

Formation of Uranium Ore Deposits

Proceedings of a Symposium
Athens
6-10 May 1974



INTERNATIONAL ATOMIC ENERGY AGENCY, VIENNA, 1974

FORMATION OF URANIUM ORE DEPOSITS

The following States are Members of the International Atomic Energy Agency:

AFGHANISTAN	HAITI	PAKISTAN
ALBANIA	HOLY SEE	PANAMA
ALGERIA	HUNGARY	PARAGUAY
ARGENTINA	ICELAND	PERU
AUSTRALIA	INDIA	PHILIPPINES
AUSTRIA	INDONESIA	POLAND
BANGLADESH	IRAN	PORTUGAL
BELGIUM	IRAQ	ROMANIA
BOLIVIA	IRELAND	SAUDI ARABIA
BRAZIL	ISRAEL	SENEGAL
BULGARIA	ITALY	SIERRA LEONE
BURMA	IVORY COAST	SINGAPORE
BYELORUSSIAN SOVIET SOCIALIST REPUBLIC	JAMAICA	SOUTH AFRICA
CAMEROON	JAPAN	SPAIN
CANADA	JORDAN	SRI LANKA
CHILE	KENYA	SUDAN
COLOMBIA	KHMER REPUBLIC	SWEDEN
COSTA RICA	KOREA, REPUBLIC OF	SWITZERLAND
CUBA	KUWAIT	SYRIAN ARAB REPUBLIC
CYPRUS	LEBANON	THAILAND
CZECHOSLOVAK SOCIALIST REPUBLIC	LIBERIA	TUNISIA
DENMARK	LIBYAN ARAB REPUBLIC	TURKEY
DOMINICAN REPUBLIC	LIECHTENSTEIN	UGANDA
ECUADOR	LUXEMBOURG	UKRAINIAN SOVIET SOCIALIST REPUBLIC
EGYPT, ARAB REPUBLIC OF	MADAGASCAR	UNION OF SOVIET SOCIALIST REPUBLICS
EL SALVADOR	MALAYSIA	UNITED KINGDOM OF GREAT BRITAIN AND NORTHERN IRELAND
ETHIOPIA	MALI	UNITED STATES OF AMERICA
FINLAND	MEXICO	URUGUAY
FRANCE	MONACO	VENEZUELA
GABON	MONGOLIA	VIET-NAM
GERMAN DEMOCRATIC REPUBLIC	MOROCCO	YUGOSLAVIA
GERMANY, FEDERAL REPUBLIC OF	NETHERLANDS	ZAIRE, REPUBLIC OF
GHANA	NEW ZEALAND	ZAMBIA
GREECE	NIGER	
GUATEMALA	NIGERIA	
	NORWAY	

The Agency's Statute was approved on 23 October 1956 by the Conference on the Statute of the IAEA held at United Nations Headquarters, New York; it entered into force on 29 July 1957. The Headquarters of the Agency are situated in Vienna. Its principal objective is "to accelerate and enlarge the contribution of atomic energy to peace, health and prosperity throughout the world".

PROCEEDINGS SERIES

FORMATION OF URANIUM ORE DEPOSITS

PROCEEDINGS OF A SYMPOSIUM ON THE
FORMATION OF URANIUM ORE DEPOSITS
ORGANIZED BY THE
INTERNATIONAL ATOMIC ENERGY AGENCY
AND HELD IN ATHENS, GREECE, 6-10 MAY 1974

INTERNATIONAL ATOMIC ENERGY AGENCY
VIENNA, 1974

FORMATION OF URANIUM ORE DEPOSITS
IAEA, VIENNA, 1974
STI/PUB/374
ISBN 92-0-040274-7

FOREWORD

The increase in uranium production which will be required during the remainder of this century is unprecedented in the history of mineral development and poses a major challenge to uranium geology and exploration. Basic to any exploration effort is knowledge and understanding of how uranium deposits are formed. Increased knowledge of the chemical, mineralogical and geological controls and of the regional, tectonic and geochemical distribution of uranium is required to support the exploration programmes of the future.

The International Atomic Energy Agency, conscious of the importance of the study of uranium geology and exploration techniques, first sponsored a panel meeting in April 1970 to discuss uranium exploration geology and, as a result of that meeting, a number of Working Groups were set up to study genetic concepts, the various principal types of uranium deposits and their formation. It was later recommended that a further and more broadly based meeting be held to discuss all aspects of the formation of uranium deposits.

As a result, a Symposium on the Formation of Uranium Ore Deposits was convened by the Agency and held from 6 to 10 May 1974 in Athens at the invitation of the Government of Greece. A total of 220 participants from 40 countries and two international organizations attended the Symposium, at which 43 papers were presented. The subject of the Symposium proved to be timely and important because recent changes in the world energy situation compel even greater emphasis to be placed on the future development of nuclear power.

Uranium deposits in sandstones and quartz-pebble conglomerates at present form the bulk of known uranium resources. Yet there is reason for believing that there may, in the future, be geological limitations to the continued discovery of such deposits in numbers sufficient to meet the envisaged needs; work is needed here to determine whether there are in fact such limits, and if not, how the deposits yet undiscovered can be rapidly identified. New types of deposits, low in grade but larger in size, may have to supply the bulk of future resource additions, and investigation is required on the characteristics of such deposits and the means of identifying them.

At the Symposium, these problems were discussed and all subjects related to the genesis and formation of uranium ore deposits were reviewed under the topic headings of the six Working Groups, each of which also prepared a summary report. The papers, discussions and Working Group reports are presented in these Proceedings.

The Agency is grateful to all those who contributed papers and took part in the Working Groups and in the general discussions. Thanks are especially due to the General Chairman, Mr. R.D. Nininger, Assistant Director, Division of Production and Materials Management, USAEC, and the eight

session chairmen. The Agency also wishes to thank the chairmen of the Working Groups: Messrs S.H.U. Bowie (UK), H.H. Adler (USA), D.S. Robertson (Canada), E.E.N. Smith (Canada), J.W. von Backström (South Africa) and V. Ziegler (France). Finally, sincere gratitude is expressed for the excellent conference arrangements and the general hospitality to the participants and to the Agency staff afforded by the Government of Greece and the staff of the Democritos Centre of the Greek Atomic Energy Commission.

EDITORIAL NOTE

The papers and discussions incorporated in the proceedings published by the International Atomic Energy Agency are edited by the Agency's editorial staff to the extent considered necessary for the reader's assistance. The views expressed and the general style adopted remain, however, the responsibility of the named authors or participants.

For the sake of speed of publication the present Proceedings have been printed by composition typing and photo-offset lithography. Within the limitations imposed by this method, every effort has been made to maintain a high editorial standard; in particular, the units and symbols employed are to the fullest practicable extent those standardized or recommended by the competent international scientific bodies.

The affiliations of authors are those given at the time of nomination.

The use in these Proceedings of particular designations of countries or territories does not imply any judgement by the Agency as to the legal status of such countries or territories, of their authorities and institutions or of the delimitation of their boundaries.

The mention of specific companies or of their products or brand-names does not imply any endorsement or recommendation on the part of the International Atomic Energy Agency.

CONTENTS

INTRODUCTORY REVIEW PAPER

The world uranium supply challenge – an appraisal (IAEA-SM-183/42, Review Paper)	3
R.D. Nininger	
Discussion	18

CHEMICAL AND PHYSICAL MECHANISMS IN THE FORMATION OF URANIUM MINERALIZATION, GEOCHRONOLOGY, ISOTOPE GEOLOGY AND MINERALOGY

The geochemical distribution of uranium as a primary criterion for the formation of ore deposits (IAEA-SM-183/19)	21
J.W. Brinck	
Geochemical factors controlling the formation of the secondary minerals of uranium (IAEA-SM-183/21)	33
M. Dall'Aglia, R. Gragnani, E. Locardi	
Discussion	47
On the behaviour of uranium during crystallization of magmas – with special emphasis on alkaline magmas (IAEA-SM-183/26)	49
H. Bohse, J. Rose-Hansen, H. Sørensen, A. Steenfelt, L. Løvborg, H. Kunzendorf	
Geochemical and mineralogical studies of euxinite and its alteration products in graphitic pegmatites from Harrar, Ethiopia (IAEA-SM-183/47)	61
S.S. Augustithis, E. Mposkos, A. Vgenopoulos	
Discussion	70
Solubilisation et insolubilisation de l'uranium des granites par des bactéries hétérotrophes (IAEA-SM-183/18)	73
R. Magne, J.R. Berthelin, Y. Dommergues	
Discussion	86
A study of the influence of microflora on the genesis of uranium occurrences at Udaisagar, Udaipur District, Rajasthan (IAEA-SM-183/31)	89
K.M.V. Jayaram, K.K. Dwivedy, M.C. Bhurat, S.G. Kulshrestha	
Discussion	98
The role of organic matter in the accumulation of uranium: the organic geochemistry of the coal-uranium association (IAEA-SM-183/29)	99
I.A. Breger	
Discussion	123

Consideraciones sobre el papel que desempeñan las sustancias orgánicas naturales de carácter húmico en la concentración del uranio (IAEA-SM-183/33)	125
M. Martín Calvo	
Discussion	135

SEDIMENTARY BASINS AND SANDSTONE-TYPE DEPOSITS: NORTH AMERICAN DEPOSITS

Concepts of uranium-ore formation in reducing environments in sandstones and other sediments (IAEA-SM-183/43, Review Paper)	141
H.H. Adler	
Discussion	167
Distribution of elements in some roll-type uranium deposits (IAEA-SM-183/4)	169
E.N. Harshman	
Discussion	182
Zoning in the altered tongue associated with roll-type uranium deposits (IAEA-SM-183/6)	185
H.C. Granger, C.G. Warren	
Discussion	199
Genesis and characteristics of the Southern Powder River Basin uranium deposits, Wyoming, USA (IAEA-SM-183/5)	201
A.R. Dahl, J.L. Hagmaier	
Discussion	216
Alteration of detrital magnetite-ilmenite in continental sandstones of the Morrison Formation, New Mexico (IAEA-SM-183/36)	219
S.S. Adams, H.S. Curtis, P.L. Hafen	
Discussion	252
Sandstone-type uranium deposits in the Proterozoic strata of Northwestern Canada (IAEA-SM-183/37)	255
R.D. Morton	
Discussion	271

SEDIMENTARY BASINS AND SANDSTONE-TYPE DEPOSITS: PERMIAN DEPOSITS IN EUROPE

Review of uranium occurrences in Permian sediments in Europe, with special reference to uranium mineralizations in Permian sandstone (IAEA-SM-183/34)	277
F.H. Barthel	
Discussion	288
Permo-triassic uranium ore in the Austrian Alps – paleogeographic control as a guide for prospecting (IAEA-SM-183/25)	291
W.E. Petrascheck, E. Erkan, K. Neuwirth	
Discussion	297

Genetic characteristics of uranium deposits associated with Permian sandstones in the Italian Alps (IAEA-SM-183/22) ...	299
M. Mittempergher	
Discussion	312
Uranium ore deposits in the Permian sediments of Northwest Yugoslavia (IAEA-SM-183/7)	313
E. Lukacs, A.P. Florjančič	
Discussion	327
Caractères minéralo-géochimiques et genèse du gisement d'uranium de Žirovski Vrh (IAEA-SM-183/8)	331
C. Markov, M. Ristić	
Discussion	339
Литолого-фациальные условия локализации урановых рудопрояв- лений в пермских отложениях в Социалистической Республике Румынии (IAEA-SM-183/15)	343
И. Корничук, Т. Буртик	
Discussion	355
Facteurs contrôlant la distribution des éléments dans les shales uranifères du bassin permien de Lodève (Hérault, France) (IAEA-SM-183/3)	359
A. Herbosch	
Discussion	380

SEDIMENTARY BASINS AND SANDSTONE-TYPE DEPOSITS: SEDIMENTARY DEPOSITS IN OTHER AREAS

Uranium in Siwalik sandstones, Sulaiman Range, Pakistan (IAEA-SM-183/41)	383
M.Y. Moghal	
Discussion	400
Uranium mineralization in Siwalik sandstones from Pakistan (IAEA-SM-183/20)	405
I.R. Basham, C.M. Rice	
Discussion	417
Uranium deposits in the Karoo Supergroup near Beaufort West, Cape Province, South Africa (IAEA-SM-183/48)	419
J.W. von Backström	
Discussion	423
Controls and genesis of uranium mineralization in some geological environments in India (IAEA-SM-183/39)	425
G.R. Udas, T.M. Mahadevan	
Discussion	436
Genesis of uranium deposits of the Tono Mine, Japan (IAEA-SM-183/11)	437
N. Katayama, K. Kubo, S. Hirono	
Discussion	452
Le gîte d'uranium de Fakılı (Turquie) et sa formation (IAEA-SM-183/40)	453
H. Kaplan, S. Uz, İ. Çetintürk	
Discussion	465

Origin of uranium in Oligocene Qatrani sediments, Western Desert, Arab Republic of Egypt (IAEA-SM-183/1)	467
E.M. El Shazly, N.M.T. El Hazeq, A.A. Abdel Monem, S.M. Khawasik, Z.M. Zayed, M.E.M. Mostafa, M.A. Morsi	
Discussion	477
Analogías y diferencias de caracteres de favorabilidad en distintos terrenos sedimentarios de la Cordillera Ibérica (IAEA-SM-183/32)	479
J. Martín-Delgado Tamayo, J.A. Fernández Polo	
Discussion	491

URANIUM IN QUARTZ-PEBBLE CONGLOMERATES

Basal Proterozoic units as fossil time markers and their use in uranium prospection (IAEA-SM-183/35, Review Paper)	495
D.S. Robertson	
Discussion	512

VEIN- AND SIMILAR-TYPE DEPOSITS

Review of current concepts regarding vein deposits of uranium (IAEA-SM-183/45, Review Paper)	515
E.E.N. Smith	
Discussion	527
The concepts of supergene versus hypogene emplacement of uranium at Rabbit Lake, Saskatchewan, Canada (IAEA-SM-186/38)	531
H.D. Knipping	
Discussion	548
Uranium mineralization in the Rum Jungle-Alligator Rivers Province, Northern Territory, Australia (IAEA-SM-183/28)	551
R.G. Dodson, R.S. Needham, P.G. Wilkes, R.W. Page, P.G. Smart, A.L. Watchman	
Discussion	567
Les inclusions fluides dans les minerais des gisements d'uranium intragranitiques du Limousin et du Forez (Massif Central, France) (IAEA-SM-183/17)	569
B.P. Poty, J. Leroy, M. Cuney	
Discussion	581
Use of fluid inclusions in the genetic study of vein deposits (IAEA-SM-183/2)	583
J. Bossi	
Discussion	592
Zletovska Reka uranium deposit (IAEA-SM-183/9)	593
D. Radusinović	
Discussion	601

OTHER URANIUM DEPOSITS

Other uranium deposits (IAEA-SM-183/27, Review Paper)	605
J.W. von Backström	
Discussion	620
Uranium resources of the future – "porphyry" uranium deposits (IAEA-SM-183/12)	625
F.C. Armstrong	
Discussion	635
Uranium occurrences in Brazil (IAEA-SM-183/24)	637
J.R. de Andrade Ramos, M.O. Fraenkel	
Discussion	657

RELATION OF METALLOGENIC, TECTONIC AND ZONING FACTORS TO THE ORIGIN OF URANIUM DEPOSITS

Essai de classification métallotectonique des gisements d'uranium (IAEA-SM-183/16, étude d'ensemble)	661
V. Ziegler	
Les conditions tectono-magmatiques de la formation des gisements d'uranium de Roumanie (IAEA-SM-183/14)	679
G. Nitu	

REPORTS OF THE WORKING GROUPS

Working Group I: Chemical and physical mechanisms in the formation of uranium mineralization, geochronology, isotope geology and mineralogy	695
Discussion	697
Working Group II: Sedimentary basins and sandstone-type deposits	699
Discussion	702
Working Group III: Uranium in quartz-pebble conglomerates	707
Discussion	708
Working Group IV: Vein- and similar-type deposits	713
Discussion	719
Working Group V: Other uranium deposits	723
Working Group VI: Relation of metallogenic, tectonic and zoning factors to the origin of uranium deposits	727
General Chairman, Session Chairmen and Secretariat of the Symposium	729
List of Participants	731
Working Groups	745
Author Index	747

INTRODUCTORY REVIEW PAPER

Review Paper

THE WORLD URANIUM SUPPLY CHALLENGE - AN APPRAISAL

R.D. NININGER

Division of Production and Materials Management,
US Atomic Energy Commission,
Washington, D.C.,
United States of America

Abstract

THE WORLD URANIUM SUPPLY CHALLENGE - AN APPRAISAL.

The first Symposium on the Formation of Uranium Ore Deposits is a milestone in the expanding activities of the International Atomic Energy Agency in the field of nuclear raw materials. During this expansion, the Agency has greatly increased and improved international cooperation in uranium geology exploration and resource evaluation. In addition to stimulating an exchange of information, it has also expanded technical assistance in uranium exploration to developing countries in cooperation with the United Nations. These activities are very important at this critical point in the development of nuclear power, highlighted by recent problems in the world energy supply.

The world demand for uranium during the remainder of the century is projected at around 4 million tons. It could be greater if the trend towards the use of electricity is accelerated and if other fuels continue to become more expensive. The increase in uranium production which will be required is unprecedented in the history of mineral development and poses a major challenge to uranium geology and exploration.

World reserves at a cost of up to \$ 15/lb U_3O_8 are estimated at little more than 2 million tons and additional resources at an equivalent amount. However, the production levels needed towards the end of the century will require a resource base approaching three times the present resource estimates.

A number of questions and problems are presented by the magnitude of the uranium supply challenge and should be addressed in this Symposium. Uranium deposits in sandstone and quartz-pebble conglomerates presently represent the preponderance of uranium resources. Yet there is a question whether geological limitations on the occurrence of such deposits may preclude their discovery in numbers sufficient to meet the eventual resource needs. New types of deposits, low in grade but larger in size, representing the equivalent of the porphyry copper deposits, may supply the bulk of future resource additions. Further investigation is needed on the characteristics of such deposits and the means of their identification. Similarly, additional investigation is needed to determine whether limits on the more conventional deposits do in fact exist and, if not, what advanced approaches to rapid identification of additional such deposits might be employed.

The world probably cannot rely on the very low-grade deposits such as most uraniferous black shales for both economic and environmental reasons. There is probably a minimum grade between 100 and 500 ppm below which uranium deposits cannot be effectively exploited for nuclear power.

A number of papers at this Symposium address some of these questions, and it is hoped that the ensuing discussions will shed additional light on the means by which the world's nuclear fuel requirements will be met.

The International Atomic Energy Agency is to be congratulated on convening this first Symposium on the Formation of Uranium Ore Deposits. It is the culmination of an intensive effort by the Agency to expand and improve international cooperation in uranium geology, exploration and resource evaluation begun some seven years ago. This has included the joint Working Parties on Uranium Resources and Demand with the OECD and the Panels on Uranium Exploration Geology and

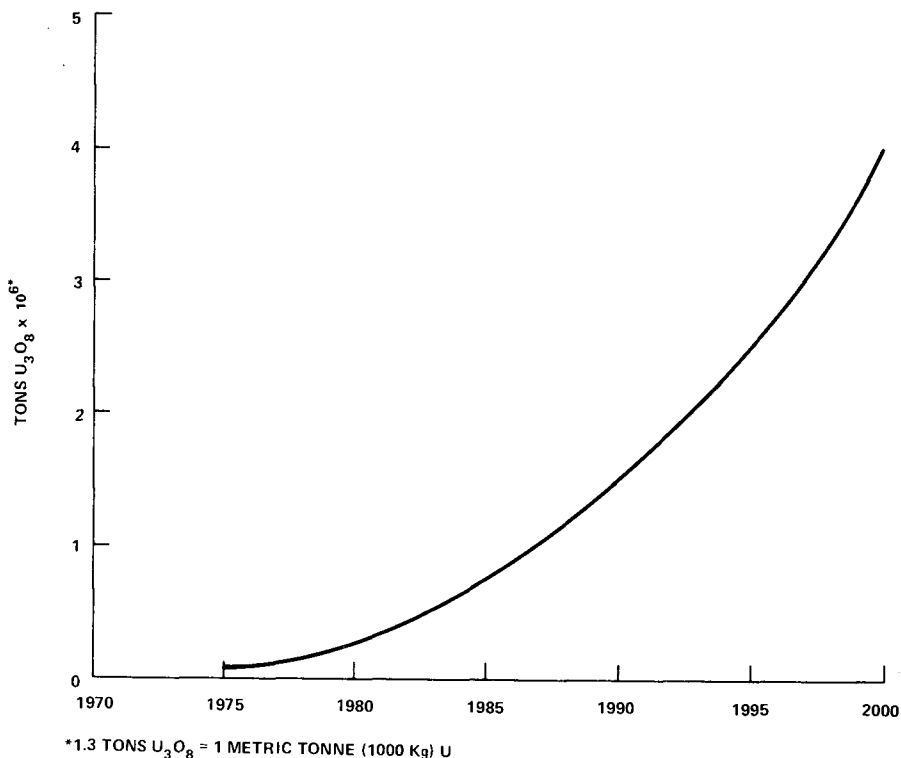


FIG. 1. World uranium requirements - cumulative. (Excludes China, USSR and Eastern Europe¹). 0.20% enrichment tails.

Uranium Exploration Methods. In addition the Agency has undertaken several long-term technical assistance programs to developing countries in cooperation with the United Nations Development Program.

This Symposium marks the end of this initial period of expanding activity in the field of uranium raw materials as well as the much needed beginning of fuller international cooperation and exchange of information in the critical area of uranium geology and exploration.

The Agency must also be congratulated for its success in attracting to this Symposium such a large and prestigious group of uranium geologists. This augurs well for its success and its impact on future uranium supply.

The convening of this Symposium is timely. This is highlighted by the most recent developments in world energy supply. The confluence of the oil embargo and the realization that the consumption of energy in the industrialized countries was rapidly outstripping the traditional supplies

have placed even greater emphasis on the development of nuclear power which was already foreseen to be the major source of the world's electricity by the year 2000. As a consequence, the projected increase in resources and production of uranium needed, unprecedented in the history of mineral development, may now be further increased. Accordingly, the challenge to uranium geology and exploration has become even greater.

What is the magnitude of the challenge; what questions and what problems does it pose; and what are some possible answers? I shall address myself very briefly to these subjects and identify a few which I hope may be explored at this Symposium. One may hope that at least the general direction in which the answers to some of the questions lie may be suggested during the ensuing discussions.

The consensus on the probable world¹ demand for uranium during the remainder of the century is about 4 million short tons of U_3O_8 (1) (Figure 1). Against this requirement, world reserves at a cost of up to \$10 lb. of U_3O_8 amount to 1.2 million tons (Figure 2).

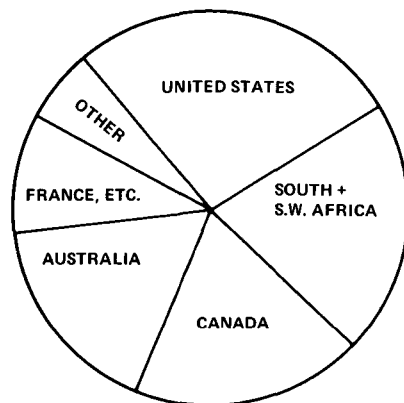
The present estimate of additional undiscovered resources in this cost range is 1.1 million tons. Incremental reserves and estimated additional resources in the \$10-\$15 range amount to another 1.7 million tons (Figure 3). Much larger resources will be needed to support the production level of about 300,000 tons per year which will be reached by 2000 (Figure 4). Demand will continue to climb for some years after 2000 even with the successful commercial introduction of breeder reactors in the 1980s. Figure 5 shows a comparison of the rate of increase in uranium production needed over the next 20 years with the maxima achieved in world production of three other minerals over similar periods in the past. Uranium production must increase at an average annual rate of more than 12 percent.

The reserves plus resources which need to be identified by the year 2000 to support the required production levels through 2000 and beyond may approximate 12 million tons, about three times the present estimate of reserves and resources at \$15 per pound (Figure 6).

These then are the dimensions of the uranium supply challenge. Now let us review some of the geologic and exploration ramifications.

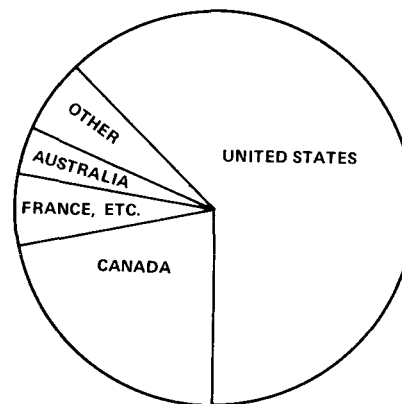
Figure 7 shows the geologic distribution of reserves and potential resources at \$10/lb U_3O_8 . Deposits in sandstones and in quartz pebble conglomerates predominate. Figure 8 shows the geologic distribution of \$10-\$15 resources. Except for the addition of the significant resources of uranium in the black shales of Sweden, the picture is much the same.

¹ "World" as used in this paper excludes China, USSR, and Eastern European states for which data are not available, with the exception of Yugoslavia.



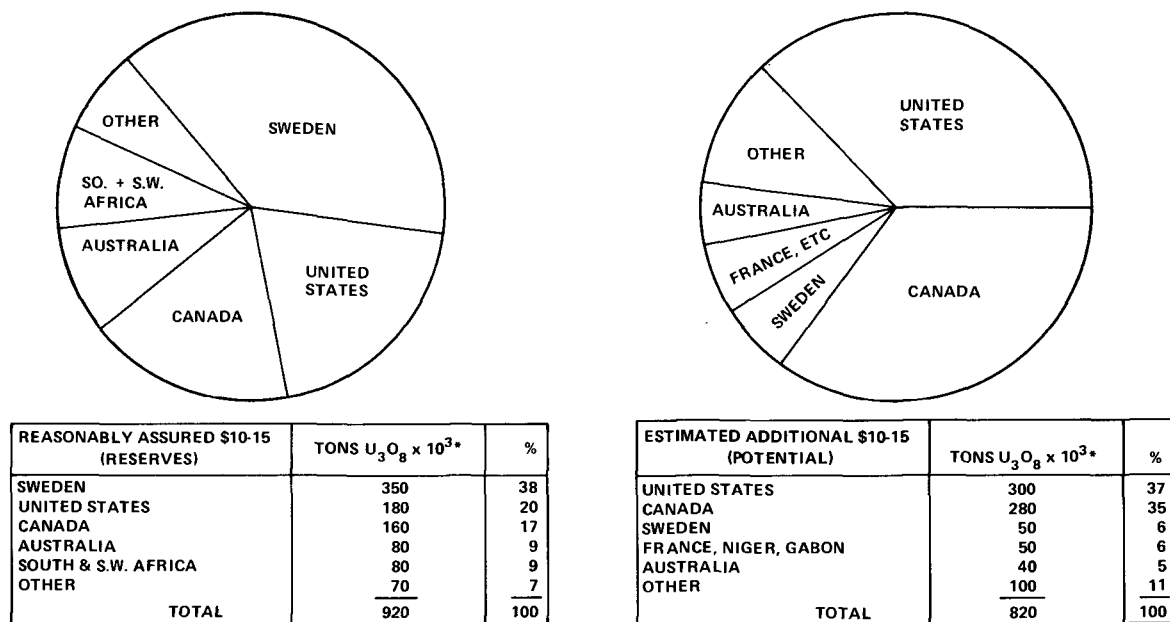
REASONABLY ASSURED — \$10/LB U_3O_8 (RESERVES)	TONS $U_3O_8 \times 10^3$ *	%
UNITED STATES	340	27
SOUTH + S.W. AFRICA	260	21
CANADA	240	19
AUSTRALIA	210	17
FRANCE, NIGER, GABON	130	10
OTHER	60	6
TOTAL	1240	100

*1.3 TONS U_3O_8 = 1 METRIC TONNE (1000 Kg) U



ESTIMATED ADDITIONAL — \$10/LB U_3O_8 (POTENTIAL)	TONS $U_3O_8 \times 10^3$ *	%
UNITED STATES	700	62
CANADA	250	22
FRANCE, NIGER, GABON	60	6
AUSTRALIA	50	4
OTHER	70	6
TOTAL	1130	100

FIG. 2. World uranium resources — \$ 10 per lb U_3O_8 . (Excludes China, USSR, and Eastern Europe¹).



*1.3 TONS U_3O_8 = 1 METRIC TONNE (1000 Kg) U

FIG.3. World uranium resources - \$ 10 to \$ 15 per lb U_3O_8 . (Excludes China, USSR and Eastern Europe¹).

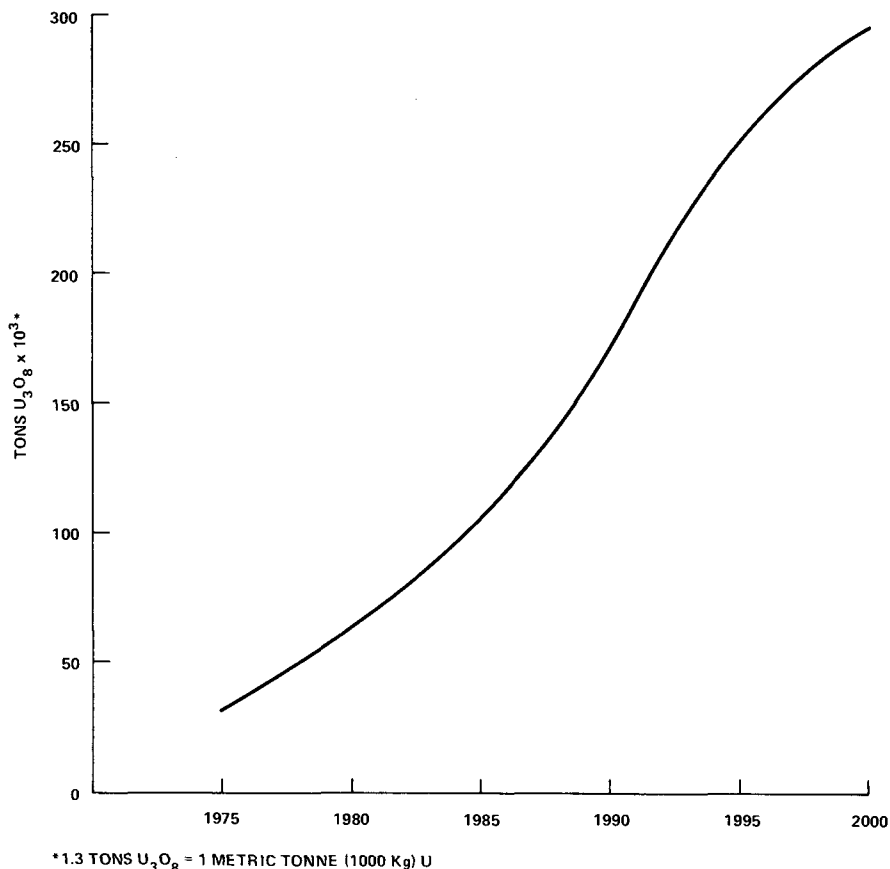


FIG. 4. World uranium requirements - annual. (Excludes China, USSR and Eastern Europe¹). 0.20% enrichment tails.

Given this situation, after 25 years of intensive exploration, what is the likelihood that these types of deposits will remain the world's main source of uranium supply and, if this is likely to be the case, how does that affect the prospects for meeting the huge demand confronting us?

Robertson (2) has suggested that, because uranium is a lithophile element, its distribution is geologically limited and resources in sandstones and conglomerates may be restricted to additional deposits of the type with which we are familiar. He suggests that the conglomerate deposits are restricted in geologic time and the sandstone deposits by special depositional conditions, greatly limiting the potential for expanding

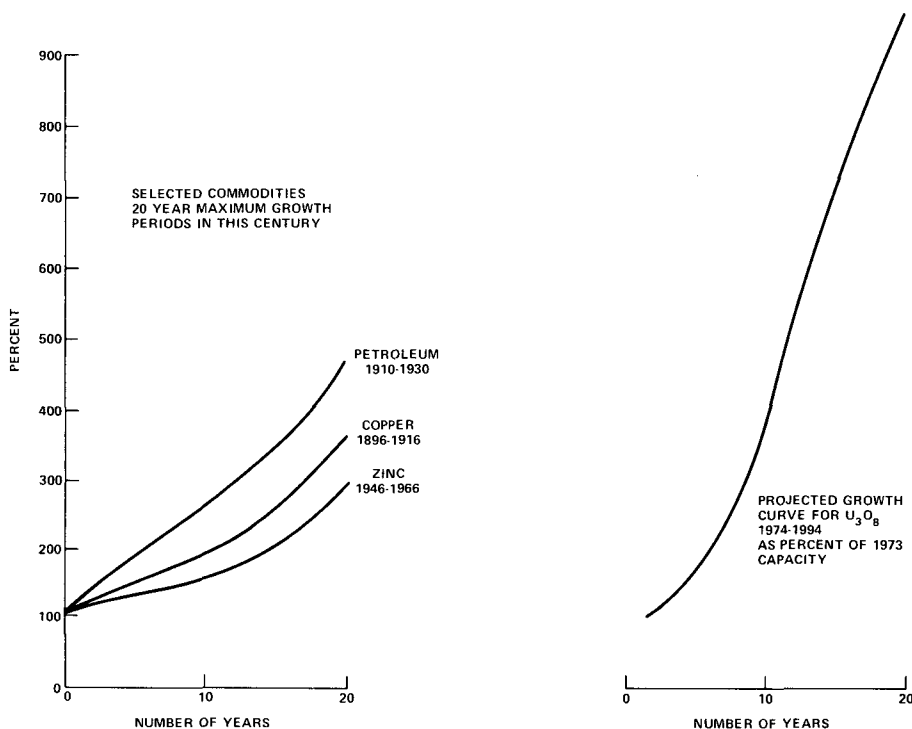


FIG.5. World annual mineral production growth comparisons. (Excludes China, USSR and Eastern Europe¹).

resources. Robertson qualifies this conclusion by tying it to resources economic under current conditions. The possibility remains of finding entirely new types of deposits exploitable at higher costs.

Investigations of sandstone deposits in the United States indicate that the resources in such deposits cannot be greatly expanded by raising the cutoff cost. Both the tonnage and grade of sandstone deposits show log-normal distributions so that the increase in total contained uranium at lower average grades of ore is relatively small. Figures 9 and 10 show the incremental and cumulative distribution of ore and contained uranium in a typical deposit. The data also indicate that the size of sandstone-type deposits is generally independent of grade. Thus, we have no evidence to suggest that there may be large uranium resources in sandstone deposits in the 500 to 1000 parts per million range. Sandstone deposits appear to represent primarily relatively high-grade deposits, the distribution of which is limited. They may not, therefore, be capable of supplying the large quantities of uranium needed.

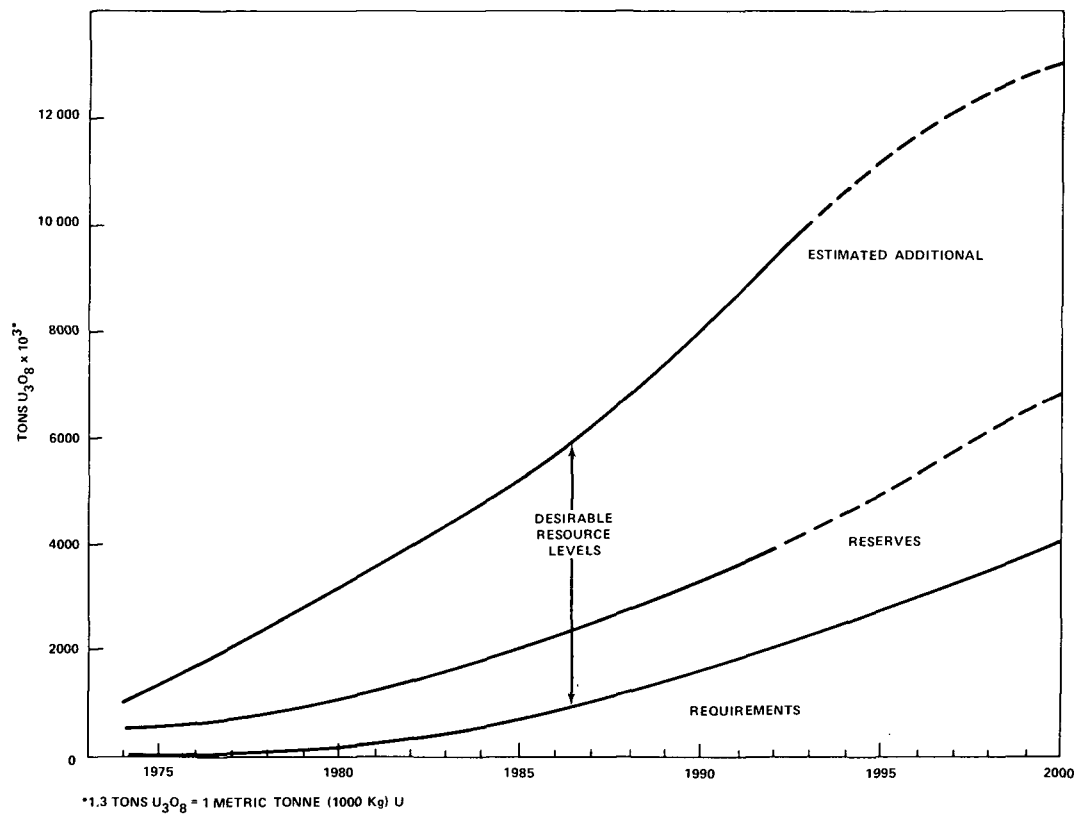
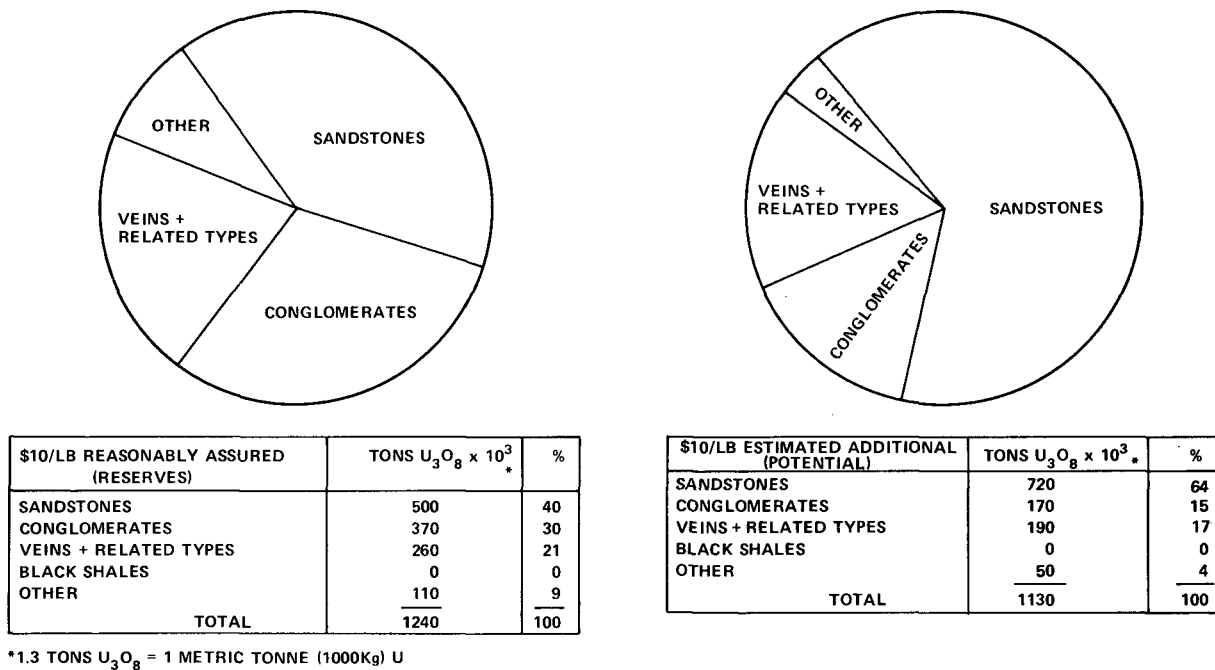
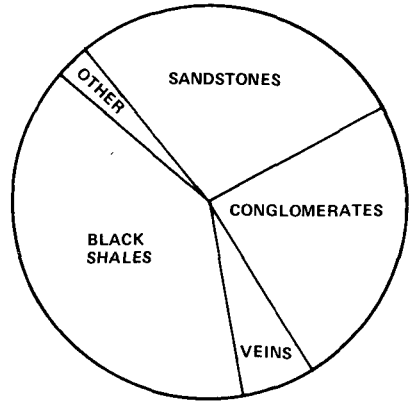
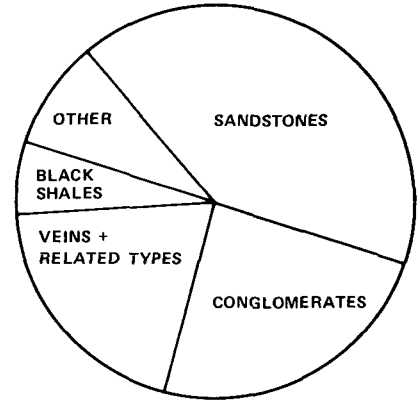


FIG. 6. Cumulative world uranium requirements, desirable levels of reserves and estimated additional resources. (Excludes China, USSR and Eastern Europe¹). 0.20% enrichment tails.

FIG.7. World uranium resources - \$ 10 per lb U_3O_8 . (Excludes China, USSR and Eastern Europe¹).



\$10-15 REASONABLY ASSURED (RESERVES)	TONS $U_3O_8 \times 10^3$ *	%
SANDSTONES	260	28
CONGLOMERATES	220	24
VEINS AND RELATED TYPES	60	6
BLACK SHALES	350	38
OTHER	30	3
TOTAL	920	100



\$10-15 ESTIMATED ADDITIONAL (POTENTIAL)	TONS $U_3O_8 \times 10^3$ *	%
SANDSTONES	340	41
CONGLOMERATES	200	24
VEINS AND RELATED TYPES	160	20
BLACK SHALES	50	6
OTHER	70	9
TOTAL	820	100

*1.3 TONS U_3O_8 = 1 METRIC TONNE (1000 Kg) U

FIG.8. World uranium resources - \$ 10 to \$ 15 per lb U_3O_8 . (Excludes China, USSR and Eastern Europe¹).

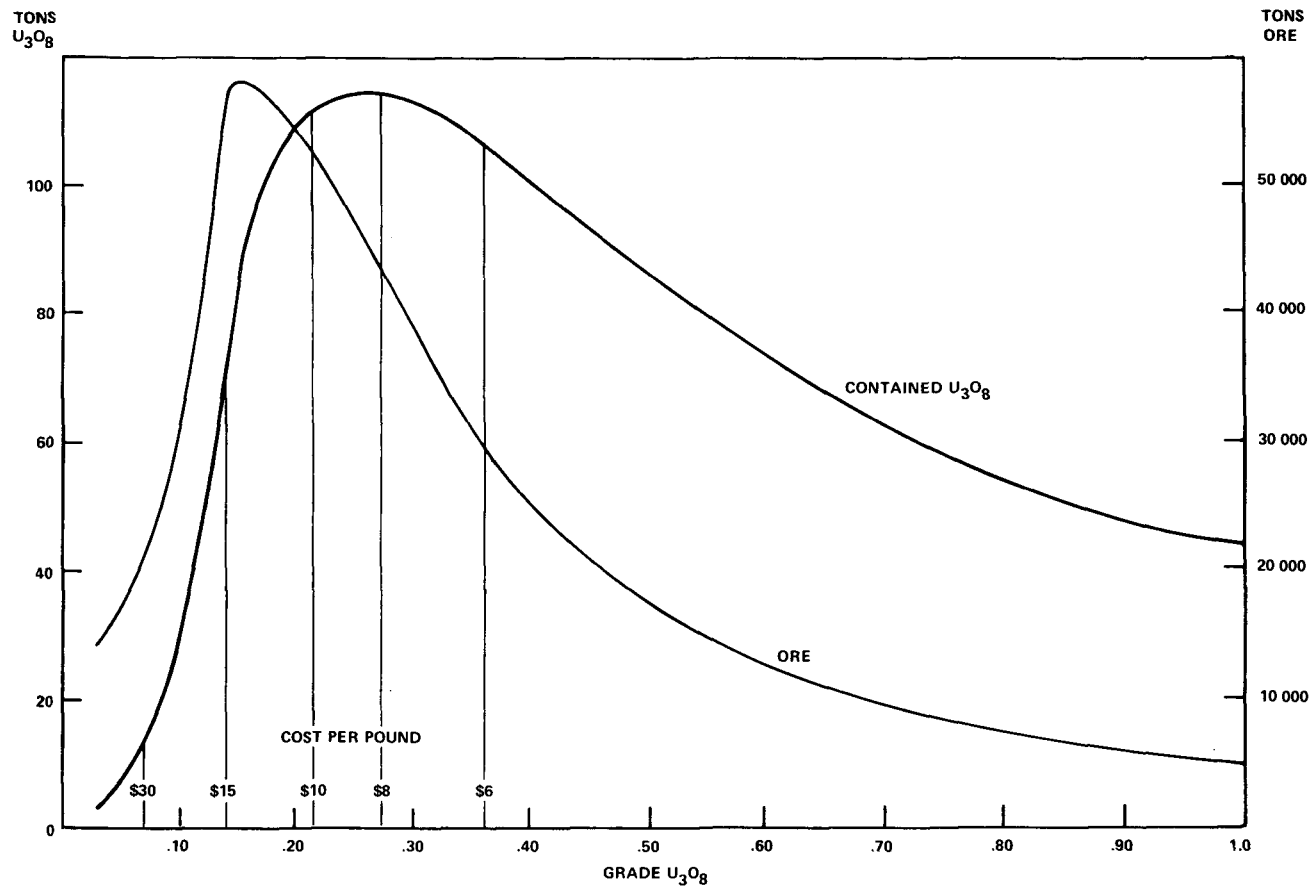


FIG. 9. Distribution of reserves by grade and cost per pound for a typical sandstone-type uranium deposit.

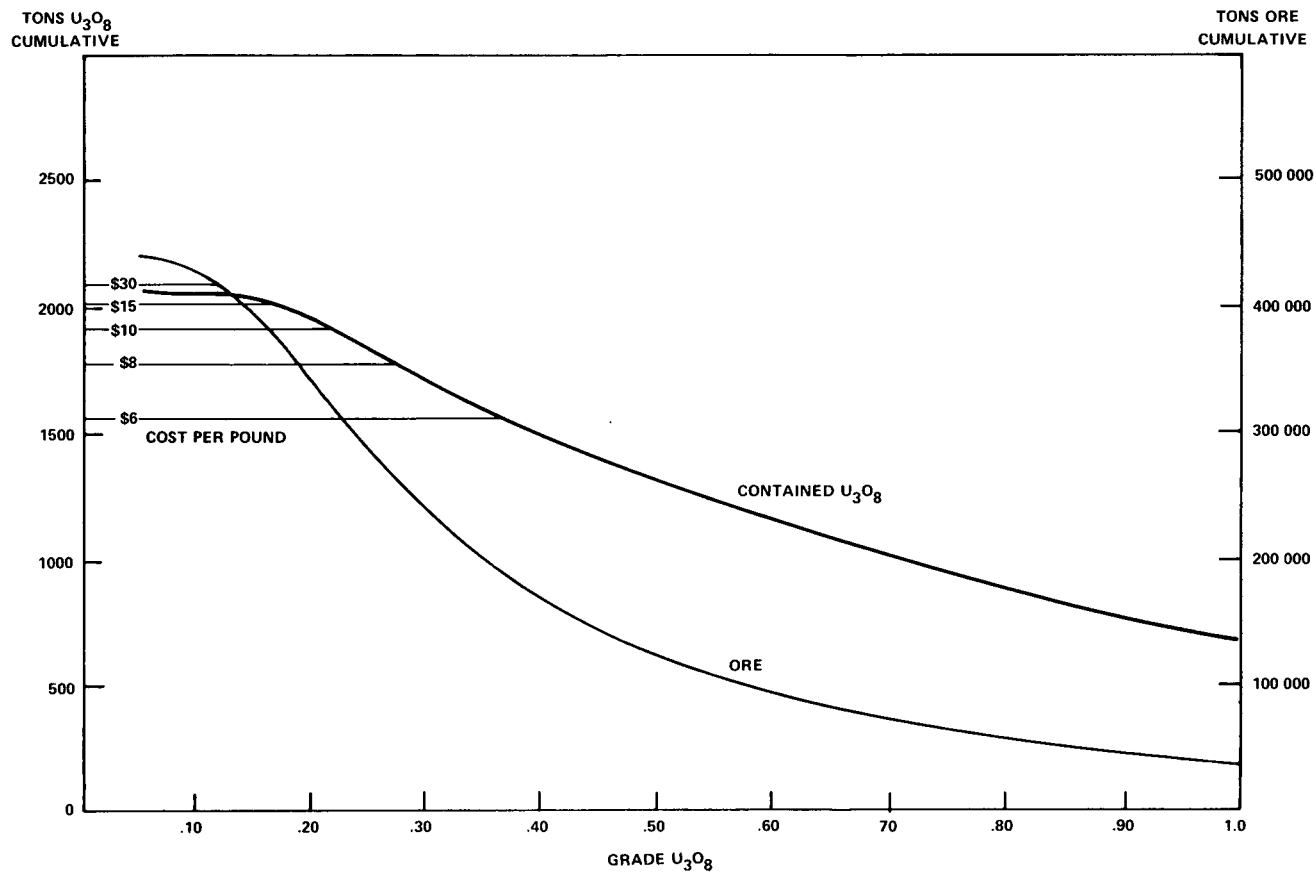


FIG. 10. Cumulative distribution of reserves by grade and cost per pound for a typical sandstone-type uranium deposit.

In spite of these possible limitations, exploration for sandstone-type deposits remains predominant, and geologic studies and genetic concepts related to them attract the major present interest. This is evidenced by the large number of papers on this subject to be presented at this Symposium relative to the papers discussing other types of deposits. This, of course, is an expectable situation because of the much greater experience and knowledge in this area; the success experienced thus far in discovering new deposits; and the human characteristic, which geologists share, of concentrating on the subject that is of primary interest at the time and which appears to offer the most available opportunities for investigation.

However, it may not be in our best interest from the standpoint of developing nuclear fuel supplies for the future to concentrate so large a proportion of effort on the geology and exploration of sandstone-type deposits relative to other resource possibilities. In this regard, the papers to be presented in Session I on chemical and physical controls in the formation of uranium minerals and ores, which may be applicable to a variety of deposits, should be of interest.

The possible limitations of sandstone-type deposits should not be overemphasized for, after all, they represent our most obvious immediate opportunity to increase world resources. In addition to further exploration for such deposits in traditional environments, the possibility of expansion on a significant scale into host rocks which have not proved of major importance to date must be considered. Thus, the paper by Morton (3) dealing with sandstone-type deposits in Proterozoic rocks will be of interest. Also, the several other papers in Sessions IV and V on uranium in Permian and Permian-Triassic sediments warrant close attention.

Unfortunately, only one paper was submitted specifically on quartz pebble conglomerates. We will be interested in Mr. Robertson's evaluation, and that of Working Group 3, of further opportunities for expanding resources of that type. Hopefully, the paper on uranium occurrences in Brazil by Mr. Ramos (4) will discuss in some detail the conglomerate deposits presently under study in that country.

I would like now to focus attention on the question of whether there may be reason to expect that large additional resources of uranium may be found in new types of deposits, most likely appreciably lower in grade than those presently being exploited but containing larger quantities of uranium per deposit. There are a number of papers which should add to our understanding and elicit discussion of such possibilities. For example, the paper by Armstrong (5) entitled, "Are there 'porphyry' uranium deposits?". There are also two other papers that describe types of deposits which may come to represent "porphyry" uranium deposits, those by von Backström (6) and Bohse et al. (7).

May there exist, in fact, substantial numbers of large, lower-grade uranium deposits which could economically provide the uranium needed to power non-breeder reactors? Once breeder reactors are fully established, there will no longer be a uranium resource problem; the quantities of natural uranium required will be relatively small and the price inconsequential. But until that time, economics and, perhaps even more important, environmental considerations may limit the minimum grade of ore which can be relied upon. The limit is probably a uranium concentration equivalent to a cost of recovery of somewhat less than \$100/lb U₃O₈.

A cost of \$100/lb of U₃O₈ is equivalent to a grade in the range of 50 to 100 parts per million. The only large deposits of this type now known are the uranium-bearing black shales in the southeastern United States which contain several million tons of U₃O₈. However, in my opinion these shales are not likely to be a viable source of uranium because of the environmental impact of mining, milling and disposing of the huge quantities -- several million tons of ore per day -- that would be mined to meet U. S. requirements alone in the 1990's.

The minimum grade imposed by environmental restraints probably lies in the range of 100 to 500 parts per million. Only the Rössing deposit in South-West Africa and the auriferous conglomerates in South Africa fall in this grade range. The auriferous conglomerates may well be unique, but the uranium-bearing alaskite intrusive at Rössing or similar deposits may be repeated elsewhere.

Singer et al. (8) have made a statistical study of porphyry copper deposits in Arizona and New Mexico. The preliminary results of this study of 37 deposits suggest that the grades of those deposits, like the sandstone uranium deposits, are not related to size. They have also found an independence of grade and tonnage in strata-bound copper deposits and inconclusive results for massive sulfide copper deposits. When all types of deposits are analyzed together, however, there is an inverse relationship between grade and tonnage.

It seems obvious that we cannot expect to discover much larger deposits of the types now known. Either new types of deposits must be found and exploited, or we must find very much larger numbers of the same size of deposits we are now exploiting, which will be a difficult task. Therefore, a critical question is: what will be the type and grade range of uranium deposits which may be the equivalent of the porphyry coppers? Are they the black shales which cannot, I think, solve the problem of long-term uranium supply? Are they deposits like Rössing which, if present in sufficient numbers, could provide an economic and environmentally acceptable source of uranium on a large scale? Or are they some yet unrecognized type?

The uranium deposits equivalent to the high-grade copper deposits could be the historical vein deposits at Shinkolobwe, Great Bear Lake and Joachimsthal rather than the sandstone-

type deposits. Vein deposits were the principal objective of exploration for 15 years until the major deposits in sandstone were found. Perhaps the latter are the porphyry equivalents. If so, the uranium supply problem may be aggravated. If the black shales are the porphyry equivalent, the supply problem may be even greater.

The importance of the recently discovered vein-type deposits in the Northern Territory of Australia and the Rabbit Lake deposit in Canada, which certainly have important implications for exploration, should not, of course, be underestimated. Papers in Session VII on those deposits will, therefore, be of interest.

In considering how the immense requirements for uranium are to be met, the importance of the developing countries must be emphasized. Exploration for uranium has continued for many years and is well advanced in the developed countries which now have the major identified resources. Substantial additions to those resources may be expected with time, but there are large areas of the world that are virgin or lightly explored, particularly in the developing countries, which may offer even greater promise for new discoveries of the conventional type of deposit or for new types of deposits. The shield and sedimentary areas of Africa and South America, comprising 30 to 40 countries, represent such favorable exploration targets. The work of the Agency in assisting such countries to investigate their uranium possibilities is to be commended because of its potential contribution to meeting the world's uranium requirements as well as to the improvement of income and standard of living in those countries.

In conclusion, it is hoped that new ideas may be presented and discussion generated at this Symposium not only on the geology of conventional uranium deposits but also on the probable characteristics and possibilities for discovery of new types of deposits. In this regard, the report by Working Group 5 under the Chairmanship of Mr. von Backström should be of particular interest.

REFERENCES

- [1] DAVIS, M., Uranium Supply and Demand: Worldwide Preview, Paper presented at Annual Meeting of Am. Inst. Mining, Metallurgical and Petroleum Engineers, Dallas, Texas (1974).
OECD Nuclear Energy Agency and IAEA, Uranium - Resources, Production and Demand, (A Joint Report by the OECD and IAEA), OECD, Paris (1973).
OFFICE OF PLANNING AND ANALYSIS, Nuclear Power 1973-2000, USAEC WASH-1139(74), (1974).
- [2] ROBERTSON, D. A., "Uranium: its geological occurrence as a guide to exploration", Uranium Exploration Geology (Proc. Panel Vienna, 1970), IAEA, Vienna (1970) 267.
- [3] MORTON, R. D., "Sandstone-type uranium deposits in the Proterozoic strata of Northwestern Canada", these Proceedings, Paper IAEA-SM-183/37.
- [4] de ANDRADE RAMOS, J. R., FRAENKEL, M. O., "Uranium occurrences in Brazil, these Proceedings, Paper IAEA-SM-183/24.
- [5] ARMSTRONG, F. C., "Uranium deposits of the future - "porphyry" uranium deposits?", these Proceedings, Paper IAEA-SM-183/12.
- [6] von BACKSTRÖM, J. W., "Other uranium deposits", these Proceedings, Paper IAEA-SM-183/27.

- [7] BOHSE, H., et al., "On the behaviour of uranium during crystallization of magmas - with special emphasis on alkaline magmas", these Proceedings, Paper IAEA-SM-183/26.
- [8] SINGER, D.A., Personal communication (1974).

DISCUSSION

R. G. DODSON: Would you venture a guess as to the grade of uranium ore that could be worked by the year 2000 as a by-product of phosphate treatment and beneficiation?

R. D. NININGER: Phosphates with a grade as low as 0.01% U can be expected to yield some uranium, but only as a by-product of phosphoric acid production or some similar chemical process. It is most unlikely that they could ever be worked for uranium alone.

G. R. UDAS: I have a question in connection with your reference to the extraction of U_3O_8 at \$30 per pound from phosphorites with 0.01% U_3O_8 . Have the methods for such extraction been finally established? And what is the basis of the cost estimate of \$30 per pound?

R. D. NININGER: We have not, in recent years, made any estimates of phosphate uranium production at \$30 per pound. We believe that all the uranium derived from phosphates - and the amounts are certain to be comparatively small - will be a by-product of phosphoric acid production or some similar process and will cost \$8 to \$10 per pound. The processes needed for this kind of extraction are available, but, as I have said, the amounts produced will not be large and will probably not exceed a few thousand tons per year between now and the year 2000.

S. A. SOUTH: The figure of 210 000 short tons of U_3O_8 that you quote for Australia's "reasonably assured" reserves at less than \$10 per pound is rather higher than current official Government estimates. I assume that this figure is based on company statements of geological resources rather than on the economically recoverable reserves known to be present in the individual deposits.

R. D. NININGER: Quite right. We assumed that the Yeelirrie deposit of Western Mining and the new Getty discovery as well as some lesser deposits were not included in the official figure of 140 000 tons.

CHEMICAL AND PHYSICAL MECHANISMS IN THE
FORMATION OF URANIUM MINERALIZATION,
GEOCHRONOLOGY, ISOTOPE GEOLOGY
AND MINERALOGY

THE GEOCHEMICAL DISTRIBUTION OF URANIUM AS A PRIMARY CRITERION FOR THE FORMATION OF ORE DEPOSITS

J. W. BRINCK

"IRC" BRINCK, International Resources Consultants B. V.,
Alkmaar, The Netherlands

Abstract

THE GEOCHEMICAL DISTRIBUTION OF URANIUM AS A PRIMARY CRITERION FOR THE FORMATION OF ORE DEPOSITS.

Outstanding questions concerning the formation of uranium ore deposits can be divided into several broad categories.

Apart from the economic aspect of ore deposits, which hardly enters at all in studies of this kind, the largely qualitative questions "how?" and "where?" generally have attracted more attention in economic geology than the at least equally important question "how much?".

The use of a log-binomial model of element distribution in the geological environment has been particularly useful in answering this last question and thus has contributed substantially to a better evaluation of the long-term supply problem for uranium. The same approach is presently used for several other mineral resources by Société des Consultants Indépendants et Neutres de la Communauté Européenne S. C. I. E. N. C. E. sprl., Brussels, under contract with the Commission of the European Communities.

Some implications of this model for making an inventory of regional mineral potential and the selection of favourable exploration areas by multi-element geochemical surveys are discussed.

1. METALLOGENESIS

A fundamental requirement to any exploration effort is the knowledge and understanding of how uranium deposits are formed. This has been the main subject of the panel meetings on uranium exploration geology held in Vienna in April 1970 and in Montreal in August 1972.

It was observed, as has been done for the ores of other elements, that most major deposit types are replicated in many areas of the world. Their formation has been attributed to a limited number of well-recognized geological processes, physical and/or chemical controls. These can be scaled down from plate tectonics, orogenies or metallotectonic zoning of global, continental or at least regional dimensions to igneous activity, erosion-sedimentation, solution-precipitation etc. of regional to local dimensions. Some of the more precise controls may act only over distances of centimetres to metres.

Such geologically favourable processes and controls have been recognized in many areas of unproved mineral potential. The subsequent discoveries of new ore deposits of the predicted types are the great successes of and the best justification for the use of metallogenetic theories as an exploration tool. These successes largely overshadow the often forgotten and rather embarrassing fact that the origin of some of the world's most important ore deposits are topics of heated scientific discussion and that in many, if not most, areas of the world such reputedly favourable processes and controls did not result in the formation of ore deposits. It is interesting to note, however, that in the latter case mineral indications or

even submarginal to marginal mineralizations may be found in direct relation with such reputedly favourable processes and/or controls. A closer study of these facts does not reveal a contradiction here.

The common characteristic of all ore-forming processes and controls is that of selective transport and/or deposition of mineral materials. The essential point is that by this migration a given part of the geological environment becomes depleted in a given element whereas, in order to maintain the material balance, at the same time another part becomes proportionally enriched. It is immaterial whether the depleted source area is adjacent to or at considerable vertical or horizontal distance from the enriched depositional area. Most of these processes and controls are of common and rather widespread occurrence both in geological time and space. Normally they are not specific for any element in particular. The physicochemical characteristics and concentration of a given element, in contrast to those of all other elements affected by each of these processes, determine the concentration efficiency of such processes for this element. Thus each element will have its own "specific mineralizability" for a given process.

A complete sequence, favourable combination and often a repetition of such processes and controls seems to be required for the formation of an ore deposit. Most often, only the very last stages of ore formation can be recognized and both the source area and the transport mechanism may remain unknown and become a subject for wild speculation.

Only the presence of metal in the right quantities and concentrations finally decides whether or not a given combination of known or unknown processes and controls has been favourable to the formation of ore. The old prospector's adage "Gold is where you find it" appears to be equally valid for uranium and, incidentally, most other elements.

2. DISTRIBUTION OF URANIUM ORE DEPOSITS IN THE EARTH'S CRUST

Uranium mineral indications and deposits are known to occur almost everywhere. Nevertheless, the really large contributions to the ore reserves are made by only a few, rather well-defined areas in the world. Such areas are known as metallogenetic provinces and are known for many different metals. According to the dominant metal(s), gold, copper, zinc-lead, tin, uranium and many other such metallogenetic provinces have been described.

About 96% of the reported world's uranium reserves are found in only 6 such provinces [1].

Colorado Plateau and Wyoming area	— USA	(30%)
Witwatersrand Basin	— South Africa	(23%)
Precambrian Shield area	— Canada	(21%)
Northern Territory	— Australia	(8%)
Hercynian area	— Europe	(6%)
Niger, Gabon, Central African Republic	— Africa	(8%)

Compared with the earth's surface as a whole, these provinces are rather small areas in which a few large or many small uranium ore deposits occur. The ore deposits in such provinces may be of different geological types and ages, indicating that in favourable areas widely different processes and controls at different times can yield different types of ore deposits for the same metal(s). Observation of the individual ore deposits seems to indicate that an inverse relationship exists between their reported grade and size. This is clearly demonstrated by the average size and grade of the uranium ore deposits making up the uranium reserves of the major producing countries.

Country	Reserves (tonnes U)	Av. ¹ ore grade (%U)	Av. ¹ size of the ore deposits (tonnes U contained)
USA [2]	259 000	≈ 0.195	≈ 2 300
Canada	185 000	≈ 0.1	> 10 000
South Africa	220 000	≈ 0.02	≈ 10 000
World reserves (1/1/73)	866 000	≈ 0.185	≈ 10 000

The South African uranium deposits represent a special case, since uranium is recovered there as a by-product of gold production. However, the low grade combined with the large size of the individual ore bodies is in line with the general observation. The metropolitan French ore reserves occupy an intermediate position between the US and Canadian deposits. Similar examples could be given for many other elements.

From an economic point of view this demonstrated "size/grade" relationship is very important as it allows, through economies of scale, the mining of large, low-grade deposits at a cost-price similar to that for the higher-grade, but generally much smaller deposits [3]. With development of the demand for uranium, a continuous trend towards larger and lower-grade deposits will be observed just as has been the case for copper deposits during the last 50 years.

In some cases mineral provinces can be subdivided into mineral districts which contain one or more ore fields or ore deposits, often of similar type and age (a good example is the Canadian Shield uranium province). These individual ore deposits and fields in turn can be divided into ore shoots. Even in ore shoots more or less widely varying concentrations of the ore metal can be found. Individual districts, fields and deposits also are known to occur outside the area of larger units.

Provinces and districts normally are considered highly favourable areas for the discovery of additional ore deposits. Generally they are characterized by higher concentrations of the ore metal than normal for areas of comparable size. The dimensions of such favourable areas may vary from

¹ Average is here used in the sense that 50% of the reported ore reserves occur in deposits with grade and/or size equal to or greater than the one indicated.

100 000 km² or more for mineral provinces to a 100 m² or less for individual deposits or ore shoots. These observations have been used in geochemical exploration to locate and delineate new deposits and districts. Many remarkable successes have been obtained and important ore deposits have been located by these methods. It also has been observed, however, that many of such apparently favourable areas did not contain the expected mineralizations. Apart from erroneous interpretation, sampling and other errors, it could be established that, in some of such apparently favourable high-background areas, the required ore-forming processes had not been operative or had resulted only in mineralizations of sub-marginal grades and sizes. Such areas appeared to be characterized by lower than normal dispersion of the measured metal concentrations around the high background [4]. This observation seems to indicate that the dispersion of the measured concentrations around the background concentration can be considered as an indication for the efficiency of the ore-forming processes in the sampled area [5].

By quantifying these observations, one may be able to determine more exactly the requirements for calling a given area favourable for the occurrence of ore grade and size mineralizations.

3. THE LOG-BINOMIAL DISTRIBUTION OF ELEMENTS IN THE GEOLOGICAL ENVIRONMENT

Different models have been proposed to describe the distribution of elements in the geological environment. Although the log-normal model [6] is most frequently used in geochemical exploration and ore reserve evaluation, it was found that the closely related log-binomial model as proposed by De Wijs [7] gives more consistent results when applied over very large probability ranges ($\gamma \pm > 3\sigma$). This model has the added advantage that it illustrates the foregoing qualitative observations on the results of geochemical exploration and the occurrence and distribution of ore deposits in a simple way [8].

In this model the geological environment (R) is considered as an inhomogenous mixture of a given element with a fixed average concentration X in a matrix material consisting of all other elements ($X \ll 1$).

Dividing the environment in two equal parts, the concentration of the given element in each of these parts will be either equal or unequal. With respect to the average concentration X one can describe the distribution of the element content M in the two parts of the environment as follows:

$$M = R \cdot X = \frac{1}{2} R \cdot X (1 - q_{1,1}) + \frac{1}{2} R \cdot X (1 + q_{1,1}) \quad (0 \leq q \leq 1) \quad (1)$$

It is easy to see an equivalence between this mathematical expression and the basic result of a hypothetical ore-forming process defined for equal volumes of the depleted and the enriched parts of the geological environment.

In this expression the value $q_{1,1}$ represents the efficiency of the given process for separating this particular element from its matrix material. Therefore the value of $q_{1,1}$ is a direct measure of the "specific mineralizability" of the element for this process.

For a value $q_{1,1} = 0$ the concentrations in both parts of the environment would be equal and the given process would not be ore-forming for this element. For a value $q_{1,1} = 1$ one part of the environment would not be a mixture any longer. By dividing the two parts of the environment again in two equal parts we find the metal content distributed as follows:

$$\begin{aligned}
 M = R \cdot X = & 0.25 R \cdot X (1 - q_{1,1}) (1 - q_{2,1}) + \\
 & 0.25 R \cdot X (1 - q_{1,1}) (1 + q_{2,1}) + \\
 & 0.25 R \cdot X (1 + q_{1,1}) (1 - q_{2,2}) + \\
 & 0.25 R \cdot X (1 + q_{1,1}) (1 + q_{2,2})
 \end{aligned} \quad (2)$$

and so on.

Continuing this subdivision it can be demonstrated that high concentrations with a pronounced tendency to group together are generated over the whole scale. Translated into the 3-dimensional geological environment such a process would result in provinces and districts and the concentrations X_i would become a regionalized variable in the sense of Matheron [6].

If $q_{1,1} = q_{2,1} = q_{2,2}$ the second and third terms of the equation would have the same concentration and metal content. However, the processes resulting in such equal concentrations could have been rather different in time and place. By choosing random values for $q_{i,j}$ around an average value Q and plotting the logarithms of the thus calculated concentrations (divided into $(i + 1)$ grade intervals) against their frequency of occurrence, a good fit with the i^{th} order binomial frequency distribution is usually obtained ($i \geq 8$). The concentrations actually found are situated on or around the probability density curve connecting the mid-points of the grade intervals, as can be observed by integrating the concentration frequencies.

Therefore, by taking an average value Q to represent the different values $q_{i,j}$, the distribution of a given element in the geological environment can be described by the general equation

$$M = R \cdot X = \sum_{k=0}^{\alpha} \frac{\binom{\alpha}{k}}{2^{\alpha}} R \cdot X (1 + Q)^{\alpha-k} (1 - Q)^k \quad (3)$$

where

α = a rational number indicating the order of subdivision of the environment

k = an integer, $0, 1, 2, \dots, N$ ($\alpha - 1 < N \leq \alpha$)

Considering the earth's upper crust with rather well-known average element concentrations as the environment of ore deposits and the reported reserves of given average size and grade as the measured probability of their occurrence in this environment, one not only can make an estimate of the value Q but can also calculate the probability of occurrence of resources for all possible size-grade specifications. Going one step further one now can estimate the exploration and exploitation costs for such resources as a function of their rarity, size and grade [9]. This has been done in Fig. 1 for uranium. The calculations are based on the uranium reserves

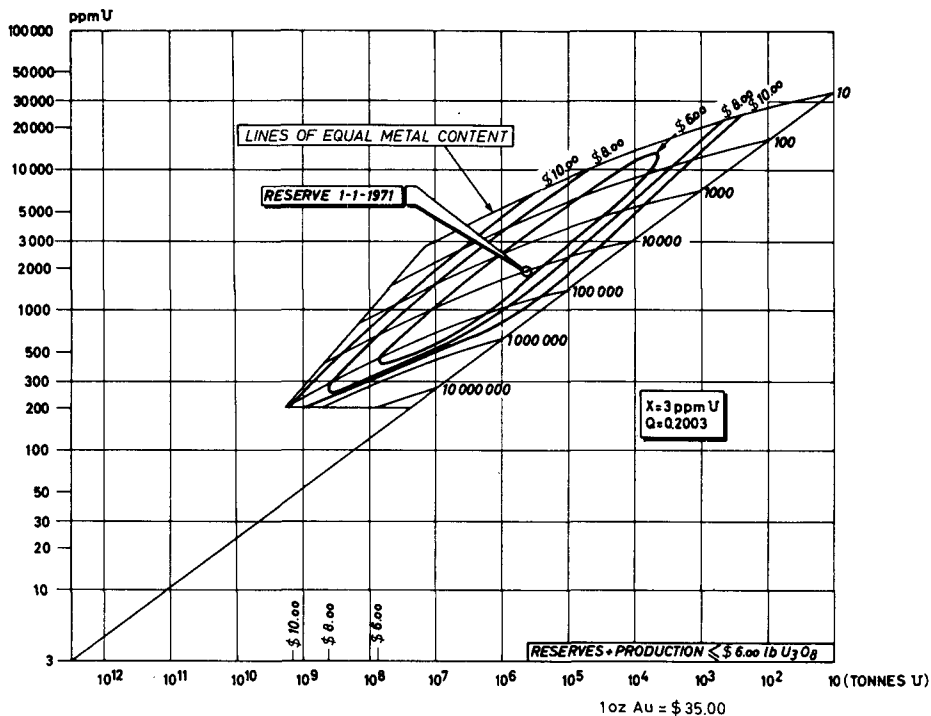


FIG. 1. Uranium resources and inferred potential reserves as estimated by the program MIMIC [9]. Numbers along diagonal refer to largest possible deposits for the given value of X and Q . Dollar values refer to estimated average exploitation costs.

which had been reported as of 1 Jan. 1971 and which have been largely confirmed by the official reserves estimate in the joint report by the OECD and the IAEA of August 1973. It should be noted that the dollar value refers to the old price of US \$35.00/oz Au. The calculations were made by the computer program MIMIC [10]. It was found that, by inserting the X and Q values for copper, lead, zinc and gold, close estimates of exploitation costs and resources also could be made for these elements without changing any of the economic parameters of the model. As a result of this observation, it was found by non-linear, multiple regression analyses on X , Q and the price that the long-term average price differences between these metals are determined within some 30% by their average concentration in the earth's upper crust and their specific mineralizability Q . Figure 2 illustrates this relation which recently has been extended to include estimates for mercury [11], molybdenum, antimony and manganese.

The long-term average price (P) for these elements per kg of contained metal in 1971 US \$ is determined to within some 30% by

$$P = \exp(8.96637 - 25.5688 Q)/(10^6 X) \quad (4)$$

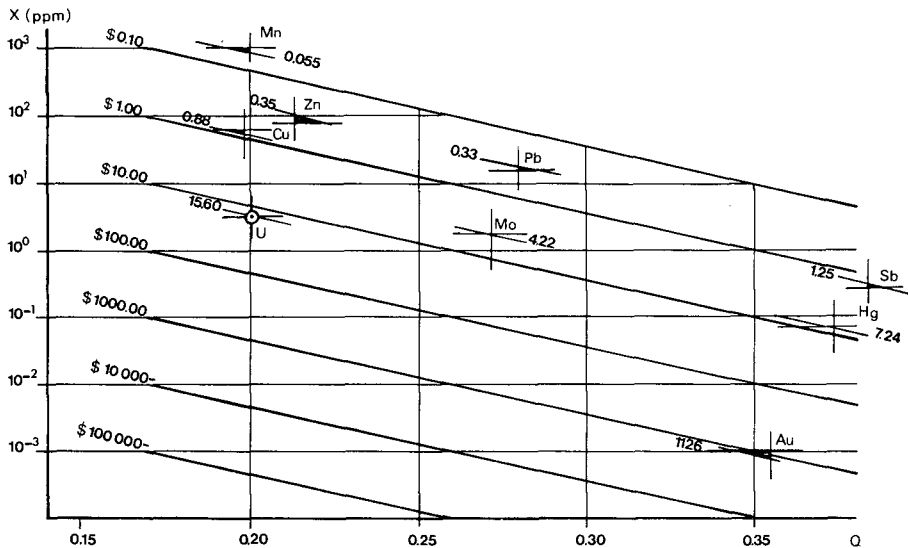


FIG. 2. Long-term average price differences of some non-ferrous metals and corresponding X and Q values as determined from reasonably assured reserves characteristics plus former production.

It is interesting to note that De Wijs found specific mineralizabilities of about 0.2 for copper, lead and zinc in hydrothermal fissure deposits of these metals and a specific mineralizability for gold in the range 0.35 - 0.45.

A geochemical stream sediment survey which was made in 1962 by the group for applied geochemistry of the Joint Research Centre (JRC) of Euratom in the Oslo Region, Norway, found Q values for copper, zinc and lead of respectively 0.197, 0.226 and 0.319. This indicates that similar values for the specific mineralizability for each of these elements can be expected to occur over the whole size-grade range of concentrations. They would be valid for regional prospecting of areas of 100 000 km² or more in which each sample may represent an area of 10 - 100 km², to the sampling of ore deposits in which each sample may represent as little as a few tonnes of material.

Figure 3 illustrates the grade-size relations for the concentration of an element with a specific mineralizability $Q = 0.2$ (uranium, copper) for the earth's upper crust. The environment for ore deposits is taken as 150 million km² of dry land surface to an accessible depth of 2.5 km. With a specific gravity of 2.7, this environment corresponds to 10¹⁸ tonnes of rock.

The standard deviation σ of the metal concentrations is a logarithmic value which depends on the value of Q and the order of subdivision of the environment (α):

$$\pm \sigma = 0.5 \sqrt{\alpha} \ln \left(\frac{1+Q}{1-Q} \right) \quad (5)$$

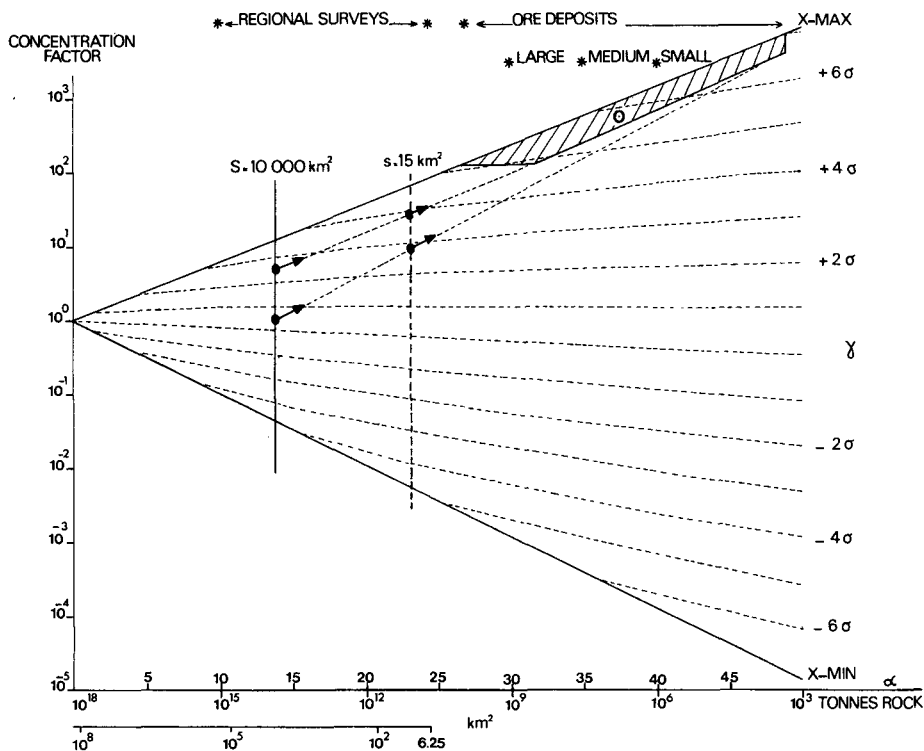


FIG. 3. Probability field for element concentrations in the earth's upper crust for a specific mineralizability $Q = 0.2$.

An estimate of the standard deviation can be made in the usual way from the results of geochemical surveys, core drilling or other sampling methods:

$$\sigma = \frac{\sum_{i=1}^n W_i (\ln x_i - \ln \gamma)^2}{(n-1) \sum_{i=1}^n W_i} \quad (6)$$

where

- n = number of samples
- x_i = concentration in the i^{th} sample
- γ = median concentration
- W_i = weight of the i^{th} sample

The median concentration γ is given by

$$\gamma = X (1 - Q^2)^{\alpha/2} \quad (7)$$

and can be estimated from survey results by:

$$\ln \gamma = \frac{\sum_{i=0}^n W_i \ln X_i}{\sum_{i=0}^n W_i} \quad (8)$$

The order of subdivision of the environment is estimated from the sample weights with respect to the sampled environment:

$$\frac{W}{w} = 2^\alpha \quad (9)$$

where

W = weight of the environment

w = average sample weight

$$w = \frac{1}{n} \sum_{i=1}^n w_i \quad (10)$$

and from Eq. (9)

$$\alpha = \frac{\ln(W/w)}{\ln 2} \quad (11)$$

With the estimated values for σ , γ and α , the specific mineralizability Q can be estimated from Eq. (5):

$$Q = \frac{e^{\sigma/0.5\sqrt{\alpha}} - 1}{e^{\sigma/0.5\sqrt{\alpha}} + 1} \quad (12)$$

For each value of α the maximum and minimum expectable concentrations are given by

$$X_{\max} = X(1+Q)^\alpha \quad (13)$$

$$X_{\min} = X(1-Q)^\alpha \quad (14)$$

All concentrations outside this range should be considered truly anomalous and not representative of the given set of concentrations and sample weights.

Ore-grade and size mineralizations corresponding to the area of possible ore reserves of Fig. 1 are indicated by vertical lines for concentrations between $\ln \gamma + (5 \text{ to } 7)\sigma$ and can be roughly divided into

Large deposits: $3 \times 10^7 - 1 \times 10^9$ tonnes ore ($30 \leq \alpha < 35$)

Medium deposits: $1 \times 10^6 - 3 \times 10^7$ tonnes ore ($35 \leq \alpha < 40$)

Small deposits: $< 1 \times 10^6$ tonnes ore ($\alpha \geq 40$)

For a Q value of 0.2 the minimum enrichment with respect to the average concentration in the crust should be about $130 \times (\approx 400 \text{ ppm U})$.

This does not necessarily mean that for elements of high average concentration in the crust (> 0.007) the Q value necessarily has to be smaller than 0.2. It only means that an upper concentration limit exists beyond which the partial environment becomes saturated. Theoretically this condition will be reached for all elements at the concentration 1. In practice, this limit will be set by the concentration of the element in its most common ore mineral. In such saturated environments (most iron ore deposits for example) the concentrations are no longer distributed log-binomially and Q values calculated for such deposits would not be representative of the environment as a whole. For uranium, with an average concentration of 3 ppm, the concentration in possible ore deposits varies between 400 ppm and some 3%, whereas the limiting concentration would be the U content of pitchblende (85% U).

In Fig. 3 a hypothetical regional geochemical survey is indicated for an area S of $10\,000 \text{ km}^2$ in which individual samples s represent independent sub-areas of average area 15 km^2 .

The survey area of $10\,000 \text{ km}^2$ represents one sample out of a possible number of $2^\alpha = 15\,000$ equal-sized areas with different average uranium contents varying between the extremes $X_{\max} = X(1+Q)^\alpha$ and $X_{\min} = X(1-Q)^\alpha$.

For a Q value of 0.2, only regions with an average uranium content of at least $5 \times$ the crust's average or 15 ppm could be considered potentially favourable for the occurrence of uranium ore deposits. Individual sample areas ($\alpha = 23.22$) should contain at least 30 times the crust's average to be indicative of possible uranium ore deposits.

Very few regional survey areas of this size would be found to contain such a high average uranium content and in view of the relative rarity of uranium ore deposits this is not at all surprising. However, for a region of size S a high specific mineralizability also could result in economic mineralization. The figure indicates that, for a regional average uranium content equal to that of the earth's crust (3 ppm), the specific mineralizability should be at least 0.267 and favourable individual samples in this case should contain 30 ppm or more.

The favourability of a given area for possible ore deposits depends not only on X and Q but also on the size of the area with respect to the size of the total environment. The equivalence between X and Q with respect to the favourability of an area is determined from expression (4). Defining P_R as the long-term average price indicated by the average concentration X_R in the earth's upper crust and the specific mineralizability Q_R as found from the ore reserves of an element, P_S would be a hypothetical price for specific mineralizability Q_S and average concentration X_S as found by the regional survey. For $P_R/P_S > 1$ the conditions in the survey area would be relatively more favourable for the occurrence of ore deposits than in a randomly selected average area of size S . The minimum value for this ratio that would indicate possible ore deposits depends on the size of S with respect to the total environment. Taking into account the equivalence of X and Q Eq. (4), Fig. 3 shows that the ratio P_R/P_S should be equal to or greater than $(1+Q)^{\alpha-5}$.

From the foregoing discussion, a dimensionless favourability index F_S can be defined as follows:

$$F_S = P_R/P_S (1+Q)^{\alpha-5} \quad (15)$$

Previously, only values for $F_s \geq 1$ would be indicative of ore potential. In practice, however, the sampling of such large areas will introduce a number of sampling, analytical and normal statistical errors, some of which may be systematic and due to geological or human factors beyond the control or correction of the sampler. Expert judgement, therefore, nearly always will be required for the interpretation of the survey results. A few generalizations can be made in this respect:

- (a) The most representative samples for regional surveys usually can be obtained from recent stream sediment. Here, nature has largely solved the problem of proportional representation of all parts of the sampled drainage basin.
- (b) The contribution of even the best-exposed average uranium ore deposit to the concentration of uranium in the regional sample is small with respect to the total contribution of the surrounding host rock. Dispersion trains from ore-grade mineralizations therefore normally will not be recognized in regional surveys.
- (c) To assure sufficient vertical representation, certain geological conditions have to be fulfilled in the survey area and the individual samples should represent average drainage basins of at least 6 km². A maximum of only S/s independent samples could be taken, the sample size s being dependent on the drainage pattern.
- (d) The statistical error for individual samples is much larger than for the regional average, whereas normally no Q values are known for the individual samples.
- (e) Most regional surveys will fail to indicate ore potential for any particular metal.
- (f) Owing to the low sample density and therefore generally high sampling cost, multi-element surveys are to be recommended. They not only reduce the cost per element per km² and increase the chances for finding at least some kind of ore potential but also enable recognition of man-made pollution of the stream sediment.

It is the considered opinion of the author from his, admittedly limited, personal experience in tropical and temperate climates that such regional geochemical surveys do reflect the metallogenetic character of the surveyed areas much better than generally believed and that favourable ore potential is not easily missed by these methods.

REFERENCES

- [1] OECD Nuclear Energy Agency and IAEA, Uranium - Resources, Production and Demand (Joint Report by the OECD and the IAEA), OECD, Paris (1973).
- [2] PATTERSON, J. A., "Character of the United States uranium resources", Uranium Exploration Geology, (Proc. Panel Vienna, 1970), IAEA, Vienna (1970) 117.
- [3] MABILE, J., "Long-range trend for uranium", Nuclear Fuel - Exploration to Power Reactors (Proc. Conf. Oklahoma City, Okla. 1968), Southern Interstate Nuclear Board, 800 Peachtree St. N.E., Atlanta, Georgia 30308 (1968).
- [4] HAWKES, H. E., WEBB, J. S., Geochemistry in Mineral Exploration, Harper & Row, New York (1962).
- [5] TAUSON, L. V., KOZLOV, V. D., KUZ'MIN, M. I., "Geochemical criteria for ore-bearing potential in granitoid intrusions" in Proc. 23rd Int. Geol. Congr., Prague, 1968; Academia Prague (1968).
- [6] MATHERON, G., *Traité de Géostatistique Appliquée*, Mém. du B.R.G.M. 1 (1962).

- [7] DE WIJS, H.J., "Statistics of ore distribution, Part II: Theory of binomial distribution applied to sampling and engineering problems", Geol. Mijnbouw 15 (1953).
- [8] BRINCK, J. W., Calculating the world's uranium resources, Euratom Bulletin 6 4 (1967).
- [9] BRINCK, J. W., "Prediction of mineral resources and long-term price trends in the non-ferrous metal mining industry" in Proc. 24th Int. Geol. Congr., Montreal, 1972; Int. Geol. Congr., 601 Booth St., Ottawa (1972).
- [10] BRINCK, J. W., MIMIC, Euro Spectra 10 2 (1971).
- [11] BRINCK, J. W., VAN WAMBEKE, L., World Resources of Mercury, 1st Int. Mercury Congr., May 1974, Univ. of Barcelona, Barcelona.

GEOCHEMICAL FACTORS CONTROLLING THE FORMATION OF THE SECONDARY MINERALS OF URANIUM

M. DALL'AGLIO, R. GRAGNANI, E. LOCARDI

CNEN - Laboratorio Geominerario,

CSN - Casaccia,

S. Maria di Galeria (Rome),

Italy

Abstract

GEOCHEMICAL FACTORS CONTROLLING THE FORMATION OF THE SECONDARY MINERALS OF URANIUM.

The formation of secondary uranium minerals directly from natural waters is examined in this paper. There is evidence of some geochemical processes which are capable of creating conditions favourable for the precipitation of secondary minerals, even when there are no primary uranium (IV) occurrences.

Direct experience indicates that at least two hydrogeochemical processes are responsible for the precipitation of secondary uranium minerals; namely (1) the leaching of crystalline rocks, even with a normal content, under particular erosion and weathering conditions in the wet temperate climatic zone. This process occurs, for instance, on the Sila Plateau in the Calabria region (Italy), where autunite is still precipitating; and (2) evaporitic processes of inland waters under arid climatic conditions, an example of which is furnished by carnotite deposits in the calcrete area of Western Australia.

In the paper the results obtained in the course of hydrogeochemical studies carried out in the Sila Plateau and in Western Australia are presented. The secondary mineral precipitation as a step towards the forming of uranium ore bodies in a multistage minerogenetic process is discussed.

1. INTRODUCTION

The last twenty years of uranium research has been marked by a constantly growing interest in deposits of sedimentary origin, and in the problems connected with their genesis. Quite recently the discovery of uranium occurrences of supergene origin, under environmental conditions hitherto considered unfavourable to the deposition of uranium (for instance the deposits in calcrete), have called attention emphatically to the genetic conditions of the secondary minerals. In the light of these new minerogenetic situations a critical examination becomes necessary of studies made in the last 10 years on the environmental and geochemical conditions controlling the formation of secondary minerals of uranium. This examination of the genetic models studied and proposed by the research workers of many countries has pointed out how our knowledge up to now was unfortunately incomplete, mostly because the studies were focused on only a few environmental and geochemical aspects of the problem, without giving due consideration to other aspects of importance equal to those studied up to now.

In particular, as far as the accumulating uranium in secondary minerals directly from natural waters is concerned, present knowledge is quite inadequate. This is easily accounted for historically by the fact that almost all the minerogenetic studies have been made on occurrences of secondary uranium minerals which were formed in the vicinity of deposits of uranium

in the reduced state, where there are favourable conditions for a very high uranium concentration in the waters.

The purpose of the present paper is to try to improve knowledge of the most important geochemical factors controlling the formation of the secondary uranium minerals. In particular, an attempt will be made to reconstruct the supergene conditions favourable to the direct precipitation of carnotite and autunite from natural waters.

From the geochemical viewpoint there are many processes that may create conditions favouring the precipitation of secondary uranium minerals from natural waters, even when there are no primary deposits of uranium. Our experience has shown that at least two geochemical processes favour the formation of secondary minerals of uranium, namely

- (a) The leaching of crystalline rocks, even with a normal uranium content, under particular erosion and weathering conditions in the wet temperate climatic zone. This process occurs, for instance, on the Sila Plateau in the Calabria region (Italy), where autunite is still precipitating
- (b) Evaporitic processes of inland waters under arid climatic conditions, an example of which is furnished by carnotite deposits in the calcrete area of Western Australia.

2. FACTORS CONTROLLING THE PRECIPITATION OF CARNOTITE AND AUTUNITE

2.1. General remarks

In the last ten years many excellent papers have been devoted to the study of the formation conditions of carnotite and autunite [1 - 4]. As has already been observed, the above papers refer to the study of the genetic conditions of secondary mineralizations of uranium formed in the vicinity of primary occurrences of uranium (IV). The results given in the above publications thus cannot be extrapolated to the minerogenetic conditions dealt with in this paper. There is, as yet, no information on the geochemistry of the waters near the secondary mineralizations still in formation.

In general, from the physicochemical viewpoint the precipitation of a secondary uranium mineral depends on

- (a) Values of physicochemical parameters such as pH, Eh, etc.
- (b) Concentrations in waters of precipitating anions, such as phosphate, vanadate, and arsenate
- (c) Concentration of uranium
- (d) Concentrations of the anions that form quite stable complexes with the uranyl ion.

The UO_2^{2+} ion forms very stable complexes with some of the major constituents dissolved in natural waters, such as carbonate, and sulphate. The reaching of the solubility products of secondary minerals also depends on the activity value of the uranyl ion. This value varies by many orders of magnitude as a function of the variation in the concentration of its chelating anions, with the uranium concentration remaining constant. Especially important in this regard is the carbonate ion which forms a very stable complex with the uranyl ion ($K = 10^{-24}$).

Even if, at present, the published free energy values (ΔF) for the most important secondary minerals of uranium seem to be basically correct, quite little is known about the kinetics of the precipitation and dissolution reactions of the secondary minerals, and about the real geochemical processes that take place in nature. In particular, information is lacking on the following aspects of the problem.

- (a) Quite little is known about the role of organic matter and clay minerals in adsorbing uranium from natural waters. This may permit the UO_2^{2+} activity to reach high values at the surface of the secondary minerals. The example provided by Muto and co-workers [2] might better define the problem. The solubility curves for carnotite and autunite, versus pH values show a minimum uranium concentration (about 10^{-7} moles) for pH 6. The adsorption curve of uranium by kaolinite shows a minimum uranium concentration, also for pH 6, but the value is much lower, i.e. 10^{-8} moles.

Organic matter and clay minerals might thus play the role of catalysers in the precipitation of the secondary uranium minerals.

- (b) Nothing is known about the role played by each of the above-mentioned variables (Eh and pH values, and the concentration of anions chelating the UO_2^{2+} ion) in precipitating the secondary uranium mineralizations found in nature. The above papers for the most part give the results of the study of the paragenesis of the minerals. They deduce from a theoretical basis the minimum uranium concentration in equilibrium with the secondary minerals as a function of physicochemical parameters (pH, Eh etc.), with the concentrations of the precipitating and chelating anions remaining constant. But neither in the papers referred to, nor in other sources, is precise information available on the role of the other factors controlling the precipitation of the secondary uranium minerals; an example may clear up what has just been said. Carnotite is the most widespread secondary mineral of economic importance. But almost nothing is known about the ways vanadium circulates in the mineralized areas, about the vanadium contents in natural waters in equilibrium with the carnotite, and about the range of the variation of its content in the waters. In other words no complete hydrogeochemical studies have been made in areas where secondary minerals of uranium had been – or still are – precipitating. Thus knowledge of the real geochemical processes, taking into account their variability due to the differences of environmental conditions, is incomplete.

2.2. The solubility of carnotite and autunite under natural conditions

To improve knowledge of the precipitation of the secondary minerals under natural conditions, field and laboratory studies were carried out as follows.

- (a) Natural waters were analysed which are presumed to be in equilibrium with carnotite and autunite.
- (b) The concentrations of uranium, vanadium and the major constituents were determined in waters which were previously maintained in contact for a long time with rock samples containing secondary uranium minerals.

TABLE I. CHEMICAL COMPOSITION OF WATER SAMPLES ASSUMED TO BE IN EQUILIBRIUM WITH CARNOTITE (SAMPLE 1) AND WITH AUTUNITE (SAMPLE 2).

Sample	pH	Ca	Mg	Na	K	HCO ₃ ⁻	SO ₄ ²⁻	Cl ⁻	SiO ₂	P ₂ O ₅	U
					(meq/l)				(mmole/l)		(pp 10 ³)
1	7.1	1.7	0.62	1.5	0.46	0.30	2.6	1.0			1.27
2	6.3	0.18	0.06	0.37	0.027	0.29	0.07	0.28	0.36	0.002	0.55

TABLE II. U AND V CONTENTS AND THE CHEMICAL COMPOSITION OF WATER SAMPLES MAINTAINED IN CONTACT FOR A LONG TIME (APPROX. 1 MONTH), UNDER CONTINUOUS MIXING, WITH ROCK SAMPLES SOME OF WHICH CONTAIN CARNOTITE, i.e. SAMPLES No. 1, 2, 5, 6, 7, 8, 9.

All the leaching tests were carried out with distilled water except sample No. 5 in which natural waters from Western Australia were used.

Sample	pH	Ca	Mg	Na	K	HCO ₃ ⁻	SO ₄ ²⁻	Cl ⁻	SiO ₂	U	V
										(pp 10 ³)	(pp 10 ³)
					(meq/l)				(m moles/l)		
1	8.6	0.50	1.67	1.06	0.29	3.1	0.18	0.096	0.19	2841	1192
2	8.5	0.77	1.37	2.22	0.57	3.5	1.0	0.18	0.42	2018	564
3	8.4	0.45	0.74	3.52	0.33	3.1	0.55	0.90	0.40	67.8	142
4	8.4	0.21	0.39	3.41	0.33	3.5	0.44	0.12	0.34	44.1	129
5	8.5	3.7	15.7	53.9	0.027	3.8	13.1	61	0.54	2171	922
6	6.7	0.095	0.067	1.48	0.34	0.26	0.37	1.2	1.2	1.08	245
7	7.1	0.39	0.20	1.0	0.013	0.58	0.27	0.074	0.78	2.64	1094
8	7.1	0.11	0.076	0.71	0.31	0.31	0.28	0.56	1.3	2.1	41
9	7.1	0.033	0.041	0.45	0.22	0.17	0.11	0.53	1.0	1.61	114

Both a sample of water squeezed out of the diatomite containing carnotite (Northern Latium) [5], as well as a sample of spring water from Sila, Calabria, which deposits autunite, have shown extremely low uranium contents, that is, of the order of $1 \text{ pp } 10^9$, and a very low bicarbonate content. The results of the analyses, given in Table I, are in considerable disagreement with the results given by Hosteltler and Garrels [1] and by Muto and co-workers [2], in the sense that the samples we analysed show a much lower uranium content than might be expected on the sole basis of the data on the solubility of the carnotite and autunite.

It is beyond the scope of this paper to establish what processes and what chemical equilibria actually take place between the various substances (waters, secondary uranium minerals, organic matter, clay minerals, etc.) which control the uranium concentration in the waters analysed. The circumstance worthy of notice is, however, that much lower uranium contents were found than expected on a theoretical basis for waters assumed to be in equilibrium with the secondary minerals of uranium.

Table II gives the analytical results for samples of water kept in contact with carnotite contained in various types of rock. The results obtained can be thus synthesized

- (a) The waters kept in contact with diatomite containing carnotite show a very low uranium content, and this agrees well with the content found in the water sample squeezed out of the diatomites. These waters are always characterized by a very low bicarbonate content, and thus a very low content of CO_3^{2-} , which is the most effective uranyl chelating ion.
- (b) The V to U ratio in the waters is found to vary widely and does not always correspond to the ratios in carnotite. The theoretical equilibria with the secondary minerals are not the only processes conditioning the U and V contents in waters. The equilibria of each of the two elements with clay minerals, organic matter, etc. are more important in conditioning the U and V content in solution.
- (c) The uranium content in the waters depends a great deal on the salinity of the waters, and even more on the bicarbonate content.

It is already possible to draw some general minerogenetic conclusions.

- (a) The equilibria established in nature are much more complicated than might be deduced from the thermodynamic data on the solubility of the uranium secondary minerals.
- (b) The uranium contents corresponding to the solubility of carnotite and autunite may vary a great deal (several orders of magnitude) as a function of the different environmental and geochemical conditions. It is to be stressed that the uranium content in waters, in equilibrium with its secondary minerals, mostly depends upon the activity of the carbonate ion.

3. GENESIS OF THE AUTUNITE MINERALIZATIONS IN SILA (CALABRIA)

On the Sila Plateau (Calabria, Southern Italy), mineralizations of autunite have been detected which do not show a genetic tie with possible primary uranium occurrences in the reduced state.

The main geological events that have intervened in the settlement of the Sila crystalline massif, may be summarized thus

- (a) During the Hercynian orogenesis, quartz-dioritic plutons and their associated metamorphic rocks were granitized, migmatized, and intruded by epi-granites.
- (b) During the Mesozoic the massif gradually uplifted, and only its borders are mantled by marine sediments.
- (c) During the Apenninic orogenetic period (Cenozoic) the tectonic was of a compressive type, and gave rise to large-scale overturnings and overthrusts. On the marginal parts of the massif the crystalline formations overlap phyllitic formations or unmetamorphosed Mesozoic sediments.
- (d) The Miocene sediments are transgressive on almost the whole massif. An emersion followed for the whole Calabrian range, and then an uplifting, which is estimated at over a 1000 m during the Quaternary, occurred.

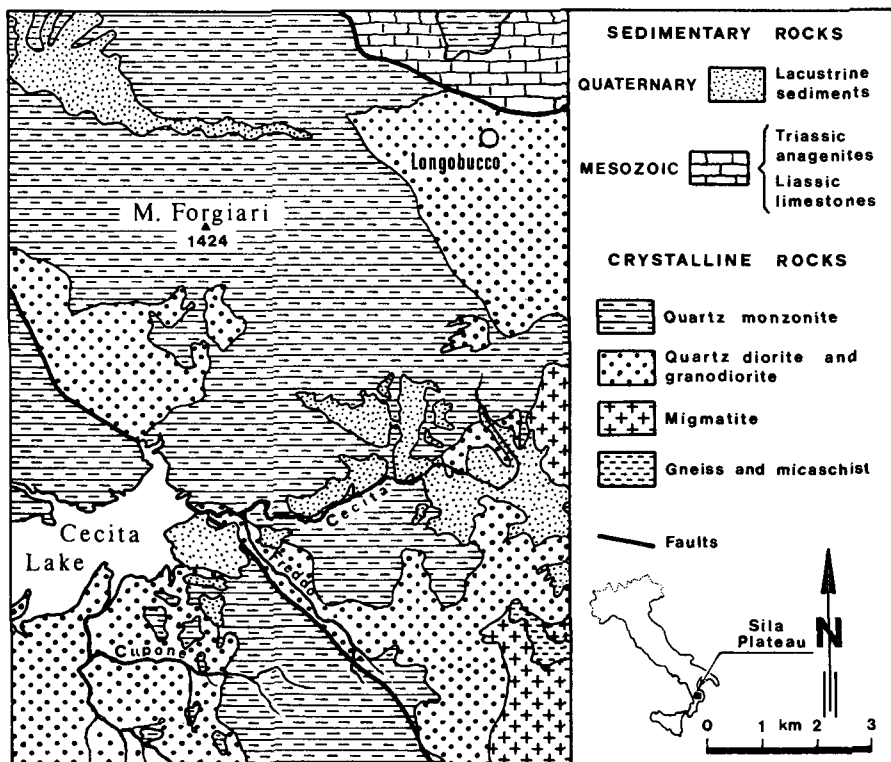


FIG.1. Geological map of the Sila Plateau area, where autunite mineralizations occur.

The central sector of the "Sila Grande", which we are considering here, most likely remained above sea level since the Upper Paleozoic. The transgressive Miocene sediments are marginal to this sector, and are found up to altitudes of 1300 m above sea level. Therefore one can assume an uplift of the central part by more than 1300 m during the Neogene. In the recent Quaternary, traces of this uplift can be found in a series of terraced lacustrine deposits.

From the height of Lake Cecita basin (1140 m), a series of unconsolidated lake sediments are deposited on progressively higher levels up to 1350 m, limited on the SW by a tectonic line that follows the course of the Freddo River, Mucone Valley (Fig. 1). This tectonic line separates two zones of differential uplift in the massif, with the relatively uplifted block in the northeastern sector. The rising is also marked by an intense morphological rejuvenation, by the erosion of the thick weathering cover which is characteristic of the Sila crystalline rocks, by the capturing of torrents and by a considerable general disequilibrium of the hydrological system.

The two sectors which are separated by the tectonic line are made up of the same lithological complex: granodiorites varyingly intruded by aprites, pegmatites and by quartz-monzonitic batholites. Even the uranium content of these complexes is uniform, being 2-3 ppm. But the radioactivity anomalies distinctly differentiate the two sectors.

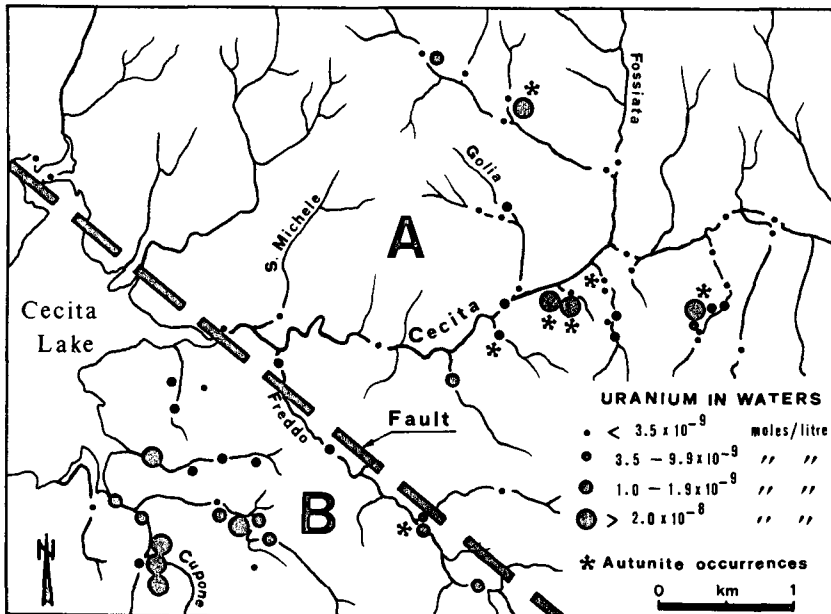


FIG.2. Uranium distribution in stream and spring waters from the Sila Plateau.

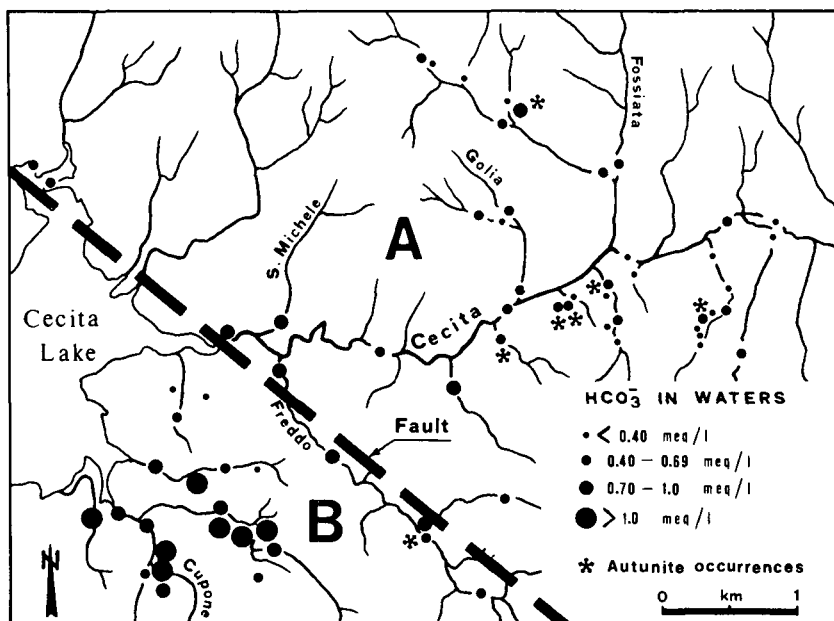


FIG. 3. Bicarbonate distribution in stream and spring waters from the Sila Plateau.

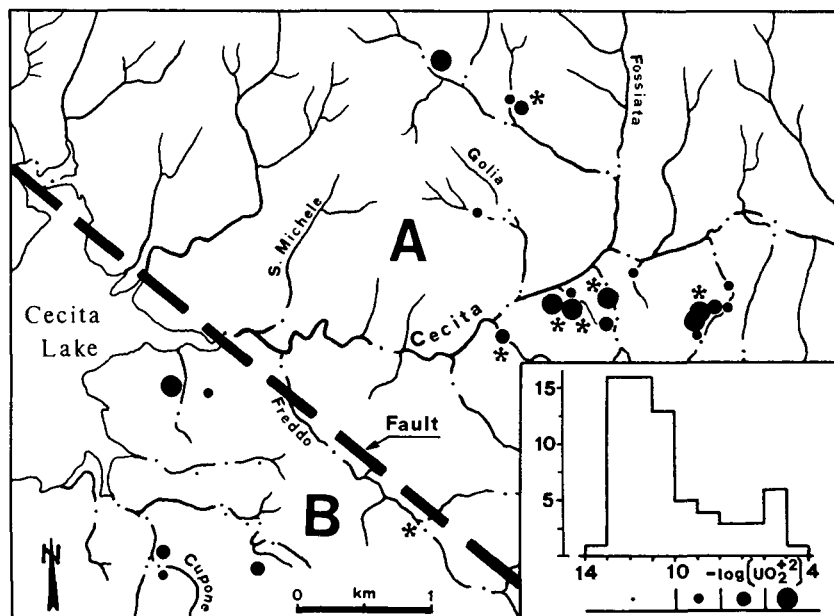


FIG. 4. Uranyl ion activity computed taking into account pH values and bicarbonate content. Spring and stream waters from the Sila Plateau.

Almost all the radiometric anomalies correspond to the block of relative uplift, and are due to:

- (a) Autunite crystallizing into lithoclasts of crystalline rocks and into lacustrine coarse sediments
- (b) Uranium adsorbed in soils and in lacustrine sediments rich in organic matter
- (c) Radon emanating from rocks and transported by the ground waters.

On the other hand, the non-rejuvenated sector is characterized by a large quantity of uranium dissolved in the surface and ground waters. Some weak radiometric anomalies are found in correspondence with radon emanations.

In the zone in which the autunite mineralization occurs, a study was made on the distribution of uranium, phosphate and the major constituents dissolved in spring and stream waters. The sampling sites are given in Fig. 2, as well as the distribution of the uranium content in waters. Figure 3 gives the distribution of the bicarbonate content, and Fig. 4 gives the distribution of the values of the uranyl ion activity, calculated on the basis of the formula

$$\log \frac{[\text{UO}_2(\text{CO}_3)_2(\text{H}_2\text{O})_2^{2-}]}{[\text{UO}_2^{2+}]} = -6.9 + 3 \log [\text{HCO}_3^-] + 3 \text{ pH}$$

The data presented suggest the following considerations.

- (a) The uranium distribution in waters reflects the different structural situations of the area studied. The sector of recent uplifting (A in the map) shows, on the average, relatively low uranium content in water; i. e. approx. $1 \text{ pp } 10^9$. It should be pointed out that the Cecita river, the waters of which leach this sector, has always shown — in different seasons — a content below $1 \text{ pp } 10^9$.

The sector SW of the tectonic line (B on the map) shows, on the other hand, average uranium content much higher, i. e. more than $10 \text{ pp } 10^9$.

- (b) The two sectors mentioned above are clearly differentiated as to the distribution of bicarbonate in waters. Unlike the low value in zone A, the bicarbonate content is much higher in zone B. The waters of the latter basin only leach crystalline rocks, and thus the relatively high bicarbonate content is attributable to the high maturity of the waters in question.
- (c) The distribution of the uranyl ion activity values (Fig. 4) shows still another clear difference between the two zones. It should be noted, however, that in area A there are waters that show higher activity, and this in apparent contrast with what was shown by the uranium distribution in waters. Here we point out the correspondence between the area in which the autunite precipitates and the area with higher uranyl ion activity in waters.
- (d) Going into greater detail, both the uranium contents and the activity values calculated for the uranyl ion present a bimodal distribution. All the water samples richest in uranium correspond to autunite mineralizations located above the present water table. Measurements of

the radioactive equilibria of the autunite mineralizations show active processes of dissolution ($Ra > U$). On the contrary, the autunite mineralization found below the present water table shows radioactive disequilibrium due to an excess of uranium.

- (e) In area A not all the uranium is concentrated in autunite; a generally higher quantity of uranium is fixed in the levels of the lacustrine sediments which show high contents of clay minerals and organic matter. Even in this case the uranium circulation is particularly intense where the water table emerges.

All of the above phenomena indicate that between very similar geological zones the process of autunite precipitation took place, and continues to do so, only in the zone corresponding to a recent uplifting of the crystalline block. This recent uplifting caused a hydrological rejuvenation, allowing, on the one hand, the circulating waters to reach formations not previously subjected to intense circulation of the waters, and causing, on the other hand, a change in chemical composition of waters towards a low salinity value. It is definitely this particular water chemism that causes the precipitation of the autunite.

4. SUPERGENE MINEROGENETIC PROCESSES IN THE CALCRETE AREA OF WESTERN AUSTRALIA

4.1. Introduction

The recent discovery of carnotite deposits in the calcrete area of Western Australia and of Somalia have called the attention of research workers throughout the world to the minerogenetic problems connected with the formation of this type of deposit under environmental conditions that were previously considered unlikely to yield uranium deposits.

There is no direct information available for the two above-mentioned uranium deposits; in fact no studies on the minerogenesis of this type of deposit have been published as yet.

However, an attempt will now be made to define the terms of the minerogenetic problem on the basis of (1) the hydrogeological studies made by the Geological Survey of Western Australia on the calcrete aquifer of this zone, (2) the information provided by the geologists of the Geological Survey of Western Australia, and (3) the hydrogeochemical data gathered in a calcrete area near the Yeelirrie deposit.

In this area a very mature morphology is the effect of erosion processes active for a very long time under conditions of high geological stability of the Archean shield. The area was deeply eroded during the Cenozoic period by a major river system. The permanent surface water has disappeared, and at present, almost only ground water circulates in the calcreted aquifer. The rainfall is low, i.e. about 10 in. a year. Under these conditions there are many small basins each of which is, roughly speaking, a geochemically closed system as regards the leaching and precipitation of the elements. In these basins the complete supergene geochemical cycle, from the leaching processes up to the concentration of soluble elements in salt lakes, is reproduced on a small scale.

4.2. Environmental conditions and hydrogeological and hydrogeochemical characteristics of Western Australia

The hydrogeology of the calcrete area of Western Australia has been the subject of exhaustive studies on the part of the Geological Survey of Western Australia [6] because calcrete constitutes the most important aquifer of the zone, which supplies the fresh and brackish water demand. From the hydrogeological and hydrogeochemical viewpoint the calcrete environment has its own peculiar characteristics.

- (a) It has already been pointed out that from the leaching of the outcropping rocks at the borders of the basin, up to the concentration of all the soluble components in the salt lake, the waters go through the whole hydrological cycle in the space of only a few kilometres, unlike elsewhere in the world where this cycle takes place over entire continents. In more general terms, water in this zone quickly matures in a short space, i.e. in only a few kilometres. This is due to the extremely low value of the hydraulic gradient (less than 0.001) of the very slow movement of water in the calcrete drainage, and to the particular climatic conditions of the area.
- (b) The evolution of the chemism of the waters along the whole length of their course shows a general behaviour dependent upon an evaporitic type process (cf. Fig.5).

Generally speaking, the succession of the minerals that precipitate from the waters along their route (carbonates and in part gypsum in the calcrete, gypsum and sodium chloride in the salt lakes) belongs to a typical evaporitic sequence.

- (c) The extremely mature morphology of the basins, the protracted water-rock interaction and the desert climatic conditions favour precisely the process of extraction from rocks, and separation and concentration of the most soluble elements by the waters. No quantitative data are available on the ratio between the transport of elements in the particulate form and in solution in this type of basin, but for the most soluble elements this ratio must be in favour of the transport into solution, as shown by the accumulation of enormous quantities of calcium and magnesium carbonate precipitated by the waters as calcrete.
- (d) The particular climatic conditions, characterized by low average rainfall (approx. 200 mm/a), by high average temperature and low average humidity, favour the rapid combustion of the organic matter produced by the small biota mass supported by these environmental conditions [7]. It is also unlikely, under such environmental conditions, for the organic matter to be present in quantities high enough to create oxido-reduction barriers.

4.3. Geochemical behaviour of uranium and vanadium under the environmental conditions of Western Australia

In the light of the above considerations, it is best to examine the geochemical supergene behaviour of uranium and vanadium to clearly identify the minerogenetic processes acting in the Yeelirrie deposit.

Uranium shows a striking tendency to pass into the water phase in the course of water-rock interaction, which occurs in the first part of

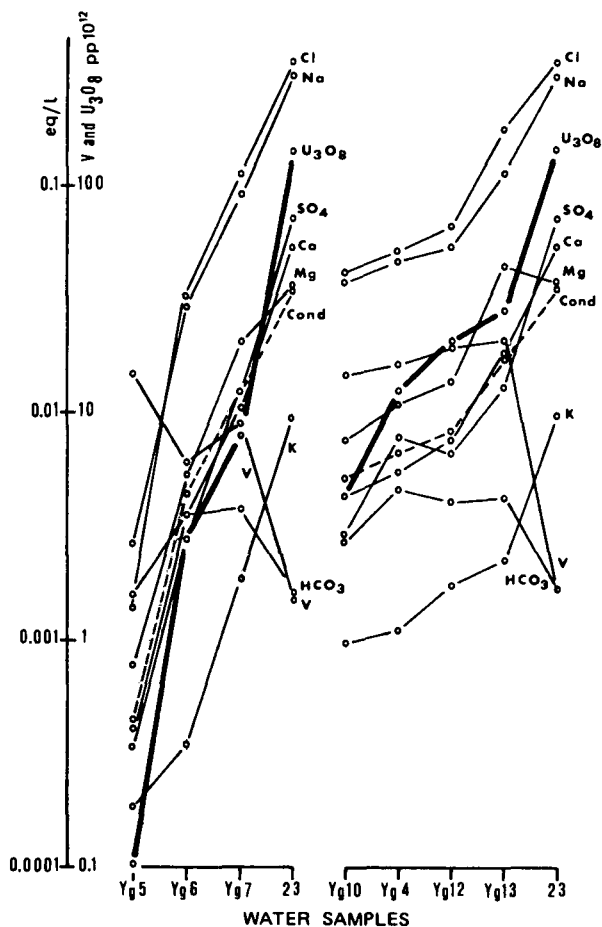


FIG. 5. U and V contents, and chemical composition of water samples from a calcreted basin from Western Australia. Samples arranged according to the increasing maturity of the waters.

the hydrological cycle, in which the meteoric waters leach the outcropping rocks. As a result of the interaction between water and the alteration products, the uranium tends to redistribute between the solid phases and water according to the equilibria that take place between waters and substances that can precipitate uranium (organic matter, and, to a lesser extent, clay minerals) [8].

During the evaporitic processes uranium tends to concentrate a great deal in the waters. The only process that can remove considerable amounts of uranium from the waters and the brines is the adsorption by the organic matter and the clay minerals in suspension [9].

It is also known that in the supergene environment, under oxidizing conditions, uranium is generally one of the most soluble and mobile trace

elements, mostly owing to the high stability of its complexes with carbonate, and to a lesser degree with sulphate and chloride.

Under the environmental conditions of the calcrete area of Western Australia, the uranium content in the waters tends to increase indefinitely as the natural waters gradually become more mature.

The primary source of uranium that accumulated in the deposit may be the granitic formations of the Archean shield that outcrop in extensive zones of numerous basins, including the Yeelirrie basin.

The supergene geochemistry of vanadium is only known in its general aspects and not so much is known about it as about uranium. Direct information as yet is lacking especially on the distribution and circulation of vanadium in fresh waters. Vanadium however seems not to have a very high geochemical mobility; its supergene geochemistry seems to be more strikingly conditioned by the presence of organic matter than in the case of uranium.

In the environment considered here, the rapid process of combustion of the organic matter, though not generally affecting the circulation of uranium, can have quite a striking effect on vanadium. Nevertheless, the vanadium content may also tend to increase in water under the environmental conditions existing in this area.

4.4. Possible minerogenetic processes of the Yeelirrie deposit

Figure 5 synthesizes the results of a hydrogeochemical study carried out in a calcrete basin not much different from the Yeelirrie one. In the diagrams presented, the composition pattern of the waters versus increasing geochemical maturity is given. The samples gathered show the different stages of the hydrological cycle, from the leaching of the granite, passing through the calcrete aquifer, up to the salt lake found at the end of the basin. The two diagrams correspond to the ground waters of independent small basins that flow into the same salt lake.

The data given show how, along with the regular increase in the salinity, there corresponds a gradual change in the chemical composition; the most soluble salt contents (CaSO_4 and NaCl) gradually increase. Moreover, there is a decrease in the HCO_3 content.

The uranium content shows a regular increase up to $120 \text{ pp } 10^9$. Also, the rate of increase of the uranium content is more than linear with respect to the salinity rate.

The vanadium distribution shows a more irregular pattern; in particular the higher salinity sample (salt lake) shows a very low vanadium content.

The uranyl ion activity is decisive in reaching the solubility product of carnotite. During the evolution of the chemism of the waters under investigation, the activity increases more than it would if it were proportional to the uranium concentration, because along with the uranium increase there is a decrease in the HCO_3 content, and thus a lower activity of the CO_3^{2-} ion that forms a very stable complex with the uranyl ion.

This uranyl ion activity may, under particular conditions, very well reach high enough values for the precipitation of the carnotite.

The vanadium concentration in the waters, and the processes controlling its circulation, may become a limiting factor in the process of direct carnotite precipitation from the waters.

We have given here a possible genetic model of the Yeelirrie deposit based on the direct precipitation of the carnotite from the waters circulating in the calcrete aquifer. This genetic model is compatible with the environmental conditions of the zone, and with the geochemical behaviour of uranium in this particular environment, as observed from studies carried out in nearby areas.

There are no direct observations or publications available on the minerogenesis of Yeelirrie and so the possibility, however small it may be, cannot be excluded that the carnotite deposit developed on a proto-ore in the reduced state.

5. CONCLUSION

This paper discussed some of the geochemical processes capable of precipitating the secondary minerals of uranium directly from circulating waters, even when there are no primary uranium mineralizations.

The first case discussed referred to the autunite mineralizations from the Sila plateau in the Calabria region, and the second was a carnotite deposit in the Yeelirrie calcrete, Western Australia.

The general conclusions to be drawn from these studies may be summarized as follows.

In the supergene ore genesis, the problem of uranium supply is mostly considered in terms of space and time. Our results show that peculiar environmental conditions are able to cause, in a short time and/or space range, an intense uranium mobilization and circulation. On the other hand, some widespread geochemical processes, which are a consequence of the above environmental evolution, are of fundamental importance in the uranium accumulation, and they behave just like traps, even if of unusual type.

There are series of geochemical processes capable of bringing about a very effective separation and concentration of uranium, with a yield extremely high for a natural system. Such processes may occur under humid temperate climatic conditions, as in the case of the Sila Plateau, at an early stage of erosion, and as the result of processes of rejuvenation of the hydrology, as well as under arid climatic conditions in zones where the morphology is very flat and the erosion is consequently very mature.

The most important geochemical process is the reaching of high UO_2 activity in circulating waters because of the low concentration or depletion of the carbonate ion which is the most effective uranyl chelating compound.

Different environmental conditions may control the uranium concentration either as carnotite or as autunite mineralizations.

The factors controlling the circulation and distribution of the compounds precipitating uranium may thus be important in determining the eventual fate of the uranium, that is, whether deposits are formed or rather really missing ore bodies, as is the case for the dispersed mineralizations.

The precipitation processes discussed in this paper may also be just one important step of the multistage minerogenetic processes which control the formation of the most important deposits; however the processes described above may by themselves account for the genesis of one of the most important types of uranium deposits in the world, the carnotite deposits in calcrete.

REFERENCES

- [1] HOSTELTLER, P.B., GARRELS, R.M., Transportation and precipitation of uranium and vanadium at low temperatures, with special reference to sandstone-type uranium deposits, *Econ. Geol.* 57 (1962) 137.
- [2] MUTO, T., HIRONO, S., KURATA, H., Some aspects of fixation of uranium from natural waters, *Kozan Chishitsu* 15 74 (1965) 287.
- [3] KAJITANI, K., A geochemical study on the genesis of ningyosite the special calcium uranous phosphate mineral, *Econ. Geol.* 65 (1970) 470.
- [4] SANTOMA, L., Estabilidad mineralogica de los fosfatos de uranilo, *Bol. Geol. Minero* 83 3 (1972) 283.
- [5] FERRETTI, O., MOLIN, D., Concentrazioni di carnotite in un bacino diatomifero del Viterbese, *Rend. Soc. Ital. Min. i Petr.* 27 (1971) 149.
- [6] SANDERS, C.C., Hydrogeology of a calcrete deposit on Paroo station Wiluna, and surrounding areas, *Geological Survey of Western Australia Bulletin* (1972) 15.
- [7] MANSKAYA, S.M., DROZDOVA, T.V., *Geochemistry of Organic Substances*, Pergamon Press, Oxford (1968).
- [8] DALL'AGLIO, M., A study of the circulation of uranium in the supergene environment in the Italian Alpine range, *Geochim. Cosmochim. Acta* 35 (1971) 47.
- [9] DALL'AGLIO, M., CASENTINI, E., The distribution of uranium between precipitates and brines in the solar salt plant of Margherita di Savoia — Geochemical and geological considerations, *Boll. Soc. Geol. Ital.* 89 (1970) 475.

DISCUSSION

H. H. ADLER: How do you account for the presence of uranium phosphate (autunite) and uranium vanadate (carnotite) when the uranyl ion is soluble and is easily complexed with these anions? What, for example, is the source of the phosphate and the vanadate? Is it possible for the uranium and phosphate, or the uranium and vanadate, to move together in supergene solution? Why is uraninite not formed? So much has been made of the formation of supergene uraninite, for example in the French granite deposits, that one would expect it to be more commonly found, even in areas where there is no organic reductant present. Why, then, is uraninite not formed in the conditions that you describe?

M. DALL'AGLIO: The uranyl ion is soluble mainly thanks to its complexes with carbonate ions. When carbonate activity is low, the activity of the uranyl ion is high. In such cases uranium can, under specific environmental conditions, attain activity adequate to reach the solubility products of carnotite or autunite.

The sources of vanadium and phosphate are not necessarily the same as the source of uranium. In the Sila Plateau, phosphorus probably originates from biological activity and its decay products, and in Western Australia vanadium probably originates from the leaching of basic rocks that crop out in the Yeelirrie Basin. For precipitation of carnotite and/or autunite to occur, it is only necessary that uranyl ion activity and phosphate and/or vanadate activity should be high enough in the same water to reach the solubility products of the secondary uranium mineral under investigation. In the conditions found in Western Australia, uranium and vanadium concentrations in natural waters may increase with advancing maturity of the water.

In the cases I have discussed in this paper, it is because oxidizing conditions exist that uraninite is not formed. In more general terms, the solubility products of autunite and carnotite are reached before uranium can be transported by water to depths where the transition and reducing environments would allow precipitation of uraninite, as happens in some vein occurrences that have originated "per descensum".

J. E. FROST: Although carnotite is reportedly the principal ore mineral at Yeelirrie, tyuyamunite is much more abundant in the other interior basins in Western Australia. Have you considered the stability relationships of carnotite as compared with tyuyamunite? Is there any apparent zoning pattern which could be used to define ore concentrations?

M. DALL'AGLIO: This is a most interesting question, but we have not studied it yet.

J. PASQUALI: You discuss two situations, one in southern Italy where there is about $1 \text{ pp}10^9$ of uranium in solution, and the other in Western Australia, with about $200 \text{ pp}10^9$ of uranium in solution in saline waters close to the solubility product of carnotite. The implication of the situation in southern Italy is that the uranium has to go through a nucleation process in which it is adsorbed on surface-active solids (iron oxides, organic matter and so on). When enough uranium has been adsorbed, redistribution by crystallization can take place.

M. DALL'AGLIO: I completely agree with you. This is a problem which we have in fact studied in some detail.

J. CAMERON (Scientific Secretary): I recently had the opportunity of visiting the Mudugh deposits in Somalia to which Mr. Dall'Aglío referred, and subsequently he and I were able to compare notes on the Yeelirrie and Mudugh deposits. There are obviously great similarities. At Mudugh carnotite is present interstitially and in cracks and cavities in calcrete, marls, clays and bentonite in the near-surface zone, and is apparently limited to the zone of the narrowly fluctuating seasonal water table. The uranium seems to occur from the surface to about 5 - 8 m depth, and none is at present known to occur below the lower level of the water table. I mention this because, given similar climatic and oxidizing conditions, other deposits similar to Yeelirrie and Mudugh are likely to be found; the Yeelirrie Basin is probably by no means unique.

ON THE BEHAVIOUR OF URANIUM DURING CRYSTALLIZATION OF MAGMAS – WITH SPECIAL EMPHASIS ON ALKALINE MAGMAS*

H. BOHSE, J. ROSE-HANSEN, H. SØRENSEN
Institute of Petrology, University of Copenhagen

A. STEENFELT
Geological Survey of Greenland, Copenhagen

L. LØVBORG, H. KUNZENDORF
Danish AEC Research Establishment Risø, Roskilde,
Denmark

Abstract

ON THE BEHAVIOUR OF URANIUM DURING CRYSTALLIZATION OF MAGMAS – WITH SPECIAL EMPHASIS ON ALKALINE MAGMAS.

In a number of series of igneous rocks the uranium content decreases towards the younger members, which is generally explained as a result of a release of uranium during crystallization of the magmas. This trend of evolution is described from the Ilímaussaq intrusion, South Greenland and is considered a result of retention of uranium in the magma owing to the formation of complex ions. It is thus possible to build up concentrations of uranium in residual melts even in rock series displaying low contents of uranium.

The distribution of uranium and thorium in igneous rocks

The behaviour of uranium during igneous crystallization deserves close attention. This is because igneous rocks are considered to be the source of most uranium deposits, either directly, when the deposits are formed from fluids expelled during crystallization of magmas, or indirectly, when the primary content of uranium is redistributed by hydrothermal or meteoric solutions. Uranium-rich igneous rocks constitute low grade resources for the future.

Uranium and thorium are generally enriched in the youngest, most felsic, most silicic and most potassic members of comagmatic suites of igneous rocks (1). There is, however, a number of examples of uranium varying inversely with the above-mentioned factors (2-5). In these cases thorium increases or remains more or less constant. Decreasing Th/U ratios are more rare (4).

* Contribution to the Mineralogy of Ilímaussaq No.35.

Decreasing contents of uranium in late stage rocks are commonly explained as a result of oxidation of U^{4+} ions and a subsequent removal of UF_6 or mobile uranyl complex ions (e.g. 2, 4, 5). A removal of uranium from the melt by early uranium-rich minerals finds no support in the known distribution of uranium between the phases of igneous rocks (3, 6, 7).

There is still another way of explaining decreasing uranium contents in igneous rock series. Uranium may, during crystallization, be partitioned strongly into the melt, thus becoming accumulated in residual melts. In this connection it should be mentioned that agpaitic rocks¹, which represent products of crystallization of highly evolved magmas, are richer in "residual" elements, including uranium and thorium, than most other igneous rocks (8, 9, 10).

The relation between uranium and the volatile components of magmas

Uranium and thorium are finely dispersed in acid volcanic glasses rich in halogens (12, 13, 14) and are retained even in hydrated glasses. This demonstrates a strong preference of uranium for acid melts rich in fluorine and chlorine. This may also explain the late precipitation of uranium in many granites (15). Uranium and the halogens are expelled during crystallization of the glasses (14) while thorium is retained. Uranium minerals are consequently associated with fluorite in many deposits (12, 16, 17). Thorium-rich veins often have a gangue of carbonate minerals (18). That uranium may be removed with the gas phase during magma consolidation is well documented (19, 20).

The importance of volatiles for the retention of residual elements is demonstrated in the case of the ekerite of the Oslo Province. Massive varieties are rich in residual elements, while miarolitic varieties, which have lost their gas phase during crystallization, are depleted in these substances (21).

Uranium and thorium are able to migrate within magmas to be concentrated in the most water-rich rocks (22, 23) or in the apical parts of magma chambers (24, 25).

¹ Agpaitic rocks are peralkaline nepheline syenites and phonolites enriched in rare elements and halogens and containing complex zirconium and titanium silicates such as eudialyte and rinkite (11).

These examples illustrate that uranium may be partitioned into the melt in magma systems rich in fluorine and chlorine. This indicates that the formation of complex halide compounds rather than increasing oxygen fugacity prevent uranium from precipitation. Therefore, decreasing contents of uranium in a succession of igneous rocks does not necessarily mean that these rocks crystallized from uranium-poor magmas. This trend is particularly well demonstrated by the agpaitic rocks of the Ilfmaussaq intrusion in South Greenland (8).

On the behaviour of uranium during crystallization of the Ilfmaussaq intrusion

The Ilfmaussaq intrusion, which is made up mainly of peralkaline, agpaitic nepheline syenites, is an example of extreme enrichment in uranium and thorium during igneous crystallization and differentiation (8). The latest intrusive phases have in places more than 0.1 % U and 0.5 % Th. There are furthermore late veins rich in radioactive minerals (26) and in the roof zone in the northern part of the intrusion the roof rocks are strongly fenitized. The uranium deposit at Kvanefjeld is a part of this fenitized complex (25). (See Fig.1).

The following account is based on the preliminary results of a thorough investigation of the behaviour of uranium during the crystallization of the Ilfmaussaq rocks.

The agpaitic nepheline syenites are considered to have crystallized from one batch of magma in a fairly closed system. The roof of the intrusion is preserved at a number of places; the bottom of the magma chamber is not exposed.

The rocks of the upper roof zone crystallized by plastering of crystals on the roof and present a gradual sequence downwards from pulaskite through heterogeneous foyaite and sodalite foyaite to a poikilitic sodalite-rich nepheline syenite, the naujaite (see table I). At the naujaite stage of crystallization, crystals of sodalite floated in the top part of the magma. In all the rocks of the roof zone eudialyte is an interstitial mineral.

The lowermost exposed part of the intrusion is made up of a layered series of nepheline syenites, the kakortokites, which clearly formed by bottom accumulation of crystals and

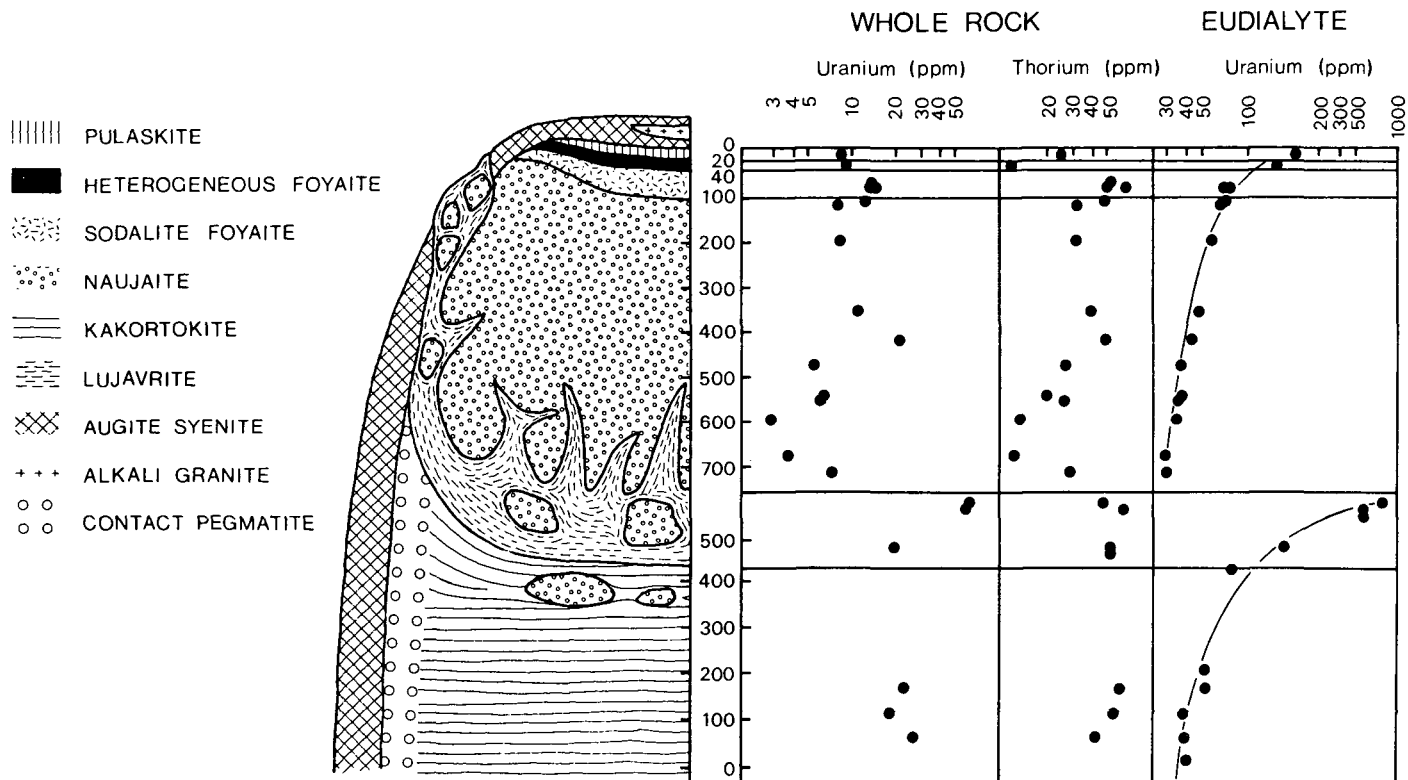


FIG.1. Schematic section through the exposed part of the Ilímaussaq intrusion. In the top sequence of rocks, the height (= structural level in the intrusion) is measured downwards from the upper contact of the pulaskite. For the bottom sequence the height is measured upwards from the lowermost layer of kakortokite. Heights are given in meters. Uranium and thorium determinations as given in Table II.

Table I The major agpaitic rock types and some radioactive minerals from the Ilmaussaq intrusion.

Rock type	Texture, grain size	Essential minerals	Uranium-bearing minerals
pulaskite and heterogeneous foyaite	massive, medium to coarse	alkali feldspar, alkali pyroxene, alkali amphibole, nepheline	apatite, eudialyte
sodalite foyaite	massive, coarse	alkali feldspar, nepheline, sodalite, alkali pyroxene, alkali amphibole	eudialyte, rinkite
naujaite	poikilitic, coarse	sodalite, alkali feldspar, alkali pyroxene, alkali amphibole	eudialyte, rinkite
kakortokite	laminated, layered, medium	alkali feldspar, nepheline, alkali amphibole	eudialyte, rinkite
lujavrite	laminated, fine; and massive, layered, medium to coarse	microcline, albite, nepheline, alkali amphibole, alkali pyroxene	britholite, eudialyte, monazite, pyrochlore, rinkite, steenstrupine

Mineral	U (ppm)	Th (ppm)
Britholite $(\text{Na,Ce,Ca})_5\text{F}(\text{SiO}_4, \text{PO}_4)_3$		6900
Eudialyte $(\text{Na,Ca,Fe})_6\text{Zr}(\text{OH,Cl})(\text{Si}_3\text{O}_9)_2$	50-869	30-340
Monazite $(\text{La,Ce})\text{PO}_4$	138-12800	300-57300
Pyrochlore $(\text{Ca,Na})_2(\text{Nb,Ta})_2\text{O}_6(\text{O,OH,F})$	2000	7000
Rinkite $(\text{Ca,Na,Ce})_{12}(\text{Ti,Zr})_2\text{Si}_7\text{O}_{31}\text{H}_6\text{F}_6$	3000-12000	3000-4300
Steenstrupine $(\text{Na}_2\text{Ce}(\text{Mn,Nb,Fe})\text{H}_2((\text{Si,P})\text{O}_4)_3$	2000-15000	2000-74000
Thorite $(\text{Th,U})\text{SiO}_4$	31000	405000

which are later than the naujaite (27). Eudialyte is a liquidus phase in the kakortokites.

The kakortokites continue upwards into an about 200 m thick unit of laminated, mesocratic nepheline syenites, lujavrites, which intrude the overlying agpaitic rocks and at Kvane-fjeld also the roof of volcanic rocks (25). In these rocks eudialyte is also a liquidus phase, but some varieties of lujavrite are poor in eudialyte and are instead rich in the radioactive mineral steenstrupine (see Table I).

As shown in Table II there is a slight increase in U and Th from pulaskite-heterogeneous foyaite to sodalite foyaite. The naujaite is distinctly lower in U and Th than the sodalite foyaite.

Table II Uranium and thorium contents of some Ilfmaussaq rocks and uranium contents of their eudialyte

Rock type GGU No.	Structural position	Whole rock analyses					ppm U in eudialyte ^c
		U ^a (ppm)	Th ^a (ppm)	Th/U	Nb ^b (%)	Zr ^b (%)	
pulaskite	5	9 ^d	25 ^d	2.8			216 ^e
heterogeneous foyaite	15	10 ^d	12 ^d	1.2			165 ^e
sodalite foyaite							
154350	70	14	55	3.9			73 ^e
154351	80	14	67	4.8	0.063		
naujaite							
154357	120	9	32	3.6	0.057	0.35	70 ^e
154344	200	9	31	3.4			65
154309	360	12	40	3.3	0.105	0.91	50 ^e
154311	480	6	26	4.3	0.054	0.24	38 ^e
57041	550	7	20	2.9	0.078	0.77	32
154331	720	8	29	3.6	0.082	0.55	31 ^e
lujavrite							
119729	570	67	48	0.7			869
119719	560	62	66	1.1			534
57033	470	20	55	2.8			181
kakortokite							
60755 uppermost layer	417						81
154318 layer 12	160	23	61	2.7			54
154327 layer 4	100	19	55	2.9	0.104	1.09	39 ^e
109272 layer -9	0						40

^a Gamma-spectrometrical analyses (41). Average of three runs on at least six 200-g samples from 50-kg rock samples. Standard deviation given as the sum of the precision and the accuracy, and is ~5% for thorium and ~8% for uranium.

^b Determined by isotope-fluorescence analyses (42). The accuracy of the analyses, expressed as the sum of the counting error and the accuracy of the slope of the regression line, is less than the following values, Zr: 1.2%; Nb: 2.9%.

^c Determined by the fission track method (43). Mica is used as detector, neutron flux $\sim 1.3 \times 10^{11}$ neutrons/cm² · s, exposure time 150 s. The results have been compared with delayed neutron counting following neutron activation. The correlation is within the standard deviation on the fission track method, ~20%.

^d From Gerasimovsky (44).

^e From other samples of eudialyte in the same structural position (28).

The kakortokites are richer in U and Th than the roof zone rocks and show a lower Th/U ratio. These features are partly due to a content of rinkite.

The lujavrites have up to 1000 ppm U or more, and up to 5000 ppm Th or more and Th/U varying from 0.5 to about 5. They are, as mentioned above, accompanied by uranium mineralizations.

The trend in the contents of uranium of the various rocks has been compared with the variation in uranium in their

eudialyte as determined by fission track analyses (Table II and (28)).

The interstitial eudialytes of the pulaskite-heterogeneous foyaite-sodalite foyaite show decreasing contents of uranium with progressive crystallization. This trend continues down through the about 500 m thick zone of naujaite and thus parallels the trend seen in the rock analyses. The eudialyte accounts for most of the uranium content of these rocks.

In the kakortokites the uranium content of eudialyte increases upwards. This trend reflects a steady increase of the content of uranium in the magma from which this eudialyte crystallized as a liquidus phase. The trend continues upwards into the overlying lujavrites.

These data indicate that the kakortokites and lujavrites were formed from magmas which became progressively richer in uranium, but relatively poorer in thorium. These magmas gave rise in the late stages to uranium mineralizations. The observed trend is in accordance with the theoretical trend for uranium in magmas which display fractional crystallization.

The uranium contents of the rocks and the interstitial eudialytes of the uppermost part of the intrusion decrease, however, with progressive crystallization. As these rocks crystallized under closed system conditions, as there are no traces of uranium mineralizations where naujaite adjoins the country rocks (contrary to mineralizations in country rocks in contact with lujavrite), and as uranium and thorium are accumulated in the youngest rocks of the intrusion, the crystallization sequence pulaskite-naujaite is an example of crystallization of uranium-poor rocks from a magma steadily accumulating uranium. These features may be explained by the redox conditions of the magma, by partitioning of uranium between gas phase and magma or by the formation of complex ions.

Oxidation of uranium is the most popular explanation of decreasing content of uranium in rock series (2). The Ilfmaussaq rocks in question are rich in sodic pyroxenes and have high $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios which might indicate a high oxygen fugacity of the magma. The silica-undersaturated and peralkaline rocks of the roof zone appear, however, to have crystallized at extremely low oxygen fugacities (27), as excess sodium stabilizes Fe^{3+}

in the melt. A low oxygen fugacity is also in agreement with the presence of huge quantities of hydrocarbon gases and bitumens in these rocks (29).

The partitioning of uranium between gas phase and magma also appears unlikely since theoretical and experimental data indicate that volatile components such as fluorine and chlorine are highly soluble in undersaturated peralkaline magmas characterized by a low silica activity (30,31).

The authors favour the view that uranium and thorium have been retained in the halogen-rich magma during crystallization of the upper sequence of rocks (cf. 28). The possibility that the top sequence and the bottom sequence of rocks have been derived from separate magma masses is incompatible with the field relations. This type of explanation has also been advanced for the agpaitic rocks of the Lovozero intrusion, the Kola Peninsula (32). Fluorine, chlorine, carbonate ions and hydrocarbons are possible complex formers (28, 30, 33).

During crystallization of the lujavrites from the residual magma left after the formation of the kakortokites and the pulaskite-naujaite sequence of rocks, the concentration of uranium and thorium in the magma became so high that the thorium-rich mineral steenstrupine substituted eudialyte. The Th/U ratios of the lujavrites indicate that uranium is enriched relative to thorium. Fluids squeezed out during the crystallization of the lujavrites formed mineral veins containing steenstrupine (34). The Kvanefjeld deposit was formed where gas-rich lujavrite magma was collected in arched zones under the roof of the magma chamber (26). Fractures in the country rocks have radioactive veins having 17-1500 ppm U, 60-4500 ppm Th and Th/U 0.1-57 (35).

Conclusions

The trend demonstrated for the Ilímaussaq intrusion indicated that considerable concentrations of uranium and thorium may be built up during consolidation of undersaturated peralkaline magmas of agpaitic type. Agpaitic rocks therefore represent potential low grade deposits of uranium and thorium.

Peralkaline granitic magmas, which represent the end members of oversaturated differentiation series, will generally

generate a fluid phase and expel chlorine and fluorine as crystallization proceeds (30, 31). Metals may be extracted from magmas by such fluids (36), which may explain the successive release of uranium, thorium and other metals (37).

Granitic magmas consolidating at depth under such conditions that the fluid phase is retained may build up a concentration of uranium and thorium. When such magmas release a gas phase either because of retrograde boiling (38) or subsequent to a relief of pressure, porphyry type of deposits may be formed. The Ross-Adams deposit, Alaska (39) and the Rössing deposit, South West Africa (40) may have been formed in this way. Fluorite-pitchblende veins may originate from fluorine-rich fluids, perhaps containing UF_6 , released from acid magmas (16,17).

Publication authorized by the Director of the Geological Survey of Greenland.

REFERENCES

- (1) ROGERS, J.W., ADAMS, J.A.S., "Uranium", Ch. 92, Handbook of Geochemistry (WEDEPOHL, K.H., ed.), Springer-Verlag, Berlin (1969).
- (2) RAGLAND, P.C., BILLINGS, G.K., ADAMS, J.A.S., Chemical fractionation and its relationship to the distribution of thorium and uranium in a zoned granite batholith. *Geoch. Cosmoch. Acta* 31 (1967) 17.
- (3) BARTHEL, F., MEHNERT, K.R., Die Verteilung von Uran und Thorium im Malsburger Granit. *N. Jb. Miner. Abh.* 114 (1970) 18.
- (4) ZOLOTAREV, B.P., SEMENOV, G.S., Distribution of thorium, uranium, and potassium in rocks of tholeiite-basaltic series, *Internat. Geology Rev.* 13 (1971) 1548.
- (5) SOLOV'YEV, N.S., Behavior of uranium and thorium during evolution of Mesozoic volcanic apparatuses in Transbaykal, *Internat. Geology Rev.* 13 (1971) 1642.
- (6) COPPENS, R., "Sur la radioactivité des granites", Les roches plutoniques dans leurs rapports avec les gîtes minéraux (MORIN, P., ed.), Masson et Cie, Paris (1973).
- (7) WILLGALLIS, A., Zur Mikrosondeanalyse der U-Th-Minerale im Malsburger Granit, *N. Jb. Miner. Abh.* 114 (1970) 48.
- (8) SØRENSEN, H., "Low-grade uranium deposits in agpaïtic nepheline syenites, South Greenland", *Uranium Exploration Geology, IAEA, Vienna* (1970) 151.
- (9) VARET, J., Les phonolites agpaïtiques et miaskitiques du Cantal septentrional (Auvergne, France), *Bull. Volcan.* 33 (1969) 621.

- (10) GERASIMOVSKII, V.I., Geochemistry of agpaitic nepheline syenites (Proc.13th Int.Geol.Congress, Prague, 1968), Akademia, Prague 6 (1968) 259.
- (11) SØRENSEN, H., "Alkali syenites, feldspathoidal syenites and related lavas", Ch. II.2, The Alkaline Rocks (SØRENSEN, H., ed.), John Wiley & Sons, London (1974).
- (12) SHATKOV, G.A., SHATKOVA, L.N., GUSHCHIN, Ye.N., The distribution of uranium, thorium, fluorine, chlorine, molybdenum, and niobium in liparites and acid volcanic glasses, Geochem. Int. (1970) 1051.
- (13) LOCARDI, E., MITTEMPERGHER, M., Relationship between some trace elements and magmatic processes, Geol. Rd. 57 (1967) 313.
- (14) ROSHOLT, J.N., PRIJANA, NOBLE, D.C., Mobility of uranium and thorium in glassy and crystallized silicic volcanic rocks, Econ. Geol. 66 (1971) 1061.
- (15) LARSEN, E.S., jr., GOTTFRIED, D., Distribution of uranium in rocks and minerals of Mesozoic Batholiths in Western United States, U.S. Geol. Surv. Bull. 1070-C (1961).
- (16) STAATZ, H., OSTERWALD, F.W., Uranium in fluorspar deposits of the Thomas Range, Utah, U.S. Geol. Surv. Prof. Paper 300 (1956) 131.
- (17) KERR, P.F., "The Marysvale, Utah, uranium deposits", Ch. 50, Ore Deposits of the United States 1933-1967, The Graton-Sales Volume, Vol. 2 (RIDGE, J.D., ed.), The American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc., New York (1968) 1020.
- (18) OLSON, J.C., OVERSTREET, W.C., Geologic distribution and resources of thorium, U.S. Geol. Surv. Bull. 1204 (1964).
- (19) MACDONALD, R., UPTON, B.G.J., THOMAS, J.E., Potassium- and fluorine-rich hydrous phase coexisting with peralkaline granite in South Greenland, Earth Planet. Sci. Letters 18 (1973) 217.
- (20) LARSEN, L.M., STEENFELT, A., Alkali loss and retention in an iron-rich peralkaline phonolite dyke from the Gardar province, South Greenland, Lithos (in press).
- (21) DIETRICH, R.V., HEIER, K.S., Differentiation of quartz-bearing syenite (nordmarkite) and riebeckite-arfvedsonite granite (ekerite) of the Oslo Series, Geoch. Cosmo. Acta 31 (1967) 275.
- (22) SMITHSON, S.B., HEIER, K.S., U and Th distribution between normal and charnockitic facies of a deep granite intrusion, Earth Planet. Sci. Letters 12 (1971) 325.
- (23) SMITHSON, S.B., DECKER, E.R., K, U and Th distribution between dry and wet facies of a syenitic intrusion and the role of fluid content, Earth Planet. Sci. Letters 19 (1973) 131.
- (24) LOCARDI, E., MITTEMPERGHER, M., The meaning of magmatic differentiation in some recent volcanoes of Central Italy, Bull. Volcan. 33 (1969) 1.

- (25) SØRENSEN, H., ROSE-HANSEN, J., NIELSEN, B.L., LØVBORG, L., SØRENSEN, E., LUNDGAARD, T., The uranium deposit at Kvanefjeld, the Ilfmaussaq intrusion, South Greenland, *Geology, reserves, beneficiation*, Rep. Geol. Surv. Greenland 60 (1974).
- (26) BONDAM, J., SØRENSEN, H., Uraniferous nepheline syenites and related rocks in the Ilfmaussaq Area, Julianehaab District, Southwest Greenland, *Int. Conf. peaceful Uses atom. Energy* (Proc. Conf. Geneva, 1958) 2, UN, New York (1958) 555.
- (27) LARSEN, L.M., En kemisk undersøgelse af pyroxenerne i Ilfmaussaq-intrusionen, Sydgrønland. Unpubl. Dissertation, Univ. of Copenhagen (1974).
- (28) STEENFELT, A., BOHSE, H., Variations in the content of uranium in eudialyte from the differentiated alkaline Ilfmaussaq intrusion, South Greenland (in preparation).
- (29) PETERSILIE, I.A., SØRENSEN, H., Hydrocarbon gases and bituminous substances in rocks from the Ilfmaussaq alkaline intrusion, South Greenland, *Lithos* 3 (1970) 59.
- (30) KOGARKO, L.N., "Rôle of volatiles", Ch. VI.4, *The Alkaline Rocks* (SØRENSEN, H., ed.), John Wiley & Sons, London (1974).
- (31) STORMER, J.C., CARMICHAEL, I.S.E., The free energy of sodalite and the behavior of chloride, fluoride and sulfate in silicate magmas, *Amer. Min.* 56 (1971) 292.
- (32) SAPRYKINA, T.V., "Uranium", *The Geochemistry of the Lovozero Alkaline Massif*, vol. 2 (GERASIMOVSKY, V.I., ed.) Australian Nat. Univ. Press, Canberra (1968).
- (33) KRANTZ, R., The participation of organic compounds in the transport of ore metals in hydrothermal solutions, *Kernforschungsanlage Jülich* (1967).
- (34) SØRENSEN, H., On the occurrence of steenstrupine in the Ilfmaussaq massif, Southwest Greenland, *Meddr Grønland* 167 (1962) Part 1.
- (35) HANSEN, J., A study of radioactive veins containing rare-earth minerals in the area surrounding the Ilfmaussaq alkaline intrusion in South Greenland, *Meddr Grønland* 181 (1968) Part 8.
- (36) HOLLAND, H.D., Granites, solutions, and base metal deposits, *Econ. Geol.* 67 (1972) 281.
- (37) TROFIMOV, L.A., MITRYAYEVA, N.M., FILIMONOVA, L.Ye., SYROMYATNIKOV, N.G., Behavior of uranium and thorium during deposition of the Boshchekul ores, *Internat. Geology Rev.* 15 (1973) 183.
- (38) PHILLIPS, W.J., Mechanical effects of retrograde boiling and its probable importance in the formation of some porphyry ore deposits, *Trans. Inst. Min. Met. Sect. B* 82 (1973) 90.
- (39) MACKEVETT, E.M., jr., Geology and ore deposits of the Bokan Mountain uranium-thorium area Southeastern Alaska, *U.S. Geol. Surv. Bull.* 1154 (1963).

- (40) BACKSTRÖM, J.W., von, "The Rössing uranium deposit near Swakopmund, South West Africa", Uranium Exploration Geology, IAEA, Vienna (1970) 143.
- (41) LØVBORG, L., "Assessment of uranium by gamma-ray spectrometry", Uranium Prospecting Handbook (BOWIE, S.H.U., DAVIS, M., OSTLE, D., eds.) London Inst. Min. Met. (1972).
- (42) KUNZENDORF, H., Die Isotop-Röntgenfluoreszenz Analyse und ihre Anwendung bei geochemischen Untersuchungen in Grönland, Risø M-1610 (1973).
- (43) WOLLENBERG, H., Fission track radiography of uranium and thorium in radioactive minerals, Risø Rep. 228 (1971).
- (44) GERASIMOVSKY, V.I., Geochemistry of the Ilímaussaq alkaline massif (in Russian), Nauka, Moscow (1969).

GEOCHEMICAL AND MINERALOGICAL STUDIES OF EUXINITE AND ITS ALTERATION PRODUCTS IN GRAPHIC PEGMATITES FROM HARRAR, ETHIOPIA

S. S. AUGUSTITHIS, E. MPOSKOS, A. VGENOPOULOS

National Technical University of Athens,
Athens, Greece

Abstract

GEOCHEMICAL AND MINERALOGICAL STUDIES OF EUXINITE AND ITS ALTERATION PRODUCTS IN GRAPHIC PEGMATITES FROM HARRAR, ETHIOPIA.

Metamictic euxinite occurs in a graphic pegmatite from Harrar, Ethiopia. Owing to differential leaching by chemical weathering of the euxinite, an alteration margin has been produced, which is relatively depleted in Nb and U in comparison with the unaltered euxinite. In this alteration margin there is relatively more Y and Ti. Mineralogically the alteration margin includes relics of euxinite, anatase and perhaps ampingabeite (?). Additional studies showed that by heating the metamictic euxinite to 580°C, some lattice restoration occurred; however, complete euxinite lattice restoration occurred at 770°C.

One of the important problems of uranium geochemistry and mineralogy is uranium mobilization and the leaching of uranium out of the primary uranium minerals with the subsequent building up of secondary minerals resulting from element migration. A preliminary phase of the present studies was carried out and published about 10 years ago [1], as X-ray fluorescence spectroscopical studies on unaltered parts of an unidentified¹ Y, Nb, U mineral and its alteration margin (coating).

The following ratios have been determined:

(a) Unaffected "euxinite"

Y:Nb = 1:1

U:Th = 4:1

Y:Zr = 9:1

Y:U = 3:1

(b) Alteration margin of euxinite:

Y:Nb = 4:1

U:Th = 3:2

Y:Zr = 14:1

Y:U = 17:1

(c) Nb, Zr, Y, a little Th and U have infiltrated into the microcline of the graphic pegmatite surrounding the euxinite, and are due to the leaching out of elements from the radioactive mineral.

¹ Spectrochemically Ta, and about 14.5% Ti, have also been determined. On the basis of the Debye-Scherrer diagram, the mineral is identified as euxinite.

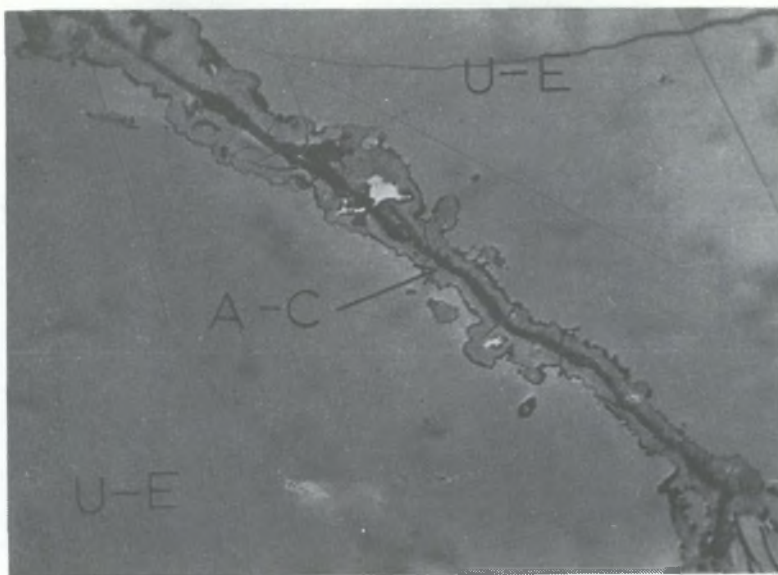


FIG. 1. Unaltered metamictic euxinite transversed by an extension of the margin alteration, which attains a channel-like appearance. U-E = unaltered metamictic euxinite. A-C = alteration channel transversing the euxinite. Polished section; without crossed nicols; oil immersion 250 X.

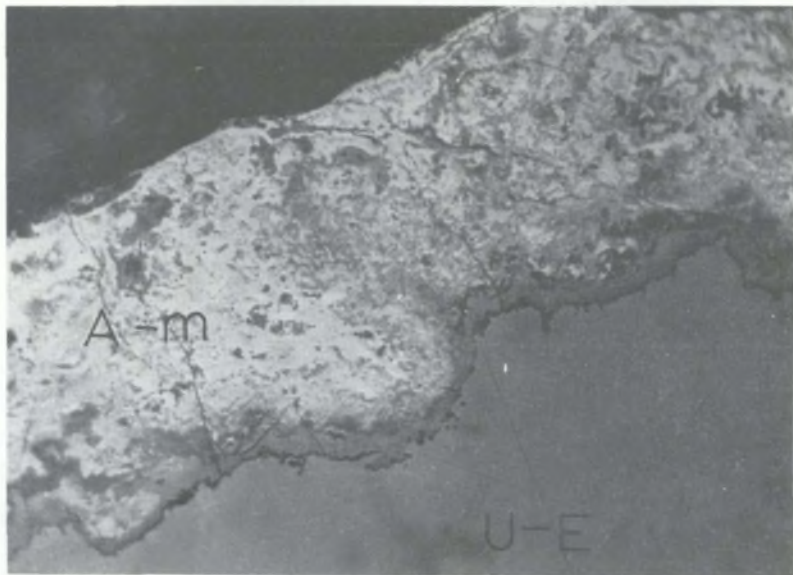
Comparison of the ratios in the unaltered euxinite and in its alteration margins shows that Nb, U and to a lesser extent Th and Zr are greatly decreased in the alteration margin of the euxinite. In this connection it should be emphasized that the ore-microscopic phenomenology clearly shows that the alteration margin was initially euxinite which, owing to mineral alteration and element leaching, has been changed. Extensions of the alteration margin protruding into the unaltered euxinite nucleus are shown in Fig.1.

In addition, all transitions of unaffected euxinite to its alteration margins have been observed and unaffected or partly affected euxinite parts (as relics) are ore-microscopically observed (see Figs 2a, b).

Ore-microscopically the unaltered euxinite is "metamictic" isotropic under crossed nicols whereas the alteration margin is transluscent and shows very strong internal reflection. X-ray goniometric studies show a metamictic "phase" without any characteristic peaks. Only when the metamictic euxinite was subjected to a differential thermal analysis and then analysed by X-rays (goniometric procedures) did it show a characteristic pattern determined to be euxinite (see Table I).

Figure 3 shows the differential thermal analysis diagram of the metamictic euxinite with curves at temperatures of 220°C, 580°C and 770°C respectively.

Figure 4 shows the X-ray goniometric diagram before the euxinite was heated up to the critical temperature and Fig.5 shows an X-ray goniometric diagram after the euxinite was heated above the critical temperature of 770°C.



(a)

FIG. 2a. Metamictic euxinite and its alteration margin. U-E = unaltered metamictic euxinite. A-m = alteration margin. Polished section; without crossed nicols; oil immersion 250 x.



(b)

FIG. 2b. Metamictic euxinite (dark) with alteration margin and extension of this margin transversing the euxinite. Polished section; with crossed nicols; oil immersion 250 x.

TABLE I. COMPARISON OF d-VALUES OF EUXINITE AS GIVEN BY THE JOINT COMMITTEE ON POWDER DIFFRACTION STANDARDS AND OF THE METAMICTIC EUXINITE HEATED ABOVE 760°C

Euxinite ^a dÅ	Metamictic euxinite heated above 760°C dÅ
7.28 ^b	7.248 ^b
3.66 ^b	3.630 ^b
3.37	3.488
3.28	3.263
2.99 ^b	2.985 ^b
2.95	2.777 ^b
2.78 ^b	2.627 ^b
2.63 ^b	2.590 ^b
2.60 ^b	2.419 ^b
2.55	2.377
2.52	2.324
2.45	2.301 ^b
2.45	2.197 ^b
2.43 ^b	2.103
2.31 ^b	2.087 ^b
2.21	2.021 ^b
2.19 ^b	1.893 ^b
2.12	1.860
2.08 ^b	1.822
2.04 ^b	1.760
1.979	1.706 ^b
1.941	1.670
1.939	1.643 ^b
1.897 ^b	1.588 ^b
1.880	1.586 ^b
1.830 ^b	1.572
1.806	1.559 ^b
1.774	1.515
1.731	1.513
1.727	1.453
1.704 ^b	1.445
1.683	1.441 ^b
1.643 ^b	1.439 ^b
1.625	1.421
1.614	1.418
1.590 ^b	
1.565 ^b	
1.540	
1.505	
1.496	
1.492	
1.488	
1.476	
1.474	
1.462	
1.441 ^b	
1.437 ^b	

^a Ref. [2].

^b Correspondence of d-values of euxinite from the literature with the metamictic euxinite heated above 760°C.

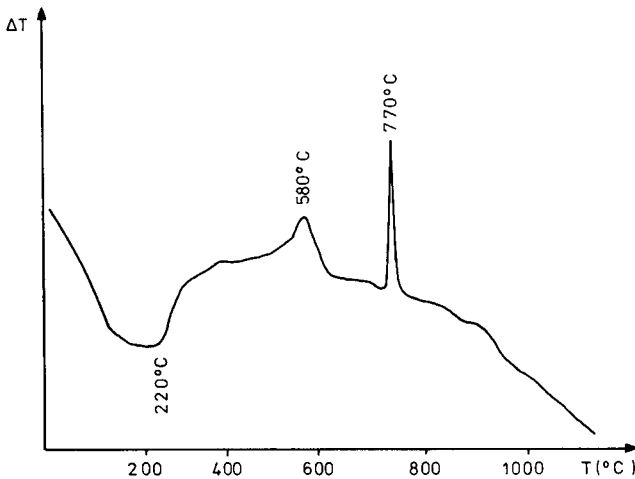


FIG. 3. Differential Thermal Analysis diagram with curves shown at the temperatures 220°C, 580°C and 770°C. As the X-ray studies show (Table II) regeneration of the euxinite lattice took place progressively as the temperature increased.

The restoration of the euxinite lattice from the metamictic state is progressively accomplished at 580°C and 770°C, as shown in Table II. However, certain irregularities are noticeable.

The alteration product is a micro-aggregate which, as mentioned, includes unaltered parts of euxinite and transition phases between euxinite and the alteration product; on the basis of X-ray studies, euxinite relics and anatase have been determined (see Table III).

As has been shown by geochemical and mineralogical studies, the leaching out of elements due to weathering of the mineral formed a "coating", and extensions of the alteration appear as a pattern of an intracrystalline network extending into the euxinite.

The alteration is caused by intergranular water (low-temperature), which formed solution paths which subsequently developed into channels of element migration.

The ore-microscopic observations show a progressive change from the dark metamictic euxinite → euxinite with internal reflection → euxinite with strong internal reflection and a fine aggregate of microanatase, translucent isotropic grains and amphoteric.

In addition to the changes of euxinite, the leaching out of elements resulted in neocrystallizations of the residuals and the formation of micro-crystalline aggregates of anatase which could be attributed to residual (less leached) Ti and its oxidation. The formation of the alteration margin is characterized by a decrease in the specific gravity, i.e. the density of powdered unaltered euxinite is about 5.3 and that of its altered margin 2.6.

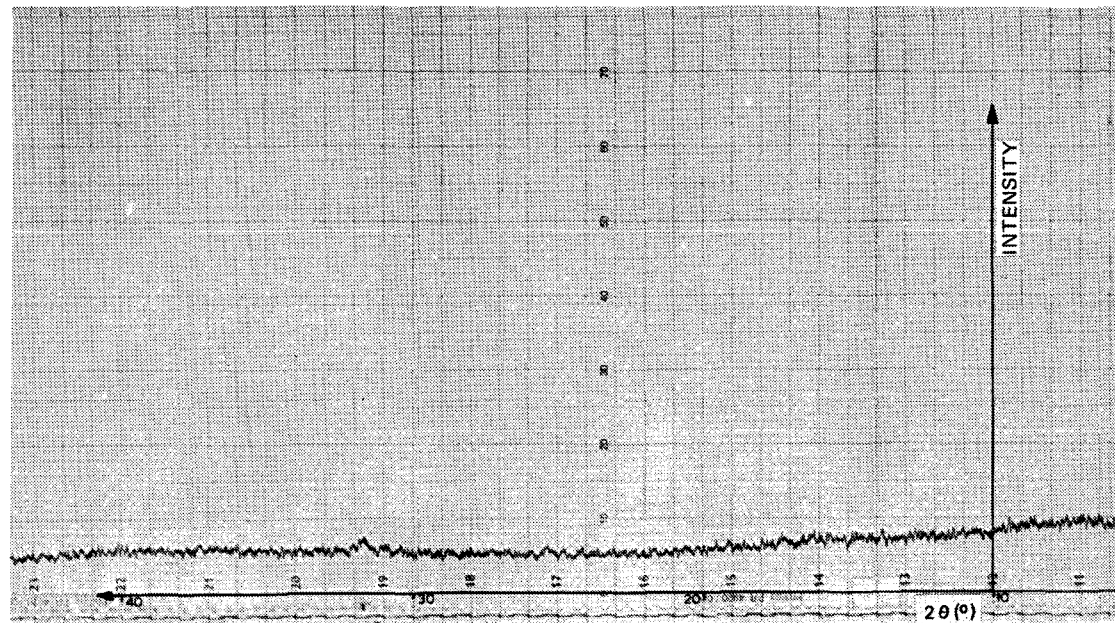


FIG. 4. Debye-Scherrer diagram of metamictic euxinite.

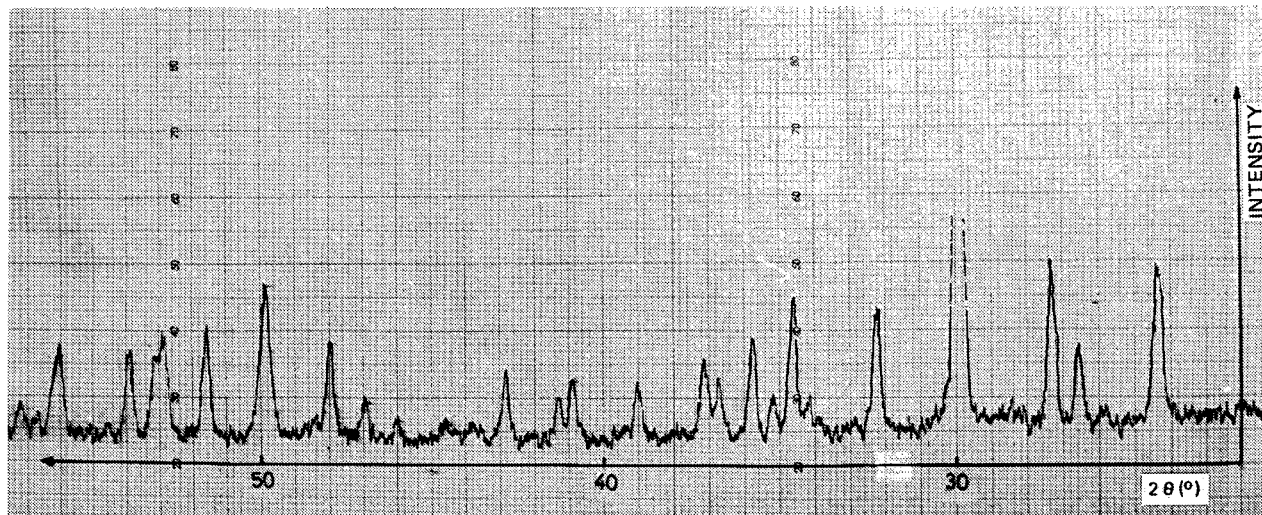


FIG. 5. Debye-Scherrer diagram of euxinite with lattice regeneration achieved by heating the metamictic euxinite to about 770°C.

TABLE II. PROGRESSIVE RESTORATION OF THE EUXINITE LATTICE FROM THE METAMICTIC STATE AT 580°C AND 770°C

<u>Metamictic euxinite at room temperature</u>	
dÅ	
2.664	
2.187	
2.024	
1.897	
1.857	
1.711	
1.675	
<u>Metamictic euxinite heated to 220°C</u>	
dÅ	
3.503	
<u>Metamictic euxinite heated to 580°C</u>	
dÅ	
2.96	
2.882	
1.675	
1.645	
<u>Regenerated euxinite heated to 770°C</u>	
dÅ	
3.610	
3.330	
3.252	
2.769	
2.583	
2.503	
2.443	
2.414	
2.301	
2.209	
2.109	
1.979	
1.939	
1.776	
1.731	
1.614	
1.570	
1.503	
1.493	
1.469	
1.444	
1.370	
1.344	
1.315	
1.302	

TABLE III. COMPARISON OF d-VALUES OF THE ALTERATION MARGIN OF THE EUXINITE WITH THE d-VALUES OF STANDARD EUXINITE AND ANATASE

Alteration margin of euxinite	Euxinite ^a	Synthetic anatase ^a	Anatase ^b
dÅ	dÅ		
4.23	7.28	3.51 ^d	3.84
3.54 ^d	3.66	2.435 ^d	3.49 ^c
3.48 ^e	3.37	2.379 ^d	2.377 ^e
3.46	3.28	2.336 ^d	2.070
3.43	2.99	1.891 ^d	1.883
3.33	2.95	1.699 ^d	1.694 ^e
3.299	2.78	1.665 ^d	1.661 ^e
2.55 ^c	2.63	1.494 ^d	1.477
2.50 ^c	2.60	1.480 ^d	1.365
2.45 ^c	2.55 ^c	1.367	1.342
2.43 ^{d,c}	2.52 ^c	1.337	1.262
2.39	2.45 ^c	1.264	1.166
2.377 ^{d,e}	2.45	1.250	
2.34 ^d	2.43 ^c	1.171	
2.27	2.31	1.1609	
2.26	2.21	1.0869	
2.13	2.19	1.0433	
2.12 ^c	2.12 ^c	1.0173	
1.98 ^c	2.08	0.9550	
1.92	2.04	0.9461	
1.91	1.979 ^c	0.9189	
1.90 ^{d,c}	1.941	0.8960	
1.85	1.939	0.8877	
1.72 ^c	1.897 ^c	0.8311	
1.714	1.880	0.8268	
1.711	1.830	0.8100	
1.693 ^{d,e}	1.806	0.7940	
1.685 ^c	1.774		
1.679	1.731		
1.670 ^{d,e}	1.727 ^c		
1.513	1.704		
1.503 ^c	1.683 ^c		
1.499	1.643		
1.495 ^{d,c}	1.625		
1.493 ^c	1.614		
1.491 ^c	1.590		
1.484 ^d	1.565		
	1.540		
	1.505 ^c		
	1.496 ^c		
	1.492		
	1.488 ^c		

^a Ref. [2].

^b LEBEDEV, L. M., Metacolloids in Endogenic Deposits, Plenum Press, New York (1967).

^c Correspondence of d-values of euxinite (from the literature) with the alteration margin of euxinite.

^d Correspondence of d-values of synthetic anatase (from the literature) with the anatase present in the "alteration margin of euxinite".

^e Correspondence of d-values of anatase (L. M. Lebedev) with the anatase present in the "alteration margin".

CONCLUSIONS

The alteration of euxinite is a case of element gradoseparation [3], which is the differential separation of elements from a mineral by leaching under chemical weathering.

In unaltered metamictic euxinite the atoms are in an amorphous arrangement; when subjected to hydration and oxidation processes by weathering, gradoseparation of the elements occurred with the more mobile hexavalent U and Nb leached out. In the alteration margin thus formed, there was a comparative enrichment of residual Y and Ti.

On the basis of microscopic and analytical data, as stated, the following transitional alteration phases are suggested, starting from unaffected metamictic euxinite → metamictic euxinite with weak internal reflection → translucent euxinite (very strong internal reflection) → neocrystallization of micro-aggregates of anatase and (?) ampingabeite.

Translucent "isotropic" grains also present in the alteration margin are considered as an amorphous and intermediate phase between the altered metamictic euxinite on the one hand and the neocrystallization of anatase and perhaps ampingabeite on the other.

Geochemically, as the comparative ratios of elements of the unaffected euxinite and its alteration margin show, the alteration margin is enriched² in the residual elements Y and Ti. However, X-ray fluorescence spectrochemical studies of the alteration margin also showed the presence of Nb, Zr, U and Th.

Consequently oxides and hydrated oxides of these elements will be the neocrystallizations of the alteration margin.

REFERENCES

- [1] AUGUSTITHIS, S.S., Geochemical and ore-microscopic studies of hydrothermal and pegmatitic primary uranium parageneses, *Nova Acta Leopoldina, Neue Folge* 28 170 (1964).
- [2] JOINT COMMITTEE ON POWDER DIFFRACTION STANDARDS, Powder Diffraction File, Joint Committee on Powder Diffraction Standards, 1845 Walnut St., Philadelphia, Penn. 19103 (1967).
- [3] PIERUCCINI, R., Einige in der Theorie und Praxis gewonnene geochemische Erkenntnisse über das Verhalten des Wassers bei der metamorphitischen Umwandlung von vulkanischen Tuffen und Sedimentgesteinen, *Ber. Geol. Ges. D.D.R., Erfurt, Sonderh.* 1 (1964) 117.

DISCUSSION

J. PASQUALI: Have you had an opportunity to analyse the solutions responsible for the leaching — that is, the stream waters of the region?

S. S. AUGUSTITHIS: No, but the weathering that occurs is typical of that prevailing in the tropical climatic conditions of the East African basement.

A. G. DARNLEY (Chairman): Mr. Augustithis' paper has wider relevance than may appear at first sight to people not familiar with the topic. This type of alteration is not confined to euxinite; it is commonly found associated with a variety of similar minerals. In work I carried out some years ago

² In the unaltered euxinite the Ti content is determined by atomic absorption to be about 14.5%, and in the alteration margin the Ti content is found to be 18.5%.

I found similar alteration in brannerite from Nkana, Zambia, and in yttrio-tantalite and samarskite from other localities in Africa. Although some examples could have been the result of supergene processes, what we observed in the brannerite from Nkana was certainly the product of either hydrothermal alteration or retrograde metamorphism. I would also draw attention to Ramdohr's "Pronto Reaction" observed in the Elliot Lake ores, where brannerite is described as forming in situ from its constituents. The converse could well be possible, the observed textures being a recrystallized alteration product.

S. S. AUGUSTITHIS: Some ten years ago we studied similar alteration phenomena due to chemical weathering (in davidite as well) and similar differential leaching processes in pegmatitic uraninite from Gordonia, South Africa. A report was published on that work at the time.³ I agree with Mr. Darnley about the significance of the differential leaching process, and I would like to suggest that this could be considered as a mechanism for the formation of secondary uranium minerals. However, in the material from Harrar studied here, the differential leaching of the uranium mineral was a part of the weathering undergone by the rock.

S. S. ADAMS: Have experimental leaching studies been done on euxenite or other uranium-bearing minerals for the information they would provide on the chemical conditions and rates of leaching?

S. S. AUGUSTITHIS: So far no experimental work has been done on the weathering of euxenite. Our research team is working on geochemical weathering, however, and has studied comparable weathering of davidite and crystalline pegmatitic uraninite from Gordonia, South Africa. Before going on to further experimental work we would like to gather more information for inductive thinking; in other words, we want to study more natural examples.

S. S. ADAMS: Mr. Darnley mentioned the Ramdohr reaction a few minutes ago, and I must confess I had not realized there was any further doubt about its validity. We have evidence for the occurrence of non-metamict (probably authigenic) davidite in the Morrison sandstone of New Mexico, suggesting that uranium and titanium do combine to form brannerite and davidite, as suggested by Ramdohr.

S. S. AUGUSTITHIS: Indeed, gradoseparation (differential leaching and mobilization of elements) could be the process. My former teacher, Professor Ramdohr, seems after all to be right as far as the formation of brannerite is concerned.

³ AUGUSTITHIS, S. S., Geochemical and ore-microscopic studies of hydrothermal and pegmatitic primary uranium parageneses, *Nova Acta Leopoldina, Neue Folge* 28 170 Leipzig (1964).

SOLUBILISATION ET INSOLUBILISATION DE L'URANIUM DES GRANITES PAR DES BACTERIES HETEROTROPHES

R. MAGNE

Centre de recherches radiogéologiques (CEA-ENSG)

J.R. BERTHELIN, Y. DOMMERGUES

Centre de pédologie biologique du CNRS,
Nancy, France

Abstract-Résumé

SOLUBILIZATION AND INSOLUBILIZATION OF URANIUM FROM GRANITES BY HETEROTROPHIC BACTERIA.

Batch cultures and semi-continuous flow perfusions are used as experimental devices to study microbial solubilization and insolubilization of uranium from granites by heterotrophic bacteria. The nutrient media are synthetic (with dextrose or amino acids) or natural (with mine water containing organic compounds). Microbial activity increases 2 to 97 times the solubilization of uranium. The processes are biosyntheses of complexing or chelating compounds. The micro-organisms involved are soil microflora and bacteria of mine water and granites. Some species are identified. Microbial insolubilizations of uranium are described in batch cultures. These processes involve biodegradation of uranium binding organo-compounds. These biodegradations occur after long periods of incubation and promote some neoformations of uranium deposits. Black and yellow deposits are observed and described. These experimental results suggest the model described in the paper. This model seems to apply easily to superficial processes of solubilization and concentration of uranium and in reworking deposits. However, in the case of primary intragranitic uranium deposits it is only an hypothesis correlated by the existence of favourable environmental conditions for bacterial growth and by some geological observations mentioned in the paper.

SOLUBILISATION ET INSOLUBILISATION DE L'URANIUM DES GRANITES PAR DES BACTERIES HETEROTROPHES.

Des incubations en cuve et des cultures en perfusion semi-continue sont utilisées comme dispositifs expérimentaux pour étudier la solubilisation et l'insolubilisation de l'uranium des granites par des bactéries hétérotrophes. Les milieux nutritifs sont synthétiques (à base de glucose ou d'acides aminés) ou naturels (eau de profondeur contenant des composés organiques). L'activité microbienne accroît de 2 à 97 fois la solubilisation de l'uranium. Ces processus de solubilisation correspondent à la biosynthèse de composés organiques complexants ou chélatants par les micro-organismes. Les micro-organismes intervenant dans ces processus sont des microflores du sol, des bactéries d'eau de profondeur et des granites. Certaines espèces ont été identifiées. Les processus d'insolubilisation microbienne de l'uranium sont mis en évidence lors d'incubations en cuve. Ils impliquent la biodégradation de complexes organiques de l'uranium. Ces biodégradations se produisent après de longues périodes d'incubation et conduisent à la néoformation de dépôts d'uranium. Des dépôts noirs et des dépôts jaunes sont observés et décrits. Les résultats expérimentaux permettent de proposer un modèle métallogénique présenté dans le mémoire. Ce modèle semble devoir s'appliquer aisément aux phénomènes de concentrations superficielles et de remaniements des gîtes. En ce qui concerne la mise en place des gîtes primaires intragranitiques, le modèle offre seulement une hypothèse qui s'appuie d'une part sur l'existence de conditions de l'environnement favorables à la croissance bactérienne, d'autre part sur quelques observations géologiques mentionnées dans le mémoire.

INTRODUCTION

Des mesures précises montrent que l'altération superficielle d'un massif granitique libère des quantités considérables d'uranium. Dans un granite appelé fertile comme certains leucogranites du Limousin ou de

Vendée, le clark de 18 à 22 ppm de la roche saine de profondeur descend à 6 ou 8 ppm pour les premiers mètres d'altération, proches de la surface, et se situe autour de 13 à 15 ppm sur les 15 m suivants. Il faut donc admettre qu'avant le décapage érosif du massif et son déblaiement, une fraction importante de l'uranium a été entraînée par la circulation des eaux qui percolent à travers le massif granitique. Le calcul montre qu'une tranche de 20 m d'épaisseur sur une surface de 1 km² libère par les altérations superficielles successives de 600 à 700 tonnes de métal; celui-ci ne quitte pas le massif par ruissellement, mais, pour une fraction appréciable, variable suivant la tectonique, est entraîné en profondeur avant déblaiement.

Différents mécanismes de solubilisation et d'insolubilisation sont généralement invoqués, les seconds étant la conséquence des premiers. Ces mécanismes peuvent être de nature chimique ou biologique. Un premier mécanisme peut consister dans l'oxydation de l'uranium tétravalent en uranium hexavalent, suivie de la formation d'uranylcarbonates sous l'action du CO₂ dissous dans les eaux. Un autre mécanisme fait intervenir des complexations par des composés organiques d'origine végétale ou microbienne. D'autres mécanismes ont également été proposés, dans lesquels interviennent des micro-organismes autotrophes ou hétérotrophes. Les bactéries autotrophes appartiennent au genre Thiobacillus et agissent par l'acide sulfurique qu'elles produisent. Parmi les hétérotrophes, dont le substrat nutritif est par définition carboné, on a signalé l'intervention des sulfatoréducteurs dans la précipitation de l'uranium, notamment dans les gîtes sédimentaires des Etats-Unis d'Amérique. Dans la nature, ces différents processus chimiques ou biologiques peuvent intervenir successivement ou simultanément.

Dans la présente étude, nous avons cherché à vérifier si d'autres bactéries hétérotrophes, provenant de sols ou de granites de profondeur, sont capables de solubiliser et d'insolubiliser l'uranium des granites. Dans nos expérimentations, le carbone organique a été fourni aux bactéries, soit sous forme de produits organiques de synthèse, soit par des eaux naturelles, percolant dans les granites, et concentrées. Ces résultats expérimentaux sont fondés sur des techniques microbiologiques et biochimiques. Leur discussion peut ouvrir quelques perspectives sur les mécanismes biologiques de l'altération des massifs granitiques, de la libération de l'uranium et de sa concentration ultérieure après transport.

1. METHODOLOGIE

1.1. Modèles expérimentaux

Deux modèles sont utilisés: dans le premier, du type cuve (batch), les incubations sont effectuées dans des flacons de 100 à 1000 cm³, où les teneurs de l'uranium solubilisé sont contrôlées à intervalles réguliers. Dans le second modèle, dit de perfusion semi-continue (semi-continuous flow), le renouvellement lent du liquide contenu dans les colonnes expérimentales permet une approche cinétique du processus; la stérilisation y est cependant plus difficile à maintenir [1, 2].

Les roches utilisées ont, selon les expériences, d'une part différentes teneurs d'uranium (arène à 6 ppm, minerai pauvre de 0,085 à 0,16%, minerai

riche de 1,5 à 30% d'uranium contenu), et d'autre part divers états d'altération (arène ou minéral sain de profondeur). Il s'agit, dans presque tous les cas, de granite (et très rarement d'épisyénite) prélevé dans les gîtes uranifères intragranitiques français (Vendée, Limousin, Forez). L'uranium y est minéralogiquement présent sous la forme d'oxydes noirs ou de pechblende. Pour ces expériences, la roche a été concassée, puis tamisée dans un intervalle défini de granulométrie (généralement entre 1 mm et 0,3 mm).

1.2. Milieux nutritifs

Les milieux nutritifs utilisés dans les expérimentations décrites sont naturels ou synthétiques.

1.2.1. Milieu nutritif naturel: eau profonde

L'eau qui percole en profondeur, à travers les fissures d'un massif granitique, et que nous appelons «eau profonde», est recueillie en mine, à 50, 80 ou 250 m de profondeur, dans un suintement naturel, à la sortie d'une diacalse par exemple. On choisit de préférence une zone de galerie dans laquelle l'amont pendage n'est pas perturbé par des travaux d'exploitation. Cette eau profonde semble être un bon milieu nutritif pour la microflore de profondeur (cf. définition infra), à condition de la concentrer préalablement environ cinq fois par évaporation à basse température (maximum 35°C).

TABLEAU I. ANALYSE DE L'EAU PROFONDE, PRELEVEE DANS UN MASSIF GRANITIQUE (VENDEE, FRANCE) A 250 m AU-DESSOUS DE LA SURFACE

R ^a	Carbone organique	Mg	Ca	K	Na	SO ₄ ²⁻	Cl ⁻
340	3,5	30	61	7,2	124	82,7	100

^a Résistivité, exprimée en ohm·cm.

Les autres valeurs sont exprimées en mg/l.

TABLEAU II. ANALYSES D'EAUX PROFONDES, PRELEVEES DANS UN MASSIF GRANITIQUE (MARGNAC, LIMOUSIN, FRANCE) ENTRE 50 ET 80 m AU-DESSOUS DE LA SURFACE

	R ^a	rs ^b	Mg	Ca	K	Na	SO ₄ ²⁻	Cl ⁻	NO ₃
Année 1969	11 500	98,75	3,68	2,30	1,53	9,68	22,16	4,91	0,87
Année 1970	9 500		2,02	6,27	0,60	10,07	27,45	5,76	nd

^a Résistivité, en ohm·cm.

^b Résidus secs.

nd = non dosé. Valeurs exprimées en mg/l.

TABLEAU III. VARIATION DE LA TENEUR EN CARBONE ORGANIQUE DES EAUX D'UN MASSIF GRANITIQUE ENTRE LE 1^{er} OCTOBRE ET LE 30 DECEMBRE (en mg/l)

Dates des prélèvements	Année 1969		Année 1970	
	A	B	A	B
1 ^{er} oct.	2,90	0,37	2,25	0,76
13 oct.	4,47	0,49	3,90	0,39
5 nov.	3,50	0,44	4,00	0,59
25 nov.	5,35	0,40	6,05	0,71
9 déc.	2,42	0,42	6,60	0,68
30 déc.	1,51	0,46	-	-

B: moyenne de six prélèvements, effectués entre 50 et 80 m de profondeur.

A: teneur de la nappe située au-dessus de ces prélèvements.

La stérilisation de cette eau est difficile. L'autoclavage présente l'inconvénient de modifier ses composants organiques, favorisant ensuite les solubilisations chimiques. La filtration sur ultrafiltres type Millipore ne donne pas toujours satisfaction.

L'eau profonde, qui a un pH voisin de 5,6 à 6,0, contient du carbone organique en plus des cations et anions minéraux habituels. L'analyse d'eau profonde prélevée en Vendée figure au tableau I.

L'eau percolant dans un massif granitique du Limousin (tableau II) a été analysée sur une plus longue période et la moyenne des six prélèvements effectués six fois par automne donne des valeurs nettement inférieures à celles trouvées en Vendée.

Le carbone organique contenu dans l'eau profonde provient de l'action pédologique. Il semble résulter de la transformation des composés végétaux et microbiens. La teneur en carbone organique des eaux varie au cours de la saison automnale, avec un décalage par rapport aux nappes superficielles. Ce décalage est fonction de la profondeur et de la vitesse de percolation (tableau III).

C'est ce carbone organique, beaucoup plus que les éléments minéraux (ces derniers sont relativement plus constants), qui paraît constituer le substrat nutritif essentiel de la microflore de profondeur. Plus précisément, il semble que l'eau collectée en novembre ou fin mars (en France) permette une meilleure activité bactérienne.

Des travaux en cours ont permis de montrer qualitativement la présence d'acides volatils, d'hydrocarbures aromatiques et aliphatiques, de composés aminés, notamment tyrosine, sans qu'il soit possible de fournir encore d'indications quantitatives. Il peut s'agir de composés d'un poids moléculaire élevé. Diverses méthodes d'analyse ont été employées après séparation sur résines échangeuses d'ions et extraction par solvants organiques: chromatographie sur couche mince et sur papier (acides aminés, acides carboxyliques, composés phénoliques); spectro-

métrie infrarouge sur culot de centrifugation après concentration très poussée de l'eau (hydrocarbures aliphatiques et aromatiques).

Les éléments organiques contenus dans ces eaux sont plus ou moins rapidement biodégradés en même temps que le pH s'élève de 5,9 à 7 ou 8. Pour éviter, en cours de conservation, même à basse température (0, -4°C) la biodégradation de ces composés organiques et leur minéralisation, la congélation à -40°C est conseillée.

1.2.2. Milieux nutritifs de synthèse

Les milieux utilisés ont été de deux types:

- Des milieux de culture glucosés à 2%, d'un emploi habituel en microbiologie. Ils conviennent très bien à la microflore du sol, utilisée pour certains expériences (milieux M2, M3) [3, 2] (Exp. 1 à 4, tableau IV).

- Des milieux à faible teneur en carbone organique. Les exigences nutritionnelles de la microflore de profondeur sont assez particulières et les milieux glucosés lui conviennent moins bien que des milieux nutritifs très pauvres: par exemple, milieu nutritif contenant 10^{-3} mole de tyrosine et 25×10^{-3} mole d'arginine en solution dans 1 litre d'eau distillée. A l'inverse de l'eau profonde, ces milieux de synthèse sont facilement stérilisables à l'autoclave (milieu II TA, tableau IV).

1.3. Stérilisation

Un certain nombre d'expériences ont été effectuées, en stérilisant les roches à l'autoclave, trois fois, de 30 min à 1 h, à 120°C (deux jours de suite, et sept jours après). Dans les cas où l'on a craint une insuffisance de l'autoclavage, nous avons stérilisé les minerais au four à moufle, dans les conditions suivantes: L'échantillon est placé au four à moufle, à 800°C, pendant 1 h, puis transféré, encore chaud, dans un flacon stérile; il est lavé à l'eau stérile, puis stérilisé à l'autoclave, deux fois 30 min à 120°C, à un jour d'intervalle, ceci pour éliminer d'éventuelles contaminations au cours des manipulations. La température de 800°C ne modifie pas les oxydes noirs d'uranium et entraîne seulement un fendillement des feldspaths ou des quartz et un grillage des sulfures. Mais la disparition de toute trace de carbone organique présent dans la roche entraîne fréquemment une diminution de l'activité bactérienne, donc une diminution de la solubilisation d'uranium.

1.4. Incubations

Les incubations sont effectuées dans l'obscurité à $23 \pm 2^\circ\text{C}$.

1.5. Expression des résultats

Tous les résultats présentés dans les tableaux et figures sont les moyennes de 3, 4 et parfois 5 répétitions par traitement. La solubilisation est suivie en dosant par fluorimétrie la teneur du milieu en uranium, soit dans le milieu de culture pour les dispositifs en cuve, soit dans l'effluent pour les dispositifs de perfusion semi-continue.

La solubilisation (microbienne + non microbienne) est mise en évidence par la teneur maxima en uranium dans les dispositifs ensemencés (tableau IV).

TABLEAU IV. SOLUBILISATION MICROBIENNE DE L'URANIUM DANS DIFFERENTES CONDITIONS EXPERIMENTALES

Expérience		Matériel expérimental		Milieux de culture	Résultats	
N°	Durée (j)	Minéral (teneur U)	Microflore provenant de		Teneur maxima ^a	Coefficient de solubilisation ^b
1. Flux semi-continu						
1	50	mineral (0, 1%)	sol	glucosé M2	3,95	3,7
2	30	arène (6 ppm)	sol + thymol	glucosé M3	0,09	2,0
3	30	granite (18 ppm)	sol + thymol	glucosé M3	0,05	4,4
4	30	mineral (0, 03%)	sol + thymol	glucosé M3	5,80	97,7
5	70	mineral (0, 03%)	profondeur	tyrosine	0,40	5,1
2. Cultures en cuves (batch)						
6	100	mineral (0, 16%)	profondeur	eau prof. ^c	34,00	2,5
7	130	mineral (32%)	profondeur	eau prof. ^c	13,40	2,4
8	100	mineral (0, 16%)	profondeur	eau prof. ^c	13,00	30,0
9	115	mineral (1, 11%)	profondeur	Mil. II TA	110,80	3,0
10	115	mineral (30%)	profondeur	Mil. II TA	50,30	2,0
11	60	mineral (0, 024%)	profondeur	tyrosine	1,85	9,0

^a La teneur maxima, exprimée en mg/l, est celle de la plus forte solubilisation mesurée dans les effluents au cours de l'expérience (flux semi-continu) ou dans le milieu liquide, à la fin de l'expérience (dispositifs en cuve).

^b Coefficient de solubilisation, défini dans le texte.

^c Eau profonde concentrée cinq fois, à 35°C.

Le rôle des micro-organismes dans la solubilisation est mesuré par le coefficient de solubilisation microbienne, qui est égal au rapport SUE:SU. Par SU, nous entendons la quantité globale d'uranium recueillie et dosée dans l'effluent des colonnes de perfusion ou dans le milieu liquide des cuves; SU intègre les phénomènes de précipitation physico-chimique ou biologique pouvant se produire dans ces colonnes ou cuves. Il s'agit donc d'une mesure de la différence entre la solubilisation totale de l'uranium et son insolubilisation.¹ Dans le cas des systèmes ensemencés, SU correspond à la solubilisation par voie microbienne et non microbienne; il est désigné ici par SUE. Dans le cas des systèmes stériles, SU correspond à la solubilisation non microbienne; il est désigné ici par SUs.

¹ Rappelons que l'insolubilisation microbienne [4] correspond à l'insolubilisation, sous l'influence des micro-organismes, de l'uranium préalablement en solution, sans préjuger des mécanismes. L'insolubilisation microbienne comprend, d'une part l'immobilisation par les cellules microbiennes, et d'autre part des processus tels que la biodégradation des complexes organométalliques, suivie de la précipitation des éléments minéraux.

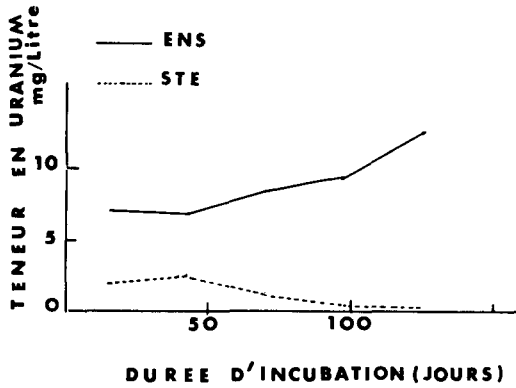


FIG.1. Expérience 8: variation, en fonction de la durée d'incubation, de la teneur en uranium du milieu liquide dans un dispositif en cuve. Microflore de profondeur. Milieu eau profonde concentrée cinq fois. Minerai à 0,16% U (100 g). ENS: Ensemencé — STE: Stérile.

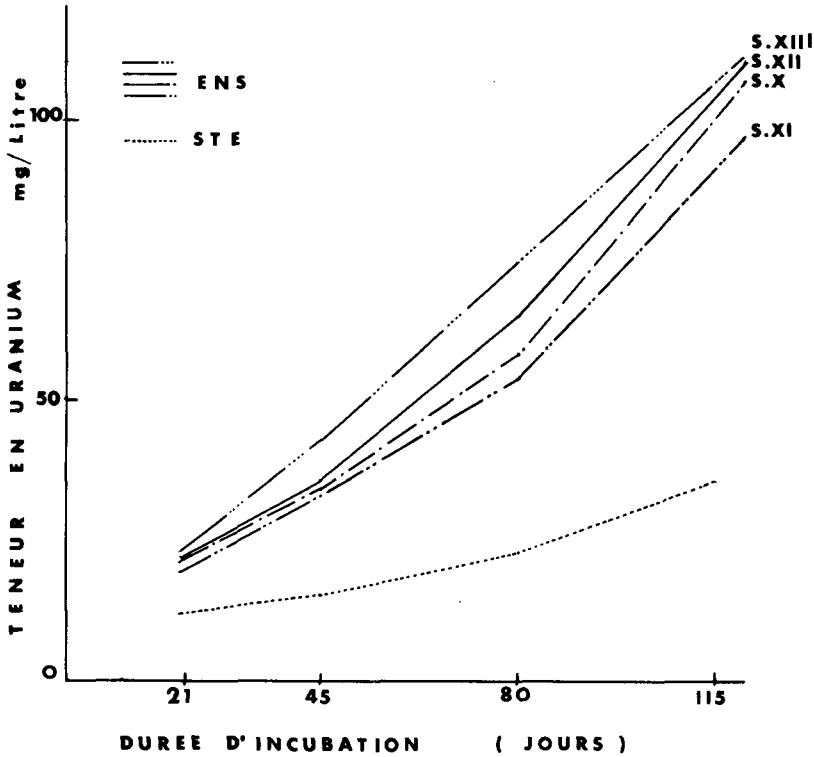


FIG.2. Expérience 9: variation, en fonction de la durée d'incubation, de la teneur en uranium du milieu liquide dans un dispositif en cuve. S.X, S.XI, S.XII, S.XIII: associations bactériennes de profondeur. Milieu II TA. Minerai à 1,1% U (5 g). ENS: Ensemencé — STE: Stérile.

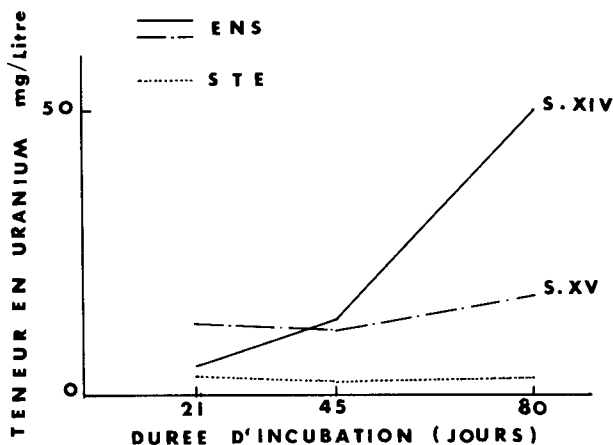


FIG.3. Expérience 10: variation, en fonction de la durée d'incubation, de la teneur en uranium du milieu liquide dans un dispositif en cuve. S.XV, S.XIV: associations bactériennes de profondeur. Milieu II TA. Minéral à 30% U (5 g). ENS: Ensemencé - STE: Stérile.

2. RESULTATS

2.1. Solubilisation

2.1.1. Rôle des micro-organismes

Les figures 1, 2 et 3 représentent les courbes de solubilisation de l'uranium en fonction du temps, obtenues dans diverses conditions expérimentales. Les milieux nutritifs sont constitués d'eau profonde concentrée (fig.1), ou d'une solution d'arginine et de tyrosine (fig.2, 3). Ces courbes, analogues à celles obtenues dans les expériences en flux semi-continu (courbes non présentées), montrent que les micro-organismes favorisent très activement la solubilisation de l'uranium des roches. Celle-ci suit une croissance régulière pendant les périodes d'incubation considérées. Le tableau IV met également en évidence ce rôle important des micro-organismes de différentes origines (sol et profondeur) et permet de constater que l'activité microbienne peut, dans certains cas, multiplier presque par 100 la solubilisation chimique non microbienne. D'autre part, une microflore de profondeur permet l'obtention de solutions contenant plus de 100 mg U/l.

2.1.2. Microflore impliquée

Dans les expériences 2, 3 et 4 (tableau IV), la microflore provenant du sol (sol brun acide sur granite) a été sélectionnée par le thymol [2, 5]. Elle est constituée par des levures isolées (non identifiées) et par quatre espèces bactériennes. L'une des souches isolées est Bacillus licheniformis; les trois autres, non identifiées, sont de petits bâtonnets d'environ $0,5 \mu\text{m} \times 2,0 \mu\text{m}$ [2]. Les Thiobacillus sont absents de cette microflore.

Dans les autres expériences citées, la microflore dite «microflore de profondeur» peut avoir trois origines:

- La roche du front de taille: des fragments de roche d'un volume unitaire de 1 à 2 cm³ sont détachés d'un front de taille frais, après un tir d'avancement de galerie, de préférence en formation filonienne, à des profondeurs de 50, 100 ou 250 m sous la surface topographique. Chaque fragment de roche est immédiatement lavé dans une solution antiseptique (formol 1%), rincé deux fois à l'eau distillée stérile, et déposé dans une enceinte stérile contenant un milieu liquide nutritif stérile. Un fragment de roche est ensuite utilisé pour effectuer les ensemencements. Il est alors placé dans les flacons à ensemercer et peut être retiré après une semaine.

- La carotte de sondage: une carotte de sondage, prélevée à 135 m de profondeur, est utilisée dans des conditions identiques.

- L'eau profonde: l'eau profonde, prélevée avec le maximum de précautions pour éviter toutes contaminations par des micro-organismes étrangers, est aussi utilisée pour effectuer les ensemencements. Ces fragments de roche ou cette eau profonde, provenant des gîtes uranifères intragranitiques de Vendée, du Limousin ou de Forez, sont utilisés, soit directement comme inoculum, soit pour multiplier, par enrichissement sur un milieu de culture défini, une association microbienne comportant un nombre limité d'espèces, qui sert d'inoculum. Les figures 2 et 3 montrent la solubilisation de l'uranium par de telles associations provenant de roches de profondeur (S. X, S. XII, S. XIV, S. XV) ou d'eau profonde (S. XI, S. XIII), dans un milieu tyrosine-arginine. Quatre microflores de profondeur et quelques-unes des espèces bactériennes les constituant ont été isolées sur milieux nutritifs gélosés. Quelques bactéries ont ainsi pu être identifiées: Pseudomonas fluorescens, Pseudomonas putida, ainsi que plusieurs espèces d'Achromobacter. Les travaux en cours permettront sans doute de déterminer plusieurs autres souches, déjà isolées, dont l'identification est rendue délicate par leur inaptitude à utiliser les glucides employés dans les tests habituels. Pseudomonas fluorescens a été signalé [6] comme bactérie susceptible de solubiliser l'uranium. Cette bactérie produit du peroxyde d'hydrogène qui est un oxydant efficace. Dans toutes ces expériences, il y a lieu de souligner que les contrôles de stérilité des témoins, effectués à l'aide d'observations microscopiques et sur des milieux divers (Nutrient Broth Difco, Nutrient Agar Difco, eau de mine concentrée gélosée, enrichie en tyrosine et arginine), montrent l'absence de micro-organismes.

2.1.3. Mécanismes de solubilisation

Les bactéries impliquées ici sont des hétérotrophes qui exigent la fourniture d'énergie sous forme de composés organiques dont on a vérifié l'utilisation par chromatographie et dosages colorimétriques. Divers résultats permettent de penser que la solubilisation de l'uranium ne résulte pas seulement de processus d'oxydation (par exemple par H₂O₂, fourni par Pseudomonas fluorescens) et de carbonatation, mais aussi de complexations organométalliques. La preuve de la complexation organo-métallique est fournie par les deux types d'observations suivantes. La première réside dans le fait que l'action des acides glutamique et aspartique en solution diluée (respectivement 0,367 et 0,333 g/l) au contact de minéral

(5,0 g à 0,08%, 1,1% et 30% U) conduisent, dans des conditions stériles, à des mises en solution de l'uranium dans le milieu liquide. Le second type d'observation découle d'expériences en perfusion semi-continue. Dans celles-ci, la microflore obtenue après stérilisation partielle en présence de thymol (tableau IV), qui favorise très activement cette solubilisation, a un métabolisme orienté vers la formation de quantités importantes de composés organiques acides complexants, de faibles masses moléculaires, comme par exemple l'acide oxalique, ainsi que de composés acides à grosses masses moléculaires (P.M. = 2000, 2500) [2], qui peuvent certainement intervenir dans la lixiviation de l'uranium.

2.2. Insolubilisation

2.2.1. Mise en évidence du processus

Lorsque le temps d'incubation des dispositifs en cuves dépasse 150 jours, la teneur en uranium soluble dans le milieu de culture ensemencé avec la microflore complexe diminue après cette date. Ceci signifie que les processus d'insolubilisation l'emportent alors sur les processus de solubilisation. La figure 4 montre une courbe typique obtenue dans ce cas, ainsi que la courbe témoin obtenue dans le cas d'un milieu stérile.

2.2.2. Mécanismes d'insolubilisation microbienne

L'insolubilisation obtenue dans l'expérience que l'on vient de citer peut être attribuée à la biodégradation de complexes organométalliques. En effet, il a été montré au paragraphe 2.1.3 que des composés organiques tels que les acides aspartique et glutamique peuvent, en milieu stérile, solubiliser l'uranium. L'uranium ainsi solubilisé est vraisemblablement sous la forme de complexes organométalliques et ces derniers peuvent être dégradés par la microflore, libérant ainsi l'uranium qui, selon l'état

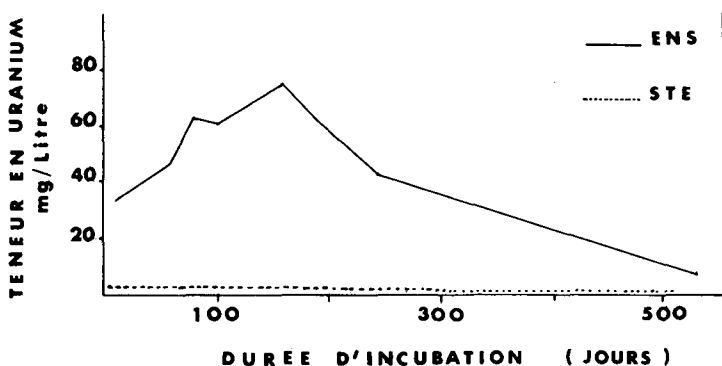


FIG. 4. Expérience préliminaire: Variation, en fonction de la durée d'incubation, de la teneur en uranium du milieu liquide dans un dispositif de culture en cuve. Microflore de profondeur. Milieu nutritif eau profonde concentrée cinq fois. Minéral à 5% U (10 g). ENS: Ensemencé - STE: Stérile.

du milieu et les composés présents, pourra précipiter. On a effectué, à partir de sols ou de roches de profondeur, l'isolement de micro-organismes capables de réaliser de telles biodégradations. En dehors des mécanismes de biodégradation des complexes organométalliques, on peut envisager l'intervention des variations du potentiel d'oxydo-réduction. Ces processus sont en cours de vérification.

2.2.3. Produits d'insolubilisation

En laboratoire, des néoformations de produits noirs et de produits jaunes ont été obtenues. Une expérience du même type que celle décrite ci-dessus (fig. 4) a été conduite en laboratoire, à la température ambiante (20 à 25°C), avec une microflore de profondeur, 10 g de minerai à 7% U, et un milieu nutritif d'eau profonde. Cette expérience a confirmé l'existence des deux phases décrites ci-dessus: une phase de solubilisation au cours de laquelle la teneur en uranium a atteint 125 mg/l, une phase d'insolubilisation à la fin de laquelle la teneur en uranium soluble n'était plus que de 1,5 mg/l. Après trois cents jours, des dépôts noirs irréguliers se sont formés sur les parois des éprouvettes. Ils ont été définis comme des sels d'uranium, à la fois par analyse chimique et par le procédé d'autoradiographie. Lors de la formation des dépôts, les éprouvettes contenaient les deux tiers du liquide initial. Dans d'autres expériences, des dépôts jaunes sont apparus.

Un des plus intéressants a été obtenu à partir d'un minerai de pechblende, à 5% U, dans un milieu d'acide aspartique et avec une microflore de profondeur. La phase de solubilisation avait entraîné une teneur de 60 mg d'uranium par litre. Plus de trois cents jours après le début de l'expérience, le dépôt jaune s'est formé sur la paroi du flacon qui contenait encore 90% du volume du liquide initial. L'analyse aux rayons X (Fe K α) d'une de ces néoformations de produits jaunes a montré des pics correspondant aux longueurs d'onde suivantes (en Å): 3,04, 3,80, 3,83, 5,55, 8,17. Les pics à 3,04 et 3,83 Å peuvent indiquer la présence de calcite. Les autres pics, dont deux de forte intensité, à 5,55 et 8,17 Å, ne permettent pas de déterminer un corps cristallisé figurant dans les tables de l'ASTM (édition de 1967, corps inorganiques). Ce produit jaune cristallisé, soumis à l'analyse qualitative par fluorescence X, a montré les raies spécifiques de l'uranium U L β 1, U L β 2, U L α 1, U L γ ainsi que les raies du calcium, à l'exclusion de tout autre élément de la classification périodique situé au-dessus du silicium. En ce qui concerne le calcium, sa présence dans l'échantillon n'est pas démontrée car le vernis de fixation en renferme. Quant aux éléments de rang inférieur à Si, c'est-à-dire, Al, Mg, Na, F, N, C, B, cette méthode ne permet pas de les déceler.

CONCLUSION

Les résultats expérimentaux obtenus permettent de proposer le modèle métallogénique représenté dans la figure 5. Ce modèle fait intervenir:

- la solubilisation de l'uranium des granites dans le manteau d'altération, processus dans lequel les micro-organismes sont susceptibles de jouer un rôle de premier ordre

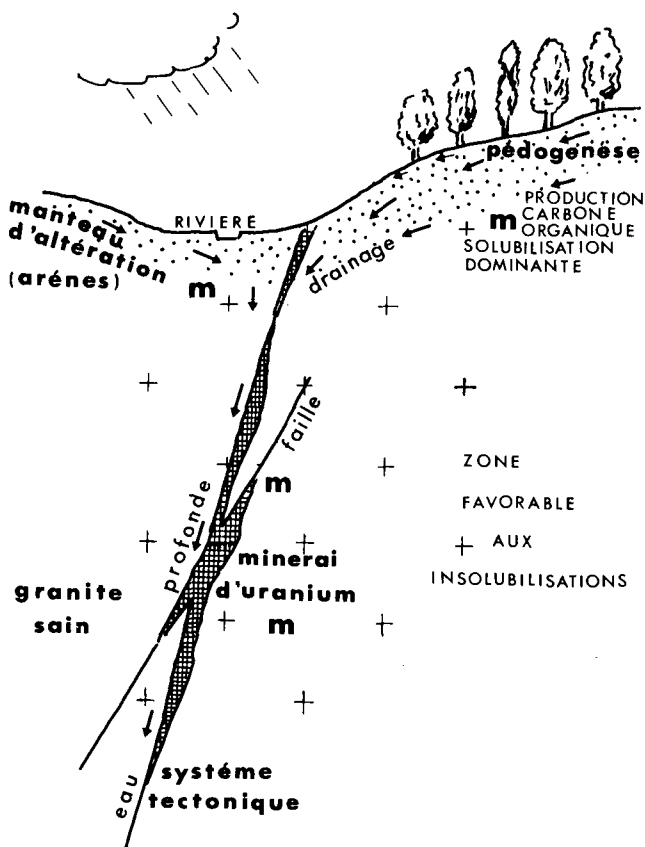


FIG. 5. Migration de l'uranium dans un sous-sol granitique (m: sites d'intervention possible des micro-organismes).

- le transport de l'uranium par les percolations des eaux naturelles dans les accidents tectoniques
- l'insolubilisation de l'uranium, qui résulte de processus physico-chimiques ou microbiens.

Ces processus peuvent être associés et intervenir simultanément aux différents niveaux; mais nous admettons que les processus de solubilisation prédominent dans le manteau d'altération alors que les processus d'insolubilisation l'emportent en profondeur.

Ce modèle s'appuie sur:

- l'existence, dans les sols, les eaux profondes et les roches de profondeur, de micro-organismes hétérotrophes capables de solubiliser ou d'insolubiliser l'uranium

- la présence de carbone organique, d'origine végétale ou microbienne, dans le sol, les granites et les eaux profondes; les teneurs en carbone organique des eaux profondes sont faibles (0,3 à 3 mg/l, mais, à la différence des niveaux gréseux sédimentaires, dans lesquels le carbone est en général enfoui avec la sédimentation, la circulation permanente des eaux dans les massifs granitiques entraîne un renouvellement relativement constant de ce carbone
- l'existence, aux profondeurs considérées, de conditions d'environnement souvent favorables (température, pH, oxygène dissous, humidité).

Le modèle proposé peut apporter une explication satisfaisante à certains faits géologiques, notamment:

- l'écart de 30 à 50 millions d'années qui sépare souvent le moment de mise en place d'un massif granitique de celui de la mise en place des gîtes uranifères de ce massif
- la quasi-disparition des minéralisations à une profondeur variant entre 250 et 400 m, bien que les structures tectoniques se poursuivent au-dessous
- l'importance du Permo-trias et du Tertiaire (périodes géologiques de forte activité continentale) pour la mise en place mondiale de l'uranium.

En outre, l'étude détaillée des gîtes uranifères du Limousin (France) montre, à des profondeurs assez constantes de 60 à 80 m, rarement 100 m, une zone d'enrichissement en uranium, du point de vue des teneurs et de la quantité du métal au mètre d'approfondissement. Cette zone d'enrichissement, appelée bulbe par certains [7], semble étroitement liée à la surface car sa position en profondeur est identique pour des gîtes très voisins se trouvant à une altitude différente.

On peut objecter au modèle proposé qu'il justifie difficilement les accumulations importantes d'uranium rencontrées dans certains cas. En fait, cette objection serait valable si on limitait l'effet des processus considérés à une colonne d'altération surmontant le gisement, en d'autres termes si l'on ne considérait que le drainage vertical. En fait, le système le plus vraisemblable, dans la nature, doit intégrer un drainage latéral qui peut collecter l'uranium sous une surface du manteau d'altération, variable selon la morphologie du terrain, et en tout cas bien supérieure au seul volume vertical situé immédiatement au-dessus du système tectonique intéressé.

Le modèle proposé semble devoir s'appliquer aisément aux phénomènes de concentrations superficielles et de remaniements des gîtes.

En ce qui concerne la mise en place primaire des gîtes uranifères intragranitiques, notre modèle constitue seulement une hypothèse que l'on peut évoquer, parallèlement aux diverses hypothèses déjà proposées par différents auteurs et dont Geffroy [8] a apporté récemment une présentation synthétique, dans le cas des gisements français.

REMERCIEMENTS

Les auteurs expriment leur reconnaissance en particulier à M. P. Blazy, Directeur de l'Ecole nationale supérieure de géologie appliquée et de prospection minière de Nancy, pour l'aide qu'il a apportée à ces recherches. Ils remercient également MM. Bussière et Morel, Mmes Boulmier et Chakroun pour leur importante collaboration à ces résultats.

REFERENCES

- [1] BERTHELIN, J., DOMMERGUES, Y., Rôle des produits du métabolisme microbien dans la solubilisation des minéraux d'une arène granitique, *Rev.Ecol. Biol. Sol Paris* **IX** 3 (1972) 397-406.
- [2] BERTHELIN, J., KOGBLEVI, A., DOMMERGUES, Y., Microbial weathering of a brown forest soil: influence of partial sterilization, *Soil Biol. Biochem.* (sous presse).
- [3] MAGNE, R., BERTHELIN, J., DOMMERGUES, Y., «Microbial solubilization of uranium from ores, granite, and granite sand», *Symp. Environmental Biogeochemistry*, Utah State University, Logan, U.S.A., 1973, Abstracts p. 20-21.
- [4] BERTHELIN, J., Altération microbienne d'une arène granitique, *Sci. Sol Paris* **1** (1971).
- [5] MAGNE, R., BERTHELIN, J., DOMMERGUES, Y., Solubilisation de l'uranium dans les roches, par des bactéries n'appartenant pas au genre *Thiobacillus*, *C.R. Acad. Sci., Sér. D*, **276** (1973) 2625-28.
- [6] ZAJIC, J.E., *Microbial Biochemistry*, Academic Press, New York (1969).
- [7] MOREAU, M., PUGHON, A., PUIBARAUD, Y., SANSELME, H., L'uranium et les granites, *Chron. Mines Recherche Minière*, n° 350 (1966).
- [8] GEFFROY, J., «Les gîtes uranifères dans le Massif Central», *Géologie, géomorphologie et structure profonde du Massif Central français* (C.R. *Symp. J. Jung*, Clermont-Ferrand, 1971), *Plein Air Service*, Clermont-Ferrand (1971) 541-79.

DISCUSSION

H. H. ADLER: The conditions that you mention in your model — presence of uraniferous granite and of humate or other organic matter, the micro-organisms involved, the presence of fractures and leaching of uranium — seem to me to be more or less ubiquitous in the earth's crust. The deposits of which your model is representative seem to form under supergene conditions in France. We see very few vein-type deposits in the United States of America and that makes me wonder why your model does not work there. Can you explain why that should be so?

J. R. BERTHELIN: This is of course a model designed to be applicable in many localities. Bear in mind, however, that our scheme of the role which microorganisms may play in the solubilization or insolubilization of uranium and in the formation of intragranitic beds is no more than a theory. We think that this scheme is most easily applicable to processes of uranium solubilization and surface concentration and to the alteration of the beds. Differences of age, tectonics and the geomorphology of granite masses may explain, in some cases, why these mechanisms do not work.

But these few remarks are perhaps not sufficient. The following examples show that relatively specific factors can sometimes intervene to guide the biological action. In three sets of experimental tests operating with the same experimental material, we have observed three different modes of uranium mobilization. In flooded experimental columns mobilization is very slight (microflora oriented towards the anaerobic); in columns containing control microflora we find weak to medium solubilization (aerobic and anaerobic microflora); and in columns containing microflora exposed to partial sterilization (by the presence of thymol) we find strong mobilization. In this last case the metabolism of the microflora is controlled by partial sterilization, and as a result the uranium is actively solubilized.

In other cases, too, a given microorganism can exhibit different types of metabolism and accordingly have a more or less aggressive influence on minerals. The orientation of its metabolism is governed, in such instances, by the presence or absence of certain mineral elements (various cations and anions).

A third example, finally, will show the importance of certain factors which are not immediately apparent and have therefore not received sufficient attention. Careful pedogenetic observations have shown that with a given type of vegetation (beech trees) and a given parent rock (rhetian sandstone) one can obtain two completely different soils: in one case an acid brown soil, and in the other a podzol only a few kilometres away. The climatic conditions were accordingly the same. The work done in this particular case¹ revealed that the different pedogenesis was linked with the presence of iron in one spot and not in the other.

R. G. DODSON: Have you done experiments in saline solutions, or in media of other composition, such as acid or alkaline?

J. R. BERTHELIN: We have used media containing only organic carbon (for example an arginine-tyrosine medium with microflora from deep horizons). However, we have also used media containing mineral anions and cations: deep water for the microflora from depth and glucose media enriched in salts such as ammonium phosphate (as growth factor) for both soil microflora and the microflora from depth. These media have also been enriched in other salts.

H. D. KNIPPING: Your paper reflects a most important piece of fundamental research. Do you know anything about bacteriological activity of this kind during the Proterozoic? We at Rabbit Lake believe that what we observe may be a form of leaching of uranium, but we have not found any evidence of bacteria.

J. R. BERTHELIN: I have no certain knowledge of bacteriological activity during the Proterozoic, but since microorganisms have been shown to have been active in Precambrian time, it is reasonable to assume that there would have been microbial activity during the Proterozoic; however, we are on purely hypothetical ground here. Isotopic fractionation studies do seem to indicate that bacteria were active on the earth from the Proterozoic onwards.

M. DALL'AGLIO: Could you tell us what the physico-chemical conditions of your experiments were?

J. R. BERTHELIN: In certain experiments we were able to establish the physico-chemical conditions. There are no difficulties of measurement as far as pH is concerned: in the arginine-tyrosine media the values were about 5.5 - 8.0 for the microflora from depth. Among the glucose media (in perfusion columns) there were some with a pH as low as 3.0 and even slightly less. In these same experiments the Eh values could be anywhere from +200 to -50 mV (in non-flooded columns with partial sterilization and strong solubilization of uranium). Eh measurements can be difficult in experiments involving tanks, because sampling alters the conditions and tends to bring about equilibrium with the ambient air. To overcome this problem one might consider working with a chemostat system that allows effective control of the redox potential.

D. S. ROBERTSON: Can you conceive of an environment in which the process you have described reverses itself? If, for example, the contributing rock volume became depleted in uranium, could the bacteria act in such a way as to disperse the previously formed deposit?

¹ TOUTAIN, Doctorat ès Sciences, Nancy (1974).

J. R. BERTHELIN: Yes, if conditions compatible with the action of the heterotrophic microorganisms we have been speaking of are present (oxygen, organic carbon, moisture, temperature), there can well be an alteration of deposits accompanied by solubilization and insolubilization. The boundary of the biosphere undoubtedly varies a great deal from one site to another, and our knowledge of deep microflora (microorganisms with specific conditions of life) is very limited. In some published works the limit of the biosphere within the earth's crust is set at a depth of 6000 ft.

A. ZERESHKI: Could you say in roughly what degree microorganisms are responsible for mobilization of uranium in the earth's crust?

J. R. BERTHELIN: We have shown that microflora can increase the solubilization of uranium by anything from 2 to 97 times, but remember that these results were obtained in experimental models; the question whether they can be extrapolated directly to in situ processes remains to be answered. Another thing to remember, however, is that although the processes which occur in the earth's crust may be of slighter intensity, they operate on a vast time scale.

A. G. DARNLEY (Chairman): Have you investigated the effect which elements such as arsenic and selenium might have on the bacterial processes? These elements would be present in many natural situations. Secondly, can the bacteria you describe be identified in the absence of uranium?

J. R. BERTHELIN: The answer to your first question is no: we have not studied the effect of arsenic and selenium.

The bacteria can be identified in the absence of uranium. We have been able to identify them because they correspond to familiar types. However, other bacteria have been isolated in the course of this work which exhibit peculiar characteristics as regards growth and nutritional requirements and do not fit in with the classes normally encountered. These are clearly microorganisms possessing unfamiliar traits — which does not mean, however, that they are definitely associated with uranium.

A STUDY OF THE INFLUENCE OF MICROFLORA ON THE GENESIS OF URANIUM OCCURRENCES AT UDAISAGAR, UDAIPUR DISTRICT, RAJASTHAN

K.M.V. JAYARAM, K.K. DWIVEDI,
M.C. BHURAT, S.G. KULSHRESTHA
Atomic Minerals Division,
Department of Atomic Energy,
New Delhi, India

Presented by G.R. Udas

Abstract

A STUDY OF THE INFLUENCE OF MICROFLORA ON THE GENESIS OF URANIUM OCCURRENCES AT UDAISAGAR, UDAIPUR DISTRICT, RAJASTHAN.

An area of 6 km² in the vicinity of Udaisar shaft was investigated to study the role of sulphur and iron-oxidizing bacteria in the mobilization of uranium in the carbonaceous phyllites and its redeposition in breccias and the fault gouge.

The Aravalli metasediments consisting of conglomerates, phyllites, impure limestones, carbonaceous phyllites and ferruginous-breccia are intruded by granites and gneisses. The general strike is: N20°-30°W-S20°-30°E with an easterly dip of 60-85°.

Uranium mineralization is confined to a fault gouge in a 6 × 200 m zone, at a depth of 25-45 m from the surface. The ore contains stringers of uraninite associated with uranyl minerals and some iron and copper sulphides. It analyses 0.7% FeO, 2.31% Fe₂O₃, 6.3% C, 2.97% SO₄²⁻, 0.85% moisture and 0.03-0.06% U₃O₈ and has a bacterial population of 2.3 × 10⁵/g of dry solids. It has a pH of 2.2 to 4.5 and a redox potential of -360 to -480 mV. The ore samples show disequilibrium in favour of uranium.

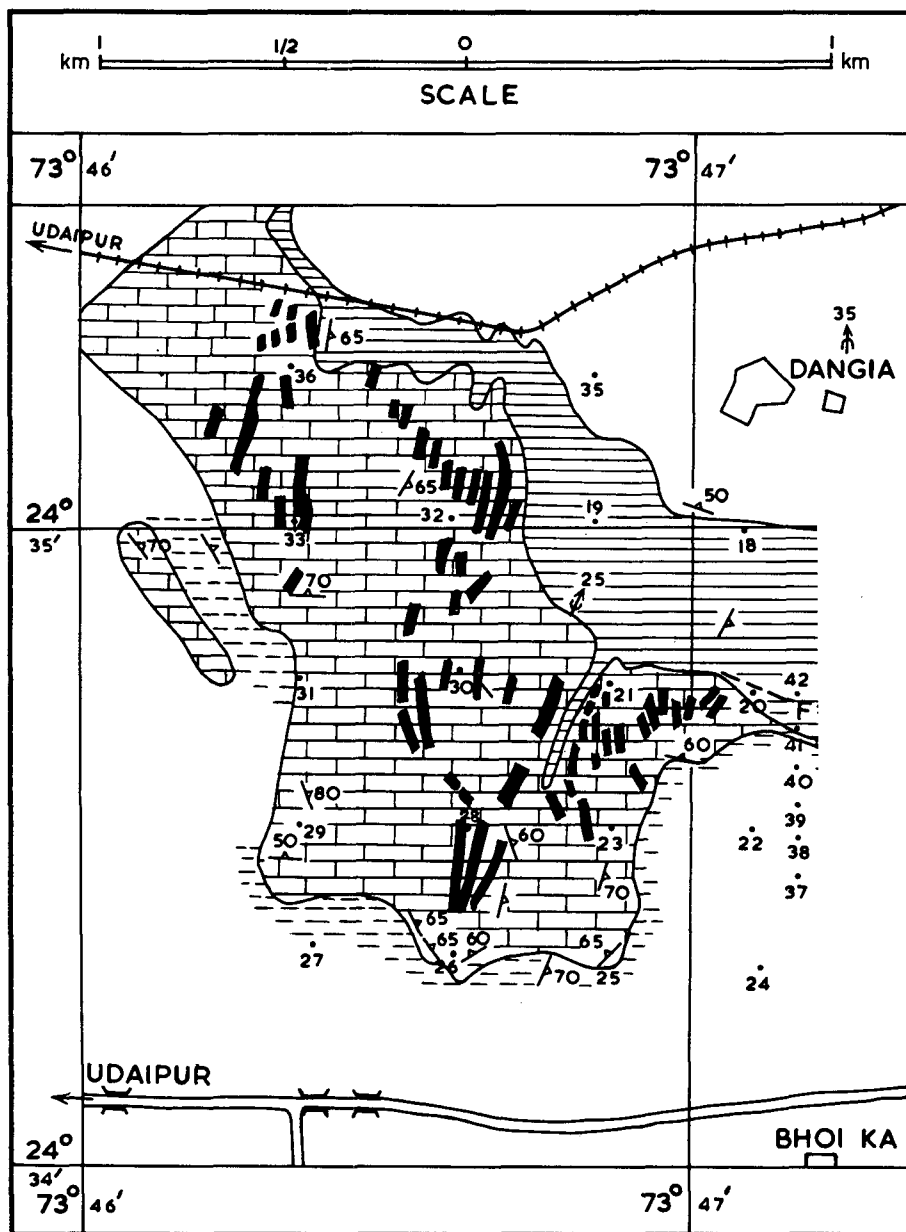
Samples of the ore analysing 0.03% and 0.06% U₃O₈ yielded a leachability of 43.3% and 67.8% respectively at 60% P.D. (solids) in 6-h leaching time, using water alone.

The carbonaceous phyllites in the immediate vicinity analyse 3.04% FeO, 2.96% Fe₂O₃, 11.2% C, 0.11% SO₄²⁻, 0.15% moisture and 0.0005 to 0.0027% U₃O₈ with a pH of 7.0 - 8.5 and a redox potential of -200 to -280 mV.

The occurrence of significantly higher radon values in the vicinity of the shaft (35.5 pCi/cm³), the shallow nature of the deposit, absence of any major channel for waterborne transportation as indicated by resistivity surveys, the presence of elemental sulphur, soluble sulphates and microflora in the ore samples and the high leachability of uranium in water alone show that uranium is mobilized from the carbonaceous phyllites and redeposited in the fault gouge.

1. INTRODUCTION

Detailed prospecting, including borehole drilling and underground exploratory mining of numerous radioactive occurrences, northwest of Udaisar Lake, about 12 km east of Udaipur City, Rajasthan, (Fig.1) revealed low-grade uranium ore (0.03-0.06% U₃O₈) in a 6 × 200 m zone, at a depth of 25-45 m from the surface [1]. Dar and Nandi [2] attributed the uranium mineralization to hydrothermal activity, whereas Phadke and co-workers [3] stressed the importance of "other circulating" solutions in the redistribution of uranium content from the carbonaceous phyllites in the area (cf. Section 2.1.) and its localization in suitable structural and lithological traps. Since uranium from the ore sample is



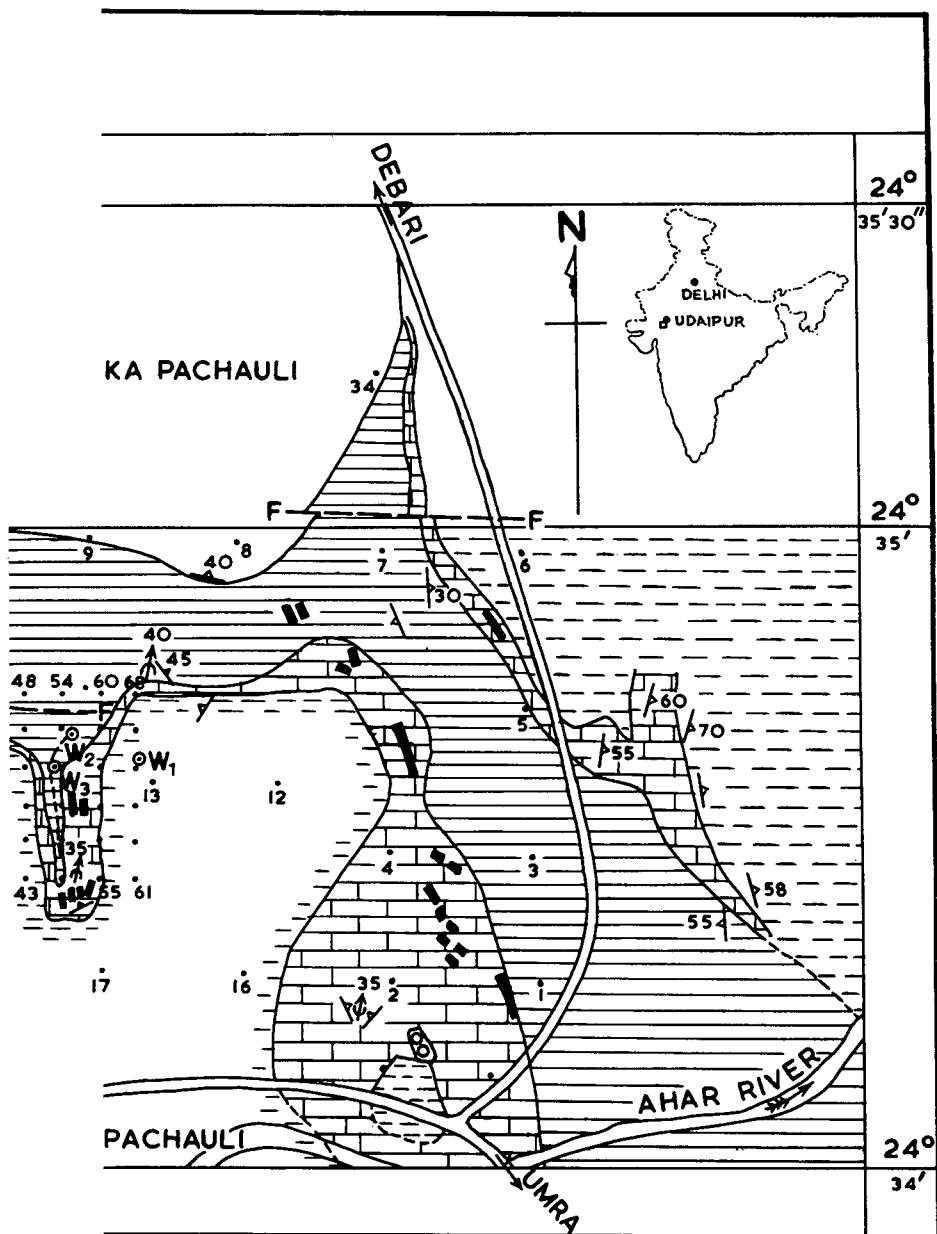


FIG. 1. Geological map of the Udaisagar area (part of toposheet No. 45H/14).

leachable in neutral water at ambient temperature [4] and a resistivity survey did not indicate any channel for transportation [5] of uranium from a known deposit and also since the ore sample contained 2.3×10^6 bacteria per gram [6], detailed investigations were carried out to evaluate the possible role of the microflora in the mobilization of uranium from the country rocks and its subsequent refixation in favourable locales. For this purpose, an area of 6 km² in the vicinity of Udaisagar prospecting shaft was investigated and surface samples were collected at 400-m intervals along NS-EW grids. Later the sampling interval was closed up to 100 m along the grid line, around the shaft area.

2. GEOLOGY

2.1. Geologically, the area represents the Precambrian Aravalli metasediments consisting of conglomerates, chloritic and biotitic phyllites, impure limestones, quartzites, black carbonaceous phyllites and breccias intruded by granites.

The stratigraphic succession of the area is as follows:

Post Aravalli	6: Granites (sometime gneissose)
Aravalli	5: Breccias – ferruginous, quartzitic
	4: Black carbonaceous phyllites
	3: Silicified and calcareous phyllites with impure limestone and quartzite
	2: Chloritic and biotitic phyllites
	1: Conglomerates

2.2. The area, which may be considered as a B 1 B' tectonite, lies on the eastern limb of the highly folded Aravalli synclinorium [7] with a general strike of N20° to 30°W to 30°E, and an easterly dip of 60° to 85°, though occasional westerly dips, due to asymmetric folds and drags, are not uncommon. Structurally the area represents a series of tight isoclinal folds, the main structure in the region of the shaft being a plunging anticline. Drag folds, plunging at 35° towards N to N20°E, nearly at right angles to the main axis, are commonly observed in the black phyllites.

2.3. The breccia bands in the "Horse-shoe hill" to the west of the shaft, which is an open syncline as compared to the tightly folded adjacent anticline in the shaft area, occupy the tensional cracks developed during folding. While most of the tensional cracks are shallow, some are relatively deep and extend well below the water table.

2.4. Among the major lineaments are two faults, one trending N20°W-S20°E and the other N80°W-S80°E. The former, although not apparent on the surface, is clearly indicated by shearing and the presence of fault breccia and gouge observed in the drill holes. This fault has a steep easterly dip and is almost parallel to the anticlinal fold axis.

3. MINERALIZATION

3.1. Uranium mineralization is confined to a kaolinized and brecciated fault gouge within the relatively downthrown western block of the fault (N20°W-S20°E), in a 6 × 200 m zone located at a depth of 10-30 m below the water table. In the ore zone, higher radioactivity is confined to regions where the cross folds form a minor depression due to the doubly plunging fold axis. Both towards north and south the radioactivity values fall rapidly.

3.2. To the west of the shaft, patches of radioactivity (0.008-0.129% U_3O_8) are noted in the limonitic breccia. The black carbonaceous phyllites, which are rich in kaolin and occur to the east of the shaft, also show patches of radioactivity. The granites, however, do not record significant radioactivity.

Samples of water taken from wells in different rock formations, outside the known mineralized area, show 3.9-15.0 pp10⁹ uranium, the higher values being confined always to the carbonaceous phyllites [8].

3.3. Uranium occurs as streaks and stringers of uraninite and sooty pitchblende together with specks of siderite, chalcopyrite (0.05 wt%) and pyrite (0.3 wt%) in an abundant clay gouge (68 wt%) containing fragments of phyllite, quartz and unaltered feldspar (32 wt%). Radioluxographs of the ore samples show general clouding, attributable to uranium adsorbed in the clay material.

4. ISOLATION AND IDENTIFICATION OF BACTERIA

4.1. The occurrence of elemental sulphur and the high oxidation state of some of the samples in the vicinity of the shaft suggested the presence of bacteria. Isolation and identification of the microflora was therefore carried out by using different media.

Heterotrophic bacteria were isolated in nutrient agar medium and the chemoautotrophic sulphur and iron oxidizing bacteria in 9K and Leathen media. The anaerobic bacteria were segregated in a medium comprising 1.0 g KNO_3 , 0.1 g $Na_2HPO_4 \cdot 2H_2O$, 2.0 g $Na_2S_2O_3$, 0.1 g $NaHCO_3$, 0.1 g $MgCl_2 \cdot 6H_2O$ in 1 litre of distilled water. The bacteria present in the above segregates were then enriched by the constant enrichment technique and identified, on the basis of morphological, cultural and physiological characteristics.

(a) The flora identified consist of:

- (i) Heterotrophic:
Pseudomonas perolans; P. chlororaphis;
Bacillus pumilis; Micrococcus luteus
- (ii) Chemoautotrophic:
Thiobacillus ferrooxidans; Thiobacillus-thiooxidans
- (iii) Anaerobic:
Desulfovibrio desulphuricans

TABLE I. DATA ON ROCK AND SOIL SAMPLES

Sample No.	Rock type	pH	mV	rH ₂	% $\underline{e}U_3O_8$	% U_3O_8	% S	% SO_4^{2-}	Oxidizing bacteria	Reducing bacteria
1	Carbonaceous phyllite	8.2	-200	23.3	0.004	0.003	n.d. ^a	n.d.	+	-
6	Soil	8.5	-245	25.5	0.0003	0.0002	n.d.	n.d.	n.d.	n.d.
16	Soil	6.6	-300	23.5	0.011	0.0115	n.d.	n.d.	n.d.	n.d.
19	Carbonaceous phyllite	8.2	-265	25.4	0.010	0.009	n.d.	n.d.	n.d.	n.d.
38	Calcareous breccia	10.2	-100	23.8	0.002	0.0011	nil	traces	-	-
49	Carbonaceous phyllite	9.0	-260	27.0	0.004	0.003	traces	0.11	+	+
52	Calcareous phyllite	9.3	-230	26.5	0.002	0.002	nil	nil	-	-
66	Limestone	8.6	-120	21.3	0.002	0.001	n.d.	n.d.	-	+
67	Ore	3.8	-380	20.7	0.043	0.053	0.92	0.18	+	+
68	Sulphurous ore	2.6	-480	21.7	0.044	0.059	3.10	2.97	+	+
69	Ore	4.0	-380	21.7	0.043	0.053	1.55	0.20	+	+

^a n.d. = not determined.

- (b) The samples collected from the fault zone and the host rocks show the presence of both chemoautotrophic and anaerobic bacteria. In the ore zone, however, a comparatively higher population of Desulfovibrio desulphuricans indicates a relatively higher reducing environment.
- (c) Chemoautotrophic bacteria start appearing in the culture media within 48-72 h but attain their maximum growth in the second and third week. They show a steady growth only between 0.5 to 3.0 pH. Their growth, however, declines between 3.5 to 7.0 pH. This indicates a favourable oxidation environment for leaching and a favourable reduction environment for refixation of uranium.

5. STUDY OF ROCK AND WATER SAMPLES

Results of tests (Tables I and II) carried out on rock samples, crushed to -74 μm size and mixed with water at a rock-to-water ratio of 1:4, show that

- (a) The pH of carbonaceous phyllite varies from 6.5 to 9.0; it varies from 2.6 to 4.0 in the sulphur-bearing samples. Similarly, the redox potential varies from -200 to -240 mV in the carbonaceous phyllites and from -360 to -480 mV in the sulphurous samples. The pH of the calcareous phyllites and limestones varies from 8.0 to 10.2, with a redox potential of -100 to -200 mV. This indicates that the samples from the shaft are comparatively more oxidized.
- (b) The sulphurous ore sample analyses 0.70% FeO, 2.31% Fe₂O₃, 6.3% C, 2.97% SO₄²⁻, 3.1% elemental sulphur, 0.85% moisture, 0.03 to 0.06% U₃O₈ and 0.026 to 0.044% U₃O₈ equivalent by γ measurements. The carbonaceous phyllite in the immediate vicinity analyses 3.04% FeO,

TABLE II. DATA ON WATER SAMPLES

	W ₁ ^a	W ₂	W ₃ (shaft)
U (pp10 ³)	76	97	452
P ₂ O ₅ (pp10 ³)	835	140	400
Fe ²⁺ (pp10 ³)	< 10	< 10	< 10
Fe ³⁺ (pp10 ³)	< 10	27.0	56.0
CO ₃ ²⁻ (mg/l)	259	232	259
SO ₄ ²⁻ (mg/l)	83	126	92
CaO (mg/l)	70	65	70
pH	8.3	8.2	7.9
mV	-50	-40	-10
rH ₂	18.3	17.7	16.1

^a W₁ = well water No. 1.

W₂ = well water No. 2.

- 2.96% Fe_2O_3 , 11.2% C, 0.11% SO_4^{2-} , traces of elemental sulphur, 0.001 to 0.004% U_3O_8 equivalent by γ measurements and 0.0005 to 0.003% U_3O_8 . The mined ore sample analyses 0.20% SO_4^{2-} , 1.55% elemental sulphur, 0.043% U_3O_8 equivalent by γ measurements and 0.053% U_3O_8 .
- The ore samples show a prolific growth of anaerobes and scanty growth of chemoautotrophic bacteria. Samples from the host rock show a significant growth of the latter and a negligible growth of the former microflora.
 - The ore samples show disequilibrium in favour of uranium. Samples of the surrounding country rock, on the other hand, show disequilibrium in favour of uranium daughters.
 - The uranium content in the shaft water decreases to 84 pp10⁹ during summer months from 542 pp10⁹ immediately after the rains. This indicates that the leached uranium is carried by percolating waters, through available channels, during the rainy season.
 - The rH_2 values vary from 21.3 to 29.0 in carbonaceous phyllites, 20.0 to 25.5 in sulphur-bearing samples and 16.1 to 17.7 in the shaft and well waters. This indicates favourable conditions for refixation of uranium below the water table.

6. LEACHING OF URANIUM

6.1. Static leaching tests (Table III) for different periods of time and at different pulp densities showed that:

- 43.3% and 67.8% of the uranium can be leached at ambient temperature in neutral water from ore samples analysing 0.033% and 0.059% U_3O_8 respectively. This shows that uranium present in the mined ore is in an oxidized state, the higher the grade of the ore the higher the content of leachable uranium.
- Addition of an oxidant (0.5 kg/t MnO_2) increases uranium leachability by only 4%.

TABLE III. LEACHING OF URANIUM

Size: 33.2% + $\frac{1}{4}$ in, 10.00% -200 M (A.S.T.M.)

Serial No.	Acid used (kg/t)	Time (h)	Pulp density (% solids)	Leachability (%)
1.	Water	2	60.0	25.7 ^a
2.	Water	2	60.0	61.1 ^b
3.	Water	6	60.0	43.3 ^a
4.	Water	6	60.0	67.8 ^b
5.	4.0	4.0	60.0	67.2 ^a
6.	4.0 + 0.5 MnO_2	4.0	60.0	71.0 ^a

^a Feed assay: 0.033% U_3O_8 .

^b Feed assay: 0.059% U_3O_8 .

7. ORE GENESIS

Of the different formations found in the area, the post-Aravalli granites and gneisses do not record any significant radioactivity. The Aravalli conglomerates and phyllites which show evidences of granitization show however a comparatively higher radioactivity. Although uranium mineralization in the fault gouge can at least in part be attributed to the late hydrothermal phase of the post-Aravalli granitic intrusions, as indicated by the presence of feldspar and kaolin in the fault gouge, it does not fully account for the increased concentration noticed in the kaolinized ore zone.

Black carbonaceous phyllites, rich in iron and copper sulphides, are the most important uranium-bearing host rocks in the area. They show higher syngenetic uranium content than other formations, although they also do not form ore zones as such. Above the water table, they show higher rH_2 and other evidence of oxidation phenomena, such as cuboidal solution cavities filled with limonitic matter. The oxidation of uranium contained in these host rocks is aided by the chemoautotrophic bacteria. This is confirmed by the presence of soluble sulphates, absence of elemental sulphur, presence of autotrophic bacteria, disequilibrium in favour of daughter products, higher radon values in the vicinity of the shaft (35 pCi/cm^3) and higher rH_2 in the host rock.

The mobilization of uranium along localized planes is confirmed by the absence of any major channel for water-borne transportation, occurrence of radioactive breccia bands at or near the carbonaceous phyllite-limestone contact, absence of radioactivity in the silicified breccia well within the limestone, and seasonal increase in the uranium content immediately after the rains in the shaft water (cf. Section 5 e).

Uranium in the ore occurs in an adsorbed state at various levels of oxidation, as UO_2 and its condensation products, viz, $U_2O_5^{2+}$ and $U_3O_8^{2+}$. This inference is supported by the absence of hydrated minerals, easy solubility in neutral water at an end pH of >3 even without the addition of an oxidant, and disequilibrium in favour of uranium.

Uranium mobilized from the carbonaceous phyllites is thus refixed on the natural mineral exchangers, like hydrous aluminosilicates, in the fault gouge into a small, localized, shallow, uranium occurrence in the zone of impeded water circulation below the water table, where the rH_2 falls to about 16 owing to the presence of active anaerobes. Thus the fault gouge provided not only a suitable structural and chemical trap for the reconcentration of uranium but also a congenial ecological environment for the proliferation of anaerobic bacteria, which aided the process of refixation.

8. CONCLUSION

From the above observations it is concluded that:

- (a) While the hydrothermal activity connected with the post-Aravalli granitic intrusions is responsible for introducing uranium into the country rock, the higher radioactivity in the black carbonaceous phyllites is due to the higher uranium content in the unaltered sediment.

- (b) The comparatively higher concentration of uranium into a shallow, low-grade deposit is brought about by the microbial leaching of the contained uranium in the continuously eroding carbonaceous phyllites and its subsequent adsorption on the natural mineral exchangers in the fault gouge below the water table, by reduction, in the presence of active anaerobes.
- (c) Since considerable reconcentration of uranium could be brought about through the agency of bacteria, areas containing sizeable thickness of suitable host rocks, autotrophic bacteria, transportation channels extending below the water table and structural and lithologic traps may yield similar deposits. A study of water and rock samples in such areas, collected before and after the rainy season, may provide guidelines for locating boreholes during subsurface exploration.
- (d) Deposits of this nature may yield economically exploitable reserves of uranium in view of its easy leachability.

ACKNOWLEDGEMENTS

We are thankful to Mr. K.K. Dar and Dr. G.R. Udas for encouragement. Help given by Dr. T.K. Bhattacharyya in the petrological examination of samples, Mr. B.N. Tikoo and his associates for chemical analysis, and Mr. A.K. Mathur, in the microbiological investigations, is acknowledged. We are also thankful to Dr. S. Viswanathan and Mr. B.D. Chatterjee for critical review of the manuscript.

REFERENCES

- [1] TATACHAR, S.R., Unpublished Annual Report, Atomic Minerals Division, Department of Atomic Energy, New Delhi (1962).
- [2] DAR, K.K., NANDI, H., in Int. Conf. Peaceful Uses Atom. Energy (Proc. Conf. Geneva, 1958) 2, UN, New York (1958) 696.
- [3] PHADKE, A.V., DWIVEDI, K.K., PARTHASARTHY, T.N., Unpublished Annual Report, Atomic Minerals Division, Department of Atomic Energy, New Delhi (1960).
- [4] JAYARAM, K.M.V., Uranium leachability tests of uraniferous clay from Udaisagar, Udaipur District, Rajasthan, India, Ind. Sc. Cong., New Delhi (1967).
- [5] LAL, Y., GHOSH, P.C., et al., Geophysical Survey Report, Atomic Minerals Division, Department of Atomic Energy, New Delhi (1968).
- [6] KULSHRESTHA, S.C., JAYARAM, K.M.V., "Effect of sulphur oxidising bacteria on uranium leaching from the Udaisagar clay, Udaipur District, Rajasthan", in Proc. Symp. Uranium in India, Jadugudah - Singhbhum - Bihar (1972), Uranium Corp. India, Jadugudah - Singhbhum - Bihar (1972).
- [7] HERON, A.M., Mem. Geol. Surv. India 79 (1953).
- [8] KAUL, R.K., SWARNAKAR, B.M., et al., Unpublished Report on Geol. Chem. Surv., Atomic Minerals Division, Department of Atomic Energy, New Delhi (1969).

DISCUSSION

H.D. FUCHS: Have other ore minerals apart from uranium been identified?

G.R. UDAS: The uranium is in the adsorbed state. Native sulphur has been identified, as well as pyrite and chalcopyrite and siderite in clays.

THE ROLE OF ORGANIC MATTER IN THE ACCUMULATION OF URANIUM

The organic geochemistry of the coal-uranium association

I. A. BREGER

US Geological Survey,
Washington, D. C. ,
United States of America

Abstract

THE ROLE OF ORGANIC MATTER IN THE ACCUMULATION OF URANIUM : THE ORGANIC GEOCHEMISTRY OF THE COAL-URANIUM ASSOCIATION.

Geochemical studies have been carried out on 64 specimens of coalified logs from Triassic and Jurassic uranium-bearing sediments of the Colorado Plateau and from Paleocene and Eocene sediments of Wyoming. These logs contain from 0.0005 to 16.5% uranium. Autoradiographic studies and observations of relative reflectivities of uraniferous and non-uraniferous specimens demonstrate that uranium was introduced into the coal epigenetically in solution along micro-faults and/or shrinkage cracks. Following its introduction, probably as a complex alkali uranyl carbonate, the uranium was reduced by the coal to form uraninite or coffinite.

Data indicate that radiation from the uranium and its equilibrium daughter products causes radiochemical dehydrogenation and demethanation of the coal. This transformation results in significantly higher reflectivity and hardness related to cross-linking that produces diamond-like clusters of carbon atoms. Irradiation of the coal does not cause its rank to rise to that of anthracite..

Organic sulphur contents up to 13.1% have been noted for coalified logs of Triassic age from the San Rafael Swell area. Such unusual values have been attributed to the interaction between the coal and hydrogen sulphide from underlying sediments at temperatures of 110 to 120°C corresponding to burial under about 3000 m of overburden. If uranium was introduced into the sediments following the interaction between the coal and the hydrogen sulphide, this mineralization could not have occurred before Late Cretaceous time.

This work, in context with previous studies, has led to a generalization of principles underlying the association of uranium with coal.

INTRODUCTION

The search for sources of uranium during the 1940's and 1950's attracted attention to the direct or indirect role of organic substances in the geochemical cycle of the element. Among such substances were the organic constituents of carbonaceous shales, the kerogen; those substances called asphaltites, some of which were later shown to be coal or coal derivatives [1, 2]; and others described by Breger and Deul [3] and other contributors to the International Conference on the Peaceful Uses of Atomic Energy held in Geneva in 1955. Although an association between uranium minerals and coalified logs on the Colorado Plateau was described as early as 1904 [4], only passing interest was shown in the coal-uranium association until the discovery of the uraniferous subbituminous coal of the Red Desert of Wyoming and the uranium-bearing lignites of western North and South Dakota in the late 1940's. Shortly after this discovery, detailed studies were carried out to elucidate the geochemistry and mineralogy of several low-rank uranium-bearing coals [5, 6].

In this paper, studies are reported of over 60 samples of coalified wood, both uraniferous and non-uraniferous, from the Colorado Plateau and

from Wyoming. The investigation was conducted over a period of nearly 20 years to obtain further insight into the most probable manner in which uranium is introduced into coal and the mechanism by which it is retained in coal. In addition, it has been possible from this study to determine the long-term effects of radiation from the uranium and its daughter products on the coal.

Such terms as coal, coalified wood, fossil wood, and log are used interchangeably, merely to avoid repetition, in referring to the coalified logs described in this work. Samples were collected in collaboration and with the assistance of field geologists from the U.S. Geological Survey and the U.S. Atomic Energy Commission. James M. Schopf and R.A. Scott accompanied the author on a tour devoted to the collection of specimens, and the former made many field notes, drew diagrams of collection sites, and photographed sections of many of the coal samples. Many geologists directed us to locations they considered to be of particular interest or where logs could be found. Among members of these field parties were D.P. Elston, C.C. Hawley, I.J. Witkind, R.C. Robeck, R. Thaden, and E.W. Grutt. Maurice Deul, L. Stieff, T. Stern, and this author were part of an earlier expedition to the Colorado Plateau when coalified logs and various other carbonaceous uranium-bearing substances were collected. To these and many other geologists who assisted us we offer our sincerest appreciation.

Discussion of the coalified logs that follows is essentially restricted to those collected from Triassic and Jurassic sediments of the Colorado Plateau area. Most samples were taken in mines in the San Rafael Swell, Emery County, Utah. One log of Paleocene age and a number of logs of Eocene age were collected in sediments in Wyoming. Their analyses are included because of their particularly high uranium values.

SAMPLES

All but a few of the samples used in this study were collected by the author from mines, many of which were operating, in Colorado, Utah, New Mexico, and Wyoming. Only those samples were chosen that had not been weathered, as indicated by the absence of associated oxidized iron or uranium minerals. Occasionally, several samples of a large coalified log were collected where field examination with a radiation detector indicated different parts of the log to contain widely differing degrees of radioactivity.

The sediments from which the specimens were collected are more or less arkosic, fluvialite sandstones in various degrees of lithification. In Colorado, Utah, and New Mexico the sediments are of Triassic or Jurassic age; in Wyoming they are of Eocene age except for one specimen of Paleocene age. Excellent descriptions of the geological settings and stratigraphy have been published by a number of authors and need not be repeated here [7-13].

The coalified wood in these sediments ranges in size from finely divided intergranular fragments visible with a hand lens to entire tree trunks many feet long and still having attached branches and roots. The larger pieces of coalified wood are compressed or uncompressed, black or brown in color, and may or may not contain siliceous, calcitic, or dolomitic fillings replacing the original pithy cores of the trunks. Some coalified fragments are still flexible when first collected but become brittle when dried. Brown and black fragments are occasionally superimposed upon each other; the former have the appearance of lignite,

whereas the latter outwardly resemble vitrain. As shown by Scott [2], all structurally preserved wood collected from the Colorado Plateau belongs to the genus Araucarioxylon Kraus, which is similar to the modern coniferous family Araucariaceae. According to Scott, "...systematic differences were not important factors affecting uranium content of fossil woods".

Prior to analysis, each sample was gently crushed to fragments approximately 2-3 cm on edge. Adhering mineral matter was then removed from each fragment by means of a hand-held electric grinding tool fitted with a thin grinding disk. Following this procedure, the fragments were again gently crushed to about one-half their original size and re-examined to ensure as complete removal as possible of visible mineral matter. The final sample was then crushed to pass a 50-mesh screen. In several instances where it was necessary to resort to sink-float separation of mineral matter in bromoform-carbon tetrachloride mixtures, residual traces of the liquids were removed by heating the coal under vacuum at 80°C for several hours. Random specimens of the samples, as collected, were reserved for petrographic and other studies.

ANALYSES

Chemical analyses of the samples are shown in Table I along with notations regarding the age of the sediment, the name of the mine, and the state in which each sample was collected. Standard coal analyses were obtained through the courtesy of Roy F. Abernethy of the U.S. Bureau of Mines using methods described by Fieldner and Selvig [14]. Sub-bituminous probably best categorizes the equivalent rank of most of the coalified non-uraniferous or slightly uraniferous wood. Such coal is said to be of low rank. Radiochemically induced changes in the composition and physical properties of coalified wood containing significant quantities of uranium (to be described below) make it difficult to establish the equivalent rank of the original coal and it must be assumed that it, too, was subbituminous in rank.

Uranium analyses were performed by chemists of the U.S. Geological Survey using methods described by Grimaldi, May, Fletcher, and Titcomb [15]. The radiometric determination entitled "equivalent uranium" [15] is intended to indicate the order of magnitude of the uranium content and is not intended to be taken as an absolute value. A significant discrepancy in orders of magnitude between chemically and radiometrically determined uranium values could indicate a disequilibrium between the uranium and its daughter products. However, no such disequilibrium is apparent from the data of Table I and the uranium appears to be in secular equilibrium with its decay products in those samples for which equivalent uranium values are available.

X-ray diffractograms were obtained by members of the analytical staff of the U.S. Geological Survey for most of the samples of Table I in a search for minerals, especially uranium minerals, in the logs. Traces of quartz and pyrite were identified in a number of samples, and barite was recognized in Sample No. 29. Similarly, uraninite was shown to be present in Sample No. 2 (2.02 % U), Sample No. 7 (7.51 % U), and Sample No. 19 (5.8 % U), and coffinite was identified in Sample No. 49 (1.31 % U), Sample No. 50 (3.08 % U), Sample No. 53 (16.5 % U), and Sample No. 54 (11.0 % U). Vanadium oxide minerals were recognized in several samples. It is interesting that no minerals were identified in other samples containing equally high or higher percentages of uranium than those in which coffinite or uraninite were found.

Table I. ANALYSES OF COALIFIED LOGS^a

Sample Number —	C %	H %	N %	O (Diff.) %	S (Total) %	S (Org.) %	Btu —	Volatile Matter %	Ash %	U (In coal) %	U (Equiv.) %	Mine ^b —	Age —
1	81.0	7.5	0.4	6.5	4.6	4.6	15860	55.7	0.5	0.001	—	1	Tr
2	72.8	5.0	0.2	7.5	14.5	13.1	14280	33.8	7.0	2.02	—	2	Tr
3	83.0	6.9	0.4	7.6	2.1	2.0	15700	61.7	1.1	0.018	—	2	Tr
4	81.7	6.6	0.3	6.7	4.7	4.1	15530	52.9	3.8	0.33	—	2	Tr
5	81.4	5.5	0.3	8.2	4.6	4.7	14930	38.3	4.0	1.3	—	2	Tr
6	75.0	6.0	0.3	17.2	1.5	0.7	13680	51.8	3.1	0.036	—	3	Tr
7	78.1	4.2	0.3	6.9	10.5	8.6	14100	29.5	19.8	7.51	—	4	Tr
8	81.3	6.6	1.0	7.1	4.0	3.0	15410	49.4	7.4	0.017	0.016	4	Tr
9	75.0	4.5	0.2	7.8	12.5	11.2	13620	37.5	19.4	3.9	3.0	4	Tr
10	79.1	6.9	0.4	11.4	2.2	1.2	15120	71.4	2.7	0.026	—	4	Tr
11	75.6	4.0	0.2	8.8	11.4	9.9	13600	33.2	22.9	7.54	—	5	Tr
12	74.6	6.2	0.4	17.2	1.6	1.4	13710	60.3	2.6	0.018	0.009	6	Tr
13	78.5	6.8	0.4	9.8	4.5	1.3	14990	70.4	5.2	0.0005	—	6	Tr
14	79.5	7.1	0.6	8.9	3.9	2.1	15380	70.5	6.8	0.015	0.014	6	Tr
15	79.8	7.1	0.6	9.0	3.5	1.9	15430	67.7	3.3	0.007	0.008	6	Tr

Table I. ANALYSES OF COALIFIED LOGS (Continued).

16	80.5	7.2	0.6	8.9	2.6	2.1	15480	69.0	6.6	0.009	0.008	6	Tr
17	81.2	7.1	0.4	8.9	2.4	1.3	15340	72.5	3.1	0.009	0.012	7	Tr
18	79.3	6.6	0.5	10.5	3.1	1.7	15000	69.3	4.4	0.004	0.002	7	Tr
19	77.6	4.4	0.3	7.7	10.0	9.3	14030	32.7	18.6	5.8	4.3	7	Tr
20	78.1	6.7	0.6	6.2	8.4	1.2	15170	66.6	8.9	0.003	0.001	7	Tr
21	79.5	6.7	0.7	8.2	4.9	1.5	15010	60.5	5.0	0.001	-	7	Tr
22	78.8	6.0	0.6	9.0	5.6	2.7	14690	57.1	8.1	0.007	0.005	8	Tr
23	79.1	4.6	0.9	10.4	5.0	4.4	13790	33.9	5.5	0.69	-	8	Tr
24	80.3	6.0	0.7	9.5	3.5	2.9	14780	52.0	3.2	0.21	-	8	Tr
25	81.7	6.4	0.6	7.8	3.5	2.7	15250	57.2	4.4	0.31	-	8	Tr
26	81.4	6.8	0.6	8.7	2.5	1.9	15390	62.6	1.5	0.011	0.009	8	Tr
27	78.6	5.1	0.4	8.1	7.8	6.5	14420	37.9	8.5	1.15	-	9	Tr
28	80.9	5.9	0.3	7.9	5.0	3.4	14990	45.1	3.6	0.42	-	9	Tr
29	79.7	5.0	0.3	14.0	1.0	0.5	14260	39.9	3.8	0.080	-	10	Ju
30	81.0	6.1	0.3	8.8	3.8	0.8	15080	60.2	5.6	0.33	0.29	10	Ju
31	82.2	5.8	0.3	9.7	2.0	0.5	15060	48.4	5.1	0.38	-	10	Ju
32	83.2	5.3	0.4	9.4	1.7	1.1	14800	36.7	8.2	0.085	-	10	Ju

Table I. ANALYSES OF COALIFIED LOGS (Continued).

33	82.8	5.3	0.4	9.9	1.6	1.0	14760	38.2	8.4	0.064	-	10	Ju
34	82.4	5.3	0.3	10.5	1.5	1.0	14710	36.9	9.3	0.048	-	10	Ju
35	82.9	6.5	0.4	9.4	0.8	0.7	15330	56.6	1.6	0.036	-	10	Ju
36	81.7	6.5	0.4	10.5	0.9	0.7	14860	56.9	1.8	0.016	-	11	Ju
37	80.2	5.6	0.2	12.5	1.5	0.6	14700	49.5	6.3	0.14	-	11	Ju
38	83.1	6.3	0.4	9.3	0.9	0.7	15320	55.5	7.0	0.18	0.13	11	Ju
39	79.8	4.7	0.4	14.0	1.1	0.6	13990	32.7	7.5	1.5	1.4	11	Ju
40	81.8	6.3	0.3	10.1	1.5	0.6	15130	60.4	5.1	0.23	0.09	11	Ju
41	84.1	6.2	0.4	8.5	0.8	0.7	15420	56.3	2.3	0.40	0.28	11	Ju
42	83.6	6.3	0.4	9.0	0.7	0.7	15450	56.9	3.3	0.14	0.12	11	Ju
43	83.9	6.1	0.4	8.7	0.9	0.7	15530	53.6	6.1	0.26	0.16	11	Ju
44	84.4	5.9	0.4	8.4	0.9	0.6	15320	47.3	8.7	0.88	0.78	11	Ju
45	82.2	6.3	0.4	10.0	1.1	0.9	15100	61.9	0.9	0.008	0.005	11	Ju
46	83.2	6.3	0.2	9.3	1.0	0.5	15280	56.1	7.4	0.94	-	12	Ju
47	81.4	5.7	0.3	10.7	1.9	0.7	14960	43.0	7.6	1.3	-	12	Ju
48	78.1	3.4	0.3	16.6	1.6	0.4	12990	29.8	23.3	6.7	-	13	Ju
49	83.6	6.0	0.4	8.0	2.0	1.2	15380	42.2	6.4	1.31	-	14	Ju
50	74.6	3.2	0.5	13.1	8.6	0.6	12790	28.0	17.4	3.08	-	15	Ju

Table I. ANALYSES OF COALIFIED LOGS (Continued).

51	74.2	5.3	0.7	19.2	0.6	0.4	12890	48.2	3.1	0.65	0.28	15	Ju
52	75.7	5.4	0.7	17.5	0.7	0.5	13350	47.4	4.2	0.46	0.21	15	Ju
53	67.2	3.2	0.3	28.7	0.6	0.5	11340	35.8	37.4	16.5	8.4	16	Ju
54	71.4	3.0	0.3	23.3	2.0	1.5	11280	32.7	23.0	11.0	6.4	16	Ju
55	73.1	3.8	1.1	19.7	2.3	2.0	11870	36.6	15.0	6.6	5.0	17	Pa
56	58.8	3.5	1.8	35.4	0.5	0.3	8420	57.5	29.9	2.5	2.2	18	Eo
57	56.3	3.3	1.3	38.5	0.6	0.03	7790	65.2	26.4	4.8	2.3	19	Eo
58	57.6	3.6	1.2	36.7	0.9	0.2	8160	59.3	23.2	2.9	1.3	19	Eo
59	56.4	3.3	1.2	38.1	1.0	0.8	7810	59.3	26.5	4.5	2.5	19	Eo
60	57.7	4.3	1.2	25.0	11.8	7.5	9940	49.0	19.0	1.6	0.7	20	Eo
61	54.2	3.5	0.6	30.4	11.3	3.0	9340	48.4	24.7	10.5	4.5	21	Eo
62	57.6	2.9	0.6	38.1	0.8	0.2	7880	62.8	20.8	2.9	2.4	22	Eo
63	57.9	3.0	0.6	37.6	0.9	0.2	8040	65.0	23.6	2.4	1.2	22	Eo
64	70.8	4.4	0.3	22.3	2.2	0.9	11830	38.5	7.0	3.5	1.5	23	Eo

a

Coal analyses (C, H, N, O, S, Btu, Volatile Matter) on a moisture- and ash-free basis. Ash values on a moisture-free basis. Analysis through the courtesy of Roy F. Abernethy and the U.S. Bureau of Mines. Uranium analyses by the staff of the Analytical Laboratories of the U.S. Geological Survey; Equivalent uranium values by F. Flanagan and B. McCall of the U.S. Geological Survey.

b

Most mine locations are described in references [6-11]. Mine 1, Robby Ford, Utah; 2, Dirty Devil No. 2, Utah; 3, A and G No. 2, Utah; 4, Vanadium King No. 7, Utah; 5, Rex No. 1, Utah; 6, North Mesa No. 2, Utah; 7, North Mesa No. 9, Utah; 8, Adams, Utah; 9, Lucky Strike No. 2, Utah; 10, Peanut, Colorado; 11, Virgin No. 3, Colorado; 12, Corvusite, Utah; 13, Lumsden No. 2, Colorado; 14, JJ, Colorado; 15, Poison Canyon, New Mexico; 16, Jackpile, New Mexico; 17, Del Claims, Wyoming; 18, Docamour, Colorado; 19, Hardy, Wyoming; 20, Lucky Mc, Wyoming; 21, Veca, Wyoming; 22, Snowball, Wyoming; 23, Phelps-Dodge Lease, Wyoming.

Semi-quantitative spectrographic analyses were obtained by the staff of the analytical laboratories of the U.S. Geological Survey for the ash prepared from each sample listed in Table I.

DISCUSSION

Trace-Element Associations

Certain elements, such as zinc, lanthanum and a number of the rare earths, yttrium in particular, appear to be somewhat more highly concentrated in these logs than in most coals. Zinc is a common constituent of coals, besides which sphalerite has been identified in some coalified logs from Utah [9]; low-rank coal is known to concentrate lanthanum and the rare earths from solution. The lead content of the logs closely follows that of the uranium, and in samples of high uranium content the lead content of the ash can reach 1 to 5 %. Correlations between uranium and other elements in the logs are difficult to evaluate.

Mineral constituents

It is quite clear that the quantities of uranium minerals present in the logs are, as a rule, too small to be detected by routine X-ray diffraction procedures. Moreover, as already noted, detectibility of a uranium mineral is not necessarily related to the uranium content of the log. The inclination from this observation would be to assume that the uranium occurs as an organo-uranium compound or complex in some logs, whereas it crystallizes as uraninite or coffinite in others. This seems to be an unlikely explanation, however, in view of the fact that sub-bituminous coal is capable of reducing the uranyl ion from a solution of uranyl sulfate and converting it to uraninite that is easily identified by its sharp X-ray diffraction pattern [16]. Even partially degraded spruce wood will reduce the uranyl ion to uraninite from the same solution, but the uraninite in this case is not as well crystallized.

From studies conducted by Moore [17], it is clear that low-rank coal and wood absorb uranium from solution avidly. It is probable, therefore, that the uranyl ion is absorbed from solution by the logs and is eventually reduced to uraninite. Although the experiments in which coal and degraded wood reduced the uranyl ion were conducted at 210°C, uraninite had formed at the end of only three days. There seems little doubt that the kinetics of the reaction are such that it could have taken place at a much lower temperature over a somewhat longer period of time.

The uranium content of the logs cannot be attributed to the original plants from which the logs were derived. Not only is uranium a trace element of most plants [3], but the extreme range of uranium values for the samples listed in Table I (0.0005 to 16.5 %) could hardly reflect initial concentrations.

In view of the above considerations, it seems plausible to conclude that at least most of the uranium in the logs listed in Table I is present in the form of discrete minerals. Reasons for the occurrence of uraninite in some specimens and coffinite in others may be related to the host environments in which the logs were buried, or to differences in the composition and properties of the solutions that carried the uranium into contact with the logs. Possible reasons for the failure to identify uraninite, coffinite or any other reduced uranium minerals in some of the samples with high uranium content by X-ray diffraction are discussed below.

Introduction of uranium

The distribution of uranium in three samples (Nos. 2, 7, 49) with high uranium content (1.31 to 7.51 %) was studied by applying stripping film to polished sections [18]. High concentrations of alpha-particle tracks along straight or curved paths indicated that uranium-bearing solutions penetrated the logs along microscopic fractures and/or shrinkage cracks. These fractures may be too small to see or may have been healed, during or after the introduction of the uranium, as a result of plastic flow of the coal such as has been observed by Scott for samples of coalified wood from the Colorado Plateau [2].

In spite of the high percentages of uranium and the known occurrence of uraninite or coffinite in these three samples, the alpha-particle tracks of Figs. 1 and 2 do not appear to emanate from specific mineral masses, thus indicating colloidal distribution of the mineral.

Observations of the distribution of uranium by alpha-particle track densities have been confirmed by the use of photomicrographs of polished sections of the same polished sections (Figs. 1, 2, and 3), among others, of the coalified logs. Thus, it has long been known, even in hand specimens, that significant percentages of uranium in these coalified logs will increase the luster of the coal. As noted by Ergun, Donaldson and Breger [19], and as will be discussed in further detail below, irradiation of the coal by the uranium results in changes both in its chemical composition and physical structure that lead to higher reflectivity and increased hardness. This phenomenon is demonstrated in Fig. 1 where the photomicrograph (Sample No. 49, 1.31 % U) indicates channelling of the uranium in the coal so that some zones are obviously metamorphosed to become highly reflecting by the radiation, whereas other zones, apparently having significantly lower percentages of uranium, are indicated by the lower reflectivity normal for low-rank coals. The same is true in Fig. 3 where the photomicrograph of Sample No. 7 (7.51 % U) illustrates particularly high reflectivity that, in this case, may actually be associated with mineral grains; uraninite has been identified in this sample. Although the sample of Fig. 2 (Sample No. 2, 2.02 % U) has a higher percentage of uranium than that of Fig. 1, its reflectance does, nevertheless, exhibit a general unchannelled distribution of uranium. An X-ray diffractogram has shown only a hint of uraninite in the sample of Fig. 2. These observations seem to indicate that in Sample No. 2 (Fig. 2), and other samples where the uranium is highly dispersed, its distribution and minute particle size make detection of uranium difficult in spite of the presence of even as much as 2.02 % of the element in a specimen (Sample No. 2, Fig. 2).

The actual composition of the uranium-bearing solution that came into contact with the coal cannot be definitively established. There is evidence [1], however, that this solution was alkaline, particularly in the San Rafael Swell area of Utah where many of the samples of Table I were collected. Inspection of a number of specimens of sandstones from this region has shown the grains to be etched and that they have re-entrants. Moreover, considerable evidence has been found for the mobilization and subsequent precipitation of silica, phenomena that reflect an alkaline solution. However, inasmuch as the uranyl ion is unstable in alkaline solution, it probably travelled as a complex uranyl carbonate, which is stable in alkaline solution. Several such complexes were suggested by Breger et al. [6] in a study of the introduction of uranium into a uraniferous subbituminous coal.

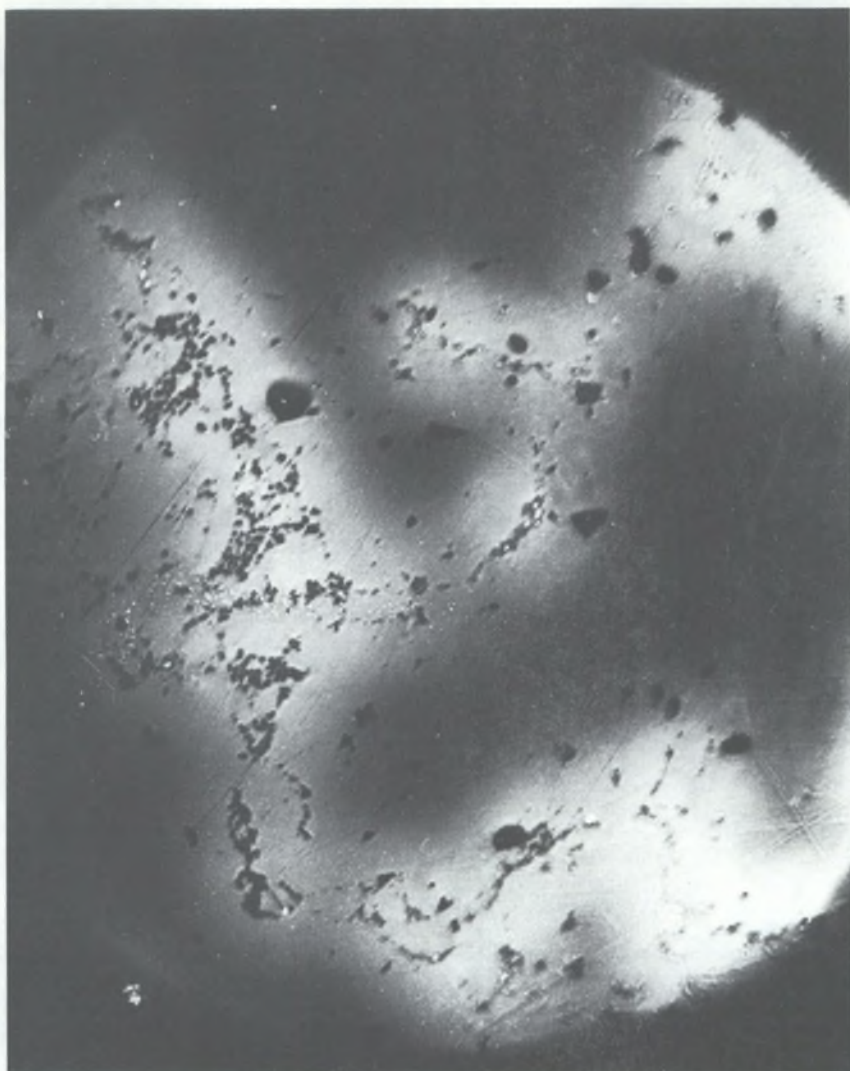


FIG. 1. Photomicrograph (75x) of polished section of coalified uraniferous log collected in the J.J. Mine, T. 46 N., R. 102 E., San Miguel Co., Colorado [20]. The log occurred in the Salt Wash Member of the Morrison Formation (Jurassic). Sample No. 49, 1.31% U, coffinite present. Coal preparation and photomicrograph by J. M. Schopf, US Geological Survey.

Petrographic description of specimen from which polished section was made: "Evident wood structure. Contains areas of abrupt transition to opaque organic matter, darkening around some rays, and small spheroids associated with disseminated pyritic (?) minerals." (J.M. Schopf, personal communication.)

Bright areas in the photograph are zones of high reflectance where the coal has been altered by radiation from uranium and its daughter products. The dull areas of low reflectance have not been affected by the radiation. Contrasting light and dark areas represent, respectively, uraniferous and non-uraniferous zones in the sample.

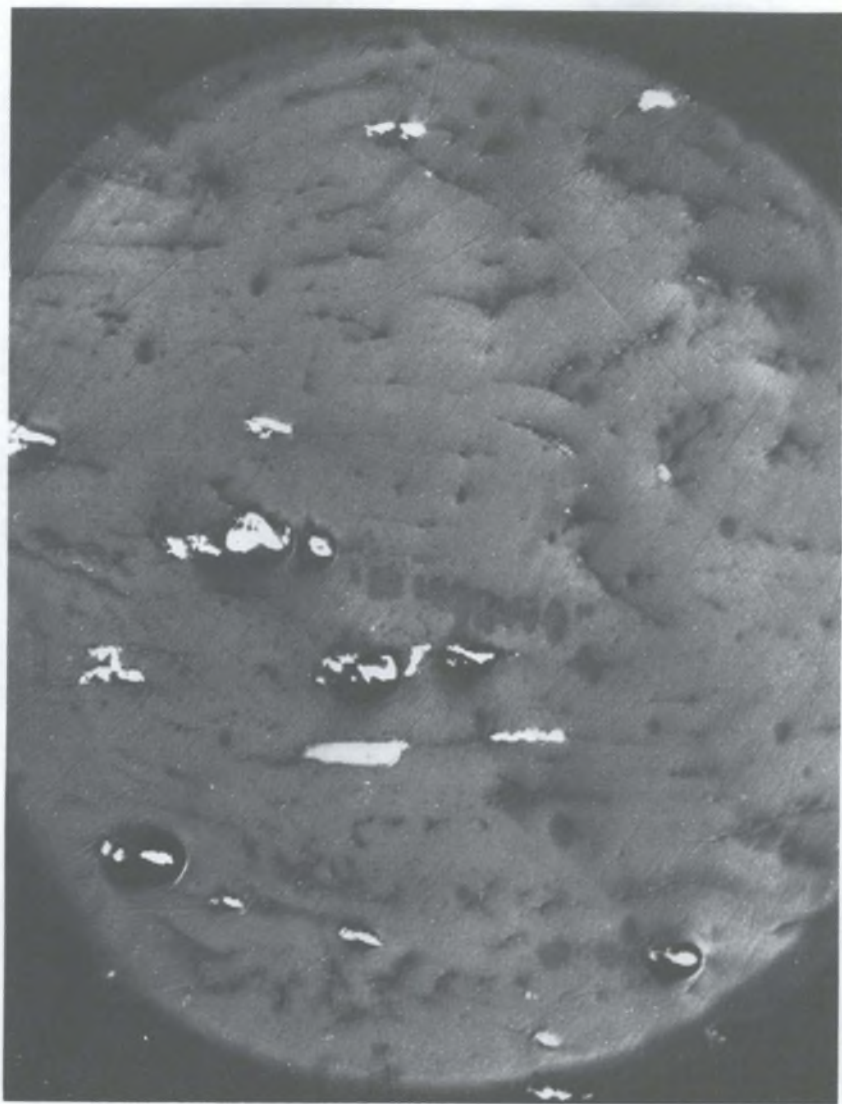


FIG.2. Photomicrograph (75x) of polished section of coalified uraniferous log collected in the Dirty Devil No.4 mine, School Section, San Rafael Swell, Emery Co., Utah [11, p.96]. The log occurred in the Moss Back Member of the Chinle Formation (Triassic). Sample No.2, 2.02% U, uraninite (?). Coal preparation and photomicrograph by J.M. Schopf, US Geological Survey.

Petrographic description of specimen from which polished section was prepared: "Questionable histologic structure. Matrix very dense, mostly opaque or brown including some translucent, ovoid organic bodies. Some of the ovoid bodies are grouped in files reminiscent of ray-resin groupings in wood. However, no cell-wall differentiation is visible. Pyritic (?) and transparent mineral matter show equivocal relation to possible histologic features." (J.M. Schopf, personal communication.)

Reflectance of the section is higher than that to be expected for non-uraniferous low-rank coal (see dark areas of Fig.1). The higher reflectance of the coal is attributed to radiation damage from the associated uranium and its daughter products. In contrast to Fig.1, the uranium appears to be very evenly distributed in this sample.



FIG.3. Photomicrograph (75x) of polished section of coalified uraniferous log collected in the Vanadium King No. 7 mine, North Adit, Middle Workings, Temple Mountain, San Rafael Swell, Emery Co., Utah. Log occurred in the Moss Back Member of the Chinle Formation (Triassic). Sample No. 7, 7.51% U, uraninite present. Coal preparation and photomicrograph by J.M. Schopf, US Geological Survey.

Petrographic description of log from which polished section was prepared: "No histologic structure. Consists principally of opaque organic matter with smaller areas of homogeneous red-translucent organic matter. A few isolated, translucent ovoid bodies, [similar to those in Sample No. 2 (Fig.2)], but lacking any organized grouping are present in the dense matrix. The transition between opaque and translucent areas is fairly abrupt and the contact has a colloidal, diffusion-type (botryoidal?) outline. Needle-shaped crystals of an opaque mineral are preferentially concentrated in red translucent areas." (J.M. Schopf, personal communication.)

It is clearly evident in the upper left-hand corner of the photograph that parts of the log from which the section shown in Fig.3 was prepared do have histologic structure. The upper left to lower right distribution of crystals does not appear to be related to the highly radioactive zones which are clearly outlined, as in Fig.1, by their high reflectance. Minerals within the highly reflecting areas may be uraninite, which is known to be present in this sample.

$\text{Na}_2[\text{UO}_2(\text{CO}_3)_2]$ Sodium uranyl dicarbonate

$\text{Na}_4[\text{UO}_2(\text{CO}_3)_3]$ Sodium uranyl tricarbonatized

On contact with the slightly acidic environment of the coalified wood, such a complex would decompose to release the uranyl ion that would then be absorbed by the coal [17]. Eventually, the coal would reduce the absorbed uranyl ion to uraninite or perhaps, in the presence of sufficient available silica in the solution, coffinite would form preferentially. Hostetler and Garrels [21] later concluded, on the basis of thermodynamic calculations, that the uranyl dicarbonate complex best explains the transport of uranium in a neutral solution, and the uranyl tricarbonatized complex in alkaline solution, both at 25°C. They also found that the uranyl tricarbonatized complex was favored in an excess of carbonate or bicarbonate ions, and that either complex could tie up considerable concentrations of uranium under slightly reducing conditions.

As is evident from the data of Table I, there is an extreme range in uranium values for the coalified logs. The explanation appears to rest on the accessibility of the mineralizing solution, during its passage through permeable channels in the sediments [10], to the coalified wood where, on contact, the uranium was absorbed and concentrated. An example of local concentration can be found in the comparison of data for Sample Nos. 2 and 3. In spite of the fact that these two samples occurred only 2.5 m apart laterally and about 50 cm apart vertically, Sample No. 2 contains 2.02 % uranium whereas Sample No. 3 contains only 0.018 % uranium. Some large logs (up to 3-4 m long), buried horizontally partly in and partly out of channel sands, were found to be uraniferous within the zone of the permeable sand, whereas that end that was buried in the relatively impermeable enclosing sediments was essentially uranium-free. Even better evidence for the absorption of uranium by the coalified logs from a mineralizing fluid is to be found in a coalified log two sides of which (separated by only about 10-12 cm) differ in uranium content by two orders of magnitude. In this case that side of the log that was protected from the uranium-bearing solution by a clay seal was hardly mineralized. Contrary to recently expressed doubts [12], there can be no question regarding the ability of coalified wood, by itself, to absorb uranium from solution under geological conditions as it does in the laboratory [16, 17]. However, the occurrence of uranium deposits even where significant quantities of coalified wood or carbonaceous materials are present may be related to other contributing factors such as hydrogen sulfide, which is also an effective precipitating or reducing agent. In this respect, any chemical reaction or physical condition that will decrease the mobility of an element will tend to increase its concentration.

The time of mineralization of the logs and their enclosing sediments has been a subject of controversy. According to some geological opinion based on field relationships, uranium was introduced within a relatively short period after deposition of the beds [7, 12]. Other opinion, based on lead and uranium isotope analyses [22] of Jurassic and Triassic uranium ore and associated galenas from the Colorado Plateau, calls for introduction of the uranium no earlier than during Late Cretaceous time, long after deposition of the sediments and in approximate correspondence with the time of the Laramide uplift.

The rapidity with which wood undergoes degradation under conditions that may be presumed to have prevailed during its burial in Triassic and Jurassic time has been studied in detail [23], and it has been shown that

its properties and composition approach those of lignite in as little as 30 000 years [24]. It is likely, then, that coalification to the sub-bituminous stage was complete prior to mineralization of the sediments.

Relationship between uranium content and coal constituents

It is evident from the data of Table I that no Triassic log has a carbon content exceeding 83.0 %, and no Jurassic log has a carbon content exceeding 84.4 %. Such data indicate that coalification has proceeded only through the biochemical stage, and that dynamochemical changes brought about through more deep-seated physical effects such as shear or heat have not occurred. These observations complement those made by Schopf [25] who, on the basis of his petrographic studies of a number of these samples, concluded that rank metamorphism is not primarily responsible for the wide range in analytical data for the coalified logs. As examples of these ranges, Triassic coals contain from 72.8 to 83.0 % C and 4.0 to 7.5 % H; Jurassic coals have a range of 67.2 to 84.4 % C and 3.0 to 6.5 % H, and Eocene coals contain from 54.2 to 70.8 % C and 2.9 to 4.4 % H. In an attempt to find explanations for such enormous variabilities, relationships were sought between the composition of the coal (on a moisture- and ash-free basis as indicated in Table I) and its uranium content.

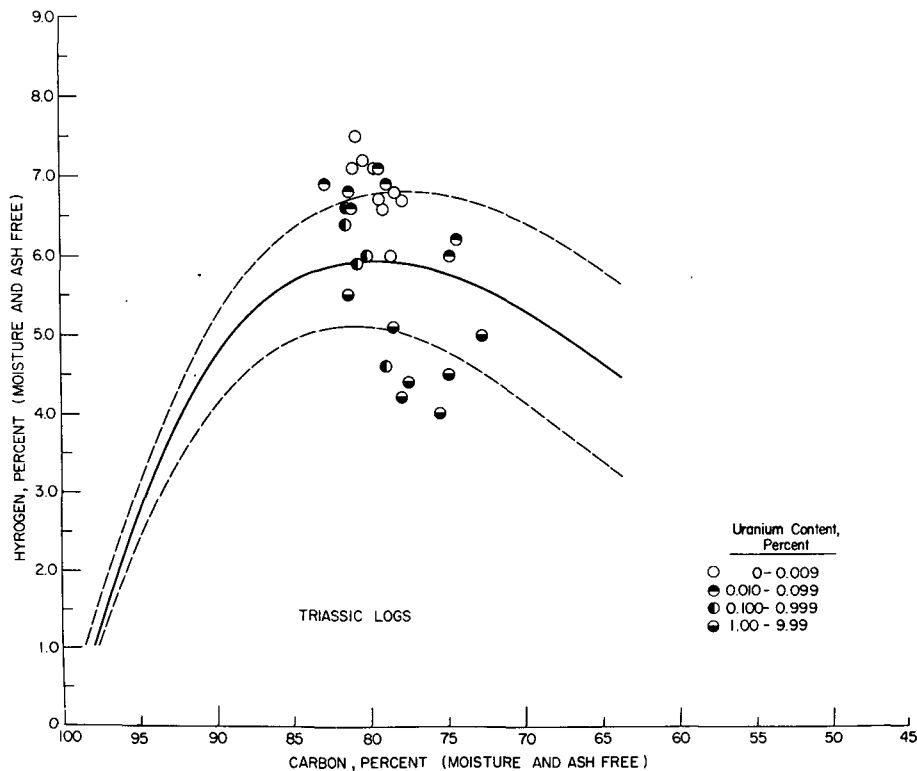


FIG.4. Carbon and hydrogen values for uraniferous coalified logs of Triassic age. Dashed lines represent Essenhigh's coal band [26] and enclose analyses for most mined coals.

Fig. 4 illustrates the relationship between the carbon, hydrogen and uranium contents for 28 Triassic logs listed in Table I; Fig. 5 shows the same relationships for 26 Jurassic logs. Although individual plots have not been prepared for the one Paleocene and nine Eocene samples, analyses of these samples follow the same trend indicated in Figs. 4 and 5. The data of these Figures have been plotted with respect to Essenhigh's carbon/hydrogen coal band, which includes the analyses of most mined coals [26].

Trends in the data of Figs. 4 and 5 clearly indicate that percentages of hydrogen and carbon both decrease as the uranium content of the coalified logs increases. Were irradiation of the coal by the alpha particles from the uranium and its daughter products (alpha particles carry approximately 75 % of the energy evolved) to bring about an increase in the rank of the coal, then the percentage of hydrogen would decrease, but that of carbon would increase as indicated by Essenhigh's coal curve. Obviously, increase in rank is not indicated by the data.

As has already been noted, increase in the uranium content of the coal is generally accompanied by an increase in its reflectance when viewed in polished section. This observation has been reported by others, in particular by Stach [27] and Jedwab [28], both of whom have also shown that uranium is introduced along fracture zones or shrinkage cracks.

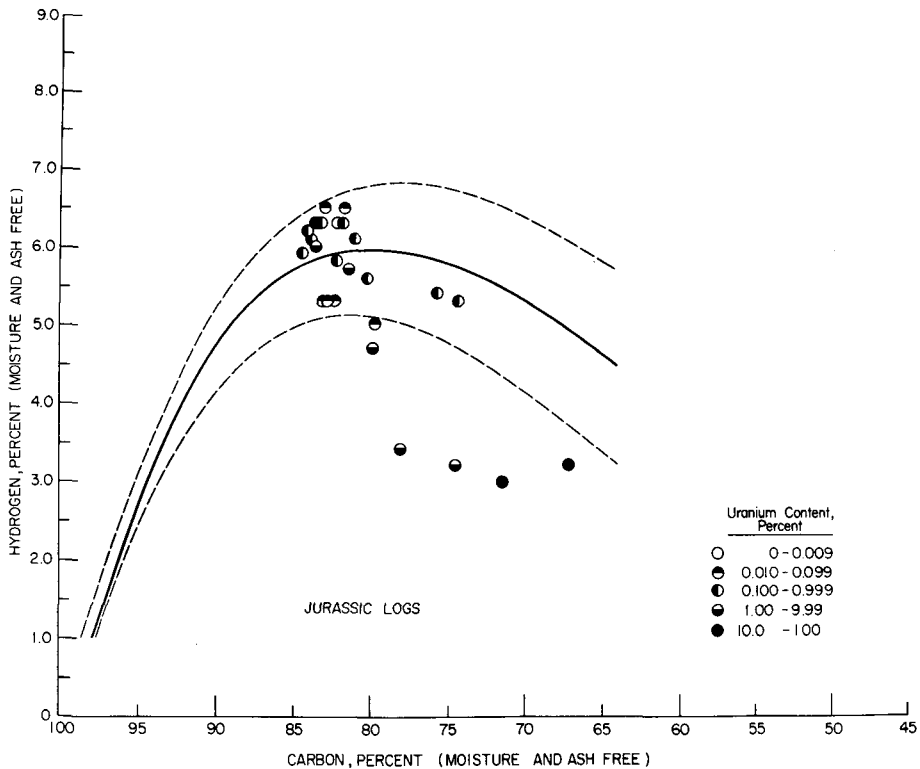


FIG.5. Carbon and hydrogen values for uraniferous coalified logs of Jurassic age. Dashed lines represent Essenhigh's coal band [26] and enclose analyses for most mined coals.

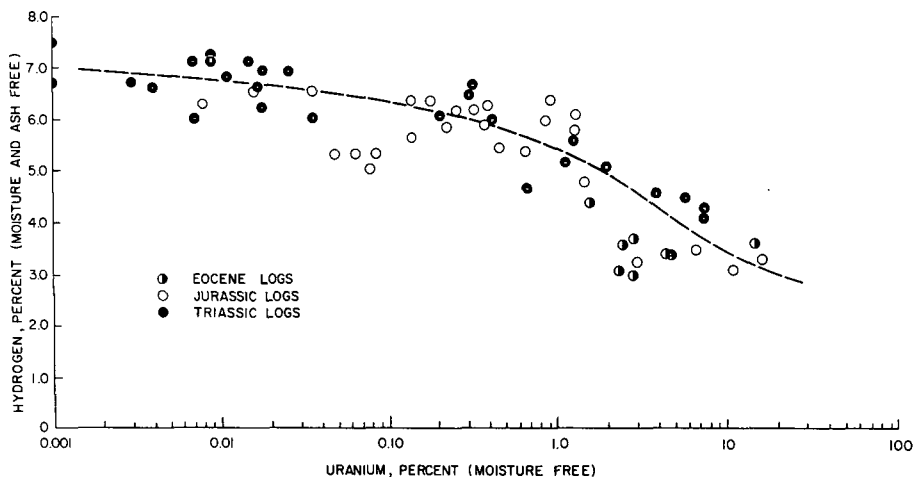
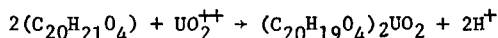


FIG. 6. Relationship between hydrogen and uranium in coalified logs.

Petrographic observation of an increase in reflectivity such as noted by Stach and Jedwab would normally be associated with increase in the rank of the coal to anthracite, a conclusion reached by Stach. It is clear from Figs. 4 and 5, however, that irradiation of the coal has not led to the formation of anthracite. Rather, examination of a number of the coalified logs by X-ray techniques has led to the conclusion that graphite-like structures in these uraniferous coals have been buckled to assume some properties of diamond. Thus, the irradiated coal becomes more highly reflecting, besides which it exhibits increased hardness [19].

The relationship between hydrogen and uranium in all the coals (Triassic, Jurassic, Paleocene, and Eocene) is shown in Fig. 6. Data are plotted on a semi-log scale for convenience, and the dashed line is intended to demonstrate the trend in hydrogen content with increasing values for uranium. The decrease in hydrogen with increasing uranium content is extremely gradual until uranium values of 0.2 - 0.3 % are reached, at which point the rate of loss of hydrogen with increasing uranium content accelerates. It is probably that changes in hydrogen content at uranium values below 0.2 - 0.3 % are so small as to be difficult to detect analytically, and that the loss of hydrogen becomes analytically detectable only at higher percentages of uranium. The curve of Fig. 6 has been extrapolated to flatten out and parallel the abscissa at uranium values above 10 % on the assumption that self-absorption of energy by uranium minerals at higher percentages of uranium, along with the lower percentages of hydrogen available for elimination from the coal, will be factors in decreasing the amount of hydrogen produced at high uranium values.

For further assurance that loss of hydrogen truly represents a radio-chemical dehydrogenation, consideration has been given to the possible replacement of hydrogen by the uranyl ion in a type reaction such as that shown below:



The composition ($C_{20}H_{21}O_4$) represents an approximate empirical formula for coals based on analytical data from Table I, and it is assumed that the uranyl ion reacts with two carboxyl groups to replace two hydrogen ions. Calculations have shown that loss of hydrogen from the coal, were it the result of such a reaction, would be linear and far smaller with increase in uranium content than is shown in Fig. 6. All evidence, therefore, points to radiochemical dehydrogenation as the explanation for the curve of Fig. 6. It may further be noted that much more hydrogen is subject to removal by radiation than by the limited chemical reactions of functional groups.

Dehydrogenation is a common phenomenon when organic compounds are irradiated, and aromatic compounds generally condense or polymerize with an accompanying low production of hydrogen [29]. In the case of coal, irradiation evidently leads to the loss of both hydrogen and carbon which, by difference, would result in the enrichment of oxygen in the product. This observation would account for the fact that coal derivatives associated with uranium ores on the Colorado Plateau and at times called "asphaltite" [1; 9, p. 93] have lower hydrogen contents and higher oxygen contents than are to be expected.

The concordance of data in Figs. 4 and 5, and especially in Fig. 6, would indicate that the coalified logs of the Triassic and Jurassic sediments were irradiated for essentially the same period of time. The scatter of points in these curves, as well as in those to follow, is undoubtedly caused by the inherent inhomogeneity of the uranium-coal associations as demonstrated by the photomicrographs of Figs. 1 and 3.

Data for the radiochemical dehydrogenation of coal, as illustrated in Fig. 6, lead to the conclusion that mineralization of both the Triassic and Jurassic sediments occurred at about the same time. The coals of Triassic age, however, tend to have higher sulfur contents than the coals of Jurassic age. Inasmuch as the specimens of Triassic age were collected in the San Rafael Swell of Emery County, Utah, it is apparent that local geological conditions in the Swell led to changes in the composition of the coal over and above those related to uranium mineralization on the rest of the Colorado Plateau.

Different forms of pyrite in the coalified logs of Triassic age from the San Rafael Swell are thought to represent different generations of formation, at least some of which are related to uranium mineralization [9, p. 68]. Of particular interest in this study is the non-mineral sulfur, that is, the sulfur that is actually part of the organic substance of the coal. This sulfur can occur in many forms such as, for example, thioethers, thiols, and heterocyclic sulfur structures, to name but several possibilities. As shown in Fig. 7, there is a definite increase in organic sulfur with increasing uranium in the Triassic samples from the San Rafael Swell in contrast to the Jurassic samples from other parts of the Colorado Plateau in which the organic sulfur and uranium contents are not related. Comparison of data plotted in Figs. 6 and 7 also indicates that the hydrogen content of the logs is independent of the organic sulfur content.

Based on the conclusion that there were no essential chemical differences between the Triassic and Jurassic coals by the time that mineralization occurred, and based on the assumption that the same mineralizing fluid came into contact with these coalified logs at some time after sedimentation of the Jurassic sediments was complete, it seems

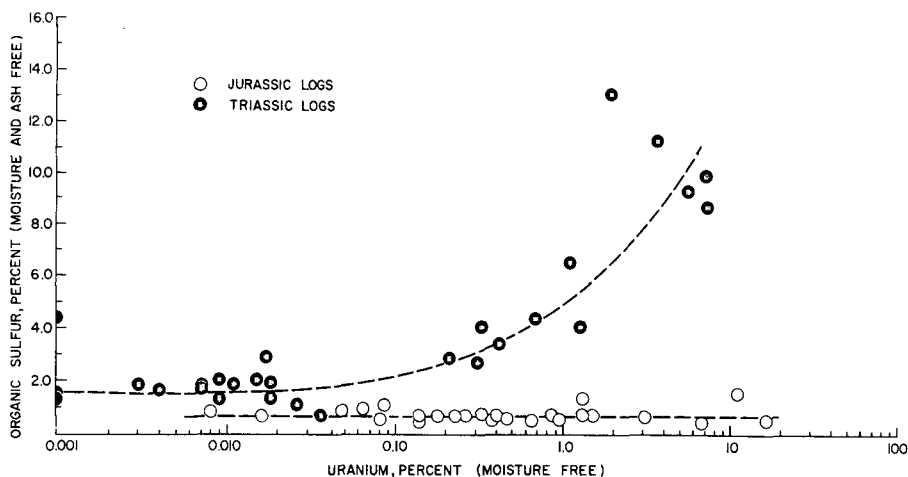


FIG. 7. Relationship between organic sulfur and uranium in coalified logs.

clear that the sharp increase in organic sulfur contents with increasing uranium values in the Triassic logs must reflect local mineralizing conditions in the San Rafael Swell.

There is a strong disposition, based on the curves of Fig. 7, to relate the increase in the organic sulfur content of the Triassic coal to the increase in uranium content. Although this would suggest that sulfur in some form accompanied the uranium-bearing mineralizing solution, the fact is that hydrogen sulfide will cause the precipitation of uraninite from solutions of complex alkali uranyl carbonates [30, 31]. Uranyl hydroxide, UO_2OH^+ , is similarly unstable in the presence of hydrogen sulfide [30]. The relationship between uranium and organic sulfur in the Triassic coals, therefore, appears to be fortuitous rather than genetic.

As noted by Hawley and his colleagues, some pyrite is definitely related to coalification, whereas a second generation of pyrite in the logs of the San Rafael Swell appears to have developed post-coalification and prior to introduction of uranium into the region [9, p. 68]. This secondary pyrite, which occurs in veinlets and as fillings in shrinkage cracks in coalified logs, requires explanation both with respect to the source of the iron and the sulfur. Moreover, consideration of the paragenetic relationships regarding the formation of this pyrite and the time of uranium mineralization have led to suggestions regarding the processes that produced the high organic sulfur contents of some of the samples of coalified wood.

The small amount of "primary" pyrite that has been defined as being associated with the process of coalification of the logs is undoubtedly similar to that found with most coals. It originates during early stages of coalification, occurs in the wood cells, and probably represents formation from sulfur inherent in the wood, and additional sulfur derived from microbiological reduction of sulfates introduced by environmental waters at the time of deposition of the sediments following their burial

to the degree necessary to exclude air and produce anaerobic conditions. The iron for this pyrite probably was also contributed by the formation water.

With burial of the sediments in which the logs were enclosed, new sources of both the sulfur and iron must be found to account for the development of the massive secondary pyrite. Several possibilities may be enumerated:

1) Ground water carrying both sulfate and soluble iron salts continued to percolate through the sediments. On contact with the reducing environment of the coal, the sulfate was reduced to the sulfide ion, the ferric iron was reduced to the ferrous form, and pyrite was formed. For this hypothesis to have merit, a supporting substrate must be found for the bacteria necessary to reduce the sulfate ion. Coal, however, does not support significant bacterial activity.

2) Separate sources can be hypothesized for the iron and the sulfur. In this case, iron would be derived from the sediments overlying the buried woody debris that is in the process of coalification. In analogy with the development of soils, meteoric water would leach the sediments and carry the iron down into contact with the coalifying wood where it would be retained.

The source of sulfur for the formation of secondary pyrite is somewhat more difficult to determine, especially if burial of the sediments, development of anaerobic conditions, and coalification of the wood precluded an effective substrate for the microbiological reduction of any sulfate that might have been present. At this point, it should be noted that thick pre-Permian marine limestones underlie the San Rafael Swell of Emery County, Utah, where all but one (Sample No. 60) of the coal samples with high organic sulfur content have been collected [9]. It is not unreasonable to hypothesize that many of the viscous crude oil residues present in the Triassic and Jurassic rocks of the Swell may have arisen in or been associated with these older limestones. Gas caps containing hydrogen sulfide are commonly found with such asphaltic crude oils, and it is suggested that such gas penetrated the sediments and came into contact with the coalified iron-rich logs to form the massive secondary pyrite. Although hydrogen sulfide may have continued to be available to the sediments containing the coalified logs, continued burial to the point of exclusion of additional iron from the overlying strata would then rule out further formation of the secondary pyrite.

In further analysis of the mineralization of the coalified wood, account must next be taken of the formation of high organic sulfur contents in certain logs. Following development of the secondary pyrite and continued burial of the sediments, the coalified logs would be subject to the geothermal gradient and, as is indicated below, were probably exposed to temperatures up to 110° to 120°C. At such temperatures, reactions between the hydrogen sulfide and the coal could be expected to produce the organic sulfur forms in the Triassic logs.

Diffusion of hydrogen sulfide from pre-Permian rocks of the San Rafael Swell into the overlying Triassic sediments may, therefore, be related to the origin of secondary pyrite and to the high organic sulfur content of a number of coalified logs. "Gaseous" odors that develop when many fragments of coalified wood are crushed appear to be related to traces of volatile organic sulfur compounds and are similar to those from contemporary anoxic marine or lacustrine sediments.

Evidence for the presence of hydrogen sulfide in the sediments of the San Rafael Swell is to be found in the alteration zones that have been described. Extensive bleached zones have been noted near collapse structures in the San Rafael Swell [9]; these structures may have served as low-resistance conduits for movement of the gas. Altered zones that have been ascribed to seepage of crude oil may also be related to hydrogen sulfide that diffused with the oil from the pre-Permian sediments.

In attempting to understand the paragenetic relationships of the uranium in these sediments, it must be kept in mind that hydrogen sulfide will cause precipitation of uraninite from solutions of uranyl salts. Uranium in these sediments is, however, generally associated with coalified wood and its derivatives. The fact that it is not more generally dispersed suggests that no significant amounts of hydrogen sulfide were present in the sediments of the San Rafael Swell during the lateral migration of the uranium-bearing mineralizing solutions. Implied in this conclusion is the additional conclusion that diffusion of hydrogen sulfide from underlying sediments had stopped before introduction of the uranium began.

Weeks and Garrels [32] have pointed out that Triassic sediments of the Colorado Plateau were buried under approximately 1500 to 3000 m of overburden by the end of Cretaceous time. At the usually accepted geothermal gradient of approximately $1^{\circ}\text{C}/30\text{ m}$, this would mean that the Triassic sediments were at 70 to 120°C and that the Jurassic sediments were at some correspondingly lower temperature. Studies of a number of the coalified logs have indicated the maximum temperature to which the Triassic logs were exposed to be 110 to 120°C , and for Jurassic logs to 100°C with most evidence for the latter pointing to temperatures below 100°C [33]. If elevated temperatures are necessary to explain the reaction between hydrogen sulfide and the organic constituents of the coal to produce forms of organic sulfur, and if the diffusion of hydrogen sulfide into the Triassic sediments had stopped before the mineralizing fluid entered the sediments, then depths of burial up to 3000 m must be invoked at the time that mineralization occurred. This could be taken as evidence that uranium was introduced into the sediments no earlier than in Late Cretaceous time.

In view of these considerations, it must be concluded that the formation of forms of organic sulfur in the logs of Triassic age and introduction of uranium into the same logs took place in two separate and unrelated stages. The curve of Fig. 7 for the Triassic logs must, therefore, represent a fortuitous rather than a genetic relationship. The fundamental factor relating the organic sulfur and uranium contents must, then, be the permeability of the sediments and the ability of gas or fluid to come into contact with some logs rather than others.

Before leaving the subject of the organic sulfur in the Triassic logs, it should be noted that Sample No. 2 has one of the highest percentages of organic sulfur (13.1 %) of any coal sample ever reported; extremely high percentages also are present in Samples No. 7 (8.6%), No. 9 (11.2 %), No. 11 (9.9 %), and No. 19 (9.3 %).

Fig. 8 illustrates the decrease in calorific values of these coalified logs with increasing uranium content. This relationship reflects the decrease in carbon and hydrogen that has already been noted and, in the case of the Jurassic logs, a corresponding differential increase in oxygen content. In still another manner, this decrease in calorific values illustrates that irradiation of the coal does not lead to an increase in its rank, as anthracitization would result in higher, not lower, thermal values.

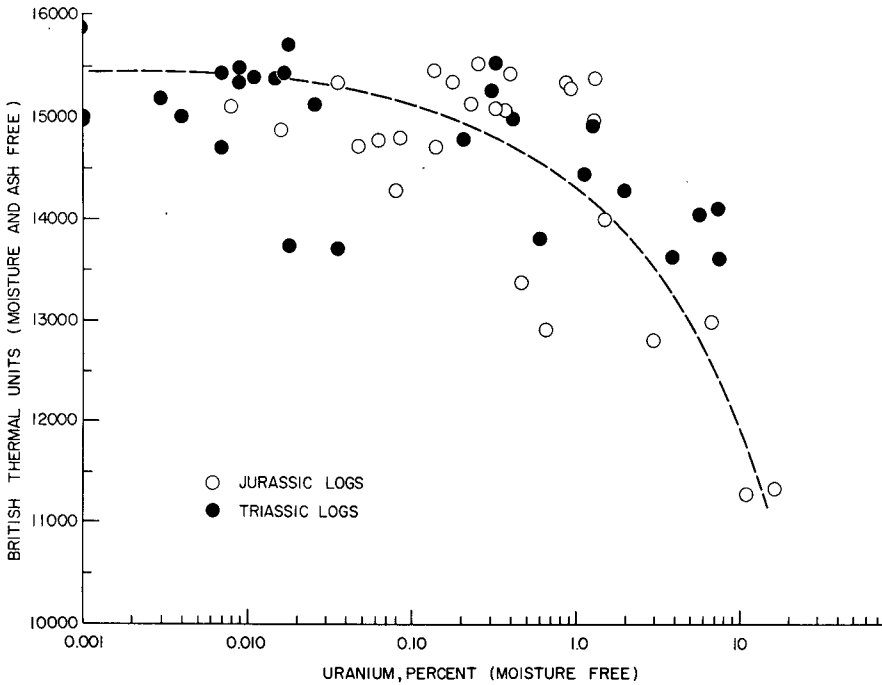


FIG. 8. Relationship between calorific values and uranium in coalified logs.

In the case of the Triassic coals, the oxygen content does not increase significantly with increasing uranium content as would be expected. In these coals, however, the total of oxygen plus organic sulfur increases with uranium content, but not to the same degree as in the case of the Jurassic coals. It is clear that forms of organic sulfur have replaced at least part of the oxygen in the coal, and analysis of the data also indicates that some sulfur may have entered the coal structure without replacing oxygen. Decrease in the calorific value of the Triassic coals with increasing uranium content reflects the fact that increasing the sulfur content has the same effect as increasing the oxygen content.

In Fig. 9 it is evident that the volatile matter values of the coalified logs drop consistently with increase in uranium content. This relationship provides excellent confirmation that radiochemical dehydrogenation of the coalified logs leads to the formation of a product of increased molecular weight.

SUMMARY AND CONCLUSIONS

Uranium, not being a significant constituent of plants, becomes associated with individual coalified logs or massive coal deposits through secondary processes. In essence, a solution carrying, in all likelihood, complex alkali uranyl carbonates, comes into contact with the coal where it

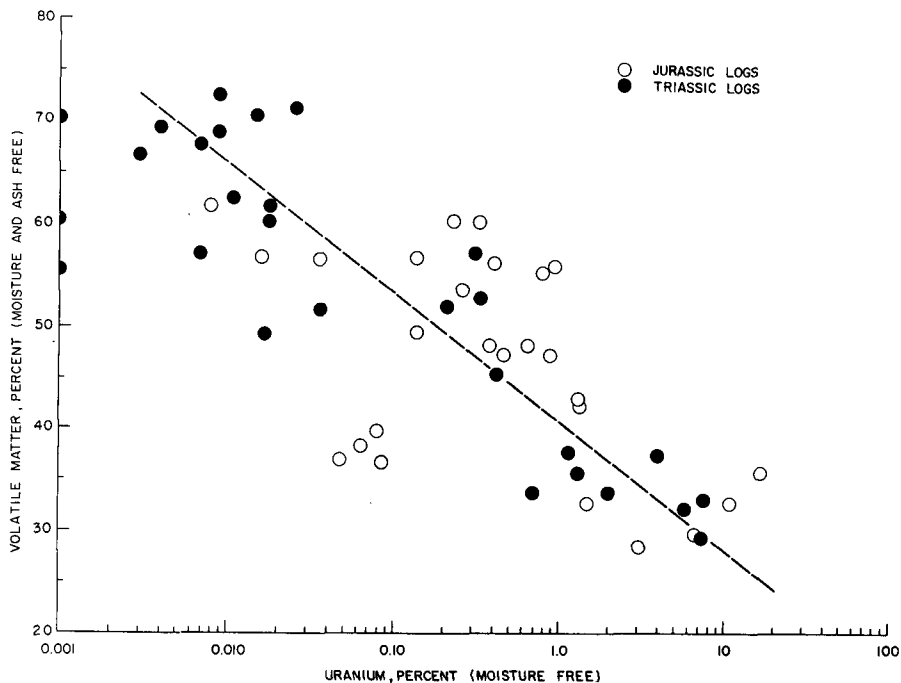


FIG. 9. Relationship between volatile matter and uranium in coalified logs.

is readily absorbed, at least in part by penetration of the solution into fracture and/or shrinkage zones in the coal. Initial retention may be in the form of complex or insoluble uranyl compounds; depending on the environment, these compounds can be reduced to form uraninite or coffinite. Where a coalified log or coal is protected from the mineralizing fluid, it will remain free or essentially free of uranium.

Study of coalified logs from the Colorado Plateau has not only advanced a generalization of the principles underlying the coal-uranium association, but has provided detailed information on secondary processes in which the nuclear radiation from the uranium and its daughter products effects radiochemical transformations in the coal structure. In concert with known effects of nuclear radiation on organic compounds, it has been found that the coal is radiochemically dehydrogenated and condensed, that it becomes more highly oxygenated by differential loss of both carbon and hydrogen, and that in the process of such changes it loses part of its calorific value. These results, when compared to previously published data on the so-called asphaltites associated with uranium ores on the Colorado Plateau, confirm earlier conclusions that those substances are coal derivatives.

Uraniferous coalified logs collected in Triassic sediments of the San Rafael Swell of Utah differ from those of the rest of the Colorado Plateau in having organic sulfur contents that increase with increasing uranium content; some of the organic sulfur contents are among the highest ever recorded for coals. Interpretation of field observations and analytical

data indicates that the association between the organic sulfur and uranium contents is fortuitous rather than genetic, that the high organic sulfur contents of the coalified logs may have resulted from an interaction between the coal and hydrogen sulfide derived from underlying sediments, that both hydrogen sulfide and, later, uranium came into contact with the coalified logs by following zones of maximum permeability in the sediments, and that the sediments in which the logs were buried and coalified were essentially free of hydrogen sulfide at the time that solutions of complex alkali uranyl carbonates were introduced. If, in all likelihood, an elevated temperature was necessary for the interaction between the coal and the hydrogen sulfide in the San Rafael Swell, then the paragenetic relationships indicate that the uranium entered the sediments considerably after their deposition, a conclusion in correspondence with published age determinations that indicate that mineralization occurred not earlier than in Late Cretaceous time.

The coalified logs of Eocene age (including one of Paleocene age) were of special interest in this study because of their particularly high uranium values (1.6 to 10.5 %). Analysis of the data, as shown in Fig. 6, clearly illustrates that they have undergone radiochemical dehydrogenation as have the Triassic and Jurassic logs.

The radiochemical degradation of coal does not lead to the formation of anthracite, but is accompanied by demethanation and dehydrogenation as the dominant processes. Analysis of the data for Triassic coals has shown that 1.7 moles of methane are evolved per mole of hydrogen that is eliminated; the ratio for the Jurassic coals is somewhat different, namely, 1.1 moles of methane per mole of hydrogen. Perhaps the somewhat higher temperature of the Triassic coals increased the rate of cleavage of carbon-carbon bonds and the formation of more methane. These relatively high ratios of methane to hydrogen may correspond to a high aliphatic/aromatic ratio for the coal and are in keeping with earlier conclusions regarding the rather high aliphatic character of low-rank coals [19].

Several assumptions have been made during the presentation of this work. As already noted, alternate hypotheses have also been proposed with respect to the time of mineralization. Other suggestions have also been made regarding the manner in which mineralization occurred. The real significance of this work, however, lies in the fact that it has been possible to achieve a coherent picture suggestive of events related to uranium mineralization on the Colorado Plateau based to a very considerable degree on an organic geochemical study of coalified logs.

REFERENCES

- [1] BREGER, I.A., DEUL, M., Association of uranium with carbonaceous materials, with special reference to the Temple Mountain region, U.S. Geol. Surv., Prof. Pap. 320 (1959) 130.
- [2] SCOTT, R.A., Fossil woods associated with uranium on the Colorado Plateau, U.S. Geol. Surv., Prof. Pap. 424-B (1961) B-130.
- [3] BREGER, I.A., DEUL, M., The organic geochemistry of uranium, Int. Conf. Peaceful Uses At. Energy (Proc. Conf. Geneva, 1955) 6, UN, New York (1956) 418.
- [4] BOUTWELL, J.M., Vanadium and uranium in southeastern Utah, Bull. U.S. Geol. Surv. 260 (1905) 200.

- [5] BREGER, I.A., DEUL, M., RUBINSTEIN, S., Geochemistry and mineralogy of a uraniferous lignite, *Econ. Geol.* 50 (1955) 206.
- [6] BREGER, I.A., DEUL, M., MEYROWITZ, R., Geochemistry and mineralogy of a uraniferous subbituminous coal, *Econ. Geol.* 50 (1955) 610.
- [7] FISCHER, R.P., Uranium-vanadium-copper deposits of the Colorado Plateau region, *Int. Conf. Peaceful Uses At. Energy (Proc. Conf. Geneva, 1955)* 6, UN, New York (1956) 605.
- [8] GRUTT, E.W., Jr., Environment of some Wyoming uranium deposits, 2nd *Conf. Nucl. Eng. Sci.*, Paper 57-NESC-69 (Phila., 1957), *Am. Soc. Mech. Engineers*, New York (1957).
- [9] HAWLEY, C.C., WYANT, D.G., BROOKS, D.B., Geology and uranium deposits of the Temple Mountain district, Emery County, Utah, *Bull. U.S. Geol. Surv.* 1192 (1965) 68.
- [10] GRANGER, H.C., Localization and control of uranium deposits in the southern San Juan Basin mineral belt, New Mexico - An hypothesis, *U.S. Geol. Surv.*, Prof. Pap. 600-B (1968) B60.
- [11] HAWLEY, C.C., ROBECK, R.C., DYER, H.B., Geology, altered rocks and ore deposits of the San Rafael Swell, Emery County, Utah, *Bull. U.S. Geol. Surv.* 1239 (1968).
- [12] FISCHER, R.P., Similarities, differences, and some genetic problems of the Wyoming and Colorado Plateau types of uranium deposits in sandstone, *Econ. Geol.* 65 (1970) 778.
- [13] RACKLEY, R.I., Environment of Wyoming Tertiary uranium deposits, *Am. Assoc. Pet. Geol. Bull.* 56 4 (1972) 755.
- [14] FIELDNER, A.C., SELVIG, W.A., Methods of analyzing coal and coke, *Bull. U.S. Bur. Mines* 492 (1951).
- [15] GRIMALDI, F.S., MAY, I., FLETCHER, M.H., TITCOMB, J., Collected papers on methods of analysis for uranium and thorium, *Bull. U.S. Geol. Surv.* 1006 (1954).
- [16] BREGER, I.A., MOORE, R.T., Preliminary experiments on the reduction of the uranyl ion to uraninite by carbonaceous substances, *U.S. Geol. Surv.*, Trace Elements Memo. Rept. 942 (1955).
- [17] MOORE, G.W., Extraction of uranium from aqueous solution by coal and some other materials, *Econ. Geol.* 49 (1954) 652.
- [18] STIEFF, L.R., STERN, T.W., Preparation of nuclear track plates and stripping films for the study of radioactive minerals, *Am. Mineral.* 37 (1952) 184.
- [19] ERGUN, S., DONALDSON, W.F., BREGER, I.A., Some physical and chemical properties of vitrains associated with uranium, *Fuel* 39 (1960) 71.
- [20] ELSTON, D.P., BOTINELLY, T., Geology and mineralogy of the J.J. Mine, Montrose County, Colorado, *U.S. Geol. Surv. Prof. Pap.* 320 (1959) 203.
- [21] HOSTETLER, P.B., GARRELS, R.M., Transportation and precipitation of uranium and vanadium at low temperatures, with special reference to sandstone-type uranium deposits, *Econ. Geol.* 57 (1962) 137.

- [22] STIEFF, L.R., STERN, T.W., MILKEY, R.G., A preliminary determination of the age of some uranium ores of the Colorado Plateau by the lead-uranium method, U.S. Geol. Surv. Circular 271 (1953).
- [23] VAROSSIEAU, W.W., BREGER, I.A., Chemical studies on ancient buried wood and the origin of humus, 3^e Congrès pour l'avancement des études de stratigraphie et de géologie du Carbonifère (C.R. Congrès Heerlen, 1951) 2, Editions Ernest van Aelst, Maestricht (1952) 637.
- [24] NARAYANAMURTI, D., et al., Note on a piece of ancient buried wood dredged from the bed of the River Ganga near Mokameh, Bihar, Holz Roh- Werkst. 18 (1960) 55.
- [25] SCHOPF, J.M., Personal communication.
- [26] ESSENHIGH, R.H., Oxygen and hydrogen in coals, Fuel 36 4 (1957) 395.
- [27] STACH, E., DEPIREUX, J., Artificial coalification by radioactivity, Brennst.-Chem. 46 1 (1965) 13.
- [28] JEDWAB, J., Radiation damage in the uraniferous Schaentzel coal, Geol. Rundsch. 55 (1965) 445.
- [29] BREGER, I.A., Transformation of organic substances by alpha particles and deuterons, J. Phys. Colloid Chem. 52 (1948) 551.
- [30] MILLER, L.J., The chemical environment of pitchblende, Econ. Geol. 53 5 (1958) 521.
- [31] RAFALSKY, R.P., The experimental investigation of the conditions of uranium transport and deposition by hydrothermal solutions, Int. Second Conf. Peaceful Uses At. Energy (Proc. Conf. Geneva, 1958) 2, UN, Geneva (1958) 432.
- [32] WEEKS, A.D., GARRELS, R.M., Geologic setting of the Colorado Plateau ores, U.S. Geol. Surv. ., Prof. Pap. 320 (1959) 3.
- [33] BREGER, I.A., CHANDLER, J.C., Extractability of humic acid from coalified logs as a guide to temperatures in Colorado Plateau sediments, Econ. Geol. 55 5 (1960) 1039.

DISCUSSION

R. BLASER: What differences are there, if any, in lithology or deposition environment between the Jurassic and the Triassic samples you investigated?

I. A. BREGER: I do not think there are any differences between the Jurassic and Triassic sediments of the plateau that would favour the mineralization of one rather than the other.

J. PASQUALI: What, in your opinion, are the implications of your work with respect to the organic matter found in the quartz-pebble conglomerates of South Africa?

I. A. BREGER: Organic matter of various types will accumulate and, under reducing conditions, ultimately reduce the uranyl ion. Higher percentages of uranium cause coal to lose significant fractions of both carbon and

hydrogen. Relatively low percentages cause changes too small to observe. The organic matter of the Rand was derived from very simple organisms, probably algae, which metamorphose towards graphite with or without uranium.

I am not certain about the ultimate products, but I would predict that the final product from the radiolysis of coal is likely to be graphite, or graphite having some aspect of a diamond-like lattice. The ultimate products from other irradiated substances would also be graphite.

CONSIDERACIONES SOBRE EL PAPEL QUE DESEMPEÑAN LAS SUSTANCIAS ORGANICAS NATURALES DE CARACTER HUMICO EN LA CONCENTRACION DEL URANIO

M. MARTIN CALVO

Junta de Energía Nuclear,
Dirección de Geología y Minería,
Madrid, España

Presentado por J.A. Fernández Polo

Abstract-Resumen

THE ROLE OF HUMIC NATURAL ORGANIC MATTER IN URANIUM CONCENTRATION.

The paper reports a short experiment on the metallogenetic aspect of the uranium-organic matter association in nature. The author carried out several experiments on uranium fixation by organic matter with different degrees of maturity. Although further studies are considered necessary, the results already obtained lead to the following conclusion: when uraniferous solutions come into contact with humic organic matter, the efficiency and nature of the uranium-organic matter association thus established depends on the degree of carbonization attained by the humic material. At the beginning of the development process, the organic matter has high chemical activity and the uranium tends to occur in stable organic phases. As the process continues, a stage is reached from which uranium tends to form its own minerals independently of organic matter. From the coalification stage onwards the tendency towards uranium-organic matter association becomes increasingly less in any form. Petrographically, the humic constituents to which uranium is closely and positively related belong to the huminite maceral group. Lastly, it is considered that when the organic matter is present as an accessory constituent in other sedimentary rocks and with quite low maturity indices, there is greater favourability for the formation of uranium deposits.

CONSIDERACIONES SOBRE EL PAPEL QUE DESEMPEÑAN LAS SUSTANCIAS ORGANICAS NATURALES DE CARACTER HUMICO EN LA CONCENTRACION DEL URANIO.

El trabajo constituye un breve ensayo de orientación metalogénica de la asociación urano-orgánica natural. El autor ha realizado varios ensayos sobre fijación de U por MO (materia orgánica) con diferentes grados de madurez. Aunque se consideran necesarias ulteriores investigaciones, los resultados obtenidos han permitido deducir lo siguiente: cuando las soluciones uraníferas se ponen en contacto con MO de carácter húmico, la eficiencia y naturaleza de la asociación urano-orgánica establecida depende del grado de carbonización alcanzado por el material húmico. Al principio de la evolución la actividad química de la MO es elevada y el U tiende a determinarse en fases orgánicas estables. Al ir avanzando el proceso evolutivo, llega un momento a partir del cual el U tiende a formar minerales propios dividuados de la MO. A partir del estadio de hullaificación va siendo cada vez más exigua la tendencia a la asociación U-MO en cualquiera de sus determinaciones. Desde el punto de vista petrográfico, los constituyentes húmicos con que el U tiene estrecha y positiva relación corresponden al grupo maceral huminita. Finalmente se considera que cuando la MO se presenta en calidad de constituyente accesorio en otras rocas sedimentarias y con índices de madurez más bien bajos, es cuando mayor favorabilidad ofrece para la formación de yacimientos de U.

INTRODUCCION

Dentro de las relaciones generalizadas entre las sustancias naturales de composición orgánica, podemos catalogar tres grandes tipos de materiales: organitas húmicas (carbones), organitas bituminosas (petróleos, asfaltos, asfaltitas y ceras naturales) y organitas kerabituminosas (kerabitumitas). Los dos últimos tipos se suelen agrupar bajo la denominación común de sapropelitas.

En la geoquímica orgánica del U., las organitas de carácter húmico son las más interesantes tanto desde el punto de vista económico como metalogénico, y es a ellas a las que nos referimos en este trabajo al hablar de M.O.

Los materiales húmicos por antonomasia son los comprendidos bajo la denominación general de carbones o compuestos carbonosos y son producto de transformación de sustancias vegetales, sobre todo, plantas terrestres; el examen microscópico no da lugar a dudas, por lo que en esto hay prácticamente unanimidad entre los autores.

Es sabido que este tipo de M.O. se presenta en la naturaleza tanto en pequeñas o grandes aglomeraciones masivas como en micro o macrofragmentos dispersos en otros sedimentos, por ejemplo, en areniscas. En ambas formas de yacimiento ejerce la M.O. gran influencia en la fijación, concentración y fijación del U.

Las ideas expuestas en este trabajo son, en parte, fruto de experiencias realizadas en el laboratorio, y en parte, corresponden a hipótesis de principio que juzgamos válidas, aunque son necesarias ulteriores investigaciones para su confirmación definitiva.

EXPERIENCIAS SOBRE LA FIJACION DE U. POR M.O.

Hemos realizado en el laboratorio diversas experiencias sobre la adsorción de U. por materiales carbonosos, algunos de cuyos resultados hemos ya publicado en un trabajo anterior [1]. La M.O. empleada corresponde a muestras carbonosas procedentes de la cuenca de Calaf (Barcelona). Empleamos soluciones de nitrato de uranilo a distintas concentraciones y se pusieron en contacto con las muestras esperando hasta alcanzar el equilibrio. Entonces correlacionamos la concentración de equilibrio del ión UO_2^{2+} en las muestras con la concentración UO_2^{2+} existentes en las soluciones, reflejando los resultados en la Fig.1a. Las fracciones de muestra a que hace relación la curva (1) contenían 60 % de A.H. (ácidos húmicos) y las correspondientes a la curva (2) contenían sólo el 3 %. El carbón de Calaf tiene en general un rango equivalente a lignitos duros brillantes según hemos podido comprobar [2]. Tal es el rango que tiene el material húmico de la muestra (2) el cual se encuentra fundamentalmente al estado de huminas; la recogimos en zonas del interior de galerías de minas no afectadas por procesos oxidantes. En cambio el material de la muestra (1) lo recogimos en zonas superficiales, fuertemente afectadas por procesos supergénicos, los cuales han dado lugar a una regeneración de los A.H. a partir de las huminas. Por eso el material orgánico de tal muestra se compone fundamentalmente de dichos ácidos, y en este aspecto, se puede asimilar a turba en la que, como es sabido, la M.O. húmica se encuentra en esencia al estado de A.H.

Observando la isoterma (1) se observa cómo la adsorción va aumentando gradual y rápidamente hasta llegar a la saturación. Es similar a las construidas por Szalay [3-4] con turbas de Hungría, Martín [5] con turbas de

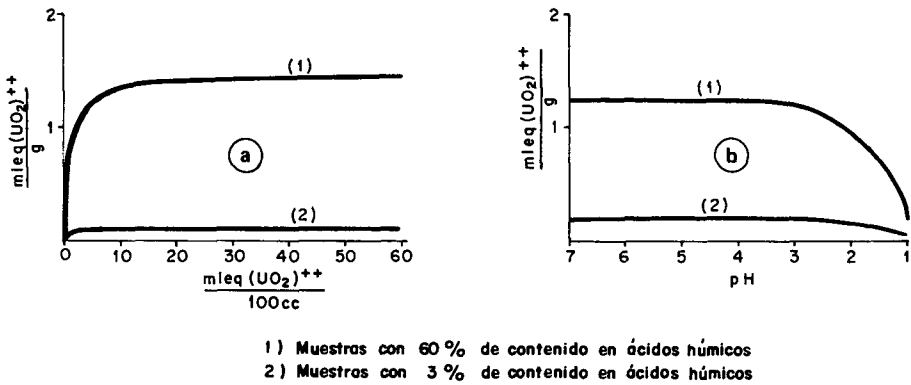


FIG.1a). Isotermas de fijación de $(\text{UO}_2)^{++}$ por lignitos. Ordenada: concentración de equilibrio de $(\text{UO}_2)^{++}$ por gramo de lignito. Abscisa: concentración de $(\text{UO}_2)^{++}$ en la fase acuosa en equilibrio.
1b). Liberación de $(\text{UO}_2)^{++}$ absorbido por el lignito. Ordenada: concentración de $(\text{UO}_2)^{++}$ retenido por el lignito. Abscisa: pH de la solución empleada en la experiencia de desorción del $(\text{UO}_2)^{++}$ del que previamente se había saturado el lignito.

Francia y Schmidt-Cellerus [6] con turbas de U.S.A. por no citar más; pero lo que deseamos puntualizar ahora es que el grado de adsorción registrado por la muestra (1) es mucho mayor que el registrado por la muestra (2) en la que puede verse que la saturación se alcanza inmediatamente. Se desprende que las huminas no poseen las propiedades características para la fijación de U. que presentan los A.H.

En la Fig.1b se esquematiza gráficamente el proceso inverso al anterior; es decir, se reflejan los resultados de ensayos sobre liberación del U. fijado experimentalmente. Las muestras se sometieron a ensayos de lixiviación a distinto pH. Se observa que a $\text{pH} > 3$ no se libera nada de U., pero al aumentar la acidez del medio, crece a su vez rápidamente el grado de desorción. Esto indica la característica de reversibilidad que presenta el proceso de adsorción.

También realizamos otro tipo de experiencias sistemáticas para ver si existía efectivamente una afinidad química entre el U. y los A.H., y si esta tenía lugar, en qué dominio de pH era mayor el grado de combinación de ambos componentes. Para ello mezclamos en una serie de frascos 250 cm^3 de solución alcalina de A.H. extraídos de lignitos de Calaf con otros 250 cm^3 de solución diluida de tricarbonato de uranilo, ajustando la mezcla a pH 2, 3, 4, 5 y 6. Los resultados se reflejan en la Fig. 2. En efecto, observamos que el U. se asocia a los A.H. y ambos coprecipitan, teniendo lugar la máxima coprecipitación entre pH 4 y 5,2. Aparte habíamos visto que ajustando a los mismos pH la solución de tricarbonato de uranilo sin A.H. no precipitaba ningún compuesto de U., pues de lo contrario no hubiera servido para la experiencia; es lo que refleja la curva (2); vemos que en todos los dominios de pH se mantiene el valor cero, es decir, no precipita nada de U.

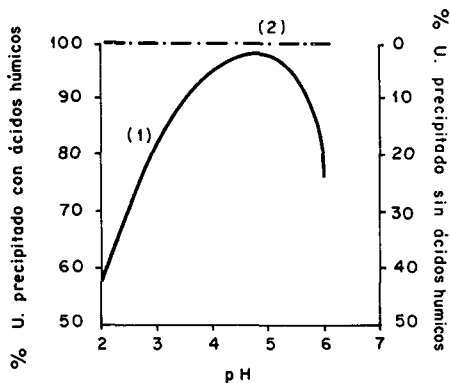


FIG.2. Precipitación del uranio a partir de soluciones con ácidos húmicos 1), y sin ácidos húmicos 2), en relación con el pH.

Por otra parte hemos realizado pruebas de adsorción sobre muestras esporádicas con M.O. de diverso rango en la escala de la carbonización. Por ejemplo hemos hecho ensayos en las siguientes muestras:

- M.O. al estado de turba procedente de Gumiel de Hizán (Burgos), en la que el U_3O_8 retenido una vez lavado el material representa el 24 % de la muestra.

- M.O. al estado de lignitos de bajo rango, procedente de Puente de García Rodríguez (Coruña), en la que el U_3O_8 retenido, siempre después de lavada la muestra, es el 12 %.

- M.O. al estado de lignitos de medio rango, procedente de Utrillas (Tehuacán) y de la mina Tres Amigos de Almatrat (Lérida); el U_3O_8 retenido representa el 5 %.

- M.O. al estado de lignitos de alto rango, procedente de Berga (Barcelona); el U_3O_8 retenido representa el 0,3 %.

- M.O. al estado de hullas de bajo rango, procedente de la mina Inesperada (Oviedo); el U_3O_8 retenido representa el 0,1 %.

En conjunto se deduce:

- Hay una gran tendencia del U. a asociarse con la M.O.
- Que dentro de la M.O. son las sustancias húmicas las responsables.
- Que el grado de asociación depende del pH del medio y del estado de dichas sustancias. El mayor grado se efectúa cuando el material húmico se encuentra al estado de A.H.; la fuerza de asociación va disminuyendo al ir aumentando el rango de la M.O., llegando a ser mínima cuando se encuentra al estado de hulla.

LA ASOCIACION URANO-ORGANICA A TRAVES DEL PROCESO EVOLUTIVO DE LA CARBONIZACION

De todas las experiencias señaladas creemos se pueden deducir además algunas orientaciones de principio sobre la metalogenia general de la asociación urano-orgánica. En los apartados siguientes exponemos un esquema de las mismas. En primer lugar señalamos las circunstancias óptimas que determinan un estado específico de la asociación U.-M.O. y en segundo lugar la evolución de los complejos urano-orgánicos fijados en los primeros estadios de la carbonización.

1. Formación de fases minerales propias o complejos urano-orgánicos

En cada yacimiento han podido jugar factores diferentes, pero hay uno común y fundamental y es el carácter evolutivo que presenta la M.O. húmica cuando las soluciones uraníferas llegan a ponerse en contacto con la misma. En ese instante, y supuestas naturalmente condiciones reductoras, se produce una especie de competencia entre dos tendencias a las que el U. queda sujeto: formación de fases minerales individualizadas (equivalentes a pechblenda o cofinita) o formación de fases orgánicas con naturaleza de complejos cualquiera que sea el tipo de los mismos. El que se produzca uno u otro estado del U. es de gran trascendencia sobre todo por las repercusiones de orden económico en lo que concierne a su recuperación en el caso de formar yacimiento explotable.

La alternativa a que ha de dar lugar dependerá de la relación entre la constante de estabilidad de los complejos urano-orgánicos y el producto de solubilidad de los minerales. Ahora bien, la constante mencionada depende a su vez del estado de la M.O. cuya actividad y capacidad de reacción varía en el proceso evolutivo de la fosilización. Por tanto la relación que acabamos de indicar será también diferente según la mayor o menor maduración de la M.O., siendo esta diferencia la que va a decidir el que el U. se determine según una u otra fase.

La mayor parte de los constituyentes biógenos se presentan al estado de A.H. en los primeros estadios de la evolución (correspondientes petrográficamente a turbas) y es cuando tienen mayor capacidad de reacción según se desprende de las experiencias antes señaladas. En ese estado, es cuando la estructura de la M.O. presenta mayor número de cadenas laterales a las que se asocian grupos activos, los cuales constituyen ligandos ideales para el U. Igualmente, los materiales húmicos manifiestan una porosidad muy elevada en ese estado, por lo que son, a su vez, cuando mayor superficie de reactividad tienen. En estas condiciones la relación entre la tendencia de dichos materiales a formar fases urano-orgánicas y el producto de solubilidad de los minerales propios favorece la formación de las fases urano-orgánicas.

Cuando el material organógeno se presenta disperso, por ejemplo en facies arenosas, una parte del U. en contacto con los A.H. precipitará en fases orgánicas, pero en los espacios intermedios el U. puede precipitar en forma

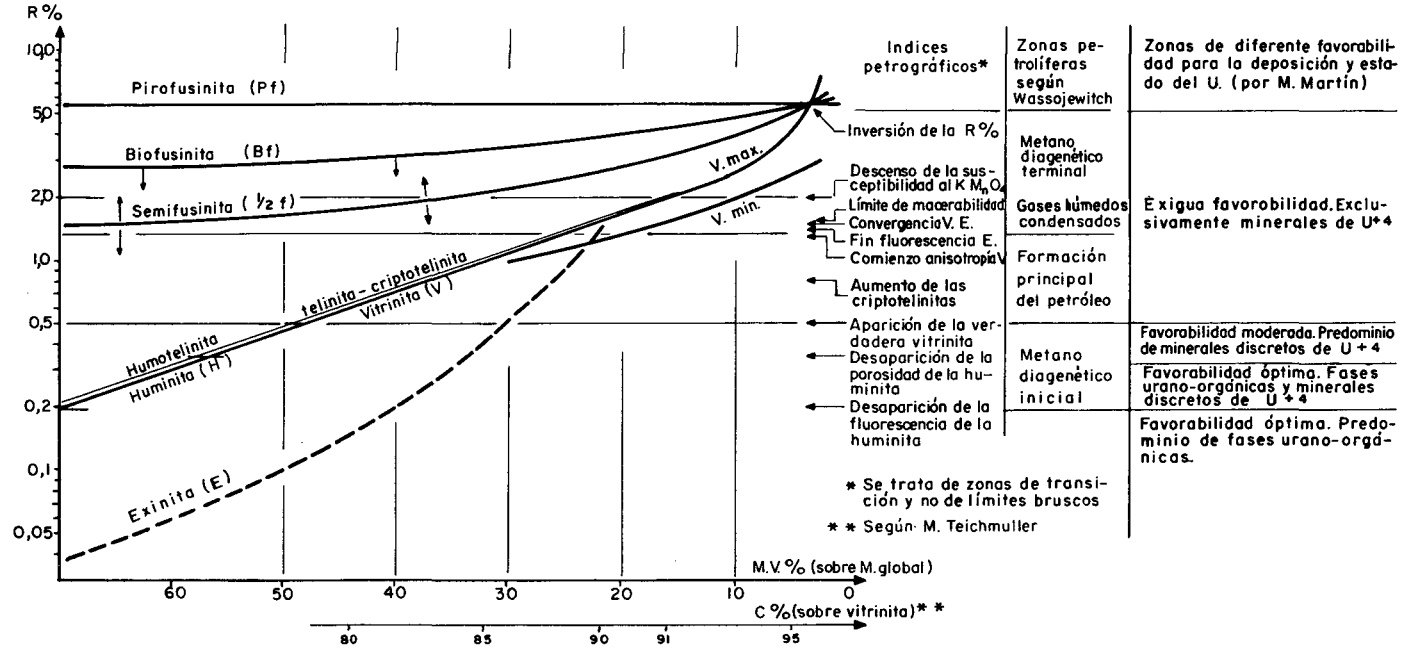


FIG. 3. Esquema de principio sobre la evolución de la reflectividad de los macerales en el curso de la carbonización (según B. Alpern).

de minerales discretos. Igualmente, si en un momento dado, el enlace U.-A.H. alcanza el grado de saturación, y aún queda U. en la solución por encima del producto de solubilidad, puede precipitar también dicho metal en fases minerales propias.

Sigue evolucionando la M.O.; al principio la evolución se manifiesta fundamentalmente por la pérdida de agua y porosidad, lo cual tiene lugar al irse comprimiendo el material. Se van modificando las propiedades físicas, químicas y petrográficas de las sustancias húmicas, alcanzando el segundo estadio importante de la fosilización: petrográficamente corresponde al estado de lignitos de bajo rango que con cierta flexibilidad podemos asimilar a los denominados lignitos blandos. La M.O. contiene todavía en esta etapa una gran proporción de A.H. y una reactividad notable. No obstante la relación entre la fuerza de afinidad química y la de formación de minerales discretos va disminuyendo progresivamente. Al principio del estadio de lignitos blandos la relación será favorable para la deposición del U. en forma de complejos; pero al progresar la evolución, llegará un momento en que dicha relación favorecerá la precipitación de fases pechblenda. Por tanto en el estadio de lignitos de bajo rango, en general, la asociación U.-M.O. puede tener lugar según los dos estados: en fases orgánicas y en forma de minerales individualizados.

La carbonización avanza y llegamos a la siguiente etapa, que asimilamos a la que petrográficamente se clasifica como estadio de lignitos duros. En este intervalo de la evolución las propiedades físicas y químicas de las sustancias húmicas sufren cambios más profundos, que, lógicamente, se patentizan en su comportamiento petrográfico, tecnológico y metalogénico. Una de esas modificaciones relevantes es el tránsito del estado de A.H. al de huminas. En tal estado las sustancias húmicas son muy poco activas; disminuye mucho su tendencia a reaccionar con el U.; es lo que se refleja en la curva (2) de la Fig.1a. La relación entre la afinidad química y la tendencia para la formación de fases minerales individualizadas favorece la formación de estas últimas.

Siguiendo el proceso de la carbonización llegamos a la última fase, la cual comprende desde el estado de hullas hasta el final de la maduración. La M.O., en tal estado, se comporta como inerte, por lo que ya no hay probabilidad de formación de fases urano-orgánicas, y si tiene lugar deposición de U. ha de ser poco eficiente y en forma de minerales. Una pequeña proporción de U. puede fijarse en cierta superficie de adsorción muy limitada y de una forma mecánica como puede suceder, por ejemplo, en el carbón de encina. Tal inercia va aumentando progresivamente a medida que avanza la carbonización hasta que llega a ser prácticamente total a partir del estado de hulla con rango elevado.

Las ideas expuestas se sintetizan gráficamente en la Fig.3. El gráfico ha sido realizado por Alpern [7], y en él, traza el esquema de principio sobre la evolución de la reflectividad de los macerales en el curso de la carbonización. Se ve cómo avanza el valor de la reflectividad de los tres grupos de macerales: el de la inertinita (pirofusinita, biofusinita, semi-fusinita), el de la huminita-vitrinita y el de la exinita. El representati

vo y característico es el de la huminita-vitrinita, ya que sus propiedades físicas y químicas varían regular y progresivamente a través de la evolución; además a él se asocia el U. Al proyectar los valores de la reflectividad sobre la curva de ese maceral, quedan marcadas las zonas de la carbonización, que corresponden, en orden de reflectividad creciente, a turbas, lignitos de bajo y medio rango, lignito de medio y alto rango, y a partir de $R > 5\%$ la M.O. alcanza sucesivamente el estado de hulla, antracita y grafito. Al lado señala Teichmüller los índices petrográficos, Wassojewitch et al. [8] el ordenamiento de las zonas petrolíferas y a la derecha indicamos nosotros el ordenamiento de las zonas con diferente favorabilidad para la deposición y estado del U.

Para terminar este apartado, diremos que la observación estadística de las condiciones de yacimiento que rodean la asociación urano-orgánica tienen también a confirmar, de algún modo, los criterios metalogénicos expuestos. Efectivamente, en los datos de observación de campo, es frecuente observar que, cuando se trata de U. singenético, lo cual supone que se depositó en los estadios tempranos de la fosilización y por tanto con la M.O. poco evolucionada, normalmente no aparecen minerales. En cambio, cuando se trata de U. epigenético, en el sentido de que se depositó en los materiales biógenos después de litificados y con la M.O. en un estado de madurez más o menos avanzado, el U. suele aparecer en forma de minerales individualizados.

2. Los complejos urano-orgánicos a través de la carbonización

Ya hemos dicho que la M.O. en el primer estadio de la carbonización tiende a enlazarse con el U. en forma de complejos. Podemos suponer que la unión U.-M.O. se ha podido verificar según procesos más o menos similares a los realizados en el laboratorio de los que hemos señalado anteriormente algunos ejemplos. Pues bien, cualquiera que sea la naturaleza de los complejos formados, parece probable que el grado de estabilidad de los mismos no fuera al principio relativamente elevado. Es lo que puede deducirse de las experiencias sobre la liberación del U. que hemos reflejado en la Fig. 1b.

Al evolucionar la M.O. las fases urano-orgánicas se van reajustando conforme a las condiciones ambientales que van surgiendo. Al transformarse los A.H. en huminas se pierden ciertos grupos polares que estaban colocados en las cadenas alifáticas que forman parte de la estructura de las sustancias húmicas; esto hace que el U., el cual va precisamente ligado a dichos grupos, se reordene, pero en el sentido de adquirir mayor estabilidad. Parece probable que, en un principio, el U. al depositarse formase con preferencia complejos, digamos, comunes, y en los reajustes que acompañan a la maduración progresiva dichos complejos vayan adquiriendo mayor fuerza de enlace, pasando por ejemplo a ser del tipo quelatos. Algunos datos experimentales sugieren también tales modificaciones metalogénicas en los complejos urano-orgánicos a través de la carbonización. Nos referimos a una serie de ensayos sobre liberación del U. que hemos realizado en lignitos uraníferos de la Cuenca de Calaf [2]. El U. se fijó en esos materiales singenéticamente, en el sentido de que tuvo lugar en los primeros estadios de

la carbonización, y constituyó fases orgánicas. Actualmente el material carbonoso, según ya hemos señalado, presenta un rango equivalente a lignitos duros brillantes. Pues bien, el U. se libera de los mismos con mucha dificultad; hay que aplicar condiciones enérgicas de ataque, y sólo destruyendo la M.O. se logran rendimientos satisfactorios. No sucede lo mismo con el U. fijado en condiciones de laboratorio, las cuales manifiestan características de reversibilidad, según se ha indicado. En los ensayos de lixiviación, a los que ahora hacemos referencia, vimos incluso que las muestras con mayor proporción de A.H., lo que equivale a M.O. menos evolucionada, liberan más fácilmente el U. que las que tienen menor proporción de A.H., en las mismas condiciones de pH. Deducimos por tanto que el U., que en la naturaleza pudo fijarse por un proceso similar al que tiene lugar en el laboratorio, al pasar el tiempo y evolucionar la misma M.O. progresivamente hasta aproximadamente el grado de lignitos duros, ha adquirido mayor fuerza de enlace, puesto que manifiesta un comportamiento diferente al que ofrece inmediatamente después de fijarse a la misma M.O., es decir, no sometida al proceso de maduración.

A partir de la hullificación, el U. se inestabiliza por efecto del intenso metamorfismo que afecta a la M.O. A partir de esta etapa los núcleos aromáticos de las huminas van adquiriendo una gran condensación, por lo que correlativamente desaparecen las cadenas laterales alifáticas y es en ellas donde van colocados los grupos portadores de U. Esto supone lógicamente que las fases urano-orgánicas se van destruyendo y el U. liberando simultáneamente. Los anteriores procesos eran de reajuste estabilizador dentro de las macromoléculas de la huminita; ahora es un proceso destructivo. Una vez liberado el U. de sus ligandos orgánicos puede dar lugar a formación local de minerales.

RELACION DEL U. CON LOS CONSTITUYENTES PETROGRAFICOS DE LA M.O.

En la Fig. 3 se representan gráficamente los índices petrográficos correspondientes a los grupos fundamentales de macerales a través de la carbonización. Pues bien, todo lo expuesto hasta ahora en torno a la metalogénia de la asociación urano-orgánica se refiere fundamentalmente a la asociación del U. con la M.O. constituida petrográficamente por huminita-vitrinita y, más específicamente, con los macerales del grupo de la huminita. La vitrinita manifiesta escasa actividad, desde el punto de vista metalogénico, pues corresponde a M.O. muy evolucionada, concretamente al estado de hullas, según la nomenclatura de los petrógrafos del carbón Alpern y Teichmüller [9], reconocida en el L.I.P.C. [10]. En cambio la huminita es el maceral que mejor caracteriza petrográficamente a la M.O. con rango inferior a hulla, y es el responsable fundamental de la asociación urano-orgánica.

La exinita constituye un grupo de macerales con importancia secundaria en la metalogénia del U.; sus componentes son más bien de naturaleza sapropelítica, por lo que presentan cierta similitud con las bitumitas, y es sabido que la M.O. de este tipo es mucho menos activa para el U. que la M.O. de carácter húmico propiamente tal.

Los macerales del grupo de la inertinita son de naturaleza húmica como la huminita pero son también muy poco activos frente a su asociación con el U. Etimológicamente el término señala inercia, y efectivamente, los petrógrafos del carbón [11] le dieron ese nombre general porque los macerales de este grupo son más inertes que los otros dos frente a ciertas propiedades tecnológicas. Pues bien, frente al U. presentan igualmente gran inercia; ello se debe a que estos macerales evolucionaron con anterioridad a su sepultura definitiva en la cuenca de sedimentación, y cuando se incorporaron al restante material biolítico ya habían perdido los grupos funcionales activos y demás ligandos con los que se relaciona el U.

Un ejemplo confirmativo del anterior aserto lo constituyen los lignitos uraníferos de Calaf [2], en los que observamos que siempre el U. se asocia esencialmente a los macerales del grupo de la huminita.

PROPORCION DE M.O. OPTIMA PARA LA FORMACION DE YACIMIENTOS DE U

En la naturaleza, la M.O. húmica se presenta, por una parte, en grandes concentraciones y con distribución más o menos homogénea, constituyendo los materiales que comúnmente designamos como carbones o pizarras carbonosas. Por otra parte, la M.O. se presenta en pequeños fragmentos dispersos en las facies sedimentarias y más bien con distribución irregular.

El interrogante que ahora nos hacemos es el siguiente: ¿cual es la proporción de M.O. óptima para provocar la formación de concentraciones de U. de economía más rentable? Parece lógico responder que no es necesario, ni mucho menos, que haya gran cantidad de sustancias húmicas para que se produzca una concentración de U. interesante. Precisamente, sobre todo desde el punto de vista económico, las acumulaciones masivas de biolitos no son las más propicias para que el factor de concentración alcance los límites normales de explotabilidad. En efecto, cuando existen grandes cantidades de sustancias húmicas, lógicamente se encontrarán más lejos del estado de saturación para una misma proporción de U. que llegue a la cuenca, por lo que en ese caso nos encontraremos siempre en la fase inicial de la isoterma de la Fig.1a. Al ir disminuyendo la proporción de material orgánico alcanzaremos puntos más altos en la isoterma. Pero también se concibe que hay un límite en la proporción ínfima de materia orgánica ideal. Entonces existe un equilibrio óptimo entre la proporción de M.O. y el U. disponible en una cuenca para que se formen yacimientos de economía rentable. Creemos que se acerca a esa proporción ideal la existencia de M.O. en calidad de constituyente accesorio, aunque dentro de este carácter sea más bien abundante. Resulta muy difícil señalar la proporción óptima exacta. Simplemente indicaremos que, por ejemplo, las concentraciones de U. singenéticas en algunas extensas formaciones de pizarras negras marinas y en algunas cuencas de biolitos húmicos masivos es difícil lleguen a formar yacimientos de explotabilidad definitivamente rentable, ya que las propiedades similares y homogéneas de las sustancias húmicas en cuanto a su afinidad físico-química por el U. hacen que este se asocie y diluya con homogeneidad por toda la masa húmica. Entonces, para que esas masas biógenas se saturen de

U. suficiente o provoquen una precipitación interesante del mismo, se necesitarían venidas y concentraciones en solución acuosa con valores ideales, difíciles de tener lugar en la naturaleza. Por el contrario la M.O. (supuestos índices bajos de madurez) al estado disperso y distribución irregular dentro de otros materiales, por ejemplo en arenisca, delimita centros de concentración preferente, lo cual puede dar lugar a masas explotables económicamente. Por eso, a la hora de valorar áreas sedimentarias de mayor favorabilidad para contener yacimientos, se juzga como signo más positivo la existencia de M.O. al estado disperso y con distribución esporádica e irregular, más que al estado de horizontes o aglomeraciones masivas.

REFERENCES

- [1] MARTIN CALVO, M., Influencia de la materia orgánica fósil en la metalogénia del uranio, I Congreso Hispano-Luso-Americano de Geología Económica, E-4-19, Madrid-Lisboa (Sept. 1971).
- [2] MARTIN CALVO, M., Sobre la petrogénesis de algunas litofacies españolas con fases urano-orgánicas, Boln geol. min., España (en prensa).
- [3] SZALAY, A., The significance of humus in the geochemical enrichment of uranium, 2^a Conf. int. util. energía atóm. fines pacíf. (Actas 2^a Conf. Ginebra, 1958) 2, Nac. Unidas, Ginebra (1958) 182.
- [4] SZALAY, A., Cation exchange properties of humic acids and their importance in the geochemical enrichment of UO_2^{+2} and other cations, Geochim. Cosmochim. Acta, 28 (1964) 1605-14.
- [5] MARTIN, J., Fixation et transport de l'uranium par les substances humiques, Rapport CEA, n° 2141 (1962).
- [6] SCHMIDT-COLLERUS, J.J., Research in uranium geochemistry. Investigations of the relationship between organic matter and uranium deposits, Part II. Experimental investigations, Denver Research Institute (Julio 1969).
- [7] ALPERN, B., Classification petrographique des constituants organiques fossiles des roches sedimentaires, Revue de l'Institut Français du petrole et annales des combustibles liquides, XXV 11 (Nov. 1970).
- [8] WASSOIEWITCH, N.B., KORTCHAGINA, J.I., LOPATIN, N.W., TCHERNICHEV, W., TCHERNIKOV, K.A., Die Hauptphase der Erdolbildung, Z. Angew. Geol. 15 (1969) 612-21.
- [9] ALPERN, B., TEICHMULLER, M., Classification et correlation des constituants de la vitrinite (houilles) et de l'huminite (lignites), C. R. Acad. Sc. Paris 272, serie D, n°13 (1971) 1717-21.
- [10] LEXIQUE INTERNATIONAL DE PETROGRAPHIE DES CHARBONS, Supplement à la 2^e édition de l'LIPC, Edit. CNRS, Paris (1971).
- [11] LEXIQUE INTERNATIONAL DE PETROGRAPHIE DES CHARBONS, Centre National de la Recherche Scientifique, Paris (1963).

DISCUSSION

S.S. AUGUSTITHIS: Do you think there is some true chemical affinity between carbon and uranium, or is it more likely to be a chance mechanical connection?

J. A. FERNANDEZ POLO: I doubt whether there is any true chemical affinity between the elements carbon and uranium, but I do think there exists a direct geochemical affinity and an indirect geophysical affinity between humic carbonaceous materials and uranium.

J. W. von BACKSTRÖM: In South Africa, evidence regarding the influence of carbonaceous material as a collector and precipitator of uranium is rather contradictory. During the early 1950s, when the first uranium boom arrived, we asked all our coals and carefully analysed them for uranium, with negative

results. In fact, the enclosing sandstone and shale of the Eccra Formation, in which the coal occurs, showed higher uranium background values. This observation was later confirmed by hundreds of radiometric logs of exploratory boreholes drilled for gold, which penetrated the coal measures present in the overlying Karoo Supergroup covering the Witwatersrand Supergroup.

In contrast, boreholes drilled through the Kalahari Beds into the coal seams of the Karoo Supergroup in South West Africa revealed high uranium values. In the Witwatersrand Supergroup the situation is very similar. Although carbonaceous material commonly occurs with gold and uranium in the quartz-pebble banket reefs, there is a lot of carbon present throughout the Witwatersrand Supergroup without this association.

J. PASQUALI: Have the groups that complex the uranium in or with the humic acids been specifically identified?

J. A. FERNANDEZ POLO: We have not identified them ourselves because we were not involved in this aspect of the research. Indirectly we can deduce that the groups in question are located in the lateral chains of the macromolecules which constitute the humic substances. For more information on this subject I would refer you to the work of Schmidt-Collerus which we cite as Ref. [6].

I. A. BREGER: If I may go back for a moment to Mr. Augustithis' question, it is true that most coals contain extremely small quantities of uranium. We have used anthracite for making background measurements with a radiation counter. For a uraniferous coal deposit to form, however, three things must be present: the coal itself, the uranium, and finally a water system capable of moving the uranium into the coal where it can be absorbed. Unless uranium is brought within the coal zone, there will be no uraniferous coal.

R. BLASER: I might add that the relationship between uranium and organic matter may be established indirectly, via the reduction of uranium ions in solution in water by the H_2S produced in an anaerobic environment as a result of bacterial action on organic matter. The H_2S could lead to the precipitation of less strongly oxidized (and less soluble) uranium compounds in the aqueous solution by reducing the originally more highly oxidized (and more soluble) uranium compounds present therein.

In shales containing large amounts of iron ($FeS \rightarrow FeS_2$) uranium may be adsorbed on the organic matter, but it might also occur in the clay matrix in the form of cryptocrystalline inorganic compounds.

In a carbonate environment, for example in bituminous marls, uranium can occur in several forms: (a) adsorbed on the surface of kerogenous organic particles; (b) incorporated in the kerogenous organic matter (possibly); and (c) as complex uraniferous hydrocarbon compounds. The occurrence of inorganic uranium minerals in bituminous marls is uncertain and to my knowledge has not been demonstrated yet.

A. HERBOSCH: I agree with Mr. Blaser. There still seems to be a lot of confusion in our minds about the relationship between uranium and organic matter. Too often we forget how important the pH of the environment is. As far as I know, organic matter will not adsorb uranium or form a chelate with it except at an acid pH, i. e. a value below 5. We seem to forget that sandstone-type deposits are often alkaline and that this process is not effective in such an environment. There is, nevertheless, a very clear relationship between uranium and organic carbon, and I think under the circumstances it must have come about indirectly: the organic carbon

provides a bacteria-rich nutrient capable of transforming sulphates to H_2S , and the uranium is precipitated either because of the prevailing reducing conditions or by the H_2S .

S. S. AUGUSTITHIS: Some of the comments we have heard highlight the role of organic carbon as a reducing agent and catalyst, but it seems to me that a true chemical affinity between uranium and carbon has yet to be demonstrated.

G. R. UDAS: We have observed that carbonaceous material is not essential to secondary concentration of uranium. We find on the one hand that the coal seams overlain and underlain by clays in the Gondwanas are not mineralized for uranium, whereas, on the other hand, Precambrian conglomerates with a pyrite and clayey matrix do show enrichment of uranium. I think, therefore, that it would be unwise to overemphasize the role of carbonaceous material in controlling uranium concentration.

J. R. BERTHELIN: Firstly, let me say that carbon is not essential to microbial action, as certain speakers seem to be saying. We have to distinguish between heterotrophic microorganisms, whose development requires organic carbon, and autotrophic microorganisms, which utilize mineral compounds as an energy source.

Moreover, carbon is not important in itself; it is the structure of the carbonaceous organic compound that is important in the uranium mobilization process: functional groups, molecular structure and so on.

Finally, anaerobic conditions do not imply, as some appear to believe, a mobilization of uranium by microflora but rather the opposite – immobilization. Experiments in anaerobic conditions utilizing acids (acetic, butyric, lactic) resulted in no mobilization of uranium, whereas other experiments have indicated that aerobic conditions (unflooded columns, microflora obtained by partial sterilization) with the formation of oxalic acid and organic acid compounds of large molecular mass (2000 - 2500) do favour solubilization of uranium. This again clearly indicates the importance of carbon compound structure.

Let me conclude with three questions to Mr. Fernandez Polo. Firstly, how do you distinguish between the different humic acids?

J. A. FERNANDEZ POLO: Mainly by their different behaviour in organic and inorganic solvents. In our research we separated the fulvic acids from the humic acids proper only to observe the relationship which each bore to uranium.

J. R. BERTHELIN: And what exactly do you understand by the distinction between humic acid and humins?

J. A. FERNANDEZ POLO: The humic acids are represented by humic carbonaceous material which has undergone little evolution (from peat to medium-range lignites, say) and which, chemically, is soluble in alkalis under normal conditions. The humins are more highly evolved humic carbonaceous substances (from the upper-range lignites on) which are chemically insoluble in alkalis unless subjected to some preliminary oxidation process.

J. R. BERTHELIN: You mentioned, in connection with the process of solubilization and insolubilization, a "limit" applicable to the different humic acids. What is this limit?

J. A. FERNANDEZ POLO: The limit is precisely this transition from humic acids to humins. It is in effect an indeterminate point which we recognize best a posteriori in analysing organic substances at different stages of evolution.

SEDIMENTARY BASINS AND
SANDSTONE-TYPE DEPOSITS:
NORTH AMERICAN DEPOSITS

Review Paper

CONCEPTS OF URANIUM-ORE FORMATION IN REDUCING ENVIRONMENTS IN SANDSTONES AND OTHER SEDIMENTS

H. H. ADLER

US Atomic Energy Commission,
Washington, D.C.,
United States of America

Abstract

CONCEPTS OF URANIUM-ORE FORMATION IN REDUCING ENVIRONMENTS IN SANDSTONES AND OTHER SEDIMENTS.

Reliance will be placed on sandstones as a source of uranium for many years to come inasmuch as they contain nearly a third of the world's resources and in excess of 95% of the US reserves.

The mobility of uranium depends on the solubility of the uranyl ion in ground water, and precipitation of the metal as ore is governed almost exclusively in sandstones by chemical reduction. The fate of uranium in sandstones is dependent primarily on the existence of a variety of conditions and circumstances under which reductants form and accumulate.

The redox recycling process which involves considerable mobility of uranium is prominently involved in the formation of uranium ores in the Wyoming basins and in the Grants area, New Mexico, but is more restricted in areas where vanadium abundantly accompanies uranium and fixes the uranyl ion as insoluble vanadate.

The major deposits in sandstone are classifiable into peneconcordant and roll types on the basis of morphological relationships; however, a further breakdown of deposits on the basis of the geochemical environment of deposition is more useful in determining where new occurrences might be found.

From a genetic standpoint roll-ore deposits may be divided into four principal types. These are the Wyoming-type, which is associated with a prominent redox interface created by oxidation of indigenous reductants by oxygenated ground waters; the Plateau-type roll, which reportedly is encircled by pyritic sandstone and has therefore been interpreted as a primary depositional feature; the Entrada- or Rifle-type, which the writer attributes to diffusion of H_2S and ore-forming cations towards a stationary interaction zone separating a trapped oil or gas pool from wedges of fresh water which press against and confine the location of the hydrocarbon- H_2S -bearing medium and its reaction interface; and the Texas-type, which is formed by H_2S introduced along faults into the host sands from underlying gas and oil deposits. Redistribution deposits formed by reworking of pre-existing tabular deposits in the Grants, New Mexico area are genetically classified with the Wyoming-type rolls.

Ore deposits in eolian sandstones, such as the ores at Rifle, Placerville, and Grants, are identified with a bleached zone overlying the normally red facies of the host rock. At Grants and Placerville, and in the intervening San Juan Basin, the bleaching appears to be related to H_2S development in the Todilto sea immediately following the end of Entrada deposition. The once-pyritic, now limonitic, bleached zone of the Entrada contains several small occurrences of ore in outcrop, and speculation is raised as to the possibilities for ore formation at depth where known deposits of oil and brackish water suggest that reducing conditions still remain.

Tabular (peneconcordant) deposits are also classifiable according to the nature and source of the reductant controlling ore deposition. Deposits associated with introduced humate substances make up a substantial part of US resources. The suggested genetic connection between these deposits and overlying paleo-bogs and swamps raises some concern regarding the replication elsewhere of resources of similar kind and magnitude.

Sandstones and other classic sediments may play a role in uranium-ore formation by serving as paleoaquifers which conduct uraniferous ground waters or other solutions towards loci in adjoining less-permeable sediments containing suitable reductants, e.g., bituminous limestones and shales. The Todilto-Entrada relationship is one example, and several deposits (some non-uraniferous) in the Permian of Europe and the Precambrian of the USA may reflect a similar association.

INTRODUCTION

Almost 75 percent of the low-cost uranium reserves of the world, exclusive of the USSR, Eastern Europe and China are contained in sedimentary rocks, particularly sandstones and conglomerates. In the U. S. A. over 95 percent of low-cost uranium reserves are in sandstone, whereas deposits in quartz-pebble conglomerate account for more than 80 percent of Canada's reserves and most of South Africa's. Virtually all of the uranium resources of Argentina, Central African Republic, Gabon, and Niger are in sedimentary rocks. Sweden has large resources in bituminous alum shales, and many nations with smaller resources also rely on sediments as their major source of ore.

A recent study (1) has shown that the U. S. A. has about one-third of the world's uranium reserves and is expected to account for just under one-half of world requirements by 1985. Further predictions reveal that by the end of this century a six- to seven-fold increase must be achieved in domestic resources in order to meet anticipated requirements without depleting the supplementary resource base which is estimated at about an 8-year forward supply. Discovery of the needed uranium is tantamount to finding 16 new uranium districts comparable in size to the largest now known in the U. S. A., i.e., the Ambrosia Lake District in New Mexico.

Because sedimentary rocks are such a productive source of uranium, they are expected to continue to play a major role in providing the uranium needed to fuel future nuclear reactors for many decades to come. It is important, therefore, to acquire an understanding of the manner in which these ores are formed, as such knowledge will be most helpful in guiding exploration into regions that are not yet explored or known to contain uranium but conceivably could add to the world's inventory of this extraordinarily useful fuel.

There are basically two principal classes of uranium deposits in sediments, those deposits that are formed by physical mechanisms and those that are formed chemically. Geological consensus would seem to identify the important Witwatersrand deposits of South Africa and the Blind River ores of Canada as placer-type occurrences. The sandstone-type deposits of the U. S. A., on the other hand, although not all alike, are clearly chemical deposits. This presumably is true also of the major deposits in Niger and Gabon which have many of the attributes of the U. S. deposits and of the enormous Swedish occurrences in shales.

This paper will confine itself largely to uranium deposits formed in sediments, particularly sandstones, in which chemical reduction is a major factor in ore formation. Although it reflects opinions and ideas already expressed in the literature on uranium ore formation, it is not intended strictly as a review paper. An attempt is also made to classify sandstone-type deposits according to reducing environment and the source of the reductant, and some views and insight are offered on the manner and conditions of formation of uranium occurrences in eolian and other rocks that are less productive but present geochemically interesting possibilities.

URANIUM MOBILITY

Uranium mobility in solution in permeable sediments is governed by the stability of its two natural valence states, U^{4+} and U^{6+} (or UO_2^{2+}). Uranium occurs largely in the tetravalent state in its two most important ore minerals, uraninite and coffinite. These compounds are stable under

reducing conditions, and there is no evidence for appreciable dissolution in oxygen-depleted ground waters. Oxidizing conditions at or near the ground surface or associated with pyrite decomposition below the water table normally render the minerals soluble. The resultant uranyl ions react in various ways with the geological environment.

In the presence of vanadium ions or ionic complexes, stable uranyl vanadates such as carnotite and tyuyamunite are likely to form, occasionally in rich but local concentrations such as the well-known carnotite log deposits of the Colorado Plateau. On the other hand the uranyl ion may re-enter the reducing environment in which hydrogen sulfide formed bacteriogenically or as the product of disproportionation of sulfur-ion species may re-reduce the U^{6+} to U^{4+} and cause uranium precipitation and renewed accumulation. The roll ores of Wyoming are formed essentially by this process.

In the absence of suitable reductants, or absorbents such as coalified wood, uranium may move through the ground-water system to be dissipated in some way that is of geochemical rather than economic importance. The fate of uranium in waters in deep basins is not known but should be of interest because of the potential for reacting with the reducing components of oil and gas, thereby chemically restricting its further movement and possibly yielding additional accumulations.

Sandstones containing coalified plant remains, humate substances, pyrite, or hydrogen sulfide make suitable host rocks for uranium ore deposits. The potential for reduction of uranium moving into these sediments in ground waters is considerable. Other elements with transitional valence states are also affected, including vanadium, iron, molybdenum, copper, sulfur, and selenium, and their reconcentration can also be accounted for largely by chemical reduction.

Black unoxidized ores containing uraninite and coffinite are normally considered to be primary deposits in relation to the yellow oxidized uranium ores. Uranium readily fluctuates between its oxidized water-soluble state and its reduced insoluble state, and thus considerable transformation from one to the other goes on. The terms primary and secondary thus tend to lose significant meaning. Episodes of oxidation-reduction are evidently frequently repeated in many ore districts, especially in the absence of vanadium, and these cyclical events lead to a constant or discontinuous mobilization of ore with gradual movement of ore away from the direction of most intense or persistent oxidation. In other words, there is a tendency for ore to "roll" away from advancing oxidation brought about by oxygenated ground waters. Recycling responsible for formation of the important black ore-roll deposits so prominent in the Wyoming basins may begin by the uranyl ion being reduced and precipitated in the presence of organic matter, decomposing pyrite, or hydrogen sulfide. Oxygenated ground water re-oxidizes and solubilizes the uranium while simultaneously causing oxidation of pyrite and H_2S and contributing to oxidative degradation of the plant matter. The uranyl ion released on oxidation re-enters the reducing environment either by ground-water movement or by diffusion and is again reprecipitated. Ore formed in this manner involves an accretionary process, relying on influx of uranium ions from some remote or external source or on an abundance of ions released nearby in the sediments.

Recycling may also contribute to the formation of tabular and lenticular deposits. Young (2) and Malan (3) have expressed the opinion that the low-vanadium ores found in paleochannels in Triassic (Shinarump Formation)

sandstones on the Colorado Plateau were formed from uranium derived from earlier-formed, now-eroded, deposits in these rocks. King and Austin (4) attribute some of the peneconcordant deposits in the Gas Hills, Wyoming, to redistribution of uranium from ores undergoing oxidation at stratigraphically higher levels. On the other hand, the Grants District, New Mexico, provides excellent examples of the manner in which the redistribution process operates to destroy pre-existing tabular deposits and simultaneously to rework this uranium into roll-like and related (stacks) forms or ore deposits.

Although there is much evidence in many ore districts for cyclical redistribution of uranium, the process does not appear to have been equally important in all places where ore is encountered, e.g., in the central Colorado Plateau region roll-ore formation appears to be a minor development. This may be accounted for by the fact that recycling can be interrupted by failure of uranium-bearing solutions to re-encounter or regenerate chemically active reducing zones, or by the complexing of uranium with vanadate, phosphate, or arsenate to form relatively insoluble uranyl compounds, thus removing uranyl ions from circulation.

Recycling generally appears to be least restricted under conditions where the uranium-fixing elements are absent or scarce, and is most frequently inhibited where particularly vanadium is abundant. Copper and molybdenum, which are not uncommon in sandstone-type ores, seem to have little or no effect on the process. Where vanadium is relatively sparse as in ores of the Shirley Basin, Powder River Basin, and Gas Hills (all in Wyoming), a large number of deposits show evidence of continuous or interrupted, but complete, recycling to form both roll-type and tabular deposits. In the Grants District, New Mexico, where few of the ores are fixed by vanadium, there are excellent examples of redistribution of uranium along the oxidized edges of primary (pre-existing) tabular deposits that are related to an earlier period of ore formation.

In areas where vanadium is abundant, as in the Urvan mineral belt, black ores appear to have been converted to yellow ores by oxidation without evidence of appreciable displacement of uranium from the original site of ore deposition. Here, the unoxidized ore-mineral assemblage consists typically of pitchblende, coffinite, and montroseite, all of which are stable in the reducing environment but are susceptible to oxidation. Low-valence vanadium silicates (micas and clays) are also present. Whereas the clays and micas do not become oxidized, the more susceptible uranium and vanadium minerals alter to a complex assortment of oxidized uranium, oxidized vanadium, and oxidized vanadium-uranium minerals. Black vanadiferous uranium ores of the Colorado Plateau may contain from 1 to 15 times more vanadium than uranium, providing considerable opportunity for uranium fixation into insoluble vanadates. The efficiency of the process is evident in the great abundance of oxidized carnotite-bearing ore deposits on the Colorado Plateau.

Unoxidized ores having lower vanadium-uranium ratios, e.g., in the Black Hills of South Dakota and Wyoming, where the V:U ratio averages between 1.5 to 1.0 (5), appear to have had considerably greater opportunity for roll-ore formation through recycling of the unfixed uranium.

Oxidation of vanadiferous black ores of the central Colorado Plateau is believed to have occurred chiefly above the water table. Enrichment of black ore by redistribution is here considered unlikely because of the rapidity and extent of oxidation, the insolubility of the carnotite formed, and the generally low sulfide content of the vanadiferous ores

(6). Recycling of uranium by oxidation and reduction within the ground-water-saturation zone is considered (7) to have been of no importance in forming the roll deposits that exist there. The writer does not agree entirely with this position.

Although fixation of uranium by vanadium was an important process on the Plateau in limiting uranium redistribution, some local redistribution of black ore deposits appears to have occurred toward paleostream-channel edges where access to re-formed black ores by ground waters was impeded by the increasing mud and clay content of the stream bank sediments. The formation of rolls would be consistent with this process.

A few words should be said about the source of the uranium. The choice seems to be narrowed to those sources that at somewhat erratic intervals during various geological periods were capable of providing uranium to permeable strata, without requiring faults or fractures, and could do so more or less simultaneously in the same formation in many different areas. The subject of source has raised a great deal of speculation and controversy, and from time to time concepts, tentatively laid to rest, seem to reappear, as once discarded but not forgotten preferences are re-examined and reiterated.

At the moment, there seem to be two, or perhaps even three, predominant points of view each with its own group of proponents. Many geologists impressed by the proximity of uranium deposits to tuffaceous rocks, existing or eroded, prefer to derive uranium by weathering from these rocks which were sufficiently widespread throughout the western U. S. A. to give ample account for the distribution of known uranium deposits. Others see granites as the principal source for the uranium carried basinward by weathering solutions toward reduction loci. Magmatic hydrothermal emanations and waters expelled by compaction of shales and other sediments have also been called upon as possible sources; and even brines have been suggested. The writer is a proponent of the tuff-leach concept and will let the matter rest there.

CLASSIFICATION OF MAJOR DEPOSITS IN FLUVIATILE SANDSTONES

Uranium deposits in fluvatile sandstones are ordinarily classified on the basis of their morphological relationships to the host rock into two types, a peneconcordant-type deposit and a roll-type deposit. Unfortunately, such a classification gives no indication of the diversity of geochemical circumstances under which sandstone-type uranium deposits form. A genetic classification, even if somewhat speculative, would seem to be of considerably greater value in resolving the problem of where to look in sandstones for new occurrences of ore.

From the genetic standpoint, peneconcordant deposits, which are commonly described as tabular or lenticular layers that lie parallel, or nearly so, to bedding, can be divided into primary and secondary deposits. The primary deposit is, in theory at least, an original accumulation of uranium not obviously derived from a pre-existing ore body. The secondary deposit, as its name implies, is ordinarily thought of as having been formed by redistribution or reconstitution of pre-existing ore, usually by superegene processes. These definitions apply to unoxidized as well as oxidized ore bodies, but further consideration in this paper will be limited to the unoxidized deposits. The commercially important blanket or trend deposits of the Grants mineral belt in New Mexico are looked upon as primary deposits, and indeed they are insofar as their relationship to

the adjacent redistributed ores is concerned. On the other hand, some, if not all, of the tabular ores in the Gas Hills area, Wyoming, are considered more likely to be the product of uranium redistribution, as heretofore noted.

Tabular deposits may be more meaningfully sorted genetically according to the nature and source of the reductant. On this basis they appear to be classifiable into at least two kinds; namely, 1) deposits associated with an essentially static indigenous reducing environment such as is generated by carbonaceous plant matter accumulated by stream action during sedimentation and 2) deposits closely connected with later-introduced reductants such as humic substances or hydrogen sulfide.

The ore occurrences scattered along the paleostream channels in Salt Wash (Jurassic) and Shinarump (Triassic) strata of the central Colorado Plateau are examples of deposits found with indigenous plant material. Their deposition can be attributed to the reducing action of organic matter as well as hydrogen sulfide formed therefrom by anaerobic bacteria. Ore deposits associated with what, on the other hand, is considered to be introduced or redistributed organic matter are prevalent in the Grants mineral belt, New Mexico. The uranium occurrences in that area are associated in large part with impregnations of water-transported humic residues believed to have been derived from boggy vegetated terrain at one time directly overlying the outcrops of the uranium host rocks (8, 9). Another type of tabular ore in the latter category is that which appears to have been deposited by hydrogen sulfide introduced into sandstone along faults from underlying gas and oil reservoir rocks, as for example in the Maybell area, Colorado.

From all indications, primary tabular deposits are more numerous and of greater commercial importance than secondary tabular deposits. Remobilization of uranium, rather than forming tabular deposits, appears to have been more productive in the formation of roll-type deposits.

Roll ores, or ore rolls, are crescent-shaped deposits which cut across sandstone bedding. They are most common in Tertiary (Eocene) fluvial sandstones, particularly in the Wyoming basins and along the Texas Gulf Coast where the majority of commercial deposits occur in this form. In these areas, rolls are for the most part independent of tabular deposits, but in the Grants area, New Mexico, deposits of a modified roll type are found along the oxidized edges of primary tabular deposits where they constitute the so-called "redistributed" and "stack" or "stacked" deposits of the Jurassic Morrison Formation.

Ore rolls can be classified into at least four types depending on their manner of formation and the nature and source of the reductant. The Wyoming-type roll is typically associated with an indigenous reducing environment made up of carbonaceous plant material and pyrite. It is characteristically bordered on one side by an oxidized limonitic and/or hematitic altered facies in the sandstone and on the other by an unoxidized pyritic unaltered facies that has a recognizable, if not measurable, reducing capacity (Fig. 1). Wyoming rolls are generally considered to be the product of cyclic redistribution of uranium involving repetitive reworking of ore by supergene oxidation-reduction processes along hydrodynamic gradients. Two concepts to account for the recycling stand out as having special merit. These will be discussed subsequently.

It has been argued (7) that the rolls found on the Colorado Plateau are not genetically related to the Wyoming-type roll, and accordingly should

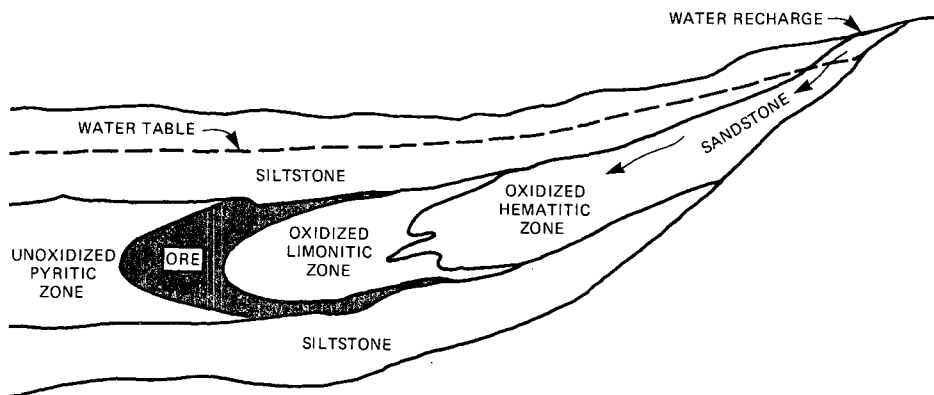


FIG. 1. Wyoming-type ore roll showing position of ore between oxidized and reduced sandstone facies.

be considered as a separate type. The rolls in question occur chiefly in fluvatile sandstones of the Morrison (Salt Wash member) and Chinle (Shinarump member) formations in the central Colorado Plateau and commonly border or otherwise accompany peneconcordant uranium deposits in these rocks. They are believed to have been formed within a locally intensive reducing environment produced by carbonaceous plant matter and related hydrogen sulfide (5). Except where oxidized by weathering, they have the appearance of having developed entirely within a pyritiferous facies of the sandstone by some process unrelated to redox recycling (7). Although genetically of interest, Plateau rolls are considered to be relatively unimportant economically in either the Morrison (10) or Chinle (2) sediments. They are not to be confused with the redistributed ore deposits in the Grants, New Mexico, area, which have a more obvious genetic relationship to Wyoming-type rolls.

Ordinarily likened to and included with Plateau-type rolls are the roll-ore occurrences found in the eolian sandstones of the Entrada and Navajo Formations of Jurassic age. These ores are restricted to the east side of the Colorado Plateau and are some distance removed from the more typical Plateau ores of the Urvan mineral belt. They are highly vanadiferous and low in uranium which is recovered only as a byproduct of vanadium production. Although having mineralogical similarities to the central Plateau ores, the Entrada-type deposits differ from those ores in some very important respects.

Most importantly, the deposits occur in rocks that are evidently totally free of fossil plant accumulations. This feature also distinguishes them from most of the ore deposits occurring in fluvatile rocks, e.g., in the Wyoming basins and at Grants, New Mexico. Unlike Wyoming rolls, these Plateau rolls show little or no apparent redox control which, as has been emphasized, is fundamental to Wyoming-roll formation. The chief clue to their origin is their location within an extensive zone of bleaching in rocks that are otherwise regionally pervasively red. The bleaching suggests to the writer that reductants, possibly petroleum and H_2S , have been introduced into the red beds and were in some way involved in ore formation. Because of these peculiar traits, the deposits should not be placed in the same classification with rolls of other types, particularly those associated with carbonaceous plant remains.

Some, if not all, roll deposits of the Texas Coastal Plain evidently belong in still another category. The rolls referred to appear to have been deposited by hydrogen-sulfide-bearing gases introduced into the host rock along fault zones from deeper oil- and gas-bearing horizons (11). The deposits are reportedly free of organic debris, although plant fragments occur elsewhere in the fluvial host rocks; and although near oxidation-reduction interfaces, the rolls appear now to bear no genetic relationship to them. It is assumed that uranium may have been released on oxidation from pre-existing up-dip deposits and subsequently redistributed within a down-dip reducing zone created by H_2S that had diffused from faults into the host sandstone. The position of the rolls down-dip from recognizable redox interfaces is attributed to the localizing effect of reducing-intensity gradients created presumably by H_2S concentration differences (11).

URANIUM-ORE-ROLL FORMATION

Several of the ore-roll types previously mentioned are associated with carbonaceous plant matter deposited within fluvial sandstones. These include the Wyoming-type rolls that are invariably associated with redox interfaces and the Plateau-type rolls formed within reducing zones in sandstone but reportedly without assistance from or relation to redox fronts. A third type of roll, also mentioned previously, is confined to eolian sandstones devoid of plant remains and is evidently not associated with a recognizable oxidation-reduction interface. A fourth type, identified here as the Texas-type, is apparently related genetically to hydrogen sulfide gas introduced along faults from gas reservoirs into stratigraphically higher sandstone units. Still another kind, found in the Grants District, New Mexico, is the result of redistribution of pre-existing tabular deposits where oxidation has penetrated in ground water and caused removal and reworking of the primary ore.

Fundamentally, rolls of the type dealt with in this paper represent rather narrow chemically active zones developed at interfaces between environments (both solution and solid) of different chemical character. These rolls constitute ore deposits only when sufficient economically usable mineral matter has accumulated. Although a complex of elements is involved, only one or two, such as uranium and vanadium, may concentrate in recoverable amounts.

The formation of Wyoming-type ore rolls and accompanying geochemical features have been described in earlier papers (12, 13) which cite references to other pertinent publications. The deposits form in sandstones containing vegetal matter decomposed in part by anaerobic bacteria. Migration of hydrogen sulfide generated by sulfate-reducing microbes acting on the organic matter extends the reducing environment from its previously fixed boundaries over a considerably larger area and thereby enhances chemical exposure and reducing activity. Oxides of iron commonly entrained in the sediments are readily transformed to pyrite which adds to the reducing capacity of the rocks.

The reduzate environment with its organic matter, pyrite, and H_2S is readily destroyed by oxidation during invasion of oxygenated ground waters. Oxidation culminates usually in formation of iron oxides such as goethite (limonite) and hematite (Fig. 1). The oxidation process occurring below the water table is responsible for the formation of elongate redox boundaries which are progressively displaced laterally away from the major paths of ground-water recharge. The invasive process replaces the reduzate facies

by an ever-enlarging tongue of epigenetically oxidized sandstone that may extend the entire distance from the redox interface to the outcrop.

The redox boundary, or roll front, marking the farthest point of oxidation advance and resulting pyrite destruction, is the locus of accumulation of elements that are susceptible to valence change with variation in natural oxidation-reduction potential. The ore deposits of economic interest are almost invariably located on the unoxidized side of the redox boundary and consist of minerals that are readily deposited and maintain stability under reducing conditions. The uranium roll-ore deposits are typically crescent-shaped in cross-section, and in plan form elongate, sinuous, frequently discontinuous, ribbon-like bodies which normally conform to the redox boundary. Where several sands overlie one another separated by impermeable mudstone, ore rolls may form separately in each sandstone bed. An excellent account of ore-roll anatomy and interrelationships has been presented elsewhere (14), and the interested reader should refer to this paper for details which will not be presented here.

Two hypotheses have been advanced to explain the deposition of uranium along the Wyoming-type roll fronts. One concept visualizes that bacteriogenic hydrogen sulfide remaining in the unoxidized carbon-trash-bearing sandstone caused precipitation of uranyl ions introduced anew in solution or through recycling from the oxidized parts of the sandstone. This hypothesis is based principally on sulfur-isotope studies (15) which suggest the involvement of bacteriogenic hydrogen sulfide in the formation of pyrite and associated uraninite within the redudate facies. The validity of this idea has, however, been questioned, firstly because H_2S is rarely encountered in newly opened mines and secondly because there is doubt that sulfate-reducing bacteria can utilize coalified wood as a substrate for generating H_2S . Ore deposits evidently young enough to have formed after coalification are thus difficult to explain by this mechanism, and there seems to be evidence in the disequilibrium conditions of many of the ores that they postdate coalification. The alternative concept (16) proposes that limited oxidation of diagenetically formed pyrite can cause formation of partially oxidized unstable sulfur-ion species which through disproportionation are capable of regenerating sulfide ions that bring about precipitation of the uranium and other metal oxides and sulfides and also re-form pyrite. From this standpoint, the presence of pyrite in sandstone becomes the critical factor in ore-roll formation. Were it not for the fact that organic matter is very often the only substrate from which the initial pyrite evolved, it would be immaterial for ore-roll formation whether carbonaceous material was present or not. Obviously, many geological situations can be envisioned in which the sulfur-ion disproportionation concept may provide opportunities for uranium-ore formation, including enlargement of the range of sedimentary environments capable of generating rolls and their accompanying ores. Sediments containing iron sulfides formed by petroleum and H_2S gas deposits should provide a suitable setting for ore-roll formation (as for example in Texas), and pyritiferous facies of marine and eolian sands through which H_2S has passed might also provide suitable conditions. Where oxidation has under proper circumstances been superimposed on pyritiferous facies of these rocks through ground-water circulation, exploration might be justified.

Features of oxidative alteration associated with formation of ore rolls and useful in guiding exploration for deposits of the Wyoming-type have been described in numerous papers, many of which have already been identified by the writer (13). Color changes accompanying oxidation of the ore-bearing sediments, their causes, usefulness in exploration, and application to recognition of potentially productive areas have been covered in particular (13, 17).

Although different in geometric aspects, the redistributed and stacked ores, otherwise known as post-fault ores, of the Grants District, New Mexico, are genetically similar to the ore rolls of the Wyoming uranium districts, including those in the Shirley Basin, Gas Hills area, and Powder River Basin. The Grants deposits, which are in the Morrison formation (Jurassic age), commonly form along the oxidized edges of tabular deposits; and although they usually do not assume the typical crescent-shaped form of the Wyoming deposits, are nevertheless associated with tongues of oxidative alteration which manifest themselves in a limonitic and hematitic facies abruptly terminating against pyritic carbonaceous ore-bearing facies of the reduzate zone. It is conceivable that the oxidation tongues extend from the ore zone all the way to the outcrop.

Both the Wyoming-type rolls and the redistributed ores at Grants, New Mexico, were presumably formed by similar geochemical processes involving chiefly oxidation of reduzate sandstone facies by oxygenated ground waters. Plateau-type rolls, on the other hand, have been distinguished from Wyoming-type rolls largely on the basis of the presence today of pyrite on both sides of the roll (7). Oxidation, which is normally well developed in the sandstone on one side of the Wyoming-type roll, is reportedly commonly absent adjacent to unweathered Plateau-type rolls. Consequently it has been assumed that the latter are not formed in the same manner or under the same circumstances as the Wyoming-type rolls. Because they are in many, if not all, cases completely surrounded by a reducing environment, the Plateau rolls appear to be features involving principally deposition rather than destructive and redepositional processes.

Roll ore bodies are less common than tabular and lenticular deposits on the Colorado Plateau (2, 18) and production from them is relatively small (10). They are nevertheless of interest because of the interpretations that have been suggested to account for them. Shawe and his co-workers (18, 19) have accounted for Plateau rolls by precipitation of minerals at an interface between solutions of different composition and density, possibly involving contact between static connate waters and ore-bearing solutions originating in and deriving their load of uranium from another formation. Their concept implies that the contacts between the warm pregnant solutions and the cooler connate waters became fixed adjacent to the mineralized solution pathways and that the metallic ions were removed and precipitated in the cooler surrounding water to form the rolls. Other studies (20), however, suggest that Plateau rolls may either be primary features or can be accounted for by partial redistribution of ore minerals by oxidation.

The viewpoint of the writer is that Plateau rolls are incidental to the formation of ore deposits whose existence is due primarily to development of localized accumulations in sandstones of carbon trash which generated considerable active reducing capacity through H_2S and pyrite formation. The reducing capacity of these trash pockets may have been diminished periodically by encroachment of oxygenated ground waters along paleostream channel courses, but was usually re-established as the rate of fresh-water recharge subsided permitting H_2S to once again diffuse outward from the organic accumulations to re-form pyrite and re-establish a peripheral reduzate facies. Under such circumstances loss of magnetite and ilmenite from the sediments, which Shawe et al. (19) attribute to the action of heated connate waters, could easily be brought about by the reducing action of H_2S and by the subsequent oxidation of pyrite to form acid solutions which readily destroy these oxides (17). Because of repeated exposure to acid attack and reduction during oxidation of pyrite and rediffusion of H_2S , it is difficult to see that much magnetite or ilmenite would remain in the sandstone surrounding such a reducing zone.

The presence of pyrite within the alteration tongue on the oxidized side of ore rolls warrants further discussion. It is not unusual for pyrite to be present on the oxidatively altered side of ore rolls, although its absence has perhaps been noted much more frequently. Pyrite has been reported within oxidatively altered ground adjacent to Wyoming-type ore rolls in the Shirley Basin (21), Gas Hills (4), and Powder River Basin (22); but it is usually limited to within a few feet or tens of feet of the redox contact. Within the oxidized zone, the grain surfaces of the pyrite may be pitted, as in one Powder River Basin deposit (22), and appear to be undergoing destruction. Here, and in the Gas Hills where the pyrite in the "oxidized" zone is euhedral (4), it may be the product of crystallization from sulfide ions that diffused from the roll-ore zone into the oxidized zone during periods of decelerated water flow. Such reintroduction of pyrite might take place during periods of extended climatic dryness reducing water recharge and flow rate or at times when the content of oxygen in the ground water was depleted by excessive concentrations of surface vegetation in the recharge areas. It is possible that much of the remnant pyrite is, by virtue of some peculiar physical or chemical attribute, less susceptible to decomposition and therefore able to withstand oxidation for a longer time.

The Texas-type roll described by Klohn and Pickens (11) is attributed to deposition of uranium by hydrogen-sulfide gas introduced into the ore-bearing sands along nearby faults. The existing uranium deposits are believed to have migrated from pre-existing rolls which form relict structures up-dip from the present ore. The relict deposits now lie within oxidized sandstone. The present roll does not lie adjacent to oxidized sand but is surrounded by an aureole of pyritic sandstone. The question here too arises whether renewed introduction of H_2S might not account for redeposition of pyrite in previously oxidized ground.

Differences in pyrite morphology would seem to suggest more than one period of sulfide formation in uranium-bearing sandstones. In the Texas deposits, aggregate crystals of pyrite predominate in the ore zone whereas a finely crystalline form persists in the reduced zone between the up-dip-pointing wings of the roll where oxidized ground is normally encountered.

King and Austin (4) have also described differences in texture and morphology of pyrite on opposite sides of the ore roll. Reintroduction of H_2S into the previously oxidized zone to account for this has been suggested in an earlier paper (12). The manner of pyrite formation and oxidation and its relationship to ore-roll formation has been subjected to intensive investigation (16, 23, 24, 25, 26) and possibly warrants further study.

DEPOSITS IN EOLIAN SANDSTONES

Although uranium deposits in eolian sandstones of the U. S. A. are commercially of minor importance, an understanding of how these deposits were formed and of the factors controlling their distribution may increase the possibility of finding additional and larger quantities of ore in these sediments.

The Entrada Formation (Jurassic age) is a highly sandy eolian red bed extending over a large area of the Colorado Plateau. Uranium deposits are found in this formation in three principal areas which include the Rifle Creek area in Garfield County, Colorado, the Placerville area in



FIG. 2. Relationships between Todilto Formation, and bleached-limonitic and red Entrada sandstone facies near Grants, New Mexico.

San Miguel County, Colorado, and the Grants-Laguna area in northwestern New Mexico. Perhaps the most significant factor bearing on uranium (and vanadium) deposition in these rocks is the confinement of ore only to bleached parts of the sandstone which normally is red in color throughout most of its areal extent.

In the Rifle area, bleaching (removal of red coloration) prevails throughout the entire thickness of Entrada Sandstone and extends through the underlying Navajo Sandstone (also typically a red eolian sand) into the upper few feet of the normally red Chinle Formation (Triassic). In the Placerville and Grants areas, bleaching is restricted in the Entrada to a zone up to several tens of feet thick at the top of the formation whereas the basal Entrada is typically dark red (Fig. 2).

From earlier accounts it is evident that the cause and significance of bleaching of the Entrada is not well understood. Bleaching has been attributed to weathering of the post-Entrada surface by Kelley et al. (27), whereas Rapaport et al. (28) suggested that the color of the Entrada is not an original feature and that the color differences in the formation are probably due to variations caused by groundwater percolating through the sediments. Neither of these explanations is adequate on geochemical grounds to account for the decoloration phenomenon.

The bleached zone is made up of white, drab (limonitic) and occasionally greenish layers as well as of irregularly shaped zones made up of these colors separated frequently along rather sharp boundaries. Limonite concretions, and pyrite concretions coated with limonite, have been found by the writer in the bleached facies, suggesting that H_2S may at one time have been present and that the bleached zone may represent a former reducing environment. The current yellow-brown limonitic appearance of the bleached zone is widespread and indicative of pervasive oxidation, perhaps of previous pyritic reduzate facies. Magnetite and ilmenite, present in the red facies, are reportedly (29) absent in the bleached zone. Although samples of rock collected by the writer from the bleached zone contained magnetic minerals, the latter seemed always to be more sparse in these samples than in those from nearby red Entrada.

According to driller's logs, bleaching has been observed in deep drill holes. Moench and Schlee (29) have noted the irregularity of the bleached/red color boundary and its obliqueness to bedding and concluded that formation of this boundary predates Jurassic folding, probably took place shortly after sedimentation, and may be related to deposition of the overlying Todilto Limestone. No explanation was, however, given for the bleaching, and the process was declared to be of unknown origin.

The obliqueness of the bleached/red color boundary to bedding (Fig. 3) indicates that it is of geochemical rather than sedimentological origin. The color relationships are in some respects similar to those observed on the Colorado Plateau in mudstones underlying organic trash pockets containing ore in the overlying Salt Wash (Morrison Formation) sands. The normally red color of the Salt Wash muds usually gives way upward to a green or grey color which thickens near and under the ore in the sand. The color transition which transgresses bedding in the mudstone is attributed to the reducing action of H_2S which penetrated downward from the trash pockets of the Salt Wash, causing reduction of Fe^{+3} to Fe^{+2} . The phenomenon has been recognized and used for some time as a guide to ore on the Plateau because of the strong correlation between thickness of ore and thickness of green mudstone directly beneath.

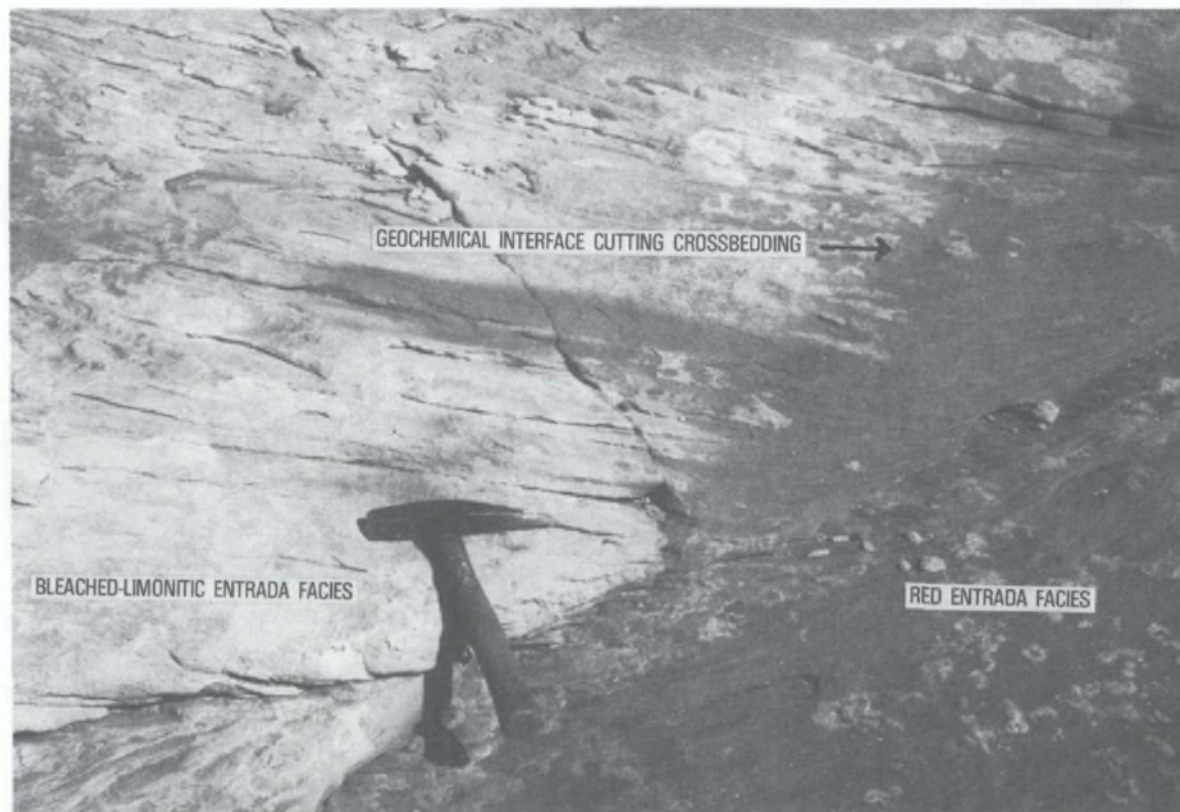


FIG. 3. Geochemical boundary cutting crossbedding and separating bleached from red Entrada sandstone facies.

Bleaching of the Entrada is in the writer's opinion related to the existence of the overlying Todilto Limestone; to be more exact, to the existence of the Todilto sea. The writer feels that the bleaching is directly attributable to reducing conditions prevailing along the bottom of the Todilto sea. The fetid nature of the limestone as well as detailed studies of limestone composition support this opinion. The studies of Anderson and Kirkland (30) indicate that the limestone must have formed in a body of water having a high organic content that undoubtedly contributed to reducing conditions persisting throughout most of Todilto time. Bacterial destruction of the organic matter, comprising phytoplankton and vascular plant fibers, would have produced large amounts of hydrogen sulfide in the bottom waters and sediments. The toxic conditions that prevailed account for the scarcity of benthonic organisms and the almost complete absence of fossils in the limestone.

It is possible to account for bleaching of the Entrada by diffusion of H_2S -bearing gases from Todilto sea water and bottom sediments into connate waters saturating the underlying Entrada sandstone. The diffusing H_2S would have caused reduction and decoloration of the upper red beds. The red/bleached color boundary evidently marks the lower limit of effective H_2S penetration (Fig. 4). With later compaction, H_2S and petroleum expelled from the Todilto into the underlying Entrada possibly augmented the bleaching and reduction.

Since reduction of red beds by H_2S can, and often does, lead to formation of pyrite, it may be assumed that the pyritic nodules found by the writer are a consequence of this event, and that the pyritic reducing environment has subsequently been oxidized with accompanying limonitic staining of sand grains. With a pyritic reducing environment having been established in the upper Entrada, one can readily visualize by reference to the Wyoming-ore-roll model (Fig. 1) what the effects of later penetration by oxygenated ground waters flowing from the basin rim might have been.

With few exceptions (29), there is little additional known pyrite in Entrada outcrops today in the San Juan Basin. All the surface exposures appear to be oxidized. However, oil has been found in the basin (31), and the Entrada may still contain an extensive reducing facies at depth. Consideration of the principles of roll-ore formation lend encouragement to the expectation in the basin of redox contacts along which uranium and vanadium could have accumulated in the basin. This opinion is reinforced by the knowledge that both metals occur in economic or near economic concentrations in the bleached facies of the formation at Rifle and at Placerville, and also by the existence of ore deposits in the Entrada in the Grants-Laguna area along the southern flank of the San Juan Basin (29). In the latter area, the ore deposits pass from the Todilto Limestone laterally into the Entrada. The Entrada ore at this locality consists of unoxidized, semi-tabular, roll-like deposits containing pitchblende, coffinite, and vanadium clays. Pyrite is distributed in and around the ore, sometimes encrusting pitchblende in concretionary masses, a relationship that is not incompatible with the concept of re-formation of pyrite through sulfur-ion disproportionation.

The Todilto sea is known to have extended northward to the Placerville area of Colorado where the fetid, bituminous, Todilto-equivalent Pony Express Limestone overlies bleached Entrada Sandstone in which numerous roll-like ore deposits are found (32). One can therefore consider the enormous region of the San Juan Basin between the southern exposures of ore near Laguna and the northern exposures at Placerville as a likely repository of a reducing Entrada facies which could have become mineralized

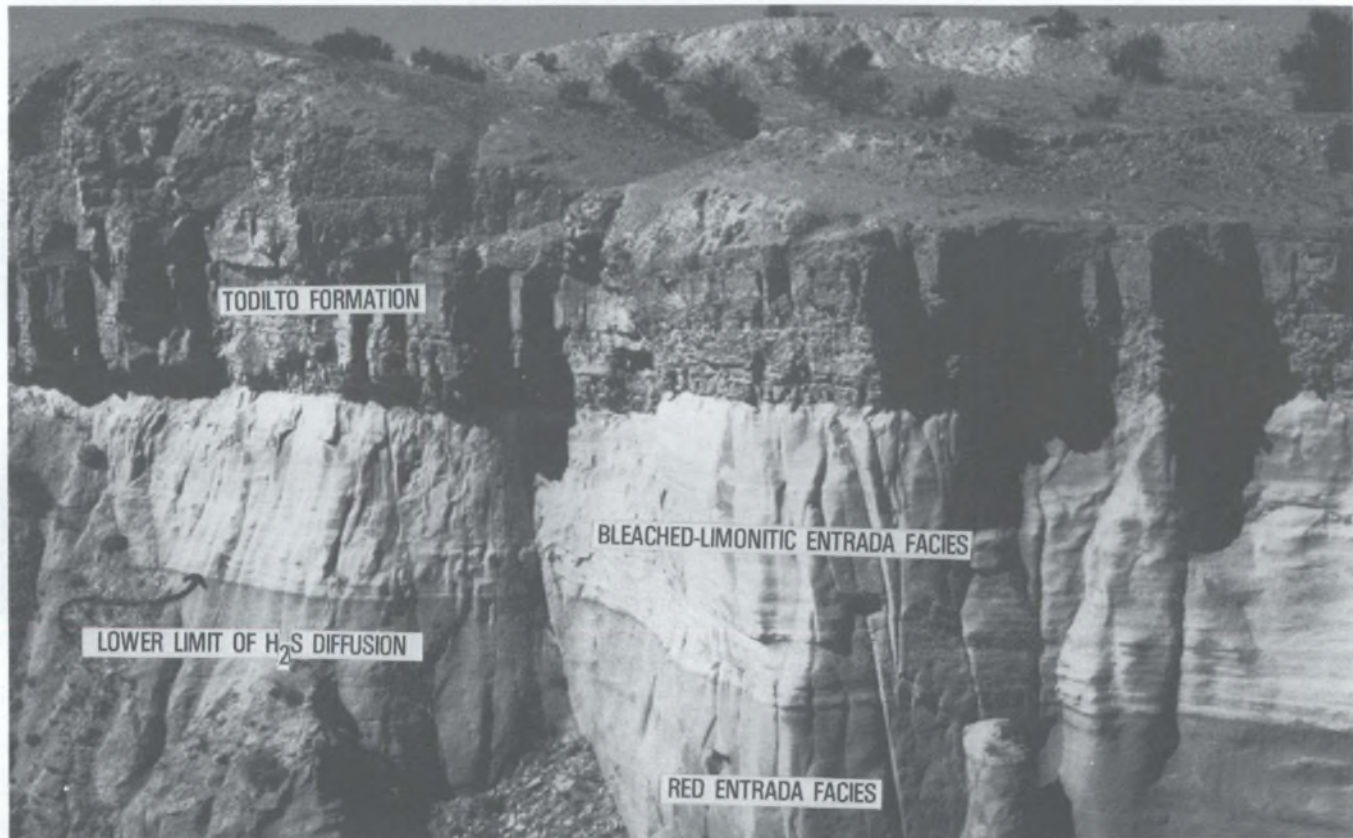


FIG. 4. Bleached/red boundary marking lower limit of H_2S diffusion in the Entrada sandstone near Grants, New Mexico. Todilto Formation consisting of limestone and overlying gypsum lies above the Entrada.

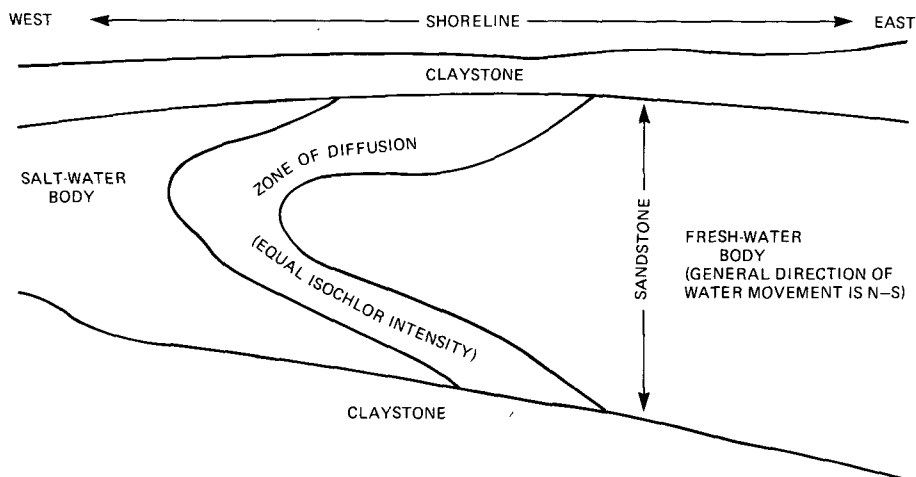


FIG. 5. Salt-water fresh-water diffusion relationship as a model for interaction between waters of different composition.

by roll-ore-forming reduction-oxidation processes. The existence today of oil and brackish water within the Entrada (31) reinforces this optimism because their presence indicates that reducing conditions still persist within the basin.

At Rifle the ore occurrence in the Entrada and Navajo formations is composed of three limbs which when projected form a large flattened S-shaped body (33) (see Fig. 6 for approximate shape of ore body). The individual limbs are in many places interrupted to form a series of smaller ore bodies which show internal roll-like features. Zoning of several metals, in particular vanadium, uranium, lead, and chromium, is a persistent characteristic (also noted at Placerville) of the limbs. Although Fischer (33) failed to recognize any localizing controls or evidence of genesis, he proposed that reaction at the interface of two solutions might account for element fractionation as well as formation of the ore layers.

The deposits at Rifle involve a far more extensive reducing zone than might reasonably be accounted for simply by diffusion of H_2S from a Morrison-age sea floor environment into subjacent water-saturated red beds. Conjecture by the writer regarding the conditions of ore formation at Rifle is based largely on the geologic information reported by Fischer (33). On the basis of his data, one can conclude that the extensive aureole of bleaching surrounding the ore is a product of reduction by H_2S probably associated with gas and oil that penetrated the pre-Morrison formations on a large scale. Both the formations (Entrada and underlying Navajo Sandstones) in which the ore is found are typical red-bed sandstones from which the normally persistent red coloration has been removed over a large area within which the Rifle ore occurs. Bleaching extends through and below the Jurassic (Navajo) beds, but terminates in the underlying Chinle (Triassic) shales or mudstones where it cuts across the less permeable Chinle bedding which evidently restricted fluid and gas migration. Joints and faults in the Chinle are bordered by a narrow band of bleaching, and the Chinle where bleached is pyritiferous. Asphaltite is present in fractures and fillings in the sandstones. Its presence suggests that the

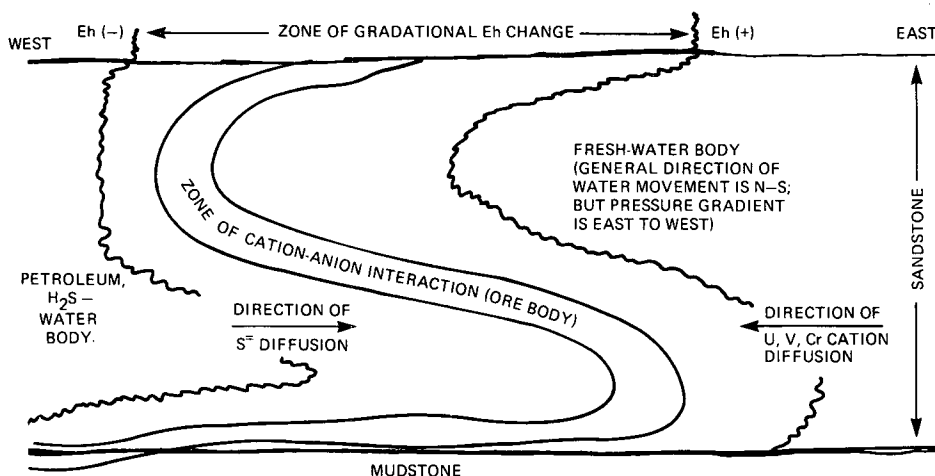


FIG. 6. Hypothetical conditions leading to formation of ore-roll deposit between fresh water and static oil or H_2S pool.

sands had contained oil at one time. Sulfides evidently postdate the brecciated and displaced vanadium-uranium ore, indicating a rather continuous penetration of the area by reducing solutions even after mineralization had taken place.

Comparison between the S-shaped roll at Rifle, Colorado, and the interface formed between fresh and salty ground water may be illuminating in regard to roll formation. The subsurface fresh-water salt-water relationships are illustrated in Figure 5, modified after Perlmutter, Geraghty, and Upson (34). Although their illustration was used to delineate the effects of salt-water displacement of fresh ground water, and no insoluble components or precipitating reactions are involved, the model is useful for depicting the simple diffusion relationships that may also operate to promote ore-roll formation. Using this model, the writer has illustrated diagrammatically in Figure 6 a possible circumstance under which the Rifle roll may have formed by incorporating components conducive to chemical formation of the mineralized zone.

Further insight into the mechanism of roll-ore formation at Rifle is provided in the experimental work of Temple and Le Roux (35). Whereas metallic ions adsorbed on clays and on ferric hydroxide were used as the cation source in their work, the writer believes that water solutions would probably be a more mobile and regenerative source of ore-forming cations under natural conditions. In the Temple-Le Roux study, both the soluble sulfide ions used as the precipitant and the "ore-forming" cations were free to diffuse toward an intervening inert medium (agar). The results showed that banded precipitates of various metals (Zn, Cu, Fe, and Pb were used in the experiments) were readily formed in the agar within a very short time (a few weeks). Moreover, a definite sequence of desorption of the cations from the clay and iron hydroxide was observed, indicating competitive displacement of cations from the contributing medium. It was concluded that the active sulfide (H_2S formed by sulfate reduction) zone would form a chemical trap in the natural environment where unconsolidated sediments, e.g., sandstone, could serve as the host for precipitation.

Oil-water and gas-water contacts are commonly located along the flanks of anticlinal and domal uplifts. The Rifle ore deposit lies on the flanks of the White River Plateau which contains many anticlinal flexures suitable for fluid entrapment. The flow of ground water along the flanks of this uplift, while still unbreached, could conceivably have created the static interface relationships favoring formation of the Rifle roll. The high-pressure gradients created by the inflowing fresh waters would allow wedges of water to develop and persist against the tightly confined gas, gaseous petroleum, or gaseous waters. No flushing or flooding of the reservoir would have occurred while the ore was being formed. Under these circumstances, chemical migration and interaction consistent with the Temple-Le Roux experiment could have created a static roll-like ore body.

TABULAR DEPOSITS IN FLUVIATILE SANDSTONES

As already mentioned, if the tabular or peneconcordant deposits in the U. S. A. are regarded in light of the nature and source of the reductant controlling ore deposition, it is possible to classify these deposits into two principal types, namely, those deposits associated with a reducing environment established by indigenous matter such as fossil plant remains (and the H_2S derived therefrom) and those deposits whose location in the host rock seems to be controlled by apparently introduced reductants such as H_2S or humate substances. Although both types of deposit are commercially important in the U. S. A., the latter, particularly those associated with material of humic origin, appear from production and resource data to be the more productive of the two. It is also noteworthy that whereas the deposits associated with plant remains are very widespread and numerous, those related to humate occurrences in sandstone appear to be very limited in geographic distribution, a fact which, as will be discussed shortly, may have considerable significance with respect to future prospects for discovery of new resources.

Many of the deposits associated with fossil plant material have a spotty distribution and occur in clusters separated usually by large areas of barren or lightly mineralized sandstone. There is such a close spatial relationship between ore and accumulations of organic matter that the presence of organic trash pockets has been used extensively as a guide to favorable ground (36).

The trash-pocket ores are abundant on the Colorado Plateau in sandstones deposited in a complex of fluvial channels interspersed with finer-grained flood-plain and overbank sediments. The channel sands occur either as aggradational accumulations distributed as blanket-like alluvial fans by streams that meandered freely over their floodplains or as degradational remnants and lag deposits in channels scoured into the underlying rocks (37). In both cases plant matter, rafted by streams and deposited in the shallow quiet-water areas of the meander channels, was buried in the sands and subjected to anaerobic conditions. Sulfate-reducing bacteria feeding on the organic debris were able to generate H_2S which diffused into the surrounding sands, reacted with detrital iron-bearing minerals to form pyrite, and created an active renewable reducing environment capable of precipitating metallic ions carried into the area by ground-water solutions.

Since it is possible to transport uranium in both oxygenated and de-oxygenated ground-water solutions, two concepts may be invoked to account for ore deposition. One provides for the concentration of uranium from

oxygenated waters which are likely to create redox fronts that reflect areas where oxygen has been removed from ground-water solution by interaction with the reductants in the sandstone. Such waters would have reacted with pyrite to produce rolls or roll-like accumulations of metallic minerals. The other alternative is that de-oxygenated ground waters carried uranium through the pyritiferous reduzate facies to areas within the channel sands where fossil plant material and H_2S were available in sufficient quantity to produce a substantial accumulation of reduced uranium. Existence of such reducing loci in basins beyond redox interfaces improves greatly the opportunities for ore discovery. Not only trash pockets but areas of possible H_2S introduction into sandstone from faults become likely exploration targets. Structures in which oil and gas have accumulated may also be of interest. Marine clastics (even Precambrian) containing organic matter may become loci of ore accumulation. For that matter, any deposit of organic matter or H_2S in permeable sediments constitutes a potential zone for uranium deposition, and either roll-like or peneconcordant accretions may be expected because of the variety of ways and circumstances under which the uranium-precipitating reaction can occur.

Peneconcordant uranium deposits associated with carbonaceous matter believed to be a water-soluble humate residue derived from decaying plant material are of special interest in the U. S. A., where they occur in the Grants area of New Mexico, because of the large quantities of uranium encountered.

The humate residue is widespread and appears to control uranium deposition in the major deposits of the area. Three sources for the carbonaceous material have been proposed (9). The preferred concept is that it was derived from vegetation decaying in a bog or swamp overlying outcrops of the subsequently mineralized sandstones into which it was carried by ground waters and deposited probably at the water table. Another view is that it was dissolved from plant matter syngenetically incorporated in the sandstone. The third hypothesis is that it was present in the same streams which deposited the sandstones and was therefore derived from plants undergoing decay at the time the sediments were being formed.

If the preferred hypothesis is correct, the likelihood of replication elsewhere of these source-to-host relationships is a matter of serious concern in evaluating the possibilities for finding additional uranium deposits of similar magnitude and importance. Although it would seem that the possibilities for uranium might increase for sandstones underlying paleocoastal areas where bogs, swamps, marshes, and the like are normally located, the geological requirements could be too limiting to have permitted formation of many other Ambrosia-Lake or Laguna-type districts elsewhere in the U. S. A. This is not a particularly comforting thought when one considers the fact that the equivalent of 16 districts of this type (in which humates exercise considerable control over uranium deposition) will have to be discovered to meet the projected uranium requirements of the U. S. A. alone, and that this particular district is by far the largest of those known in the U.S.A.

CHEMICAL REDUCTION AS A FACTOR IN ORE FORMATION IN OTHER SEDIMENTS

An overwhelming amount of evidence points to the involvement of chemical reduction as a prime factor in uranium deposition in sandstones. Only in rare instances is the evidence so sparse as to raise any question regarding the validity of this involvement. It is interesting to note

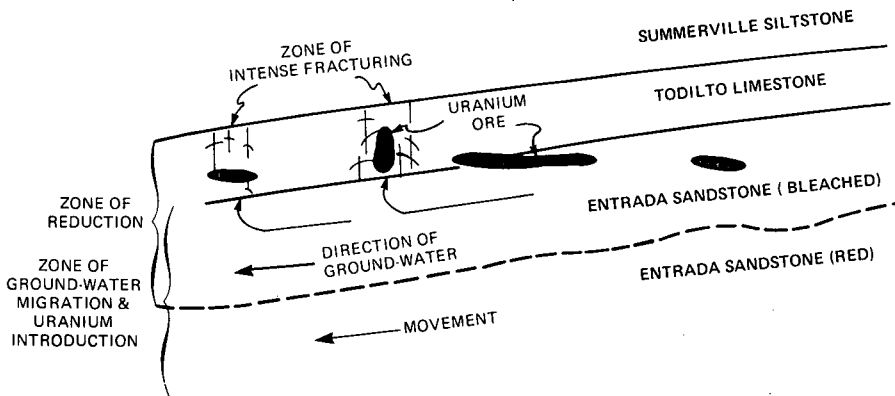


FIG. 7. Conditions of formation of uranium deposits in limestone above a sandstone paleoaquifer.

that fine-grained sediments with indigenous reducing capacity often reflect this capacity by decoloration of adjacent coarser-grained sediments (such as sandstones and conglomerates) from their normally red hues to a grey or white color, which may subsequently become drab because of limonite formation. This red to white transformation appears to be caused by H_2S which has migrated into the porous red clastics. We have noted also how coarse clastics charged with H_2S cause reduction of red underclays changing them to green or grey, e.g., in the Salt Wash member of the Morrison Formation on the Colorado Plateau.

In this section of the paper several examples will be given where reducing conditions appear to be involved in ore formation in fine-grained sediments. Although the circumstances cited relate in a few cases to the formation of deposits of metals other than uranium, the conditions represented conceivably provide opportunity for uranium deposition and should therefore be given consideration in uranium exploration planning.

Uranium ores are not commonly found associated with limestone in the U. S. A. Only two occurrences warrant mention. One is the deposit at Grants, New Mexico, where ore occurs in the Todilto Limestone of Jurassic age, and the other is in the Pryor Mountains along the Montana-Wyoming State line. The Pryor Mountain occurrence has been of little economic significance, and very little is known about the ore controls in this area. The Grants District, on the other hand, has been studied in detail and consequently a great deal has been revealed about the host rock and its relationship to ore.

The Todilto ore deposits are concentrated where the limestone has been deformed locally by intraformational folds and intensely fractured. Underlying the Todilto is a thick clean permeable eolian sandstone (Entrada Formation) consisting of an upper zone of bleached sandstone several tens of feet thick lying between the Todilto contact and the main body of red Entrada sand (Figs. 2, 4). It has been suggested on the basis of the presence of small amounts of fluorite that the Todilto uranium ores may have been deposited from solutions having a magmatic hydrothermal component. However, as the ore is not associated with faults, the only

access for mineralizing solutions is through the limestone or the underlying sandstone and probably involves movement of ground water. The Summerville Formation above the Todilto appears too impermeable to have been an aquifer.

The limestone is fetid and considered to be the source of oil now found in the underlying Entrada. Detailed examination (30) shows that the limestone is composed of repetitive laminae of quartz, calcium carbonate, and organic matter (sapropel), and that uranium has clearly replaced the organic laminae. The limestone has been a source of reductant, undoubtedly both oil and H_2S , and the underlying sandstone could easily have provided a means by which uraniferous solutions gained access to the mineralized fractures. The relationships are illustrated diagrammatically in Figure 7. The fracture zones undoubtedly served as collecting points for H_2S generated by bacterial decay of the organic matter in the limestone and also provided easy access for transfer of uranium from the underlying sandstone aquifer. Vertical and lateral diffusion of uranium may have accounted for the local accumulation of ore associated with the limestone fractures. Simultaneously, H_2S expelled into ground water in the Entrada produced small pockets of ore in the sandstone. Both limestone and sandstone ores probably formed shortly after Todilto sedimentation (29). In the writer's opinion, uranium deposition began with introduction of fresh ground waters into the Entrada.

The Kupferschiefer mineral deposits of central Europe provide another example of the involvement of reducing conditions in ore formation.

Although the prevailing genetic concepts largely indicate otherwise, the spatial relationship of the Permian marine Kupferschiefer shale of Europe to the adjacent, but discontinuous, Zechstein conglomerate may be more than coincidental in the formation of Kupferschiefer ore. Though dominantly red in color, the conglomerate is usually bleached for a short distance vertically where it underlies the shale. The bleached facies is commonly known as the Grauliegendes or Weissliegendes reflecting the reduction of hematite coloration to produce a grey or white conglomerate facies.

Interestingly, the Kupferschiefer-conglomerate relationship is in some respects not unlike the Todilto-Entrada relationship. Like the Todilto, the Kupferschiefer is bituminous, and ore (copper) extends locally from the shale into underlying Weissliegendes conglomerate. Both the Kupferschiefer Shale and Todilto Limestone were evidently formed in foul-bottom sea areas in which few marine shell fish and invertebrates were able to exist. Persistent stagnation was presumably maintained by restricted renewal of marine circulation, and in both cases H_2S diffusion probably accounted for bleaching of the underlying red-bed conglomerate.

According to several review papers on the subject (38) and (39), theories on the origin of the Kupferschiefer ores fall largely into two categories, syngenetic and epigenetic (hydrothermal). Although a considerable range of ideas and evidence has been generated in support of each hypothesis, little attention appears to have been given to the significance of bleaching in the underlying conglomerate or its relationship to the Kupferschiefer ore. With perhaps one or two exceptions, there is little note of the fact that these permeable conglomerates make ideal aquifers through which mineralizing solutions could have gained access to the shale and its fracture systems. The chief problems with this concept, where noted, are the introduction of ground-water solutions throughout the enormous areas involved in mineralization and the emplacement of the ore metals in the

impermeable shale following its consolidation. However, there is some opinion (40) that mineralization had its beginning in the biogenic formation of pyrite which was scattered over great distances in the shale, and that the pyritic iron was replaced by Cu, Pb, Zn, etc., either diagenetically or epigenetically to form sulfides of these ore metals. It seems inconceivable that uranium could be deposited in replacement of iron in this manner in such a sediment, since it forms no natural sulfides, but it could interact with the organic matter in the shale or, if transported in oxygenated solutions, could have locally been removed from solution by reducing ionic sulfur species formed on oxidation of pyrite. Alternatively, were H_2S still being produced in the host rock, the opportunity for uranium precipitation would increase considerably. In this connection, it should be pointed out that most of the tabular uranium ore deposits in the U. S. were most likely formed by diffusion or migration of uranyl ions in ground waters toward loci within sediments containing H_2S , fossil plant material, or humate matter which precipitated the uranium.

Some interesting observations on the continental alluvial (or deltaic) sandstone formations of the Middle and Upper Permian of Italy have been made by Mittempergher (41). Here the dominant uranium ore bodies are located in grey sandstone at or just below a boundary separating the grey facies from an overlying finer-grained red-colored facies. The uranium deposits are described as stratiform or lenticular and conformable with the layering. The uranium is associated with pyrite and with organic matter which sometimes consists of logs but is frequently finely comminuted and dispersed. The relationships appear not unlike many of those observed in the central Colorado Plateau. Metamorphosed equivalents of these Italian sedimentary deposits are also known (41).

Of greater genetic interest, however, from the standpoint of this paper are metamorphic occurrences in which the ore lies in lenticular bodies near the top of a green chloritic Permian schist facies (corresponding to an original argillite-graywacke sequence) close to the boundary of an overlying (presumably at one time permeable) Triassic quartzite facies. Uraninite is associated with pyrite in the ore. Mineralization in these occurrences has been attributed to the action of syngenetic sedimentary processes in littoral or lagoonal environments involving deposition within pelites and siltites containing abundant organic matter. In spite of the syngenetic interpretation given to these ores by Mittempergher (41), which may be correct, it is interesting to note that the uranium deposits occur largely close to boundaries where permeability and redox differences in the sediments could have played important roles in mineralization. In other words, fine-grained sediments containing an organic reduzate facies were obviously in contact with an overlying coarser sediment which could have functioned as a paleoaquifer from which uranium might have diffused into the underlying reduzate beds (Fig. 8). If the deposits were of syngenetic origin, it seems rather fortuitous that they should occur only near the schist-quartzite contact, as Mittempergher's illustration (41) shows.

Still another example, in this case not involving uranium, involves the deposition of copper in the sulfur-rich reducing environment of the Nonesuch Shale at White Pine, Ontonagon County, Michigan (42). The mineralization there has been ascribed to introduction of copper from underlying conglomerate (Copper Harbor Conglomerate) and replacement of indigenous pyrite by copper in the overlying organic shale. The mechanisms of solution transfer proposed are 1) infiltration of copper by solution flow from conglomerate to shale and 2) diffusion of copper through a stationary pore solution due to a chemical potential gradient. The source

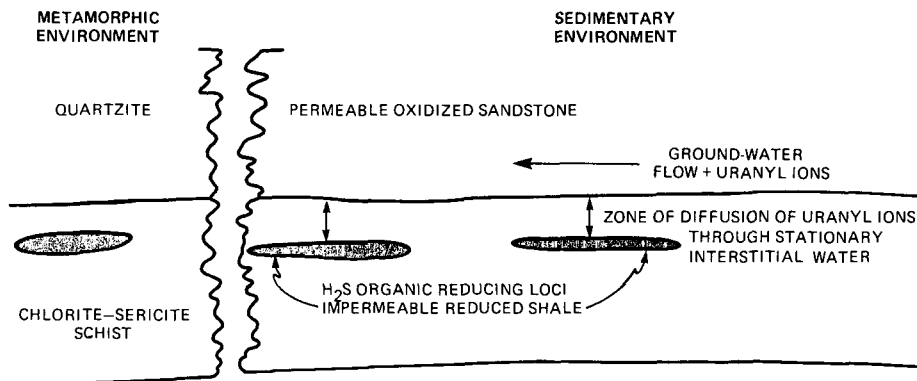


FIG. 8. Comparison between sedimentary and metamorphic environments suggesting paleoaquifer control of emplacement of uranium in underlying reductate sediments.

of the copper is thought to have been volcanic solutions, other magmatic hydrothermal solutions, or interstitial waters from adjoining rocks. It is unlikely that uranium would deposit under this circumstance since it does not replace other metals in sulfide structures. However, given the proper conditions for release of sulfide ions, as have been emphasized throughout this paper, uranium deposits might result in replacement of pyrite in such geologic environments.

The transport of uranium through an aquifer above or below a relatively impermeable sediment normally occurs by fluid flow of solutions through the pores of the aquifer. The solutions may in some cases be guided into the adjacent less-porous rock by fractures from which they may spread outward along bedding planes. To qualify as a potential host rock, the low-porosity sediment, e.g. limestone or shale, must contain an abundance of organic matter, H₂S, or iron sulfide. Sediments containing these substances were probably formed in low Eh waters and maintained this condition during their diagenetic and later evolution. Sandstones or conglomerates deposited and persisting under oxidizing rather than reducing conditions would permit migration of metal-bearing waters without interstitial deposition of the cations that precipitate readily on reduction, thereby assuring that these cations survive migration through the coarse clastic sediments.

Mineralization of the adjoining reducing shale or limestone would probably have to have been accomplished before the permeability of the aquifer rocks became prohibitively low as the result of compaction or cementation.

Although fine-grained sediments such as shale and limestone restrict the free movement of interstitial water, the rate of solute diffusion through them should not be affected unless the intergranular openings are narrower than a few ionic diameters. The entry of cations from the more permeable aquifer rocks is possible because of the continuity of solution between the more permeable and the less permeable rocks. Such continuity promotes the differential movement of solute from the solvent in one rock to the solvent in the other without any bodily movement of solution. Precipitation

would tend to generate a continuing movement of metal ions from the zone of higher solute concentration toward the zone from which the ions were being removed.

It is conceivable, as suggested by Brown (42) for the White Pine deposit, that interstitial solutions infiltrating pyritiferous shale could have caused release of sulfur resulting during replacement of pyrite by copper sulfides. Sulfide sulfur released in this manner could presumably permit reduction of uranyl ions and cause precipitation under these circumstances. However, it is more likely that where copper and uranium occur together in sediments, precipitation is directly attributable to an abundance of H_2S .

REFERENCES

1. Nininger, R. D., Uranium reserves and requirements, Nuclear Fuel Resources and Requirements, U. S. Atomic Energy Comm. WASH-1243, TID UC-51 (1973) 10-28.
2. Young, R. G., Distribution of uranium deposits in the White Canyon-Monument Valley district, Utah-Arizona, Econ. Geol. 59 (1964) 850-873.
3. Malan, R. C., The uranium mining industry and geology of the Monument Valley and White Canyon districts, Arizona and Utah, Ore Deposits of the United States, 1933-1967, Am. Inst. Min. Metall. and Petrol. Eng. (1968) 790-804.
4. King, J. W., Austin, R., Some characteristics of roll-type uranium deposits at Gas Hills, Wyoming, distr. by USAEC Grand Junction, Colo., (1965); abridged version in Min. Eng. 18 5 (1966) 73.
5. Fischer, R. P., Similarities, differences, and some genetic problems of the Wyoming and Colorado Plateau types of uranium deposits in sandstone, Econ. Geol. 65 (1970) 778-784.
6. Weeks, A. D., Coleman, R. G., Thompson, M. E., Summary of the ore mineralogy, Geochemistry and Mineralogy of The Colorado Plateau Uranium Ores, U. S. Geol. Survey Prof. Paper 320 (1959) 65-79.
7. Shawe, D. R., Granger, H. C., Uranium ore rolls - an analysis, Econ. Geol. 60 (1965) 240-250.
8. Granger, H. C., Santos, E. S., Dean, B. G., Moore, F. B., Sandstone-type uranium deposits at Ambrosia Lake, New Mexico - an interim report, Econ. Geol. 56 (1961) 1179-1210.
9. Granger, H. C., Localization and control of uranium deposits in the southern San Juan mineral belt, New Mexico - an hypothesis, U. S. Geol. Survey Prof. Paper 600 B (1968) 60-70.
10. Motica, J. E., Geology and uranium-vanadium deposits in the Uravan mineral belt, southwestern Colorado, Ore Deposits of the United States, 1933-1967, Am. Inst. Min., Metall., and Petrol. Eng. (1968) 805-813.
11. Kohn, M. L., Pickens, W. R., Geology of the Felder uranium deposit, Live Oak County, Texas, Soc. Min. Eng. A.I.M.E. preprint 70-1-38 (1970) 19 p.

12. Adler, H. H., Sharp, B. J., Uranium ore rolls - occurrence, genesis, and physical and chemical characteristics, Utah Geol. Soc. Guidebook No. 21 (1967) 53-77.
13. Adler, H. H., Interpretation of colour relations in sandstone as a guide to uranium exploration and ore genesis, Uranium Exploration Geology, Int'l. Atomic Energy Agency, Vienna (1970) 331-344.
14. Armstrong, F. C., Geologic factors controlling uranium resources in the Gas Hills district, Wyoming, 22nd Ann. Field Conf., Wyo. Geol. Assoc. Guidebook, Casper, Wyo. (1970) 31-44.
15. Jensen, M. L., Sulfur isotopes and the origin of sandstone-type uranium deposits, Econ. Geol. 53 (1958) 598.
16. Granger, H. C., Warren, C. G., Unstable sulfur compounds and the origin of roll-type uranium deposits, Econ. Geol. 64 (1969) 160.
17. Adler, H. H., Exploration for uranium in sandstones: geochemical, remanent magnetic, and sulfur-isotope applications, Uranium Exploration Methods, Int'l. Atomic Energy Agency, Vienna (1973) 155-166.
18. Shawe, D. R., Significance of roll ore bodies in genesis of uranium-vanadium deposits on the Colorado Plateau, U. S. Geol. Survey Prof. Paper 300 (1956) 239-241.
19. Shawe, D. R., Archbold, N. L., Simmons, G. C., Geology and uranium-vanadium deposits of the Slick Rock district, San Miguel and Dolores Counties, Colorado, Econ. Geol. 54 (1959) 395-415.
20. Elston, D. P., Botinelly, T., Geology and mineralogy of the J. J. Mine, Montrose County, Colorado, Geochemistry and Mineralogy of The Colorado Plateau Uranium Ores, U. S. Geol. Survey Prof. Paper 320 (1959) 203-211.
21. Melin, R. E., Description and origin of uranium deposits in Shirley Basin, Wyoming, Econ. Geol. 59 (1964) 835-849.
22. Rubin, B., Uranium roll front zonation in the southern Powder River Basin, Wyoming, Wyo. Geol. Assoc. Earth Sci. Bull. (Dec. 1970) 5-12.
23. Warren, C. G., A method for discriminating between biogenic and chemical origins of the ore-stage pyrite in a roll-type uranium deposit, Econ. Geol. 66 (1971) 919-928.
24. Warren, C. G., Sulfur isotopes as a clue to the genetic geochemistry of a roll-type uranium deposit, Econ. Geol. 67 (1972) 759-767.
25. Warren, C. G. and Granger, H. C., The concept of growth and maturity of ore-stage pyrite in roll-type uranium deposits, U. S. Geol. Survey Jour. Research 1 (1973) 151-155.
26. Granger, H. C., Warren, C. G., "Zoning in the altered tongue associated with roll-type uranium deposits", these Proceedings, Paper IAEA-SM-183/6.
27. Kelley, V. C., Kittel, D. F., Melancon, P. E., Uranium deposits of the Grants region, Ore Deposits of The United States, 1933-1967, Am. Inst. Min. Metall. and Petrol. Eng. (1968) 752-769.
28. Rapaport, I., Hadfield, J. P., Olson, R. H., Jurassic rocks of the Zuni uplift, New Mexico, U. S. Atomic Energy Comm. RMO-642 (1952) 49 p.

29. Moench, R. H., Schlee, J. S., Geology and uranium deposits of the Laguna district, New Mexico, U. S. Geol. Survey Prof. Paper 519 (1967) 117 p.
30. Anderson, R. Y., Kirkland, D. W., Origin, varves, and cycles of Jurassic Todilto Formation, New Mexico, Bull. Am. Assoc. Petrol. Geol. 44 (1960) 37-52.
31. Wengard, S. A., Origin and habitat of oil in the San Juan basin of New Mexico and Colorado, Habitat of Oil, L. G. Weeks, ed., Am. Assoc. Petrol. Geol. Tulsa, Okla. (1958) 366-394.
32. Fischer, R. P., Haff, J. C., Rominger, J. F., Vanadium deposits near Placerville, San Miguel County, Colorado, Colo. Sc. Soc. Proc. 15 (1947) 117-134.
33. Fischer, R. P., Vanadium-uranium deposits of the Rifle Creek area, Garfield County, Colorado, U. S. Geol. Survey Bull. 1101 (1960) 52 p.
34. Perlmutter, N. M., Geraghty, J. J., Upson, J. E., The relation between fresh and salty ground water in southern Nassau and southeastern Queens Counties, Long Island, New York, Econ. Geol. 54 (1959) 416-435.
35. Temple, K. L., Le Roux, N. W., Syngeneses of sulfide ores: desorption of adsorbed metal ions and their precipitation as sulfides, Econ. Geol. 59 (1964) 647-655.
36. Weir, D. B., Geologic guides to prospecting for carnotite deposits on Colorado Plateau, U. S. Geol. Survey Bull. 988-B (1952) 15-27.
37. Stokes, W. L., Stratigraphy of primary sedimentary features of uranium occurrences of southeastern Utah, Guidebook to The Geology of Utah, Utah Geol. Soc., Salt Lake City, Utah (1967) 32-52.
38. Dunham, K. C., Neptunist concepts in ore genesis, Econ. Geol. 59 (1964) 1-21.
39. Trask, P. D., The origin of the ore of the Mansfeld Kupferschiefer, Germany, a review of the current literature, Econ. Geol. 20 (1925) 746-761.
40. Love, L. G., Biogenic primary sulfide of the Permian Kupferschiefer and marl slate, Econ. Geol. 57 (1962) 350-366.
41. Mitterpergher, M., Characteristics of uranium ore genesis in the Permian and Lower Triassic of the Italian Alps, Uranium Exploration Geology, Int'l. Atomic Energy Agency, Vienna, (1970) 253-264.
42. Brown, A. C., Zoning in the White Pine copper deposit, Ontonagon County, Michigan, Econ. Geol. 66 (1971) 543-573.

DISCUSSION

R. BLASER: Why do uranium accumulations and Pb-Zn ore accumulations not occur at the same localities in carbonate rocks, and why should Pb-Zn deposits be abundant in such rocks whereas uranium deposits are rare? Conversely, why are uranium deposits common in sandstone whereas Pb-Zn deposits are rare? I suppose I could formulate these questions in

more general terms by asking what the specific geochemical conditions or processes are that favour uranium deposition and how they differ from the specific conditions that result in lead and zinc precipitation.

H. H. ADLER: That is a very broad question, and not an easy one to answer. There is of course a divergence of geochemical properties between the two groups of elements, and this undoubtedly plays a role in their different geochemical behaviour. For example, the mobilization and accumulation of uranium is largely a function of its sensitivity to redox conditions in the sandstone environment, whereas the deposition of lead and zinc does not appear to be governed by valence differences. Then there is the question of source. There are many theories of the origin of lead and zinc that point to a connection with carbonate environments under marine circumstances. Uranium, on the other hand, is associated predominantly with continental environments, and its access to carbonates would be primarily through permeable adjacent aquifer sands. Only bituminous limestones would act as a chemical trap under these conditions.

Mobility early in the history of sandstones and limestones may be a governing condition, with the result that elements associated with marine sources move and deposit entirely in marine circumstances. Uranium would then be excluded from deposition in carbonates inasmuch as its predominant source is considered to be continental tuffs and granites. The paleoaquifer concept of the introduction of lead and zinc into karsts in limestone might seem to offer some scope for uranium mobility, but examination of such lead and zinc deposits has revealed no uranium. We have wondered about this.

The deposits in the Central African Republic may provide a clue to the mechanisms of uranium accumulation in limestones, but as they are more or less unique it seems unlikely that they will suggest a general concept which could be followed in exploring limestones for uranium. On the other hand, the uranium-limestone association in the Grants district of New Mexico, in the United States of America, can be explained as the result of epigenetic introduction of uranium through an underlying sandstone aquifer. This suggests a very useful model, although the number of such occurrences may be small because of the numerous factors that have to combine to provide a favourable prospect for mineralization.

T. S. ARY: Did Fischer agree that the Rifle deposit resulted from events that could be explained in terms of the Temple-Le Roux theory? I believe that Rifle is a V_2O_5 deposit and not a uranium deposit.

H. H. ADLER: Fischer's publication is dated 1960 and the Temple-Le Roux experiments were described in 1964. I doubt, therefore, whether Fischer could have known anything about the Temple-Le Roux results, and his paper gives no indication that he was aware of the concept that can be derived from those results.

It is true that Rifle is a vanadium deposit containing a small uranium by-product, but the concept outlined in my paper would apply to uranium as well as vanadium inasmuch as the two elements are so commonly associated under similar conditions on the Colorado Plateau. In fact, the Entrada Formation to the south of Rifle, particularly at Grants, New Mexico, contains deposits which were mined for uranium but also contain vanadium. Thus the formation can host either uranium or vanadium deposits, with different ratios of the two elements.

DISTRIBUTION OF ELEMENTS IN SOME ROLL-TYPE URANIUM DEPOSITS

E. N. HARSHMAN,
US Geological Survey,
Denver, Colo.,
United States of America

Abstract

DISTRIBUTION OF ELEMENTS IN SOME ROLL-TYPE URANIUM DEPOSITS.

Roll-type uranium deposits are crescentic in cross-section and elongate along the margins of large tongues of altered sandstone. The alteration was produced by the ore-bearing solutions. Host rocks are arkosic or siliceous sandstone interbedded with siltstone. They are late Mesozoic to late Tertiary in age, and of continental or marginal marine origin.

Analyses of close-spaced samples — taken in suites across ore bodies in Karnes and Live Oak Counties, Texas; the Gas Hills and Shirley Basin areas of Wyoming; and the Black Hills area of South Dakota — show that elements were added to and removed from the host sandstone in bands or zones that show a remarkably consistent pattern. Similar genetic processes therefore appear to account for all deposits studied.

Twelve elements are discussed, five of them in detail for their particular genetic significance. Uranium, selenium, vanadium, molybdenum, and ferrous iron-bearing minerals have been deposited outwards from the edge of the altered tongue in exactly the same sequence as required by their redox potentials. Furthermore, these elements are ones that can or must be transported in neutral to somewhat alkaline solutions. Elements such as copper, that are mobile only in acid solutions, are not present in the ore in significant amounts.

Roll-type uranium deposits seem best explained by transport of elements in neutral-to-alkaline oxidizing solutions, and by deposition of component minerals by a drop in Eh that reached a minimum with deposition of jordanite at a considerable distance from the edge of the oxidized tongue.

INTRODUCTION

Roll-type uranium deposits lie at the edges of large tongues of altered (oxidized) sandstone that vary widely in size, but typically are a few tens of meters thick, a few kilometers wide, and 10 kilometers, more or less, long. The alteration was produced by the ore-bearing solutions. Host rocks are predominantly reduced arkosic or siliceous sandstones of continental or marginal marine origin, interbedded with siltstones and claystones. Host rocks range from late Mesozoic to late Tertiary in age. Figure 1 is a plan of two altered tongues in the Shirley Basin, Wyoming.

Ore bodies are in sharp contact with the altered tongues, extend a few centimeters to a few tens of meters outward from them, and grade gradually into unaltered (reduced) unmineralized sandstone. They are generally crescentic in cross-section and cut sharply across bedding of the host rock. Some ore, in small tabular bodies, is found on the top and bottom surfaces of the altered tongues. Figure 2 is a vertical section through an ore body and the edge of a tongue. The length of an ore body along a tongue's edge is many times its width normal to the edge. The edge of a tongue is everywhere mineralized but it is not everywhere ore-bearing. In the United States, deposits of this type are found in the Wyoming basins, the Black Hills of South Dakota, and in the south Texas Gulf Coastal Plain. Soviet geologic publications describe similar deposits in Mesozoic-Cenozoic sedimentary rocks of that country.

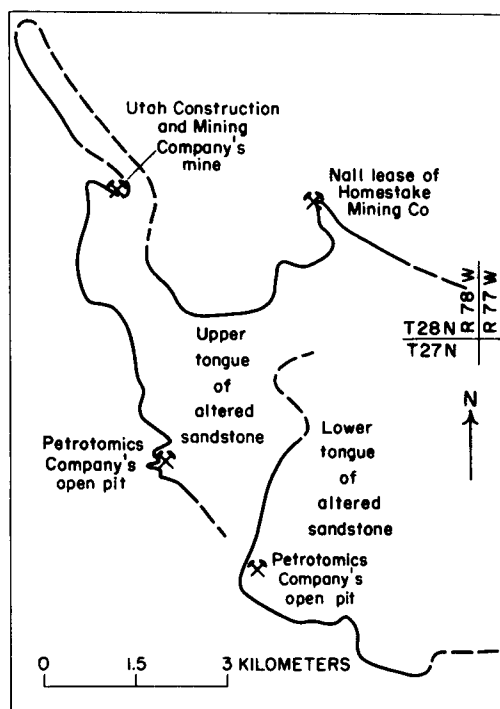


FIG. 1. Plan map showing outline of upper and lower altered sandstone tongues, Shirley Basin, Wyoming.

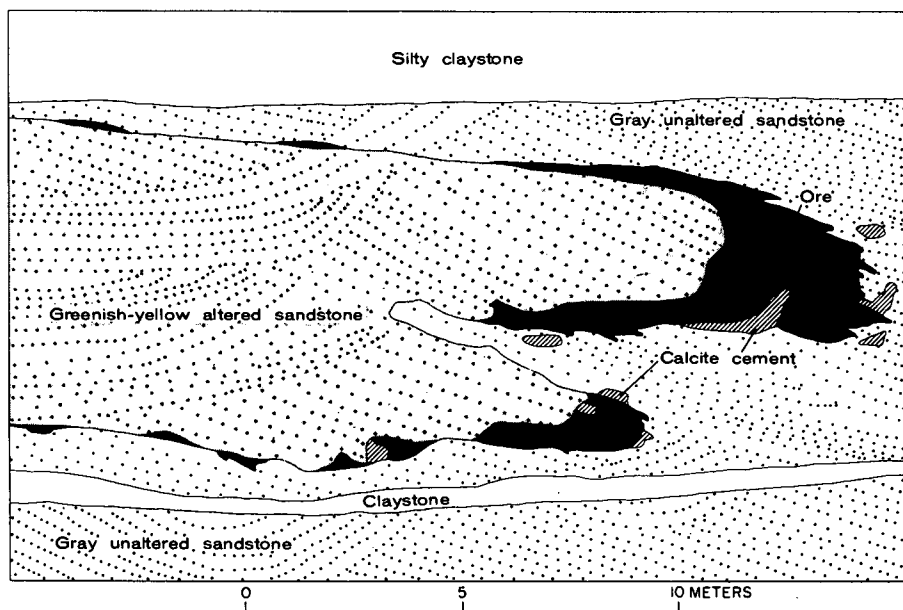


FIG. 2. Section normal to edge of altered sandstone tongue showing distribution of ore.

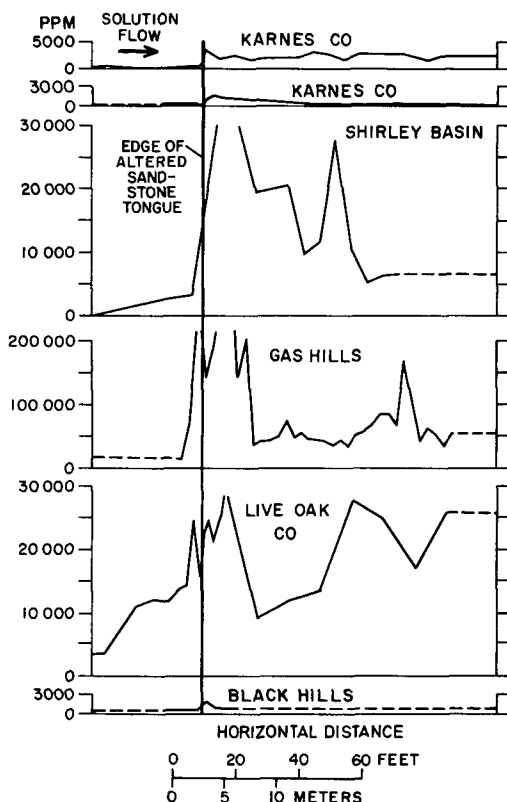


FIG. 3. Distribution of pyrite.

Much has been written on the geochemistry of uranium at low temperatures and pressures but an acceptable genetic theory for roll-type uranium deposits must explain the distribution of all elements in the ore bodies. This paper will present the analytical data from an extensive sampling program carried out in the principal roll-type uranium mining areas of the United States. These data can be used to guide speculation on the source or sources of the elements in the deposits, the character of the ore-bearing solutions, and the nature of the reductants responsible for ore deposition. The paper will conclude with some general geochemical implications of the data.

Roll-type uranium deposits in the Shirley Basin and Gas Hills areas of Wyoming, the Black Hills area of South Dakota, and the Karnes and Live Oak Counties areas of Texas were sampled on close-spaced centers (15 cm to 2 m); and the samples were analyzed chemically for uranium, ferric and ferrous iron, sulfate and sulfide sulfur, organic and mineral carbon, selenium, arsenic and phosphate and radiometrically for equivalent uranium. The amounts of 54 elements in the samples were determined spectrographically. The sample suites extended from altered (oxidized) sandstone, through ore, and into unaltered (reduced) sandstone.

The analytical data show that certain elements were added to parts of the host sandstone during the ore-forming process and that other elements were taken from it. Addition and depletion of elements took place in zones that show a consistent pattern in the deposits studied, a fact suggesting the geographically widely separated deposits were formed by similar geochemical processes. The distribution patterns of 12 elements and pyrite are shown graphically in illustrations that follow. The illustrations are sections across the edges of altered sandstone tongues and the ore associated with them. In each illustration the ore-bearing solution moved from left to right (shown by the heavy horizontal arrow) and the edge of the altered tongue is marked by a heavy vertical line. Dashed lines show analytical data projected into plane of section.

ANALYTICAL DATA

Pyrite (fig. 3) has been added to and is most abundant in reduced sandstone at the edges of the altered tongues; it gradually decreases in amount away from the edges and in most deposits pyrite extends farther into the unaltered reduced sandstone than does uranium. Pyrite has been destroyed in most of the altered tongues, although some tongues contain minor amounts of pyrite, particularly near their edges, where it is thought to be residual or post-ore.

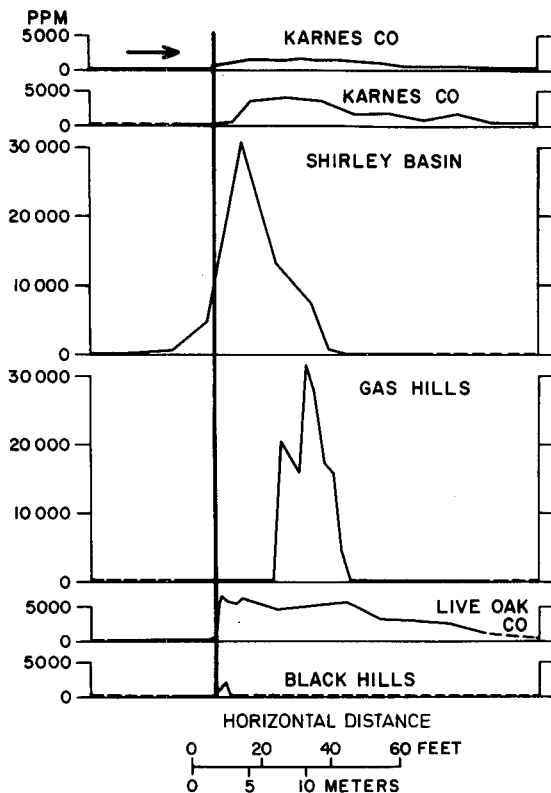


FIG. 4. Distribution of uranium.

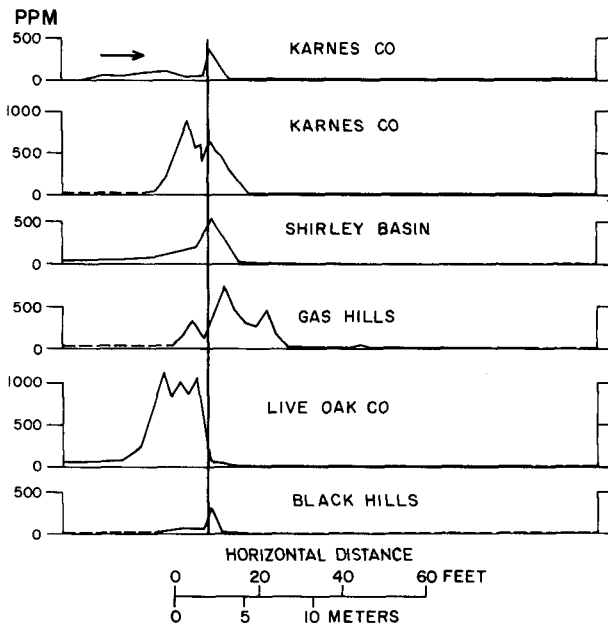


FIG. 5. Distribution of selenium.

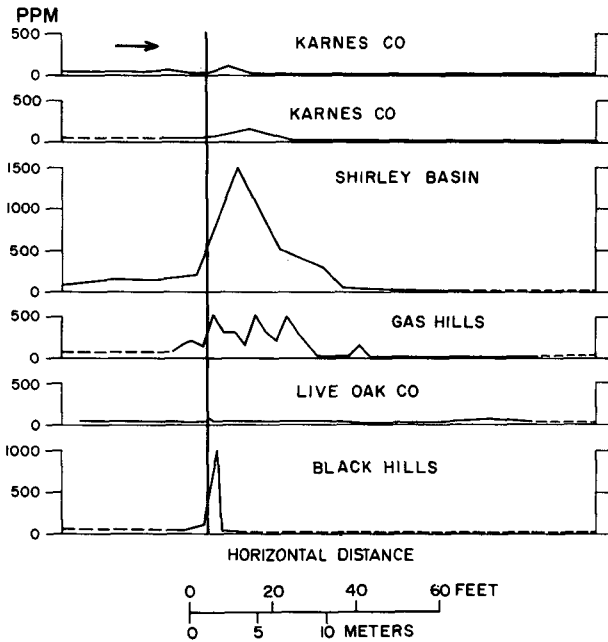


FIG. 6. Distribution of vanadium.

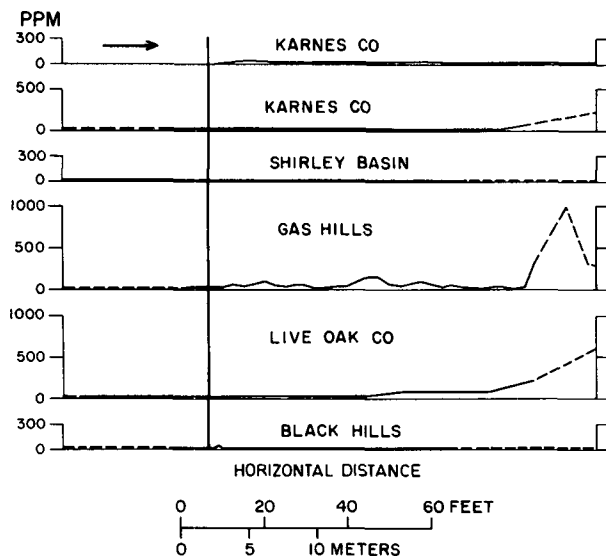


FIG. 7. Distribution of molybdenum.

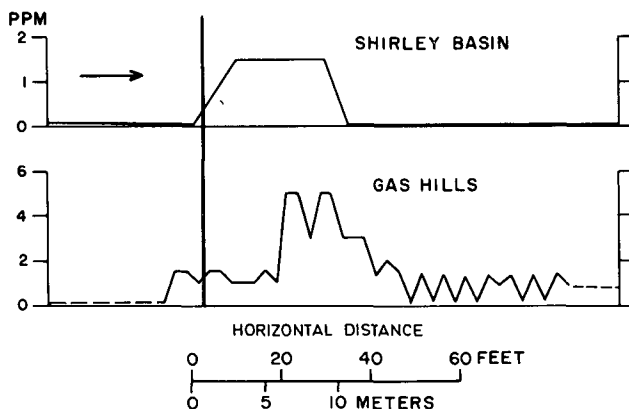


FIG. 8. Distribution of beryllium.

Uranium, shown in figure 4, has been added to reduced sandstone in zones close to or in contact with the edges of altered sandstone tongues. The redox interface for uranium coincides with that for iron in about half the deposits studied; in the other half the uranium redox interface is separated from the iron interface by as much as 5 meters of pyrite-bearing reduced sandstone. The uranium content of altered sandstone is slightly greater than that of unmineralized reduced sandstone.

Selenium (fig. 5) present in all ore bodies studied, has been deposited in narrow zones at the outer edges of the altered tongues, astride the edges, or in reduced sandstone close to the edges. The altered sandstone contains ferroselite (FeSe_2), the reduced sandstone contains native selenium. Analytical data indicate that most of the selenium in reduced sandstone is not contained in pyrite. Selenium in altered sandstone is at least one order of magnitude greater than selenium in unmineralized reduced sandstone.

Vanadium (fig. 6) content of roll-type uranium deposits is low but, in each area sampled, vanadium has been deposited in a narrow zone of reduced sandstone at or very close to the edge of the altered sandstone tongue. The zones of vanadium deposition are independent of the zones of deposition for uranium, selenium, or pyrite. The altered sandstone of most deposits contains more vanadium than does unmineralized reduced sandstone, probably admixed with iron oxides.

Molybdenum (fig. 7) has been deposited in reduced sandstone in three of the six deposits sampled. It is found as the mineral jordisite (MoS_2 ?) in a broad zone at, or several hundred meters beyond, the outer edges of the uranium and pyrite-bearing zones. The molybdenum content of altered sandstone is as low or slightly lower than that of unmineralized reduced sandstone.

Beryllium (fig. 8) has been deposited with uranium in two of the six deposits studied. Amounts in the ore are small (1.5-5 ppm) but there is an unmistakable correlation between uranium and beryllium. Beryllium contents in both altered and unmineralized reduced sandstone are below the limits of detectability (<1.5 ppm).

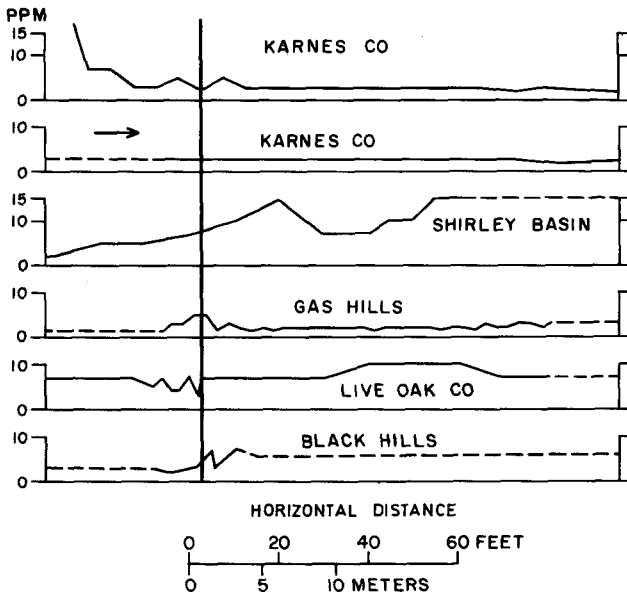


FIG. 9. Distribution of copper.

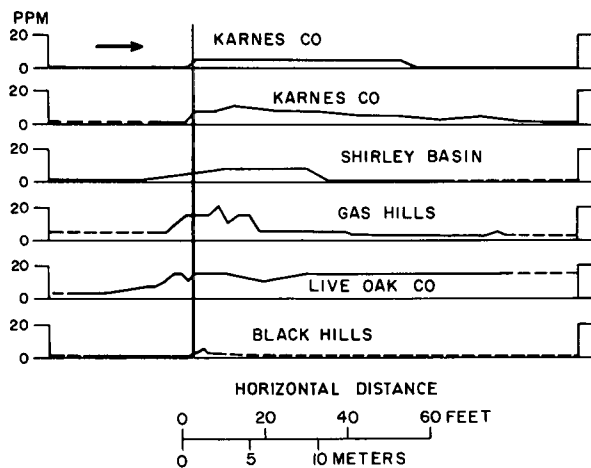


FIG. 10. Distribution of cobalt.

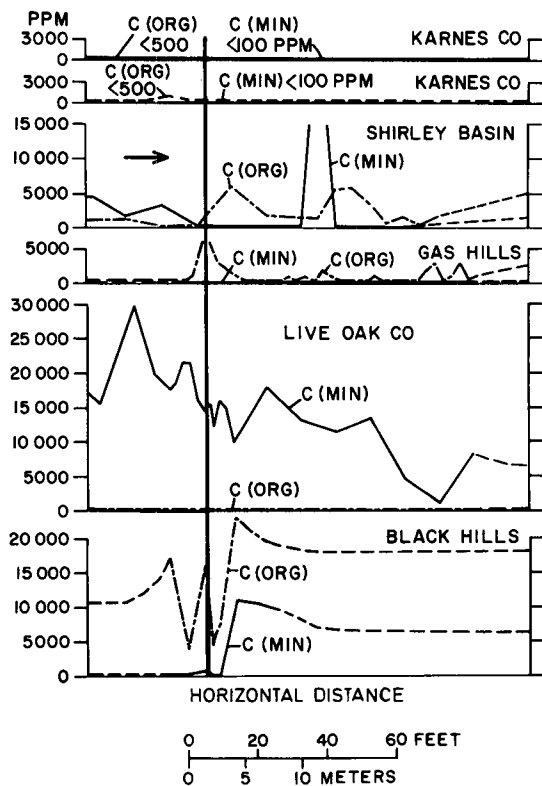


FIG. 11. Distribution of mineral (MIN) and organic (ORG) carbon.

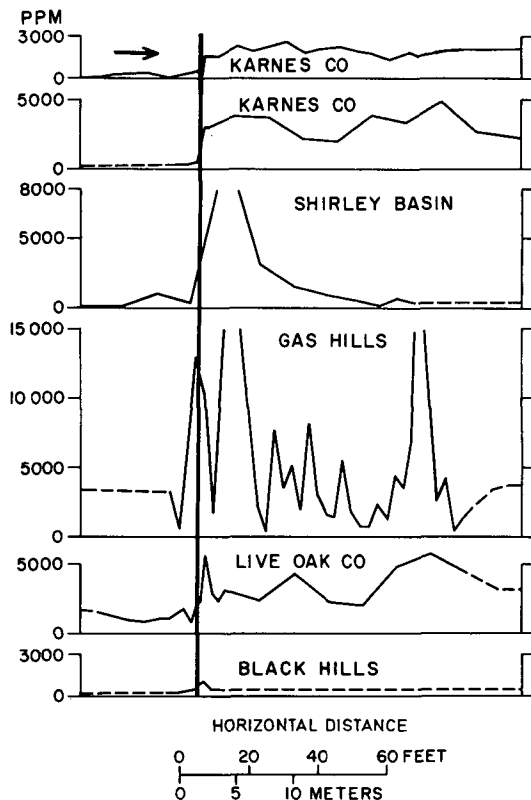


FIG. 12. Distribution of sulfate sulfur.

Copper (fig. 9) has not been deposited in the reduced sandstone sampled during this investigation and there is no indication that it was deposited in reduced sandstone not exposed for examination and sampling. In some deposits very minor amounts of copper may have been leached from the altered sandstone.

Cobalt (fig. 10) has been deposited in reduced sandstone near the edges of the altered tongues. In some deposits the zone of cobalt deposition coincides with the zone of high pyrite; in others cobalt was deposited with uranium in reduced sandstone. The position of cobalt deposition thus seems to be somewhat independent of the deposition of other elements or minerals.

Carbon (fig. 11), both mineral and organic, ranges greatly in amount and distribution. Organic carbon content is less than 0.05 percent in all facies of some deposits and is as high as 2 percent in the reduced facies of others. Similar ranges are shown for mineral carbon. Generally both organic and mineral carbon are higher in reduced sandstone than in altered sandstone. Figure 11 shows no direct correlation between the uranium and the organic carbon contents of the samples studied, a fact that places considerable doubt on the belief that organic carbon was directly involved in the formation of roll-type uranium deposits.

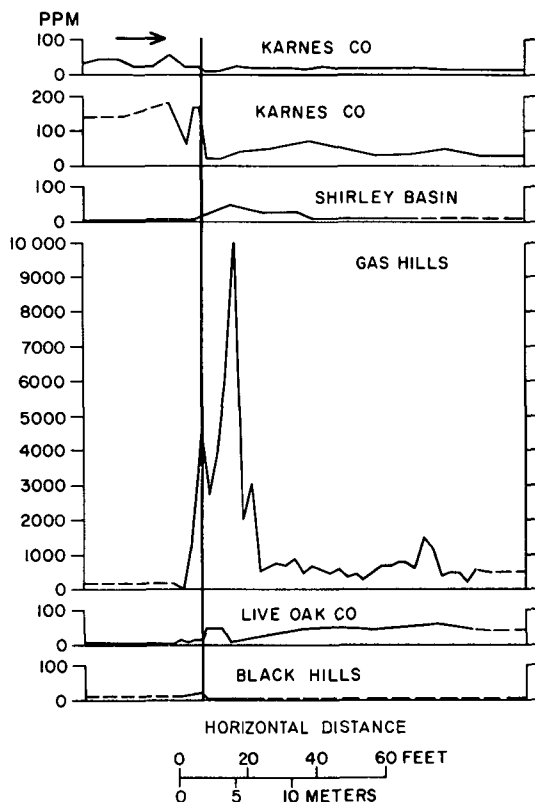


FIG. 13. Distribution of arsenic.

Sulfate Sulfur (fig. 12) appears to have been added to the reduced sandstone during ore deposition, probably as an iron sulfate mineral not yet identified. It has been leached from the altered sandstone where it originally was present as gypsum.

Arsenic (fig. 13) shows no consistent pattern of distribution. In one deposit it correlates well with pyrite and appears to be contained in that mineral; in two deposits it is found in reduced sandstone. Three deposits contain very little arsenic in reduced sandstone but have anomalously high amounts in altered sandstone where it may be associated with iron oxides.

Iron (fig. 14), principally as pyrite, has been added to reduced sandstone at and for some distance beyond the edges of the altered tongues. In some deposits the amounts added were small and there is little change in the total iron content of samples taken across the roll feature. In other deposits ore may contain 10 times as much iron as does reduced unmineralized sandstone. Ferric iron predominates in altered sandstone, and ferrous iron predominates in unaltered reduced sandstone.

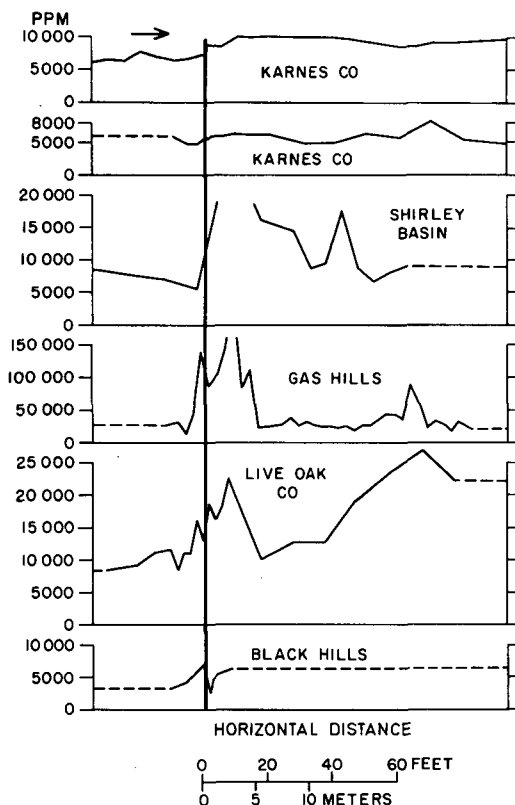


FIG. 14. Distribution of total iron.

SUMMARY AND CONCLUSIONS

If similar genetic processes account for the formation of the deposits described in this paper, as the similarity of their every aspect suggests, then the geochemistry of their formation can be surmised from the alteration produced by the ore-bearing solutions, from the elements carried by them, and from the sequence of deposition of the ore minerals.

Figure 15 is a graphic summary of the distribution of the principal elements in five of the deposits investigated. As in the preceding illustrations, the flow of the ore-bearing solution was from left to right (heavy arrow) and the edges of the altered (oxidized) tongues are marked by the heavy vertical line. There can be little doubt that the ore-bearing solutions were oxidizing, for in each altered tongue the passage of these solutions resulted in increasing the amount of ferric iron at the expense of ferrous iron, decreasing the amount of mineral and organic carbon, and converting pyrite to goethite and/or hematite. Significantly, the principal elements in the ore generally form soluble compounds that either must or can be readily transported in neutral to somewhat alkaline solutions; elements that require acid solutions for mobility, such as copper, are lacking in the ore. This evidence together with

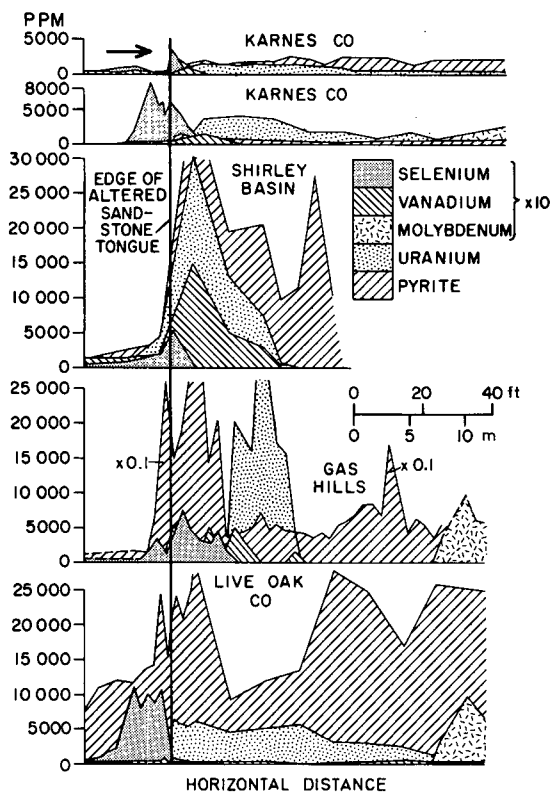


FIG. 15. Sequence of deposition of some elements in roll-type uranium deposits.

the fact that the host rocks and the tuffaceous material in them or associated with them are an alkaline environment, suggests that the ore-bearing solutions had a pH in the range of 7 to 8 or 8 1/2.

Deposition of the ore minerals required a reductant, the character of which is difficult to ascertain. Figure 16 is an Eh-pH diagram based on data by Garrels [1], Hostetler and Garrels [2], Lakin [3], Lisitsin [4], and Hansuld [5]. It shows the equilibrium conditions between soluble and insoluble forms of selenium, vanadium, uranium, and molybdenum and between pyrite and two ferric iron compounds, at conditions of temperature, pressure, content, and concentrations approximating those thought extant at the time of ore deposition. Also shown is the field of mobility for copper. The diagram undoubtedly is oversimplified, but assuming an ore-bearing solution of pH 7 1/2 and reducing the Eh from +300 mV to -300 mV (heavy arrows), the diagram indicates that the principal elements in the ore will be deposited in the same order shown on figure 15 outward from the edge of the oxidized tongue.

Granger and Warren [6] have shown that intermediate sulfur species produced by oxidation of pyrite at the edge of the oxidized tongue may act as reductants for some of the elements in the ore, a proposal that requires the most reducing

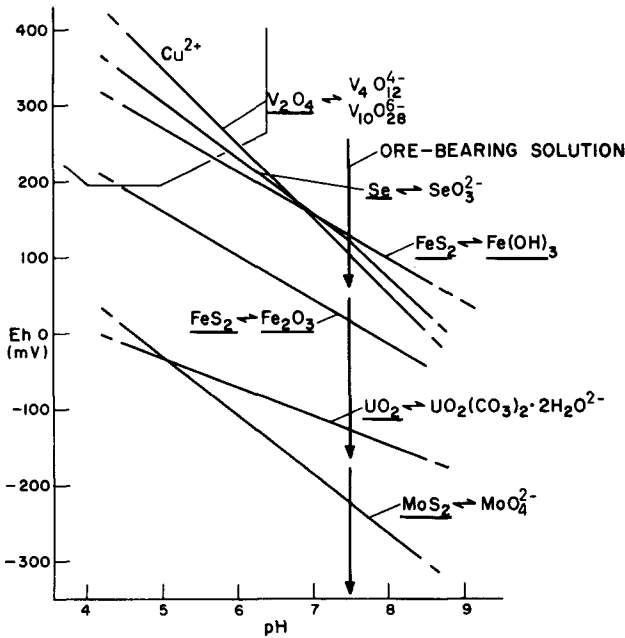


FIG. 16. Composite Eh-pH diagram for the principal elements in roll-type uranium deposits, and for copper. Solid phases are underlined.

conditions to be near the edge of the tongue. The results of this study suggest that, at least for those deposits containing jordisite (?) (MoS_2), an additional reductant may be required because the sequence of mineral deposition away from the tongue is in the order of decreasing Eh with jordisite, the most difficult (requiring the lowest Eh) mineral to precipitate, found at the greatest distance from the tongue's edge. The concept that sour gas, H_2S of biogenic origin, or H_2 has been an important factor in the genesis of some roll-type uranium deposits has merit, particularly in those areas such as Texas and the Gas Hills of Wyoming, where the uranium deposits are underlain by accumulations of oil and gas.

REFERENCES

- [1] GARRELS, R. M., Mineral Equilibria, New York, Harper and Brothers (1965) 174, 210.
- [2] HOSTETLER, P. B., GARRELS, R. M., Transportation and precipitation of uranium and vanadium at low temperatures, with special references to sandstone-type uranium deposits, *Econ. Geol.* 57 (1962) 147.
- [3] LAKIN, H. W., "Geochemistry of selenium in relation to agriculture", Selenium in Agriculture (ANDERSON, M. S. et al.), US Dept. of Agriculture Handbook 200 (1961) 11.
- [4] LISITSIN, A. K., Conditions of molybdenum and selenium deposition on exogenous epigenetic uranium deposits, *Lithology and Min. Resources* (translated from Russian) 5 (1969) 542.
- [5] HANSULD, J. A., Behavior of molybdenum in secondary dispersion media, *Mining Engineering* 18 12 (1966) 75.
- [6] GRANGER, H. C., WARREN, C. G., Unstable sulfur compounds and the origin of roll-type uranium deposits, *Econ. Geol.* 64 (1964) 160.

DISCUSSION

S. S. AUGUSTITHIS: The association of Mo, As, Se and Co found in the sandstone deposits you have described is in fact very similar to what we find in the hydrothermal vein uranium deposits. Have you found in the sandstone uranium deposits any elements of the pegmatitic uranium parageneses - thorium, zirconium or rare earths for example?

E. N. HARSHMAN: It is true that many of the elements found in the roll-type deposits are also found in the hydrothermal vein-type uranium deposits. Since we find these same elements in the tuffs and granites in or near the basins containing the ore deposits, I prefer to postulate that the deposits were formed from elements leached from tuffs and/or granites and transported by ground water. Possibly my prejudice shows here. Elements other than uranium associated with pegmatites, such as rare earths, are present in detectable amounts only in a few odd samples that I have collected.

H. D. FUCHS: Is the uranium content of the reduced sandstone higher than that of a normal sandstone, or is all the uranium introduced in solution from some outside source?

E. N. HARSHMAN: Data on the Wyoming roll-type deposits suggest that the altered sandstone contains slightly more uranium than unaltered, unmineralized sandstone. In the Shirley Basin we find about 6 ppm U in the altered tongue and 4 ppm in the barren grey sandstone. This suggests that the uranium was introduced from an outside source. Selenium exhibits an external origin much more clearly, because it is an order of magnitude more abundant in the altered sandstone than in the unaltered, unmineralized sandstone.

R. D. MORTON: Going back for a moment to Mr. Augustithis' remarks about the element association, I might say that one is immediately struck by the lack of nickel in these deposits. Does any nickel occur within the rolls? And could you give us any information about Ni:Co ratios in the tuffs which are thought possibly to have acted as "donors" within the sedimentary sequence?

E. N. HARSHMAN: Nickel occurs in very small amounts with cobalt in the ore and unaltered or reduced sandstone, but does not seem to show any significant concentration in the ore as does cobalt. If I remember correctly, the Ni:Co ratios in the tuff are 1:1 or less; but both elements are present in very small amounts.

S. ANZALONE: You have spoken for the most part about single roll fronts. Have you studied any regions where two roll fronts have collided and coalesced to form a mineral accumulation of a higher grade? How, for example, is the geochemistry affected at such points of collision? I should think they would be promising regions to explore if the uranium contained in the two single fronts does in fact combine to form a zone of high-grade mineralization in the merger region.

E. N. HARSHMAN: I have not seen nor have I read about the coalescing of two roll fronts. If such a merger did occur, it should, as you say, be a good spot to look for high-grade ore. I have noted that the highest grade of ore in the Shirley Basin of Wyoming occurs at changes in strike of the roll front, and I feel that such irregularities in trend are excellent exploration targets.

R. H. DE VOTO: As we continue to explore the sedimentary basins and our need for more sophisticated exploration techniques increases, it will be important to follow these trace element concentrations farther from the uranium ore deposits. Have you sampled the host sandstone at great distances from the ore, i.e. miles away? If so, have you found selenium enrichment in the altered tongue at great distances from the ore?

E. N. HARSHMAN: Unfortunately, I have not been able to get good samples at great distances from ore. I am limited to sampling mine openings, which of course are in or near ore. I do have samples of altered sandstone from as much as 1000 or 1500 feet behind the roll front, and have definitely found selenium enrichment there, but I cannot say how much enrichment may occur 5000 feet behind the front.

S. H. U. BOWIE: In what form does the beryllium occur? The distribution of elements shown in Fig. 15 looks like what one might expect to occur in partition chromatography with a sandstone medium. Would you care to comment on this possibility?

E. N. HARSHMAN: Beryllium occurs in such small amounts - from 1.5 to 5 ppm - that it has been impossible to determine what beryllium mineral is present in the ore. I agree with your observation that the distribution of elements in the roll-type uranium deposits is suggestive of chromatographic separation, but I prefer to conclude that the separation results from a decrease in pH.

ZONING IN THE ALTERED TONGUE ASSOCIATED WITH ROLL-TYPE URANIUM DEPOSITS*

H. C. GRANGER, C. G. WARREN

US Geological Survey, Denver, Colo.

and

Colorado State University, Fort Collins, Colo.,

United States of America

Abstract

ZONING IN THE ALTERED TONGUE ASSOCIATED WITH ROLL-TYPE URANIUM DEPOSITS.

The altered tongues associated with roll-type uranium deposits commonly include a border zone that separates the hematitic core of the tongue from enclosing reduced pyritic rocks. This border zone — herein called the alteration envelope — can have characteristics that range from limonitic orange to bleached in appearance. The authors speculate that a metastable mineral assemblage developed in this zone during genesis of the roll deposits.

A tentative model of roll formation is proposed, in which oxygenated ground waters percolating through the hematitic core zone react abruptly with authigenic siderite and elemental sulphur in the alteration envelope. This results in the creation of soluble ferric thiosulphate complex ions, $\text{Fe}(\text{S}_2\text{O}_3)^+$, which can flow past the siderite and sulphur without significant change. When the ferric thiosulphate ions contact pyrite, however, they react to release ferrous iron, elemental sulphur, and thiosulphate. Some of the ferrous iron precipitates as siderite and the remainder is transported ahead in solution with the thiosulphate to be reprecipitated as iron sulphides.

Upon termination of roll formation, the zone containing siderite and elemental sulphur can be leached or can alter slowly to limonite or pyrite. The various characteristics of the alteration envelopes are therefore believed to be attributable to mild post-ore processes.

INTRODUCTION

Roll-type deposits now occupy a fairly clear-cut classification in the geologic literature; they are characterized by their spatial and genetic relation to an irregular tongue-shaped zone of altered (commonly called oxidized) host rock whose borders ordinarily contrast sharply with the enclosing unaltered rock. Unaltered host rocks are typically light-gray to pale-drab-brown sandstones that contain a few tenths of a percent disseminated pyrite where not affected by ore-stage processes. Altered rock, on the other hand, contains little or no pyrite and can be white, grayish green, yellowish green, buff to orange, or red. The contact between altered tongue and unaltered rock forms a distinctly visible surface commonly referred to as the redox interface (fig. 1). The part of the redox interface that curves across the host strata and forms the distal edge of the tongue is called the roll front. Although a relatively thin layer of ore or mineralized rock—called limb ore—commonly borders the upper and lower surfaces of the altered tongue, most economic ore deposits are localized in the unoxidized rock adjacent to the roll front.

Most altered tongues associated with uranium deposits in New Mexico, Wyoming, and Texas (fig. 2) seem to be divisible into two distinct zones on the basis of differences both in color and mineral content. Rock composing

* Publication authorized by the Director, US Geological Survey.

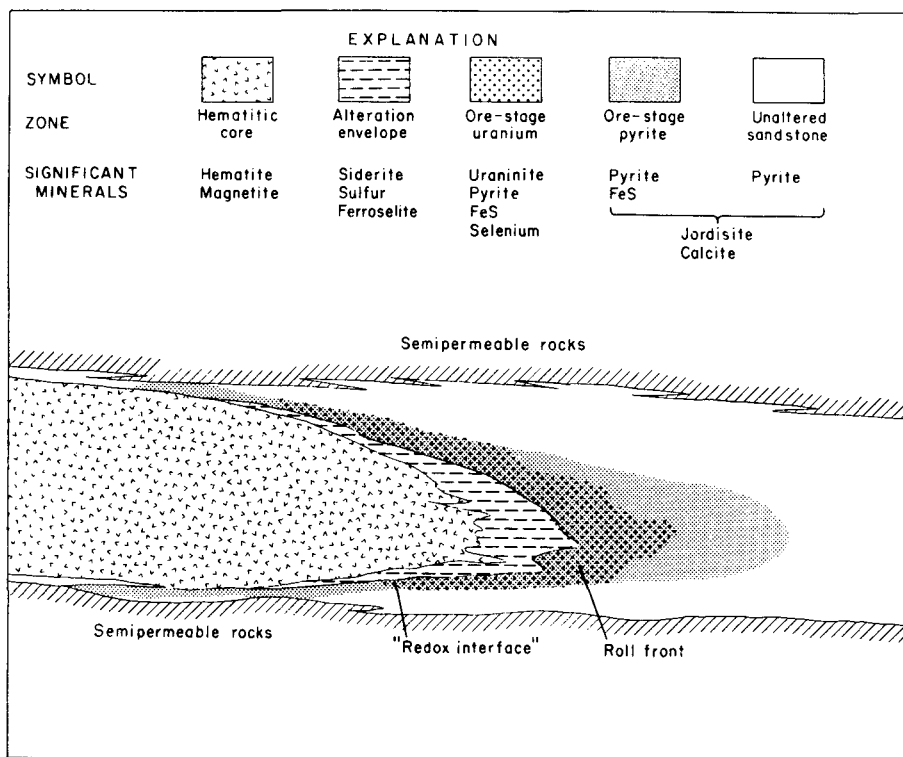


FIG. 1. Idealized cross-section showing minerals involved in genesis of roll-type uranium deposits.

the core of an altered tongue can commonly be distinguished from bordering altered rock of the tongue, which we will refer to as the alteration envelope. The alteration envelope, in turn, is bordered by the so-called redox interface that seemingly marks an abrupt change from altered rock to reduced pyrite- and uranium-bearing rock. These zones have previously been recognized and described, but, in our opinion, the origins have not been adequately explained. Any view that the altered tongues are fairly uniform bodies, in terms of alteration geochemistry, is much too simple. Most of the tongues are evidently zoned bodies, with at least two distinguishable subdivisions that may contain subtle, but extremely important clues to understanding the geochemical processes involved in the genesis of roll-type ore bodies.

Rock in the core zone (fig. 1) of most altered tongues is oxidized and characterized by brownish-red to pink tints that reflect the content of finely divided hematite and of hematite-stained clays. In some instances, at least, this zone also contains authigenic subhedral magnetite grains, partly altered to hematite.

The alteration envelope can be as much as a few hundred meters thick just back of the roll front. Adjacent to the redox interface along the upper and lower limbs it is markedly thinner and may be missing. Even adjacent to the



FIG. 2. Map of index to localities.

roll front it can be extremely narrow. Rock in this envelope is characterized variously by almost total bleaching, by bleaching coupled with sparse, disseminated, fresh pyrite crystals, or by a buff to pale-orange zone that contains goethite stain and, locally, a few goethite pseudomorphs derived from pyrite. Much of the color can result from goethite-stained clay.

Unoxidized, apparently pristine host rock outside the tongue and beyond the ore zone invariably contains pyrite, and may or may not contain some detrital magnetite and hematite grains in the heavy mineral fraction. The clays are commonly nearly white to very pale gray or pale olive.

GEOLOGIC OBSERVATIONS AND PREVIOUS WORK

Evidence for a bipartite division of the oxidized zones or altered tongues is given below. It should be acknowledged that the visible characteristics of these zones are not identical from district to district. A similarity in their genesis, however, is an assumed premise incorporated in this paper; an attempt to relate the deposits genetically will be emphasized, rather than any attempt to prove them fundamentally different.

Ambrosia Lake district, New Mexico

Most ore in the Ambrosia Lake district is in the form of strata-bound, peneconcordant, layered, humic impregnations that contain coextensive accumulations of uranium [1]. In parts of the district, however, one or more altered tongues have encroached on this earlier ore and have produced redistributed ore bodies having characteristics very similar to classical roll-type deposits elsewhere.

Within the Ambrosia Lake district the altered hematitic core ranges from pale to intense red and is bordered by an envelope of buff to pale-orange limonitic rock as much as 100 meters thick near the roll front. This envelope may locally be missing, and so the red hematitic rock directly contacts reduced pyritic rock and redistributed ore. In some places the limonitic envelope is narrow enough that the whole sequence can be shown in a single thin-section slide. Within a few millimeters of the contact with reduced rock, there commonly are goethite pseudomorphs derived from pyrite, but these do not seem to persist far into the alteration envelope. Ferroselite grains are found as much as a few centimeters from the redox interface into the alteration envelope but are not known to exist in the hematitic core zone. (Much of the ferroselite is not confined to the goethite blebs as was implied in an earlier paper [2].)

Gould and others [3] briefly described the sharp transitions from unoxidized gray ore-bearing sandstone, to buff, and, thence, to red barren sandstone. In their figure 3, they provided a convincing illustration of the sequence at one place in the Section 23 mine. MacRae [4] has described a similar sequence in the nearby Smith Lake district where the Black Jack No. 1 ore body is largely confined to bleached and gray sandstone surrounded by an orange, yellow, and brown halo that grades into enclosing brick-red rocks.

Powder River Basin, Wyoming

The characteristics of altered rock spatially related to ore zones in the Powder River Basin seem to vary from place to place. Sharp and others [5] generally recognized only two color phases in the near-surface host rocks of the northern part of the basin: (1) drab sandstones which contain the ore, and (2) hematitic red sandstones adjacent to the ore. Some of their descriptions, however, suggest the presence of an alteration envelope. For example, on p. 566, they report that uranium minerals occur where pod-like tongues of red sandstone extend into buff sandstone or where a wedge of buff sandstone underlies a red-colored zone.

Langen and Kidwell [6], working in the southern part of the basin, noted that goethite characterizes the rock in contact with the uranium deposits, but that hematite occurs in the altered rocks farther from ore.

Davis [7, p. 135 and Plate 4] summarized his observations of the altered rocks in the basin: "The most widespread and without doubt the most distinguishable alteration is the pinkish-red hematite stain. This red zone exists for great distances back from the mineralized zone. A narrow zone of limonite staining and occasionally an interval of almost white bleached sandstone occur adjacent to the mineralization."

Granger [2] described ferroselite from bleached altered rock adjacent to the roll front in the Mrak No. 2 mine and suggested that the bleached rock is either the unweathered equivalent to the widespread red hematitic sandstone or a bleached zone between the red and drab-colored sandstones.

Although the data are not consistent, and there seems to be evidence that the limonitic and bleached envelope is more extensively developed in the southern than in the northern parts of the basin, there can be no doubt that an alteration envelope with variable characteristics borders at least some parts of the hematitic cores of the altered tongue(s) in the Powder River Basin.

Gas Hills district, Wyoming

Nearly all the altered rock in the Gas Hills district is reportedly very pale gray to nearly white. It was described as bleached dead-gray by King and Austin [8]. The samples of these authors are largely from altered zones within about 15 m of the ore zone, but King and Austin also observed rocks much farther from ore. They illustrated a transition zone separating the altered tongue from ore, but the description of this zone is brief and lacks detail. One of the distinctive differences between altered and unaltered rock that they described is in the shapes and sizes of pyrite grains that they found in each of the zones. Although sparse, pyrite found in the altered tongue is very fine grained, shiny, and euhedral (see also [9]). No limonite specks were noted in the altered zone. In contrast, the ore zone (mineralized ground) contains even finer-grained pyrite, but in clusters or aggregates that are less shiny than in altered rock, and which are associated with scattered limonite specks. These clusters of pyrite are tarnished and alter quickly after exposure to air. King and Austin also suggested that some amorphous iron sulfide may be present.

Unoxidized rock away from ore contains untarnished coarser-grained crystals of pyrite associated with some magnetite. Magnetite has been destroyed in the altered zone.

Shirley Basin, Wyoming

The altered tongues in the Shirley Basin are dominantly light-yellowish-green zones whose coloration results from a few percent of iron-rich montmorillonite or nontronite, and generally small amounts of goethite and hematite. No well-defined alteration envelope has been recognized. Unaltered rock is very light gray and contains about the same amount of clay as the altered rock, but of a more iron-poor variety. Harshman [10] presented heavy mineral data showing that hematite and goethite are essentially absent in unaltered rock and ore, rise to about 0.06 percent in altered rock within about 2 m of ore, then decrease to about 0.01 percent in the remainder of the altered tongue. (It should be noted that hematite and limonite stain or extremely fine particles attached to coarser and less dense minerals might not show up in the heavy mineral fraction, but the relative amounts reported are probably significant). Scattered hematitic calcite concentrations in the ore zone are prominent because of their color contrast but not abundant enough to be significant in the averages.

Pyrite averages about 0.60 percent of the unmineralized unaltered rock, about 0.90 percent of the rock in the uranium ore zone, and only 0.15 percent of the altered rock within about 2 m of ore [10]. There is so little pyrite in altered rock more than 2 m from ore that it can be considered absent for all practical purposes. Melin [11] also observed that coarse-grained pyrite is virtually absent from altered rock. What little remains, he stated, is within about 30 cm of ore and it assumes corroded shapes, devoid of associated limonite, that contrast with the euhedral grains of pyrite found in the ore and unaltered rock.

Black opaque minerals, including a little magnetite, are fairly uniformly distributed at about 0.10 percent throughout altered and unaltered rock. Hornblende and epidote show little if any differences in altered and unaltered rock, except in and adjacent to ore where they are only about half as abundant as elsewhere.

In summary, Harshman's data show iron oxide minerals to be most abundant in the altered rock within 2 m of ore, pyrite to be virtually nil in altered rock, and hornblende and epidote to be least abundant in and near the ore zone.

Benevides deposit, Gulf Coastal Plain, Texas

In some ways the Benevides deposit provides the best data to support a bipartite division of the altered tongue and also contains a mineral suite that limits the possible explanations for the ore-forming and altering geochemical processes.

Unaltered and essentially unmineralized rock, as much as half a kilometer in advance of the roll front, contains, at most, a trace of magnetite, about 0.1 percent ilmenite, and nearly 1.0 percent pyrite (written communication, Westinghouse Electric Corp.). Just back of the roll front the altered rock is pale orange and the ilmenite content has dropped to about half its abundance in unaltered rock; magnetite, partly altered to hematite, is present (Granger, unpubl. data) to the extent of a few hundredths of a percent; goethite makes up between 0.1 and 0.2 percent of the rock, and pyrite is absent. Nearly a kilometer back of the roll front, the altered rock is pale red and contains between 0.1 and 0.2 percent authigenic magnetite, partly altered to hematite (martite); the ilmenite content has risen to about 0.3 percent (suggesting that some martite was mistakenly called ilmenite), and both pyrite and goethite are essentially absent. Even total heavy mineral content--of which iron minerals compose the bulk--is less than half as great in the alteration envelope as in either the unaltered rock or magnetite-rich hematitic core zone. Clay fractions are a pronounced red in the hematitic core zone, distinct yellow in the alteration envelope, and very pale gray in the unaltered rock. Observations given here were made on disaggregated drill core samples (provided by Russell Honea and the Westinghouse Electric Corp.), so the abruptness of the contacts among the various zones could not be determined.

Felder deposit, Gulf Coastal Plain, Texas

Klohn and Pickens [12] first described the Felder deposit, Live Oak County, Tex., from drill data acquired before the deposit was exposed by open pit mining operations. According to their description, the deposit has most of the geometric and element distribution characteristics of clastic roll-type deposits, with the exceptions that the rock in the bleached, altered tongue contains pyrite and that there is about as much pyrite in unaltered rock away from ore as in the ore itself. Magnetite seemingly is very sparse in all the pyritic rock.

The pre-mining cross-sections included among Klohn and Pickens' illustrations of the Felder deposit were borne out by actual relations later seen in the open pit. Their sections illustrated a surficial weathered zone that terminates downward near the upper limb of the ore zone. From their description, it seems that magnetite is much more abundant in some of the oxidized rock than in the pyritic rock. When one of us (H.C.G.) observed the pit in 1971, a typical roll ore body was well exposed in the pit wall and the weathered zone could be seen about 10 m above it. Local redistribution of ore from the original deposit would be expected wherever weathering affected the ore; this fact was noted and illustrated as various irregularities in ore distribution and radioactive equilibrium by Klohn and Pickens [12]. Perhaps the altered tongue at the Felder deposit once had a typical bleached alteration envelope and a hematitic core, but recent surficial weathering has obliterated the original distinctions in many places.

U.S.S.R.

Geologists in the U.S.S.R. [e.g., 13] have reported the presence of elemental sulfur and ferrous carbonate (siderite) in the altered tongue, which they commonly refer to as the zone of limonitization. As shown in the parts that follow, these are important observations that have contributed to the synthesis of our geochemical model. We believe it is probable that these substances were also present in the alteration envelopes of U.S. deposits during roll genesis, but have since been largely destroyed or dissolved and removed.

Summary

The core zones of altered tongues in most districts, other than the Shirley Basin and Gas Hills districts, Wyoming, seem to be consistently characterized by shades of red caused by finely disseminated hematite. Clay fractions that have been separated from this zone are typically reddish. At the Benevides deposit, Texas, it can be seen that at least much of the hematite has resulted from oxidation of epigenetic magnetite, but this is certainly not obvious in most other districts.

The alteration envelope is varied in its characteristics, typically being buff colored from disseminated limonite, or nearly white, seemingly from bleaching. It may or may not contain a little pyrite that can either appear to be: (1) euhedral, shiny, and fresh; (2) corroded but seemingly unoxidized; or (3) partly oxidized to limonite. In the Shirley Basin district, Wyoming, the alteration envelope either is very narrow, is not present, or has subtle characteristics. Corroded pyrite [11] and increased limonite content (E. N. Harshman, oral commun., 1973) near the redox interface suggest that an alteration envelope is present but poorly delineated.

Unweathered host rock that was beyond the influence of alteration and the ore-forming process is light gray to nearly white. The clay fraction is white or pale greenish gray. Pyrite is invariably disseminated in the pristine rock, although it may be sparse.

Organic matter [15] is generally present, at least in small quantities, in the unaltered rock and is ordinarily geochemically similar to coal or humates. This material is almost entirely destroyed [10] in the alteration envelope of the altered tongue.

Magnetite seemingly shows no consistency in its occurrences in various districts but, in spite of this, may provide extremely useful clues to unravelling the geochemistry of alteration. Harshman [10] observed virtually no change in quantity or alteration of detrital magnetite between unaltered rock and the altered tongue in the Shirley Basin. At Ambrosia Lake, N. Mex., magnetite is virtually absent in all the zones. King and Austin [8], on the other hand, reported that detrital magnetite in the unaltered rock of the Gas Hills district had been destroyed in the altered tongue. On the other hand, unaltered host rocks of the Benevides and Felder deposits contain very little magnetite. There, the alteration envelopes are also almost devoid of magnetite, but a significant quantity of authigenic magnetite, partly altered to hematite, is contained in the hematitic cores of the altered tongues and was seemingly formed there during the alteration process.

A band of anomalous selenium content spans the redox interface in nearly all deposits and includes at least a few centimeters of the alteration envelope. Ferroselite has been identified in back of the redox interface in this band at Ambrosia Lake, the Powder River Basin, and Shirley Basin. In the reduced zone, ahead of the redox interface, elemental selenium is the dominant selenium mineral in the band.

PROPOSED ORIGINS OF THE ALTERATION ENVELOPE

The generally prevailing theory is that an influx of oxygen-bearing ground waters percolating subparallel to gross stratification produced the altered tongue by reacting with pyrite at the redox interface. Typical current concepts assume or imply that most of the pyrite was abruptly oxidized to ferric iron minerals such as hydrous iron oxides and goethite. We also had previously made this assumption [14 and 15].

Because of the presence of fresh-appearing pyrite in the altered tongue and limonite specks in the ore zone in the Gas Hills district, Wyoming, King and Austin [8] implied that oxidation was not the principal process that produced the altered tongue. Adler and Sharp [16] suggested that there may have been two types of pyrite--one readily oxidized and the other more resistant, causing it to lag behind in the altered tongue. Adler and Sharp [16] also suggested that H_2S might have diffused back into the alteration envelope, causing pyrite to reform in the dominantly oxidized environment. Because the pyrite near ore in the altered tongue of the Shirley Basin was corroded, but not accompanied by limonite, Melin [11] suggested that some agency other than oxygen had attacked the pyrite. Sharp and others [5] implied that the hematitic zone in the Powder River Basin, Wyoming, was once characterized by hydrated iron oxides that were at least partly dissolved in a CO_2 -rich environment and then reprecipitated as hematite. Adler [17] suggested that limonite was formed initially by oxidation of pyrite and subsequently dehydrated to hematite. He proposed that dehydration might have been episodic and accelerated during warm climatic conditions when the ground-water temperatures were slightly elevated. In 1972, Adler [18] also suggested the possible role of aging in converting limonite to hematite. Conversely, Davis [7] attributed the limonite and bleaching near the uranium deposits to reduction of hematite near the point of ore precipitation. He proposed that this limonite might become "re-oxidized" under weathering conditions and thus become indistinguishable from hematite derived initially from pyrite oxidation.

According to our observations, none of these suggestions adequately explains the alteration envelope and its varying characteristics from district to district. Some investigators may assume that, when roll-formation ceased, the environment was frozen into the characteristics we can now observe. Others entertain the idea of subsequent changes, but have given explanations that can be applied only to a certain district and may not be applicable to roll-formation in general. To overcome these deficiencies, our efforts have been directed toward developing a concept that explains the differing properties of various alteration envelopes within the context of one overall hypothesis of roll development.

SYNTHESIS OF THE GEOCHEMICAL MODEL

Any hypothesis devised to explain the genesis of the alteration envelope must have the latitude to provide a logical explanation for a variety of seemingly conflicting characteristics. The similarities in shape, apparent mode of origin, host rock and host rock environment, ore mineralogy, and altered zones among the various roll-type ore deposits strongly suggest a common genetic geochemical process. If this premise is accepted, it becomes apparent that there is, or was, some obscure similarity among the various alteration envelopes that seemingly take on quite dissimilar characteristics from district to district. The buff zone of Ambrosia Lake, the white zone in the Powder River Basin and Gas Hills, and the limonite-bearing zone in the Shirley Basin and Benevides deposits may have been very similar during the ore-forming process, but may now look different because of differences in subsequent events. How can this be explained?

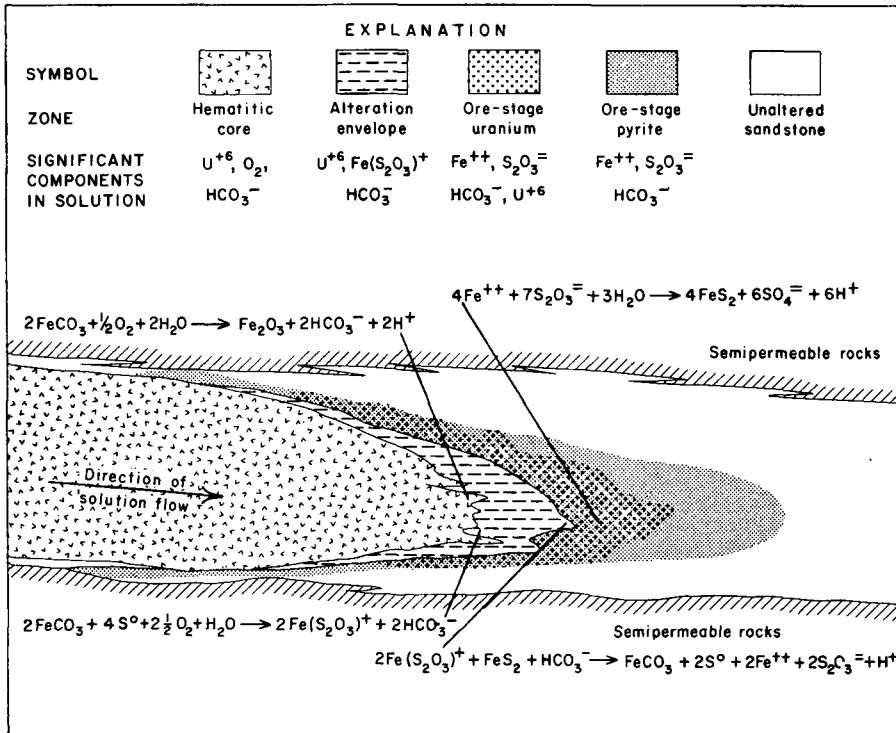


FIG. 3. Idealized cross-section showing some solution components and summary reactions in the Fe-S-O-CO₂ aqueous system during roll formation.

Fairly sharp and distinct contacts between the hematitic core and alteration envelope and between the alteration envelope and pyritic ore zone suggest that two different chemical reactions occurred between the altering solution and certain components of the host rocks. There can be little doubt that the altering solution was initially oxidizing and was essentially in equilibrium with the hematitic core zone; but where it encountered the alteration envelope, it must have undergone reactions that changed both its composition and oxidizing capacity. During transit through the alteration envelope, reactions were inhibited either because the solutions were in chemical equilibrium with the rock or because potential reactions were kinetically sluggish. At and near the redox interface, however, pyrite was essentially destroyed, selenium compounds were mobilized and redeposited, and uranium compounds were dissolved. Beyond the redox interface iron sulfides and uranium were redeposited [14, 15] and complementary reactions occurred that equilibrated the solution with its new environment.

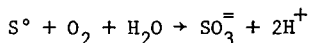
We initially investigated the possibility that the alteration envelope once contained metastable iron sulfides by making a comparison with some modern shallow marine environments, such as in the Black Sea [19, 20] where the topmost sediments are oxidized and are successively underlain by layers containing metastable iron sulfides and finally pyrite. We speculated that reactions with pyrite at the redox interface might remove some sulfur and produce a

residual iron sulfide such as greigite (Fe_3S_4), troilite (FeS), or mackinawite ($\text{FeS}_{0.9}$). This concept had the advantages that the metastable iron sulfides could be readily oxidized to limonite, dissolved under mildly acid conditions, or could be converted to pyrite by aging and disproportionation long after the ore-forming process was arrested. Additionally, the altered hematitic core and pyritic ore would barely be affected by such mild conditions.

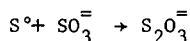
Although it is simple enough to convert ferric iron to ferrous sulfide and, thence, to pyrite, in the presence of H_2S , the process seems to be irreversible along the same path. Pyrite is relatively so much more stable than the sulfur-deficient iron sulfides of low-temperature origin that these sulfides cannot exist in an environment in which pyrite is being destroyed. However, a concept that the alteration envelope once contained a metastable mineral that could convert to various products under mild conditions or aging was so attractive that we continued to examine alternative systems. Only one such system seems to accommodate the requirements and forms the basis for the model that follows.

As the oxygenated ground water leaves the hematitic core zone in which it has achieved equilibrium (fig. 3), it enters the alteration envelope. At that time this zone contains elemental sulfur, and ferrous iron combined largely as FeCO_3 (fig. 1); some ferrous iron is also partly adsorbed on and in exchangeable positions in montmorillonite clay. Where the water contacts the alteration envelope, the free dissolved oxygen is completely consumed, releasing bicarbonate ions and forming a rather stable, colored ferric thiosulfate complex. The reactions can be represented as follows:

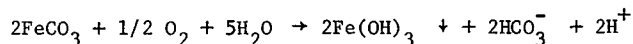
Oxidation of elemental sulfur:



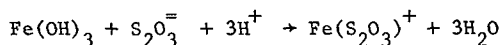
Followed by:



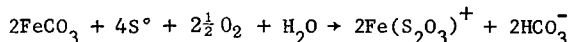
Oxidation of ferrous carbonate:



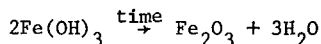
and reaction with thiosulfate:



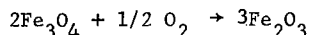
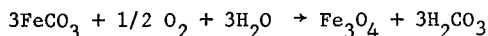
Summarizing the reactions:



Any freshly precipitated $\text{Fe}(\text{OH})_3$ that fails to react with S_2O_3^- will ultimately age to goethite or hematite:



Unreacted ferrous carbonate can oxidize first to magnetite and then to hematite:

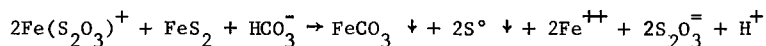


The free energy losses in each of these reactions indicates that they are favorable from a thermodynamic viewpoint, although we cannot completely judge their kinetic favorability. If some of the reactions are more sluggish than others, a rather uneven contact could be formed between the completely oxidized and the ferrous-carbonate and elemental-sulfur-bearing zones.

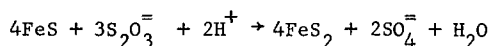
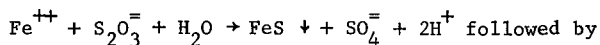
It can be seen that the well-oxidized rocks will ultimately contain considerable hematite, although residual magnetite may persist locally. Of utmost importance to the model we are proposing is the fact that some ferric iron has been combined in a soluble complex ion that is fairly stable at low and intermediate pH values and will not react readily with either the ferrous carbonate or elemental sulfur.

Ferric iron seems to oxidize pyrite at a much faster rate than does dissolved free oxygen [21, 22]. The ferrous iron in pyrite does not directly contribute to such a process; rather the ferric iron in solution is reduced and sulfide sulfur is oxidized. The simplest of these reactions involves oxidation of the sulfide sulfur only as far as elemental sulfur. A major complication, however, is keeping ferric iron in solution in any but the most acid solutions. This is one reason why our model requires a soluble ferric iron complex such as $\text{Fe}(\text{S}_2\text{O}_3)^+$, which is relatively stable at low concentrations over a fairly wide pH range. Additionally, our experiments suggest that ferric iron either does not react or tends to be kinetically sluggish toward any reaction with elemental sulfur, unless oxygen is present. FeCO_3 also is not affected because ferrous iron is not susceptible to oxidation by ferric iron. Soluble ferric iron can, therefore, be transported past elemental sulfur and FeCO_3 without appreciable change.

In this model, the interface that has been termed the roll front or redox interface is not contacted directly by dissolved oxygen, but is a narrow zone of reaction between pyrite and complex ferric ions being carried in solution. Oxidation of sulfide sulfur produces elemental sulfur, which is only stable under very restricted, acid conditions. The summary reaction is about as follows:

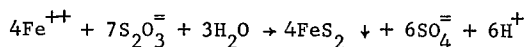


Probably some of the ferrous iron is precipitated as ferrous carbonate by the bicarbonate ions in solution [24] and some ferrous iron may be adsorbed or held in exchangeable positions by montmorillonite clay; some of the ferrous iron, however, remains soluble. The soluble products are continually moved ahead in solution and probably react in two steps to produce ore-stage pyrite:

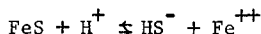


Most investigators now seem to agree that pyrite never forms directly at low temperatures but develops from the sulfidization of some early formed species such as mackinawite ($\text{FeS}_{0.9}$) [25, 26].

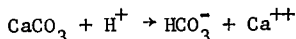
However, we can represent the summary reaction as:



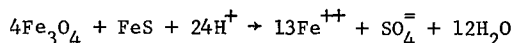
It can be seen that the production of H^+ ions will tend to lower the pH in the zone in which iron sulfide is forming. This can be buffered by several reactions, such as (1) by low-intensity alteration of alkali feldspars in the sandstone host, (2) by dissolution of the early formed iron sulfide:



which is readily reversed upon neutralization of the hydrogen ions, or (3) by dissolution of calcite:



Destruction of detrital magnetite in the host rock could be a powerful buffer in the ore zone:



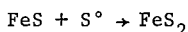
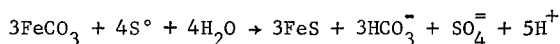
Ultimately, the reactivity of the solution is spent and it flows out of the system in virtual equilibrium with its environment.

Another critical consideration in our model is the ease with which selenium can be transported in solution, as a passenger on certain sulfur-bearing ions such as SeS^- and SeSO_3^- . Such ions contribute to the formation of ferroselite in the presence of ferrous iron [23] or can release elemental selenium under acid conditions. The presence of ferroselite in the selenium band on the oxidized side of the redox interface implies that some forms of sulfur and ferrous iron were present in the alteration envelope during ore formation. As noted above, we feel justified in assuming that both FeCO_3 and elemental sulfur were once present in the alteration envelope because they have been reported by Soviet geologists [13], even though they may have been destroyed in most U.S. deposits.

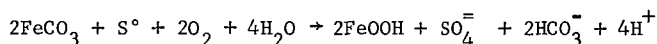
Depending on conditions that exist in individual situations, the $\text{Fe}(\text{S}_2\text{O}_3)^+$ -bearing solution can traverse various distances through the ferrous carbonatite-elemental sulfur-bearing rocks without undergoing significant changes. Critical factors may include variations in the content of reactive minerals, velocity of ground-water flow, temperature (thiosulfate is less stable under higher temperatures), and Eh and pH.

Now, let us turn our attention to what might happen if the ore-forming process is terminated--perhaps caused by some structural event, or a change in ground-water recharge due to diversion or arrest by continued deposition of overlying fluvial sediments. The thoroughly oxidized hematitic tongue is stable and contains iron-rich clays, hematite, magnetite, and (or) limonite (which will eventually dehydrate to hematite). The ore-stage pyrite zone is also relatively stable, except for the newly deposited FeS, unless there is a change to strongly oxidizing conditions. The ferrous carbonate-elemental sulfur-bearing zone is much less stable, because of the small but significant solubility of FeCO_3 and the metastability of disseminated sulfur.

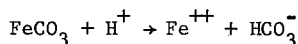
All that is required is time, if the pH is kept nearly neutral, for the ferrous iron and sulfur to form FeS and, ultimately, pyrite.



Slightly oxidizing post-ore conditions could dissolve and remove the sulfur while converting the ferrous iron to limonite:



Bleaching could be largely the result of converting the FeCO_3 to FeS_2 , as shown above, or could be principally by solution and removal of the FeCO_3 under mildly acid conditions that do not significantly affect the elemental sulfur.



In summary, this model system could explain the features we now see at many of the U.S. districts that contain roll-type deposits. It is also compatible with the selenium system that seems to be associated with all known roll-type deposits. Although many laboratory experiments were conducted concurrently with the investigation on which this paper is based, some of the reactions have not been thoroughly tested. The proposed geochemical system is based on sound thermodynamic principles, however, and is far more probable than several alternative models which were considered but proved to be untenable.

REFERENCES

- [1] Granger, H. C., Santos, E. S., Deane, B. G., and Moore, F. B., "Sandstone-type uranium deposits at Ambrosia Lake, New Mexico--An interim report", *Econ. Geol.* 56 7 (1961) 1179.
- [2] Granger, H. C., "Ferroselite in a roll-type uranium deposit, Powder River Basin, Wyoming", in *Geological Survey Research 1966*, U.S. Geol. Survey Prof. Paper 550-C (1966) 133.
- [3] Gould, W. R., Smith, R. B., Metzger, S. P., and Melancon, P. E., "Geology of the Homestake-Sapin uranium deposits, Ambrosia Lake area", in *Geol. and Technol. of the Grants uranium region, New Mex. Bur. Mines Memoir 15* (1963) 66, New Mex. Bureau Mines, Socorro, New Mex.
- [4] MacRae, M. E., "Geology of the Black Jack No. 1 mine, Smith Lake area", in *Geol. and Technol. of the Grants uranium region, New Mex. Bur. Mines Memoir 15* (1963) 45.
- [5] Sharp, W. N., McKay, E. J., McKeown, F. A., and White, A. M., "Geology and uranium deposits of Pumpkin Buttes area of the Powder River Basin, Wyoming", *U.S. Geol. Survey Bull.* 1107-H (1954) 541.
- [6] Langen, R. E., and Kidwell, A. L., "Geology and Geochemistry of the Highland uranium deposit, Converse County, Wyoming", *Soc. of Mining Engineers of AIME*, presented at AIME Centennial Annual Meeting, New York, N. Y., Preprint 71-I-37 (1971) 17 p.
- [7] Davis, J. F., "Uranium deposits of the Powder River Basin", *Contrib. to Geol., Wyo. Uranium Issue*, 8 2 (1969) pt 1, 131.

- [8] King, J. W., and Austin, S. R., "Some characteristics of roll-type uranium deposits at Gas Hills, Wyoming", *Mining Engineering* 18 5 (1966) 73.
- [9] Anderson, D. A., "Uranium deposits of the Gas Hills", *Contrib. to Geol., Wyo. Uranium Issue*, 8 2 (1969) pt 1, 93.
- [10] Harshman, E. N., "Uranium ore rolls in the United States", *Uranium Explor. Geol., I.A.E.A., Vienna* (1972) 219.
- [11] Melin, R. E., "Uranium deposits in Shirley Basin, Wyoming", *Contrib. to Geol., Wyo. Uranium Issue*, 8 2 (1969) pt 1, 143.
- [12] Klohn, M. L., and Pickens, W. R., "Geology of the Felder uranium deposit, Live Oak County, Texas", preprint of paper presented before the Soc. of Mining Engineers of AIME, Denver (1970)
- [13] Kashirtseva, M. F., "Mineral and geochemical zonation of infiltration uranium ores", *Translated from Soviet Geol.* 10 (1964) 51.
- [14] Granger, H. C., and Warren, C. G., "Unstable sulfur compounds and the origin of roll-type uranium deposits", *Econ. Geol.* 64 2 (1969) 160.
- [15] Granger, H. C., and Warren, C. G., unpublished data on dissolved oxygen and the genesis of roll-type uranium deposits.
- [16] Adler, H. H., and Sharp, B. J., "Uranium ore rolls--occurrence, genesis, and physical and chemical characteristics", *Guidebook to the Geol. of Utah, Uranium districts of southeastern Utah, Utah Geol. Soc., Salt Lake City, Utah*, 21 (1967) 53.
- [17] Adler, H. H., "Interpretation of color relations in sandstone as a guide to uranium exploration and ore genesis", *Uranium Explor. Geol., IAEA, Vienna* (1970) 331.
- [18] Adler, H. H., "Exploration for uranium in sandstones: geochemical, remanent magnetic, and sulfur-isotope applications", *Uranium Explor. Geol., IAEA, Vienna* (1972).
- [19] Volkov, I. I., and Ostroumov, E. A., "The form of sulfur compounds in the interstitial waters of the Black Sea sediments", *Geochemistry* 4 (1957) 397.
- [20] Love, L. G., "Sulphides of metals in Recent sediments", *Sedimentary Ores, Ancient and Modern* (Proc. of the 15th Inter-University Geol. Cong., Univ. of Leicester, England, 1967) Univ. of Leicester (1969) 31.
- [21] Singer, P. C., and Stumm, Werner, "Acidic mine drainage: the rate determining step", *Science* 167 (1970) 1121.
- [22] Meyers, R. A., Hamersma, J. W., Land, J. S., and Kraft, M. L., "Desulfurization of coal", *Science* 177 (1972) 1187.
- [23] Warren, C. G., "The synthesis of ferroselite from an aqueous solution at low temperature", *Econ. Geol.* 63 4 (1968) 418.
- [24] Stashchuk, M. F., "The oxidation-reduction potential in geology", *Amer. Edition, Consultants Bur.; Plenum, New York* (1972).

- [25] Sweeney, R. E., and Kaplan, I. R., "Pyrite framboid formation: Laboratory synthesis and marine sediments", *Econ. Geol.* 68 5 (1973) 618.
- [26] Berner, R. A., "Thermodynamic stability of sedimentary iron sulfides", *Amer. Jour. of Sci.* 265 9 (1967) 773.

DISCUSSION

A. DURANDAU: You discussed various chemical models for roll deposits. Could you say what are in your opinion the optimum conditions of sandstone permeability and grain size for promoting these chemical exchanges in such a way as to yield a good accumulation of uranium?

H. C. GRANGER: I do not believe that we can easily relate favourability to an optimum permeability or grain size; nor do I think that the hydraulic conductivities measured at present are necessarily representative of the permeabilities that existed at the time of ore deposition. Certainly the rocks had to be permeable enough to permit a fairly unrestricted flow of ground water parallel to the stratification. If the flow had been too slow, no altered tongues of the sizes now seen could have been formed; and if it had been too fast, the reactions could not have reached the continuous quasi-equilibrium required. Probably the permeabilities at the time of deposition were similar to those of relatively clean, very fine- to medium-grained alluvial sands such as are deposited today. Ore bodies may have been trapped or temporarily restrained where the permeability was sharply reduced. The lateral margins of altered tongues, particularly where restricted by intercalated finer-grained units as at the edges of paleochannels, might be particularly favourable locations. Ore bodies that had been swept into such a protected setting might then be bypassed by the advancing altered tongue.

The deposits occur in rocks that range from very fine-grained to coarse-grained sandstone, and from poorly to rather well-sorted sandstone. The critical factors are probably more closely related to adequate permeability and to pre-ore-stage pyrite than to grain size. This paper, however, deals with the alteration associated with ore formation and not with ore formation as such. I doubt whether we are prepared yet to state why ore is now found at certain places along a roll front and not at others.

S. H. U. BOWIE: I have no difficulty in accepting that hematite is authigenic, but find it more difficult to attribute the same mode of origin to magnetite. Detrital magnetite was almost certainly present, and could have been partly or completely replaced by hematite. How important do you think this fact is for your excellent model?

H. C. GRANGER: The authigenic magnetite is not a critical part of the model, and in most deposits it was probably such a fleetingly transient phase that little or no trace of it can now be found. The chemistry of the model allows for it, however, and where the hematitic core contains two or three orders of magnitude more magnetite than the unaltered sandstone, we seem to be forced to consider the possibility that it is authigenic.

J. E. FROST: In response to Mr. Bowie's question, I might say that there is a distinct zoning pattern of hematite to magnetite to pyrite as one approaches the Live Oak County ore bodies in Texas. This zoning extends laterally for approximately 20 km from the Felder deposit.

R. H. DE VOTO: How do your findings compare with the valuable observations of Mr. Harshman regarding the virtual absence of sulphate minerals in the altered sand and their abundance in ore, and what is their mineralogy in the unaltered sand?

H. C. GRANGER: Mr. Harshman said that sulphate is probably present in small amounts as gypsum in the unaltered sand and that the anomalous amount of sulphate in ore is in a soluble but unidentified form, possibly iron sulphate. Both the elemental sulphur which we have suggested was present in the alteration envelope during ore formation and the metastable iron sulphide which we have suggested was originally present in ore could easily oxidize to form sulphate minerals. We believe that this could have occurred after ore deposition ceased without significantly affecting the more stable ore-stage minerals.

GENESIS AND CHARACTERISTICS OF THE SOUTHERN POWDER RIVER BASIN URANIUM DEPOSITS, WYOMING, USA

A.R. DAHL

Exxon Company, USA, Denver, Colo.

J.L. HAGMAIER

Exxon Company, USA, Casper, Wyo.,

United States of America

Abstract

GENESIS AND CHARACTERISTICS OF THE SOUTHERN POWDER RIVER BASIN URANIUM DEPOSITS,
WYOMING, USA.

Uranium deposits in the southern Powder River Basin of Wyoming are excellent examples of large roll-type ore bodies. The host rocks are Paleocene sandstones deposited as point bars by a meandering stream. The source of uranium is tuffaceous and arkosic debris indigenous to the sedimentary sequence containing the host rocks. The largest deposits of highest grade occur near the distal margins of permeable, slightly dipping sandstones where they grade laterally into organic-rich siltstones, claystones and lignites deposited in backswamp or flood basin environments. The deposits are epigenetic in origin, formed by precipitation of uranium from groundwater solutions that moved through the host rocks from a recharge area southwest of the deposits towards a discharge area northeast of the deposits. The deposits are large because the host rocks are extensive and the groundwater system remained relatively stable. Pyrite formed early in and around the host units through a biogenic process utilizing sulphate-reducing bacteria. This was important in establishing a permissive geochemical environment for later ore genesis. Oxidation of pyrite by incursing groundwater caused sulphite to form. Sulphite disproportionation into SO_4^{2-} and HS^- developed the final reducing mechanism for uranium precipitation in the ore rolls. Deposit characteristics and associated alteration products are compatible with the chemical theory of Granger and Warren.

Introduction

In 1968 Exxon Company, U.S.A. discovered uranium in the Highland area of the southern Powder River Basin in east-central Wyoming. Subsequent exploration and development by Exxon have defined several deposits which contain a total of about 9 million metric tons of ore grading between one and three kilograms of U_3O_8 per metric ton. Discovery of additional deposits in the area by other operators has confirmed a uranium district of major importance. Part of the Exxon deposits are now being mined by open-pit methods and processed in a mill with a design capacity of 1 800 metric tons per day. Exxon has begun development of underground mines to recover ore that occurs at greater depths.

Uranium in the Highland area is present as roll-type deposits formed within Tertiary fluvial sandstones. It occurs where the sandstones grade laterally into finer-grained facies equivalents. The sandstones are permeable, dip slightly into the basin and are altered updip from uranium accumulations.

The objectives of this paper are to set forth the regional geologic and groundwater setting of the southern Powder River Basin, describe the characteristics of the Highland deposits and interpret the geologic and

geochemical sequence of events that contributed to their genesis. Only those deposits controlled by Exxon have been studied by the authors and used to develop a genetic model. However, it is assumed that adjoining deposits of other operators have a similar origin.

The authors are grateful to colleagues within Exxon Company, U.S.A. and Esso Production Research Company for their assistance.

Regional Geology

Exxon's Highland uranium deposits are located in the southern Powder River Basin, Converse County, Wyoming (Fig. 1). The Powder River Basin is a large structural and topographic basin bounded on the south by the Laramie Range and the Hartville Uplift, on the east by the Black Hills and by the Big Horn Mountains and Casper Arch on the west. To the north, it gradually terminates in Montana.

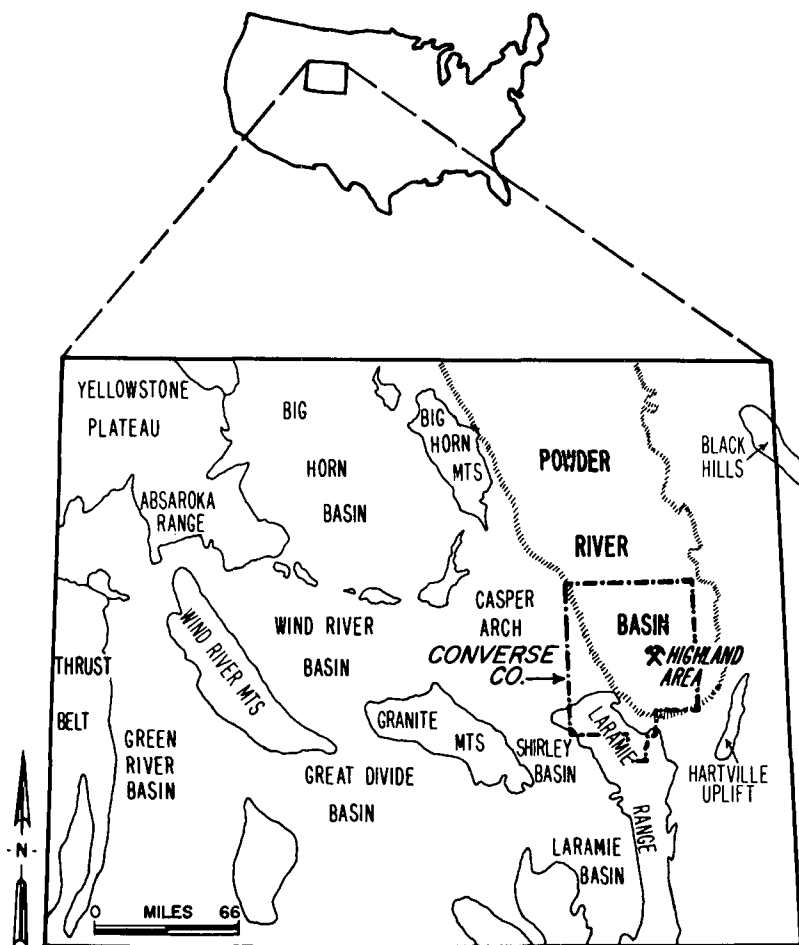


FIG. 1. Index map showing location of the Powder River Basin and the Highland uranium deposits in Converse County, Wyoming.

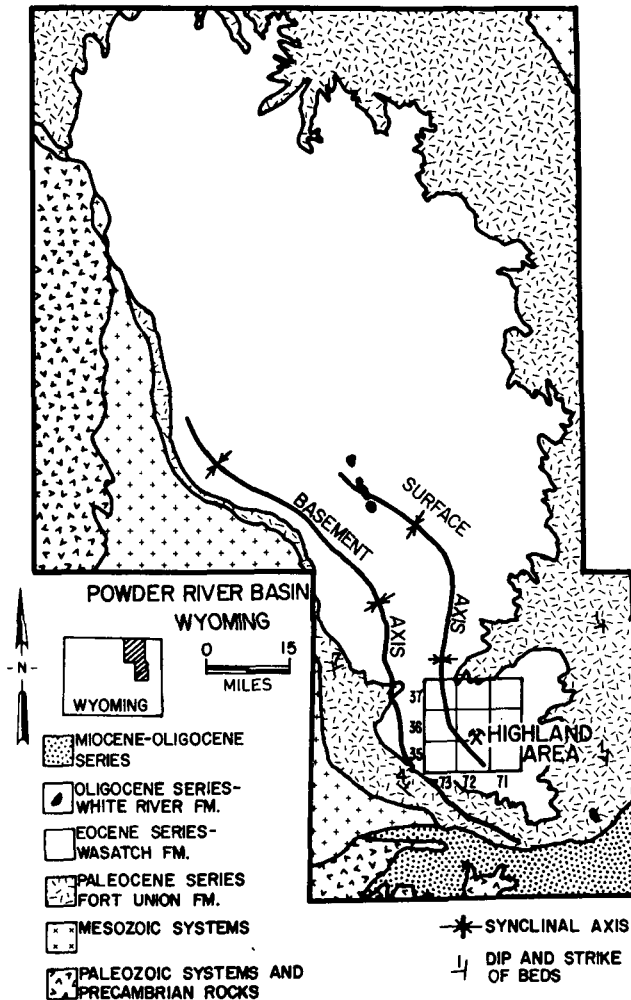


FIG.2. Geological map of the Powder River Basin, Wyoming. (FM = Formation).

Structurally the basin is a north-south aligned asymmetric syncline (Fig. 2). The Precambrian basement axis lies in the western part of the basin. The axis has shifted as the basin filled and the present surface axis as measured from dips on Tertiary rocks now lies several miles east of the basement axis and in close proximity to the known uranium deposits. This structural feature has influenced the position of Tertiary fluvial systems that built into the basin from the south as well as subsequent groundwater movement into the basin. Dips are slight ($1-3^{\circ}$) in the southern part of the basin, particularly on the east side. They increase to the west and southwest near the basin margin.

The surface of the Powder River Basin is primarily underlain by sedimentary rocks deposited during the Cenozoic Era. Around the uplifted margins of the basin, older sedimentary rocks deposited during the Paleozoic and Mesozoic Eras crop out (Fig. 2).

Three stratigraphic units deposited during the Cenozoic period are recognized in the Powder River Basin. They are the Paleocene Fort Union Formation, the Eocene Wasatch Formation and the Oligocene White River Formation (Fig. 3). The host sandstones for the Highland uranium deposits are in the upper Fort Union Formation.

The Fort Union Formation thickens from an erosional featheredge on the southern margin to as much as 1 000 meters in the central part of the basin. It is composed of interbedded fine-to-coarse-grained sandstone, siltstone, claystone, lignite and coal. It conformably overlies the Cretaceous Lance Formation and is unconformably overlain by the Eocene Wasatch Formation. In the southern part of the basin, the Fort Union Formation is composed of sedimentary material derived from erosion of Mesozoic and Paleozoic sedimentary rocks, the Precambrian crystalline complex of the Laramie and Granite Mountains and volcanic debris from the Absaraka volcanic center in western Wyoming (Fig. 1).

Streams generally flowing northward into the southern part of the basin during the early Tertiary deposited clastic sediment within a fluvial framework. The physiography of the area at that time is interpreted to have been one of a low-relief vegetated plain that contained one dominant river system and flanking freshwater lakes and swamps. The climate is interpreted to have been warm and humid. This interpretation is based on the abundance of plant fossils, lignite and coal in the Fort Union Formation within the basin.

ERA	PERIOD	EPOCH	
CENOZOIC	TERTIARY	PLEISTOCENE	Post-Oligocene units removed by erosion
		PLIOCENE	
		MIOCENE	
		OLIGO- CENE	WHITE RIVER FORMATION
		EOCENE	WASATCH FORMATION
		PALEO- CENE	FORT UNION FORMATION
MESOZOIC	CRETACEOUS		Lance Formation

FIG. 3. Tertiary stratigraphic nomenclature for the Powder River Basin.

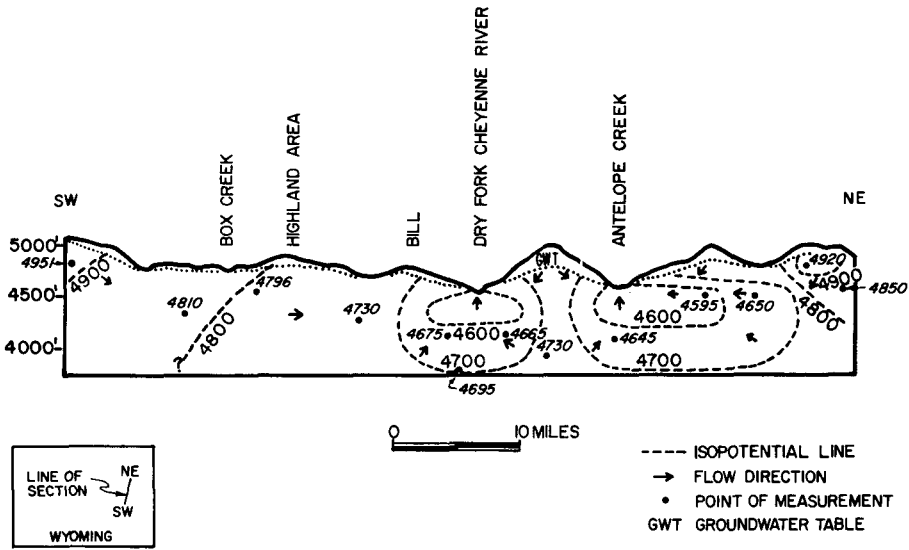


FIG.4. Pattern of regional groundwater flow in the Dry Fork Cheyenne River flow system, near Highland Area, Wyoming.

Regional Groundwater Flow and Chemistry

Transportation and precipitation of uranium in the Highland area is directly related to groundwater movement in the southern Powder River Basin. Regional groundwater recharge and discharge areas of the present groundwater-flow systems (Hagmaier, 1971)[1] are interpreted to have been at approximately the same locations as those of the early Tertiary groundwater-flow systems because the general structural-topographic configuration of the Powder River Basin has been reasonably stable since the early Paleocene Epoch. That is, the major mountain uplifts and fold areas of Wyoming were either rejuvenated or initiated during the Laramide Revolution in late Cretaceous and were well-defined by the Paleocene.

Present-day regional groundwater flow through the Highland area is from the southwest to the northeast (Fig. 4). This is compatible with local alteration data from the mineralized area; configuration of the oxidation-reduction front at Highland indicates that mineralizing groundwater flowed from the southwest toward the northeast at the time the uranium deposits were formed (Fig. 8).

The present-day groundwater in the southern Powder River Basin undergoes a chemical change along its regional flow path where the groundwater passes through the area of the Highland uranium deposits. The chemistry changes from a sulfate-rich groundwater with minor bicarbonate in the recharge area southwest of the Highland area to a bicarbonate-rich groundwater in the discharge area northeast of the uranium deposits. The general chemical facies sequence from recharge to discharge areas is stated in its simplest form as sulfate and bicarbonate facies grading to a bicarbonate facies (Fig. 5). This change in groundwater chemistry is attributable to sulfate reduction. The direct effect of sulfate reduction

GROUNDWATER RECHARGE AREA SW POWDER RIVER BASIN

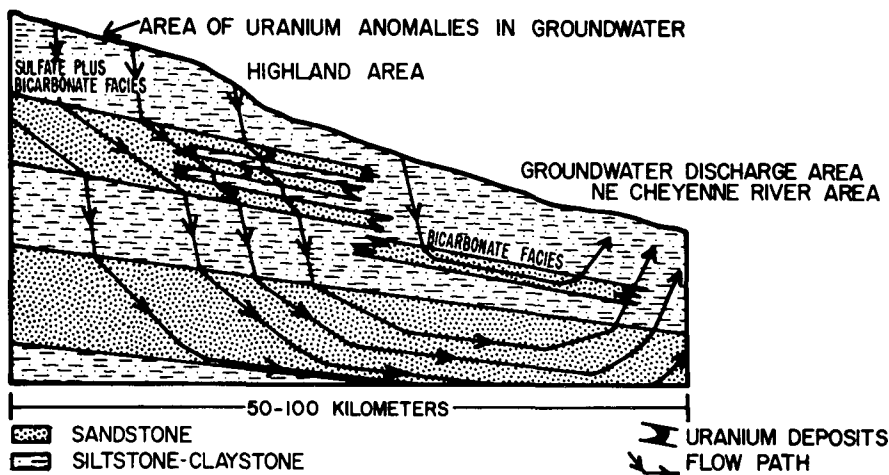


FIG. 5. Generalized diagram showing the chemical facies of the groundwater flow system in the Southern Powder River Basin and its relationship to the Highland uranium deposits. (Modified from Hagmaier [1].)

on groundwater chemistry is to decrease sulfate concentration and increase bicarbonate concentration. The change in groundwater chemical facies near the Highland uranium deposits was probably caused by the same reductant that precipitated uranium from groundwater solution during ore genesis. Hagmaier (1971) [1] demonstrated that anomalous amounts of uranium in groundwater occur only in the sulfate-rich facies updrift from the Highland area (Fig. 5). No anomalies were observed from groundwater samples taken in the bicarbonate-rich facies after it had passed through the Highland area. This is not meant to imply that the ore deposits at Highland are very recent, although some slight remobilization and deposition is likely taking place at the present time. It does imply that the coincidence of uranium deposits and recently-measured groundwater chemical change is likely in a basin like the Powder River where the hydrodynamic framework in terms of recharge-discharge positions has remained relatively stable since deposition of the host sandstones.

Highland Sandstone System

The sandstones that host the Highland uranium deposits are collectively and informally referred to in this section as the Highland sandstone unit. This unit underlies a large area of the southwest Powder River Basin and exhibits relatively consistent lateral continuity. The authors feel that this lateral continuity is an important factor in the origin of the large Highland deposits.

The Highland sandstones are arkosic in composition, loosely consolidated, have excellent permeability (1 000 millidarcies is common) and contain substantial organic debris and tuffaceous material.

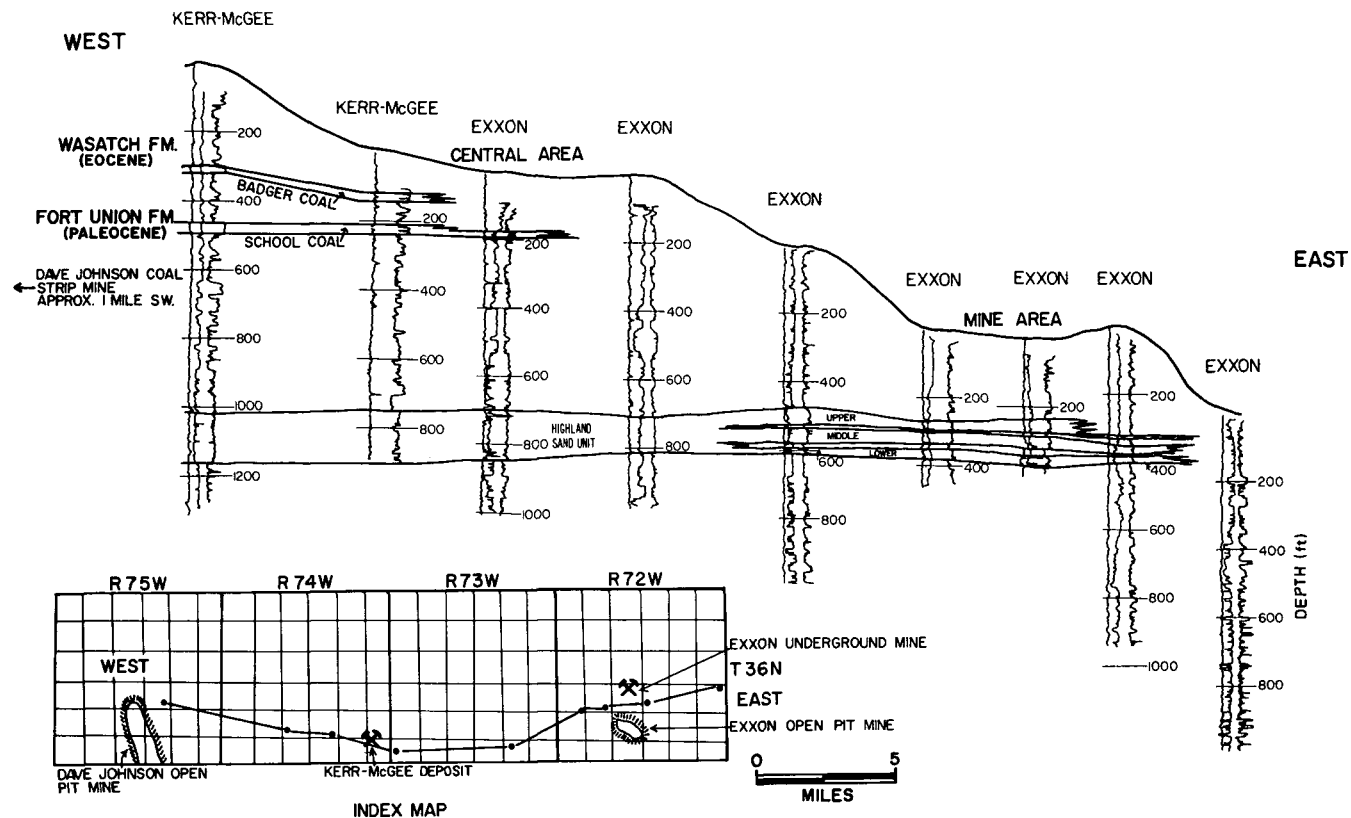


FIG.6. Stratigraphic cross-section between Dave Johnson Coal Field and Highland Area. (FM = Formation.)

Stratigraphically the Highland sandstones are located in the upper part of the Fort Union Formation. The stratigraphic position of the sandstones in relation to key marker beds (coal seams) can be documented by drill hole electric log correlations from the Dave Johnson Coal Field near the southwest extremity of the basin to the Highland area (Fig. 6). The School and Badger coal seams being surface-mined in the Dave Johnson Coal Field are positioned stratigraphically near the top of the Fort Union Formation. Locally the top of the Badger coal is used to mark the boundary between the Fort Union and Wasatch Formations. The Highland sandstone unit is positioned about 200 meters below the Badger coal.

The time-stratigraphic position of the sandstones has been established on the basis of palynology. Samples from drill holes taken during exploration and more recently from the northwest wall of the first open-pit mine contain a suite of spores and pollen representative of Paleocene Zone III or late Paleocene in age.

The sandstones that host ore at Highland were deposited primarily as point bars and to a lesser extent as channel bars by sand-laden streams. The fluvial environment is represented by upper low-flow regime and to a lesser extent by lower high-flow regime. These conclusions are based on field observations of primary sedimentary structures, sediment characteristics and facies relationships as seen in the Highland open-pit mine area, outcrops along Box Creek south of the mine and outcrops along the southwest margin of the basin. The basal part of the thicker sandstones exhibit large-scale coarse-grained festoon crossbeds. The middle zone is characterized by medium-scale crossbeds and the upper part by even, parallel laminae, small-scale current ripples and clay drapes. The entire point-bar sequence exhibits a decrease in grain size upward. Figure 7 is a diagrammatic cross-section illustrating the various sedimentary characteristics observed in the point bar sandstones.

Individual sandstones that contain the uranium deposits are tongue-like extensions off the edge of the central Highland sandstone unit.

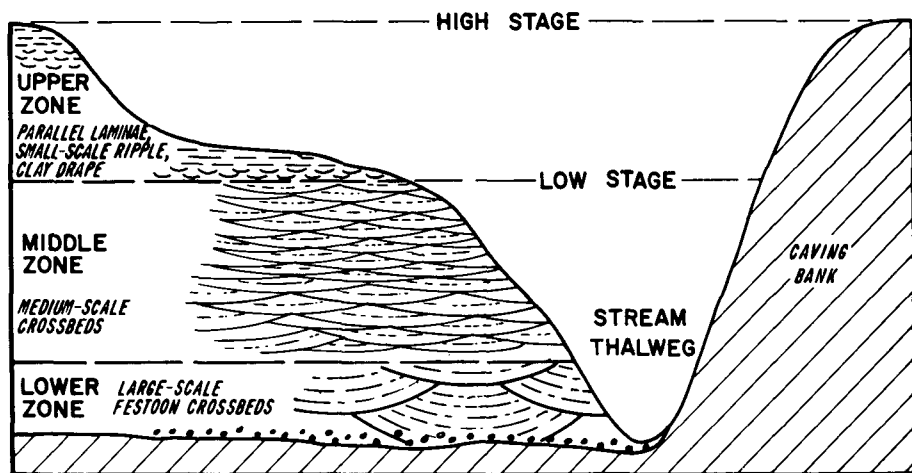


FIG.7. Diagrammatic cross-section showing sedimentary characteristics of point bar deposits.

This central unit is located about 8 kilometers west of the open-pit mine and is illustrated by electric logs on the western end of the cross section shown on Figure 6. The sandstone in the central part is massive and attains a total thickness of 50 meters. It is interpreted to be located near the axis of the meander belt of the Highland fluvial system. A breakup of the massive sandstone into laterally continuous and discrete sands toward the Exxon mine area is interpreted to be the result of an eastward lateral migration of point bars (note electric logs in mine area of Fig. 6). Each sandstone represents the lateral migration of a large individual point bar system to the eastern edge of the ancient meander belt, a subsequent neck cut-off and a return of the river to the axis of the meander belt. This is characteristic of meandering streams as illustrated by detailed studies of the present-day Missouri River (Dahl, 1961)[2]. The process of lateral migration and neck cut-off occurred three times at Highland as the river system aggraded and resulted in the three major sandstones that contain uranium ore. In the Exxon mine area the sandstones are separated vertically by siltstones, claystones and lignites deposited in upper point bar, natural level and back swamp or flood basin environments. Laterally the sandstones exhibit facies changes into carbonaceous claystone and lignites deposited in a flood basin environment.

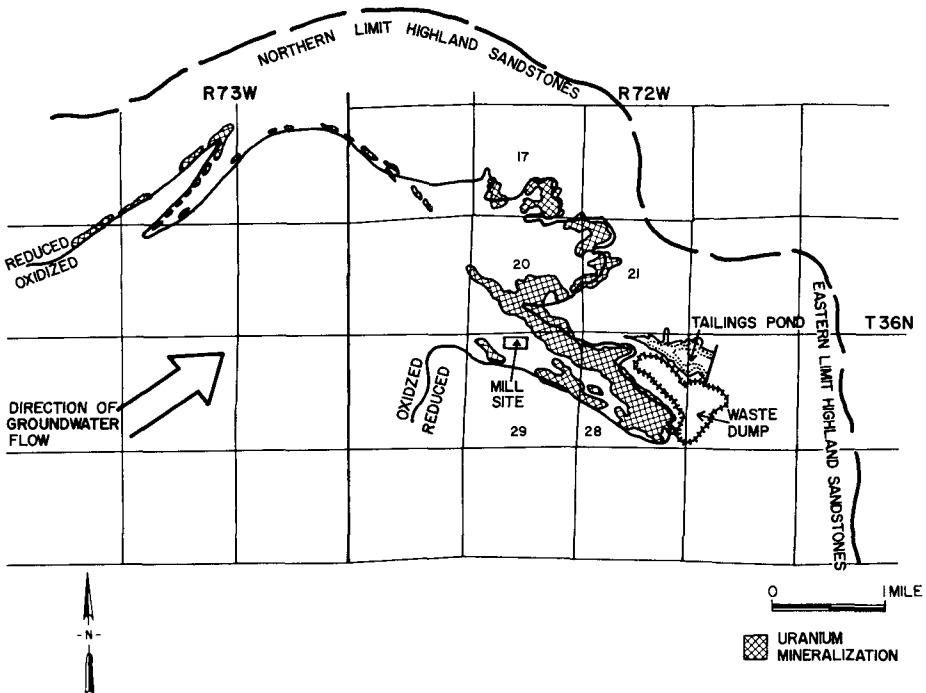


FIG.8. Geological summary map of Highland Area showing relationship of uranium mineralization, limit of Highland sandstone unit, oxidation-reduction boundary and groundwater flow path.

TABLE I. COMMON CONSTITUENTS OF THE HIGHLAND HOST SANDSTONES

<u>Constituent</u>	<u>Percent of Total Composition</u>	<u>Comments</u>
Crystalline Quartz	50-60%	Some smokey but mostly clear quartz.
Feldspar	20-30%	Both K-feldspars and plagioclase are present. The K-feldspars show only limited alteration along cleavage planes. The plagioclase feldspars usually show alteration to kaolinite and/or sericite in the oxidized sands.
Chert and Rock Fragments	10-15%	The chert and rock fragments are reworked from Paleozoic and Mesozoic sedimentary rocks.
Clay Minerals	2- 8%	Montmorillonite is the common clay mineral. Minor kaolinite is present. The other clay minerals such as illite, sedimentary chlorite, and mixed layer aggregates are present only in trace amounts.
Organic Matter	0- 3%	Organic matter consists of carbonized wood and lignite fragments that are disseminated throughout the sediments in the form of lenses, partings, and individual angular fragments.
Mica and Chlorite	1- 2%	
Green Hornblende	0- 2%	Green hornblende is always present except in the hematite-stained oxidized sandstones.
Other Minerals	0- 1%	Heavy minerals present include garnet, epidote, zircon, apatite, sphene, magnetite, hematite, and ilmenite. The oxidized sandstones contain only heavy minerals that are chemically stable and does not contain minerals such as pyroxene, hornblende, and biotite all of which are present in the protore sands.

Deposit Geology

The Highland uranium deposits exhibit many of the geologic characteristics of the sandstone roll-type that are considered epigenetic in origin. Ore grade uranium occurs near the margin of sandstones where they grade laterally into finer-grained equivalents. Mineralized trends are subparallel to the sandstone pinchouts for each sandstone and are well-defined by oxidation-reduction phenomena within each sandstone. Figure 8 is a geologic summary map relating known uranium deposits, sandstone limits, regional oxidation-reduction boundary and interpreted groundwater flow direction in the area. Most of Exxon's ore is near the eastern limit of ancient meander loop migration. In this area there is both a physical and chemical relationship between uranium occurrence and sandstone boundary. Physically the finer-grained units near the edge of the sandstone bodies tended to direct mineralizing groundwater into the boundary area where the higher organic content was instrumental in producing a reducing environment necessary for mineral deposition.

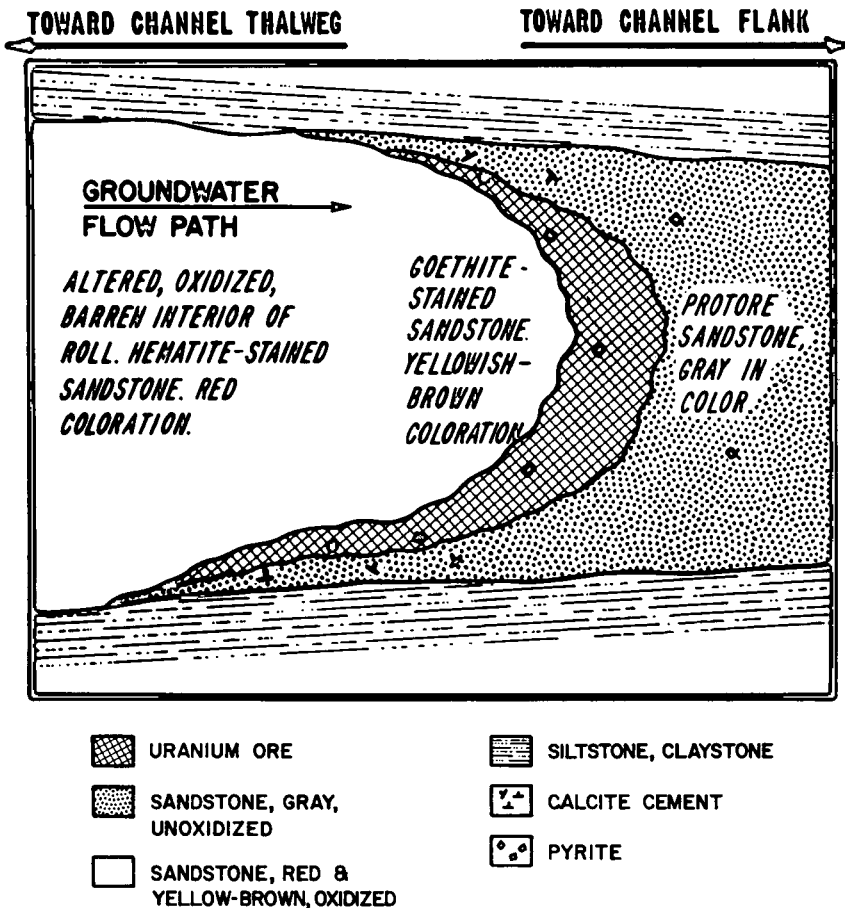


FIG.9. Generalized cross-section of ore roll in Highland Area. (Modified from Langer and Kidwell [3].)

The three separate sandstones that host ore are designated Highland upper, middle and lower. These sandstones are usually separated by 3 to 7 meters of siltstone and claystone except where channel scour has removed the interbeds and brought the sandstones into vertical continuity. Dip of the host sandstones in the mine area is slight, being less than 1 degree to the northwest. A description of the average mineral composition of the host sandstones is presented in Table I.

In cross-section the uranium deposits are characterized geometrically by C-shaped or roll-type mineralization (Fig. 9). In plan view the deposits are tongue-shaped (Fig. 8) and best developed near the sandstone margin. Mineralization extends for several kilometers but is not everywhere of economic grade along the tongue. The ore mineral is primarily coffinite with lesser uraninite. Coffinite occurs in the form of thin sooty layers and irregular spherical or botryoidal masses (generally less than 10 microns thickness) on individual detrital mineral grains in the sandstone.

Alteration associated with mineralization is strongly manifested in the Highland deposits. It is represented by red hematite-stained sandstone within the oxidized concave interior of a roll (Fig. 9). Hematite grades into a narrow brown-colored goethite zone close to and within the roll. The goethite-stained sandstone grades into gray unoxidized sandstone (protore) on the convex side of the roll. These color changes associated with alteration provide guides for following mineralization during exploration. The mineralizing solutions flowed in directions generally normal to the regional trend of the roll front (Fig. 9). Highest-grade ore of minable thickness is most frequently located within a band of varying width (20-200 meters) along the goethite-protore contact.

Pyrite is widely distributed within the ore zones and unaltered protore. It is more abundant (enriched) in the mineralized zones than in un-mineralized rock. The principal mode of occurrence is spherical aggregates of from 10 to 100 micron in size, occurring in the clay matrix and on the surfaces of sand grains. The spherical aggregates are more abundant in the mineralized zone and tend to concentrate mainly in direct contact with sand grains and occasionally with coffinite. Because of the extremely small size, an accurate visual estimate of pyrite is difficult in the field. Estimates from thin sections average 1 percent.

Calcite is present as a cement matrix in thin seams along the top and base of mineralized sandstones. It is generally absent in the oxidized, altered sandstone updip from ore except for scattered occurrences.

Metals that are sometimes associated with uranium in other mining districts in the United States are not diagnostic as pathfinder elements at Highland. Selenium is not common and its distribution is extremely erratic. Some slightly anomalous concentrations of vanadium coincide with uranium but some uranium-enriched sandstones show no vanadium enrichment. Molybdenum was not present in any of the samples tested from Highland. Lead, zinc, manganese, nickel and cobalt are all present but the concentrations are in a few parts per million and show no particular relationship to uranium mineralization.

A comparison of chemical analyses of cores and equivalent uranium calculated from natural gamma-ray logs of mineralized zones indicates that the deposits are essentially in radioactive equilibrium. For grades

less than 0.08 percent U_3O_8 the U/gU ratio is slightly less than 1, whereas grades greater than about 0.12 percent U_3O_8 have a U/gU ratio slightly greater than 1.

Origin and Geochemistry

The source of uranium for the Highland deposits is considered to be tuffaceous and/or arkosic debris indigenous to the host sandstones, their nearby facies equivalents and overlying sedimentary units. Unaltered sandstone, siltstone, and claystone with admixed tuff from the Fort Union Formation of the Powder River Basin yield uranium values ranging from 1 to 8 ppm. Oligocene and Miocene tuffs (White River and Arikaree Formations) from the Hartville Uplift east of Highland yielded values of 1 to 4 ppm. Each or both types of rock could serve as an adequate source.

The authors favor a tuffaceous source. Volcanism took place throughout the Tertiary, but as long as debris fell into a landscape undergoing fluvial sedimentation (such as is the case with the Paleocene and Eocene of the southern Powder River Basin), the tuffaceous material became incorporated and reworked into alluvial sediments. The coexistence of host sands and tuffaceous source greatly enhanced the availability of uranium to the host sandstones. It also simplified the process and timing of mineralization in that the same framework involved in fluvial sedimentation could be utilized for subsequent groundwater fluid movement and the indigenous volcanic debris could immediately undergo hydrolysis in a moist environment and the uranium released became part of the fluid system.

The transporting groundwater fluid is interpreted to have been an oxidizing, slightly alkaline, sulfate-bicarbonate type. The bicarbonates that are a part of the groundwater today are excellent complexing agents for uranium. In this system uranium would be carried as uranyl carbonate complexes (probably $UO_2(CO_3)_2^{--}$ and $UO_2(CO_3)_3^{---}$) until precipitation by reduction occurred.

Both biogenic hydrogen sulfide and inorganic hydrogen bisulfide are interpreted to be important in the total ore-forming process. Biogenic H_2S is significant during an initial phase of pyrite generation and HS^- during ore deposition and a second phase of pyrite generation.

The first generation of H_2S and pyrite in the sediments is a diagenetic process utilizing anaerobic sulfate-reducing bacteria. This process likely starts very early in the diagenesis and lithification of fluvial sediments as the genus Desulfovibrio are present in almost any environment containing organic matter and sulfate in solution. Hydrogen sulfide is being generated today in organic-rich (0.5-1.5% organic matter) flood basin sediments of the Missouri River (Dahl, 1961)[2].

The likelihood of sulfate-reducing bacteria being present in the Tertiary Basins of Wyoming is supported by the work of Jensen (1958)[4], Cheney and Jensen (1966)[5] and Austin (1970)[6]. Hagmaier (1971)[1] showed that conditions favorable for Desulfovibrio growth are present in the Powder River Basin. These authors suggest that hydrogen sulfide of biogenic origin likely provided the sulfur for pyrite that is associated with many Wyoming deposits in Tertiary rocks. This same hydrogen sulfide may have been the reducing agent which caused precipitation of the uranium. However, the authors interpret the biogenically-produced sulfides (those present in unaltered protore rock) to be an important but genetically unrelated factor in the formation of roll-type deposits in

the Powder River Basin. A similar interpretation has been made for the uranium deposits in the Gas Hills district of Wyoming by Cheney and Trammell (1973)[7]. The early-formed pyrite is a necessary step in building a geologic framework for later mineralization and is considered to be a form of geochemical host-rock preparation.

Inorganic HS^- of the type developed in the experimental model of Granger and Warren (1969)[8] is likely the final reducing agent for economic concentrations of uranium and for precipitation of second-generation pyrite enriched in the roll deposits. Their laboratory work and chemical theory indicates that groundwater moving through the host units may cause oxidation of preexisting sulfides (pyrite) to sulfite which decomposes to SO_4^{2-} and HS^- .

Some factors which make an inorganic reductant source attractive for the southern Powder River Basin deposits are:

1. The timing of mineralization is simplified and follows a natural, unbroken sequence of events from deposition of the host to precipitation of mineral.
2. The distribution of mineralization along the distal margins of the sandstones is compatible with the theory. The most important chemical control is the presence of pre-ore pyrite and this is concentrated and controlled by the facies boundaries. That is, more pyrite is located where anaerobic sulfate-reducing bacteria feed on the organic material most prevalent in the back swamp clays and silts. In the Highland area, the bulk of commercial mineralization is located near the easternmost extension of the host sandstones into backswamp sediments. Lack of continuous ore-grade mineralization along the northern part of the tongue can be explained by the local presence or absence of pyrite and perhaps calcite which would modify Eh-pH conditions along the oxidation front.
3. The juxtaposition of ore bodies strongly suggests one major geochemical control. There seems to be no question but that the ultimate location of the southern Powder River Basin deposits, although locally controlled by facies boundaries and their associated geochemical effects, is at a position where semi-regional (several kilometers) chemical equilibrium was reached between recharging oxidizing groundwater and a reduced sedimentary pile. Utilizing the ideas of Granger and Warren, this zone is positioned at a place updip from which pyrite within the host is oxidized and downdip from which pyrite is in chemical equilibrium with the groundwater solutions.
4. The shape and size of pyrite associated with ore at Highland is similar to that synthesized inorganically by Granger and Warren. No pyrite pseudomorphs of bacterial shapes or bacterial casts have been observed in ore at Highland to suggest that bacterial growth was taking place simultaneously with ore genesis.
5. The alteration products at Highland are compatible with the groundwater geochemistry developed by oxidation of pyrite. Since pyrite has largely been destroyed in the oxidized updip portion of the host sandstones, it can be assumed the original or re-charging solutions had an oxidizing Eh relative to pyrite and a slightly alkaline pH due to reactions with silicates (Hostetler

and Garrels, 1962)[9]. However, the oxidation of pyrite lowered the pH along an advancing front, apparently below that required for the stability of calcite, and left behind products (feldspar alteration and destruction of calcite) compatible with a slightly acid solution. Uranium concentrated during the process is compatible to early ideas put forth by Gruner (1956)[10]. The color changes associated with the boundary between oxidized rock and mineralization is dependent on the type of fixation of ferric iron in the oxidized zone. Goethite is the common alteration product of pyrite and it, in turn, dehydrates to hematite.

Summary - Sequence of Events

The Highland uranium deposits in Wyoming are model examples of large roll-type bodies. The requirements and sequence of events leading to their interpreted genesis are outlined below.

1. Deposition of permeable fluvial host sandstones and associated facies which contain organic debris. A master stream system flowed northward into the Powder River Basin depositing clastics in an alluvial complex. Its location was sympathetic with the synclinal axis of the basin.
2. Early formation of pyrite in the host sands and surrounding sediments. This was a diagenetic process with the iron sulfides being formed by the action of H_2S on available iron. The H_2S was generated by an anaerobic biogenic process utilizing sulfate-reducing bacteria.
3. Persistence of the structural and topographic configuration of the basin. This created a compatible and similar hydrodynamic framework for the movement of groundwater through the Highland sand system. Fluid movement was from the southwest (groundwater recharge area) to the northeast (discharge area). Early Tertiary uplift around the southern periphery of the basin allowed the hydrodynamic groundwater system to operate effectively after deposition and burial of the host sediments.
4. Source of uranium in the tuffaceous and arkosic debris indigenous to the host and surrounding units.
5. Steady intake of oxidizing meteoric water in the recharge area.
6. Slow laminar flow of this fluid through the Tertiary rocks with flow lines converging toward the host sandstones which are below the water table. This provided a leach and transportation mechanism for uranium ions taken into solution.
7. Oxidation of early-formed pyrite in and around the host units with a subsequent lowering of pH, below that required for the stability of calcite. This oxidation of biogenically-produced pyrite results in unstable sulfite ions which disproportionate into inert sulfate ions and bisulfide ions (Granger and Warren, 1969 [8]). Uranium in this environment would be taken into solution as carbonate ions.
8. Continuation of this dynamic process concentrated uranium to economic levels within the host sandstones at an interface bounded

by oxidized sandstone updip and reduced sandstone downdip. The interface is an equilibrium surface updip from which pyrite has been depleted by oxidizing solutions and downdip from which it is in chemical equilibrium with the spent or neutralized solutions. The reductant responsible for precipitation of uranium, pyrite, and calcite within the interface zone is considered to be inorganic bisulfide (HS^-).

REFERENCES

- [1] HAGMAIER, J. L., Groundwater flow, hydrochemistry, and uranium deposition in the Powder River Basin, Wyoming, unpublished Ph.D. thesis, Grand Forks, North Dakota, library, University of North Dakota (1971).
- [2] DAHL, A. R., Missouri River studies: alluvial morphology and Quaternary history, unpublished Ph.D. thesis. Ames, Iowa, library, Iowa State University of Science and Technology (1961).
- [3] LANGEN, R. E., KIDWELL, A. L., Geology and geochemistry of the Highland uranium deposit, Converse County, Wyoming (abs.), Econ. Geol. 66 1 (1971) 207.
- [4] JENSEN, M. L., Sulfur isotopes and the origin of sandstone-type uranium deposits, Econ. Geol. 53 5 (1958) 598.
- [5] CHENEY, E. S., JENSEN, M. L., Stable isotope geology of the Gas Hills, Wyoming, uranium district, Econ. Geol. 61 1 (1966) 44.
- [6] AUSTIN, S. R., Some patterns of sulfur isotope distribution in uranium deposits, Earth Sci. Bull. 3 2 (1970) 5.
- [7] CHENEY, E. S., TRAMMELL, J. W., Isotopic evidence for inorganic precipitation of uranium roll ore bodies, Amer. Assoc. Petrol. Geol. 57 7 (1973) 1297.
- [8] GRANGER, H. C., WARREN, C. G., Unstable sulfur compounds and the origin of roll-type uranium deposits, Econ. Geol. 64 2 (1969) 160.
- [9] HOSTETLER, P. B., GARRELS, R. M., Transportation and precipitation of uranium and vanadium at low temperatures, with special reference to sandstone-type uranium deposits, Econ. Geol. 57 2 (1962) 137.
- [10] GRUNER, J. W., Concentration of uranium in sediments by multiple migration-accretion, Econ. Geol. 51 6 (1956) 495.

DISCUSSION

R. H. DE VOTO: This is the first time I have heard mention of tuffaceous material in the Paleocene deposits. What specific evidence do you have of the tuff? You apparently believe that ground water moved through the shales and siltstones, i. e. relatively impermeable rocks. Is this true?

A. R. DAHL: With the aid of a hand lens, white tuffaceous material can be recognized in the Paleocene sediments; it is quite abundant in the Eocene, too. Most of it is weathered, and a good deal has gone to bentonite (montmorillonite). Occasionally a few doubly terminated bipyramids of high-temperature quartz can be recognized, probably representing a contribution from volcanic material.

P. C. ELLSWORTH: Could you tell us how sharp and complete the loss of sulphate is?

A. R. DAHL: I can give you some median values. In the shallow ground water the recharge areas show a mean sulphate of 700 ppm, while the discharge areas show a mean of 140 ppm. Deep ground water in the recharge areas has a mean sulphate of 23 ppm, and in the discharge areas 5 ppm.

P. C. ELLSWORTH: Have you any information on the down-dip changes in pH?

A. R. DAHL: Only in a general range. The pH values do increase with increasing flow-path length, and this of course suggests a higher pH in the down-dip direction.

I. A. BREGER: If the enclosing sediments supposedly contain uranium, does the associated coal also contain it?

A. R. DAHL: The stratigraphically closest coals that are being mined - the Badger and School coals about 600 ft above the ore sandstones - contain little or no uranium. The thinner coals and lignites in close stratigraphic proximity to the ore sandstones contain trace amounts of uranium. Some organic trash within the best sandstones also contains ore-grade uranium.

J. BERNAZEAUD: I gather you take the tuffaceous material in the sandstone to be the principal source of uranium in the Highlands deposit. Presumably you have some numerical data on the concentrations in tuffaceous rock as compared with other enclosing formations. Could you give us some indication of these concentrations?

A. R. DAHL: Yes. In the relatively unaltered sandstone, siltstone and claystone of the Fort Union Formation in the southern Powder River Basin, with admixed tuff, the concentration ranges from 1 to 8 ppm. Pure tuffs from the Hartville Uplift east of the Powder River Basin have yielded values of 1 to 4 ppm uranium.

J. PASQUALI: From the presentations of Adler, Harshman and Granger, I have the impression that large volumes of water must flow to form uranium deposits. In this sense it puzzles me that you should be suggesting a flow of water through claystones, lignites and so on. Are you puzzled too?

A. R. DAHL: Not at all. I agree of course that the formation of an ore body requires huge quantities of ground water carrying relatively small amounts of uranium in solution (a few parts per 10^9) which are precipitated by a reducing trap. However, you seem to be assuming that the sediments were lithified at the time when the uranium deposits were formed. I doubt whether this was so, because I interpret the deposits to have been formed relatively early - although they were certainly buried. The fact of the matter is that the Paleocene "rocks" of the Powder River Basin are hardly "rocks" even today; they are only loosely consolidated and could hardly be called lithified in the normal sense.

S. H. U. BOWIE: Is there any evidence in the Powder River Basin or elsewhere in the United States of America of leached and unleached tuffs which would demonstrate that uranium had been derived from such rocks? It should be possible to demonstrate depletion and enrichment zones.

A. R. DAHL: A very pertinent question, but one to which I cannot give a satisfactory reply. The problem is to find an unleached tuff, or at least one you could reasonably interpret to be unleached.

F. C. ARMSTRONG: Leaching of the altered arkosic sandstone prism hardly strikes me as an adequate source for the uranium in the deposits. Conservative materials balance calculations in the Gas Hills did not supply nearly enough uranium for the deposits, not to mention the non-ore uranium-bearing rock. Have you done any materials balance calculations, and, if so, how did they come out? What assumptions did you make, particularly as regards the efficiencies of extraction and precipitation?

A. R. DAHL: I have done materials balance calculations as an academic exercise, and they came out satisfactorily. I do not remember exactly how many cubic miles of rock were involved. The computation was made within the interpreted ground-water flow network up-gradient from the Highlands deposits, using a 50% efficient recovery factor.

A. G. DARNLEY: How did Exxon discover the deposits you have been describing?

A. R. DAHL: Essentially by applying the familiar procedures of exploration geology. We began studying the basin late in 1966. It was an obvious place to explore in view of the general characteristics of the region: other Tertiary basins in Wyoming hold major uranium deposits. There were also some old, small open-pit mines in the Wasatch Formation that had produced uranium in small quantities in the 1950s. Late in 1966 and early in 1967, field work was performed along the outcropping rocks at the southern margin of the basin. We mapped the host characteristics, recorded uranium shows, noted the direction of sediment transport and observed alteration characteristics. By means of oil and gas test holes the potential hosts were mapped into the subsurface. A small amount of drilling was done late in 1967; in 1968 a larger drilling programme was undertaken, and the actual discovery took place in August 1968.

I. WENDT: Does the supposedly leached tuffaceous material show a lower U:Th ratio than tuffaceous material which has obviously not been leached? Thorium is probably not leached as strongly as uranium, so one would expect to find different ratios corresponding to different degrees of leaching.

A. R. DAHL: Your question is akin to Mr. Bowie's, and I cannot give you a satisfactory answer because I do not know what "obviously unleached" tuff is. In principle, however, I should say that you are probably right.

ALTERATION OF DETRITAL MAGNETITE-ILMENITE IN CONTINENTAL SANDSTONES OF THE MORRISON FORMATION, NEW MEXICO

S.S. ADAMS, H.S. CURTIS, P.L. HAFEN

The Anaconda Company,

Uranium Division,

Grants, N.Mex.,

United States of America

Abstract

ALTERATION OF DETRITAL MAGNETITE-ILMENITE IN CONTINENTAL SANDSTONES OF THE MORRISON FORMATION, NEW MEXICO.

Minor amounts of magnetite and ilmenite are now present locally in the fluvial sandstones of the Morrison Formation. Where these minerals are absent or strongly altered, particularly within and adjacent to uranium deposits, the sands contain authigenic leucoxene, anatase, and perhaps other titanium oxide minerals. Studies of thin sections and heavy mineral concentrates from drill-hole cuttings and core have identified stages in the alteration of ilmenite and magnetite. These alterations are interpreted to have occurred in oxygen-deficient ground waters through the selective dissolution of iron from the magnetite and ilmenite. This dissolution may have been promoted by dissolved organic species. The sites of altered titaniferous magnetite and ilmenite are now occupied by clots of titanium oxides. The intensity of a series of periods of alteration, resulting from variations in the oxidation potential within the ground waters, can be recognized in some instances. It is suggested that the chemical conditions which produced the alteration assemblages described here are essentially those under which the uranium deposits formed. Most important, the interpretation of these alteration assemblages in thin sections and drill cuttings is a useful exploration guide for those deposits in which there is an antipathy between detrital ilmenite and magnetite and uranium mineralization.

INTRODUCTION

The sandstones, siltstones, and shales of the Morrison Formation of Northwestern New Mexico and adjacent areas locally contain from trace amounts to approximately one-half percent detrital magnetite, hematite, and ilmenite. The paucity of these detrital iron minerals in the proximity of uranium deposits in sandstones has been noted by many investigators (for example, [1]). Such observations have been interpreted as evidence that these minerals were destroyed by either oxidizing or reducing ground waters which may have been related to formation of the uranium deposits.

This paper presents observations on the alteration of ilmenite and magnetite noted during the examination of several hundred thin sections

TABLE I Stratigraphy and proportional composition of the Morrison Formation, Colorado Plateau, Western United States [2].

		MAJOR ROCK TYPES (%)	
<u>Stratigraphic Unit</u>	<u>Volume (%)</u>	<u>Sandstone and Conglomerate</u>	<u>Mudstone, Siltstone, Claystone, and Miscellaneous</u>
Jackpile Sandstone	(a)	80 ^(b)	20 ^(b)
Brushy Basin Member	34	11	89
Westwater Canyon Member	12	83	17
Recapture Member	15	73	27
Salt Wash Member	<u>39</u>	61	39
Total	100		

(a) Data for the Jackpile sandstone is not given separately in the reference cited [2] but the total volume percent of the total Morrison Formation is negligible.

(b) Authors' estimates.

of Westwater and Jackpile sands collected from outcrops and drill core in Northwestern New Mexico and adjacent areas. The alteration of these minerals is interpreted to have occurred after deposition of the sediments through the action of oxygen-deficient ground waters which produced associated alteration assemblages and ultimately contributed to the formation of the uranium deposits. In this study, the black opaque minerals magnetite, ilmenite, and lesser hematite were identified by X-ray methods in some heavy mineral concentrates but were not identified in thin sections. Throughout this paper, these heavy minerals will collectively be referred to as magnetite-ilmenite.

The stratigraphic units of the Morrison Formation are given in Table I. The principal uranium deposits of the Salt Wash Member in the Four Corners Region are in the Slick Rock District and Uravan Mineral Belt, Colorado and the Lukachuka Mountains District, New Mexico (Figure 1).

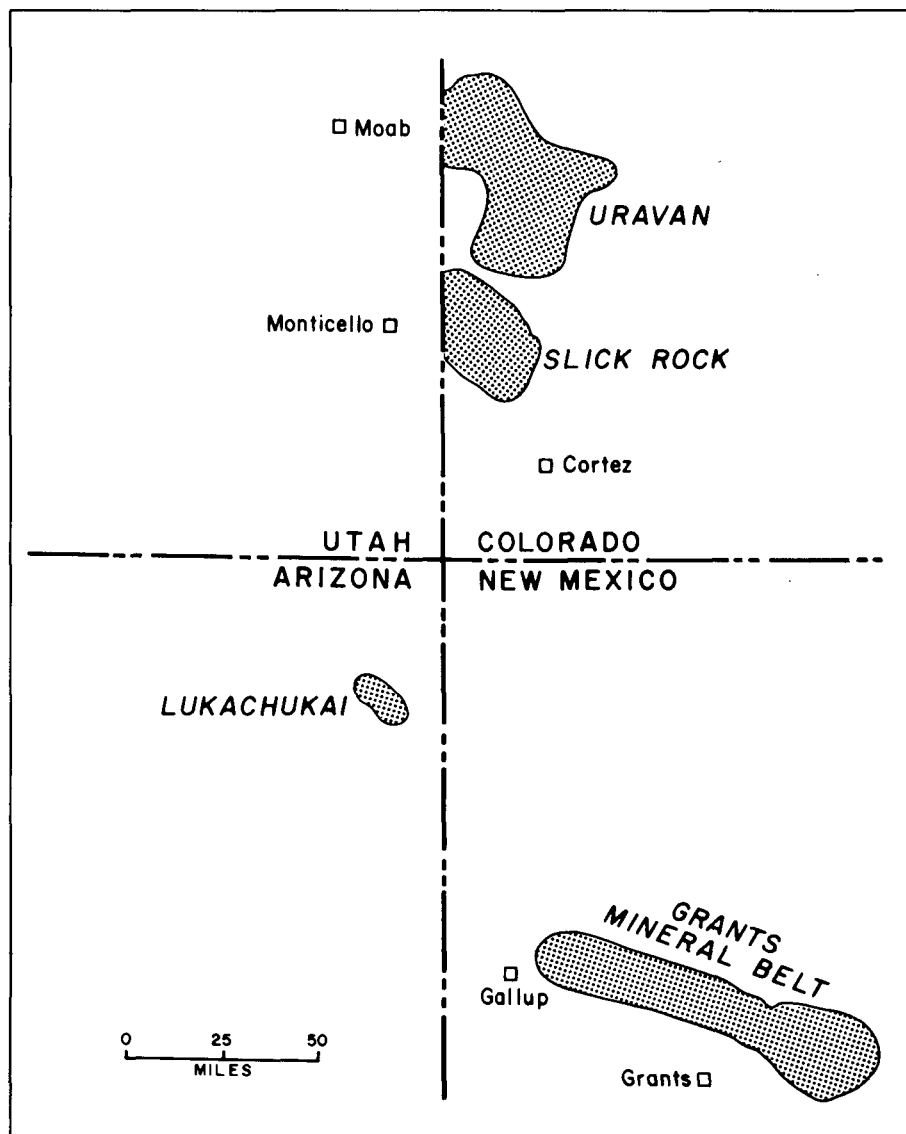


FIG. 1. Location map for the principal uranium districts of the Morrison Formation in the Four Corners Region, Colorado Plateau, Western United States.

TABLE II Stability of detrital heavy minerals (modified after [3]).

Very Unstable	Unstable	Moderately Stable	Stable	Ultrastable
Olivine	Hornblende	Epidote	Apatite	Rutile
	Actinolite	Kyanite	Garnet (iron poor)	Zircon
	Augite	Garnet (iron rich)	Staurolite	Tourmaline
	Diopside	Sillimanite	Monazite	Anatase
	Hypersthene	Sphene	Biotite	
	Andalusite	Zoisite	Ilmenite	
			Magnetite	

The extensive deposits of the Grants Mineral District are in the Westwater Canyon Member and the Jackpile sandstone.

This paper has been prepared and presented with the generous permission and support of The Anaconda Company. The staff of that company has contributed substantially, in particular H. Salek, G. Stanton and D. Gamel.

Magnetite-Ilmenite in Sandstones

As background to the discussion of magnetite-ilmenite in the Morrison Formation, the abundance, distribution, and alteration of magnetite-ilmenite in other sandstones, including some uranium-bearing sandstones, is briefly described in the following paragraphs.

Magnetite and ilmenite are common accessory minerals in many clastic sediments, their abundance depending upon: a) their concentration in the source rocks, b) weathering and abrasion during transport,

TABLE III Concentrations of black opaque (largely magnetite and ilmenite) and other heavy minerals in selected sandstones (a)

	Number of Samples	Total Heavy Minerals	Black Opaque Minerals (b)	Non- Opaque Minerals (c)	Pyrite
Shirley Basin, Wyoming (d)					
Wasatch Formation					
Unaltered Sandstone	11	2.79	.13	2.03	.63
Altered Sandstone more than 5 ft. from ore	11	2.22	.15	2.07	
Altered Sandstone less than 5 ft. from ore	10	2.08	.13	1.79	.16
Unaltered Sandstone with more than .1% U_3O_8	7	3.04	.18	1.71	1.15
Slick Rock Dist., Colorado (e)					
Morrison Formation					
Brushy Basin Member					
light red-brown sandstone	24	.38	.247	.131	traces
light gray sandstone	32	.45	.131	.314	.005
Salt Wash Member					
light reddish-brown sand- stone	66	.31	.183	.127	traces
light gray carbonaceous unmineralized sandstone	32	.16	.067	.091	.002
light gray sandstone adja- cent to mineralized layers	74	.11	.002	.100	.008
Colorado Plateau (f)					
Morrison Formation					
Salt Wash Member	253	.23 (g)	.123 (j)	.107	
Recapture Member	59	.44	.305 (j)	.135	
Westwater Member	58	.47 (h)	.341 (j)	.129	
Brushy Basin Member	49	.32 (i)	.201 (j)	.119	
Laguna Dist., N.M. (h)					
Morrison Formation					
Jackpile Sandstone					
less than .01% U_3O_8	112	.093	nil	.074	.019
greater than .01% U_3O_8	31	.219	nil	.128	.091

(a) All data presented as average weight percent of whole rock

(b) Largely magnetite and ilmenite

(c) Includes zircon, tourmaline, rutile, anatase, leucoxene, hornblende, epidote, garnet, barite, and possibly other minerals.

(d) Source: modified after [7]

(e) Source: modified after [8]

(f) Source: modified after [2]

(g) Average of 266 samples

(h) Average of 59 samples

(i) Average of 53 samples

(j) Includes all opaque minerals, hence any pyrite and leucoxene which might be present

(k) Source: this paper

c) sorting during deposition, and d) alteration after deposition. These minerals are comparatively resistant to destruction under earth surface conditions. Among the detrital heavy minerals, Pettijohn, Potter, and Siever [3] rank ilmenite and magnetite as "stable" together with biotite, monazite, and apatite (Table II). Ilmenite and magnetite are to be expected, therefore, in clastic sediments derived from ilmenite and magnetite-bearing source rocks. The combined ilmenite and magnetite content of most arenaceous sediments is between .13 and .75 weight percent [4] [5] [6]. Data for some sandstones which have yielded important uranium deposits are given in Table III. The source for these concentrations may be basic igneous rocks, which contain 5 to 8 weight percent combined ilmenite and magnetite, or granite rocks which contain only 1 to 5 combined weight percent, but which are generally more abundant in the earth crust [9]. Coarse clastic sediments and their metamorphic equivalents may also be important source rocks. The source of the ilmenite and magnetite deposited in the sands and shales of the Morrison Formation is not known with certainty. The abundance of detrital volcanic, plutonic, metamorphic, and older sedimentary clasts suggests, however, that contributions were probably received from all these rock types.

Heavy minerals may be uniformly disseminated within clastic sediments, concentrated in heavy mineral suites along bedding planes, or in more massive concentrations such as placer sands. Within the Westwater and Jackpile sandstones, zircon, tourmaline, rutile, ilmenite and magnetite (or their alteration products) and minor amounts of other heavy minerals generally occur as disseminated grains. Concentrations in thin zones are occasionally found along bedding planes.

The original concentrations of ilmenite and magnetite in the sands of the Morrison Formation are not known with certainty due to the widespread post-depositional destruction of these minerals. Bowers and Shawe [8]

give an average of .31 percent black opaque, heavy minerals for the light red sands of the Salt Wash Member. As ilmenite and magnetite commonly constitute the majority of the black opaque, heavy minerals and as these minerals are least altered in the light red sands, this is the best estimate of the detrital concentration of these minerals. The gray and mineralized sands, by contrast, contain .16 and .11 percent black opaque minerals indicating reduction and leaching of iron. The titanium content of the unmineralized Salt Wash sands, expressed as a geometric mean, is approximately .05 percent Ti compared with .095 for uranium-bearing mill pulps. The titanium content of the Jackpile and Westwater sands (Table IV) is in the same general range (.05 to .18 percent titanium) with uranium-rich samples showing some enrichment in titanium, particularly according to the data of Kendall [10] for the Westwater Member. It is likely, therefore, that the concentration of magnetite and ilmenite in the Jackpile and Westwater sands were comparable to the Salt Wash Member.

Stearn [9] has estimated that the average magnetite content of sandstones is .58 percent; the average ilmenite content is .25 percent. Magnetite and ilmenite are present as accessory minerals in many sandstones which are not known to contain uranium deposits in concentrations ranging from nil to several percent. Magnetite and ilmenite are present but irregularly distributed in most sandstones which contain uranium deposits. In some of these sandstones, heavy minerals have been destroyed by processes related to the formation of uranium deposits, while in others they are essentially unaltered. In the uranium-bearing Wasatch Formation of the Tertiary Basins of Wyoming, for example, detrital magnetite and ilmenite have not been significantly altered even by the processes which have formed the uranium roll front deposits. Files [15] found magnetite and ilmenite in almost all the samples from ore, altered sandstone, and unaltered sandstones in the Gas Hills, Crooks Gap, and Shirley Basin

TABLE IV Estimated average titanium content of sandstones which contain significant uranium deposits.

Stratigraphic Unit	Rock or Ore Type	Number of Samples	Titanium (percent)	Footnote
CUTLER FORMATION		14	.09	(a)
CHINLE FORMATION - Shinarump and Moss Back Members	Unmineralized Sandstone	97	.092	(a)
MORRISON FORMATION				
Salt Wash Member	Uranium-bearing mill pulps from 215 mines	215	.095	(b)
Basal Strata		29	.05	(a)
Intermediate Strata		42	.05	(a)
Upper Strata		25	.05	(a)
	Red Mudstone	13	.10	(a)
	Green Mudstone	19	.14	(a)
Westwater Canyon Member				
	Sandstone - less than .01% U_3O_8	8	.181	(c)
	Sandstone - more than .01% U_3O_8	8	.324	(c)
	Shale	6	.296	(c)
	Primary Ore	193	.12	(d)
	Jordisitic Sandstone	31	.12	(d)
	Redistributed Ore	59	.09	(d)
	Gray barren sandstone	88	.13	(d)
	Tan barren sandstone	65	.10	(d)
	Green claystones	15	.26	(d)
Brushy Basin Member				
	Bentonitic Mudstone	14	.25	(a)
	Non-bentonitic Mudstone	14	.30	(a)
Jackpile Sandstone				
	Sandstone - less than .01% U_3O_8	16	.051	(e)
	- more than .01% U_3O_8	90	.053	(e)
	Sandstone - less than .01% U_3O_8	11	.043	(f)
	- more than .01% U_3O_8	9	.086	(f)
WASATCH FORMATION				(g)
Crooks Gap District, Wyoming	Unaltered Sandstone	3	.101	
	Ore (>1.0% U_3O_8)	2	.090	
	Altered Sandstone	3	.099	
Gas Hills District, Wyoming	Unaltered Sandstone	2	.085	
	Ore (>1.0% U_3O_8)	2	.073	
	Altered Sandstone	2	.074	
Shirley Basin District, Wyoming	Unaltered Sandstone	1	.169	
	Ore (>1.0% U_3O_8)	2	.098	
	Altered Sandstone	2	<.073	

- (a) Analyses by semi-quantitative spectroscopy; average given as geometric mean [6].
- (b) Average given as geometric mean [11].
- (c) Analyses by X-ray fluorescence [10].
- (d) Data compiled by Squyres [12] from data of Granger [13]; analyses by semi-quantitative spectroscopy.
- (e) Analyses by semi-quantitative spectroscopy [14].
- (f) Analyses by X-ray fluorescence (source, this paper).
- (g) Analyses by X-ray fluorescence [15].

Districts. He noted, however, that some ilmenite in ore was partially surrounded by pyrite. He also noted that the abundance of ilmenite was highest in the Shirley Basin and lowest in the Crooks Gap District. In the Shirley Basin, Harshman [7] noted that "the black opaque minerals from altered and unaltered sandstone are similar, and that they constitute 4.5 to 7.0 percent of the heavy-mineral samples" (Table III). In contrast to the preceding observations, King and Austin [16] reported that in the Gas Hills magnetite is characteristic of remote barren (unaltered) ground, apparently having been "removed from barren interior and mineralized ground in the course of mineralization." In the Slick Rock District, Colorado, Bowers and Shawe [8] identified three types of sandstone in the Salt Wash Member of the Morrison Formation, each with its characteristic total heavy mineral and black opaque mineral content (Table III). They noted that the abundance of black opaque minerals decreased in the sequence light red sandstone, light gray sandstone remote from uranium ore bodies, to light gray sandstone near ore bodies. This decrease is accompanied by an increase of anatase which they interpret as having formed from the alteration of ilmenite.

Magnetite and ilmenite are rare in the Jackpile and Westwater sandstones of the Morrison Formation, particularly in the vicinity of uranium deposits. Squyres [12] and Kendall [10] studied suites of samples from the operating mines in the Ambrosia Lake District and found a virtual absence of ilmenite and magnetite. Nash [17] made the same observation for the Jackpile sandstone in the Laguna District. These observations have been confirmed in this study with several hundred thin sections and heavy mineral separates from outcrop and drill core samples of the Jackpile sandstone and Westwater and Brushy Basin Members of the Morrison Formation. These studies indicate that permeable sandstones within several hundred feet of uranium deposits are essentially devoid of black opaque minerals. By contrast, siltstone, bentonitic shale, and sandstones

hydrologically isolated by these impervious rocks, together with sandstones remote from known uranium deposits, commonly contain unaltered or only partially altered ilmenite and magnetite. This pattern of ilmenite and magnetite distribution, together with the pervasive distribution of authigenic leucoxene and anatase in magnetite- and ilmenite-free sandstones, suggest that these detrital minerals have been destroyed over wide areas of the Westwater and Jackpile sandstones.

The concentration of titanium in sandstones provides additional information for study of the abundance of titanium-bearing detrital minerals and the mobility of titanium in ground water during the post-depositional alteration of these minerals. The average titanium content of sandstones is .31 percent titanium [18], essentially the same as the estimated average titanium content of the earth's crust (.33 percent titanium). Sandstones of the Colorado Plateau (.02-.07 percent titanium) and important uranium-bearing sandstones, by contrast, contain significantly less titanium (.05-.17 percent titanium). Estimates of the titanium content of sandstones which contain significant uranium deposits are compiled in Table IV. The lower titanium concentration in these sandstones is due, in part, to the arkosic lithology of most uranium-bearing sandstones, in contrast to quartzites and mature sandstones in which detrital magnetite-ilmenite are commonly more concentrated. It may also reflect a low crustal abundance of titanium in the Colorado Plateau and possibly some post-depositional leaching of titanium.

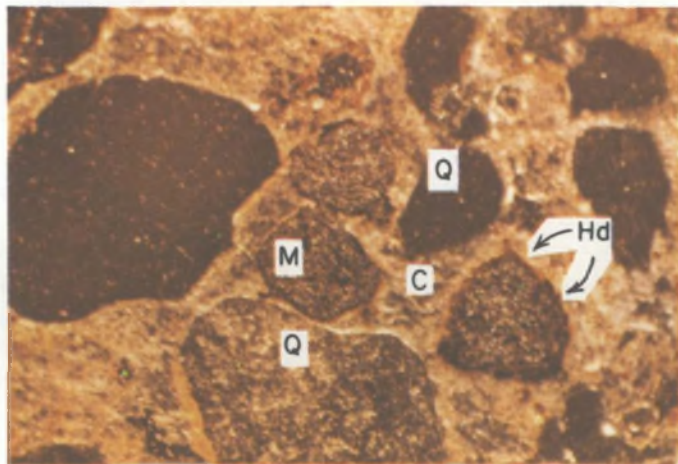
Alteration of Magnetite-Ilmenite

The alteration of detrital magnetite-ilmenite in the Morrison sands is variable with iron dissolution ranging from negligible to complete. Whereas alteration appears to be completely transitional, the degree of iron dissolution from magnetite-ilmenite grains in any given thin section is generally of the same magnitude. The altered grains are readily

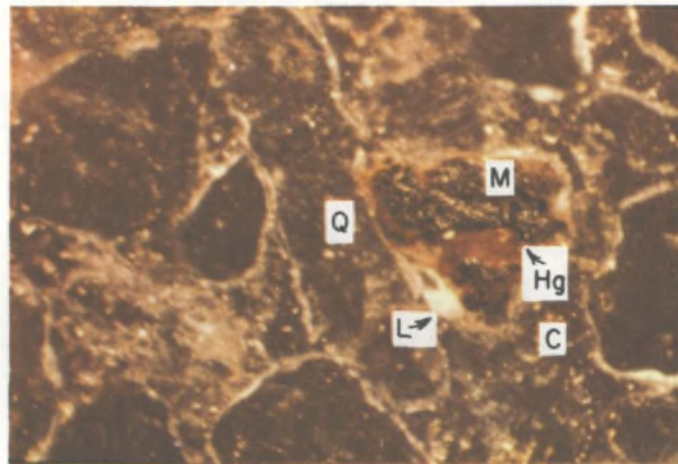
apparent in thin section when examined under oblique reflected light. Where local variations in the degree of iron dissolution do occur they are likely the result of variations in permeability resulting from sorting and cementation of the sandstone. Appropriate pE-pH-log activity diagrams indicate that optimum conditions for iron dissolution from magnetite-ilmenite grains in a sedimentary environment would have occurred under reducing, neutral to acid conditions.

The degree of iron dissolution from detrital magnetite-ilmenite in Westwater and Jackpile sands may be conveniently discussed as negligible, moderate, and intense. In some instances much of the iron has been sulfidized to pyrite in proximity to the parent magnetite-ilmenite grains, whereas in other instances the iron has been transported away from detrital iron minerals leaving only TiO_2 as evidence of the previous detrital sites. The four photographs in Figure 2 are examples of sandstones that initially contained detrital magnetite-ilmenite and show respectively, negligible iron dissolution, moderate iron dissolution, intense iron dissolution and sulfidation, and intense iron dissolution and removal. The following is a brief description and interpretation of the degree of magnetite-ilmenite alteration observed in these Westwater sandstone samples.

Figure 2(a). The metallic to submetallic magnetite-ilmenite grains have experienced negligible iron dissolution, alteration consisting only of dusty hematite rims around the detrital iron minerals. The dusty hematite which locally penetrates into the magnetite-ilmenite grains along fractures and crystal planes may have formed during weathering and transport or may have developed during the post-depositional exposure to oxidizing ground waters or a combination of both. It does not appear that significant iron leaching occurred during weathering and transport under oxidizing conditions. We interpret this sample as not having been exposed to a strong reducing environment as explained in a later section.

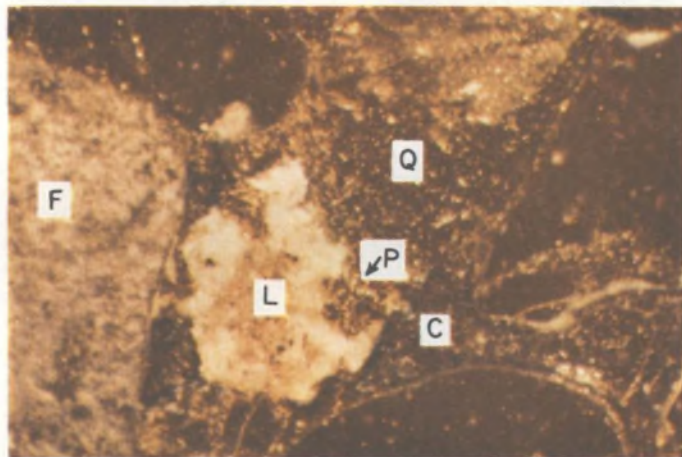


(a) Negligible iron dissolution

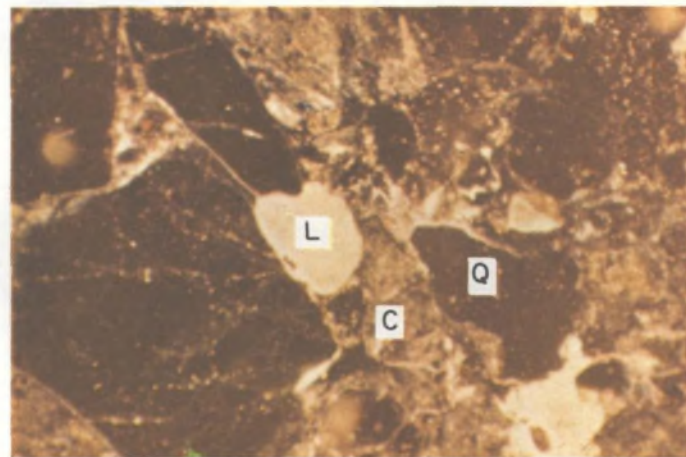


(b) Moderate iron dissolution

0 0.5 mm



(c) Intense iron dissolution, iron sulfidized to pyrite



(d) Intense iron dissolution, iron removed

EXPLANATION

M: magnetite-ilmenite; P: pyrite; Q: quartz; L: leucoxene;
Hd: dusty hematite; Hg: glassy hematite; C: clay

FIG.2. Photographs of detrital magnetite-ilmenite alteration in the Westwater sandstone, oblique reflected light.

Figure 2(b). TiO_2 is present as rims around, and patches within, the detrital magnetite-ilmenite grains which contain residual metallic to sub-metallic magnetite-ilmenite. Some hematite wash is evident within the detrital grain, suggesting that a period of oxidation preceded the reducing environment in which the iron-free TiO_2 formed. We believe this sample was exposed to an oxidizing environment followed by a reducing environment of insufficient intensity or duration to effect complete iron dissolution from the detrital magnetite-ilmenite grains.

Figure 2(c). This sample illustrates intense iron dissolution from ilmenite-magnetite and the incorporation of the iron into pyrite. The TiO_2 is clear and apparently free of iron, suggesting intense leaching. Pyrite occurs as patches within, and adjacent to, the parent detrital heavy mineral. We suggest that this sandstone has been subjected to an intensely reducing geochemical environment in which sufficient sulfide was available to sulfidize the iron to pyrite. There is no evidence of either an earlier or a later (post-pyrite) period of oxidation.

Figure 2(d). This sample illustrates detrital magnetite-ilmenite alteration where intense iron dissolution and mobilization have occurred. The available iron has been taken into solution and transported away from the parent detrital grains. Leucoxene remains as the only evidence of the original detrital iron minerals. We interpret this alteration as having occurred in a strongly reducing, sulfide-deficient, geochemical environment.

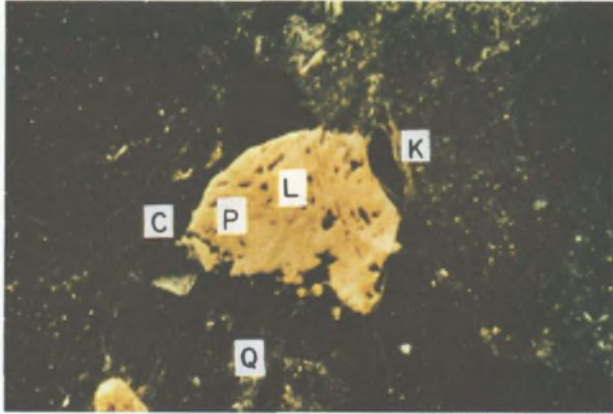
The photographs in Figure 3 are examples of altered iron-bearing detrital grains which could not have survived transport and deposition in the present form, hence must have been altered in place.

Figure 3(a). The fragile TiO_2 grain form, preserving the sub-rounded shape of the original detrital mineral, is common in the Jackpile and Westwater sands where intense iron dissolution has occurred. The internal fabric of TiO_2 laths and voids, probably reflecting primary structural

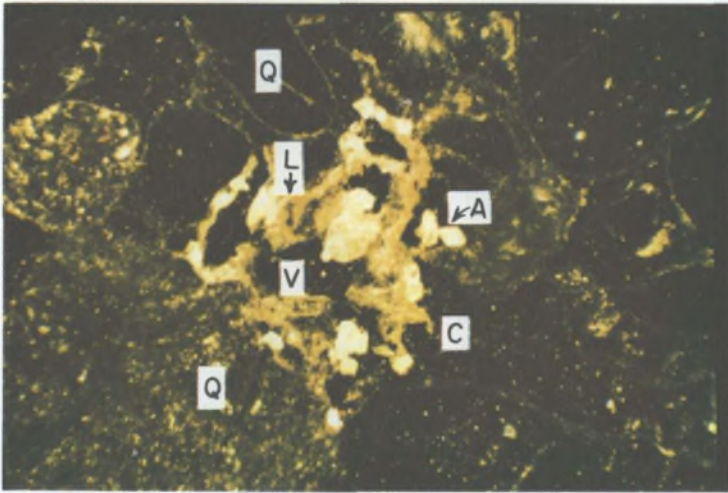
and chemical features of the detrital mineral, has been accentuated by the removal of iron. This fragile open structure could not have survived the abrasion of transport and deposition, hence the alteration must have occurred within the sands at a later time. Note the small bleb of authigenic pyrite between the TiO_2 laths. The embayed portion of the leucoxene grain resulted from collapse of the open lath structure adjacent to a small quartz grain.

Figure 3(b). The space originally occupied by a detrital titanium-bearing grain is now indicated only by recrystallized TiO_2 around the margin of a void. The relatively small amount of TiO_2 compared with the size of the void suggests the detrital grain may have been a titaniferous magnetite or other titanium-bearing, iron-rich mineral. Considerable iron has been leached and removed from the vicinity of the grain.

Detrital magnetite-ilmenite in Morrison sandstones survived the oxidizing environments of weathering, transport, and early post-depositional oxygenated ground waters. Whereas hematite formed on and within the grains, there does not appear to have been strong leaching and removal of iron. During diagenesis, however, particularly within permeable sands in the vicinity of organic concentrations, virtually all of the iron was removed from detrital iron minerals, leaving only TiO_2 as evidence of their previous existence. As illustrated in Figures 2 and 3, the TiO_2 commonly retains the sub-rounded detrital form of the parent magnetite-ilmenite grains. It is proposed that studies of detrital magnetite-ilmenite alteration can: 1) aid recognition of originally organic-rich sediments from which the organic material has been removed or redistributed, and 2) define permeable channels along which organic-rich solutions have migrated. As both organic material and permeable sands are critical to the formation and localization of the uranium deposits in the Morrison sands, these alteration studies are useful in the exploration for new deposits.



(a) TiO_2 lath-like texture inherited from detrital grain



(b) Anatase, leucoxene and void space in detrital grain site

0 0.4 mm

EXPLANATION

Q: quartz; L: leucoxene; C: clay matrix; A: anatase;
P: pyrite; K: potassium feldspar; V: void

FIG. 3. Photographs of types of TiO_2 resulting from magnetite-ilmenite alteration in the Westwater sandstone, oblique reflected light.

DISCUSSION

The alteration minerals described in the preceding paragraphs are typical of assemblages formed under low temperature, aqueous conditions. Other authigenic minerals in the Morrison Formation, such as kaolinite, quartz, and calcite, also formed during low temperature diagenesis and post-depositional alteration of the sediments. In this section we consider aspects of the chemistry of the ground waters in which these mineral assemblages were formed. The assemblages will first be considered in an inorganic system and then in a "limited" organic system in which the organic material is assumed to have participated only by lowering the pH and oxidation potential of the ground water. These systems are discussed by means of thermodynamic data presented as pE-pH-activity diagrams at 25°C. Consideration will then be given to the possible role of soluble, organic material in the leaching of iron from magnetite and ilmenite.

Three pE-pH-activity diagrams (Figures 4, 5 and 6), involving the iron and titanium phases of interest, have been constructed from the thermodynamic data in Table V. The boundaries for phases and aqueous species in the diagram were constructed with data given in Appendix I.

Relations for the oxides of iron and titanium in the system Fe-Ti-O-H are presented in Figure 4. Although goethite is stable relative to hematite at 25°C and an activity of water (a_{H_2O}) greater than about 0.5 [20], kinetic and grain-size factors render fine-grained goethite less stable than hematite. Anatase is stable relative to rutile and hydrous titanium oxide ($TiO_2 \cdot H_2O$) throughout the pH and pE ranges of interest. As anatase is also a common mineral in alteration assemblages of the Morrison Formation, it has been used as the stable titanium oxide phase in the construction of all diagrams. Anatase and hematite have a wide stability range relative to ilmenite and magnetite. Throughout the stability fields of these phases, detrital ilmenite and magnetite would

TABLE V Thermodynamic data for Fe-Ti-S-O-H system

Formula	Name	Gram Formula Weight	Free Energy of Formation (Cal/G.F.W.) ^a	Reference
H ₂ O	Water	18.015	-56688 ± 20	[19]
TiO ₂	Anatase	79.899	-212626 ± 120	[19]
FeTiO ₃	Ilmenite	151.745	-277065 ± 390	[19]
Fe ₂ O ₃	Hematite	156.692	-177728 ± 310	[19]
Fe ₃ O ₄	Magnetite	231.539	-243094 ± 510	[19]
FeS ₂	Pyrite	119.975	-38296 ± 410	[19]
FeS	Troilite	87.911	-24219 ± 360	[19]
Fe ⁺⁺⁺ _{aq}	Ferric Ion	55.847	-2520 ± 50	[19]
Fe ⁺⁺ _{aq}	Ferrous Ion	55.847	-20300 ± 100	[19]
HSO ₄ ⁻ _{aq}	Bisulfate Ion	97.070	-180684	[19], [23]
SO ₄ ⁼ _{aq}	Sulfate Ion	96.062	-177970 ± 100	[19]
H ₂ S _{aq}	Hydrogen Sulfide-aqueous	34.080	-6654	[19], [23]
HS ⁻ _{aq}	Bisulfide Ion	33.072	+2880 ± 200	[19]
S ⁼ _{aq}	Sulfide Ion	32.064	+20500 ± 200	[19]
TiO ₂	Rutile	79.899	-212559 ± 110	[19]
Fe(OH) ₃	Goethite	106.853	-175340	[20]
Fe(OH) ₃	Lepidocrocite	106.853	-173970	[20]
Fe(OH) ₃	Amorphous Ferric Hydroxide	106.853	-165720	[20]
TiO ₂ H ₂ O	White Hydrated TiO ₂	97.916	-252990	[22]
Ti(OH) ₃	Titanous Hydroxide	98.924	-250905	[21]
Ti ⁺⁺⁺ _{aq}	Titanous Ion	47.90	~ -83600	[20]
TiO ⁺⁺ _{aq}	Titanyl Ion	63.899	~ -138000	[21]
HTiO ₃ ⁻ _{aq}	Titanate Ion	96.908	-228460	[21]

^a G.F.W. = gram formula weight.

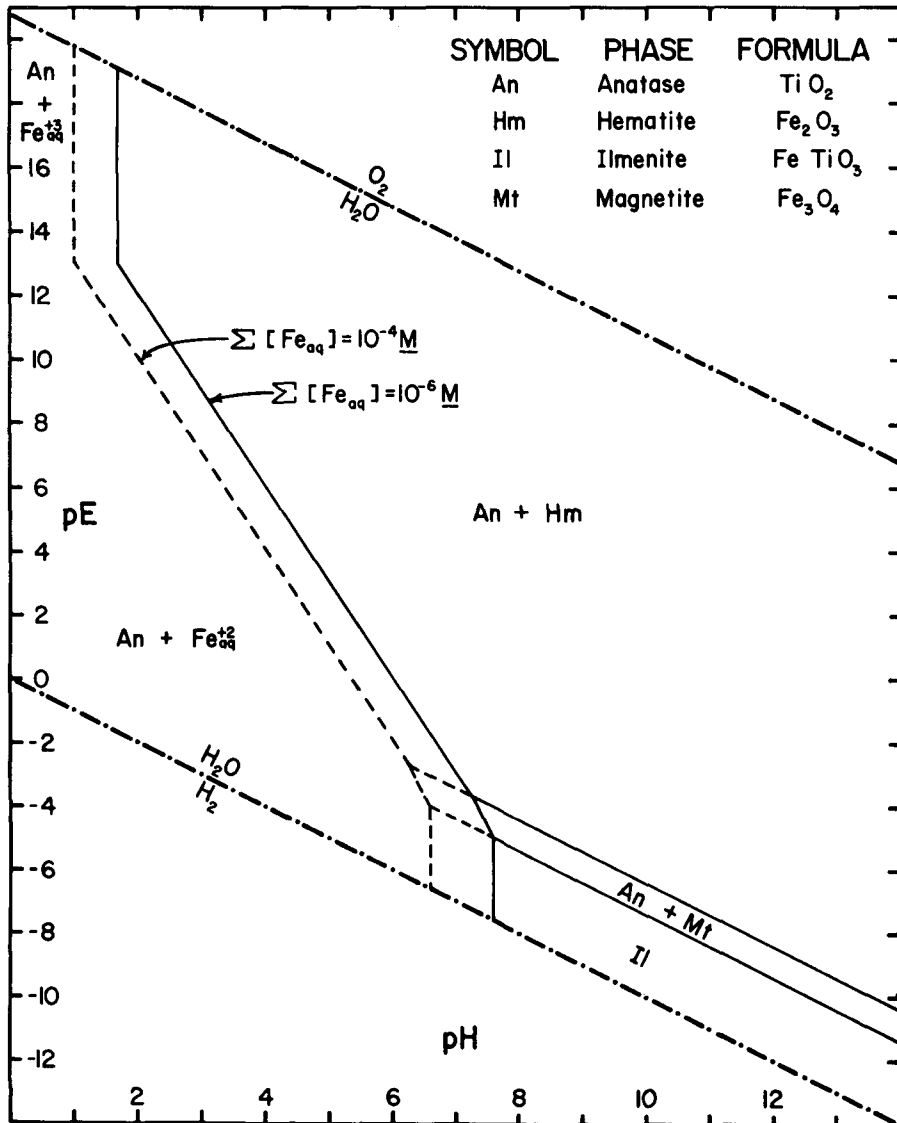


FIG.4. Stability relations in the system Fe-Ti-O-H for hematite (25°C).

be expected to oxidize to Fe_2O_3 and TiO_2 through the development of surface coatings and the diffusion of oxygen into the grains [24]. Only under acid conditions within the field of ferrous iron would magnetite and ilmenite be significantly altered by the leaching of iron. The pH required for iron leaching depends on pE and the concentration of iron in solution, but would be at or below pH7. There is no obvious mechanism whereby, in the absence of organic material, the pH and pE could have been sufficiently lowered to lead to the leaching of iron as Fe^{+2} . On the contrary, the abundant detrital volcanic glass in the Morrison sands would probably have buffered any reaction leading to a pH significantly below pH7. Ilmenite and magnetite are unlikely to have altered in these sands, therefore, in an organic-free system.

Organic material is capable of lowering both the pH and pE of ground water through the dissociation of organic acids and the oxidation of carbon. The detrital carbon content of the Morrison sands was substantial as indicated by silicified logs and locally, residual carbonaceous plant trash. The degradation and dissolution of this material may have promoted the development of a more acid-reducing ground water in which iron would have been more soluble. As the ground water may also have contained sulfate ions and the sulfate-reducing bacteria *Desulfovibrio*, sulfide ion should be considered as a component in the magnetite-ilmenite alteration system. As demonstrated experimentally by Gruner [25], ilmenite may be altered to pyrite and leucoxene in the presence of H_2S at temperatures as low as 200°C . Carroll [26] has suggested that at least part of the pyrite in the authigenic TiO_2 -bearing Cretaceous sediments of the Maryland coastal plain was probably formed by the alteration of ilmenite in ground waters. In the Morrison Formation of Northwest New Mexico, Austin [27], "found evidence that authigenic kaolinite, pyrite, and anatase superseded and partially replaced detrital feldspar and vanished detrital magnetite and ilmenite, and probably were all formed during a single period of post-

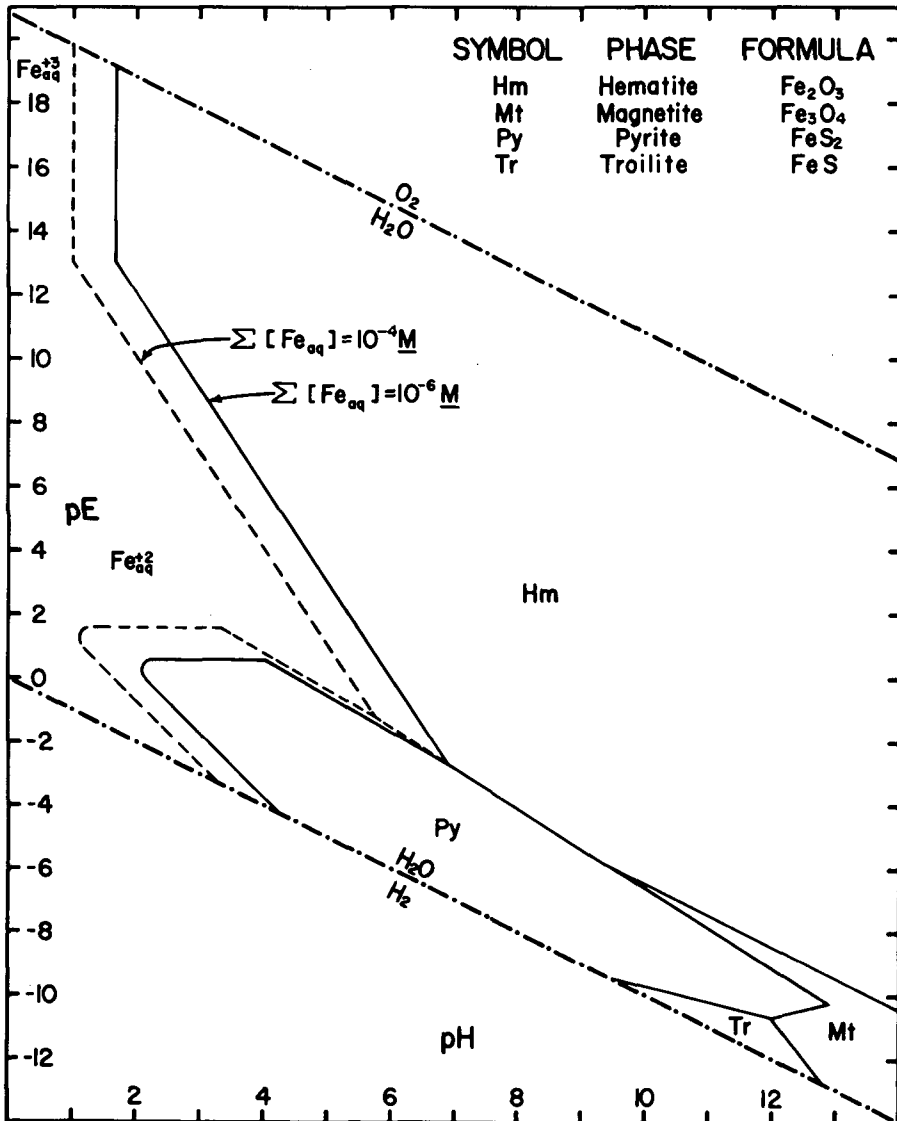


FIG. 5. Stability relations in the system Fe-S-O-H for hematite (25°C and $\Sigma [\text{S}_{\text{aq}}] = 10^{-3} \text{ M}$).

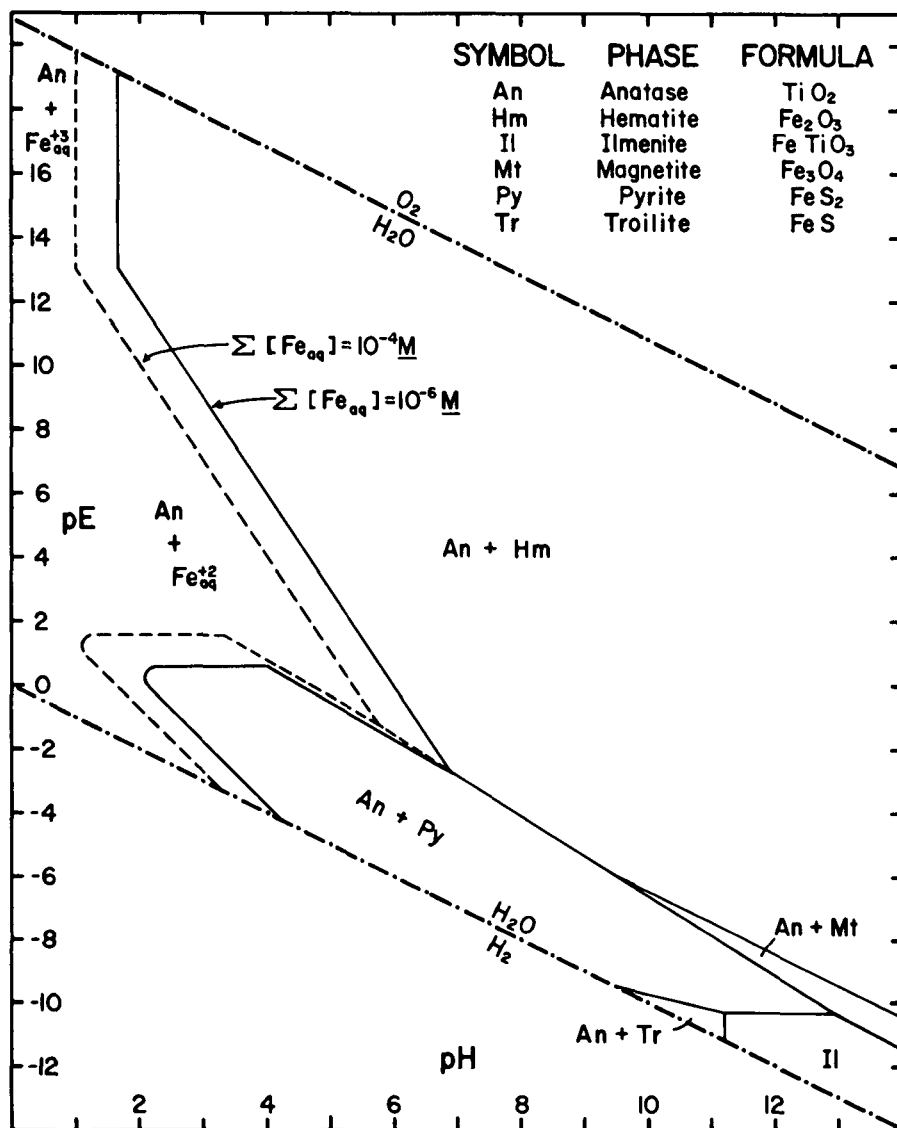


FIG. 6. Stability relations in the system Fe-Ti-S-O-H for hematite (25°C and $\Sigma[\text{S}_{\text{aq}}] = 10^{-3} \text{ M}$).

depositional alteration. Thus, an acid-reducing environment is postulated in which alteration was accomplished by fluids containing possible combinations of humic and sulfuric acid, H_2S , and the compound and complexes of sulfur." Variable but generally minor amounts of pyrite do occur within the sands and shales of the Morrison Formation, particularly below the zone of surface oxidation and in the vicinity of uranium deposits. Crystals are common, although erratic, within and on leucoxene clots, suggesting a possible relationship between the alteration of ilmenite and magnetite in the formation of pyrite. The relations for iron minerals in the system Fe-S-O-H are shown in Figure 5. This diagram is constructed for a sum of sulfur species activities equal to 10^{-3} , equivalent to 100 parts per million SO_4^{--} , as about 75% of analyses of natural waters contain less than this concentration [28]. The system Fe-Ti-S-O-H is shown in Figure 6. By comparison with the sulfide-free systems, pyrite largely replaces the stability fields of magnetite and ilmenite. In the presence of sufficient S^{--} , therefore, magnetite and ilmenite would be replaced, respectively, by pyrite and pyrite and leucoxene. However, the low and erratic concentration of pyrite in the Morrison sands, particularly within leucoxene clots, does not suggest the quantitative sulfidization of iron in magnetite-ilmenite. On the contrary, many sands contain leucoxene clots without pyrite or other authigenic iron minerals suggesting that iron was leached and removed in solution. The paucity of pyrite suggests, therefore, that ilmenite and magnetite were not altered in a sulfate-rich ground water in which low pH and pE were controlled by organic material. It is possible, however, that the alteration of magnetite and ilmenite occurred in a sulfate-poor system in which the solubility of iron was not controlled by pyrite. Had organic material maintained the pH at 7 or lower and the pE below +2 (Figure 6) iron would have been soluble as ferrous iron. It is not known whether the volcanic glass of the sands would have buffered the pH above pH7, hence the alteration

may have occurred in a sulfate-poor low pH and pE ground water controlled by organic material.

Iron is complexed by certain dissolved and dispersed organic molecules and is essential to some organisms. Although these aspects of iron geochemistry are generally not well known, certain data and observations permit one to speculate on the organic geochemistry of iron in the Morrison sandstones. As summarized by Hem [29], "iron is capable of combining with certain organic ions and some inorganic ones to produce anion or cation complexes sufficiently stable and soluble to affect the transport of iron in surface waters, soil moisture, and ground water." Soluble complexes of ferric and ferrous iron with organic matter are common. Hem [30] investigated a complex involving ferrous iron and tannic acid which had an oxidation half-life in contact with air of approximately 30 days at pH values near 8.0 compared to an oxidation half-life of a few minutes for the oxidation of uncomplexed ferrous iron. In laboratory experiments Lynd [31] found that a humic acid solution of pH 3.5 was twice as effective in removing iron from ilmenite as a sulfuric acid solution of the same pH. Schnitzer [32] investigated the formation of complexes between fulvic acid and a series of metal ions. Fulvic acid is a product of plant decay and is a "highly oxidized, biologically stable, water soluble, naturally occurring, complexing agent that can complex di- and tri-valent metal ions and hydroxylated metal compounds and that can interact with clay minerals." Particularly noteworthy, at pH 5, were the high solubility of complexes between fulvic acid and Fe^{+3} , Cu^{+2} , Pb^{+2} , Fe^{+2} , and possibly Al^{+3} . The soluble products of plant decay, in particular the humic and fulvic acids, are capable, therefore, of complexing and thereby promoting the solubility of both ferric and ferrous iron. As the Morrison sands contained abundant plant trash, much of which was dissolved after deposition, this mechanism was probably important in the leaching of iron and, to a lesser extent, titanium from detrital ilmenite and magnetite.

TABLE VI Major element composition of carbonaceous organic material from the Jackpile sandstone and Florida beach sands.

	Percent Ash-Free Basis					<u>Reference</u>
	<u>C</u>	<u>H</u>	<u>O</u>	<u>N</u>	<u>S</u>	
Jackpile Sandstone	81.68	4.59	13.46 ^(a)	.27	-	[14]
Jackpile Sandstone	77.2	4.7	16.7 ^(b)	<.25	1.4	This paper
Florida Humate	55.0	4.4	38.4	1.4	0.7	[34]

(a) Oxygen plus sulfur determined by difference.

(b) Oxygen determined by difference.

The possible role of dissolved organic material in the alteration of magnetite and ilmenite may also be examined by considering the "secondary" organic material in the Morrison sandstones and similar organic material described in the beach sands of Florida. The extensive uranium deposits of the Jackpile sandstone and Westwater Member of the Morrison Formation contain similar abundant, structureless, uranium-bearing, organic material ([33], [14]). Analyses of samples of the material are given in Table VI. Within the ore-bearing sands the organic material fills voids, coats detrital grains, and stains leucoxene clots. Within essentially barren sands adjacent to ore bodies in the Jackpile sandstone, organic material seems to occur preferentially within or on leucoxene clots. The association between organic material and titanium is also indicated by the slight enrichment of titanium in the higher-grade uranium-bearing sands of the Westwater and Jackpile sandstone (Table IV), suggesting that minor amounts of titanium are dissolved, transported, and concentrated in the

TABLE VII Minor element composition of carbonaceous organic material from Florida beach sands (a)

A. Approximate average composition (weight percent) of humate cemented sand (9 spectrographic analyses).					
Si	>10	Mn			.0003
Al	.7	B			.001
Fe	.07	Ba			.001
Mg	.02	Cr			.0005
Ca	.02	Cu			.0003
Ti	.05	Zr			.007
B. Average composition (weight percent) of residue from chemically extracted and reprecipitated humate (9 spectrographic analyses).					
Si	3.0	Na	1.5	Cr	.01
Al	7.0	Ti	.3	Ni	.0015
Fe	.3	Mn	.0007	Pb	.003
Mg	.07	Ba	.007	V	.005
Ca	.02	Co	.0005	Zr	.005

(a) Modified after [34].

organic material of the uranium deposits. The low titanium content in the redistributed ores of the Westwater sandstone is to be expected as these areas are characterized by low concentrations of organic material. Iron is also concentrated in the organic material, at least in part, as pyrite.

Humate-cemented beach and dune sands of recent age in Northwest Florida have been investigated by Swanson and Palacas [34]. They found that this brown to black organic material is soluble in alkaline solutions and has the composition given in Table VII. The organic material was

derived from the leaching of soil humus by rain and introduced into the brackish coastal waters as tea-colored streams and ground water. There it was precipitated in the matrix of the sands, probably largely by the formation of humate salts. The authors believe that the origin, composition, and chemical behavior of the organic material in the uranium deposits of the Morrison sands were essentially the same as the Florida humates. The present differences in their chemical composition (Table VI) is due to the loss of oxygen during the aging of the older material in the Morrison sands. Such deoxygenation is typical of the diagenesis of plant-derived carbonaceous material and may have been promoted by radiation. We consider it significant that the soluble extract of the Florida humate contains 0.3 percent iron and 0.3 percent titanium indicating that these elements are complexed on the soluble humic acids. The carbonaceous organic material of the uranium deposits, by contrast, is essentially insoluble in both alkaline solutions and organic solvents due, presumably, to its deoxygenated, degraded state. We suggest, however, that at the time of deposition it exhibited the same ability to complex and transport iron and titanium and was probably important in the leaching and alteration of magnetite-ilmenite.

The alteration of ilmenite has been studied in connection with other ore deposits, particularly in beach sands and bauxite deposits. Evidence suggests that the ilmenite of most beach sands is more or less altered to an amorphous or finely crystalline titanium-ferric iron oxide or mixture of titanium and ferric iron oxides. According to Bailey and co-workers [35] this amorphous material, which is grayish and opaque with no internal reflections, in turn alters to leucoxene with well-developed internal reflections and color typical of rutile. Iron leaching accompanies the alteration of the amorphous oxides to leucoxene. The amorphous alteration product of ilmenite recognized by Flinter [36] in Malayan beach sands is probably similar to the leucoxene of Bailey and co-workers [35].

This material, which has a higher TiO_2 content and a higher $\text{Fe}_2\text{O}_3/\text{FeO}$ ratio than ilmenite, "gives a diffused rutile pattern (and possibly anatase and brookite) and in reflected light the mineral has lower reflectivity and shows reddish internal reflections with a metallic mottling" [36]. The alteration of ilmenite in beach sands, therefore, is essentially a process of oxidation of iron followed by some iron leaching during the recrystallization of TiO_2 . This amorphous mixed oxide material has not been recognized as a systematic stage in the alteration of magnetite-ilmenite in the Morrison sands, although a gray opaque material has been noted in some thin sections. Furthermore, intensity of ilmenite alteration in the Morrison sands is greater than in the beach sands, suggesting that the mechanism and environment of alteration were different [37].

Temple [38] presents data for the Trail Ridge, Florida deposit in which strong iron leaching of the titanium mineral is limited to the portion of the deposit above the water table. Whereas one might conclude that this is the effect of oxidation, Temple's data shows that the iron of the ilmenite is almost completely oxidized to at least 40 feet below the water table with only minor iron leaching. It is likely that the iron leaching above the water table has resulted from the downward movement of organic-rich waters which have selectively complexed iron from minerals above and close to the water table.

The alteration of ilmenite in bauxites [39] is not the same as in beach sands. Instead of proceeding along crystal planes, the grains alter to leucoxene from the rims inward. In a second type of alteration, ilmenite is replaced by fine-grained aggregates of anatase that have light yellow to moderately deep red internal reflections. This type of alteration, accompanied by strong iron leaching, is similar to the magnetite-ilmenite alteration of the Morrison sands and was probably promoted by dissolved organic material in strong ground-water movement.

CONCLUSIONS

The alteration of detrital magnetite-ilmenite grains provides information on the oxidation-reduction history of Morrison sandstones. The alteration of ilmenite and magnetite includes both the formation of hematite and limonite under oxidizing conditions and the dissolution of iron, presumably under reducing conditions. It is the dissolution of iron which characterizes magnetite-ilmenite alteration in the vicinity of uranium deposits in the Morrison sands. The intensity of iron dissolution varies from negligible to complete, the end product being essentially iron-free TiO_2 . The iron leached from magnetite-ilmenite may be incorporated into authigenic pyrite or clays or transported away from the immediate vicinity of the parent detrital grains. The distribution and habit of hematite and limonite provide additional information on the geochemical environments to which the sandstones have been subjected, including oxidation that occurred: a) during weathering and transport, b) within early post-depositional ground waters (roll front type alteration), and c) late post-depositional oxidation related to uplift and erosion.

The leaching of iron from magnetite-ilmenite in the Morrison Formation could have occurred in reducing, neutral to weakly acid ground water in which the low pE and, to a lesser extent, pH were maintained by the alteration of detrital organic material. The low and erratic concentration of pyrite in the sands suggest the ground water had a low sulfate content. However, information on the composition of plant-derived carbonaceous material similar to that in the Morrison sands, together with iron-leaching experiments for ilmenite in humic acids, suggest that soluble organic species were directly involved in the leaching of iron from magnetite-ilmenite in the Morrison sands. The antipathy of magnetite-ilmenite and uranium deposits in the Morrison sands should be a useful guide in the exploration for this type of deposit.

APPENDIX I

Reactions and the corresponding equations represented in pE-pH diagrams for the system Fe-Ti-S-O-H

REACTION	EQUATION
$O_2 + 4H^+ + 4e^- = 2 H_2O$	$pE = 20.781 - pH - (1/4) \log(O_2) + (1/2) \log(H_2O)$
$2H^+ + 2e^- = H_2$	$pE = 0.000 - pH + (1/2) \log(H_2O)$
$Fe^{+++} + e^- = Fe$	$pE = 13.035 + \log(Fe^{+++}) - \log(Fe^{++})$
$Fe_2O_3 + 6H^+ = 2Fe^{+++} + 3 H_2O$	$pH = -0.320 - (1/3) \log(Fe^{+++}) - (1/2) \log(H_2O) + (1/6) \log(Hm)$
$Fe_2O_3 + 6H^+ + 2e^- = 2Fe^{++} + 3H_2O$	$pE = 12.076 - 3pH - \log(Fe^{++}) - (3/2) \log(H_2O) + (1/3) \log(Hm)$
$3Fe_2O_3 + 2H^+ + 2e^- = 2Fe_3O_4 + H_2O$	$pE = 3.554 - pH - (1/2) \log(H_2O) - \log(Mt) + (3/2) \log(Hm)$
$Fe_3O_4 + 8H^+ + 2e^- = 3Fe^{++} + 4H_2O$	$pE = 16.337 - 4pH - (3/2) \log(Fe^{++}) - 2 \log(H_2O) + (1/2) \log(Mt)$
$FeTiO_3 + 2H^+ = TiO_2 + Fe^{++} + H_2O$	$pH = 4.601 - (1/2) \log(Fe^{++}) - (1/2) \log(H_2O) + (1/2) \log(I1) - (1/2) \log(An)$
$Fe_3O_4 + 3TiO_2 + 2H^+ + 2e^- = 3FeTiO_3 + H_2O$	$pE = 2.534 - pH + (1/2) \log(H_2O) + (3/2) \log(I1) - (1/2) \log(Mt) - (3/2) \log(An)$
$Fe^{++} + 2S^0 + 2e^- = FeS_2$	$pE = 6.597 + (1/2) \log(Fe^{++}) + \log(S_{aq}^0) - (1/2) \log(Py)$
$FeS_2 + 4H^+ + 2e^- = Fe^{++} + 2H_2S$	$pE = -1.718 - 2pH - (1/2) \log(Fe^{++}) - \log(H_2S_{aq}) + (1/2) \log(Py)$
$Fe^{++} + 2SO_4^{= } + 16H^+ + 14e^- = FeS_2 + 8H_2O$	$pE = 6.052 - (8/7) \log(Fe^{++}) + (1/7) \log(SO_4^{= }) - (1/14) \log(Py) - (4/7) \log(H_2O)$
$Fe_2O_3 + 4SO_4^{= } + 38H^+ + 30e^- = 2FeS_2 + 19H_2O$	$pE = 6.454 - (19/15) \log(Fe^{++}) + (2/15) \log(SO_4^{= }) + (1/30) \log(Hm) - (1/15) \log(Py) - (19/30) \log(H_2O)$

<u>REACTION</u>	<u>EQUATION</u>
$3\text{FeS}_2 + 4\text{H}_2\text{O} + 4\text{e}^- = \text{Fe}_3\text{O}_4 + 6\text{HS}^- + 2\text{H}^+$	$\text{pE} = -21.231 + (1/2)*\text{pH} - (3/2)*\log(\text{HS}^-) - (1/4)*\log(\text{Mt}) + (3/4)*\log(\text{Py}) + \log(\text{H}_2\text{O})$
$\text{FeS}_2 + \text{H}^+ + 2\text{e}^- = \text{FeS} + \text{HS}^-$	$\text{pE} = -6.216 - (1/2)*\text{pH} - (1/2)*\log(\text{HS}^-) - (1/2)*\log(\text{Tr}) + (1/2)*\log(\text{Py})$
$\text{Fe}_3\text{O}_4 + 5\text{H}^+ + 3\text{HS}^- + 2\text{e}^- = 3\text{FeS} + 4\text{H}_2\text{O}$	$\text{pE} = 23.813 - (5/2)*\text{pH} + (3/2)*\log(\text{HS}^-) + (1/2)*\log(\text{Mt}) - (3/2)*\log(\text{Tr}) - 2*\log(\text{H}_2\text{O})$
$\text{Fe}_3\text{O}_4 + 6\text{SO}_4^{=2-} + 56\text{H}^+ + 44\text{e}^- = 3\text{FeS}_2 + 28\text{H}_2\text{O}$	$\text{pE} = 6.520 - (14/11)*\text{pH} + (3/32)*\log(\text{SO}_4^{=2-}) - (7/11)*\log(\text{H}_2\text{O}) + (1/44)*\log(\text{Mt}) - (3/44)*\log(\text{Py})$
$\text{TiO}_2 + \text{FeS}_2 + \text{H}_2\text{O} + 2\text{e}^- = \text{FeTiO}_3 + 2\text{HS}^-$	$\text{pE} = -13.309 - \log(\text{HS}^-) + (1/2)*\log(\text{H}_2\text{O}) + (1/2)*\log(\text{An}) + (1/2)*\log(\text{Py}) - (1/2)*\log(\text{Il})$
$\text{FeTiO}_3 + \text{HS}^- + \text{H}^+ = \text{TiO}_2 + \text{FeS} + \text{H}_2\text{O}$	$\text{pH} = 14.186 + \log(\text{HS}^-) + \log(\text{Il}) - \log(\text{An}) - \log(\text{Tr}) - \log(\text{H}_2\text{O})$

Key: Symbols in parentheses represent activities of constituents

An - Anatase TiO_2
Hm - Hematite Fe_2O_3
Il - Ilmenite FeTiO_3
Py - Pyrite FeS_2
Tr - Troilite FeS

R E F E R E N C E S

- [1] ELLIS, J.R., AUSTIN, S.R., DROULLARD, R.F., Magnetic susceptibility and geochemical relationships as uranium prospecting guides, USAEC, AEC-RI (1968).
- [2] CADIGAN, R.A., Petrology of the Morrison Formation in the Colorado Plateau, USGS Prof. Paper 556 (1967) 113 p.
- [3] PETTIJOHN, F.J., POTTER, P.E., SIEVER, R., Sand and Sandstone: Springer-Verlag, New York (1972) 618 p.
- [4] SABINE, P.A., Geochemistry of sedimentary rocks; 1. Petrography and chemistry of arenaceous rocks, Inst. of Geological Sciences, Report No. 69-1 (1969) 168 p.
- [5] PETTIJOHN, F.J., Chemical composition of sandstone - excluding carbonate and volcanic sands in Data of Geochemistry, USGS Prof. Paper 440-S (1963) 12 p.
- [6] NEWMAN, W.L., Distribution of elements in sedimentary rocks of the Colorado Plateau - a preliminary report, USGS Bull. 1107-F (1962) 337-445.
- [7] HARSHMAN, E.N., Geology and uranium deposits, Shirley Basin Area, Wyoming, USGS Prof. Paper 745 (1972) 82 p.
- [8] BOWERS, H.E., SHAW, R.R., Heavy minerals as guides to uranium-vanadium ore deposits in the Slick Rock District, Colorado, USGS Bull. 1107-B (1961) 169-218.
- [9] STEARN, N.H., A background for the application of geomagnetics to exploration, AIME Tech. Pub. No. 150 (1928) 28 p.
- [10] KENDALL, E.W., Trend ore bodies of the Section 27 Mine, Ambrosia Lake uranium district, New Mexico, Ph.D. Thesis, Univ. of Calif., Berkeley (1971) 167 p.
- [11] MIESCH, A.T., Distribution of elements in Colorado Plateau uranium deposits - a preliminary report, USGS Bull. 1147-E (1963) E1-E57.
- [12] SQUYRES, J.B., Origin and depositional environment of uranium deposits of the Grants region, New Mexico, Ph.D. Thesis, Stanford University (1970) 228 p.
- [13] GRANGER, H.C., Analytical data on samples collected at Ambrosia Lake, New Mexico - 1958 through 1962, USGS Open File Report, Den. Fed'l Center, Denver, Colo. (1966).
- [14] MOENCH, R.H., SCHLEE, J.S., Geology and uranium deposits of the Laguna District, New Mexico, USGS Prof. Paper 519 (1967) 117 p.
- [15] FILES, F.G., Geology and alteration associated with Wyoming uranium deposits, Ph.D. Thesis, Univ. of Calif., Berkeley (1970) 113 p.
- [16] KING, J.W., AUSTIN, S.R., Some characteristics of roll-type uranium deposits at Gas Hills, Wyoming, Min. Engng 18 5 (1966) 73-80.

- [17] NASH, J.T., Geology and uranium deposits of the Jackpile mine area, Laguna, New Mexico, Ph.D. Thesis, Columbia University (1967) 216 p.
- [18] BEUS, A.A., Titanium distribution in the lithosphere, Chem. Geol. 8 (1971) 247-275.
- [19] ROBIE, R.A., WALDBAUM, D.R., Thermodynamic properties of minerals and related substances at 298.15°K (25.0°C) and one atmosphere (1.013 bars) pressure and at higher temperatures, USGS Bull. 1259, (1968) 256 p.
- [20] LANGMUIR, D., Particle size effect on the reaction goethite = hematite + water, Am. J. Sci. 271 (1971) 147-156.
- [21] POURBAIX, M., Atlas of electrochemical equilibria in aqueous solutions, Pergamon (1966) 644 p.
- [22] LATIMER, W.M., The oxidation states of the elements and their potentials in aqueous solutions, 2nd ed., Prentice Hall (1952) 392 p.
- [23] HELGESON, H.C., Thermodynamics of hydrothermal systems at elevated temperatures and pressures, Am. J. Sci. 267 (1969) 729-804.
- [24] GALLAGHER, K.J., FEITKNECHT, W., MANWEILER, U., Mechanism of oxidation of magnetite to γ -Fe₂O₃, Nature 217 (1968) 1118-1121.
- [25] GRUNER, J.W., The decomposition of ilmenite, Econ. Geol. 54 (1959) 1315-1316.
- [26] CARROLL, D., Ilmenite alteration under reducing conditions in unconsolidated sediments, Econ. Geol. 55 3 (1960) 618-619.
- [27] AUSTIN, S.R., Ilmenite, magnetite and feldspar alteration under reducing conditions, Econ. Geol. 55 (1960) 1758-1759.
- [28] DAVIS, S.N., DeWiest, R.J.M., Hydrogeology, John Wiley & Sons (1966) 447 p.
- [29] HEM, J.D., Stability field diagrams as aids in iron chemistry studies, Am. Water Works Jour. 53 2 (1961) 211-228.
- [30] HEM, J.D., Chemistry of iron in natural water - complexes of ferrous iron with tannic acid, USGS Water Supply Paper 1459-D (1960).
- [31] LYND, L.E., Study of the mechanism and rate of ilmenite weathering, AIME Trans. 217 (1960) 311-318.
- [32] SCHNITZER, M., Reactions between fulvic acid, a soil humic compound and inorganic soil constituents, Soil Sci. of Am. Proceedings 33 1 (1969) 75-81.
- [33] GRANGER, H.C., SANTOS, E.S., DEAN, B.G., MOORE, F.B., Sandstone-type uranium deposits at Ambrosia Lake, New Mexico - an interim report, Econ. Geol. 56 7 (1961) 1179-1210.
- [34] SWANSON, V.E., PALACAS, J.G., Humate in coastal sands of Northwest Florida, USGS Bull. 1214-B (1965) 29 p.

- [35] BAILEY, S.W., CAMERON, E.N., SPEDDEN, H.R., WEEGE, R.J., The alteration of ilmenite in beach sands, *Econ. Geol.* 51 3 (1956) 263-279.
- [36] FLINTER, B.H., The alteration of Malayan ilmenite grains and the question of Arizonite, *Econ. Geol.* 54 (1959) 720-729.
- [37] LYND, L.E., Conditions for ilmenite alteration, *Econ. Geol.* 56 (1961) 994-995.
- [38] TEMPLE, A.K., Alteration of ilmenite, *Econ. Geol.* 61 (1966) 695-714.
- [39] HARTMAN, J.A., The titanium mineralogy of certain bauxites and their parent materials, *Econ. Geol.* 54 (1959) 1380-1405.

DISCUSSION

R. RODRIGUEZ TORRES: Is it considered possible that mineralogical changes from magnetite to other minerals of iron could be responsible for changes in surface radioactivity values? If so, has any attempt been made to map such measurements?

S. S. ADAMS: I would not expect the alteration of magnetite and ilmenite to change the radioactivity of the sandstone. Magnetic susceptibility should decrease, however, and this suggests the possibility of magnetic measurements.

I. A. BREGER: I congratulate Mr. Adams on a very fine paper. What is the grade of the uranium associated with the organic matter? If high enough, it might condense the organic matter and render it insoluble, as has happened with some of our coals.

S. S. ADAMS: The grade of the primary ore is commonly in excess of 0.5% U_3O_8 , and sometimes as high as 2.0% U_3O_8 . As you say, it is quite likely that radiation has contributed to the alteration of the organic matter, rendering it insoluble and non-reactive.

H. H. ADLER: It appears from your paper that organic matter in solution plays a significant role in the removal of magnetite as well as iron from ilmenite in sandstones, leaving Ti behind. It also seems obvious that, where lignitic deposits are present, adjoining red beds have been decoloured - that is, have evidently suffered hematite destruction. I wonder whether we can conclude from this - given the appropriate circumstances - that if we note a loss of iron such as you have described we may also assume a movement of humic or other organic agents through the sands, organic matter which may have precipitated down-dip (or further along the hydrological gradient) in the manner suggested by Granger, and may thereby have provided sites of uranium accumulation. If such a conclusion were justified, we might be able to judge the prospects for uranium-humate deposits at depth from up-dip or outcrop evidence of iron loss such as you have described. I would appreciate your comments on this possibility.

S. S. ADAMS: I think that your inference is sound. This would mean, for example, that exploration for the primary Grants-type ore might be concentrated on portions of the sandstones which show magnetite-ilmenite destruction. We should be cautious about basing our search for roll-front deposits too heavily on magnetite-ilmenite destruction, however, because,

as Granger and Warren have suggested, magnetite may be an authigenic phase within the altered interior, and possibly not all detrital magnetite-ilmenite was destroyed with the passing of the roll front. The question of authigenic magnetite might be resolved by analysis of the magnetite grains: authigenic magnetite should contain very little TiO_2 and should be quite uniform in composition.

S. H. U. BOWIE: Has the phase troilite (FeS) shown in Fig. 5 been identified in Morrison Formation sandstones? What happens to the titanium remaining after the removal of iron from minerals such as ilmenite? Can it be accounted for in the anatase and rutile known to be present, and in the organic concentrations you have shown to be present?

S. S. ADAMS: Troilite has not been identified. It was included in the figure only because it is a thermodynamically stable phase in the system. As for the mass balance of titanium in the sands, we lack the analyses to demonstrate that the residual TiO_2 of the altered heavy minerals and the TiO_2 in the urano-organic ore is equivalent to the titanium content of unaltered magnetite-ilmenite sands.

J. R. BERTHELIN: Have you been able to establish any analogy between the processes you have observed or deduced and the podzolization processes that take place in pedogenesis?

S. S. ADAMS: The heavy-mineral alteration in the Morrison sands took place under neutral to alkaline conditions, as is shown by the lack of any H^+ metasomatism of the feldspar. Podzolization probably proceeds under more acid conditions, and in this respect is different from the alteration I have discussed.

SANDSTONE-TYPE URANIUM DEPOSITS IN THE PROTEROZOIC STRATA OF NORTHWESTERN CANADA

R.D. MORTON
Department of Geology,
University of Alberta
Edmonton, Canada

Abstract

SANDSTONE-TYPE URANIUM DEPOSITS IN THE PROTEROZOIC STRATA OF NORTHWESTERN CANADA.

Epigenetic uranium deposits within a Proterozoic, marine to continental, volcanic-sedimentary sequence are described from the Great Slave Lake region of NW Canada. Mineralization occurs in faulted and folded, fluvialite arenites and rudites, in part metamorphosed to a maximum of the zeolite facies of regional metamorphism. The sediments carry interstitial, disseminated uranium minerals which clearly replace pre-existing sulphides and are associated with hematite or graphite. Genetic hypotheses are forwarded and it is suggested that these deposits, being possibly generated by metamorphic fluids, might be of a type intermediate between those associated with younger sandstones at shallow levels and syn-metamorphic vein deposits.

The realization that Canada's present annual uranium production will probably need to be tripled to 13600t U_3O_8 /yr by 2000 A.D., in order to satisfy the nation's domestic reactor requirements, has, despite the poor short-term market outlook, encouraged a diminished but continued quest for nuclear resources on the Canadian Shield.

Traditionally, prospecting programs have been biased towards the search for conglomeratic deposits of the Elliot Lake-Agnew Lake type and for pegmatitic and vein types associated with regionally metamorphosed or igneous rocks, similar to those of the Bancroft district of Ontario and the western margin of the shield respectively. To date some 20 Proterozoic basinal provinces within the Northwest Territories, Saskatchewan, Manitoba, Ontario and Quebec have been investigated. The potentials and reserves of these provinces were recently reviewed by Little [1]. During the past five years these investigations have proven fruitful and, apart from many occurrences of radioactivity, at least one major uranium ore deposit has been discovered by Amok Ltd. who recently announced [2] the discovery of a small but rich U- (Au, V, Cu, Ni, Bi, Se, As) orebody, composed of pitchblende and coffinite (together with arsenides, selenides and native Au) within argillaceous strata intercalated with orthoquartzites of the Paleohelikian Athabasca Formation in the Carswell Lake area of N. Saskatchewan. This orebody, some 90m x 15m x 9m in size, carries an average grade of around 10% U_3O_8 .

This paper summarizes the findings of the author, Vestor Explorations Ltd. and earlier workers (Lang [3]; Lang et al [4] and Little [5]) concerning uranium mineralization within the Proterozoic basinal sequence occurring in the Great Slave Lake area of Canada's Northwest Territories.

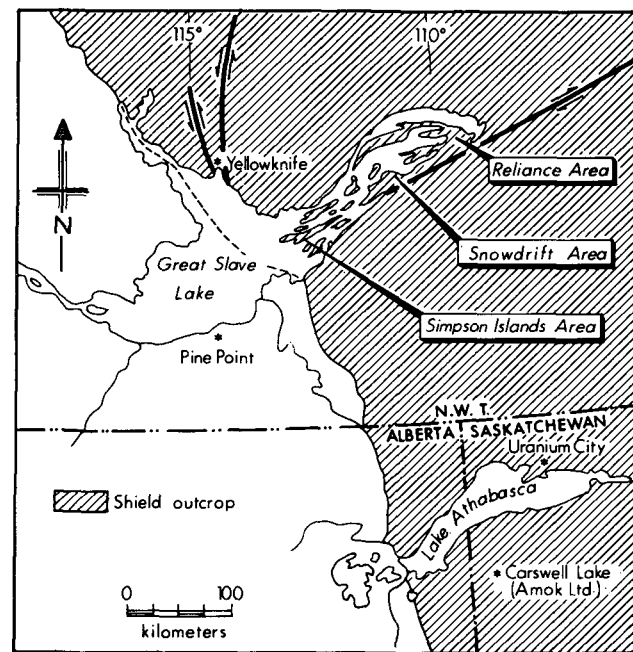
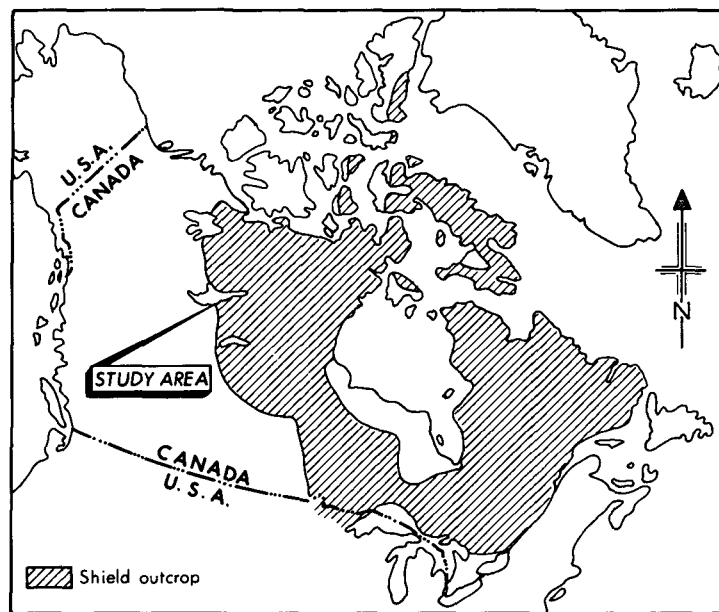


FIG. 1. Location maps showing the location of the uraniferous localities described.

Location and General Geology

The East Arm region of Great Slave Lake, situated between longitudes 104°00' W and 135°45' W and latitudes 61°30' N and 62°50' N, lies near the western exposure margin of the Canadian Shield, (figure 1). The area is composed of a NE-SW trending belt of folded and faulted Precambrian rocks occupying the so-called Athapuscow aulacogen. This aulacogen is sited upon the boundary between the Slave and Churchill structural provinces of the shield (Hoffman [6]) and is coextensive with a major system of high angle faults cutting the basement. The local basement is composed of Archean metamorphic and plutonic rocks, 2300 to 2600 m.y. old. Unconformable upon the Archean complex are sequences of Proterozoic (Aphebian) sediments and volcanics cut by Aphebian and Helikian intrusions.

The stratigraphy of the Athapuscow aulacogen, after Hoffman [7], is summarized in figure 2. The aulacogen contains some 12 km of Proterozoic rocks in the SW part of the region which thin to minima of ~2 km in the NE near Fort Reliance and to ~1.5 km where they onlap the Archean Slave province, E of Yellowknife. These rocks were probably deposited between 2200 m.y. and 1650 m.y. ago; (Hoffman [8], Olade and Morton [9]). Hoffman considers the aulacogen analogous to those described from the U.S.S.R. by Salop and Scheinmann [10] and to have possibly been initiated as one branch of a RRR-type triple-junction system. The two active western arms developed into a geosyncline (the Coronation geosyncline), whilst the abandoned intracontinental arm generated the aulacogenic rift basin. The history of the aulacogen and its environs illustrated in figures 3 and 4 was:

- Phase I : Deposition of the Union Island Group and the paraconformable, (non-marine) fluvialite Hornby Channel and littoral Duhamel Formations during active rifting.
- Phase II : Downwarping, folding and faulting accompanied by deposition of a predominantly marine, sedimentary and volcanic sequence (Kluziai to Portage Inlet Formations); the lower and upper members being deposited under fluvialite and continental conditions respectively.
- Phase III: Transcurrent faulting and the deposition of an ~4 km thick continental and fluvialite terrigenous sequence accompanied by minor volcanism.

Hoffman [11] recognized 6 volcanic episodes within the Aphebian sequence and noted an absence of any regional metamorphism. However, recent work in the SW sector of the aulacogen, where the sequence is thickest, has revealed evidence of a zeolite facies burial metamorphism which must be anticipated beneath up to 12 km of strata.

Uranium mineralization

Vein-type uranium mineralization in the East Arm region was first discovered by Eldorado Nuclear Ltd. in 1952. These deposits were first described by Lang [3] and Lang et al [4] who noted vein deposits both within diorite stocks cutting the Stark Formation and in arenaceous algal dolomites of the Duhamel Formation; see figure 2.

The existence of uranium mineralization in the non-marine arenites of the region was first realized in 1969 when Vestor Explorations Ltd. discovered showings of yellow uranium silicates in hematized rocks on South Simpson Island. Subsequently

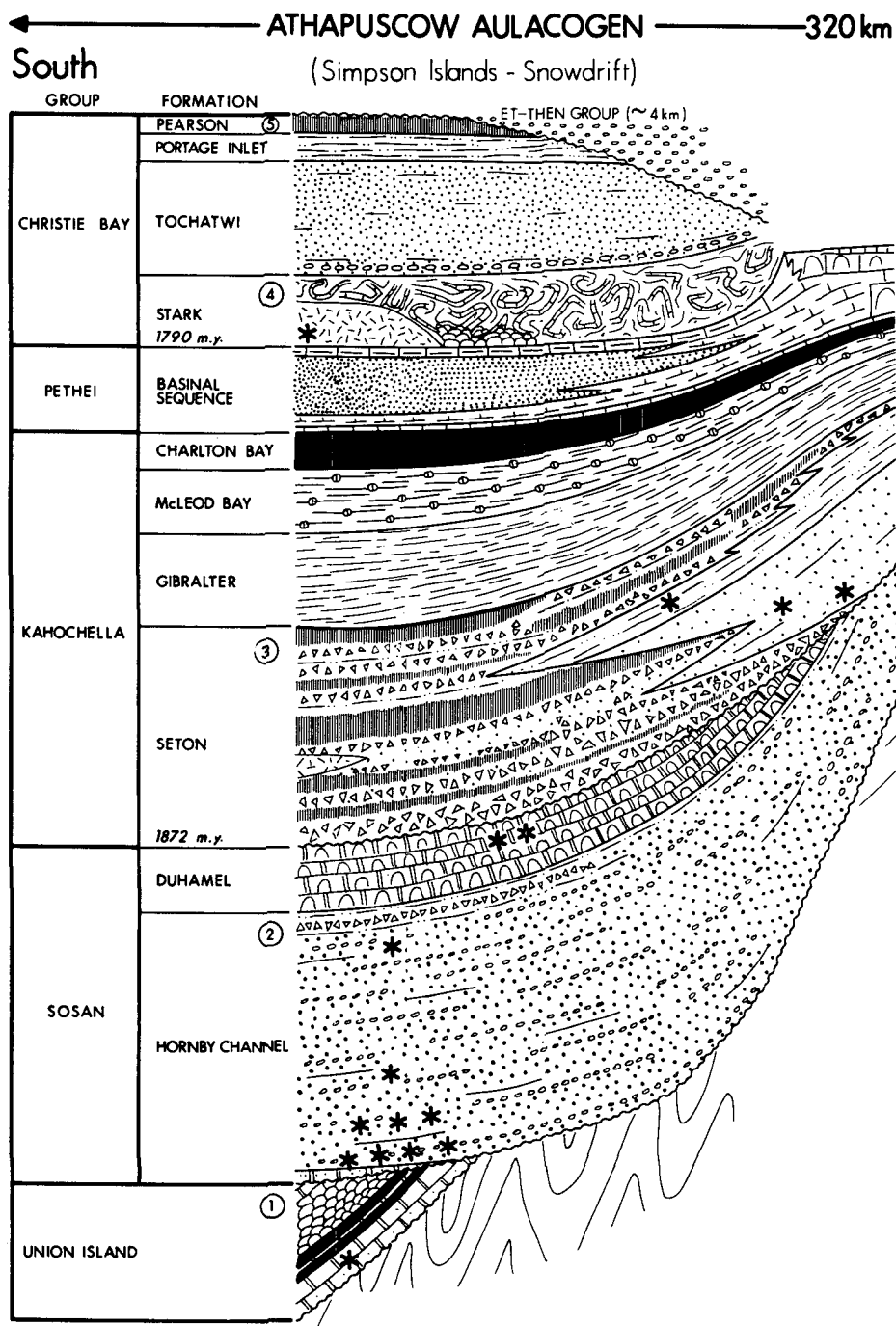
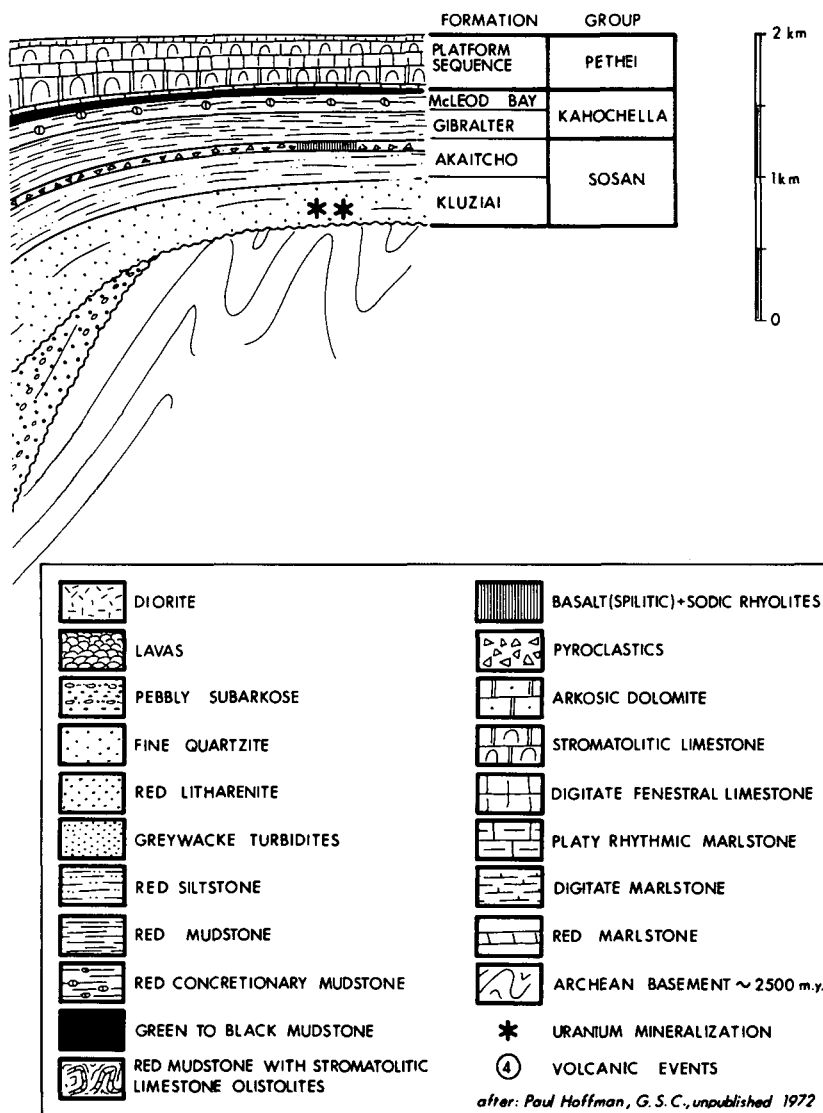


FIG.2. Schematic cross-section of the Athapuscow aulacogen showing the stratigraphic positions of known uranium mineralization.

SLAVE PLATFORM

(Reliance)

North



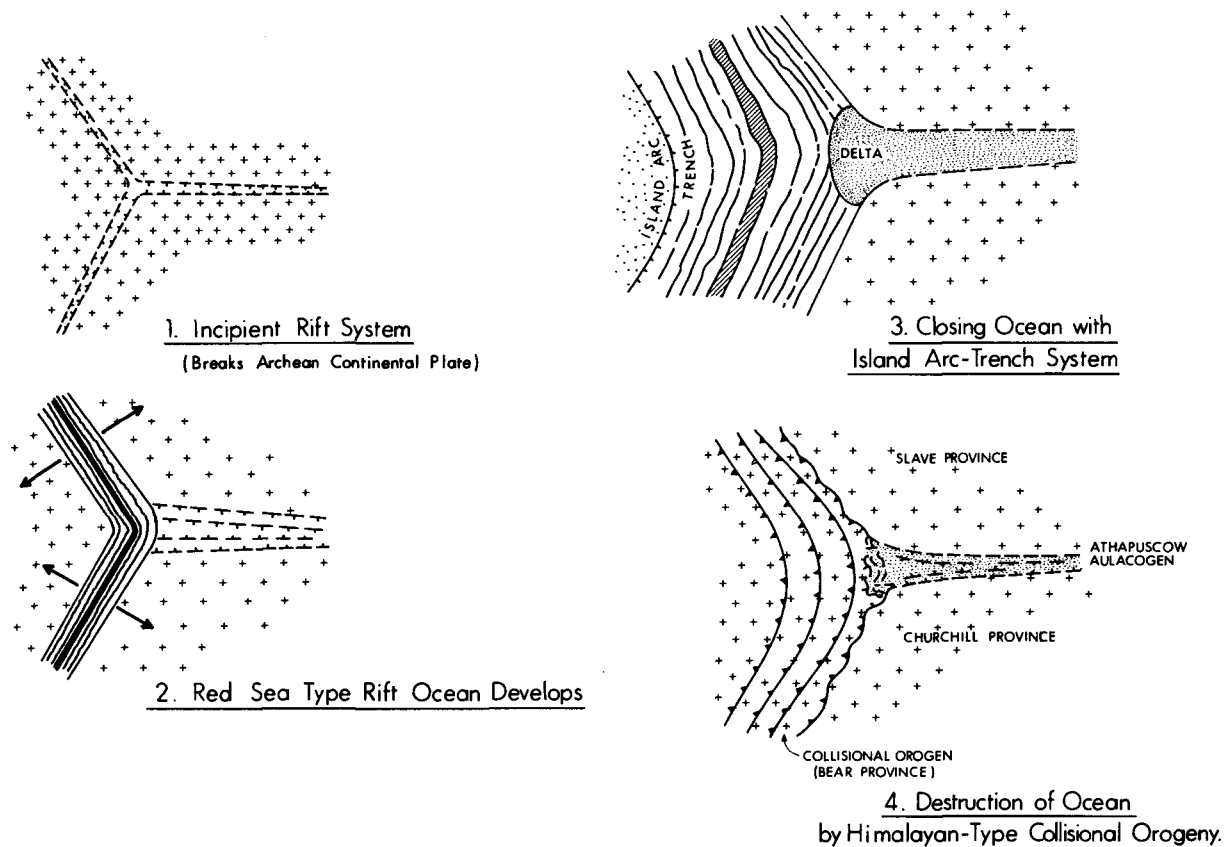


FIG.3. Geotectonic evolution of the Athapuscow aulacogen and environs (after Hoffman [13]).

mineralized sandstones, in part conglomeratic, within the Hornby Channel and Kluziai Formations have been revealed by ground scintillometric surveys in 3 areas, namely: the Simpson Islands, the Snowdrift area and the Reliance area.

1. The Simpson Islands occurrences

The Simpson Islands are situated 143 km SE of Yellowknife at latitudes $61^{\circ}40' \text{ N}$ to $61^{\circ}55' \text{ N}$ and longitudes $112^{\circ}10' \text{ W}$ to $112^{\circ}40' \text{ W}$. 10 apparently sub-concordant zones (average 330m x 30m at outcrop) and some 200 occurrences of uranium mineralization have been found in the Hornby Channel Formation strata which unconformably overlie Archean biotite granites and upper amphibolite facies paragneisses with pegmatites. 85% of the uranium mineralization occurs in the lower 450 m of a 1500-m-thick succession of mature, thick-bedded to massive, poorly sorted, coarse orthoquartzitic and subarkosic sandstones, grits and conglomerates. These arenites exhibit festoon cross-stratification and bear lenses of green shale, finer micaceous sandstone, dolomitic sandstone and boulder diamictite. The mineralized arenites are noticeably lacking in fresh detrital magnetite and ilmenite whereas zircons are common. Locally the beds are cut by diatreme breccias, diabase, syenite and bostonite dykes. Silicification and stringers of quartz veins are developed adjacent to faults which generally trend NE-SW. Minor radioactivity was detected in: (a) hematite and heavy mineral-rich foresets (predominantly Th) and (b) red, fine-grained, argillaceous sandstones and siltstones.

The uraniferous zones were mapped by scintillometry and have been examined by trenching and 26 short diamond drill holes. At surface they are expressed either by red hematite enrichment or by outcrops covered with yellow and green secondary uranium minerals; see table 1. In depth the uranium deposits are clearly discordant and epigenetic and manifest themselves as 3-m to 9-m-broad 'fronts' at 30° to 90° to the bedding; see figure 5. The mineralized arenites and rudites are either (a) dark grey in colour, sulfide-rich and carry a fine-grained, interstitial 'reduced' mineralization or rarely a network of oxide-sulfide veinlets, (b) brick red in colour (hematite rich), or (c) buff-coloured, goethite-bearing, leached types. The dark grey lithologies carry 0.4 to 1.5% U_3O_8 , 1 to 5% pyrite, are in apparent isotopic equilibrium, have Th/U ratios of ~ 0.05 to 0.07 and up to 0.3% Cu, 1g/t Au and 14g/t Ag. The associated red lithologies carry only between 0.05 and 0.5% U_3O_8 and have Th/U ratios of 0.13 to 0.5, whilst the apparently leached, goethite-bearing rocks carry $<0.05\%$ U_3O_8 and have Th/U ratios of around 0.12.

Microscopic and electron microprobe studies of the mineralized strata show interstitial euhedral pyrite and chalcopyrite, in part replacing ilmenite (and magnetite?) have been replaced by fine-grained anhedral uraninite. The uraninite is clearly replaced by anhedral coffinite-bearing euhedral galena. Primary sphalerite and cobaltite accompany the above sulfides. The uraninite is associated with bladed hematite and subhedral to euhedral anatase.

2. The Snowdrift occurrences

The uranium-bearing sediments of the Snowdrift area are located around Toopon Lake, 19 km ESE of Snowdrift, at latitudes $62^{\circ}20' \text{ N}$ to $62^{\circ}22' \text{ N}$ and longitudes $110^{\circ}20' \text{ W}$ and $110^{\circ}29' \text{ W}$. 3 mineralized zones and 50 radioactive occurrences have been found over a strike length of 3 km. The uranium mineralization is discordant within a 180-m-thick sequence of massive to thick-bedded, well-sorted,

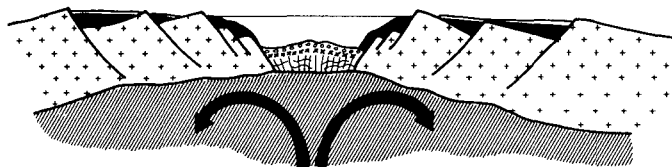
RIFT - SYSTEM



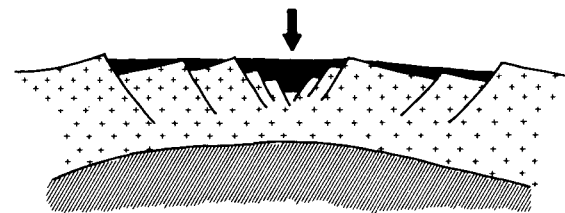
CRUSTAL DOMING WITH CRESTAL GRABEN
 FILLED BY CONTINENTAL SEDIMENTS & ALKALI
 BASALT—RHYOLITE

GEOSYNCLINE

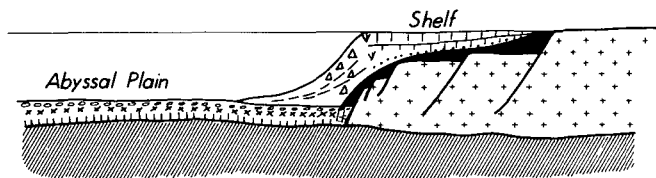
AULACOGEN



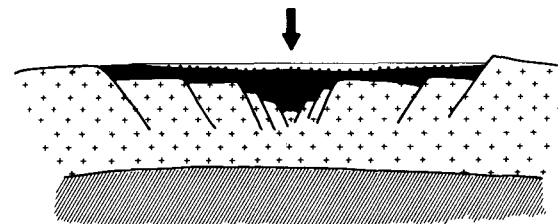
RED SEA TYPE RIFT OCEAN WITH NEW LITHOSPHERE



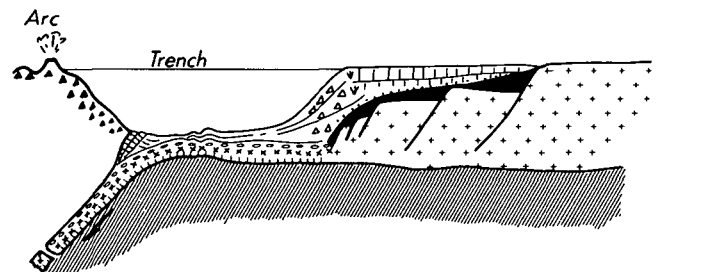
DOWNWARPING



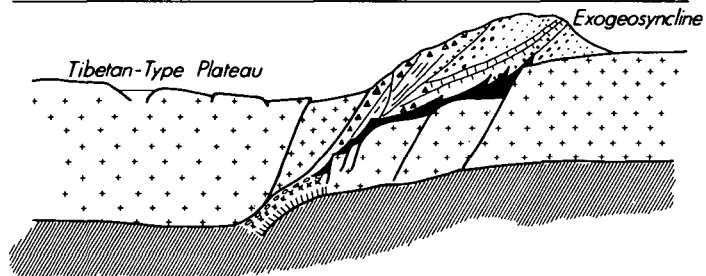
MIO-GEOCLINAL STAGE



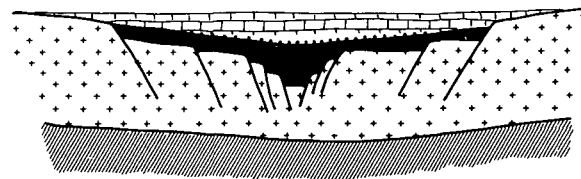
DOWNWARPING & MANTLE CONTRACTION



VOLCANIC ARC-TRENCH & CONTINENTAL MARGIN APPROACH



CONTINENTAL COLLISION



FOUNDERING OF GRABEN

FIG. 4. Evolution of the Coronation geosyncline and Athapuscow aulocogen (after Hoffman [13]).

TABLE I. PARAGENETIC SEQUENCES OF THE E. ARM OCCURRENCES

	<u>Phase I</u>	<u>Phase II</u>	<u>Phase III</u>	<u>Phase IV</u>	<u>Supergene oxidation at surface</u>
<u>SIMPSON ISLANDS</u>	<u>Ilmenite (?)</u> <u>Magnetite (?)</u>	<u>Pyrite</u> <u>Chalcopyrite</u> <u>Cobaltite</u> (Sphalerite)	<u>Anatase</u> <u>Hematite</u> <u>Uraninite</u> (Dolomite)	<u>Coffinite</u> <u>Galena</u>	Goethite Covellite Erythrite Uranophane Compreignacite Liebigite Cuprosklodowskite Soddyite Becquerelite Vandendriesscheite (?) Billieite (?)
<u>RELIANCE</u>	<u>Ilmenite (?)</u> <u>Magnetite (?)</u>	<u>Pyrite</u> <u>Chalcopyrite</u> <u>Cobaltite</u> <u>Safflorite</u> <u>Arsenopyrite</u>	<u>Hematite</u> <u>Uraninite</u> <u>Brannerite</u> <u>Calcite</u> (Barite)	<u>Coffinite</u> <u>Galena</u>	Unidentified yellow secondary U minerals
<u>SNOWDRIFT</u>	<u>Ilmenite (?)</u> <u>Graphite</u>	<u>Pyrite</u> <u>Chalcopyrite</u> <u>Cobaltite</u>	<u>Hematite</u> <u>Brannerite</u> <u>Uranian titania</u> (Barite)		Goethite Covellite Cuprosklodowskite Soddyite

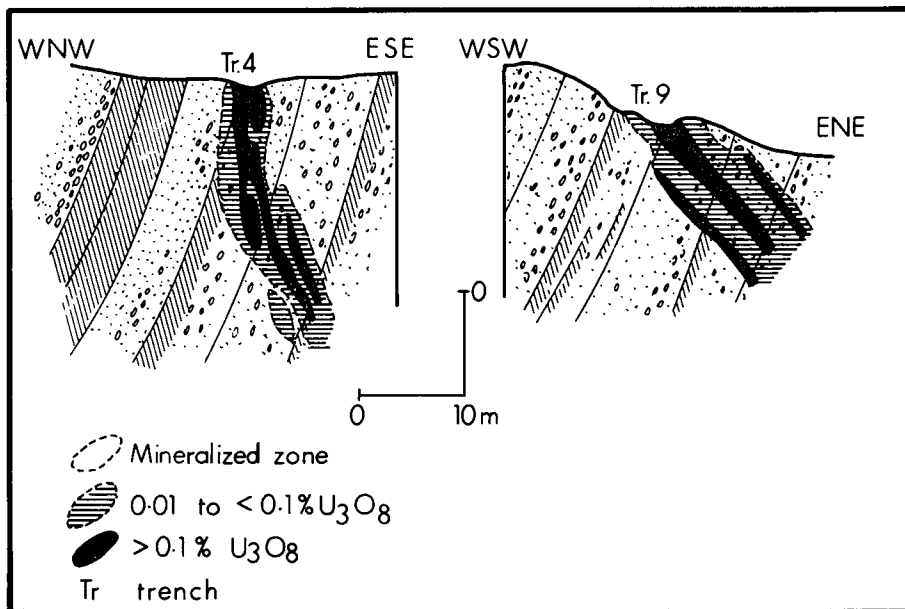


FIG. 5. Cross-sections of the uranium deposits on S. Simpson Island as revealed by drilling.

medium- to fine-grained, non-marine orthoquartzites of the Kluziai Formation. The host strata contain frequent partings of green shale, exhibit cross-stratification and ripple marks and contain intraformational shale breccias in their upper part.

Three varieties of low-grade mineralization, similar to those of the Simpson Islands, are intimately associated, namely: (a) a sulfidic, 'reduced' type with dark grey quartzite-carrying disseminated, interstitial and micro-veinlet concentrations of graphite, U-Ti minerals, pyrite, chalcopyrite, cobaltite and barite; see table I. (b) an 'oxidized' type where interstitial uranium minerals are associated with abundant hematite; (this type occurs as coronas around the type (a) sulfidic mineralization) and (c) a 'supergene-leached' type with pale buff arenites, clearly controlled by joint sets, carrying yellow uranium salts and goethite; (this type clearly replaces types (a) and (b)).

The grey, sulfidic sectors carry up to 0.56% U_3O_8 , 0.2% Cu, 0.02% Co, 8.2g/t Ag and a trace of Au. In contrast the 'oxidized' zones contain only up to 0.1% U_3O_8 and the 'leached' zones only a maximum of 0.05% U_3O_8 .

In polished thin sections the interstitial sulfides pyrite and chalcopyrite are clearly replaced in part by brannerite and what appears to be uranian anatase. Small veinlets of barite cut the mineralized rocks.

TABLE II. PARTIAL CHEMICAL ANALYSES OF REPRESENTATIVE MINERALIZED ARENITES FROM GREAT SLAVE LAKE, N. W. T.

Locality	SIMPSON ISLAND				SNOWDRIFT			RELIANCE
Specimen No.	T4	T6	T6-4	T6-5	SP-2N	SP-2W	SP3-N	RP-4
SiO ₂ (%)	>90	>90	>90	>90	>90	>90	>90	84.71
Al ₂ O ₃ "	1.98	2.38	4.96	5.54	2.53	3.13	2.48	2.52
Σ FeasFe ₂ O ₃	1.19	1.39	0.99	0.40	tr	tr	tr	9.69
MnO "	n.d.	n.d.	n.d.	n.d.	0.01	0.01	0.01	0.02
MgO "	0.25	0.45	0.35	0.10	0.10	0.10	0.10	0.10
CaO "	n.d.	0.40	0.40	tr	tr	tr	tr	0.10
Na ₂ O "	0.02	0.24	0.26	0.01	0.62	0.02	tr	0.07
K ₂ O "	0.41	0.67	1.53	1.87	2.24	1.50	1.21	0.67
TiO ₂ "	0.08	0.04	n.d.	0.77	0.20	0.22	0.04	0.08
U ₃ O ₈ "	0.54	0.39	0.21	0.01	0.41	0.4	<0.01	1.50
I.L. "	0.96	0.71	0.84	1.02	0.72	0.66	0.76	1.15
Th (ppm)	350	232	26	-	-	-	-	530
Ba "	109	129	114	139	1122	800	1241	163
Sr "	59	79	55	54	40	50	40	10
Co "	135	133	127	168	179	124	174	217
Cr "	55	65	42	61	42	28	10	<10
Cu "	89	10	30	10	30	10	337	30
Ni "	22	40	34	10	40	10	10	64
V "	49	69	69	20	20	10	10	35

^a U, Th determination by gamma spectrometry, Univ. of Alberta; all other elements by arc spectrography - K. Govindaraju, C.R.P.G., Nancy). I.L. = loss on ignition.

3. The Reliance occurrences

Uranium mineralization also occurs in coarse, often conglomeratic, poorly sorted, non-marine sandstones of the Kluziai Formation, E of Meridian Lake at latitude 62°37' N and longitude 109°19' W. Three zones, comparable in surface area to those of Simpson Island, occur within dark-red, hematitic arenites which often carry yellow uranium salts on joints and fractures. To date little work has been done on these occurrences which were discovered in late 1970, and drilling is planned for 1974. Grab assays from trenches on a 120m x 335m zone show remarkably high grades of 2.6 to 6.7% U_3O_8 .

In polished thin sections, abundant, interstitial lamellar hematite is accompanied by 1 μ m to 5 μ m diameter spherules or hollow spherical shells of radiating uraninite (or rarely brannerite) clearly replaced by secondary coffinite in part. The uranium oxides have replaced primary pyrite and chalcopyrite. Occasional cubes of uraninite, ~5 μ m thick, are rimmed by coffinite. Calcite, safflorite and cobaltite are also present in the uraniferous rocks.

Geochemistry of the occurrences

Gamma spectrometric and fluorimetric analyses for U and Th are presently being performed on the mineralized suites and their associated lithologies. Electron-microprobe analyses of the constituent mineral phases are also planned.

Table II presents partial chemical analyses for comparative purposes. The quartzitic aspect of the mineralized arenites is clearly demonstrated by their high silica contents and concomitantly low concentrations of alumina, alkalis and alkaline earths. It is noteworthy that the Simpson Island and Snowdrift specimens have high Ti contents related to the observed anatase and brannerite contents. The Reliance sample also shows distinctly higher Ni and Co concentrations due to its arsenide content and a distinctly high Fe content related to its hematitic character. The barite-rich nature of the Snowdrift rocks is clearly shown by the Ba content. Cu and Cr enrichment appears to characterize the Simpson Island occurrences.

Geochronology

Preliminary U-Pb isotope studies by H. Baadsgaard and the author on material from Reliance indicates that the epigenetic deposits must have been originally deposited from solution between 1800 and 1550 m.y. ago.

This age may be compared with that of 1625 m.y. for the earliest stage of mineralization at Port Radium on the east shore of Great Bear Lake given by Thorpe [12]. It is also significant that Hoffman et al [13] consider that the extensive vertical movement associated with the final development stage of the aulacogen-graben, which resulted in the deposition of a thick fanlomerate sequence, took place around 1650 m.y. ago and definitely terminated prior to 1310 m.y. ago.

Genetic considerations

(A) Origin of the uranium

The uraniferous solutions which gave rise to the mineralization in the Great Slave Lake region may have been derived from the following sources:

- (i) Detrital uranium minerals from the surrounding Archean craton
- (ii) 'Exhalative' uranium supplied to the aulacogen during one of the volcanic phases

- (iii) Uranium leached from either arkosic sands or volcanics of the Proterozoic sequence during diagenesis or burial metamorphism
- (iv) 'Fugitive' uranium from the Churchill province during the late (retrograde) stages of metamorphism and extreme cataclasis of the Hudsonian episode.

(B) Precipitation of the uranium

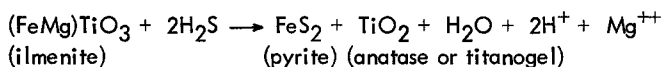
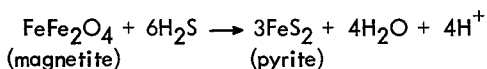
In this case one must distinguish between the main discordant type of mineralization and the very low-grade 'secondary' type rarely found adjacent to fault zones, which obviously represents very local redistribution. The precipitation of the uranium from solution could have been effected by:

- (i) reduction or chelation by active bacterial and/or algal floras during sedimentation
 - (ii) reduction or chelation by organic fractions in the sedimentary rocks
 - (iii) reaction with preexisting sulfide minerals in or without the presence of bacteria
- or
- (iv) reaction with and/or adsorption on to Ti oxides.

(C) Possible genetic framework

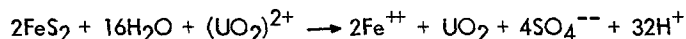
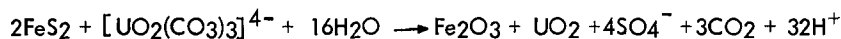
At the present stage of investigation the following tentative hypothetical scheme of metallogenesis is proposed:

Around 2000 m.y. ago erosion of the Archean basement resulted in the deposition of magnetite- and ilmenite-bearing sands within the aulacogen. The extensive eruption of submarine volcanoes around 1870 m.y. ago may have caused S, Fe, Cu, Co, As, Ca and U(?) -bearing fluids to pervade the sedimentary pile, resulting in the destruction of the detrital Fe- and Ti-oxides due to 'sulfurization' reactions of the type:



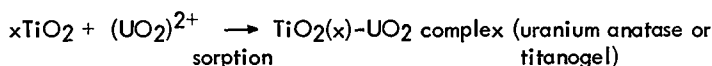
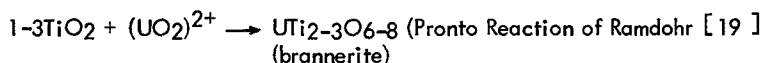
It must also be noted that such 'sulfurization' might well have been a result of biologic activity or due to the breakdown of sulfur-bearing organics.

Thus a suite of secondary sulfides such as pyrite and chalcopyrite would be accompanied by Ti-oxides such as anatase and 'titanogels'. Arsenides and carbonates might also be precipitated at this stage. The long sedimentary history of the aulocogen terminating 1600 to 1500 m.y. ago resulted in the burial of the lowermost Proterozoic sediments and associated volcanics under a maximum of 11 km of sediments and igneous rocks. Such burial would inevitably lead to the burial metamorphism of the older rocks of the suite up to grades approximating at least to the prehnite-pumpellyite facies ($\sim 270^\circ\text{C}$ and $\sim 3.3\text{kb}$ minimum). At this time U-bearing solutions derived either from resident connate waters, by leaching of the volcanic suites or from the underlying Churchill basement (which was undergoing cataclasis and taphrogenic activity), would attack the secondary sulfide assemblage. This would result either in the production of uraninite pseudomorphs after sulfides or a replacive assemblage of uraninite + hematite:



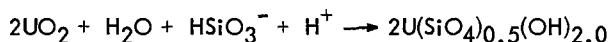
It is noteworthy that the presence of barite in some of the occurrences is accounted for by these reactions.

At the same time it is possible that the Ti oxides produced by the degradation of ilmenite might either react with or adsorb U from the solutions:



The presence of organics in the rocks would at this grade of metamorphism be manifested by graphite which in turn might act as a reductant or adsorbant of U. The organics could also be a source of sulfide ion species when degraded.

The presence of HSiO_3^- in the solutions would at the same time account for the association of coffinite with uraninite; the reaction being perhaps of the type:



Conclusions

The uraniferous fluvatile arenites of the Great Slave Lake region are in many respects analogous to the epigenetic sandstone-type deposits of the west-central U.S.A. and especially, with respect to their quartzitic hosts, to those of the Black Hills in southwestern S Dakota and NE Wyoming. Their association with a Proterozoic intracratonic basin and the local redistributional features noted adjacent to certain faults is reminiscent of the deposits of the Franceville basin, Gabon ([14] and [15]). There is however, a possibility that the Canadian deposits might be the first examples of a 'sandstone-type' generated by metamorphic fluid regimes rather than by the circulation of groundwaters at shallow crustal levels. In this respect they perhaps constitute a sub-class of deposits between the classic sandstone-type deposits of younger eras on the one hand and the mobilized, syn-metamorphic types exemplified by the vein deposits of Eldorado, N Saskatchewan and Port Radium-Echo Bay, NW Territories discussed previously by Morton and Sassano ([16], [17] and [18]) and by Robinson and Morton [20] and Badham et al [21].

Whilst the study of the Great Slave Lake occurrences is far from complete, the observations and genetic hypotheses mentioned herein do widen the possible exploration horizons for future low-cost nuclear resources. That is, such deposits might in future be sought within either fluvatile or marine basins containing thick sedimentary-volcanic sequences, deposited on or adjacent to regions which subsequently or penecontemporaneously underwent regional metamorphism and extensive disruptive deformation.

Acknowledgements

The generous assistance of Vestor Explorations Ltd. is acknowledged. Prof. D.G.W. Smith has greatly assisted in the electron microprobe analyses performed in his laboratory at the University of Alberta. Prof. H. Baadsgaard's help in the geochronological studies is gratefully acknowledged. M.A.D. Olade and R. Walker are thanked for their aid in the assembly of data and materials. This work was funded through N.R.C. grants Nos. A4242 and A4254.

References

- [1] LITTLE, H.V., Uranium deposits in Canada - their exploration, reserves and potential. *Canad. Inst. Mining and Metallurgy Bull.*, 67, no. 743 (1974) 155.
- [2] ANON., Mokta's uranium deposits hold intriguing potential. *Northern Miner*, July 5 (1973).
- [3] LANG, A.H., Canadian deposits of uranium and thorium. *Geol. Survey of Canada, Econ. Geol. Series*, No. 16 (1960).
- [4] LANG, A.H., GRIFFITH, J.W., STEACY, H.R., Canadian deposits of uranium and thorium. *Geol. Survey of Canada, Econ. Geol. Series*, No. 16, (2nd ed.) (1952).
- [5] LITTLE, H.V., Uranium in Canada (Project 670029). *Geol. Survey of Canada, Paper 72-1 part A, Report of Activities* (1972) 81.
- [6] HOFFMAN, P.F., Evolution of an early Proterozoic continental margin: the Coronation geosyncline and associated aulacogens of the NW Canadian Shield, in "Evolution of the Precambrian Crust". *Phil. Trans. Royal Soc. London* (1973) 1.
- [7] HOFFMAN, P.F., Proterozoic paleocurrents and depositional history of the East Arm fold belt, Great Slave Lake. *Canadian Jour. Earth Sci.*, 6 (1969) 441.
- [8] HOFFMAN, P.F., FRASER, J.A., MCGLYNN, J.C., The Coronation geosyncline of Aphebian age, district of Mackenzie. *Geol. Survey of Canada, Paper 70-40* (1970) 201.
- [9] OLADE, M.A.D., MORTON, R.D., Observations on the Proterozoic Seton Formation, East Arm of Great Slave Lake, Northwest Territories, *Canad. Jour. of Earth Sciences* 9, no. 9 (1972) 1110.
- [10] SALOP, L.T., SCHEINMANN, Y.M., Tectonic history and structures of platforms and shields. *Tectonophysics* 7 (1969) 565.
- [11] HOFFMAN, P.F., Aphebian supracrustal rocks of the Athapuscow aulacogen, East Arm of Great Slave Lake, District of Mackenzie. Project 660009. *Geol. Survey of Canada, Paper 73-1A* (1973) 151.
- [12] THORPE, R.I., Lead isotopic evidence on the age of mineralization, Great Bear Lake. *Geol. Survey of Canada, Paper 71-1B* (1971) 72.
- [13] HOFFMAN, P., DEWEY, J.F., BURKE, K., Aulacogens and the reconciliation of Belousovian and Wilsonian tectonics (1973) in press.
- [14] BOURREL, J., PFIFFELMAN, J.P., La province uranifère du bassin de Franceville (République Gabonaise), *Mineralium Deposita* 7 (1972) 323.
- [15] WEBER, R., Une série Précambrienne du Gabon: Le Francevilien. *Mém. du Service de la Carte Géol. d'Alsace et de Lorraine*, 28 (1968) 328 p.

- [16] MORTON, R.D., SASSANO, G.P., Structural studies on the uranium deposit of the Fay Mine, Eldorado, Northwest Saskatchewan, Can. Jour. Earth Sci. 9, no. 11 (1972) 1368.
- [17] SASSANO, G.P., FRITZ, P., MORTON, R.D., Paragenesis and isotopic composition of some gangue minerals from the uranium deposits of Eldorado, Saskatchewan, Can. Jour. Earth Sci. 9, no. 2 (1972) 141.
- [18] SASSANO, G.P., The nature and origin of uranium mineralization at the Fay Mine, Eldorado, Saskatchewan, Ph.D. thesis, Dept. of Geology, University of Alberta (1972).
- [19] RAMDOHR, P., The ore minerals and their intergrowths, (1969) Pergamon-Oxford.
- [20] ROBINSON, B.W., MORTON, R.D., Geology and geochronology of the Echo Bay area, N.W.T., Canada, Can. Jour. Earth Sci. 9, no. 2 (1972) 158.
- [21] BADHAM, J.P., ROBINSON, B.W., MORTON, R.D., The geology and genesis of the Great Bear Lake silver deposits, (Proc. 24th. Int. Geol. Congr. Montreal, 1972), Sect. 4, Mineral Deposits, IGS, 601 Booth st., Ottawa (1972) 541.

DISCUSSION

J. C. ROWNTREE: Are the known uranium deposits within the Proterozoic contemporaneous with the enclosing rocks?

R.D. MORTON: Yes; but they have certainly, as you would expect, undergone remobilization.

J. C. ROWNTREE: Is there some definite relationship between the gold and the uranium?

R.D. MORTON: The amount of gold that has been detected in the area is very small indeed. The occurrence that actually stimulated the research in the first place turned out to be a small vein associated with an intrusion nearby. It was sampled, quite accidentally, at the wrong site.

H. W. LITTLE: I believe that roll-type deposits can occur in Proterozoic basins. When I visited the Carswell Dome area, the first discovery I was shown looked like a roll deposit. When excavated it was about the size of a large cabbage, and it is my opinion that a roll had been formed and subsequently largely destroyed by oxidizing ground-water solutions. A U-Pb age determination on pitchblende from the deposit showed Early Tertiary, but not too much weight should be attached to this because there was great disequilibrium.

In the deposits you described from Simpson Islands in Great Slave Lake, which I visited a few years ago, the dark material you mentioned is to the best of my recollection in the form of round spots surrounded by hematized zones which are of irregular shape and rather widely spaced. Apart from the dark spots — which are highly radioactive — the hematized zones are quite radioactive, and the activity seems to be proportional to the degree of hematization. These zones are all close to fractures. Would you therefore consider that these deposits might be of hydrothermal origin?

R.D. MORTON: There is a distinct possibility that hydrothermal readjustment took place. Unquestionably, the deposits that you saw in the Simpson Islands had been modified to some extent by faulting. The deposits that have been found since your visit are more typically of the roll type;

they are much larger in size, and the grades are, as you know, as high as 6.7% U_3O_8 in the Reliance area. These deposits have little connection with faults, as the faults are at a very considerable distance. I agree, however, that the faults are so numerous that they must have affected the situation in some way.

R.G. WILSON: What relationship, if any, have you found between primary and secondary (surface) mineralization?

R.D. MORTON: If you are referring to the oxidized facies of the surface, it is difficult to say exactly what the relationship is. We are doing an age determination at the moment, and although it might well turn out to be Tertiary, it could also be Precambrian. It is probably best not to speculate for the time being.

R.G. WILSON: Is there any clear relationship between the mineralization that has been found and the proximity of the volcanic members of the sequence?

R.D. MORTON: We are analysing all the volcanics in the region by gamma spectrometry and studying uranium-thorium ratios to determine whether these volcanic members have acted as contributors. But of course there is the further problem — encountered also in the Colorado Plateau, for example, and in many other places — that if the solution has passed through these volcanic members it will have added uranium to them too. We have analysed the spilitized rocks, and although they show the typical thorium-uranium ratio of one, they also show — and this is perhaps typical for spilites — a uranium enrichment of something like five times the normal. Thus, while I would like to see these members depleted, unfortunately they are very enriched.

H.H. ADLER: What do you postulate as the source of the sulphide?

R.D. MORTON: The source of the sulphide could be volcanic; there might have been exhalative sulphur contributions in the form of sulphide ion species entering the waters either during sedimentation or later. Then one has to remember the other possibility, namely a biogenic contribution, which we are studying by isotopic analyses. A better answer will be possible when the sulphur isotopes have been thoroughly analysed.

H.H. ADLER: If you postulate a biogenic origin, what is the source of the organic material? I ask this question in view of the fluvial nature of the host rock, which presumably would contain no plant remains as we know them in younger rocks containing sandstone-type deposits.

R.D. MORTON: The sequence is characterized by vast thicknesses of stromatolitic limestones in which both algal flora and bacterial flora have been present. The origin would be brackish in the marginal area, and partly marine farther to the southwest. From these sources the sulphur could have migrated into the fluvial facies.

A.G. DARNLEY: I am not able to comment on the ultimate significance of the uranium occurrences which you have described from the East Arm of Great Slave Lake, but I would draw attention to the fact that very prominent potential source areas for uranium concentration lie both to the north and to the south of the East Arm. Regional uranium enrichment occurs over an area of several thousand square miles, the enrichment being among the most extensive so far discovered in the Shield. Therefore, if the various theories about the necessity of having suitable source areas for sedimentary uranium are valid, the East Arm would seem to be a very obvious place to look for mineralization.

R.D. MORTON: Yes, your surveys have shown clearly that the material is there. I would tend to favour the south side, however.

A.G. DARNLEY: But it would be wrong to underestimate the importance of the Slave Province as a source area. Data released in April this year clearly demonstrate this fact.

J. PASQUALI: Once you have found a basin such as you have described, what suggestions do you have for locating uranium deposits within the basin?

R.D. MORTON: In this particular instance I am postulating that the metamorphic fluids were probably the mineralizing solutions. Accordingly, one might be tempted to look first in the deeper parts of the basin. On the other hand, we know that the fluids will tend to move outward as well. One useful approach would be to try to determine the paleo-environment in terms of the heavy mineral suites, because the oxides control the development of the sulphides, and the oxide facies will accordingly be the primary controlling factor. The sulphides in turn control the deposition of uranium, so the sulphide facies – the replacing sulphides – will also afford a lead. Thus you have, as it were, two mineralogical guides to follow, oxides and sulphides, as well as the uranium itself.

S.H.U. BOWIE: Would you agree there is a distinct possibility that uranium phases such as uraninite and coffinite were derived from detrital minerals such as brannerite, euxenite or columbite? The residual titanium would form minerals such as anatase and rutile. The evidence from many Proterozoic deposits is that anatase and rutile pseudomorph pre-existing detrital minerals.

R.D. MORTON: I have seriously considered the possibility that uranium may have come from original detritals. It is certainly a theory that deserves further discussion. I believe people shy away from the concept of uranium associated with metamorphism, possibly because we know so little about the relationship.

SEDIMENTARY BASINS AND
SANDSTONE-TYPE DEPOSITS:
PERMIAN DEPOSITS IN EUROPE

REVIEW OF URANIUM OCCURRENCES IN PERMIAN SEDIMENTS IN EUROPE, WITH SPECIAL REFERENCE TO URANIUM MINERALIZATIONS IN PERMIAN SANDSTONE

F.H. BARTHEL

Bundesanstalt für Bodenforschung,
Hanover, Federal Republic of Germany

Abstract

REVIEW OF URANIUM OCCURRENCES IN PERMIAN SEDIMENTS IN EUROPE, WITH SPECIAL REFERENCE TO URANIUM MINERALIZATIONS IN PERMIAN SANDSTONE.

This summary from the literature reviews the uranium occurrences in Permian sediments in Europe. It covers primarily the most important, mineable uranium occurrences in sandstone in France, Italy, Yugoslavia and Hungary.

Uranium in sandstone most commonly occurs in fluvial, lacustrine and deltaic deposits and is related to the presence of plant remains, carbonized wood, and pyrite as reducing agents. Concentration processes are strongly influenced by the presence of clayey horizons. A feature of the lithology and facies which was observed is a relation between uranium concentrations and a change of colour of the sandstone from grey to red.

In connection with the genesis of the sandstone mineralization, the occurrences in mixed sedimentary and volcanic deposits are treated in detail. The mineralization related to volcanism and Permian volcanic rocks may have had an influence on the later enrichment processes in the sediments. Examples are used to illustrate the processes in the course of the metamorphism of uranium enrichments of sedimentary origin. Finally, the genetic conditions accompanying the enrichment of uranium in bituminous shales and in coal are reviewed.

1. INTRODUCTION

Among the uranium occurrences in sandstone throughout the world, the nonmarine Mesozoic and Tertiary deposits in the United States of America are of primary importance. When the paleogeographical and sedimentological conditions which led to uranium enrichments there are compared with those prevailing in Europe at the end of the Paleozoic, certain parallels may be seen between European and US strata, especially in the Lower Permian rocks. Locally, commercial-quality uranium mineralization occurred in continental clastic deposits. Such concentrations are present not only in psammitic rocks but also in a wide range of other clastic sediments including sedimentary-volcanic deposits. For a genetic interpretation of the mineralization in Permian sandstone in Europe, it is worthwhile to consider in somewhat more detail the manifold nature of the uranium enrichments.

This paper reviews the literature on uranium enrichments in Permian sediments in Europe with particular emphasis on the various forms of enrichment. The different points of view about genesis will not be balanced against each other or used to derive a new theory.

2. THE LOWER PERMIAN IN EUROPE

The most important features of the Permian deposits will be considered here. For the distribution of uranium concentrations, only the nonmarine Lower Permian strata are important. Various names are in use in geological literature such as "Rotliegende" in Germany, "Autunien" or "Saxonien" in France, and "Verrucano" in the Alpine region. Three large paleogeographic provinces may be distinguished for the Lower Permian deposits.

2.1. Northern or sub-Variscan province

This province comprises parts of the United Kingdom, the North Sea, Northern Germany, Denmark, Holland and Belgium. Permian sedimentation began in depressions with the accumulation of conglomeratic strata commonly accompanied by volcanism. Towards the top of the section, the predominantly psammitic deposits become finer grained. A red colour is characteristic. The southern part of the province had several troughs striking north or north-northeast. These received sediments from the surrounding uplands.

2.2. Central or Variscan province

This province extends from southwest England and France over the central part of the Federal Republic of Germany, southern Democratic Republic of Germany, and part of Czechoslovakia reaching as far as Poland. In this province typically late Variscan conditions continued into the Permian. Commonly, sedimentation continued from the Late Carboniferous into the Permian without interruption.

Sedimentation began with grey or greyish red fluviatile or limnic deposits. Limestone, coal seams and bituminous shale are common. Deposition in intramontane basins is characteristic for the region. The composition of the sediments is influenced by relief, volcanism and tectonics. In the upper Rotliegende are red sediments and fanglomerate as a result of arid conditions.

2.3. Southern or Verrucano province

This province is restricted to the Alpine and Apennine basins. Many features of these mountain basins are identical with those of the Variscan province, for instance, inexact boundaries of the nonmarine Carboniferous sediments and gradational contacts with Triassic deposits. Not only intramontane basins but also regions which probably were partly connected with the Tethys Sea were sites of sedimentation.

The basal strata are primarily conglomerate. They are followed by grey and red sediments of fluviolacustrine facies. The differentiation into channels, closed basins, and fresh-water lakes led to a substantial variety of sedimentary types. Contemporaneous volcanism resulted in the formation of mixed sedimentary and volcanic deposits.

At the end of the Early Permian, deposition of the Kupferschiefer north of the Variscan mountains formed a transition to the marine Zechstein. This littoral, shallow-water deposit extends from the United Kingdom to

the Soviet Union and contains substantial concentrations of non-ferrous metals within its 0.5-2 m thickness of sandy, marly, and clayey bituminous strata.

3. URANIUM MINERALIZATIONS IN SANDSTONE

3.1. Federal Republic of Germany

In the Lower Rotliegende several small uranium concentrations are known to exist in the Sarre and Nahe trough. Near Obermoschel, six uraniferous horizons occur at contacts between sandstone and claystone in the lower part of a grey sedimentary sequence [1]. The uranium is related primarily to carbonaceous material (wood) and lenticular pyrite concentrations and is contained in carburan, pitchblende and coffinite. The uranium minerals are accompanied by pyrite, marcasite, some chalcopyrite and sphalerite. The fact that the claystone contains practically no uranium suggests epigenetic mineralization by circulating solutions which precipitated their metal ions in a reducing environment. The claystone acted as a stratigraphic trap. At present, only areally restricted concentrations are known.

Other uranium occurrences in the Upper and Lower Rotliegende are probably related to Permian volcanism. Commonly the sandstone is mineralized near the contact with rhyolitic rocks or the sandstone contains conglomerate with mineralized volcanic pebbles. A mineralization of a completely different nature occurred in a Lower Rotliegende sandstone and resulted in a uranium-vanadium concentration within spheroidal bodies [2]. These bodies contain between 0.005 and 0.3% U besides 0.5% to < 10% V and between < 1% and > 10% carbon. The dark grey to black cores are surrounded by bleached haloes which are considered to have resulted from removal of hematite pigment. The genesis has not been satisfactorily determined to date.

3.2. France

Uranium occurs in the basins around the Massif Central. The most well known is the Lodève basin [3]. Permian deposition began with Autunian strata over a dissected, pre-Permian basement. A basal conglomerate is followed by fine-grained sandstone with mud cracks, bituminous limestone, and shale with plant remains. On top of these are reddish and grey psammitic and pelitic deposits.

The depositional environment was initially swampy and had a rich flora. In individual lagoons, sediments accumulated in deep and tranquil water. Temporarily flooded, relatively stable areas are distinguished by terrestrial vegetation (conifers). The climate was tropical, moist, and hot with intermittent drier periods. Another characteristic feature of the Autunian sequence is the occurrence of acid volcanic ash horizons with high alkali contents. Mineralized horizons are found mostly on the flanks of channels. They occur as about 50 silt-clay intercalations in the region where the sandstone changes from grey to red. The mineralized horizons contain abundant plant remains and bitumen and their carbonate content increases stratigraphically upwards (increase of evaporation).

Mud cracks are also present. The uranium minerals present are carburan and some pitchblende. The mineralized zone is lenticular and stratified and it formed under lithological as well as tectonic control. In all probability the enrichment was syngenetic. The uranium was probably supplied by solutions formed during weathering of granite within the Massif Central. In the depositional basin the uranium was precipitated under reducing conditions during sedimentation. In joints and traps subsequent enrichment probably occurred under the influence of migrating bitumen. In most areas there is a good correlation between the carbon and uranium contents. Besides uranium mineralization, enrichment of Pb and Cu also occurred. Zinc is also concentrated along some joints. The uranium is accompanied by V, Mo, Mn, Ba, Sr, Sn, As and, in lesser quantities, Ni, Co and Sb [3, 4]. Two samples gave radiometric ages of 158 m.y. (Jurassic) and 230 m.y. (Permian) on the basis of the ratios $^{207}\text{Pb}/^{235}\text{U}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ respectively.

Further Autunian age occurrences are located along the southern and southwestern borders of the Massif Central (St. Affrique, Rodez, Brive, Laguèpie-Monesties). Mineralization was generally related to clay, bituminous clay and sandy clay. Carburan enrichments are found in arkose and secondary mineralization occurred in conglomerate and coarse-grained sandstone [5]. The mineralization took place where organic material is present in iron oxides as well as where grain sizes change. As a rule, enrichment was restricted to where the colour of the sediment changes from grey to red. The uranium content is usually not high (0.04-0.09%).

3.3. Italy

In the Verrucano province, uranium enrichment was restricted to individual basins or parts of basins some of which contain more than 100 tons of uranium.

The sandstone mineral occurrences can be classified into alpino-type and germano-type facies areas on the basis of paleogeography [6, 7]. In both facies areas, substantial magmatic activity (granite and acid volcanic rocks) was contemporaneous with Early Permian sedimentation and resulted in accumulation of sedimentary-volcanic strata.

The major uranium occurrences (Val Rendena, Val Daone) are located in areas with very thick sedimentary sequences (6000-8000 m) such as, for instance, the Lombardy trough. The mineralization occurred primarily in the basal transition between coarse-grained grey sandstone and fine-grained red sandstone (Grödener sandstone). These sediments are fluvial or deltaic with lacustrine or lagoonal intercalations. Characteristic features are poor sorting, cross-bedding, ripple marks, and load casts. The uranium enrichments are concordant with stratification. Commonly, several thin horizons occur one above the other. However, lenticular, diffusely mineralized zones also occur. Coarse- to medium-grained arkose and silty and pelitic horizons containing carbonized wood are mineralized. Besides uranium, pyrite, and occasionally also sphalerite, tetrahedrite, galena, and chalcopyrite occur. Mineralization in the alpino-type zones is considered epigenetic. The uranium presumably present in the volcanic rocks, either finely distributed or as hydrothermal enrichments, was carried away by circulating solutions and deposited in suitable horizons as uraninite.

In basins with restricted sedimentation, a synsedimentary uranium enrichment in epicontinental pelite and siltite is assumed to have taken place under the influence of organic material and pyrite. Remobilization is not completely excluded [8].

Near Bolzano, uranium is associated with galena and forms a syngenetic, stratiform, red-bed concentration. The lenticular enrichments are most common in medium-grained grey sandstone containing plant remains. Uraninite is present and, in zones influenced by tectonic phenomena, also colloform pitchblende as a result of mobilization. These deposits are generally small and contain from 500-8000 ppm uranium. The metals originated from the volcanic rocks.

3.4. Switzerland

The uranium mineral occurrences of the Mürtschenalp (Canton of Glarus) in the Helvetian nappe belong to the Verrucano province. The sequence begins with red conglomerate, continues as conglomeratic sandstone, and ends with mudstone. The sediments in these strata are considered to have been produced by the arid erosion of the Variscan blocks. Tectonism resulted in intense jointing and the circulation of solutions which caused part of the sediments to turn grey in colour. These phenomena led to the formation of sericite and chlorite as well as the development of carbonate and quartz veins. This was accompanied by a mesothermal or epithermal copper mineralization resulting in the replacement of pitchblende which was probably sedimentary in origin [9]. Sedimentological relicts suggest such uranium deposition, presumably under the influence of organic material.

Other Permian uranium occurrences in Switzerland bear still stronger imprints of tectonic and mobilization processes and so will be treated with the metamorphically altered deposits.

3.5. Austria

Near Fieberbrunn, in the northern greywacke zone of Tyrol, a uranium enrichment has been found in grey sandstone within a Permo-Triassic sequence [10]. This sequence begins with coarse-grained sandstone followed by red sericite quartz sandstone and sericitic schist. Intercalated between these are beds of carbonate-containing, grey to grey-green sandstone with hematite, pyrite and marcasite. Locally magnesite enrichments are also present. The carbonates are interpreted to be authigenic, syndiagenetic deposits. The grey sandstone locally contains plant remains. Along many horizons are presumably synsedimentary copper enrichments as well as pyrite and pitchblende. Together with pyrite, the uranium ores fill the cell walls and pores of carbonized plant remains.

The mineralization occurred during the Triassic and mineralized the lagoonal-brackish, shallow-water deposits. The uranium was precipitated syndiagenetically from metalliferous weathering solutions when they encountered reducing conditions during sedimentation. These deposits are comparable with those in Northern Italy or Yugoslavia.

Near Schladming in the Lower Tauern, uranium is enriched in Permian sericitic quartzite and sericitic phyllite. Whether the processes which formed this deposit are comparable to those producing the sandstone

mineralizations is not yet resolved. Some features indicate a mineralization comparable to the mineralizations (discussed below) of the greenschist facies in the Alps.

In the case of the uranium mineralization of the Mitterberg copper deposit (Salzburg) the uranium is presumed to have been derived by metamorphic mobilization processes from sedimentary concentrations in the Permian sandy shale of the greywacke zone [11].

3.6. Yugoslavia

In the Lower Permian Gröden sandstone, uranium is concentrated in lenses in grey fluviatile sandstone near Žirovski Vrh (Slovenia) [12]. Continental sediments extend from the Upper Carboniferous to the Upper Permian. The lower strata are about 800 m of grey to grey-green sandstone with intercalations of red siltstone. Above is red sandstone with grey intercalations [13]. The grey to red colour-change parallels bedding.

The uranium is in lenses in the lower grey sandstone, which are from 0.5-1.5 m thick and extend over areas of several hundred to several thousand square metres. The uranium is restricted to a sequence about 150-m thick and is contained in pitchblende which occurs either in the cement or finely distributed in organic matter. In part, the uranium is related to locally higher pyrite contents. An association with galena and chalcopyrite is rare. Sphalerite, tetrahedrite, bornite, realgar, marcasite, arsenopyrite, covellite, ilmenite, Cr-spinel, and pyrrhotite occur independently of uranium. Where present, the uranium content varies between 0.05 and 0.25% U_3O_8 . Reserves are estimated to be more than 5000 tons of uranium.

Cyclic sedimentation is recognizable in the mineralized sandstone. Oblique- and cross-bedding are rare. Schistosity has obliterated the original sedimentary structure. The composition of the sediments suggests the presence of volcanogenic detritus and intercalations of tuffite are present locally. A geochemical investigation of the sandstone showed the presence of less than 50 ppm of V, Cr, Ni and Cu (in order of decreasing concentration). The grey, unmineralized sandstone has a higher uranium content and lower thorium content than the red sandstone. The uranium in the grey sandstone is easier to dissolve than that in the red sandstone. This feature was probably important for the concentration of the uranium in the grey sandstone.

3.7. Hungary

In the Mecsek Mountains, about 500 m of Upper Permian fluviatile sandstone contain uranium enrichments. The deposits are composed of arkosic sandstone and siltstone with siliceous and calcareous cement as well as lenticular claystone intercalations which are preponderantly grey in colour (indicating a low redox potential). Above is red sandstone with iron-rich argillaceous and calcareous cement (indicating an elevated redox potential) [14].

The uranium occurs along the borders of swampy to fluviatile deposits, whose lenticular form derives from the original sedimentation of fine-grained deposits rich in vegetable matter in association with arkose. The paleogeographic setting suggests that deposition was on a fluviatile talus fan. The material must have been transported over a distance of

some 10 km. It was derived from the erosion of granitic rocks enriched in Bi, Co and Ni [15].

The uranium mineralization took place along the banks of a meandering stream with an abundant flora. Migration of the stream bed led to the formation of numerous pools and flooded areas with coarse-grained arkose and fine-grained clays. Low precipitation favoured an infiltration of mineralized waters into the border zone (with dead vegetation) and permitted the uranium ore to be precipitated as uranite.

The uranium concentrated primarily within arkose intercalations the detritus of which was derived mostly from granitic rocks. At the same time, some basic igneous detritus was also deposited as is shown by the presence of chromium-containing hydromicas. They also contain vanadium. The U, Cr and V content of the sandstone varies greatly, ranging from 0.008-0.015% U_3O_8 , 0.16-3% Cr_2O_3 and finally 0.03-0.08% V. In mineralized zones a substantial increase of the uranium content is observed.

Geochemical and sedimentological observations suggest that the uranium mineral occurrences formed shortly after the deposition of the permeable sandstone. The lower permeability of the lacustrine clays severely restricts their uranium content. The uranium in these early epigenetic products was in part mobilized during diagenesis; however only minor concentrations resulted. Uranium mineralization was accompanied by formation of Pb, Zn, Cu, Ni and Co sulphides or arsenides.

Uranium in Permian sandstone has also been described by geologists in Czechoslovakia [16] and Poland [17]. These occurrences are in the intramontane basins of Northern Bohemia and the Sudeten area which contain conglomerate, sandstone and claystone together with coal seams and organic matter. They were deposited under either fluvial or lacustrine conditions.

In the Northern Bohemian trough, U and V are concentrated in carbonate concretions and bleached haloes in coal and dark shale. Presumably, the enrichments originated post-depositionally by selective precipitation from mineralizing solutions, which was favoured by a warm, dry climate [18].

4. MIXED SEDIMENTARY-VOLCANIC MINERALIZATIONS

In various parts of Europe, Permian volcanism led to hydrothermal uranium mineralization or volcanogenic metal impregnations. These processes attained substantial importance in Northern Italy and Czechoslovakia and resulted in the development of mixed sedimentary-volcanic deposits.

In Czechoslovakia such mineralization occurs in the Slovakian Erzgebirge, a part of the Western Carpathian Mountains. The stratigraphic sequence begins with the conglomerate having intercalations of sandstone, siltstone and quartz-porphyry. On top of these are volcanoclastic beds with quartz porphyry, tuffite, sandy shale and sandstone [19]. These grade into greywacke, shale, marl and evaporite deposits. Volcanic activity occurred primarily during the deposition of the middle and upper parts of the sequence. In the middle part, volcanism led to a uranium-molybdenum mineralization of the country rock. The upper complex underwent a uranium-copper mineralization. In both cases there were auto-metasomatic alterations. The quartz porphyry has been enriched in pitch-

blende, black oxides, molybdenite and copper sulphides [20, 21] as well as galena, sphalerite and arsenopyrite.

5. URANIUM MINERALIZATIONS IN METAMORPHIC ROCKS

The types described are restricted to Switzerland, Northern Italy and Austria.

In Northern Italy, uranium has been concentrated in rocks of the greenschist facies. In all probability the epimetamorphic quartz-mica schist, sericitic phyllite, and sericitic quartzite were originally greywacke and impure sandstone. Commonly, the original relationship between the microcrystalline uraninite and plant remains can be recognized in only slightly metamorphosed rocks. Occasionally a relation with graphite and apatite (phosphorite) can be observed. This signifies marine ingressions. Geologically, the occurrences were usually related to the Pennine zones. Frequently, the composition and age of the original rocks can no longer be proven with absolute certainty [22].

Detailed observations of the metamorphic mobilization processes are available from the Preit Valley in the Cottian Alps [22]. Here, the original rocks were clastic sediments which were metamorphosed to sericitic-chloritic schist. The uranium was originally associated with pyrite and plant remains. During metamorphism, uranium ore and sulphides were mobilized. The first products to form were nodular and lenticular enrichments. Hard ores such as pyrite and pitchblende show cataclastic deformation. In pressure shadows there are intergrowths which show the different stages of mobilization. With softer ores such as sphalerite, some myrmekitic intergrowths formed. Occasionally the mobilized pitchblende segregated into reniform or scaly structures which closely resemble hydrothermal products. These mobilized deposits are characterized by lack of order in the sequence of segregation as well as by the presence of the same ore in different stages of transformation.

Within the Penninic St. Bernhard nappe in the Canton of Valais in Switzerland, chloritic-sericitic schist and sericitic-albitic gneiss (Cassana Series) contain a metamorphically altered U-Cu-Pb-Mo mineralized zone. The original rocks were a sequence of Upper Carboniferous to Lower Triassic sedimentary rocks. The mineralized horizons are thought to be Lower Permian. Presumably the uranium and non-ferrous metal mineralization was originally sedimentary [23], but the genetic relationships are ambiguous. During Alpine metamorphism, the minerals were mobilized and underwent complicated recrystallization. In part, the mobilization caused the ores to migrate to the neighbouring rock.

In greenschist of the Eastern Alps in Austria, sericitic quartzite and sericitic phyllite contain slightly metamorphosed uranium concentrations.

6. URANIUM MINERALIZATIONS IN SHALE AND COAL

The uranium occurrences of the Kupferschiefer are one of the most common types of mineralization.

The Kupferschiefer is a transgressive marine deposit at the base of the Upper Permian Zechstein limestone. It was deposited in a shallow-water area 2500 km long and 300 km wide. The usual sequence begins with

a conglomerate or fine-grained, light-grey sandstone (Weissliegendes). Over this is the bituminous Kupferschiefer which is about 1 m thick. It consists of very bituminous clay (up to 15% bitumen), bituminous clay-marl, slightly bituminous marl, and dolomitic limestone part of which is sandy. The Kupferschiefer is characterized by a horizontal and vertical zoning of the metal distribution. The greatest Cu contents (2-3%) are encountered in coastal regions, whereas farther away from the coast are higher Pb (approx. 0.5%) as well as Zn (approx. 2%) contents.

In the Mansfeld region is a vertical zoning [24, 25] in which in the lower, argillaceous horizons Cu was deposited, followed by Pb as a filling of calcareous shells and by Zn as an incrustation on these shells. The segregation sequence is believed to have resulted from changes in redox conditions and pH values both of which influence the solubility products of the metal ions. Involved were probably poorly aerated minor basins and marginal bays. As a rule the accompanying elements have fewer possibilities for correlation. Silver is assumed to have been deposited parallel with Cu while Co and Ni are related to the carbon content and V and Mo are associated with clay minerals. Presumably, the uranium was precipitated early and was related to an obviously polymerized bitumen (pitchy horizon) in the lower part of the sequence. Here, the uranium is closely associated with thucholite.

The average uranium content of the Kupferschiefer is of the order of 0.004% although locally it reaches about 0.02% and more.

The uniform precipitation of the non-ferrous metals and uranium over broad areas and the fact that the zoning depends on both the solubility product and the paleogeography are arguments for syndimentary or syndiagenetic origin.

Also present are epigenetic enrichments along vein fissures [25]. Here, a paragenetic association of Bi-Co-Ni with barite as well as U-Mo-Re enrichment was followed by a copper mineralization rich in Ag and Ge. Part of this paragenesis is presumed to have been dissolved by migrating bitumen and then redeposited as thucholite beds.

In the Mansfeld region, pebbles of propylitized volcanic rock in the Weissliegende and the underlying Permian have undergone a Cu-Pb-Zn mineralization. Consequently, the following relations of the genetic cycle of the Kupferschiefer deposits may be reconstructed.

- (a) Cu-Pb-Zn mineralization of propylitized Permian volcanic rocks.
- (b) The formation of depressions prior to deposition.
- (c) Erosion under arid conditions and deposition of the resultant detritus in sedimentary basins.
- (d) Mixing of the metal-bearing water of these basins with transgressive marine water.
- (e) Precipitation of the metals in stagnant areas under the influence of microorganisms.
- (f) Subsequent mineralization with Bi, Co, Ni, Ag, Mo, U, Re and Ge along veins.

Metal deposits comparable to the Kupferschiefer are contained in bituminous shale of some intramontane basins. In a bituminous shale (paper shale) from 3-5 cm thick in the Sarre-Nahe depression, there appears to have been a seasonal change between deposition of very calcareous and

slightly bituminous laminations on the one hand and very bituminous and slightly calcareous horizons on the other. In the very bituminous material, uranium is enriched to 0.005%. Besides uranium there is up to 0.05% Cu, 0.1% Pb, 0.05% Zn, 0.035% V, 0.01% Mo, 0.015% Ni, 0.02% Cr and 0.004% Co. These enrichments were apparently syngenetic.

Coal of the Rotliegende depressions (such as the Sarre-Nahe depression) is commonly enriched in uranium. The uranium content fluctuates from 0.002-0.005% but may rise to about 0.04%. Mostly the uranium is adsorbed on the coal and the adjacent shale.

The coal seams of the Stockheim basin in Lower Franconia have substantial uranium contents in certain areas. The uranium mineralization has affected the coal as well as the shale. Investigation of the general area has shown that the uranium is undoubtedly related to the coal seams.

Near Dresden, the Rotliegende coal of Freital is enriched in uranium [26]. The uranium minerals are probably related to the non-ferrous metal-containing shale in the sequence. The ashes may contain as much as 0.12-1% U_3O_8 . The mineralization is considered to have been syngenetic.

7. CONCLUSION

In summary it can be concluded that, among the numerous uranium enrichments in Permian sediments of Europe, the concentrations in sandstone are of primary importance. They occur in fluviatile deposits, preferably where argillaceous beds were deposited together with the sandstone (such as in the Mecsek Mountains of Hungary). The mineral deposits related to the change of colour from grey to red within the sandstone may be considered a subtype of fluviatile deposits (Žirovski Vrh, Yugoslavia; Val Rendena, Italy). Another type of mineralization is related to silty and pelitic intercalations in the sandstone. The uranium minerals were produced by syngenetic processes controlled by sedimentological and tectonic events (Lodève, France). Uranium mineralization in sedimentary-volcanic deposits (Czechoslovakia, Northern Italy) is considered to be a special case. Part of the uranium which is concentrated in metamorphic rocks in the Alps was derived from uranium enrichments of sedimentary origin. Relative to the uranium sandstone, the last two types of occurrences are of subordinate economic importance. This is also true for uranium enrichments in shale and coal.

REFERENCES

- [1] REE, Ch., et al., *Sedimentäre Uranvorkommen in Rheinland-Pfalz* (1973), unpublished.
- [2] EICHHOFF, H.H., et al., *Uran-Vanadinkerne mit Verfärbungshöfen*, Neues Jahrb. Mineral. Monatsh. 11/12 (1952) 294.
- [3] GARRIC, J., *L'uranium dans le Carbonifère et le Permien de l'Hérault*, Les minerais uranifères français, Bibl. Sciences Techn. Nucl. 2, Presses Universitaires de France, Paris (1965).
- [4] GANGLOFF, A., "Notes sommaires sur la géologie des principaux districts uranifères étudiés par le CEA", Uranium Exploration Geology (Proc. Panel Vienna, 1970), IAEA, Vienna (1970) 77.
- [5] CARRIQU, L., *Les gîtes et indices sédimentaires du Massif Central*, Les minerais uranifères français, Bibl. Sciences Techn. Nucl. 2, Presses Universitaires de France, Paris (1965) 95.
- [6] MITTEMPERGER, M., "Characteristics of uranium ore genesis in the Permian and Lower Triassic of the Italian Alps", Uranium Exploration Geology (Proc. Panel Vienna, 1970), IAEA, Vienna (1970) 253.

- [7] MITTEMPERGHER, M., "The paleogeographical, lithological and structural controls of uranium occurrences in the Alps" (Proc. Symp. Bled, 1971), Geoloski Zavod, Ljubljana (1972); Razpr. in Poročila 15 (1972) 63.
- [8] CEVALES, G., Erzmikroskopische Untersuchung von zehn Uranvorkommen des italienischen Perms der West- und Ostalpen, Neues Jahrb. Mineral., Abh. 94 (1960) 733.
- [9] BÄCHTIGER, K., Die Kupfer- und Uranmineralisation der Mürtschenalp (Kt. Glarus, Schweiz), Beitr. Geol. Schweiz, Geotechnische Serie 38 (1963).
- [10] SCHULZ, O., et al., Eine Uranerzlagerstätte in permotriadischen Sedimenten Tirols, Tscherma's Mineral. Petrogr. Mitt. 14 (1970) 213.
- [11] SIEGL, W., Die Uranparagenese von Mitterberg (Salzburg, Österreich), Tscherma's Mineral. Petrogr. Mitt. 17 (1972) 263.
- [12] JOKANOVIĆ, V., et al., "The uranium deposit of Žirovski Vrh" (Proc. Symp. Bled, 1971), Geoloski Zavod, Ljubljana (1972); Geologija, Razpr. in Poročila 15 (1972) 91.
- [13] PROTIČ, M., et al., "Terrigene Permablagerungen als uranführende Sedimente in Slowenien" (Proc. Symp. Bled, 1971), Geoloski Zavod, Ljubljana (1972); Geologija, Razpr. in Poročila 15 (1972) 77.
- [14] BARABAS, A., et al., Mechanism of formation of sedimentary uranium ores at the Mecsek deposit, Lithol. Miner. Resour. 8 (1966) 247.
- [15] KISS, J., Constitution minéralogique et genèse du gisement uranifère de la Montagne Mecsek (II), Ann. Univ. Sci. Budapest, Rolando Eotvos Nominatae, Sect. Geol. 14 (1971) 79.
- [16] PLUSKAL, O., "Uranium mineralization in the Bohemian massif", Uranium Exploration Geology (Proc. Panel Vienna, 1970), IAEA, Vienna (1970) 107.
- [17] MORAWIECKI, A., Occurrence of uranium minerals in Poland, Kwart. Geol. 4 (1960) 869.
- [18] SKOČEK, V., Vanadium and uranium accumulation in the Permo-Carboniferous sediments of central and northeastern Bohemia, Cas. Miner. Geolog. 12 (1967) 419.
- [19] DRNŽIK, E., et al., Some remarks about geological boundaries between Permian and Werfenian in the Novoveska Huta area, Geol. Průzkum Bratis. 30 (1963) 39.
- [20] ROJKOVIČ, J., Mineralogical-geochemical characterization of U-Mo-Cu-mineralization in the Permian of the Spísko-Gemerské Rudohorie Mts, Geol. Zb. Bratislava, Geol. Carpath. 19 (1968) 179.
- [21] ROJKOVIČ, J., Petrography and geochemistry of Permian quartz-porphyrries in relation to U-Mo-Cu-mineralizations, Geol. Zb. Bratislava, Geol. Carpath. 20 (1969) 87.
- [22] CEVALES, G., Metamorphe Mobilisationsvorgänge in der Uranlagerstätte des Preitales (Kortische Alpen), Neues Jahrb. Mineral. Abh. 96 1 (1961) 112.
- [23] HÜGI, Th., et al., Die Uranvererzung bei Isérables (Wallis), Beitr. Geol. Schweiz, Geotechnische Serie 42 (1967).
- [24] KNITZSCHKE, G., Zur Erzmineralisation, Petrographie, Hauptmetall- und Spurenelementführung des Kupferschiefers im SE-Harzvorland, Freiburger Forschungshefte, Mineral. u. Lagerstättenlehre C 207 (1966).
- [25] SCHÜLLER, A., Metallisation und Genese des Kupferschiefers von Mansfeld, Abh. Deut. Akad. Wiss. Berl., Kl. Chemie, Geologie, Biologie 6 (1958).
- [26] ZIEHR, H., Uranhaltige Kohlen in Europa, Glückauf 97 (1961) 1370.

BIBLIOGRAPHY

- D'AGNOLO, M., "Manifestazioni uranifere connesse ad arenarie permiane nel Trentino Sud-Occidentale", Atti Symp. Internaz. Giacimenti Minerari Alpi (Proc. Symp. Trento, Italy, 1966) 2, Economia Trento della C.C.I.A.A. (1966) 253.
- D'AGNOLO, M., "Manifestazioni uranifere nell'arco alpino occidentale", Atti Symp. Internaz. Giacimenti Minerari Alpi (Proc. Symp. Trento, Italy, 1966) 2, Economia Trento della C.C.I.A.A. (1966).
- BARABAS, A., et al., "The genesis and sedimentary petrographic character of enrichment of uranium ore in Mecsek Mt.", Int. Conf. Peaceful Uses Atom. Energy (Proc. Conf. Geneva, 1958) 2, UN, New York (1958) 388.
- von BRAUN, E., Die mit Bundesmitteln unterstützte Uranprospektion der Jahre 1956-1962, Gersbach, Munich (1965).
- BRONDI, A., et al., Uranium and Heavy Metals in Permian Sandstones near Bolzano (Northern Italy), Int. Union Geol. Sci. Series A 3 (1973) 65.

- DYBEK, J., Zur Geochemie und Lagerstättenkunde des Uran, Clausthaler Hefte 1 (1962).
- FALKE, H. (Ed.), *Rotliegend: Essay on European Lower Permian*, E.J. Brill, Leiden (1972).
- HEINRICH, E., *Mineralogy and Geology of Radioactive Raw Material*, McGraw-Hill, New York (1958).
- HERZBERG, W., Die Uranführung der Unterrotliegend-Sedimente insbes. der Mittleren Lebachter Schichten, Ph.D. Dissertation, Technical Univ. Berlin (1962).
- IPPOLITO, F., "The uranium-bearing formations of the sediments of the late Alpine Paleozoic", Int. Conf. Peaceful Uses Atom. Energy (Proc. Conf. Geneva, 1958) 2, UN, New York (1958) 612.
- JANTSKY, B., et al., "A characteristic case of uranium migration observed in the foothills along the shore of Lake Balaton", Ibid., p.64.
- KISS, J., "Uraniferous chromium ore and its paragenetic role in the Mecsek Permian aggregate", Ibid., p.398.
- KISS, J., Constitution minéralogique, propriétés et problèmes de genèse du gisement uranifère de la Montagne Mecsek (I), Ann. Univ. Sci. Budapest Rolando Eotvos Nominatae, Sect. Geol. 9 (1965) 139.
- LENOBLE, A., et al., "The present state of knowledge of thorium and uranium deposits in France and the French Union", Int. Conf. Peaceful Uses Atomic Energy (Proc. Conf. Geneva, 1958) 2, UN, New York (1958) 569.
- OPPERMANN, H., Uran- und Spurenelementführung von Kohlen und anderen Sedimenten des Stefan C und des Unterrotliegenden der Saar-Nahe-Senke, Ph.D. Dissertation, Technical Univ. Berlin (1967).
- PANTIĆ, R., et al., "Present state of exploration and reserves of nuclear raw materials in Yugoslavia", Int. Conf. Peaceful Uses Atomic Energy (Proc. Conf. Geneva, 1971) 8, IAEA, Vienna (1972) 73.
- REE, Ch., Uranvorkommen im Saar-Nahe-Gebiet (Rheinland-Pfalz), Abd. Hess. Landesamt Bodenforschung 56 (1970) 163.
- RUZICKA, V., Geological Comparison between East European and Canadian Uranium Deposits, Geological Survey of Canada Paper 70-48 (1971).
- WEDEPOHL, K.H., Untersuchungen am Kupferschiefer in NW-Deutschland, ein Beitrag zur Deutung der Genese bituminöser Sedimente, Geochim. Cosmochim. Acta 28 (1964) 305.
- WEDEPOHL, K.H., Kupferschiefer as a Prototype of Syngenetic Sedimentary Ore Deposits, Soc. Mining Geol. Japan, Spec. Issue 3 (1971) 268.

DISCUSSION

B.P. POTY: You mentioned a uranium deposit, probably of sedimentary origin, in the Verrucano of Switzerland. Since it appears that this deposit underwent alpine metamorphism, I wonder whether you could say what modifications occurred in the mineralization during this process.

F.H. BARTHEL: There appears to have been strong metamorphic remobilization of the primary pitchblende, followed by pitchblende deposition in sedimentary rock together with the enrichment of other elements, presumably during metamorphism. It is assumed that these processes were sedimentary in origin.

H.H. ADLER: I am impressed, when I read the literature on copper and other minerals, by the preponderant opinion that metallization in the Permian formations of Europe – and this seems to apply particularly to the Zechstein and Rotliegende relationships – is syngenetic. What, in your opinion, is the ratio of syngenetic to epigenetic uranium deposition in the Permian uranium deposits of Europe?

F.H. BARTHEL: The literature I have reviewed does suggest a preponderance of syngenetic formations with epigenetic enrichment playing a more limited role. It is difficult to suggest a ratio for syngenetic versus

epigenetic enrichment, but on the evidence available 3:1 would seem to be a reasonable estimate.

M. MITTEMPERGHER: I believe that most occurrences of uranium in the Permian are epigenetic. In some cases, particularly when the sediments are very strongly metamorphosed, it is possible to conclude in favour of syngenetic metallization, often from the evidence offered by stratigraphic composition. Stratigraphically, we find, in the Alps, uranium occurrences in close proximity to marine sediments, quartzite and limestone. In such environments there is generally a lot of apatite and organic matter near the uranium minerals. Only in these cases, I feel, can we speak with reasonable conviction of syngenetic origin. But these deposits represent a much smaller fraction of the total than the epigenetic deposits.

H.H. ADLER: Yes, that is what I would have expected.

PERMO-TRIASSIC URANIUM ORE IN THE AUSTRIAN ALPS – PALEOGEOGRAPHIC CONTROL AS A GUIDE FOR PROSPECTING

W.E. PETRASCHECK, E. ERKAN
Montanistische Hochschule Leoben,
Leoben

K. NEUWIRTH †
Bergbau- und Mineralgesellschaft Vienna,
Vienna
Austria

Abstract

PERMO-TRIASSIC URANIUM ORE IN THE AUSTRIAN ALPS – PALEOGEOGRAPHIC CONTROL AS A GUIDE FOR PROSPECTING.

Since 1968, a large-scale prospecting campaign for uranium ore has been carried out in Austria. Research in the Western and Southern Alps was concentrated on the sandstone facies of the Permian and Lower Triassic. These beds, partly developed as red and grey sandstones, partly as semi-metamorphic quartzites and sericite-chlorite schists, are terrestrial and lagoonal in origin, while their upper parts are of shallow marine origin. After rearrangement of these deposits, which appear in their original position in the different overthrust nappes systems, distinct troughs and platforms can be delineated according to the variations of the thickness of the beds. These features interfere with the general E-W strike of the Alpine geosyncline, following predominantly a transversal direction, which was conditioned by the prealpine Hercynian structures. The comparatively larger uranium layers are situated in or nearest the areas of greater thickness, that is, in the Permian troughs. A remobilization and reconcentration of uranium happened in those localities where younger hydrothermal solutions have penetrated into uraniferous sandstones.

Almost all of the uranium ore deposits in Europe are related, directly or indirectly, to the Hercynian orogenic and metallogenic belt. Therefore, when uranium prospecting in Austria began in 1957, it was mostly carried out in the southernmost part of the Bohemian massif and in those parts of the Central Alps which are considered to be regions of Hercynian intrusions and metamorphism. These investigations were unsuccessful. Thorough radiometric surveying of the tertiary lignite mines led to the detection of a few considerable local uranium enrichments in coal seams, north of the Alps, explainable by their geologic environment, but of no economic significance [1]. Finally, regarding the experience in the Western and the Southern Alps in France, Switzerland, Italy and Yugoslavia, where uranium was found in Permian sandstones and sericite-quartzites and phyllites, Petrascheck [2] directed the attention of the prospecting organization to the metamorphic Permo-Skythian schists in the Central Alps, but this too failed and was given up, owing partly to insufficient equipment, and partly to the fall of the uranium prices in the early sixties.

A new and modern prospecting campaign was started in 1968 by the Bergbau- und Mineralgesellschaft in Vienna. This campaign concentrated on the areas of the nonmetamorphic Gröden Sandstein (Permian) in

† Deceased.

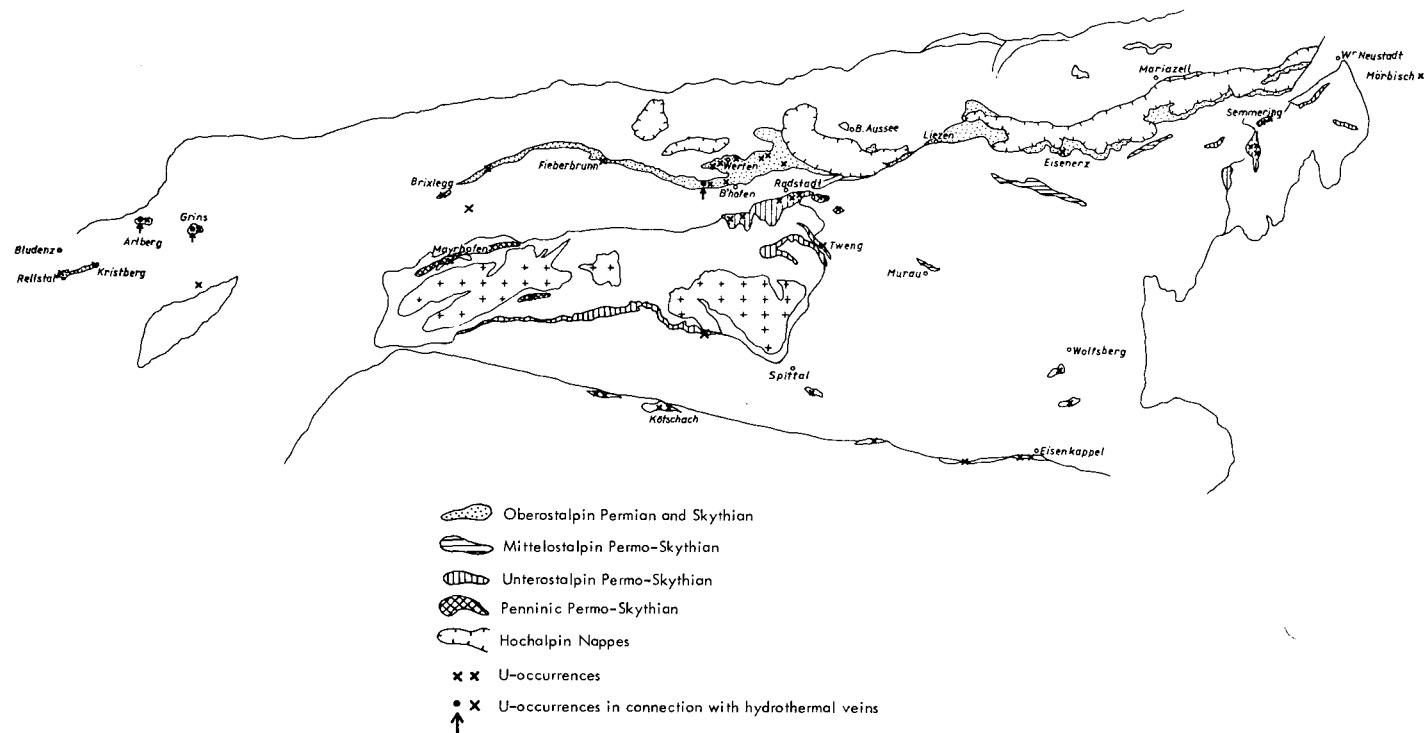


FIG. 1. Uranium-occurrences in the Austrian Alps.

Southern Austria, on the nonmetamorphic Buntsandstein and Werfen schists (Permian and Lower Triassic) in the Northern Kalkalpen and on the epimetamorphic sericite-chlorite quartzites (Permo-Triassic) in the Central Alps. The Permo-Skythian areas are distributed along the main tectonic zones in the E-W direction; their total surface is about 1300 km². The initial prospecting was carborne; important anomalies were investigated by prospecting on foot and later by drilling, sampling and in Forstau also by galleries. About 60 places with strongly anomalous radioactivity have been found; 20 of them deserve exploration. The single ore bodies are layer- or lense-shaped; their length varies between approximately ten to a few hundred metres. The extension of the ore-bearing zones is a few kilometres, always elongated in the alpine E-W direction. The content of the ore is between 0.05 and max. 2% U. The leader of the prospecting organization was one of the authors (K. Neuwirth, Ref. [3]) who died accidentally in November 1973. Prospecting for uranium ore in Austria is not yet completed, but the encouraging results achieved so far give an idea of the factors which controlled the distribution of uranium ore in Austria.

The Permo-Skythic beds in the Eastern Alps have a psammitic facies, their upper parts having a more pelitic facies. These beds are of fluvial, lagoonal and shallow marine origin, with increasing marine influence in the higher levels. They were formed under semi-arid conditions which are documented by their predominantly reddish color and by the occurrence of evaporites in the Upper Permian.

These deposits are exposed in the different longitudinal tectonic zones of the Eastern Alps (Figs 1 and 2). The northernmost zone is represented by Buntsandstein and Werfener Schiefer; this is called "Oberostalpin". In the Central Alps the Permo-Triassic quartzite and schists appear in three tectonic units, the "Mittelostalpin", the "Unterostalpin" and the "Penninic". In all these units which are characterized by a very reduced thickness of the overlying Triassic limestones, the rocks are metamorphic. (The distinction between Unterostalpin and Mittelostalpin, adapted here according to Tollmann, is still disputed, because the facies, the sequence and the metamorphism of these two series are very similar.) In the Southern Alps, the Permian Grödener Sandstein with its well-known intercalation of quartz porphyry lies above gray shales and sandstones of Upper Carboniferous age.

Uranium mineralizations are known to occur in all of these units, e. g. in the "Oberostalpin" Buntsandstein near Fieberbrunn (Tyrol), in "Mittelostalpin" quartzites of the Rannach Series (Styria), in the "Unterostalpin" sericite quartzites of Forstau (Salzburg) and the Semmering (Styria), in the Penninic schists near Mayrhofen (Tyrol) as well as in the Grödener Sandstein of the Gailtaler Alpen and Karawanken (Carinthia). Anyhow, the sericite-chlorite quartzites of the "Unterostalpin" seem to be the most favourable schists. An excellent review of the Permo-Skythian stratigraphy is given in the volume of the "Verrucano Symposium", Vienna (1972), and particularly in an article by Mostler [5], dealing with Tyrol and Salzburg.

When we spread out the tectonic nappes and rearrange them into their original position, we came to the picture of Fig. 2. The lowest nappe system, the Penninic, was deposited in the northernmost area, whereas the highest nappes (Oberostalpin) have been transported and overthrust from a trough in the South. The Mittel- and Unterostalpin sediments have

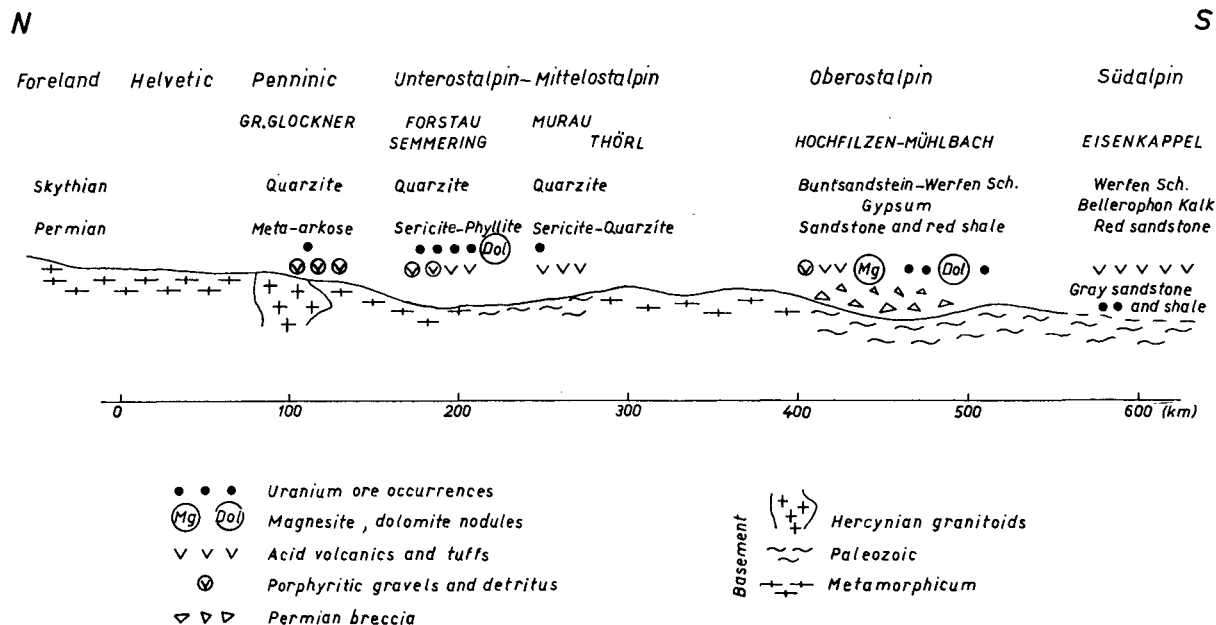


FIG. 2. The rearrangement of the tectonic zones of the Eastern Alps.

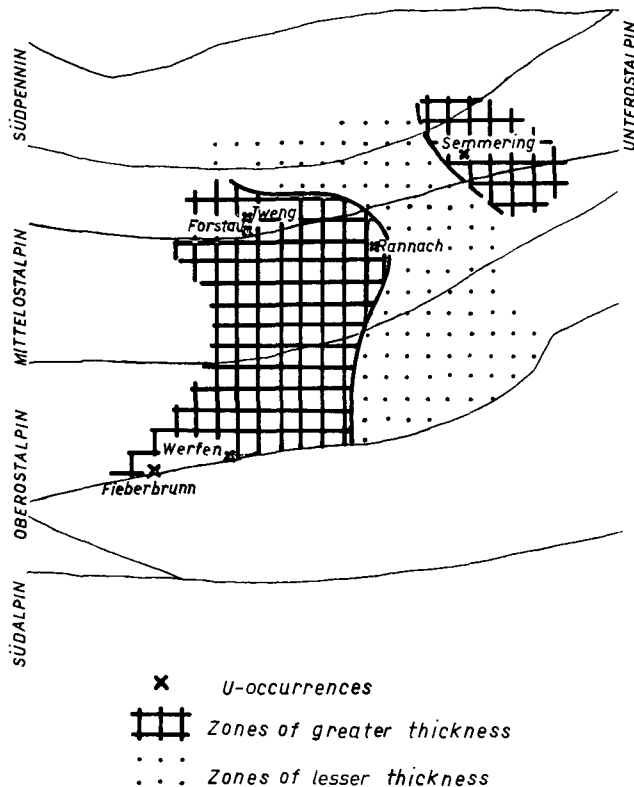


FIG. 3. Upper Permian facies zones in the eastern part of the Austrian Alps (Erkan, 1973).

been at least partly deposited at somewhat higher levels of the prealpine basement. Farther to the south, the Grödener Sandstein lies more or less in its original position.

However, this arrangement, which reflects very well the depositional conditions since middle Triassic time (exactly since the Anisian), is not completely valid for the Permian and the Skythian. Current investigations by one of the authors (E. Erkan) have shown that one has to distinguish between areas of greater and lesser thickness of the Permo-Skythian and that these areas extend transversal to the E-W direction of the present tectonic zones (Fig. 3). This observation fits perfectly well with analogous statements in the Grödener zone of the Italian Alps, published by Mittempergher [6]. The Permian of the greater thickness — 500 m on the average — begins with a thin layer of conglomerate and consists mainly of greyish and reddish shales and sandstones, locally containing nodules of magnesite, dolomite or gypsum and very few intercalations of acid volcanic tuffs; these are covered by gypsum deposits. The Permian having the lesser thickness — 30 to 300 m — begins with a conglomerate and consists

predominantly of arkoses and quartzites. Between these two areas sections with a basal breccia and more interbedded carbonates can be recognized; here again thick layers of gypsum form the top of the Permian. It seems that the important uranium occurrences are confined to the thicker sequence.

The thick Permian sequence partly represents the deposits of the beginning ingression of the Tethys Sea, coming from the South, whereas the thin Permian sequence seems to be mostly terrestrial. These different areas are conditioned by the pre-Permian relief of the Hercynian underground. Further detailed investigations by Erkan hope to show whether the different series correspond to separate N-S troughs and ridges, or whether they indicate depressions and elevations within initial epirogenic E-W structures of the alpine geosyncline. Also marine and fresh-water sediments will have to be distinguished by additional criteria.

Considering the well-founded assumption that the NNE-SSW directed tectonic zones of the Bohemian massif have entered the area which later was occupied by the Tethys geosyncline and then was overworked by the alpine orogenesis [7], one might even try to find out what were the surroundings of the Permian basins and from where the uranium in the sediments could be derived. It seems that the depressions can be correlated to zones of soft paleozoic schists, whereas the elevations correspond to high metamorphic underground or to paleozoic limestones. Thus there is an erosion relief.

If one tries to find the provenance of the uranium by paleogeographical considerations, conflicts arise. Uranium-bearing granites are known in the Hercynian north of the Alps (Schwarzwald, Bohemia). In the Western Alps, uranium occurrences in Hercynian granites and gneisses are reported from the autochthonous massif of Mont Blanc, which is situated north of the uranium-bearing schists of the Penninic nappes (see map by Hügi and co-workers [8]). In the Eastern Alps, the syenite of Gastein, belonging to the Penninic system of the Tauern and assumed to be a rejuvenated Hercynian rock, has a higher uranium content, up to 70 ppm. However, the northernmost Permian trough, the Penninic one, is the poorest in uranium. One will have to assume source areas which are now buried under alpine nappes. A heavy mineral study might help answer the question.

Mitttempergher has shown that almost all of the uranium occurrences in the Italian Alps are connected with acid volcanics. The greatest concentrations are found in the structural lows, where volcanic rocks are extensively present. This correlation exists in the Austrian Alps too, but is not nearly so apparent. Almost all the Permian deposits with uranium contain porphyritic intercalations or volcanic detritus, but there is no correlation between the intensity of mineralization and the frequency of volcanics. In the Buntsandstein, volcanics are scarce and in the Skythian Werfener Schiefer, where remarkable occurrences of ore exist, acid volcanics are absent.

It might be mentioned, however, that in the Western United States of America acid volcanics are considered an essential metallotect for sandstone-type uranium deposits [9].

Finally, one observation might be described here which shows a particular mode of uranium concentration in sandstone deposits. The well-known hydrothermal copper vein of Mühlbach near Bischofshofen cuts black siluric schists; these schists are overlain by violet quartzites of probably lower Permian age. These quartzites contain small stratiform layers of very

fine-grained uranium ore (uraninite and brannerite). The chalcopyrite-ankerite vein enters into the violet quartzite bed, but here it is less rich. On both sides of the vein, black nodules of uranium ore have been detected, some of them having a size of a few centimetres. In spite of their concretionary shape they proved to be uraninite, as a result of the careful investigations of Siegl [10]. As these nodules occurred along the hydrothermal copper-ankerite vein only, they can be explained by the leaching and redeposition of the sedimentary ore in the quartzite. But the surprising phenomenon was that the uraninite nodules contained native gold in their cracks. The copper vein does not have a commercial content of gold, and only traces of gold have been found in the ore.

The explanation of the precipitation of gold from very poor solutions by the uranium ore might be found in the reduction effect of tetravalent uranium when it gets oxidized to hexavalent uranium. To check this hypothesis, one of the authors (E. Petrascheck) asked the Head of the Department of Analytical Chemistry of the University of Vienna, Professor Dr. F. Hecht, whether gold can be precipitated by UO_2 solutions. Dr. E. Schmid of this department was kind enough to dissolve some uraninite from Morogoro in H_2SO_4 and to add AuCl_3 -solution; up to 68% of the gold was precipitated.

The occurrence of uranium enrichment near the copper vein of Mühlbach might indicate the value of further prospecting. Some radioactive anomalies have been found in the vicinity of hydrothermal ankerite near Permian sandstones in Western Tyrol. Therefore the intersection of hydrothermal ore veins with uranium-bearing sediments deserves attention.

REFERENCES

- [1] PETRASCHECK, W.E., SCHUBERT, H., VOHRYZKA, K., Über uranhaltige Kohlen und Kohlenschiefer in Österreich, Berg- u. Hüttenm. Monatsh. 104 1 (1959).
- [2] PETRASCHECK, W.E., Methoden und Aufgaben der Lagerstättensuche in Österreich, Almanach d. Österr. Akad. Wiss. 120 (1970).
- [3] NEUWIRTH, K., Uran – ein neuer Energierohstoff, Das Kernkraftwerk 15 5/6 (1973).
- [4] SCHULZ, O., LUKAS, W., Eine Uranlagerstätte in permotriadischen Sedimenten Tirols, Tschermaks Mineral. Petrogr. Mitt. 14 (1970) 213.
- [5] MOSTLER, H., Zur Gliederung der Permoskyth-Schichtfolge im Raume zwischen Wörgl und Hochfilzen (Tirol), Verh. Geol. Bundesanstalt, Wien (1972) 155.
- [6] MITTEMPERGER, H., "Characteristics of uranium ore genesis in the Permian and Lower Triassic of the Italian Alps", Uranium Exploration Geology (Proc. Panel Vienna, 1970), IAEA, Vienna (1970) 253.
- [7] CLAR, E., Bemerkungen für eine Rekonstruktion des variskischen Gebirges, Z. Dtsch. Geol. Ges. 122 (1970) 161.
- [8] HÜGI, Th., DE QUERVAIN, F., HOFFMÄNNER, F., Übersichtskarte der Uran- und Thorium-Mineralisationen der Westalpen, Schweizerische Geotechnische Kommission, Bern (1962).
- [9] GRUTT, E.W., "Prospecting criteria for sandstone-type uranium deposits (US)", Uranium Prospecting Handbook (BOWIE, S.H.U., DAVIS, M., OSTLE, D., Eds), (Proc. Nato-sponsored Adv. Study Inst. on Methods of Prospecting for Uranium Minerals, London, 1971), Inst. Min. Metall. London (1972) 47.
- [10] SIEGL, W., Die Uranparagenese von Mitterberg (Salzburg), Tschermaks Mineral. Petrogr. Mitt. 17 (1972) 263.

DISCUSSION

S.H.U. BOWIE: Could you tell us something more about the nature of the brannerite and uraninite near Mühlbach? Does it appear that these

deposits are detrital or of epigenetic origin? Age determination studies on this material would probably shed a lot of light on the genesis of the occurrence.

W.E. PETRASCHECK: Yes, as I said, the brannerite and uraninite that we find in the sandstone near Mühlbach are very fine-grained materials. On both sides of the hydrothermal vein lie the uraninite nodules which were investigated by W. Siegl, by electron-microscopic scanning among other things. Siegl confirmed that, though the material was anisotropic, it definitely consisted of brannerite and uraninite; and, as we point out in our paper, a surprising finding was that the uraninite nodules contain native gold in their cracks. You are quite right that age determination would be valuable. Among other things it might reveal the age of the vein itself, which has given rise to much controversy: some consider it to be a remobilization product from some stratiform Silurian schist. In any case, we have sent samples to Zürich for age determination, and I shall be pleased to let you know the results.

GENETIC CHARACTERISTICS OF URANIUM DEPOSITS ASSOCIATED WITH PERMIAN SANDSTONES IN THE ITALIAN ALPS

M. MITTEMPerGHER
CNEN - Laboratorio Geominerario,
CSN - Casaccia,
S. Maria di Galeria (Rome),
Italy

Abstract

GENETIC CHARACTERISTICS OF URANIUM DEPOSITS ASSOCIATED WITH PERMIAN SANDSTONES IN THE ITALIAN ALPS.

The Permian continental sandstones of the Alps show numerous small uraniferous, stratiform epigenetic occurrences.

The most interesting occurrences are related to a basal member mainly composed of grey sandstones and conglomerates, which represent sediments formed in a piedmont environment. These sediments are not oxidized and differ from the overlying red sandstones (typical of an environment strongly oxidized) of alluvial and coastal plain sedimentation. The control of the mineralization was seen to be linked to the permeability and the reducing environment caused by the presence of organic matter in the piedmont sediments.

The continental sedimentary basin that began to form in the Lower-Middle Permian evolved during the Triassic-Permian into a marine basin, lasting through the whole Mesozoic. This evolution of the basin did not cause processes of remobilization of the pre-existing mineralizations, while the effects of the diagenesis and of the Alpine metamorphism hardly modified the structure of the deposits.

INTRODUCTION

Uraniferous mineralizations are continuously present in the Permian continental sandstones, which occur in the whole Alpine range. These mineralizations have been classified as stratiform epigenetic, even if locally the effects of diagenesis and of metamorphism have caused modifications in the mineralogical pattern and in the geometry of the deposits. The mineralizations in the zones of major interest and frequency (Val Rendena, Val Daone, Val Pescara in Italy, Žirovski Vrh in Yugoslavia) are characterized by a close association of uranium with grey, grey-green coloured sandstones which represent a basal horizon of the Permian series, made up otherwise of red coloured sandstones.

From studies carried out so far it is clear that the control of the mineralizations was due in part to the presence of organic matter (diffused or concentrated) in the grey sandstone. It has been more problematic so far to define the stratigraphic, sedimentological and hydrological processes that caused the precipitation of the uranium minerals within the grey sandstone horizon near the contact with the overlying red sandstone. Another genetic problem concerns the shape and the distribution of the occurrences, and their relationships to the geotectonic evolution of the zone. To clear up the main points of this problem all of our geological and minerogenetic knowledge

contained in previous scientific works was re-evaluated and stated in a more organized way. We also compiled all the sedimentological information on sandstone formation occurring in Italian territory.

1. DISTRIBUTION AND CHARACTERISTICS OF MINERALIZATIONS

Figure 1 gives the geographic distribution of the Permian sandstone outcrops in the Italian Alps and the main uraniferous mineralizations connected with these sandstones are indicated. The mineralizations are particularly located in a zone trending NE-SW, which includes the Val Rendena - Val Daone and the Val Pescara - Val D'Ultimo areas. All the occurrences are stratiform; in some cases they are lens-shaped and concordant, in other cases they are composed of thin overlain layers. The deposits can be divided into two groups (Fig. 2):

(a) Deposits contained in the basal grey sandstone, in areas where the sandstone formation is made up of a basal grey member and a red upper one. These are the uraniferous deposits of major interest and are the most common in Val Rendena, Val Daone and Val Pescara.

(b) Deposits contained within grey sandstone intercalated in the red sandstone formation. These deposits are of no economic interest and are scattered on the whole outcropping area of the Permian sandstones.

The distribution of the uraniferous mineralizations within the sandstone complex is closely related to the presence of grey sandstone facies. These facies are almost always found interbedded with red sandstone facies. Only in the Val Rendena, Val Daone and Val Pescara area do the grey sandstones make up a thick basal member in the Permian sedimentary sequence. In this basal member the most important uraniferous mineralizations are concentrated.

The structural characteristics of the deposits and the mineralogical and chemical composition of the mineralizations are, in general, uniform.

The differences in their characteristics do not permit genetic distinctions and mostly depend on local conditions.

The deposits are always stratiform. Within the layer the mineralizations can be lens-shaped and show different uranium contents. Pitchblende and microcrystalline uraninite (black oxides) are the only uraniferous minerals in the ores and are minerals often diffused in the sandstone matrix or in the groundmass of small volcanite pebbles [1].

Where the sandstone has been subjected to weak metamorphism, the pitchblende forms layers locally massive and often associated with levels of coal. Chalcopyrite, pyrite, galena, sphalerite, arsenopyrite, tennantite, etc. often occur in random variable quantities. Where the uraniferous mineral is scattered in the sandstone matrix, the sulphides of Cu, Pb and Zn are also diffused without revealing paragenetic succession.

Wherever the pitchblende shows characteristics of synmetamorphic or syndiagenetic redeposition, the other minerals also reveal replacement structures. The spatial extent of this remobilization was quite restricted.

Generally, apart from the deposits affected by thermal halo due to Mesozoic granitic intrusion (of Alpine age), this remobilization has not altered the structural features of the deposits and their stratiform character. The dominant geochemical association is characterized by the presence of U with Pb, Zn, As, Fe.

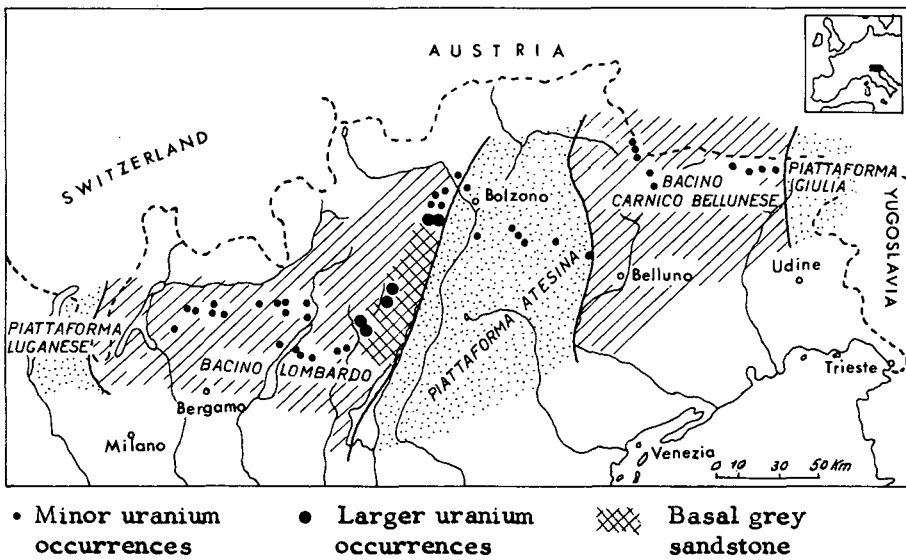


FIG.1. Geographical distribution of uranium occurrences and of basal grey sandstone.

MARGINAL PART OF VOLCANIC PLATFORM

CENTRAL PART OF VOLCANIC PLATFORM

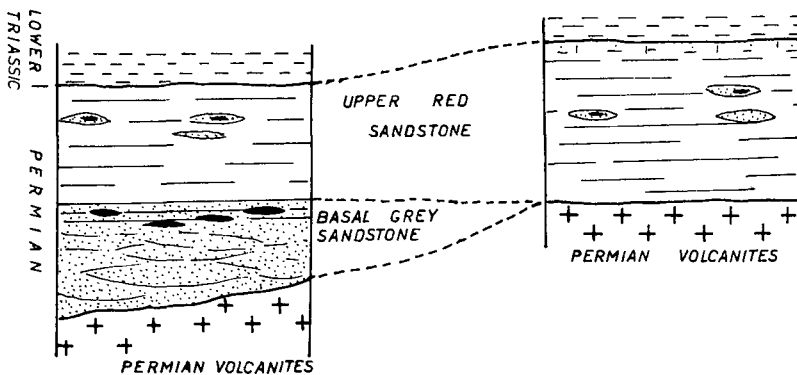


FIG.2. Uranium occurrences.

The amounts of these elements vary. Sometimes Pb and Zn are more abundant than uranium. The less frequent association is that of uranium with copper. Copper occurs in greater amounts mostly in the mineralizations contained in grey sandstone interbedded with the red sandstone. In this case considerable amounts of carbonates occur. The organic matter, both as log remnants more or less carbonized to fusitic terms, as well as scattered in the matrix, always occurs in the uraniferous mineralizations. Even in the case of remobilization of mineralizations, the carbonaceous material represented an ideal situation for the redeposition of pitchblende and sulphides. The recognition of the factors controlling the mineralizations has been difficult because of poor outcropping conditions and the effects of diagenesis on the original features of sediments.

The primary epigenetic character of these mineralizations, located in a littoral basin [2] subjected to a slow subsidence, results from their structural and paragenetic features. The distribution of the deposits within the sedimentary sequence and their preferential association with the basal grey sandstone were determined by means of sedimentological, paleogeographical and tectonic studies. The results of this research will permit defining the most likely controls for these mineralizations and the modifications by which they have been affected.

2. RESULTS OF THE SEDIMENTOLOGICAL STUDY ON PERMIAN SANDSTONES

During the last 15 years several specific studies have been carried out on Permian sandstones of Italian Alps. Other studies have been performed on the analogous sedimentary formations of Slovenia (Yugoslavia). From the overall results of these studies, and from the research going on at present at the CNEN, it is possible to define the mineralogical, chemical and sedimentological characteristics of the Permian sandstones and to reconstruct the main sedimentation processes and evolution of this continental clastic formation. To find the controlling factors of uraniferous mineralizations it is necessary to describe the differences between the red and the basal grey sandstones. The basal grey sandstone occurs only in a limited portion of the area considered (Val Rendena, Val Pescara).

According to grain-size studies, a stratigraphic section analysed in Val Rendena [3] shows a clear distinction between basal grey sandstone (Fig. 3), with coarse to very coarse grain size, and the overlying red sandstone, characterized by medium to very fine grain size. These differences in grain size correspond to different deposition environments.

Within the grey sandstone the grain-size classes have a predominantly lens-shaped distribution, typical of a very rapid deposition, while in the red sandstone extensive layers of rather uniform thickness and grain size prevail. This suggests a lower environmental energy and a flatter deposition environment.

The mineralogical composition is rather uniform throughout the whole sequence and is represented by rock fragments, quartz, feldspars, muscovite, clay-seritic matrix or, in places, limonitic, calcitic or chalcedony cement. In the grey sandstone, the K-feldspar is almost wholly altered into sericite, while the matrix remains clay-seritic. In the red sandstone the feldspars are well conserved and the matrix contains limonite and

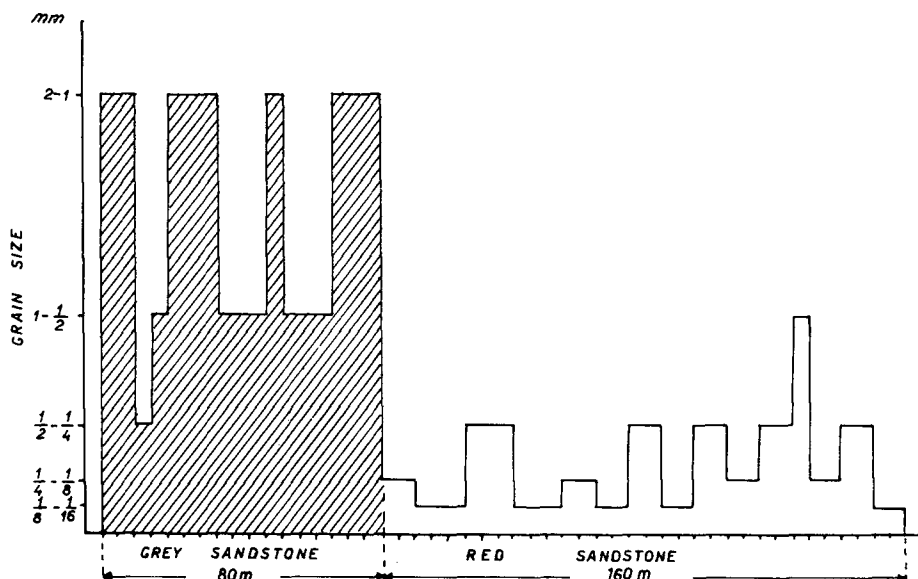


FIG. 3. Size composition of sandstones of Val Rendena series.

calcite. The classification of the sandstones, as summarized in Fig. 4, indicates that generally the grey sandstones tend to fall in the quartz-sandstone field, while the red ones fall between the feldspathic sandstone and the subgreywacke fields. The greater mineralogical maturity found in the grey sandstones is usually due to the almost complete weathering of the K-feldspar contained. The mechanical character of their maturity is demonstrated by the low roundness index, which indicates the very low morphoscopic maturity of grey and red sandstones.

The origin of the components of the sandstones is much the same for both grey and red sandstones [3]. In the zones where the basement of the Permian sedimentary sequence is represented by the volcanites of the lower Permian, the percentage of volcanic clasts can reach values as high as 70-75%. In Val Rendena average values of 50% were found. In general, in the basal grey sandstone there is a higher percentage of components derived from the volcanites than in the red sandstone. In the last case and in particular in their finer facies there are very abundant micas derived from the erosion of the metamorphic basement. This would indicate a progressive widening of the erosion basin towards zones of prevailing outcrops of a crystalline basement.

A series of determinations of K and Na content allows one to define better some mineralogical differences between the grey and red sandstones in Val Rendena [4]. The Na_2O content averages 0.85% in grey sandstone and 2.47% in red sandstone, while K_2O averages 2.52% and 3.32% in grey and red sandstones respectively (Fig. 5). These differences are in part connected with the alteration and sericitization of feldspars contained in the grey sandstone and with the larger amount of white mica in the red sandstone.

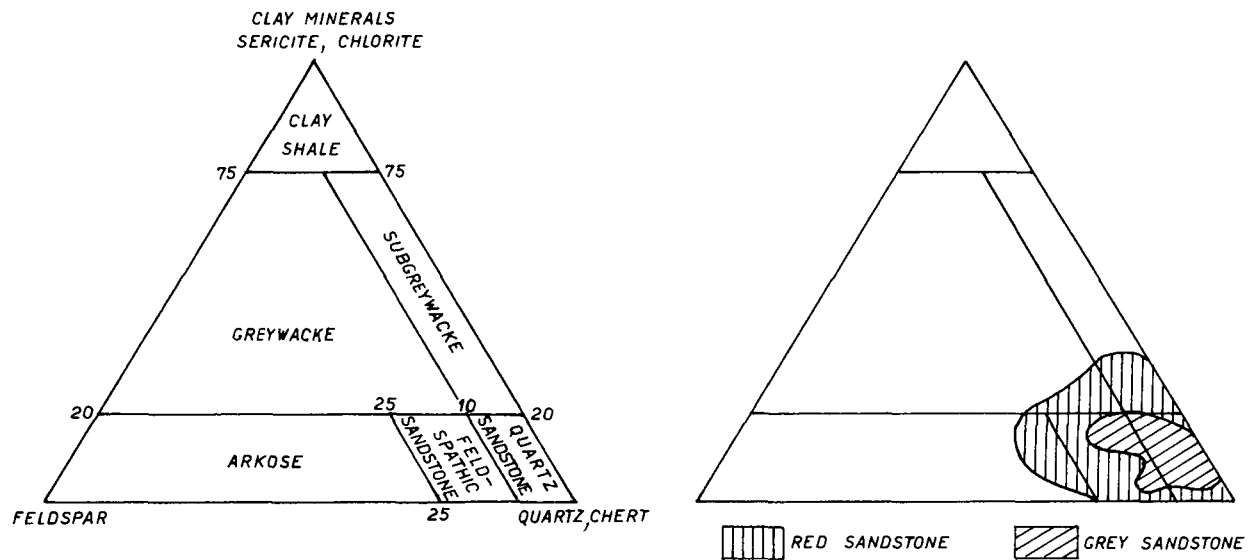
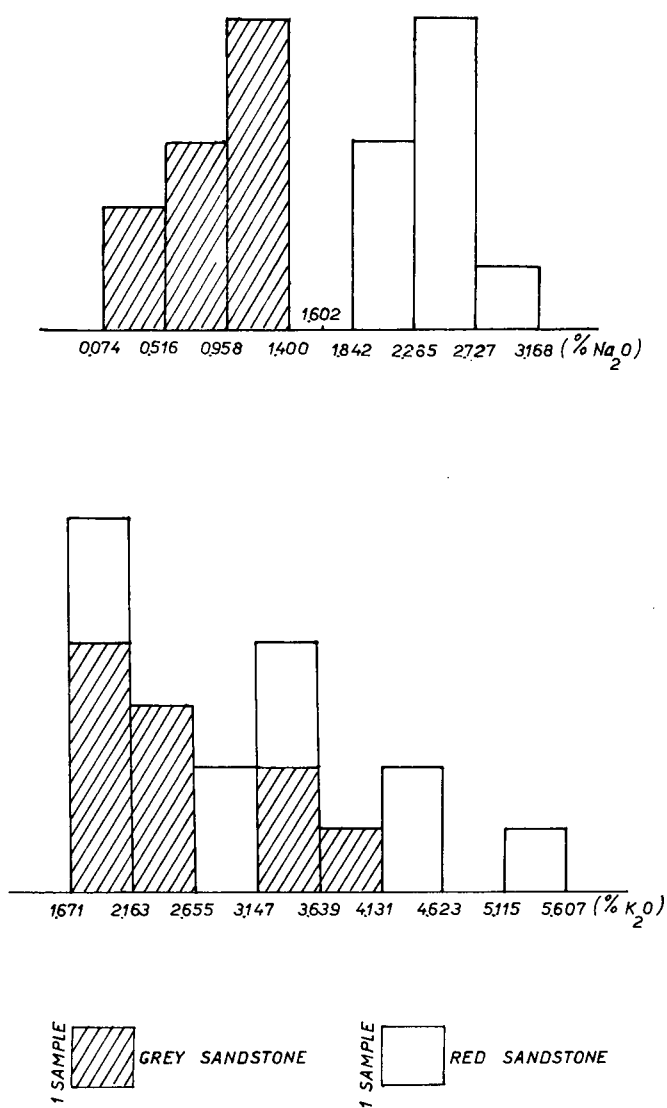


FIG. 4. Classification of sandstones of Val Rendena series.

FIG. 5. Na_2O and K_2O distribution in sandstones of Val Rendena series.

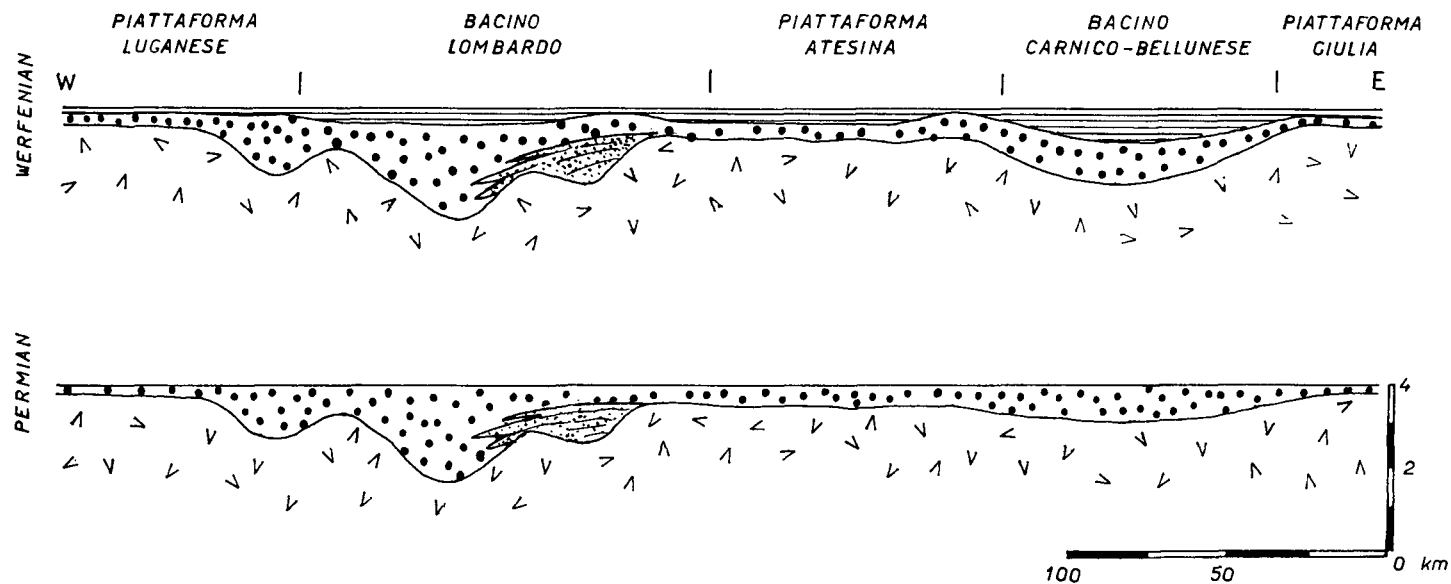


FIG. 6. Sedimentary basin during the Permian and Werfenian (modified after Bosellini [5]).

The alteration of the feldspar in the grey sandstone is presumably due to presence of a reducing environment. Scattered organic matter always occurs in the grey sandstone [1, 3]; in the red sandstone carbonized and silicified logs and wood occur.

Diagenetic processes in Permian sandstones caused the transformation of the clay matrix into sericite and chalcedony. The process of removing the matrix, determined by the natural arrangement of the grains, is limited, while almost no "pressure solution" effects are shown. Small veins and geodes of quartz, present in some areas, are most likely related to weak hydrothermal activity, connected perhaps in part with the Tertiary magmatism.

Summarizing, the analyses of the mineralogical and sedimentological characteristics of Permian sandstones suggest the following conclusions:

- (a) The basal grey facies show the characteristics of (1) a coarse-grained sedimentary phase of piedmont type, (2) rapid accumulation and (3) high permeability. The red sandstone mostly corresponds, from a sedimentological point of view, to a sedimentary cycle of alluvial and deltaic type, more regular and uniform.
- (b) Passing from piedmont conditions to "alluvial and deltaic" environments, a widening of the erosion basin took place. This is shown by the variation in the origin of the clasts.
- (c) The red sandstone deposited in an "alluvial and coastal plain" environment should contain more organic matter than the grey sandstone deposited under piedmont conditions. In the red sandstone the organic matter occurs in massive accumulations. It is likely that dominant oxidizing conditions have caused the destruction of the original scattered organic matter while only massive accumulations were preserved. On the other hand, in the basal grey sandstone, traces of diffused organic matter are always found. This means that this facies was prevalently involved with reducing conditions. The grey sandstone corresponds therefore to a non-oxidized sediment, in part also because of the speed of accumulation. The red sandstone is, on the other hand, completely oxidized.
- (d) The grey sandstone, in which uraniferous mineralizations occur, has not shown chemical, mineralogical or sedimentological characteristics different from similar but barren facies.

From the above it is possible to conclude that the main uraniferous mineralizations contained in Permian sandstones of the Alps are connected with non-oxidized clastic sediments of piedmont environment. Smaller mineralizations are connected with organic accumulations in oxidized sandstones of alluvial deltaic facies.

3. GENESIS AND EVOLUTION OF THE SEDIMENTARY BASIN

Permian sandstones of the Italian Alps generally represent, as has been mentioned, the products of a fluvialite sedimentation which has gradually filled a basin in slow subsidence. The formation and evolution of the basin is closely related to a disjunctive tectonic which dominated during the post-Hercynian period. In fact the basal part of the transgressive sequence on the Hercynian metamorphics is mainly represented by acid volcanites of

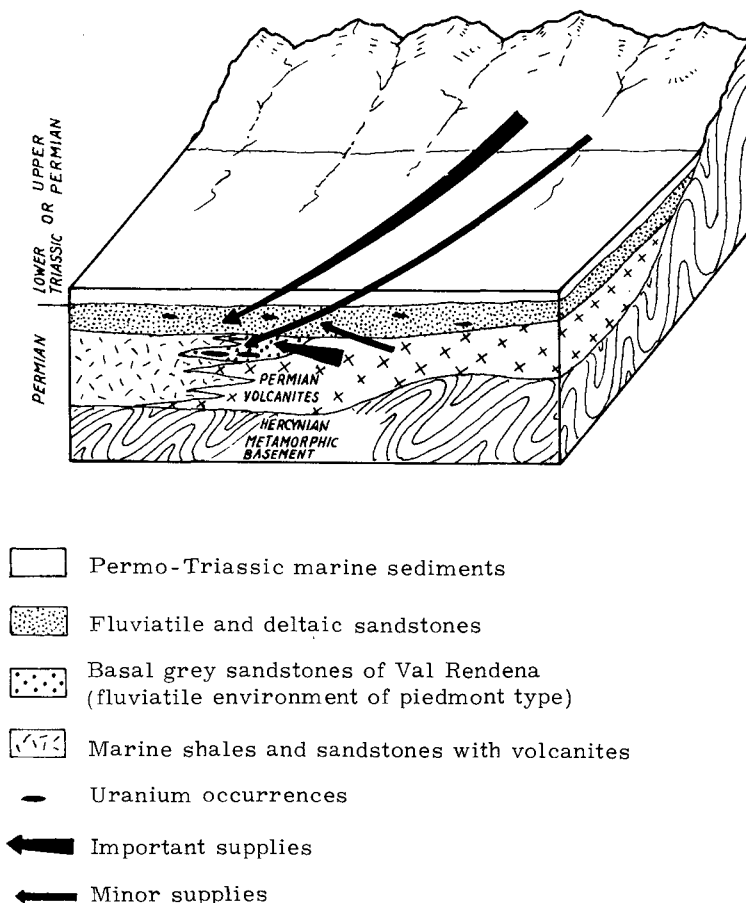


FIG. 7. Diagram showing eastern slopes of the Lombard Basin.

lower Permian. As shown in Fig. 6, the speed of the basin subsidence was different in the different zones of the Southern Alps. Within the large subsiding basin there were recognized zones with different rates of subsidence [2]. These zones are located along an East-West trendline; within these zones, more stable areas alternate with more evolved ones, the subsidence of which began in the lower Permian.

In these troughs, and especially in the largest of them known as the Lombard Basin, the basal Permian sediments are typical of marine environment and often are over 1000 m thick. These marine sediments, together with the associated volcanics, have temporarily filled up the Lombard Basin. In the entire basin of the Southern Alps, in the Middle Permian, continental

sandstone sediments were deposited. Along the border of the Lombard Basin, the basal sediments are continental and heteropic with the upper marine sediments of the central part of the same basin. They show piedmont character and correspond to the grey sandstone and conglomerates occurring along the eastern slopes of the basin towards the Permian volcanic plateau (Fig. 7). These sediments contain the uraniferous mineralizations of Val Rendena, Val Daone and Val Pescara. Apart from these piedmont facies of high permeability, which are non-oxidized and rich in organic remnants, the overlying sediments are more oxidized. The continental sedimentation went on until the Upper Permian with deposition of more and more fine-grained and oxidized sediments.

When the filling material was insufficient to compensate the gradual subsidence of the area, the marine ingressions took place and deposition of evaporitic lagoonal sediments started (Bellerophon strata); further sedimentation developed in the lower Triassic with deposition of Werfenian siltstones and argillites. The subsidence continued for almost the whole Mesozoic, during which the area of the Southern Alps most likely represented a part of the southern margin of the Tethys Sea. The uplift of the Southern Alps that took place during the Paleogene period led to the emersion and to a new tectonic phase.

To define the character of ore genesis that affected the continental formations of the basin, it is better to point out that the uplift and the emersion of the sediments took place after the diagenetic and metamorphic processes. These processes considerably modified and stabilized the structure and the physical characteristics of the original sedimentary rocks.

In short the Permian basin of the Southern Alps can be considered as a marginal basin which, until the formation of the Alpine Range, has always been affected only by movements of subsidence.

4. THE GENESIS OF THE URANIFEROUS DEPOSITS

Within the Permian sedimentary basin, defined above, the uraniferous occurrences can be classified in two groups:

- (a) The major deposits are connected with basal piedmont facies made up of grey sandstone and conglomerates which represent the transition from the Permian volcanic continental area and the Lombard Basin.
- (b) Numerous small deposits scattered within the red sandstone sequence in thin horizons of grey sandstone rich in organic matter.

The control of the deposits of group (a) was most likely provided by permeability factors and by regional draining conditions for the underground waters.

The differences in permeability have been shown by plotting the grain-size distribution against the whole sandstone sequence (Fig. 3); within the grey member the mineralizations are distributed in the upper part, that corresponds to the upper part of the ground water contained in the piedmont sediments. This layer, overlain by the red sandstone, and lying on almost impermeable volcanites, must have had a flow from east to west. The regional conditions of the ground-water circulation were controlled by the dipping of this grey sandstone. Considering their piedmont character and the presence of a trough situated westward, these sediments must have drained

ground water fed by a basin located to the east and made up mostly of acid volcanites. The regularity and the wideness of the mineralized horizon indicates the persistence in time of this water table. The great amount of uranium concentrated in these sediments indicates a considerable transport of uranium by waters mostly leaching acid volcanites and their products of weathering. The concentration of uranium only on the eastern slope of the Lombard Basin, which connects the Basin itself with the continental volcanic area, is an important indication of the preferential provenance of uranium contained in the basal grey sandstones. Also on the basis of previous studies [6] the origin of the uranium contained in the sediments was mostly connected to the erosion of the acid volcanites and of the epithermal uraniferous concentrations they contained. As seen above, the rapid accumulation of the basal grey sandstone within the piedmont environment favoured the preservation of the organic matter; in this reducing environment uranium was therefore precipitated, mostly at the freatic surface. For this reason the mineralizations are now located, with lateral transitions, in lenses of sandstones characterized by different grain sizes. The mineralizations of the (b) group, always of small size and poorly developed, are related to local reducing horizons and because of the presence of organic matter are scattered in the oxidized continental sedimentary sequence.

These local reducing environments caused the subsequent precipitation of the uranium.

Both types of mineralizations were formed during the general subsidence of the Southern Alpine basin. Since this Permian basin was not uplifted before the diagenetic and metamorphic processes, the uraniferous deposits did not go through the remobilization and reconcentration phases that are typical of the classical uraniferous basins throughout the world. In fact the grey sandstone containing mineralization does not show those particular geochemical and mineralogical characteristics of the deposits involved in such processes.

Apart from the local effects of diagenesis, the present features of the deposits are typical of primery epigenetic ones. The minerogenetic environment of the Permian sedimentary sequence of the Alps is therefore quite similar to that occurring in the coastal subsiding basins of Texas. The fact that successive remobilization and reconcentration processes did not take place represents a restricting factor for the economic value of the occurrences, even in the case of the most important and large ones contained in the basal grey member in Val Daone, Val Rendena and Val Pescara.

On the other hand, after diagenesis and local metamorphism, the tertiary uplift of the Permian sandstones, already consolidated, did not establish a hydrological circulation by permeability but rather along fractures and bed joints. As a consequence, aside from the local surface oxidation caused by the present hydrology, the mineralizations show the original structural characteristics, weakly modified by diagenetical processes. The diagenetic processes influenced the recrystallization of the minerals rather than the remobilization and circulation of the elements on a regional scale. Various determinations of age, made on minerals remobilized by diagenesis as well as on primary minerals, have consistently provided an average age of 220 m.y., corresponding to Upper Permian-Lower Triassic. These constant values support the idea that syndiagenetical mineralizations were very limited, and processes of spatial separation of the elements of the uranium family did not occur.

An evaluation of the effect of diagenesis on the economic importance of the deposits is more problematic. The problem involves much of the uraniferous mineralizations of the pre-Mesozoic basin. It would be better solved by taking into account simpler situations than those that characterize the Permian of the Alps.

In general terms, it seems one can conclude that even if the diagenetic processes, which affected mostly the uraniferous mineralizations in the Permian sandstone, were responsible for local anomalous concentrations of uranium, they have not been favourable for producing uranium deposits of economic importance.

REFERENCES

- [1] D'AGNOLO M., Manifestazioni uranifere connesse ad arenarie permiane nel Trentino Sud Occidentale, Atti Symp. Int. sui Giacimenti Minerari delle Alpi, 2, Trento (1966).
- [2] MITTEMPERGHER M., "Characteristics of uranium ore genesis in the Permian and Lower Triassic of the Italian Alps", Uranium Exploration Geology (Proc. Panel Vienna, 1970), IAEA, Vienna (1970) 253.
- [3] TEDESCO C., Studio petrografico comparativo delle differenti facies delle arenarie permiane delle Alpi Orientali, Studi e Ric. Div. Geom., CNEN, Rome (1958).
- [4] FALCHI G., Distribuzione di sodio, potassio e calcio nelle arenarie permiane e nelle mineralizzazioni uranifere connesse, Studi e Ric. Div. Geom., CNEN, Rome (1958).
- [5] BOSELLINI A., Lineamenti strutturali delle Alpi Meridionali durante il Permo-Trias, Mem. del Museo di Storia Naturale della Venezia Tridentina, Vol. 15, Part 3 (1965).
- [6] MARINELLI G., MITTEMPERGHER M., Provenienza e modalità di deposizione dell'uranio nei giacimenti italiani del tardo paleozoico, Notiziario CNEN 8 12 (1962) 57.

BIBLIOGRAPHY

- BRONDI, A., CARRARA, C., POLIZZANO, C., "Uranium in heavy metals in Permian sandstones near Bolzano (Northern Italy)", Ores in Sediments (AMSTUTZ, G. C., BERNARD, A. J., Eds), (Proc. 8th Int. Sedimentological Congr. Heidelberg, 1971), Int. Union Geol. Sci., Series A, No. 3, Springer-Verlag, Berlin, Heidelberg, New York (1973).
- DROVENIK, F., DROVENIK, M., GRAD, G., "Kupferführend Gröden Schichten Sloweniens", Mineral Deposits of the Alps (Proc. 2nd Int. Symp. Bled, 1971), Geological Transactions and Reports 15, Geološki Zavod, Ljubljana, Parmova 33 (1972).
- FALCHI G., NERI D., SERRINI G., Distribuzione di alcuni elementi associati all'uranio nei giacimenti delle Alpi italiane, Studi e Ric. Div. Geom., CNEN, Rome (1958).
- MITTEMPERGHER M., Il giacimento uranifero della Val Rendena, Studi e Ric. Div. Geom., CNEN, Rome (1958).
- MITTEMPERGHER M., Il giacimento uranifero della Val Daone (Trentino Sud-occidentale), Studi e Ric. Div. Geom., CNEN, Rome (1958).
- PANTIĆ R., SIMIĆ V., JOKANOVIĆ V., ANTONOVIĆ A., "Present States of Exploration and Reserves of Nuclear Raw Materials in Yugoslavia", Int. Conf. peaceful Uses atom. Energy. (Proc. Conf. Geneva, 1971) 8, IAEA, Vienna (1972) 73.
- PROTIĆ M., RADOSEVIĆ S., GRAD K., "Terrigene Permablagerungen als uranführende Sedimente in Slowenien", Mineral Deposits of the Alps (Proc. 2nd Int. Symp. Bled, 1971), Geological Transactions and Reports 15, Geološki Zavod, Ljubljana, Parmova 33 (1972).

DISCUSSION

A. DURANDAU: Could you tell us what the extent and thickness of these mineralized beds in the grey sandstone are? And have you observed any channel structures in these formations?

M. MITTEMPERGER: The uranium mineralizations in grey sandstone are seen as outcroppings along a northeast-southwest line 60 or 70 km long. In the best locations the thickness of the mineralization is 3 to 4 m. We recognize many lens-shaped structures of alluvial origin in the grey sandstone, but up till now we have not seen any channel structures.

S.S. ADAMS: I am interested in the stratigraphic relations of the grey sandstone. Does it overlie the volcanics or is it interbedded with them? Does the oxidation-reduction boundary between the grey sandstone and the overlying red sandstone coincide with a stratigraphic horizon or does it cut across the strata?

M. MITTEMPERGER: The basal grey sandstone ore rests on a lateral slope of the great volcanic plateau; the sandstone accordingly overlies the oldest volcanics and is heteropic with the younger volcanic formations that crop out farther eastward. The boundary between red and grey sandstones is concordant with the stratigraphy, although there is a transitional phase extending for some 10 or 12 m.

URANIUM ORE DEPOSITS IN THE PERMIAN SEDIMENTS OF NORTHWEST YUGOSLAVIA

E. LUKACS, A. P. FLORJANČIČ

Geološki Zavod,
Ljubljana, Yugoslavia

Abstract

URANIUM ORE DEPOSITS IN THE PERMIAN SEDIMENTS OF NORTHWEST YUGOSLAVIA.

Experts of the Belgrade Institute for Geological and Mining Research and Nuclear Materials Analysis, applying aeroradiometric prospecting techniques in the area under consideration, have discovered over 60 radioactive anomalies in the Middle Permian Groeden formation. They have delimited five areas as productive uranium deposits. These areas, with the exception of the central part of the Žirovski Vrh, are still insufficiently explored.

On the Žirovski Vrh one finds sandstone, siltstone, slate and conglomerate mainly of a red colour but, especially in the lower part, there are productive green and grey horizons. Stratigraphically, the mineralization depends only on the greenish-grey formation. The spatial distribution of mineralization by uranium shows that the largest concentrations of uranium are in formations characterized by a wide variety of reduction and precipitation conditions. It has also been established that the most important mineral of the deposit is pitchblende. The morphological characteristics provide the basis for a classification by types of the ore bodies which are indicative of the genesis of the deposit. The authors assume that this deposit is of complex formation and they classify it as syndiagenetic.

1. INTRODUCTION

In the Sava Folds which are an extension of the Julian Alps, several ore deposits occur. The best known are the Idrija mercury ore deposits, and the copper ore deposit Škofje, which was already under exploitation a hundred years ago. The smaller ore deposits Litija (Pb, Zn), Pleše (Pb, Zn), Knap (Pb, Zn), Knapovž (Pb, Zn, Hg) and Sv. Ana (Hg) have been abandoned. In the last ten years, in the Middle Permian terrigenous sediments of the so-called Groeden (Val Gardena) beds, the uranium ore deposit Žirovski Vrh was found, as well as numerous widespread uranium ore occurrences (Fig. 1). Of these occurrences the most interesting is in the locality Bodovlje, where uranium ore in economic quantities and also up to 2% of copper were found in samples from the surface.

The experts of the Institute for Geological and Mining Research and Nuclear Materials Analysis, Belgrade, carried out regional aeroradiometric surveys in the area shown in Fig. 1, and found over 60 localities with radioactive anomalies. Most of these were checked by terrestrial radiometric surveys. The northern part of the same area has also been explored by geochemical prospecting methods (hydrochemical prospecting, analyses of stream sediments). Some of the geochemical anomalies coincide with the aeroradiometric anomalies.

The area of Middle Permian clastic rocks in the west of Ljubljana have been explored by regional reconnaissance radiometric terrestrial survey and partly by detailed surveys. The results of these studies were described by Omaljev [1]. Exploration carried out up to now in NW Yugoslavia indicated five areas which are promising for uranium ore deposits. They are

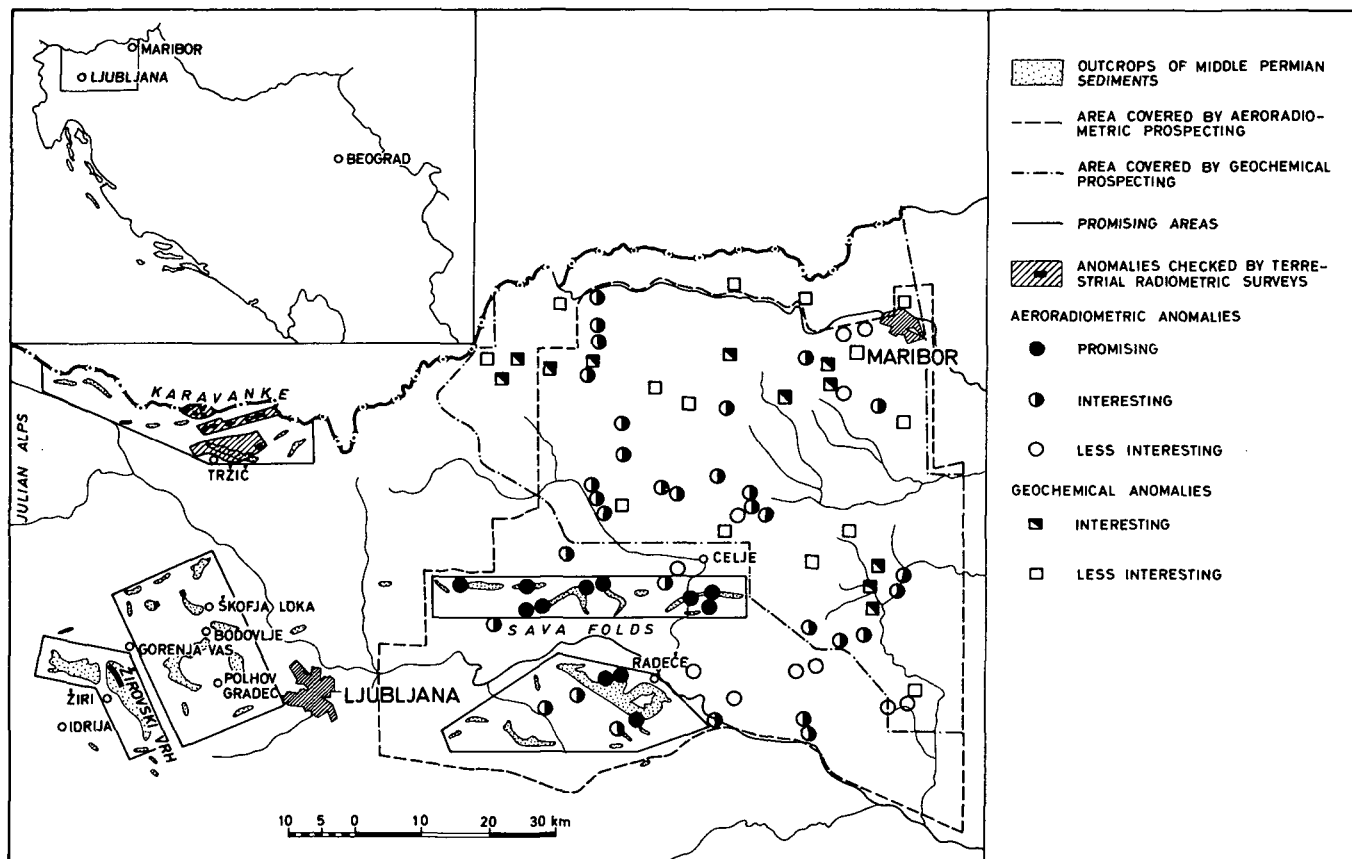


FIG.1. Map of mineralizations in Permian sediments.

Žirovski Vrh, the surroundings of Škofja Loka, the surroundings of Tržič, the southern slopes of the Celje basin, and the surroundings of Radeče. With the exception of the immediate vicinity of Žirovski Vrh, explorations in these areas are in a rudimentary stage.

2. MIDDLE PERMIAN SEDIMENTS IN THE SAVA FOLDS

The Lower and the Middle Permian sediments in the Sava Folds contain no fossils, therefore the age of these rocks is rather vaguely defined. However, the whole Permian has been rather continuously deposited in the nearby Karavanke region. Upper Schwagerina limestone occurs in the Lower Permian (Rattendorf series). The Trogkofel series with reef limestone and Tarviso breccia belongs to the lower part of the Middle Permian. Its lateral equivalent is dark grey quartz sandstone, alternating with shale and conglomerate, or with limestone containing index fossils. The mainly red, and more rarely grey Groeden beds overlie in the Karavanke mountains either the Trogkofel limestone and breccia, or their clastic equivalent. The Groeden beds are overlain in the Sava Folds as well as in Žirovski Vrh by Upper Permian bedded limestone that is rich in fossils, and by dark grey dolomite. As the Groeden beds do not contain any fossils, their age was determined only according to their stratigraphic position with respect to the underlying and overlying beds.

Detailed descriptions of lithology and geochemical characteristics of the uranium-bearing Groeden beds in the Sava Folds have been given by Protić [2], Protić, Radošević, and Grad [3], and M. Drovenik, F. Drovenik, and Grad [4]; and for the neighbouring Italian region by Mittempergher [5].

The widest extent of the Groeden beds in NW Yugoslavia is found in the Sava Folds, which is a region 130 km long and 24 km wide. This is an area of complicated tectonics at the juncture of the Alps and the Dinarids. Detailed uranium prospecting has been carried out mainly in the part of this belt that lies in the west of Ljubljana. The Groeden beds there lie in the imbricated nappe structure of the Idrija-Žiri region, which is a final stage of deformation of a large recumbent fold [6]. The areas of interest for uranium prospecting, Idrija-Žiri and Škofja Loka-Polhov Gradec, as well as the ore deposit Žirovski Vrh, belong to the same nappe. The fold and the nappe structure originated most probably during the Alpine orogenesis.

In the Sava Folds the Groeden beds consist of sandstone, siltstone, slate and conglomerate. Their colour is mainly red, some of the layers, especially in the lower part of the beds, are green, greenish grey and grey. The red colouring is caused by trivalent iron oxide. The grey colouring is mainly caused by organic matter, often containing pyrite; the green colouring probably originates from bivalent iron.

All known uranium occurrences in NW Yugoslavia are found in greenish grey sediments of the Lower part of the Groeden beds. In the explored areas the greenish grey layers contain numerous red sandstone and siltstone intercalations, both of which are interbedded in the ore-bearing horizon. The thickness and the composition of the various lithological units vary widely in both vertical and lateral directions. Microscopic examination has shown that in qualitative mineralogical composition the red sandstone, the barren green sandstone and the ore-bearing greenish grey sandstone show nearly no differences. The quantitative mineralogical composition however shows that the red sandstone is

somewhat richer in carbonates, and the greenish grey in clayey minerals, mica, and feldspars. In the greenish grey strata, medium-grained sandstone prevails, with grains of 0.2-0.4 mm diameter. The ratio between grains and cement varies from 3 : 1 to 1 : 1. The grains consist mainly (60-80%) of quartz from magmatic and metamorphic rocks, and feldspars amount up to a few per cent. In conglomerates, from 5-20% of quartz porphyry and keratophyre fragments are found, as well as shale fragments. Besides quartz, there are, in the cement, feldspars, carbonates, clay minerals, sericite, chlorite, anthracite and pyrite. In the red sandstone, finely grained hematite and iron hydroxide can be found.

It is difficult to decide on the origin of these sediments. The sedimentological investigation is difficult because of the alpine-type tectonic and the diagenesis. Only some exposures of cross-bedding, the cyclic character and the tendency of finer grading of sediments in the upward direction can be a proof of alluvial origin [2]. The possibility that a part of the sediments was deposited in the near-shore belt of sedimentary basins cannot be excluded.

3. THE ORE DEPOSIT ŽIROVSKI VRH

Geological studies and drilling have shown that the ore deposit Žirovski Vrh lies in Middle Permian sediments in one of the sheets of the imbricated structure of an overthrust that overlies Triassic autochthon rocks. Together with the Middle Permian, Permo-Carboniferous sediments have been overthrust as well. The contact plane between Permo-Carboniferous and the overlaying Groeden beds is not very clearly defined. It is not definitely known if there exists, besides the tectonic nonconformity, an erosion nonconformity as well. However, along the fault in the mine, besides manifestations of a strong faulting, very essential differences in lithologic characteristics and in texture of both facies are observed.

By comparing the Groeden beds of Žirovski Vrh with those elsewhere in the Sava Folds, where their development is normal and continuous, the clastic rocks of Žirovski Vrh are attributed to Middle Permian. In their lower part they are grey and more coarsely grained, in their upper part they are mainly red and of finer grain size. The thickness of the Groeden beds has up to now been assumed to be about 600 m, about 200 - 250 m belonging to the grey series and 350 - 400 m to the red series. In our opinion the proper thickness is probably much less; a secondary thickening most probably took place by folding processes, that have not been taken into consideration by previous authors.

Exploration of the grey sandstone series in Žirovski Vrh has shown three macrocycles. The first, lowest, cycle consists of basal conglomerate and conglomeratic sandstone. These sediments contain no uranium mineralization. Larger or smaller fragments of magmatic, metamorphic and sedimentary origin prevail. As the grains are mainly subangular and there is nearly no graded bedding, it is practically impossible to observe any stratification. The cycle is concluded by the first stratum of red clastites. The second stratum of red clastites overlaying grey sandstone concludes the second cycle. Closely above it, the first uranium mineralizations occur. The bedding of the grey sandstones and conglomerates is somewhat better discernible, and in some places the first elements of a stratification of grains can be seen. The lower, basal, part of this cycle has often a pseudoconglomerate appearance, but is not a conglomerate, as the main part of the white

quartz fragments consists of lenticular quartz concretions of metasomatic origin. The third, so-called ore-bearing cycle, has in its basis a characteristic reddish brecciated conglomerate of varying thickness. The bedding of the sediments in the ore-bearing middle part is quite distinct; here cross-bedding is frequent, and is very discernible especially near places where sandstone alternates abruptly with conglomerate. In this cycle the quantity of conglomerate, in relation to the prevailing sandstone, decreases even more than in the former cycle. The clayey component of these clastites prevails more in the cement, and less in the larger shaly pebbles that can be found mainly in the lower cycles. The increasing content of organic matter causes a darker colouring of the rock. This third grey cycle is considered to be the last grey cycle, although soon in the red series one sequence of grey clastites occurs again.

4. GEOLOGICAL STRUCTURE OF THE ORE DEPOSIT

Lately it has been assumed that uranium mineralization was connected to a subvertical elongated body, in which the strata, with the exception of the fold on its top, strike at about 230° with a dip of $15-35^\circ$ (Fig. 2). During exploration of the 530-m level it was found by drilling vertically downwards that the main mineralized intervals dip just in the opposite direction, i. e. 60° (Fig. 3). Exploratory work on the 480-m level confirmed that the character of this inverse direction was not of local significance only.

The cross-section (Fig. 3) of the ore deposit gives a rather clear picture of the position of the ore-bearing bed, which is a stratum in the middle of the grey series. Owing to the so-called "S" structure, an apparent repetition of the strata occurs, which caused a wrong interpretation in the initial stage of the exploration (Fig. 2).

A very distinctive feature of the deposit is the marked cleavage that often conceals the stratification and prevents comparison of the rocks.

Characteristic are also the calcareous concretions that originated by migration of calcite from the cement of the sandstone. The concretions are of slaty, lenticular shape, parallel to the bedding plane. Two kinds of concretions are distinguished: those inside the ore-bearing bed, and the others outside of it. From 1-10 m below the ore-bearing bed the so-called basal stratum of calcareous concretions occur. Their size is in the range of some centimetres; at the surface they are grey, and inside mainly white. Inside the ore-bearing bed the concretions are of a grey-pinkish colour, and of a very dense structure. Their variations in size and shape are larger than those observed in the grey basal concretions. The highest "hanging wall" stratum of calcareous concretions usually appears close above the highest peripheral ore bodies. Outside the ore-bearing bed, numerous concretions occur as well.

5. MINERALIZATION

The ore-bearing bed consists of rocks in three basic colours, red, grey and green; the layers are of irregular thickness, and thin out laterally. There is no marker horizon, and also facial changes are frequent. Therefore it is often impossible to connect the sequences of strata even between

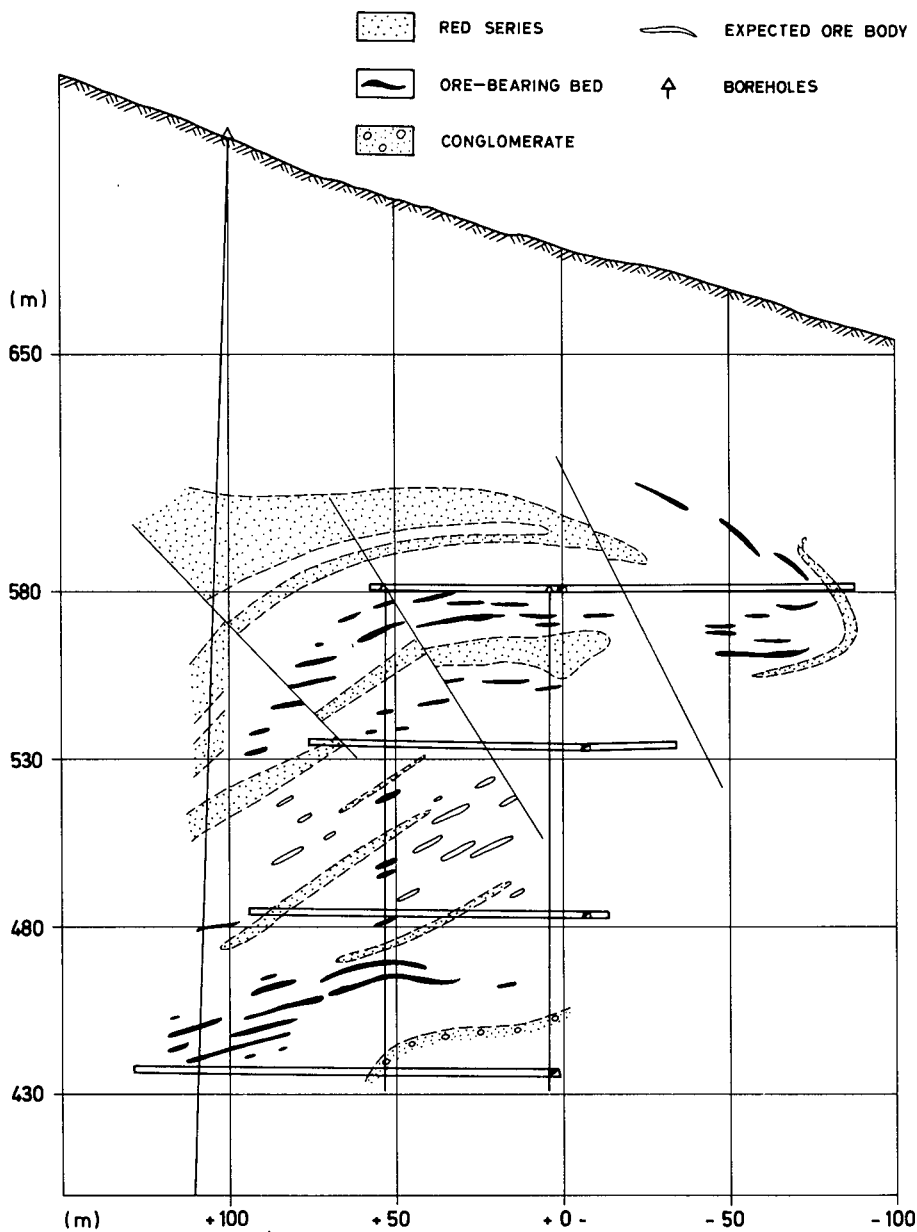


FIG.2. Geological cross-section through the Žirovski Vrh uranium deposit. Original interpretation.

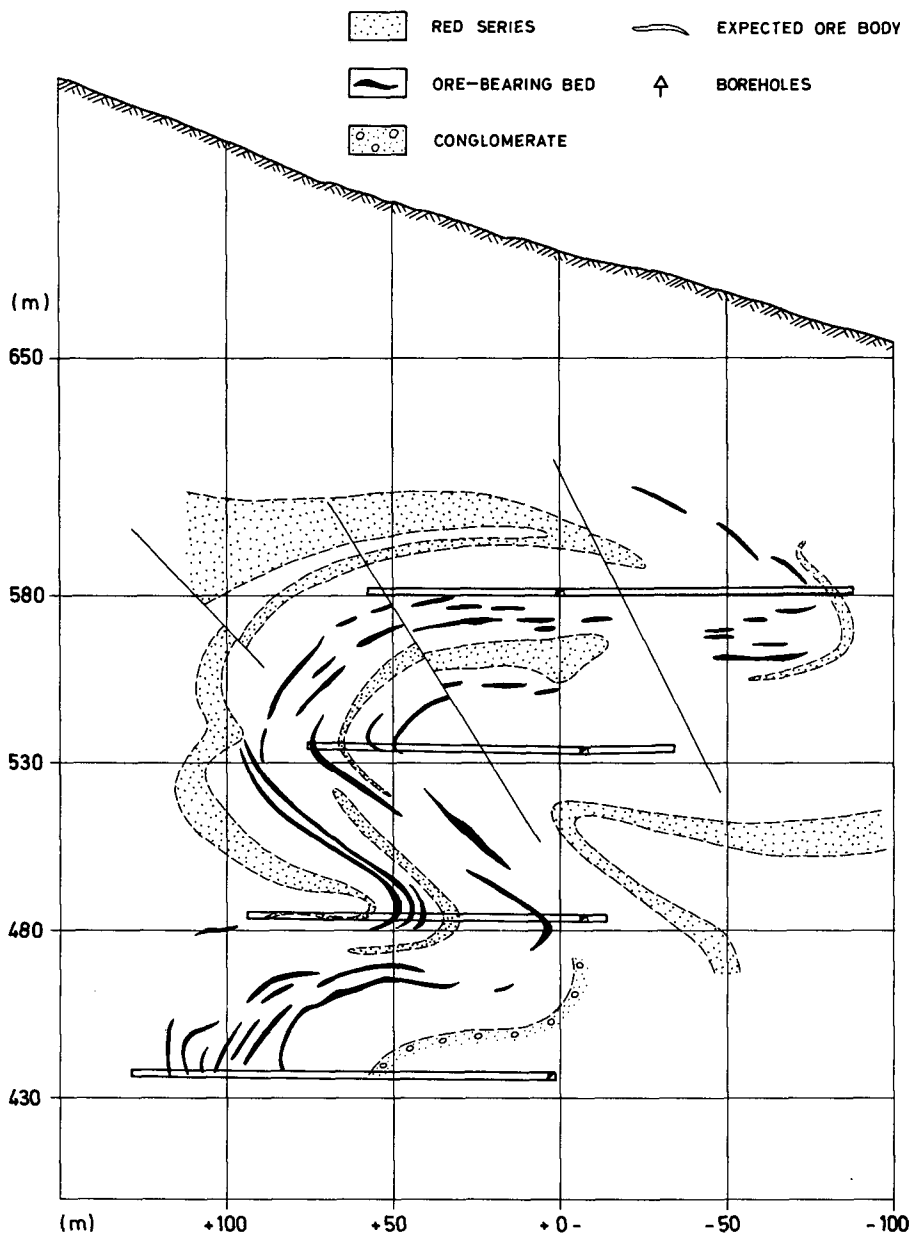
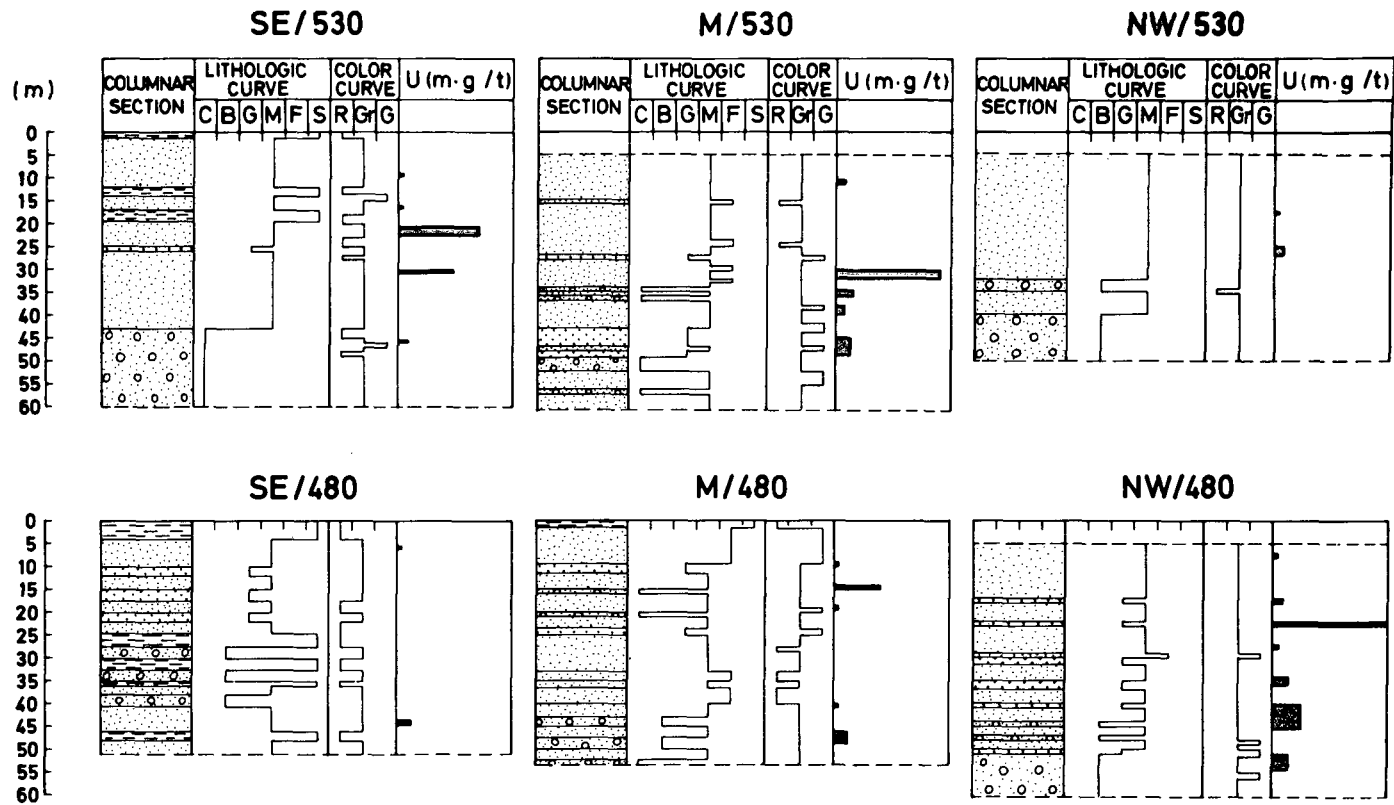
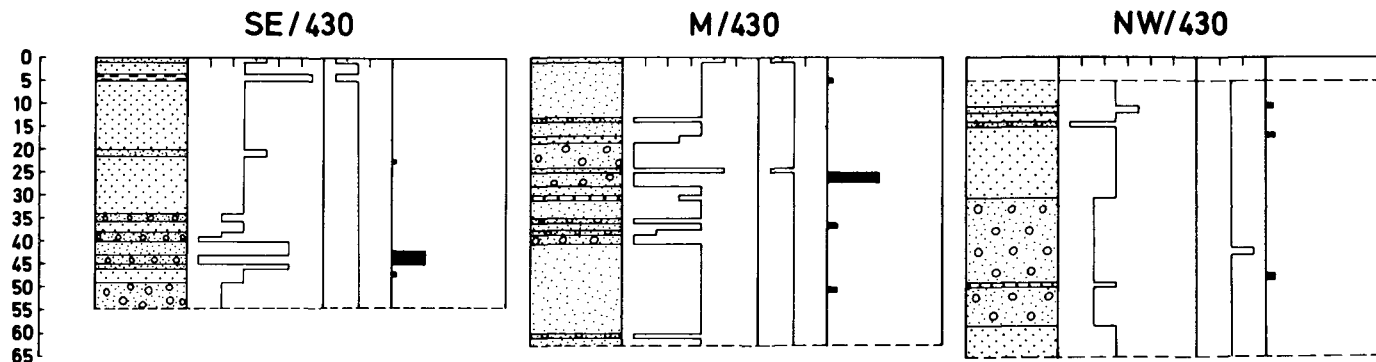


FIG.3. Geological cross-section through the Žirovski Vrh uranium deposit. Recent interpretation.





EXPLANATION:

SE SOUTHEAST PART OF DEPOSIT
M MIDDLE PART OF DEPOSIT
NW NORTHWEST PART OF DEPOSIT
530 MINE LEVEL 530 m
480 MINE LEVEL 480 m
430 MINE LEVEL 430 m

LITHOLOGIC CURVE:

C CONGLOMERATE
B CONGLOMERATIC SANDSTONE
G COARSE-GRAINED SANDSTONE
M MEDIUM-GRAINED SANDSTONE
F FINE-GRAINED SANDSTONE
S SILTSTONE

COLOUR CURVE:

R RED
Gr GREY
G GREEN

FIG.4. Diagrams illustrating the relation of mineralization to lithology and colour of Groeden sediments.

very closely drilled exploratory bores. The green rocks occur in the upper and lower parts of the greenish grey ore-bearing bed. It seems that they are spaced between oxidized and reduced rocks.

Because of the complicated structure of the productive facies and owing to the very irregular distribution of differently coloured rocks, it was necessary to introduce systematic methods to determine the mineralization by observations of rocks colours. The distribution of colours was studied in the vertical as well as in the lateral direction. Up to now a marker horizon could not be found; therefore as a starting point the contact plane between the hanging-wall red intercalation and the greenish grey productive series has been chosen. The geological boundary in the bottom of the productive beds could not yet be determined. Only the so-called geophysical floor beds have been determined on the basis of a low background of radioactivity, and partly by measurements of the Th/U ratio which increases outside the ore-bearing beds.

From the drilling logs averages have been calculated for three parts of the ore deposit and for three levels, as shown in Fig. 4. These data show the incidences of (1) red and green intercalations, (2) siltstone, (3) fine-, medium- and coarse-grained sandstone and (4) conglomerate in relation to depth. These data were compared with data from gamma logs of the cored exploratory bores. Their most representative parameter is the linear productivity, i.e. thicknesses of mineralized borehole intervals multiplied by their respective average mineral contents.

On the basis of these data, productivity curves were compiled for the vertical (530 m - 480 m - 430 m) and horizontal (SE-M-NW) distributions of colours and grain size (Fig. 5). The diagrams show that high linear productivities correspond to one, two or three of the following factors: overall large thickness of the bed, large thickness of the grey strata, and large thickness of medium-grained sandstones. Figure 6 shows the diagrams of the averages in the horizontal direction. Here an additional relationship of mineralization and thickness of red intercalations is evident.

The first data about uranium mineralization were obtained on outcrops with secondary mineralization. Primary, non-oxidized ore was later found in boreholes and in mining works. The uranium mineralization is connected with the greenish grey series exclusively. The ore-bearing horizon of 30 - 60 m thickness lies in the third cycle. In the ore-bearing horizon there are three to five ore bands, two of which are of economic interest. These two ore bands are usually separated by a discontinued intercalation of red, slaty sandstone. Below and above the ore-bearing horizon there are discontinued, red sandstone intercalations as well, therefore the mineralization is in close relationship with the red intercalations. In the upper part of the second cycle there are only poor and few traces of uranium mineralization; in the hanging-wall sandstone uranium concentrations are in some parts very high, but as the ore bodies are very widely dispersed, they are of no economic interest. The ore is found most frequently in dark grey, medium- to coarse-grained sandstone. Other characteristics of the ore-bearing sandstone are better than average bedding, less distinct cleavage, and augmented occurrence of sulphides.

The mineralogical composition of the ore has been studied by Ristić and Markov [7], and by Radusinović [8]. The most important ore mineral of the deposit is pitchblende. Dispersed in the sandstone cement, it usually occurs as a finely grained aggregate, where the individual grains are smaller

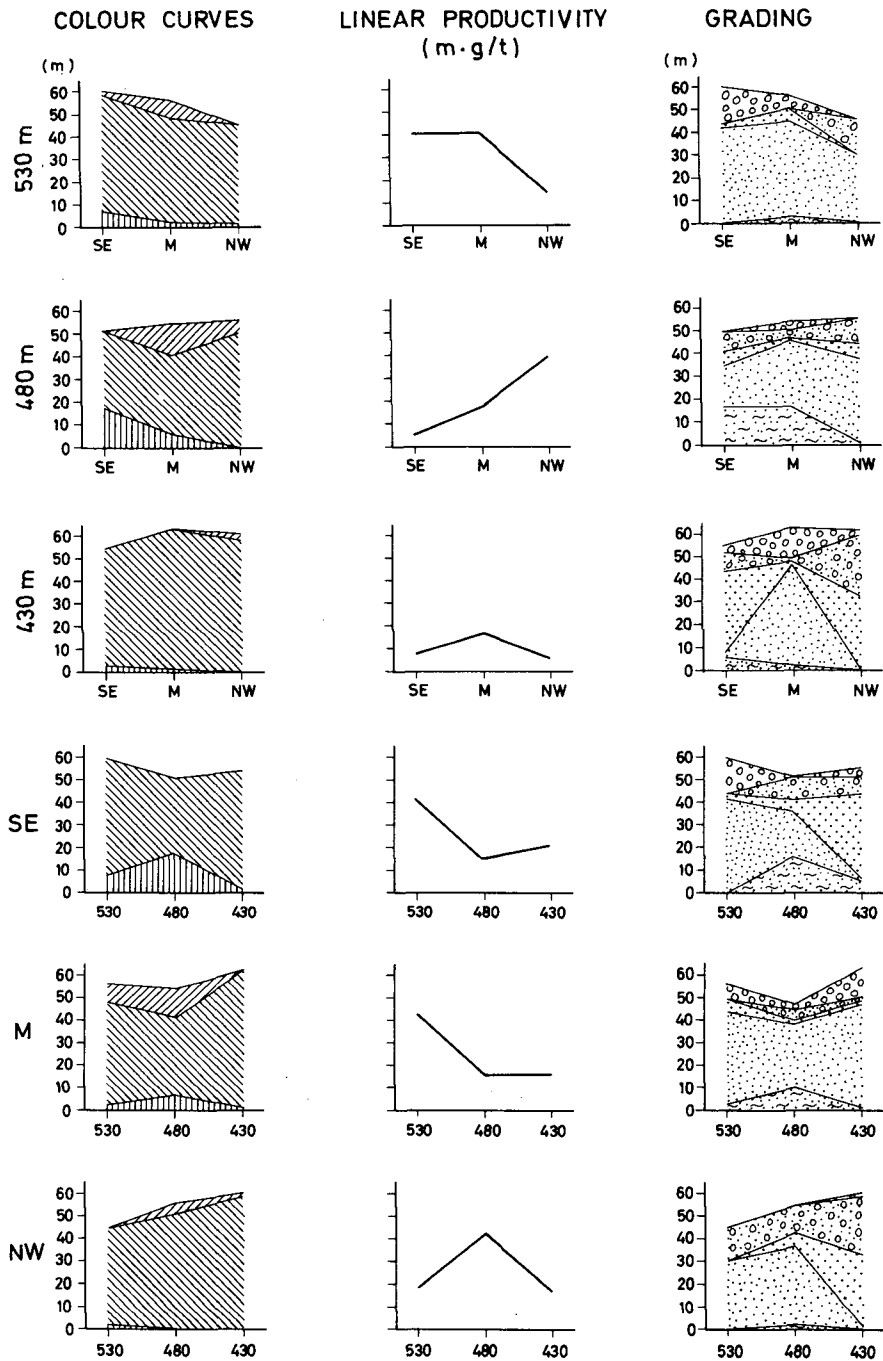


FIG. 5. Diagrams illustrating the dependency of the linear productivity on colour and grading of the ore-bearing bed in the horizontal (SE-M-NW) and vertical (530-480-430) directions. For explanation see Fig. 6.

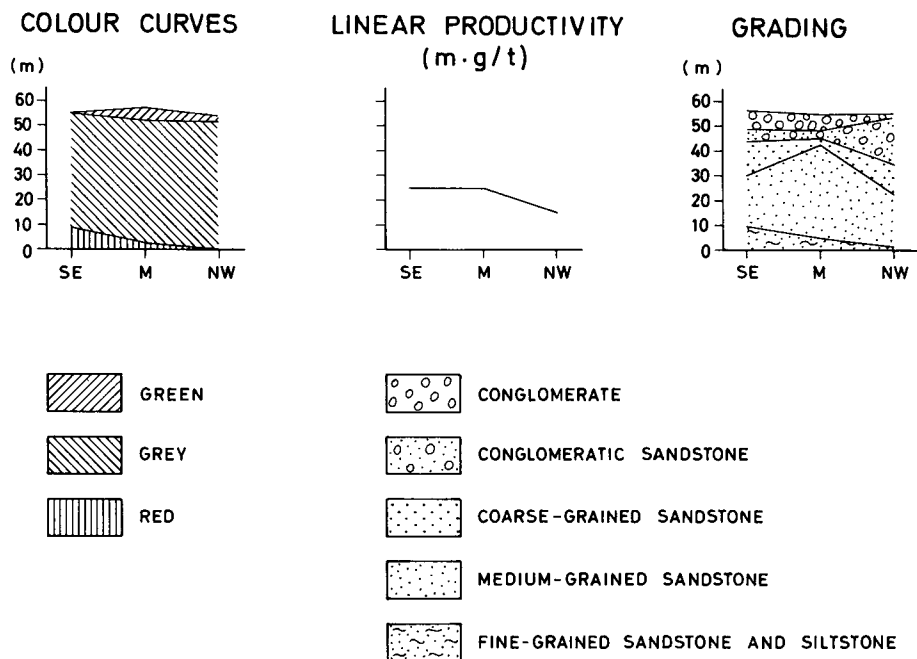


FIG. 6. Diagrams of averages (Fig. 5) in the horizontal direction.

than $10\ \mu\text{m}$. Most frequently encountered are associations with sulphide minerals, mainly arsenopyrite, pyrite, galena and chalcopyrite. It was found that the uranium mineralization is connected to the parts of the sandstone with higher organic content, but as a rule is not in direct contact with it. Paragenetic relations between pitchblende and the sulphides are difficult to determine; but it is clear that pitchblende is younger than the organic matter. On the outcrops the ore is oxydized. Determined were secondary minerals: dumontite, torbernite, autunite, the series phosphuranylite-renardite, and gummite. Secondary minerals have been found down to 200 m below the surface.

It is interesting to note that the copper deposit at Škofje occurs in the upper part, but the Žirovski Vrh uranium deposit is in the lower part of the Groeden beds [4].

Lately our studies were directed also to the increase of knowledge about the morphological types of the ore occurrences. Although the studies are in their beginning, some rather good comparative examples have been found similar to those described by Virág and Vincze [9] from the ore deposit Mecsek. The banded type consists of a band of ore up to 20 cm thick, parallel to the bedding of fine- or medium-grained ore. The ore band is either uniform or composed of several thinner bands. The concentration of pitchblende in the bands can be very high. Micro-layered disseminated ore consists of a series of thin (up to a few millimetres thick) associations of carbonized vegetal remnants and minerals of

uranium oxides in fine-grained sandstone or bordering siltstone. Ore which is connected with larger carbonized wooden remnants is rarer, but can cause extraordinarily high pitchblende concentrations. Ore bands, ribbons and rounded structures which intersect the bedding planes have also been observed. The most heterogeneous ore bodies are those of the disseminated ore type. Here, inside the ore body, patches with ore concentration varying from high to barren are distributed at random. Ore in joints has been found to represent partial secondary mineralization along cleavage planes.

The most frequent types of ore bodies in the deposit are of the banded and the disseminated ore type. The shape and size of the ore lenses depend on the extent and frequency of the bands or on the distribution of ore patches. When bands or patches join, massive ore is obtained [10]. The morphological types of the ore indicate that the existing distribution of uranium ore is not the result of one continuous process, but of several phases of transportation and accumulation. Ore bodies containing one single morphological type of mineralization are scarce; most ore bodies present associations of several types.

Ore bodies of the same mineralized horizon represent the "ore belt". Their shape, direction and distribution reflect the geological environment of their origin and the structure of the deposit. By imagining the fold (Fig.3) straightened out, the discontinued bands of ore bodies would assume a step-like shape, and the stratigraphically younger strata, higher in their assumed position, would become more mineralized with uranium ore.

6. GENESIS

The foregoing description indicated a rather well-marked correspondence between the stratiform ore lenses and the enclosing rocks, as well as a conformity of the ore belt in the fold and fault dislocations respectively. The post-ore character of these tectonic disturbances is beyond any doubt.

The first interpretation of the structure of the ore deposit (Fig.2) rendered the hypotheses about its genesis rather difficult; therefore previous authors were of differing opinions. However all of the authors agree that hydrothermal processes had no influence on the genesis of the ore deposit. The majority of the authors connect the mineralization with ground water that transported the epigenetic uranium [7, 8, 10]. Kovačević [11] however thinks that the deposit is of syngenetic origin.

On the basis of the latest exploration and studies, we are of the opinion that the uranium in Žirovski Vrh was transported into the sediments during their deposition, and later redistributed.

The composition of the rocks implies that the source of the sediments as well as that of the uranium was the keratophyric basement, as keratophyre fragments prevail in the deposit [10]. The source of the material for the cement of the sandstone was most probably metamorphic rock, as might be proved by the inclusions of schist fragments. Before the Permian erosion affected the rocks, these rocks seem to have been exposed to weathering during a long period. In addition to uranium the weathered rocks undoubtedly contained other heavy minerals such as Pb, Zn, and Cu. Erhart [12] thinks that in the next phase the heavy metals would be leached out from a partly weathered basement just when the terrigenous phase is eroded from the

same basement. Samama [13] has some doubts, since this model does not explain one of the main characteristics of the sandstone-type deposit: where the basement contains many elements, only one or two heavy metals are concentrated in a deposit. This characteristic can only be explained by continental supplies selectively enriched because of the different behaviour of Pb, Zn, Cu and U during weathering. This would mean that of primary importance in sandstone-type deposits were the weathering processes, which have been described in detail by Samama [13].

Alluvial areas of meandering rivers, smaller floodplains, periodic lakes and moors were favourable for the deposition of uranium, and the simultaneous deposition of the sediments. In the ore deposit many cases of cross-bedding and load cast were encountered which prove, together with the lenticular and step-like thinning out of the red and green sandstones, that the uranium-bearing sediments are of fluvial origin. The grey, green and red redox facies that overlay each other in the geological column (Fig. 4) often lie along each other; they replace each other and are therefore heteropic facies.

During the transport of uranium and of copper, the waters were oxidizing in character, with a pH value between 7 and 8. Under such circumstances uranium can be transported as a complex uranyl carbonate ion, as the uranyl-hydroxide ion, as well as in colloidal aggregates of uranylhydroxide sols [9].

The precipitation of uranium in stagnant waters was influenced by processes such as adsorption to organic matter, forming of organic uranium compounds, coagulation of uranium-hydroxide polymeric ions into colloid aggregates, and simultaneous sedimentation with adsorbing feldspar and silica minerals. The formation of microlayered, disseminated and ribbon-shaped types of ore bodies started with these processes; these ore bodies were later enriched by diagenesis. The differentiation between individual elements was achieved primarily by geochemical barriers and by different solubilities of carbonates and sulphates of heavy metals.

The concentration of uranium in the early syndiagenetic phase was probably low. In sites where the rich vegetal remnants caused a higher concentration of H_2S , reduction processes took place in the uranium-bearing solutions during the diagenesis. Part of the uranium was precipitated, the concentration of the solution was reduced and caused a diffusion of ions from other parts of the sediments.

Sinking of the beds followed, and the reductivity of the environment increased. According to Virág and Szolnoki [14], in addition to the reduction by H_2S , reduction without H_2S also became important. This reduction was caused (1) by underground waters that contained no oxygen but did contain CO_2 and CH_4 , that originated from anaerobe bacteria, and (2) by organic acids. From studies of the isotope ratio $^{32}S/^{34}S$ Ristić and Markov [7] confirmed the biogenetic origin of the sulphur in the sulphides of the uranium-bearing horizon.

It is assumed that during further sinking and subsequent upthrust of the beds, new migrations and precipitation of uranium again took place. Significant quantities of uranium could be transported only from the red series, where there existed no reductive environment. Studies carried out by Protić, Radošević and Grad [3] on the ratio of soluble uranium to the total uranium content, confirmed this assumption. By examining numerous samples, they found a relatively high percentage (more than 40%) of soluble uranium in greenish grey sandstone, whereas this percentage in the red series amounted to only 10% on the average.

In the late epigenesis, orogenesis also affected the ore deposit, as it caused fissuring in the beds. At higher temperatures and pressures the most mobile constituent was silica. It migrated from unbroken parts into the fissured parts of the rock and formed numerous metasomatic and dilatation quartz veins. During upthrusting in the more recent tectonic phase the Permian beds were disturbed again, and numerous fissures, veins and veinlets were formed which contained well-developed idiomorphs of quartz, calcite and dolomite and, in the uranium-bearing horizon, sulphides as well.

REFERENCES

- [1] OMALJEV, V., Prospekcijska radioaktivnih kamenin v Sloveniji, *Geologija razprave in poročila Ljubljana* 14 (1971) 161.
- [2] PROTIĆ, M., Litološki odnosi i geohemijska obeležja grodenskih peščara Savskih bora, *Radovi Instituta za geološko-rudarska istraživanja i ispitivanja nuklearnih i drugih mineralnih sirovina, RADOVI Beograd* 4 (1968) 57.
- [3] PROTIĆ, M., RADOŠEVIĆ, S., GRAD, K., "Terrigene Permablagerung als uranföührende Sedimente in Slowenien", *Mineral Deposits of the Alps (Proc. Symp. Bled, 1971), Geological Transactions and Reports* 15, Geološki Zavod, Ljubljana, Parmova 33 (1972).
- [4] DROVENIK, F., DROVENIK, M., GRAD, K., "Kupferföührende Grödenener Schichten Sloweniens," *Mineral Deposits of the Alps, (Proc. Symp. Bled, 1971), Geological Transactions and Reports* 15, Geološki Zavod, Ljubljana, Parmova 33 (1972).
- [5] MITTEMPERGER, M., "The paleogeographical, lithological and structural controls of uranium occurrences in the Alps", *Mineral Deposits of the Alps (Proc. Symp. Bled, 1971), Geological Transactions and Reports* 15, Geološki Zavod, Ljubljana, Parmova 33 (1972).
- [6] MLAKAR, I., Krovna zgradba idrijsko žirovskega ozemlja, *Geologija razprave in poročila Ljubljana* 12 12 (1969) 5.
- [7] RISTIĆ, M., MARKOV, C., Mineraloško-geohemijski indikatorji orudnjenja i način postanka ležišta urana Žirovski vrh, *RADOVI Beograd* 6 7 (1971) 1.
- [8] RADUSINOVIĆ, D., Mineraloški sastav i geneza uranskog ležišta Žirovski vrh, *RADOVI Beograd* 3 3 (1967) 1.
- [9] VIRÁGH, K., VINCZE, J.A., Mecseki uránérclelőhely képződésségének sajátosságai, *Földtani Közlöny Budapest* 97 1 (1967) 39.
- [10] OMALJEV, V., Razvoj gredenskih slojeva i uranove mineralizacije u ležištu Žirovski vrh, *RADOVI Beograd* 3 (1967) 33.
- [11] KOVAČEVIĆ, R., Über Uranerzvorkommen im Vorgebirge der Julischen Alpen, *Freiberger Forschungshefte C* 231 (1968) 175 (Breithaupt Kolloquium).
- [12] ERHART, H., Biorhexistasie, biostasies évolutives, hétérostasie, *C.R. Acad. Sci. Paris* 263 (1966) 1048.
- [13] SAMANA, J.C., "Ore deposits and continental weathering", *Ores in Sediments (Proc. 8th Int. Sedimentological Cong. Heidelberg, 1971), (AMSTUTZ, G.C., BERNARD, A.J., Eds), Int. Union. Geol. Sci., Series A, No.3, Springer-Verlag, Berlin, Heidelberg, New York* (1973).
- [14] VIRÁGH, K., SZOLNOKI, J., Baktériumok szerepe a mecseki uránérc keletkezésében és későbbi áthalmazásában, *Földtani Közlöny Budapest* 100 1 (1970) 43.

DISCUSSION

A.G. DARNLEY: I was fortunate in having the opportunity to visit this mine recently, through the kind invitation of Mr. Lukacs, and I was struck by the great difficulty of visually distinguishing ore from unmineralized rock. Clearly, exploitation will have to be carefully controlled by instruments. Is this lack of visible characteristics a feature of other primary uranium mineralization in the region?

E. LUKACS: That is a very difficult question to answer, because only here have we done detailed exploration work and penetrated to the primary

ore; at other sites in the region we have explored only the upper parts of the deposits, the oxidized portions, where secondary minerals of a yellow and green colour occur. Here we can in fact see the ore body clearly, but not in the primary ore.

J. CAMERON: I also found the extreme difficulty of identifying the boundaries of the primary ore very striking. Even with a pitchblende containing only 0.20% U_3O_8 one would expect to be able to see the colour difference. What is the mineralogical reason for this feature, and for the dark colour in the non-ore zone?

E. LUKACS: We attribute the dark colour of the unmineralized rock to organic matter.

H. H. ADLER: Have you done sulphur isotope analyses to elucidate the relationships between your ores and their environment or source? It would be interesting to know whether you find the typical range of sandstone-type sulphides on which such extensive data are available in United States publications.

E. LUKACS: Our own group has not yet done such analyses, but they would undoubtedly be instructive.

H. H. ADLER: Yes, I think the answer, or at least part of the answer, to the question of what the environment of deposition was like might emerge from isotope determinations.

A. ZERESHKI: You mentioned, I believe, that you found an increasing Th/U. Could you say how this ratio was measured? It would also be interesting to know whether you have done detailed microscopic petrographic studies, and, if so, what inclusions you found.

E. LUKACS: The thorium-uranium ratios were determined by chemical analyses. However, this work was done not by us but by the group of Markov and Ristić whose paper¹ is to be presented tomorrow. It will, I think, provide the answers to your questions.

A. DURANDAU: This is a question which I would like to address to Mr. Lukacs, but also to Mr. Petrascheck and Mr. Mittempergher. Have you found copper associated in any appreciable quantities with the uranium of the Permian occurrences in Europe?

W. E. PETRASCHECK: No, certainly not in appreciable quantities. There are trace amounts of copper virtually everywhere in association with sulphides, but nothing that is economically extractable.

E. LUKACS: We have one copper ore deposit about 20 km from Žirovski Vrh, but it is located in the upper part of the Greden formation.

W. E. PETRASCHECK: An interesting question is whether there is any marked difference of shape between the deposits occurring in shallow marine sandstones and those found in terrestrial sandstone. Perhaps some of you would care to comment on this. It seems that the Austrian deposits were formed in a marine or lagoon environment and that they are tabular in shape.

H. H. ADLER: My first reaction is to ask where the uranium deposits in marine sandstones are, because we simply do not see them in the United States of America. I have spoken with our French colleagues about the origin of the deposits they have explored in the Niger and in Gabon, and when I raise the question of the marine affinity they assure me that the origin is marginal, not marine. Nevertheless, although we have not seen uranium deposits

¹ MARKOV, C., RISTIĆ, M., these Proceedings, Paper IAEA-SM-183/8.

in genuine marine sandstones, there is no reason why we should not expect to find one, provided the enclosing rock is in fact a true sandstone. We are assured by sedimentologists that deltas and off-shore bars are good areas for the accumulation of logs and other marine debris, so one might well expect them to evolve geochemically into zones where uranium could concentrate.

R. BLASER: The fact that uranium concentrates usually – if not exclusively – in terrestrial sandstones rather than marine ones may be due to the relative rarity of hydrodynamic water flow through marine sandstones (at the margins of sedimentary basins). In many marine sandstones the conditions of permeability are just as favourable as in terrestrial sandstones, so I feel we must look for some other explanation of the rarity of uranium deposition in marine sediments.

H. H. ADLER: I am not entirely happy with your explanation, because we regard the origin of the sandstone deposits as epigenetic, not syngenetic. This means that in theory the deposits could have been inserted long after the marine sediments had been uplifted and had become subject to water-table effects, that is, to essentially the same hydrodynamic gradients as terrestrial sandstone.

W. E. PETRASCHECK: In some of the sandstones where uranium ore deposits occur in Austria we find a rhythmic graded bedding and nodules of magnesite, features which we regard as convincing evidence of a marine or at least lagoonal origin. The uranium deposits in these sandstones seem to be strictly stratiform. We feel that these characteristics would be difficult to explain if the sandstone were of fluvial origin.

J. W. KING: I think possibly the unfavourable feature of the marine environment is its uniformity. Mineralization is favoured by change; the farther seaward we go the less change we find and – if my theory is correct – the more unlikely it becomes that the environment would have favoured uranium mineralization.

M. MITTEMPERGER: While we are on the subject of deposition and the conditions of deposition in the Permian and lower Triassic sandstones and siltstones of the Alps, I might say that it should always be possible, by appropriate sedimentological studies, to differentiate the continental from the marine sediments. In the Italian Alps the Permian sandstones are continental sedimentary rocks; the lower Triassic siltstones are marine sediments.

I. A. BREGER: Surely it does not matter whether a sediment is marine, lagoonal, fluvial or terrestrial. The important thing is that the sediment must be permeable to permit the introduction of the uranium-bearing solution, and that it must have a means for trapping the uranium. Marine sands are probably free of organic matter under normal conditions but could serve as a trap if they obtained organic matter from some external source, or perhaps hydrogen sulphide.

CARACTERES MINERALO-GEOCHIMIQUES ET GENESE DU GISEMENT D'URANIUM DE ŽIROVSKI VRH

C. MARKOV, M. RISTIĆ

Institut pour les investigations
géologo-minières,
Belgrade, Yougoslavie

Abstract-Résumé

MINERAL-GEOCHEMICAL CHARACTERISTICS AND GENESIS OF THE ŽIROVSKI VRH URANIUM DEPOSIT.

The Žirovski Vrh uranium deposit is situated in the Gorenja Vas region, to the west of Ljubljana, Slovenia – a region of Permian and Triassic sediments. The uranium ore occurs in grey gredonian sandstone or – more rarely – in slightly metamorphized conglomerates and breccias. These rocks are composed of: quartz, fragments of quartz porphyry and metamorphic rocks; then, mica, feldspar and silico-sericitic cement; lastly, carbonates, organic matter, resistant heavy minerals, sulphides and uranium ore.

The mineralized bodies are in the form of bands or lenticles distributed within the sedimentary stratum, which is about 20 m thick. The uranium ore is pitchblende. The concentration of uranium in the ore is 0.01-5%, amounting to over 10% in a very few places.

In the sandstone and conglomerates of the grey uraniferous series there are a number of elements (Cu, Zn, Pb, As, Y, etc.) of which the greater part was precipitated epigenetically in that series, where their distribution is very dependent on the distribution of the carbonates, the organic matter, the sulphides and the pitchblende.

The uranium and other metals were precipitated from underground waters and deposited at the limit of the oxidation and reduction media, which represented the geochemical barrier. Gradual metamorphism of the sandstones led to the transformation of the argillaceous cement into chlorite and sericite and of the organic matter into anthracite, with the fractionation and deposition of uranium.

CARACTERES MINERALO-GEOCHIMIQUES ET GENESE DU GISEMENT D'URANIUM DE ŽIROVSKI VRH.

Le gisement d'uranium de Žirovski Vrh est situé dans la région de Gorenja Vas, à l'Ouest de Ljubljana, en Slovénie. Cette région est constituée par des sédiments permien et triassiques. Les minerais d'uranium se trouvent dans des grès gredoniens gris, plus rarement dans des conglomérats et des brèches peu métamorphisés. Ces roches se composent de quartz, de fragments de porphyre quartzifère et de roches métamorphiques, puis de mica, de feldspath et de ciment silico-séricitique, ensuite de carbonates, de matière organique, de minéraux lourds résistants, de sulfures et de minerai d'uranium. Les corps minéralisés se présentent sous forme de bandes ou de lentilles, et sont distribués dans l'alternance du rythme sédimentaire, dont l'épaisseur est à peu près 20 mètres. Le minerai d'uranium est la pechblende. La teneur en uranium du minerai varie entre 0,01 et 5% et ne dépasse qu'exceptionnellement 10%. Dans les grès et les conglomérats de la série grise uranifère se trouvent des éléments (Cu, Zn, Pb, As, Y, etc.) dont la plus grande partie a précipité épigénétiquement dans cette série, où leur distribution dépend étroitement de la distribution des carbonates, de la matière organique, des sulfures et de la pechblende. L'uranium et les autres métaux des eaux souterraines ont précipité et se sont déposés sur la limite des milieux d'oxydation et de réduction, qui représentait la barrière géochimique. Le métamorphisme progressif des grès a produit la transformation du ciment argileux en chlorite et séricite et de la matière organique en anthracite, avec fractionnement et dépôt de l'uranium.

INTRODUCTION

La région de Žirovski Vrh est située sur le flanc sud des Alpes Juliennes, à l'Ouest de la ville de Ljubljana. C'est une contrée montagneuse avec un relief ramifié, une importante couverture d'humus et un climat humide.

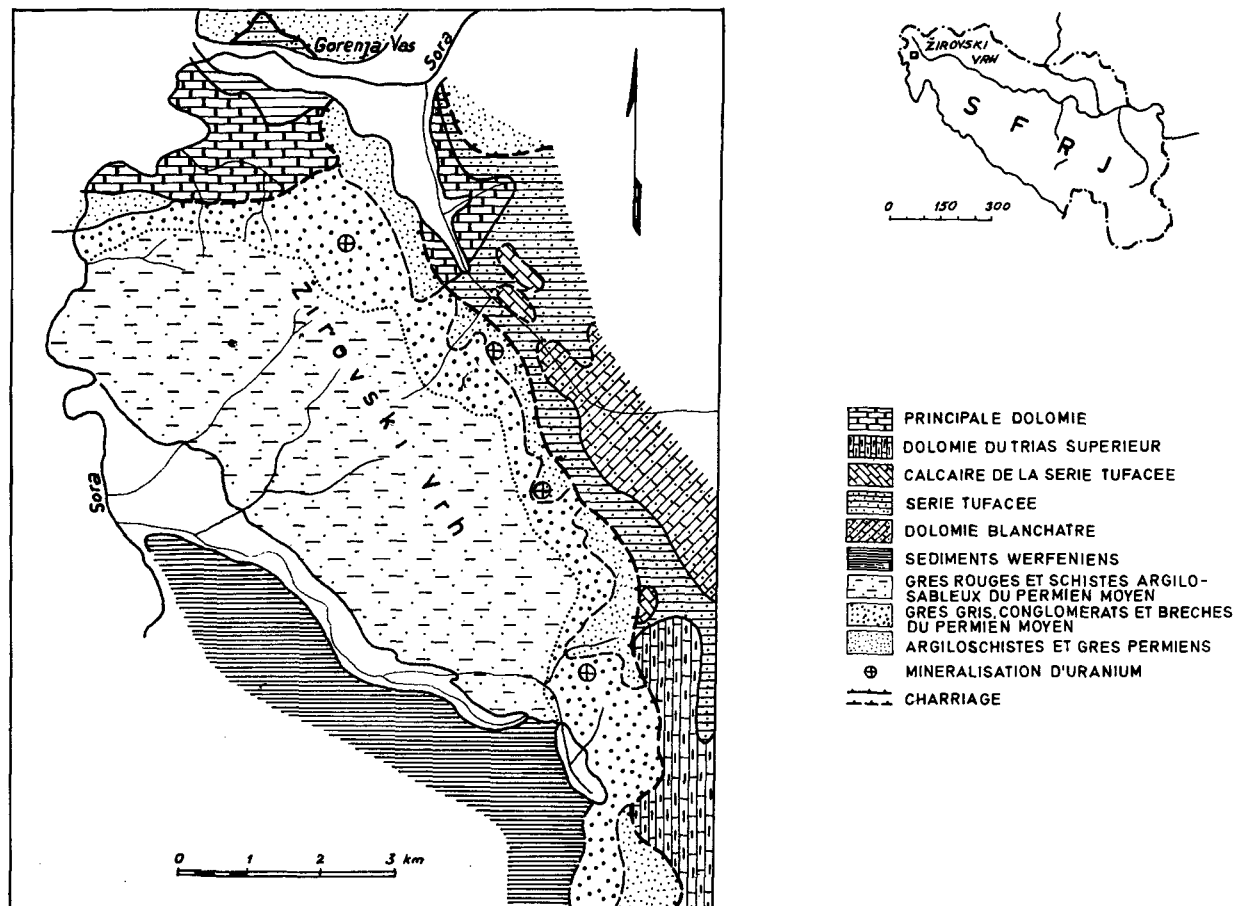


FIG.1. Carte géologique de la région de Gorenja Vas (d'après IGRI, Belgrade).

Les premières anomalies de radioactivité dans cette région ont été observées en 1951, lors d'une prospection radiométrique non systématique, mais le gisement a été découvert en 1960, grâce à une prospection systématique, et à partir de ce moment il a été reconnu et préparé pour l'exploitation.

A proximité du gisement on trouve [1-3] des carbonates sédimentaires du Permien et du Trias (fig. 1), qui forment une bande d'une longueur de 20 km orientée du Nord-Ouest au Sud-Est. Les schistes argileux et les grès du Permien moyen et inférieur remontent souvent sans limite définie dans les couches du Permien moyen gredenien, et celles-ci dans les calcaires à bélorofones.

Les grès gredenienens comprennent deux parties qui se distinguent par la couleur. La partie inférieure a une épaisseur de plusieurs dizaines de mètres, et elle se compose de grès gris-verts et de couches (lentilles) intercalées d'alévrolites rouges; l'autre partie a une épaisseur de quelques centaines de mètres et elle est formée de grès et d'alévrolites rouges avec des couches intercalées (lentilles) d'alévrolites gris et gris-verts. Dans les deux parties de la série se trouvent des concentrations de carbonates qui se sont créés pendant la diagenèse; la silicification et la carbonatation ont eu lieu au stade épigénétique. En plusieurs lieux la silicification s'est faite au-dessus et au-dessous des grès minéralisés.

La zone de stratification oblique [4, 5] se trouve dans la série inférieure et peut s'expliquer par l'activité intensive de courants qui ont interrompu le dépôt normal horizontal, ou par la sédimentation à proximité de la côte.

Dans les grès gris se trouvent plusieurs niveaux de couches intercalées avec la matière carbonifère proprement dite, constituée en majeure partie par des fragments d'anthracite [6]. Pour cette raison leur couleur a été attribuée à l'existence de milieux réductifs lors de leur dépôt, due à la présence de matière organique non décomposée. Les couches intercalées de grès gris et d'alévrolites dans la série rouge clastique dans lesquelles ne se trouvent pas de traces de matière organique sont interprétées comme résultant d'une décoloration locale pendant la diagenèse des sédiments rouges.

LES CARACTERISTIQUES MINERALO-GEOCHIMIQUES

Les grès sont composés [5] de fragments et de grains de porphyre quartzifère et de quartz volcanogène, de fragments de roches métamorphiques, de quartz non volcanogène, de chlorite et de grains de plagioclase, de muscovite et de séricite. Le ciment de ces grès est maintenant micro-cristallin; il est constitué de matière silico-séricitique, sporadiquement remplacée par de la matière carbonatée. A l'origine le ciment était argileux.

Les grès rouges de la partie supérieure de la série gredenienne ont presque la même composition minéralogique [5], mais le matériel volcanique est plus difficile à distinguer. Les fragments de roches volcaniques se trouvent aussi dans des parties conglomératiques, mais en moindre quantité.

La composition moyenne (47 échantillons) des grès gris dans le voisinage et dans les corps minéralisés d'uranium est la suivante:

quartz	29%	fragments de roches	28%
feldspath	3%	ciment silico-séricitique et autres minéraux	31%
mica	9%		

Les grès gris, outre les minéraux énumérés, contiennent encore des minéraux lourds résistants, de la matière organique, des carbonates, des sulfures avec des produits de transformation; les parties minéralisées contiennent des minéraux d'uranium.

Les minéraux lourds résistants se trouvent dans la masse cimentatoire des roches, plus rarement dans les fragments de roches, et leur concentration est à peu près 0,1%. Ils se sont déposés en même temps que les minéraux pétrogènes, sauf une partie de la barytine qui caractérise les parties de grès minéralisés à l'exception des filons silico-quartzeux. De ces minéraux les plus abondants sont le zircon, le rutile (leucoxène), les minéraux métalliques, le plus souvent magnétite avec martite, rarement ilménite et plus rarement encore spinelle; on trouve des traces de tourmaline, apatite, allanite, zoisite, staurolite, disthène, monazite, scheelite et corindon.

La matière organique était primitivement composée de petits détritux végétaux et de morceaux de bois qui se sont transformés dans des conditions anaérobies en charbon, qui a quelquefois une structure cellulaire ligneuse, imprégnée de pyrite [6]. Elle est métamorphisée en anthracite. Outre la matière anthracique non dissoute il existe aussi en plus petite quantité dans le ciment du grès de la matière organique dissoute, mais elle n'a pas été explorée en détail. Souvent la matière organique est associée à des sulfures, surtout pyrite, plus rarement à la pechblende. La teneur de la matière organique dans les grès et les conglomérats de la série grise grede-nienne varie entre 0,02 et 4,31% ($\bar{x} = 0,26\%$), avec une tendance évidente à augmenter dans les corps minéralisés, mais il n'existe pas dans ceux-ci une corrélation plus significative de la teneur en matière organique avec la teneur en uranium.

Dans les grès et les conglomérats gris se trouvent de la calcite, de la dolomie, de l'ancérinite, de la cérusite, de la malachite et de l'azurite de minéraux carbonatés. La calcite peut être mélangée au ciment séricito-siliceux, se présenter sous forme de filons plus ou moins petits, ou se trouver dans des filons quartzo-calcitiques. Sa teneur varie entre 0 et 19% ($\bar{x} = 4\%$). Les teneurs les plus élevées se rencontrent dans les couches de minerai autour desquelles les teneurs en uranium sont les plus basses. Dans les corps minéralisés cependant, il n'existe pas de corrélation entre la teneur en calcite et la teneur en uranium, mais il existe une corrélation positive linéaire significative entre les teneurs en calcite et en manganèse ($r = 0,83$). La dolomie et l'ancérinite se trouvent dans le ciment des roches; elles se sont déposées avant le minerai. La cérusite, la malachite et l'azurite sont les produits de la transformation des sulfures et se trouvent dans la zone d'oxydation.

Les minéraux sulfurés se trouvent dans les corps minéralisés et dans les parties non minéralisées de grès gris, mais en quantités peu considérables. La teneur en sulfures augmente aux environs des corps minéralisés et dans les filons quartzo-calcitiques.

Dans les corps minéralisés on a trouvé les minéraux sulfurés suivants: la pyrite, qui est la plus abondante et contient les transformations de la marcasite, ensuite la blende, la galène, la mispickel, la chalcopryrite avec les transformations en bornite, covellite et chalcocite, puis le cuivre gris. Ces minéraux se trouvent dans le ciment du grès sous forme de grains isolés associés à la matière organique ou à deux ou plusieurs autres minéraux sulfurés, ou encore à la pechblende. Le plus souvent ils sont

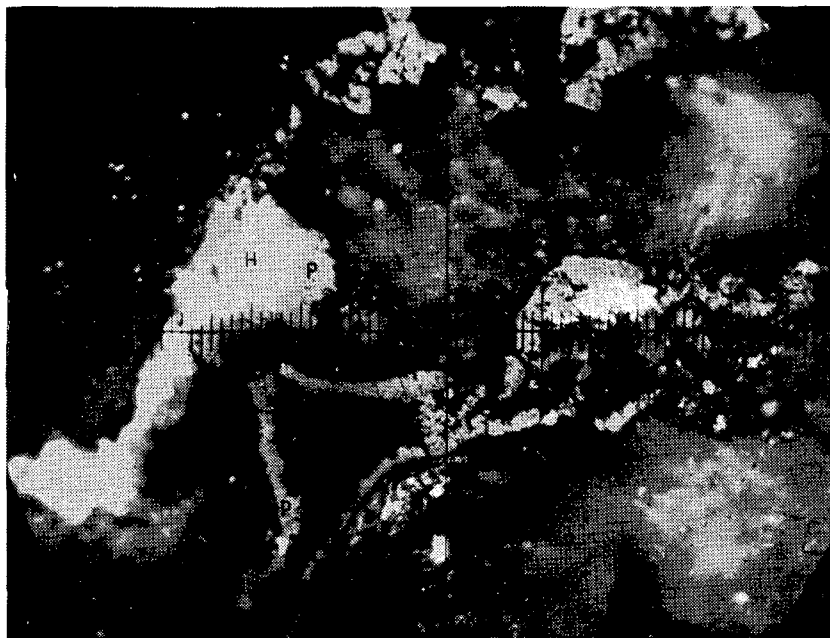


FIG.2. Mine de Žirovski Vrh: pechblende (P) et chalcocite (H) (grossissement 150x, section polie).

disséminés dans la masse de ciment. L'association de l'anhracite avec la pyrite est la plus fréquente; elle est plus rare avec les autres sulfures qui se trouvent dans les fissures de l'anhracite. Les relations paragenétiques mutuelles des minéraux sulfurés sont rarement visibles, car la plus grande partie se trouve dans des grains isolés, mais la paragenèse se manifeste dans la formation en plusieurs générations de la pyrite, de la chalcoppyrite et autres sulfures, qui résulte des conditions primaires de leur création et des processus métamorphiques ultérieurs. La taille des grains varie de dimensions submicroscopiques à quelques centaines de microns. Dans les conditions d'oxydation ces minéraux se transforment en limonite, arsénolite, malachite, azurite et cérusite.

La pechblende est le seul minéral d'uranium; sa teneur dans les corps minéralisés varie entre 0,01 et 5%; elle ne dépasse 10% qu'exceptionnellement. Elle se présente sous forme de grains submicroscopiques distribués inégalement dans le ciment du grès, ou sous forme d'agrégats grenus; dans ce dernier cas elle est visible au microscope; ses dimensions sont parfois de 10 μm , mais le plus souvent de 3 à 7 μm (fig. 2 et 3). Les agrégats de pechblende peuvent atteindre des dimensions remarquables. Elle se présente dans le minéral comme des agrégats grenus isolés, sous forme irrégulière dans le ciment et au contact des fragments de roches et des minéraux pétrogènes avec le ciment, et associée avec les sulfures dans le ciment des grès. La pechblende et les sulfures sont les plus jeunes minéraux de l'ensemble gréseux, sauf les petits filons de calcite et les minéraux de la zone d'oxydation.



FIG. 3. Mine de Žirovski Vrh: pechblende (P) et chalcopyrite (HK) avec transformation en chalcocite (H) (grossissement 150x, section polie).

Les relations paragenétiques de la pechblende avec les sulfures: chalcopyrite et produits de transformation (fig. 3) – chalcocite et covellite – pyrite, galène et blende, sont rarement visibles, mais la pechblende est quelquefois plus jeune.

L'autunite, la chalcolite, la djumontite, la phosphuranylite-renardite et l'uranotile sont des minéraux secondaires créés à partir de la pechblende dans les conditions d'oxydation. Ils se trouvent dans les parties supérieures et superficielles du gisement et quelquefois dans la profondeur des fissures, mais il n'y a pas eu de migration notable d'uranium pendant ces processus.

Dans tous les grès se trouvent à plusieurs niveaux des intercalations de matière carbonifère composée de petits filons et de fragments d'anthracite, et dont la couleur s'explique par l'existence d'un milieu réductif lorsqu'elle s'est déposée.

Dans les grès et les conglomérats de la série grise se trouvent en quantités microscopiques, outre l'uranium, les éléments suivants: Cu, Zn, Pb, As, Y, Mn, Ba, Sr, V, Zr, Ti, Th, Sb, Ag, Co, Ni, Mo, Sn, Cr, Ga, Sc et La. Quelques-uns de ces éléments se trouvent en grande partie dans des roches clastiques grises, par suite de processus épigénétiques.

Les teneurs en Sb, Ni, Cr, Th et Ga sont insignifiantes; les teneurs en Ag, Mo, Sn, Sc et La sont irrégulières. Les éléments Sb, Ag, Co, Mo et une partie du Ni sont liés aux sulfures et surtout sont déposés épigénétiquement. Les éléments Cr, Th, Ga, Sc et La sont liés aux minéraux pétrogènes et aux minéraux résistants et n'ont pas de relation avec le minerai d'uranium.

Cependant, la relation Th/U peut être utilisée comme indicateur du minerai d'uranium, car dans les parties de grès non minéralisé le thorium prédomine tandis que dans la zone de dissémination d'uranium épigénétique autour des corps minéralisés, c'est l'uranium qui l'emporte.

L'élément Ti est lié aux minéraux lourds résistants, leucoxène, rutile et ilménite; une partie insignifiante en est liée à la magnétite et la martite. Une importante quantité de zirconium est liée au zircon, et une autre partie en est mélangée aux autres minéraux détritiques. Il n'y a pas de différence de teneur en ces éléments dans les roches clastiques minéralisées et non minéralisées.

Les éléments Mn et Sr sont en partie liés aux carbonates, et en partie aux minéraux détritiques, ce qui rend leur distribution hétérogène.

Une partie des éléments Ba, V et Y est épigénétiquement introduite dans l'ensemble des grès. Ba se présente sous forme de barytine ou est mélangé aux feldspaths; il caractérise quantitativement le minerai d'uranium et son voisinage immédiat. Ba se trouve aussi dans les filons quartzo-calcitiques. Une partie de V se trouve dans la matière organique et les minéraux lourds résistants (magnétite entre autres) et l'autre partie dans le minerai d'uranium, quand il est épigénétique. La teneur en Y est insignifiante dans les grès non minéralisés, mais elle augmente considérablement dans le minerai d'uranium, où il existe une corrélation positive linéaire visible avec l'uranium ($r = 0,74$).

Les éléments Pb, As et Cu sont, outre le Fe, les principaux éléments de la minéralisation sulfurique et ils ont été introduits dans les grès et les conglomérats gris épigénétiquement; ils caractérisent alors quantitativement des parties de grès contenant du minerai d'uranium ou leur voisinage immédiat. Ces éléments, en outre, se trouvent dans les minéraux purs, ou ils sont disséminés dans les autres minéraux, surtout dans la pyrite.

LA GENESE

L'étude de la genèse du gisement uranifère de Žirovski Vrh a une grande importance pour l'identification des ensembles pétrographiques uranifères et pour la découverte de gisements aveugles dans ceux-ci hors du voisinage immédiat du gisement lui-même. Sur la genèse de ce gisement il existe plusieurs opinions [1, 2, 6, 7] mais elles ne se distinguent pas beaucoup. La création du minerai d'uranium a été un processus complexe, qui a commencé sur la terre ferme, a continué avec le dépôt des roches clastiques et leur diagenèse et avec la création du gisement, et s'est terminé par le métamorphisme. La genèse peut être expliquée de la manière suivante:

Après le Carbonifère s'est formé dans la région de Žirovski Vrh un bassin dans lequel se sont déposées des couches du Permien inférieur ou moyen; puis des couches gredeniennes se sont déposées dans le faciès continental, dont la partie inférieure est grise. Cette couleur des roches clastiques est primitive, et n'est pas due à la décoloration de sédiments rouges. Elle résulte du dépôt [4] du matériau clastique dans le milieu marin, ou a été provoquée [7] par les conditions climatiques et l'érosion sur la terre ferme. Pendant la saison des pluies, une quantité de détritiques organiques a été entraînée dans le bassin, formant un milieu réductif et expliquant la couleur grise de l'ensemble grès-conglomérats.

Aujourd'hui, on ne peut pas estimer la longueur du chemin parcouru par les grains de sable d'après leur rondeur, car ils ont certainement changé durant la longue diagenèse et le métamorphisme.

Des eaux souterraines et superficielles ont transporté, jusqu'au bassin et dans les grès gris, l'uranium et les autres éléments lessivés de roches volcaniques ayant une teneur en uranium élevée ou des minéralisations d'uranium et des auréoles de la dissémination d'uranium endogène.

Si les eaux hydrothermales ont circulé à travers les grès, les grains des feldspaths auraient dû être transformés en kaolinite, qui aurait dû être à son tour transformée durant le métamorphisme en dickite et hydromica. Nous n'avons pas trouvé ces minéraux, et les grès minéralisés ont la même composition que les grès non minéralisés. Cela, ainsi que des résultats d'analyses isotopiques du soufre (on constate une légère augmentation des isotopes), montre que le mode de création du minerai d'uranium n'était pas, à l'origine, hydrothermal. En outre, dans les accidents tectoniques qui coupent la série grise et la minéralisation même, on n'a trouvé aucun produit d'altération hydrothermale, ni de traces de minéralisation, mais seulement des matériaux de grès gredeniens gris fortement milonitisés.

Les quantités d'uranium qui ont pu se déposer par la voie chimique de solutions aqueuses acides et qui ont circulé à travers les grès gris sont insignifiantes, à cause de la très basse concentration d'uranium dans ces solutions. De même, seules des quantités négligeables d'uranium des eaux souterraines ont pu être fixées par les colloïdes minéraux - oxydes d'aluminium, de fer, de silice et phosphates -, en raison des très faibles quantités habituellement présentes dans de tels sédiments.

La formation du minerai a commencé après la compression provoquée dans les sédiments par la cimentation, c'est-à-dire quand les matériaux argileux et alévolitiques ont commencé à constituer des écrans pour les solutions aqueuses et pour les gaz. Elle a duré jusqu'au moment où, à cause de la cimentation et du métamorphisme, la porosité des grès a diminué et a empêché la circulation des eaux souterraines uranifères. La plus grande partie de l'uranium s'est déposée pendant la cimentation, quand les bords des minéraux siliceux se sont dissous et la silice s'est déposée dans les interstices entre les grains des minéraux pétrogènes qui avaient ralenti la circulation des eaux souterraines, et quand le dépôt de minéralisation d'uranium et de sulfures a augmenté. La création du ciment siliceux confirme que les eaux souterraines ont circulé à basse température et à basse pression.

L'uranium et les autres métaux, ainsi que d'autres éléments des eaux souterraines, se sont déposés sur des barrières géochimiques [8] dans les grès gredeniens gris, processus déterminé par la présence de détritiques carbonifères qui avaient servi de source d'énergie [9, 10] aux bactéries anaérobies qui ont provoqué la décomposition de ce détritiques et la libération de H_2S , dont la concentration était conditionnée par la création du milieu réductif. L'uranium et d'autres éléments se sont déposés sur la limite entre les milieux d'oxydation et de réduction. La concentration de ces éléments a été déterminée par la teneur en H_2S et par leur concentration dans les eaux souterraines. Un déplacement de cette limite a pu se produire de temps en temps. En conséquence, l'uranium déjà déposé a pu parvenir dans la zone d'oxydation et être transformé en uranium hexavalent, puis être réintroduit dans le milieu réductif par les eaux souterraines. De cette manière [10] des corps minéralisés de plus en plus grands ont pu se créer. Ainsi

l'uranium s'est déposé comme de la «suie d'uranium» dans le ciment du grès. Avec l'uranium se sont déposés les grains de sulfures, le plus souvent isolément, jusqu'à ce que la création du milieu aseptique interrompe l'activité des bactéries.

Dans la phase finale, il s'est produit un métamorphisme progressif de faible intensité qui a transformé la matière argileuse du ciment en séricite et chlorite et la matière carbonifère en anthracite, avec fractionnement et séparation de l'uranium tétravalent sous forme d'inclusions de pechblende, où l'uranium reste dans le ciment du grès, uni aux fractions de matière carbonifère. Le métamorphisme se produit à une température d'environ 200°C, qui correspond à la température de transformation de la matière carbonifère en anthracite. Des restes d'eaux réchauffés jusqu'à cette température ont facilité la recristallisation des sulfures et la création des inclusions de pechblende. Ainsi s'est terminée la création du gisement uranifère de Žirovski Vrh.

Dans les conditions d'oxydation, pendant le processus de désintégration superficielle, la pechblende et les sulfures se sont transformés en produits secondaires qui représentent les plus jeunes formations du gisement. Mais il n'y a pas eu à ce moment d'importante migration d'uranium et d'autres éléments. Pour le gisement uranifère de Žirovski Vrh, ces processus n'ont pas d'intérêt pratique.

REFERENCES

- [1] OMALJEV, V., Bucl. Ener. Belgrade 3 3 (1967).
- [2] OMALJEV, V., Radovi, Geoinst. Belgrade 3 (1967) 33.
- [3] OMALJEV, V., Radovi, Geoinst. Belgrade 3 (1967) 125.
- [4] PROTIĆ, M., Radovi, Geoinst. Belgrade 1 (1961) 91.
- [5] RADOŠEVIĆ, S., Radovi, Geoinst. Belgrade 5 (1969) 157.
- [6] RADUSINOVIĆ, D., Radovi, Geoinst. Belgrade 3 (1967) 1.
- [7] RISTIĆ, M., MARKOV, C., Radovi, Geoinst. Belgrade 7 (1971) 1.
- [8] PEREL'MAN, A.I., Geohimiya epigeneticheskikh protsessov, Nedra, Moscou (1968).
- [9] JENSEN, M.L., Econ. Geol. 54 3 (1959) 374.
- [10] NININGER, D., et al., Proc. 21th Int. Geological Congress, Copenhagen, 1960, 15 (1960) 40.

DISCUSSION

H.H. ADLER: You mention recycling of uranium as the mechanism which produced the concentration now observed in this deposit, and you suggest that this process took place before metamorphism. Do you see any evidence of oxidation such as limonite and hematite bordering solution fronts (reduction-oxidation interfaces) along one or more borders or edges of the ore deposit? As you know, these manifestations are quite commonly associated with recycling of uranium in the United States of America.

M. RISTIĆ: As there is a fairly heavy covering of humus in the Žirovski Vrh region, it is impossible to examine the surface outcrops for evidence of oxidation products such as are seen in the US deposits. However, underground mining work in the mineralized zones has not yet revealed any such demarcation. Recycling of uranium occurred to us when we compared

the dimensions of the mineralized bodies at Žirovski Vrh with the mineralized bodies in a number of uranium deposits contained in the sandstone of Tertiary basins, where we discovered small lenses with oxidized ore and, further on in the same bed, larger lenses exhibiting the typical uranium "soot".

H.H. ADLER: It would be interesting to compare the sulphur isotope ratios of sulphides associated with the unmetamorphosed and with the metamorphosed deposits, both of which are found in the Permian strata. We have fairly copious data on sulphides from various sources, but to my knowledge no comparison of this kind has been made. In my opinion it would be very worthwhile, because it might show us whether metamorphism produces some distinct change in sulphur isotope ratios that distinguishes these deposits from unmetamorphosed deposits.

M. RISTIĆ: To determine the isotopic composition ($^{32}\text{S}/^{34}\text{S}$ ratios) we analysed monomineralic sulphide concentrates from the Žirovski Vrh uranium deposit and also from other deposits of lead, zinc and copper. The standard used in presenting these results was the troilitic phase of the Cañon Diablo meteor, for which we took a value of 22.22. The results were as follows:

Žirovski Vrh	Mispickel	-20.8 and -18.2
	Chalcopyrite	-25.1
	Pyrite	-33.6 and -33.8
Sovoden	Chalcopyrite in red sandstone	-10.2‰
	Chalcopyrite in ore	-13.7‰
	Pyrite	+2.5‰

W. BOURRET: What is the average grade of the uranium in the deposit?

M. RISTIĆ: The uranium content of the deposit is not at all uniform; the grade varies from 0.01 to 5% U_3O_8 (in a few exceptional cases to more than 10%). However, the mean content of the mineralized bodies in the ore is above 0.1%.

W. BOURRET: How were your samples taken?

M. RISTIĆ: Samples were taken in the mine by means of core holes and percussion drill holes with gamma logs. The samples were analysed chemically and by gamma spectrometry.

W. BOURRET: What are the dimensions of the mineralized area?

M. RISTIĆ: The mineralized areas vary from a few tens to a few hundreds of square metres in size. The zone as a whole extends over several kilometres.

C.T. MEYERTONS: What are the average concentrations of sulphides found in the ore? Did you analyse for molybdenum and for selenium and vanadium, and, if so, what were the concentrations of these elements? Do they exhibit some type of zoning with the ore?

M. RISTIĆ: The sulphide concentration in the mineralized bodies varies from trace amounts to 5%. Molybdenum is sporadic, generally showing only trace values, but the concentration rises somewhat within the mineralized bodies. The vanadium content of the mineralized bodies varies from 28 to

1000 ppm ($\bar{X}$ = 305 ppm), and in the unmineralized sandstone we find from trace amounts up to 15 ppm. The concentrations of certain other elements are as follows:

Fe	trace to 6.30%	$\bar{X}$ = 1.60%
Cu	0.00 to 0.40%	$\bar{X}$ = 0.05%
As	0.00 to 0.33%	$\bar{X}$ = 0.10%
Pb	0.00 to 2.58%	$\bar{X}$ = 0.28%
Zn	0.00 to 0.68%	$\bar{X}$ = 0.26%

There is a very definite zoning pattern, because the concentrations of these elements consistently diminish as one moves away from the mineralized bodies.

ЛИТОЛОГО-ФАЦИАЛЬНЫЕ УСЛОВИЯ ЛОКАЛИЗАЦИИ УРАНОВЫХ РУДОПРОЯВЛЕНИЙ В ПЕРМСКИХ ОТЛОЖЕНИЯХ В СОЦИАЛИСТИЧЕСКОЙ РЕСПУБЛИКЕ РУМЫНИИ

И.КОРНИЧУК

Министерство горной, нефтяной
промышленности и геологии,
Бухарест

Т.БУРТИК

Государственный комитет по атомной энергии,
Бухарест
Социалистическая Республика Румыния

Abstract—Аннотация

LITHOLOGICAL FEATURES AND FACIES OF URANIUM ORE DEPOSITS IN FORMATIONS IN THE SOCIALIST REPUBLIC OF ROMANIA.

Some of the uranium ore occurrences associated with multicoloured rocks of Permian-carboniferous age in Romania show concentrations great enough to encourage exploitation. Although they have certain features in common (lithological and structural controls, mineralogical composition, and so on) some geological characteristics of the formations in which the mineralization (which does not always crop out) is localized tend to hamper exploration and prospecting. Generally speaking, the uranium ore deposits occur in a series of multicoloured rocks representing a transitional stage between series of grey and red rock. In this transition the ore is associated with grey and grey-green rocks consisting of conglomerates, gritstones and sandstones. The rocks most favourable for uranium accumulation exhibit great permeability and sharp lithological contrast, and were formed in alluvial and lacustrine-alluvial facies. Important in the ore deposition process was the presence of lithological, tectonic and structural screening that promoted its accumulation. The ore bodies are stratified and lenticular in shape, lie concordant with the strata for the most part, and exhibit sharply defined lithological control. The uranium mineral is pitchblende, finely dispersed segregations of which are observed inside bitumen. Less frequently one encounters pitchblende and uranium black unassociated with bitumen, but always lying close to it. Several theories have been put forward with regard to the genesis of these occurrences (such as syngenetic, exogeno-epigenetic, or hydrothermal origin), but clearly the genesis of these ore deposits was highly complex and both exogenic and endogenic factors must have contributed to their formation.

ЛИТОЛОГО-ФАЦИАЛЬНЫЕ УСЛОВИЯ ЛОКАЛИЗАЦИИ УРАНОВЫХ РУДОПРОЯВЛЕНИЙ В ПЕРМСКИХ ОТЛОЖЕНИЯХ В СОЦИАЛИСТИЧЕСКОЙ РЕСПУБЛИКЕ РУМЫНИИ.

Урановые рудопроявления, связанные с комплексом пестроцветных пород пермско-каменноугольного возраста, иногда представляют собою концентрации урана промышленного значения. Несмотря на то, что они имеют некоторые общие черты (литологический и структурный контроль, минералогический состав и т.д.) некоторые геологические особенности формаций, в которых локализована минерализация, иногда не имеющая выхода на дневную поверхность, делают трудным поиски и разведку. Как правило, эти рудопроявления урана локализованы в комплексе пестроцветных пород, которые представляют собою переходный интервал от комплекса пород серого цвета к комплексу красноцветных пород. В этом интервале рудопроявления приурочены к отложениям пород серого и серо-зеленоватого цвета, представленных конгломератами, гравелитами и песчаниками. Породами, благоприятными для накопления урановой минерализации, являются те породы, которые имеют повышенную проницаемость, резкий литологический контраст и образовались в условиях аллювиальных и озерно-аллювиальных фаций. Важную роль в локализации минерализации играет присутствие литологических, тектонических и структурных экранов,

которые благоприятствуют ее накоплению. Рудные тела имеют пластообразную, линзовидную форму, в общем залегают согласно с напластованием и имеют резкий литологический контроль. Урановым минералом является настуран, тонкодисперсные выделения которого наблюдаются внутри битума. Реже встречаются настуран и урановая чернь, не связанные с битумом, но всегда по соседству с последним. В отношении генезиса было высказано несколько гипотез (сингенетическое происхождение, экзогенно-эпигенетическое, гидротермальное). Очевидно, что образование этих рудопоявлений очень комплексно и в их формировании принимали участие как экзогенные, так и эндогенные факторы.

В реферате коротко излагаются некоторые результаты геологических исследований (стратиграфических, фациально-литологических, палеогеографических и структурных), проведенных в районе с целью определения некоторых закономерностей, связанных с распространением и накоплением урановой минерализации, приуроченной к комплексам осадочных пород пермско-каменноугольного возраста. Проблемы, связанные с поисками месторождений этого типа, сложные и настоящий материал предлагает обсуждение только некоторых наиболее важных вопросов, относящихся к данной минерализации.

1. ОСНОВНЫЕ ОСОБЕННОСТИ ГЕОЛОГИЧЕСКОЙ СТРУКТУРЫ РАЙОНА

Главной геологической структурой района является синклинорий – грабен субмеридионального направления, сложенный палеозойскими и мезозойскими образованиями. Ограниченное распределение имеют кайнозойские отложения.

По интенсивности разломов, степени метаморфизации и магматическим комплексам выделяются три структурных этажа.

Нижний структурный этаж

Нижний структурный этаж сложен кристаллическими сланцами, которые по возрасту относятся к верхнему допротерозою, и кристаллическими сланцами верхнего протерозоя с переходом к палеозою (палеозой докарбоновый). Породами более древнего возраста, чем верхний протерозой, считаются слюдистые сланцы, прорванные гнейсогранитами и гранитоидами.

Верхний протерозой – докарбоновый палеозой представлены слабо-метаморфизованными хлоритовыми и серицитовыми сланцами, которые образовались из осадочных и эффузивных пород.

Средний структурный этаж

Средний структурный этаж представлен толщей терригенных пород, слабометаморфизованных (песчаники, алевролиты, конгломераты, известняки), которые относятся к верхнему палеозою и мезозою. Эти породы трансгрессивно и несогласно залегают на кристаллических сланцах. Отложения среднего этажа делят на два осадочных цикла.

Нижний осадочный цикл представлен терригенными континентальными отложениями серого или красного цвета, которые по возрасту

относятся к верхнему карбону и перми. Ограниченное распространение имеют эффузивные формации.

Верхний осадочный цикл представлен юрскими и меловыми отложениями, в большинстве случаев известняками и мергелями.

Верхний структурный этаж

Верхний структурный этаж представлен кайнозойскими формациями, очень слабо дислоцированными. Ограниченное распространение имеют кислые эффузивные породы.

Геологическая структура района сформировалась в течение пребайкальского, герцинского и альпийского тектонических циклов.

Движения альпийского тектонического цикла закончили образование современной геологической структуры района. Отложения были смяты в линейные складки субмеридионального направления, осложненные тектоническими нарушениями (рис.1).

С альпийским тектоническим циклом в районе связано и вторжение кислых интрузивных пород, которые локализованы по линии регионального разлома [1].

В упомянутых комплексах пород урановая минерализация имеет неравномерное распределение. Так, в формациях верхнего и нижнего этажа до настоящего времени не были обнаружены рудопоявления и месторождения урана, несмотря на то, что отмечаются отдельные радиоактивные аномалии, связанные с кристаллическими сланцами. Большинство радиоактивных аномалий, все рудопоявления и месторождения урана локализуются в пределах формаций среднего структурного этажа и связаны с верхнепалеозойскими терригенными образованиями.

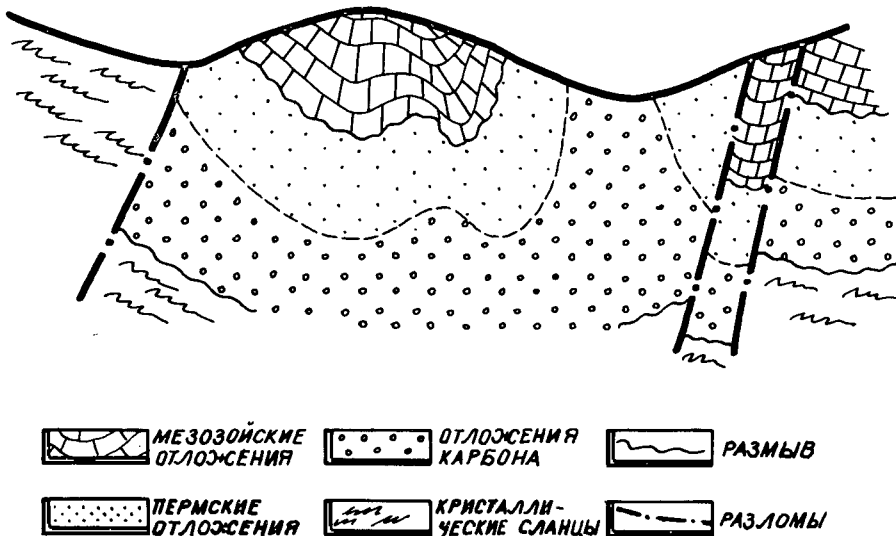


Рис.1. Схематический геологический разрез.

группа	субтема	отдел	свита	форм. фонд	мощь	краткая характеристика состава
П А Л Е О З О Й	П Е Р М Ь		ВЕРХНЯЯ		> 1500	КОНГЛОМЕРАТЫ, ПЕСЧАНИКИ МЕРГЕЛЯ, ИЗВЕСТНЯКИ.
				V	> 150	КРАСНЫЕ И СЕРЫЕ АЛЕВРОЛИТЫ И ПЕСЧАНИКИ ГЛИНИСТЫЕ СЛАНЦЫ
				IV	120-200	СЕРЫЕ КОНГЛОМЕРАТЫ И ПЕСЧАНИКИ, ПЕСЧАНИКИ КРАСНОГО ЦВЕТА, ГЛИНИСТЫЕ СЛАНЦЫ
				III	40-90	КРАСНЫЕ И СЕРЫЕ ПЕСЧАНИКИ
				II	20-100	КРАСНЫЕ КОНГЛОМЕРАТЫ И ПЕСЧАНИКИ, ТУФЫ
				I	20-100	КРАСНЫЕ И СЕРЫЕ ПЕСЧАНИКИ И КОНГЛОМЕРАТЫ
			НИЖНЯЯ		250-350	ПЕСЧАНИКИ, ГЛИНИСТЫЕ СЛАНЦЫ, ГЛИНИСТЫЕ БИТУМИНОЗНЫЕ И УГЛИСТОГЛИНИСТЫЕ СЛАНЦЫ
					250-400	СЕРЫЕ ПЕСЧАНИКИ, ПЕРЕСЛАИВАЮЩИЕСЯ С ТЕМНЫМИ, АЛЕВРОЛИТАМИ, ТЕМНЫЕ БОГАТЫЕ ОРГАНИЧЕСКИМ ВЕЩЕСТВОМ АЛЕВРОЛИТЫ
					250-350	КОНГЛОМЕРАТЫ, ПЕСЧАНИКИ С ПРОСЛОЯМИ ГРАВЕЛИТОВ И КОНГЛОМЕРАТОВ
					180-400	СРЕДНЕГАЛЕЧНЫЕ И КРУПНОГАЛЕЧНЫЕ КОНГЛОМЕРАТЫ С ПРОСЛОЯМИ ПЕСЧАНИКОВ
	КАРБОН	ВЕРХНИЙ КАРБОН	ВЕРХНЯЯ		0-700	КОНГЛОМЕРАТЫ, СРЕДНЕЗЕРНИСТЫЕ И МЕЛКОЗЕРНИСТЫЕ ПЕСЧАНИКИ С ПРОСЛОЯМИ ГРАВЕЛИТОВ И АЛЕВРОЛИТОВ
					0-650	ВАЛУННЫЕ КОНГЛОМЕРАТЫ, КОНГЛОМЕРАТЫ И ГРАВЕЛИТЫ С ПРОСЛОЯМИ ПЕСЧАНИКОВ.
			НИЖНЯЯ			
						КРИСТАЛЛИЧЕСКИЕ СЛАНЦЫ

Рис. 2. Стратиграфическая колонка верхнепалеозойских отложений.

2. ВЕРХНЕПАЛЕОЗОЙСКИЕ ОТЛОЖЕНИЯ И ЛИТОЛОГИЧЕСКИЕ ОСОБЕННОСТИ ПРОДУКТИВНЫХ ГОРИЗОНТОВ

Осадочные формации верхнего палеозоя занимают центральную часть синклиория и представлены терригенными континентальными отложениями серого цвета (те что относятся к верхнему карбону) или пестроцветными отложениями пермского возраста.

Весь комплекс пород характеризуется ритмичностью отложений, которая была обусловлена различными палеогеографическими условиями района во время отложения осадков.

Согласно принятой классификации формации верхнего палеозоя разделяются на несколько серий, стратиграфическая колонка которых показана на рис.2.

Из стратиграфической колонки вытекают следующие особенности: начиная с верхнего карбона зона была подвержена погружению и начинает накапливаться материал, транспортируемый большей частью водами. В результате этих процессов образовались обломочные породы, отложенные в условиях континента и эпиконтинентального бассейна, залегающие трансгрессивно и несогласно на кристаллическом фундаменте.

В пределах отложений верхнего карбона имеют место и прослои битуминозных алевролитов.

В нижней перми котловинный характер района обостряется еще больше, образовавшиеся породы представлены битуминозными алевролитами.

После отложения битуминозных алевролитов, характерных для нижней перми и залегающих в ее основании, осадочный бассейн подвергается поднятию, что выражается в разрушении верхней части подсерии.

На битуминозных алевролитах трансгрессивно залегают снова континентальные отложения и отложения бассейна. Эпиконтинентальный бассейн занимает меньшую площадь и образовавшиеся формации представлены алевролитами с прослойками известняков. Континентальные образования представлены отложениями палеорок, конусов выноса, озерными отложениями и отложениями затопляемых площадей [2].

Особенностями пермско-карбонных отложений являются:

- вертикальная зональность, выражающаяся в смене цвета пород, а именно, в основании лежит комплекс пород исключительно серого цвета, на которых залегают комплекс пестроцветных пород, представленный переслаиванием отложений серого и красного цвета и, наконец, комплекс красных пород;

- присутствие битуминозных и угленосных алевролитов, которые считаются источником битумов, локализованных в продуктивных горизонтах;

- ритмичность отложений (рис.3). Основные рудопроявления урана в районе связаны с верхней серией пермских отложений, а именно, с пестроцветным комплексом пород.

Минерализация урана локализована в прослоях песчаников и конгломератов серого и серо-зеленоватого цвета.

По литологическим признакам пестроцветный комплекс делится на 5 горизонтов. Эти горизонты характеризуются ритмичностью отложений, каждый микроритм всегда начинается базальными конгломератами и кончается мелкозернистыми отложениями. Каждый горизонт может состоять из одного или нескольких микроритмов [3].

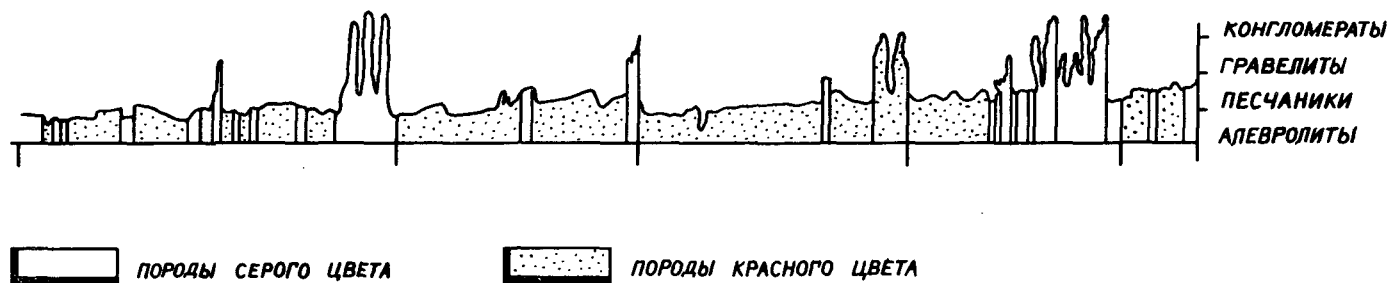


Рис.3. Ритмичность пермских пестроцветных отложений.

Урановая минерализация приурочена к трем из этих горизонтов, вследствие чего они были названы продуктивными горизонтами.

Осадочный горизонт I состоит из 20-25 микроритмов. В основании каждого микроритма замечают конгломераты, гравелиты и песчаники серого цвета, отложенные ритмично и имеющие косую слоистость. Компоненты, слагающие конгломераты, представлены обломками метаморфических пород. Гравелиты имеют тот же состав, что и конгломераты с той разницей, что содержат большее количество розового полевого шпата. Песчаники имеют серый цвет, обломки, входящие в их состав, слабо сортированы и в основном слюдистые и глинистые. Верхняя часть микроритмов обычно представлена битуминозными алевролитами. Осадочный горизонт I заканчивается песчаниками и алевролитами красного цвета. К этому горизонту приурочено урановое оруденение.

Осадочный горизонт II. В основании горизонта залегают конгломераты с обломками кварцевых порфиров серого, темно-серого, почти черного и красного цвета; обломки, входящие в состав конгломератов, имеют повышенную степень окатанности и сцементированы красно-фиолетовой массой. В этом горизонте присутствуют туфы, туффиты серого, серо-зеленоватого или красного цвета, песчаники и алевролиты того же цвета.

Этот осадочный горизонт очень выдержан на большом пространстве и является литологическим репером.

Осадочный горизонт III. В основании горизонта лежат отложения потоков, представленные конгломератами и гравелитами серого цвета с косой слоистостью. Горизонт содержит прослойки песчаников и туфо-песчаников серого и серо-зеленоватого цвета. На них залегают тонкозернистые песчаники и глинистые сланцы красно-фиолетового цвета с прослойками мергелей. В этом горизонте радиоактивные аномалии встречаются редко.

Осадочный горизонт IV. В этом горизонте выделяются 3-4 осадочных микроритма, представленные конгломератами, гравелитами и песчаниками серого и серо-зеленого цвета с косой слоистостью. Обломки, которые входят в состав конгломератов и гравелитов, представлены в основном кварцем. В лежащем боку осадочных ритмов находятся среднезернистые песчаники зеленоватого цвета с повышенным содержанием угловатых обломков изверженных пород. Верхняя часть осадочного горизонта IV сложена песчаниками и глинистыми сланцами серого и красного цвета с прослойками черноватых известняков и глинистых сланцев. Этот осадочный горизонт также является рудоносным.

Осадочный горизонт V. В основании этого горизонта лежат крупно- и среднезернистые глинистые и слюдистые песчаники серого цвета, переслаивающиеся с серыми и красными песчаниками, залегающими в виде линз. Верхняя часть горизонта сложена тонкозернистыми песчаниками и глинистыми сланцами красного цвета. К этому осадочному горизонту приурочено урановое оруденение.

3. НЕКОТОРЫЕ СВЕДЕНИЯ О ЛОКАЛИЗАЦИИ УРАНОВЫХ РУДОПРОЯВЛЕНИЙ В РАЙОНЕ

Детальный анализ аномалий, рудопроявлений и месторождений урана в районе дает возможность сделать следующие заключения:

- грубые терригенные отложения, относящиеся к верхнему карбону и находящиеся ниже уровня битуминозных алевролитов из верхней серии верхнего карбона и основания нижней перми являются пустыми с точки зрения урановой минерализации;

- в битуминозных и углистых алевролитах из верхней серии верхнего карбона и основания перми выявляется ряд аномальных зон на большом протяжении по простиранию и падению, так называемых битуминозных горизонтов с пониженным содержанием урана;

- основные урановые оруденения района находятся в верхней серии перми (пестроцветный комплекс) и локализованы в осадочных горизонтах I, IV, V.

В осадочном горизонте I известно несколько типов рудопроявлений, находящихся в его основании и локализованных в углистых, битуминозных алевролитах, песчаниках и конгломератах с карбонатным цементом.

Рудные тела имеют пластообразную форму и уран связан с присутствием органического вещества (битум или уголь).

В осадочном горизонте IV находится несколько рудных тел. Главное рудное тело имеет столбообразную форму; урановая минерализация локализована в сером горизонте, сложенном конгломератами, гравелитами и песчаниками с карбонатным цементом.

В лежачем боку рудного тела находятся среднезернистые песчаники зеленоватого или серо-зеленоватого цвета с глинистым цементом и содержат обломки изверженных пород.

Висячий бок рудного тела сложен песчаниками и глинистыми сланцами с прослойками серо-черных известняков и углистых сланцев.

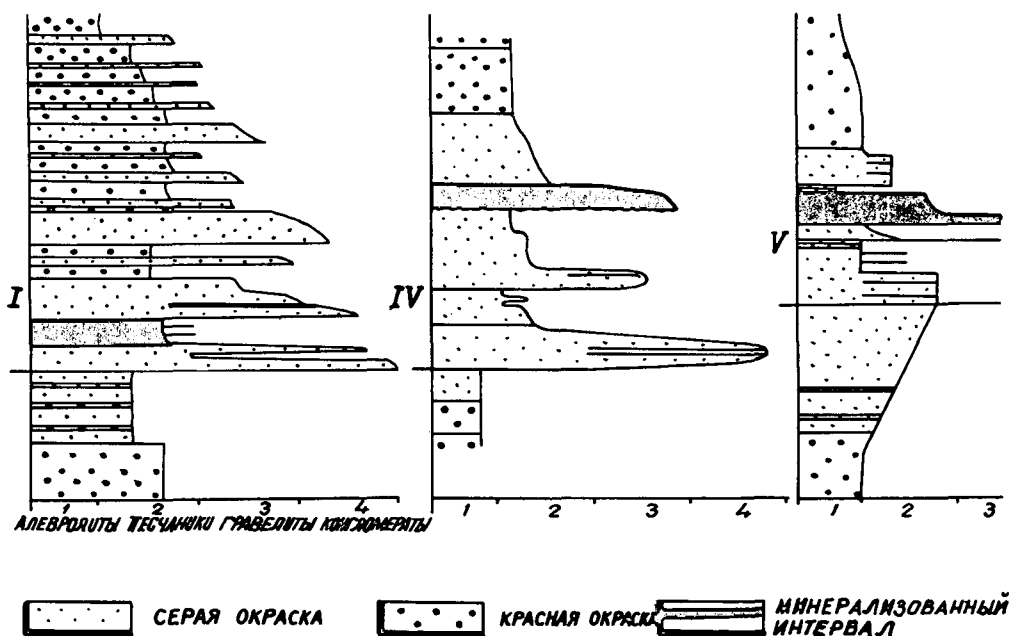


Рис. 4. Особенность стратиграфических горизонтов.

Твердые битумы, содержащие уран, замещают частично или полностью карбонатный цемент обломочных пород или находятся в сильно раздробленных зонах, заполняя трещины. В битумах настуран находится в виде тонкодисперсных выделений.

В осадочном комплексе V урановая минерализация локализована в средне- и мелкозернистых песчаниках с карбонатным цементом. Лежащий бок минерализованной зоны сложен серо-зеленоватыми песчаниками, которые содержат обломки изверженных и метаморфических пород и имеют глинистый цемент.

Рудные тела имеют пластообразную или линзообразную форму и сильно усложнены тектоническими нарушениями. Урановая минерализация в рудных телах распределена неравномерно и связана с битумами.

Битум в рудных телах находится в массе песчаников в форме гнезд, прожилок или в форме точечных остатков по трещинам или плоскостям напластования. Урановым минералом является настуран.

В приведенной схеме показано расположение минерализованных зон в пределах продуктивных горизонтов (рис.4).

4. ГЛАВНЫЕ ФАКТОРЫ, КОНТРОЛИРУЮЩИЕ МИНЕРАЛИЗАЦИИ УРАНА

Урановые минерализации в районе являются результатом наложения нескольких геологических процессов. Главными факторами, которые привели к образованию урановых минерализаций в районе, являются стратиграфический, литолого-фациальный, структурный и минералогический факторы. Условия, при которых они влияли на локализацию минерализаций, приводятся кратко ниже.

Стратиграфические условия

Урановая минерализация связана с битумным или угольным веществом и локализована исключительно в породах серого цвета из пестроцветных пермских отложений, а именно в песчаниках, гравелитах, конгломератах и реже в алевролитах.

Сравнивая стратиграфические разрезы минерализованных зон с разрезами зон неминерализованных, вытекает следующая особенность: стратиграфические разрезы минерализованных зон характеризуются контрастностью составляющих пород, то есть быстрой сменой по разрезу слоев крупнозернистых пород (конгломераты, гравелиты) слоями пород более мелкозернистых (песчаники, алеволиты): стратиграфические разрезы неминерализованных зон обычно монотонны.

Литолого-фациальные условия

Одним из главных факторов, необходимых для локализации минерализаций, является проницаемость пород. Породы, которые обладают большой проницаемостью, формируются только в определенных фациальных зонах, а именно, в условиях аллювиальных и прибрежно-озерных фаций.

Минерализации урана в пределах осадочного горизонта I и IV локализованы в аллювиальных отложениях русел рек, а в осадочном горизонте V — в аллювиальных дельтовых или озерно-прибрежных отложениях.

Такие отложения широко распространены и входят в состав многих микроритмов, но урановая минерализация локализована только в ограниченном числе микроритмов.

Микроритмы, содержащие минерализации урана, обычно залегают с отчетливым несогласием на размытой поверхности отложений лежащего бока и обычно представлены алевролитами или песчаниками с глинистым цементом. Обломочный материал в минерализованных породах представлен кварцем, в меньшей степени полевым шпатом или обломками эффузивных пород, хорошо обкатанных и отсортированных, и содержат в цементе небольшое количество глинистых частиц. Обычно эти микроритмы заканчиваются мелкозернистыми породами — алевролитами темносерого цвета и содержат тонкие прослойки карбонатных пород (доломитов).

В минерализованных породах ясно наблюдается параллельная или косая слоистость.

Микроритмы, не содержащие урановую минерализацию, в общем имеют следующее строение.

В основании микроритмов залегают серые конгломераты и гравелиты, состоящие из слабообкатанных и слабосортированных обломков: в верхней части микроритмов находятся крупно- и мелкозернистые породы красного цвета, неслоистые, и обломочный материал, входящий в их состав, сортирован слабо.

Это позволяет сделать вывод, что формирование пород, благоприятных для локализации минерализации, происходило в условиях потоков с постоянным водным режимом и активной динамикой водной среды.

Породы, не содержащие минерализацию урана, образовались в общем в условиях потоков с изменчивым режимом, в которых короткие периоды сильных затоплений сменялись засушливыми периодами.

Структурные условия

Структурные условия выражаются, в первую очередь, в локализации минерализаций в складчатых структурах и, во-вторых, во влиянии на формирование благоприятных фаций.

То, что было упомянуто в характеристике литолого-фациальных условий, в которых происходило образование формаций, благоприятных для уранонакопления, определяется тектоническим режимом в период осадконакопления.

Разрезы отложений с резким гранулометрическим контрастом, в которых локализованы рудопроявления урана, образовались в условиях интенсивных колебательных движений как зоны осадконакопления, так и эрозионной зоны.

Динамика водной среды, периоды максимальной транспортировки материала, как и положение поверхностей эрозии в пределах зоны, определяются тектоническим режимом периода осадконакопления.

Большинство рудопроявлений и особенно те, которые имеют повышенное содержание урана, локализованы в антиклинальных альпийских структурах (рис.5).

В пределах антиклинальной структуры наблюдается зональность в распределении рудопроявлений. Рудопроявления с повышенным содержанием урана находятся обычно в ядре антиклинали, а с меньшим содержанием урана — в ее крыльях.

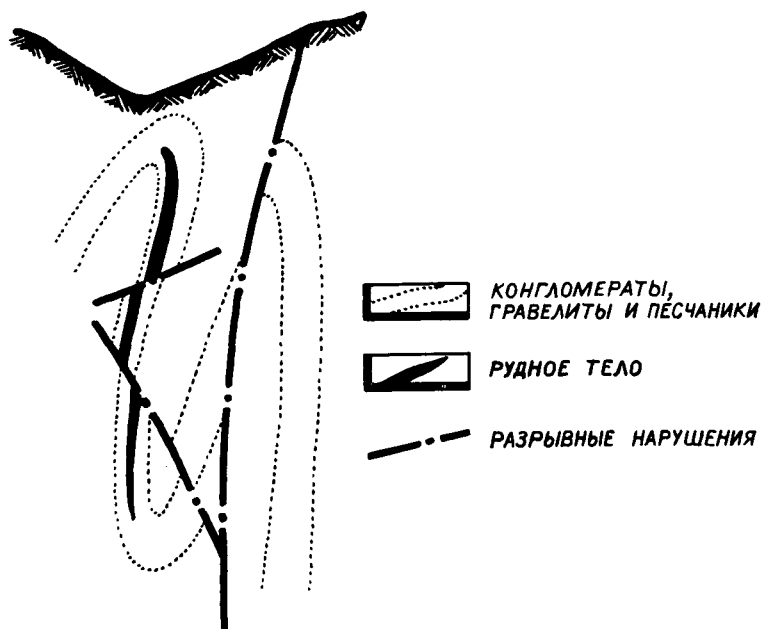


Рис.5. Схематический структурно-геологический разрез.

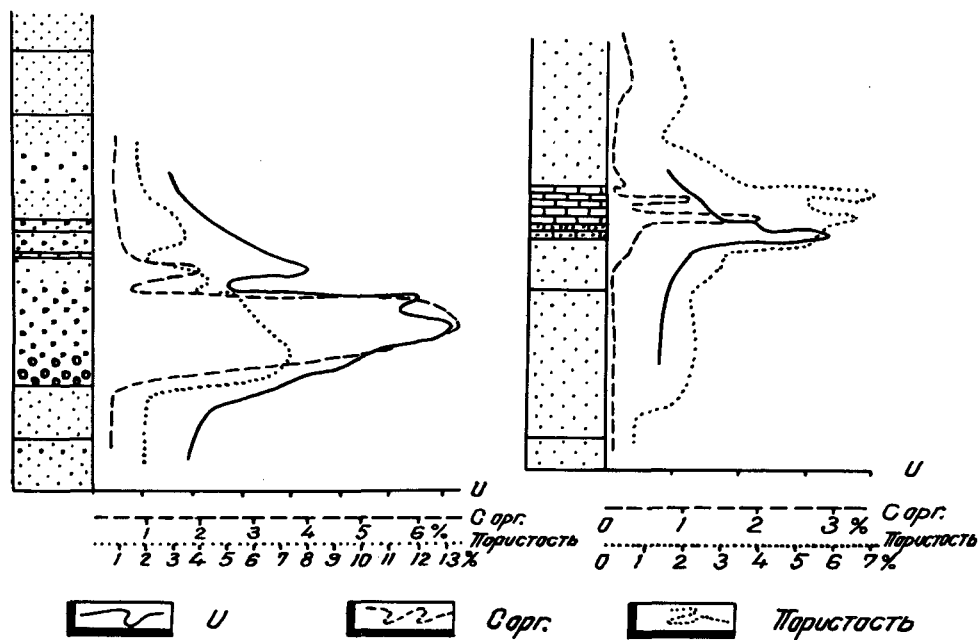


Рис.6. Зависимость между пористостью пород и количеством битума и урана.

Благоприятными для локализации рудопроявлений урана являются зоны альпийских антиклиналей, сложенные аллювиальными отложениями палеорек и расположенные наклонно по отношению к оси антиклинали.

Необходимо также отметить значение тектонических разрывов в распределении минерализаций урана в пределах пород. Сильно трещиноватые зоны всегда имеют повышенное содержание урана.

Не нужно также пренебрегать и значением тектонических разломов как путей проникновения битумов и урана, а также их экранирующей ролью [4].

Минералогические условия

Урановая минерализация в районе всегда связана с органическим веществом (битум). По этой причине присутствие в породе битумов указывает на присутствие и урана (рис. 6).

Из краткого анализа главных факторов, принявших участие в локализации рудопроявлений, вытекает, что рудоносные площади оконтуриваются только в зонах, где эти факторы участвовали совместно.

5. УРАНОВАЯ МИНЕРАЛИЗАЦИЯ И ЕЕ СВЯЗЬ С БИТУМОМ

По характеру связи урановой минерализации с породами-коллекторами и с органическим веществом, которое создавало восстановительные условия, урановая минерализация может быть разделена на следующие группы:

- сингенетическая минерализация урана, локализованная в битуминозных и углистых уровнях в тонкозернистых породах ("битуминозные горизонты" верхнего карбона и основания пермских отложений);
- эпигенетическая минерализация урана, локализованная в пестроцветных породах пермского возраста, связанная с присутствием твердых битумов, образовавшихся из жидких и газообразных углеводородов, вероятно мигрирующих из нижележащих битуминозных отложений.

Интерес представляют только эпигенетические минерализации урана, связанные с твердым битумом.

Твердые битумы присутствуют в форме неправильных включений, точечных остатков или линз, а также замещают частично или полностью карбонатный цемент обломочных пород, а иногда даже обломочные зерна.

Большинство твердых битумов в рудных телах имеют один и тот же возраст, но по степени окисления могут быть разделены на несколько разновидностей.

Содержание урана в битуме колеблется в широких пределах — от долей процента до 10–15%, более богатые битумы окислены сильнее.

Урановым минералом является настуран, присутствующий в форме тонкодисперсных включений в битуме. В меньшем количестве настуран находится в форме включений в цементе песчаников, в трещинках включений битума и вокруг него.

Характер распределения битумов, его форма, замещение карбонатного цемента и обломочных зерен битумом указывают на эпигенетический характер по отношению к породе.

Что касается отложения урановых минерализаций, то здесь, кажется, существовало две фазы.

Первая фаза начинается вторжением углеводородов и преобразованием их в твердые битумы, которые затем при отложении окислов урана окисляются, полимеризуются и превращаются в твердые черные битумы.

Присутствие урановых минералов, не связанных с битумом, а также распределение настурана вокруг зерен битума или по трещинам последнего указывают на наличие более молодой фазы минерализации, в которой вмешательство гидротермальных растворов имело решающую роль [5].

Этот тип минерализации носит ограниченный характер и развит по соседству с тектоническими нарушениями.

ЗАКЛЮЧЕНИЕ

1. Основные рудопроявления урана локализованы в пестроцветных пермских отложениях в пределах стратиграфических разрезов, которые имеют резкий литологический контраст и всегда связаны с твердыми битумами.

2. Распределение минерализаций урана, связанных с твердым битумом, обусловлено присутствием некоторых благоприятных факторов, таких как стратиграфический, литолого-фациальный и структурный.

3. В пределах развития благоприятных фаций распределение урановых минерализаций определяется и рядом дополнительных факторов, особенно присутствием складчатых структур.

ЛИТЕРАТУРА

- [1] GIUȘCĂ, D., CIOFLICĂ, G. SOVUM, Caracterizarea petrologică a provinciei Banatitice. Anuar Comit. Geologic XXXV Buc. 1966.
- [2] EMIL SAULEA, Geologia istorică, Editura didactică și pedagogică, București, 1967.
- [3] РУХИН, Л.Б., Основы Литологии, Гостоптехиздат, 1953.
- [4] NITU, GHEORGHE, Condițiile tectonico magmatice de formare a zăcămintelor de uraniu din R.S. România.
- [5] Геология и Вопросы Генезиса Эндогенных Урановых Месторождений, АН СССР, Изд-во "Наука", М., 1968.

DISCUSSION

R. H. DE VOTO: Your excellent description of these deposits makes me wonder whether they might not be related to fossil oil fields. Would you care to comment on this possibility?

I. CORNICIUC: The elemental composition of these bitumens clearly indicates that they belong to the strongly metamorphosed varieties of the petroleum series, the anthraxolites. Their frequency can be explained only as a result of the migration of oil and its concentration in porous and fissured rocks with subsequent metamorphism. Most investigators believe that the relatively fine-grained deposits with high concentrations of organic material may be derived from oil. We are more inclined to think that the oil-related formations in this region are the dark organic-rich intercalated

siltstones and sandstones — rocks belonging to upper Paleozoic horizons, in particular the upper Carboniferous.

S.S. ADAMS: Your description of the bitumen in the sands is interesting because it sounds like secondary, reprecipitated humic material, perhaps similar to the organic material in the Grants-type primary ores. The presence of detrital beds containing plant trash perhaps reinforces this possibility. What is the evidence that the bitumen has been oxidized (this would imply alteration) and has not simply retained oxygen from the organic humate material? Also, what is the uranium mineral?

I. CORNICIUC: As I said, the highest state of oxidation is found in the bitumens containing the largest amounts of uranium. This can be explained in the following way. Firstly, the bitumens now seen to be richest in uranium may have been those which were most heavily washed by the uraniferous solutions, as a result of which they were strongly oxidized. Secondly, alteration of the uranium-rich bitumens may have been subject to the oxidizing action of radiation. Also, the waters of the oxidation zone undoubtedly exerted some influence on the alteration of these bitumens.

On the other hand, the observed oxidation of the bitumens reduced their hardness and increased their brittleness; the intense lustre disappeared, the combustion temperature dropped, and the specific weight may have increased.

The uranium mineral is pitchblende in the form of finely dispersed inclusions within the bitumen. Uranium may be associated with other minerals too, however, and may even be present in the adsorbed state.

A.P. FLORJANČIČ: Have you observed any carbonate nodules or any decoloration of the enclosing rock around the mineralized bodies?

I. CORNICIUC: The formations in which the uranium mineralization is localized in this region have in fact undergone important alteration processes, some of them resulting in green or white coloration, and the intensity of this alteration of the rock is directly related to the size of the ore bodies. It is a familiar fact that in oil-rich regions the green coloration of red and grey strata is associated with migration and concentration of bitumens.

The chemism of this process has not been thoroughly studied as yet. We think that it is associated not only with the formation of hydromica and a reduction in the amount of iron present in oxide form (with some decrease in all forms of iron), but also with silicification and carbonization of the rock beyond the confines of the ore zones.

Some evidence of this can be seen in the development of powerful replacement processes accompanying the accumulation of bitumens, in the course of which large amounts of carbonate and silica should be liberated. In our region these alteration processes (green and white coloration) are being used as a guide to prospecting.

S.H.U. BOWIE: I am very interested in the presence of hydrocarbons or oxyhydrocarbons (bitumen) with pitchblende. The evidence I have derived from the study of several similar occurrences in various parts of the world suggests that the hydrocarbon probably polymerized from a gaseous phase through a liquid phase to the solid, which then aged. I should like to ask whether you have any evidence of pitchblende actually being replaced by hydrocarbon. This could happen both in vein-type and in stratiform deposits.

I. CORNICIUC: The uranium is present in the form of oxides which can sometimes be observed under the microscope at large magnification. Normally these are scattered sub-microscopic inclusions of pitchblende

reminiscent of a "rash". In the uranium-rich bitumens we find larger deposits of pitchblende along with these small inclusions. In a few individual cases we have seen pitchblende inclusions in the cement of gritstones and sandstones and in shrinkage cracks within the bitumen. This pitchblende appears to be associated with later formations.

Our observations to date do not suggest actual replacement of pitchblende by the hydrocarbon. However, the work is still in progress, and since you are interested in this question I shall be glad to inform you of any new results.

J. HRUBÝ: How do you reconcile the idea of strict control of uranium formation by the oxidized bitumens with the assumption that a large part of the uranium was associated with bitumen even before polymerization?

I. CORNICIUC: The bitumens acted as ion-exchange resins. They possessed this capacity apparently during the process of oxidation, when they were at their most active. Oxidation of petroleum bitumen, as we know, increases its content of the carboxyl group - COOH - and this in turn increases the sorptive capacity of the material. A process of uranium sorption and desorption accordingly took place.

During subsequent carbonization of the bitumens, uranium separated out in the form of oxides. The observed processes of uranium segregation within the bitumens provide evidence of repeated recrystallization and redistribution of uranium during polymerization of the bitumens.

The ore beds appear to have been formed in three main stages:

- (i) deposition of bitumens in favourable structural and lithological conditions;
- (ii) precipitation of uranium from the circulating solutions by bitumen; and
- (iii) carbonization and oxidation of the bitumens, with recrystallization and redistribution of uranium during the alteration processes.

FACTEURS CONTROLANT LA DISTRIBUTION DES ELEMENTS DANS LES SHALES URANIFERES DU BASSIN PERMIEN DE LODEVE (HERAULT, FRANCE)

A. HERBOSCH

Laboratoire de géochimie,
Université libre de Bruxelles,
Bruxelles, Belgique

Abstract-Résumé

FACTORS GOVERNING THE DISTRIBUTION OF ELEMENTS IN THE URANIFEROUS SHALES OF THE LODEVE PERMIAN BASIN (HERAULT, FRANCE).

Detailed petrographic, chemical and mineralogical studies were performed with about a hundred samples taken from the carrier beds of a stratiform regional anomaly (uranium and to a lesser extent molybdenum, lead and astatine). These beds, consisting of finely laminated dolomitic and bituminous pelite, point to lacustrine episodes which occurred cyclically in the Lower Permian within a thick continental pelite-sandstone fill of the "red beds" type. Besides the heavy-metal anomaly, these rocks are distinguished by their extremely small grain size, the presence of finely dispersed organic matter and an abundance (30-60%) of minerals of recent origin: ankerite, low-temperature albite, chlorite and sulphides. Factorial analysis in the R mode with 21 chemical variables enables one to describe 78% of the initial variance in terms of eight correlated factors which take into account all the intercorrelations. Identification of these factors with the fundamental geological processes involved in the formation of these rocks (diagenesis of the sulphides in a reducing medium, agitation of water, aggradation of diocahedral clays, detrital clays, alkalization, production of organic matter, diagenetic migration of sulphides) makes it possible to reconstruct with a high degree of accuracy the medium in which sedimentation occurred and the paleogeographic environment. From the stratigraphic point of view, the mathematical model enables one to characterize objectively and quantitatively this excellent example of "areas of retarded sedimentation", which is in this case a "metallotect" for uranium.

FACTEURS CONTROLANT LA DISTRIBUTION DES ELEMENTS DANS LES SHALES URANIFERES DU BASSIN PERMIEN DE LODEVE (HERAULT, FRANCE).

Une centaine d'échantillons des couches porteuses d'une anomalie régionale stratiforme en U et accessoirement en Mo, Pb, As ont fait l'objet d'investigations pétrographiques, chimiques et minéralogiques détaillées. Ces niveaux, formés d'une pelite dolomitique et bitumineuse finement laminée, sont les témoins d'épisodes lacustres qui apparaissent cycliquement à l'Autunien au milieu d'un épais remplissage périto-gréseux continental de type «red-beds». Outre leur anomalie en métaux lourds, ces roches se caractérisent par une extrême finesse, la présence de matières organiques finement dispersées et l'abondance (30-60%) de minéraux de néoformation: ankérite, albite de basse température, chlorite et sulfures. L'analyse factorielle en mode R effectuée sur 21 variables chimiques permet de décrire 78% de la variance initiale en termes de huit facteurs corrélés qui rendent compte de l'entière des intercorrélations. L'identification de ces facteurs avec les processus géologiques fondamentaux qui ont présidé à la formation de ces roches: diagenèse des sulfures en milieu réducteur, agitation des eaux, aggradation des argiles dioctaédriques, argiles détritiques, alcalinité, productivité organique, migration diagénétique des sulfures, permet de reconstituer d'une manière très précise le milieu de sédimentation et son environnement paléogéographique. Au point de vue géologique ce modèle mathématique permet de caractériser objectivement et quantitativement ce bel exemple «d'aires de sédimentation ralentie» qui constitue ici un métallotect pour l'uranium.

1. INTRODUCTION

1.1. La géologie

Le bassin permien de Lodève est situé dans l'Hérault à une cinquantaine de km au N-W de Montpellier. C'est le dernier représentant méridional d'une série de bassins carboniféro-permiens (déroit de Rodez, Saint-Affrique, Lodève) localisés en bordure W du golfe sédimentaire des Causses, à l'extrémité S du Massif Central (Fig. 1). Limniques, intra-montagneux, d'axes approximativement E-W, ils ont récemment fait l'objet d'une série de travaux (1 à 7) surtout motivés par la présence de nombreux indices d'U et accessoirement de Cu.

Jusqu'à présent seul le bassin de Lodève semble susceptible de présenter un intérêt économique, ses réserves sont estimées à 13000 t d'U métal (8).

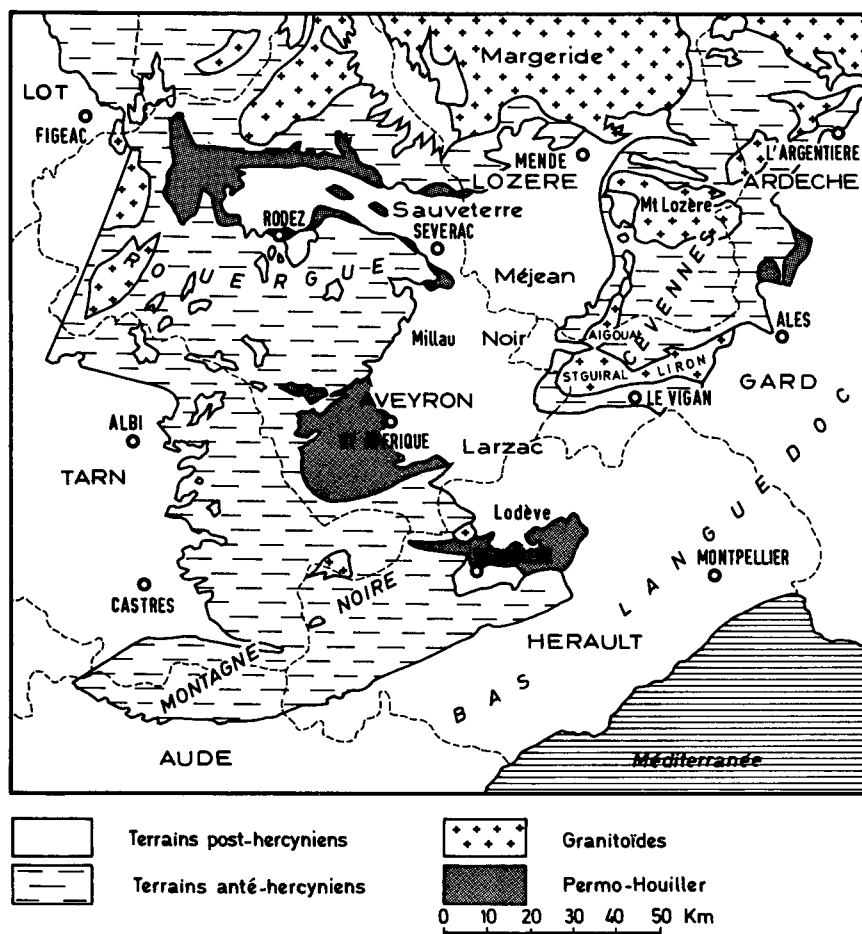


FIG.1. Localisation des bassins permien du sud du Massif central.

A la lumière de ces travaux, on peut dire que ce Carboniféro-Permien, comprenant le Stéphanien, l'Autunien et le Saxonien, constitue un ensemble post-orogénique fortement influencé dans la composition et la répartition de ses sédiments par la nature, la structure et les derniers mouvements épirogéniques du vieux socle hercynien. Sans trop schématiser, on peut considérer qu'à l'échelle de l'étage, le Stéphanien et l'Autunien correspondent à une ère de biostasie évolutive (9), qui conduit d'une manière insensible de la "biostasie des hygrophytes westphaliennes" à la rhexistasie saxonnienne. Le déplacement d'équilibre paraît plus lié à l'évolution de la topographie (tectonique) qu'à des changements climatiques radicaux. Une légère augmentation de l'aridité du climat tropical à saisons alternées se marque cependant au Saxonien (10).

Le bassin de Lodève, dont on trouvera une description géologique détaillée dans GARRIC (6), présente une structure monoclinale régulière et une puissance de 2000 m dont 600 m d'Autunien et 1400 m de Saxonien à faciès "red-beds". Seul l'Autunien nous intéresse ici, franchement transgressif il débute par un conglomérat auquel succède un épais remplissage de pélites fluvio-lacustres, plus ou moins silteuses, à ciment carbonaté fréquent. Grises et dolomitiques sur les 280 premiers mètres, ces pélites deviennent progressivement rouges (hématites) dans les 120 mètres suivants. Elles envahissent totalement les 200 derniers mètres annonçant les faciès bariolés du Saxonien. Les levés et nombreux sondages effectués par le C.E.A. ont permis de mettre en évidence dans l'Autunien des niveaux remarquables : peu épais (50 à 200 cm) et d'une grande extension latérale, ils fournissent d'excellents repères stratigraphiques. Les lithotopes de ces niveaux s'ordonnent en une série idéalement représentée par la "couche type autunienne" (Fig. 2). Ils forment un microcycle sédimentaire complet (biséquence + -), comprenant à la base une période ingressive à faciès relativement grossier, puis une période d'équilibre représentée par des dépôts lacustres fins, et enfin, une période dégressive avec sursaturation et traces de dessiccation. Ces épisodes lacustres, surtout bien ordonnés dans la partie médiane de l'Autunien, confèrent à la sédimentation un caractère cyclique fort proche du cyclothème limnique carbonifère.

Seul terme constant de cette séquence, le shale dolomitique et bitumineux finement laminé, et sa variante plus dolomitique et massive (voir Fig. 2), constituent la couche au sens strict et au sens minier. Les travaux géochimiques (1) couplés aux travaux stratigraphiques et miniers (6) montrent, en première approximation et malgré de nombreux phénomènes de remobilisation, que l'uranium est localisé dans les "couches autuniennes", plus précisément dans les shales dolomitiques du coeur, qui constituent donc les niveaux porteur d'une anomalie géochimique en U et accessoirement en Mo, Pb, ...

Ces shales feront l'objet exclusif de la présente étude.

I. 2. Buts et méthodes

Si le caractère stratiforme du gisement et son contrôle lithostratigraphique paraissent démontrés à l'échelle du bassin, par contre, à l'échelle locale aucun critère déterminant ne permet d'expliquer l'accumulation de l'U au sein de certaines couches. L'aspect génétique n'ayant pratiquement pas été abordé, nous porterons tous nos efforts dans cette direction, ce qui, vu le caractère stratiforme du gisement, implique en tout premier lieu l'étude de la roche encaissante et la reconstitution de son milieu de dépôt.

A cette fin, une centaine d'échantillons provenant de carottes de sondage ont été prélevés (district du Mas Alary, couches I à IO), en ayant soin d'éviter les zones remobilisées. Ils ont ensuite fait l'objet d'une étude pétrographique, minéralogique et géochimique détaillée. Cependant, vu les difficultés d'interprétation rencontrées par les études précédentes (1, 6) et les difficultés d'application des méthodes d'investigation classiques à ce matériel (finesse, déséquilibre thermodynamique, etc...), une autre méthode d'approche s'imposait. C'est la raison pour laquelle nous avons tenté d'analyser les structures de dépendance parmi l'ensemble des variables à l'aide de méthodes d'analyse multivariées.

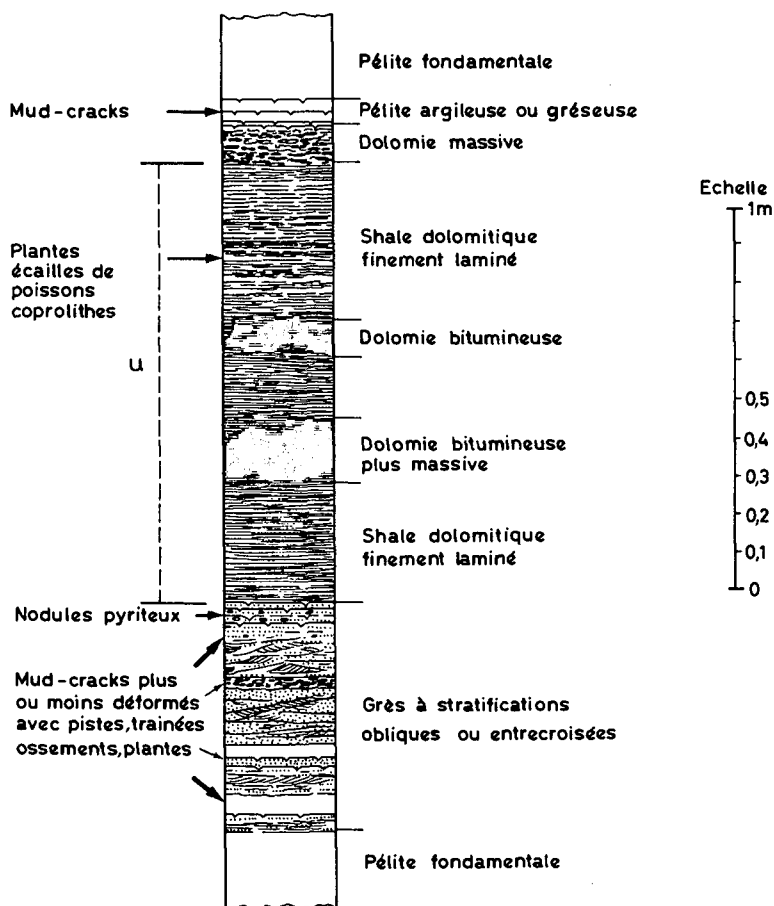


FIG.2. La couche-type autunienne (d'après Garric (6)).

2. TECHNIQUES ANALYTIQUES

2. I. Chimie

Les analyses chimiques ont toutes été effectuées par spectrofluorescence de rayons X (XRF), sauf le carbone organique dosé indirectement par les pertes au feu entre 135 et 500° C. Les éléments majeurs : SiO_2 , TiO_2 , Al_2O_3 , Fe_2O_3 total, MgO , CaO , K_2O , MnO ont été analysés sur des pastilles de verre obtenues par coulage direct du produit de fusion des échantillons avec un fondant au borate de Li, additionné de lanthane comme absorbant (11). Les effets de matrice, très faibles pour Na et S dans les roches silicatées (12), ont permis leur dosage par calibration linéaire directe sur produits crus finement broyés et pastillés.

Les mineurs : V, Ni, Cu, Zn, As, Y, Sr, Mo, Pb, U ont été analysés sur ces mêmes pastilles crues par une méthode originale de correction mathématique des effets de matrice (13). Valable pour les éléments lourds en traces dans une matrice silicatée légère, cette méthode est basée sur les propriétés (a) de constance des absorptions relatives des éléments majeurs entre leurs discontinuités d'absorptions (14), (b) de proportionnalité des absorptions primaires et secondaires dans certaines conditions bien précises (12). Elle permet le calcul, à partir de l'analyse des majeurs, d'un facteur de correction unique valable depuis le Ni, et au delà, pour les raies K, et depuis Yb, et au delà, pour les raies L.

La calibration linéaire à partir d'étalons synthétiques, commune à toutes ces techniques, permet un contrôle objectif de la validité des résultats. La reproductibilité, estimée par répétition (à un niveau de confiance de 95 %) est meilleure que 5 % relatifs pour les majeurs (sauf Na). Etroitement liée aux teneurs absolues pour les traces, elle varie depuis 50-100 %, au niveau des limites de détection, jusqu'à environ 5 % pour quelques dizaines de p.p.m.. La précision, contrôlée par l'analyse d'étalons internationaux, est comprise dans l'intervalle de confiance des erreurs statistiques pour les majeurs, et à ± 10 % près pour les traces.

2. 2. Minéralogie

La méthode de diffraction X (XRD) quantitative utilisée pour le dosage du quartz et de l'albite, complète celle développée en XRF pour les traces : basée sur des mesures absolues, elle utilise à nouveau et les échantillons pastillés, et les facteurs de correction d'absorption massique. La combinaison, avec optimisation au point de vue expérimental, de l'analyse chimique des majeurs, mineurs et traces, par XRF avec la XRD quantitative est entièrement neuve. Rares sont les méthodes capables de rivaliser avec ses qualités de souplesse et de rapidité.

L'ankérite, identifiée par coloration de surface et par analyse thermique différentielle, a été dosée quantitativement par volumétrie (manocalcimètre). La quantité globale d'argiles a été estimée approximativement par différence : $100\% - (\text{quartz} + \text{albite} + \text{ankérite}) = \Sigma \text{argiles}$. Leur identification s'est faite sur la fraction inférieure à $5\mu\text{m}$ suivant un schéma classique.

3. COMPOSITION MINÉRALOGIQUE

Le tableau I donne la composition minéralogique moyenne des échantillons étudiés ainsi, qu'à titre de comparaison, celle de roches ordinaires détritiques (15, 16).

TABLEAU I. COMPOSITION MINÉRALOGIQUE MOYENNE DES 79 SHALES DOLOMITIQUES AUTUNIENS COMPAREE A D'AUTRES MOYENNES PLUS GÉNÉRALES (%)

	Shales dolomitiques			300 shales		96 red-beds
	$\bar{x}$	s	étendue	$\bar{x}$	s	$\bar{x}$
Quartz	10.6	8.6	0-40	33.6	15.	33.
Albite(feldspath)	24.1	9.3	10-50	3.6	4.8	-
Ankéríte(carbonate)	24.0	9.2	8-51	2.7	8.4	11.
Argiles	41.5	9.0	18-60	64.1	9.4	56.
Autres minéraux	<2.	-	-	2.	-	-
Matière organique	3.3	2.4	0-15	1.	-	-

Le caractère le plus étonnant est sans conteste l'abondance d'albite, que ne laissait absolument pas présager l'observation microscopique. De nombreux arguments géologiques comme : sa finesse et son imbrication avec les autres minéraux, la faible abondance ou même le manque de quartz, l'absence de feldspaths K (étonnante alors que dans les sols ferrugineux tropicaux ces derniers sont conservés préférentiellement aux plagioclases (17), s'opposent à une origine détritique de l'albite. La présence de kaolinite excluant tout métamorphisme, l'hypothèse de sa néoformation in situ dans le lac s'impose. Elle est étayée par l'analcite et l'albite authigènes observées dans les faciès red-beds des bassins permians avoisinants (7, 18) et par la nature vraisemblablement endoréique du lac autunien. L'étude minéralogique détaillée de l'albite, rendue très difficile par sa finesse ($<10\mu\text{m}$), montre outre des profils diffractométriques identiques pour tous les échantillons, qu'il s'agit d'une albite terme extrême (l'absence de Ca et K a été vérifiée à la microsonde) du type basse température mais assez désordonnée. En effet, les films obtenus avec une chambre Guinier montrent en plus de réflexions diffuses, mal définies et élargies, une obliquité égale à : $\Delta(\theta) = 1.25 \pm 0.05^\circ 2\theta$ ce qui est nettement trop élevé pour une albite pure dont l'ordre Si-Al serait parfait (19, 20). Ces caractères ne paraissent pas en contradiction avec l'hypothèse de néogénèse; en effet, si les albites authigènes des roches carbonatées (les seules pour lesquelles on possède des données) semblent plutôt bien ordonnées (21), ce n'est pas une règle absolue (20 à 22) et de toute manière l'extrapolation au cas présent paraît hasardeuse (lithologie, teneurs trop différentes).

L'ankéríte se présente avec une très grande variété d'habitats, le plus fréquent est constitué de cristaux automorphes de 20-30 μm dispersés dans la matrice argilo-albitique très fine, suggérant une formation précoce.

L'illite, bien cristallisée, est toujours présente, la kaolinite, fréquente et la chlorite, en plages xénomorphes de néoformation, peu abondante. La matière organique, très finement dispersée, est responsable de la couleur et bien souvent du litage de ces roches. Elle s'accumule parfois dans certains niveaux et donne naissance à des bitumes en lentilles ou en filaments.

Les mouchetures de pyrite et de blende sont ubiquistes, celles de galène plus rares. La pyrite est également abondante dans des lits silteux. L'observation microscopique couplée à l'analyse par microsonde des niveaux les plus riches en matières organiques, a montré la présence de blende, galène, löllingite, coffinite et uraninite, ces deux dernières étant étroitement associées à des plages bitumineuses.

L'appellation de shale ou plus précisément, de shale dolomitique et bitumineux, n'est satisfaisante qu'au niveau macroscopique. Pétrographiquement il s'agit d'argiles silteuses (plus de 50 % < 4 μ m) et dans une classification triangulaire silt-clay-carbonate (23) de "dolomitic mudstones". C'est avant tout le caractère mixte (mélange de constituants détritiques et chimiques) et le caractère diagénétique (les minéraux authigènes sont quantitativement majoritaires et leur formation liée aux processus de diagenèse) de ces sédiments lacustres qui ressortent des investigations minéralogiques. Ces traits, dont NICOLINI (24) souligne à plusieurs reprises les caractères métallotectiques favorables, sont généralement considérés comme typiques d'une sédimentation ralentie.

4. COMPOSITION CHIMIQUE

4. I. Eléments majeurs

Comme le laissait présager l'étude minéralogique et le caractère mixte de ces sédiments, leur composition chimique moyenne est assez particulière et ne correspond à aucune des catégories classiques (Tableau II). Leur similitude avec les shales de plateforme, plus riches en carbonates que ceux des

TABLEAU II. COMPOSITION CHIMIQUE MOYENNE DES SHALES DOLOMITIQUES AUTUNIENS COMPAREE A DES MOYENNES GENERALES (%)

	Shales dolomitiques			Shale moyen (a)	Shale moyen (b)	Granodiorite moyen (c)
	$\bar{x}$	$\tilde{x}$	s			
SiO ₂	47.1	46.5	7.2	58.9	50.7	67.9
TiO ₂	0.48	0.47	0.1	0.78	0.78	0.38
Al ₂ O ₃	12.7	12.8	2.8	16.7	15.1	15.5
Fe ₂ O ₃	4.5	4.6	1.2	6.9	6.7	3.9
MnO	0.14	0.12	0.12	0.09	0.08	0.05
MgO	4.3	4.1	1.6	2.6	3.3	1.7
CaO	6.7	6.4	2.4	2.2	7.2	1.9
Na ₂ O	3.1	3.4	1.2	1.3	0.8	3.3
K ₂ O	3.7	3.8	1.1	3.6	3.5	4.1
P ₂ O ₅	~0.1	-	-	0.16	0.10	0.2
S	0.34	0.19	0.39	0.24	0.2	-
Corg.	3.3	2.7	2.4	0.6	0.7	-
p.f.	15.0	13.5	4.8	~6.3	~11.1	~1.0

a: de géosynclinaux [25]; b: de plateforme [25]; c: Massif Central [26].

géosynclinaux, est nette, sauf en ce qui concerne les teneurs en soude qui n'ont d'équivalents que dans les roches magmatiques acides. L'appauvrissement en silice, et dans une moindre mesure en alumine et fer, comparé à l'enrichissement en soude, magnésie et chaux, s'explique aisément si l'on tient compte de ce que TARDY (27) appelle : "la chromatographie des ions dans le paysage". En période biostasique et sous un climat de type sahélien, la savane arbustive ne constituant pas un filtre parfait, les éléments les plus fins de la phase résiduelle (argiles) arrivent avec les alcalins et alcalino-terreux de la phase migratrice et s'accumulent dans le lac sans issues.

Au tableau II figurent en plus de la moyenne ($\bar{x}$), la médiane ($\tilde{x}$) et l'écart-type (s), valeurs qui permettent de constater que les distributions des éléments majeurs des roches sédimentaires n'obéissent pas systématiquement à une loi normale (28). En effet, si Si, Ti, Al, Na et K s'y conforment (la critique de l'ajustement a été effectuée par un test de χ^2), Ca, Mg, et Fe obéissent par contre à une loi lognormale qui est celle à laquelle répond la distribution de l'ankérite. Les mineurs Mn, S, Corg. sont aussi distribués lognormalement ($\tilde{x} < \bar{x}$).

4. 2. Éléments en traces

La comparaison des teneurs moyennes des éléments en traces, telle qu'elle est couramment pratiquée, nous paraît peu recommandable vu le caractère inévitablement biaisé de la moyenne arithmétique comme estimateur de tendance centrale. Ces éléments très dispersés ont en effet des distributions à dissymétrie gauche prononcée parfois assimilables à une loi lognormale (29) (cas de V, As, Sr, Pb). En conséquence, la comparaison des moyennes géométriques ou à défaut des médianes (plus faciles à calculer) est certainement plus proche de la réalité et moins sujette à des distorsions causées par quelques valeurs extrêmes.

TABLEAU III. ABONDANCE MOYENNE DES ELEMENTS EN TRACES DES SHALES DOLOMITIQUES AUTUNIENS COMPAREE A DES SHALES MOYENS (p. p. m.)

	Shales dolomitiques				Shale moyen $\bar{x}$ (31)	Black shale moyen (30) valeur enrichissement minimum	
	$\bar{x}$	s	$\bar{x}_g$	$\tilde{x}$		$\tilde{x}$	
V	156	40	151	145	130	150	1000
Ni	41	28	27	53	68	50	300
Cu	21	49	4	3	45	70	200
Zn	425	1560	81	55	95	<300	1500
As	219	401	64	60	10	-	-
Sr	259	179	205	206	300	200	1500
Y	108	169	58	39	41	30	70
Mo	443	747	60	69	3	10	200
Pb	454	991	91	96	20	20	100
U	4110	7056	381	170	4	-	30

$\bar{x}_g$ = moyenne géométrique.

Compte tenu de ces remarques théoriques, la comparaison avec les données moyennes concernant 800 "black shale" (30) paraît préférable à d'autres (31, 32), d'autant plus que les teneurs en Corg. ($\bar{x} = 3.2\%$) y sont beaucoup plus proches des échantillons étudiés ($\bar{x} = 2.7\%$). La comparaison des médianes (Tab. III) permet de classer les éléments en traces analysés en trois catégories distinctes : 1° appauvris : Cu,

2° normaux : V, Ni, Zn, Sr,

3° enrichis : As, Y, Mo, Pb, U.

Les deux premières catégories possèdent des dispersions beaucoup plus faibles que la troisième. En ce qui concerne cette dernière, la comparaison des valeurs individuelles avec ce que VINE & TOURTELOT (30) appellent le "minimum enrichment factor" permet de montrer que : 25 % des échantillons pour Y, 35 % pour Mo, 45 % pour Pb et 79 % pour U, peuvent être considérés comme anormalement enrichis en ces métaux.

Une telle accumulation de métaux lourds est aussi jugée comme un critère de sédimentation extrêmement ralentie mais en milieu réducteur.

5. ANALYSE DES DONNEES

5. 1. Généralités

Ces résultats analytiques forment un vaste ensemble de valeurs numériques (25 variables x 80 échantillons = 2000 données) dont le nombre et le caractère interdépendant rendent toute synthèse, par le seul jeu des facultés mentales, impossible ou très fragmentaire. Les données brutes, les corrélations inter-éléments (totales et partielles), l'analyse en composantes principales et enfin l'analyse factorielle en mode R ont été utilisées conjointement pour analyser les structures de dépendance parmi ces variables. Si nous ne présentons ici que les résultats de l'A.F., c'est pour éviter toute répétition et parce que cette technique fournit les résultats les plus significatifs sous une forme condensée et facilement déchiffrable.

5. 2. L'analyse factorielle

Développée par les psychologues dès le début du siècle, perfectionnée par des statisticiens, l'A.F. s'est rapidement étendue à d'autres domaines dès l'après-guerre. Introduite beaucoup plus tardivement en géologie (33), elle est de nos jours largement utilisée en géochimie pour l'interprétation des données analytiques concernant : des minéraux (34 à 36), des sédiments anciens (16, 37 à 39) et récents (40 à 42), la prospection géochimique (43), etc...

Parmi les nombreux traités et articles concernant les aspects théoriques de l'analyse, nous citerons HARMAN (44), une remarquable revue du sujet et de l'esprit de son utilisation (45), enfin les travaux de SPENCER (46) en géochimie.

Le principal but de l'A.F. est d'expliquer les relations observées entre un grand nombre de variables en termes de relations plus simples et surtout plus fondamentales. Une telle résolution est centrale à tout travail scientifique et correspond à la création d'un petit nombre de variables hypothétiques (les facteurs) dans l'espoir qu'elles vont permettre de trouver un ordre simple sous-jacent aux variables observées. Par l'interprétation des facteurs on peut tenter d'en obtenir une explication : dans un domaine inconnu l'A.F. apparaît donc comme une méthode d'exploration créatrice d'hypothèses.

Transposons au niveau des roches sédimentaires : la distribution des éléments y est caractérisée par la présence de groupes géochimiquement

cohérents, c'est-à-dire de groupes d'éléments qui sous des conditions données se comportent de la même manière (covariants). La distribution et la nature de ces groupement naturel sont influencées par des facteurs fondamentaux comme par exemple : la vitesse de sédimentation, les processus diagenétiques, l'éloignement des lignes de rivage, le pH, etc...

L'A.F. fournit un moyen mathématique de repérer ces groupes d'éléments cohérents, ou facteurs, et de mesurer l'influence de l'entière teneur du groupe sur un échantillon particulier, ou cote en facteurs (R-score). Muni de ces renseignements et du poids de chacun des éléments dans ces groupes, ou saturations, il devient possible d'émettre des hypothèses au sujet des facteurs de base qui ont influencé la distribution des éléments.

Pour diverses raisons, que nous avons analysées en détail et qui seraient trop longues à exposer ici, la technique rigoureuse dénommée "ouverte" (45) ou "en facteurs communs et spécifiques" (47) a été utilisée de préférence à celle plus directe généralement employée en géochimie (46, 48). Malgré ses nombreux avantages pratiques, nous pensons que la méthode directe introduit un bruit de fond néfaste qui gonfle spécieusement les facteurs et risque de fausser l'interprétation. En conséquence, le carré des corrélations multiples a servi de base à l'estimation des communautés, et la matrice des composantes principales obtenue par diagonalisation de la matrice des corrélations réduites.

Une structure simple orthogonale (le modèle impose des facteurs non corrélés) a ensuite été recherchée par rotation suivant le critère analytique varimax (48). Ce critère qui tend à maximaliser les saturations nulles et élevées, a pour effet de rendre l'interprétation des facteurs beaucoup plus facile puisque seules quelques variables possèdent encore des saturations significatives.

L'essence des phénomènes naturels est telle qu'un modèle orthogonal est peu probable : l'expérience montre que les facteurs obliques sont la loi dans la nature (45, 46). En conséquence, des rotations de ce type ont été effectuées suivant le critère promax pour différentes valeurs du paramètre d'obliquité (k_{min}). La solution finale retenue, est celle pour laquelle un accroissement de k_{min} ne produit plus qu'une faible augmentation des obliquités.

Pour terminer, les cotes en facteur sont calculées.

L'ensemble de ces opérations, effectuées par un ordinateur (une version assez fortement modifiée du programme de CAMERON (48) a été utilisée), ne constitue que l'étape simplificatrice en elle-même peu intéressante pour le chercheur. Elle débouche sur ce qui est certainement l'aspect le plus important de l'A.F. en tant que méthode scientifique : l'interprétation. C'est une tâche inductive qui exige une grande familiarité avec la matière sur laquelle porte l'analyse.

6. RESULTATS DE L'ANALYSE FACTORIELLE

Les données minéralogiques ont été exclues de l'analyse mais peuvent, comme nous le verrons par la suite, être corrélées aux cotes en facteur ce qui permet d'en vérifier l'interprétation. La raison en est double : (1) l'imprécision de leur dosage risque d'introduire une variance d'erreur substantielle (2) elles forment un ensemble à somme constante très réduit (4 variables), situation qui fausse certainement les corrélations (49). Peu importante dans le cas des variables chimiques, l'incidence de cette source de distorsion a été investiguée à partir des corrélations partielles. Toutes les variables dont la distribution n'était pas normale ont subi une transformation logarithmique.

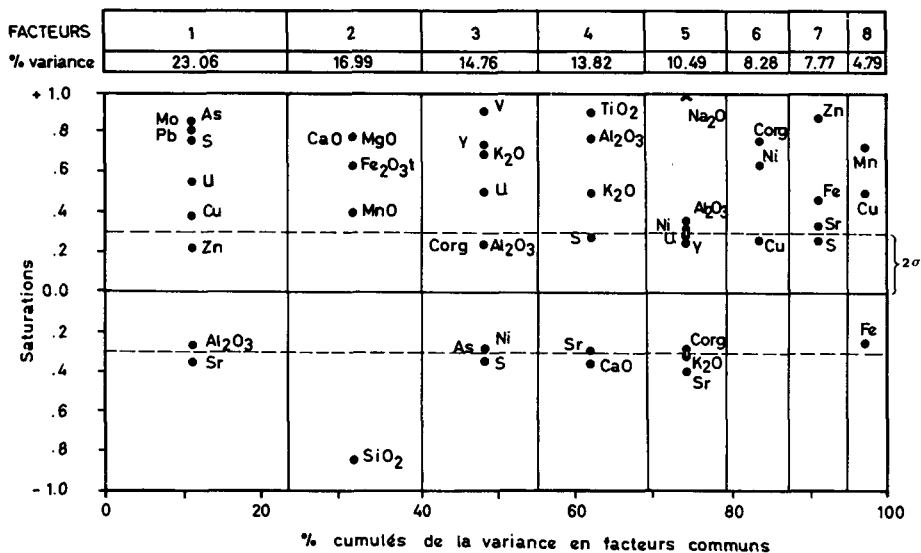
TABLEAU IV. MATRICE FACTORIELLE VARIMAX RELATIVE AUX SHALES DOLOMITIQUES AUTUNIENS

Elément	Facteur								Communauté h^2
	1	2	3	4	5	6	7	8	
SiO ₂		-.834	-.287						.868
TiO ₂				.844					.790
Al ₂ O ₃				.768	.383				.881
Fe ₂ O ₃		.601					.493	-.321	.742
MgO		.808							.801
CaO		.818		-.437					.929
Na ₂ O					.855				.796
K ₂ O			.647	.457			-.285		.719
Corg	.329		.283			.725			.797
S	.693		-.348				.329		.783
V			.753						.605
MnO		.425						.547	.606
Ni	.297			.297	.298	.666			.760
Cu	.524					.308		.424	.611
Zn							.748		.648
As	.823					.348			.876
Sr	-.348		.628	-.438	-.549		.320		.802
Y	.278						-.273		.760
Mo	.834				.369				.796
Pb	.846		.325						.941
U	.612		.588		.344				.870
Contribution des facteurs à la variance totale									Σh^2
%	17.99	13.26	11.52	10.78	8.19	6.47	6.06	3.74	16.38
% cumulés	18.0	31.2	42.7	53.5	61.7	68.2	74.3	78.0	

Les saturations < 0,25 ont été omises.

Huit facteurs communs représentant 79 % de la variance des données initiales rendent compte de l'entière des corrélations entre les 21 éléments des shales autuniens. La solution orthogonale présentée au tableau IV donne les saturations, les contributions des facteurs à la variance totale et les communautés. Ces dernières ou variances communes ne donnent pas uniquement, comme le notent la plupart des scientifiques, la fraction de la variance de chacun des éléments qui est expliquée par les facteurs mais, ce qui est beaucoup plus fondamental, la part de la variance des variables qui rend compte uniquement des intercorrélations.

La valeur élevée des communautés montre que la distribution des éléments dans ces sédiments lacustres n'est pas soumise à des variations aléatoires trop importantes. La figure 3 donne le schéma de la solution oblique finale et le tableau V les corrélations entre les facteurs correspondants (cosinus de l'angle qu'ils font entre eux). Ce schéma, plus explicite que des chiffres, sert de base à l'interprétation. Les facteurs y sont représentés dans un rectangle dont l'ordonnée représente leur contribution respective à la variance en facteurs communs (c'est-à-dire leur importance), et l'abscisse (saturation) le poids de chacune des variables initiales dans chacun des facteurs. Les groupes covariants sont ainsi clairement mis en évidence. Seules les valeurs supérieures à deux fois l'estimation de l'erreur standard sur les saturations (44) sont considérées comme significatives.

FIG.3. Schéma factoriel de la solution oblique promax $k_{\min.} = 4$.TABLEAU V. MATRICE DES CORRELATIONS ENTRE LES FACTEURS PROMAX $k_{\min.} = 4$

Facteur	1	2	3	4	5	6	7	8
1	1.00							
2		1.00						
3			1.00					
4		-0.25		1.00				
5	0.28	-0.24	0.33	0.34	1.00			
6	0.41			0.22		1.00		
7		0.22	-0.49		-0.47		1.00	
8			0.28	-0.41				1.00

Les corrélations < 0.2 ont été omises.

La comparaison du tableau IV avec la figure 3, montre que le passage d'un modèle à l'autre élimine quelques saturations faibles et augmente les plus fortes, ce qui va bien dans le sens recherché de la structure la plus simple.

Des 8 facteurs qui "expliquent" la distribution des éléments de ces shales, 7 ont pu être identifiés avec succès, le dernier n'étant probablement pas significatif.

Facteur I : "diagénèse des sulfures en milieu réducteur"

Statistiquement le plus important, ce facteur est fortement saturé par une série d'éléments très groupés (Mo, Pb, As, S), puis par l'U légèrement en retrait, plus faiblement ensuite par le Cu, et enfin par le Zn à la limite de la signification. Le carré d'une saturation donnant la fraction de

variance de l'élément qui est expliquée par le facteur on voit que, pour le premier groupe, elle l'est pour ainsi dire entièrement par le facteur 1. Pour le modèle orthogonal (le modèle oblique ne permet plus ce calcul) et, par exemple, pour le Mo, on a : $(0.85)^2 = 0.72$ ce qui fait 72 % de la variance totale ou plus exactement, par comparaison à sa communauté, 90 % de ses intercorrélations ($0.72/0.79 = 0.90$).

Excepté l'U, ce sont tous des éléments chalcophiles bien connus pour la facilité avec laquelle ils précipitent à l'état de sulfures pour des teneurs en ions extrêmement faibles (50) et pour leur aptitude à se concentrer dans les milieux euxiniques (30 à 32). Les nombreux travaux (bibliographie dans 51 à 53) consacrés à la formation synsédimentaire des sulfures de métaux lourds dans les sédiments réducteurs anciens et modernes, montrent que la réduction bactérienne des sulfates en H_2S est le processus fondamental responsable du "piégeage" de ces métaux durant la diagenèse précoce. Les travaux de RICKARD (53) prouvent en outre, à partir d'un modèle mathématique, que la production bactérienne de soufre, dans un sédiment réducteur, est nettement suffisante pour amener des concentrations en sulfures métalliques importantes. Les conditions favorables à une forte production de H_2S sont d'une part des teneurs importantes (le calcul montre qu'environ 1 % de Corg. est nécessaire par % de métal fixé) en matières biodégradables et d'autre part une sédimentation lente en milieu calme (maintien du déficit en oxygène). Ces conditions étant largement répandues dans la nature, c'est manifestement la disponibilité en métaux qui contrôle la syngénèse des sulfures.

La confrontation avec ces observations permet d'identifier le facteur 1 avec le processus de diagenèse des sulfures en milieu réducteur générateur d'hydrogène sulfuré. Si la concentration métallifère apparaît comme syngénétique, son expression minéralogique sous forme de sulfure est, elle, diagenétique. L'exactitude de cette hypothèse est confirmée de manière indirecte par la nette corrélation ($r = 0.41$) avec le facteur 6 représentatif de la sédimentation organique. Cette obliquité est non seulement induite par les contingences énergétiques de la réduction bactérienne, mais sûrement aussi par le fait que la précipitation, la chélation et l'adsorption des métaux en solution sont favorisées par la sédimentation très ralentie qui préside à l'accumulation du matériel organique.

L'U, dont la moitié de la variance est expliquée par le facteur 1, doit certainement son association avec les chalcophiles à son caractère réductible. De très nombreux auteurs (cf. 54, 55) invoquent, en effet, une réduction de U^{6+} (généralement en solution sous forme de complexe bicarbonaté) en U^{4+} insoluble, pour justifier sa concentration dans les milieux réducteurs. Son comportement dans les milieux dépourvus d'oxygène n'est cependant pas clair et différentes hypothèses sont communément avancées : (1) la réduction par H_2S (2) la réduction pour des potentiels d'oxydo-réduction très négatifs ($Eh < -0.20$ mV) (3) l'interaction avec les matières organiques (réduction, adsorption, complexation, chélation, etc...). L'absence de saturation du facteur 1 par Corg. (ainsi que celle du facteur 6 par U) permet d'exclure le dernier processus, ce qui n'a rien d'étonnant vu le caractère alcalin des eaux. Par contre, la réduction par (1) et/ou (2) paraît probable, d'autant plus que l'uraninite et la coffinite ont été observées (rarement cependant).

La nature ultra-détritique de la sédimentation, l'abondance de minéraux authigènes et de matières organiques préservées, la parfaite conservation du litage, la présence de nombreux sulfures, sont quelques-uns des nombreux arguments qui témoignent en faveur d'un lac stratifié de type

eutrophique (riche en matières nutritives). Entouré d'une végétation hygrophytique jouant le rôle de filtre, les eaux calmes et stagnantes favorisent le développement d'une vie intense en surface (algues, poissons, etc... (4)), d'un hypolimnion anaérobie riche en H_2S en profondeur et enfin d'un sapropel au fond.

Facteur 2 : "agitation des eaux superficielles"

C'est un facteur bipolaire qui oppose fortement SiO_2 à une série de saturations positives clairement représentatives de l'ankérite (Ca, Mg, Fe, Mn). Des travaux récents (56) sur la formation et la diagenèse inorganique des carbonates Ca-Mg en milieu lacustre suggèrent, vu les caractères primaires de l'ankérite, une formation par diagenèse précoce d'une calcite magnésienne précipitant périodiquement dans les eaux superficielles (épilimnion), sous l'effet probablement combiné de l'évaporation, de l'élévation de température et de l'augmentation de pH due à l'activité photosynthétique du phytoplancton. Les exemples actuels montrent que le rapport moléculaire Mg/Ca des eaux est un facteur essentiel, qui contrôle et, la formation du précurseur ($2 < Mg/Ca < 12$), et sa transformation en dolomite ($7 < Mg/Ca < 15$). Ces rapports ne nécessitant pas un confinement élevé, il est probable que les eaux de l'épilimnion étaient relativement douces, de type bicarbonaté calco-magnésien ou sodique avec, à cause de l'effet tampon de Ca et Mg, un pH proche de 8.

Le remplacement, dans la structure naissante de la dolomite, d'une forte proportion du Mg par Fe et Mn, pourrait être attribué à la mobilisation de ces deux cations dans l'environnement très réducteur des eaux interstitielles du sapropel (à partir des enduits des minéraux détritiques des sols rouges tropicaux). Leur barrière d'hydratation plus faible que celle de Mg (57) a ensuite permis leur incorporation préférentielle dans le réseau.

Une série d'observations convergentes (58) montrent en outre, que la dolomitisation semble favorisée par un milieu confiné, riche en matières organiques, réducteur et de pH très élevé, ce qui est l'image même de l'hypolimnion.

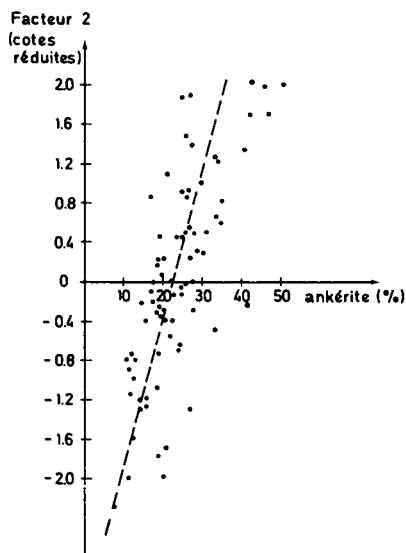


FIG. 4. Cotes du facteur 2 en fonction des teneurs en ankérite.

La bonne corrélation entre les teneurs en ankérite et les cotes du facteur 2 (fig. 4) montre que ce facteur traduit une relation inverse entre la phase carbonatée et l'ensemble des autres phases qui sont silicatées et jouent le rôle de diluant. Cependant, si l'on admet (nous verrons par la suite pourquoi) que l'albite se forme essentiellement à partir des argiles détritiques, cette relation traduit alors l'opposition entre les périodes calmes, favorables à une saturation en carbonates, et les périodes plus agitées, favorables aux apports détritiques (fluviaux ?). L'alternance de saisons sèches et humides (climat tropical à saisons alternées) en est probablement la cause et permet d'expliquer l'aspect parfois varvaire de ces shales.

Facteur 3 : "agradation des argiles dioctaédriques"

L'association de fortes saturations pour V, Y, K₂O suggère un processus d'agradation vers l'illite des phases à équidistance variable, fortement dégradées et hydratées, provenant des sols ferrugineux tropicaux qui se développaient sur le continent (5). Si, dans le milieu confiné du lac, une "cicatrisation" rapide du matériel micacé le moins dégradé se conçoit aisément (17), ce facteur implique certainement aussi l'évolution diagenétique ultérieure de toutes les argiles 2 : 1 vers un pôle illitique. La nette corrélation avec le facteur 5 confirme l'importance du confinement.

Malgré des teneurs en U qui atteignent fréquemment quelques milliers de p.p.m., la majorité de ces shales ne montre (microscopie, autoradiographie, microsonde) aucun minéral porteur de l'U. L'hypothèse d'une liaison organo-métallique, avancée (1, 6) sur la base d'arguments fragiles, semble totalement infirmée par les résultats de l'A.F. Le facteur 6 (productivité organique) n'est pas saturé par l'U, ce qui exclut toute concentration biogène (59), tandis que la nette saturation avec le facteur 3 suggère une adsorption par les argiles. Les travaux expérimentaux (60) confirment la possibilité de ce processus, il pourrait s'agir de l'entraînement des produits colloïdaux résultant de l'hydrolyse des carbonates complexes d'uranyle dans le milieu basique du lac avec les argiles les plus dégradées, très fines et réactives.

Facteur 4 : "argiles héritées"

Saturé seulement par TiO₂, Al₂O₃, K₂O, ce facteur représente les argiles détritiques issues de l'altération sur le continent hercynien qui, comme le confirme l'abondance de kaolinite, était soumis à une intense monosiallisation. La liaison avec le facteur 6, d'origine mécanique, est bien connue des sédimentologues, et l'opposition avec le facteur 2 tout à fait logique, puisqu'en période de calme les apports détritiques sont réduits au maximum.

Facteur 5 : "alcalinité"

Très fortement saturé par Na₂O et beaucoup plus faiblement par Al₂O₃, ce facteur est évidemment lié à la néoformation de l'albite. Le Na totalement libéré lors des hydrolyses est, du fait de sa grande mobilité, intégralement évacué par les eaux de drainage (61, 27) et s'accumule donc obligatoirement dans ce lac sans issue, lui conférant un caractère sodique accentué. Si la néoformation de minéraux sodiques s'impose, les données de la littérature concernant des environnements semblables montrent qu'il s'agit de silicates non alumineux (62, 63) ou de zéolites (64, 65) mais pas d'albite, surtout en si forte quantité. Thermodynamiquement stable dans les conditions de P, T normales (66, 67), sa formation

semble nécessiter un rapport $[Na^+]/[H^+]$ très élevé, fait confirmé expérimentalement par GREGOR (68) qui est parvenu à synthétiser l'albite à partir d'illite pour des rapports supérieurs à 108.

Seule une stratification chimique du lac, impliquant un hypolimnion dense c'est-à-dire une saumure carbonatée sodique, semble capable de présenter les conditions nécessaires à la genèse de l'albite tout en restant compatible avec le modèle déjà élaboré. Ce phénomène, assez fréquent dans des lacs semi-arides, est beaucoup plus stable qu'une simple stratification thermique et, en conséquence, ses effets sur la sédimentogenèse beaucoup plus marqués (présence constante d'albite). Formées par évaporation des eaux issues de l'environnement essentiellement cristallin, ces saumures, à Na^+ , HCO_3^- et CO_3^{--} dominants, étaient fortement alcalines (69) ($9 < pH < 11$) ce qui est favorable à de très fortes concentrations en silice dissoute (70) et à la formation de zéolites à faible rapport Si/Al (65), proches de l'albite.

Dans ces conditions assez particulières, l'albite aurait pu se former directement par hydrolyse des argiles, hypothèse déjà invoquée pour la néoformation pédogénétique de l'analcime (71) et de la mordénite (72).

Facteur 6 : "productivité organique"

Ce facteur n'est saturé que par Corg., Ni et à la limite de la signification par Cu.

Les caractères pétrographiques et chimiques (6) de la matière organique, la rareté des restes de plantes démontrent son origine autochtone à partir des nombreux organismes (4) et surtout microorganismes (plancton) qui peuplaient le lac. Son abondance témoigne et d'une forte productivité (eutrophication), et d'un mécanisme de préservation (hypolimnion anaérobie). Le comportement du Ni, fortement contrôlé par ce facteur, suggère une concentration biogène (plancton ?).

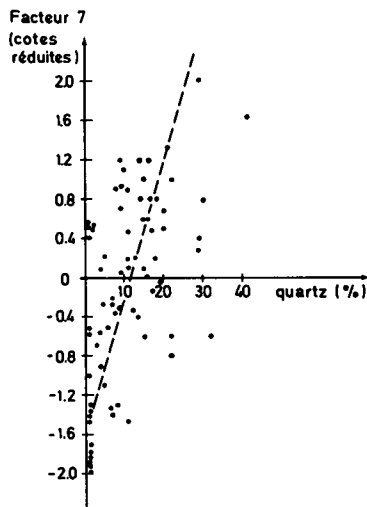


FIG. 5. Cotes du facteur 7 en fonction des teneurs en quartz.

Facteur 7 : "migration diagénétique des sulfures"

Fortement saturé par Zn et plus faiblement par Fe, Sr et S, ce facteur n'a pu être identifié que par un examen particulier des échantillons ayant une forte cote.

Il se caractérise par la formation préférentielle de pyrite et dans une moindre mesure de blende dans les niveaux silteux, observation confirmée par une relation assez nette entre les teneurs en quartz et les cotes du facteur 7 (fig. 5), ainsi que par une forte opposition avec les facteurs 5 et 3 (caractéristiques d'une sédimentation lente). Le processus, pareil à celui décrit théoriquement par BERNER (73), de diffusion du H_2S bactérien des niveaux riches en matières organiques vers les niveaux silteux plus riches en Fe et Zn réactifs, rend bien compte de ce phénomène qui n'est en fait qu'un cas particulier du facteur 1.

7. CONCLUSIONS

La technique de l'A.F. en "facteurs communs et spécifiques" suivant un modèle oblique fournit une description succincte parfaitement raisonnable de la distribution des éléments en termes de processus fondamentaux. Sept facteurs résument les intercorrélations entre 21 éléments analysés dans 79 shales qui sont les niveaux-porteurs d'une anomalie régionale en U. L'interprétation de ces facteurs et de leurs interactions, nous a permis d'élaborer un "modèle limologique" du lac autunien qui rend parfaitement compte et des phénomènes contrôlant la distribution des éléments et des résultats de nos observations pétrographiques et minéralogiques tout en confirmant la paléophysionomie générale du paysage autunien telle qu'elle ressort d'autres études.

Au point de vue géologique ce modèle mathématique permet pour la première fois de caractériser non seulement objectivement mais aussi quantitativement un métallotecte sédimentologique. En l'occurrence, un nouveau (milieu lacustre) et très bel exemple de ces "aires de sédimentation ralentie" (74), situées à la périphérie de masses continentales importantes et souvent minéralisées en Cu, Zn, Pb, Ba et U. La minéralisation de ces aires requiert la coïncidence spatio-temporelle d'une série d'événements géologiques inhabituels :

- 1° une géométrie de piège,
- 2° une sédimentation ralentie, ultra-détritique et adsorbante,
- 3° un milieu réducteur producteur de H_2S ,
- 4° un influx terrigène exceptionnel en métaux lourds.

Nous y ajouterons une autre condition, qui paraît spécifique à l'U :

- 5° un milieu confiné alcalin.

L'analyse de la littérature montre, en effet, que des symptômes de confinement très net, le plus souvent marqués par la présence de zéolites, sont pour ainsi dire présents dans tous les "sandstone-type deposits" (par exemple le bassin du Niger (75), le Gulf Coast des U.S.A., etc...).

Si les trois premières conditions sont amplement satisfaites, la dernière, qui concerne plutôt les deux premiers volets de la trilogie source-transport-dépôt (76), sort du cadre de cet article qui se proposait uniquement de reconstituer le milieu de dépôt. Disons cependant que, compte tenu des fortes teneurs en U qui caractérisent assez souvent les granites hercyniens (granites fertiles (77)), de fortes présomptions d'héritage géochimique de socle à couverture (78, 79) existent.

Au point de vue génétique, en admettant que la source des éléments est grosso modo la même pour les couches et l'U (c'est-à-dire terrigène), il s'agit d'un gisement stratiforme syngénétique-familier (76, 78).

En utilisant l'A.F. pour résoudre ce problème génétique particulier, nous n'avons montré qu'une facette de ses immenses possibilités. Son aspect rigoureux, quantitatif et automatisable devrait pouvoir s'adapter à l'exploration minérale en terrains sédimentaires. Les perspectives sont nombreuses : recherche des facteurs responsables des concentrations, report sur carte ou sur sondage des cotes en facteur (déjà utilisé par les pétroliers sous forme de log (δO)), sélection des éléments les plus intéressants à analyser, etc...

REMERCIEMENTS

Ce travail n'aurait pas vu le jour sans l'aide apportée par le C.E.A. qui nous a aimablement fourni les échantillons, ni celle, matérielle, du F.N.R.S. Qu'ils trouvent ici l'expression de nos remerciements. Nous sommes aussi très reconnaissants à Monsieur P. KUMMERT de l'assistance fournie lors de la programmation des problèmes statistiques, et au Professeur JEDWAB pour ses critiques constructives ainsi que ses encouragements.

REFERENCES

- (1) BRANCHE, G., CALIFET, Y., DEBYSER, J., SCEMAMA, C. Observations sédimentologiques et géochimiques sur le bassin permien de Lodève. *Advance in Organic Geochem. Pergamon* (1964) 173.
- (2) CARIOU, L. Les gîtes et indices uranifères sédimentaires du Massif Central. in: *Les Minerais Uranifères Français III* 2 (1965) 95.
- (3) DAVID, A. Etude géologique du bassin permien de Belmont-sur-Rance et minéralisations uranifères et cuprifères. Thèse 3^e cycle, Clermont-Ferrand (1967).
- (4) DOUBINGER, J., KRUSEMAN, G.P. Sur la flore du Permien de la région de Lodève. *Bull. Soc. Géol. Frç.* 7 (1965) 541.
- (5) FUCHS, Y. Contribution à l'étude géologique, géochimique et métallogénique du détroit de Rodez. Thèse, Nancy (1969).
- (6) GARRIC, J. L'uranium dans le Carbonifère et le Permien de l'Hérault. in: *Les Minerais Uranifères Français. II* (1965) 149.
- (7) KRUSEMAN, G.P. The permian climate of the basin of Lodève, Hérault. *Geol. en Mijnbouw* 46 (1967) 61.
- (8) Rapport Annuel du Commissariat à l'Energie Atomique (1963).
- (9) ERHART, H. La genèse des sols en tant que phénomène géologique. Masson et Cie., Paris (1967).
- (10) Séries d'articles in: Colloque sur la biogéographie du Permo-Carbonifère. Société de Biogéographie, Paris (1962).
- (11) NORRISH, K., HUTTON, J.T. An accurate X-ray spectrographic method for the analysis of a wide range of geological samples. *Geochim. Cosmochim. Acta* 33 (1969) 431.
- (12) NORRISH, K., CHAPPEL, B.W. X-ray spectrographic methods. in: *Physical Methods in Determinative Mineralogy. Academic Press chap.4* (1967).

- (13) HERBOSCH, A. Géochimie de l'uranium dans le bassin permien de Lodève. Thèse, Univ. Libre Bruxelles (à paraître en 1974).
- (14) HOWER, J. Matrix correction in the X-ray spectrographic trace element analysis of rocks and minerals. *Am. Min.* 44 (1959) 19.
- (15) SHAW, P.B., WEAVER, C.E. The mineral composition of shales. *Journ. Sed. Petr.* 35 (1965) 213.
- (16) COSGROVE, M.E. The geochemistry and mineralogy of the permian red beds of southwest England. *Chem. Geol.* 11 (1973) 31.
- (17) PAQUET, H. Evolution géochimique des minéraux argileux dans les altérations et les sols des climats méditerranéens et tropicaux à saisons contrastées. *Mem. Ser. Géol. Als. Lorr.* 30 (1970).
- (18) MAUREL, P. Sur la présence d'albite dans le Permien supérieur des environs de S^t Affrique et de Lodève. *Compt. Rendu Acad. Sc. Paris* (1962) 3003.
- (19) BAMBAUER, H.U., CORLETT, M., EBERHARD, E., VISWANATHAN, K. Diagrams for the determination of plagioclase using x-ray powder methods. *Bull. Suisse Min. Petr.* 47 (1967) 330.
- (20) MARTIN, R.F. The hydrothermal synthesis of low albite. *Contr. Min. Petr.* 23 (1969) 323.
- (21) KASTNER, M. Authigenic feldspars in carbonates rocks. *Am. Min.* 56 (1971) 1403.
- (22) BASKIN, Y. A study of authigenic feldspar. *Journ. Geol.* 64 (1956) 132.
- (23) PICARD, M.D. Classification of fine grained sedimentary rocks. *Journ. Sed. Petr.* 41 (1971) 179.
- (24) NICOLINI, P. Géologie des concentrations minérales stratiformes. Gauthier-Villars (1970).
- (25) WEDEPOHL, K.H. in: *Data of Geochemistry I* (1969) chap.8
- (26) DIDIER, J., LAMEYRE, J. Les granites du Massif Central français: étude comparée des leucogranites et granodiorites. *Contr. Min. Petr.* 24 (1969) 219.
- (27) TARDY, Y. Géochimie des altérations, étude des arènes et des eaux de quelques massifs cristallins d'Europe et d'Afrique. *Mem. Serv. Geol. Als. Lorr.* 31 (1969).
- (28) DEBRABANT, P. Typologie géochimique des calcaires. Application à l'étude de l'origine des calcaires métamorphiques des Massifs Hercyniens français. Thèse, Fac. Sciences Lille (1971).
- (29) SHAW, D.M. Element distribution laws in geochemistry. *Geochim. Cosmochim. Acta* 23 (1961) 116.
- (30) VINE, J.D., TOURTELOT, E.B. Geochemistry of black shale deposits. A summary report. *Econ. Geol.* 65 (1970) 253.
- (31) WEDEPOHL, K.H. Environmental influences on the chemical composition of shales and clays. *Phys. and Chem. Earth* 8 (1968) 307.
- (32) WEDEPOHL, K.H. Untersuchungen am Kupferschiefer in Nordwestdeutschland, ein Beitrag zur Deutung der Genese bituminöser Sedimente. *Geochim. Cosmochim. Acta* 28 (1964) 305.
- (33) IMBRIE, J., PURDY, E.G. Classification of modern Bahamian carbonate sediments. in: *Classification of Carbonates Rocks*. *Mem. Am. Ass. Petr. Geol.* (1962) 253.

- (34) WEBB, W.M., BRIGGS, L.I. The use of principal components analysis to screen mineralogical data. *Journ. Geol.* 74 (1966) 716.
- (35) SAXENA, S.K., EKSTROM, T.K. Statistical chemistry of calcic amphiboles. *Contr. Miner. Petr.* 26 (1970) 276.
- (36) MOTTANA, A., SUTTERLIN, P.G., MAY, R.W. Factor analysis of omphacites and garnets: a contribution to the geochemical classification of eclogites. *Contr. Miner. Petr.* 31 (1971) 238.
- (37) SPENCER, D. Factors affecting element distributions in a Silurian graptolite band. *Chem. Geol.* I (1966) 221.
- (38) HIRST, D.M., KAYE, M.J. Factors controlling the mineralogy and chemistry of an upper Visean sequence from Rookhope, County Durham. *Chem. Geol.* 8 (1971) 37.
- (39) REEVES, M.J., SAADI, T.A.K. Factors controlling deposition of some phosphate bearing strata from Jordan. *Econ. Geol.* 66 (1971) 451.
- (40) SPENCER, D., DEGENS, E.T., KULBICKI, G. Geochemical factors governing the distribution of elements in sedimentary rocks. in: *Origin and Distribution of the Elements*. U.N.E.S.C.O., Paris (1968) 981.
- (41) RUMEAU, J.L., VANNEY, J.X. Caractères géochimiques et origine des sédiments récents du plateau continental Atlantique dans le nord du golfe de Gascogne. *Bull. Centre Rech. Pau, S.N.P.A.* 3 (1969) 125.
- (42) SUMMERHAYES, C.P. Geochemistry of continental margin sediments from northwest Africa. *Chem. Geol.* 10 (1972) 137.
- (43) ARMOUR-BROWN, A., NICHOL, I. Regional geochemical reconnaissance and the location of metallogenic provinces. *Econ. Geol.* 65 (1970) 312.
- (44) HARMAN, H.N. *Modern Factor Analysis*. Univ. Chicago Press, 2nd. ed. (1967)
- (45) CATTELL, R.B. Factor analysis: an introduction to essentials. *Biometrics* 21 (1965) part I 190, part II 405.
- (46) SPENCER, D.W. Factor analysis Woods Hole Ocean. Inst. part I (1966) part II: oblique solution (1967). Unpubl. Manuscript.
- (47) LEBART, L., FENELON, J.P. *Statistique et informatique appliquée*. Dunod, Paris (1972).
- (48) CAMERON, E.M. A computer program for factor analysis of geochemical and other data. *Canad. Geol. Surv. Paper* 67-34 (1967).
- (49) CHAYES, F. On correlation between variables of constant sum. *Journ. Geoph. Res.* 65 (1960) 4185.
- (50) MICHARD, G., ALLEGRE, C.J. Comportement géochimique des éléments métalliques en milieu réducteur et diagrammes (logS, pH). *Mineral. Deposita* 4 (1969) 1.
- (51) LOVE, L.G. Sulphides of metals in recent sediments. in: *Sedimentary Ores* Proceed. 15th. Inter-Univ. Geol. Congress. Univ. Leicester (1969) 31.
- (52) BERNER, R.A. *Principles of Chemical Sedimentology*: McGraw-Hill (1971)
- (53) RICKARD, D.T. Limiting conditions for synsedimentary sulfide ore formation. *Econ. Geol.* 68 (1973) 605.
- (54) RICHARDS, F.A. Anoxic basins and fjords. in: *Chemical Oceanography I* Ed. RILEY, J.P., SKIRROW, G. (1965) 630.
- (55) MANSKAYA, S.M., DROZDOVA, T.V. Geochemistry of Organic Substances. *Inter. Ser. Monographs Earth Sciences* 28 (1968) Pergamon.

- (56) MULLER, G., IRION, G., FORSTNER, U. Formation and diagenesis of inorganic Ca-Mg carbonates in the lacustrine environments. *Naturwiss.* 59 (1972) 158.
- (57) LIPPMANN, F. *Sedimentary Carbonate Minerals*. Springer, Berlin (1973).
- (58) BOURROUILH-LEJEAN, F. Les dolomies et leur genèse. *Bull. Centre Rech. Pau, S.N.P.A.*, 7 (1973) 180.
- (59) VOROTNISKAYA, I.E. Biogenic uranium circulation in a closed basin with mean salinity. *Int. Symp. on Hydrogeochem. Biogeochem. Tokio Japan Abstracts* (1970).
- (60) GAUTHIER, M. Contribution à la géochimie de l'uranium des roches sédimentaires et en particulier des schistes carbonifères. *Bull. Serv. Carte Geol. Als. Lorr.* 14 (1961) 179.
- (61) MILLOT, G. *Géologie des Argiles Masson et Cie.* (1964).
- (62) MAGLIONE, G.F., MAGLIONE, M.H. Etude thermodynamique de silicates néoformés en milieu carbonaté sodique. *Sci. Géol. Bull.* 25 (1973) 231.
- (63) EUGSTER, H.P. Inorganic bedded cherts from the Magadi area, Kenya *Contr. Minera Petr.* 22 (1969) 1.
- (64) HAY, R.L. Zeolites and zeolitic reactions in sedimentary rocks. *Geol. Soc. Am. Spec. Paper* 85 (1966).
- (65) MARINER, R.H., SURDAM, R.C. Alkalinity and formation of zeolites in saline alkaline lakes. *Sciences* 170 (1970) 977.
- (66) HESS, P.C. Phase equilibria of some minerals in the K_2O - Na_2O - Al_2O_3 - SiO_2 - H_2O system at 25° C and 1 atmosphere. *Am. Journ. Sci.* 264 (1966) 289.
- (67) THOMPSON, A.B. Free energy from hydrothermal data. Implications for Phase equilibria and thermodynamic quantities for phase in $NaAlO_2$ - SiO_2 - H_2O . *Am. Min.* 58 (1973) 277.
- (68) GREGOR, C.B. The geochemical behaviour of Na. Thèse, Utrecht (1967).
- (69) GARRELS, R.M., MACKENZIE, F.T. Origin of the chemical composition of some springs and lakes. in : *Advance in chemistry series 67. Am. Chem. Soc.* (1967) 222.
- (70) JONES, B.F., RETTIG, S.L., EUGSTER, H.P., Silica in alkaline brines *Science* 158 (1967) 1310.
- (71) FRANKART, R., HERBILLON, A.J., Présence et genèse d'analcmite dans les sols sodiques de la basse Ruzzi (Burundi). *Bull. Groupe Franç. Argiles* 12 (1970) 79.
- (72) MAGLIONE, G., TARDY, Y., Néof ormation pédogénétique d'une zéolite, la mordénite associée aux carbonates de sodium dans une dépression interdunaire des bords du lac Tchad. *C.R. Acad. Sc. Paris* 272 (1971) 772.
- (73) BERNER, R.A., Migration of iron and sulfur within anaerobic sediments during early diagenesis. *Am. Journ. Sc.* 267 (1969) 19.
- (74) BERNARD, A., A propos du rôle métallogénique de la précipitation et de l'adsorption sédimentaire. In : *Sedimentology and Ore Genesis*. Ed. G.C. AMSTUTZ, Elsevier (1964) 1.
- (75) GANGLOFF, A., Notes sommaires sur la géologie des principaux districts uranifères étudiés par le C.E.A., *Uranium Exploration Geology*. (C.R. Groupe d'étude Vienne, 1970), AIEA, Vienne (1970) 77.

- (76) ROUTHIER, P. Essai critique sur les méthodes de la géologie. Masson et Cie. Paris (1969)
- (77) MOREAU, M., PUGHON, A., PUIBARAUD, Y., SANSELME, H., L'uranium et les granites. *Chronique des Mines* (1966) 47.
- (78) Some major concepts of metallogeny (consanguinity, heritage, province). Illustrated by examples *Miner. Deposita* 8 (1973) 237.
- (79) SAMAMA, J.C., Ore deposits and continental weathering : a contribution to the problem of geochemical inheritance of heavy metal contents of basement areas and of sedimentary basins. in : *Ores in Sediments* Springer, Berlin (1973) 247.
- (80) KULBICKI, G., SOURISSE, C., Aspects actuels du traitement sur ordinateur des données géochimiques au C.R.P.G. *Bull. Cen. Rech. Pau* 2 (1968) 191.

DISCUSSION

R. H. DE VOTO: The model you propose looks very similar to the Eocene Green River "oil shales" of the Western United States of America. In the Green River environment, which actually consists of sapropelic-rich dolomite mudstones, we find that volcanic ashes and tuffs from the edges of the salinity/density-stratified lakes have been altered to zeolites and feldspar in the centre of the lake. Do you find any volcanic ash and salts (evaporites) in the Lodève deposits?

A. HERBOSCH: I am familiar with quite a few papers devoted to the Green River basin. The Lodève basin does not, to my knowledge, have any appreciable thicknesses of evaporites such as gypsum, halite and so on. Only at the top of the typical sequences do we find some evaporite characteristics, but the material here is dolomitic. We do not find any appreciable thicknesses of vitreous tuffs, either, nor any indirect evidence of their having played a role, apart from a few shallow beds resembling tonsteins. I doubt, therefore, whether vitreous tuffs could have provided a source of albite and/or uranium.

M. MOREAU: Let me say a little bit more about products of volcanic origin in the Lodève basin, deposited either as layers of vitreous tuff or as a mixture of various elements in combination with detrital elements (we find, for example, sandstones containing fragments of glass). Whereas Mr. Herbosch's sampling at Mas d'Alary in the upper part of the grey Autunian shows large concentrations of sodium and albite, the more recent sampling done at Mas Lavayre in the lower part of the same series has revealed heavy concentrations of potassium. The cycle terminations are rich in evaporites in the form of gypsum deposits, very often changed epigenetically to ankerite.

A. HERBOSCH: I am grateful to Mr. Moreau for this additional information, which presumably has not appeared at all in the literature or has been published only in very condensed form. I nevertheless remain sceptical about the quantitative importance of these vitreous tuffs, which, after all, contribute only a few metres' depth to the 600 m of Autunian. I should very much like to see the fragments of glass or other evidence of tuffaceous debris in the shales I studied, which make up the sediments of the biostatic part of the cycle during which the uranium was concentrated.

SEDIMENTARY BASINS AND
SANDSTONE-TYPE DEPOSITS:
SEDIMENTARY DEPOSITS IN OTHER AREAS

URANIUM IN SIWALIK SANDSTONES, SULAIMAN RANGE, PAKISTAN

M. Y. MOGHAL

Atomic Energy Minerals Centre,
Lahore, Pakistan

Abstract

URANIUM IN SIWALIK SANDSTONES, SULAIMAN RANGE, PAKISTAN.

Uraniferous lenses are known to occur in seven localities over a strike length of more than 100 miles along the foothills of the Sulaiman Range in Pakistan. The best exposures are at Baghal Chur where extensive drilling has been done. The uranium mineral at Baghal Chur and other localities is metatuyamunite in the oxidized zone, while in the unoxidized zone it appears to be uraninite or coffinite. The mineralized lenses are up to 300 ft in length and width and 7 to 9 ft thick. No ore controls have yet been recognized. The denudation of the rising Himalayas is considered to have been the original source of the uranium found in this area. Its mode of transport and deposition in the Sulaiman Range is still under investigation.

1. INTRODUCTION

A carborne radiometric survey in 1959 discovered uranium mineralization 30 miles west of Dera Ghazi Khan in the Middle Siwalik formation (Middle Miocene to Lower Pliocene) flanking the Sulaiman Range. Reconnaissance during subsequent field seasons disclosed some 50 radiometric anomalies of which seven have visible showings of uranium mineralization. The most significant of these is at Baghal Chur.

These occurrences are in extremely rugged and remote terrain. Until a road was built to Baghal Chur in 1970, all supporting equipment and supplies for prospecting, geological mapping and drilling were transported by camels. The field seasons run from late October to mid-April owing to summer temperatures exceeding 120°F. Several thousand feet of drilling has been done at Baghal Chur, which has indicated several hundred tons of uranium ore of minable grade. This paper summarizes the structural and sedimentary framework within which the uranium-bearing host rock was deposited. It also discusses the mode of occurrence of the uranium and makes tentative suggestions as to the genesis of these deposits.

2. GEOLOGY

2.1. Structure

The Himalayan region during the Tertiary era underwent four successive mountain-building movements, which can be dated approximately as being Upper Cretaceous, Upper Eocene, Lower to Middle Miocene and Early to Late Pleistocene. The third mountain-building movement was perhaps the most violent episode of the four. This was accompanied by a considerable raising up and folding of the strata, which were previously laid down in the Tethys Sea, into mountain ranges. Consequently a long narrow foredeep

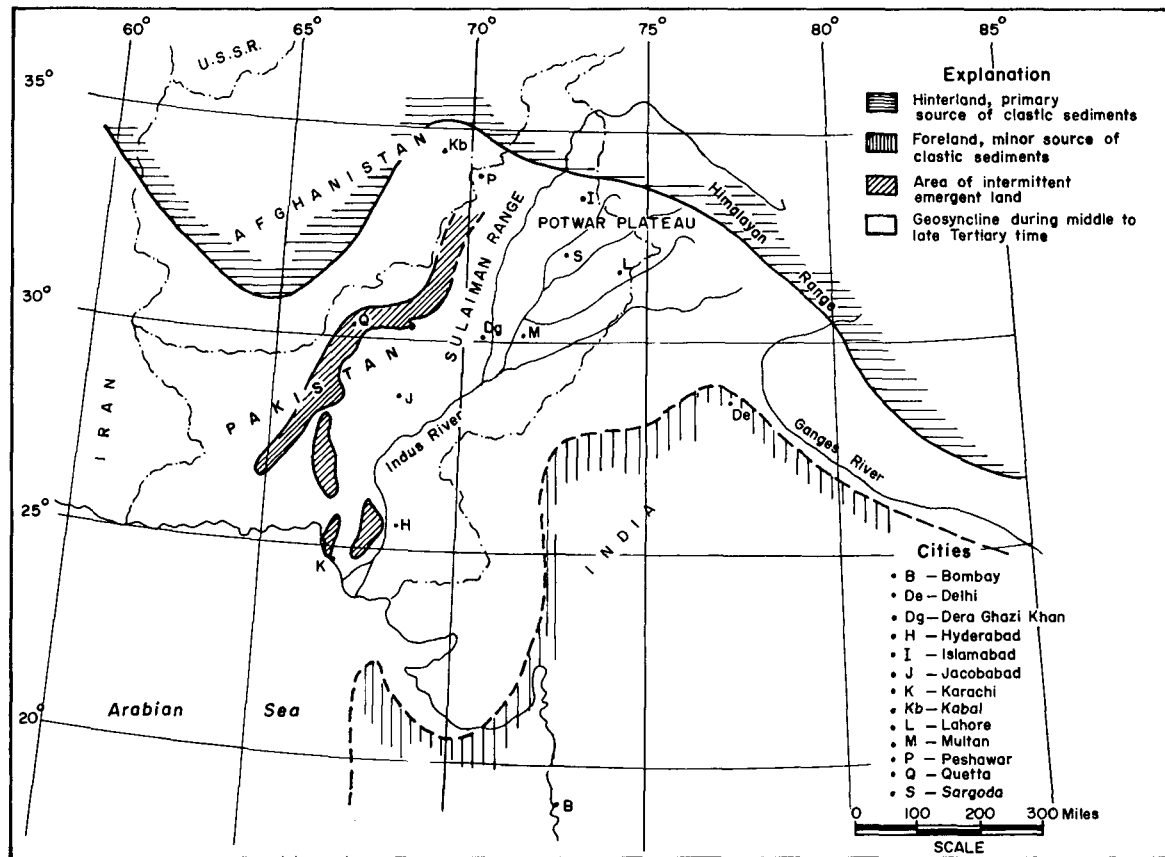


FIG.1. Mid-Tertiary geosyncline. Modified after Templeton [1].

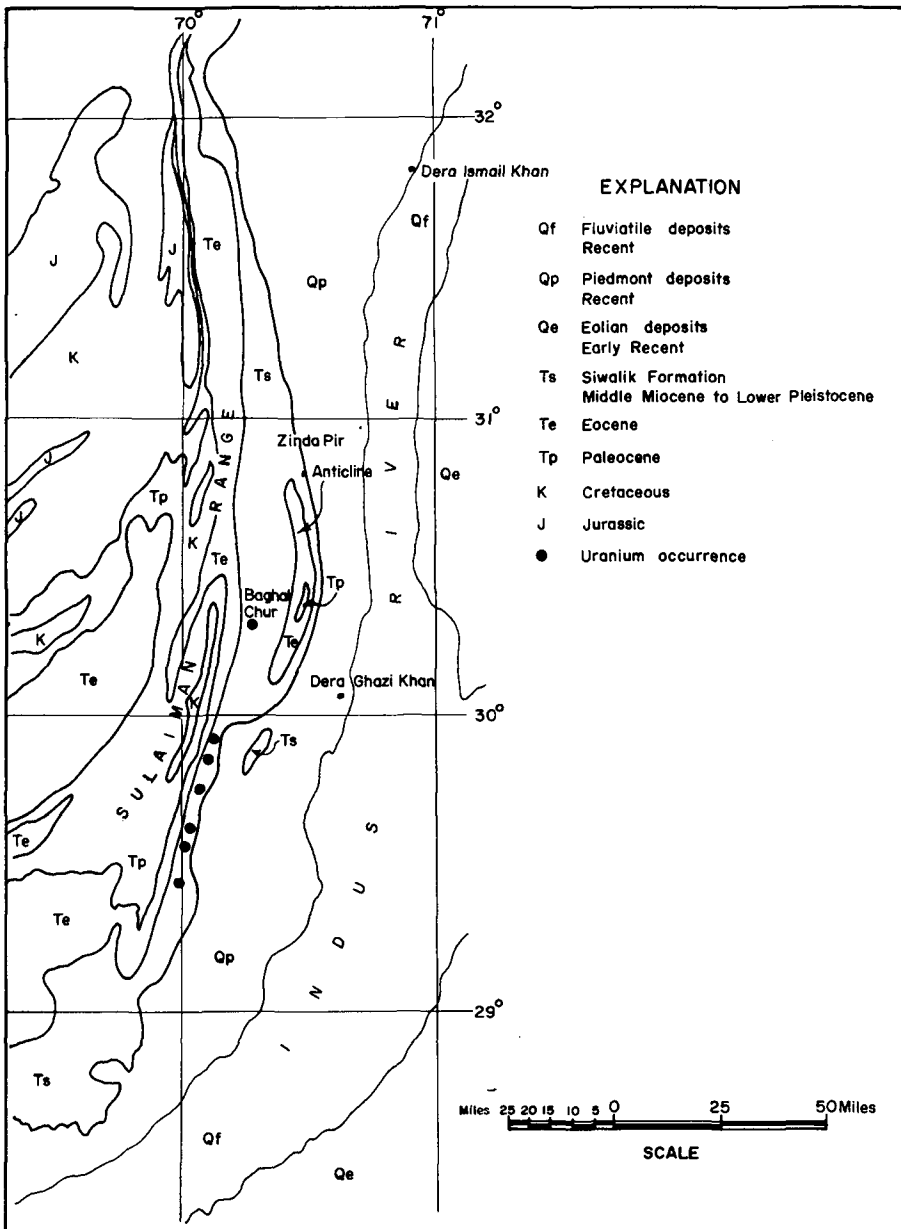


FIG. 2. Geological map, Sulaiman Range.

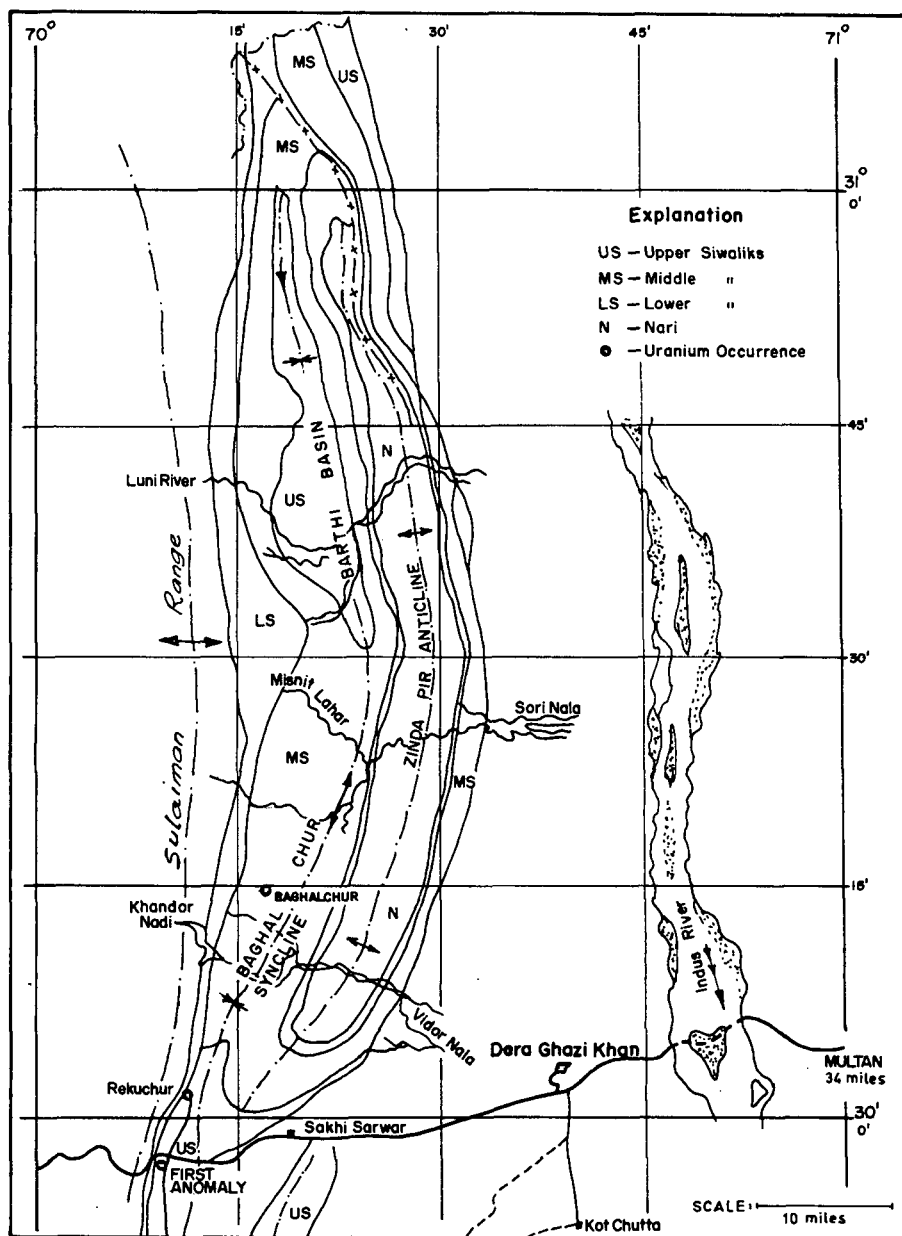


FIG. 3. Geological map, Baghal Chur area.

was formed between the rising mountains and the Indian Shield. The sediments filling this depression belong to the Siwalik System, and are well developed all along the Himalayas and in Sulaiman Range. This is illustrated in Fig.1. The Himalayan Range formed the hinterland and provided the majority of the clastics and the Indian Shield acted as the foreland, thereby limiting the deposition of Siwalik sediments. The Indian Foreland probably contributed very little clastic material.

The Siwaliks have been involved in the later phases of Himalayan orogeny. They have been folded, faulted and overthrust and are lying at steep angles against older formations.

The Sulaiman Range marks the western boundary of the Indus Plain in Central Pakistan. It consists of a series of long, narrow and parallel anticlines, trending north-south. Rocks from Jurassic to Pleistocene age are exposed (Fig.2) and the central core is marked by the presence of basic and ultrabasic intrusions.

Baghal Chur lies on the western flank of a long asymmetrical syncline extending all along the eastern flanks of the Sulaiman Range. The syncline is bounded towards the east by the Zinda Pir anticline which has a double plunge.

The syncline is asymmetrical. The eastern (Zinda Pir) flank dips at an angle of 30° to 50° towards the west. The major portion of the syncline shows gentle and uniform 7° to 10° easterly dips which then increase sharply near the western anticline. The uranium occurrences are restricted to the western flank of the syncline and no significant anomaly has been reported in other limbs of the folds.

Secondary superimposed folding extends across all structures. At Baghal Chur the large syncline has been slightly raised causing it to have a double plunge. The area north of the bulging is called the Barthi Basin. The area south of the bulge is called the Baghal Chur syncline (Fig.3). The Upper Siwaliks are absent within the crest area of this superimposed fold. All the seven showings referred to above with visible uranium mineralization occur south of this minor structural bowing.

2.2. Stratigraphy

The Siwalik formation ranges in age from Middle Miocene to Lower Pleistocene and has been divided into three divisions: Lower, Middle and Upper.

TABLE I. SIWALIK SUCCESSION (Modified after D.N. Wadia [2])

Upper Siwalik (6000 - 8000 ft)	Coarse boulder conglomerates, thick earthy clays, whitish grey sands and grit.
Middle Siwalik (6000 - 8000 ft)	Grey massive sandstones with clays and shales of grey and drab colours.
Lower Siwalik (5000 ft)	Bright red and purple shales and dark hard sandstones and minor conglomerates.

As can be seen from Table I, the Siwalik System is composed of detrital rocks such as coarsely bedded sandstones, clays and conglomerates. Although local breaks exist at places, the whole formation is a connected and complete sequence of deposits from the beginning of Middle Miocene to the close of the Siwalik deposition.

The Lower Siwaliks consist of fine-grained, micaceous sandstone which is more or less consolidated. It is distinguished by its interbedded shales of bright red, brown and occasionally purple colour.

The Middle Siwalik Group is composed of thick, massive beds of coarse micaceous sandstones which are soft, friable, poorly sorted, cross-bedded, grey coloured, and are interbedded with sparingly developed clays and shales of brown and dominantly grey colour. Some thin conglomerates and hard sandstone lenses are also present. The cementation is very unequal, much of the cement being concentrated in hard, cigar-shaped concretions which at times enclose fossil teeth, skulls or bones, leaving the main part of the rock soft.

The Upper Siwaliks are generally more argillaceous than the underlying strata. There are finer sandstones of whitish grey colour, bedded earthy clays and silts. The Upper Siwaliks in the area of interest are capped by a thick, extremely coarse siliceous boulder conglomerate.

Silicified wood and often whole tree trunks are abundant throughout the Siwalik sandstones. There are leaf impressions in the shales. In the area of interest, the wood and trees are almost always completely limonitized to a soft earthy ochre.

2.3. Distribution

The Siwaliks extend continuously along the foothills of the Himalayas from the Brahmaputra valley in the east to the Potwar Plateau and through the Balnu plains on the west towards the Sulaiman Range. The rock groups have been named differently in different areas. They constitute the Siwalik System along the outer Himalayas; the Manchhar System in Sind; the Mekran Series in Baluchistan; the Dihing Series in Assam and the Irrawady System in Burma [3].

3. URANIUM OCCURRENCES

A radioactive anomaly was discovered during a carborne survey in 1959, 30 miles west of Dera Ghazi Khan, in the Middle Siwaliks along the Sulaiman Range. The fluvial characteristics of the sediments are similar to the Colorado Plateau and Wyoming Basin type uranium-bearing sediments in the United States of America. This, combined with the discovery of uraniferous mineralization, warranted that the Siwaliks in general and the Middle Siwaliks in particular should be checked for uranium deposits. A systematic checking of Middle Siwaliks was therefore initiated in 1962 by making foot traverses across the strike. The field parties discovered over 50 radioactive anomalies, spread over an outcrop length of more than 100 miles along the foothills of the Sulaiman Range. These anomalies occur both north and south of the anomaly originally discovered. Among these, seven showings are significant and have visible uranium mineralization. Out of these seven the most favourable showing, with widespread mineralization outcrops, is at Baghal Chur.

An aeroradiometric survey using a fixed-wing aircraft was carried out in the area in 1964, but it did not add any significant anomalies to those already discovered during foot traverses. The area north of Baghal Chur has been recently reflight using a helicopter, and more widespread radioactive anomalies have been found. The data obtained are still being processed to determine the magnitude of the anomalies.

4. BAGHAL CHUR

The Baghal Chur showing lies about 25 miles NNW of Dera Ghazi Khan, and is located about 10 miles south of the edge of the Barthi Basin (Fig. 3). As this showing was considered the most favourable for exploration, an extensive trenching programme was undertaken in the area. Results were encouraging and indicated the possibility of the mineralization continuing into the subsurface. To confirm this possibility a small portable drill was put into operation and later more small drills were commissioned. Since the completion of the access road, a drill capable of reaching 500 ft and another with the capacity of drilling up to 1500 ft has complemented the small portable machines.

4.1. Lithology

At this locality, the mineralization, both on the surface and subsurface, is restricted to the unit called Baghal Chur sand¹ which is about 200 to 250 ft thick. This sandstone is enclosed by the underlying Bogo shale¹ and the overlying Vidor shale¹ (Fig. 4).

The Baghal Chur sand outcrops on a bedrock dip slope about 1000 ft wide dipping 9°SE with a strike bearing of 45°.

The Bogo shale underlying the Baghal Chur sand is grey in colour and within the prospect area attains a thickness of 40 ft. Elsewhere it thins out considerably. The shale is at places somewhat silty and sometimes contains lenses of siltstone which may be only a few feet thick. The shale dips conformably with the overlying sandstone.

The Vidor shale overlies the sandstone and is brown to dark brown in colour. It is comparatively more continuous than the underlying shale and it retains a thickness of about 80 ft. It is also silty at places.

The Baghal Chur sand is light grey, mostly medium-to-fine grained, soft, friable and poorly sorted. Erratic pebbles and cobbles occur sporadically throughout the section. These can be quartzite, limestone or calcareous clay balls. The sandstone also contains abundant heavy minerals which frequently outline cross-bedding. Magnetite constitutes the major portion of the heavy minerals.

Within Baghal Chur sand there are numerous lenses of grit and conglomerate. These lenses are usually 2 to 3 ft thick but sometimes can be up to 10 ft thick. They can persist in a north-south direction for some hundreds of feet, but seem to pinch out rapidly in an east-west direction. These lenses have lately been recognized [4] as marking paleochannels, which accounts for their pinching out in the east and west directions. They are

¹ Local informal names.

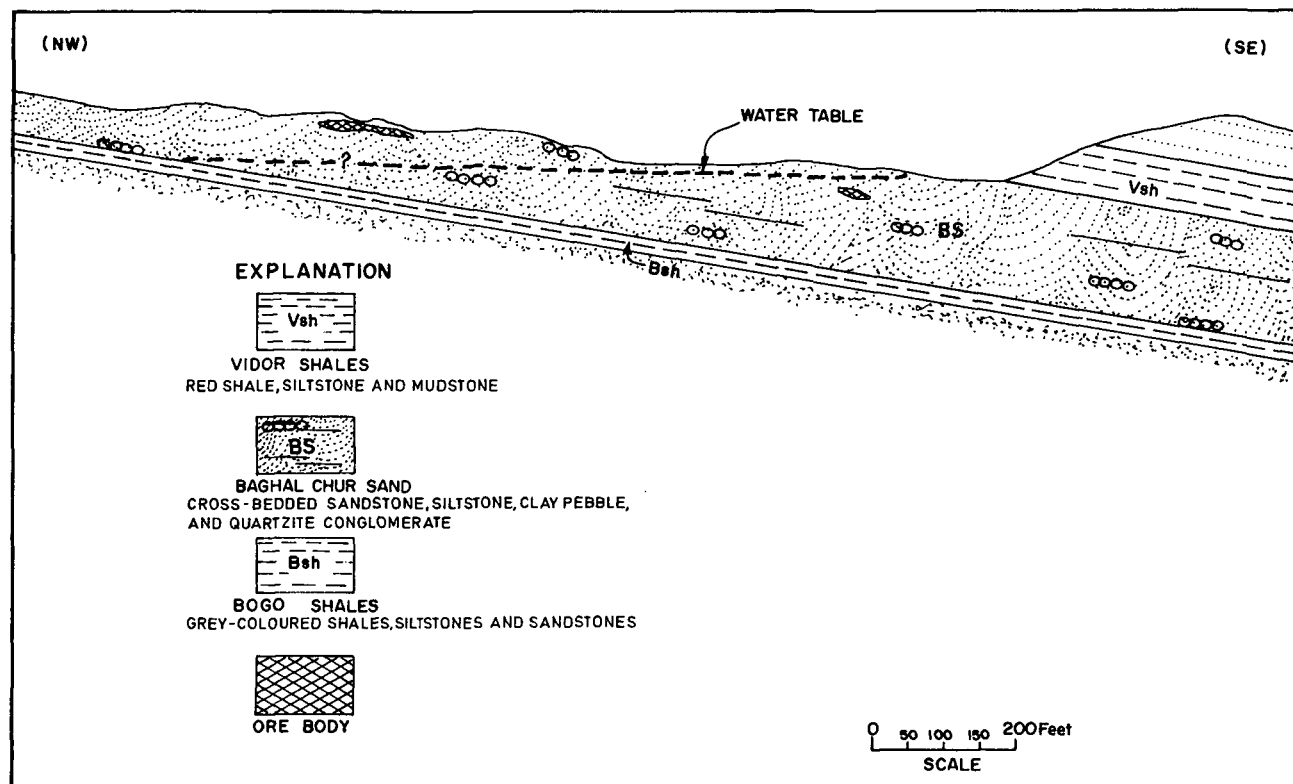


FIG.4. Geological cross-section, Baghal Chur area.

composed of rounded to subrounded pebbles and cobbles of quartzite and limestone in a silty, sandy and clayey matrix. They are usually somewhat reddish in colour.

The amount of calcareous cement in the sandstone varies laterally as well as vertically. At some places it is absent while in some zones the sandstone is relatively well cemented. No megascopic sedimentary feature such as sorting or grain size has been observed which controls the distribution of the cement.

The Baghal Chur sand was deposited primarily as sheets of clastics flooding the region in a fluvial environment. Cross-bedding and lineation of the paleochannels and orientation of the logs indicate the flow direction to have been north-south.

4.2. Mineralization

There are approximately 100 surface showings occurring over an area 10 000 ft by 1 000 ft which range from 0.05% U_3O_8 to more than 0.5% U_3O_8 . These patchy shows vary from less than 1 ft to 4 ft in thickness and from 2 ft to 100 ft in length and width. Drilling has extended some of these surface showings into the subsurface along the strike and dip directions, and has also encountered new lenses of similar mineralization.

The drilling by small machines is mostly done on a regular grid. A section of boreholes along one of the grid lines is shown in Fig.5. The section which is drawn along the dip is about 1000 ft long. One of the lenses can be seen to extend for more than 300 ft and is about 8 ft thick in the middle.

With the help of drilling, an area has been delineated which contains a group of overlapping lenses of uranium mineralization at shallow depth. The thickness of the individual lenses varies from 1 ft to more than 9 ft, with a minable grade. The configuration of the area delineated is shown in Fig.6. The darker shade indicates the area in which mineralization has been blocked by equispaced boreholes while the lighter shaded area indicates the possible subsurface extension of the mineralization. This extension is based on the positive results of two boreholes, drilled about 1000 ft from the closely gridded area, downwards from the trend of a possible subsurface paleochannel.

The deep drills have been used for widely spaced drill holes, mostly for scanning the area outside the limits of known surface mineralization. Some of the holes drilled have indicated the presence of oxidized minerals above the water table, as well as unoxidized mineralization below the water table. The thickness of such sections of unoxidized mineralization is as much as 7 ft in some places.

4.3. Ore controls

At this stage of the development no definite ore controls are recognized. The mineralization shows no preference for accumulating in any facies of rock. It occurs as elongated lenses or amoeba-like patches. It can be concordant or discordant with dip in the stratigraphic section. It sometimes follows cross-bedding planes which may or may not have associated heavy minerals. The mineralization boundaries are difficult to mark visually as they are not sharp but form halos of continuously decreasing intensity.

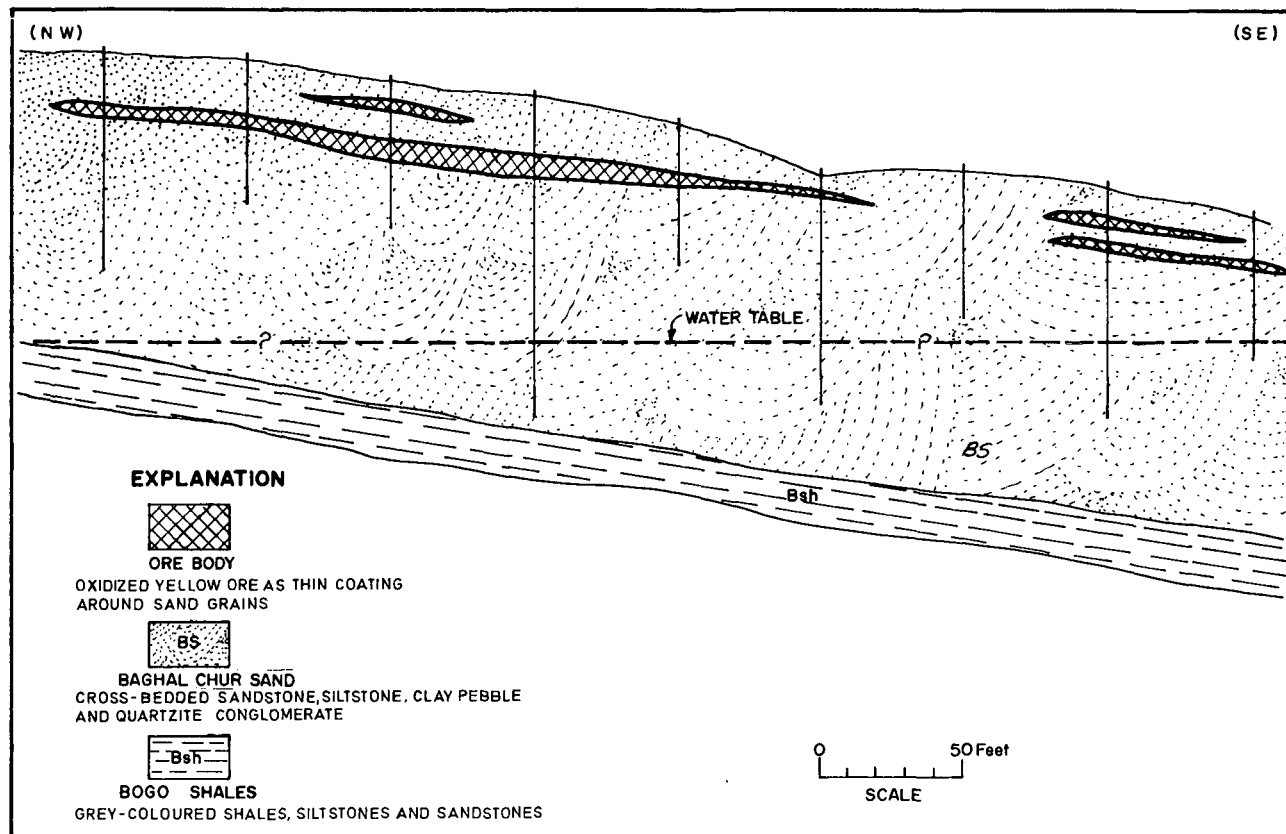


FIG. 5. Cross-section along a grid line, Baghal Chur area.

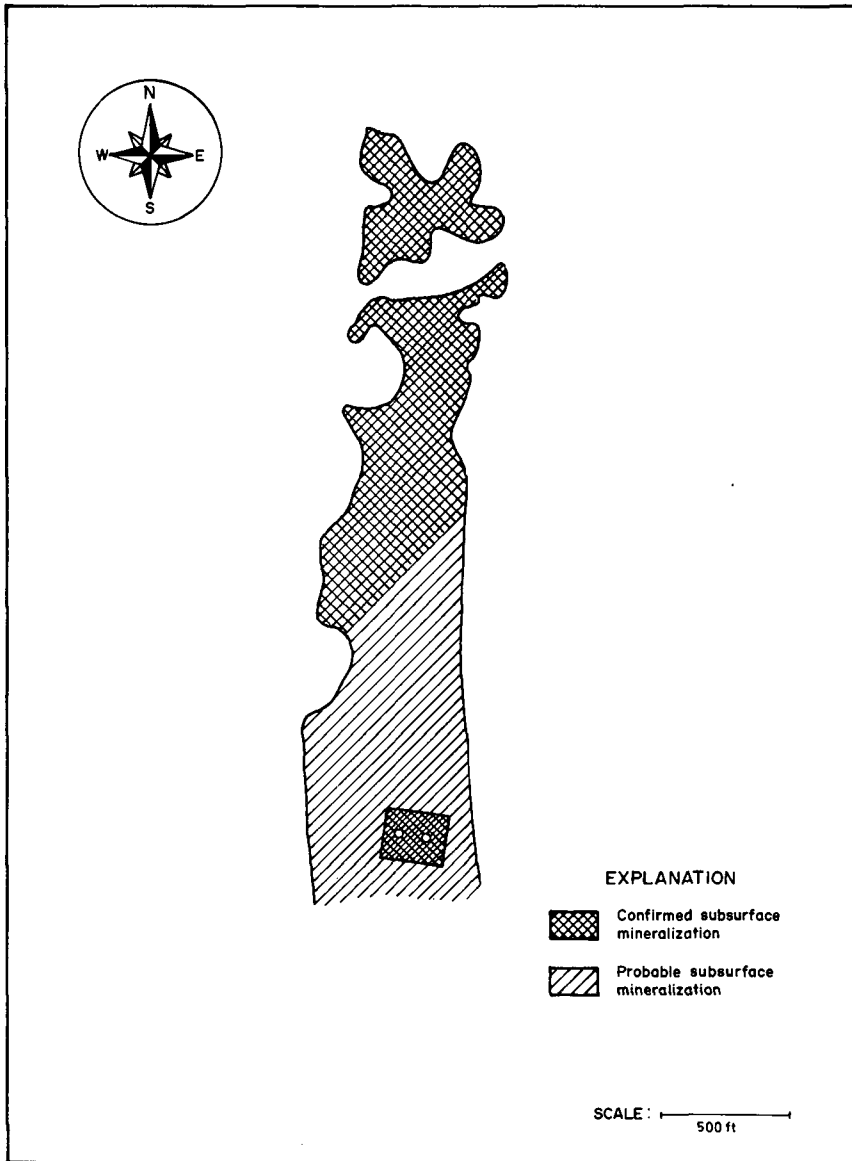


FIG. 6. Subsurface trend of mineralization outlined by drilling at Baghal Chur.

The highest concentrations are often associated with completely limonitized plant remains, logs or individual pieces of silicified bone. However not all of this type of material is radioactive.

No evidence of roll front development has yet been recognized. Dual gamma log kicks have been noted [5], suggestive of fronts, but this has not been confirmed from other data. In any case the classical mineralogical and rock colour relationships known in the United States of America are not present.

4.4. Paleochannels

As stated above, the conglomerate lenses in the area have lately been assumed to mark paleochannels. Such channels have been reported to host uranium ore bodies in the Colorado Plateau and the Wyoming Basin of the USA. One such channel in the area has visible uranium mineralization, and it is possible that these channels may host major uranium ore bodies. If the uranium mineral were brought in along with the clastics, it should concentrate, owing to its heavier specific gravity, in coarse sediments of the channel. On the other hand, if it came in solutions, the conglomerates in the paleochannels, being relatively more porous, again become the most favourable site for the entry of the solutions and consequent deposition of uranium. With this in view, one channel is being exploratory drilled and, from the data of the few holes drilled, it appears that these paleochannels may have played an important role in the concentration of uranium ore bodies.

4.5. Petrography

The sandstone is mainly composed of quartz, plagioclase and microcline feldspars, muscovite and biotite. Clay and silt rock fragments are also common. Among the accessory minerals, magnetite hornblende,

TABLE II. MICROMETRIC ANALYSIS OF BAGHAL CHUR SANDSTONE

Sample No.	Quartz & chert (%)	Feldspar & altered feldspar opaques (%)	Ferro-magnesian minerals (%)	Voids (%)	Clay & siltstone fragments (%)	Matrix clays & calcite (%)	Nature of matrix
1	27.28	21.63	7.65	10.98	11.98	20.46	Argillaceous calcite.
2	26.62	13.81	7.32	0.85	14.80	36.60	Calcite predominant.
3	25.16	16.22	11.92	19.53	7.61	19.53	Argillaceous calcite

garnet, epidote, apatite, clinozoisite, zircon, chlorite, fluorite, ilmenite and hematite are present. Their relative abundances vary in different samples but magnetite usually predominates.

Rahman [6] has done modal analysis on thin sections of three homogeneous samples free from heavy minerals. His results are shown in Table II.

4.6. Petrology

Both oxidized and unoxidized minerals are present in the area. The oxidized mineral, which is metatyuyamunite, occurs on the surface as well as in the subsurface above the water table, while the unoxidized mineral usually occurs below the water table, although a few grains have been noted in the limonitized wood logs along with concentrations of the oxidized mineral. The unoxidized mineral has not been identified petrologically but tentative identification from hand specimens indicate it to be uraninite or coffinite.

The oxidized mineral occurs as a bright greenish yellow amorphous powder impregnating the interstices between clasts or as a coating around pebbles, grains and clay balls. Occasionally the mineralization is restricted to parallel cross-beds of heavy minerals. Well-defined bands of yellow uranium mineral about $\frac{1}{2}$ in. thick follow the $\frac{1}{4}$ - $\frac{1}{2}$ in. black bands. The yellow mineralization may occur above or below or on both sides of the black, primarily magnetite, heavy mineral cross-beds.

5. OTHER SHOWINGS

Besides Baghal Chur, there are six other showings of uraniferous mineralization in the Middle Siwaliks of the Sulaiman Range. All of these occur in the same stratigraphic horizon. Their locations are given in Fig.2. Except for the showing which was first discovered, all the showings are quite inaccessible. Hence it has not been possible to do any significant exploratory work on them.

All these anomalies, as in Baghal Chur, show bright yellow mineralization in lenses mostly elongated along the strike of the sandstone. Sometimes a single lense is continuous for as much as 200 ft. At two of these sites the mineralization lenses, both large and small, are scattered over a distance of 2 to 3 miles along the strike, while at the others the mineralization in lenticular form is scattered over half a mile on each site. Limonitized wood logs, though present in these areas, are less common. In brief, some of the showings are as interesting and attractive as Baghal Chur, but the dips are rather high and consequently the terrain is more difficult. However, it is planned that exploratory work on all of these showings will be undertaken in the near future.

Besides these showings, three more areas with widespread radioactive anomalies have also been located recently in the southern part of the Barthi Basin. The varying radioactivity in each area is spread over a distance of more than 2 miles. Uranium mineralization, both oxidized and unoxidized, is rare and wherever seen is associated with limonitized wood logs. The conglomerate beds are common in these areas, and are assumed to mark the braided paleochannels. As evidence of uranium mineralization

at the surface exists, it is planned that these channels will be exploratory drilled in the near future to confirm the presence or absence of uranium mineralization in the subsurface.

6. ORIGIN

No definitive statement as to the origin of the uranium occurrences in the Middle Siwaliks can be made. The research facilities available have been limited so that previous work has been restricted to attempting to block out viable ore bodies. Concentrations of mineralization are seen on the one hand limited to the cross-beds with or without heavy minerals and on the other hand associated with the limonitized wood logs. Furthermore the random nature of the occurrences and lack of mineral preference for any sedimentary, textural or structural feature of the host rock preclude deriving at this time a conclusion as to genesis.

Two working hypotheses of the origin of the uranium are being investigated. These are (1) clastic origin and (2) ground-water movement.

6.1. Clastic origin

According to this hypothesis the uranium was originally brought into the sediments as clastic heavy mineral particles. Presumably the uranium was in the form of uranothorite or as an admixture or accessory element of heavy minerals such as allanite, sphene or zircon. An unrecognized chemical process related to the desert climate and ground-water regimen caused these clastic particles to lose their uranium ions into the surrounding sandstone. There the uranium was reprecipitated into the black uranium mineral which retained its form below the water table but was transformed into a vanadate in the oxidizing environment.

An alternative source might have been an unoxidized uranium mineral such as uraninite, which was transported from a Himalayan source area during a limited period of Middle Siwalik times. The instability of uraninite in the oxidizing environment of the outcrop has caused its change in situ into metatyuyamunite.

However, with this hypothesis it is not possible at this time to account for the presence of vanadium in the oxidized minerals and the absence of thorium in the area.

6.2. Ground-water movement

This theory is based upon the sedimentary, textural and mineralogical similarities of Baghal Chur with sedimentary deposits of Western United States. The original source of the uranium is postulated to have been in the Himalayas. The hypothesis contends that uranium was and is being transported by the ground water of the regions.

The limited size and grade of the mineralization found to date may be a function of (1) undersaturated uranium-bearing solutions, (2) the limited amount of time for uranium accumulations or (3) limonitized rather than carbonaceous vegetal remains in the stratigraphic section.

TABLE III. COMPARISON OF BAGHAL CHUR WITH SEDIMENTARY DEPOSITS OF THE UNITED STATES OF AMERICA

Regional criteria	US deposits	Baghal Chur
Age	Jurassic, Triassic, Tertiary	Tertiary
Host rock	Fluviatile	Fluviatile
Provenance	(a) Eroded granitic or metamorphic source of sediments (b) Acid volcanic centres (c) Overlying tuffaceous rocks	(a) Eroded granitic and metamorphic source of sediments (b) Mostly basic volcanics during time preceding Siwalik; contemporaneous andesitic volcanism (c) Tuffaceous rocks not recognized
Special stratigraphic features	(a) Near unconformities (b) Truncated beds	(a) Intraformational unconformities not recognised; continuous sedimentation (b) None present
Type host rock	(a) Feldspathic (15% feldspar) (b) Arkose (feldspar 40%) (c) Tuffaceous (10%)	(a) Feldspar (10-25%) (b) Classed as subarkose (c) Not recognised
Physiographic province	Colorado Plateau or Wyoming Basins	Sulaiman province of Indus Basin
Tectonic element	Cordilleran Foreland (Laramide ranging in age from Cretaceous to Oligocene)	Himalayan geosyncline (Miocene to mid-Pliocene)
Local criteria	US deposits	Baghal Chur
Type of Deposits		
(1) Blanket	(a) Concordant (b) Amoeba-shaped to elongate (c) Commonly 3-15 ft thick (d) Tenor ranges from 0.15 - 0.40% U_3O_8	(a) Generally concordant to slightly discordant (b) Amoeba-shaped to elongate (c) 1.0 - 8.0 ft thick (d) Tenor of 0.05 - 0.50% U_3O_8
(2) Rolls	(a) "C"-shaped in cross-section; roll fronts or solution fronts in Wyoming Basin, complex "C" rolls in Colorado Plateau (b) Recognized by colour, mineralogy and physical relationships	(a) Not recognized in pits, trenches or adits; gamma logs suggest miniature 2-4 ft roll "tails" (b) No colour or mineralogical changes observed
(3) Stacks	Fault and fracture fillings	Not present

TABLE III. (cont.)

Local criteria	US deposits	Baghal Chur
Sedimentary features		
(1) Grain size	Fine to coarse; medium to coarse, poorly sorted sand preferred	Fine to coarse, but no preference; poor to medium sorting
(2) Colour manifesting reducing conditions	(a) Grey, green or tan sandstones with interbedded grey or green mudstones (b) Finely divided pyrite in unoxidized zone (c) Bleaching of red and tan rocks (d) Limonite- or hematite-stained outcrops	(a) Grey to tan sandstone with interbedded grey and red to brown shale (b) Very fine but sparse pyrite, unoxidized zone not well studied (c) Bleaching not observed (d) Minor limonite staining, very limited hematite-stained outcrops
(3) Sand-to-shale ratios	1:1 to 4:1	4:1
(4) Formation dip	(a) Normally less than 5° (b) Allows slow migration of ground water with minimal flushing action (c) Large outcrop area to facilitate recharge	(a) 5° to 10° at Baghal Chur, other mineralized localities in Siwaliks have dips approaching 50° to 60° (b) Speed of water migration unknown but probably moderately fast (c) Limited recharge area
Associated elements	Vanadium, molybdenum, selenium, arsenic, phosphorous, manganese, copper	Only vanadium and possibly selenite recognized at present
Reducing agents	(a) Carbonaceous vegetal remains (b) Structureless humic compounds (Ambrosia Lake) (c) Dead oil (d) H ₂ S gas (e) Silicified mineralized bone	(a) Very rare vegetal remains, almost always completely limonitized to soft and earth-coloured ochre (b) Not present (c) Not present (d) Not present (e) Silicified, frequently mineralized bone

TABLE III. (cont.)

Local criteria	US deposits	Baghal Chur
Other factors	(a) Radiometric anomalies 5× background (b) Radioactivity in coal and lignite (c) Geochemical anomalies greater than 5 ppm U_3O_8 (d) Bicarbonate ground water mixing with sulphate water (e) Ellipsoidal-shaped calcareous concretions reflecting mineralized ground-water flow (f) Ground-water anomalies 10 ppm U_3O_8 (g) Oxidized mineral on outcrops	(a) Radiometric anomalies 5× to 10× background (b) Coal and lignite not present (c) No geochemical work done (d) No data (e) Slightly mineralized ellipsoidal (cigar-shaped) calcareous concretions in mineralized formation trending normal to direction of sediment transport but in direction of ground- water flow (f) Data too limited (g) Oxidized mineral on outcrops

The presence of unoxidized black mineral below the water table, however, is taken as an encouraging sign, being interpreted as an indication that roll-front processes have been active, although not recognized. Therefore, there is the distinct possibility of a significant ore body.

7. COMPARISON OF BAGHAL CHUR WITH SEDIMENTARY DEPOSITS OF THE UNITED STATES OF AMERICA

There are many obvious similarities of the uranium deposits in Baghal Chur with those of Western United States, on a regional as well as local scale. Grutt [7] has prepared a summary of the characteristics of sedimentary uranium deposits of Western United States. A comparison of these characteristics with those observed in Baghal Chur is presented in Table III.

8. CONCLUSION

The Middle Siwaliks along the flank of the Sulaiman Range are a favourable horizon for the formation of uranium deposits. In many respects these occurrences resemble the US sedimentary deposits. At the present time seven significant mineralizations are known. One of these at Baghal Chur has sufficient mineralization to warrant serious consideration as a viable mining operation in terms of Pakistan's economics and national requirements. Future exploration is expected to contribute materially to understanding the genesis of these deposits and discovering new ore bodies. However the search for new ore bodies is a formidable challenge. All possible knowledge and skill is needed to increase the chances of success.

ACKNOWLEDGEMENTS

The author is extremely grateful to Dr. J. Cameron of the IAEA for his encouragement and to Mr. Munir Ahmad Khan, Chairman of the Pakistan Atomic Energy Commission, for permission to publish, and to both and their agencies for financing his visit to Greece to present this paper. He is also grateful to Mr. Muhammad Aslam, Director of the Atomic Energy Minerals Centre, Lahore, Dr. J.W. Hoadley, Project Manager of the UNDP Project in Pakistan and Mr. M.A. Samad Baig, Geologist with the Atomic Energy Minerals Centre, Lahore for helpful suggestions. Mr. G.W. Chase contributed to a better understanding of the field relationships. Mr. J.L. Bowman critically reviewed the manuscript. His collaboration in preparing this paper is gratefully acknowledged.

Thanks are also due to the staff of the Atomic Energy Minerals Centre for help in typing of the manuscript and drafting of the illustrations.

REFERENCES

- [1] TEMPLETON, R. S. M., "Ideas on the Tectonics of Afghan-Pakistan Geosyncline", *GEO'NEWS*, Geological Survey of Pakistan 3 1 (1973).
- [2] KRISHNAN, M. S., *Geology of India and Burma*, Higginbothams (Private) Ltd. Madras, India (1956).
- [3] WADIA, D. N., *Geology of India*, Macmillan & Co. Ltd., London (1961).
- [4] CHASE, G. W., Verbal communication.
- [5] BOWMAN, J. L., Verbal communication.
- [6] RAHMAN, M. A., Sedimentary metatuyamunite deposits in Dera Ghazi Khan District, Pakistan, *The Nucleus*, Quarterly Journal of the Pakistan Atomic Energy Commission, Islamabad, 9 1-2 (1972).
- [7] GRUTT, E. W., Jr., "Prospecting criteria for sandstone-type uranium deposits", *Uranium Prospecting Handbook* (BOWIE, S. H. U., DAVIS, M., OSTLE, D., Eds), (Proc. NATO-sponsored Adv. Institute on Methods of Prospecting for Uranium Minerals, London, 1971), *Inst. Min. Metall.*, London (1972) 47.

DISCUSSION

F. R. JOUBIN: The Baghal Chur area seems to have almost everything in its favour for sandstone-type deposits, with the possible exception of one vital factor, namely promising source rocks for the material, in particular the uranium. Those of us who are familiar with the district feel some concern about the absence of a reasonably close basin rim with source material likely to provide substantial ore bodies. It would be interesting to hear how much importance the sandstone basin experts attribute to the basin rim being in reasonable proximity to the area under exploration.

G. R. UDAS: In a very similar setting in the Himalayas we have what are known as Chor granites, and these together with the north Himalayan gneisses are considered to be the source rock for most of the Siwalik sediments that occur on our side of the border. They contain 8-10 ppm uranium.

J. CAMERON: The problem of there being no apparent nearby source rock for the uranium is something which Mr. Joubin, Mr. Moghal and I were recently discussing at the Baghal Chur site. My own view is that it is not at all unreasonable to identify a source in the rising Himalayas some hundreds of miles to the north. The wide Indus flood plain lies only 30 miles or so to the east of Baghal Chur and parallel with the north-south

Siwalik basin. The contemporary sands in the Indus flood plain are very similar to the Tertiary Siwaliks and undoubtedly have the same origin in the Himalayas. The Indus sands exhibit an extensive suite of heavy minerals, including thorium uraninite. Uranium is therefore clearly moving, in the physical sense, in this region; the question that needs to be answered relates to the mode of leaching, mobilization, transport, and later fixation of the uranium in its present locations in the Siwalik deposits. In my view the source of the Siwalik basin uranium deposits lies to the north, in the Himalayas.

J. A. FERNANDEZ POLO: I believe that the visible mineralization at Baghal Chur consists of small lenses, but that other sizable deposits are sure to be present in the reducing zone below the water table. It seems to me that the indications are good and that we may assume a large ore potential in parts of the Siwalik basin at some distance from the radiometric anomalies observed to date.

M. Y. MOGHAL: Yes, I quite agree, and we are in fact expanding our exploration programme.

R. I. RACKLEY: If you want some consolation for your failure to identify a roll front in the oxidized zone, I might mention that roll fronts are not recognized in the oxidized zones in most Wyoming districts either. As to the question about the source of the uranium, I doubt whether there is any relationship between the topographic rim of a basin and the ore deposits, because basin rims tend to be much more recent than the mineralization.

E. N. HARSHMAN: I agree that the erosional rims cut in Tertiary rocks which are found in many of the uranium-bearing areas of Wyoming have no direct genetic relationship with the ore deposits. The rims are relatively recent features, whereas the ore deposits in the Gas Hills and Shirley Basin areas of Wyoming are at least 20 m. y. and possibly as much as 30 m. y. old. I see no reason why there should be any particular limitation on the distance over which the ore elements are transported by ground water, once the elements are in solution. Given a hydraulic gradient to cause flow, the elements could move 3 or 30 miles, or more.

J. W. KING: Very often, I think, too much importance is attributed to the source. In the areas where we all work we have found uranium, revealed by prospecting and by radioactive anomalies. Despite many years of work in the Colorado Plateau, in Wyoming and elsewhere, there is little agreement about the source of the uranium; but we find it nevertheless. A source undoubtedly exists, but it does not determine our approach to exploration or to exploration methods.

S. S. ADAMS: In the Grants region we do not worry much about the source rock; there was clearly at least an acceptable source in the thick bentonitic members of the Morrison Formation. I would, however, take exception to what I understand Mr. King to have said, namely that the source is unimportant. In wildcat exploration, source is a good criterion for the selection of favourable areas because, in my experience, every significant uranium district is located in proximity to rocks, either volcanic or granitic, of anomalous uranium content.

J. W. KING: That is true of course. I take it for granted that the selection of an area for exploration will always be based on sound theoretical considerations of source, or on the presence of anomalies. But the pursuit

of a source as a sort of academic exercise, after substantial deposits have already been found, seems to me a less practical endeavour.

A.M. GANGLOFF: I think we should be careful not to form unduly rigid concepts about the distance between mineralized zones and possible sources of uranium. Many hypotheses deserve consideration. It is also important to specify whether one is seeking the source of the detrital material constituting the basin fill or the presumed source of the uranium itself. In the case of the Niger mineralization, sedimentological and paleogeographic studies seem to indicate that the origin of the sediments constituting the host rock lies several hundred kilometres to the south of the deposits.

It should not be forgotten either that in many cases volcanic elements are found to be present in uraniferous basins; and we may consider these, too, as a possible source of uranium. I should therefore like to ask Mr. Moghal whether any volcanic elements have been observed in the formations of the Sulaiman Range.

M.Y. MOGHAL: We are not sure about the presence of true volcanic elements, but volcanic rock fragments are reported to be present in the sandstone which serves as host for the uranium.

S.H.U. BOWIE: It seems to be assumed that a source rock is essential. I am quite sure that there are many uranium deposits in the world derived not from more or less distant source rocks but from a deep-seated source. Nearly all the major uranium deposits known occur in, or immediately overlying, a Precambrian basement. If we must have a source rock, we need look no further than these Precambrian rocks. The modes of derivation from such rocks may have been quite various in different parts of the world.

R. WYLLIE: Mr. Moghal has mentioned individual grades of ore ranging from 0.05 to 0.5% U_3O_8 . I wonder whether he could suggest a figure for the average grade in the several hundred tons which these reserves are thought to contain.

M.Y. MOGHAL: It is difficult to quote a definite figure, but I should say that the average lies around 0.15%. This is expected to improve as we drill deeper.

F.C. ARMSTRONG: As Mr. Bowie says, it is usually very hard to demonstrate where a given uranium deposit has come from. In some cases, however, the evidence is such as to allow a fairly strong presumption. Rosholt and Peterman have shown for example that the rocks of the Granite Mountains in Wyoming are very depleted in ^{238}U and correspondingly enriched in radiogenetic ^{206}Pb . Concordant ages derived from Rb/Sr , $^{232}Th/^{208}Pb$ and $^{206}Pb/^{238}U$ ratios all showed about 2300 m.y., whereas the $^{238}U/^{206}Pb$ result was more than four times as high as it should have been. Calculating in reverse, they decided that the rocks must have contained 25 - 33 ppm uranium to account for the observed amount of ^{206}Pb . The logical conclusion, it seems to me, is that the uranium was leached and subsequently formed the ore deposits.

As to the source of the uranium in lignites, Denson and his colleagues have made a convincing case for its having originated from overlying tuffaceous material (White River). In Texas there are no granitic rocks in the vicinity at all but an abundance of tuffs, so the case is perhaps even clearer.

Thus there are many possible sources, and at a given site it may be difficult to say with conviction exactly how much uranium came from granite and how much from tuffs; but there are instances where I think it can be satisfactorily demonstrated that the uranium has been leached.

As for exploration, it is obviously important that the presumptive sources of uranium should be considered in planning the work to be carried out. Some sort of hypothesis is essential.

URANIUM MINERALIZATION IN SIWALIK SANDSTONES FROM PAKISTAN

I. R. BASHAM

Institute of Geological Sciences,
London

C. M. RICE

Department of Geology and Mineralogy,
Marischal College, University of Aberdeen,
Aberdeen,
United Kingdom

Presented by S.H.U. Bowie

Abstract

URANIUM MINERALIZATION IN SIWALIK SANDSTONES FROM PAKISTAN.

The mineralogy of a sandstone uranium deposit in the fluvial Siwalik sandstones of the Sulaiman Range in Pakistan has been studied by a variety of techniques including fission track radiography and electron probe analysis.

Uraninite and coffinite characterize the non-oxidized zone whereas the principal uranium-bearing mineral in the oxidized zone is tyuyamunite. Uranium concentrations are also found associated with goethite, hematite, martite, biotite and plant debris.

Uraninite and coffinite are considered to be authigenic together with Häggite, anatase, an expanding clay mineral, heulandite and calcite and ground-water behaviour is therefore an important control on mineralization. Mineralization is commonly associated with plagioclase undergoing solution and with quartz mica schist fragments (carbonaceous varieties possibly being preferred).

The source area for the Siwaliks lay to the north and comprised predominantly low-grade schists and slates. A possible source of the uranium is detrital uranium minerals derived from the rising Himalayas.

1. INTRODUCTION

Sandstone uranium deposits occur in the foothills of the Sulaiman Range in the Dera Ghazi Khan District of Pakistan. They are confined to a single horizon, more or less conformable with the host rocks, near the base of the Middle Siwalik member of the Siwalik formation. This formation is composed of 16 000 - 18 000 ft of fluvial sediments and extends from the Middle Miocene to the Lower Pleistocene (Krishnan [1]). In this area the Siwaliks form a narrow north-south trending belt, about 190 miles long and dipping to the east. The core samples on which the present study is based were obtained from the best known development of mineralization at Baghal Chur in the northern part of the outcrop (Fig. 1). According to Krishnan [1] three main rock types are present in the Middle Siwaliks (600-800 ft thick): brown and hard grey sandstones, gravel beds, orange clays and drab shales. The samples examined in this study are all of the first type (the local informal name is Baghal Chur sand) which characterizes the lower part of the Middle Siwaliks. They are considered to be representative of non-oxidized (below water table) and oxidized (above water table)

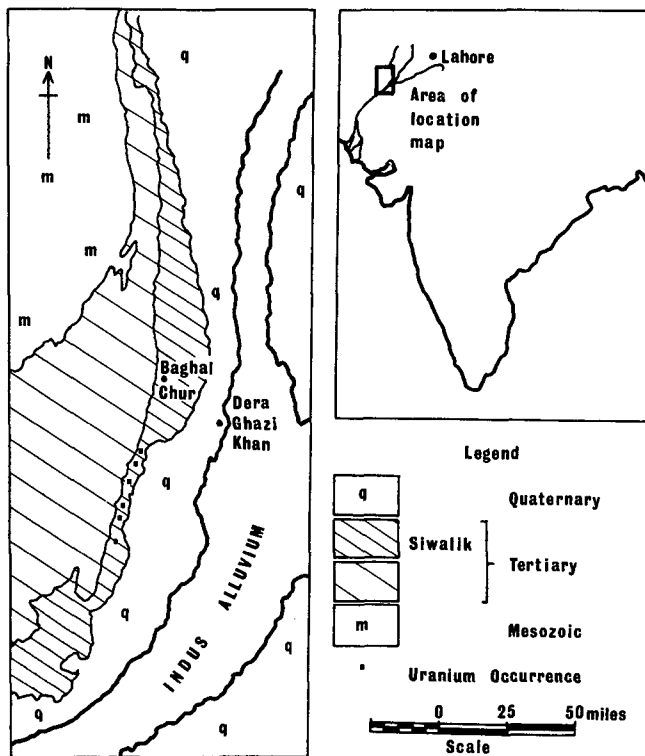


FIG. 1. Location map of uranium occurrences in the Baghal Chur region, Pakistan. (Modified after Moghal [2]).

uranium mineralization. In addition, a sample from the transition zone, apparently without uranium mineralization, is included. The object of this paper is to describe the mineralogy of the host rock and contained uranium minerals and to use these data to comment on the possible genesis of the deposits. The structural and sedimentary framework within which the uranium-bearing host rock was deposited and the mode of occurrence of the uranium are discussed by Moghal [2].

2. GENERAL MINERALOGY

The host rock for uranium mineralization is a grey, fine to medium grained, rather friable subgreywacke (definition of subgreywacke after Pettijohn [3]). It is dominantly composed of metamorphic rock fragments and quartz, accompanied by feldspar, hornblende and biotite (Table I). This is essentially the same assemblage as that described by Krynine [4] for Siwalik "low rank greywackes" to the northeast of this area. The detrital components are well sorted and in places are cemented by calcite

TABLE I. MODAL ANALYSES OF THE NON-OXIDIZED AND OXIDIZED ZONES OF MINERALIZATION FOR SIX COMPONENTS (500 POINTS COUNTED PER SAMPLE)

Sample No.	Non-oxidized zone			Oxidized zone
	2-73, 250	125-72, 255	W1	1 13
	(%)	(%)	(%)	(%)
Quartz	28,5	36,0	27,0	25,0
Rock fragments	44,0	20,5	33,0	18,0
Feldspar	10,5	11,5	14,0	8,5
Biotite	4,0	2,0	2,0	1,5
Hornblende	2,0	6,0	4,0	2,5
Calcite	6,0	14,0	15,0	39,0
Rest	5,0	10,0	5,0	5,5
	100,0	100,0	100,0	100,0

with subordinate but fairly common heulandite. The latter mineral occurs as small ($< 100 \mu\text{m}$), colourless, euhedral crystals and forms coatings around some rock and mineral fragments.

Häggite and an expanding clay mineral (possibly vanadiferous) occur as coatings on detrital grains in the most radioactive sample so far examined (GD3AA). The häggite is best developed as cavity infillings (Fig. 2) but most commonly occurs as black lustrous acicular crystals dispersed in a blue-grey clay coating. It is a rare mineral, previously described intergrown with a doloresite-type mineral from sandstone uranium deposits in the United States of America (Evans and Mrose [5]).

The metamorphic rock fragments are predominantly of low-grade, fine-grained schists with some slates (occasionally pyritiferous) and quartzites. The following schist fragments have been recognized: quartz biotite (the most common), quartz-epidote, quartz-muscovite, quartz-muscovite-biotite and rare chlorite, graphite and talc schists. Some of these are extensively replaced by calcite and occasionally by heulandite. The finer-grained schists commonly contain feldspar and variable amounts of carbonaceous material. Fragments of red sandstone, dolerite, porphyry, highly altered (igneous?) rock and serpentinite also occur rarely in the assemblage.

The low density (< 3.3) monomineralic grains principally consist of quartz, feldspar and biotite with some muscovite, chlorite, jasper. Some calcareous mud pellets are also present. Quartz commonly shows strain shadows and occasionally corroded margins. Coarse flakes of biotite (sometimes partially altered to chlorite) and muscovite are fairly common. The feldspars include microcline, orthoclase and plagioclase, with K-feldspar approximately equal in amount to plagioclase. Many feldspar

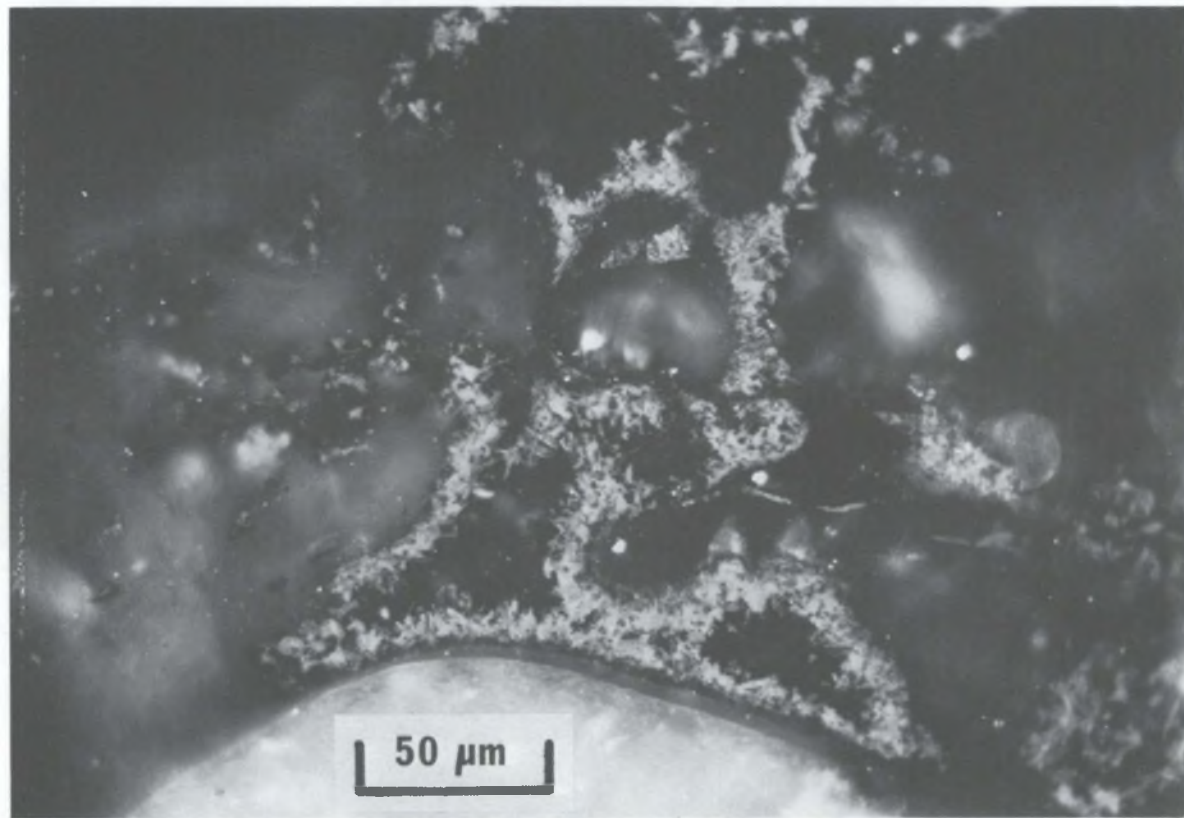


FIG. 2. Photomicrograph (reflected light, oil immersion), showing coatings of acicular haggite on detrital grains (sample GD 3AA).

grains, particularly of plagioclase, are altered and corroded and in some cases only cavernous pseudomorphs remain. Alteration is to sericite and/or calcite and fine-grained unidentified material. In general, though, the detrital component is fresh.

The most abundant heavy mineral is hornblende, followed by ilmenite, garnet, epidote and kyanite in roughly equal amounts, with smaller quantities of staurolite, sphene, rutile, tourmaline, zircon and hypersthene. Krynine [4] also reported apatite and authigenic barite. Magnetite is commonly magnetized and there are foxy red and amber varieties of rutile and pink and red garnets.

The barren transition zone is composed of a friable, biotite-rich, medium to coarse grained siliceous sandstone not containing rock fragments. Muscovite, plant debris (frequently pyritiferous) and disseminated pyrite are common. The last occurs in part as aggregates up to 1 cm in diameter. Rarely, rutile, graphite, garnet and epidote are also present.

3. URANIUM MINERALIZATION

The distribution of uranium has been studied using fission-track radiography and autoradiography, radiometric assays on various rock fractions and bulk samples, and bulk rock chemical analyses for U_3O_8 as well as Th, V and Cu. The technique of fission-track radiography used is based on that described by Kleeman and Lovering [6]. Neutron irradiation was 5×10^{14} thermal neutrons/cm².

3.1. Non-oxidized mineralization

The tenors of U_3O_8 (Grutt [7]) and V (Table II) are comparable to those found in the sandstone uranium deposits of the United States of America. Copper is low relative to U_3O_8 and V, which is consistent with the observation by Stanton [8] that few deposits of this type are enriched in both V and Cu. Thorium is not significantly enriched.

The bulk rock ($(\beta + \gamma)/\gamma$) radiometric ratios show that uranium is out of equilibrium and that this is due to a deficiency of daughter products. This is in keeping with the discrepancy between equivalent and chemical U_3O_8 and the low alpha-particle flux for uranium minerals.

Fission track radiographs show that uranium is localized and associated mainly with detrital grains of various types, although some interstitial pockets also occur. Examination of uraniferous areas by reflected light microscopy shows that most of the uranium is located in aggregates of minute ($< 1 \mu m$) granules with the aggregates often showing colloform textures. The optical properties of these aggregates are consistent with those of fine-grained uraninite (Uytenbogaardt and Burke [9]). Uraninite and coffinite have been confirmed by X-ray diffraction on handpicked specimens from microscope slides and grains separated from lightly crushed rock.

Electron probe analyses of uraninite-rich areas are shown in Table III, single uraninite crystals being too small for individual analysis. The analyses are noteworthy for their high Ti (analysis 1 only), Si and V. In addition, traverses across these areas indicate that U, Ti and V are evenly distributed. X-ray powder photographs of these and optically similar areas

TABLE II. BULK ROCK ANALYSES (ppm) FOR U_3O_8 , Th, V, Cu, eU_3O_8 AND $(\beta + \gamma)/\gamma$ FROM THE MINERALIZED AND TRANSITION ZONES

Sample	U_3O_8			eU_3O_8	$(\beta + \gamma)/\gamma$	Th	V	Cu(Cu*)
	*	DNA	XRF					
Non-oxidized mineralization								
W1	1850	n.d.	900	700	1.1	30*	1200*	8 40
2-73,250	n.d.	1500	1700	1400	2.2	7	570	10
125-72,255	n.d.	900	900	800	1.7	7	710	11
GD 3AA	n.d.	6300	7300	4000	1.4	5	9800	12
Oxidized mineralization								
I13	1910	n.d.	1500	1050	b	30*	1400	10 60
Transition zone								
M5	24	n.d.	n.d.	n.d.	n.d.	30*	100*	n.d. 66

^a Radiometric assays carried out using mica end-window Geiger-Müller tube equipment. U_3O_8 (DNA), and Th and V carried out by neutron activation analysis on the Herald Reactor facility at A.W.R.E., Aldermaston.

* $U_3O_8^*$, Th*, V* and Cu* = Personal communication, J. Cameron, IAEA. Analyses by the IAEA Siebersdorf Laboratory on different splits of the same sample. Cu analysis carried out at I.G.S. by atomic absorption; analyst: D. Hutchison.
n.d. = not determined.

^b γ -activity very low.

show essentially oxidized uraninite with some patterns having a few weak additional lines which could be attributed to minor amounts of ilmenite, quartz and anatase. The apparent insignificance of these associated minerals suggests that elements such as Si, Fe, Ti and V are not wholly present in discrete mineral phases.

The uranium minerals commonly form a skin around partially or completely altered plagioclase feldspar and also line the cavities occurring within the altered portions. The other main location is within the quartz-mica schist fragments in which quartz is often corroded and sometimes mineralization is so intense as to make the schist opaque. Schists with carbonaceous material seem to be preferred as sites for uranium mineral development. A bulk biotite separate was found to contain 1075 ppm V and 2070 ppm U_3O_8 (neutron activation analysis) suggesting that it also is a site of uranium enrichment.

TABLE III. ELECTRON PROBE ANALYSIS^a OF THREE URANINITE-RICH AREAS IN SAMPLE NUMBER 2-73.250

Area	1	2	3
	(%)	(%)	(%)
SiO ₂	11.21	9.48	4.93
UO ₂	60.88	74.98	66.95
TiO ₂	17.26	0.76	0.19
V ₂ O ₅	3.68	10.21	22.96
CaO	1.40	2.99	3.28
PbO	1.38	0.76	tr.
FeO	1.96	0.75	1.31
	97.77	99.93	99.62

^a Analyst, G.D. Taylor.

Radiometric assays of various rock fractions provide quantitative evidence that the bulk of the radioactivity is closely associated with rock and mineral fragments of SG < 3.3 (Table IV). These data show that 98.8% and 85.9% of total eU_3O_8 are located in material with an SG < 3.3 and magnetic separations demonstrate a concentration of eU_3O_8 in the medium to non-magnetic fractions (Tables V and VI), where the schist fragments, biotite and feldspar predominate.

Considerable enrichment of eU_3O_8 occurs in the heavy minerals and in sample number 125-72.255 they contain 14.1% of the total eU_3O_8 (Table IV). This radioactivity is spread through the various magnetic fractions with the least value in the non-magnetic fraction (Tables V and VI). However, the medium to strongly magnetic fraction (sample 125-72.255) contains the highest proportion of total eU_3O_8 and X-ray diffraction studies have demonstrated the common occurrence of uraninite. Its apparent high magnetic susceptibility is so far unexplained. Martite occasionally contains high levels of uranium but no inclusions of uranium minerals have been found and presumably the uranium is adsorbed.

Uranium concentrations also occur in some of the rounded grains of goethite and hematite but, as with martite, no discrete uranium minerals have been found in this material.

3.2. Oxidized mineralization

Samples from this zone contain amounts of U_3O_8 , V, Th and Cu (Table II) comparable to those from the non-oxidized zone and, as in the latter, the uranium is out of equilibrium. Tyuyamunite is the only uranium mineral identified and it forms yellow coatings on some detrital

TABLE IV. DISTRIBUTION OF eU_3O_8 WITH GRAIN SIZE AND DENSITY FOR TWO SAMPLES FROM THE ZONE OF NON-OXIDIZED MINERALIZATION

Fraction		wt%(W)	$\frac{eU_3O_8}{(\%)}$	% of total $\frac{eU_3O_8}{(T)}^a$	Concentration (T/W) factor
Density	Grain size BS mesh				
Sample 2-73,250					
< 2.7	-30 + 60	68.0	0.11	56.9	0.84
	-60 + 120	13.1		9.0	0.69
	-120	5.7		8.7	1.53
		86.8		74.6	
2.7-3.3	-30 + 60	9.8	0.27	20.1	2.05
	-60 + 120	1.8		2.2	1.22
	-120	1.4		1.9	1.36
		13.0		24.2	
> 3.3	Total	0.2	0.81	1.2	6.0
	heavies				
			Bulk rock	0.14	
Sample 125-72,255					
< 2.7	-60 + 120	64.1	0.05	47.4	0.74
	-120	18.5		16.4	0.89
		82.6		63.8	
2.7-3.3	-60 + 120	13.5	0.10	19.9	1.47
	-120	2.5		2.2	0.88
		16.0		22.1	
> 3.3	-60 + 120	0.5	0.56	4.1	8.20
	-120	0.9		10.0	11.11
		1.4		14.1	
			Bulk rock	0.08	

^a Normalized.

TABLE V. DISTRIBUTION OF $\underline{e}\text{U}_3\text{O}_8$ WITH MAGNETIC SUSCEPTIBILITY^a FOR THREE DENSITY FRACTIONS FROM SAMPLE 2-73.250

Magnetic fraction	wt% (W)	$\underline{e}\text{U}_3\text{O}_8$ (%)	% of total $\underline{e}\text{U}_3\text{O}_8$ (T) ^b	Concentration (T/W) factor
<u>SG < 2.7 (-30 + 60 BS mesh)</u>				
Highly magnetic	0.1	0.10	0.1	1.0
Strongly magnetic	4.8	0.22	7.4	1.5
Medium magnetic	6.4	0.30	13.5	2.1
Weakly magnetic	17.5	0.18	22.1	1.3
Non-magnetic	39.3	0.05	13.8	0.4
	<u>68.1</u>		<u>56.9</u> (see Table IV)	
<u>SG 2.7-3.3 (-30 + 60 BS mesh)</u>				
Highly magnetic	0.8	0.41	2.2	2.8
Strongly magnetic	0.5	0.38	1.3	2.6
Medium magnetic	5.5	0.30	11.1	2.0
Weakly magnetic	1.5	0.39	4.0	2.6
Non-magnetic	1.5	0.15	1.5	1.0
	<u>9.8</u>		<u>20.1</u> (see Table IV)	
<u>SG > 3.3 (Total heavies = 0.2%)</u>				
Highly magnetic	n.d.	0.49	-	-
Strongly magnetic	n.d.	0.41	-	-
Medium magnetic	n.d.	0.65	-	-
Weak to non-magnetic	n.d.	0.26	-	-

^a Magnetic separations by Frantz isodynamic separator. Magnetic cuts are arbitrary but taken so that magnetite, ilmenite, garnet and epidote characterize the highly, strongly, medium and weakly magnetic fractions respectively.

^b Normalized; n.d. = not determined.

TABLE VI. DISTRIBUTION OF $\underline{e}\text{U}_3\text{O}_8$ WITH MAGNETIC SUSCEPTIBILITY FOR THREE DENSITY FRACTIONS FROM SAMPLE 125-72.255

Magnetic fraction	wt% (W)	$\underline{e}\text{U}_3\text{O}_8$ (%)	% of total $\underline{e}\text{U}_3\text{O}_8$ (T) ^a	Concentration (T/W) factor
<u>SG 2.7 (-60 + 120 BS mesh)</u>				
Highly magnetic	0.2	0.13	0.5	2.5
Strongly magnetic	1.3	0.14	3.3	2.5
Medium magnetic	4.3	0.12	9.4	2.2
Weakly magnetic	1.7	0.10	3.1	1.8
Non-magnetic	56.6	0.03	31.1	0.6
	<u>64.1</u>		<u>47.4</u>	
<u>SG 2.7-3.3 (-60 + 120 BS mesh)</u>				
Highly magnetic	7.4	0.12	12.3	1.7
Strongly magnetic				
Medium magnetic				
Weakly magnetic				
Non-magnetic	6.1	0.09	7.6	1.3
	<u>13.5</u>		<u>19.9</u>	
<u>SG 3.3 (-60 + 120 BS mesh)</u>				
Highly magnetic	0.08	0.60	0.6	7.5
Strongly magnetic	0.11	0.80	1.1	10.0
Medium magnetic	0.21	0.64	1.6	7.6
Weakly magnetic	0.05	1.04	0.6	12.0
Non-magnetic	0.05	0.35	0.2	4.0
	<u>0.50</u>		<u>4.1</u>	

^a Normalized.

grains and also occurs interstitially. The bulk of the radioactivity (99%) is in the < 3.3 SG fraction, as the tyuyamunite is closely adherent to the detrital grains and is not easily liberated.

3.3. Transition zone

This zone is not significantly enriched in uranium and the only uraniferous material is pyritiferous plant debris where the uranium is presumed to be adsorbed. Vanadium is much lower than in the mineralized zones but Th and Cu values are comparable.

4. POSSIBLE ORIGIN OF THE URANIUM MINERALIZATION

There is very good evidence that uranium enrichment occurred subsequent to sedimentation, a situation typical of sandstone uranium deposits. It seems reasonable at this stage to ascribe an authigenic origin to the uranium minerals and also to h aggite, anatase and the (vanadiferous?) clay. Heulandite (Hay [10]) and calcite are common authigenic minerals in freshwater lithic sandstones and the present authors consider that "a sharp distinction cannot be drawn between the authigenic minerals formed by diagenetic alteration and the uranium ore ..." as noted by Weeks and Eargle [11] for Texas sandstone uranium deposits. Thus ground-water behaviour must be an important control on mineralization. On the microscopic scale further controls have been recognized. Mineralization tends to occur close to areas of relatively high silica activity such as dissolving plagioclase and quartz and is also associated with biotite. Earthy phases such as goethite and hematite also concentrate uranium probably by adsorption. It is well known that carbonaceous material can produce strongly reducing conditions suitable for uranium deposition and there is some evidence that the carbonaceous schists are favoured areas for deposition. On the other hand the transition zone contains considerable plant debris but is only weakly enriched in uranium.

This zone may represent a position above the permanent water table from which uranium has been leached. The high calcite content of the oxidized zone (Table I) may be attributed in part to the present (and past?) aridity of the climate. Loss of CO₂ from ground water would precipitate uranium by reaction with vanadate ions to form tyuyamunite.

The absence of equilibrium due to a relative deficiency of daughter products is interesting. This situation could arise either from the uranium being "young" and not having attained equilibrium or because daughter products have been removed by selective leaching.

Although the mineralizing solutions were ground waters rich in carbonate (judging by the common calcite cement), the ultimate origin of the uranium (and vanadium) is less clear. One possibility is that circulating ground waters leached uranium from detrital uranium minerals and precipitated it where conditions were suitable, but so far no detrital uranium minerals have been found. Moghal [2] reports that the Baghal Chur sand was derived from the north and the present study confirms the conclusion of Krynine [4] that the source area was dominated by low-grade metamorphic rocks, principally schists and slates.

Such rocks characterize the Precambrian in the Lower Himalayas of the western Punjab region (Gansser [12]) which form part of the source area for the present-day Indus gravels. Further, more detailed comparisons between the source areas for the Siwaliks and Indus gravels can be made. Quartzites, chlorite schists, ultrabasic rocks and kyanite, hornblende and garnet-bearing metamorphic rocks are common to both. Thorian uraninite and uranothorite occur in the Indus gravels (Bowie [13]), but are probably absent from the Siwalik samples, judging by the low bulk-rock thorium contents (neutron activation values preferred). Also, pegmatitic uraninite has been recorded from the Precambrian of Rajasthan (Choudari et al. [14]). Although detrital uranium minerals could provide a source for the uranium, they do not account for the vanadium concentrations and the authors feel that any theory to account for the origin of the uranium must also explain the origin of the vanadium.

5. CONCLUSIONS

The uranium mineralization in the Siwalik sandstones is comparable in many respects with the sandstone deposits of the United States of America. The uranium minerals identified in the non-oxidized zone are uraninite and coffinite while tyuyamunite occurs in the oxidized zone. Uraninite and coffinite are authigenic minerals together with haggite, heulandite, anatase, (vanadiferous?) clay and calcite, and ground-water behaviour is therefore an important control on mineralization. Mineralization is commonly associated with plagioclase undergoing solution and with quartz mica schist fragments (carbonaceous varieties possibly being preferred). In addition, uranium concentrations are found in goethite, hematite, martite, biotite and plant debris. The mineralization is out of equilibrium but the reason, as yet, is unknown. The source area for the host rock was dominated by low-grade schists and slates and in terms of its direction and geology seems comparable to that of the present-day Indus whose gravels contain uranium minerals. It is possible that the original source of the uranium is detrital uranium minerals derived from the rising Himalayas, but this hypothesis does not explain the origin of the vanadium.

ACKNOWLEDGEMENTS

The authors would like to thank Dr. S.H.U. Bowie for constructive criticism and presentation of the paper. They would also like to thank the A.W.R.E. Aldermaston for neutron activation analysis, Mr. D. Atkin of I.G.S. for X-ray identification, and Mr. G.D. Taylor of the Department of Geology and Mineralogy, Aberdeen, for electron probe analysis. The paper is produced by permission of the Director, Institute of Geological Sciences.

REFERENCES

- [1] KRISHNAN, M.S., *Geology of India and Burma*, Higginbothams (Private) Ltd, Madras, India (1956).
- [2] MOGHAL, M.Y., "Uranium in Siwalik sandstones, Sulaiman Range, Pakistan", these Proceedings, Paper IAEA-SM-183/41.

- [3] PETTIJOHN, F.J., *Sedimentary Rocks*, Harper, New York (1957).
- [4] KRYNINE, P.D., *Petrography and genesis of the Siwalik series*, *Am. J. Sci.* **34** (1937) 422.
- [5] EVANS, H.T., MROSE, M.E., *A crystal chemical study of the vanadium oxide minerals, h aggite and doloresite*, *Am. Mineral.* **45** (1960) 1144.
- [6] KLEEMAN, J.D., LOVERING, J.F., *Uranium distribution studies by fission track registration in Lexan plastic prints*, *At. Energy Aust.* **10** (1967) 3.
- [7] GRUTT, E.W., "Prospecting criteria for sandstone-type uranium deposits", *Uranium Prospecting Handbook* (BOWIE, S.H.U., DAVIS, M., OSTLE, D., Eds), (Proc. NATO-sponsored Adv. Institute on Methods of Prospecting for Uranium Minerals, London, 1971), *Inst. Min. Metall.*, London (1972) 47.
- [8] STANTON, R.L., *Ore Petrology*, McGraw-Hill, New York (1972).
- [9] UYTENBOGAARDT, W., BURKE, E.A.J., *Tables for Microscopic Identification of Ore Minerals*, Elsevier, Amsterdam (1971).
- [10] HAY, R.L., *Zeolites and Zeolitic Reactions in Sedimentary Rocks*, *Geol. Soc. Am. Special Paper No. 85* (1966).
- [11] WEEKS, A.D., EARGLE, D.H., "Relation of diagenetic alteration and soil forming processes to the uranium deposits on the southeast Texas coastal plain", *Clays and Clay Minerals*, (Proc. 10th Nat. Conf. Clays and Clay Minerals; Austin, Tex., 1961), MacMillan, New York (1963).
- [12] GANSSER, A., *Geology of the Himalayas*, Wiley Interscience, London (1965).
- [13] BOWIE, S.H.U., "Uranium - the present and future", *Mining and Petroleum Geology* (Proc. 9th Commonwealth Min. Metall. Congr. London, 1969) **2**, *Inst. Min. Metall.*, London (1970) 405.
- [14] CHOUDARI, R., KOSZTOLANYI, C., COPPENS, R., *Etude d'une uraninite provenant de la pegmatite de Rajasthan (Inde)*, *Bull. Soc. Fr. Mineral. Cristallogr.* **90** (1967) 77.

DISCUSSION

S.S. ADAMS: One of your slides showed coffinite and uraninite in a thin band surrounding what I believe were titanium-bearing grains. Do you believe that this phenomenon - the replacement of a detrital titanium-bearing mineral by uranium - adds any useful evidence in favour of the "Pronto Reaction" and reinforces the suggestion that the brannerite of the Blind River ores was formed in precisely this manner?

S.H.U. BOWIE: All the evidence suggests that the brannerite in the Blind River field post-dates the main detrital minerals, such as zircon and monazite, which are about 2000 m.y. old. I believe the oldest brannerite - and I am speaking from memory here - is around 1750 m.y. old. There is evidence, in sections, of the breakdown of that brannerite to rutile; thus one finds ghost brannerite grains now represented by laths of rutile. There is no uranium in them. But, closely associated with these brannerite grains that have been altered to rutile, one finds what appears to be a late-phase generation of uraninite itself: beautiful euhedral crystals of uraninite, not rounded in any way as are some of the older crystals. The oldest of these have been dated by Canadian geologists and mineralogists at 1500-1600 m.y., and the more recent euhedral crystals are as young as 500-600 m.y. Hence this has obviously been a long process, in the course of which some kind of remobilization was in progress. It seems to have been, if I may say so, the "Pronto Reaction" in reverse.

S. CONSTANTINO HERRERA: How much significance would you attach to the sample in which uranium is associated with magnetite? Our observations in Mexico suggest that the likelihood of finding a good uranium occurrence increases with decreasing magnetite. Were your specimens from core drillings or were they channel samples?

S.H.U. BOWIE: The samples were taken from core drillings. Only in sample 125-72.255 was an appreciable amount of uranium associated with the martite. We have here what appears to be a fairly highly magnetic uraninite. Since this is hardly likely, it seems that there must be some remnants of hematite-martite left in the grains which superficially look like uraninite. However, this association remains so far unexplained.

G.R. UDAS: In Table III we find large differences in the TiO_2 content of the three areas: 17.26, 0.76 and 0.19%. Could this be due to the fact that the samples were collected in oxidizing zones?

S.H.U. BOWIE: Areas 1 and 3 were selected to show the main differences of composition in the samples. The large amount of vanadium in area 3 is attributable to the presence of vanadium minerals.

G.R. UDAS: If uranium is thought to be derived from a breaking up of thorian uraninite, where has the thorium gone? Our experience in the Indian Shield indicates deposition of huttonite, co-precipitating with hematite, and mobilization of uranium with ground water. Would you care to comment on this?

S.H.U. BOWIE: The uranium has precipitated from ground water. However, the absence of thorium and presence of vanadium do make it difficult to explain a derivation of uranium from Indus-type thorian uraninite, as the authors suggest.

G.R. UDAS: Do you think that the presence of amphiboles might be utilized to locate the source rock?

S.H.U. BOWIE: Yes, it might well provide information on the source rock.

R.I. RACKLEY: Radiometric disequilibrium is a common feature of sandstone-type deposits in the United States of America. If reduced portions of the roll fronts are immediately down-dip, uranium leached from the oxidized zone is redeposited on the front immediately below the ground-water table. This enrichment may be of the order of 200-300%, and the depletion of the radioactive sections of the oxidized-weathered zone may be almost complete.

URANIUM DEPOSITS IN THE KAROO SUPERGROUP NEAR BEAUFORT WEST, CAPE PROVINCE, SOUTH AFRICA

J. W. von BACKSTRÖM
Geology Division,
Atomic Energy Board,
Pretoria, South Africa

Abstract

URANIUM DEPOSITS IN THE KAROO SUPERGROUP NEAR BEAUFORT WEST, CAPE PROVINCE, SOUTH AFRICA.

During the past two years sporadic occurrences of uranium mineralization of variable grades have been discovered in the Beaufort Group of the Karoo Supergroup of sedimentary rocks in the area around Beaufort West, Cape Province. Up to now, uranium mineralization has been confined to the Lower Formation of the Beaufort Group. Although the tenor of surface mineralization varies from trace amounts to more than 2%, average grades are below $\pm 0.05\%$. The principal surface manifestation of uranium mineralization in the Karoo rocks is the bright green and yellow coloration displayed by the secondary uranium minerals, mainly along joint planes. No attempt has been made to evaluate the resources of the newly discovered uranium deposits in the Karoo Supergroup, since the exploration and investigations to date are still regarded as inadequate and it is too early to predict their significance and true potential. An understanding of the origin of the Karoo deposits is paramount if their exploration is to be pursued intelligently.

1. INTRODUCTION

During the past two years sporadic occurrences of uranium mineralization of variable grades have been discovered in the Beaufort Group of the Karoo Supergroup of sedimentary rocks in the area around Beaufort West, Cape Province (Fig.1). The credit for this discovery must go to the geologists of the Union Carbide Company of the United States of America.

Rocks assigned to the Karoo Supergroup cover about 40% of South Africa and the whole of Lesotho, and are found in large areas of Swaziland, in Mozambique, in the western part of Rhodesia and over much of Botswana; they are also present in South West Africa and Angola.

The Beaufort Group derives its name from the two towns of Beaufort West and Fort Beaufort, and comprises a thick sequence of fine clastic sediments that reaches a maximum thickness of 5000 m. It contains an abundant and diversified fauna of fossil reptiles, most of which are assignable to the order Therapsida which are mammal-like reptiles. This fauna is the primary source on which present-day understanding of the reptile-to-mammal evolutionary transition is based.

The beds of the Beaufort Group are generally horizontally disposed and produce a topography characterized by broad plains and flat-topped hills and mountains. Although this simple topography is diversified by the legions of sills and dykes of resistant dolerite, most of the mineralization found to date, except that in the Fraserburg district, is generally situated to the south of the termination of the well-known imaginary "dolerite line".

Within South Africa, strata of the Karoo Supergroup form a huge and very gently dipping structural basin, measuring over 1300 km in an east-west, and 650 km in a north-south direction. This enormous expanse forms

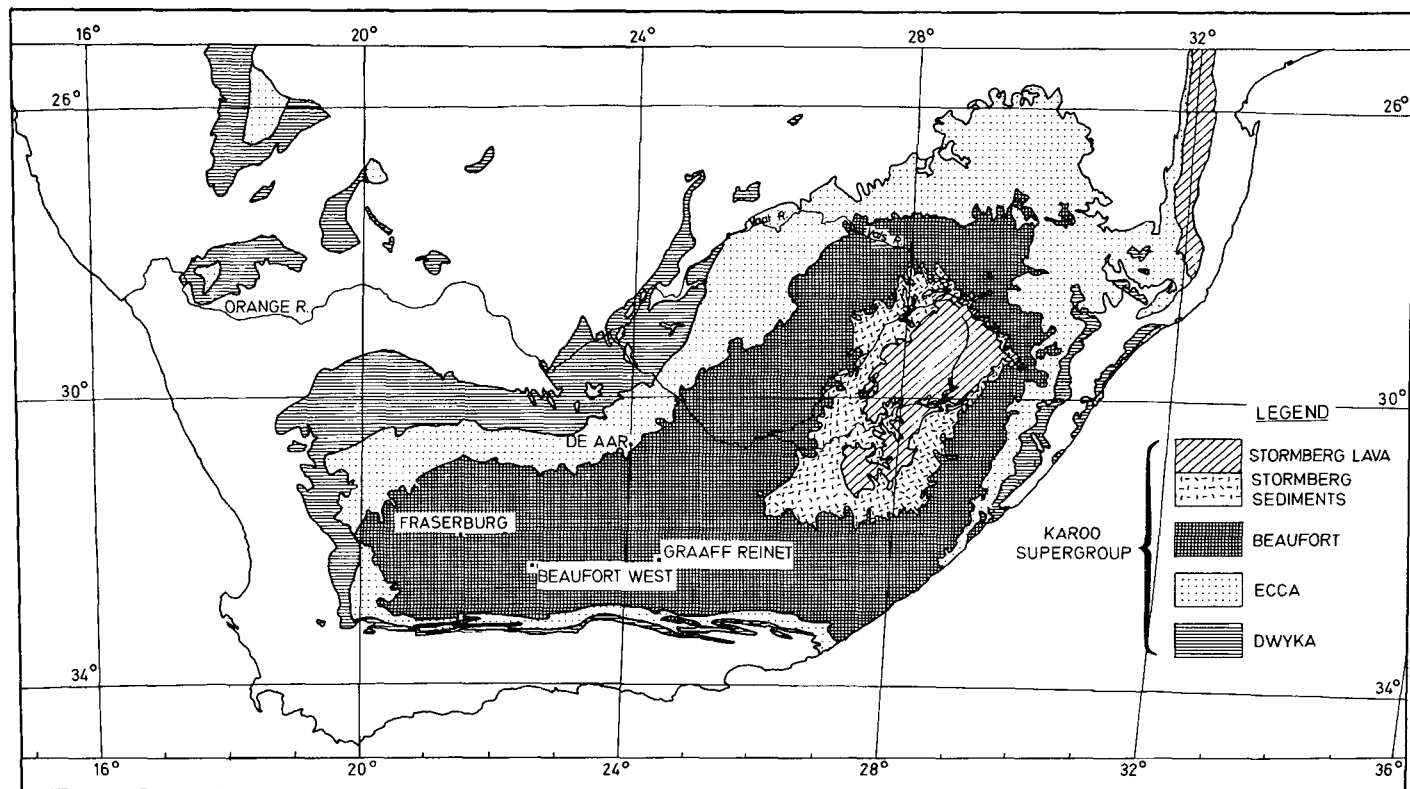


FIG. 1. Areal distribution of the Karoo Supergroup.

TABLE I. SUCCESSION WITHIN THE KAROO SUPERGROUP

Group	Formation	Biozone
Stormberg	Drakensberg lava Cave sandstone Red beds Molteno	
Beaufort	Upper Middle Lower	Cynognathus Lystrosaurus Daptocephalus Cistecephalus Tapinocephalus
Ecca	Upper Middle Lower	
Dwyka	Upper Tillite	

the type area for the group, and developed within it is a sequence of glacial deposits, sandstones, mudstones and shales, largely of continental deposition, and thick flows of lava, all intersected by and interlayered with dykes and sheets of dolerite. The presence of workable seams of coal and fossil plants and abundant remains of fossil vertebrates – fishes, amphibia, reptiles – have made the group one of outstanding interest to geologists; this interest has now been further enhanced with the recent discovery of uranium mineralization.

2. GEOLOGY

On both lithological and paleontological grounds the Karoo Supergroup has been subdivided into formations, members and biozones in the following order, from above downwards, in the type area (Table I).

No detailed study of the geology has been published to date but the following facts appear to be fairly well established:

- (a) Up to now, uranium mineralization has been confined to the Lower Formation of the Beaufort Group. Lithologically, the Beaufort Group in this area is differentiated from the Upper Stage of the underlying Ecca Group by the appearance of purplish shales and mudstones. Both groups consist of bands of spheroidally weathering greenish or bluish sandstones, greenish flagstones, coloured mudstones and shales, and calcareous concretions. Green cherty bands and clay pellet conglomerates occur along certain zones, especially near the base in the area north of Prince Albert.
- (b) Hand specimens of the above-mentioned rocks are fairly dense and non-porous in appearance although the beds themselves may be permeable, owing to bedding and joint planes.

- (c) The irregularities in the bedding are a striking feature which results in the fact that a particular lithological unit can seldom be traced for more than a few kilometres.
- (d) Uranium mineralization is most often associated with deposits formed along erosion channels and washouts.
- (e) Clay pellet conglomerate lenses, fragments of clay, rolled pieces of bone and major carbon trash accumulations are common. These may be either fossil flora, fossilized bones or carbonaceous material.
- (f) Geographically very similar sedimentary deposits reach far beyond the Lower Beaufort Formation, and no known sound geological reasons exist why similar uranium discoveries should not also be made in some of the other formations or groups.
- (g) The uranium deposits in the Lower Beaufort Formation are thinly bedded lenses in which the uranium minerals occur along the bedding planes and joint fissures. In places the uranium-impregnated beds reach a metre in thickness.
- (h) Although the tenor of surface mineralization varies from trace amounts to more than 2%, average grades are below $\pm 0.05\%$. Mineralization naturally gradually fades into the country rock along the bedding far beyond where the cutoff values are taken.
- (i) There appears to be widespread association of uranium with organic remains or fossils, either fossil flora, fossilized bones or carbonaceous material.
- (j) Yellow and green discoloration due to the presence of secondary uranium minerals is common, but some prominent radioactivity anomalies were encountered in dark brown to black rocks which exhibited no bright colours on the outcrop.
- (k) Some discrete grains of primary uraninite have been found in borehole cores recovered from below the water table.

3. MINERALIZATION

The principal surface manifestation of uranium mineralization in the Karoo rocks is the bright green and yellow coloration displayed by the secondary uranium minerals, mainly along joint planes. It is also present as discretely disseminated grains and small sporadic pods in sandstones, greywackes and clay-pellet conglomerates.

Petrographic examination revealed the presence of a complex variety of secondary uranium-bearing minerals, primarily bright green metazeunerite, bright yellow arsenuranylite and pale yellow uranophane, derived from the primary minerals uraninite and coffinite.

The uranium minerals are associated with some minor sulphides which in some areas are responsible for discoloration in the surface rocks. Heavy mineral concentrates contain pyrite, chalcopyrite, arsenopyrite, bornite, ilmenite, digenite, rutile and martite.

4. POTENTIAL

No attempt has been made to evaluate the resources of the newly discovered uranium deposits in the Karoo Supergroup, since the exploration and investigations to date are still regarded as inadequate and it is too early

to predict their significance and true potential. Drilling programs are in progress and, from the limited information available, it would appear that they are mainly shallow, flat-lying deposits. Geological knowledge indicates that there is good reason to believe similar deposits will be found in areas like those already discovered, but any attempt to quantify the potential of these undiscovered resources on the basis of the extent of unexplored but favourable ground will, at this stage, amount to mere guesswork. Furthermore, the ideas of what is conceivably discoverable and producible will surely change with the development of new knowledge about the origin and occurrence of uranium in the Karoo, and advances in mineral recovery, extraction metallurgy and use technology.

5. ORIGIN

An understanding of the origin of the Karoo deposits is paramount if their exploration is to be pursued intelligently. At this early stage of exploration not much is known about the requisite geological environment, conditions of deposition, etc. since so little work of a fundamental nature has been undertaken.

The uranium in the deposits are of both syngenetic and secondary origin. Whether all the secondary uranium is derived from the syngenetic uraninite is an open question. The Karoo Supergroup rests on granite basement in the Southern Karoo but is also overlain by more than 1000 m of volcanic rocks in Lesotho and elsewhere. So the question of the origin of the secondary uranium at this stage is still a wide open one.

DISCUSSION

H.C. WHITESIDE: Perhaps I should add, after Mr. von Backström's discussion of the uranium deposits in the Beaufort Formation at Beaufort West, that uranium occurrences have been recorded at a number of sites in the Karoo System. In the Livingstonia District of Malawi, uranophane is to be found in sandstone, probably above the coal horizon of the Middle Eccia Series. In Zambia there are occurrences near the Zambesi rift valley. In Rhodesia the uranium is found in post-Karoo faults and is probably derived from Karoo beds. Yellow uranium oxides have been found in sandstones below the Coal Measures in North and South Botswana. In general, I think it is fair to say that uranium is more widespread in the Karoo System, both laterally and vertically, than is realized.

R.G. DODSON: How were the deposits discovered in the first place?

J.W. von BACKSTRÖM: The uranium deposits near Beaufort West were first discovered with a carborne scintillation counter, by geologists of the Union Carbide Company of the United States of America, who undertook a systematic survey of the area.

R.G. DODSON: Do you have any idea what the uranium content of the coal seams in this district is?

J.W. von BACKSTRÖM: I do not know whether they have been tested for uranium, but I have been told that the pseudo-coal veins of the Merweville area are radioactive.

J. PASQUALI: Could you say anything about the relationship, if there is any, between the dolerites of the Karoo and the uranium mineralization recently found?

J. W. von BACKSTRÖM: There is no evidence at all that the dolerite played any role in the genesis of the recently discovered uranium mineralization in the Karoo rocks.

R. H. DE VOTO: You mention detrital uraninite in these rocks. Is it possible, in your opinion, for detrital uraninite to be transported by rivers? If so, how far do you think the material could be effectively carried from its source, and what are the effects of mechanical destruction, oxidation and weathering and so on likely to be? I have in mind Mr. Cameron's suggestion regarding the uraninite in the modern Indus River bedload.

J. W. von BACKSTRÖM: This is undoubtedly a very interesting question, but I am not yet able to answer it. At this early stage of our investigations, little if any attention has been given to theoretical considerations of the source of the detrital uranium found in the sedimentary rocks.

T. S. ARY: I have a general comment to make. It seems to me that the Working Groups would be wise to give careful consideration to the question which Mr. Joubin raised after Mr. Moghal's paper. It is an important question; so important, in fact, that it sums up the justification for holding this Symposium. "Where and what is the source of uranium?" — this is perhaps the most fundamental question an exploration geologist has to consider. The theoretical aspects of uranium deposition are more than an idle academic exercise: they provide us (we hope) with the basic information we need to evolve a rational plan of exploration.

Thus it is important that we should discuss questions of source, transport, distance from source and chemistry. The importance of these questions in relation to particular sites will vary, of course, depending on the stage that has been reached in exploration or exploitation. As others have said, it makes a big difference whether one has an operating mine or is in a virgin area looking for a new deposit. Our discussions here have been largely "after the fact" in the sense that they bear on known deposits; but if we are to discover those new deposits to which Mr. Nininger referred, we will have to draw on all the experience available to us which can suggest practical guides for exploration. The Working Groups would therefore do well to consider Mr. Joubin's question and solicit written statements on the subject which could be included in the Symposium Proceedings.

A. DURANDAU: It is important, I agree, that the papers presented here should suggest practical guides to prospecting. Perhaps the most critical thing is not to gauge the exact distance between the uranium source (granitic rocks or volcanic formations) and the deposit — we know that in the case of granite the distance can vary from a few kilometres to more than a hundred kilometres — but rather to seek that concurrence of favourable factors which permitted disaggregation of the parent rock with subsequent mobilization, transport and fixation of uranium. In the paleogeographic study carried out on any region of interest, paleoclimatology should occupy an important place, because it governs the oxidation-reduction potential and other critical factors.

CONTROLS AND GENESIS OF URANIUM MINERALIZATION IN SOME GEOLOGICAL ENVIRONMENTS IN INDIA

G. R. UDAS, T. M. MAHADEVAN
Atomic Minerals Division,
Department of Atomic Energy,
New Delhi, India

Abstract

CONTROLS AND GENESIS OF URANIUM MINERALIZATION IN SOME GEOLOGICAL ENVIRONMENTS IN INDIA.

The favourability factors influencing localization of uranium are discussed in relation to some selected geological environments in India, namely, the Tertiary Siwalik sedimentary basin along the Himalayan foothills, the Permian Motur and Bijori beds on the Satpura Gondwana basin in Central India, the Palaeozoic phosphorites of the Mussoorie Krol-Tal basin, certain Precambrian conglomerates and sandstones in the Dongargarh system of Central Madhya Pradesh, and some syenitic and granitic rocks from different parts of India. The association of uranium with the copper-lead-zinc mineralization in the Bihar-Madhya Pradesh-Rajasthan metallogenic province and the tectonic controls in localization of uranium are briefly discussed. Instances of fluorite-uranium association in India are cited which support the use of fluorite as a favourable clue in the search for uranium.

1. INTRODUCTION

Exploration for uranium carried out in India in the past laid great emphasis on identifying and developing structurally controlled uranium deposits in the Precambrian metamorphic complexes. With the increased need for augmenting uranium resources to meet future nuclear power programmes, the priorities in exploration are being shifted to locate sedimentary types of uranium deposits, in which better grades and large reserves may be expected. Significant zones of enrichment of uranium have been located in two major sedimentary basins, in quartz-pebble conglomerate types, phosphorites and granitic rocks. Although commercially workable resources are yet to be identified in some of these environments, the data that have accrued on the geotectonic, geological and geochemical controls influencing the localization of these zones of uranium enrichment are of relevance to discussions on the formation of uranium deposits. Data on some selected mineralized zones are presented in this paper and it is hoped that the interest that they evoke at this Symposium will help to refine further the exploration strategy.

2. URANIUM IN SEDIMENTARY BASINS

2.1. Uranium in sandstone-shale-conglomerate sequences

Significant uranium concentrations are located in (a) the Siwalik formations of Tertiary age along the Sub-Himalayan foothills, and (b) the Permian Motur beds deposited in a graben as part of the Gondwana sequences in Central India.

2.2. Uranium in Siwalik formations

The Siwalik formations constitute a thick sequence of fresh water mollasse deposited in a long narrow foredeep formed to the south of the rising Himalaya during the third phase of the Himalayan orogeny. These formations are traceable in India from Jammu in the west to the Brahmaputra valley in the east.

The Siwalik formations consist of an interbedded sequence of fine- to coarse-grained sandstones, maroon and chocolate-coloured clays, silt, conglomerate and boulder beds. They were subjected to folding, faulting and overthrusting during the last phase of the Himalayan orogeny, which continued into the late Pleistocene. The fold axis, the faults and thrust planes have a NW-SE trend and the bedding dips are generally moderate and to the NE, but become steep along the fault and thrust zones. The whole sequence has been broadly classified into three divisions, the Lower, Middle and Upper on mainly lithological and partly palaeontological evidence. In the Lower Siwaliks, the sandstones are highly compact and well-cemented, have low porosity and permeability and the clay-sandstone ratio is generally near unity. The Middle Siwalik formations are less compact and have more favourable parameters of porosity and permeability and the sandstones predominate over clays. The Upper Siwaliks comprise loose sands, pebbles and boulder beds with subordinate clays and are highly permeable and porous.

The Siwalik sediments were deposited under lacustrine, piedmont, channel and flood-plain conditions and these environments shifted in time and space, resulting in both vertical and lateral variations [1]. Cycles of humid and arid tropical climates are inferred.

2.3. Uranium in fossils

The discovery of uranium in the vertebrate fossils in some museum collections helped to localize the search for uranium in the extensive Siwalik formations. The vertebrate fossils from the Upper Siwalik formations of Pinjor region were found to contain values of 0.05% to 0.34% U_3O_8 with no thorium. Uranium in the fossils is generally in disequilibrium in favour of the parent, suggestive of accretion of uranium into the fossils even in sub-recent times. These fossils are phosphatized and contain up to 33% P_2O_5 . The phosphate mineral is a fluorapatite. The uranium is fixed in it from circulating ground waters which had dissolved uranium from the rocks traversed by them. The Upper Siwalik sandstones hosting the fossils, however, are poor at present in uranium and, considering their high porosity and permeability, it seems possible that uranium from them may have been leached away by ground-water action; and in the event of its having migrated to subsurface zones favourable for precipitation of uranium, such zones would be of interest for exploration.

2.4. Uranium in lithic units

Concentrations of uranium occur mainly in a zone encompassing the upper part of the Lower Siwalik and the Middle Siwalik formations in the Ramshahr-Kalka-Morni region (near Chandigarh) Himachal Pradesh-Haryana [2,3] and in the area near Jammu [4]. Much of the Siwalik belt remains to be examined. The most promising concentrations are in hard grey to

greenish sandstones and the interbedded intraformational clay conglomerates which carry unoxidized greyish mudstone, shale and siltstone fragments, carbonaceous and sulphide material. The sandstones are of subgreywacke type, and carry numerous rock fragments. They are feldspathic and micaceous and have a calcite cement. Uranium values range from 0.02% to as high as 0.6% U_3O_8 . The primary uranium minerals are under identification. Uranium also occurs adsorbed in the clayey fraction of the sandstones. Uranophane is the most common secondary mineral. No significant alteration zones have been met with in the vicinity of the mineralized zones. The uranium concentrations are strata-bound; but transgressive relationship to bedding has been noted in a few locales. Uranium concentrations are confined to the Siwalik sequence where greenish sandstones predominate over reddish or maroon clay beds. These features indicate that the uranium concentrations are of the remobilized syngenetic type. There are, however, chances of locating epigenetic mineralization in the thrust and fault zones.

Available heavy mineral [1] and palaeocurrent data reveal that the Siwalik sediments were derived partly from the Himalayan region and partly from the Peninsular shield areas. These provenance areas have many zones of known uranium mineralization.

2.5. Uranium in Gondwana sediments

The Gondwana sediments were deposited in a graben and comprise four successive series. (1) The basal Talchir series consists of boulder beds (glacial or fluvioglacial?), sandstones and greenish to greyish needle shales. (2) These are overlain by the Barakars which consist of sandstones, clays and coal seams. The Barakars pass into (3) Moturs and Bijoris, and (4) the Pachmarhi beds in order of time sequence. The Barakars have been deposited in a lacustrine environment while the Moturs, Bijoris and the Pachmarhis are largely fluvial deposits. Significant uranium concentrations are contained in the Motur beds (Fig. 1) while thorium and uranium occur in the Bijori and to a lesser extent in the Pachmarhi sediments [5-7].

The Motur beds consist of current-bedded immature gritty greenish and grey feldspathic sandstones, clays and shales and lenses of conglomerates and pebble beds. The pebbles are of massive quartz, chert, jasper, and granite. Fragments of anthracitic coal are present locally. The Motur beds have low to moderate dips (5° - 20°) to the north, but are, however, locally folded into broad anticlines and synclines.

The Bijori beds are characterized by pale green and buff-coloured gritty and arkosic sandstones with pods and nodules of clays. They are thus similar in lithology to the Moturs but are, however, more carbonaceous and carry remains of fossil wood. While the remains in the Barakars are calcified, those in the Bijoris and Moturs are generally silicified and carbonaceous, a fact that reflects the differences in the oxidation conditions during the diagenesis and consolidation of the sediments in the two formations.

The Pachmarhi beds consist of white sandstones with quartz pebbles and feldspar fragments and reddish clays.

Significant uranium concentrations are met with in the Motur beds at Polapathar, Mansingpura, Bodipani, Chirmatekri and Kaoleri. In Polapathar, uranium deposition is influenced by differences in the permeability of the sandstones, in Mansingpura by interfingering of clay beds, in Bodipani by braided channels, and in Chirmatekri and Kaoleri by permeable sandstones

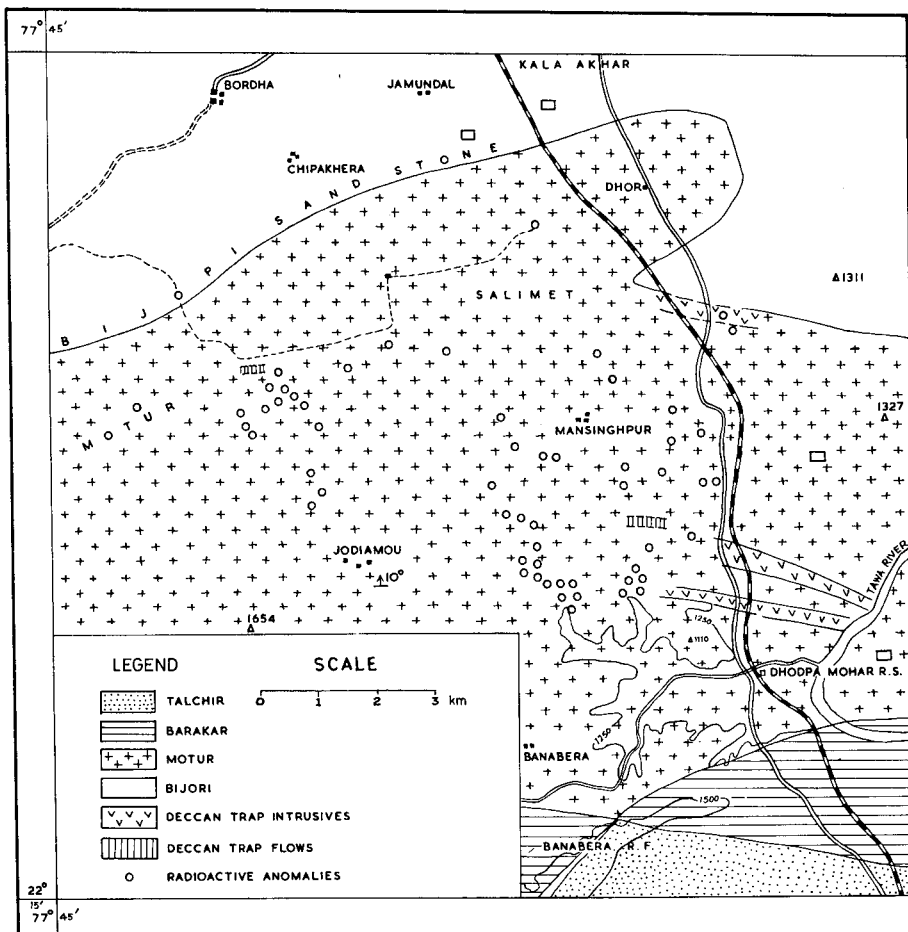


FIG. 1. Uranium anomalies in the Motur beds of Satpura basin.

enclosed by clay beds. In other words, contrasting physical and chemical discontinuities have favoured localization of uranium. The uranium occurrences in the Moturs are controlled by bedding, and roll-type mineralization has not so far been met with. They fall into four categories: (1) zones where uranium has been leached resulting in disequilibrium in favour of uranium; (2) zones where radioactive equilibrium prevails; (3) zones where uranium has been enriched and there is disequilibrium in favour of uranium; and (4) zones where thorium predominates over uranium. Most of the zones of enrichment of uranium are met with in depth (intersected by boreholes). The nature of disequilibrium conditions indicates remobilization of uranium and its enrichment in suitable locales by ground-water action.

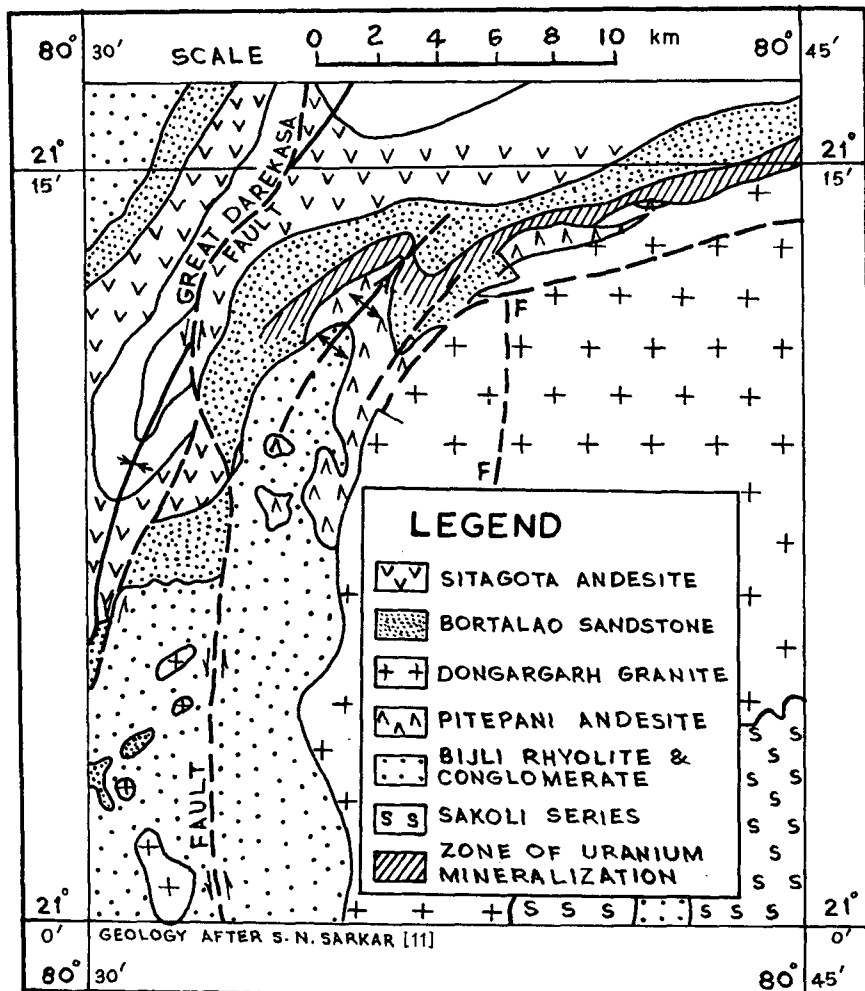


FIG. 2. Geological map of the Dongargarh area showing uranium occurrences.

Uranium occurs in the Motur sandstones in the form of black oxide of uranium, as coffinite and adsorbed in clays. The uranium values range from traces to as high as 0.2% U_3O_8 . Bluish coatings containing as much as 0.3% Mo are present in the sandstones. Vanadium is notably absent.

The Bijori sediments and to a lesser extent the Pachmarhi beds contain concentrations of Th-U minerals, mostly monazite, and zircon, occurring in association with ferruginous gritty sandstones, pebbly beds and conglomerates. The U:Th ratio ranges from 1:10 to 1:40 and can be related

to the zircon and monazite content in the sandstones. Enrichment of uranium is, however, met with in the ferruginous cappings on the sandstones as a result of weathering of the granites in the provenance area.

The presence of concentrations of uranium in the Moturs and the refractory nature of the radioactive minerals in the overlying Bijori indicate that the uranium in the Moturs has been introduced from either external sources by circulating waters or by redistribution of uranium in the Moturs themselves and may not have been derived from the overlying Bijori formations.

Palaeocurrent studies [8] indicate that the uranium concentrations in the Motur beds occur at the interface of two palaeocurrent directions intersecting each other at moderate to high angles. The provenance for the sediments are the Amla granite bodies in the southeast which contain 8 to 10 ppm of uranium.

The present ground waters draining the Amla granite have a pH of 9.5 to 9, which falls to 6.5 to 7 when the waters pass through the basal Talchir beds of the Gondwanas, and to 4.5 to 4 as they flow over the Moturs. If the present is the key to the past, these variations in pH reflect the conditions of deposition of uranium by ground waters in this basin [6].

2.6. Source of uranium and its mode of transport

In sedimentary formations, like the Siwalik and the Gondwanas, which have witnessed no magmatogenic hydrothermal activity, the prime source of uranium has to be intrinsic to the formations. Immature sediments would contain more of the rocks and mineral fragments and where the provenance is uraniferous these fragments would carry uranium minerals, thereby providing an internal source of uranium which could be mineralized and concentrated by ground water.

A fact that brings out the need for an immature sedimentary pile is that the relatively more mature Subathu and Kasauli beds underlying the Siwalik, which have many characteristics that favour concentration of uranium in them, are nevertheless devoid of any significant uranium concentrations. Similarly the Barakar sandstones underlying the Motur beds are also relatively more mature and are devoid of any uranium concentrations.

An important tectonic feature that would favour development of immature sediments is the rapid uplift of the provenance, a fact borne out by the Siwalik sediments which were deposited during the most intense period of Himalayan uplift. Such uplift of the provenance, therefore, seems to be an important favourability factor.

3. URANIUM IN PHOSPHORITE FORMATIONS

Although there are a large number of phosphatic rock deposits known in India, significant concentrations of uranium are met with only in the phosphorites of the Mussoorie syncline in the Lesser Himalayan region of Uttar Pradesh. These occurrences have been described in detail by Saraswath and Sankaran and co-workers [9]. The phosphorites in this area outcrop along the periphery of a doubly plunging syncline for some 120 km. The synclinal axis extends in a NW-SE direction for about 20 km. The syncline is 10 km where it is widest. The phosphorite horizon occurs at

the transition zone between the underlying Krol limestone and the overlying Tal shales and sandstones and has intercalations of chert and black shales. The phosphatic rock is generally dull grey to brownish in colour, and may be nodular, platy, laminated or granular. It is composed mostly of collophane and minor amounts of francolite and dahlite.

Although the phosphorite horizon is traceable over a larger part of the perimeter of the Mussoorie syncline, significant concentrations of uranium are confined to the area between Mussoorie and Sahasradhara in its southern limb. The uranium content in this zone averages 0.03% U_3O_8 over significant strike lengths, the width of the phosphorite being however only about a metre. The overlying black shales also contain uranium of the order of 0.01% to 0.02% U_3O_8 . It has been noted that there is no direct correlation between U and P_2O_5 in these phosphorites. This absence of correlation seems to be due to the fact that chemogenic precipitation of phosphates is possible under a much wider range of Eh-pH conditions than uranium.

Comparing the geological features of uraniferous and non-uraniferous phosphates in India, it is observed that the latter are characterized by the presence of stromatolitic structures, as at Jhamarkotra, Udaipur district, Rajasthan and the Pithoragarh district, Uttar Pradesh. It would appear that the algal and bacterial life that gave rise to the stromatolitic structures thrive only under conditions where oxygen is available, and such an environment does not help to build up the required redox potentials for precipitation of uranium.

In comparison with the Permian phosphorites of the USA, the uraniferous phosphorites of Mussoorie are characterized by relatively higher enrichment of Ni, Mo, V, Mn, Ba, Co, lesser amounts of Cr, La, and Sc and comparable amounts of Sr, Th, Y, and Zr. The Ni and Mo contents in some sections are as high as 0.2% and 0.16% respectively over significant strike lengths. The enrichment of these elements and the association with black shales bear out the extreme Eh conditions which favour uranium enrichment.

4. URANIUM IN QUARTZ-PEBBLE CONGLOMERATES

Of interest because of their special geological setting are the uranium occurrences observed in the Bartalao conglomerates occurring between two andesitic flows in the Dongargarh area of Madhya Pradesh [10, 11]. The formations are part of a volcanic-sedimentary sequence of the Dongargarh system of Precambrian age and occur along the periphery of an eugeosyncline. They are underlain by rhyolites, rhyolitic conglomerates and tuffaceous sandstones of the Bijli sequence, which rests on highly folded and metamorphosed gneisses and schists. Occurring close to these formations is the Dongargarh granite believed to be intrusive into the Bijli sequence. (Fig. 2.)

Uranium and thorium concentrations occur in the conglomerates at Kolarghat, Bartalao, Khampura, Burhanchhapur, Lachna, Bunnara, Udrichhappar and Bagadwani, the first four localities being mostly uraniferous while both uranium and thorium are found in the other localities. Uranium values in the surface samples are low, being of the order of 0.02% to 0.03% U_3O_8 , but higher spot values of 0.1% U_3O_8 are present. The uranium-thorium ratios where the two are associated range from 1:2 to 1:12. High

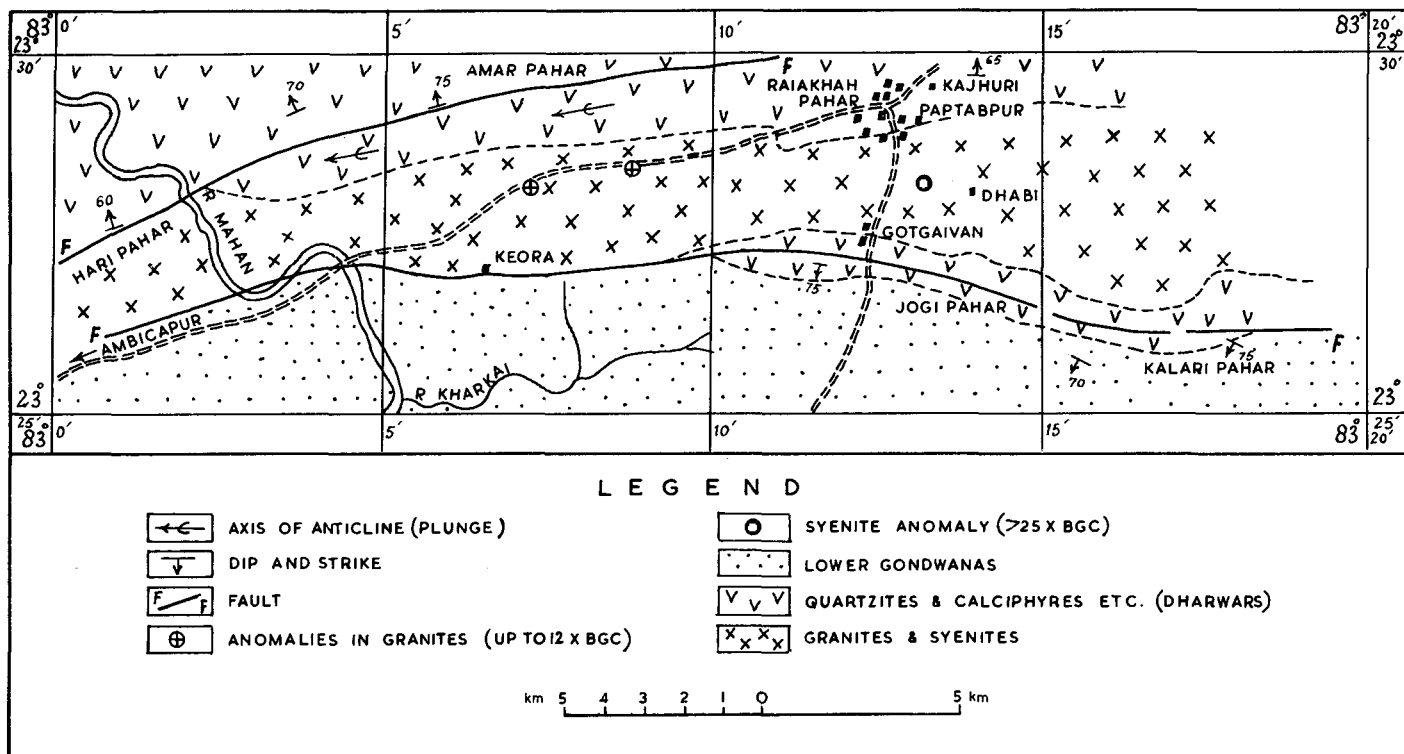


FIG. 3. Geological map of the Dhabhi-Pratabpur areas showing radioactive anomalies — District Sarguja (Madhya Pradesh), Sheet No, 64M/SW.

thorium values in the surface appear to be due to huttenite with uranium locked up in hematite. Drilling at Udrichhappar has indicated higher concentrations of uranium in depth and the presence of coffinite and uraninite with pyrite, these concentrations having been possibly affected by the action of ground water, the underlying andesite flow acting as a barrier.

The Dongargarh granites and associated pegmatites, over which the andesitic flows and Bortalao sandstones rest, themselves contain in places disseminations of uranothorite, thorogummite and uranophane. The rhyolitic tuffs and sandstones at the base of the Dongargarh system are also radioactive and show radioactivity of the order of 0.01% to 0.02% U_3O_8 .

4.1. Vein type of uranium deposits

Veins of pitchblende occur in a number of localities along tension joints in the crests of anticlinal folds in a quartzite of the Jaunsar sequence (palaeozoic) which forms a more or less persistent horizon in the Lesser Himalayan tectonic province, traceable from the Doda district of Jammu-Kashmir in the west to the Nepal border in the east. Clusters of these veins with variable vein-density have been located in Kishtwar in Jammu and Kashmir [12], Chhinjra-Jari-Kashapat area in Himachal Pradesh [13, 14] and in the Almorah-Pithoragarh districts of Uttar Pradesh [15]. The geological setting in most of these areas is similar, in that the quartzites are overlain by chlorite schists and gneisses, all these formations being folded and now preserved in synclines.

The pitchblende veins vary in thickness from a fraction of a centimetre to 3 cm and are traceable for over a length of as much as 10 m. They extend only to shallow depths of 5 m from the surface. Pitchblende also occurs as intergranular fillings in the quartzite along the vein margins. In some locales, as at Kiroli in Pithoragarh, the veins occur along sheared fractures. Pyrite, chalcopyrite and chalcocite occur with pitchblende in minor amounts. Secondary uranium minerals like vandendriesscheite, uranogummite and beta-uranophane have been identified in these veins. Colloform structures in the pitchblende and occurrence of sooty varieties indicate that the mineralization took place at low temperatures.

The mineralizing solutions which gave rise to these pitchblende veins are believed to be of magmatogenic hydrothermal origin, emanating from some granite sources [14]. Support of this hypothesis is obtained in the recent discovery of uraniferous granites in the Central Himalayan gneissic complex in the Simla area. However, the age of these granites is not certain. Further, it cannot be overlooked that the veins could have been deposited by circulating ground waters which imbibed uranium from the overlying chlorite schists and from gneisses which are radioactive in places.

5. URANIUM DEPOSITS CATEGORIZED AS UNUSUAL OCCURRENCES

Concentration of uraninite and coffinite occur in the syenitic rocks of the Precambrian age at Dhabi, Madhya Pradesh [16]. These granitic gneisses have an E-W strike of foliation and steep dips of 60-70° to the NW. They are traversed by tear faults, and a number of oblique faults along which the granite rocks have been sheared and these have later become locales of hydrothermal activity. Zeolitization of the feldspars and occurrence

of uraninite, pyrite, arsenopyrite and quartz crystals mark these zones. Values of uranium as high as 0.2% U_3O_8 have been determined over a few metres in some of the boreholes.

Uranium concentrations also occur in the granitic rocks of a number of other areas in India, such as Wanaparathi, Dongargarh and Newania in the Peninsular shield and the Chaura-Tarandadhar area in the Himalayas. In most of these granitic rocks no primary minerals have been located. Uraninite and coffinite along with arsenopyrite, pyrite and fluorite, however, occur in vugs along fractures in some of the granites at Wanaparthi and Dongargarh. Secondary minerals occur along joints and other fractures in all the granites and result from oxidation of the primary uranium oxides in the rocks.

From comparison of the uranium mineralization in the granitic rocks of Dhabi with the others referred to above, it would appear that late-stage shearing and hydrothermal activity is an essential condition for the development of uranium concentration in the granitic rocks.

6. RELATIONSHIP OF METALLOGENIC, TECTONIC AND ZONING FACTORS TO THE ORIGIN OF URANIUM IN DEPOSITS

6.1. Uranium-copper metallogenic province

Uranium occurs in certain tectonic zones in the well-known Singhbhum Thrust Belt in Bihar and in parts of the Khetri-Dariba area in Rajasthan in close association with copper mineralization. Extending westwards from the Singhbhum region into Madhya Pradesh and then into Rajasthan is a metallogenic province, encompassing formations of the Iron-ore series, the Gangpur series, the Sakoli series and the Aravalli and Delhi systems, in which numerous locales of copper-uranium-lead-zinc mineralization have been observed. The locales of mineralization are themselves mostly zones of tectonization, although lithology has aided in some areas. The base-metal mineralizations belong to hypothermal to mesothermal and epithermal types. The tectonism in this region is mainly related to early to middle Precambrian fold movements, except in the Rajasthan region where an orogenic cycle of the late Precambrian has been superposed on the Archaean fold movements.

From an analysis of the tectonic styles, the metamorphic history of the areas, the mineralogy and paragenetic sequences in mineralization and the relative positions of the locales of copper-lead-zinc vis-a-vis uranium mineralization, the following conclusions are drawn on the metallotectonic controls relevant to an understanding of the processes of concentration of uranium in specific locales, which would ultimately lead to development of deposits:

- (a) Most of the mineralization is syntectonic to late tectonic.
- (b) Relatively high uranium values are found in the zones of intense tectonization and fall off away from them.
- (c) While relatively high temperature assemblages such as pyrrhotite-pentlandite-chalcopyrite-uraninite or pyrrhotite-chalcopyrite-uraninite tend to concentrate in the same structural locales along with uraninite and sooty pitchblende, there is, at the same time, large concentration

- of the latter, to the exclusion of the former, in parts of the same shear zone, but in parallel shear planes, as at Jaduguda and Khetri-Kolihan.
- (d) Vertical zoning has been observed in the uranium-mineralized zones in that there is an increase in Ni and Mo content in depth. Uranium vis-a-vis copper ores do not bear any distinct zonal relationship, possibly due to the fact that the tectonic zones are steep and confined to relatively narrow linear zones.
 - (e) The host rocks of uranium mineralization are of the green schist to amphibolite facies and higher granulite facies appear to inhibit uranium mineralization.

6.2. Association of fluorite veins

A characteristic geochemical association of fluorite with uranium mineralization is observed in a number of areas. The fluorite occurrences in the Chandidongri area of Madhya Pradesh are matched by the uranium mineralization in the Dongargarh area. In the vicinity, the fluorite occurrences at Chapoli in Rajasthan are matched by the high-temperature uranium mineralization in the Khandela area. There are major fluorite deposits [17] associated with alkaline igneous rocks and carbonatites in India with which uranium is associated, as for example at Ambadungar in Gujarat where uranium minerals (uranothorite?) are known and at Sevattur in Tamil Nadu where uranium pyrochlore deposits are known. Fluorite-bearing pegmatites in the Bhilwara district of Rajasthan have many uranium minerals in them. These associations support earlier views [18] expressed on the use of fluorite as a clue in the search for uranium.

REFERENCES

- [1] SAHNI, M.R., MATHUR, L.F., Stratigraphy of the Siwalik Group (Proc. 22nd Int. Geol. Congr. Delhi, India, 1964, Geol. Soc. India) Geol. Survey India, Calcutta (1964).
- [2] RAJENDRA SINGH, TIWARI, K.N., SWARNAKAR, B.M., KAZANCHI, B.N., Annual Report for the Field Season 1969-70; Unpublished Rep., Atomic Minerals Division, (AMD), Dept. of Atomic Energy, New Delhi.
- [3] SWARNAKAR, B.M., Annual Report for the Field Season 1970-71, Unpublished Rep. AMD, Dept. of Atomic Energy, New Delhi.
- [4] SETH, D.K., BARGAJE, V.B., Progress Report for the Field Season 1972-73, Unpublished Rep., AMD, Dept. of Atomic Energy, New Delhi.
- [5] UDAS, G.R., Annual Report for the Field Season for 1964-65, Unpublished Rep., AMD, Dept. of Atomic Energy, New Delhi.
- [6] RAO, V.V., Annual Report for the Field Season for 1965-66, Unpublished Rep., AMD, Dept. of Atomic Energy, New Delhi.
- [7] RAMA RAO, B.V., HANSOTI, S.K., Annual Report for the Field Season 1970-71, Unpublished Rep., AMD, Dept. of Atomic Energy, New Delhi.
- [8] VIRNAVE, S.N., Annual Reports for the Field Seasons 1968-69 and 1969-70, Unpublished Reps, AMD, Dept. of Atomic Energy, New Delhi.
- [9] SARASWAT, A.C., SANKARAN, A.V., VARADARAJU, H.N., TANEJA, P.C., BARGAJE, V.B., Geochemical Data on the Uraniferous Phosphorites of Mussoorie, Dehra Dun District, U.P., India, UNESCO-ECAFE Session on "Geochemical Prospecting", Colombo, Ceylon, 1970, ECAFE, Paris (1971).
- [10] SHARMA, D.S., Annual Report for the Field Season 1970-71, Unpublished Rep., AMD, Dept. of Atomic Energy, New Delhi.
- [11] SARKAR, S.N., Stratigraphy and tectonics of the Dongargarh System: a new system in the Precambrian of Bandara-Drug-Balaghat area, Bombay and Madhya Pradesh., J. Sci. Eng. Res., Ind. Inst. Techn. Kharagpur 1 (1957) 237; 2 (1958) 145.

- [12] KAUL, R., NIKAM, P. S., SAXENA, D. N., Uranium Investigations in Parts of Districts of Doda, Anantnag and Jammu, Jammu and Kashmir State, Unpublished Rep., AMD, Dept. of Atomic Energy, New Delhi (1969).
- [13] SARASWAT, A. C., DWIVEDY, K. K., Annual Report for the Field Season 1961-62; Unpublished Rep., AMD, Dept. of Atomic Energy, New Delhi.
- [14] PHADKE, A. V., "On the geology of uranium occurrences in the Kulu Valley (Punjab)", Symposium on Uranium Prospecting and Mining in India, Jaduguda Mining Project, Jaduguda, Bihar, India, 1964, AMD, New Delhi (1964).
- [15] VASUDEVA RAO, M., Annual Report for the Field Season 1970-71, Unpublished Rep., AMD, Dept. of Atomic Energy, New Delhi.
- [16] SESHADRI, K. V., Progress Reports for the Field Seasons 1969-70 and 1970-71, Unpublished Reps, AMD, Dept. of Atomic Energy, New Delhi.
- [17] MURTHY, Y. G. K., Certain aspects of the Occurrence of Fluorites in India and its Exploration, (Proc. Indo-Soviet Symp. on Recent Trends in Exploration of Minerals, Oil and Ground Water, Indian National Science Academy, New Delhi, 1973), to be published by the Wadia Inst. of Himalayan Geology.
- [18] GABLEMAN, J. W., in Uranium Exploration Geology (Proc. Panel Vienna, 1970), IAEA, Vienna (1970) 374.

DISCUSSION

M. Y. MOGHAL: How extensive are the significant mineral occurrences that you mentioned?

G. R. UDAS: The largest runs for 300 m in the strike direction.

M. Y. MOGHAL: Have you found any paleochannels in your Siwaliks?

G. R. UDAS: No, not as yet.

M. Y. MOGHAL: You said that the mineralization occurs at the contact between lower and upper Siwaliks. At Baghal Chur we find the main mineralized area in the centre of the middle Siwaliks, and as we follow the strike southwards the mineralization tends to approach the contact between upper and middle Siwaliks. Do you think that this shift from upper horizons in the south to lower horizons in the north and east has any special significance?

G. R. UDAS: I doubt it. Uranium becomes concentrated wherever a suitable impermeable trap is available to control the ground water. At Morni the compact, well-cemented conglomerate serves as an impermeable bed. However, our present knowledge of the subject is such that it would probably be unwise to draw any general conclusion from the fact that the mineralization appears to drop to lower horizons as one moves from south to north or from west to east.

GENESIS OF URANIUM DEPOSITS OF THE TONO MINE, JAPAN

N. KATAYAMA, K. KUBO, S. HIRONO

Power Reactor and Nuclear Fuel Development Corporation,
Tokyo, Japan

Abstract

GENESIS OF URANIUM DEPOSITS OF THE TONO MINE, JAPAN.

The uranium deposits of the Tono mine, Gifu Prefecture, Japan, occur in the basal part of the Toki group of Miocene age, and are distributed in the tributaries or at the head of channels on the plane of unconformity under the formation. These features characterize the basal ground-water type of uranium deposit, and they are unique in that their typical ore mineral is a zeolite of the heulandite-clinoptilolite group, uranium being adsorbed in it.

The paper presents the history of formation of the Tsukiyoshi deposits, the most intensely explored in the Tono mine. The matrices of conglomerates and sandstones of the Toki group usually contain tuffaceous material, which has been montmorillonitized or zeolitized diagenetically. The conduit of uranium-bearing ground waters that migrated from the basement granites into the Tertiary sediments was controlled by the impermeable barriers, which are rocks in which montmorillonite predominated, or by the Tsukiyoshi fault, as well as by channel structures. Where the waters became rather stagnant, uranium was adsorbed in zeolite from them.

Enrichment of uranium further proceeded locally as follows. Pyrite was oxidized to produce sulphuric acid solution which leached the uranium that had been adsorbed in zeolite. The pH of the uranium-rich solution became higher and higher in the course of migration and, as soon as it reached about 4, the uranium in the solution was again adsorbed in zeolite, the uranium content of which may have been enriched up to 0.9%. Coffinites have been formed where uranium was accumulated over the adsorption capacity of zeolite or where strongly reducing conditions were maintained by carbonaceous matter.

1. INTRODUCTION

The indication of uranium deposits in the Tono mine, Gifu Prefecture, Japan, was first detected by a carborne survey team of the Geological Survey of Japan in 1962, and the results of subsequent studies by the Survey were published in Report No. 232 of Geological Survey of Japan [1]. In 1967, the Power Reactor and Nuclear Fuel Development Corporation (PNC) took over the exploration work in the Tono area from the Atomic Fuel Corporation (AFC) in the course of the absorption of the AFC by the newly established PNC. The exploration by AFC and PNC [2] resulted not only in the discovery of ore reserves of over 4500 t of uranium but also in discoveries of interesting features of uranium ores and deposits that are worthwhile to report. It is the main object of this paper to elucidate those interesting features and the genesis of the ore deposits, especially of the Tsukiyoshi deposits, which have been explored rather intensively.

2. GEOLOGICAL SETTING (Fig. 1)

The basement of the area is mainly composed of granites, late Cretaceous to early Tertiary in age. They contain considerable amounts of leachable uranium. The Tertiary system overlying the basement

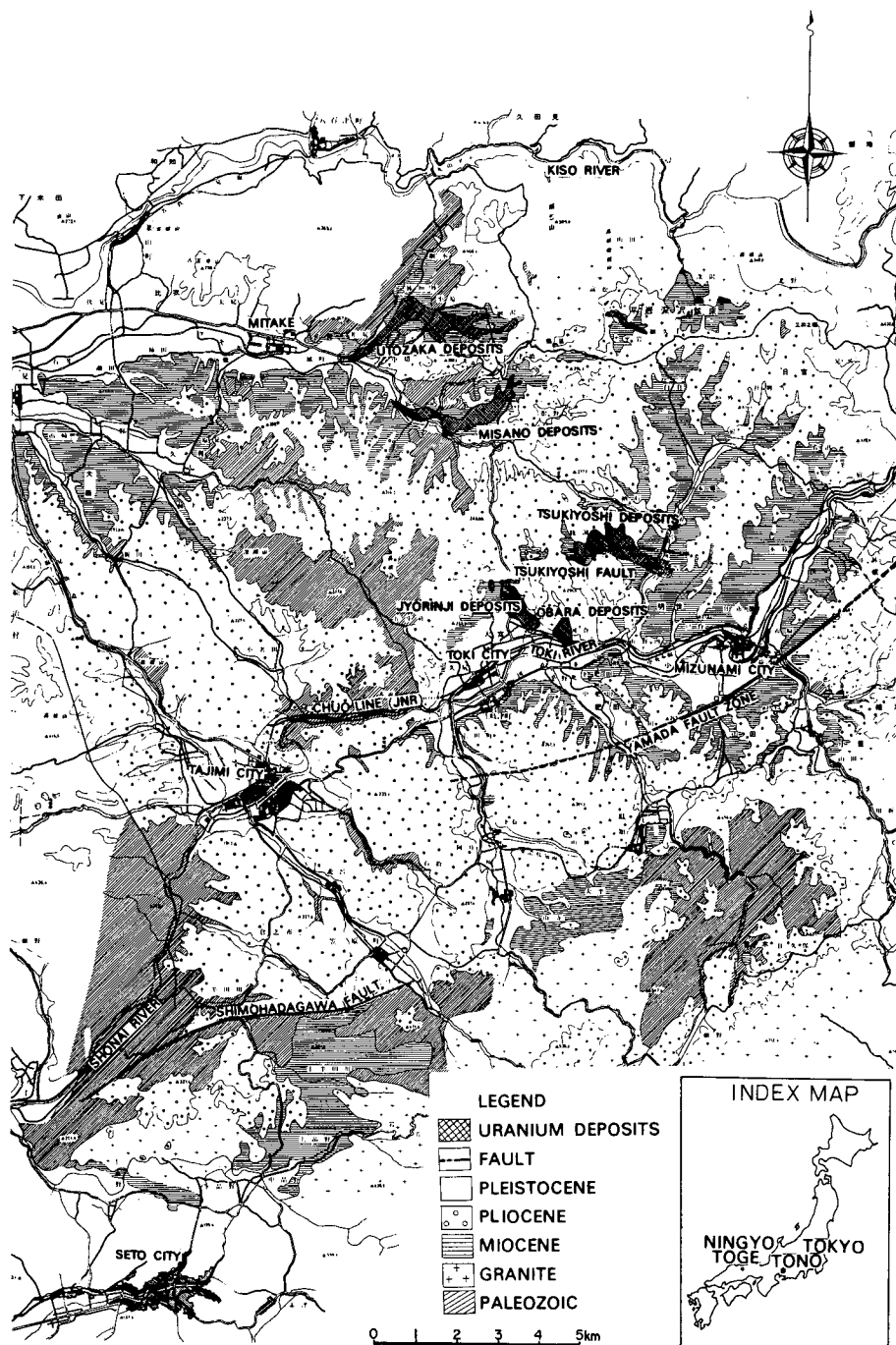


FIG. 1. Geological map of the area including major uranium deposits of the Tono mine.

is divided into three groups, Toki, Mizunami and Seto in ascending order. The Toki group is middle Miocene in age, and is represented by the Toki lignite-bearing formation in most of the area, and composed of conglomerates and carbonaceous mudstones and sandstones, with sporadic lignite beds. Most of the uranium deposits in this area occur within the Toki group. The Mizunami group contain many fossils of marine fauna which indicate middle Miocene age. The basal part of the Mizunami group is composed of various facies that were deposited in a stage of marine transgression. Overlying unconformably the Mizunami group, there is the Seto group of Pliocene age, the lower members of which are composed of clay and quartz sand, and the upper members of thick gravel beds.

Though there was no volcanic activity within the area in the Miocene, accumulation of volcanic ash was remarkable through the Toki and Mizunami ages, and even the matrices of sandstones and conglomerates contain heavy minerals of volcanic origin [3]. Heavy minerals of granitic origin occur exclusively in the Toki group.

A considerable part of the volcanic ash has been montmorillonitized; and especially in the Toki group and lower parts of the Mizunami group it has been diagenetically zeolitized [4-6]. Most of zeolites in this area belong to the heulandite-clinoptilolite group (abbreviated to H-C zeolite in the following), and are an effective adsorbent for uranium.

There is a reverse fault named Tsukiyoshi Fault, E-W, 65° - 70° S, with a throw of 35 m. It cuts the Tsukiyoshi deposits and seems to be relevant to the enrichment of uranium.

3. URANIUM ORE DEPOSITS

There are four groups of uranium deposits in the Tono area which have been explored successfully. They are the Jorinji, Tsukiyoshi, Misano and Utozaka deposits; at Tsukiyoshi the driving of an exploration gallery is now in progress. They are almost exclusively formed within the Toki group and their distribution is generally controlled by channel structures on the plane of unconformity above the basement (Figs 2 and 3). That is, they are upstream of channels or adjacent to the basement against which the Toki group abuts, and broad main channels, which are over hundreds of metres in width and over several kilometres in length, are usually barren.

There is a unique ore mineral in the Tono uranium deposits, namely H-C zeolite, which adsorbs uranium up to about 1%. The description of this mineral is left to another section.

In some cases, uranium is found adsorbed in carbonaceous matter or montmorillonite. In high-grade ores coffinite usually appears, especially in carbonaceous matter. Uraninite is contained in local high-grade ores, accompanied by coffinite and pyrite. There is another type of high-grade ore which is mainly composed of uranium calcite, cementing the matrix of the conglomerate with siderite and pyrite. In the Jorinji Deposits, there is an oxidized ore body which contains uranocircite as a main ore mineral [7]. Barium may have been leached from the weathered feldspars of the basement granites, and precipitated not only as uranocircite but also as barite in weathered granite [3]. It was also reported that the barium content of the Tertiary sediments of the Tono area reaches the order of 10^3 ppm [8].

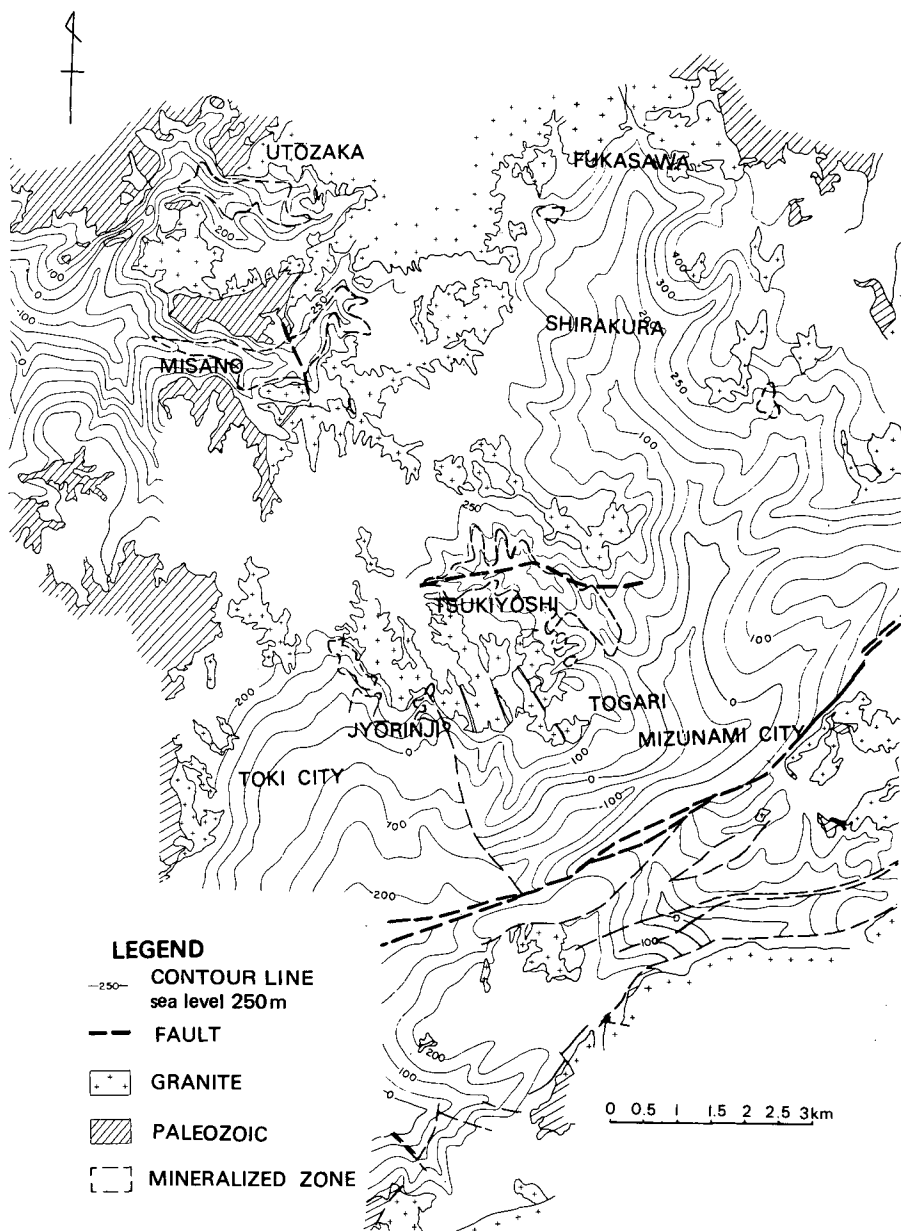


FIG. 2. Underground contour map of the plane of unconformity above the basement of the Tono area.

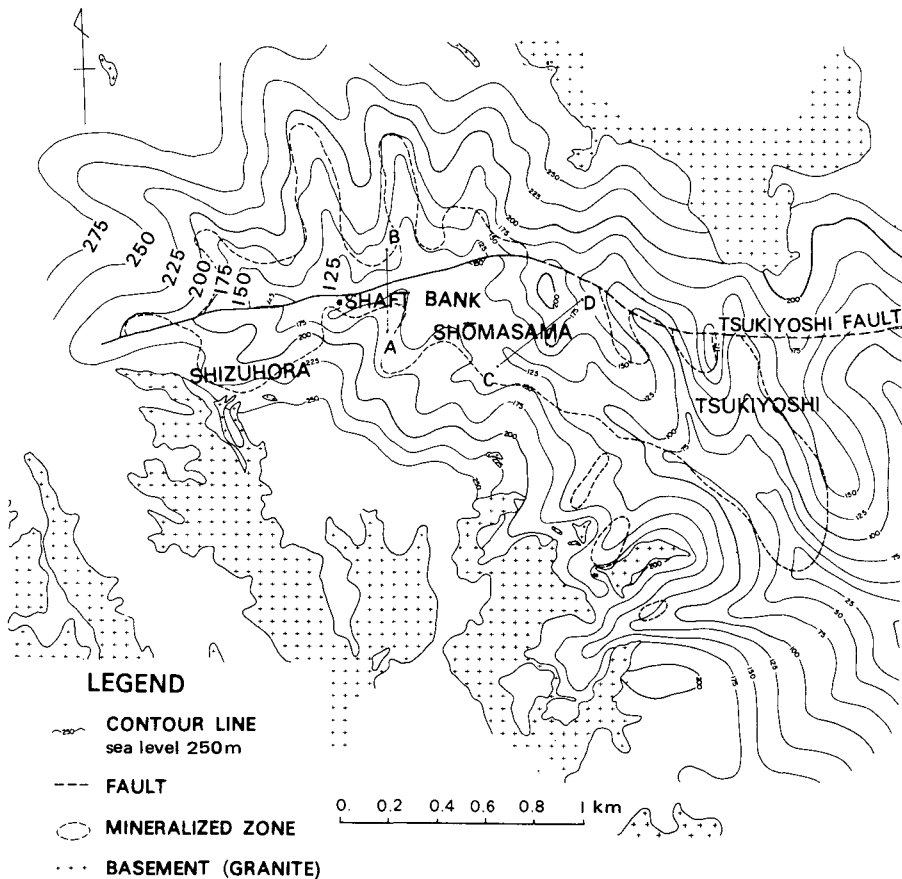


FIG. 3. Underground contour map of the plane of unconformity above the basement of the Tsukiyoshi area.

4. THE TSUKIYOSHI DEPOSITS

Since exploration work at this moment is concentrated on the Tsukiyoshi deposits, a more detailed description will be given of their features. As depicted in section AB of Fig. 4, they are formed in conglomerates and sandstones of the Toki group and shifted by the Tsukiyoshi fault, which means the mineralization of uranium preceded the movement of the Tsukiyoshi fault or deposition of the Pliocene. On the other hand, as inferred from Fig. 5, which shows concentration of uranium in the neighbourhood of the fault, some later mineralization of uranium may have taken place. This can be interpreted as follows: because the Tsukiyoshi fault is an impermeable wall, new traps for ground water may have been formed along the fault, and there additional concentration of uranium has occurred.

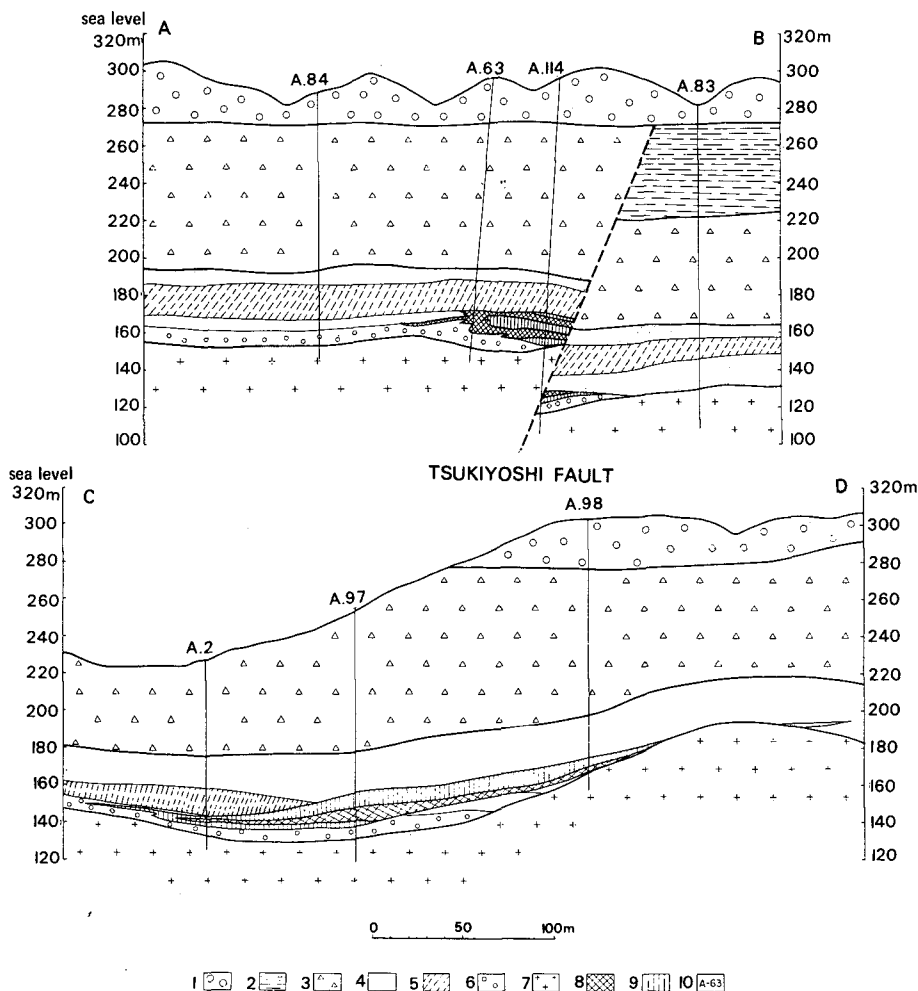


FIG. 4. Geological cross-sections of the Tsukiyoshi deposits. (1) Seto group; (2) upper members of the Mizunami group; (3) lower members of the Mizunami group; (4) sandstones and shales in the Toki group; (5) carbonaceous sandstones in the Toki group; (6) conglomerates in the Toki group; (7) basement granite; (8) high-grade ores; (9) low-grade ores; (10) borehole.

The boundary between the high-grade ore body near the fault and the barren zone is usually very sharp (Figs 6 and 7), and easily recognizable by the naked eye, for the ore is chocolate brown and the other greenish to bluish grey in colour (Fig. 8). The chocolate brown colour may be attributed to the irradiated zeolite in the ore, and the greenish to bluish grey colour to montmorillonite. Granite boulders show original colour and are not mineralized.

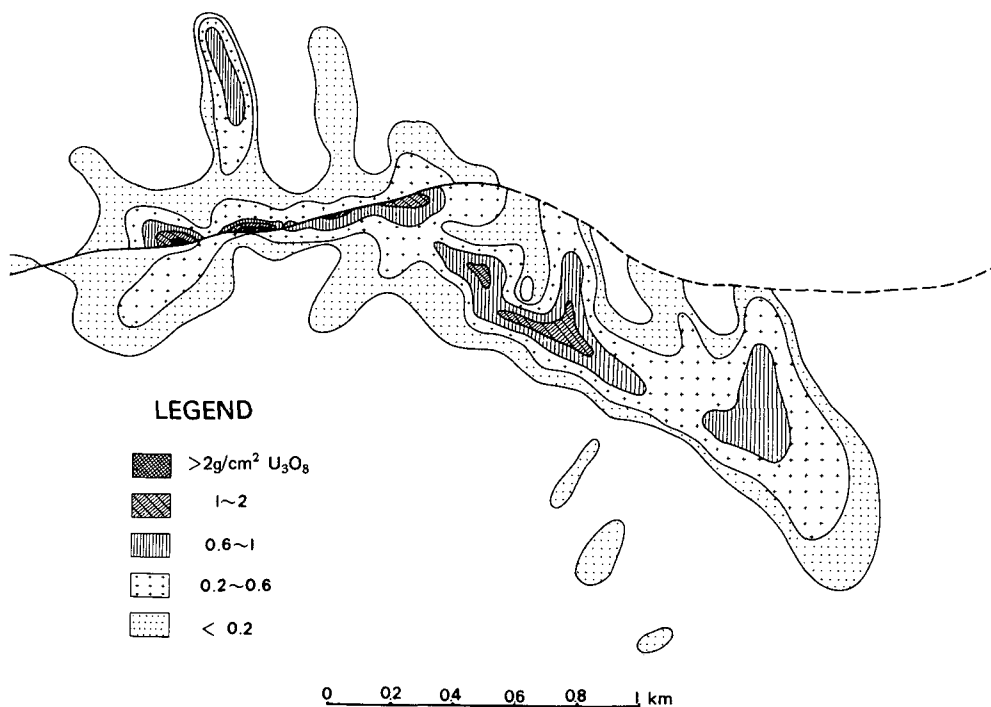


FIG. 5. Uranium content per unit area of the Tsukiyoshi deposits.

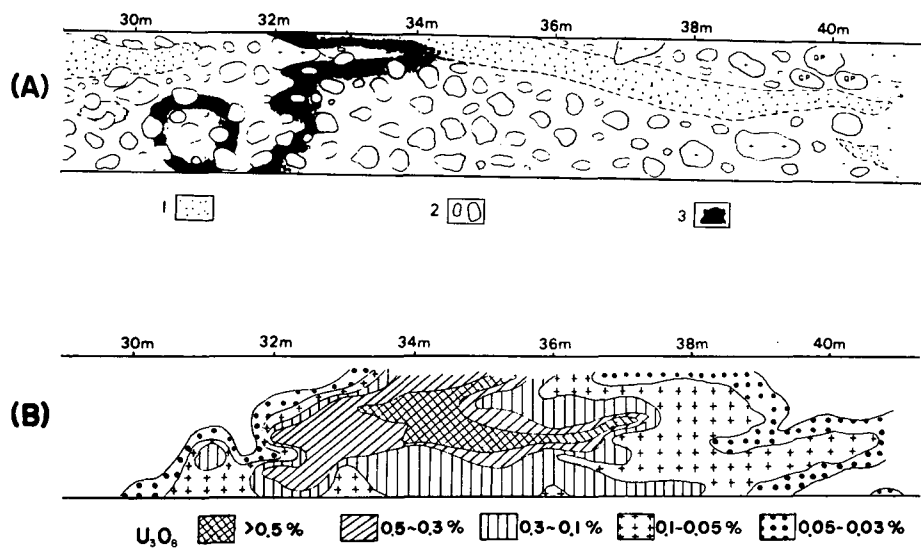


FIG. 6. Sketch (A) and assay plan (B) of the western wall of a S-N gallery at Tsukiyoshi. (1) Coarse sandstone; (2) boulders; (3) southern border of the chocolate-coloured ore body.

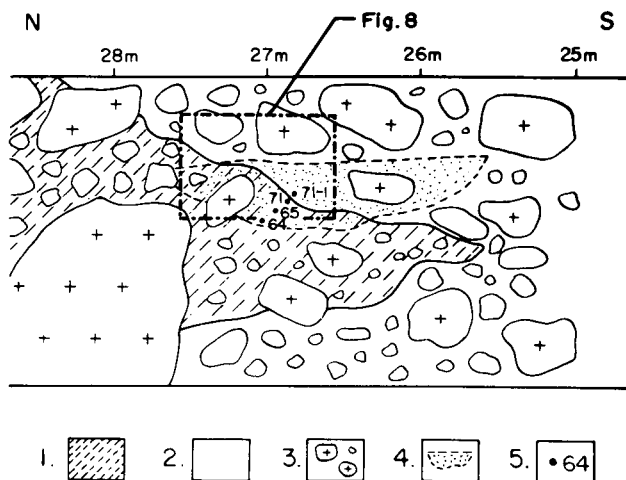


FIG. 7. Sketch of a boundary between the high-grade ore body and barren zone of the Tsukiyoshi deposits at the eastern wall of a S-N gallery. (1) Chocolate-coloured ore; (2) greenish or bluish grey coloured barren zone; (3) boulders of granite; (4) coarse sand matrix; (5) location of samples for Fig. 10.

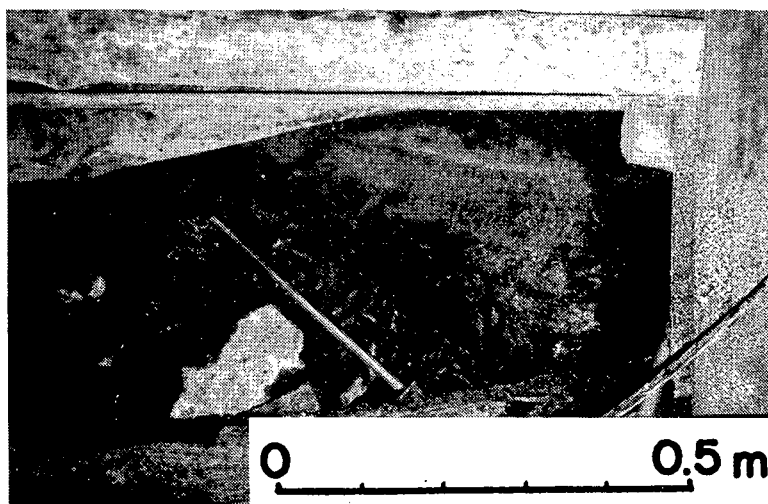


FIG. 8. Photograph of the boundary between the high-grade ore and barren zone at the location shown in Fig. 7.

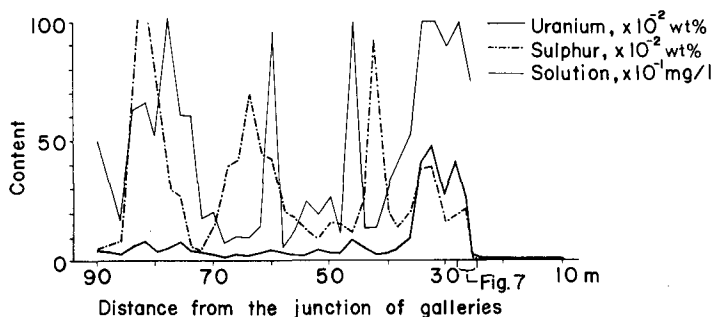


FIG. 9. Variation with distance, along the eastern wall of a S-N gallery at Tsukiyoshi, of the contents of uranium and sulphur in the ore and of the concentration of uranium in the solution assumed to have been in equilibrium with the uranium adsorbed in H-C zeolite.

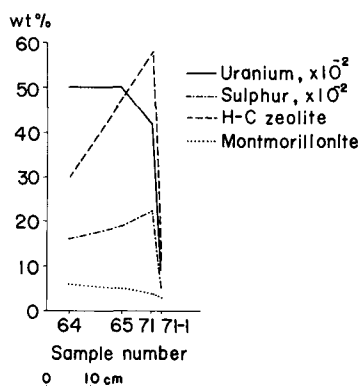


FIG. 10. Variation of the contents of uranium, sulphur, H-C zeolite and montmorillonite around the boundary depicted in Fig. 7.

Figure 9 shows variations along a wall of the gallery of uranium and sulphur contents in the conglomerate exclusive of boulders. Figure 10 shows the variations of the contents of those elements and H-C zeolite and montmorillonite around the boundary depicted in Fig. 7. The mineral compositions were determined by comparing the areas under X-ray powder peaks of each sample with those of standard mixtures of the minerals. A glance at Figs 9 and 10 will show that the ore body is characterized by H-C zeolite and sulphur, most of which occurs as pyrite of fine grain.

The correlation coefficients between those elements, H-C zeolite and montmorillonite were calculated using 41 samples from the ore body and the results are tabulated in Table I. The negative correlation between H-C zeolite and montmorillonite is remarkable.

TABLE I. CORRELATION COEFFICIENTS BETWEEN URANIUM, SULPHUR, H-C ZEOLITE AND MONTMORILLONITE IN THE ORE FROM THE TSUKIYOSHI DEPOSITS

	H-C	Mont	S
U	+ 0.55	- 0.49	+ 0.54
	H-C	- 0.70	+ 0.61
		Mont	- 0.52
			S

Mont: montmorillonite.

H-C: H-C zeolite.

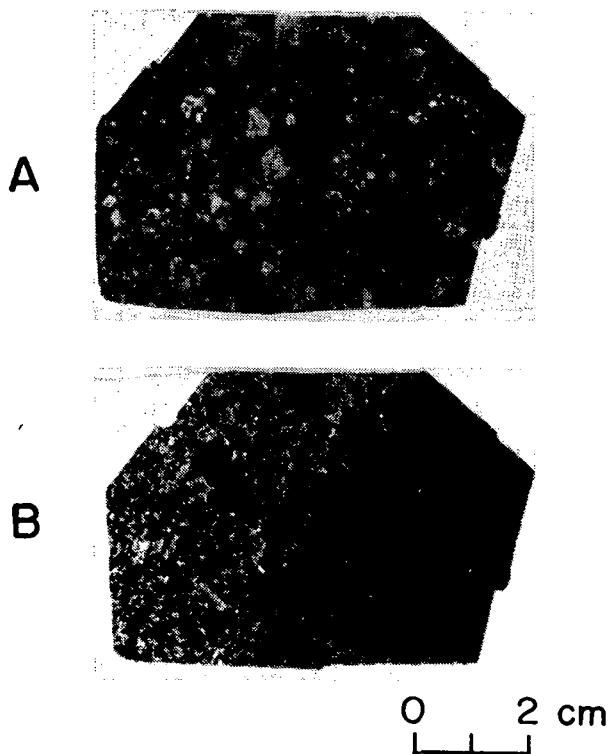


FIG. 11. Polished section of an ore specimen from the Tsukiyoshi deposits (A) and its radioluxograph (B).

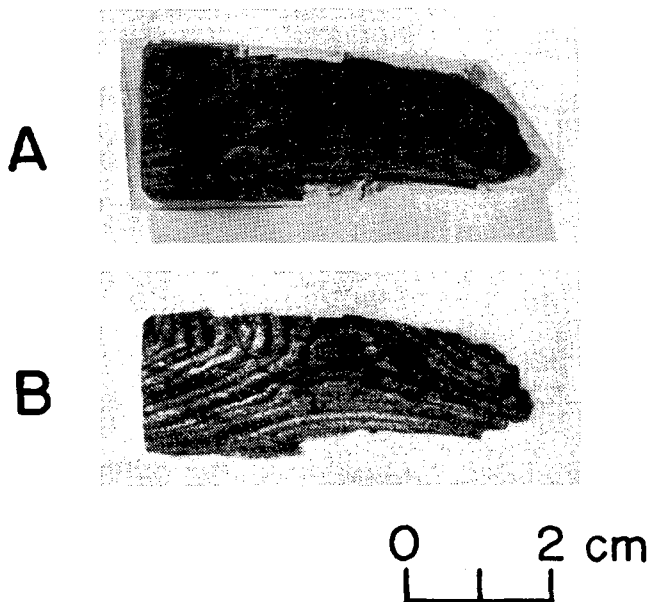


FIG. 12. Polished section of a fossil tree enriched with coffinite (A) and its radioluxograph (B).

The distribution of uranium in the ore is clearly displayed by radioluxography. Photograph B in Fig. 11 is the radioluxograph of a specimen containing the boundary between the high-grade ore and the barren zone. The uranium is concentrated in the matrix of the conglomerate. Photograph B in Fig. 12 is the radioluxograph of a fossil tree with an extraordinarily high content of uranium, and it shows that the concentration of coffinite is controlled by the texture of the annual ring.

5. ZEOLITE OF THE HEULANDITE-CLINOPTILOLITE GROUP AS A URANIUM ORE MINERAL

A practically pure material of H-C zeolite was obtained from a zeolitized tuff from Mizunami by repeated separation using heavy liquids. The X-ray powder patterns of the pure material and the material that has been heated at 300°C for 6 h are given in Fig. 13. The patterns of the untreated material indicate that it belongs to the heulandite-clinoptilolite group. Those of the heated material coincide with the features of heulandite B, the high-temperature form of heulandite. Since the dispute about the variation in composition between typical heulandite and typical clinoptilolite seems not to be quite settled [9-11], the authors will leave the precise classification an open question and will designate the mineral as H-C zeolite, as mentioned above.

One gram of the pure material was immersed in 100 ml of perchloric uranyl solution for 3 d, the pH being controlled in the range of 5.0 to 5.5,

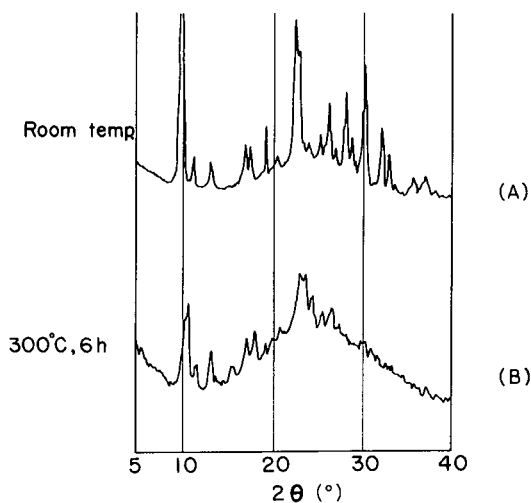


FIG. 13. X-ray powder patterns of (A) H-C zeolite from Mizunami and (B) H-C zeolite that has been heated at 300°C for 6 h (identified by $\text{CuK}\alpha$ X-rays).

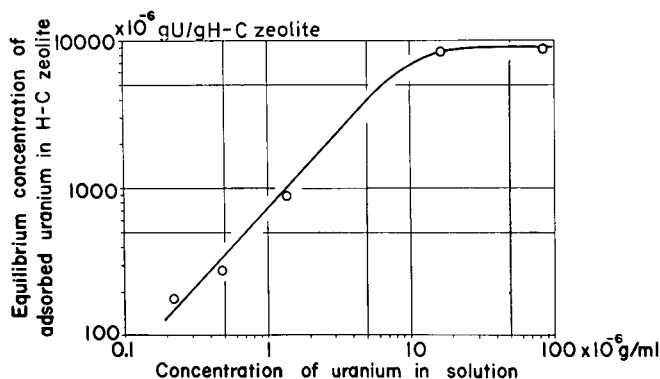


FIG. 14. Relation between the adsorbed uranium in H-C zeolite and the uranium concentration in solution at equilibrium.

and subsequently the respective concentrations of uranium in the zeolite and the solution were measured. Thus, the diagram of the relation of the variation of the uranium distribution in the zeolite and the solution was obtained (see Fig. 14). It shows that the partition coefficient of uranium between H-C zeolite and the solution will be about 700 in the middle range given in Fig. 14, and that saturation of uranium adsorption in H-C zeolite will take place at about 0.9% U.

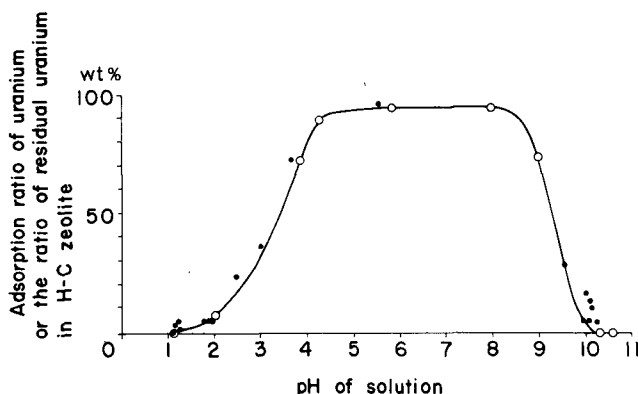


FIG. 15. Curve of the adsorption ratio of uranium in H-C zeolite versus the pH values of the solution, with plots of the ratio of residual uranium in the leaching test (solid circles).

The effect of variation of pH value was measured following the same procedure as described above and using perchloric acid or sodium carbonate to adjust the pH values. The result is plotted as small circles in Fig. 15, where the curve is drawn through the circles. The small solid circles in Fig. 15 denote the content of residual uranium in H-C zeolite after leaching tests at various pH values. They are near the curve, which means the adsorption of uranium in H-C zeolite is quite reversible. From Fig. 15 it can be concluded that, between pH values of 4.5 and 8.5, H-C zeolite is an effective adsorbent for the uranyl ion, and that leaching should be carried out at pH ranges lower than 3 or higher than 9.

6. URANIUM ORE FROM THE EXPLORATION GALLERY

Boulders were hand-picked from the ore from the exploration gallery at Tsukiyoshi and the remainder was used as the material for size analysis and leaching tests. The average grade and mineral composition of the material was as follows: 0.113% U, 11% H-C zeolite, 5% montmorillonite. The distribution of the weight of the grain size and the distribution of components for the respective grain sizes is depicted in Fig. 16. Then the material, having been milled to powders under 0.5 mm, was applied to a leaching test under the following conditions: pulp density: 50% solid, temperature: room temperature (10°-16°C), for acid leaching: 5% H_2SO_4 , 0.5% NaClO_3 , for carbonate leaching: 5% Na_2CO_3 , 1% NaHCO_3 , 0.5% KMnO_4 . The results are shown in Fig. 17 as a graph of the variation of the uranium extraction ratio with time. The high efficiency in extraction that is displayed clearly in Fig. 17 may be due to the state of the uranium which is adsorbed in H-C zeolite.

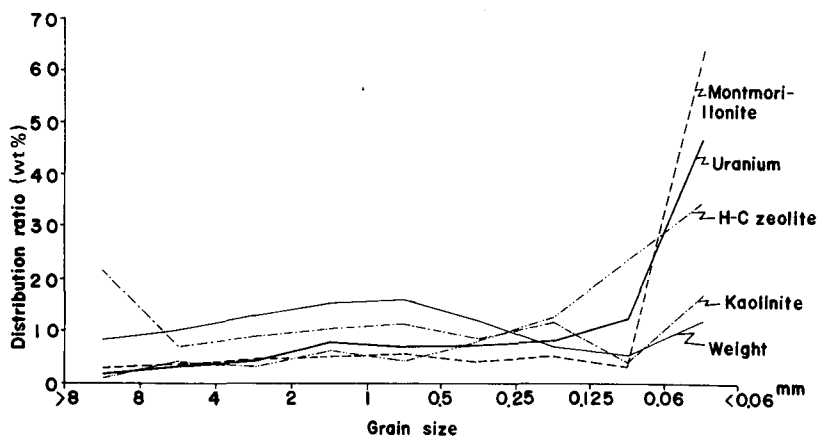


FIG. 16. Results of the size analysis of the ore from the Tsukiyoshi deposits.

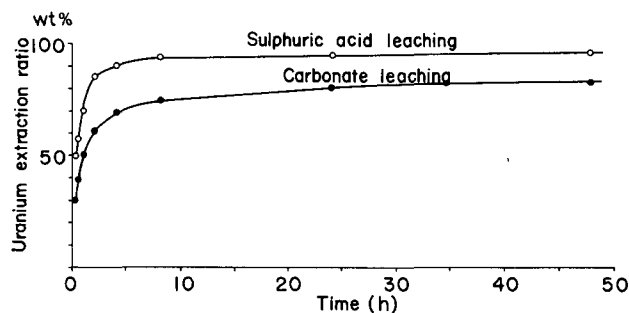


FIG. 17. Results of the leaching test of the ore from the Tsukiyoshi deposits.

7. GENESIS OF THE TONO URANIUM DEPOSITS

The Tono uranium deposits are located in the basal part of the Miocene sediments and their distribution is typically controlled by channel structures of the plane of unconformity under the Miocene. These features characterize the basal ground-water type of uranium deposit, according to Katayama [12]. The ore of the deposits is unique in that most of the uranium occurs as adsorbed in H-C zeolite, at least in the Tsukiyoshi deposits. This enables the following history of formation of the Tsukiyoshi deposits to be presented rather precisely.

The zeolitization was still in progress at the stage of sedimentation of the Mizunami group [4-6], and has been suspended since the upheaval corresponding to the unconformity between the Mizunami and the Seto

groups. On the other hand, montmorillonitization preceded zeolitization, and the densely montmorillonitized zone became an impermeable barrier for ground water. The conduit of uranium-bearing ground waters, which migrated from the basement granites into the Tertiary sediments, was controlled by those montmorillonitized zones and the channel structure of the plane of unconformity. Where the ground waters became rather stagnant, uranium was adsorbed in H-C zeolite.

Figure 9 gives the estimated uranium concentrations in the solution that were assumed to have been in equilibrium with the adsorbed uranium in H-C zeolite in the ore. Each high peak of the uranium concentration in the solution appears at a location slightly shifted from a high peak for sulphur contents in the ore, which usually contains a small amount of gypsum around such points. Those facts suggest that the sulphuric acid solution, which was produced sporadically as a result of oxidation of pyrite, leached uranium from H-C zeolite that had adsorbed it and became concentrated with it. Subsequently, as soon as the pH of the solution increased to over 4 (Fig. 15), producing gypsum in the course of migration, uranium was again adsorbed in H-C zeolite up to about 0.9% (Fig. 14).

Coffinite was formed while in and around carbonaceous matter, where strongly reducing conditions were maintained, and where the uranium introduced was more than could be adsorbed in H-C zeolite. The coffinite was formed because migration of free silica usually accompanies zeolitization [5].

The accumulation of uranium is a result of the balance between the rate of migration of uranium into the Tertiary sediments and the volume of that part of the sediments where uranium is to be deposited. So, uranium deposits may be formed in tributaries or at the heads of channels rather than in the main channels. The original form of the Tsukiyoshi deposits had been established before the outbreak of the Tsukiyoshi fault or the deposition of the Pliocene. The Tsukiyoshi fault, being an impermeable wall in itself, brought about small traps of ground water, and there uranium was further accumulated to make higher-grade ores. Recent migration of uranium in the Tsukiyoshi deposits is not noticeable because the radio-active equilibrium in ores is not disturbed significantly, except in weathered zones.

REFERENCES

- [1] HAYASHI, S., OBI, I., Uranium Deposits in the Tono District, Gifu Prefecture, Japan, Rep. 232 Geol. Surv. Japan, Tokyo (1969) 25.
- [2] HAYASHI, S., "Uranium occurrences in small sedimentary basins in Japan", Uranium Exploration Geology (Proc. Panel Vienna, 1970), IAEA, Vienna (1970) 233.
- [3] SATO, Y., Non-opaque Heavy Minerals in Sandstones of Miocene Age in Mitake and Hiyoshi Districts, Gifu Prefecture, Rep. 232, Geol. Surv. Japan, Tokyo (1969) 803.
- [4] KATAYAMA, N., FUJIMOTO, J., in Uranium Deposits and Geology in the Tono Area, Gifu Pref., (Proc. Symp. Gifu-City, 1965), J. At. Energy Soc. Japan 7 (1965) 97.
- [5] UTADA, M., MINATO, H., HATTORI, N., Migration of Chemical Components of Vitric Tuff Accompanying Zeolitization and Formation of Calcareous Nodules, Sci. Papers, College Gen. Educ., Univ. Tokyo 17 (1967) 121.
- [6] UTADA, M., Occurrence and Distribution of Authigenic Zeolites in the Neogene Pyroclastic Rocks in Japan, Sci. Papers, College Gen. Educ., Univ. Tokyo 20 (1970) 191.
- [7] HAYASHI, S., in Uranium Ore Deposits and Geology in the Tono Area, Gifu Pref., (Proc. Symp. Gifu-City, 1965), J. At. Energy Soc. Japan 7 (1965) 74.

- [8] ANDO, A., Preliminary Study on the Geochemistry of Uraniferous Toki District, Gifu Prefecture, Distribution of the Minor Elements, Rep. 232, Geol. Surv. Japan, Tokyo (1969) 285.
- [9] MINATO, H., UTADA, M., "Clinoptilolite from Japan", Advances in Chemistry Series No. 101, Molecular Sieve Zeolites-I, American Chemical Society, Washington, D.C. (1971) 311.
- [10] ALIETTI, A., Polymorphism and crystal chemistry of heulandites and clinoptilolites, Am. Mineral. 57 (1972) 1448.
- [11] BOLES, J.R., Composition, optical properties, cell dimensions, and thermal stability of some heulandite group zeolites, Am. Mineral. 57 (1972) 1463.
- [12] KATAYAMA, N., "Genesis of uranium deposits in sedimentary rocks", Genetic Problems of Uranium Deposits, Proc. 21st Int. Geol. Congress, Det Berlingske Bogtrykkeri, Copenhagen 15 (1960) 7.

DISCUSSION

P. C. ELLSWORTH: Do you know of any other instances where uranium has been concentrated on zeolites?

N. KATAYAMA: Yes, we have found several sites where zeolites have adsorbed uranium, but no exploration work has been carried out yet except at Tsukiyoshi.

S. H. U. BOWIE: Is there any evidence in the Tsukiyoshi deposit of uranium moving either up or down in the plane of the fault, which clearly post-dates the mineralization?

N. KATAYAMA: The Tsukiyoshi fault is a closed or compressed fault, and there is no detectable water migrating along it at present.

D. S. ROBERTSON: In this instance the source rocks appear quite clearly to be the Cretaceous granites. Have you identified any uranium minerals in the granites?

N. KATAYAMA: No. Leachable uranium is usually found in minute cracks of zircon and other minerals.

LE GITE D' URANIUM DE FAKILI (TURQUIE) ET SA FORMATION

H. KAPLAN, S. UZ, İ. ÇETİNTÜRK

Institut d'études et de recherches

minières de Turquie,

Ankara, Turquie

Abstract—Résumé

THE FAKILI (TURKEY) URANIUM DEPOSIT AND ITS FORMATION.

The Fakılı deposit is situated in the Aegean region, in the west of Turkey. The rocks in the vicinity of the deposit consist principally of the metamorphic series of the Menderes Massif and Neogene sediments. The metamorphic series, comprising mainly augen-gneisses, constitutes the basement rock of the Neogene sedimentary basin. The Neogene sediments can be divided into three categories: the detrital series lowest down, above that the marl series and then lacustrine limestone. The detrital series consists of clays, silts, sands, gravels and conglomerates. The lower parts are distinctly fluvial, with intersecting stratification. Higher up within the series, starting at the lower fluvial sediments, are the lacustrine sediments, with horizontal beds providing for lateral continuity. The marl series consists of alternating clay and tuffite layers with silts, sandstone and marls; it is inhomogeneous and irregular, with many changes of facies. At the same stratigraphic level, however, there are two distinct facies: the first is generally representative of the series and contains marls; the second is the Fakılı facies, distinguished from the first by a number of characteristics — variegated colouring, absence of marl, presence of secondary gypsum and sedimentary pyrites, and a generally higher level of radioactivity. The Fakılı uranium deposit is located in this facies. The lacustrine limestones are the youngest sediments of the Neogene lake.

The Fakılı uranium deposit was created in two phases: syngenetic precipitation and epigenetic concentration. At the start of the sedimentation of the marl series, the lake water was rich in dissolved uranium. The Neogene detrital series became enriched in sulphate compounds near the base of the Fakılı facies; the sulphate concentration is at a maximum above the contact with the Fakılı facies and decreases as one moves upwards. This high sulphate concentration is the result of evaporation in this part of the lake. Evaporation, which concentrated the sulphate compounds to the point where they precipitated, also concentrated the dissolved uranium, which was abundant in this level of the lake. The waters of the lake were first acidic, but then became neutral — owing partly to the decline in the sulphate concentration and partly to an increase in the CaCO_3 concentration. The uranium, which cannot remain in solution in neutral water, began to precipitate intensively following the anhydrite; this was the first phase — syngenetic precipitation of the uranium in the lake. At the end of the Neogene, the lake receded and the Neogene sediments began to undergo alteration and erosion through atmospheric influences. During the filtration of vadose waters, the uranium, which had passed into solution for the second time, precipitated as sulphate compounds in the heterogeneous zones above the contact at the base of the Fakılı facies. This process of epigenetic concentration explains the present characteristics of the lenses in the Fakılı uranium deposit.

LE GITE D'URANIUM DE FAKILI (TURQUIE) ET SA FORMATION.

Le gisement de Fakılı se trouve au nord de la région de l'Egée à l'ouest de la Turquie. Les roches principales des environs du gisement sont constituées par la série métamorphique du Massif de Menderes et des sédiments néogènes. La série métamorphique contient en général des gneiss ocellés; elle constitue le soubassement du bassin de sédimentation néogène. Il est possible de diviser les sédiments néogènes en trois catégories: à la base la série détritique, au-dessus la série marneuse, et au sommet les calcaires lacustres. La série détritique est constituée par des argiles, des silts, des sables, des cailloux et des conglomérats. Les parties inférieures ont un caractère nettement fluvial avec une stratification entrecroisée. En remontant dans la série à partir des sédiments fluviaux inférieurs, on rencontre la sédimentation lacustre, qui commence par des couches horizontales offrant une continuité latérale. La série marneuse se compose d'alternances d'argiles aux niveaux tuffitiques, de silts, de grès et de marnes. Cette série n'est pas homogène et régulière. On y rencontre beaucoup de changements de faciès. Mais on remarque en général au même niveau stratigraphique deux faciès distincts. Le premier représente le caractère général de la série et contient des marnes. Le deuxième est le faciès de Fakılı. Il se distingue du premier par les

caractères suivants: couleur bariolée, absence de marne, présence de gypse secondaire et de pyrite sédimentaire, et augmentation générale de la radioactivité. Le gisement d'uranium de Fakılı se situe dans ce faciès. Les calcaires lacustres sont les sédiments les plus jeunes du lac néogène.

La mise en place du gîte d'uranium de Fakılı s'est effectuée en deux phases: précipitation syngénétique et concentration épigénétique de l'uranium. Au début de la sédimentation de la série marneuse, l'eau du lac est riche en uranium à l'état de solution. La série détritique du Néogène s'enrichit en sulfate vers la base du faciès de Fakılı. La teneur en sulfate atteint une valeur maximum au-dessus du contact avec le faciès de Fakılı; elle diminue vers le haut. Cette richesse en sulfate provient d'une évaporation dans cette partie du lac. L'évaporation qui amène le sulfate à la concentration de précipitation concentre aussi l'uranium, qui abonde, à l'état de solution, à ce niveau du lac. L'eau du lac offre d'abord un caractère acide, puis elle devient neutre, d'une part par suite de la diminution du sulfate et d'autre part du fait de l'augmentation de la teneur en CaCO_3 . L'uranium, qui ne peut pas rester en solution dans l'eau neutre, commence à précipiter abondamment après l'anhydrite. C'est une précipitation syngénétique de l'uranium dans le lac. A la fin du Néogène, le lac se retire. Les sédiments néogènes s'altèrent et s'érodent par suite des influences atmosphériques. Pendant la filtration des eaux vadoses l'uranium, qui a passé pour la seconde fois à l'état de solution, précipite sous forme de composés de sulfate dans les parties hétérogènes, au-dessus du contact de base du faciès de Fakılı. Cette concentration épigénétique explique les caractéristiques actuelles des lentilles dans le gisement d'uranium de Fakılı.

INTRODUCTION

Les gîtes d'uranium explorés jusqu'à maintenant en Turquie se groupent dans la région de l'Egée, à l'ouest du pays. Les sédiments néogènes couvrent en général le complexe métamorphique dénommé « Massif de Menderes », très étendu dans la région de l'Egée. Au cours des études récentes, on n'a pas rencontré de dépôt exploitable dans ce complexe métamorphique constitué en général par des gneiss et des micaschistes. Tous les dépôts reconnus se trouvent à la base détritique des sédiments néogènes qui couvrent la série métamorphique. Pour le moment, le gîte de Fakılı constitue probablement la seule exception. Il se trouve à la base du faciès du type Fakılı, qui n'est qu'un faciès différent de la série marneuse couvrant la série détritique de base. Les gîtes d'uranium des sédiments néogènes sont constitués par l'uranium contenu dans des roches métamorphiques et dont la teneur est de l'ordre du ppm. Des eaux vadoses descendantes ont lessivé les roches métamorphiques et ont transporté l'uranium qui a précipité sous l'action de divers processus dans les sédiments néogènes.

GEOLOGIE GENERALE DES ENVIRONS DU GITE

Les roches principales des environs du gîte de Fakılı sont des roches métamorphiques, des calcaires cristallisés, des serpentines et différentes roches néogènes (fig.1).

La série métamorphique contient en général des gneiss ocellés, des micaschistes et, en petites quantités, des quartzites, des gneiss granitisés et des granites d'anatexie. Dans les diverses roches métamorphiques, on rencontre parfois une radioactivité élevée. Pourtant on observe généralement une radioactivité augmentant avec le degré de métamorphisme. Les micaschistes ont une valeur minimum. Par contre les gneiss granitisés et les granites d'anatexie présentent une radioactivité plus élevée. La série métamorphique forme le soubassement du bassin de sédimentation néogène (fig.2). Elle constitue la source primaire de l'uranium trouvé dans les sédiments néogènes.

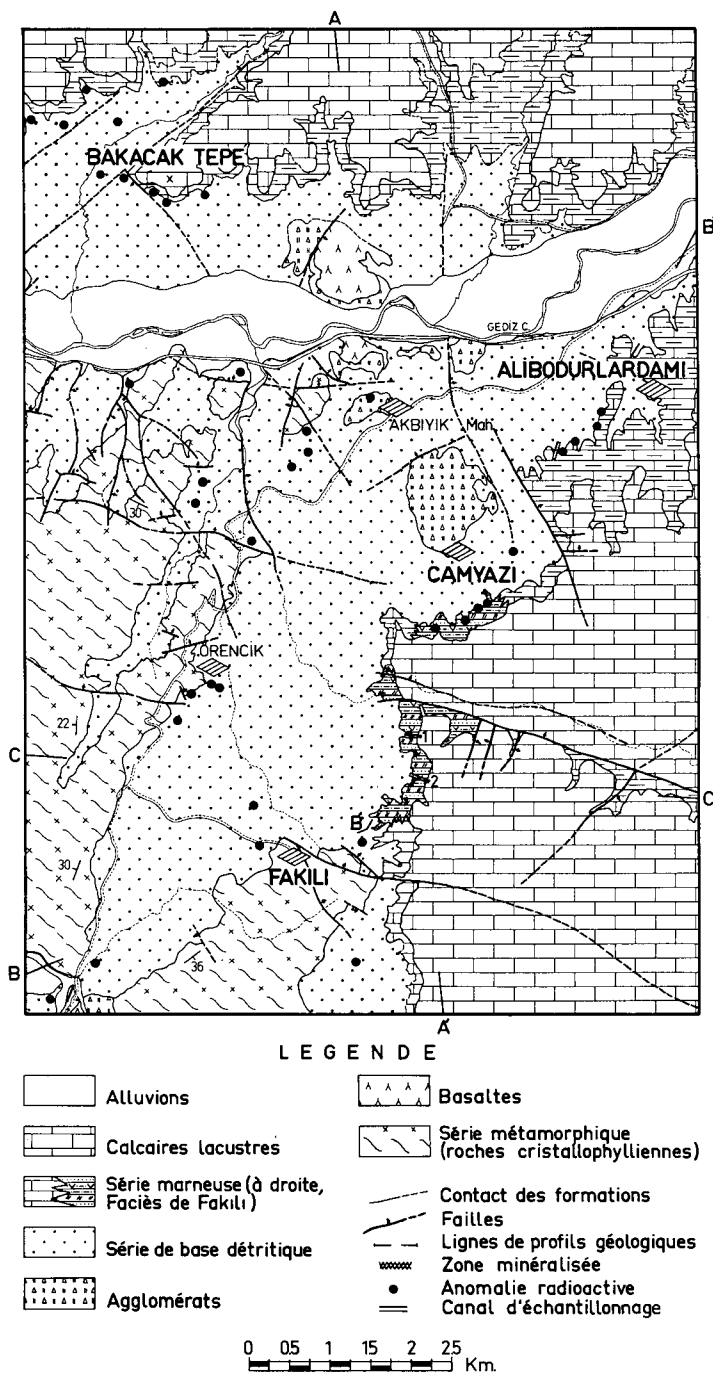


FIG. 1. Carte géologique des environs de Fakılı-Alibodurlardami.

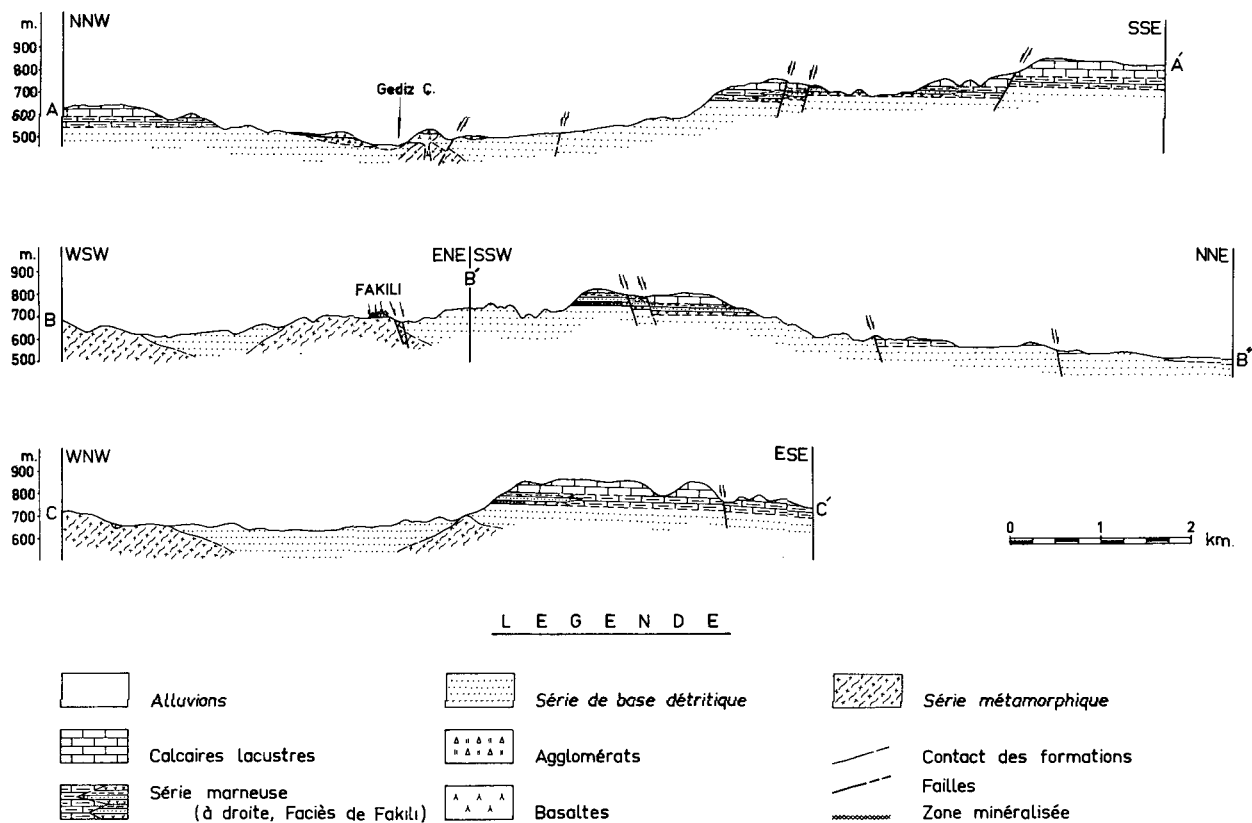


FIG. 2. Profils géologiques des environs de Fakılı-Alibodurlardamı.

On trouve des calcaires cristallisés et des serpentines au nord de la région étudiée.

Il est possible de diviser les sédiments néogènes en trois catégories: à la base la série détritique, au-dessus la série marneuse et au sommet les calcaires lacustres.

La série de base détritique

Elle est constituée par des argiles, des silts, des sables, des cailloux et des conglomérats. Les parties inférieures montrent un caractère nettement fluviatile avec une stratification entrecroisée. L'argile n'est en général présente qu'en quantités insignifiantes. Les composants de cette série proviennent en grande partie des roches métamorphiques et en petite quantité des roches andésitiques ou autres. Ces éléments ne sont pas fortement consolidés; ils sont friables. Ce n'est que dans des conglomérats bréchiques qu'on observe une cimentation. La puissance des conglomérats diminue à mesure qu'on s'éloigne du contact de la série métamorphique et disparaît en formant des lentilles entre les sables, les silts, etc. En remontant dans la série à partir des sédiments fluviatiles inférieurs, on rencontre la sédimentation lacustre, qui commence par des couches horizontales offrant une continuité latérale plus homogène.

Au-dessous des sédiments lacustres, on observe des agglomérats discordants dans la série détritique de base. Les agglomérats se composent d'éléments andésitiques et on y rencontre par endroit des coulées ayant l'aspect de scories andésitiques en contradiction avec la stratification. Une couche de basalte couvre en concordance les agglomérats de base. Le passage des agglomérats aux basaltes se fait par des basaltes poreux, et vers la partie supérieure on observe les laves à débit en coussins (pillow-lava). Dans les agglomérats présents sur les basaltes, on voit les blocs de basaltes poreux. Les agglomérats offrent des passages latéraux à la série détritique néogène par diminution des quantités des matériaux volcaniques.

Les parties supérieures de la série détritique de base contiennent des gypses abondants près du gisement d'uranium de Fakılı. D'autre part, les matériaux tuffitiques commencent à paraître à la partie supérieure et on constate une diminution des dimensions des éléments lorsqu'on s'éloigne du faciès littoral peu profond.

La série marneuse

Cette série représente les parties franchement lacustres et se trouve en concordance avec la série précédente. Elle est constituée par des alternances d'argiles aux niveaux tuffitiques, de silts, de grès et de marnes. Cette série n'est pas homogène et régulière. On y rencontre beaucoup de changements de faciès. Mais en général, au même niveau stratigraphique on remarque deux faciès distincts.

Le premier représente le caractère général de la série et contient des marnes sans gypse. Il est gris-blanc.

Le deuxième est le faciès de Fakılı. Il se distingue du premier par les caractères suivants:

Couleur: Dans le faciès du type Fakılı, il y a des bandes jaunes, jaunes brunâtres, jaunes rougeâtres, rouges et violettes. La couleur

générale de ce faciès est jaune brunâtre-rougeâtre. Il est facile de le distinguer par cette coloration bariolée. Le passage à l'autre faciès se fait progressivement, avec perte de la coloration.

Absence de marne: Dans le faciès de Fakılı il n'y a pas de marne.

Gypse: Le gypse secondaire est abondant jusqu'à une puissance de 20 m à partir de la base du faciès de Fakılı. En dépit de son abondance à la base, le gypse diminue au fur et à mesure qu'on s'élève, pour disparaître complètement à partir de 20 m. Les cristaux de gypse occupent l'espace formé par des cassures et ne sont pas parallèles à la stratification.

Pyrite sédimentaire: On observe ici et là des pyrites sédimentaires en forme de rognons dans le faciès de Fakılı.

Augmentation générale de la radioactivité: Dans le faciès de Fakılı, on observe une augmentation de la radioactivité à partir de la base du faciès jusqu'à une puissance de 10 à 35 m. D'ailleurs, le gisement d'uranium de Fakılı se situe à ce niveau.

En outre, les matériaux tuffitiques sont beaucoup plus abondants dans le faciès de Fakılı.

La puissance de la série marneuse varie de 50 à 60 m. Dans la direction nord-est de Fakılı les dimensions des éléments diminuent à cause de l'augmentation de la profondeur du lac et ainsi les bancs de calcaires pénètrent dans l'alternance. Cette situation se présente surtout aux environs d'Alibodurlardamı.

Les calcaires lacustres

Ce sont les sédiments les plus jeunes du lac néogène et ils sont en concordance avec la série précédente. Ils commencent généralement par les calcaires noduleux, dont les nodules sont cimentés par un ciment calcaire; ils ont une texture oolithique ou pisolitique. Mais les nodules sont en général plus grands que ceux d'une pisolithe et peuvent atteindre parfois une taille de 30 cm au maximum. Le centre des nodules est souvent occupé, entre autres, par des grains de gneiss. Les dimensions des noyaux du centre peuvent atteindre parfois jusqu'à 3 cm. Les nodules ne sont pas toujours sphériques, ils peuvent être ovales par exemple. Les nodules de ces dimensions semblent se former dans une eau très agitée, sursaturée et assez chaude.

Les calcaires lacustres se présentent comme des alternances de grès, d'argiles, de calcaires argileux et de calcaires dans le faciès littoral peu profond. Dans les régions profondes du lac, les calcaires ont un aspect plus homogène.

GENESE DU GITE

La mise en place du gîte d'uranium de Fakılı s'est effectuée en deux phases: précipitation syngénétique et concentration épigénétique de l'uranium.

La précipitation syngénétique de l'uranium

Le gîte d'uranium de Fakılı se trouve à la base du faciès de Fakılı en forme de lentilles. On observe une radioactivité élevée à partir de la base



L E G E N D E

	Calcaires Lacustres		Contact des formations
	Série marneuse (à droite, Faciès de Fakili)		Fautes
	Série de base détritique		Sondage dont le résultat est positif
	Gneiss ocellés		Sondage dont le résultat est négatif
			Zone minéralisée
			Canal d'échantillonnage

FIG. 3. Emplacements des sondages effectués dans le gisement de Fakili.

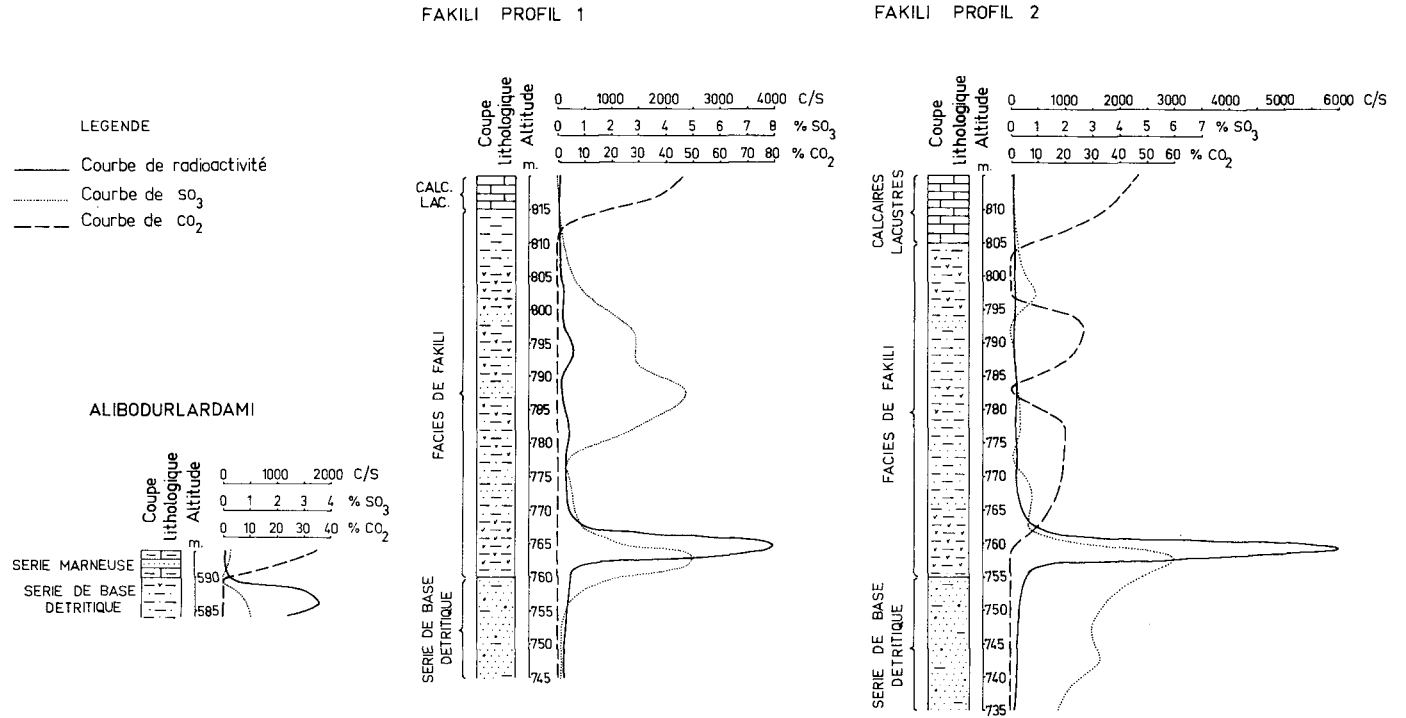


FIG. 4. Relation entre roche, radioactivité, SO_3 et CO_2 dans la région de Fakılı-Alibodurlardami.

du faciès et jusqu'à 10 ou 35 m d'épaisseur. A la surface, la zone de radioactivité élevée forme une bande conforme à la stratification. La formation d'une telle radioactivité par épigénèse n'est pas possible. Il est plus normal de retenir la précipitation syngénétique de l'uranium qui possède une telle radioactivité. D'ailleurs, les conditions nécessaires pour cette précipitation existent dans le milieu de sédimentation.

Au commencement de la sédimentation de la série marneuse, l'eau du lac est riche en uranium à l'état de solution. Toutes les anomalies radioactives qui montrent une continuité latérale parallèle à la stratification se trouvent au bord du contact de base de la série marneuse aux environs de Fakılı, de Çamyazı, d'Alibodurlardamı et de Bakacak Tepe (fig.1 et 3). Si nous représentons le contact de base de la série marneuse par une ligne, nous allons voir que les anomalies radioactives à la base du faciès de Fakılı se placent au-dessus de cette ligne, et les anomalies aux environs d'Alibodurlardamı et de Bakacak Tepe au-dessous, ce qui montre que les conditions de la précipitation de l'uranium sont un peu différentes dans ces deux faciès. Dans le faciès du type de Fakılı, deux faits jouent un rôle important dans la précipitation de l'uranium en solution dans l'eau du lac. Mais aux environs d'Alibodurlardamı et de Bakacak Tepe, l'un de ces deux faits a une importance prépondérante.

La série de base détritique du Néogène devient riche en sulfate vers la base du faciès de Fakılı (fig.4). La teneur en sulfate atteint une valeur maximum au-dessus du contact avec le faciès de Fakılı; le sulfate diminue et disparaît à mesure qu'on s'élève, en faisant des pics d'importance variable. On observe une telle richesse en sulfate dans le faciès de Fakılı seulement, mais pas aux environs d'Alibodurlardamı et de Bakacak Tepe. Cette richesse en sulfate dans le faciès de Fakılı provient d'une évaporation dans cette partie du lac, c'est un produit d'évaporation. Il est intéressant de remarquer que la précipitation de CaSO_4 a lieu par suite d'une évaporation qui se produit seulement dans cette partie du lac. D'après nos observations sur le terrain, on rencontre le sulfate en abondance ici seulement; les venues des matériaux tuffitiques sont aussi beaucoup plus abondantes dans cette partie. Naturellement, la température de l'eau du lac augmente avec les abondantes venues de cendres et de lapillis volcaniques brûlants dans le lac. Dans ces conditions il y a une évaporation. CaSO_4 est saturé et atteint facilement une concentration de précipitation à cause de cette évaporation. Une solution saturée de CaSO_4 dépose à froid du gypse et, à partir de 66°C , de l'anhydrite¹. La précipitation de l'anhydrite au lieu du gypse est normale dans un lac qui a une température plus élevée. Nous n'avons pas une opinion décisive au sujet de la source du sulfate qui abonde à cet endroit. Il est probable que le sulfate vient des alentours, ou bien des sources sulfureuses volcaniques dans le lac.

L'évaporation qui amène le sulfate à la concentration de précipitation peut concentrer aussi l'uranium, qui est présent en grande quantité à ce niveau du lac, à l'état de solution. L'eau du lac est acide, à cause de l'abondance de sulfate, et devient neutre peu à peu avec la précipitation de l'anhydrite. L'uranium ne peut pas rester en solution dans l'eau neutre et commence à précipiter après l'anhydrite. C'est une précipitation syngénétique de l'uranium dans le lac. Du reste, l'apparition des pics de radioactivité tout de suite après les pics de SO_3 confirme ce fait (fig.4, profils 1 et 2).

¹ FISCHESSE, R., Données des principales espèces minérales, J. Sennac, Paris (1955).

D'autre part, du côté sud de la lentille principale d'uranium, les grès à ciment calcaire apparaissent après la diminution de la radioactivité dans le faciès de Fakılı. Ensuite, la teneur en carbonate augmente et diminue selon les endroits, et on passe aux calcaires lacustres avec les calcaires noduleux. Il est intéressant de constater que la radioactivité baisse avec l'apparition des grès à ciment calcaire (fig. 4, profil 2). Nous savons que les calcaires précipitent dans des milieux à pH d'environ 8. Ce n'est que le commencement d'un milieu basique. L'eau du lac, d'abord acide, devient neutre à partir de la base du faciès de Fakılı, par suite d'une part de la diminution du sulfate et d'autre part de l'augmentation de la teneur en CaCO_3 . Dans les parties supérieures elle présente un caractère partiellement basique. La diminution de la radioactivité avec l'apparition des grès à ciment calcaire est liée à l'acidité du milieu, dont le caractère passe de neutre au basique. Le milieu neutre des eaux du lac a permis une précipitation syngénétique de l'uranium. Quand ce milieu a pris un caractère partiellement basique, il n'y avait plus d'uranium à précipiter dans l'eau du lac.

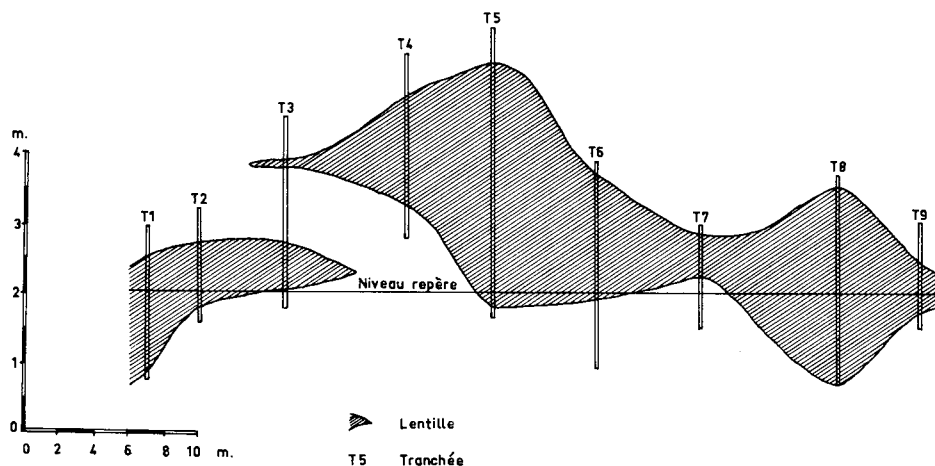
Aux environs d'Alibodurlardamı et de Bakacak Tepe, l'augmentation de CaCO_3 seulement joue un rôle important dans la précipitation de l'uranium en solution dans l'eau du lac. Aux alentours d'Alibodurlardamı, la série marneuse commence par les alternances de calcaires, de marnes, d'argiles et de grès. Des bancs des calcaires argileux se trouvent immédiatement sur la partie radioactive (fig. 4). Aux environs de Bakacak Tepe, la série marneuse commence par les couches de marne. On ne constate pas d'abondance de sulfate dans ces deux endroits. Les anomalies radioactives montrent une continuité latérale, parallèle à la stratification. La radioactivité est liée aux argiles tuffitiques situées au-dessous du contact de base de la série marneuse et au-dessus de la série de base détritique. Mais les valeurs de la radioactivité sont basses et la puissance radioactive est assez faible. Cette situation montre clairement que l'augmentation rapide de CaCO_3 dans l'eau du lac a influencé le passage du caractère acide du milieu au caractère à peu près basique. Le changement de l'acidité de l'eau du lac a causé la précipitation syngénétique de l'uranium. Dans ces lieux il n'y a pas une évaporation suffisante. Ainsi, la concentration de l'uranium en solution dans l'eau du lac est assez faible et, par conséquent, la précipitation syngénétique de l'uranium n'est pas considérable. C'est pour cela que les anomalies radioactives aux environs d'Alibodurlardamı et de Bakacak Tepe ont des valeurs basses et des puissances faibles.

La concentration épigénétique de l'uranium

A la fin du Néogène, le lac se retire. Les sédiments néogènes subissent une altération et une érosion par suite des influences atmosphériques. Des eaux vadoses filtrent vers les parties inférieures du faciès de Fakılı à partir des calcaires lacustres. Elles acquièrent un caractère acide à cause de l'abondance de sulfate dans le milieu. Pendant nos recherches sur le terrain, nous avons versé de l'eau potable sur un bloc du gypse fibreux provenant d'une des tranchées pour le nettoyer dans notre camp. Nous avons vu avec étonnement que les eaux qui ont atteint le sol calcaire après avoir lessivé l'échantillon ont provoqué une vive effervescence. Cette réaction est due à l'acide sulfurique qui se forme pendant que l'eau descend

de la surface de l'échantillon vers le sol. D'autre part, les eaux qui circulent dans le faciès de Fakılı prennent un caractère acide à cause de la pyrite sédimentaire qui se trouve par endroit dans ce faciès. Les études effectuées au laboratoire ont montré que, quand on verse de l'eau normale sur le minerai de Fakılı, une fraction de 50% de l'uranium passe à l'état de solution en une heure à la température normale. Au bout de 15 heures, 71% de l'uranium est mis en solution, car les composants de la roche forment avec ceux de l'eau de l'acide sulfurique quand on verse de l'eau sur le minerai.

Au cours de leur filtration, les eaux vadoses, qui acquièrent facilement un caractère acide, lessivent les roches des zones qui contiennent une grande quantité d'uranium syngénétique dans le faciès de Fakılı. L'uranium repasse à l'état de solution dans ces eaux. Pendant la filtration de ces eaux vadoses, l'uranium, qui se trouve pour la deuxième fois à l'état de solution, précipite en composés de sulfate, dans les parties hétérogènes, au-dessus du contact de base du faciès de Fakılı. C'est une précipitation épigénétique de l'uranium. En réalité, cette concentration épigénétique de l'uranium n'est pas indépendante de la transformation de l'anhydrite en gypse. Les eaux acides perdent leur sulfate dans des milieux propices et le sulfate qui précipite donne naissance aux gypses secondaires. Les eaux en circulation perdent partiellement leur acidité avec la disparition du sulfate et l'uranium commence à précipiter. D'ailleurs, malgré le pic de SO_3 assez élevé entre les altitudes de 780 à 805 m, on ne rencontre pas de gypse ici. A ces altitudes il y a beaucoup d'anhydrite (fig. 4, profil 1). Par contre, les cristaux du gypse secondaire commencent à paraître au-dessous de l'altitude de 780 m, où ils remplissent les fissures. Les dimensions des cristaux du gypse secondaire sont variables et atteignent parfois jusqu'à 10 cm. La quantité de gypse atteint une valeur maximum au-dessus du contact de base du faciès de Fakılı. Il diminue puis disparaît dans les parties plus basses. Il y a un accroissement de volume au cours de la formation du gypse secondaire, accroissement qui conduit à la formation de fissures de diverses dimensions dans la roche. Ces fissures assurent la circulation des eaux même dans les argiles, argiles tuffitiques, etc. Au cours de nos recherches de l'année précédente sur le gisement de Fakılı, nous avons observé la minéralisation de l'uranopilite dans l'une des tranchées. Les cristaux d'uranopilite se trouvent dans les gypses secondaires, parfois ils sont sur les cristaux de gypse. Mais aujourd'hui les cristaux d'uranopilite sont beaucoup plus abondants que l'année précédente, dans la même tranchée. D'autre part, au cours des mêmes recherches, nous avons creusé une tranchée à deux gradins, avant le commencement de l'hiver. Le premier gradin était semblable à un puits et le deuxième avait la radioactivité maximum. D'abord, nous n'avons vu aucune minéralisation dans cette tranchée, ni à l'œil nu ni sous la lumière ultraviolette. Mais au printemps suivant nous avons observé sur les surfaces du premier gradin un minéral qui est fluorescent en vert jaunâtre sous la lumière ultraviolette. Ce minéral n'était pas visible à l'œil nu et il se trouvait comme un crêpi avec le gypse sur les surfaces du puits. Il est très probable qu'il s'agisse d'uranopilite. Cet incident peut être expliqué très simplement. Les eaux de pluie ont lessivé la couche radioactive et ont rempli le premier gradin. Ensuite, le sulfate et l'uranium ont précipité avec l'évaporation des eaux. Tout cela démontre que ces phénomènes continuent à se produire encore de nos jours.



Note :- Les niveaux donnant une valeur supérieure à 1000 C/S sont considérés dans la zone de minerai.

- L'activité maximum est de 10500 C/S.

- On a produit la projection des tranchées dans un plan vertical ayant la direction N-S.

FIG. 5. Disposition du minerai en forme de lentilles entre les tranchées 1 et 9 dans le gisement de Fakılı.

Donc, à cause d'une concentration épigénétique, les lentilles ont pris leur forme actuelle dans le gisement d'uranium de Fakılı (fig.5). On peut relever ici deux facteurs qui influencent la concentration épigénétique de l'uranium: l'un de ces facteurs est la texture hétérogène qui attire l'attention dans les parties où se trouvent les lentilles; le deuxième est la présence d'argiles.

En résumé, à Fakılı, les caractéristiques générales du minerai sont: couleur bariolée, présence de gypse secondaire, structure hétérogène, présence de pyrite sédimentaire, augmentation générale de la radioactivité.

Dans le gisement de Fakılı, on trouve des cristaux d'uranopilite à deux endroits seulement. Mais ces cristaux sont très rares et ne peuvent pas caractériser le gisement. On ne peut pas voir à l'œil nu le minéral essentiel qui caractérise le gisement. Les études minéralogiques se poursuivent encore pour déterminer ce minéral. Mais les analyses chimiques ont montré que l'uranium est sous forme de composé de sulfate. La teneur moyenne du gisement n'est pas élevée: elle est de 0,044% d' U_3O_8 .

Aux environs d'Alibodurlardamı et de Bakacak Tepe on trouve également une concentration épigénétique, mais elle n'est pas importante.

DISCUSSION

W.E. PETRASCHECK: Are there any indications of uranium in the Neogene basins that contain the borate deposits?

H. KAPLAN: No, the borate deposits are not in the immediate neighbourhood of the uranium mineralization.

S. CONSTANTINO HERRERA: Since you speak of this anomaly as a deposit, it would be interesting to know what the ore grades are.

H. KAPLAN: The average concentration is 0.044% U_3O_8 .

ORIGIN OF URANIUM IN OLIGOCENE QATRANI SEDIMENTS, WESTERN DESERT, ARAB REPUBLIC OF EGYPT

E.M. EL SHAZLY, N.M.T. EL HAZEK, A.A. ABDEL MONEM,
S.M. KHAWASIK, Z.M. ZAYED, M.E.M. MOSTAFA, M.A. MORSI
Atomic Energy Establishment,
Cairo, Arab Republic of Egypt

Abstract

ORIGIN OF URANIUM IN OLIGOCENE QATRANI SEDIMENTS, WESTERN DESERT, ARAB REPUBLIC OF EGYPT.

Uranium mineralization has been discovered in the Oligocene sediments in the northern part of the Western Desert of Egypt by the Egyptian Atomic Energy Establishment. The mineralization occurs in various forms as uraniferous phosphatic sandstone, uraniferous ferruginated sandstone, uraniferous carbonaceous clay, uraniferous clay, uraniferous limestone, uraniferous tubes and uraniferous fossil wood. The mineralization has been investigated in the field and in the laboratory by various techniques which helped to elucidate its conditions of deposition, characteristics and genesis.

A theory is advanced to account for the origin of Qatrani sediments whereby the uranium has been mainly carried by thermal brines of acidic oxidized nature initiated by Oligocene subvolcanic activity indicated by the presence of relics of geysers. The tectonic elements operating at that time are comparable to those acting on the Oligocene stage of development of the Red Sea, and transcurrent faulting has been in operation. The environment of deposition is dominantly fluviatile to fluviomarine where the sediments have been transported to the site of sedimentation by a river system draining higher areas located to the SE or ESE. Qatrani area and its vicinity were at that time the site of a delta under subtropical climatic conditions with abundant fauna and flora. Uranium has been laterally distributed in the media of this environment according to the favoured stratigraphic horizons, lithology and structure.

1. URANIUM MINERALIZATION

The Qatrani area is located in the northern part of the Western Desert of Egypt southwest of Cairo and north of Lake Qarun (Fig. 1). It is covered by Tertiary and Quaternary foreland sediments with an intercalated flow of Mid-Tertiary age.

The presence of uranium mineralization in the area has been reported by Abu Zeid and Abdel Monem [1] and Higazy and co-workers [2]. Further interest has been aroused on the completion of an aerial radiometric survey by Fouad and co-workers [3] for the area. Cameron [4] studied uranium distribution in the uraniferous carbonaceous clays and the factors influencing the concentration of this element in them in Qatrani area. Ground radiometric proving of the radiometric anomalies has been carried out by Khawasik and co-workers [5] while Pejatovic [6] studied the depositional conditions affecting the distribution of uraniferous carbonaceous clay beds. Further studies on the geology and mineralization of the area have been carried out by Mostafa [7] and Morsi [8], and interesting geochemical and mineralogical investigations on the uranium mineralization are found in the work of El Shazly and co-workers [9], Abdel Gawad and co-workers [10], Khattab [11], Zayed [12] and Girgis [13].

The uranium mineralization is of wide extension in the lower part of the sedimentary Oligocene succession, and it is manifested in several forms,

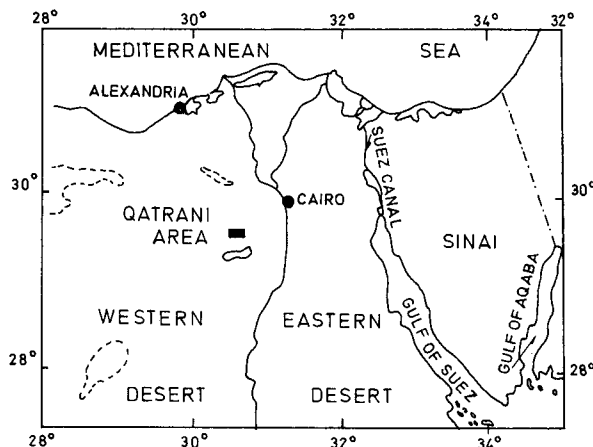


FIG. 1. Location map of the Qatrani area.

namely uraniferous carbonaceous clay, uraniferous clay, uraniferous ferruginous sandstone, uraniferous phosphatic sandstone, uraniferous impure limestone, uraniferous tubes and uraniferous fossil wood. No uranium or uranium-bearing mineral has been identified in the mineralization, except for francolite carrying a high uranium content in the uraniferous phosphatic sandstone; otherwise uranium has been found to be very finely dispersed in the mineralization by the nuclear emulsion technique. In all cases uranium has been detected in only the hexavalent state. The mineralization normally occurs in a bedded form as lenses several centimetres to several metres thick within the beds of various thicknesses which may reach hundreds of metres, with the beds themselves extending up to tens of kilometres. Sometimes the mineralization has been reported as veins cutting the bedding or controlled by cross-bedding in the case of some occurrences of the uraniferous phosphatic sandstone and uraniferous ferruginous sandstone or in fractures in limestone. Furthermore, the occurrence of the enrichment of mineralization along fault lines (NW-SE, NE-SW) has been observed.

The uranium content in the mineralization is highly variable while thorium is not anomalously enriched. In the uraniferous phosphatic sandstone mineralization, uranium is abnormally high in the separated francolite mineral (0.6% U), while in the mineralization it ranges from 0.02 to 0.21% U. The radiometric equilibrium in the uraniferous phosphatic sandstone is given as unity, indicating that the mineralization is essentially in equilibrium and radon gas has not been lost, but anomalous concentration of Ra E is given as the most probable factor causing the relatively excessive beta activity [11]. The uraniferous phosphatic sandstone shows a certain spatial and stratigraphic relation to the bone beds within the Oligocene sediments.

The uraniferous carbonaceous clay is associated with clay beds containing decayed organic matter of the humic type between overlying and underlying sandstone beds. The uranium content is variable in the

mineralization, and may reach 0.07%. An investigation has been carried out on equilibrium-disequilibrium conditions in three locations where the carbonaceous clay layer forms a trough, with the limbs occupied by locations 7 and 22. Uranium concentration has been found to be higher in the trough as compared to the limbs, and in the periphery of the layer as compared to its centre. The histogram of eU/eRa (P) shows a bimodal distribution at 0.9 and 1.3 on both sides of the equilibrium value of unity. At location 7, $\bar{X}P$ is 0.87 in the surface samples and is unity in the subsurface samples. It has been accordingly suggested that both U and Ra have been mobilized post-depositionally in the carbonaceous clay layer by surface agents with U more highly mobilized towards the troughs, while P of the least affected mineralization is considered as unity. It has been also noted that U increases with increasing ash content and decreases with the organic matter content of the carbonaceous clay [7]. The conditions prevailing in the carbonaceous clay are considered in general comparable to those of the uraniferous coaly beds [14, 15].

Interesting mineralization is noted in Oligocene fossil wood, where the uraniferous silicified wood is ferruginated, and in tubes which are also ferruginated and which are associated with faults or in sandstone in the Oligocene Lower Sandy Member. The uraniferous fossil trees are ferruginated and they have been occasionally found with thin roots in situ, thus indicating that uranium solutions containing significant iron content have been active in the present site of mineralization.

2. STRATIGRAPHY AND URANIUM MINERALIZATION

Uranium has been found in the Oligocene sedimentary succession of the Qatrani area. For this reason stress will be laid on the stratigraphy of the Oligocene sediments although Eocene and Miocene sediments are also represented.

The Oligocene Gebel Qatrani Formation overlies conformably the Upper Eocene Qasr El Sagh Formation. The latter attains a maximum thickness of 155 m and consists of limestones and clays, changing towards the top into sandstones and sands. It shows the presence of land animals, coalified plants and marine fossils, especially of the shallow water kind. Gebel Qatrani Formation, on the other hand, is overlain by a basalt sheet, belonging to the Mid-Tertiary volcanicity, of about 20 m thickness, and they are separated by an erosional unconformity surface (Fig. 2). The Lower Miocene Gebel El Khashab Formation overlies unconformably the eroded surface of the basalt, the former being an accumulation of sands and gravels with scattered fossil trees.

The Gebel Qatrani Formation consists of variegated sandstones, sands and clays with recurring beds of impure limestones and is subdivided into three members [7], namely the Lower Sandy Member, Middle Clayey Member and Upper Sandy Member. The Lower Sandy Member consists of pale reddish to white sandstones and sands with clay intercalations, and it is notable for the presence of beds with bones, and fossil trees and tubes. It encloses uraniferous brown clay, uraniferous phosphate sandstone, uraniferous fossil trees, uraniferous ferruginous sandstone and uraniferous tubes. The Middle Clayey Member consists of grey to green clays with intercalations of limestones and sandstones. It is notable for the

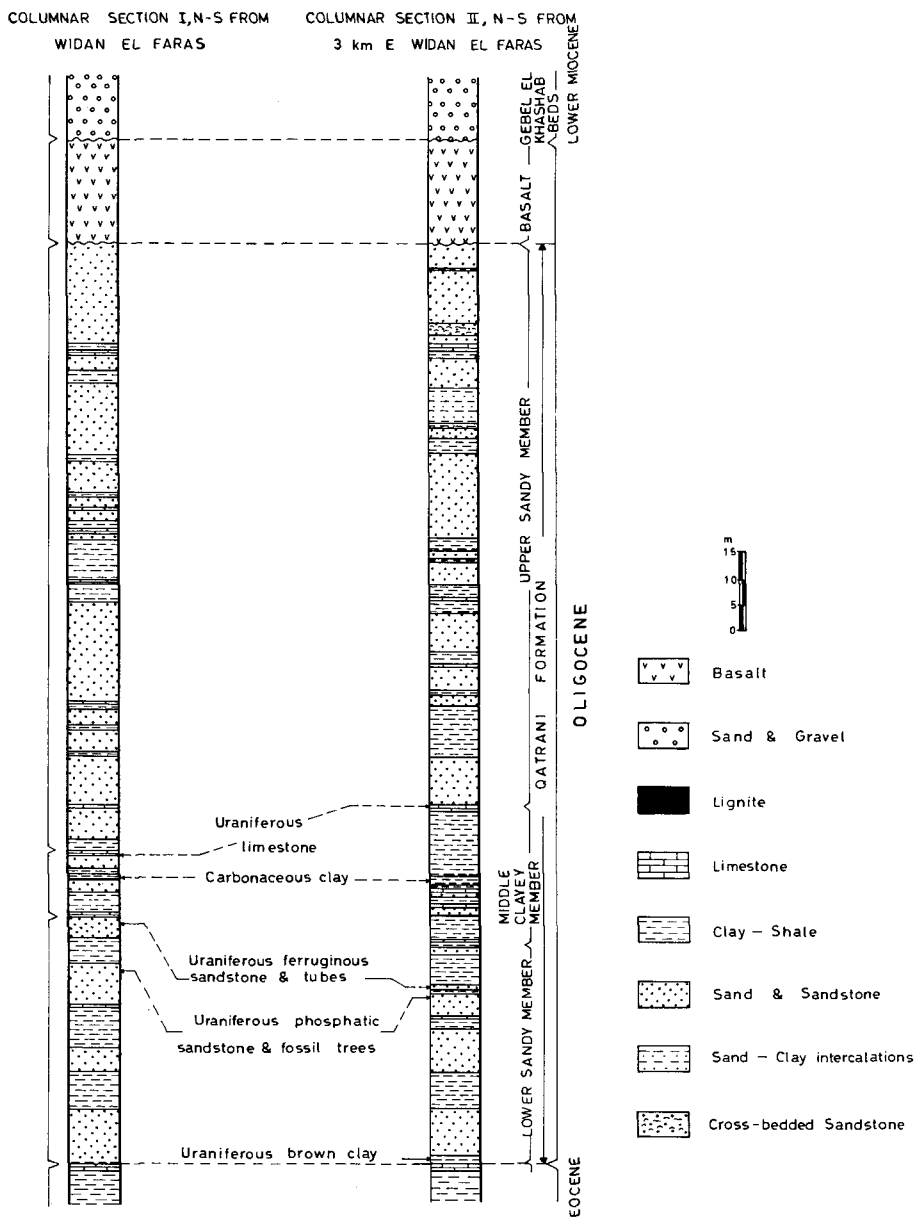


FIG.2. Stratigraphy and uranium mineralization, Qatrani area.

presence of the layer of uraniferous carbonaceous clay. The Upper Sandy Member is composed of pale reddish and white sands and sandstones with impure limestone and clay beds. Uranium mineralization is noted in an impure fractured limestone bed in the Upper Sandy Member.

The Gebel Qatrani Formation has a thickness of about 170 m; however, it is changing laterally in lithology and thickness. An example of the stratigraphy and uranium mineralization of the Oligocene rocks of the Qatrani area is given as two columnar sections at Widan El Fares and 3 km east of it (after Morsi [8]), where the thickness of the Qatrani Formation is 180 m and the overlying basalt 20 m (Fig. 2). The position of the uranium mineralizations encountered in these columnar sections is shown.

It is evident that the sedimentation conditions prevailing during the Oligocene are the continuation of those of the Upper Eocene leading to the predominance of fluvial to fluviomarine conditions. A delta of an important river system was coming into existence in the area and the vicinity, and was moving towards the north in Miocene times, with the regression of the Tethys (predecessor of the Mediterranean Sea). The sedimentation parameters of the sediments [16] suggest either long transport or the passing through of several cycles of sedimentation. It has been suggested by Pejatovic [6] that alternating reducing and oxidizing conditions existed during the deposition of Qatrani Formation. Accordingly, the Middle Clayey Member may be considered as deposited generally under a reducing environment, and the Lower and Upper Sandy Members under a general oxidizing environment. It is very difficult at present to assess the degree of reducibility of the environment of the Middle Clayey Member in spite of the presence of coalified material, iron in a predominantly ferric state and uranium exclusively in the hexavalent state, and owing to the fact that the investigations carried out on Qatrani mineralization have mainly been conducted in the top parts where oxidation conditions prevail at present. However, it can be assumed that conditions have never been strongly reducing, and that oxidizing acidic conditions may have been brought to the site of deposition with the uranium-bearing solutions.

3. VOLCANICITY AND URANIUM MINERALIZATION

A Mid-Tertiary basalt flow occurs between the Oligocene sediments and Lower Miocene sediments in the Qatrani area (Fig. 2). No relation has been found to exist between uranium mineralization and this particular flow. However, tubes have been observed in the eastern part of the Qatrani area in association with faults, as well as in the sandy extension of the bone bed encountered in the Lower Sandy Member of the Oligocene Gebel Qatrani Formation. In the former case the tubes have been found together with ferruginous sandstone in the Lower Sandy Member along the zones of three faults, namely Nos 25, 9 and 14. Faults Nos 25 and 9 belong to the NW-SE set with No. 25 showing remarkable horizontal displacement of 6-8 km, while fault No. 14 is of the NE-SW set.

Normally the tubes range from 0.5 to 20 cm in diameter and from 10 to 170 cm in height. Their outer shell consists of hard dense ferruginous sandstone, while the core is filled in part with ferruginous sand. Some of the tubes are radioactive and the outer shell is more radioactive than the core; the radioactivity decreases with depth, both in the outer shell and

the core, until it is equal to the radioactivity of the enclosing sediments. In the examined outcropping tubes the radioactivity of the outer shell ranges from 30-70 $\mu\text{R/h}$, while the core may reach 25 $\mu\text{R/h}$. The association of uranium with tubes in the Qatrani area supports, at least in part, the idea of the transport of this element by geysers.

4. STRUCTURE AND MINERALIZATION

The primary structures in the Gebel Qatrani Formation are represented by the bedding and cross-bedding of the sediments. As a general rule the bedding is extremely gentle (1° - 3°) towards the north, conforming with the general regional dip towards the Mediterranean. Cross-bedding is exhibited by some sandstones in the formation. Measurements of the direction of cross-bedding in the calcareous sandstones indicate that the sediments have been transported by a river system from the SE, ESE and NE directions as one goes from the older to the younger sediments within the formation. The interpretation of this is that the source of the Gebel Qatrani Formation is generally from the east, with the material at an early stage coming from the southeast and at a later stage from the northeast. The Eastern Desert from which the sediments are derived was higher towards the south in the earlier Oligocene, while its northern part was uplifted in the later Oligocene times. Examination of the direction of the fossil trees in the Lower Sandy Member indicates that they have been transported by a river system running from the SE and ESE towards the NW and WNW [8], which is in agreement with the analysis of cross-bedding. The fossil trees are represented mainly by species which essentially flourish under subtropical climate – and these species are mostly observed transported and rarely found with their roots in the Lower Sandy Member in the Qatrani area. The uranium mineralizations in the Gebel Qatrani Formation have been mostly reported as lenses of variable dimensions parallel to the bedding planes; however, in some cases uranium mineralizations have been considered cutting across the stratification in a vein-like form, e.g. uraniferous phosphatic sandstone [11]. Morsi [8] reported the association of uranium in the uraniferous sandstones with cross-bedding.

Secondary structures are found in the Qatrani area as faults, folds and joints. The faults are usually of the normal, mostly strike-slip type, with some showing rotational features. Two generations of fault systems are distinguished, an older one having NW-SE and NE-SW faults, and a younger E-W, WNW-ESE and ENE-WSW system. The older set has evidently developed in conjunction with the land emergence in Upper Eocene and Oligocene, whose sediments are cut by this set. This set is correlated with the Gulfs of Suez and Aqaba trends and is related to one structural stage of Red Sea development. The faults show notable horizontal displacement, exhibited in particular by No. 25 (transcurrent fault) (see Fig. 3) which has a horizontal displacement of 6-8 km, thus bringing Oligocene against Upper Eocene sediments. Uranium mineralizations are notably present along this set of faults represented by uraniferous ferruginous sandstone and uraniferous tubes, as illustrated by fault No. 25 in Fig. 3. The younger set of faults traverses all the rocks outcropping in the area including the basalt sheet and the Lower Miocene sediments. This set is believed to

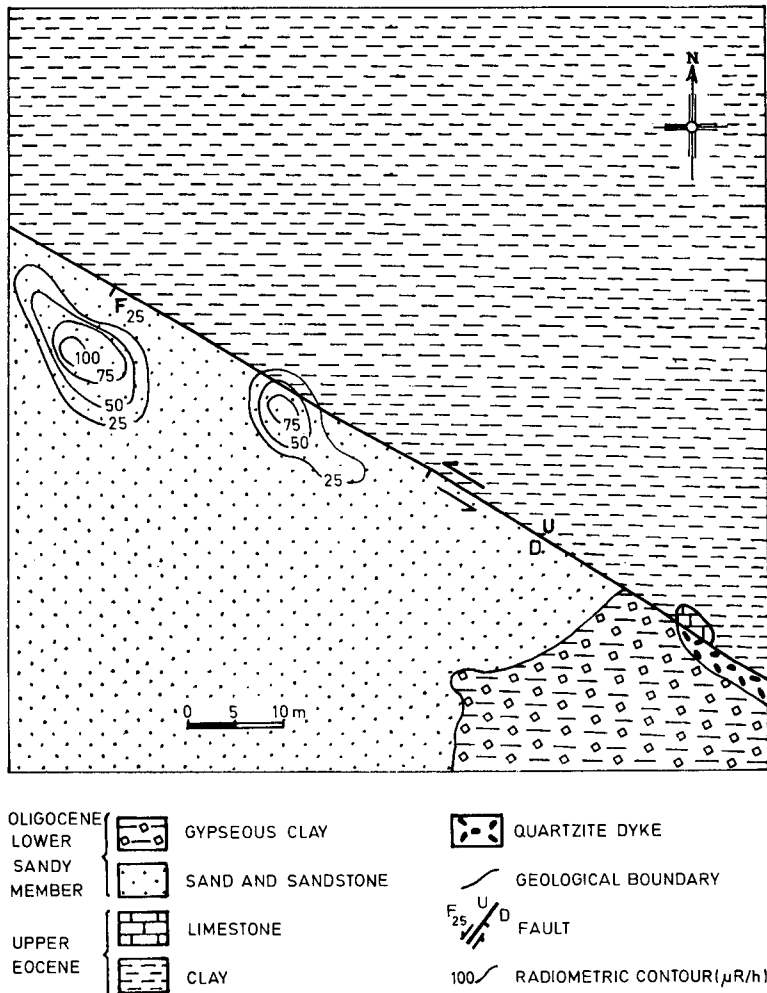


FIG.3. Uraniferous ferruginous sandstone anomaly on fault No.25, Qatrani area.

belong to Mediterranean tectonism, and is evidently connected to the Miocene land subsidence, although its duration is suspected to extend to the Pliocene or later. The fault planes of both sets are steeply inclined and their vertical displacement is within the range of metres or tens of metres.

A major anticline is present in the Qatrani area superimposed on the Oligocene sediments with parallel minor anticlines and synclines. The axis of the major anticline is E-W plunging 6° to W and is apparently symmetrical [8]. If this anticline is considered as resulting from the

same movements producing the NW-SE and NE-SW faults, the axis of major stress would be N-S. On the other hand, the axis of major stress is considered E-W in the case of the younger set of faults. Soft sediment deformation such as crumbling or slumping, disrupted bedding, penecon-temporaneous folding and dykes are common in the Qatrani area where they reflect the instability prevailing during the deposition of the Gebel Qatrani Formation. Interbedded anticline and syncline have been observed in sand and clay within the Lower Sandy Member with a N-S axis and attaining lengths of tens of metres.

5. GEOCHEMISTRY AND MINERALOGY OF THE URANIFEROUS CARBONACEOUS CLAY

Special stress will be placed in this respect on the uraniferous carbonaceous clay, because it has been analysed in a greater number of samples than the other uranium-bearing sediments. The mineralogical composition of this clay is very complex, as it contains appreciable quartz (6.65%), iron oxides: hematite and goethite (10.96%), gypsum (8.40%), carbonates: dolomite (3.89%) and calcite (0.38%), organic matter (16.22%), and soluble salts (8.28%). The clay essentially represented by montmorillonite amounts to 45.22%, which is less than half of the total rock. Other minor minerals present include native sulphur, pyrite, altered feldspars mainly as sericite, fine octahedra of magnetite, biotite and cllophane. Gypsum occurs as crystalline aggregates or as fibrous radiants, while veinlets of gypsum cutting the clay are common. Quartz occurs in anhedral to subhedral disseminated grains, and carbonates appear as fine anhedral to subhedral crystals embedded in clayey matrix with fine iron oxides and carbonaceous matter. The latter is mainly of humic nature, and coal of low rank has been occasionally observed.

Complete chemical analysis has been carried out for 25 samples of the uraniferous carbonaceous clay from anomalies Nos 52, 63, 68, 71 and 77. $\bar{X}$ in wt% for the chemical composition of these samples is as follows: SiO₂ 30.28, Al₂O₃ 9.63, FeO 0.93, Fe₂O₃ 10.10, CaO 5.69, MgO 1.50, Na₂O 1.73, K₂O 0.06, CO₂ 2.15, SO₃ 4.29, P₂O₅ 0.10, S 0.28, H₂O 7.64, organic matter 16.79, soluble salts 8.53 and humic acid 3.64. The mean soluble salts have been reported as follows in wt%: Na 12.47, K 7.27, Mg 5.54, Ca 7.39, Cl 39.37, SO₄ 18.47, not determined 9.49.

The correlation coefficient calculated for U in the clay versus the various constituents is given as follows: SiO₂ -0.38, Al₂O₃ -0.37, Na₂O (insoluble) +0.22, Ca (soluble) +0.38, Na (soluble) +0.34, Cl (soluble) +0.46, water soluble salts +0.51, humic acid -0.12, calcite 0.01, FeO +0.04, Fe₂O₃ +0.11, CO₂ +0.37, Mg (soluble) +0.61, SO₄ (soluble) 0.02, K (soluble) 0.12, organic matter -0.42, dolomite +0.58 and gypsum -0.02. It is striking to notice the negative correlation coefficient with organic matter and humic acid. Strong positive correlation with uranium is noted in the case of the soluble salts (and their constituents Mg, Cl and Na), and in the case of dolomite.

Assuming the salts present in Qatrani uraniferous carbonaceous clay represent brine circulating in these sediments, they would be enriched in K, Mg, Ca and SO₄ and depleted in Na and Cl compared to sea water. On

the other hand, the hot Red Sea brines compared to sea water are enriched in Na and Ca, and depleted in Mg and SO_4 and they are acidic while the sea water is alkaline (see Ref. [17]). However, both possess in common a high Ca:Cl ratio. The comparison can generally be only due to the transformation in the composition of the soluble salts in Qatrani and the difficulties encountered in determining the authentic chemical composition of the brines.

It is also of particular importance to compare the mineral composition of the deep sediment samples provided by the research vessel Atlantis II (from where hot brines have been discovered in the Red Sea) with the mineral composition of Qatrani uraniferous carbonaceous clay. Both contain montmorillonite-type clay, quartz and feldspar and are rich in iron minerals. The iron minerals found in Atlantis II deep sediments are mainly poorly crystallized or amorphous iron hydroxide, while pyrite could be identified by X-ray diffraction [17]. Furthermore, the Miocene detrital sediments exposed in St. John's Island — on the periphery of the axial trough of the Red Sea — and influenced by the Red Sea Miocene metasomatic phenomena are found to be generally uraniferous and their radioactivity may reach four times the background [18].

During the leaching experiments conducted on the uraniferous carbonaceous clay, uranium was found in the hexavalent state; this is also true for the uranium present in the uraniferous ferruginous sandstone as reported by El Shazly, El Hazek and Zayed [9] and in the uraniferous fossil wood. Here it should be mentioned that Girgis [13] found that uranium is only found in the hexavalent state in Qatrani uraniferous phosphate mineral, while the element is present both in the tetravalent (about 70%) and hexavalent (about 30%) states in sedimentary bedded phosphorites of marine origin in the Red Sea and the Nile Valley regions [19, 13].

Several investigators including Abdel Gawad, Faris and Khattab [10], have found that the uranium-bearing phosphate mineral in Qatrani is francolite. It was also found [10] that francolite is highly enriched in uranium in the pure mineral containing 0.6% U. Differences have been noted, however, between the sedimentary phosphorites and the Qatrani francolite [13] regarding the resemblance of the latter to synthetic hydrothermal carbonate apatite prepared by Coles [20], in that the band at about 980 cm^{-1} in their infrared spectrograms was missing. Geochemically Nb is enriched in Qatrani uraniferous phosphatic sandstone (166 ppm Nb), and impoverished in V (not detected) and Y and Yb (60 and 3 ppm respectively) as compared to the sedimentary marine phosphorites of Safaga. Nb, Yb and V have been reported in sea water; however, the reason for the selective incorporation of some of these elements in Qatrani or marine sedimentary francolite is most probably due to the variable physico-chemical conditions of transport and deposition of the phosphate mineral in both cases. It is most probable that Nb is enriched under the relatively high temperature and/or acidic environment believed to be prevailing during the deposition of Qatrani francolite. A black titaniferous material is also characteristic of Qatrani uraniferous phosphatic sandstone [11]. All this evidence leads to the assumption that the phosphate mineral "francolite", which is the uranium-bearing mineral in the uraniferous phosphatic sandstone, has been deposited by hydrothermal solutions (e.g. hot brines) by a mechanism radically different from the francolite mineral deposited under the well-established marine phosphorites. The authors

agree with Abdel Gawad, Faris and Khattab [10] that the source of P is the animal bones abundant in Qatrani bone beds; however, these authors favour ground-water transport for uranium, and we do not agree with this.

6. CONCLUSIONS

The weight of evidence indicates that uranium in the Oligocene Qatrani sediments has been deposited during Oligocene times where certain endogenic and exogenic conditions prevailed. The exogenic conditions are manifested in the action of geysers representing subvolcanic conditions as indicated by the presence of uraniferous ferruginated tubes. Furthermore, the active fault lines considered as channels for this subvolcanic action are the NW-SE and NE-SW faults, which are transcurrent faults closely related to one of the tectonic stages of the development of the Red Sea. Mineralization of uraniferous ferruginous sandstone and uraniferous ferruginated tubes has been noted along the zones of these faults or in close spatial relation to them.

The exogenic conditions prevailing during uranium deposition are fluvial to fluvio-marine, giving a clastic sequence of sandstone and clay with occasional thin beds of impure limestone. The Qatrani area and its vicinity have been a site of a delta where sediments are brought by a river system running from SE and ESE towards the NW and WNW in the earlier Oligocene and changing course in the later Oligocene. Trees have been brought by these rivers and are characteristic of a subtropical environment; also trees and animals were present in the site. The authors' investigations indicate that the normal silicified trees have been transported by the river system while the uraniferous ferruginous trees have been mineralized in the site of deposition at the Qatrani area. Oscillating conditions prevailed, but they generally were related to the rising of the land mass, while the Tethys shores were moving generally northwards. The notable presence of uranium mineralization in association with clay and sandstone beds and to a lesser extent in limestone beds is an indication of its stratigraphic and lithologic control by various beds present.

Although uranium has been found mainly in the tetravalent state and to a lesser extent in the hexavalent state in marine phosphorites (in Egypt) exposed to weathering by surface agents, the presence of uranium in the hexavalent state indicates that it was deposited originally in the hexavalent state although partly mobilized in the easily weathered carbonaceous clay layer. Hot brines, which are of an acidic oxidized nature, are considered as the solutions carrying the uranium mineralization, owing to the abundance of salts in the uraniferous carbonaceous clay and their strong positive correlation with uranium. The association of uranium with ferruginated trees, its increase with the increasing ash content and its negative correlation with organic matter and humic acid indicate that the time of deposition of uranium was shortly after the burial of the trees and did not give them enough time to go through the diagenetic processes. The fixation of uranium in the phosphatic sandstone is thought to be brought about by the abundance of phosphorus in the animals which were flourishing in the environment. Although the source of recent hot brines in the Red Sea and their environment is still controversial [21], it is however believed that the brines carrying the uranium in the Qatrani area are of

subvolcanic derivation or at least activated by the volcanicity, and have been circulated and deposited in the sediments under the prevailing previously described exogenic environment. The presence of uranium mineralizations at various stratigraphic levels and in different forms shows that the mineralizing solutions have been introduced in several intermittent pulses and not in a single phase.

REFERENCES

- [1] ABU ZEID, S., ABDEL MONEM, A.A., The Discovery of Uranium-bearing Quartzitic Veins at Gebel Qatrani Area, Internal Rep., Geology and Raw Materials Dept., AEE, Cairo (1957).
- [2] HIGAZY, R.A., et al., "The Discovery of Uranium Ores in Egypt", Int. Conf. Peaceful Uses Atom. Energy (Proc. Conf. Geneva, 1958) 2, UN, New York (1958) 97.
- [3] FOUAD, K.M., et al., Airborne Radiometric Prospection of Qatrani area, Western Desert, Internal Rep., Geology and Raw Materials Dept., AEE, Cairo (1966).
- [4] CAMERON, J., Report to the Government of the United Arab Republic on Nuclear Raw Materials Prospecting and Evaluation, Technical Assistance Rep. 362, IAEA, Vienna (1968).
- [5] KHAWASIK, S.M., et al., Prospection for Uranium in Qatrani area, Western Desert, Internal Rep., Geology and Raw Materials Dept., AEE, Cairo (1968).
- [6] PEJATOVIC, S., Geological Regularities in Situation of Coaly Clay-bearing Uranium Manifestation at Gebel Qatrani Area, Fayum District, Internal Rep., Geology and Raw Materials Dept., AEE, Cairo (1968).
- [7] MOSTAFA, M.E.M., M.Sc. Thesis, Faculty of Science, Cairo University (1972).
- [8] MORSI, M.A., M.Sc. Thesis, Faculty of Science, Cairo University (1974).
- [9] EL SHAZLY, E.M., EL HAZEK, N.M.T., ZAYED, Z.M., "Leaching experiments on uraniferous shales and sandstones from Qatrani, Western Desert, United Arab Republic", The Recovery of Uranium (Proc. Symp. São Paulo, 1970), IAEA, Vienna (1971) 57.
- [10] ABDEL GAWAD, A., FARIS, M.I., KHATTAB, K.M., Geochemistry in Relation to Origin of Uranium at Gebel Qatrani Area, Western Desert, Programme and Abstracts, Geol. Soc. Egypt, Cairo (1966) 15.
- [11] KHATTAB, K.M., M.Sc. Thesis, Faculty of Science, Ain Shams University, Cairo (1965).
- [12] ZAYED, Z.M., M. Sc. Thesis, Faculty of Science, Cairo University (1971)
- [13] GIRGIS, L.A., Ph. D. Thesis, Faculty of Science, Ain Shams University, Cairo (1974).
- [14] VINE, J.D., TOURTELOT, E.B., Geochemistry of black shale deposits, Econ. Geol. 65 3 (1970) 253.
- [15] SZALAY, A., "The significance of humus in the geochemical enrichment of uranium", Int. Conf. Peaceful Uses Atom. Energy (Proc. Conf. Geneva, 1958) 2, UN, New York (1958) 182.
- [16] DABBOUR, G.A., Mineralogy and Sedimentation Properties of Black Sand Sample, Qatrani Area, Western Desert, Internal Rep., Geology and Raw Materials Dept., AEE, Cairo (1972).
- [17] DEGGENS, L.T., ROSS, A., Eds, Hot Brines and Recent Heavy Metal Deposits in the Red Sea, Springer, New York (1969).
- [18] EL SHAZLY, E.M., et al., Personal communication.
- [19] EL SHAZLY, E.M., EL HAZEK, N.M.T., EL MAHROUKY, F.A., Geochemistry of East Luxor rock phosphate as a basis for its technology, Trans. Arab Mining Petroleum Association, Cairo, 27 2 (1972) 199.
- [20] COLES, J.L., Ph.D. Thesis, Univ. Utah (1963).
- [21] ROSS, DAVID A., Red Sea hot brine area: revisited, Science 175 (1972) 1455.

DISCUSSION

J. A. FERNANDEZ POLO: What was the uranium enrichment process that took place in the Qatrani clays? Is it an adsorption process that you observe in the sandstone-bounded clay horizons?

N. M. T. EL HAZEK: The enrichment process in the uraniferous Oligocene carbonaceous clay layer of the Qatrani Formation is thought to have involved calcium precipitation with the soluble salts from hot brines.

Adsorption of uranium on clays or iron oxides was in any case, as is evident from the negative or very weak correlation, not the main concentration mechanism.

H. H. ADLER: You do, I believe, associate uranium adsorption on clays with certain aspects of ore formation, and there have been many references in other papers to the role that uranium adsorption plays in ore formation. Have you done yourself, or do you know of, any experimental work aimed specifically at determining the concentrations of uranium that can effectively be held on montmorillonite, and, more important still, the quantity of uranium this might represent if we were interested in clays as a potential source of low-grade, high-cost uranium?

N. M. T. EL HAZEK: No such specific experimental work has been done on the uranium-bearing carbonaceous clay layer of the Qatrani Formation. However, as I said a moment ago, it is believed that most of the uranium concentration in these clays is due to a process other than adsorption; this is evident from the correlation coefficients.

A. HERBOSCH: Gauthier has reported experimental work¹ on adsorption or co-precipitation of uranium by different types of clay. If my memory is correct, he found that it was mainly the effect of entrainment on very fine particles that was important, especially at alkaline pH values.

W. E. PETRASCHECK: Mr. Adler's question about the adsorption of uranium on clays raises a real problem, especially for those of us who have been inclined to consider uraniferous schists as source beds from which uranium was leached to be redeposited in sandstone host rocks.

H. H. ADLER: We have in the United States of America sandstone-type occurrences with vanadium micas in which a certain amount of uranium is contained in the structure (a roscoelite-carnotite type of material). These are actual ore deposits; but here we are dealing not with uranium adsorption on montmorillonite or zeolite but with discrete mineral formation.

N. KATAYAMA: We have found many localities where uranium is adsorbed on clay minerals adjacent to basement granites. Our experiments suggest that the optimum pH range for uranium adsorption on clay minerals is narrower than for adsorption on zeolite. Thus clay minerals may represent an important stage in uranium concentration, but they do not adsorb it stably enough to form an ore body.

S. S. ADAMS: I, too, am doubtful about the significance of adsorption directly on clays as a uranium concentration mechanism. Worthy of note, however, is the association of considerable uranium with clay galls and lenses in the Grants district. The mechanism leading to this association is probably an adsorption of organic matter on the clays and, in turn, complexing of uranium by the same organic material. The absence of thorium in association with the clays is most likely a result of its insolubility, which prevents it from entering the solution.

Partly because of this lack of strong adsorption of uranium on clays, devitrifying volcanic-rich shales readily release their contained uranium to solutions which, during compaction, move into adjacent aquifers where the uranium may be precipitated.

¹ Bull. Service Géologique Alsace-Lorraine 14 (1961) 179.

ANALOGIAS Y DIFERENCIAS DE CARACTERES DE FAVORABILIDAD EN DISTINTOS TERRENOS SEDIMENTARIOS DE LA CORDILLERA IBERICA

J. MARTIN-DELGADO TAMAYO, J. A. FERNANDEZ POLO

Junta de Energía Nuclear,
Madrid, Spain

Abstract-Resumen

SIMILARITIES AND DIFFERENCES IN FAVOURABILITY CRITERIA FOR VARIOUS SEDIMENTARY FORMATIONS IN THE IBERIAN CORDILLERA.

The paper describes the geological features of the Iberian cordillera and its adjacent zones where prospecting and exploration of uranium deposits in sedimentary formations are now in progress. The authors specify the most significant data and the standards which can serve as a guide in evaluating the nature and degree of favourability. A description is given of the best-known types of deposits and their similarities to, and differences from, other localized anomalies. Thus, the authors define the Picofrentes type in the Lower Cretaceous of Soria, the Mazarete type in the Lower Triassic, the Miocene paleochannels of Palencia and the lignite-containing basins.

ANALOGIAS Y DIFERENCIAS DE CARACTERES DE FAVORABILIDAD EN DISTINTOS TERRENOS SEDIMENTARIOS DE LA CORDILLERA IBERICA.

En el presente informe se describen los caracteres geológicos de la Cordillera Ibérica y zonas adyacentes, actual campo de los trabajos de prospección y exploración de yacimientos uraníferos en terrenos sedimentarios. Los autores se concretan a especificar los datos más significativos y las normas que puedan servir de guía para valorar el carácter y grado de favorabilidad. Finalmente se presentan los tipos de yacimientos más conocidos y sus analogías y diferencias con otras anomalías localizadas; así definimos el tipo Picofrentes del Infracretácico de Soria, el tipo Mazarete del Triás Inferior, los paleocauces miocenos de Palencia y las cuencas lignitíferas.

INTRODUCCION

Nuestro interés ha sido desplazado hacia la investigación de los terrenos sedimentarios continentales, especialmente mesozoicos y terciarios, después de un estudio intensivo de los yacimientos filonianos en granitos y pizarras; estos no han perdido totalmente su interés, dado que en ellos han sido descubiertas las actuales reservas de uranio que poseemos, clasificadas así: Recursos razonablemente asegurados a menos de 10\$/libra de U_3O_8 (equivalentes a 11 000 toneladas cortas de U_3O_8), 8000 tm de uranio metal; recursos razonablemente asegurados entre 10 y 15\$/libra de U_3O_8 , 7700 tm de U (ENEA-OIEA, de Agosto de 1973).

Por la razón antes expresada, hace aproximadamente algo más de una década que, mientras se conclúan los trabajos de evaluación, cubicación y explotación de algunos yacimientos en materiales cristalinos, se iniciaba un estudio geológico de nuestras cuencas sedimentarias, desarrollando programas de prospección regional, itinerarios de radiometría autoportada y, posteriormente, de prospección aérea. En la actualidad consideramos nuestros terrenos sedimentarios como preferentes por aparecer en los mismos caracteres suficientemente favorables, especialmente en alguna cuenca que ha sido objeto de exploración más intensa.

Entre las condiciones de favorabilidad, que sirven como «guías» orientativas para este tipo de prospección, destaca, en primer lugar, la consideración de la amplitud y morfología de cada una de las cuencas, su evolución geológica, grado de tectonización, litología, paleohidrogeología, etc.

Dentro del conjunto de cuencas sedimentarias continentales en nuestro país, hemos creído oportuno presentar las descripciones que se refieren a algunas de las áreas de la Cordillera Ibérica, por ser la que estimamos ofrece, hasta el momento presente, un conjunto de caracteres de favorabilidad mayor, así como un potencial inducido, a través de los estudios efectuados hasta el presente, de mayor entidad.

Teniendo en cuenta los factores de favorabilidad más significativos, anteriormente citados, nos encontramos con una primera clasificación por orden de importancia que sería la siguiente: en primer lugar los depósitos de arenas y areniscas del Infracretácico; en segundo lugar, las areniscas del Trías Inferior y, por último, los depósitos detríticos del Terciario.

NORMATIVA EN LA INVESTIGACION DEL SEDIMENTARIO DE LA CORDILLERA IBERICA

Aunque se trata de fundamentos básicos de tipo doctrinal, y aplicación bastante generalizada, creemos conveniente exponer a continuación las normas principales que nos sirven de orientación:

- Carácter de continentalidad de los sedimentos.
- Delimitación, evolución geológica y caracteres generales de cada cuenca.
- Estudio estratigráfico, facies litológicas y procesos sedimentológicos.
- Buzamiento de las capas y sus cambios en diferentes áreas de cada cuenca.
- Grado de tectonización de un área y su influencia en la estructura de los sedimentos.
- Determinación de los estratos de interés por caracteres macroscópicos, tales como existencia de materia orgánica, cambios granulométricos, niveles arcillosos intercalados, etc.
- Intensidad, magnitud y distribución de las anomalías radiactivas; grado de equilibrio o desequilibrio; localización de anomalías geoquímicas y su relación con el ambiente geológico.
- Existencia de colores de alteración significativa.

La interpretación de estos datos conduce a:

- Un levantamiento cartográfico más detallado, planificación de trabajo en superficie mediante calicatas o pequeños pozos, muestreos, etc.
- Programa de sondeos para un primer reconocimiento.
- Plan sistemático de sondeos geológicos en mallas amplias y su interpretación para confección de esquemas tridimensionales, a través de: a) estudio de niveles característicos; b) obtención de cuttings y estudio en laboratorio; c) correlaciones de capas; d) mapa de datos entre zonas de oxidación y reducción.

Todo ello conduce a la selección de áreas especiales para efectuar programas de sondeos mediante mallas más densas con objeto de localización de posibles cuerpos mineralizados (véase el cuadro).

AREA DE CADA UNA DE LAS ZONAS CON CARACTERES LITOLOGICOS DE INTERES (véase la figura 1)

	km ²
Margas continentales alternando con areniscas	28 800
Conglomerados calcáreos o mixtos, no masivos, alternando con areniscas o margas continentales detríticas	17 600
Conglomerados silíceos no masivos, alternando con areniscas o arcillas continentales detríticas	9 600 ^a
Areniscas silíceas alternando con algunas capas de areniscas calcáreas (areniscas de aljibe)	3 200
Arcillas continentales alternando con areniscas	1 760
Arcillas, arcósicas continentales, arenas y areniscas feldespáticas poco cementadas y arcillas (facies de Madrid)	22 400 ^a
Idem y aglomerados de bloques y gravas derivados de los macizos graníticos y nefísicos	800 ^a
Conglomerados, areniscas silíceas masivas o alternando con arcillas detríticas; facies Buntsandstein; permotrfas o similares	5 600 ^a
Argilitas y areniscas alternando; facies wealdense	1 760 ^a
Areniscas silíceas en bancos potentes alternando con margas y arcillas continentales (Weald cantábrico)	3 840 ^a
Argilitas y areniscas silíceas, facies wealdense, con algunas intercalaciones calcáreas o margosas	270 ^a
Argilitas y areniscas cuarcíticas, a veces conglomeráticas; facies wealdense	1 760 ^a
Idem en grandes bancos	910 ^a
Argilitas detríticas y cuarcitas	1 760
Argilitas, areniscas cuarcíticas y alguna capa calcárea: facies wealdense	480 ^a
Areniscas poco cementadas, arenas y conglomerados silíceos, arcillas caolínicas detríticas, en general poco cementadas, pueden alternar con alguna capa margoso-calcárea, facies Utrilla o Weald detrítico	10 240 ^a
Total	110 780

^a Series de mayor significación.

CARACTERES GEOLOGICOS DE LA CORDILLERA IBERICA

La Cordillera Ibérica constituye un sistema orogénico definido, con orientación general NW-SE, que enlaza la Cordillera Cantábrica con la extremidad más oriental de las Béticas, bordeando la Meseta. Se trata de un plegamiento de edad alpina, cuyo núcleo es el Paleozoico, y los materiales fundamentales, que a nosotros nos interesan, son los correspondientes a los depósitos continentales del Mesozoico, especialmente los del Cretácico Inferior; subsidiariamente, las areniscas del Triásico Inferior, además de algunas cuencas terciarias. Junto al carácter continental, debemos destacar la extensión de algunas cuencas, siendo las más importantes la Numantina en las provincias de Soria y Burgos, las cuencas de Peñalén, Peralejo de las Truchas y Molina de Aragón en

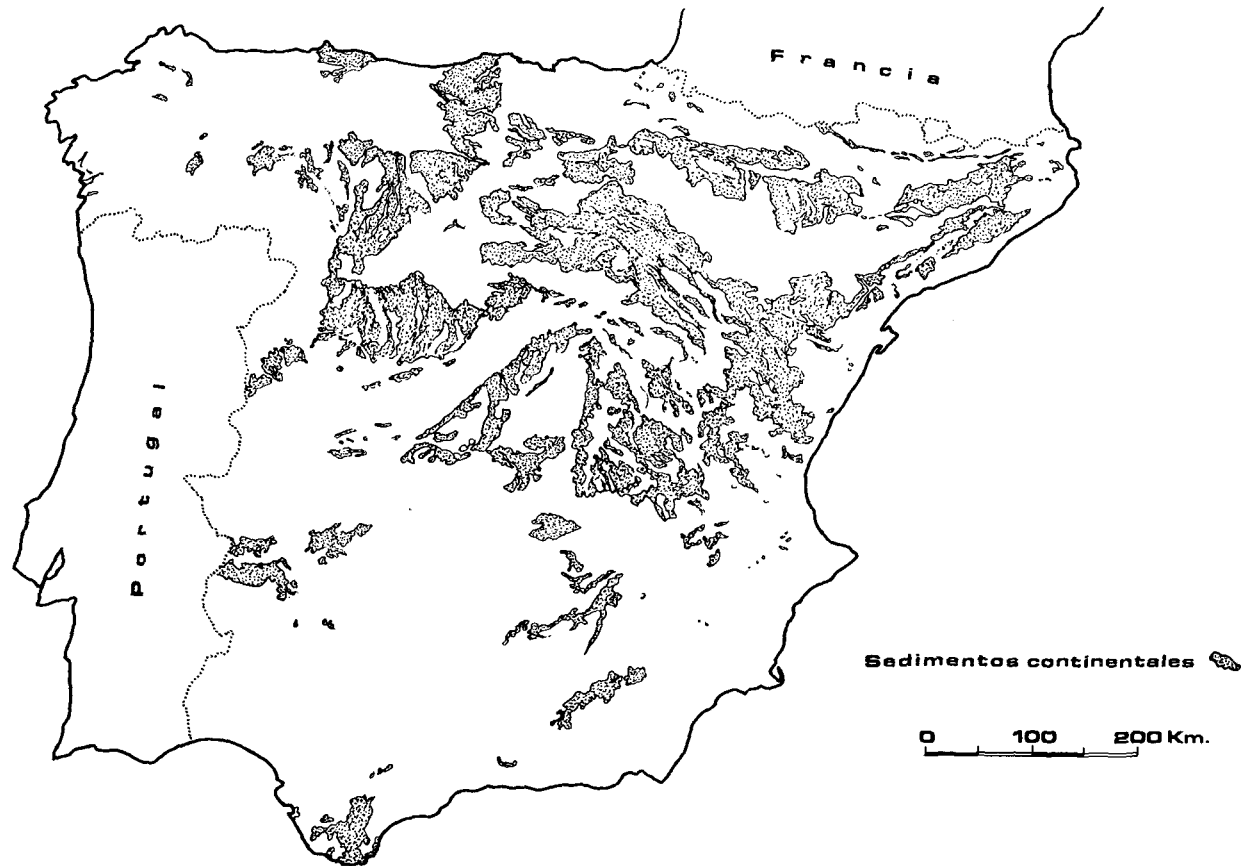


FIG. 1. Cuencas sedimentarias continentales interesantes.

Guadalajara y el complejo del Maestrazgo en las provincias de Teruel, Castellón y Valencia. Dentro de los materiales arenosos, de todas las formaciones antes citadas, se conoce la presencia de numerosas anomalías radiométricas y geoquímicas, materia carbonosa dispersa, piritas limonitizadas en superficie y en algunos casos minerales uraníferos visibles.

El carácter estructural, tanto en sus aspectos de plegamiento como de fracturación, posee gran diversidad en cuanto al grado de intensidad de ambos. Por lo que se refiere al primero, que repercute directamente sobre la inclinación de las capas, nos encontramos con áreas de considerable extensión en que el plegamiento es de efecto tectónico suave y de «estilo sajónico».

Por lo que se refiere a las dislocaciones hay, ciertamente, polígonos de mayor complejidad, que dan lugar a basculamiento de bloques y presencia de estructuras y fallas que pueden influir negativamente en el carácter favorable de algún área, aunque ello no sea un signo taxativamente excluyente. Es muy frecuente observar en los estratos la presencia de coloraciones de alteración supergénica; éstas pueden ser muy significativas dentro de un área, aunque no puedan extrapolarse de una formación a otra. Finalmente hay que indicar que son frecuentes las alternancias estratigráficas con la existencia de niveles arcillosos, intercalados entre las arenas o areniscas.

Organización básica (figura 2)

A efectos tácticos y de organización, la Cordillera Ibérica y zonas marginales ha sido dividida en cuatro zonas, designadas por los nombres de las ciudades donde se halla situado el centro de cada sector, y son: 1) Burgos; 2) Soria; 3) Teruel y 4) Cuenca. En cada una de ellas existen cinco o seis Centros de Prospección, dispersos en el área de su dominio. Cada una posee un gabinete de dibujo y administración, un laboratorio de campo, archivos y documentación, taller de reparación de gammámetros, etc.; asimismo dispone de toda ayuda necesaria por parte de los Departamentos Centrales de la División, tales como la Sección de Mineralogía, Servicio de Geoquímica, Geoestadística, Laboratorio de Electrónica, de Análisis, etc.

Resumen de los datos de prospección efectuados en cada zona

Zona 1) Burgos

Las formaciones sedimentarias de este sector comprenden una gran extensión de afloramientos de las areniscas infracretácicas, tanto albares como wealdenses y son las que tienen mayor interés. En algunas zonas de estos terrenos aparecen recubiertos por las calizas marinas del Cretácico Superior. De la base del Trías merecen ser citadas las areniscas que bordean el macizo de la Sierra de la Demanda. El Paleozoico constituye el núcleo del bloque levantado de esta Sierra y tiene un interés propio muy limitado. Los depósitos terciarios de tipo lacustre ofrecen escaso interés, a pesar de existir anomalías radiométricas en algunos niveles arenosos y en margas con material carbonoso; mayor interés tiene el paleógeno arcósico de la cuenca de Haro, típicamente depositado en régimen fluvial.

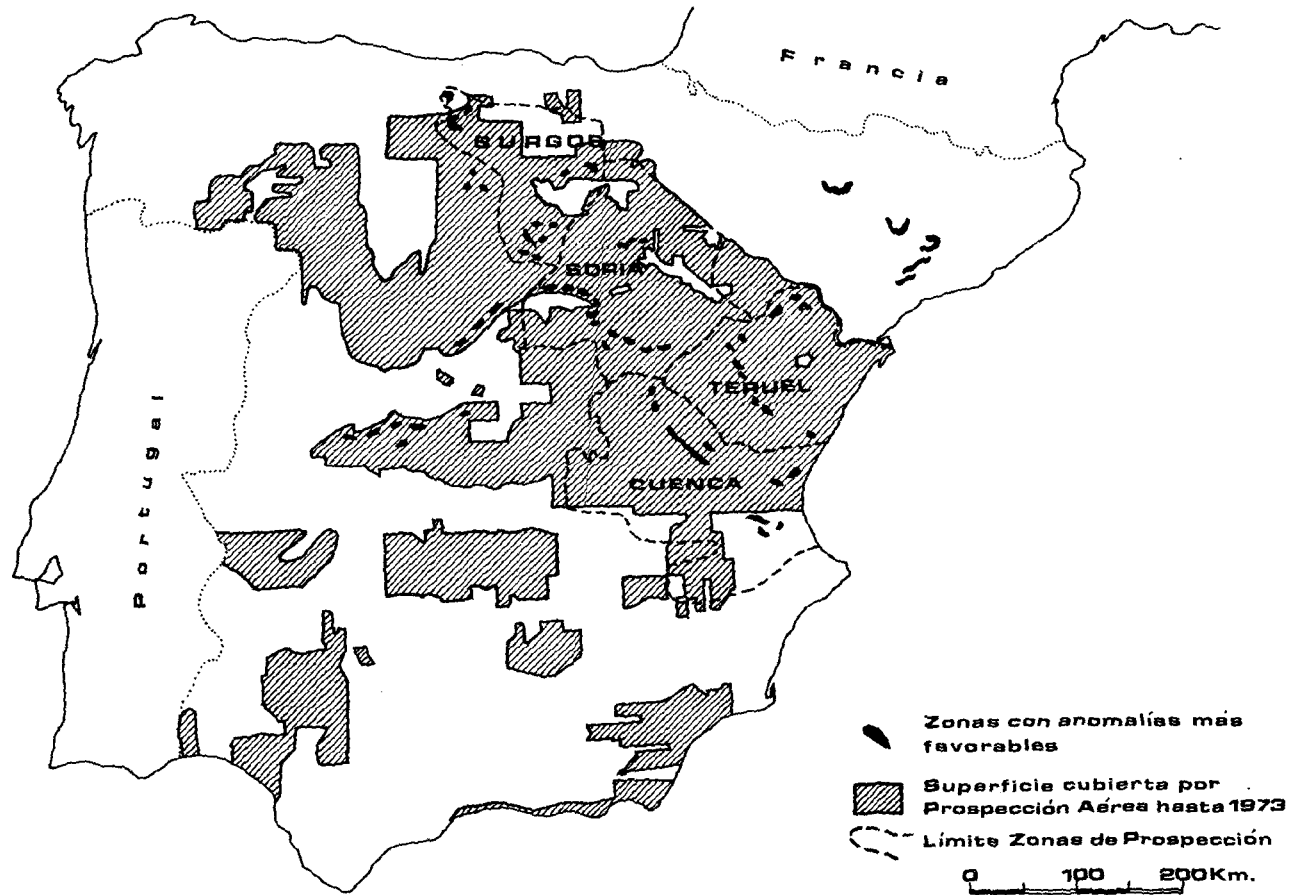


FIG.2. Algunas cuencas con anomalías actuales.

Area cubierta por prospección aérea	73% de la zona
Area cubierta por prospección autoportada	50%
Area cubierta por prospección a pie	12%
Area no prospectada	25%

Esta última corresponde fundamentalmente a la Sierra de la Demanda y parte del Cantábrico.

Por supuesto, en esta zona y en las que se consignan a continuación, los distintos tipos de prospección han cubierto el terreno independientemente, superponiéndose, total o parcialmente, sobre las mismas áreas y suministrando datos que se complementan.

Zona 2) Soria

Los materiales sedimentarios de tipo continental, correspondientes al Infracretáceo, constituyen aproximadamente el 50% de la zona y completan la unidad de la cuenca con los terrenos encajantes de la zona 1. Otros afloramientos satélites de igual naturaleza se presentan en distintos puntos, tales como Burgo de Osma, Arnedo, etc. Le siguen en interés las areniscas del Trías Inferior de Arnedo, Agreda y tronco sur, que se desarrolla en dirección a Molina de Aragón, así como en la ramificación norte de la Ibérica desde Agreda hacia Ateca. Tienen un interés muy limitado los afloramientos del núcleo paleozoico, a pesar de presentarse en las mismas rocas volcánicas ácidas. Prácticamente quedan descartados los terrenos terciarios de tipo lacustre, aun cuando han sido localizados en ellos niveles carbonosos con anomalías radiactivas, como Tarazona; no obstante, es necesario comprobar la posible existencia de paleocauces arenosos, al igual que en el caso de la lengua Ateca-Calatayud.

La cuenca de Soria será objeto, más adelante, de una descripción especial en el presente informe.

Area cubierta por prospección aérea	90% de la zona
Area cubierta por prospección autoportada	75%
Area cubierta por prospección detallada a pie	60%
Area considerada poco favorable	40%

Zona 3) Teruel

A grandes rasgos, puede decirse que es el área donde confluyen diversos plegamientos ibéricos, para volver a ampliarse hasta dar una forma de abanico; enlaza hacia el norte con la cadena Costero-Catalana y al sur con las Béticas. En conjunto, forma un área meridional con respecto al Valle del Ebro, siendo los materiales constitutivos más abundantes y de interés para la prospección los correspondientes al Cretácico Inferior aflorante en grandes extensiones.

Al norte de todo el sistema aparecen los depósitos oligocenos, con material carbonoso y litología diversa, sobre los que se presenta el Mioceno lacustre horizontal y en el que se desarrollan numerosas paleocauces arenosos, unas veces silíceos y otras molásicos.

La base de dichos materiales está constituida normalmente por areniscas y margas triásicas de desarrollo coincidente con la dirección general Ibérica, mientras que al sur, tanto el Triásico como el Jurásico, tienen un alargamiento según los ejes de plegamiento Ibérico y Bético.

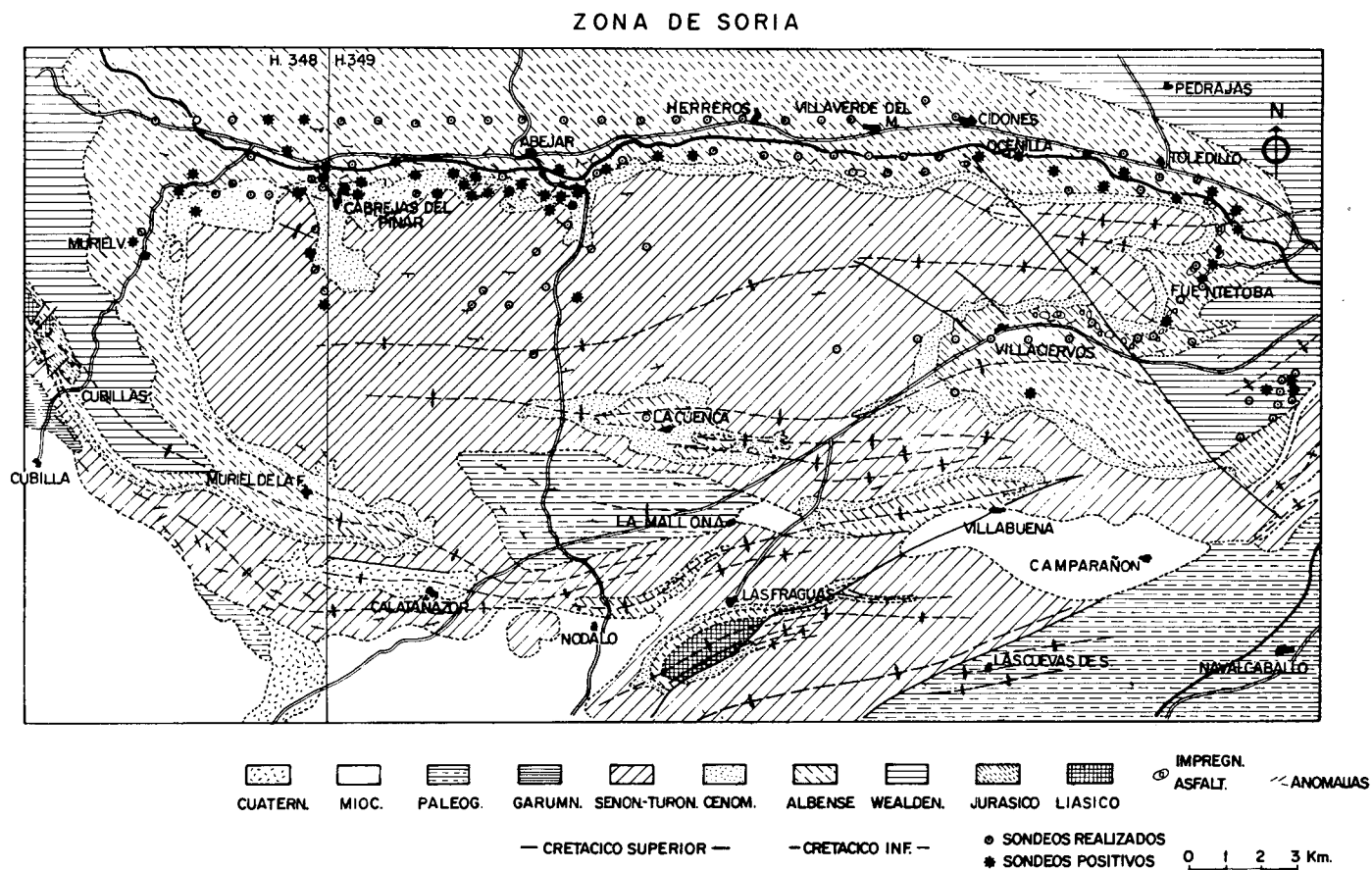


FIG. 3. Mapa geológico de Soria con plan de sondeos.

Los materiales de interés siguen siendo los del Infracretáceo, especialmente albenses y de facies utrillas, sobre todo cuando los mismos están localizados en áreas de plegamiento suave y fracturación escasa. La base del Trías, de tipo arenoso, debe ser estudiada cuando presenta caracteres de reducción, materia orgánica y tránsitos diferenciales en su granulometría.

Area cubierta por prospección aérea	90% de la zona
Area cubierta por prospección autoportada	45%
Area cubierta por prospección a pie	10%
Area considerada poco favorable	50%

Zona 4) Cuenca

En este sector geológico (provincia de Cuenca, parte de Albacete y Valencia) la labor investigadora empieza a realizarse sobre interesantes mineralizaciones en los conglomerados del Buntsandstein.

Son muy variadas las formaciones sedimentarias que se integran en esta zona: Ordoviciense y Silúrico pizarroso-cuarcitoso, Carbonífero, Triásico de facies germánica y alpina. Cretácico de gran extensión y en el cual el inferior, facies utrillas (albense) arenoso, presenta más interés, estando la facies wealdense escasamente representada. El Terciario, bien definido, corresponde al Mioceno continental o al Paleoceno de facies masiva y de amplitud más reducida.

Hasta el momento, son las mineralizaciones de los niveles de conglomerados de la base del Trías las que revisten más importancia. En cambio, indicios y anomalías sobre niveles y series detríticas del Cretácico o del Mioceno pueden representar, en un futuro más o menos próximo, áreas de gran interés para su investigación.

Area cubierta por prospección aérea	85% de la zona
Area cubierta por prospección autoportada	75%
Area cubierta por prospección a pie	10%

ZONA DE SORIA: CUENCA DE PICOFRENTES-SIERRA LLANA Y CUENCA DE MAZARETE

Dada la brevedad del presente trabajo para informar sobre la favorabilidad de existencia de yacimientos uraníferos en la Cordillera Ibérica, creemos oportuno tomar como base de la descripción dos cuencas dentro de la zona de Soria, que son: la cuenca de Picofrentes-Sierra Llana, constituida por sedimentos continentales del Cretácico Inferior, y la cuenca de Mazarete, formada por areniscas triásicas del Buntsandstein. A partir de las mismas situaremos aquellas otras áreas o cuencas que presenten cierta analogía o diferencia con las antes citadas (figura 3).

Cuenca de Picofrentes-Sierra Llana

Como resultado de unos trabajos de prospección autoportada realizados en la segunda quincena del mes de septiembre de 1967, se localizaron una serie de anomalías radiactivas al Oeste de Soria. Inmediatamente se pasó

a realizar prospección detallada a una malla de 50 - 100 metros por toda la zona, en combinación con la autoportada. De esta forma se localizaron numerosas manifestaciones radiactivas distribuidas en una extensión de más de 40 kilómetros que comprende los términos de Cabrejas del Pinar, Abejar, Herreros, Villaverde del Monte, Cidones, Ocenilla, Fuentetoba, Carboneras y Villaciervos.

La cuenca infracretácica de Soria posee un conjunto de caracteres generales y específicos suficientemente alentadores y que justifican el proseguir su investigación.

Nos concretamos a citar sucintamente los datos que consideramos más destacables y en relación más directa con la existencia de posibles mineralizaciones:

- Litología propicia, por su carácter arcósico, bajo grado de clasificación y granulometría diferenciada.
- Presencia de anomalías radiométricas notorias por su extensión, número y distribución.
- Contenidos expresivos de uranio, tanto en algunos afloramientos como en calicatas o niveles cortados por sondeos.
- Presencia de minerales secundarios visibles.
- Aparición de anomalías radiactivas no sólo en niveles arcillosos, o localizadas en muestras singulares con materia orgánica, sino en capas netamente arenosas.
- Resultado positivo de la investigación geoquímica, efectuada en una amplia zona dentro de la cuenca.
- Caracteres de alteración hematítico-limonítica en numerosas zonas dentro de toda la cuenca, contrastados por la aparición de coloraciones no sin genéticas.
- Determinación, en estudios recientes, de ámbitos alterados y no alterados, mediante estudios de «cuttings» de sondeos.

No hubo duda desde el principio de la investigación de que el proceso debía corresponder al originado por mecanismos de circulaciones acuosas y que los posibles enriquecimientos serían de tipo supergénico, lo que establecía una analogía cuyo modelo podía corresponder al de los depósitos uraníferos en areniscas de Estados Unidos y otros países. El problema básico a resolver era, y sigue siendo, la morfología, extensión y desarrollo de los posibles yacimientos, su distribución y localización; cuestión ésta que incide directamente en la escala de la exploración sistemática.

Los datos que iban obteniéndose por la prosecución del estudio en las primeras etapas, así como los resultados de la investigación geoquímica, apuntaban hacia una relación más compleja entre anomalías de superficie y yacimientos, sin que disminuyera la favorabilidad del conjunto.

Resumen de algunos trabajos de exploración efectuados

Hay que tener presente que en la citada cuenca, existe una superficie de 200 km² que será necesario explorar por sus características favorables. Se han realizado hasta la fecha 200 sondeos a una profundidad comprendida entre los 250 y 400 metros. Muchos de ellos han cortado fuertes anomalías radiactivas, llegándose a detectar la presencia de uraninita; se acompaña un mapa esquemático de conjunto con indicación de algunos sondeos.

Estos resultados unidos a un sistemático estudio de los sondeos han servido para seleccionar una serie de áreas en donde se están intensificando los trabajos. En la selección se han tenido en cuenta todos los factores de favorabilidad posibles tales como: facies, tectónica, anomalías radiactivas, contraste de alteraciones, etc.; definiéndose de este modo y en primera selección cinco zonas en las que concurren en grado suficiente todos o la mayor parte de los caracteres mencionados. Las zonas estarían situadas en las proximidades de Cabrejas del Pinar, Abejar, Herreros, Pico Frentes y Villaciervos.

Por el contrario se han relegado a segundo plano otras áreas cuyas condiciones de favorabilidad son menores que en las anteriormente citadas.

En la Cordillera Ibérica existen varias zonas, ya localizadas, con características similares a la de Picofrentes-Sierra Llana, en cuanto a facies y condiciones generales de favorabilidad. Entre ellas destacan las siguientes:

Zona de Salas de los Infantes. Situada al NO de Soria, es en realidad la prolongación natural de la cuenca citada y aunque de menores dimensiones será en su día objeto de un plan de investigación adecuado. Sus caracteres diferenciales podrían ser la abundancia de mineralizaciones de óxidos de cobre y el menor espesor del albense.

Zona de Peñalen. Situada en la provincia de Guadalajara, tiene una extensión de unos 60 km², facies y tectónica favorable, así como fuertes manifestaciones radiactivas en areniscas con leyes próximas al 1%. En esta zona se encuentran muy avanzados los trabajos previos de investigación y la puesta en marcha de un plan de sondeos es inmediata.

Zona de Ariño-Alloza-Alcorisa. En este área se observa una tectónica muy variada, con granulometría muy fina y homogénea; es de notar la existencia de frecuentes formaciones ferruginosas de tipo «paleosuelos». En el Maestrazgo podemos encontrar ciertos caracteres de similitud, también con anomalías y alteraciones de color, pero con una mayor complejidad tectónica y estratigráfica.

Yacimientos tipo Mazarete

Así como en la zona de Picofrentes y otras cuencas del Infracretácico los posibles yacimientos tendrían una morfología comparable a la de Wyoming; el yacimiento recientemente localizado en Mazarete podríamos referirlo al tipo de los existentes en Utah.

La formación corresponde al Trías Inferior de areniscas rojas; a favor de un proceso erosivo se descubrió en prospección autoportada un extenso nivel aflorante decolorado por alteración supergénica en condiciones de reducción, cuya potencia varía entre los 2 y 20 metros con franjas de anomalías radiactivas y considerable continuidad; la potencia de dicha banda radiactiva puede llegar a ser de 12 metros como ha sido comprobada en algunos sondeos de testigo. Dentro de la banda reducida se aprecian variaciones granulométricas además de existencia de materia orgánica dispersa. Estos caracteres nos impulsaron a pasar inmediatamente a una exploración mediante sondeos sistemáticos de localización cuyo resultado

es, hasta ahora, muy satisfactorio tanto en lo que se refiere a potencias como a leyes; el número de sondeos de testigo realizados hasta ahora es de 60 prosiguiéndose el plan con dos orientaciones, una de exploración extensiva y otra de una primera evaluación.

Zonas comparables a la descrita son las de Barruelo de Santullán, Reinosa (Santander), recientemente descubierta por prospección aérea; Valdemeca (Cuenca) donde la mineralización abundante se presenta en el conglomerado inferior del Bunt. Existen otras muchas anomalías en las citadas areniscas triásicas de escasa favorabilidad por aparecer la mineralización ligada a estructuras y diaclasas exclusivamente; un caso intermedio sería el de Agreda (Soria) donde simultáneamente se presentan niveles radiactivos peniconcordantes y enriquecimientos ligados a fracturas transversales.

Cuencas terciarias

Los depósitos detrítico-continetales en la Península Ibérica son muy variados, presentándose, unas veces, como rellenos masivos de amplias cuencas, caso típico de las arcosas de los bordes norte y sur del Sistema Central; en ellas han sido localizadas muy escasas anomalías. Un caso de mayor interés está representado por los paleocauces del Mioceno en la provincia de Palencia, donde los materiales arenosos contienen materia orgánica dispersa y anomalías radiométricas importantes. Un tipo independiente lo constituyen las formaciones lacustres con lignitos del Oligoceno y Mioceno, con leyes muy bajas aunque uniformes, las cuales podrían presentar en la actualidad un interés económico dada su gran extensión y la subida de los precios del uranio; entre las mismas merece citarse la de Calaf, Mequinenza, Santa Coloma de Queralt, etc., situadas al norte de la Cordillera Ibérica.

BIBLIOGRAFIA

- BOWIE, S. H. U., «World uranium deposits», Uranium Exploration Geology (Actas Panel Viena, 1970), OIEA, Viena (1970) 23.
- CASTAÑON, A., Zona de Soria. Características Generales, Informe JEN (Enero 1972).
- CASTAÑON, A., Características uraníferas de las formaciones detríticas de la Cordillera Ibérica, Informe JEN (1974).
- CASTAÑON, A., SANTOMA, L., Sistemática de la investigación geológica del uranio en terrenos sedimentarios, Energía Nuclear, N° 83, Año XVII (1973).
- FERNANDEZ POLO, J. A., Caracteres de algunos yacimientos uraníferos del Pakistán, Energía Nuclear, N° 63, Año XIV (1970).
- FERNANDEZ POLO, J. A., Caracteres geológicos, estructurales y genéticos de los yacimientos uraníferos de Salamanca, Energía Nuclear, N° 64, Año XIV (1970).
- FERNANDEZ POLO, J. A., Uranium prospection methods, Interregional Training Course on Uranium Ore Analysis, Organismo Internacional de Energía Atómica y Junta de Energía Nuclear de España, Madrid (1970).
- LUCINI, M., Estudio de sulfuros en la zona de Soria, Informe JEN (1974).
- MARTIN-DELGADO TAMAYO, J., ARTEAGA RODRIGUEZ, R., FERNANDEZ POLO, J. A., «Programa de prospección de yacimientos uraníferos en España: Evolución de técnicas y métodos», Uranium Exploration Methods (Actas Panel Viena, 1973), OIEA, Viena (1973) 23.
- MARTIN-DELGADO TAMAYO, J., Evolución de la investigación de los minerales radiactivos, Energía Nuclear, N° 60, Año XIII (1969).

NININGER, R.D., «Uranium reserves, future demand and the extent of the exploration problem», Uranium Exploration Geology (Actas Panel Viena, 1970), OIEA, Viena (1970) 3.

OSTLE, D., «Criteria for the selection of exploration areas in the United Kingdom», Ibid., pág.345.

PATTERSON, J.A., «Character of the United States uranium resources», Ibid., pág.117.

ROBERTSON, D.S., «Uranium: its geological occurrence as a guide to exploration», Ibid., pág. 267.

DISCUSSION

J. PASQUALI: I am most impressed by the vast amount of work that has been done in Spain; you deserve to be congratulated. It seems surprising, however, that your exploration work should have begun with igneous and metamorphic rocks. What is the explanation for this?

J. MARTIN-DELGADO TAMAYO: The fact that prospecting started in the rocks of the crystalline horizon reflects the experience and the knowledge of metallogenesis that existed at the time the work was being done. Spain went through a series of "fashions" in this matter, just as did her neighbours Portugal and France. Exploration was begun in the deposits that had already been exploited for radium, was continued with the investigation of granites and shales, which is where our present reserves are located, and eventually arrived at sedimentary rocks of continental origin, which offer very real promise of yielding workable deposits. The sedimentary horizons have in fact been under study for some time, although not until recently have they received such exclusive attention.

R. BLASER: In some of your slides (shown in the oral presentation) of uranium-bearing sandstones one could see a yellowish zone which looked as though it contained sulphur. Is this yellow colour due to secondary uranium-bearing minerals or to some other cause?

J. MARTIN-DELGADO TAMAYO: The yellow colour of the sandstone is not due to the presence of large amounts of uranium but rather to supergenic alteration. These colours are characteristic of each type of terrain and each particular zone, and their origin is understood in detail only by local geologists working on the spot, who, over the years, have acquired abundant experience of supergenic or syngenetic coloration phenomena in their own regions.

S. CONSTANTINO HERRERA: It seems to me that, although a great deal of emphasis has been placed on sedimentary deposits at this Symposium, we should not overlook the importance of other types. An illustration of this point is to be found in the northwestern part of Mexico, where we are finding and evaluating what appear to be very promising occurrences in volcanic rocks.

J. MARTIN-DELGADO TAMAYO: Yes; we have no wish to depreciate the importance of deposits other than sedimentary. Earlier we did what could be described as virtually exhaustive exploration work in the crystalline horizons of Spain, and it was precisely in these granitic and metamorphic rocks that we found the ores which constitute our present reserves. Ultimately, however, our evaluation of the possibilities offered by those hosts was considered to be complete, and we are now devoting every possibly effort to sedimentary horizons of continental origin, as they seem to hold out good prospects of increasing our reserves. Thus we are at present concentrating exclusively on a type of terrain which earlier received only intermittent attention.

URANIUM IN QUARTZ-PEBBLE CONGLOMERATES

Review Paper

BASAL PROTEROZOIC UNITS AS FOSSIL TIME MARKERS AND THEIR USE IN URANIUM PROSPECTION

D. S. ROBERTSON

David S. Robertson & Associates Ltd,
Toronto, Ontario, Canada

Abstract

BASAL PROTEROZOIC UNITS AS FOSSIL TIME MARKERS AND THEIR USE IN URANIUM PROSPECTION.

Pyritic, uranium-bearing, quartz-pebble conglomerates have been found in Canada, in South Africa, in Brazil and in Australia. All are similar in lithology and mineralogy. All overlie a contorted greywacke-greenstone sequence and are overlain by rock units containing red clastics and shales.

All are of similar age, where datable, being developed between 2800 m.y. and 2200 m.y.

Uranium content derives from detrital, heavy minerals carried to and preserved in the rocks because of an anoxic atmosphere prior to 2200 m.y.

Recognition of the environment of origin reflected by the conglomerates or the change in environment reflected by the sequence of rock units described permits assignment of an age range, frequently more meaningful than that derivable from usual dating methods.

Uraniferous conglomerate ores can only be found below the oldest red-colored rock units.

INTRODUCTION

Proterozoic units that are basal, in the sense that they lie immediately above Archean rocks, vary considerably in their character from place to place.

These variations relate not only to the character of source area and environment of deposition indicated by the sediments above the Archean but also to the age of the Proterozoic materials deposited.

The uraniferous, sometimes gold-bearing, quartz-pebble conglomerate ores are considered herein to be fossil expressions of a limited period of geological time, following an earlier comment [1] which pointed out certain similarities between various conglomerate deposits that suggested restriction of their time of origin. "They are restricted in geological time to a period after the development of extensive acid crust . . . but before the development of an oxidizing atmosphere. . .". This suggested pronounced restriction of the areas of the earth in which such deposits can be found.

Roscoe [2] has expanded on this concept and discussed the evidence suggestive of restriction of these kinds of rocks to a time interval between 2.7 m.y. and 2.2 m.y. in the past.

There are now eight large areas of the earth's crust in which we have worked with these rocks. The areas contain a much larger number of discrete occurrences of this type of mineralized unit.

While the areas, and the discrete units within the areas, vary considerably in detailed character and while mode of origin

varies somewhat, the pronounced similarities between the conglomerates and their enclosing rocks and the very obvious differences with all other rocks in the sedimentary column, certify an environment of origin different from that of such other rocks.

This paper describes and compares the environments in which the conglomerates lie and comments on their age, their origin, their use as a stratigraphic marker at the base of the Proterozoic and the utility, in uranium prospecting, of recognition of their special environment.

OCCURRENCES IN CANADA

The rocks of interest have been found to date in three areas and possibly four. The three known areas include 1) Elliot Lake and region in Ontario, 2) Montgomery Lake - Padlei area in the Northwest Territories, and 3) the Sakami Lake area in northwest Quebec. The fourth area is that of the Otish Mountains in Quebec. (Figure 1).

In each of these areas, relatively small remnants of basal Proterozoic (basal Aphebian) sediment are preserved beneath much more widely spread, younger Proterozoic sediment. The basal Aphebian sediments are all similar in color, in texture, and in composition. They all (with the possible exception of Otish) carry oligomictic, quartz-pebble conglomerate with pyrite and with uranium. They are all overlain either immediately or regionally

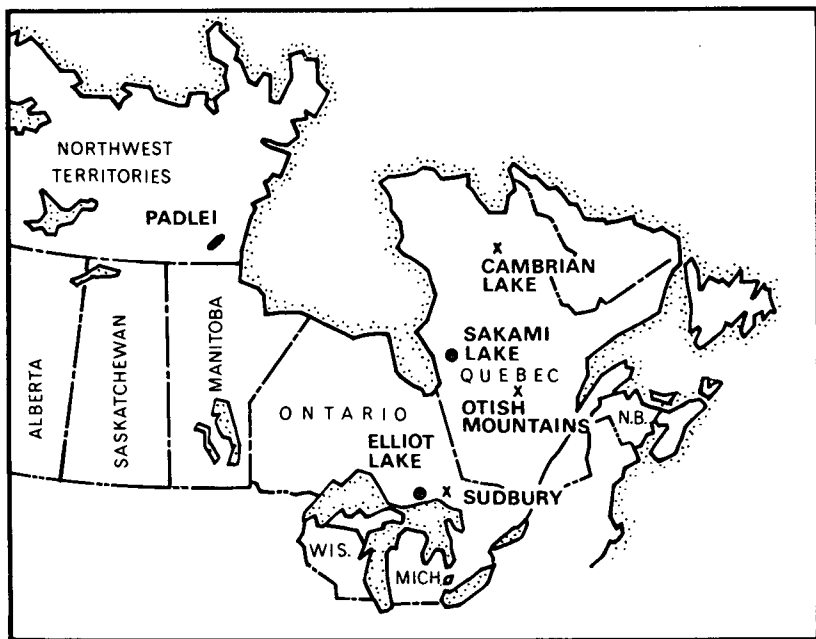


FIG. 1. Basal Aphebian quartz-pebble conglomerates in Canada.

by younger sediments different in color, texture and maturity or composition. These younger sediments always have their iron in the red form and they carry no pyrite in their conglomerates. While they are frequently radioactive, such radioactivity is always mainly due to thorium in monazite.

Elliot Lake and Region

The rocks of interest in this region comprise the lower part of the Huronian Supergroup [3]. The outcrop area in which conglomerates are found stretches in a linear belt from Sault Ste. Marie to the northwest of Sudbury, a distance of about 150 miles. However, their original depositional extent was probably much greater and may have stretched in a long, south-facing, discontinuous arc from Wisconsin to Labrador. The lower units are yellow-green to grey quartzites and arkoses with interbeds of quartz-pebble conglomerate containing pyrite and uranium.

The upper part of the Huronian Supergroup, the Gowganda and Lorraine Formations, has much broader distribution than the lower. The Lorraine rocks are reddish and their quartz-pebble conglomerates carry hematite and monazite. Similar rocks are found in the northern United States well to the west of Elliot Lake as well as in Quebec to the northeast.

The economic conglomerates of the Huronian are found at Elliot Lake and at Agnew Lake (Figure 2). The gravel sheets as previously described [1,4], are discontinuous layers developed below the point of debauchment of a major stream system, which carries the physical load from the up-country weathering process and deposits it at, or below, the sea level interface against which the stream loses its competence and drops its load. The sheets moving progressively north (Figures 3 and 4) indicate that the point of debauchment and strand line were moving progressively northward as the sea encroached on the land.

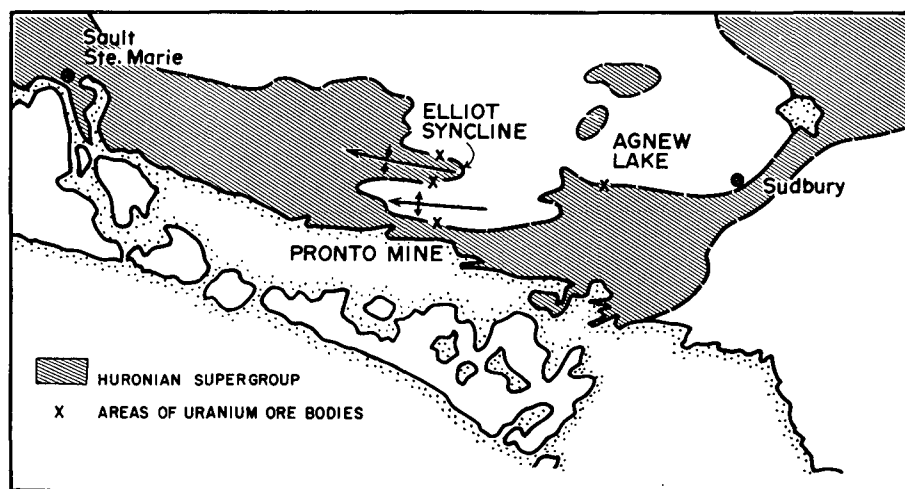


FIG.2. Huronian on the north shore, Elliot Lake area.

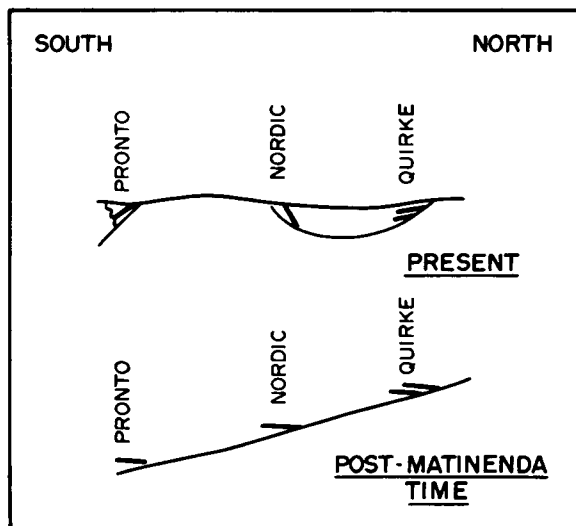


FIG.3. Sections (past and present) through the Elliot Lake area.

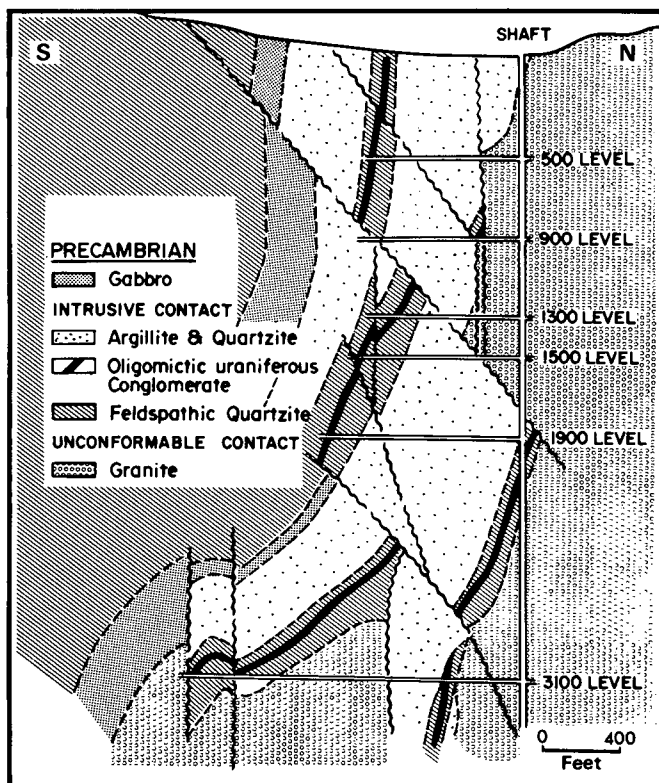


FIG.4. Shaft section, Agnew Lake mine.

While thin, discontinuous conglomerate units are found at many places in the region, the zones of major conglomerate development are discrete and almost abrupt. They reflect relatively high energy development in the transporting medium, in other words, major drainage. The conglomerate units reflect this in being very well washed and packed and in having very high concentrations of heavy minerals.

The discrete, abrupt nature of conglomerate development is not obvious in all areas where rocks of this kind evolve. In many such areas, the clastics surrounding the conglomerates are relatively dirty and unsorted, and facies changes are frequent and rapid in contrast to the clean quartzite-arkose sequence with limited lateral facies change which, in the Huronian Supergroup, is an expression of cleaning and sorting in a marine environment.

The main ore minerals at Elliot Lake are brannerite and uraninite with secondary minerals such as gummite. Other heavy minerals are present, including plentiful monazite.

At Agnew Lake the main ore mineral is uranothorite, but many other heavy minerals, including monazite, are present.

It is generally agreed by workers with the rocks [5,p.38] that uranium was deposited syngenetically although the degree to which the ore consists of a heavy mineral concentrate or to adsorption from solution, remains undecided.

Regional dating indicates that the Huronian Supergroup is between 2.5 and 2.2 m.y. in age.

Montgomery Lake - Padlei Area

Over an extensive area west of Hudson's Bay, discontinuous belts of sediment, largely typified by pink quartzites, green to red slates, dolomite and polymictic conglomerates, represent the remnants of a large Aphebian basin lying on the Archean Shield. The rocks comprise the Hurwitz Group. Their clastic formations are similar in many respects to the Lorraine Formation, the upper part of the Huronian Supergroup. In particular, they are frequently of pronounced red color.

In a small part of the area, between Montgomery Lake and Padlei, the typical Hurwitz Group rocks are unconformably underlain by a drab, yellowish green to grey sequence of clastics, the Montgomery Lake Series, which lies directly on the Archean.

These rocks, locally comprising more than 3,000 feet in thickness, strongly resemble the basal part of the Huronian Supergroup and contain oligomictic quartz-pebble conglomerates with pyrite, uranium and gold.

The conglomerate beds in the region are widely distributed although they vary in thickness from a few feet to in excess of 8 feet. Thicker conglomerate beds have larger pebbles and, normally, noticeably more pyrite than thinner beds.

Where the conglomerates have been drilled for gold, they are thin and poorly packed with pebbles up to 1/2 inch. Gold assays up to 0.1 oz per ton over 2 feet have been obtained. Where conglomerates are thicker, radioactivity is more intense. Drilling has encountered grades as high as 0.52 pounds U_3O_8 and 0.70 pounds ThQ_2 over 2 feet of conglomerate.

The principal radioactive minerals are uranothorite, a titanium-bearing complex, and zircon.

In general, the conglomerates are not as well sorted as those of Elliot Lake and assay results suggest the absence of the abundance of heavy minerals necessary for the generation of ore. This

is probably partly due to the character of the surrounding terrain which is largely made up of Archean sediments and greenstones. However, the character of the conglomerates themselves suggests that it is also due to a lack of very strong drainage that would have cleaned up the conglomerates. In spite of this, the rocks are typical of those carrying pyrite and uranium in other places.

The general appearance of these rocks, including their color and texture and their development of oligomictic quartz-pebble conglomerates containing pyrite, gold and uranium, indicates the strong similarity to the rocks of the lower part of the Huronian Supergroup.

The sequence of drab clastics with uranium-bearing conglomerates overlain by a red sequence is analogous to that described in the Elliot Lake region.

Regional dating indicates that the Montgomery Lake sediments and the Hurwitz Group were laid down between 2500 m.y. and 1800 m.y. They are thus similar in time of origin to the rocks of the Huronian Supergroup.

Sakami Lake

On the west side of Sakami Lake in northern Quebec, a thin sequence of rocks occurs which carries uraniferous, pyritic, quartz-pebble conglomerates. These rocks vary from coarse-grained, yellow-grey, dirty quartzite to white, fine, even-grained quartzite. Conglomerate beds are thin with small pebbles but they locally occur through significant thickness of section. They locally carry in excess of 10% pyrite and have heavy concentrations of uranium-bearing minerals.

These rocks strongly resemble the basal part of the Huronian Supergroup. In addition, they lie unconformably on tightly folded greywacke and greenstone of Archean age, and they are followed in the stratigraphic sequence by the Sakami Formation, the lower part of which is a redbed suite of conglomerate, arkose and siltstone, very similar in character to the Chakonipau Formation to the east and to the Lorraine, the upper part of the Huronian Supergroup.

The conglomerates carry uraninite, which contains about 10% ThO_2 , and a thorium silicate either thorite or allanite. The uranium content is locally high.

Whole rock dates on the basement rocks indicate that they have been affected by the Kenoran event at 2500 m.y. The conglomerates of interest are also intensely deformed and of amphibolite facies. They too appear to have been involved in the Kenoran event and are thus older than 2500 m.y.

The identity of sequence, red rocks overlying drab-colored rocks, and the uranium-bearing conglomerates of the drab rocks indicate a pronounced similarity to the environment in which the rocks of Elliot Lake and those of Montgomery Lake were formed.

OCCURRENCES IN BRAZIL

Pyritic, quartz-pebble conglomerates with uranium and gold have been found at three localities around the edge of the São Francisco Craton; at Jacobina in Bahia, near Belo Horizonte, in Minas Gerais, and near Pitangui to the west of Belo Horizonte (Figure 5).

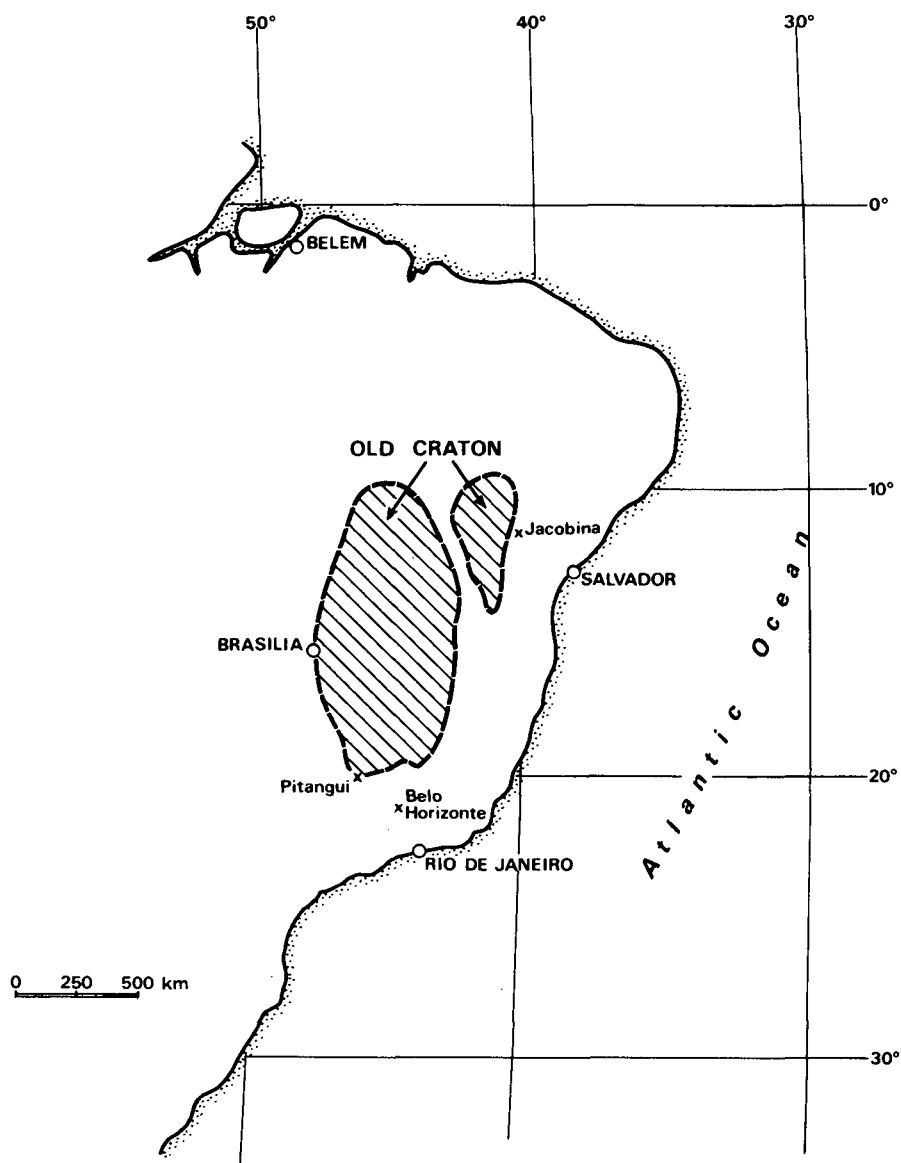


FIG.5. Uraniferous quartz-pebble conglomerates of Brazil.

Jacobina

The conglomerates of Serra de Jacobina are well developed over a strike distance of some fifteen miles along the length of the Serra which appears to be a long fault block. Pyrite, gold and minor amounts of uranium are found in the conglomerates. The conglomerates and enclosing rocks are clean, well washed and recrystallized to a high degree. They lie well up in the section in excess of 500 feet above the basal unconformity.

The quartzites are overlain by hematite-bearing sediments, similar in character to those of the Itabir Group of Minas Gerais.

While it has been suggested that the direction of sedimentation forming the conglomerates was from the east [6], analysis of regional geology shows that this is highly improbable and it is assumed that the rocks are developed from debris shed by the So Francisco Craton which was exposed in basal Proterozoic time.

Almeida [7] suggests that the rocks are part of the Trans-Amazonian cycle of South America at between 1800 and 2000 m.y. In fact, these rocks must be considerably older than this event, the dates cited by Almeida reflecting an event occurring later than the formation of the rocks of interest.

Belo Horizonte

Radioactivity in the conglomerates of the Moeda Formation, the basal part of the Caraa Group of the Minas Series, was discovered by geologists of the Comisso Nacional de Energia Nuclear of Brazil in 1970. Work prior to and subsequent to the discovery is described by Ramos [8].

The rocks of the region have been mapped and described by Dorr [9] and by others.

The Moeda lies with profound unconformity on highly metamorphosed rocks of the Nova Lima Group of the Rio das Velhas Series. Overlying the Moeda is the Batatal Formation, a phyllitic, graphitic siltstone and then red, hematitic iron ores of the Itabir Group.

The rocks of the Moeda Formation are highly quartzose. A coarse-grained facies, which contains the quartz-pebble conglomerates of interest (Figure 6), stretches through the central part of the mapped region. The rocks are greenish-grey to white in color. A finer-grained facies around the edges of the coarse-grained rocks comprises fine-grained quartzite and phyllite.

Dorr states [9, p.A-38], "The distribution of the coarser facies . . . strongly indicates that the source of the material was to the west and that the coarse facies was a deltaic deposit, . . .".

The conglomerates vary in thickness and in pebble size and are locally, intensely, physically metamorphosed. This metamorphism relates to the intense thrust faulting which appears to be part of the last structural event in the region.

Uranium-bearing minerals in the conglomerates include brannerite, xenotime and zircon. A prominent mineral, at least locally, is thucholite in rounded balls which carries inclusions of uraninite which have a relatively high thorium content. Some of the conglomerates also carry significant amounts of gold.

Hertz [10, p.B-9] proposes that the Minas Series was deposited later than 1930 m.y. Based on the conclusions reached herein, these rocks must have originated prior to 2200 m.y. and the

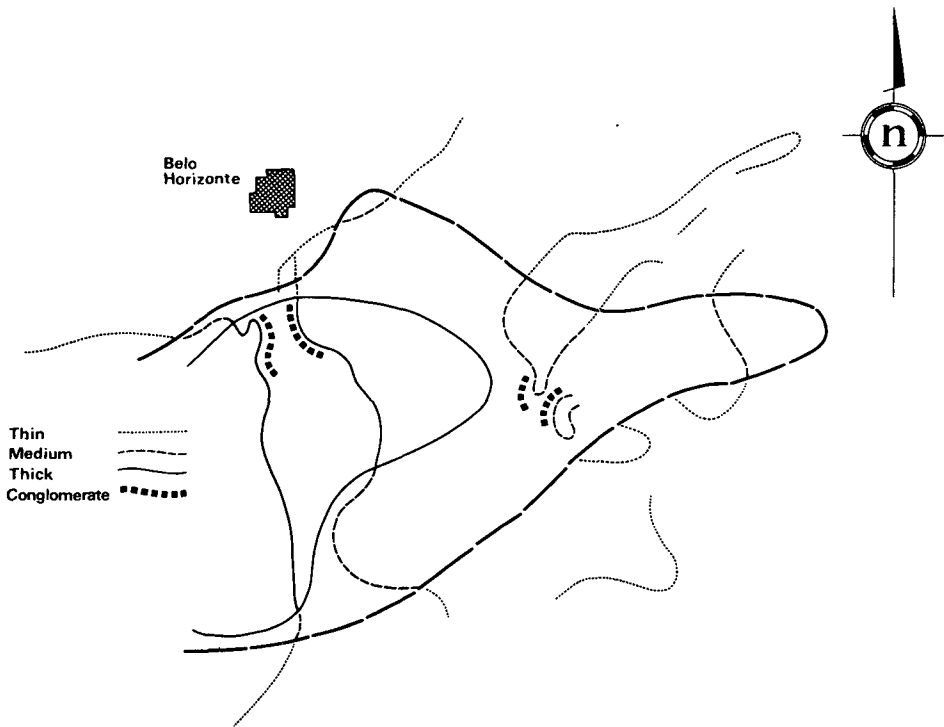


FIG. 6. Sketch of generalized thickness variations in the Moeda Formation.

assigned dates do not properly reflect rock ages, being an indicator of the existence of some relatively young event.

The conglomerates and enclosing rocks are similar in every lithological aspect and in mineralogy to the rocks previously described. They are somewhat less well washed and sorted.

The sequence of drab-colored rocks with pyrite and uranium followed by red, iron-bearing rocks is diagnostic of the time-restricted environment referred to earlier.

Pitangui

To the northwest of Belo Horizonte, near the town of Pitangui, undeformed, basal Proterozoic quartzites and arkoses lie on highly deformed schist and gneiss of the Nova Lima Group. The Proterozoic rocks include quartz-pebble conglomerates carrying uranium and gold in amounts similar to those at Belo Horizonte.

It is believed that prior to 2200 m.y. the São Francisco Craton was shedding clastic debris off its flanks. The rocks of this time suggest that the craton carried uranium-bearing heavy minerals over much of its area, which were available for concentration where this was facilitated by major drainage.

OCCURRENCES IN SOUTH AFRICA

The rocks of the Witwatersrand of South Africa comprise a sequence of clastic sediments and interlayered volcanics carrying gold and uranium. These metals occur in conglomerates and on thin grit bands (all locally called 'reefs'), at various stratigraphic levels of the section which is in excess of 25 000 feet thick.

The conglomerates are enclosed in clastic units, chiefly arkose and quartzite, with interbedded silt units. All are greenish to yellowish grey to white in color. The sequence is normally of low dip and only slightly metamorphosed. It overlies a profoundly distorted and metamorphosed basement and is overlain by rocks of the Transvaal Supergroup, the clastic rocks of which are of red color and in which a large part of South Africa's iron ore reserves lie.

In parts of the mining area, notably the Central Rand where the conglomerates outcrop and where gold was first recognized, the conglomerates are robust and thick, very similar in appearance to those of Elliot Lake. Such conglomerates could only have been deposited by a medium of great competence.

Elsewhere in the region, however, the conglomerates are very thin, frequently only an inch or so in thickness, with the pebbles milled down to grit size.

The concept advanced by Brock and Pretorius [11] views the Rand Basin as a negative tectonic block and the conglomerates as originating at different distances from the apexes of four great deltas, places of major drainage entry (Figure 7).

The main ore minerals in the Rand conglomerates are native gold and uraninite, both minerals being intimately involved with thucholite. An analysis of uraninite from the Dominion Reef [12, p.9] shows the presence of 63.29% uranium oxide, 6.52% thorium oxide and 3.43% rare earths. Other radioactive minerals are uranotorite and zircon. Monazite is abundant only in the Dominion Reef and possibly in the Central Rand.

The lavas of the Dominion Reef system yield a Pb/U age of 2800 ± 60 m.y. [13, p.976]. The Ventersdorp lavas appeared at 2300 m.y., and the Transvaal Group is believed to have originated between 1950 m.y. and 2350 m.y. [13, p.982].

The similarities of appearance, mineralization, sequence of rock units and age all confirm that the rocks of the Witwatersrand originated at the same time and in the same gross environment as that of the rocks heretofore described.

OCCURRENCES IN AUSTRALIA

Old Proterozoic conglomerates are known only in the Nullagine area of Western Australia (Figure 8) where they occur at the base of the Mount Bruce Supergroup on the northern margin of the Hamersley Basin.

In the Hamersley Basin, the lowest subdivision of the Mount Bruce Supergroup, the Fortesque Group, reaches a maximum development of 12 600 feet of basic pillow lavas and pyroclastics with a thin arkosic unit at the base. On the northern rim of the basin in the Nullagine and Marble Bar areas, the basal Fortesque is

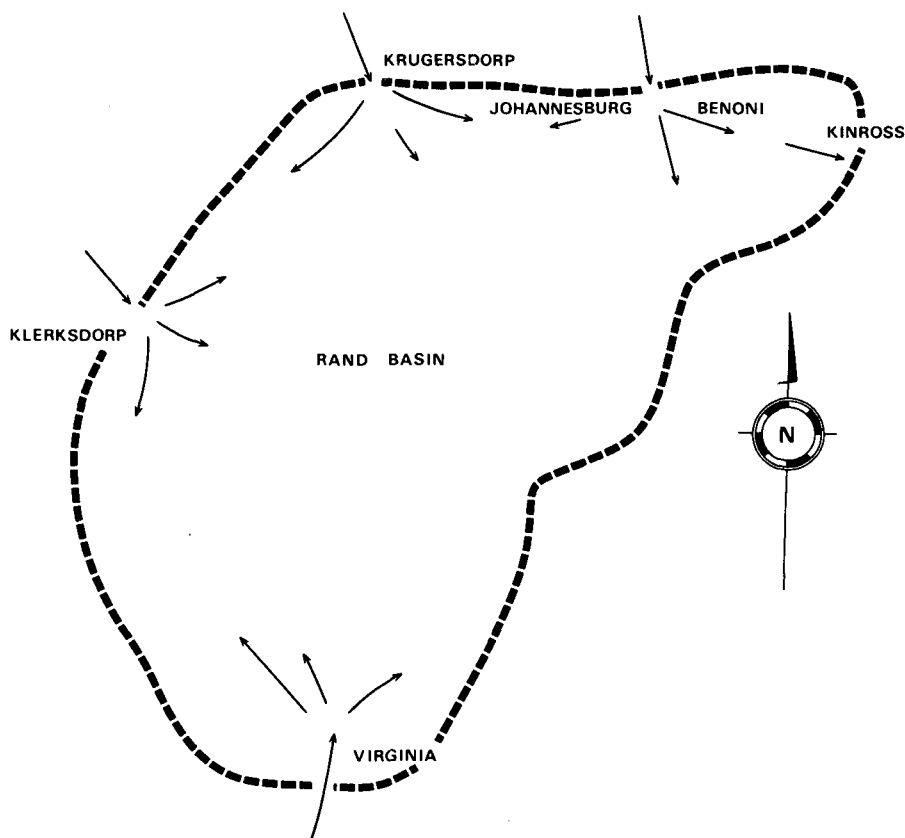


FIG. 7. Rand Basin showing location of major drainage entry.

represented by a sequence containing well-developed conglomerates deposited in shallow depressions or structural basins on the Archean land surface.

The Beaton's Creek conglomerates near the Township of Nullagine are polymictic boulder conglomerates of erratic distribution. They are pyritic and reportedly carry rounded and water-worn nuggets of gold.

Where present this conglomerate is conformably overlain by up to several thousands of feet of acid to intermediate volcanics which elsewhere rest unconformably on the Archean. The volcanics are conformably succeeded by up to 5 000 feet of shale and siltstone with occasional sandstone and conglomerate, the Glen Herring Formation, followed by the Green Hole Formation.

Quartz-pebble conglomerates in the Green Hole range generally from a few feet to 15 feet in thickness. They are unusually persistent, permitting reliable correlation between the several sub-basins of the area over distances in excess of 60 miles.

Clasts, predominantly vein quartz, vary from fist-sized cobbles to 1/2 inch pebbles, all lying in a greenish-grey, arkosic matrix.

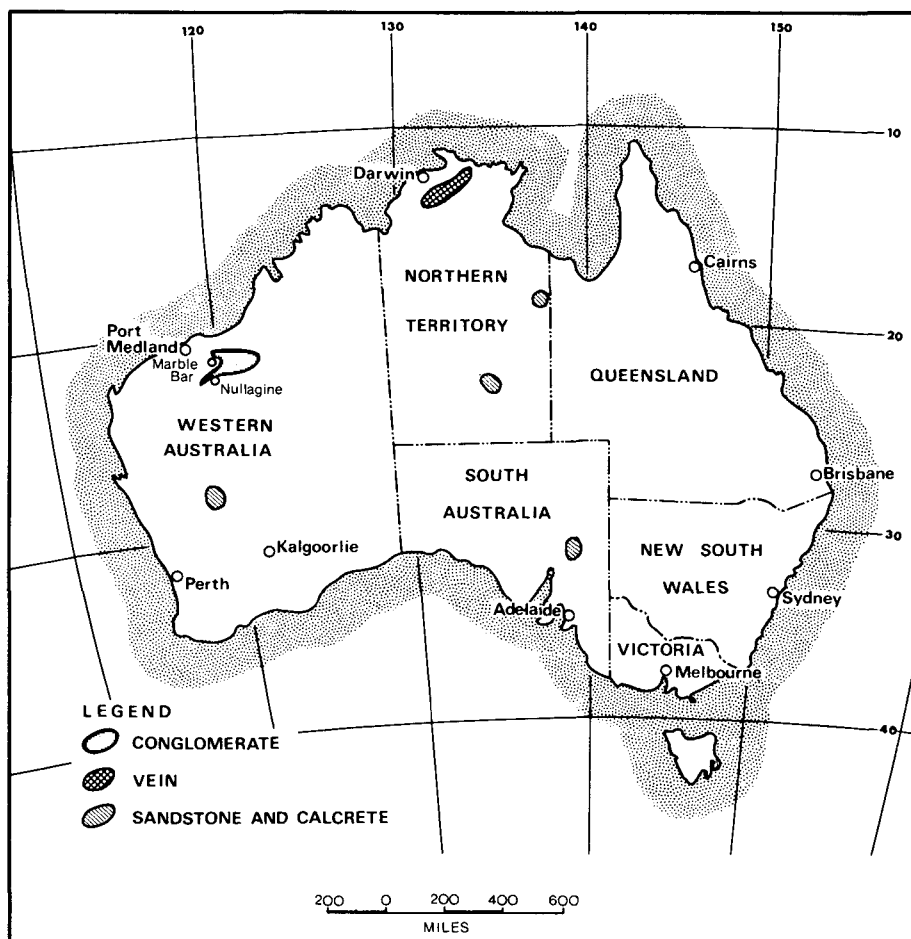


FIG. 8. Significant uranium-bearing areas of Australia.

Pyrite generally occurs in small amounts, locally being prominently concentrated on bedding planes. Heavy minerals are not abundant but monazite and zircon are found.

The conglomerates are generally weakly radioactive, in the range of 0.1 to 0.2 pounds U_3O_8 per ton. One assayed diamond drill core returned values of 0.85 pounds per ton over 5 feet. In this case, uranium is associated with thucholite pellets; associated heavy minerals are pyrite, monazite, zircon and anatase.

The conglomerates are relatively unsorted rocks. However, even where sorted and size-graded, they have weak heavy-mineral collections, probably reflecting the abundance of volcanic and meta-sedimentary material in the source areas.

The Green Hole Formation is succeeded by a thick sequence of basic volcanics and interbedded dolomite. These beds are not restricted to the sub-basins containing the Green Hole sequence

and are correlated with the volcanics of the Fortesque Group in the Hamersley Basin which are conformably overlain by the important hematitic iron formations of the Hamersley Group.

Dating indicates that the basal Proterozoic rocks of the region were deposited between 2600 and 2000 m.y.

As in the areas previously described, a drab-colored, arkosic sequence with pyritic, quartz-pebble conglomerates carrying uranium lies below younger rocks in which the iron forms red oxide. The apparent age of formation of the Green Hole conglomerates is similar to the age of deposition of like conglomerates elsewhere.

ORIGIN OF THE CONGLOMERATE ORES

Pyritic, uranium-bearing, quartz-pebble conglomerates have been found in Canada, in South Africa, in Brazil and in western Australia. The conglomerates are all of similar aspect and the minerals of interest are of similar character.

The rocks in which the conglomerates lie are also similar yellow-green to grey clastics, some clean and well washed as at Elliot Lake and some being poorly sorted and dirty. They are, with one exception, only very slightly metamorphosed, they lie with profound unconformity on highly metamorphosed strata and they underlie a red rock sequence which contains no pyrite.

It is the opinion of the author that the conglomerates are all of similar age (2.2 to 2.8 m.y.), of the same origin and that they

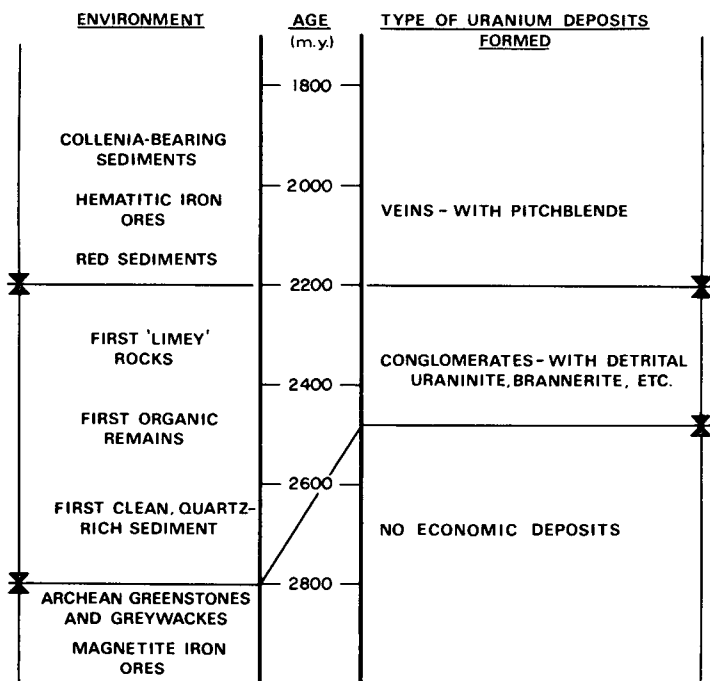


FIG.9. Uranium deposits and geochronology.

are unique to their special part of geological time, a time which preceded the formation of the epigenetic deposits, as shown in Figure 9. During this period of time, the earth's atmosphere was anoxygenic and syngenetic uraninite from pegmatite and gneiss areas was carried in detrital form to be deposited as a heavy mineral in what are now 'fossil' placers.

Various kinds of evidence have been adduced to support the concept of a detrital origin for the deposits. The author believes the uranium minerals to be largely detrital for the following reasons:

1. They exist within a normal detrital assemblage and occur in the same way as other detrital minerals. In particular, the distribution of $\text{ThO}_2/\text{U}_3\text{O}_8$ ratios varies in a manner explicable by concepts of gravity grading [14].
2. The minerals are compositionally of a kind which is accessory in granitic rocks. The uraninite, for example, with its high content of thorium and rare earths, is distinctly different from the pitchblende which forms from ground-water transport.
3. There is no connection between the uranium minerals and faults, veins or other 'late' phenomena.
4. At places where the ore units are eroded by younger conglomerates, the radioactive debris from the former contaminates the latter which are otherwise essentially non-radioactive. The distribution of radioactivity is clearly related to the erosion process and implies the existence of uranium mineral in 'older' conglomerate beds prior to the development of the 'younger' conglomerate beds.

USE AS A STRATIGRAPHIC MARKER

The worldwide distribution of the environment reflected by the existence of rocks of the kind described and the unique association between these oldest of "Proterozoic" rocks and rocks lying below and above them is shown in Tables I and II.

On each of the four continents represented, a typical, contorted, metamorphosed sequence of greywackes and volcanics with abundant granite is overlain by quartz-rich, drab-colored sediment of limited distribution, carrying pyrite and uranium. Some carry gold. These younger rocks, where datable, appear to be of age between 2800 m.y. and 2200 m.y., approximately.

In all four continents, these rocks are conformably overlain by red-colored rocks carrying hematite. Quartz-pebble conglomerates in these red rocks, while frequently radioactive, normally carry only monazite, a thorium-rich species. These younger conglomerates can be seen in at least five areas of North America and in the Kimberly Mountains of Australia.

This sequence of rock types seems so widespread as to be a fossil indicator of approximate age frequently superior to that available from published dates which too often reflect relatively young events.

Indeed, recognition of the change from typical Archean sedimentation to the quartz-rich sedimentation of the uraniferous conglomerate environment may provide a more meaningful limit to the concepts expressed by Archean and Proterozoic, than provided by the usual method of utilizing dated events.

In Canada, for example, this change in the type of sedimentation can be recognized locally over much of the craton and it reflects a change in sedimentation as fundamental as the change in atmosphere reflected by the appearance of red sediment at about 2200 m.y.

Dates suggest, however, that the conglomerate at Sakami Lake is much older than those at Elliot Lake and Montgomery Lake, having been involved in the Kenoran event at 2500 m.y., while the latter two have not. The abrupt, never-to-be-repeated, change in sedimentation appears to be a more profound reflection of evolution of the lithosphere than does orogeny.

USE IN EXPLORATION

It now seems well established that conglomerate ores do not exist except in environments reflecting sedimentation through the period of the earth's evolution in which the atmosphere was non-oxidizing.

TABLE I. TYPICAL GEOLOGICAL SEQUENCE

Rocks	Comment
Hematitic Iron Ores	Shelf rocks, normally of wide-spread distribution.
Red-colored clastic rocks	Where containing quartz-pebble conglomerates, which are not uncommon, radioactivity is due largely to thorium in monazite. These rocks never carry pyrite.
Grey-green, drab quartz-rich clastic rocks	Normally, relatively sparsely exposed. Of restricted distribution during sedimentation. Pyrite always present. Quartz-pebble conglomerates always uraniferous.

UNCONFORMITY

Interbedded greywacke and volcanic materials	Normally, contorted and metamorphosed to greater degree than overlying rocks. Clean quartzites limited to absent. Quartz-pebble conglomerates not found.

TABLE II. ROCK UNITS ILLUSTRATING EVOLUTION OF THE EARTH

ENVIRONMENT	CANADA			SOUTH AFRICA	BRAZIL	AUSTRALIA
	Elliot Lake	Montgomery Padlei	Sakami		Belo Horizonte	Nullagine
Red-colored rocks	Lorraine Formation	Hurwitz Group	Sakami (Chakonipau) Formation	Transvaal Supergroup	Itabirã Group	Hamersley Group
<u>"OXIDIZING"</u>						
<u>"NON- OXIDIZING"</u>						
Drab-colored pyrite-bearing quartz-rich sediments with uranium	Elliot Lake Group (uranium)	Montgomery Lake Sequence (gold and uranium)	Unnamed (uranium)	Witwatersrand System Dominion Reef System (gold and uranium)	Moeda Formation (gold and uranium)	Green Hole Formation (uranium)
Interlayered Greywackes and volcanic material	"ARCHEAN"					

One must look for ores of this kind stratigraphically below the oldest red sediments.

These rocks were likely deposited in relatively restricted basins prior to the development of the younger, red, Aphebian cover rocks, the Cobalt Group, the Hurwitz Group, the Transvaal Series and other such rock units.

As they have been subjected, normally, to the maximum number of orogenies and 2 000 000 000 years of erosion, they normally can be looked for only around the edges of the younger, red rocks where they have been protected from erosion.

REFERENCES

- [1] ROBERTSON, D.S., "Uranium, Its Geological Occurrence as a Guide to Exploration". (Uranium Exploration Geology). IAEA, Vienna (1970) 267-282.
- [2] ROSCOE, S.M., "The Huronian Supergroup, a Paleo-Aphebian Succession Showing Evidence of Atmospheric Evolution". GAC-Sp.Paper 12 (1973) 31-47.
- [3] FRAREY, M.J., ROSCOE, S.M., "The Huronian Supergroup North of Lake Huron". (Symposium on Basins and Geosynclines in the Canadian Shield). GSC 70-40 (1970) 143-157.
- [4] ROBERTSON, D.S., STEENLAND, N.C., "On the Blind River Uranium Ores and Their Origin". Economic Geology 57 (1960) 659-694.
- [5] GUIDEBOOK, Field Excursion C-67, "Uranium Deposits of Canada". International Geological Congress, Ottawa XXIV (1972).
- [6] GROSS, W. H., "Evidence for a Modified Placer Origin for Auriferous Conglomerates, Canavieiras Mine, Jacobina, Brazil". Economic Geology 63 (1968) 271-276.
- [7] ALMEIDA, F.F., "Geochronological Division of the Precambrian of South America". Revista Brasileira de Geociências I (1971) 13-21.
- [8] RAMOS, J.R., "Possibilidades e Prospectivas do Uranio Brasileiro". Mineração Metalurgia 334 (1972) 36-41.
- [9] DORR, J.V.B., "Physiographic, Stratigraphic and Structural Development of the Quadrilátero Ferrífero, Minas Gerais, Brazil". USGS-Prof.Paper 641-A (1969).
- [10] HERZ, N., "Gneissic and Igneous Rocks of the Quadrilátero Ferrífero, Minas Gerais, Brazil". USGS-Prof.Paper 641-B (1970).
- [11] BROCK, B.B., PRETORIUS, D.A., "Rand Basin Sedimentation Tectonics". The Geology of Some Ore Deposits in Southern Africa 1 (1964) 549-599.
- [12] HIEMSTRA, S. A., "The Mineralogy and Petrology of the Uraniferous Conglomerate of the Dominion Reef Mine, Klerksdorp Area". Trans.Geol.Soc.South Africa LXXI (1968) 1-66.

- [13] BEUKES, N. J., "Precambrian Iron Formations of Southern Africa". *Economic Geology* 68 7 (1973) 960-1004.
- [14] ROBERTSON, D. S. "Thorium and Uranium Variations in the Blind River Ores". *Economic Geology* 57 (1962) 1175-1184.

DISCUSSION

R. G. DODSON: You stressed the presence of pyrite in the uranium- and gold-bearing conglomerates. What significance do you attribute to pyrite in this environment?

D. S. ROBERTSON: Pyrite is of no significance, except that its presence is one of the means by which one recognizes these particular rocks and their environment. Pyrite presumably takes the place of magnetite and ilmenite, which one might expect as detrital, heavy minerals in these rocks, but which in fact are never found.

G. R. UDAS: Do you think that the pyrite content of these rocks controls the uranium content and its mineralization?

D. S. ROBERTSON: No, I think the pyrite content has no effect on the degree of concentration of uranium. Each is essentially a heavy mineral concentrated, initially, by detrital processes.

C. T. MEYERTONS: What do you think the source of the uranium in these conglomerates was?

D. S. ROBERTSON: The uranium came from syngenetic uranium accessory minerals in the granites, pegmatites and gneisses of the source areas, which provide the detritus for the major streams.

C. T. MEYERTONS: Are vein-type uranium occurrences likely to be found in these source areas?

D. S. ROBERTSON: Vein-type occurrences of much younger age might be found, but they could not of course be contributors of detrital material because of their age. In fact, most veins are found in younger Proterozoic rocks.

F. R. JOUBIN: Within a radius of 50 miles or somewhat more around the Blind River basal conglomerate uranium deposits, we find numerous diabase dykes that cut the crystalline basement complex. These are accompanied by calcite veinlets, some of which contain botryoidal pitchblende. This phenomenon has been studied and described in *Economic Geology*. One of the authors, I believe, was Daniels, of the University of Chicago, who concluded that lamprophyric intrusives such as diabase dykes had acted as "soakers" or collectors of uranium from the rocks they traversed. I suggest that they are a useful indication of source rocks for sedimentary uranium deposits.

J. R. de ANDRADE RAMOS: We have quite recently been informed of the existence of uraniferous metaconglomerates at the northwestern boundary of the São Francisco craton, not far from a town called Cavalcante, in the northern part of the State of Goiás (Brazil). These conglomerates overlie micaschists, believed to be of Archaean age, and they may be correlated with the Minas series near Belo Horizonte.

VEIN- AND SIMILAR-TYPE DEPOSITS

Review Paper

REVIEW OF CURRENT CONCEPTS REGARDING VEIN DEPOSITS OF URANIUM

E. E. N. SMITH

Eldorado Nuclear Ltd,
Ottawa, Canada

Abstract

REVIEW OF CURRENT CONCEPTS REGARDING VEIN DEPOSITS OF URANIUM.

The primary uranium mineral filling cracks, fissures, pore spaces, breccias and stockworks is pitchblende, a thorium-deficient variety of uraninite. A wide range of rocks may contain vein uranium suggesting that, in some cases, it is the structural trap created by the rock rather than its chemical composition which makes it a suitable host.

Vein deposits form an integral part of the uranium geochemical cycle which includes all types of uranium deposits, and which governs the repeated transport and deposition of uranium from one geological setting to another. Because of this cyclic interdependence, different types of deposits may be found together within a specific uranium province.

In Canada, uranium in veins, pegmatites and sediments may all be found in the geosynclinal belts surrounding provinces and sub-provinces of the Precambrian shield. More than one type is invariably present within a small area, although all types may not form ore bodies. Age determinations on several deposits within a specific setting often indicate a long period of repeated concentration, transportation and redeposition such that the same uranium may have occupied different deposits during different periods of the cycle.

Two major periods of the earth's geological history appear to have provided the original setting for most of the world's deposits of uranium in veins. These are the Carboniferous-Permian period and the Middle Proterozoic period. In both cases the first vein pitchblende was deposited during a period of long and intense weathering. Some geologists feel that repetition of these exogenic conditions has moved and redeposited the uranium several times up to the present. Other geologists consider that the uranium is carried to its host from a fertile source by thermal waters which may originate from late stages of granitic evolution or from acid vulcanism.

The vein deposits of uranium are those in which uranium minerals fill cavities such as cracks, fissures, pore spaces, breccias, stockworks and so on. The dimensions of the openings have a wide range, from the massive veins of pitchblende at Jachymov and Port Radium to the microscopic pitchblende-filled cracks, pores and disseminations of some of the ore-bodies in northern Saskatchewan and northern Australia.

There is an equally wide range of host rocks - granites, diabase dykes, sediments, acidic and basic volcanics, and even laterites, both ancient and modern.

Because of their high grade and the very high price of radium, it was the vein deposits of Jachymov, Shinkolobwe and Port Radium which made this class so important in the pre-dawn era of nuclear energy. However, the actual dawn brought so great a demand for uranium that the lower grade, high tonnage deposits in sediments eventually took over as the major supplier, and uranium in vein deposits were relegated to a lesser share

of the market. From our present day knowledge of the geologic setting of uranium deposits it would appear that it is not likely that these roles will be reversed in the future. This is not to say that vein deposits are not important. The most significant discoveries of new reserves in recent years have been the addition of new vein deposits to the long established uranium districts in northern Saskatchewan, Canada, and the Northern Territory, Australia.

Most geologists today readily recognize that vein deposits of uranium are not something unique and completely separate from other types of uranium deposits. Rather, they form an integral part of the complete geochemical cycle which governs the repeated transport and deposition of uranium from one host to another. This concept has been thoroughly developed and discussed in an excellent series of papers as represented by Bigotte [1] and as extended by Barnes and Ruzicka [2].

Essentially the concept holds that uranium moves from a host, such as a crystalline or sedimentary rock or the oceans, via processes of solution, metamorphism, or sedimentation. Provided conditions are proper for entrapment or precipitation, the uranium may be reconcentrated in a new host ready to participate in the next phase of the cycle. All three basic types of uranium deposits with their many variations are links in the complete chain and, in a sense, are dependent upon each other.

This interdependence is emphasized by the recognition that uranium is largely confined to specific geologic settings, and that within each of these regions, deposits may be found of several types and of several ages of deposition. This is particularly evident in the Precambrian shield of Canada where the geologist has been greatly aided by excellent maps of regional tectonics by the Geological Survey of Canada [3].

Here uranium is closely identified with the geosynclinal belts which circumscribe geologic sub-provinces of the Precambrian. Intense tectonic zones within these belts are usually an expression of the collision and grinding together of proto-continental masses, and they are a favourable resting place for uranium. However, in a few regions, uranium is also recognized within the continental plates themselves, where it tends to concentrate at the base of Middle Proterozoic cratonic cover sediments such as the Athabasca and Dubawnt formations of northern Canada.

While the continental core in any particular region may have contributed the first uranium to the geosyncline, once the uranium moved to the edge of the mass and entered the belt and especially the tectonic zone, it appears to have remained, to be distributed and reconcentrated possibly several times in several different ways. In one part of the system it may have been deposited syngenetically in sediments while in others it may have filled cracks and fissures in rocks or soils. These different events may not necessarily have taken place within the same time frame and, in fact, it is quite possible that the same uranium could have participated in

several depositional events. The important point is that once within the tectonic setting most of the uranium remained and moved as in a closed system or cycle. Several uranium districts illustrate this association quite well, even though some of the deposits may be of little economic interest.

The Elliot Lake uraniferous quartz pebble conglomerates form the base of Lower Proterozoic sediments which were derived from and lie along the south edge of a great mass of Archean rocks which contain uraniferous pegmatites and granites. Some 100 miles west of the main Elliot Lake deposits there are many small veins of younger pitchblende concentrated in the Archean rocks just below the unconformity with younger Proterozoic sequences [4].

A similar association has long been recognized in the Beaverlodge or Athabasca uranium district of northern Saskatchewan where older uraninite-bearing pegmatites are spatially related to veins of pitchblende, and sedimentary deposits of uranium are recognized in overlying quartz sandstones and quartz pebble conglomerates [5].

The Makkovik region of Labrador is a further Canadian example of a complete uranium province with pitchblende filling fractures, sedimentary deposits in quartzites and uraninite in pegmatites [6].

Not to be outdone, the Rum Jungle region of Australia, along with its well-known vein deposits, also displays uranium in quartz pebble conglomerates and in pegmatites, all within the structural setting of the district [7]. It is understood that some of the exploration which led to the major new discoveries east of Darwin was originally designed to investigate potential deposits in radioactive granites which were partially exposed through the lateritic soils which were eventually recognized as one of the hosts of the orebodies.

With the increasing availability of age-dating facilities it has become evident that many of the world's uranium provinces have had a long history of repeated uranium concentration, transport and redeposition. This is particularly evident in deposits formed initially during the Precambrian, thus providing a longer time interval for reworking. It may not be so evident in districts blanketed by relatively young sequences of sedimentary deposits.

Earlier, it was noted that vein deposits of uranium are found in all types of rocks, the granites of the Vendée, the metasediments, volcanics and granite gneisses at Beaverlodge, the mica chlorite schists at Jabiru, and so on. Veins often crosscut several rock types. The chemical composition of the rock thus appears to have less bearing on the deposition of vein uranium than does its degree of competency which permits it to develop a structural trap for the uranium-bearing solutions.

On the other hand, common host rocks like the mica chlorite schists of Beaverlodge and northern Australia may

have exerted a form of chemical control on the more diffuse bodies of uranium, or these rocks themselves may have been the immediate source of the uranium now concentrated in fractures and disseminated bodies.

It also seems evident that much of the vein uranium in any particular structural complex is usually in the last or near to last stage of tectonic activity in the region. If emplaced within earlier fracture patterns, later movement often appears to have had some influence on removing it from its original setting and redepositing it.

Some rock types appear to be ubiquitous, though not necessarily economic, hosts for vein deposits of pitchblende. As an example, there are few vein deposits in the world that do not have dykes of diabase close by, with pitchblende filling cracks either within the dyke or along its walls [8]. Some geologists have suggested that uranium and diabase may have a common parentage while others are satisfied that the emplacement of the dyke has merely relocated some pre-existing uranium. Detailed age determinations in a uranium district might help to solve this interesting association.

Age determinations of both uranium and its host rocks have played a major role in establishing the geological setting of vein deposits. Two major periods of the earth's geologic history, including two major tectonic orogenies, appear to have been the original setting for most of the world's deposits of uranium in veins. These are the Carboniferous-Permian period across Europe and along the east coast of North America, and the Middle Proterozoic period as represented in Canada and Australia. Naturally, lack of geologic information about large sectors of the world tempers these statements, but the fact remains that these two periods have been responsible for most of the uranium found in vein deposits.

The Proterozoic setting for major deposits of uranium is one with which I am most familiar, for the vein deposits of the Precambrian of Canada fall in this category.

In northern Saskatchewan uranium occurs as uraninite, uranothorite and allanite in pegmatites, coarse-grained granites and granite gneisses of Archean and/or Lower Proterozoic (Aphebian) age. At least two periods of syngenetic uraninite deposition have been recognized (2270 and 1930 million years) [5,9] representing granitization of Archean or Lower Proterozoic metasediments and volcanics. These rocks were involved in the world-wide post-Lower Proterozoic orogeny, termed the Hudsonian in Canada, at about 16-1800 million years. A product of this orogeny was the deposition in intermontane basins of typical red bed sequences of basal conglomerates, arkoses and siltstones intercalated with flows of andesite and sills of basalt (Martin formation). Later (about 12-1400 m.y.) the southern section of the region was covered by a relatively shallow basin of quartz sandstone with some quartz siltstones and basal quartz pebble conglomerates (Athabasca formation). Although vein deposits of pitchblende have been found in rocks of all three periods, geologists working in the district have long recognized

that they are invariably found within about 200 metres of the two separate unconformities upon which these Middle Proterozoic (Martin and Athabasca) formations lie [10].

While the pitchblende-filled fractures lie close to these unconformities, the unconformities themselves and the ancient soil horizons coating them are particularly favourable for vein uranium. At the Eldorado Nuclear Limited property, concentrations of uranium in the old soil or regolith zone at the base of the Martin formation have provided substantial high-grade ore for the mill, while the orebodies of the Rabbit Lake (Gulf Minerals Canada Ltd.) and the Cluff Lake (Amok Ltd.) properties lie within or close to the regolith-covered unconformity at the base of the Athabasca formation. Vein uranium deposits have been recognized in several other parts of northern Canada with the same spatial association with Middle Proterozoic unconformities.

A similar setting has been recognized in the Northern Territory of Australia [11,12]. Here the pitchblende deposits at Rum Jungle, South Alligator Rivers and the new Arnhemland properties are caught in structural traps in Archean or Lower Proterozoic metasediments and granites. All are spatially located close to or along the unconformity with the overlying Middle Proterozoic rocks. In most cases, erosion of the flat-lying Middle Proterozoic sediments has exposed the deposits at their base; several other deposits are partly protected by these cover rocks [13].

These and other examples of the affinity of vein uranium for the basal unconformity underlying Middle Proterozoic rocks are sufficient to cause one to conclude that the great hiatus about 16-1800 million years ago at the end of the Lower Proterozoic provided a particularly receptive horizon for the epigenetic deposition of thorium-deficient uranium minerals. This is in spite of current information which indicates that the bulk of the uranium seems to have been deposited following the period of sedimentation which covered the erosion surface. Several pitchblende ages, however, in the 17-1800 million year range have been recorded [9] at Beaverlodge and other parts of northern Canada, and this confirms that some uranium, at least, was deposited during the long period of erosion. Incidentally, I am not aware of any vein pitchblende throughout the world with an age older than this orogeny at the end of the Lower Proterozoic.

The other major period when primary vein uranium was deposited took place following the emplacement of Hercynian granites in Europe during the Carboniferous period. Deep weathering during the following Permian coated uranium-rich Hercynian granites with a thick soil formed in situ, within which uranium concentrated in zones of fracturing or high porosity [14,15]. Some of the uranium became caught in fracture systems in the metamorphosed rocks surrounding the granite massifs [16,17]. None of these uranium deposits stray very far away from the edge of the granite bodies. Moreover, they invariably lie within 150-250 metres of the present land surface.

This spatial relationship of uranium with late Hercynian and present erosion surfaces bears a kindred resemblance to uranium at the erosion surfaces of the Middle Proterozoic. Because the much younger age of these deposits enables one to study them almost under conditions of formation, it should be possible to apply some of the knowledge gained to investigations of the older Precambrian vein deposits. On the other hand, the tremendous time period of the Precambrian deposits enables one to study on an expanded scale several specific periods of uranium redeposition, each of which may have been caused by different processes.

Thus far, I have been stressing the deposits in Canada, Australia and western Europe. There are, of course, significant vein deposits of uranium in other regions which bear a geologic resemblance to those being discussed.

In Gabon, near Franceville [18], Precambrian sandstones and shales with an age of about 1745 million years flank Archean granite massifs. Pitchblende and coffinite form economic sedimentary deposits which are further concentrated in structural and sedimentary traps in favourable horizons of the sandstones. The deposits all lie within 200 metres of the present surface. Although Proterozoic in age the similarity of the geologic setting with the Hercynian deposits in western Europe is obvious.

A variety of vein deposits throughout the western United States [19] has characteristics individually similar to deposits in other parts of the world. Most of these deposits appear to be of the silica, sulphide type and are Tertiary in age although the host rock ranges from Precambrian to Tertiary.

The mineralogy of the vein deposits of uranium has been well described by many authors [10, 20, 21] and thus will be only briefly summarized here. The primary uranium mineral is invariably the variety of uraninite called pitchblende, which in Canadian usage, as qualified by Robinson [10], is a variety of uraninite containing negligible amounts of thorium and rare earths. It is commonly found as a vitreous to dull black, massive or botryoidal mineral coating breccia fragments and filling or lining the walls of fractures, microcracks and pore spaces. Occasionally, pitchblende is found as euhedral crystals.

Secondary uranium minerals are common in most pitchblende deposits as a product of near-surface alteration; in some properties they form the orebodies. They consist essentially of hydrated uranium oxides, phosphates and silicates with minor amounts of other elements, notably copper and vanadium. Sooty pitchblende and the uranium silicate coffinite are relatively common. The uranium titanium mineral brannerite, which is an ore mineral in the Elliot Lake quartz conglomerate beds, is finely dispersed as euhedral lath-like crystals through the pitchblende veins of the Eldorado property in northern Saskatchewan and thus may be providing a clue to the history of formation of these deposits.

The mineral assemblages found with pitchblende have been subdivided by Little [21], Gangloff [15] and Ruzicka [20] into simple and complex groupings. Representative of the complex types are the cobalt, silver, nickel, bismuth, arsenic assemblages associated with the pitchblende deposits of Port Radium [22], Czechoslovakia [20], Shinkolobwe [23], and parts of northern Saskatchewan [10] and northern Australia [11]. The simpler groups, which are composed of pitchblende with minor amounts of other minerals, may also be represented by other sectors of the deposits at Port Radium, Czechoslovakia, northern Saskatchewan and Australia. The silica, sulphide association is quite common in the European deposits [15, 24].

The native elements copper, gold, platinum, tin and silver are found in varying amounts in some deposits in Czechoslovakia, Canada, and Australia. The iron vanadate, nolanite, is a common constituent of the pitchblende ores of the Beaverlodge area, but does not seem to occur in other deposits, while the uranium, vanadium mineral francevillite is found in the orebodies of Gabon [18]. On the other hand, selenium minerals of copper, lead, mercury and cobalt have been recognized at several uranium deposits throughout the world.

In several of the vein uranium districts a rough psuedo-zoning is apparent of simple to complex mineralogy. In the case of the deposits in the Beaverlodge district of northern Saskatchewan, over a range of up to 8 kilometres, there are sectors individually rich in selenium minerals, or in the cobalt, nickel group, or in vanadium, or in sulphides, or in native metals. All sectors contain copious quantities of quartz and calcite.

Paragenetic studies and age-dating of some of these deposits have established that some of the element and mineral groupings were introduced during separate periods in the long history of mineral deposition and redeposition and, therefore, may be an indication of the nature of the source material at the particular time, or the environment through which the uranium was passed and filtered en route to its host rock.

Hematite, quartz, calcite, graphite and chlorite are probably the most common of the gangue and wall rock minerals although they are not as equally abundant in all deposits. In veins they occur as massive fillings, as drusy masses and coatings, or as euhedral crystals coating the walls of fractures or breccia fragments. Calcite is usually the dominant gangue mineral in the veins of the Beaverlodge area where it shows evidence of having been deposited before, with and after the pitchblende. On the other hand, it is essentially absent in the orebodies at Ranger in Australia. Quartz is less abundant, occurring in massive, banded and comb textures with a range of colours from milk white through pink, red and amethyst [10] at Beaverlodge, to the beautifully banded smoky quartz of the Bois Noir [15] and other European deposits [20].

The principal chlorite mineral appears to be penninite with minor amounts of prochlorite. Both calcite and chlorite are usually found disseminated within the immediate wall rocks

but, whether in veins or the host rocks, they both may show an intimate association with pitchblende. Faint wisps and grains of pitchblende are often found in chlorite masses both within the vein and disseminated in the wall rocks. Pitchblende and calcite have such a close affinity that one may replace the other in some parts of a vein with the roles reversed in other parts. Spherules of alternating shells of calcite and pitchblende at Beaverlodge illustrate the depositional contemporaneity of the two [8].

Hematite, with its pervasive colour, is often the most conspicuous accessory mineral with pitchblende in some vein deposits. Not only does it appear as tiny flakes of specularite throughout the pitchblende, calcite and quartz in the vein, but it imparts a strong red colouration to the wall rocks [10]. The genetic relation of the wall rock colouration to the period of uranium mineralization may be deceptive, however, as it is not common in some other deposits such as those of northern Australia [12], where chlorite is the dominant product of alteration. Hematitization of the country rocks is particularly widespread in northern Saskatchewan, even colouring the wall rocks of fissures that contain no uranium (conversely, a few uranium-bearing fractures may not have a noticeable red colouration of their walls). This has caused some geologists to propose that much of the red colouration is a product of normal weathering of the unconformity on top of the Lower Proterozoic.

In earlier days, vein deposits of pitchblende were usually incorporated into Lingren's detailed classification of hydrothermal epigenetic mineral deposits. Based on the evidence of the time these deposits were largely classified as mesothermal to epithermal or, as Robinson [10] suggested, Graton's intermediate leptothermal classification; that is, uranium carried by solutions into openings in the host rocks at rather moderate temperatures and at moderate depths below the surface. The source of these solutions was often somewhat of a mystery. For some deposits it was often convenient to link the source of the uranium-bearing fluids with the introduction of a nearby granite body or volcanic flow. Failing this, it was more likely that the solutions were described as moving upward from depth - depth being vaguely defined as some place below the lowest working levels of the mine. At any rate, with the field information and the laboratory instruments of the time, these conclusions were reasonable and acceptable. Lingren's classification has weathered the years and is still a most useful and serviceable system.

In examining the literature on current thinking regarding the origin of uranium-bearing solutions and, in fact, many other metallic deposits, it is apparent that many geologists now tend to discount transport from great depths or by way of direct igneous emanations in favour of rather shallow and more local sources. These thoughts are especially well expressed by Haddon King [25] and Duncan Derry [26] in the Distinguished Lecture Series of the Society of Economic Geologists.

Our French colleagues have developed two mechanisms by which uranium might be transported and deposited in rock cavities, supergene exogenic weathering and hydrothermal endogenesis. These hypotheses have evolved from the series of most informative papers on the uranium cycle which was referred to earlier. Moreau, et al [14] describes the exogenic weathering process as one where the land surface of the Hercynian granites has been subjected to an extended and repeated period of deep erosion featuring torrential rains interspersed by long periods of hot arid climate. Under such conditions, uranium has been leached from the eroding granites and has migrated until caught in a structural trap, either within the granite itself or in the surrounding rocks. Similar explanations by Fernandez Polo [16] and Matos Dias [17] are ascribed to the formation of uranium deposits in Spain and Portugal where the uranium is held in veins and disseminations in metamorphosed mica schists at the edge of Hercynian granites. This theory of supergene epigenesis has also been applied by Knipping, in the paper following, to describe the formation of the uranium deposits at Rabbit Lake, Saskatchewan.

The endogenic hydrothermal hypothesis favoured by other French geologists has been most recently summarized by Gangloff [15]. Based on laboratory decrepitation studies it was concluded that uranium was carried by thermal waters at temperatures in the range of 200-300°C. Acid volcanics carrying 3-4 ppm U are suggested as the source of the hydrothermal solutions in contrast to the fertile Hercynian granites which contain 9-11 ppm U.

In much the same sense, Barnes and Ruzicka [2] have developed a flow diagram model of the geochemical cycle which stresses the source areas of all types of uranium deposits. Although they conclude that it is not possible to differentiate between uranium derived from early crust and from uranium recycled via granitization or lateral secretion, they suggest two major mechanisms by which uranium is transported and deposited. The first is caused by chemical and mechanical weathering of the source rocks leading to the deposition of primary uranium minerals by mechanical concentration. In the second, uranium is carried either by surface and/or connate waters under conditions of low to moderate temperature and pressure, or by solutions formed under high temperature and pressure conditions.

It is the latter classification which governs the deposition of vein deposits, and they further subdivide this group into monomineralic and polymetallic associations.

In discussing the processes governing the deposition of vein pitchblende, Barnes and Ruzicka call upon both low to moderate temperatures and pressures "per descensum" for deposits such as Rabbit Lake, Nabarlek and the Massif Centrale, and upon moderate to high temperatures and pressures for solutions "per lateral secretion or per ascensum" for deposits such as Beaverlodge, Pribram, Great Bear Lake and Jachymov.

Thus it appears that they are accepting, albeit under somewhat more complex conditions, both processes suggested by the French geologists.

If the solutions which effected the release, transportation and deposition of uranium in veins have relatively low to moderate temperatures and pressures and appear susceptible to climatic conditions, then the source of the uranium is surely close at hand. Most European geologists appear to agree that the Hercynian fertile mica granites [14] with an average of 9-11 ppm U are the primary source of the uranium concentrated in fractures both in the weathered granite and in the metamorphosed rocks bordering the granites.

Some time ago, Getseva [27] discussed redistribution of uranium by the process of intense metamorphism of uranium-bearing sediments. More recently, in northern Saskatchewan, Tremblay [28] noted a higher than average content of uranium in Archean quartzites and metachists and he concluded that granitization and later dynamic metamorphism at the end of the Lower Proterozoic caused the uranium to be mobilized and to be reconstituted in fracture systems. Pitchblende veins in these mica schists and epidotic amphibolites in the Eldorado mine, although displaying networks of fractures, tend to follow specific stratigraphic peculiarities of the host rocks with a remarkable uniformity of both grade and total content per unit of depth, and with a down dip continuity of about 2000 metres.

The close association of vein pitchblende with zones of intense structural deformation, retrograde metamorphism or mylonitization is well recognized, not only in northern Saskatchewan, but in several similar settings throughout the Precambrian of northern Canada. Moreau [14] recognizes a similar relationship in Europe, but notes that the uranium is more likely to be along the edge of the zone of deformation, rather than in it. The South Alligator River deposits are described by McQueen [29] as being in rocks that are folded, faulted and sheared.

Recognizing the relative ease with which uranium is able to move about in much younger sedimentary rocks, it is not unreasonable to assume that similar processes might have permitted concentration in earlier Precambrian sediments. In addition, the much longer time period has enabled geologic forces to concentrate the dispersed uranium into open spaces to form viable orebodies.

Earlier, I referred to the decrepitation studies [15] which led some French geologists to conclude that some uranium was probably carried by hydrothermal solutions. On the basis of decrepitation studies of dolomite and quartz in pitchblende veins at Rabbit Lake, Little [30] decided that colloform pitchblende along with dolomite, quartz and calcite was probably deposited from solutions in the temperature range of 180-225°C. Badham et al [31] are of the opinion that uranium along with nickel, cobalt, bismuth and silver were deposited from hot brines to form the ore deposits at Port Radium. On the lower levels of the Eldorado mine in northern Saskatchewan, connate waters rich in calcium, magnesium and sodium chloride flow from rock cracks; the present rock temperature is a comfortable 20°C. Recently, on the 32nd level of this mine, fractures were found filled with pitchblende and solid chlorides.

In contrast to these higher temperatures, Miller [32] was able to precipitate uranium from solutions at 25°C to form a hemispherical, botryoidal pitchblende which he claimed had a microscopic texture similar to the pitchblende at Port Radium. At higher temperatures (100 to 215°C) he found that the solubility of both uranous and uranyl ions was much lower, resulting in more pitchblende precipitating from solution but with much coarser crystallite dimensions. Recognizing, therefore, that the stability of uranous and uranyl complex ions decreases with increasing temperature, he calculated that neutral solutions of uranyl carbonates, fluorides or hydroxides could react with H₂S to precipitate pitchblende at relatively cold temperatures. He also found that pressures up to 5000 pounds per square inch had little effect on the stability of the uranium ions other than to keep the system closed and to increase the solubility of the gases in solution.

Earlier I noted that, although the bulk of Precambrian uranium was deposited later, the oldest vein pitchblende appears to have been emplaced during the hiatus between the Lower and Middle Proterozoic. Several pitchblende ages within this 1600-1800 million year range have been recorded in northern Canada [9] and several similar ages have now been reported from northern Australia. I am convinced that we will soon confirm that this was the period of major primary deposition, now partly indistinct because of later movement and redeposition. It simply does not make sense to me that uranium being deposited during a younger period of the earth's history would arbitrarily select as a host a very much older structural setting on a completely world-wide basis.

Rejuvenation and remobilization of the uranium appears to have taken place during later tectonic periods, whether or not the orogeny has been recognized as a major tectonic event in the uranium district itself. For instance, pitchblende in Canada and Australia, in a rather rough way, appears to have been mobile during the orogenies at the beginning and at the end of the Upper Proterozoic. Some rejuvenation is again displayed, in the case of the Canadian deposits, at the beginning and end of the Mesozoic, or roughly the same periods affecting the west European deposits.

Obviously far more information is required before any definite conclusions can be drawn. Tentatively, there is a suggestion that periods of major continental movement were particularly sensitive times for uranium. A pattern may yet evolve to show a relationship between the remobilization of uranium and world-wide plate tectonics. An excellent start has already been made in the thoughtful work of Gabelman [33] on metallogenetic sequences in intracratonic belts.

In this review of some of the concepts currently in fashion governing the vein uranium deposits, it is obvious that I have not attempted to cover all aspects. For instance, it did not seem useful to discuss the nature of the ore-forming fluids when it was apparent that this would receive more than adequate treatment in other papers at this symposium. Rather it is hoped that the few points considered will complement the papers to follow and will serve as a foundation for our later discussions.

REFERENCES

- [1] BIGOTTE, G., "Cycle de l'uranium", 22 IGC, Part V, Section V, Genetic Problems of Ores, India (1964) 351
- [2] BARNES, F.Q., RUZICKA, V., A genetic classification of uranium deposits, 24 IGC, Section IV, Mineral Deposits (1972) 159
- [3] Tectonic Map of Canada, Geol. Surv. Can. 1251A (1969)
- [4] NUFFIELD, E.W., Geology of the Montreal River Area, Ont. Dept. Mines, Toronto Vol. LXIV, Part 3 (1955)
- [5] TREMBLAY, L.P., Geology of the Beaverlodge Mining Area, Sask., Geol. Surv. Can., Mem. 367 (1972)
- [6] BEAVAN, A.P., The Labrador Uranium Area, Geol. Assoc. Can. 10 (1958) 137
- [7] WALPOLE, B.P., et al, Geology of the Katherine-Darwin Region, Northern Territory, Bur. Min. Res., Bull. 82 (1968)
- [8] SMITH, E.E.N., Structure, wall-rock alteration and ore deposits at Martin Lake, unpublished PhD thesis (1952) Harvard Univ.
- [9] KOEPEL, V., Age and History of the Uranium Mineralization of the Beaverlodge Area, Sask., Geol. Surv. Can. Paper 67-31 (1968)
- [10] ROBINSON, S.C., Mineralogy of Uranium Deposits, Goldfields Sask., Geol. Surv. Can. Bull. 31 (1955)
- [11] TAYLOR, J., Origin and Controls of Uranium Mineralization in South Alligator Valley, Aust. Inst. Min. Metal, Atomic Energy in Australia 12 4 (1969) 18
- [12] DODSON, R.G., "Some environments of formation of uranium deposits", Uranium Prospecting Handbook, Inst. Min. Met., London (1972) 33
- [13] ROWNTREE, J.C., Descriptive geology of the Jabiluka uranium deposits, Geological Discussion Group, Toronto (Oct. 1973), unpublished
- [14] MOREAU, M., PUGHON, A., PUIBARAUD, Y., and SANSELME, H., L'uranium et les granites, Chronique des mines et de la recherche minière, Paris, No. 350 (1966)
- [15] GANGLOFF, A., "Notes sommaires sur la géologie des principaux districts uranifères étudiés par le CEA", Uranium Exploration Geology, (Proc. Panel Vienna, 1970), IAEA, Vienna (1970) 77
- [16] FERNANDEZ POLO, J.A., "Genesis de los yacimientos uraníferos en metasedimentos de Salamanca (España)", Ibid., p.243.
- [17] MATOS DIAS, J.J., SOARES de ANDRADE, A.A., "Uranium deposits in Portugal", Ibid., p.129.
- [18] BOURREL, J., PFIFFELMANN, J.P., La province uranifère du bassin de Franceville (République Gabonaise), Mineral Deposita 7 (1972) 323

- [19] EVERHART, D.L., "Uranium-bearing vein deposits in the United States", Int. Conf. Peaceful Uses Atom. Energy (Proc. Conf. Geneva, 1955), 6, UN, New York (1956) 257.
- [20] RUZICKA, V., Geological comparison between East European and Canadian uranium deposits, Geol. Surv. Can. (1971) Paper 70-48
- [21] LITTLE H.W., "Distribution of types of uranium deposits and favourable environments for uranium exploration", Uranium Exploration Geology (Proc. Panel Vienna, 1970), IAEA, Vienna (1970) 35.
- [22] JORY, L.T., Mineralogical and isotopic relations in the Port Radium pitchblende deposit, Great Bear Lake, Canada, unpublished PhD thesis, Cal. Inst. Tech. (1964)
- [23] DERRICKS, J.J., VAES, J.F., "The Shinkolobwe uranium deposit: Current status of our geological and metallogenic knowledge", Int. Conf. Peaceful Uses Atomic Energy (Proc. Conf. Geneva, 1955) 6, UN, New York (1956) 94.
- [24] CAMERON, J., Structure and origin of some uranium-bearing veins in Portugal, Junta de Energia Nuclear, Paper 22 (1959)
- [25] KING, H.F., Some antipodean thoughts about ore, Bull. Soc. Ec. Geol. 68 8 (1973) 1369
- [26] DERRY, D.R., Ore deposition and contemporaneous surfaces, Bull. Soc. Ec. Geol. 68 8 (1973) 1374
- [27] GETSEVA, R.V., "The nature of sedimentary-metamorphic uranium mineralization", The Geology of Uranium, Consultants Bureau Inc., New York (1958)
- [28] TREMBLAY, L.P., The significance of uranium in quartzite in the Beaverlodge area, Sask., Can. Jour. Earth Sci. 7 2 (1970) 280
- [29] McQUEEN, A.F., Uranium Exploration in Australia, Aust. Inst. Min. & Met. (1970) 15
- [30] LITTLE, H.W., Uranium in Canada, Geol. Surv. Can. Paper 74-1, Part A (1974) 137
- [31] BADHAM, J.P.N., ROBINSON, B.W. and MORTON, R.D., The Geology and Genesis of the Great Bear Lake Silver Deposits, 24th IGC, Section 4, Mineral Deposits (1972) 541
- [32] MILLER, L.J., The chemical environment of pitchblende, Geol. 53 (1958) 521
- [33] GABELMAN, J.W., Metallogenic evidence for continental drift, USAEC WASH-1205 (1971)

DISCUSSION

R.D. MORTON: When you refer to an association of uranium mineralization with the hiatus of 1600 to 1800 m.y. ago, you, like many others, imply that this has some genetic significance. How, then, do you explain

the results of fluid inclusion studies and stable isotope composition analyses which have been published by members of the University of Alberta? The research in question indicates temperatures of formation of up to 470°C for the mineralizing fluids and clearly shows that the fluids equilibrated with their host metamorphic rocks at high temperatures during metamorphism.

E.E.N. SMITH: It should, of course, be evident from my paper that I do attach genetic significance to the association you have mentioned. I have no comment to offer on the interpretation of fluid inclusion studies. In this review paper I merely reported the results that have been obtained.

R.D. MORTON: You refer to the lack of Archaean vein deposits; but recent unpublished work of Baadsgaard and co-workers in western Greenland has revealed gneisses about 3900 m.y. old which are remarkably depleted in uranium compared with younger and apparently identical gneisses. This observation may be significant for our understanding of the availability of uranium during the Archaean, and of the geochemical evolution of the continental lithosphere.

E.E.N. SMITH: I can only repeat that I know of no vein deposits of pitchblende older than the orogeny at the end of the Lower Proterozoic.

S. ANZALONE: Have you observed any fluorite in a zoned relationship at the periphery of the veins bearing U_3O_8 ? I ask this question because there appears to be a vague relationship between U_3O_8 mineralization and fluorspar at such sites as Bokan Mountain, Alaska, Rexspar, British Columbia, and the U_3O_8 veins in the Front Range of Colorado — particularly near Jamestown, Colorado, where fluorspar mines are at present being worked.

E.E.N. SMITH: I have no additional information, but Mr. Little of the Geological Survey of Canada may be able to answer your question.

H.W. LITTLE: I know of only one uranium deposit in Canada where such a relationship might be thought to exist, namely the Rexspar property in British Columbia. At Rexspar, however, there appear to be two quite separate bodies, one containing fluorite and the other uranium, which overlap slightly. There is no true relationship between them.

I have a question of my own for Mr. Smith. How do you account for the large vertical range of the deposit at Eldorado, which, with more than 5000 ft, is greater than the depth of any other such deposit?

E.E.N. SMITH: The explanation seems to be that the erosion surface at the base of the Martin Formation and the underlying metasediments which form the host were folded and that one limb was fortuitously protected down dip by the St. Louis fault.

H.W. LITTLE: And how do you account for the ore bodies in the hanging wall of the St. Louis fault by this process?

E.E.N. SMITH: They are a continuation of the same sequence of folded metasediments which have been offset by the fault system.

A.O. SERGIADES: Uraniferous pegmatites and uraniferous deposits in the Grenville structural province of Canada, north of the St. Lawrence River, are thought to occur at the horizon, now folded, between the reworked Archaean basement and the younger reworked Proterozoic sediments. I mention this point to emphasize the significance of the Lower Proterozoic unconformities.

B.P. POTY: The apparent contradiction between fluid inclusion data as reported by Little and the concept of supergene formation of deposits such as that at Rabbit Lake should not, it seems to me, be impossible to

resolve. Light metamorphism coming after the deposition of pitchblende, and involving nearly stagnant fluids poor in CO_2 , would not unduly affect the quantity or position of the ore. It would, however, yield some gangue minerals responsible for the published results.

H.D. KNIPPING: I might just point out that temperature determinations based on $^{16}\text{O}/^{18}\text{O}$ ratios often give only half the value found by the decrepitation method.

F.R. JOUBIN: I wonder whether Mr. Smith could supplement his account of the Eldorado uranium deposits by describing the position of the St. Louis fault system. How is the position of the fault related to the oxidized land surface of the non-conformity which you feel "positions" the ore lenses?

E.E.N. SMITH: The footwall of the fault plane is roughly parallel to and just at the Hudsonian erosion surface, which is coated by a regolith capped by the Martin basal conglomerates. The fault tends to slice and plane the irregular erosion surface.

THE CONCEPTS OF SUPERGENE VERSUS HYPOGENE EMPLACEMENT OF URANIUM AT RABBIT LAKE, SASKATCHEWAN, CANADA

H. D. KNIPPING

Gulf Minerals Canada Ltd. ,

Toronto, Ontario, Canada

Abstract

THE CONCEPTS OF SUPERGENE VERSUS HYPOGENE EMPLACEMENT OF URANIUM AT RABBIT LAKE, SASKATCHEWAN, CANADA.

The Rabbit Lake uranium deposit occurs in Lower Proterozoic metasediments below a major unconformity overlain by Middle Proterozoic sandstone. The metasediments were deformed and metamorphosed during the Hudsonian orogeny about 1800 million years ago. After peneplanation of the Hudsonian orogen surface, weathering generated a porous and permeable regolith of varying thickness which later was covered by sandstone and faulted up by a reverse fault. Primary uranium mineralization of massive and colloform pitchblende occurred about 1000 million years ago and has no relationship to the Hudsonian orogeny. The ore paragenesis is simple and monotonous. Only very few sulphides such as pyrite, marcasite and chalcopyrite are present and closely associated with pitchblende. The hypothetical process of ore emplacement is as follows. Uranium solutions entered a structurally high block of strongly brecciated and altered calcareous metasediments, and pitchblende was deposited on the surfaces of fractures, vugs and pores. Calcite, massive and euhedral quartz and euhedral dolomite overlie the pitchblende and protected it partly from leaching. Some of the pitchblende was leached and re-deposited at varying periods in other parts of the ore body. This process is still going on. Alteration and uranium emplacement are related to the surface and do not extend more than 300 to 400 ft below the unconformity. Though paleotemperature determinations on gangue minerals indicate low to elevated temperatures, the results are at present equivocal. The bulk of the evidence favours a supergene emplacement mechanism for uranium at Rabbit Lake with later leaching and re-deposition of sooty pitchblende and rare coffinite. Hexavalent uranium minerals such as uranophane, sklodowskite and boltwoodite occur only near the present surface.

INTRODUCTION

Since the discovery of the Rabbit Lake uranium deposit in northern Saskatchewan by Gulf Minerals Canada Limited in 1968, a large amount of geological data have been collected from diamond drill holes and from rock trenches. The orebody is located under and south of Rabbit Lake, a small lake three miles west of Wollaston Lake.

The following studies and concepts are based on the necessity to generate a valid model for the emplacement of uranium at Rabbit Lake which could be utilized for successful exploration planning. The investigations are not yet complete, and therefore this discussion is a progress report.

Exploration is proceeding very actively on Gulf's land holdings in Saskatchewan. Almost weekly, new evidence is obtained which adds to the knowledge of the genetic process.

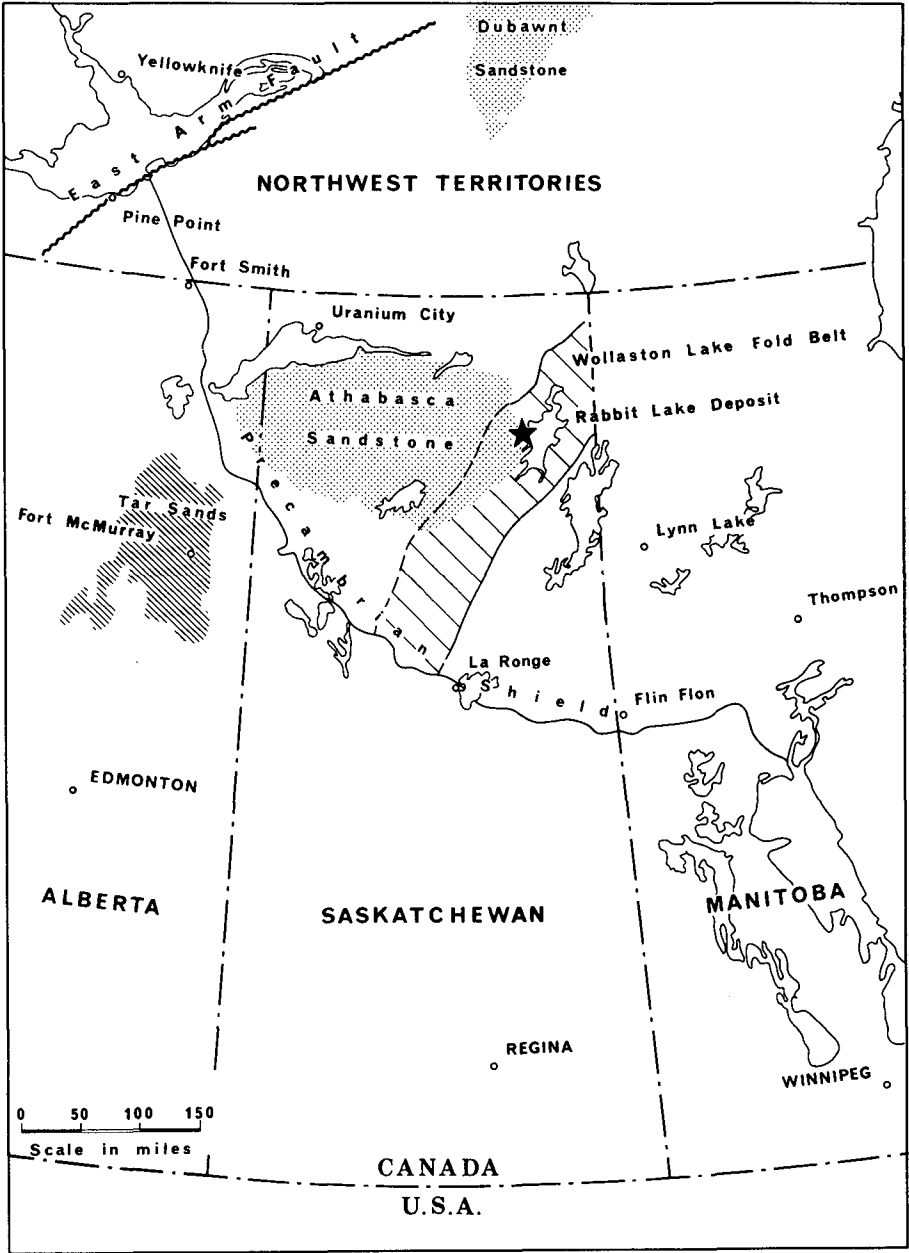


FIG. 1. Location map of Rabbit Lake deposit.

GEOLOGICAL FRAMEWORK

The Rabbit Lake uranium deposit is located within rocks of the Wollaston Lake Fold Belt in the southwestern part of the Canadian Shield [fig. 1]. The Wollaston Lake Fold Belt is a discrete unit within the Churchill structural province of the Canadian Shield as defined by C. H. Stockwell [1].

The portion of the Churchill province within the borders of Saskatchewan contains a large diversity of Precambrian units, not only in terms of composition and metamorphic grade, but also in structural trends. During the Lower Proterozoic [Aphebian], several northeast trending troughs formed on the Archaean basement. These troughs were filled with sediments derived from the Archaean uplands bordering its rims.

The Wollaston Lake Fold Belt, the most prominent of the Lower Proterozoic sedimentary belts, is a zone of dominantly supracrustal rocks. The belt is at least 400 miles long from the southern edge of the Canadian Shield northeast to the border of Manitoba and the North-West Territories. The width is 10 to 50 miles.

Archaean rocks, the source of the sediments in the Wollaston Lake Fold Belt, are mainly of granitic composition, which is reflected in the generally arkosic character of the strata. Several groups of sediments are recognized but correlation between them is not yet possible.

Meta-arkose, hornblende-biotite rocks, acidic meta-volcanics and quartzites occur in the southern part of the belt indicating eugeosynclinal conditions.

In the Rabbit Lake area, meta-arkose, biotite paragneiss and calc-silicate rocks with marble form the main rock units indicating miogeosynclinal conditions for sedimentation.

The sedimentary assemblage was deformed and metamorphosed during the Hudsonian orogeny. Tight or isoclinal folds with northeast trending axes are the result of the orogeny and metamorphism proceeded to the cordierite-amphibolite stage of the Abukuma facies series.

Conformable and crosscutting pegmatites are ubiquitous. Foliated and unfoliated granites are present but do not occur in the close vicinity of the Rabbit Lake deposit. The foliated granites are believed to be remobilized Archaean granites which intruded the Lower Proterozoic sediments during the Hudsonian orogeny.

The Middle and Upper Proterozoic Athabasca formation is not metamorphosed and overlies the Lower Proterozoic unconformably. The formation comprises quartz sandstone and conglomerate up to 5 000 feet in thickness.

A few northwest trending diabase dykes intrude the Precambrian formations. Unconsolidated glacial formations of great variety blanket the entire area.

GEOCHRONOLOGY

Samples of meta-sediments and granites were collected within a 30-mile radius from Rabbit Lake for potassium-argon age dating, which was

TABLE I
ISOTOPIC AGE DATES (by Gulf Research & Development Company)

LOCATION	ROCK TYPE	FRACTION DATED	K/Ar AGE (10^9 yr)	U_{38} CON- TENT (ppm)	^{40}Ar (%)
A	Granite*	Biotite Feldspar	2.03 1.79	1.6	97.4 93.9
B	Pegmatite	Total Biotite	1.52 1.69	31.0	98.6 91.8
C	Meta-arkose	Feldspar Chlorite	1.63 1.56	2.2	97.9 89.2
D	Granite Gneiss	Biotite Feldspar	1.89 1.87	2.9	98.9 98.4
E	Granite Gneiss	Biotite Muscovite	2.0 1.76		97.8 99.6
F	Granite**	Biotite	2.04		98.3
G	Granite*	Biotite	2.11		99.5
H	Granite Granite* Kaolinized Rock	Total Total Total	1.68 (1.51) (1.29)		95.6 97.9 95.5
I	Diabase Granodiorite	Total Biotite	1.13 1.85		94.6 71.4

* Foliated

** Strongly Foliated

carried out by Gulf Research and Development Company in Pittsburgh [Table 1]. Two groups of ages were established. Ages around 1800 million years for the meta-sediments reflect the Hudsonian orogeny, and ages of 2000 to 2100 million years for the foliated granites are believed to be survival ages of an older orogeny, the Kenoran orogeny. The youngest age obtained is 1130 million years for a diabase, which cuts the Athabasca formation. The Athabasca formation, therefore, was deposited between about 1700 and 1100 million years ago [fig. 2].

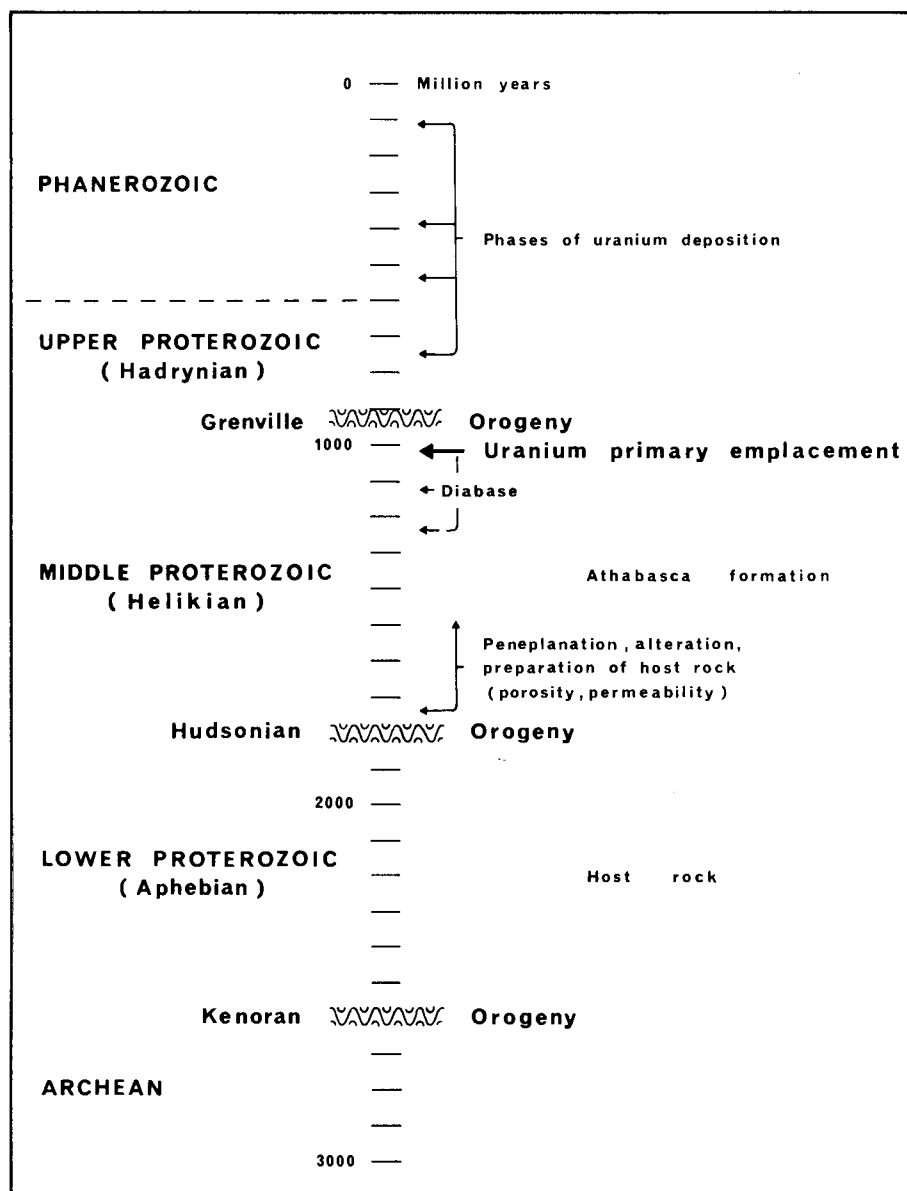


FIG. 2. Geological time frame for uranium emplacement at Rabbit Lake.

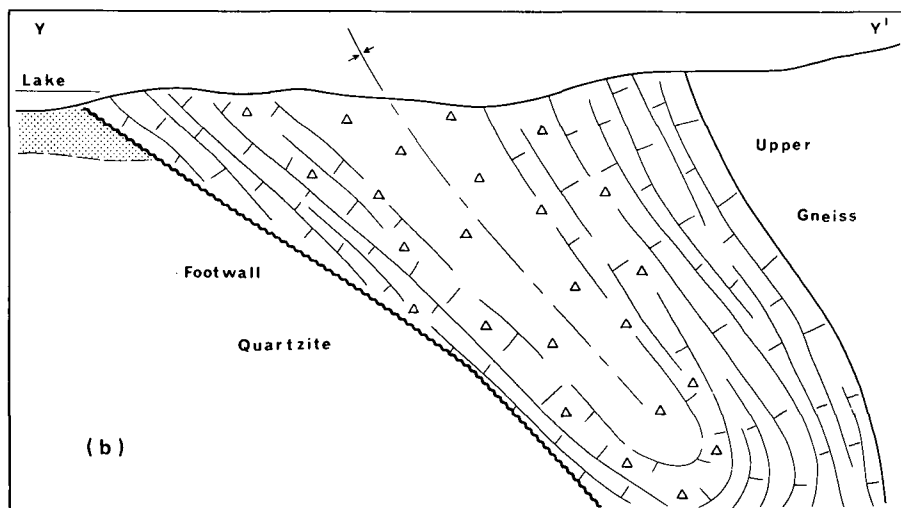
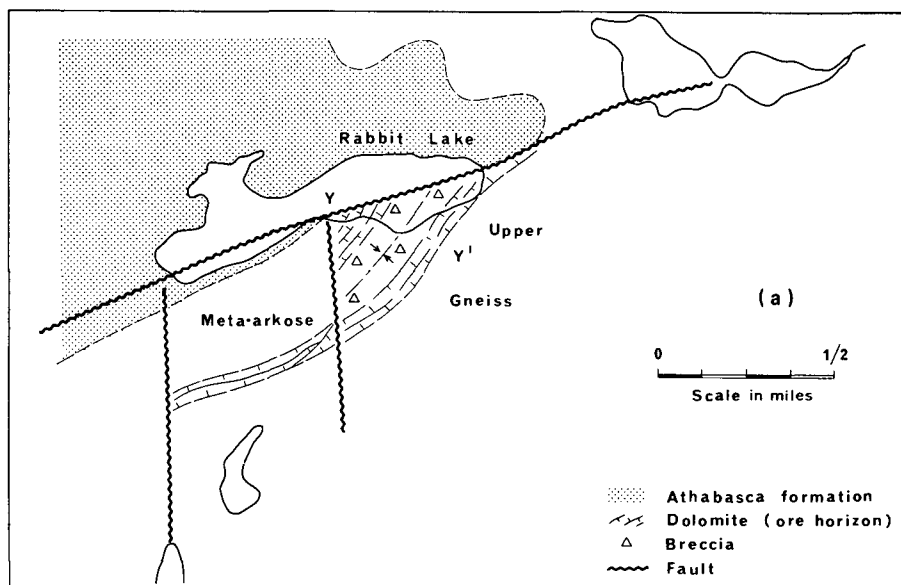


FIG. 3. (a) Geological sketch of Rabbit Lake area; (b) idealized section Y-Y'.

THE RABBIT LAKE URANIUM DEPOSIT

The schematic geologic setting of the Rabbit Lake deposit is presented in Figure 3, (the geological sketch map and cross-section).

The Lower Proterozoic rocks south of Rabbit Lake are asymmetrically folded. The main structural feature is a synform with a northeast trending axis. The axial plane of the synform dips steeply to the southeast. The west limb of the synform dips gently at about 40 degrees to the southeast, whereas the east limb is overturned and is dipping almost vertically near the surface.

The axial region of the synform was strongly sheared and brecciated. This brecciated axial region is the ore zone at Rabbit Lake. Generally, the ore zone has the shape of an irregular pipe trending northeast, and plunging very gently to the northeast.

A young cross-cutting reverse fault, with east-northeast strike, limits the ore zone on the north end. The beds involved in this structure are dolomitic and calcareous meta-sediments of the Lower Proterozoic and the Athabasca formation of Middle Proterozoic age.

The Footwall Quartzite [FWQ] formation below the young cross-cutting Rabbit Lake thrust fault is a calc-silicate and quartzite horizon, greenish-grey in colour and very fine-grained. It does not outcrop at the surface.

The cross-cutting Rabbit Lake thrust fault consists of a one to twenty foot wide zone of green to black talcose and crushed rock. Soft gouge is common.

The hanging wall block of the cross-cutting thrust fault is composed of the Dolomite Horizon or simply termed the "Ore Horizon", because the orebody occurs within it. The Dolomite Horizon is strongly altered. Pegmatites and granitic rocks invaded the Dolomite Horizon during the metamorphism of the Hudsonian orogeny and have subsequently been altered in the ore zone.

Alteration minerals identified by Gulf Research and Development Company utilizing X-ray diffraction techniques are kaolinite, vermiculite, chlorite and dickite. In addition, hematite, calcite, dolomite and massive and euhedral quartz are present. Montmorillonite and magnesite are present in very small amounts. Rutile, sphene and other titanium minerals have been altered to anatase.

Zoning of alteration minerals is not evident. The alteration is limited strictly to the highly brecciated axial zone of the synform and to associated fractures. It is very intense in the upper 300 feet from the surface and decreases rapidly downward. There is only fresh unaltered rock below the alteration zone, which bottoms at around 450 feet below the surface.

The paragenetic relationship of the alteration minerals to each other is very complex and requires much additional study. The alteration process increased the porosity and permeability in the altered zone. Uranium emplacement started after the alteration process was terminated.

The uranium solutions entered the porous rock and uranium minerals were deposited on the walls of pores and fractures. The deposition appears to be a simple process of coating the open spaces. In thin

TABLE II

CHEMICAL COMPARISONS (composition of Rabbit Lake
orebody, Beaverlodge and Great Bear Lake)^a

Element	Orebody	Rabbit Lake Area		Eldorado	Beaverlodge
		Showing A	Showing B	Port Radium ^b	Fay Mine ^c
Sb				0.12	NR
As				8.5	NR
Ba	0.03	0.1	0.05	NR	0.02
BeO				Trace	
Bi				0.68	
B				NR	
Cd				NR	NR
Ce				NR	0.3
Cr				Trace	0.01
Co				4.6	
Nb ₂ O ₅				NR	
Cu	0.01-0.02	0.0001	0.05	4.8	0.005
Ga				NR	NR
Ge				NR	NR
In				NR	NR
Fe	0.05-5	10 +	0.5	10.8	5.0
Pb		0.1	0.1	2.56	0.5
LiO ₂				NR	NR
Mn	0.01	0.01	0.01	0.7	0.1
Hg				NR	NR
Mo				0.05	
Ni				2.9	0.003
Ag	< 0.1 oz/t	< 0.1 oz/t	< 0.1 oz/t	0.09	0.002
Ta ₂ O ₅				NR	NR
ThO ₂	0.01			NR	0.05-0.2
Sn				NR	
Ti	0.02-0.05	0.05	0.1	0.14	2.0
W				NR	NR
U ₃ O ₈	10 +	15	14.85	13.81	5.0
V	Trace	0.01		0.09	1.0
Zn				NR	NR
ZrO ₂	< 0.005			Trace	0.03

^a Spectrographic estimates. Values in per cent, except for silver.

NR = not reported.

Blank space = not detected.

Elements present in Rabbit Lake ore:

A. Major	B. Low	C. Traces
U ₃ O ₈	Ba	BeO Ni
Fe	Pb	Cr Ag
	Ti	Cu V
		Ga ZrO ₂
		Mn

^b Port Radium from G. Mursky, GSC Mem. 374.

^c Fay Mine from V. Ruzicka, GSC Paper 70-48.

sections this process can be observed to the smallest detail, where pitchblende coats the fracture planes of chlorites. Some open spaces near the surface are large cavities and have probably resulted from karst formation. Primary uranium minerals at Rabbit Lake are colloform and massive pitchblende, sooty pitchblende and rare coffinite. Secondary uranium minerals are boltwoodite, uranophane and sklodowskite. The pitchblende is often overlain by massive or euhedral quartz and calcite. Some euhedral dolomite occurs on the tips of the euhedral quartz crystals and is therefore younger than the quartz. Often sooty pitchblende coats the euhedral quartz. This pitchblende is the youngest pitchblende observed in the deposit.

The paragenetic succession is always identical in different parts of the orebody. The sequence is:

Alteration of host rock - development of porosity and permeability - deposition of pitchblende on the walls of void space - deposition of massive quartz or calcite - deposition of euhedral quartz - euhedral dolomite - deposition of sooty pitchblende.

Often one or several stages of this paragenetic sequence are missing. The process of leaching and deposition is going on at the present time. Waters issuing from fractures in the orebody or from diamond drill holes are strongly uraniferous.

Within the orebody are a few blebs and specks of sulphides, such as pyrite, marcasite, chalcopyrite and galena. Some of these sulphide blebs are intimately associated with the pitchblende, suggesting syngenetic deposition. Hematization is common, adjacent to but not pervasive in the orebody. Its distribution is not yet fully understood in relation to pitchblende deposition. Many high-grade sections of the orebody are not hematized. Sulphides such as pyrrhotite and niccolite have been observed as rare occurrences within the structure but are not related to pitchblende mineralization. The chemical composition of the ore is very simple. The ore is very clean uranium oxide with very few trace elements [Table II]. It appears as if uranium passed through a geological filtering process in which other elements previously associated with uranium were filtered out. There are areas of fresh white and pink dolomite with several vugs and large pores but without pitchblende mineralization. The entire ore zone appears to be green and soft and one could classify the alteration as "green alteration".

The Upper Gneiss [U.G.] occurs only east of the orebody and comprises a variety of lithologies which still defy subdivision into sub-units. The upper gneiss consists of well-banded biotite paragneiss with intercalations of meta-arkose, dark green and fine-grained dolomitic rocks, metaquartzites and other minor lithologies. Pegmatites, granite sills and dykes are common and cause migmatization in many places. Mineralization is completely absent in the upper gneiss.

URANIUM EMPLACEMENT AND GEOCHRONOLOGY

Studies of mineral parageneses on drill cores at Rabbit Lake indicated a relative sequence of mineral deposition in time and space. However, absolute ages for the formation of some minerals were needed in order to construct a reasonable model of uranium metallogenesis. For this purpose, systematic sampling of pitchblende and other minerals from drill cores at Rabbit Lake was carried out. The samples were taken

TABLE III

ISOTOPIC AGE DATES (By Gulf Research & Development Company)

LOCATION: Rabbit Lake

MATERIAL DATED: HARD, COLLOFORM AND SOOTY PITCHBLENDE

SAMPLES FROM: DIAMOND DRILL HOLES (DEPTH 50 FEET TO 300 FEET)

	ISOTOPES	MINERAL	COMMON Pb CORRECTION	AGE OF FORMATION
DDH I	$^{206}\text{Pb}/^{238}\text{U}$ $^{207}\text{Pb}/^{235}\text{U}$ $^{207}\text{Pb}/^{206}\text{Pb}$	Sooty Pitchblende	No	508 M. Y. 662 M. Y. 1240 M. Y.
DDH II	$^{206}\text{Pb}/^{238}\text{U}$ $^{207}\text{Pb}/^{235}\text{U}$ $^{207}\text{Pb}/^{206}\text{Pb}$	Sooty Pitchblende	Yes	190 M. Y. 220 M. Y. 564 M. Y.
DDH III	$^{206}\text{Pb}/^{238}\text{U}$ $^{207}\text{Pb}/^{235}\text{U}$ $^{207}\text{Pb}/^{206}\text{Pb}$	Sooty Pitchblende	No	1200 M. Y. 903 M. Y. 384 M. Y.
DDH IV	$^{207}\text{Pb}/^{206}\text{Pb}$	Galena	Yes	820 M. Y.
DDH V	$^{206}\text{Pb}/^{238}\text{U}$ $^{207}\text{Pb}/^{235}\text{U}$ $^{207}\text{Pb}/^{206}\text{Pb}$	Colloform Pitchblende	No	929 M. Y. 989 M. Y. 1127 M. Y.
DDH VI	$^{206}\text{Pb}/^{238}\text{U}$ $^{207}\text{Pb}/^{235}\text{U}$ $^{207}\text{Pb}/^{206}\text{Pb}$	Colloform Pitchblende	No	1320 M. Y. 1248 M. Y. 1124 M. Y.

generally between fifty and three hundred feet below the surface, from diamond drill holes penetrating different parts of the orebody.

The samples were investigated at Gulf Research and Development Company in Pittsburgh, Pennsylvania, utilizing isotopic age dating methods [Table III]. Since in each pitchblende sample different generations of pitchblende were present, a very careful procedure was instituted to collect only samples of one generation for age dating methods adapted from Koeppel [2]. This procedure guarded against dilution of the sample which would have resulted in a hybrid age.

The ages obtained from the lead-uranium and lead-lead ratios vary widely from 190 to 1320 million years. The Physics Department of the University in Alberta studied Rabbit Lake pitchblende independently and determined their age of formation, which is identical to the age obtained by Gulf Research and Development Company.

The most reliable primary emplacement age of Rabbit Lake pitchblende appears to be about 1000 million years ago. This age was derived from a sample completely composed of one generation of colloform pitchblende in diamond drill hole V.

H. W. Little [3], plotting the isotope data on a concordia diagram, obtained an age of 1075 million years ago for the initial uranium mineralization at Rabbit Lake, which is in close agreement with previously established data. The process of leaching and redeposition of pitchblende is believed to still be continuing at the present time.

THE CASE FOR SUPERGENE EMPLACEMENT OF URANIUM AT RABBIT LAKE

It has been known for some time that many economic uranium concentrations are located within a few hundred feet of major unconformities or show a close relationship to old land surfaces or peneplanation areas. The Rabbit Lake uranium deposit is located in direct contact with one of the most pronounced unconformities known in the Canadian Shield. The unconformity marked by the basal conglomerate of the Athabasca formation is within 50 feet above the present top of the Rabbit Lake orebody.

In the following a list of facts is given, which are in direct relation to the ore emplacement process at Rabbit Lake. Any reasonable hypothesis of the origin of uranium at Rabbit Lake has to fit each of these facts.

1. The ore deposit is in direct contact with a major unconformity.
2. Uranium mineralization decreases with depth below the unconformity and bottoms at about 350 feet.
3. Alteration which envelopes and pervades the orebody is younger than the metamorphism of the host rock but older than the primary uranium ore emplacement. The alteration is related to the unconformity and terminates at fairly shallow depth.
4. Alteration and ore deposition are directly related to brecciation and fractures which produced porosity and permeability in the host rock. The structural deformation preparing the ground for alteration and uranium emplacement occurred during or after deposition of the Athabasca formation and has no relationship in time to the Hudsonian orogeny.

5. The ore deposit occurs only in the upthrown hanging wall block of the young cross-cutting Rabbit Lake fault. To date, no uranium mineralization has been found within the footwall block of the Rabbit Lake fault, though strong alteration is present in places. The Rabbit Lake fault does not contain any uranium, nor is there any evidence that ascending solutions passed along the fault.
6. Primary ore emplacement can be dated at 1000 to 1100 million years ago, which is 500 to 600 million years younger than the Hudsonian orogeny. In any event, uranium deposition occurred after peneplanation of the Hudsonian orogen.
7. The ore paragenesis at Rabbit Lake and showings A and B in the vicinity is very sparse and monotonous. Uranium and iron are the major elements present in the ore. Minor constituents are lead, barium and titanium. Only a few trace elements are present [Table II], and many elements such as cobalt, bismuth and thorium associated with uranium in historically well-known uranium deposits as Jachymov in Czechoslovakia, and Port Radium (Eldorado) at Great Bear Lake are completely absent.
8. The ore emplacement appears to have been a simple coating process involving the smallest detail. Uraniferous solutions carried the metal as oxide or in complex compounds into the previously prepared porosity, where pitchblende was precipitated against the walls of the void spaces. The pitchblende was in turn coated by massive quartz, calcite or euhedral quartz, which protected the pitchblende from leaching.
9. Decrepitation analyses, carried out by Gulf Research and Development Company, of massive quartz and calcite which coats the pitchblende, and is therefore younger, resulted in a temperature of formation of less than 100 degrees C.

H. W. Little [3] reported formation temperatures of 180 to 225 degrees C for similar material from Rabbit Lake using thick sections on a heating stage. There is some doubt that these determinations are conclusive. Chemical composition and oxygen isotope ratios of fluid inclusions at Rabbit Lake are not yet known. These may have a strong bearing on the determination of the temperature at the time these minerals were formed. Robinson [4] compared palaeotemperatures on gangue minerals in vein-type uranium deposits of the Lake Athabasca region of northern Saskatchewan. The method using oxygen isotope ratios $^{18}\text{O}/^{16}\text{O}$ resulted in temperatures approximately one-half of those determined by decrepitation methods.

Oxygen isotope work has not yet been carried out on Rabbit Lake gangue minerals.

The evidence presented in the foregoing appears to be sufficient to formulate a plausible hypothesis of uranium emplacement at Rabbit Lake. Despite some conflicting data, the bulk of the evidence presently favours a supergene emplacement mechanism. The hypothetical process can be described as follows:

Uraniferous waters circulated through the porous host rock which acted as a trap during a certain geological time interval when changing pH-Eh values produced the exact conditions for precipitation of quadrivalent uranium. The movement of the waters was downward, or at least the main component was "descending" and not "ascending".

There is no system of open fractures or faults at depth nor is there alteration below the orebody. Below about 400 feet from the surface only fresh rock is present in numerous diamond drill holes, and not the slightest evidence of possible feeder channels through which ascendent uraniferous waters could have moved has been discovered to date.

The entire uranium phenomenon at Rabbit Lake appears to be closely associated geologically with sedimentation, hydrology, climatic factors, surface weathering, leaching, precipitation and changes in pH and Eh of the transporting fluids. These processes are related to the surface and affect generally only a very small slice of the rocks to a depth of not more than a few hundred feet.

The concept of a geochemical cycle of uranium as proposed by G. Bigotte [5] has very strong applications in the case of Rabbit Lake. The geochemical cycle of uranium can be generally divided into a hypogene segment and a supergene segment, both with many variations. Bigotte [6] later stated: "the most powerful processes for economic concentration occur in the sedimentary environment, during the so-called supergene part of the cycle".

Similar views had been previously expressed by Gruner [7], who in discussing the "availability of uranium in igneous and other rocks" in the western United States shows that an enormous amount of uranium has been leached and transported during erosion of rocks. Later the uranium was trapped under suitable conditions.

The uranium ore at Rabbit Lake is 800 to 1000 million years older than the ore in the western United States. Very little is known about the climatic conditions during the Proterozoic. Of particular importance would be a knowledge of the climatic conditions during the extensive hiatus after the Hudsonian orogeny and before the deposition of the Athabasca formation.

There is some indication that after peneplanation of the Hudsonian orogen a hot humid climate interspersed with arid hot conditions existed in the region. Strongly weathered Lower Proterozoic rocks have been encountered in diamond drill holes below the unconformity of the Athabasca formation. The thickness of the regolith varies from a few feet to over 300 feet. Marble and calc-silicate horizons at the surface are more susceptible to weathering than granite gneiss and quartzite.

The case for interpreting the alteration at Rabbit Lake as a result of surface weathering is fairly substantial. Not only can the depth limit of alteration be cited in support, but also minute detail in drill cores of Rabbit Lake point to the fact that surface waters percolated downward through the fractures and pores and increased porosity and permeability by leaching.

The formation of alteration minerals such as hematite, kaolinite, montmorillonite, vermiculite, chlorite, anatase and others have been well documented by R. Maignien [8] in his discussion on lateritic weathering. All the above-cited alteration minerals are present at Rabbit Lake. But many processes leading to laterite formation are not yet fully understood, despite a fairly extensive knowledge of the climatic factors involved.

There is very little known concerning Proterozoic climatic conditions and the formation of Precambrian soils or regoliths. Though there are many similarities of the Rabbit Lake regolith to products of modern or

geologically recent lateritic weathering processes, many facts cannot be recovered from the geological record. For example, nothing is known of the biological activity at the weathering surface below the Athabasca formation.

H. Erhart [9] studied soil formation as a geological phenomenon and his studies culminated in the theory of "bio-rhexistatie". Though Erhart's studies are concerned only with Phanerozoic and recent soil formation, the principal processes may have been active during long intervals of the Proterozoic. According to Erhart, biochemical weathering during long periods of tropical hot humid climate separated the elements in the rock at and near the surface into the migratory phase and the residual phase. Uranium belongs to the migrating phase with e.g. sodium, potassium and others. After long periods of "biostatie", which weathered the rocks fairly deeply, events occurred which interrupted these processes and the entire slice of soft weathered rocks was eroded and removed. On the resulting fresh rock surfaces a new period of deep weathering could commence.

The theory of bio-rhexistatie has many fruitful applications. A modified version of this theory may be applicable in our interpretation of the processes leading to the formation of the Rabbit Lake uranium deposit.

The theory of "bio-rhexistatie" was applied by M. Moreau [10] et al. for the interpretation of vein-type uranium deposits in Variscan granites in France. According to Moreau et al., large surface areas of fertile granites were leached during at least three phases of bio-rhexistatic climatic conditions and the uranium deposited in open fractures within structurally high blocks. The evidence presented in Moreau's paper is very convincing and has many parallels to the genetic theory concerning Rabbit Lake.

Temperature determinations on gangue minerals in France by J. Leroy and B. Poty quoted in G. Ranchin's [11] investigation on uranium geochemistry are the main objections to the "exogenic weathering" theory and "endogenic weathering" has now been substituted for explaining the origin of uranium according to Gangloff [12].

Theories representing exogenic weathering and supergene emplacement mechanism have been presented for vein-type uranium deposits of the Iberian Peninsula by J. A. Fernandez-Polo [13] and J. M. Matos Dias, and A. A. Soares de Andrade, [14] and the evidence cited in the discussions has many parallels to Rabbit Lake.

The ubiquitous presence of barium and copper in Rabbit Lake ore and in uranium showings in the vicinity may have strong genetic implications as shown by Dall'Aglia [15]. In the supergene environment uranium, copper and barium exhibit approximately the same geochemical mobility and their presence in the Rabbit Lake trap therefore should be expected.

According to figure 2, primary uranium emplacement at Rabbit Lake occurred after deposition of the Athabasca formation. Fahrig [16] has shown that the sediments of the Athabasca formation were derived from the east and moved westward into the intracratonic basin. The palaeoslope direction was to the west during the entire time of deposition. Therefore, it is reasonable to assume that, during the deposition of the uppermost clastics of the Athabasca formation, the subsurface waters flowed westward along the unconformity within the very porous and permeable base of the Athabasca formation, carrying uranium into the Rabbit Lake

trap, which had been faulted up above the peneplained surface of the Lower Proterozoic. The uranium in the waters was probably derived from leaching the igneous and metamorphic rocks east of the Rabbit Lake deposit. The structurally high position of the Rabbit Lake trap provided the hydrological conditions which enabled the uraniferous waters to percolate through the host rock. With this hypothesis the absence of uranium in the footwall block of the Rabbit Lake reverse fault can be explained. Another source of the uranium could have been a pre-existing sedimentary uranium deposit within the Athabasca sandstone, which was later completely leached and deposited downward into the Rabbit Lake trap.

The Rabbit Lake host rock has acted as a "geochemical barrier" [6] to the migrating uraniferous solution during a probably very long period of geological time. Perelman [17] in his discussion on geochemical barriers states: "The orebodies are confined to strata which carried water. The impermeable inter-calations remain barren". In addition, Perelman cites a large amount of facts concerning the transport and fixation of uranium during supergene migration.

There is some slight indication of variation of the ^{235}U to ^{238}U ratios within the Rabbit Lake deposit. Much more work will have to be carried out to relate isotopic uranium composition to the supergene migration and to different generations of pitchblende.

THE CASE FOR HYPOGENE EMPLACEMENT OF URANIUM AT RABBIT LAKE

Historically, the main vein-type uranium deposits have been considered to have originated through hydrothermal processes from a magma chamber. Later, the magmatic hydrothermal concept evolved into the tectonic hydrothermal concept, which was lucidly documented by Gabelman [18].

There is some evidence supporting a tectonic hydrothermal emplacement mechanism of uranium at Rabbit Lake:

1. Palaeotemperatures derived from decrepitation analysis of gangue minerals in excess of 180 degrees centigrade.
2. Presence of a large amount of light green chlorite in the alteration zone.
3. Strong argillation of the host rock prior to uranium emplacement.
4. An almost total lack of sulphides or organic material in the ore deposit which could have indicated processes during which soluble hexavalent uranium was reduced and precipitated as quadrivalent uranium.

The foregoing evidence is equivocal as previously shown, but it is partly contradictory to the supergene emplacement hypothesis.

It could very well be argued that tectonic movements, such as reverse faults and wrench faults during the Middle and Upper Proterozoic, generated enough heat that surface waters entering these faults leached uranium and other elements from the strongly fractured zones of the host rock. The heated waters caused the alteration and deposited pitchblende and later the gangue minerals in the open spaces.

The depth limit of the ore could be explained by a simple experiment carried out by Robinson [4] in which he dissolved significant amounts of uranium in an autoclave at 200°C and under CO₂ pressure of 180 pounds per square inch with an addition of small amounts of sodium bicarbonate. If the temperature and pressure in this system is decreased, pitchblende will be formed.

Similar hypotheses have been proposed by A. P. Vinogradoff for the uranium deposits of the "Erzgebirge" of the German Democratic Republic as reported by Gangloff [12].

Tectonically heated brines have also been responsible for leaching and depositing uranium, silver, nickel (cobalt), arsenides and bismuth in dilatant fault zones in the Great Bear Lake area of Canada, according to Badham et al. [19].

Further paragenetic and physico-chemical studies on Rabbit Lake ore will undoubtedly reveal more evidence.

A magmatic source for the uranium at Rabbit Lake is not apparent. The granites in the area are believed to be mainly remobilized Archaean granites, and cannot be classed in the fertile group as described by Moreau [10]. The uranium content in the granites within a 30 mile radius of Rabbit Lake does not exceed 3 ppm.

CONCLUSIONS

In the foregoing, it has been shown that some questions related to the concentration of uranium at Rabbit Lake cannot be unequivocally solved with the evidence at hand. Much of the evidence is circumstantial because some critical facts as e.g. the biochemical activity at the peneplained surface of the Lower Proterozoic are not known.

At the present time, the bulk of the evidence favours the hypothesis of supergene uranium emplacement. The uranium was deposited by supergene solutions in a regolith acting as a trap, prepared during a long weathering interval after the erosion and peneplanation of the Hudsonian orogen. The uraniferous solutions originated east of the Wollaston Lake area and flowed westward during the deposition of the Athabasca formation. The uraniferous waters percolated through the porous and permeable regolith below the unconformity because structurally the block was in a "high" position, a condition noted also by Moreau [10] as a condition for the French uranium deposits. Rabbit Lake fulfills all the conditions necessary for entrapment of large amounts of uranium in the supergene segment set out by G. Bigotte in his definition of the geochemical cycle of uranium [5]

The extraordinary sparse metal paragenesis of the Rabbit Lake ore indicates that the uranium passed through a geological filtering process during which other metals normally associated with uranium in hydrothermal environment, viz. Co, Ag, Bi, Sb, were completely filtered out.

The understanding of the emplacement mechanism of uranium in supergene deposits of the Rabbit Lake type is substantially aided if the following work is carried out:

1. Detailed studies of temperatures of formation of the gangue minerals including oxygen isotope methods.

2. Study of Precambrian soils, climate and weathering processes, particularly during the Middle and Upper Proterozoic. Origin of kaolin, chlorite, vermiculite, montmorillonite, and other alteration minerals, in the host rock.
3. Electron microprobe work to document mineral paragenetic successions at the smallest scale.
4. Critical age dating of uranium minerals followed closely by:
5. Determination of ^{235}U content relative to age of emplacement (different generations of pitchblende).
6. Detailed studies of the future open pit faces to corroborate the findings from core studies and to enlarge on the structural picture related to the orebody.

REFERENCES

- [1] Stockwell, C. H., "A tectonic map of the Canadian Shield" in: The Tectonics of the Canadian Shield, Roy. Soc. Can. Special Publication No. 4, Editor J. S. Stevenson (1962).
- [2] Koepfel, V., "Age and History of the Uranium Mineralization of the Beaverlodge Area, Saskatchewan", Geol. Survey Canada Paper 67-31, [1968].
- [3] Little, H. W., "Uranium in Canada", Geol. Surv. Can. Paper 74-1, Part A, Report of Activities [1974] 137-139.
- [4] Robinson, S. C., "Mineralogy of Uranium Deposits, Gold Fields, Saskatchewan", Geol. Surv. Can. Bull. 31 [1955] 98,99.
- [5] Bigotte G., "Cycle de l'uranium", International Geol. Congress, 22nd Session, Part V, Section V, Genetic Problems of Ores, India [1964] 351-358.
- [6] Bigotte, G., "Origin of Uranium Deposits", Mineralium Deposita, 4, 4 [1969] 415.
- [7] Gruner, J. W., "Concentration of Uranium in Sediments by Multiple Migration-Accretion," Econ. Geol. Vol. 51, No. 6 [1956] 496-497.
- [8] Maignien, R., "Review of Research on Laterites", Natural Resources Research IV, Unesco, Paris [1966].
- [9] Erhart, H., "La genèse des sols en tant que phénomène géologique", 2nd Ed., Collection: Evolution des Sciences, Masson et Cie, Paris (1967).
- [10] Moreau, M., Poughon, A., Puibaraud, Y. and Sanselme, H., "L'uranium et les granites", Chronique des mines et de la recherche minière, Paris, No. 350 [1966].
- [11] Ranchin, G., "La géochimie de l'uranium et la différenciation granitique dans la province uranifère du Nord-Limousin", Rapport-CEA-R4034 [1971] 319.

- [12] Gangloff, A., "Notes sommaires sur la géologie des principaux districts uranifères étudiés par le CEA", Uranium Exploration Geology (Proc. Panel Vienna, 1970) IAEA, Vienna (1970) 77.
- [13] Fernandez-Polo, J.A., "Genesis de los yacimientos uraniferos en metasedimentos de Salamanca (España)", Ibid., p. 243.
- [14] Matos Dias, J. J. and Soares de Andrade, A.A., "Uranium Deposits in Portugal", Ibid., p. 129.
- [15] Dall'Aglia, M., "Planning and Interpretation Criteria in Hydrochemical Prospecting for Uranium", Uranium Prospecting Handbook, The Institution of Mining and Metallurgy, London (1972) 122, 123.
- [16] Fahrig, W. F., "The Geology of the Athabasca Formation", Geol. Surv. Can. Bull. 68 [1961].
- [17] Perelman, A. I., "Geochemistry of Epigenesis", Plenum Press, New York [1967] 213 pp.
- [18] Gabelman, J.W., "Speculations on the uranium ore fluid", Uranium Exploration Geology (Proc. Panel Vienna, 1970), IAEA, Vienna (1970) 315.
- [19] Badham, J. P. N., Robinson, B. W. and Morton, R.D., "The Geology and Genesis of the Great Bear Lake Silver Deposits", 24th IGC, Section 4, Mineral Deposits [1972] 541-548.

DISCUSSION

R.H. DE VOTO: I am greatly impressed by the thoroughness of your observations, your data collection and your interpretations. However, I am not sure I understand your theory of the chemistry of uranium precipitation at this deposit.

H.D. KNIPPING: We have considered various processes, but are still not clear on this point. Mr. Berthelin's paper¹ strikes me as extremely important in this connection. For quite some time we have suspected that biological activity, either algal or bacterial, may have played an important role. Perhaps the most serious obstacle to any demonstration of this theory is the great age of the rocks and the fact that they are partly polymetamorphic. To detect any clear indication of biological activity is thus a formidable task, so we are not yet beyond the speculative stage.

H.W. LITTLE: I should point out that the fluid inclusion temperatures to which Mr. Knipping has referred were measured not by me but by André Boyer, who did very careful work. The temperatures of 180°C and 225°C are minimum temperatures based on low salinity of the solutions. If the salinity was higher, so were the temperatures.

The age of 1075 m.y. was obtained by plotting the uranium-lead isotope data on a concordia diagram; all the results except for one "maverick"

¹ BERTHELIN, J.R., DOMMERGUES, Y., MAGNE, R.A., these Proceedings, Paper IAEA-SM-183/18.

fell on a chord and indicated this age for the initial deposit, with no subsequent events. The Athabasca Formation has been shown by Fahrig to be at least 1250 m.y. old, and so is probably at least 200 m.y. older than the deposit. Under these circumstances I do not see how the deposit could have been formed in the manner you suggest. My own contention is that hydrothermal solutions rose through the fracture zone and that the Athabasca Formation provided a good trap for them. The age of the deposits at Cluff Lake is about the same, but the deposits at Beaverlodge are much older — about 1760 m.y. How can these deposits all have been formed by the same process?

H.D. KNIPPING: Our interpretation applies, strictly speaking, only to Rabbit Lake. Nevertheless, I should point out that, according to the supergene hypothesis, the primary emplacement of pitchblende is related in time and space to the unconformity. The age of Beaverlodge — 1760 m.y. — could, in my opinion, easily be related to the basal Martin Formation unconformity, which is quite a bit older than the Athabasca.

The basal Athabasca conglomerate is still very porous near Rabbit Lake and must have been exceptionally porous and permeable for a long time after initial sedimentation until diagenetic processes slowly filled the pore spaces.

H.W. LITTLE: The basal member of the Athabasca has been eroded at Rabbit Lake, but at other sites I have observed that it is a conglomerate with an argillaceous matrix which could form a trap. Hydrothermal activity can produce argillization, and indeed has in many places.

H.D. KNIPPING: I find it difficult to see how the conglomerate or the base of the Athabasca Formation could have acted as a seal to hypogene solutions, even if we postulate argillization by these fluids. The Athabasca is still an aquifer, and must have been an exceptionally strong aquifer during the Proterozoic. For this reason it would be particularly instructive to find paleo-watertables in this formation.

URANIUM MINERALIZATION IN THE RUM JUNGLE-ALLIGATOR RIVERS PROVINCE, NORTHERN TERRITORY, AUSTRALIA*

R. G. DODSON, R. S. NEEDHAM, P. G. WILKES,
R. W. PAGE, P. G. SMART, A. L. WATCHMAN
Bureau of Mineral Resources, Geology and Geophysics,
Department of Minerals and Energy,
Canberra, Australia

Abstract

URANIUM MINERALIZATION IN THE RUM JUNGLE-ALLIGATOR RIVERS PROVINCE, NORTHERN TERRITORY, AUSTRALIA.

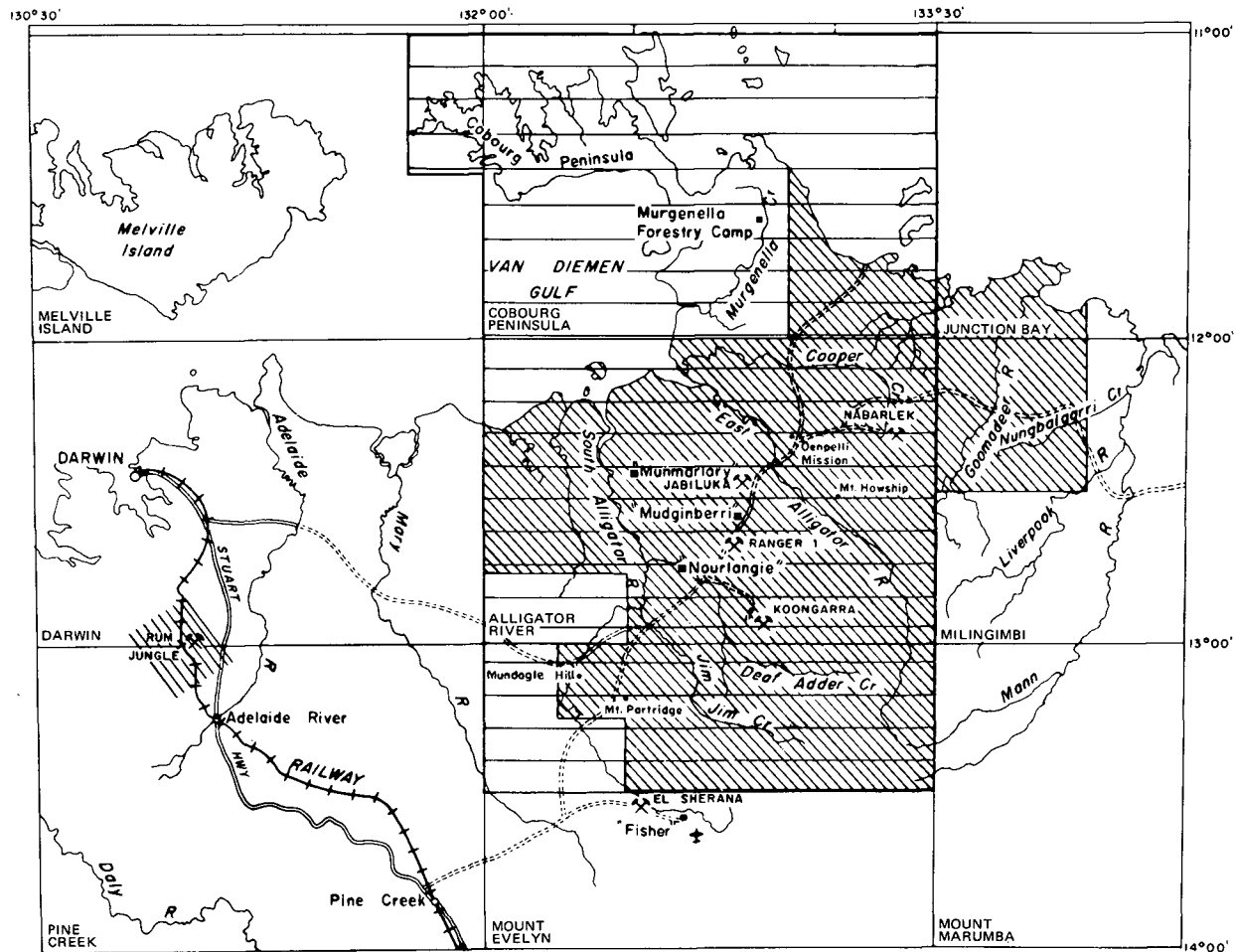
Renewed interest in uranium exploration in northern Australia in the late 1960s led to the discovery of one of the most important uranium fields in the world. To obtain an understanding of the geological setting of the uranium deposits, and to provide guidelines for future exploration, the Bureau of Mineral Resources (BMR) undertook an investigation which included semi-detailed mapping, aided by geophysical surveys, isotopic dating, and stratigraphic drilling. From the results so far obtained and from the important data made available by mining companies engaged in exploration in the region, a pattern of uranium mineralization can be recognized, particularly in relation to the Lower Proterozoic sedimentation of the region.

INTRODUCTION

In a review of the more important environments of Australian uranium deposits, Dodson¹ pointed out that 'Future exploration of the Alligator Rivers area will be greatly assisted if the genesis of uranium ore is established.' Since delivery²⁻⁴ of the paper (September 1970), semi-detailed geological mapping⁵ and geophysical surveys by the Bureau of Mineral Resources (BMR), and investigations by mining companies, have added considerably to our knowledge of the geological setting of these deposits. Although certain assumptions cannot be fully substantiated at present, we believe that we are close to understanding the origin of the ore. Conversely, certain hypotheses put forward in the past appear less likely as new data are obtained.

Following the discovery of uranium at Rum Jungle in 1949, the Katherine-Darwin region was mapped at reconnaissance scale by BMR⁶. The survey established the main outlines of the regional geology, and identified the most favourable environments for uranium. The resulting 1:250 000 geological maps formed the basis for more detailed mapping and the planning of exploration when interest in uranium was revived at the close of the 1960s. In 1970, following the

* Published by permission of the Director, Bureau of Mineral Resources, Geology and Geophysics, Canberra, Australia.



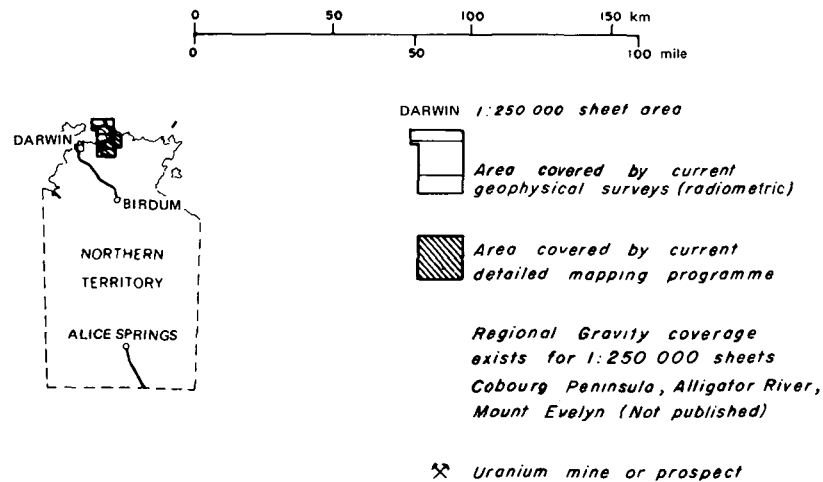


FIG. 1. Locality map of the Rum Jungle-Alligator Rivers uranium province.

discovery of high-grade uranium ore in the Alligator Rivers area about 250 km east-northeast of Rum Jungle, a start was made on semi-detailed geological mapping aided by geophysical surveys, isotopic dating, and stratigraphic drilling. The area being mapped consists of the whole of the Alligator River 1:250 000 Sheet area and parts of the Cobourg Peninsula, Junction Bay, Milingimbi, and Mount Evelyn Sheet⁷ areas (Fig. 1.) A similar but more restricted program at Rum Jungle commenced in 1972. The aim of the current program is to determine the geological setting of the newly discovered uranium deposits, to correlate the geology of the uraniferous areas with each other, and to establish the origin of the mineralization.

GEOLOGY OF THE URANIUM DEPOSITS

With the exception of a few minor prospects, all known uranium deposits of the province occur in Lower Proterozoic sediments of the Pine Creek geosyncline. The deposits are concentrated in three areas: Rum Jungle, South Alligator River valley, and an area between the South Alligator River and Cooper Creek, known for convenience as the Alligator Rivers area. Perhaps the most important clue to the origin of uranium in this province that has resulted from the present investigation is the recognition of a stratigraphic control on the distribution of uranium. In the Alligator Rivers area, both the uranium deposits and untested uranium prospects lie in the same sequence, and there are sound reasons for correlating the succession at the Alligator Rivers area with those of the South Alligator River valley and Rum Jungle. Both the Rum Jungle⁸ and South Alligator River valley^{9,10} deposits have been described in detail, and are therefore only briefly outlined in this paper. The more recently discovered deposits of the Alligator Rivers area are less well known; details of their environment are only now becoming available as geological and geophysical investigations in the area progress.

Rum Jungle

Lower Proterozoic sediments are draped around a core of the Pine Creek Geophysical basement, the late Archaean Rum Jungle Complex. The sediments dip steeply away from the complex, indicating post-Archaean updoming of the complex at the close of sedimentation in the Pine Creek Geosyncline. Further evidence of this updoming has been provided by the discovery of a sheared contact between the Rum Jungle Complex and the Lower Proterozoic sediments (K. Johnson, pers. comm., 1974).

Rhodes¹¹ distinguished six major units in the southern part of the Rum Jungle Complex, in order of decreasing age: Schists and gneisses, granite gneiss, metadiorite, coarse granite, large feldspar granite, and leucocratic granite. Banded ironstone and quartzite have also been

recorded in the complex. The uranium contents of these rocks range from a low 2.8-4.5 ppm in the metadiorite to 10-28 ppm in the leucocratic granite¹². Rb-Sr dating of the leucocratic granite has yielded a whole-rock isochron of about 2400 m.y., and three zircons from different parts of the complex yielded an extrapolated U-Pb age of around 2550¹³ m.y. Evidence of post-Archaean activity in the complex is provided by the presence of quartz-tourmaline veins radiating from centres in the complex and invading the overlying Lower Proterozoic rocks (K. Johnson, pers. comm., 1974).

The complex is cut by the Giant's Reef Fault, which strikes northeast and has a horizontal displacement of about 6 km.

During the Lower Proterozoic, sediments of the Batchelor Group (Beestons Formation, Celia Dolomite, Crater Formation, and Coomalie Dolomite; see Fig. 2) were deposited against and around the Rum Jungle Complex. The Batchelor Group sediments were in turn overlain by sediments of the Goodparla Group, represented at Rum Jungle by the Golden Dyke Formation and the Acacia Gap tongue, which underlies and interfingers with the Golden Dyke Formation. The Batchelor Group sediments were deposited in littoral to neritic conditions; the overlying Goodparla Group sediments were deposited in a shallow marine, partly euxinic environment. Both the Batchelor Group and the Goodparla Group sediments were overlain by the Finnis River Group, represented in the Rum Jungle area by the Noltinius Formation. The Burrell Creek Formation is a lateral facies variation of the Noltinius Formation.

The five small uranium deposits were in Lower Proterozoic schist, siltstone, and shale of the Golden Dyke Formation of the Goodparla Group. The lodes were located in shears, faults, and, at Rum Jungle Creek South, in a tight fold, the host rock being carbonaceous sediments or chloritic slate, near the contact with the underlying Coomalie Dolomite.

South Alligator River valley

The Lower Proterozoic sediments of the South Alligator River valley area are lithologically similar to and are stratigraphically relatable to the Lower Proterozoic sediments of the Rum Jungle area.

Basement rocks of the Pine Creek Geosyncline are not exposed in the valley. The Stag Creek⁶ Volcanics, tentatively assigned to the Archaean by Walpole et al., are considered in the light of recent field work to be Lower Proterozoic; the unit occurs in sequence with Lower Proterozoic sediments at the top of the Masson Formation, underlying the Mount Partridge Formation, both of the Goodparla Group. In the South Alligator River valley the Mount Partridge Formation is overlain by the South Alligator Group, consisting of the Koolpin Formation

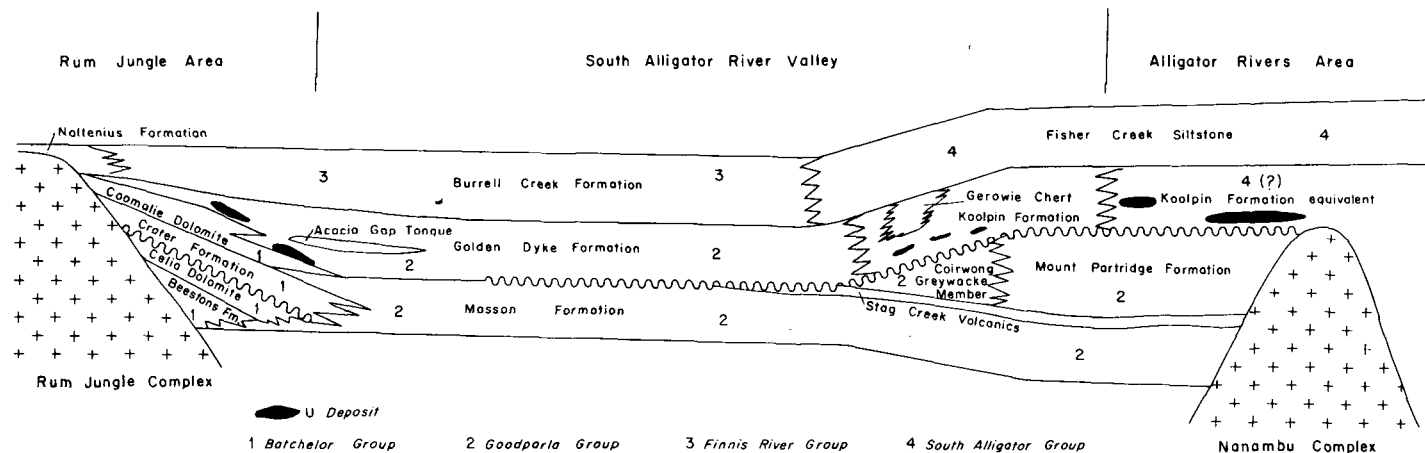


FIG. 2. Relationship of the Lower Proterozoic rock units, Rum Jungle-Aligator Rivers uranium province. The distribution of groups shown here was proposed by Walpole and co-workers in 1968 [6], and is subject to amendment pending completion of field mapping now in progress. The formation correlations shown are based on the recent mapping.

and its facies variant, the Gerowie Chert, and the overlying Fisher Creek Siltstone.

Allowing for lateral facies changes, the Lower Proterozoic successions at Rum Jungle and the South Alligator River valley are similar. K. Johnson (pers.comm., 1974) believes that sediments of the Batchelor Group lens out within a short distance of the Rum Jungle Complex, and are interbedded with sediments of the Masson Formation and Golden Dyke Formation, as shown in Figure 2. In the vicinity of Mundogie Hill north of the South Alligator valley, the Masson Formation is overlain by the Stag Creek Volcanics and The Mount Partridge Formation, which is overlain by the Koolpin Formation, a unit similar lithologically to the Golden Dyke Formation.

The uranium deposits of the valley consisted of thirteen small but mostly high-grade deposits distributed along a 19km section of a fault zone along the South Alligator River valley. Almost all the uranium ore in the Lower Proterozoic rocks is in steeply dipping Koolpin Formation black carbonaceous shale. Uranium is also contained in volcanics and sandstone of the Carpentarian Edith River Volcanics at Coronation Hill and Saddle Ridge, and in sandstone of the Carpentarian Kombolgie Formation at Palette. Where pitchblende occurs in the sandstone, the host rock is mostly in contact with carbonaceous shale of the Koolpin Formation. The lodes are in the form of veins, stringers, or pods located in shears and cross-fractures along the main fault zone, which strikes north-northwest.

Alligator Rivers area

The geology of the Alligator Rivers area is dominated by two large complexes - the Nanambu and Nimbuwah Complexes - surrounded by Lower Proterozoic metamorphic rocks which grade into unmetamorphosed sedimentary units of the Goodparla and South Alligator Groups. Rb-Sr geochronological studies by BMR have demonstrated that the geological histories of the two complexes are different. The Nanambu Complex (Fig. 3) extends over about 3500 sq km in the centre of the area and consists of a core of granitoid rocks, leucogneiss, and migmatite, mantled by Lower Proterozoic sediments. It is surrounded by metamorphosed Lower Proterozoic sediments. Metamorphic grade decreases away from the complex, and arkose, sandstone, and siltstone are exposed southwest of Jim Jim Creek. Isotopic dating has revealed that the granitoid core of the complex is Archaean, suggesting that the Lower Proterozoic rocks that now form the outer mantle of the complex were draped around a basement high. The antiquity of part of the granitoid core of the Nanambu Complex has been established by Rb-Sr total-rock isochrons, the oldest of which is 2520 ± 30 m.y. (initial Sr 87/Sr 86 = 0.704 ± 0.001). Other parts of the complex yield isochron ages of around 1800 and 2000 m.y., but with rather high initial Sr 87/Sr 86 ratios (up to 0.78). The Lower Proterozoic ages represent partial or complete resetting of the

total rocks at the time of the 1800 m.y. metamorphism. Mica ages, obtained by K-Ar and Rb-Sr methods, also reflect the 1800 m.y. event.

The Nimbuwah Complex to the northeast extends over about 10 000 sq km. Its northeastern and southern extents are masked by Carpentarian and younger sediments; its true extent may exceed 20 000 sq km. Walpole et al.⁶ ascribed an Archaean age to schist and quartzite (Myra Falls Metamorphics)¹⁴ which crop out mainly east of the East Alligator River. Needham et al.¹⁴, however, have shown these rocks to be metamorphosed and mylonitized equivalents of the Lower Proterozoic South Alligator Group, and that in migmatized form they constitute the outer zones of the Nimbuwah Complex. The complex has been divided into zones which represent increasing degrees of migmatization and/or mobility towards the centre. The zonation represents a classical gradation of migmatite types from incipiently migmatized schists to completely homogenized and mobilized granitoid anateixites in the centre. All of the migmatite types described by Mehnert¹⁵ have been recognized. South Alligator Group sediments have been fully incorporated into the outer zones of the Nimbuwah Complex, and in the Myra Falls Inlier cross-bedded quartzite, carbonaceous schist, dolomitic marble, and amphibolite within banded and lit-par-lit gneiss masses are considered to be metamorphic equivalents of the Koolpin Formation. The inner zones of the complex may also have been formed by migmatization of Lower Proterozoic units which have been highly migmatized. Field evidence is not conclusive, however; the Nimbuwah Complex could have an Archaean core like the Nanambu Complex. An 1840 m.y. Rb-Sr total-rock isochron age obtained for the Nimbuwah Complex represents the time at which Rb and Sr became fixed in the rocks shortly after the peak of the migmatization and metamorphism.

Altered pink biotite granites, all anomalously radioactive, are thought to be anatectic and produced by mobilization of migma developed in the centre of the Nimbuwah Complex during migmatization. They are probably comagmatic with the Edith River Volcanics, a series of acid volcanics best exposed in the South Alligator valley where they unconformably overlie folded South Alligator Group sediments. The acid igneous rocks mark the last Lower Proterozoic event.

Lower Proterozoic sediments of the Alligator Rivers area comprise the Masson and Mount Partridge Formations of the Goodparla Group and the Koolpin Formation equivalent and Fisher Creek Siltstone of the South Alligator Group (Fig. 2).

Masson Formation rocks are the oldest sediments in the Pine Creek Geosyncline, and crop out between the South Alligator River and McKinlay River and Mount Bundey. The formation is predominantly quartz greywacke, carbonaceous siltstone, calcareous siltstone, and conglomerate about 3000 m thick.

Arkosic sandstone, siltstone, and conglomerate of the Mount Partridge Formation conformably overlie the Masson Formation. The Mount Partridge Formation appears to be wedge-shaped, and has a maximum thickness of about 3000 m; deposition was probably confined to the west and southwest flanks of the Archaean core of the Nanambu Complex. The formation thins out westwards, and west of the South Alligator River valley is continuous with the Coirwong Greywacke.

The South Alligator Group unconformably overlies the Goodparla Group and appears to onlap the Archaean core, although this relation is not clearly observable in the field. The Koolpin Formation metamorphic equivalent of the Alligator Rivers area also differs lithologically from the Koolpin Formation type section of the South Alligator Valley; it is composed of chlorite-muscovite schist, carbonaceous schist, amphibolite, quartzite and gneiss with lenses of massive carbonate rock near the base of the sequence.

The Fisher Creek Siltstone gradationally overlies Koolpin Formation and its equivalent. It is a homogeneous sequence of siltstone and arenaceous siltstone, metamorphosed to phyllite and schist north of Jim Jim Creek. The Fisher Creek Siltstone is the youngest Lower Proterozoic unit to be deposited in the Alligator Rivers and South Alligator River valley areas, and is believed to be the lateral equivalent of the Burrell Creek Siltstone and Noltenius Formation farther west.

Two series of basic igneous rocks intrude Lower Proterozoic rocks: the Zamu Complex diorite, dolerite, and differentiates which were emplaced as numerous sills prior to migmatization, and subsequently altered in places to amphibolite, and the Oenpelli Dolerite¹, emplaced as a large undulating flat-lying discordant sheet soon after metamorphism and migmatization. The absence of hornfelsing adjacent to the dolerite where it intrudes the inner zones of the Nimbuwah Complex suggests that the Oenpelli Dolerite was emplaced before the migmatite complex had cooled.

Phonolitic and sodic trachyte dyke swarms intrude one small area, near Mudginberri homestead in the Nanambu Complex (Mudginberri Phonolite¹).

The Carpentarian Kombolgie Formation sediments unconformably overlie Lower Proterozoic rocks, and form the most prominent feature in the region, the Arnhem Land Plateau. The Kombolgie Formation consists of lower (about 300 m) and upper (about 150 m) medium to coarse sandstone units separated by the basic Nungbalgarri Volcanic Member which consists of one or more flows with minor intercalated sediments. The volcanic member ranges from 0-70 m in thickness. The upper sandstone unit includes a thin (up to 3 m) volcanic layer comprising

¹ Informal name.

tuff, tuffaceous siltstone, and basalt known as the Gilruth Volcanic Member¹. The Carpentarian plateau sandstone covers most of the north-east, east, and southeast of the region mapped.

Post-Carpentarian rocks in the region cover extensive areas. They include terrestrial Mesozoic sediments which form low plateau in the northern part and underlie Cainozoic sand plains in the centre. A recent coastal submergence has resulted in extensive alluvial accumulation along major rivers; the flood plains are seasonally inundated by brackish water up to 100 km inland during the wet season.

During parts of 1971 and 1972, BMR made an airborne magnetic and gamma-ray spectrometric survey of the Alligator Rivers area¹⁵. The airborne geophysics was designed to assist the semidetalled geological mapping and the uranium search in the area particularly where the surface geology is covered by superficial deposits (see Figs 1, 3). It was hoped that the radiometric and magnetic characteristics of individual rock units would prove sufficiently distinctive to allow recognition of hidden rock units. The survey was of a regional nature; east-west lines were flown 150 metres above the ground with a spacing of 1.5 km.

Many of the magnetic anomalies are of shallow or surface origin, and their correlation with geological units has been helpful in tracing these units beneath the extensive overburden which covers much of the area to the west and north of the Arnhem Land Plateau escarpment. The more magnetic of the geological units appear to be the Stag Creek Volcanics, Koolpin Formation, Koolpin Formation equivalent, Zamu Complex dolerite, and Oenpelli Dolerite.

The magnetic data show that the Nanambu Complex is only weakly magnetic (anomalies generally less than 30 gammas). This complex is surrounded by rocks of Koolpin Formation equivalent, and locally by Oenpelli Dolerite. Both of these exhibit stronger magnetic expression (anomalies up to 300 gammas). Mapping these magnetic features permits indirect interpretation of parts of the margin of the complex. Magnetic interpretation has also indicated the likelihood of two further areas of Nanambu Complex to the north of the main mass, and this has been confirmed by shallow drilling. The Nimbuwah Complex, however, has a very variable and complex magnetic expression, and its extent seems impossible to determine from the magnetic and radiometric data.

The Koolpin Formation equivalent exhibits very variable magnetic expression, with anomaly amplitudes ranging from less than 10 gammas (in the Myra Falls Inlier) to possibly as high as 300 gammas (to the west of Koongarra.) This makes it difficult to trace its full extent, and also to see whether it is continuous with the Koolpin Formation.

Dolerites appear to be much more widespread than originally mapped. Magnetic anomalies are associated with both the Zamu Complex dolerite and the Oenpelli Dolerite. Interpretation of the magnetic data indicates that many of the surface exposures are parts of larger continuous dolerite bodies in the subsurface.

The airborne radiometric results have identified areas of higher than average radioactivity, and provided an indication of the predominant sources of the radioactivity - i.e., whether due to uranium, thorium, or potassium.

The radiometric anomalies of highest amplitude were recorded over three of the major uranium deposits (Ranger 1, Nabarlek, and Koongarra), various uranium prospects, granite masses, and a large hill of Mount Partridge Formation (Mount Basedow). The BMR survey did not fly directly over the Jabiluka uranium deposit, which appears to have been too far from the nearest lines to be detectable.

Forty anomalies were classified as 'uranium anomalies'. For this purpose a uranium anomaly was defined as one where potassium was not the major source and the uranium-to-thorium ratio was roughly two or greater (assuming equilibrium to be achieved in both the uranium and thorium decay series). The host rocks for these 'uranium anomalies' are Nanambu Complex, Nimbuwah Complex, Koolpin Formation equivalent, Mount Partridge Formation, and laterites associated with the volcanic members of the Kombolgie Formation.

All the granite masses are anomalously radioactive, potassium and thorium being the major sources. Similarly, the anomalous radioactivity of the large hill of Mount Partridge Formation, referred to earlier, is due to potassium and thorium.

The sandstone of the Kombolgie Formation is very low in radioactivity. However, certain laterites that developed down-slope from the Nungbalgarri Volcanics and the Gilruth Volcanic Member are somewhat radioactive, with moderately high uranium-to-thorium ratios. It is considered that these are only surface features, and that the laterite is a concentrating agent for the uranium.

The Alligator Rivers uranium deposits were briefly described by Dodson¹ in 1971. Since then exploration has proved extensions of known lodes, and much has been learnt about the geology of the deposits through drilling and trenching. From north to south the deposits are: Nabarlek (Queensland Mines Ltd), Jabiluka (Pancontinental Mining Ltd), Ranger 1 (Peko Wallsend - E.Z. Industries Ltd), and Koongarra (Noranda Ltd).

Nabarlek^{16,17} consists of two high-grade lensoid lodes composed of ore richer than 10 percent U_3O_8 , surrounded by a zone of lower-grade

ore 230 m long and up to 20 m wide. Massive pitchblende coated with secondary minerals was intersected at 1.5 m below the surface, and the ore extends to a depth of about 70 m, lensing out above a thick flat-lying dyke of Oenpelli Dolerite. Disseminated uranium minerals occur along strike for a total of about 270 m. The lode strikes north-northwest, parallel to the schistosity of the host rock (quartz-chlorite-muscovite schist of the Koolpin Formation equivalent), and dips to the east at 30-45°.

In two deep drill-holes at Nabarlek, granite was intersected about 500 m below the surface.

Nabarlek has estimated reserves of 9540 tonnes U_3O_8 (402 000 tonnes of ore of an average grade of 2.37 percent U_3O_8).

Jabiluka¹⁷ is situated about 50 km southwest of Nabarlek, close to the Arnhem Land Plateau. Pancontinental Mining Ltd announced the discovery of Jabiluka 1 in January 1973. The lode trends west-southwest away from the Arnhem Land Plateau and dips south at about 45°. The ore zone is up to 30 m thick and about 150 m long, and extends to a depth of about 105 m. Primary ore is pitchblende in quartz-chlorite carbonaceous schist of the Koolpin Formation equivalent. Pyrite and chalcopyrite are minor constituents in the lode, and gold is locally present. Secondary uranium ore is disseminated through a narrow zone in the Kombolgie Formation sediments, possibly deposited by hypogene enrichment.

In September 1973 Pancontinental Mining Ltd announced the discovery of Jabiluka 2, about 480 m to the east of Jabiluka 1 and beneath the Kombolgie Formation sediments of the Arnhem Land Plateau. Jabiluka 2 is similar in geological setting to Jabiluka 1 but it is much larger: the ore zone is up to 49 m thick, and at depths of between 61 m and 192 m below the surface. The length of Jabiluka 2 has not been fully tested.

Ore reserves announced by Pancontinental Mining Ltd on 20 December 1973 were: Jabiluka 1-3490 tonnes U_3O_8 ; Jabiluka 2-19 580 tonnes U_3O_8 .

An anomalous zone in the same exploration licence area known as Prospect 7J is as yet not fully tested. Secondary uranium minerals are present at the surface and gold values as high as 23 g/tonne were recorded in the ore.

Ranger 1^{18,17} consists of six radiometric anomalies grouped in a roughly north-trending arc-like zone about 6.5 km long and up to 1 km wide, approximately 25 km south of Jabiluka. Of the six anomalies, Nos. 1 and 2 have been fully tested; ore-grade uranium has been intersected at anomalies 2, 4, and 5. The host rocks at Ranger 1 are known to the company geologists as the 'Mine Series' or 'Mine Sequence' - a

sequence readily divisible into upper and lower units. The Mine Series is considered by BMR geologists to be part of the Koolpin Formation equivalent. The Lower Mine Series consists of biotite-feldspar-quartz schist overlain by a discontinuous band of dolomite and biotite-quartz schist. In the mineralized part, the schist is chloritized. Carbonaceous schist is locally present in the sequence. The Mine Series is intruded by pegmatite and dolerite, both of which are heavily altered in the mineralized parts.

The uranium is present mostly as primary pitchblende-rich chloritic veinlets infilling cracks and fissures, mainly in the Lower Mine Series but also in the Upper Mine Series. In the Upper Mine Series, uraniferous veinlets tend to be concentrated around fragments of brecciated chlorite schist. Pitchblende is also present as fine grains disseminated through veins and in mineralized zones in chloritic host rocks. Copper, lead, and gold are erratically distributed through the ore. Ore reserves for anomalies 1 and 3 announced by Peko Wallsend Ltd (1972-73 Annual Report) confirmed an earlier estimated figure (1972) of 100 350 tonnes U_3O_8 . On 29 March 1974 Peko Wallsend Ltd announced an increase in the reserves to 100 350 tonnes U_3O_8 .

The Koongarra^{19,17} deposit is located about 20 km south-south-west of Ranger 1. The deposit lies close to the southern side of the Mount Brockman massif, an outlier of Kombolgie Formation sandstone. The mineralized zones are roughly conformable with the schistosity of the host rock and parallel to a major reverse fault dipping at about 60° to the southeast. The fault plane coincides with the southeastern margin of the Mount Brockman massif, and has brought the Lower Proterozoic host rock into contact with unmineralized Kombolgie Formation sandstone. The faulted contact is intensely brecciated and marks the footwall of the mineralized zone; the hanging wall is a carbonaceous horizon, some 70 m above and nearly parallel to the fault. The orebodies consist of a series of en echelon zones of disseminated uranium minerals. The zones enclose cores of higher-grade ore. Host rock to the ore is Lower Proterozoic quartz-chlorite-muscovite schist of the Koolpin Formation equivalent. Graphite and garnet are accessory minerals. In the primary ore the uranium mineral is pitchblende; minor pyrite, chalcopyrite, galena, and a trace of gold are associated with the ore.

To date no announcement has been made on the ore reserves of Koongarra.

GENESIS OF THE ORE

The current BMR program has shown that metasediments originally considered to be Archaean are the metamorphosed equivalent of Lower Proterozoic sediments (South Alligator Group) exposed in the South Alligator River valley. Field investigations have provided evidence

for the correlation of the Koolpin Formation, host rock to most of the uranium deposits in the South Alligator River valley, with the Koolpin Formation equivalent, which is the host rock to the uranium deposits at Nabarlek, Jabiluka, Ranger, and Koongarra (See Fig. 3.) and also, we believe, with the Golden Dyke Formation, host rock to the uranium deposits at Rum Jungle. The concentration of uranium in the Koolpin Formation and its correlatives suggests a syngenetic enrichment of uranium during sedimentation. The source of uranium is not known, but it is assumed that the provenance was sufficiently enriched in uranium to make uranium available during sedimentation. (Archaean rocks at Rum Jungle, from which some of the sediment was derived, have anomalously high uranium content, ranging from 2.8 to 28 ppm $U_{3.08}^{238}$). The high carbonaceous content of the Koolpin Formation and equivalents (upto 30 percent) would provide a reducing environment, during sedimentation, capable of precipitating uranium.

Assuming syngenetic enrichment of uranium in favourable units in the Lower Proterozoic sequence, there remains an important consideration: the mechanism responsible for the concentration of uranium into ore deposits.

The orebodies occupy faults, shears, and breccias or, as at Rum Jungle Creek South deposit, are contained in a fold. This relation may be due to the squeezing-out of mineralized solutions from a sedimentary pile into centres of low stress during a tectonic event as suggested by Roberts²⁰. However, the proximity of the major deposits to the mantled gneiss domes suggest that mineralization was also related to orogenic activity responsible for the rejuvenation of Archaean igneous masses, and the intrusion of other igneous masses at about 1800 m.y. Extensive zones of alteration, mostly chloritization and sericitization, around the deposits of the Alligator Rivers area in particular indicate a mesothermal mineralization temperature range. Uranium-lead ages and lead isotopic compositions of ore from the Alligator Rivers area point to at least four pitchblende ages: 1880, 1700, 900, and 500 m.y. The ages support the suggestion of syngenetic deposition of uranium in the Lower Proterozoic sediments before 1880 m.y. and uranium concentration at 1700 m.y., perhaps by remobilization of pre-existing uranium accumulations, followed by periods of lead loss at 900 m.y. and 500 m.y. - ages which cannot be related to an igneous or tectonic event. (Hills & Richards, pers. comm., 1974)

The spatial distribution of uranium deposits and prospects around the Nanambu and Rum Jungle Complexes suggests a relation between the mineralization and a major igneous phase (1700-1800 m.y.) responsible for the renewal of activity in the pre-existing Archaean masses and for the emplacement of large granitic masses in the province and elsewhere in northern Australia. The nature of this relation is not known, but judging from the comparatively low grade of hydrothermal alteration in ore zones throughout the province, we

consider that the mineralizing solutions did not originate from the granitic masses. More probably the mineralizing solutions were fluids isolated by lithification of the Lower Proterozoic sediments and mobilized during the igneous and contemporaneous tectonic phases.

The uranium deposits of the South Alligator River valley occur close to, and in some places in, volcanics and sediments of the Edith River Volcanics. The uranium content of these volcanic rocks has been considered as a possible source of the ore in this area. However, the Edith River Volcanics could not have been responsible for the formation of deposits elsewhere in the province. We believe therefore that the part played by the Edith River Volcanics in uranium mineralization is small, if not insignificant.

During the current investigations, attention has been paid to the Kombolgie Formation, a massive Carpentarian sedimentary sequence which might be considered as a source rock²¹ from which uranium was leached and then precipitated in a suitable environment. As previously stated, the Kombolgie Formation consists of lower and upper sandstone units separated by the basic Nungbalgarri Volcanic Member composed of interbedded volcanics and sediments. The upper sandstone unit includes a thin volcanic unit, the Gilruth Volcanic Member. The sandstone components of the Kombolgie Formation are composed of compact quartz sandstone and interbeds of pebble conglomerate, both being characteristically low in radioactivity. The Nungbalgarri Volcanic Member is also of low radioactivity. However, significant radiometric anomalies have been recorded over laterite developed locally down-slope from the volcanic members. Anomalous radioactivity is a feature common to most laterites in the Rum Jungle-South Alligator River valley and the Alligator Rivers area.

Concentration of ore near the present-day land surface at some deposits in the Rum Jungle area and at Saddle Ridge in the South Alligator River valley suggests that supergene enrichment has taken place locally, probably by solution and accretion as the surface has been lowered by erosion. At the other deposits, such as Palette in the South Alligator River valley, uranium in the overlying Kombolgie Formation sediments is believed to be a product of hypogene enrichment.

We concluded that the following sequence of events has been responsible for the formation of the uranium deposits of the Rum Jungle-Alligator Rivers Province:

- (1) Syngenetic enrichment of uranium in carbonaceous sediments during the Lower Proterozoic.
- (2) Concentration of ore-grade deposits of uranium minerals in favourable places from mineralized solutions mobilized during a major igneous/tectonic event.
- (3) Relocation of uranium by circulating solutions through leaching and redeposition not far away.

REFERENCES

- [1] DODSON, R. G., "Some environments of formation of uranium deposits", Uranium Prospecting Handbook (BOWIE, S. H. U., DAVIS, M., OSTLE, D., Eds), (Proc. NATO-sponsored Adv. Study Institute on Methods of Prospecting for Uranium Minerals, London, 1971), Inst. Min. Metall., London (1972) 33-44.
- [2] NEEDHAM, R. S., SMART, P. G., Progress Report, Alligator River Party N.T. 1971, Rec. Bur. Miner. Resour. (1972/1) unpublished.
- [3] NEEDHAM, R. S., WILKES, P. G., SMART, P. G., WATCHMAN, A. L., Alligator Rivers Region Environmental Fact Finding Study, Rec. Bur. Miner. Resour. (1973/208) unpublished.
- [4] SMART, P. G., WILKES, P. G., NEEDHAM, R. S., WATCHMAN, A. L., The Geology and Geophysics of the Alligator Rivers Region (in preparation).
- [5] HORSFALL, K. R., WILKES, P. G., Cobourg Peninsula Alligator River and Mount Evelyn (part) Airborne Magnetic and Radiometric Survey 1971/2, Rec. Bur. Miner. Resour. Aust. (in preparation).
- [6] WALPOLE, B. P., CROHN, P. W., DUNN, P. R., RANDAL, M. A., Geology of the Katherine-Darwin Region, Northern Territory, Bull. Bur. Miner. Resour. Aust. 82 (1968).
- [7] JOHNSON, K., Progress Report: Geological Review and Revision of the Rum Jungle Area, Northern Territory, 1973, Rec. Bur. Miner. Resour. Aust. (in preparation).
- [8] BERKMAN, D. A., "The geology of the Rum Jungle uranium deposits", Proc. Symp. Uranium in Australia, Melbourne, Australasian IMM (1968) 12-31.
- [9] PRICHARD, C. E., "Uranium ore deposits of the South Alligator River", Geology of Australian Ore Deposits, 2nd Edn (McANDREW, J., Ed.), 1, Melbourne Congress and Australasian IMM (1965) 207-9; Publications 8th Commonwealth Min. Metall. Congr. Australia, N.Z. (1965).
- [10] TAYLOR, J., "Origin and controls of uranium mineralization in the South Alligator Valley", Proc. Symp. Uranium in Australia, Melbourne, Australasian IMM (1968) 32-44.
- [11] RHODES, J. M., The Geological Relationships of the Rum Jungle Complex, Northern Territory, Bur. Miner. Resour. Aust. Rep. 89 (1965).
- [12] HEIER, K. S., RHODES, J. M., Thorium, uranium and potassium concentrations in granites and gneisses of the Rum Jungle Complex, N.T., Australia, Econ. Geol. 61 3 (1966) 563-71.
- [13] RICHARDS, J. R., BERRY, H., RHODES, J. M., Isotopic and lead-alpha ages of some Australian zircons, Geol. Soc. Aust. 13 1 (1966) 69-96.
- [14] NEEDHAM, R. S., SMART, P. G., WATCHMAN, A. L., Regional Geology of the Alligator River Uranium Province, Northern Territory, Australia, Rec. Bur. Miner. Resour. 1973/64.
- [15] MEHNERT, K. R., Migmatites and the Origin of Granitic Rocks, Elsevier, Amsterdam (1968).
- [16] ANTHONY, P., Nabarlek. Specialist Group in the Genesis of Ore Deposits, Symp. Geol. Soc. Aust. Sydney (1973) unpublished.
- [17] INGRAM, J. A., Uranium Deposits, Bur. Miner. Resour. Aust. Mineral Resources Rep. 6 (in preparation).
- [18] ELLISTON, J., EUPENE, G. S., Ranger 1. Specialist Group in the Genesis of Ore Deposits, Symp. Geol. Soc. Aust. Sydney (1973) unpublished.
- [19] PEDERSEN, C., Koongarra. Specialist Group in the Genesis of Ore Deposits, Symp. Geol. Soc. Aust. Sydney (1973) unpublished.
- [20] ROBERTS, W. M. B., Dolomitization and the genesis of the Woodcutters lead-zinc prospect, Northern Territory, Australia, Miner. Deposita (1973) 835-58.
- [21] BARNES, F. Q., in Uranium Prospecting Handbook (BOWIE, S. H. U., DAVIS, M., OSTLE, D., Eds), (Proc. NATO-sponsored Adv. Study Institute on Methods of Prospecting for Uranium Minerals, London, 1971), Inst. Min. Metall., London (1972) 45.

DISCUSSION

H. H. ADLER: How do you suppose uranium could have been "squeezed out" or concentrated from sediments with a presumed concentration of 1% U or less to such a pure and highly concentrated pitchblende deposit as that at Narbalek without leaving any dispersion of uranium in the nearby environment?

R. G. DODSON: I believe that Narbalek is a classic example of relocation (and concentration) of uranium within a source rock. Uraniferous solutions deposited pitchblende in a favourable structure, which appear to be a slip

shear, at comparatively low temperature, probably less than 200°C. The high-grade ore is surrounded by zones of lower-grade ore. But, quite obviously, the original relocation which took place some 1700 m.y. ago was followed by a long and intensive process of enrichment.

H.H. ADLER: A comparison of $^{235}\text{U}/^{238}\text{U}$ ratios is interesting in this connection. We find, for example, that the ratios measured in Narbalek samples are quite similar to those measured in our own sandstones, and not at all like the values prevailing in the Congo mineralizations.

M. MOREAU: A strong concentration factor must have been operative in the Lower Proterozoic at Franceville, Gabon, because we know that the Oklo fossil reactor would have required a concentration of at least 20% U to function as it apparently did.

R.H. DE VOTO: Has any attempt been made to sample the uranium content of the unmetamorphosed carbonaceous shales and to trace the changes of uranium content as the areas of metamorphism and the ore deposits are approached?

R.G. DODSON: No, but I agree that a study of that kind would be valuable.

F.J. DAHLKAMP: Going back for a moment to Mr. Adler's comments, I think there is a very significant difference between vein-type deposits such as these, which are more or less monomineralic and contain microcrystalline colloform pitchblende, and the deposits at Shinkolobwe and Great Bear Lake, or in the Erzgebirge of the German Democratic Republic and Czechoslovakia, which contain paragenetic cobalt and nickel as well as some silver and bismuth. Shinkolobwe has yielded macroscopic crystals of U_3O_8 — cubes of up to 2 cm in size — which also contain thorium in their lattice. These facts and some others suggest a classical hydrothermal origin, possibly at a katathermal stage. Another obvious difference is to be found in the vertical extension of the deposits: the known vein-type deposits extend not more than 150–200 m below the surface, whereas the hydrothermal deposits I have mentioned go far deeper.

LES INCLUSIONS FLUIDES DANS LES MINERAIS DES GISEMENTS D'URANIUM INTRAGRANITQUES DU LIMOUSIN ET DU FOREZ (MASSIF CENTRAL, FRANCE)

B. P. POTY*, J. LEROY**, M. CUNÉY*

* Centre de recherches pétrographiques et
géochimiques, Vandœuvre-lès-Nancy

** Ecole nationale supérieure de géologie appliquée
et de prospection minière, Nancy,
France

Abstract-Résumé

FLUID INCLUSIONS IN URANIUM ORES FROM INTRAGRANITIC DEPOSITS IN LIMOUSIN AND FOREZ
(MASSIF CENTRAL, FRANCE).

Fluid inclusion studies have been performed utilizing a variety of techniques: crushing stage, micro-thermometry and gas chromatography on samples from uranium deposits located in granites from Massif Central: Limousin and Forez.

In Limousin uranium is mined from veins and in hydrothermally altered pods of the Saint-Sylvestre two-mica granite. Only the second type of occurrence has been studied. Fluid inclusions show that a clear relation exists between uranium grade and CO₂ concentration in the fluid, that boiling occurred at the time of trapping, and that deposition occurred at a temperature of 340-350°C and a pressure close to 700-800 bars. This strongly suggests transport of uranium as uranyl carbonate complexes, and a deposition due to unmixing of the solution. Reduction of the uranyl ion is not fully understood. A reaction coupled with oxidation of ferrous iron does not seem adequate since hematitic alteration is not ubiquitous.

In Forez (Bois Noirs - Limouzat vein) a detailed paragenesis in six stages has been worked out.

The deposition of quartz-marcasite-pitchblende and pyrite (1st stage), is followed by hematitic quartz (2nd stage). At that time pitchblende was slightly altered into coffinite and epidote + adularia grew in the surrounding rocks. Then banded smoky quartz (3rd stage), fluorite, carbonates, and whewellite (4th stage) were formed. A late generation of quartz + bismuthinite crosses most previous generations (5th stage) and supergene alteration during alpine orogeny and present time ended the evolution of this vein (6th stage).

Characteristic fluids have been isolated for the first five stages. Temperatures and compositions varied quite widely and suggest a complex genesis for this vein-type deposit. Fluids associated with pitchblende deposition as well as those associated with bismuthinite are rich in CO₂ and suggest, as in the case of Limousin, transport of uranium through uranyl carbonate complexes. Reduction of the uranyl ion was probably controlled by a constituent of the solution.

LES INCLUSIONS FLUIDES DANS LES MINERAIS DES GISEMENTS D'URANIUM INTRAGRANITQUES DU
LIMOUSIN ET DU FOREZ (MASSIF CENTRAL, FRANCE).

Les inclusions fluides ont été étudiées au moyen de plusieurs techniques: platine à écrasement, micro-thermométrie et chromatographie en phase gazeuse.

Au Limousin l'uranium est exploité dans des filons et des amas du granite à deux micas de Saint-Sylvestre ayant subi une altération hydrothermale. Seuls les amas ont été étudiés. L'étude des inclusions montre qu'il existe une relation nette entre la teneur en uranium et la concentration en CO₂ du fluide, qu'une ébullition s'est produite au moment du piégeage des solutions et que le dépôt de la pitchblende a eu lieu à une température proche de 340-350°C et à une pression voisine de 700 à 800 bars. Ceci suggère un transport de l'uranium sous forme de complexes d'uranylcarbonates, et un dépôt lié à l'ébullition des solutions. La réduction de l'ion uranyle n'est pas entièrement comprise. Une réaction couplée avec l'oxydation de Fe²⁺ semble peu probable puisque l'altération hématitique n'est pas systématique.

Dans le Forez (filon des Bois Noirs - Limouzat) une succession minéralogique détaillée en six épisodes a pu être établie. Le dépôt de l'association quartz-marcasite-pitchblende-pyrite (premier épisode) est suivi par

celui du quartz hématitique (deuxième épisode). La pechblende est alors légèrement altérée en coffinite et dans les roches encaissantes croissent l'épidote et l'orthose adulaire. La succession se poursuit par la venue de quartz enfumés et rubanés (troisième épisode), de fluorine, de carbonates et de whewellite (quatrième épisode). Une génération tardive de quartz et de bismuthinite recoupe la plupart des générations antérieures (cinquième épisode). Une altération supergène, continue, depuis l'orogénèse alpine jusqu'à nos jours, termine l'évolution de ce filon (sixième épisode).

Des fluides caractéristiques ont pu être associés à chacun des cinq premiers épisodes. Les températures, pressions et compositions chimiques varient très largement et indiquent une genèse très complexe pour ce gisement. Les fluides associés au dépôt de la pechblende sont riches en CO_2 , comme ceux associés à la bismuthinite, et suggèrent comme au Limousin le transport de l'uranium sous forme de complexes d'uranyl-carbonates. La réduction de l'ion uranyle a probablement été contrôlée par une espèce en solution.

Parmi les gisements d'uranium intragranitiques français [1], deux font actuellement l'objet de recherches au moyen des techniques d'étude des inclusions fluides : ceux du Limousin [2] [3] et ceux du Forez [4] [5]. Ces recherches visent essentiellement à définir les caractéristiques physicochimiques des fluides associés au dépôt des différentes minéralisations.

Les techniques utilisées sont au nombre de trois :

- écrasement de grains de minéraux sous le microscope dans la glycérine anhydre [6] [7]. Ce procédé simple est extrêmement efficace pour détecter la présence, dans les inclusions, de gaz sous pression : CO_2 et/ou hydrocarbures légers.

- microthermométrie, ou étude sous le microscope des changements de phases dans les inclusions fluides lorsque la température varie. Dans ce travail le domaine de température est compris entre - 180 et + 400°C. Par cette méthode peuvent être déterminés : l'abaissement du point de fusion de la glace qui donne une valeur de la concentration en sels dissous en se reportant au système $\text{H}_2\text{O}-\text{NaCl}$ [8], la présence de gaz par formation de clathrates, des températures minimales de formation, par homogénéisation des fluides qui étaient miscibles lors de leur capture par le cristal, un ordre de grandeur des pressions par chauffage de l'échantillon jusqu'à décrépitation [9].

- chromatographie en phase gazeuse des gaz extraits des inclusions soit par décrépitation au cours d'un chauffage progressif, soit par écrasement sous vide.

I - Les amas épiisyénitiques minéralisés du Limousin

Les gisements d'uranium du Limousin sont localisés dans le granite à deux micas de Saint-Sylvestre [10] granite à histoire deutérique complexe qui a fait récemment l'objet d'une étude détaillée [11]. Deux grands types de gisement ont été reconnus : des ensembles filoniens, et des amas de granite altéré appelés "épiisyénites". Il existe deux types de ces épiisyénites : l'une essentiellement feldspathique qui n'est jamais minéralisée, l'autre essentiellement micacée qui l'est souvent. Toutes deux apparaissent comme une des manifestations ultimes de l'évolution deutérique du granite à deux micas de Saint-Sylvestre [12] [2] [13]. L'épiisyénite micacée se caractérise par la disparition quasi totale du quartz du granite, la déstabilisation des feldspaths - surtout du feldspath sodique - et l'abondance des micas. C'est une roche très poreuse, parfois pulvérulente [13].

Seuls les gisements en épiisyénites ont été étudiés du point de vue des inclusions fluides. Les filons n'ont fait l'objet de recherches que tout à fait préliminaires [13].

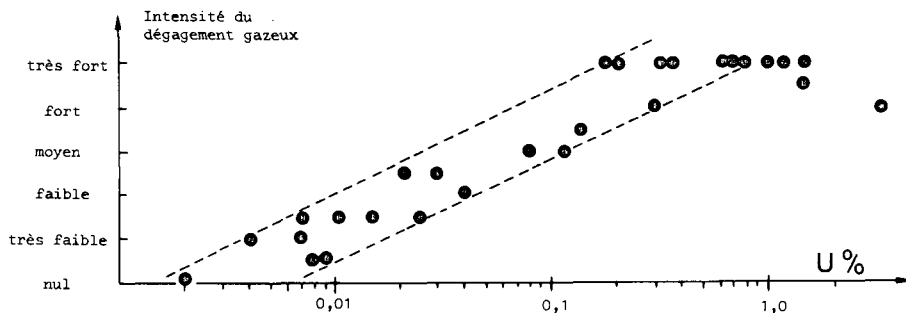


FIG. 1. Ecrasement dans la glycérine anhydre de grains de quartz provenant d'échantillons ayant des teneurs en U variables. Gisement de Margnac, point 132 (Limousin).

A) Les différents fluides observés dans les épi-syénites minéralisées du Limousin

L'étude a été réalisée au point 132 de Margnac qui est un amas épi-syénitique de forme très irrégulière reconnu sur une hauteur de 80 mètres. Sept niveaux ont été échantillonnés sur toute la hauteur de l'amas et les échantillons ont été prélevés dans le granite sain, dans la zone de transition progressive entre granite et épi-syénite dont la puissance oscille entre 10 et 50 cm, et dans l'épi-syénite. Les teneurs en uranium de ces échantillons varient de 20 ppm à 1,2 %.

Les inclusions fluides ont été observées dans les quartz reliques du granite, que l'on retrouve encore dans la zone de passage entre le granite et l'épi-syénite, et également, mais plus rarement, dans l'épi-syénite.

L'écrasement des grains de quartz dans la glycérine anhydre montre un dégagement gazeux (CO_2 et/ou hydrocarbures) proportionnel à la concentration en Uranium (fig. 1). Cela indique un lien entre un fluide riche en CO_2 et le dépôt de l'uranium.

Dans la zone de passage entre granite et épi-syénite, on peut en fait distinguer trois groupes d'inclusions fluides :

- a - des inclusions aqueuses à deux phases fluides dont le point de fusion varie de -7 à -4°C (salinité : 10,5 à 6,5 % d'équivalent poids NaCl) et les températures d'homogénéisation varient de $+140$ à $+200^\circ\text{C}$. Ces inclusions se retrouvent partout dans le granite sain à 2 microns et doivent être les témoins des fluides présents durant la phase deutérique du granite.
- b - des inclusions aqueuses à deux phases fluides dont la concentration en sels dissous est plus forte (9 à 14,5 % eq. NaCl) et croît avec la profondeur dans l'amas. Les températures d'homogénéisation sont plus élevées, comprises entre 270 et 300°C .
- c - des inclusions qui montrent trois phases fluides à la température ordinaire, c'est-à-dire des inclusions riches en CO_2 .

La relation nette entre le dégagement de CO_2 et la teneur en uranium des échantillons indique qu'il faut associer le groupe c au dépôt de l'uranium.

Le groupe b, qui n'est jamais observé dans le granite sain, n'est pas lié à la teneur en uranium, et se retrouve dans les épi-syénites non minéralisées, est purement spécifique de l'épi-syénite. Il doit être associé au processus d'épi-syénitisation.

B) Les fluides contemporains du transport et du dépôt de l'uranium

Les inclusions du groupe c sont observées dans des fractures cicatrisées des cristaux de quartz.

A la réfrigération les inclusions à 3 phases fluides forment un clathrate qui ne se dissocie pas à $10,5^{\circ}\text{C}$, comme le clathrate de CO_2 pur, mais à une température beaucoup plus basse : entre $+4$ et $+6^{\circ}\text{C}$ (fig. 2). Ceci témoigne de la présence dans le fluide d'hydrocarbures autres que le méthane [14].

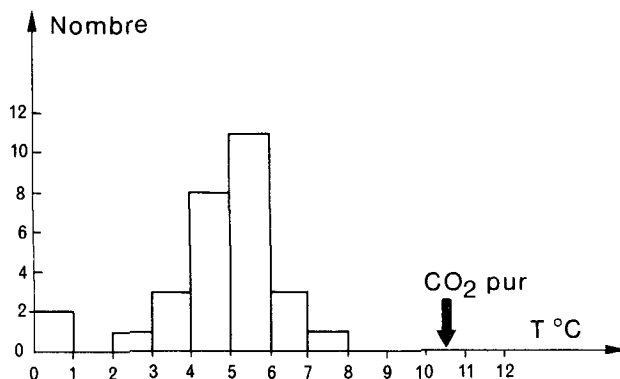


FIG. 2. Température de dissociation du clathrate des inclusions à trois phases fluides des quartz des épi-syénites. Gisement de Margnac, point 132 (Limousin).

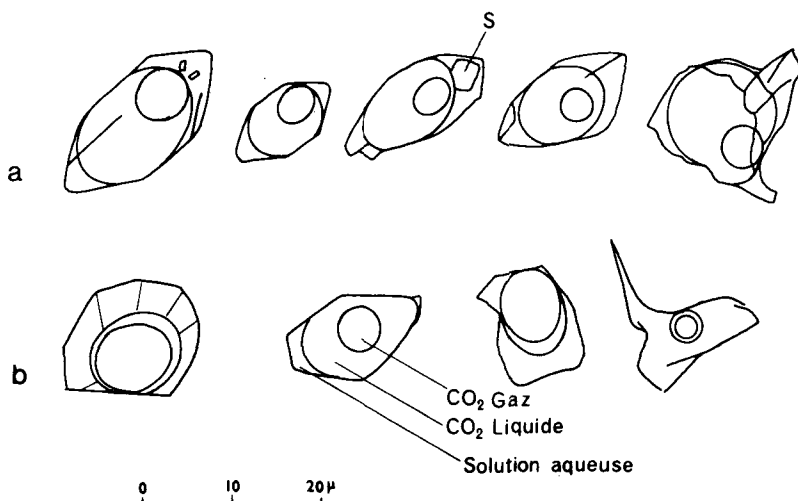


FIG. 3. Inclusions à trois phases fluides. Gisement de Margnac, point 132 (Limousin). a - inclusions identiques appartenant à la même fracture, b - inclusions différentes appartenant à la même fracture.

L'analyse des gaz par chromatographie montre que, outre le CO_2 qui est dominant, on détecte un peu de CH_4 , mais surtout des hydrocarbures éthyléniques C_2H_4 , C_3H_6 et C_4H_8 . Enfin SO_2 a été identifié. Sa libération parallèle à celle du CO_2 témoigne de la présence dans le fluide d'une espèce contenant du soufre.

Suivant que ces inclusions appartenant à une même fracture sont toutes identiques (fig. 3 a) ou différentes (fig. 3 b), on peut en déduire que le fluide était, au moment de sa capture, un fluide unique, homogène, ou bien un mélange de deux fluides non miscibles. Les observations montrent que ces fluides riches en CO_2 étaient, selon la position dans l'amas épisyénitique et selon le moment de leur capture par les cristaux, soit homogènes, soit hétérogènes. Autrement dit le fluide était soumis à une ébullition.

L'homogénéisation de ces inclusions est difficile à réaliser. La plupart d'entre elles explosent avant ou au moment de l'homogénéisation. Toutefois les mesures indiquent une température comprise entre 340 et 350°C qui semble être restée stable durant tout le processus. Compte tenu du fait que la décrépitation se produit aux environs de cette température, on peut considérer [9] que la pression était de l'ordre de 700 à 800 bars.

II - Le gisement d'uranium des Bois Noirs - Limouzat

Le gisement d'uranium des Bois Noirs - Limouzat est formé d'un groupe de filons localisés dans des zones fracturées et broyées de direction E-W et N 135°E du granite des Bois Noirs [10] et [15]. Son extension longitudinale est d'environ 1500 mètres et sa profondeur reconnue d'environ 500 mètres.

A) Succession minéralogique

L'apparition des minéraux dans le filon a été subdivisée en six épisodes [4] [5] (fig. 4) :

- Episode I : quartz - sulfures - pechblende.

Sur les épontes broyées du granite, on observe parfois un quartz en peigne, microcristallin et hématitique à la base, puis de mieux en mieux cristallisé. Rarement la löllingite apparaît dans ces quartz. Au sommet sur les zones de croissance on observe des dépôts de pechblende et de pyrite.

Ce dépôt de quartz peut se reproduire plusieurs fois, mais généralement l'association sulfures-pechblende est déposée directement sur le granite, avec la succession suivante : marcasite en peigne, pechblende, pyrite enfin. Parfois la pyrite renferme des demi-sphérules de pechblende sur ses zones de croissance. Cette trilogie marcasite-pechblende-pyrite peut se répéter 2 à 3 fois [16].

- Episode II : les silices rouges.

Le dépôt des silices rouges s'accompagne de transformations très importantes de la minéralisation uranifère (épisode I).

La marcasite est très corrodée et remplacée par la silice. Suivant le mode de remplacement le faciès de la silice varie. Parfois la pseudomorphose est réalisée avec conservation du faciès de la marcasite, parfois le quartz présente son faciès habituel. Dans ce cas, il est difficile à distinguer du quartz de l'épisode I [16]. D'une façon générale la silice est calcédonieuse en début de croissance, et s'organise progressivement pour former des cristaux automorphes de quartz parsemés de paillettes d'hématite en fin de croissance.

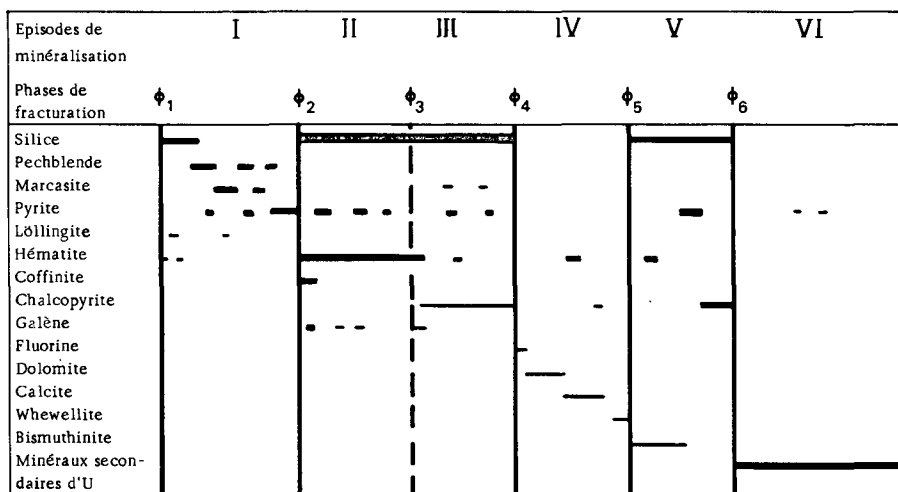


FIG.4. Succession minéralogique. Gisement des Bois Noirs-Limouzat (Forez).

Les reliques de marcasite, quand elles existent, sont presque toujours transformées en pyrite. On retrouve alors les anciennes macles de la marcasite. La pyrite est attaquée le long de ses zones de croissance, particulièrement lorsqu'elles contiennent des demi-sphérules de pechblende. La pechblende est alors emballée dans la silice rouge, et on constate qu'elle est peu ou pas corrodée.

Les bisulfures de fer semblent être à l'origine de l'hématite qui pigmente en rouge la silice. Néanmoins la pyrite peut cristalliser sporadiquement durant cet épisode II.

- Episode III : les quartz rubanés et enfumés.

Les quartz rubanés et enfumés succèdent à l'épisode II soit en continuité, soit après une bréchification. Ils contiennent de la chalcopyrite.

- Episode IV :

Les géodes restantes sont comblées par des carbonates : dolomite et calcite, parfois par de la fluorine, exceptionnellement par de la whewellite.

- Episode V :

Une génération de quartz à bismuth, bismuthinite, pyrite, chalcopyrite, recoupe les épisodes I et II. Elle est vraisemblablement postérieure à l'épisode III mais sa position par rapport à l'épisode IV n'a pas encore pu être déterminée. Fait remarquable, la pechblende est légèrement remobilisée durant cet épisode.

- Episode VI :

Enfin une phase de remaniement supergène, commençant vraisemblablement au moment de la tectonique alpine tertiaire, a transformé une partie des minéralisations précédentes, donnant surtout des produits secondaires d'uranium, noirs (UO_2 néoformé) et colorés (chalcolite essentiellement).

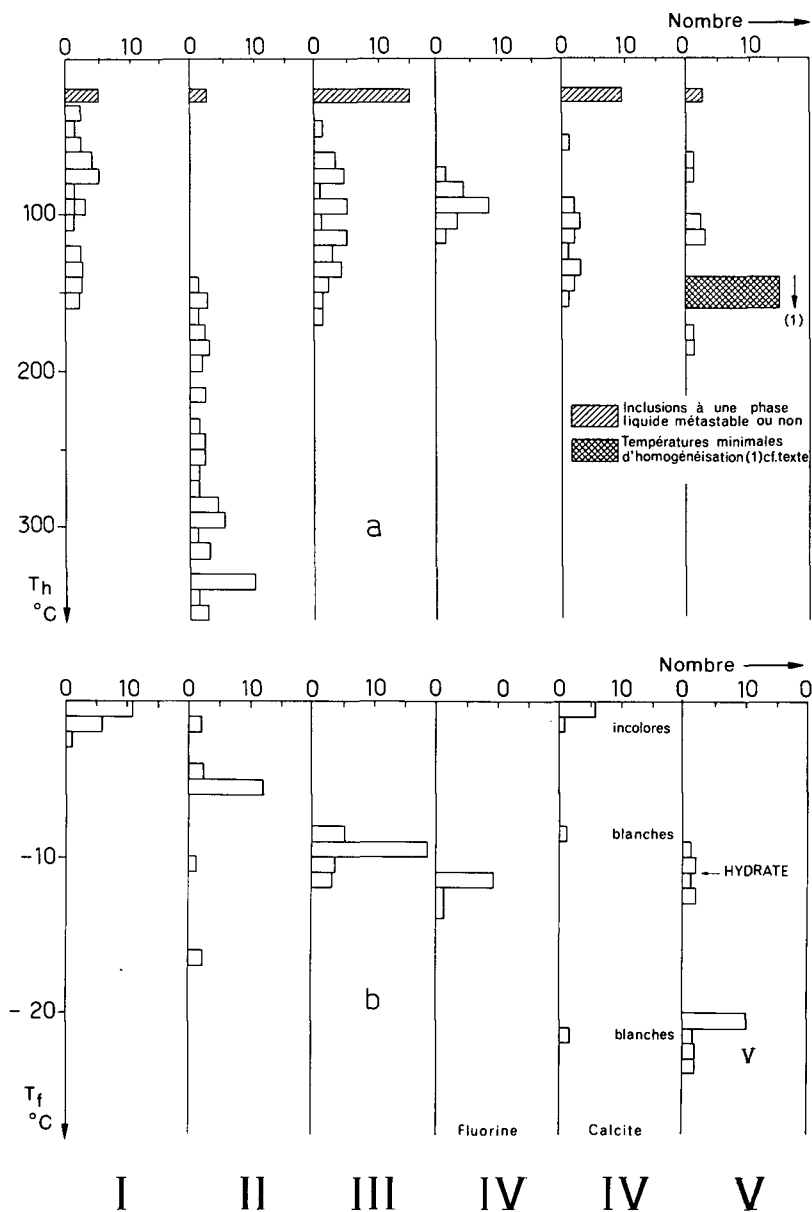


FIG. 5. Résultats de l'étude microthermométrique. Gisement des Bois Noirs-Limouzat (Forez). a - températures d'homogénéisation, b - températures de fusion.

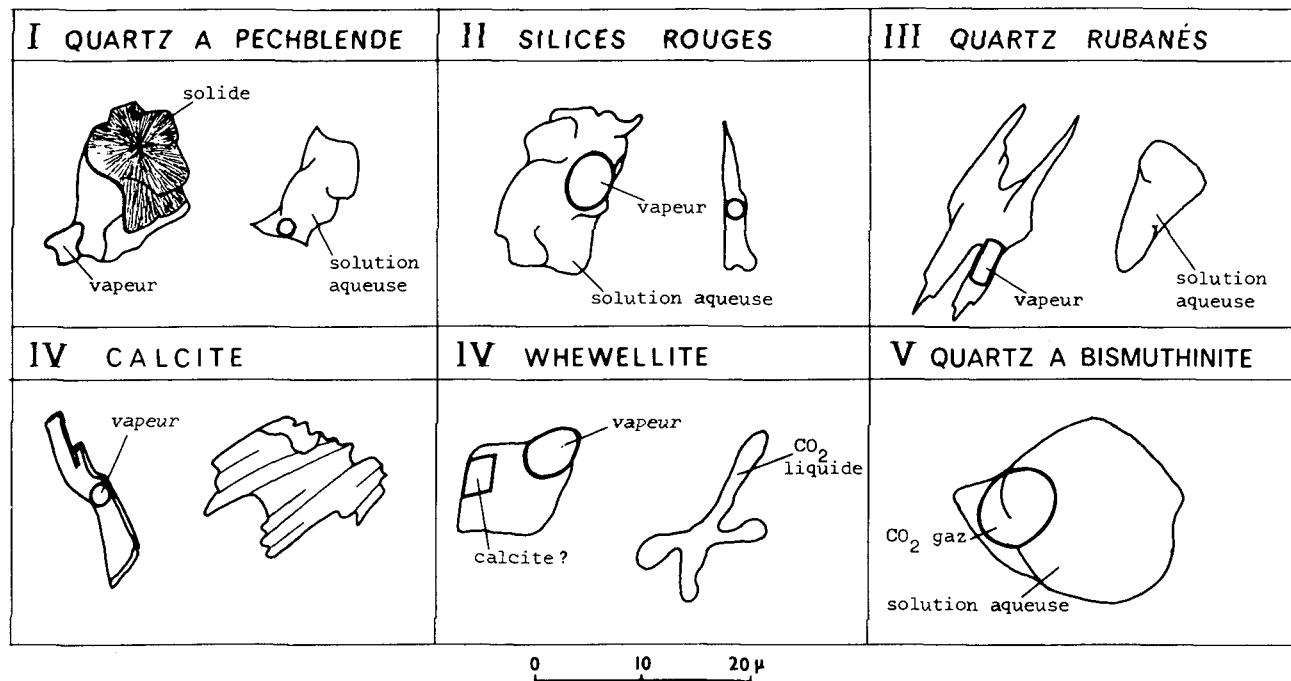


FIG. 6. Inclusions typiques des différents épisodes minéralisateurs dans le filon des Bois Noirs-Limouzat (Forez).

Les épontes ont subi des transformations minéralogiques importantes qu'il n'est pas toujours possible de relier aux différents épisodes de minéralisation. Toutefois à l'épisode II on peut associer une paragenèse à quartz, orthose adulaire, hématite, calcite et une autre à quartz, zoïsite, pistachite, hématite. Des paragenèses à quartz, kaolinite, séricite, montmorillonite ont été identifiées de la surface au niveau - 400. Dans certains cas, elles paraissent nettement contemporaines du remaniement supergène (épisode VI), mais le plus souvent il n'est pas possible de les relier à un épisode déterminé.

B) Analyse des phases fluides associées

Il est remarquable qu'à chacun des épisodes I à V corresponde un fluide spécifique (fig. 5 et 6).

- Episode I : quartz - sulfures - pechblende.

A la platine à écrasement ces quartz montrent un dégagement de CO_2 net, mais d'importance variable selon les zones de croissance. Les inclusions primaires ont des températures d'homogénéisation comprises entre 50 et 150°C, avec un pic entre 60 et 100°. L'abaissement du point de fusion de la glace est de 0,9° en moyenne (1,7 % eq. NaCl). Mais les inclusions renferment fréquemment de volumineux solides biréfringents, qui pourraient être de l'Alumohydrocalcite $\text{Ca Al}_2 (\text{CO}_3)_2 (\text{OH})_4 \cdot 2\text{H}_2\text{O}$.

- Episode II : les silices rouges.

Les fluides des silices rouges n'ont pu être étudiés que lorsque la silice était suffisamment cristalline et claire pour permettre l'observation des inclusions.

A l'écrasement dans la glycérine anhydre des quantités très faibles de gaz sous pression sont mises en évidence. Les inclusions primaires et secondaires sont pour l'essentiel à deux phases fluides et s'homogénéisent entre 350 et 150°C, avec une baisse progressive de la température au cours de la croissance. Les salinités sont de l'ordre de 9 à 12 % eq. NaCl.

- Episode III : les quartz rubanés et enfumés.

A l'écrasement, on n'observe pas de dégagement de gaz sous pression. Les inclusions primaires sont toutes aqueuses, à deux phases fluides au début de la croissance des cristaux et à une phase fluide en fin de croissance. Les températures d'homogénéisation montrent, comme pour les silices rouges, et en prenant leur relai, une baisse graduelle de la température, de 150 à 50°C. Les salinités sont par contre assez constantes : 13 à 15 % eq. NaCl.

- Episode IV : les carbonates, la whewellite et la fluorine.

Les calcites ne montrent aucun dégagement de gaz sous pression à l'écrasement. Leurs inclusions à deux phases fluides s'homogénéisent aux environs de 100°C. Les salinités sont très élevées pour les générations précoces (jusqu'à 20 % eq. NaCl) et très faibles pour les générations tardives. La whewellite se caractérise par un dégagement exceptionnellement intense de gaz sous pression lors de l'écrasement. Elle renferme deux types d'inclusions :

. des inclusions aqueuses, contenant des solides rhomboédriques biréfringents (calcite ?). L'homogénéisation n'a pu être obtenue avec ce minéral qui se déstabilise dès 170°. Mais la taille variable de la bulle de vapeur est probablement due à la grande fragilité du minéral, c'est-à-dire à des fuites.

. des inclusions sans phase aqueuse contenant un mélange de CO_2 et d'hydrocarbures qui s'homogénéisent en une seule phase fluide entre - 10° et - 25°.

Par chromatographie en phase gazeuse on détermine, outre CO_2 dominant, la présence de CH_4 et C_2H_4 .

La fluorine contient des fluides de caractéristiques proches des fluides des carbonates : absence de gaz sous pression, températures d'homogénéisation proches de 100° et salinité assez constante, aux environs de 16 % eq. NaCl.

- Episode V : les quartz à bismuthinite.

Ces quartz montrent un très fort dégagement de gaz sous pression. Les inclusions à deux phases fluides sont abondantes. Elles n'ont pu être homogénéisées car dès 150° , elles décrépitent. A cette température la pression est de l'ordre de 700 à 800 bars [9]. La température d'homogénéisation probable devrait être comprise entre 160 et 200°C . La salinité est très forte, et l'abaissement du point de fusion, plus grand que celui de l'eutectique du système $\text{NaCl-H}_2\text{O}$, indique la présence d'ions bivalents tels Ca^{++} . Un hydrate se dissocie à -11°C , confirmant la présence de CO_2 et/ou d'hydrocarbures. Mais l'absence de liquide immiscible à température ordinaire indique que les teneurs ne doivent pas dépasser quelques moles pour cent.

III - Discussion

Les résultats de l'étude des inclusions fluides pour ces deux types de gisements [17] [18] laissent apparaître un certain nombre de points communs, mais aussi des différences.

Au Limousin, plusieurs faits sont solidement établis : le minéral est lié à un fluide riche en CO_2 et ce fluide était en ébullition. On peut donc logiquement se référer au modèle de transport de l'uranium sous forme d'uranyle carbonates [19] [20] [21], le dégazage de la solution par ébullition entraînant la déstabilisation de ces carbonates pour libérer l'ion uranyle UO_2^{2+} . Ce processus a été déjà discuté [13] [12]. En suspens, reste le problème de la réduction de l'ion uranyle, c'est-à-dire de la précipitation de la pechblende. D'après les études en cours il ne semble pas que l'on puisse invoquer une réaction couplée avec l'oxydation du Fer, puisque la pyrite paraît stable durant ce processus.

Les températures d'homogénéisation mesurées sur des fractures contenant des inclusions toutes identiques (fluide homogène) ou différentes (fluides immiscibles) permettent de situer le dépôt entre 340 et 350°C , sans modifications notables de la température au cours du temps. Compte tenu de la décrépitation abondante à cette température, la pression devait être de l'ordre de 700 à 800 bars. Pour une densité de roches moyenne (2,65) cela donne une profondeur d'environ 2,6 à 3 km.

Ces températures sont élevées, de beaucoup supérieures à celles mesurées sur les minerais d'uranium de l'Erzgebirge [22]. Toutefois le fluide est ici plus riche en CO_2 (jusqu'à 20 moles %) et ne pourrait pas avoir été véhiculé sous la forme d'un fluide unique aux températures trouvées pour les minerais de l'Erzgebirge.

Aux Bois Noirs, une succession particulièrement nette de paragenèses minéralogiques, associées chacune à des fluides caractéristiques rend l'histoire du gisement beaucoup plus claire. La pechblende se dépose à une température basse, de l'ordre de 100°C , à partir d'un mélange $\text{CO}_2\text{-H}_2\text{O}$ en partie hétérogène. Cette hétérogénéité est probablement à l'origine du dépôt de la pechblende, par déstabilisation des uranyle carbonates. Là également et de façon plus nette encore, la réduction de l'ion uranyle n'est pas couplée à une oxydation de l'ion ferreux puisque les bisulfures de fer sont stables. L'agent réducteur se trouve probablement dans la solution.

La silicification très importante qui fait suite à l'épisode à pechblende s'individualise très nettement par ses caractéristiques physicochimiques : température plus élevée, concentration en sels plus forte, quasi-absence de CO_2 . Durant cette silicification la coffinite se forme en petites quantités. Dans l'ensemble la pechblende est peu mobilisée, ce qui n'est pas surprenant compte tenu du fait que la solubilité de UO_2 est faible dans l'eau pure, et décroît lorsque la température s'élève [21].

La pechblende n'est remise en solution que lors de l'épisode à quartz-bismuthinite. Les fluides associés à cette minéralisation sont d'ailleurs riches en CO_2 . Mais cet épisode est également remarquable en ce sens qu'à une température d'environ 160°C la pression était proche de 700 à 800 bars, ce qui revient à dire que la paragenèse à quartz bismuthinite s'est déposée à une profondeur minimum de 3000 m.

Conclusion

Ces résultats d'études en cours sur les fluides associés au dépôt des minerais d'uranium dans les épihyénites du Limousin et le filon des Bois Noirs mettent en évidence un certain nombre de particularités nettes :

- le dépôt de la pechblende s'est fait à partir d'une solution riche en CO_2 . Dans les deux cas, le moteur du dépôt n'est pas une modification de la température, mais une modification des caractéristiques du solvant. Cela explique la rareté des gangues dans ces gisements : un dépôt de silice nécessite en effet une modification de la température.

Cette modification des caractéristiques du solvant est au moins dans le cas du Limousin, une ébullition. Compte tenu de la structure du diagramme CO_2 - H_2O [23] [13] une baisse de pression paraît être le phénomène le plus apte à obtenir l'immiscibilité du fluide et on retrouve ici l'importance des fractures qui mettent le système en communication intermittente avec la surface. Le rôle de la tectonique dans la mise en place des gisements d'uranium a été maintes fois souligné [12] [10]. Si les conditions de T et P sont trop élevées on ne pourra d'ailleurs pas obtenir de démixtion et cela explique peut-être pourquoi les gîtes filoniens d'uranium ne peuvent pas être directement rattachés à l'activité magmatique.

Un gisement comme celui des Bois Noirs résulte de la succession d'événements qui ne semblent pas liés les uns aux autres. La venue des silices rouges ne nous apparaît pas génétiquement associée au dépôt de la pechblende. De fait, si de nombreux gisements filoniens d'uranium montrent ces faciès hématitiques d'autres comme la colonne Henriette en sont dépourvus [10] [24]. La nature de cette liaison non obligatoire mais fréquente, reste donc à élucider.

Le quartz à bismuthinite semble lui aussi appartenir à un autre cycle d'événements. Aux Bois Noirs il serait donc souhaitable de différencier les âges du dépôt de la pechblende, du dépôt des silices rouges, grâce à la coffinite associée, et du dépôt des quartz à bismuthinite qui remanient la pechblende. Ceci rejoint les conclusions des travaux sur les gisements d'Uranium de l'Erzgebirge [25] [26].

Enfin sur un plan pratique, l'uranium étant transporté par des fluides riches en CO_2 , la détection sur le terrain du CO_2 contenu dans les inclusions fluides à l'aide d'une platine à écrasement pourrait être une méthode supplémentaire, et simple, à ajouter à celles que l'on utilise généralement pour la prospection de l'uranium.

REFERENCES

- [1] GANGLOFF, A., "Notes sommaires sur la géologie des principaux districts uranifères étudiés par le C.E.A.". Uranium exploration Geology. (IAEA, Vienne) (1970) 77.
- [2] LEROY, J., "Épisyénitisation et dépôt de l'uranium dans l'épisyénite du point 132. Mine de Margnac (C.E.A. - Limousin - France)". Réunion annuelle des Sciences de la Terre, Paris (1973) 271.
- [3] LEROY, J., Les épisyénites non minéralisées dans le massif de granite à deux micas de Saint-Sylvestre (Limousin - France). Equilibres entre minéraux et solutions. Thèse Univ. Nancy I (1971).
- [4] CUNEY, M., "La succession paragénétique du gisement uranifère des Bois Noirs - Limouzat (Forez). Introduction à l'analyse des phases fluides associées". Réunion annuelle des Sciences de la Terre. Pont-à-Mousson (1974) 127.
- [5] CUNEY, M., Le gisement uranifère des Bois Noirs - Limouzat (Forez - France). Relations entre minéraux et fluides associés. Thèse. Univ. Nancy I (1974).
- [6] DEICHA, G., Essais par écrasement de fragments de minéraux pour la mise en évidence de gaz sous pression. Bull. Soc. fr. Miner. Cris. 73 (1950) 439.
- [7] ROEDDER, E., Application of an improved crushing microscope stage to studies of the gases in fluid inclusions. Bull. Suisse Miner. Petr. 501 (1970) 41.
- [8] ROEDDER, E., Studies of fluid inclusions I : Low temperature application of a dual purpose freezing and heating stage. Econ. Geol. 57 (1962) 1045.
- [9] TUGARINOV, A.I., NAUMOV, V.B., Relation entre la température de décrépitation, la composition des inclusions gazeuses et liquides et la dureté des minéraux. Dok. Akad. Nauk SSSR. 195 1 (1970) 182.
- [10] ROUBAULT, M., Les minerais uranifères français. Presses Univ. France. (1962).
- [11] RANCHIN, G., La géochimie de l'uranium et la différenciation granitique dans la province uranifère du Nord Limousin. Serv. Cent. Doc. C.E.A. R-4034 (1971).
- [12] MOREAU, M., RANCHIN, G., "Altérations hydrothermales et contrôles tectoniques dans les gîtes d'uranium". Les roches plutoniques dans leurs rapports avec les gîtes minéraux. (Morin, Ph., Ed.) Masson, Paris (1971) 77.
- [13] LEROY, J., POTY, B., Recherches préliminaires sur les fluides associés à la genèse des minéralisations en uranium du Limousin (France). Miner. Dep. (Berlin) 4 (1969) 395.
- [14] DEATON, W.N., FROST, E.M., Gas hydrates and their relation to the operation of natural gas pipe lines. US Bureau of Mines, Monograph 8 (1946).
- [15] FAURE, J., Le gisement uranifère des Bois Noirs (Loire). Le piège structural. Sc. de la Terre, Nancy. 13 (1968) 233.

- [16] ARNOLD, M., CUNEY, M., Une succession anormale de minéraux et ses conséquences sur l'exemple de la minéralisation uranifère des Bois Noirs - Limouzat (Forez - Massif Central français). C.R. Acad. Sc. (1974) sous presse.
- [17] GEFFROY, J. SARCIA, J., La notion de gîte épithermal uranifère. Bull. Soc. Géol. Fr. 8 (1958).
- [18] GEFFROY, J. "Les gîtes uranifères dans le Massif Central". Symposium J. Jung : Géologie, géomorphologie et structure profonde du Massif Central français. (Plein Air Serv. Ed.) Clermont-Ferrand (1971) 541.
- [19] NAUMOV, G.B. Quelques caractéristiques physico-chimiques du transport de l'uranium dans les solutions hydrothermales. Geokhimiya. 2 (1961) 115.
- [20] NAUMOV, G.B., MIRONOVA, O.F. "Sur la migration de l'uranium dans les solutions hydrothermales carbonatées (d'après les données physico-chimiques)". Problèmes de géochimie. Ed. Nauka. Moscou. (1965) 158.
- [21] LEMOINE, A., "La solubilité de UO_2 en milieu aqueux à haute température et haute pression". Réunion Annuelle des Sciences de la Terre. Pont-à-Mousson (1974) 255.
- [22] TUGARINOV, A.I., NAUMOV, V.B. Conditions de température et de pression pour la formation des gisements hydrothermaux d'uranium. Geokhimiya. 2 (1969) 131.
- [23] TAKENOUCHI, S., KENNEDY, G.C. The binary system H_2O-CO_2 at high temperatures and pressures. Am. J. Sc. 262 (1964) 1055.
- [24] GEFFROY, J., SARCIA, J. Contribution à l'étude des pechblendes françaises. Sc. de la Terre, 2, 1 et 2 (1954).
- [25] BAUMAN, L., Sur le problème de la minéralisation hercynienne et post-hercynienne dans l'Erzgebirge, Saxe (R.D.A.). Freiburger Forsch. H, C, Dtsch., 209 (1967) 15.
- [26] LEUTWEIN, F., Alter und paragenetische Stellung der Pechblende Erzgebirgischer Lagerstätten. Geologie 6 2 8 (1957) 797.

DISCUSSION

H.D. KNIPPING: Why does the episyenite at Margnac and Farrray in the Crouzille district of France not extend much below the ore - below a few hundred metres from the granite surface?

B.P. POTY: Most episyenite pods have been discovered from outcrops on the surface, where observations are easier than at depth in the mines. But I am not so sure that what you say is an established fact.

M. MOREAU: I think possibly Mr. Poty did not lay enough stress on the fact that CO_2 and hydrocarbons co-existed in the fluids which accompanied pitchblende deposition. In fact, I believe there must be equilibrium between U^{IV} and U^{VI} for pitchblende deposition to occur. If the CO_2 fluid is too highly oxidized, there will be a deposition of hematite and destruction of pitchblende. If the equilibrium is displaced towards reducing Eh values, on the other hand, there will be no remobilization.

B.P. POTY: I agree with Mr. Moreau. Fluids were always close to the pyrite-hematite boundary, on the pyrite side during deposition and on the hematite side after deposition. This has been observed very clearly by Mr. Cuney at Bois Noirs: in the first case we find a mass of pyrite and occasionally a few flakes of hematite, and in the second case a mass of hematite and only occasional crystals of pyrite.

S.S. ADAMS: If I understood you correctly, you find pyrite commonly co-existing with pitchblende. Now the literature is full of references to a supposed association between uranium and hematite. Have you ever found such an association?

B.P. POTY: No.

S.S. ADAMS: Presumably, then, where they are seen as members of a paragenetic sequence, they are of different age.

B.P. POTY: Yes; there is no relationship.

USE OF FLUID INCLUSIONS IN THE GENETIC STUDY OF VEIN DEPOSITS

J. BOSSI

Facultad de Química,
Montevideo, Uruguay

Abstract

USE OF FLUID INCLUSIONS IN THE GENETIC STUDY OF VEIN DEPOSITS.

The formation process of the "properly uraniferous" type of uranium vein deposits (according to Geffroy and Sarcia) is still under discussion.

In this paper the systematic application of the study of fluid inclusions is proposed in order to contribute to the interpretation of the genetic process.

The behaviour of fluid inclusions of a vein deposit of lead-zinc in the south of the French Central Massif, which, in the author's opinion, is believed to be *per descensum* (deposited by solutions moving downwards) is taken as a model and it is proposed that such a criterion be applied to uraniferous deposits.

The aim of the paper is to interpret the genesis of these uranium vein deposits, in the belief that this will be of great importance in assessing guides for provisional prospecting, once the theoretical conditions that control the supergenic process are known.

1. INTRODUCTION

Two main types of vein uranium deposits are known and were already defined by Geffroy and Sarcia [1]: a polymetallic type containing normally Ag-U-Bi-Ni-Co (example: the Erzgebirge ore bodies) and a "properly uraniferous type" with a very simple paragenesis. To this type belong the main French deposits.

This polymetallic type seems undoubtedly to be of endogenous origin, closely related to granitic plutons, with zoned distribution and with mesothermal deposit conditions. This type has been described by several authors, principally Schneiderhoehn [2].

The properly uraniferous type, on the other hand, seems to have more than one possible origin, or more accurately, its genetic process is under discussion since Moreau and co-workers [3] suggested an origin by descending infiltration for the French deposits in Hercynian granites.

This supergenic process is accepted by Matos Dias and Soares de Andrade [4] for the discordant uranium deposits in Portugal. Fernandez Polo [5] arrives at the same conclusion for the vein deposits in Salamanca (Spain).

However, later works of Leroy and Poty [6] on some French deposits seem to point to an endogenous process of pitchblende accumulation as most probable. This process, according to Gangloff [7], would be one of selective leaching by means of the action of re-heated waters in a late orogenic phase, a model already proposed by Geffroy and Sarcia [1].

The possibility of metallic concentrations (especially lead and zinc) by descending infiltration of meteoric waters has already been demonstrated by direct observations as well as by physicochemical analysis.

Theoretical conditions of the process were pointed out by Garrels [8] and successively improved by Garrels and Christ [9], Michard [10] and Michard and Allegre [11].

From the geological point of view, these deposits are related to paleokarsts or to strongly fractured regions in horst-graben style.

The intrakarstic metallogenic model proposed by Callahan [12] was explained in its physicochemical mechanism by Bernard [13].

The concentration of lead and barium in areas submitted to block tectonics, as was pointed out by Roger [14], has been analysed by Bossi [15] who proposed a model explaining all direct observations by descending infiltration. In the case of uranium, Fuchs [16] and Barbier [17] established the conditions in which its concentration would be possible by means of infiltration of meteoric waters.

From the point of view of provisional prospecting in metamorphic and granitic areas, knowing the origin of these vein deposits is obviously of great importance.

Very few techniques seem capable of interpreting the genetic process and in every case several techniques must be applied simultaneously. Among them, the study of fluid inclusions should be applied more frequently because of its simplicity and low cost.

This method seems potentially very useful, especially after the recent progress reached in its quantitative interpretation by means of the physicochemical studies of Roedder [18-20], Poty [21], Yajima and Touray [22], Smith [23], Ovchinnikov and Chelishchev [24].

The detailed study of a lead-zinc deposit in Lot (France) allowed the establishing of an apparently sound criterion to define a mineralization by descending infiltration.

The study of fluid inclusions is not taken into account as frequently as expected in the discussions on genesis in the literature and therefore it seemed useful to present this criterion to help differentiate endogenous from exogenous vein deposits, provided the samples are adequately selected and offer good observation conditions.

2. PROPERLY URANIFEROUS VEIN DEPOSITS

This type of deposit, described by Geffroy and Sarcia [1] for some vein deposits in France and Portugal, can at present be extended to other French deposits, to some Canadian deposits in the area of Beaverlodge according to descriptions of Bowie [25] and Ruzicka [26] and to the Spanish deposits in the province of Salamanca recently described by Fernandez Polo [5].

Essentially, these deposits can be described by the following types, taking into consideration the descriptive parameters proposed by Routhier [27] and modified by Bernard [28]. They have a very simple paragenesis, based on pitchblende, pyrite, marcasite and quartz (especially jasper and chalcedony). The weathering processes have transformed pitchblende into gummities, down to a considerable depth. The uranium content is high, averaging 0.2% in U_3O_8 . The tonnage can be estimated to be between 5000 - 10 000 t for separate deposits. They are located in fractures of strongly tectonized areas which are generally of a horst-graben type, and have a variable lithology but always with high uranium content (more than 15 ppm).

These mineralized ore bodies are veins, normally with banded structure and wall rock strongly hematitized. The veins are connected with the surface (or with a paleo-surface) and disappear with depth, having a vertical development no deeper than 400 m. The age of mineralization is younger than that of the country rock and coincides sometimes with a period of peneplanation.

French deposits of this type are represented by the areas of Vendée, Forez and Limousin. From the genetic point of view two different hypotheses can account for the metallic concentration, recently described by Gangloff [7]: (a) selective endogenous leaching in the fractured zones, by the action of re-heated waters during a late orogenic phase (this theory was proposed by Geoffroy and Sarcia [1]) and (b) descending infiltration of uranium-laden meteoric waters. This genetic model was presented by Moreau and co-workers [3].

More recently, Barbier [17] discovered a striking parallelism in the observable characteristics of certain French deposits and the sedimentary deposits of the Wyoming type (roll-type) – fundamentally the sequence of minerals in both types of deposits is the same, namely: pitchblende, marcasite, pyrite, hematite, calcite.

Samama [29] developed the following model for the French deposits in the Central Massif: high continental metamorphic areas containing granite with a high uranium content submitted to strong tectonic actions. Pseudo-lateric weathering conditions free the uranium. The freed uranium percolates through the granite by means of a net of fractures and concentrates at depth if there exist such traps as structural or lithological heterogeneities.

For the deposits in the area of Ace-Verna in Beaverlodge, Canada, Robinson [30] recognized six mineralization periods in the sequence: plagioclase, hematite, pyrite, calcite, chlorite, quartz, pitchblende, arsenides, sulphides, selenides.

Tremblay [31] recognizes the following chain of events: (a) uranium-rich sediment deposits; (b) mobilization and concentration of uranium during a granitization; (c) remobilization during processes of mylonitization; (d) new remobilization, later than the fracture stage. According to that author, the economically exploitable uranium has been concentrated in this last stage and he recognizes the presence of lithological and structural control in the most representative deposits of the Beaverlodge area: Fay, Ace-Verna, Belger Hab and Gunner. Ruzicka [26] describes the mineralization as filling up fractures in a Precambrian metamorphic basement with a high average content of uranium, 4.5 ppm.

All the geological characteristics of this area, summarized by Bowie [25], seem to point to a late concentration by means of an exogenous process. However, the conclusions of Robinson [30] would indicate formation temperatures higher than 150°C.

Matos Dias and Soares de Andrade [4] have described the discordant deposits in Portugal and, according to them, the present geological characteristics are compatible with an exogenous origin. The most significant facts are: rapid decrease of mineralization with depth, and ages coinciding with peneplanation periods.

Fernandez Polo [5] also proposes a supergenic origin for the vein deposits in Salamanca, Cáceres and southern Spain.

On the whole, various authors describe sequences of geological phenomena that allow considering descending infiltration as a logical model to explain the uraniferous concentration.

But this "per descensum" model disagrees with the theory of uranium concentration by means of a selective endogenous process.

In every case the mineralization occurs later and is independent of the formation process of the country rock, which acts only to preconcentrate the uranium.

From the point of view of provisional prospecting in new areas, it would be of fundamental importance to be able to demonstrate with certainty that at least one of the deposits of this type has been produced by a super-genic process and it would be of still greater interest to discuss the formation process of each of them.

If the supergenic concentration process is possible, the crystalline areas to be prospected are those which have a high uranium content and which in a certain moment of their geological history have been submitted to horst-graben tectonics in continental conditions of arid climate with short periods of intense rain. If the process can only be endogenous, only those areas presenting orogenic reactivations in the later phases must be prospected.

3. THE LEAD-ZINC MINERALIZATION IN ASPRIERES-BOUILLAC (FRANCE)

This area of the southwest French Central Massif has been recently studied by Bossi [15] from the geological and physicochemical points of view, and from both methods a metallogenic process by means of descending infiltration (per descensum) could be demonstrated.

The mineralization is based on blende and galena with gangue of silicified barytine. Galena is rich in Sb and Ag and very poor in Bi; blende is rich in Cd, Ga and Sb. Mineralization is found in discordant veins in a medium-grade metamorphic complex formed by amphibolites, gneisses, leptynites and micaschists, all of which have high contents of Ba, Pb and Zn.

Veins have been formed by filling up fractures and their thickness decreases with depth, together with a division into several branches. The structure is always banded and normally symmetric. The bands are alternatively formed by silicified intercrossed tabular barytine from the wall-rock side with blende-galena in the axis of the vein and microcrystalline quartz. Sulphides are found only in the bands with silicified barytine. The silicification of barytine increases with depth, together with a decrease in the size of the crystals.

The country rock became a stable basement approximately 350 m.y. ago, when it suffered an injection of diorites. Later this basement was crossed by porphyritic veins, 260 m.y. ago. Mineralization occurred later and therefore independently of all deep magmatic phenomena in the area.

The mineralization was affected later on by the fault of Villefranche and it can be undoubtedly deduced that its formation coincides with the time when the block containing it was the highest of the area. The age of mineralization, between 260 and 200 m.y., coincides with climatic conditions that made possible a removal, by means of leaching, of Pb, Zn and Ba in the rocks exposed to weathering.

The banded structure resulting from differential slips between high and sunken blocks, the mineralization associated with silicified barytine and the total independence of deep magmatic processes as well as the geometry of the vein, permit one to conclude a supergenic origin by descending infiltration from the geological point of view.

The source of the Ba, Pb and Zn is found in metamorphic country rock. The solubility of the metals in the prevailing climatic conditions accounts perfectly well for the accumulated tonnage. Precipitation takes place when the solution reaches zones of impeded circulation and the environment becomes reductive.

The study of fluid inclusions was carried out carefully taking into consideration the sampling sites and the host mineral. The salinity of the solutions as well as the temperature of homogenization were studied.

At the moment of the deposit of the barytine, the solution contained 8% equivalent weight of NaCl. Quartz was deposited from solutions with 13% equivalent weight of NaCl. Blende, on the contrary, was deposited from solutions with concentrations between 3.5 and 4.0 moles of a mixture NaCl-Cl₂Ca. At least in the case of quartz, the solution is extremely rich in SO₄²⁻ with a ratio SO₄²⁻/Cl⁻ greater than 1. For those saline concentrations, and according to the curves of solubility of quartz and barytine of Holland [32] and Uchameshvili and co-workers [33], silicification of barytine is not possible with temperatures higher than 50°C.

The first contributions of the study of fluid inclusions were:

- (a) Detecting the abundance of SO₄²⁻ in the mineralized liquid
- (b) Defining a salinity at which the silicification of barytine cannot be produced above 50°C.

Another important contribution was the distribution of homogenization temperatures with regard to depth of mineralization. Figure 1 shows frequency histograms of homogenization temperatures of fluid inclusions to different depths and for each mineral. It is possible to see that with an increase of depth there is an increase also in the proportion of fluid inclusions with one liquid phase in every mineral; also very high homogenization temperatures (above 150°C) are present only at upper levels.

From the different hypotheses worked out to explain these results, the only plausible explanation to account for all the observed phenomena has been the heterogeneity of the fluid at the moment of its trapping. Liquid with gas bubbles has been adsorbed by the growing crystal in the upper levels and, according to Klia and Laemmlein [34], this leads to abnormally high homogenization temperatures.

This hypothesis is on the other hand the only one which would explain the striking fact of a quasilinear variation with depth of the percentage of inclusions with one or two fluid phases, as shown in Fig.2.

The model is then defined as a liquid which in the upper levels contains air in suspension and as it percolates is dissolved by greater pressure or is eliminated by reaction in a reductive environment.

It must be noted that in this study the inclusions of one liquid phase were expressly taken into consideration, which demanded special care in the handling of samples. These inclusions are often unnoticed because of insufficient contrast, especially regarding host minerals of low refraction index. It is recommended, therefore, that the samples systematically

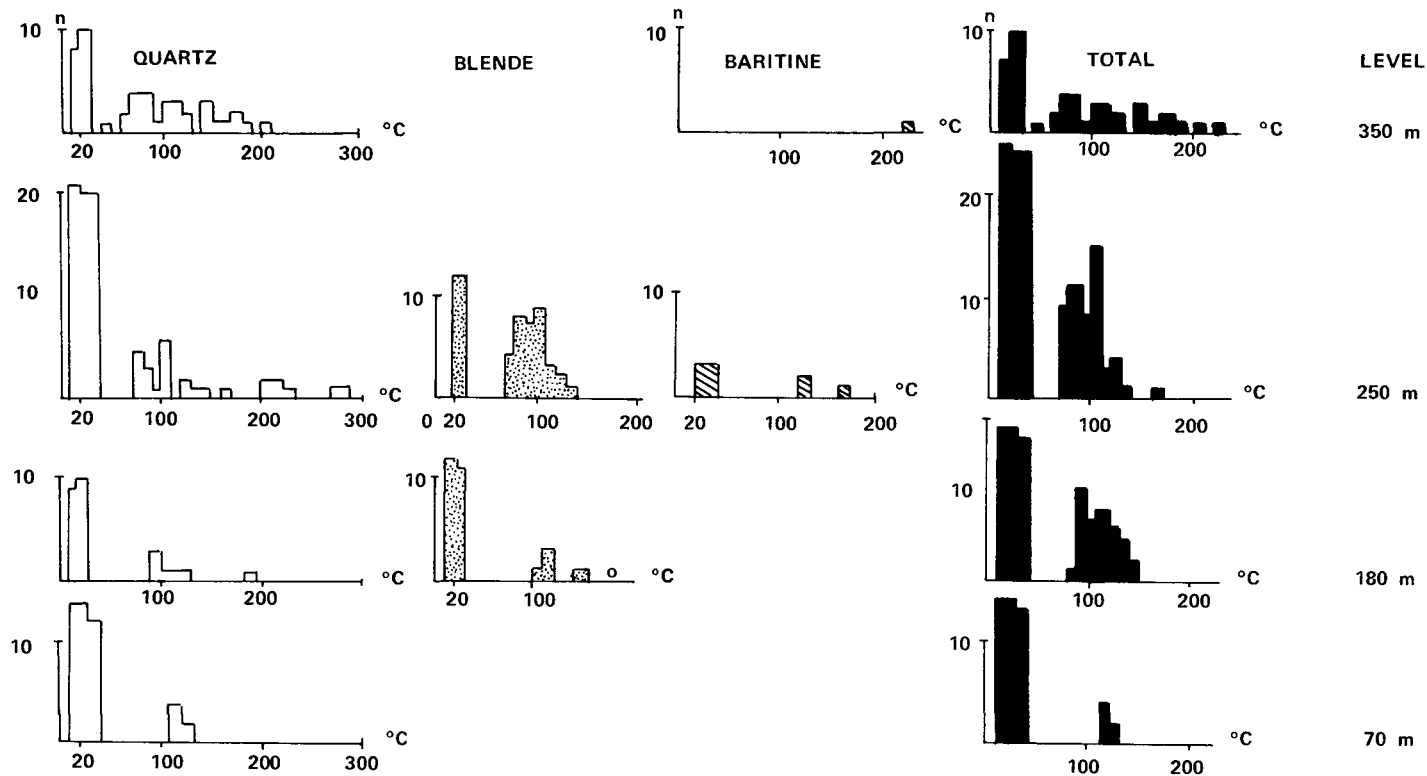


FIG. 1. Frequency histograms of homogenization temperatures of fluid inclusions at different levels and for each analysed mineral. Vertical axis: number of analyses; horizontal axis: homogenization temperature in °C.

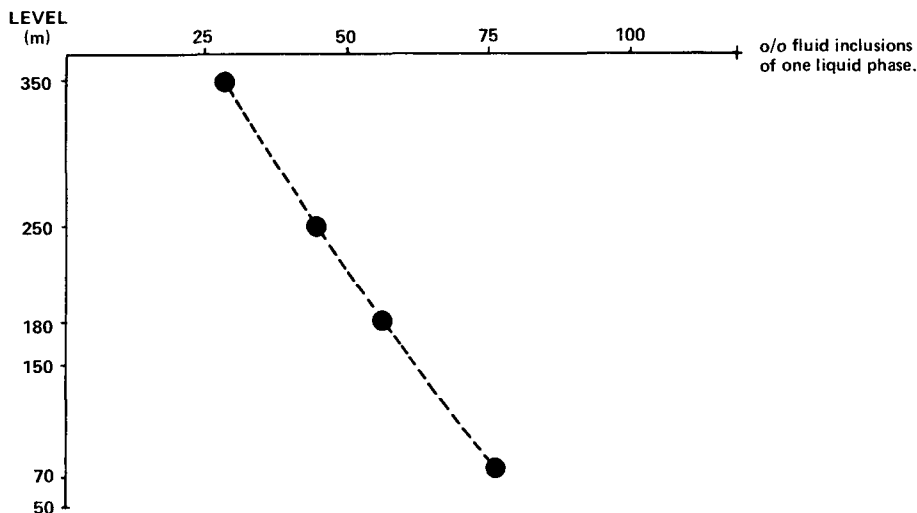


FIG. 2. Variation with depth of the percentage of fluid inclusions with one or two phases.

be submitted to cooling, at least in the first stages of the study, until one has become familiar with the characteristics of the samples under natural light and normal observation. This recommendation seems useful when one considers that very few references in the literature are made to inclusions of only one liquid phase.

4. POSSIBLE APPLICATION TO URANIUM DEPOSITS

For the deposits formed by descending infiltration, fluid inclusions must be only monophasic or, as in the case described here, its percentage should increase with depth.

This information together with the geological data is generally enough to define the process. The only limiting factor is finding adequate samples for the study.

Some of the uranium vein deposits, the origin of which is still under discussion (superficial or deep genesis), present siliceous gangue and banded structure.

Such is the case, for instance, with the deposit of l'Ecarpière, Vendée, France, described by Gerstner and co-workers [35]. It is a zone of veins affecting the northern border of the Mortagne batholite, with strong tectonics WNW.

The thickness of the veins varies between 0.20 m and 3 m. These veins are surrounded by hematitized clayey wall rock. The country rock is a breccia with granitic elements cemented by gangue of silica and fluorite. Mineralizations are banded and symmetric. From the red granitic wall rocks towards the axes of the vein the following sequence can be observed: red granitic breccia, fluorite, cryptocrystalline silica, fluorite, pyrite, pitchblende, silica with pyrite and fluorite in the axes.

In this type of vein it seems possible to apply the technique of the study of fluid inclusions for the gangue minerals of different bands and to different depths.

The appearance of liquid monophasic primary fluid inclusions exclusively or according to the Asprières-Bouillac vein distribution would indicate undoubtedly a supergenic origin. If, on the other hand, they contain an important amount of CO₂ at high pressure, this would indicate an endogenous process of the type described by Geffroy and Sarcia [1]. The transport of uranium by an endogenous process is a result of the pressure of CO₂, as has been proved by Naumov and Mironova [36] and Khitarov [37].

5. CONCLUSIONS

- (a) Either by theoretical considerations or by geological observations, the possibility of uranium concentration in vein deposits by means of descending infiltration (per descensum) must be accepted.
- (b) For this metallogenic model the conditions to be met in order that the process may lead to economically exploitable deposits are already known.
- (c) Once it can be demonstrated that the process has evidently taken place, it will provide a valuable basis for provisional prospecting.
- (d) The probable behaviour of fluid inclusions for deposits of undoubtedly "per descensum" origin is already known after the study of the deposit of lead-zinc at Asprières-Bouillac (France).
- (e) It seems very useful to try to extend this criterion to uranium vein deposits, the origin of which is still under discussion. Systematic research will help establish more accurate guidelines for provisional prospecting.

ACKNOWLEDGEMENTS

The author wishes to express his gratitude to the Staff of the Centre de Recherches Pétrographiques et Géochimiques, Nancy, Professors Poty and Leroy, Mr. Schwarzkopff and Mr. Jachimovich for their contribution to the author's training in the techniques of fluid inclusions and their applications to geological problems. Thanks are also due to Miss S. Darré for her encouragement and collaboration in translating and typing this paper.

REFERENCES

- [1] GEFFROY, J., SARCIA, J. A., La notion de gîte épithermal uranifère et les problèmes qu'elle pose, Bull. Soc. Géol. Fr., 6^e série 8 (1958) 173.
- [2] SCHNEIDERHOEHN, H., Vergleich der Uranerzvorkommen des mittleren Schwarzwaldes mit anderen Lagerstaetten, Mitt. Bad. Geol. Landesanst., (1951).
- [3] MOREAU, M., POUCHON, A., PUIBARAUD, Y., SANSELME, H., L'uranium et les granites, Chron. Mines Rech. Min n° 350 (1966) 47.
- [4] MATOS DIAS, J. M., SOARES de ANDRADE, A. A., "Uranium deposits in Portugal", Uranium Exploration Geology (Proc. Panel Vienna, 1970), IAEA, Vienna (1970) 129.

- [5] FERNANDEZ POLO, J. A., "Génesis de los yacimientos uranfíferos en metasedimentos de Salamanca (España)", *Ibid.*, p. 243.
- [6] LEROY, J., POTY, B., Recherches préliminaires sur les fluides associés à la genèse des minéralisations en uranium du Limousin (France), *Miner. Deposita* 4 (1969) 395.
- [7] GANGLOFF, A., "Notes sommaires sur la géologie des principaux districts uranifères étudiés par la C.E.A.", *Uranium Exploration Geology (Proc. Panel Vienna, 1970)*, IAEA, Vienna (1970) 77.
- [8] GARRELS, R. M., Mineral species as a function of pH and oxidation-reduction potentials, with special reference to the zone of oxidation and secondary enrichment of sulfide on deposits, *Geochim. Cosmochim. Acta* 5 4 (1953) 153.
- [9] GARRELS, R. M., CHRIST, C. L., Equilibre des minéraux et leurs solutions aqueuses, Gauthier Villars, Paris (1967).
- [10] MICHARD, G., Signification du potential redox dans les eaux naturelles, *Miner. Deposita* 2 (1967) 34.
- [11] MICHARD, G., ALLEGRE, C. J., Comportement géochimique des éléments métalliques en milieu réducteur et diagrammes (log₅, pH), *Miner. Deposita* 4 (1969) 1.
- [12] CALLAHAN, W. H., "Paleographic premises for prospecting of stratabound base metal deposits in carbonate rocks", *Symp. Mining Geology, Central Treaty Organization (CENTO), Ankara, Turkey (1964)* 191.
- [13] BERNARD, A., "Metallogenic processes of intrakarstic sedimentation", *Ores in sediments (AMSTUTZ, G. C., BERNARD, A., Eds), (Proc. 8th Int. Cong. Sedimentation, Heidelberg, 1971)*, Springer-Verlag, Berlin (1971) 43.
- [14] ROGER, G., Relation entre quelques gisements filoniens et leurs terrains encaissants; contrôles et sources de la minéralisation, Thèse D. S. W., Fac. Sci. Paris, Ronéo (1971).
- [15] BOSSI, J., La minéralisation plombo-zincifère d'Asprières-Bouillac (Aveyron-Lot, France): essai génétique, Univ. Nancy, France, Thèse 3^e cycle, Ronéo (1972).
- [16] FUCHS, Y., Quelques exemples de remobilisations dans le domaine épicontinental, *Convegno Sulla Rimobilizzazione dei Minerali Metallici e non Metallici, Cagliari, Italy (1969)* 161.
- [17] BARBIER, J., Conséquences géochimiques et métallogéniques de certains remaniements météoriques dans les granites, Applications pratiques dans le cas de l'uranium, Univ. Nancy, Fac. Sci., Thèse D. S. N., Ronéo (1971).
- [18] ROEDDER, E., Studies of fluid inclusions. I: Low temperature application of a dual-purpose freezing and heating stage, *Econ. Geol.* 57 (1962) 1045.
- [19] ROEDDER, E., "Fluid inclusions as samples of ore fluids", *Chap. 12, Geochemistry of Hydrothermal Ore Deposits (BARNES, H. L., Ed.), Holt, Rinehart and Winston, N. Y. (1967)* 515.
- [20] ROEDDER, E., Fluid inclusion evidences on the environment of formation of mineral deposits of the southern Appalachian Valley, *Econ. Geol.* 66 (1971) 777.
- [21] POTY, B., La croissance des cristaux de quartz dans les filons, sur l'exemple du filon de La Gardette (Bourg d'Oisans) et les filons du Massif du Mont-Blanc, Univ. Nancy, Thèse D. S. N., Ronéo (1969).
- [22] YAJIMA, J., TOURAY, J., Analyse thermométrique du gisement de fluorite d'El Hamman (Maroc), *Miner. Deposita* 5 (1970) 23.
- [23] SMITH, F. C., *Physical Geochemistry*, Ch. 17, Addison-Wesley, Reading, Mass. (1963).
- [24] OVCHINNIKOV, L. N., CHELISHCHEV, N. F., Statistical estimation of the physicochemical conditions of mineral formation, *Geochem. Int.* (1967) 1084.
- [25] BOWIE, H. U., "World uranium deposits", *Uranium Exploration Geology (Proc. Panel Vienna, 1970)*, IAEA, Vienna (1970) 23.
- [26] RUZICKA, V., Geological Comparison Between East European and Canadian Uranium Deposits, *Geol. Surv. Canada, Paper 70-48*, Ottawa (1971).
- [27] ROUTHIER, P., Sur la notion de "types" de gisements métallifères, *Bull. Soc. Géol. Fr.*, 6^e série 8 (1958) 237.
- [28] BERNARD, A., "Les types de gisement", *Paper at Conférences et séminaires de recyclage de métallogénie*, Univ. Nancy, France, Ecole Nat. Sup. Géol. Appliquée (1968) 1.
- [29] SAMAMA, J. C., "Les surfaces continentales et leur géochimie", *Conférences et Séminaires de Recyclage*, Univ. Nancy I, Ecole Nat. Sup. Géol. Appliquée, Nancy, France (1972).
- [30] ROBINSON, S. C., Mineralogy of uranium deposits, Goldfields, Saskatchewan, *Geol. Surv. Can. Bull.* 31 (1955).
- [31] TREMBLAY, L. P., The Geology of the Beaverlodge Area, Saskatchewan, *Geol. Surv. Can. Mem.* 367 (1968).
- [32] HOLLAND, H. D., "Gangue minerals in hydrothermal deposits", *Ch. 9, Geochemistry of Hydrothermal Ores (BARNES, H. L., Ed.), Holt, Rinehart and Winston, N. Y. (1967)* 366.

- [33] UCHAMESHVILI, N.E., MALININ, S.D., KHITAROV, N.L., Solubility of baryte in concentrate chloride solutions of some metals at elevated temperatures in relation to problems of the genesis of baryte deposits, *Geochem. Int.* (1966) 951.
- [34] KLIA, M.O., LAEMMLEIN, G., Inclusions primaires de gaz dans les cristaux, *Zap. vsejov. Mineral. ob. S.S.S.R.* 90 (1961) 260.
- [35] GERSTNER, A., et al., in *Les minerais uranifères français* (ROUBAULT, M., Ed.), Presse Univ. France, Paris 2 (1962) 323.
- [36] NAUMOV, G.B., MIRONOVA, O.F., Oxidation-reduction equilibrium in the system uranium-iron in a carbonate environment and its significance to geochemistry, *Geochemistry* 3 (1969) 286.
- [37] KHITAROV, N.I., Report on new experimental work in the field of deep-seated processes, *Geochemistry* 9 (1967) 909.

DISCUSSION

H.H. ADLER: The concept of supergene formation in what is obviously a vein-type configuration is important. I have heard one explanation of this process that relies on reduction of uranyl to uranous ions, which then precipitate to form pitchblende. This is a bacteriogenic mechanism. I am not convinced, however, that it is universally applicable; otherwise such deposits would be found more commonly in granitic areas. What is it that precipitates pitchblende so near the surface in a vein-type deposit when there is no physical evidence of a reductant? It is obviously not a high-temperature reaction.

B.P. POTY: I am inclined to think that it is. But would not hydrocarbons or H_2S promote the precipitation, even at lower temperatures?

H.H. ADLER: Yes, but what is the source of the H_2S ? I quite agree: if organic material was moved into the vein before the introduction of uranium, or simultaneously with it, pitchblende would be effectively precipitated. But one would then expect to find more pyrites associated with such veins.

B.P. POTY: But we do. The precipitation of both pitchblende and pyrite requires the presence of hydrogen sulphide. Where the source of the H_2S lies is a more difficult question to answer.

H.H. ADLER: It is an important question, however, because if we could put our finger on the source of H_2S we would be in a better position to predict where uranium deposits of this type might be found.

J. BOSSI: Presumably the sulphide source is the same as the source of the other elements: sulphide minerals disseminated through the enclosing rock.

ZLETOVSKA REKA URANIUM DEPOSIT

D. RADUSINOVIĆ

Institute for Geological and Mining Exploration and
Investigation of Nuclear and Other Mineral Raw Materials,
Belgrade, Yugoslavia

Abstract

ZLETOVSKA REKA URANIUM DEPOSIT.

The Zletovska Reka uranium deposit is located inside the Tertiary volcanites which were produced during the final phase of volcanic activity in the Zletovo-Kratovo metallogenetic area. The uranium has most probably originated from a deep-seated magmatic source, activated after the consolidation of volcanites; accordingly, the uranium deposit is in a paragenetic rather than in a direct genetic relation with volcanites. The mineralization is controlled by the fault-type structures, and the ore bodies, mainly vein-type, are located inside the sheared zones. The deposit has been formed during the epithermal phase of hydrothermal activity, and during one of the last stages of the mineralizing processes. The uranium mineralization has been deposited subsequent to the main phase of sulphide mineralization, which produced the important lead and zinc deposits in the Zletovo-Kratovo area. The well-defined depositional succession, starting with copper, via lead-zinc, to uranium mineralization, has been observed. Such formation of mineral parageneses has been reflected in their definite zoning, indicating some sort of differentiation of mineralizing solutions which resulted in increased uranium concentration in the late stages of hydrothermal activity and formation of the Zletovska Reka uranium deposit.

1. INTRODUCTION

The Zletovska Reka uranium deposit is located in the Osogovo Mountain, the Zletovo-Kratovo volcanic area, Macedonia (Fig. 1). The complex of volcanic rocks in this area consists of several types of dacites, andesites and their pyroclastics, produced by the Tertiary intermediate magmatic activity, and represents the most extensive volcanic complex in Yugoslavia.

In a structural sense, the Zletovo-Kratovo area belongs to the Vardar zone, a part of the large Dinarides unit. More precisely, the Zletovo-Kratovo volcanic area represents an independent magmatic and structural region, located between the Dinarides and the Serbo-Macedonian mass.

Several important lead and zinc deposits as well as numerous copper and uranium mineral occurrences belonging to the Alpine metallogenetic epoch are located in the Zletovo-Kratovo volcanic area.

2. GEOLOGICAL AND STRUCTURAL FEATURES

The geology of the area around the uranium deposit is relatively complex. The basement consists of Paleozoic crystalline schists, composed mostly of chlorite-sericite and amphibole-chlorite schists, some mica-schists and phyllites, and subordinate amphibolites and gneisses. This basement has been intersected and, in the area of the Zletovska Reka deposit, covered by extrusive volcanic rocks; frequently, the crystalline schists from the basement form the xenoliths and enclaves in the volcanites.

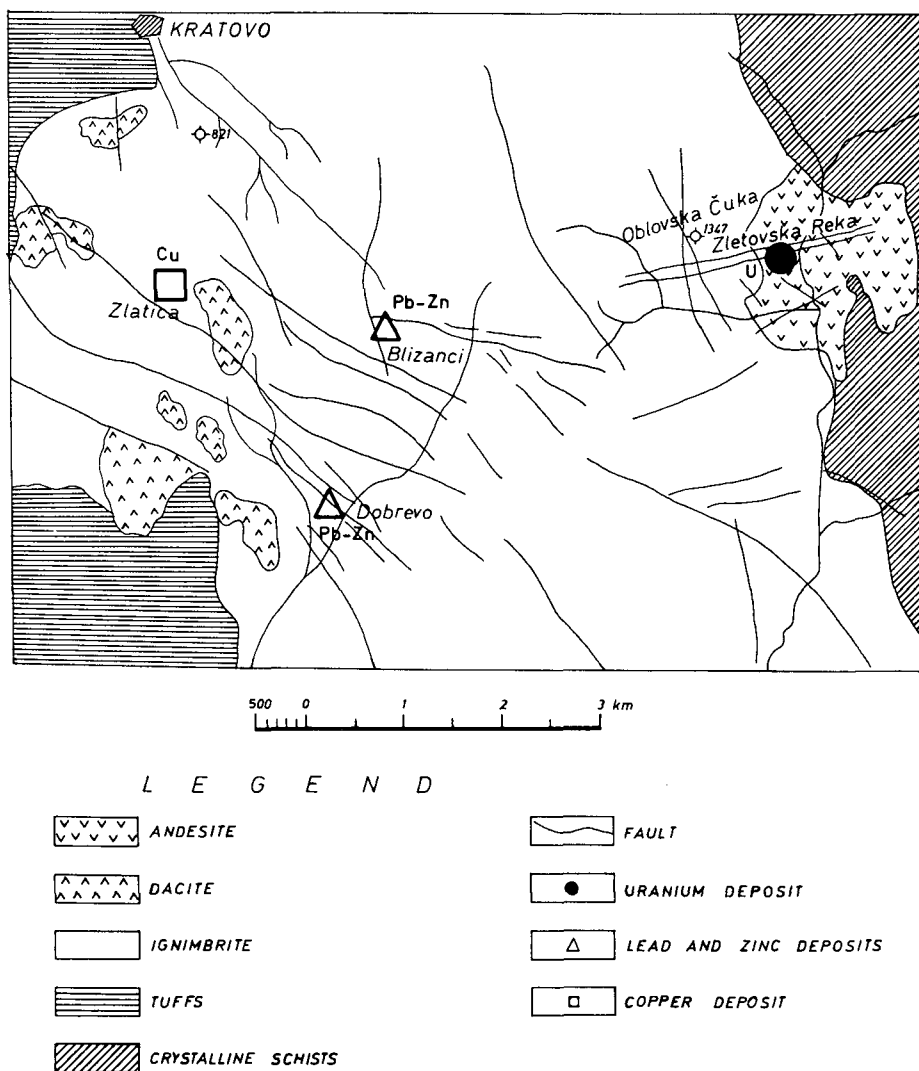


FIG. 1. Metallogenetic sketch map of the Zletovo-Kratovo area.

Actually, the Zletovska Reka area represents the contact zone between the volcanites and the crystalline schists belonging to internides of the Serbo-Macedonian mass (Fig. 2).

In addition to the above-mentioned schist, a gabbroid massif is located about 8 km southwards; this massif has been intruded into the chlorite-sericite schists along the boundary structure which separates the Zletovo-Kratovo volcanic area and the Serbo-Macedonian crystalline schists. The gabbro is highly cataclastic and partly, but intensively, uralitized. As stated earlier, both the gabbro and the crystalline schists represent the lower structural unit in the Zletovska Reka area.

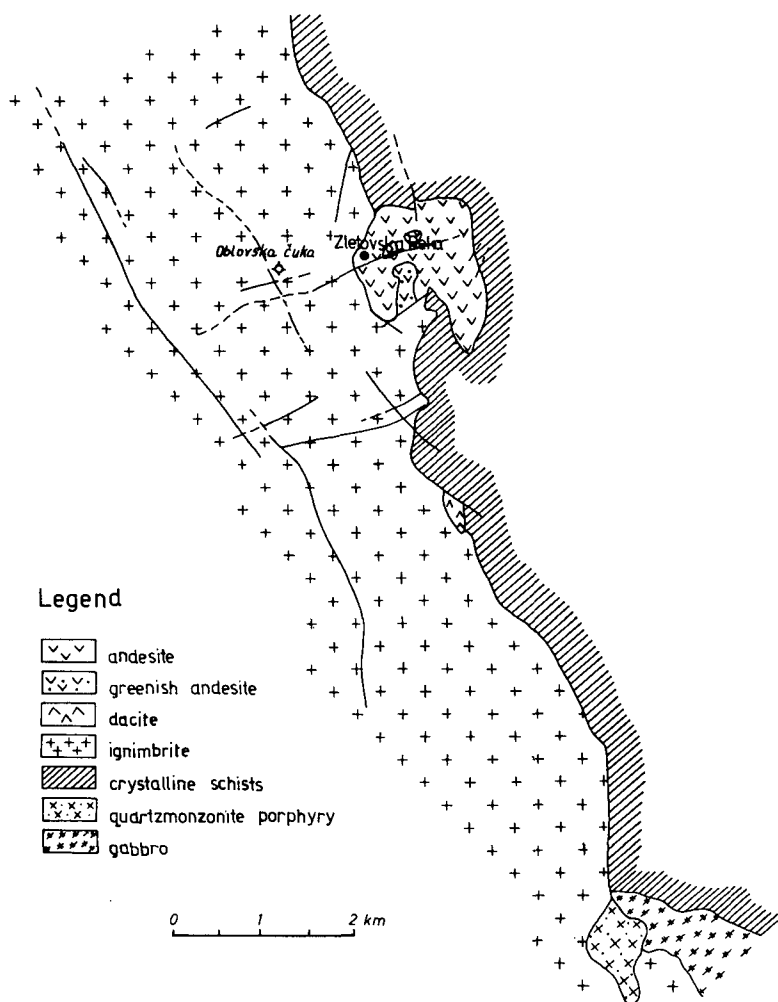


FIG. 2. Schematic geological map of the Zletovska Reka.

The upper structural unit has developed in the Tertiary, after the intensive, mainly the extrusive and effusive, magmatic activity was initiated. This unit consists of thick andesitic and dacitic pyroclastics, andesitic and quartz-latic dykes and flows, and one quartz-monzonite porphyry intrusive body. Generally, the four main phases of volcanic activity have been recognized in the Zletovo-Kratovo area; however, only three of these phases were identified around the Zletovska Reka deposit.

The volcanic activity in the Zletovo-Kratovo area started in the Eocene [1] by the hornblende-biotite andesite flows; these rocks are particularly well developed in the Zletovska Reka deposit, where they cover the most

extensive area. The andesite flows were associated with a pyroclastic phase, composed of andesitic tuffs and breccias as well.

The second phase of volcanic activity consisted of a sequence of dacitic ignimbrites, produced by the violent incandescent cloud-type explosions. The incandescent clouds were composed of fragments of previously consolidated volcanic rocks, numerous phenocrysts and pulverized pyroclastic material, and of fragments of rocks in the basement which magma has brought to the surface during its upward movement; all these fragments represented a sort of emulsion, saturated by water vapour and other easily vaporized substances. The incandescent clouds of this material, ejected through the craters, were deposited inside the lower parts of the paleorelief over extensive areas.

The third phase was relatively quiet. The previously formed andesites and ignimbrites were intruded by younger andesites of a characteristic green colour, and partly propylitized. The green colour was produced by the presence of celadonite. These rocks are actually amphibole-biotite andesite, and their presence in the deposit is relatively subordinate. In addition to the andesite described, this volcanic phase in the area surrounding the mineral deposit is also marked by the dacite, latite and dacitic-andesitic intrusions, which frequently form the low and rounded hills in the pyroclastics and ignimbrites formed in the second phase. The quartz-monzonite intrusive body probably belongs to this phase as well.

In the area immediately surrounding the deposit, the preserved topographic forms indicate that the centres of volcanic activity were located in the volcanic domes. Actually, the Zletovska Reka deposit is located near one such dome-like volcanic centre, Oblovska Čuka. In the broad area around the deposit, the ring-like calderas, craters, necks and lava flows were identified as well.

The main structures in the area are the fault-type structures, produced because of the position of the Zletovo-Kratovo area inside a highly mobile zone during the Alpine orogenesis. During this phase of structural development, the fold-type structures were replaced by the fault-type structures, with magmatic activity related to the latter. The fault-type structures are grouped into the systems characterized by regular distribution and trends. Four such groups were identified in the area, but only the eastern group is developed around the deposit. The individual systems of fault-type structures correspond to individual phases of volcanic activity; this activity is closely related to phases of structural deformations [2], such as the replacement of andesitic by dacitic phases, pyroclastic extrusions and minor subvolcanic intrusions. The subsequent post-magmatic activity was also related to fault-type structures, and the individual structural and magmatic phases were followed by mineralizing processes. The most important fault-type structures have NNW-SSE to N-S and ENE-WSW to E-W trends, with very steep to vertical dips.

The longitudinal NNW-SSE fault served as feeders for hydrothermal solutions with sulphide mineralization. The lead and zinc sulphide mineralizations are located in these structures, and their most important concentrations are located in the central parts of the Zletovo-Kratovo area.

The ENE-WSW or almost E-W faults are produced by the subsequent strains in the already consolidated structural frame-work; the Zletovska Reka uranium mineralization, situated in the eastern part of the Zletovo-Kratovo area, is located inside this fault system.

3. ROCK ALTERATIONS

The rock alterations are intensively developed around the deposit. These alterations have been partly produced by autohydroatation processes, partly by the action of hydrothermal solutions, and partly by supergene processes. The propylitization phenomena were particularly active in the dark minerals amphibole, pyroxene and locally biotite, over the extensive area. The hydrothermal alterations are confined to structural zones, and are well developed in the mineral deposit only.

The products of hydrothermal alterations generally marked the direction of channels where the mineralizing solutions have moved and these products introduced changes in the mineral composition of adjacent rocks. According to the most frequent new minerals, the following types of hydrothermal alterations can be identified: carbonitization, argillization, chloritization, sericitization, silicification, alunitization and zeolitization. The carbonitization was rather extensive and influenced practically all rocks in the deposit; it consists mainly of calcite, and very infrequently of siderite. The argillization, consisting of kaolinite, montmorillonite and illite, is also extensive and particularly intensive near the ore bodies. Silicification consists of quartz, chalcedony and sometimes of opal. Quartz is not particularly frequent and was formed before chalcedony and opal, which were related directly to mineralizing processes and which are mineralized by uranium as well. The other minerals produced by hydrothermal alterations, except for chlorite, are present in lesser quantities; chlorite is relatively frequent, but present in very low concentrations.

The alteration products indicate their horizontal zoning around the mineral deposit; near the ore bodies the concentration of calcite is reduced, both in foot walls and hanging walls, and the clay minerals are increased.

Similar phenomena were observed with accessory minerals as well. The concentrations of magnetite, hematite and ilmenite are reduced towards the mineral bodies and are completely absent in the mineralized zones; pyrite has the opposite behaviour, and its concentrations increase from traces in the surrounding rocks to several per cent in the ore bodies. Consequently, there is a characteristic zoning in the distribution of accessory minerals in mineralized zones which is related to the influence of uranium-bearing hydrothermal solutions.

4. MINERAL COMPOSITION

The mineral composition in the Zletovska Reka mineral deposit is relatively complex, and consists of uranium minerals, associated sulphides and gangue minerals.

Pitchblende is the most important uranium mineral. It can be observed by the unaided eye along the fissures, where it forms stains and veinlets; in the rocks, it is finely disseminated and can be observed by microscope only. It usually forms individual colloidal grains, but also locally intergrows with sphalerite and, less frequently, with pyrite and only occasionally with galena. The contacts of pitchblende with other sulphide minerals were not observed, and it can be concluded that the pitchblende is younger than sphalerite and pyrite, with which it is associated. Owing to the oxidation, the pitchblende has been destroyed locally and transformed into the numerous

secondary minerals such as autunite, torbernite, kasolite, uranophane and uranospathite. In the reductive environment a thin cementation zone has been formed, where the only uranium mineral is "sooty pitchblende". All these secondary minerals are present inside a zone which is tens of metres thick near the surface, and completely disappear with depth.

Among the sulphide minerals, the most frequent are sphalerite and pyrite; the other minerals are scarce, and actually only a few grains of galena, tetrahedrite, bravoite and marcasite have been observed. Sphalerite is fine-grained and transparent. It is sometimes intimately intergrown with pitchblende. Pyrite is also fine-grained, and occurs as idiomorphic crystals or as irregular grains. Some idiomorphic grains of pyrite are associated with bravoite. Pyrite is partly transformed into limonite and infrequently into marcasite. Galena is present in traces and contains minor tetrahedrite inclusions. Consequently, the sulphides represent only the minor associated minerals with the uranium mineralization.

The gangue minerals - siderite, barite, fluorite, quartz and chalcedony - area also present in traces, usually as individual grains, except for chalcedony, which forms the thin veinlets locally.

5. ORIGIN OF THE DEPOSIT

The Zletovska Reka uranium deposit was formed during a separate (and the youngest) phase of mineralizing processes related to Tertiary magmatic activity in the Zletovo-Kratovo area. The formation of the deposit has been influenced by the previous tectonic activity, which has produced the intensive fault-type structures in the volcanic complex. These structures were, depending on the local conditions, later mineralized; the volcanites represented the previous magmatic activity, and only after the volcanites were consolidated and subsequently faulted, were the necessary conditions satisfied for circulation of hydrothermal solutions near the surface during the later phases of magmatic activity. During the post-magmatic activity, the lead, zinc, copper and uranium mineral deposits were formed. The magmatic and tectonic phases were developed successively, with the resulting characteristic zoning in mineral deposits in the Zletovo-Kratovo area. Accordingly, all the mineralizing solutions originated from the same, deeply seated magmatic chamber, formed in the final phase of the Alpine metallogenetic epoch. The uranium deposit represented the last phase of the mineralizing processes in the Zletovo-Kratovo area, which have already formed the important deposits of different metals. During this last phase, the old fractures were reactivated and the new were formed, and have been used by the hydrothermal solutions with uranium. The WNW-ESE to E-W fault structures were the most favourable for mineralizing solutions, and it is there that the most important uranium mineralizations have been deposited. This is the most important structural feature of these uranium deposits, contrary to previously formed phases, where the NW-SE structures were favourable for the important lead-zinc and other sulphide mineralizations. The mineralizing solutions with uranium have introduced hydrothermal alterations into the surrounding rocks; the alteration products are, both in mineral composition and in the spatial distribution, highly similar to those produced by earlier sulphide mineralizations.

The genetic relations and the same magmatic source of both the lead-zinc and uranium deposits are reflected in the similar mineral composition. The Zletovska Reka uranium deposit contains the minerals found in lead-zinc parageneses and, in the Dobrevno and other lead-zinc deposits, uranium minerals are present. The most frequent sulphide minerals in Zletovska Reka are sphalerite, pyrite and, infrequently, galena; although galena is infrequent, some lead is always present in traces, and the uranium-lead correlation coefficient is 0.85. The other elements with positive correlation coefficients are molybdenum (0.81) and yttrium (0.98). However, both molybdenum and yttrium were found in trace concentrations only, and their minerals have not been identified so far.

The oxidation zone has secondary uranium minerals and is well developed. This zone also contains some ore bodies, but the zone of oxidation and transformation of primary minerals is relatively thin and disappears with depth, so the secondary minerals are of no economic importance. The primary ore minerals are located along the fractures and fissures, where they form the veinlets of weak impregnations in sheared and altered rocks. The highly sheared and hydrothermally altered parts of the deposit contain the impregnation-type mineralization where the ore bodies can have an appreciable ore grade. In places where the rocks are compact, only the fissures contain the ore minerals, and such parts of the deposit are of low ore grade. Consequently, the uranium deposition is influenced more by the physical and mechanical, rather than the petrochemical characteristics of the surrounding rocks.

The mineralizations are localized inside the sheared fault zones, and the ore bodies generally follow the trend of these zones; the higher uranium concentrations are located along the intersection of different fault zones. The ore veins form the local lenses and irregular lodes or, sometimes, the discontinuous "ribbons" as well. The mineralization is always structurally controlled. In some ore bodies, pitchblende is the only ore mineral. The ore bodies which contain the associated sulphides usually contain higher uranium concentrations, and there the pitchblende surrounds the sulphide grains. The reductive environment, favourable for sulphide deposition, was also favourable for uranium deposition from circulating hydrothermal solutions.

According to available data, it is difficult to determine exactly to which magmatic rock the uranium mineralization is genetically related. The author is inclined to accept the paragenetic rather than the direct genetic relation between the uranium mineralization and the particular magmatic rocks. Owing to the fact that the uranium mineralization is related to the youngest phase of magmatic activity, it can be supposed that at some depth below the volcanites a larger intrusive body is located, where the different magmatic and post-magmatic phenomena originated. It is possible that the small quartz-monzonite intrusive body, located about 8 km in the south of the uranium deposit, is related to this supposed large intrusive. This small intrusive body is younger than the surrounding volcanites, but has a geochemical and petrological composition highly similar to other volcanic rocks in the Zletovo-Kratovo area. Owing to the fact that the uranium is concentrated in the late magmatic differentiation, it can be considered possible that the post-magmatic processes related to intrusions of quartz-monzonite magma have introduced uranium mineralization in the Zletovska Reka deposit.

No zoning was observed in the deposit so far, except for the vertical zoning produced by transformation of primary ore components. The weathering and oxidation zone extends up to a maximum depth of about 60 m, followed by an appreciably thinner cementation zone, and by the zone of primary uranium mineralization. However, the general zoning of the Zletovo-Kratovo area as a whole is of particular interest from the metallogenetic point of view. This zoning resulted, most probably, from the pulsatory alternations of structural and magmatic activities and related mineralizations. Such activities have produced the different rock sequences and different mineral parageneses, although all the eruptive phases were not associated with the corresponding extensive phase of mineralization. Apparently the explosive volcanic phases, which produced the ignimbrites and other pyroclastics, were not associated with a larger phase of mineralization.

The mineralizing solutions which introduced the mineralization in the Zletovo-Kratovo area have changed their chemical composition in the course of geological evolution and, owing to their differentiation related both to time and space, the different mineral deposits have been formed. A general sequence of mineral parageneses, from those of copper, via lead-zinc, to those of uranium, have been observed. Spatially, these relations are confirmed by the presence of copper mineralizations in the western part of the Zletovo-Kratovo area, those of lead and zinc in the central part of this area, and those of uranium in the eastern parts of the Zletovo-Kratovo area. The mineral composition of a particular paragenesis depends on the place and the time of deposition. The mineral parageneses replaced each other with respect to the main metals, but the general interdependence has been preserved when dealing with the contribution of minerals occurring in individual phases. This interdependence is demonstrated by the fact that the mineral paragenesis in one phase contains the traces of minerals which represent the main ore metals in the next phase. The copper parageneses at the Zlatica copper mineral occurrence contain the traces of lead and zinc parageneses, which occur as the main metals in the next phase. Owing to the fact that the earlier phases, which preceded the copper phase, are not known, it may be inferred from the traces of gold in copper parageneses that the earlier phases contained the gold as the main metal.

The lead and zinc parageneses at Dobrevu always contain some minerals from the earlier copper phase; in the final stages of the lead and zinc mineral phase occur the uranium parageneses, indicating the next phase with uranium mineralization.

The uranium mineral parageneses contain the traces of lead and zinc minerals from the preceding phase; owing to the fact that the uranium mineralization does not contain the younger mineral parageneses, it can be concluded that uranium mineralizations represent the end of endogene mineralization in the Zletovo-Kratovo area.

According to the data presented, it can be concluded that the Zletovska Reka uranium deposit genetically corresponds to hydrothermal mineralization formed in the epithermal environment and originating from a deep magmatic source related to the final phase of the Alpine metallogenetic epoch.

REFERENCES

- [1] MIJALKOVIĆ, N., PEŠIĆ, D., Referati VI Savetovanja geologa Jugoslavije, Ohrid (1966) 158.
 [2] MAKSIMOVIĆ, B., SIKOŠEK, B., Trudovi na Geozavod na SRM sv.4, Skopje (1954).

BIBLIOGRAPHY

- TOMIĆ, J., Vesnik Instituta kralj., Belgrade 6 (1938) 221.
 CISSARC, A., RAKIĆ, S., Vesnik Zavoda za geološka i geofizička istraživanja NRS, Belgrade 1 (1956) 224.
 PANTIĆ, R., RADUSINOVIĆ, D., SIKOŠEK, B., OBRENOVIĆ, M., "Uranium deposits in tertiary volcanic rocks of northeastern Macedonia", Int. Conf. peaceful Uses atom. Energy (Proc. Conf. Geneva, 1964) 12 UN, New York (1964) 55.
 RADUSINOVIĆ, D., Radovi sektora za istraživanje nuklearnih i dr. mineralnih sirovina, Belgrade 1 (1961) 77.
 PUTNIK, S., SARIĆ, V., Internal Rep. 1531, Inst. Nucl. Raw Materials, Belgrade (1969).
 DIVLJAN, S., Comptes rendus des séances de la Société serbe de géologie, Belgrade (1964).
 MIJALKOVIĆ, N., STANIĆ, B., DIVLJAN, S., PEŠIĆ, D., RONČEVIĆ, G., Comptes rendus des séances de la Société serbe de géologie, Belgrade (1964).
 TEOFILOVIĆ, M., VUJANOVIĆ, V., Bulletin du Musée d'histoire naturelle, Série A, Livre 25, Belgrade (1971).
 MIJALKOVIĆ, N., MILUTINOĆ, D., ISAILOVIĆ, S., PEŠIĆ, D., Internal Rep. 1476, Institute Nucl. Raw Materials, Belgrade (1964).

DISCUSSION

J. A. FERNANDEZ POLO: Have you found what you interpret to be a genuine paragenetic relationship of uranium with other metals such as lead and zinc, or is what you have seen more likely to be a chance association?

D. RADUSINOVIĆ: We feel certain that it is not a chance association but a genuine paragenesis. The lead and zinc veins contain numerous uranium occurrences which are of course inter-related, but which also show a distinct relationship to the other metals and are consistently of a younger age than the sulphides.

J. A. FERNANDEZ POLO: What relationship does the supergene process bear to the hydrothermal deposits?

D. RADUSINOVIĆ: The supergene process is limited to the surface zone. In the mineralized sectors it was effective through the first 60 m or so of depth, which contain the secondary uranium minerals and occasional ore bodies. Below 60 m we find a zone of cementation with uranium "soot", and, beneath that, the zone of primary mineralization which reaches to a depth of 200 or 300 m.

OTHER URANIUM DEPOSITS

Review Paper

OTHER URANIUM DEPOSITS

J. W. von BACKSTRÖM

Geology Division,

Atomic Energy Board,

Pretoria, South Africa

Abstract

OTHER URANIUM DEPOSITS.

Other Uranium Deposits (group 4) includes deposits which could not readily be classified with groups 1, 2 and 3, in the classification of uranium ore deposits established by the International Atomic Energy Agency at Montreal in September 1972. This group makes provision for many diverse types of uranium mineralization, and deposits are classified according to origin as orthomagmatic; diatremes; shear zones and breccias; supergene; brines; marine. In the present paper a number of representative uranium deposits from each group are described. Orthomagmatic deposits cover uranium mineralization associated with granites, syenites, carbonatites and pyroxenite in Scotland, Alaska, Greenland, Brazil, South Africa, Madagascar and the United States of America. Uranium mineralization associated with diatremes in the United States of America, Canada and Italy, is described. Occurrences associated with shear zones and breccias in the two first-named countries and in India are also described. Examples are given of supergene deposits occurring in Canada, Portugal, Spain, Australia and Southern Africa, and of brines in the United States of America. Conditions for the formation of uranium deposits in closed basins are also mentioned. Finally, under uranium of marine origin a summary on uraniferous phosphatic rocks is quoted; the paper concludes with a description of some continental shelf deposits.

Hundreds of uranium deposits have been discovered in many geologic environments. However, significant deposits or districts which have produced large quantities of uranium, or which contain noteworthy reserves, are relatively few. All the most important producing fields have uranium associated with quartz-pebble conglomerates, sedimentary basins or sandstone-type deposits, or veins and similar deposits. It is to be expected that new uranium reserves will be developed by extending existing ore bodies or by exploring favourable areas within known fields.

It will, however, be necessary to discover new uranium deposits in areas which lack the above-mentioned favourable geologic features, since they may hold the clues for major future discoveries. In favour of such an approach is the fact that no one rock type consistently appears as preferred host for uranium mineralization; neither is this mineralization tied to any particular epoch or era or to any form, type or intensity of structural deformation. Such deposits are reviewed in the present paper and may be classified as follows:

1. Orthomagmatic
2. Diatremes
3. Shear Zone and Breccia Deposits
4. Supergene Deposits
5. Brines
6. Uranium of Marine Origin

1. ORTHOMAGMATIC

Vinogradov (1962) gives the following average uranium content for igneous rocks derived from data based on the accuracy of the analytical method, on the largest possible number of

determinations and on multiple determinations on standard samples taken from all over the world:

Rock group	Uranium content (ppm)
Ultramafic (dunite, peridotite, pyroxenite)	0,03
Mafic (basalt, gabbro)	0,5
Intermediate (diorite, andesite)	1,8
Felsic (granite, granodiorite)	3,5
Sedimentary (clay, shale)	3,2
Meteorites (chondrite)	0,015
Earth's crust (two parts felsic, one mafic)	2,5

Data for stony meteorites (chondrites) and for sedimentary rocks, clays and shales that constitute most of the earth's sedimentary cover are given for comparison. Very tentative figures for the "average content of the earth's crust", obtained by assuming that the earth's crust is composed of two parts of granite and one part of basalt, are also given. The enrichment of uranium in intrusives rich in silica and alkalis is also observable in volcanics, and it is generally thought that the maximum concentration of uranium is found in the youngest member of the series.

1.1 Granite

1.1.1 Caledonian granites of Scotland

According to Davis *et al.* (1972), of about 2 500 km² of northern Scotland which were surveyed, the Caledonian granites of Helmsdale exhibit by far the best evidence of uranium mineralization. Small occurrences of autunite, metatorbernite and kasolite were found, associated with fractures in the Helmsdale granite which was intruded into Precambrian schist. Because of the extensive peat and drift cover, the area is not amenable to investigation by systematic surface or aeroradiometric survey techniques. The technique adopted was therefore based on geochemical sampling of stream water and sediment, and the selective traversing of favourable areas using portable radiation detectors. It showed an association of uranium anomalies in stream sediments with newer Caledonian granites. Numerous radioactive anomalies were discovered in the granite itself. Although secondary uranium minerals were identified locally in the granite, it was not possible to establish the existence of high-grade primary mineralization. Drilling demonstrated the persistence of weathering and low-level radioactivity to a depth of 30 metres in one locality in adamellite. Although this may be regarded as a uranium province, no significant deposit of uranium has been located to date.

1.1.2 Alkali granite of Ross-Adams, Alaska

The Ross-Adams uranium-thorium deposit has been described by MacKevett (1958). It is situated within a small stock or boss of alkali granite about 300 metres from its margin. The age is probably late Cretaceous or Tertiary. The country rocks in order of age are metamorphosed Devonian sediments and volcanics, black slate and hornfels, diorites, granodiorite, aplite and alaskite. The youngest intrusive rock, excluding dykes, is the alkali granite which forms a small stock or boss about 8 km² in areal extent. It contains abnormal quantities of certain minor elements, notably uranium, thorium, yttrium, lanthanum, niobium, cerium and rare earths.

The Ross-Adams ore body represents an uncommon type of uranium deposit in mineralogy and shape, and in its genetic affiliation with alkali granite. The dominant ore minerals are uranorthorite and uranoan-thorianite. The ore body consists of a core of high-grade ore containing more than 0,50 per cent U₃O₈ and enveloped by a uraniferous zone between one and six metres thick which contains less than 0,50 per cent U₃O₈. Texturally, the ore resembles its alkali granite

host rock. The formation of the deposit is attributable to two processes, viz. a local concentration of probably late-stage accessory uranorthorite and uranoan-thorianite in the alkali granite, followed by the emplacement of numerous uranium-bearing and thorium-bearing veinlets at the side of the lode.

1.1.3 Midnite Mine, Spokane, Washington, USA

Barrington and Kerr (1961) have described a potentially important deposit of uranium 80 km northwest of Spokane, in which uranium ore occurs at the contact between regionally metamorphosed Precambrian sediments and an intrusive Cretaceous granite. It is a coarse-grained, holocrystalline, intrusive rock with aplitic and pegmatitic phases, but without visible primary uranium mineralization. The latter occurs in a zone along the contact of the granite and the sediments.

Ores are found within and near associated fractures and shear zones. Secondary, oxidized uranium minerals, principally autunite and meta-autunite, lie above a fluctuating water table, while below this water table there occurs a zone of partially oxidized, sooty and compact uraninite with which sulphides are associated. The action of hydrothermal solutions is indicated by the presence of minerals such as kaolinite, illite, montmorillonite and adularia.

Several open-pit mines have been developed in the area since uranium mineralization was first reported in 1954. The average uranium content of the first 710 tonnes shipped was 0.285 per cent U_3O_8 . In the period August 1957 to end 1959, 496 716 tonnes of ore were mined and 1 834 030 tonnes of waste stripped.

1.1.4 Austen, Lander County, Nevada, USA

Quartz monzonite of probable Jurassic age are in contact with metamorphosed sedimentary rocks, predominantly quartzite and phyllite, with minor silicified limestone and hornfels in the Reese River silver-mining district, where uranium mineralization was discovered 5 km south of Austen in 1953.

Sharp and Hetland (1954) have described autunite and metatorbernite in faults and fractures in both the intrusive quartz monzonite and the metamorphosed sedimentary rocks, and also as disseminated ore in small roof pendants of the latter near the contact of these units. The quartz monzonite acted as host to narrow siliceous and intermediate dykes, as well as to numerous mineralized fracture zones which served as conduits for ascending uraniferous solutions. Fracture zones are from two to 30 metres wide, and from 20 to more than 1 000 metres long. Uranium minerals are associated with silver, gold, copper and iron in a gangue of sericite with varying amounts of vein quartz.

Select samples from the area contained as much as six per cent U_3O_8 , and grab samples averaged 0.151 per cent.

1.2 Syenite

1.2.1 Ilimaussaq, South Greenland

The Gardar province of South Greenland is made up of a number of major intrusions, of many generations of dyke swarms and of basaltic lavas. At Ilimaussaq, Sørensen (1970) has described a highly mineralized agpaite nepheline syenite intrusion which measures about 100 km². It is the youngest major intrusion and has been dated at 1 000 million years. It is a lujauvritic nepheline syenite locally enriched in uranium and thorium and contains potential deposits of eudialite, stienstrupine, monazite, thorite and rare minerals containing beryllium, lithium and niobium. Uranium content ranges from 100–3 000 ppm, and that of thorium from 50–1 300 ppm.

The uranium deposits are low-grade ores characterized by a very heterogeneous distribution of uranium and thorium. The volumes occupied by rocks having more than 400 ppm

uranium are rather small. Future exploitation can only be considered in conjunction with occurrences of Nb, Be, Zr, Li, F, etc.

1.2.2 Pocos de Caldas, Brazil

Pocos de Caldas, as described by Távora (1964), is an elliptical laccolith consisting of alkaline rocks which crop out over an area of 800 km² close to the boundary of the Minas and Parana basins. The most common rocks are syenites (foyaïtes), microsyenites (tinguaïtes), phonolites and associated tuffs.

In the central part there is a dense net of thin veins, from five to 25 cm thick, of so-called "caldesite"—a mixture, in variable proportions, of zircon, baddeleyite and other minerals. Apart from the *in situ* deposit, eluvial and alluvial material cover the slopes surrounding the deposits and are found along the drainages over an area of roughly 450 km².

Uranium is either associated with the zirconium minerals as inclusions and chats, which association gives high and fairly cheap recoveries of uranium in extraction plants, or is present in the crystal structure of the zircon, which fact gives rise to an uneconomical refractory "ore". Unfortunately the latter type of deposit, with an average grade of 0.1 per cent, is highly pre-dominant.

1.2.3 Pilanesberg, South Africa

The Pilanesberg intrusive complex, rising abruptly about 600 metres above the Bushveld plain of norite and red granite, is wonderfully regular in outline, is almost circular, and has a diameter of 27 km. The complex contains both extrusive and plutonic rocks which are divisible into two main petrologic groups—alkaline syenites and trachytes, and foyaïtes and phonolitic rocks. Associated with the extrusive rocks are breccias and tuffs.

Rare-earth mineralization occurs as veins in tinguaites, and as veins and blebs in marginal parts of green foyaïtes. Average percentage rare-earth oxides (REO) varied between 7.45 and 19.5, ThO₂ between 1.3 to 4.3, and U₃O₈ from 0.005 to 0.025. Although this deposit has been under active investigation for the past five years it is not a viable proposition at this stage.

1.3 Carbonatite

The search for ore deposits in carbonatites was, to a large extent, inspired by discoveries of mineral wealth. Major reserves of metalliferous ores of great importance to the mining industry have been discovered in carbonatite-bearing complexes. The results from a nuclear-mineral economic point of view have, however, been disappointing although minor concentrations of rare-earth minerals, associated with uranium, are being produced from the carbonatite of the Phalaborwa Igneous Complex in the northeastern Transvaal.

A detailed description of the Phalaborwa Complex was given by Hanekom *et al* (1965), and of Ondurakorume, Tweerivier and Glenover by Verwoerd (1967).

1.3.1 Phalaborwa, South Africa

The Phalaborwa Complex consists of pyroxenite, syenite, olivine-diopside-phlogopite-pegmatoid, fennite and carbonatite. Most of the members are intrusive into the granite gneiss of the Archean Complex, but some are regarded as products of metasomatism. The pyroxenite was intruded first, followed by the syenite and lastly by a centrally located core of transgressive carbonatite which is surrounded by a serpentine(olivine)-magnetite-apatite rock to which the name "phoscorite" has been given. The phoscorite is regarded as original dunite which has been enriched in magnetite and apatite under pneumatolytic pegmatitic conditions. Apatite is an important mineral constituent of pyroxenite, phoscorite and some of the pegmatoid bodies. Large concentrations of vermiculite occur in the most northerly pegmatoid body, and the carbonatite forms the host for concentrations of copper sulphides. Small concentrations of

baddeleyite and uranothorianite occur in the phoscorite and carbonatite. At present copper, apatite, vermiculite and magnetite are mined intensively, and baddeleyite and uranium are being recovered as by-products. Reserves of copper available for an open-pit mine to a depth of 400 metres, at a grade of 0,7 per cent, are estimated at several hundred million tonnes; of thorium, at a grade of 0,01 per cent, at 36 000 tonnes; and of uranium, at a grade of 0,004 per cent, at 11 000 tonnes.

1.3.2 Tweerivier, Brits District, South Africa

The Tweerivier Carbonatite Complex is a roughly pear-shaped body, 5,4 km long and between 1,6 and 3,2 km wide, entirely surrounded by red Bushveld granite. The most prominent surface manifestations are three volcanic vents. On Tweerivier North the Complex consists of a heterogenous assemblage of dolomitic carbonatite with intercalated sövite and tremolite schist, into which an outer group of bifurcating and coalescing parankeritic beforite dykes was intruded, whilst on Tweerivier South quite different rock types, viz. gabbro, anorthositic gabbro, white crystalline limestone and a radioactive silicified ferruginous rock are met with.

On account of both the limited resources and the low average grades there is no indication of an economic uranium deposit, as is borne out by the following assay values (per cent) : U_3O_8 : 0,002–0,006; ThO_2 : 0,03–0,18.

1.3.3 Glenover, Thabazimbi District, South Africa

The Glenover Carbonatite Complex is almost devoid of outcrops and occupies a shallow circular depression about 13 km² in extent. Owing to differences in vegetation, the outline of the deposit could be traced by means of aerial photographs. A low hill 20 metres high, referred to as Breccia Hill, marks the centre of the plug. It consists of high-grade apatite breccia, and mining operations, together with boreholes and prospecting pits, have exposed the geology of the plug.

Two main types of carbonatite are present, viz. beforite and sövite. An extensive program of pitting has revealed that carbonatite is subordinate to biotite-pyroxenite and actually occurs in the form of dykes and sills traversing the latter. Large segments of the complex between lines of pits are unexplored and there is some justification for postulating an irregular, pipelike carbonatite body approximately at the centre of a biotite-pyroxenite plug, with core sheets and irregular intrusions of carbonatite emanating from the pipe.

Because of the extensive cover of surficial material, radioactivity is difficult to trace and interpret satisfactorily, but there seems little doubt that the Complex possesses a low but definite radioactivity. Radiometric assays of channel and borehole samples from several exposed radioactive zones ranged from 0,01 to 0,05 per cent U_3O_8 .

Green monazite is quite plentiful in some portions of the apatite breccia. It was deposited on apatite, quartz, specularite and brown limonite and is characterized by a very low thorium content of between 0,03 and 0,1 per cent.

There is no production of either uranium or thorium from this deposit and no viable deposits have been proved to date.

1.3.4 Ondurakorume, South West Africa

The Ondurakorume carbonatite is situated 55 km southwest of Otjiwarongo, where it projects as a prominent conical mountain approximately 300 metres above the plain.

The country rock consists of varied formations of the Damara Supergroup, amongst which marble, schist and granite are predominant. The outcrop expression of the intrusive is roughly circular, measuring between 1 200 and 1 000 metres in diameter. Drilling has established the vertical attitude of the body as well as its complex composition. In order of age, the predominant phases are as follows:

1. Intrusive primary white sövite, mainly poorly mineralized calcium carbonate, with cubes and aggregates of magnetite and crystalline apatite.

2. Moderately radioactive greenish-black beforsite, forming an irregular mass near the core and minor outlying lenses and plugs. Contains radioactive iron-rich veins and some apatite.
3. Brown beforsite, consisting of mixed Ca, Mg and Fe carbonates heavily impregnated with apatite which is present as plugs, lenses and ring dykes.
4. Moderately radioactive small lenses and ring dykes of dark grey-blue beforesite heavily impregnated with blue riebeckite, iron carbonate, strontium and rare-earth carbonates.

Apart from the widespread occurrence of apatite, very little mineralization is seen. Even magnetite associated with sövite is only locally prominent. Detailed mineralogical work showed that, in addition to the carbonates calcite and ankerite, ancylite, strontianite and carbocernaite were developed, as well as accessory amounts of monazite, pyrochlore, cerianite, zircon, columbite, pyrite and riebeckite.

Owing to certain extraction metallurgical difficulties and low average grades the deposit is not considered to be viable at the present stage, although indicated tonnages of some of the minerals are significant.

Average grades were as follows (percentages): U_3O_8 : 0,002; Th_2O_5 : 0,003; Nb_2O_5 : 0,24; $SrCO_3$: 2,5; REO : 3,0.

1.4 Pyroxenite

1.4.1 Fort Dauphin, Southern Madagascar

According to Raubault (1956), uranium-bearing rocks are located along an arc, approximately 150 km long and between 30–40 km wide at best, between Fort Dauphin and the basin of the Mandrarè River in Southern Madagascar. The uranothorianite is closely associated with masses or lenses of pyroxenite which contain diopside and are interstratified in Precambrian crystalline schists which are very common. Lenses vary in length and may reach several hundred metres. Uranothorianite occurs *in situ*, associated with masses of phlogopite, calcite and anorthite, but may also be disseminated in the pyroxenite. Secondary alluvial and eluvial deposits of uranium are considered to have been derived from earlier deposits.

2. DIATREMES

2.1 Navajo and Hopi Reservations, Arizona, USA

Uranium deposits have been found in, or associated with, diatremes in widely separated parts of the Navajo and Hopi Indian Reservations in Arizona, where some 250 are known to occur. Some of these diatremes have several features in common with the diamond pipes of South Africa and contain pyroclastic material similar to kimberlite in composition. They have been described by Schoemaker (1956).

A fully developed diatreme in its upper portion is filled with bedded tuff and limestone, and in places with thinly laminated clay and siltstone, evaporites and even some bedded chert. Lower in the vent these sediments give way to more massive tuff, breccia, huge blocks of country rock, agglomerate, and ultimately to solid igneous rock.

The volcanic rocks associated with the diatremes are nearly all alkaline basalts which may be classified as manchiquites and minettes. Both types are usually compared with Colorado Plateau olivine basalts and contain average equivalent uranium (eU) of 0,001 2 and 0,004 6 per cent, respectively. Radioactivity is due to concentrations of both uranium and thorium minerals which are largely not acid-soluble.

For the most part the mineralized rock contains no visible uranium minerals; these are so fine-grained that even microscopic identification is difficult. Carnotite, becigite and metatyuyamunite have been identified, together with trace amounts of silver, cobalt, nickel, lead and thallium. Although small deposits approaching ore grade are present in a few diatremes, no viable deposit is known.

Schoemaker (1956) suggests a syngenetic origin and that the uranium could have been derived from hydrous, phosphate-rich, moderately uraniferous monchiquite magma, situated at depth beneath and in the diatremes.

2.2 Spors Mountain, Juab County, Utah, USA

More than 40 fluorspar deposits containing uranium are known to occur on Spors Mountain, Juab County, Utah, USA. The rocks of Spors Mountain are chiefly marine limestone, shale, quartzite and dolomite, ranging in age from Lower Ordovician to Middle Devonian. These rocks are cut by Tertiary plugs and dykes of latite, rhyolite, and dellenite; volcanic explosion pipes filled with breccia are common along the east side of Spors Mountain. The fluorite deposits are of three types: pipelike bodies, veins and disseminated deposits. The most abundant ore is soft white to dark purple and occurs as pulverulent masses or as boxworks.

The uranium content of the pipes varies considerably between 0,003 and 0,33 per cent uranium. Only four of 19 pipelike bodies from which fluorspar has been produced contained more than 0,01 per cent uranium, and only one of these yielded a sample containing more than 0,20 per cent uranium. There is also a sharp decrease in uranium content with depth.

Both the fluorspar and the uranium are believed to have been derived from the same magma and to have formed during the closing stages of the vulcanism that was responsible for the plugs and dykes of Spors Mountain.

2.3 Mokta, Carswell Area, Saskatchewan, Canada

Three most interesting uranium deposits have been discovered recently very close to the contact of the Archaean basement and younger sandstone in the above-mentioned area, in which uranium is associated with gold, vanadium, platinum, selenium, copper and nickel.

All the deposits are found close to Cluff Lake, which is on the south side of the prominent, circular Carswell structure, within the Athabasca sandstone basin. It is outlined by a discontinuous ring of dolostones (fragmental dolomite) of the Carswell formation that, in contrast to the surrounding flat-lying Athabasca sandstone, are folded and, in places, overturned about axes that commonly parallel the outline of the structure. Outside and inside diameters of the collar or annulus of the structure are 40 km and 29 km respectively. A core of uplifted basement rock underlies the central zone which is about 18 km in diameter.

The Carswell structure has been variously interpreted as a possible cryptovolcano, a diapiric structure and eroded impact crater. Volcanic-like rocks termed Cluff breccias occupy dykes and veinlets in places.

Of the three deposits discovered so far, the one marked "D", although small, is particularly rich, averaging 10 per cent U_3O_8 . It measures 100 x 20 metres at surface and is 10 metres deep.

The Cluff Lake deposit occurs close to a fault, and coffinite and uraninite are always associated with organic matter. The deposit is roughly 30 metres long and 50 metres wide. Ore-containing beds are from 0,3 to 3 metres thick in a sequence of 130 metres. Average grades are 1,2 per cent U_3O_8 . The third deposit occurs in a highly faulted area between two magnetically different basement-rock types.

No satisfactory explanation for the genesis of these deposits has been forthcoming at this early stage of the investigation. Pitchblende occurs with shale in a shale-sandstone sequence, probably overturned and overlain by basement, the whole structure forming an antiform.

2.4 Quaternary of Central Italy

Mittempergher (1970) has described uranium and iron sulphide exhalative supergenic mineralization from three volcanic districts in central Italy. These volcanics are Pleistocene in age; they are built up by alkaline-potassic rocks and are characterized by the feldspathoids leucite, kalsilite and melilite. Ignimbrites and tuffs prevail over lava flows, and petrochemically the volcanites are represented by K-trachytes, undersaturated latites and phonolitic tephrites.

The mean uranium content of the volcanites is 25 ppm, and the maximum 50 ppm, and of thorium 130 ppm and 240 ppm, respectively. The uranium mineralization is related to magmatic H₂S exhalations and to supergenic weathering of exhalative pyrite and marcasite. Furthermore, the ore deposits are controlled by the surficial and underground hydrology. Common to all mineralized areas is the emission of CO₂ gas with small amounts of H₂S.

The mineralized areas all exhibit zonation with thick layers of bleached, silicified and kaolinized volcanic rocks at the top followed by alternate bands containing iron sulphides (pyrite and marcasite) and uranium, at depth. Mineralization follows a hydrostatic and not a stratigraphic horizon, and exhibits a regular slope with respect to drainage valleys. The author classifies the mineralization as exhalative-supergenic and states that

"Uraniferous bodies have been found around small rivers, the thickness of the mineralized beds is between two and three metres and the content of uranium decreases going away from the exhalative zone. The best and most regular deposits are about one km long and some hundred metres wide. Inside these bodies the U content is variable. Maximums have been recorded but the average determined till now has not exceeded 300 to 400 ppm of U".

3. SHEAR ZONE AND BRECCIA DEPOSITS

3.1 Singhbhum Thrust Belt, Bihar, India

Uranium deposits occur in an arcuate thrust zone 160 km long, which swings around the northern margin of the cratonic block of Singhbhum granite in South Bihar. Although the mineralization has been described as hydrothermal in nature and of the vein type, some uranium is also widely disseminated in crush and breccia zones and therefore also qualifies for inclusion under Other Uranium Deposits.

The following description has been culled from the paper by Bhola, K.L. *et al.* (1964):

The Singhbhum Thrust Belt is well known for its copper, apatite-magnetite and kyanite deposits. It trends east-west and traverses Precambrian metasediments comprising closely folded mica schists, quartzites, conglomerates and metamorphosed basic lavas. The rocks have been overfolded and sometimes overthrust, accompanied by severe crushing and mylonization along a zone from 100 metres to 300 metres wide.

Uranium occurs as lenses in *en échelon* pattern both along the strike as well as at depth. The shear zones appear to form the main control for uranium as well as copper, although the lithological characters of the host rocks have also partly influenced the pattern and grade of mineralization. Workable concentrations of uranium are, however, observed only where cross folding and later fractures are dominant.

There are a number of uranium deposits along the belt in various stages of exploration in the rocks of the Iron Ore Series, which were mylonitized to various degrees in various places. At Jaduguda, the main deposit, the thrust zone is composed mainly of quartzite which is crushed, fractured and brecciated. Uranium mineralization is present as disseminations in a 120-metre wide zone in quartzite breccia. The main ore minerals are uraninite, torbernite and autunite which occur frequently in the surficial zone. The average grade is 0.067 per cent U₃O₈.

Studies of mineral paragenesis indicate that mineralization along the thrust belt took place over a long period, the minerals being deposited in two stages, the first to form being apatite and magnetite, closely followed by uranium mineralization, and the sulphides, including chalcopyrite, were the last to be deposited.

3.2 Golden Gate Canyon, Jefferson County, Colorado, USA

Pitchblende and secondary uranium minerals are found in or near Laramide fault zones that cut gneiss, schist and pegmatite of Precambrian age in the above-mentioned area. The fault zones, or "breccia reefs", are extensive structures as much as seven metres wide and possibly many kilometres long. They consist of ankerite and potash feldspar as a matrix enclosing partly replaced rock fragments. Pitchblende and base-metal sulphides occur as thin films, or more commonly as colloform masses less than 0,1 mm in diameter, that densely coat crystals of ankerite of comparable size. They are irregularly distributed through intensely altered wall rock, and are replaced in varying degrees by later sulphides.

The localization of uranium mineralization appears largely to be the result of the composition and texture of the wall rock and was probably effected by the oxidation of ferrous to ferric iron. The studies made during this investigation lead to the conclusion that pitchblende-bearing veins of the carbonate type can be expected where ample ferrous iron is available in the wall rocks, and that, in a sulphide environment, conditions resulting in the oxidation of either iron or sulphur may precipitate pitchblende.

Three mines and several prospects lie in an area of about 8 km². Shipments of ore from the Ascension Mine in 1956 amounted to 466,9 tonnes containing 0,23 per cent U₃O₈. In 1960 the mine shipped a further 1 026 tonnes of ore containing 0,27 per cent U₃O₈.

3.3 Gunnar Mine, Athabasca Region, Saskatchewan, Canada

Since the discovery in 1952 of frost-heaved radioactive boulders in muskeg close to St. Mary's Channel, an ore body about 80 metres in diameter, plunging from surface to a depth of 300 metres below the shoreline of Lake Athabasca, was outlined by drilling. Between 1955 and 1961 total production from open-pit and underground mining amounted to 5,6 million tonnes of ore of an average grade of 0,175 per cent U₃O₈ which was remarkably constant throughout the ore body.

The country rock is fine-grained paragneiss overlain conformably by coarse-grained granitized gneisses and metasomatic granite, referred to collectively as the Gunnar granite. Albitization of the latter caused the formation of small, irregular, tabular-shaped bodies less than 500 metres long and 125 metres wide, composed primarily of albite with minor amounts of quartz and dark accessory minerals, termed "syenite", which acted as host to the uranium mineralization. The ore body consisted of brecciated and mineralized parts of the syenite mass. Its surface expression was roughly circular, with a diameter of some 150 metres. It plunged from surface at 45 degrees. The ore minerals were pitchblende and uranophane, the latter representing only a small fraction of the total uranium present. The uranium minerals are finely disseminated in the syenite and are for the most part not visible macroscopically. The only important gangue minerals are calcite and hematite.

The ore was considered to be of hydrothermal origin, and uranophane was believed to be primary except near the surface. The impression is that the breccia pipe bears a spatial relationship to a number of large faults in the area and that one or more of these faults provided a conduit for ore fluids.

4. SUPERGENE DEPOSITS

4.1 Athabasca Region, Saskatchewan, Canada

Supergene occurrences of uranium due to surficial secondary enrichment were widely recognized in the Beaverlodge area of the Athabasca region where there was uranium mineralization; however, they were not economic, probably mainly because most of them were formed since the Pleistocene. The Athabasca region was above sea level during much of the Phanerozoic and underwent a long period of denudation resulting in peneplanation. Supergene deposits

undoubtedly formed during this period and their absence at the present time is due to erosion by the Pleistocene sheet. Secondary minerals are found in only minor amounts at or near to the surface of deposits, except in a few of the ore zones located on major faults, where supergene alteration has extended to depths of around 50 metres.

The supergene deposits are generally superimposed on, and transitionally downward into, the other types of deposits. The most common secondary uranium minerals formed are uranophane and liebegite. They invariably form only a thin zone at the surface, and very rarely occur at depth along a fault zone.

The two best-known showings of supergene uranium were at Middle Lake, 16 km east of Stony Rapids, described by Beck (1970), and the 1 525 tonnes of uranium-rich material at Balger, east of Verna Lake, which averaged 0,7 per cent U_3O_8 .

4.2 Uranium Deposits in Portugal

Dias and de Andrade (1970) consider all the uranium deposits of Portugal to be supergene in origin. They are correlated with the contact between metasediments, considered to be Precambrian to Neo-Devonian in age, and Hercynian younger granites which have a high radioactivity background.

The aureole of contact metamorphism does not extend beyond a width of 3 km. Uranium deposits are always confined to this aureole and rarely extend further than 50 m in depth.

Mineralization occurs in fractures close to the roof and walls of the granite and in metasediments. These brecciated structures normally originated under tangential tectonic movements which caused shear faults and mylonitization without any recrystallization of the rock elements. The most common associated wall-rock alterations are hematization, limonitization and seritization which all form favourable loci for uranium deposition. Mineralization is also always associated with surfaces of peneplanation, and where this has been destroyed no mineralization occurs.

The most common uranium minerals are pitchblende and coffinite, which are associated with near a dozen secondary coloured minerals of which the most common are autunite, torbernite uranocirrate and sabugalite. Rarely found are uranophane, beta-uranophane, saléeite, phosphuranylite, parsonite, uranopilite and zippeite. Only pyrite and marcasite appear regularly as non-uraniferous minerals, and galena, chalcopyrite, sphalerite and arsenopyrite are found only sporadically.

4.3 Uranium Deposits in Spain

Uranium deposits very similar to those described as occurring in Portugal also occur in Spain; they have been described as occurring in the Salamanca Province by Fernandez Polo (1970), and in the Badajoz Province near Don Benito by Ramirez (1969).

At Salamanca, Hercynian granodiorite and adamellite, intrusive into Cambrian pelitic sediments, are responsible for a thermal aureole along which spotted slates and hornfels occur in a succession, together with quartzite and limestone.

Mineralization occurs along bedding and joint planes together with some organic material and, although lenticular in nature and intermittent, is fairly large in size and is economically viable. This mineralization is in the form of stockworks, is of supergene origin and is confined to the metamorphic aureole which may be from 200 metres to a kilometre wide. The uranium ore comprises pitchblende, uranophane, autunite and torbernite, with minor phosphuranylite, renardite, saléeite, ianthenite and uranopilite. Associated accessory minerals are pyrite, chalcopyrite, galena and melnikovite. The gangue minerals are mainly quartz, jasper, barite and calcite.

4.4 Yeelirrie, Western Australia

Yeelirrie is a semi-arid, open scrubland forming part of an ancient plateau approximately 500 metres above sea level, which is underlain by Archaen rocks consisting largely of granite.

During the Tertiary, the area was deeply eroded by a major river system draining in a south-easterly direction toward the Great Australian Bight. Although the average yearly rainfall for the area is 250 mm, permanent surface water has disappeared. The present drainage system contains an aquifer which carries appreciable quantities of subterranean water varying in quality from potable to highly saline.

The Yeelirrie mineralization has formed in sediments comprising sand, clay and calcrete, which fill one of these old river channels. The uranium was deposited as carnotite from ground-water percolating through the river fill, and occurs as thin films in horizontal layers lining the voids and cavities along 45 km of the channel, principally within eight metres of the surface.

Reconnaissance exploration at Yeelirrie has outlined an area of 45 km by 3 km, which contains anomalous uranium values; ten kilometres of the area was tested in detail by drilling. An ore zone measuring 6 000 metres by 5 000 metres, and eight metres thick, was proved; this zone is estimated to contain 46 000 tonnes U_3O_8 at an average grade of 0,15 per cent, of which 24 000 tonnes are above 0,36 per cent. As the ore is close to the surface, is of a high grade and can be easily mined, it is quite clear that an economic operation can be undertaken.

4.5 West Coast, Southern Africa

Semi-arid and desert areas border the coast of Southern Africa from north of the Oliphants River mouth (approximately 32° south latitude) for more than 1 500 km, throughout South West Africa and into Angola. It forms a windswept, barren, desolate belt varying in width from 25 to 150 km. The coast is for most of its length either rock-bound or, as is more often the case, bordered by great expanses of yellowish sand, often piled up into hills as high as 200 metres in the area south of Walvis Bay. Raised beaches, salt-pans and dried-up lagoons, the surfaces of which are covered with crystals of gypsum and encrustations of salt, are encountered at numerous localities along the coast and testify to its recent uplift relative to the sea. This uplift has been dated as post-Miocene by Wagner (1916), but he also states "that it has been in progress for a very considerable time".

The desert everywhere rises fairly rapidly towards the interior and, in consequence, attains a considerable elevation within a comparatively short distance of the coast. It therefore has the character of a sloping plain, underlain by eluvial material derived from ranges of hills of characteristic jagged outline, half-smothered in their own débris, and by isolated eminences of the inselberg type.

The area as a whole is poorly watered, as the rainfall is generally extremely low. Mean annual rainfall is less than 100 mm. The many episodic rivers north of Walvis Bay, which rise near the escarpment edge, are normally run-off courses and are effectively barred to the sea by coastal dunes. Over wide areas they effectively cover ancient dry river courses which, like all those exposed at surface south of the Cunene River, provide evidence of Pleistocene pluvial and interpluvial periods. There can be little doubt that the continental margin at present receives considerably less terrigenous sediment than has been the case in the past.

Groundwater, where encountered in certain parts of the desert, has a high content of various salts, particularly carbonates and bicarbonates, which are effective uranium solvents. Destruction by weathering and erosion of uranium-rich rocks and veins have, over a considerable period of time, released uranium, some of which has become reconcentrated in suitable environments—over a hundred localities have been traced by aerial spectrometer surveys—whilst an unknown amount of uranium has been transported to the sea by circulating waters.

A number of factors, both continental and marine, exerted a strong influence upon the sedimentation, stratigraphy, structure and history of the west coast. The history of the formation of the coastal plain probably began in Cretaceous times, or even earlier. There is evidence of marine transgression in Upper Cretaceous times and in the Eocene, of uplift in the Miocene, and

of intermittent movements during the late Tertiary and Quaternary. Along its inner edge inselbergs of old rocks are frequent. Stocken has indeed shown that, since the Pleistocene, there have been four marine regressions, each followed by successively smaller transgressions accompanied by differential longitudinal warping.

It can thus be taken for granted that the plain was submerged over long eons of time during the Eocene (16 million years) and Oligocene (19 million) years. The basement rocks constituting the plain must have been completely filled with water and circulation must have been at a minimum, if not zero. This means that, under these conditions, oxidation was non-existent for a period of 35 million years. Diffusion was the only important operative mechanism and probably caused the introduction of various salts into the rocks. At times of uplift above sea level, potential sites of uranium deposition could be removed by denudation, and uranium concentration of groundwater and seawater would again increase.

Over a considerable period of the Quaternary up to the present time, these rocks have experienced an arid climate and have been above the permanent water table which is adjusted to the number of large rivers, such as the Swakop and Khan, which drain the plain. There is much sulphate left, e.g. gypsum and other minerals, but the chlorides, which must have been present, have disappeared. The sulphates are intimately associated with uranium minerals, but gypsum is just as common in places not containing any uranium.

There is no reason to doubt that a number of marine transgressions affected the plain from Upper Cretaceous times, through the Eocene and Miocene, right up to the Pleistocene, but, as the above speculation illustrates, it would be nigh impossible to reconstruct the history of sedimentation and denudation of older uraniferous plain deposits, even granting that such deposits were preserved at all.

The historical evidence indeed strongly endorses the results of field observations and of study of these surficial deposits which all bear the stamp of being very recent in origin. Many of them are confined to present-day water courses and it would not come as a surprise if most of them were formed since the last Pleistocene transgression.

5. BRINES

5.1 Oil Field Brines Containing Uranium, USA

About 200 asphalt-bearing Paleozoic and Mesozoic rocks from 49 areas in south, central and western United States were analyzed for uranium. The average uranium content for seven areas ranged from 0,028 to 0,376 per cent. In 13 additional areas the average uranium content ranges from 0,02 to 0,068 per cent uranium in the ash of the extracted oil. Although petroleum is therefore capable of transporting small amounts of uranium, this process is not important in the formation of uranium ore deposits.

Uranium related to petroleum-bearing and gas-bearing structures have been described as occurring in Texas, Wyoming, Utah, New Mexico and Oklahoma. The important uranium-producing areas of Wyoming, Utah and New Mexico are underlain in part by oil-producing and gas-producing formations which give rise to asphalt and gas seeps with which deposits of uranium are often closely associated. Uraniferous asphaltite or piobitumen is a very common type of uranium ore at Ambrosia Lake, Temple Mountain and other places on the Colorado Plateau. It has been suggested that this uraniferous asphaltite represents dead oil left behind in a breached or partially flushed oil trap.

Host rocks in which the asphalt is found include sandstone arkose, tuff, limestone, diatomite and alluvium. The uranium was concentrated as an organo-uranium complex in the asphalt, and not in the host rock. Apparently the uranium occurred as an original constituent of the oil or was introduced during the migration of the oil. Several uranium ore deposits are located above or near producing oil fields such as Lance Creek, Wyoming and Cement, Oklahoma.

5.2 Closed Basins

Uranium, like other elements, can be concentrated in mineralized water in a closed basin. For this to occur, it is necessary to have special conditions, viz.:

1. The environment must consist of uranium-bearing rocks.
2. The area must be a desert or semi-desert where the evaporation of water is higher than the rainfall. Because of this, the rainwater in this basin flows in deep levels beneath the basin and is concentrated.

The uranium content of the liquid depends on the length of time during which the basin is closed. High concentrations are found only in very old basins. These conditions exist not only now, but also prevailed in earlier geological times. It is, therefore, necessary to know the paleogeographical and paleoclimatological conditions of an area. The closed basin is found in both banded deserts and semi-deserts such as occur in Asia, Africa and Australia. It is recommended that geochemical studies be made in these regions to find this unusual type of uranium occurrence.

6. URANIUM OF MARINE ORIGIN

Marine areas constitute 71 per cent of the world, as against the 29 per cent consisting of solid earth, so it is easy to understand why speculation concerning mineral resources in this largely unexplored region generates a high interest.

Seawater contains 0,000 15–0,001 6 ppm of uranium. Although this is a very low concentration, the total amount of uranium in seawater is very large. It seems reasonable to suppose that a small amount of byproduct uranium will be recovered in the near future from desalination plants or from plants recovering magnesium from seawater.

The continental shelves, which form the near-shore division of the continental margins, were almost entirely exposed as dry land during Pleistocene time when much of the world's water was locked up in ice caps and glaciers, causing the oceans to retreat almost to the shelf edges. Fluvial sand and gravel, deposited at this time, were reworked by wave action as the sea rose again and inundated the shelves at the close of the Ice Age.

Mineable concentrations of minerals (diamonds, tin, iron, limestone, sulphur, barite) occur on the continental shelves in buried river and beach placers, in submerged residual concentrations, in surficial deposits of bulk commodities such as sand and gravel, and in consolidated stratified deposits, either exposed or buried beneath the sea.

As has been demonstrated by the diamond-dredging operations which were conducted off the west coast of South West Africa between 1961 and 1971, offshore mining of semi-consolidated deposits using conventional mining equipment adapted to the marine environment is technically feasible in shallow water, although operating costs are high in a hostile physical environment.

6.1 Uraniferous Phosphatic Rocks

Finch *et al* (1972) give the following excellent summary on uraniferous phosphatic rocks:

"Most phosphatic rocks are uraniferous and their uranium content generally increases with the phosphate content. Marine phosphorite is the dominant source of phosphate and constitutes a very large resource of uranium. In such rocks, geosynclinal facies tend to be more uraniferous than platform facies. Uraniferous marine phosphorite deposits, commonly 5–10 feet thick, underlie hundreds of square miles, and their uranium content generally ranges from 0,007 to 0,07 per cent U_3O_8 . Phosphorite beds in the Phosphoria Formation of Permian age underlie 135 000 square miles of Idaho, Montana, Utah, and Wyoming (McKelvey and Carswell, 1956). Their uranium content ranges from 0,001 to 0,075 per cent U_3O_8 , but beds more than three feet thick

and with more than 31 per cent P_2O_5 generally average 0,012–0,024 per cent U_3O_8 . Phosphorite in the Bone Valley Formation of Pliocene age in the land-pebble phosphate field in Florida ranges in thickness from six to seven feet over several hundred square miles and averages 0,012–0,024 per cent U_3O_8 and 20–30 per cent P_2O_5 (Altschuler and others, 1956). Uranium in marine phosphorite deposits was probably deposited from seawater during sedimentation, or in some places possibly later by downward percolating groundwater.

"Large portions of extensive deposits of marine phosphorite in countries along the Mediterranean Sea from Morocco to Israel contain at least 0,01 per cent U_3O_8 (Davidson and Atkin, 1953). Near Recife, Brazil, deposits of phosphorite somewhat like those in Florida yield phosphate products that contain 0,02 per cent U_3O_8 . Phosphorite that fills large depressions formed by solution of dolomite in the Central African Republic are also uncommonly rich in uranium (Mabile, 1968). Deposits of aluminium phosphate in Senegal and Nigeria are also uraniferous. Marine phosphorite of Cambrian age in the Kara-Tau Mountains, Kazakhstan, USSR, resemble the Phosphoria Formation and are probably uraniferous."

6.2 Continental Shelf Deposits off Walvis Bay

A number of investigators have described four separate basins on the continental shelf opposite the coast of South West Africa, which contain offshore muds. By far the best developed basin extends north and south of Walvis Bay, with a protrusion, representing a sediment-filled scour channel, opposite the Swakop River at Swakopmund. Similar smaller basins exist off the coast between the Unjab and Hoanib Rivers (bisected by latitude 20° south); north of Hollams Bird Island (bisected by $24^\circ 25'$ south latitude) and opposite Naribus (bisected by 25° south latitude).

The bathymetric maps show a depth of water of between 50 and 150 metres over these basins, and depths of diatomaceous mud of from less than two up to 15 metres thick have been proved in them by core drilling.

The results of a shallow-penetration seismic and bottom-sampling program, in an attempt to outline the distribution and thickness of uraniferous muds found off the west coast of Southern Africa during a Scripps Institution campaign in 1968, have been described by Meyer (1973).

The survey was undertaken with the "Gemsbok", a 314-ton, 45-metre-long vessel, equipped with a Decca Mark 21 navigation system, a 18-kHz ELAC echo sounder and a 10-metre barrel-length pistol corer plus handling device.

Within less than a month, four mud basins with a total surface area of 19 000 km² and a mud thickness of 15 metres at maximum, were traced within a total area of nearly 40 000 km² which was surveyed. At the same time, distribution and thickness of mud were continuously evaluated on board with the help of seismic records which covered a length of nearly 4 000 km.

The mud is generally olivine-green-grey, soft, and homogeneous, with an ubiquitous smell of H_2S . The mud was sampled and examined with the help of 41 piston cores (201 metres in length) of which 21 penetrated the whole mud sequence and reached the underlying strata which consists of hard siltstone, stiff clay and brecciated terrestrial material. The mud is extremely fine-grained, with 70–80 per cent grains finer than six microns. It consists for 53–73 per cent of siliceous matter, the rest being made up of material derived from foraminifera, ostropods, pteropods, gastropods, lamellibranchs, bentonite and sharks' teeth. The highest uranium concentrations of 44–51 ppm occurred opposite $22^\circ 50'$ and 25° south latitude. Values ranged between five and 93 ppm, with an average value of 21 ppm, which exceeds the maximum of the range (10–20 ppm) for the Black, Caspian and Baltic muds.

The only other significant values obtained were for molybdenum (range 20–120 ppm, average 62 ppm) and vanadium (range 60–180 ppm, average 112 ppm).

REFERENCES

- ADAMS, J.W. AND STUTGARD, F. JNR. (1955) : Wall-rock Control of Certain Pitchblende Deposits in Golden Gate Canyon, Jefferson County, Colorado, Peaceful Uses of Atomic Energy. Proc. 1st Int. Conf., Geneva, v. 6 p. 279.
- BARRINGTON, J. AND KERR, F. (1961) : Uranium Mineralization at the Midnite Mine, Spokane, Washington. Econ. Geol. v. 56(2) p. 241.
- BECK, L.S. (1969) : Uranium Deposits in the Athabasca Region. Rep. 126. Dep. Mines. Res. Sask. Canada.
- BHOLA, K.L.; UDAS, G.R.; MEHATA, N.R. AND SAHASRABUDHE, G.H. (1958) : Uranium Ore Deposits at Jaduguda in Bihar State, India. Peaceful Uses of Atomic Energy. Proc. 2nd Int. Conf., Geneva, v. 2 p. 704.
- DAVIS, M.; BOWIE, S.H.U.; OSTLE, D.; LOOSEMORE, W.R.; SMITH, S.E. AND WHITE, P.A. (1971) : United Kingdom Research and Development Work in Aid of Future Uranium Resources. Peaceful Uses of Atomic Energy. Proc. 4th Int. Conf., Geneva, v. 8 p. 59.
- EVOY, E.F. (1961) : Geology of the Gunnar uranium deposit, Beaverlodge area, Saskatchewan. Ph.D. thesis, University of Wisconsin (unpublished).
- FERNANDEZ POLO, J.A. (1970) : Caracteres geologicos estructurales y genéticos de los yacimientos uraniferos de Salamanca. Energia Nuclear—Ario XIV—Marzo—Abril 1970 de la Revista.
- FINCH, W.I.; BUTLER, A.P.; ARMSTRONG, F.C.; WEISSENBORN, A.E.; STAATZ, M.H. AND OLSON, J.C. (1972) : United States Mineral Resources—Nuclear Fuels. USGS Prof. Paper 820.
- GRIFFITH, J.W. (1967) : The Uranium Industry—It's History, Technology and Prospects. Min. Rep. 12. Min. Res. Div. Ottawa, Canada.
- HAIL, W.J. Jr.; MYERS, A.T. AND HERR, C.A. (1955) : Uranium in Asphalt-bearing Rocks. Peaceful Uses of Atomic Energy. Proc. 1st Int. Conf. Geneva, v. 6 p. 489.
- HANEKOM, H.J.; VAN STADEN, C.M.; SMIT, P.J. AND PIKE D.R. (1965) : Geology of the Palabora Igneous Complex. Mem 54. Geol. Surv. S. Afr.
- MacKEVETT JR., E.M. (1958) : Geology of the Ross-Adams Uranium Thorium Deposit, Alaska. Peaceful Uses of Atomic Energy. Proc. 2nd Int. Conf. Geneva, v. 2 p. 502.
- MATOS DIAS, J.M. AND SOARES DE ANDRADE, A.A. (1970) : Uranium Deposits in Portugal. Uranium Exploration Geology. Proc. Panel. p. 142. IAEA Publ. Vienna.
- MEYER, K. (1973) : Uran-Prospektion vor Südwestafrika. Erzmetall. Bd. 26(7) p. 313.
- MITTEMPERGER, M. (1970) : Exhalative-supergenic uranium mineralization in Quaternary alkaline volcanic rocks in central Italy. Uranium Exploration Geology, Proc. Panel, p. 177. IAEA Publ. Vienna.
- PARBO, A.H. (1972) : Yeerillie Uranium Deposit. Western Mining Corporation, Director's report.

RAMIREZ, E. (1969) : Estudio geológico de los yacimientos uraníferos de "Mesas de Poyato" y "Hoya del Lobo", La Serena (Badajoz).

ROUBAULT, M. (1956) : The Uranium Deposits of France and French Overseas Territories. Peaceful Uses of Atomic Energy. Proc. 1st Int. Conf., Geneva, v. 6 p. 152.

RUSSELL, R.T. (1958) : Relationship of Uranium Ore Deposits to Petroleum and Gas-bearing Structures. Peaceful Uses of Atomic Energy. Proc. 2nd Int. Conf., Geneva, v. 2 p. 358.

SHARP, B.J. AND HETLAND, D.L. (1954) : Preliminary report on uranium occurrences in the Austen area, Lander County, Nevada. USAEC RMF-2010.

SCHOEMAKER, E.M. (1956) : Occurrence of Uranium in Diatremes in the Navajo and Hopi Reservations, Arizona, New Mexico, and Utah. Peaceful Uses of Atomic Energy. Proc. 1st Int. Conf., Geneva, v. 6 p. 412.

SORENSEN, H. (1970) : Low-grade uranium deposits in agpaitic nepheline syenites, South Greenland. Uranium Exploration Geology, Proc. Panel p. 151 IAEA Publ. Vienna.

STAATZ, M.H. AND OSTERWALD, F.W. (1956) : Uranium in the Fluorspar Deposits of the Thomas Range, Utah, USA. Peaceful Uses of Atomic Energy. Proc. 1st Int. Conf., Geneva, v. 6 p. 275.

TÁVORA, E. (1964) : Nuclear Fuel Supply : Programme and Results in Brazil. Peaceful Uses of Atomic Energy. Proc. of 3rd Int. Conf., Geneva, v. 12 p. 64.

THURLOW, E.T. (1956) : Uranium deposits at the contact of metamorphosed sedimentary rocks and granite intrusive rocks in western United States. US Geol. Surv. Prof. Paper 300 p. 85.

TREMBLAY, L.P. (1972) : Geology of the Beaverlodge Mining Area, Saskatchewan. Mem. 367. Geol. Surv. Canada.

VERWOERD, W.J. (1967) : The Carbonatites of South Africa and South West Africa. Handbook 6, Geol. Surv. S. Afr., Pretoria.

VINOGRADOV, A.P. (1962) : Average contents of chemical elements in the principal types of igneous rocks of the earth's crust, *Geokhimiya*, no. 7 p. 555.

WAGNER, P.A. (1916) : The geology and mineral industry of South West Africa, Mem. 7, Geol. Surv. S. Afr., Pretoria.

DISCUSSION

H. D. FUCHS: To my knowledge you are the first to have attempted to classify the so-called calcrete or Yeelirrie-type deposits, and I see that you have described them as supergene deposits. I wonder whether this is really justified. If supergene deposits include any that are formed by uranium leached from source rocks and precipitated in a favourable environment, we would have to put the sandstone deposits in this category too. I think, therefore, that we might be wise to wait for some time before

classifying calcrete deposits, until more detailed studies have been done. From the little knowledge I have of them, I would be inclined to call them evaporite deposits.

J. W. von BACKSTRÖM: I quite agree with your suggestion that it would be wise to wait a while before attempting any firm classification. I called the calcrete deposits supergene here simply for want of a better place to put them, but the classification should certainly be reviewed later.

J. E. FROST: The Yeelirrie deposits should in my opinion be classified as evaporite or efflorescent deposits, and the mechanism of formation does appear to be similar to that of the calcrete or caliche deposits.

J. CAMERON: I must take issue with Mr. von Backström - or more correctly with his sources Messrs Matos Dias and Soares de Andrade - about the classification of all the uranium deposits of Portugal as supergene.

In my view such a classification gives a wrong impression as the uranium occurrences in the granites are in vein structures and these deposits should be classified as "vein deposits" and indeed are included, in my view, correctly, in Mr. Smith's review paper¹ as part of the Western European vein deposits.

The source of the uranium in the Portuguese vein deposits is, however, perhaps worth discussing. As a result of many years of work on these deposits, two papers² of mine were published in 1959 and 1960 and if I may briefly summarize the conclusions and add some more recent information, it may be of interest.

The veins are of the siliceous-pyrite-galena type and four main districts in the Beira granites of north-central Portugal are recognized, Urgeiriça, Reboleiro, Guarda and Bendada. The host granite is of Hercynian age with a high uranium content (40-50 ppm) and the veins follow a complex but generally NE-SW orientated fracture system related to the uplift of the Serra da Estrela mountain block during Alpine movements. The uranium-bearing fractures and the contained pitchblende can be dated as Tertiary in age.

Three main vein types occur, red jasper, ferruginous white quartz and black and white banded quartz veins. The red jasper type contains the best uranium values. Alteration of the granite wall rock plays an important role, the two principal types of alteration being sericitization which is the earlier in age and hematitization. Sericitization is the most common type and shows a selective attack on the normal granite, first altering the biotite and then, with more intensive alteration, the oligoclase, orthoclase and quartz and producing, under intense alteration, a massive green-coloured rock in which only fragments of muscovite and quartz from the original granite remain visible. There is a selective removal of Fe, Al, Mg, Na and Ca and an addition of SiO₂. This is probably due to the action of alkaline hydrothermal solutions with temperatures of above 100°C. Each type of alteration may occur by itself or hematitization may overlie sericitization to produce a green-pink speckled rock.

From a study of many drill holes in the Urgeiriça district, it was found that around individual ore shoots there was a general tendency that the greater the width of sericitic alteration the poorer were the uranium values

¹ SMITH, E. E. N., these Proceedings, Paper IAEA-SM-183/45.

² CAMERON, J., Structure and Origin of Some Uranium-bearing Veins in Portugal, Junta de Energia Nuclear, Lisbon, Technical Paper No. 22 (1959); The Ore Controls of Some Uranium Vein Deposits in Portugal, Junta de Energia Nuclear, Lisbon, Technical Paper No. 26 (1960).

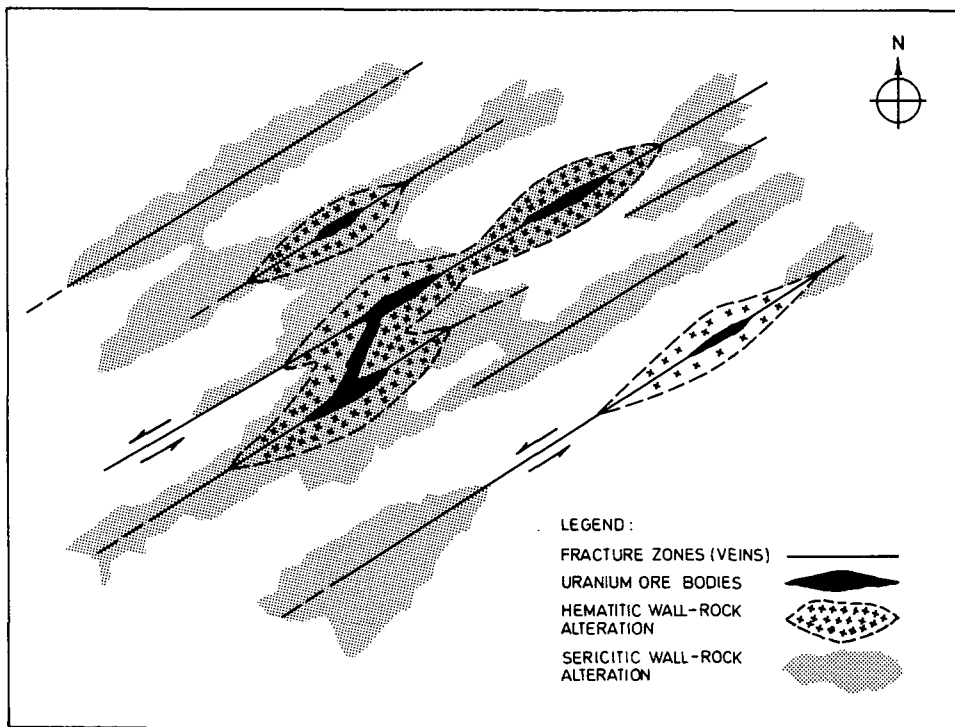


FIG. A. Diagrammatic representation of the relationship between uranium ore bodies, sericitic and hematitic wall-rock alteration, Urgeiriça district, Portugal.

in the enclosed fracture. On the other hand it was very clear that the greater the width of hematitic alteration, the greater was the uranium content in the enclosed fracture.

A diagrammatic representation of the relationships is shown in Fig. A.

On a district scale, however, the total amount of sericitization is directly relatable to the total U_3O_8 content of that district. The surface areas of sericitization were measured from detailed base maps of 40-km² blocks at the centre of each district and these figures were compared with the total extracted plus measured, indicated and inferred ore reserves in each district. The results are shown in Table I.

This relationship between uranium content, hematitic alteration and sericitization, together with the known high uranium content of the Beira granite, led to a hypothesis on the source and mode of deposition of the uranium. It is suggested that the uranium and iron originally present in accessory minerals in the sericitized zones of the Hercynian granite were leached and mobilized during Tertiary movements, concentrated and re-deposited in the more open sections of fracture systems. Relatively low-temperature hydrothermal fluids capable of the leaching action are not difficult to visualize as hot springs exist on parallel fractures in the region. Three hot springs on parallel fractures are located within 10 km of the Urgeiriça mine, the largest in the whole region.

TABLE I. RELATIONSHIP BETWEEN TOTAL SERICITIZATION IN A DISTRICT AND TOTAL U_3O_8 CONTENT

District	Surface area of sericitization per km ²	Relative total content of U_3O_8
	m ²	
Urgeirica	50 000	1.000
Bendada	8 000	0.388
Reboleiro	1 000	0.044
Guarda	500	0.009

Some evidence to further support these views has been obtained more recently from four samples provided to the speaker by the Junta de Energia Nuclear, Lisbon and analysed at the IAEA Seibersdorf Laboratory in Austria by differential gamma spectrometry and neutron activation analysis. The samples were from the wall-rock zone of the Urgeirica Mine and represented fresh unaltered granite and sericitized granite without hematitic alteration. The results are summarized below.

	U (ppm)	Th (ppm)
No. 1. Unaltered granite	46	25-30
No. 2. Unaltered granite	44	25-30
No. 3. Sericitized granite	29	25-30
No. 4. Sericitized granite	33	25-30

Materials balance calculations indicated that if only 25% of the original uranium content of the granite was removed from the sericitic zones to the depths explored and mined, this would be more than sufficient to provide the known uranium content of the vein deposits. This would appear to be satisfied by these recent analyses.

In general, the hypothesis is that Tertiary structural movements in the Hercynian granite caused fractures and released low-temperature hydrothermal fluids resulting in extensive sericitization, leaching of uranium and iron from the granite and re-deposition of these elements in suitable structural traps in the enclosed fractures. The fractures were subject to repeated movement over a long period, and movement may be continuing to the present time.

S. H. U. BOWIE: I wonder whether Mr. von Backström would care to comment on what the relative importance of these "other uranium deposits" will be in the future - that is, the extent to which they are likely to contribute to uranium requirements over the next 20 or 30 years.

J. W. von BACKSTRÖM: I think important uranium ores will be found in Recent deposits, including semi-consolidated and unconsolidated superficial materials and large river deltas. Intrusive complexes rich in alkali minerals with a substantial content of uranium offer another promising

possibility; these include the carbonatite pipes of Africa, Brazil and Canada. To be economically viable, however, they will have to command a higher price than the ores in Recent deposits.

If there should in fact be a very sharp increase in the price of uranium, the sedimentary rocks themselves, including grit horizons, parting planes and other sedimentary features (apart from the quartz-pebble conglomerates of the old Precambrian formations), should be carefully re-examined. Finally, I might point out that, whereas on the Witwatersrand quartz-pebble conglomerates with a high gold/uranium ratio have been widely explored, the converse is not always true, because viability has so far relied on high gold prices and not on high uranium prices. This could change.

URANIUM RESOURCES OF THE FUTURE — "PORPHYRY" URANIUM DEPOSITS

F.C. ARMSTRONG,
US Geological Survey,
Spokane, Wash.,
United States of America

Abstract

URANIUM RESOURCES OF THE FUTURE — "PORPHYRY" URANIUM DEPOSITS.

The economics of the electrical utility industry indicate that nuclear fuels will largely replace fossil fuels in large generating plants of the future. This use will cause a large demand for uranium; it will also cause the price of U_3O_8 to increase perhaps as much as threefold, and will release fossil fuels for other more beneficial uses. In the next quarter century, the uranium mining industry will probably undergo changes similar to those experienced by the copper mining industry in the last half century. With increased price and large assured market, deposits containing as little as 0.04% U_3O_8 will become economically exploitable, and the large sums of capital necessary for their development will become available.

Deposits containing 0.03-0.05% U_3O_8 occur in late magmatic differentiates. Alaskite, leucocratic granite, biotite granite, and biotite quartz monzonite that are intruded by networks of aplite and pegmatite dikes of similar composition are the favourable host rocks for "porphyry" uranium deposits. Uraninite and radioactive black minerals are the principal ores. Uranium also occurs as ionic and molecular disseminations.

Possible examples of "porphyry" uranium deposits are Rössing, South West Africa; Charlebois Lake, Canada; Crocker Well, Australia; and certain areas in central Idaho and northeastern Washington. The deposits will be easiest to find in arid climates, and unmetamorphosed rocks are perhaps the most likely hosts.

INTRODUCTION

Recent sharp increases in the prices of oil and natural gas and, to a lesser degree, coal, have focused attention on the growing worldwide shortage of energy source materials. Because of the high cost of fossil fuels, electrical utility companies are evaluating alternative fuels for use in new generating plants. In 1969 the 600 MW(e) Haddam Neck reactor generated electricity for 5-3/4 mill/kWh. whereas eight large fossil-fuel plants in New England averaged about 7-1/2 mill/kWh, [1]. In 1970 that part of the cost of generating electricity that was attributable to the cost of fuel was about 39 percent for fossil fuels [2] and about 5 to 8 percent for U_3O_8 in 1973 (written communications, 1973, Atomic Energy of Canada Ltd. and Kerr-McGee Corp.).

A forecast for the period 1981-1996 estimates the cost of oil will contribute 55 percent of the total cost of generating electricity, and coal will contribute about 36 percent [3]. The same forecast estimates that the cost of U_3O_8 will contribute about 5 percent, about the same as it contributes today, to the total cost of generating electricity.

Increased cost of fossil fuels increases the economic advantage of nuclear fuels in generating electricity. The cost of generating electricity by nuclear reactors is about 5.0 or 6.0 mills per kilowatt hour. Therefore, tripling the price of U_3O_8 would increase the cost of electricity less than 1.0 mill per kilowatt hour. Similar increases in the prices of oil and coal result in large increases in the cost of electricity. With the increasing cost of fossil fuels, their large contribution to the cost of generating

electricity, and their more beneficial use in other industries, it seems inevitable that the generation of electricity at central power stations will be largely taken over by nuclear fuels.

As a result of these developments in the electrical utility industry, a large demand for uranium is forecast and the price of U_3O_8 will go up. Denison Mines Limited's recent tentative agreement with Japan for 1984-1993 delivery of U_3O_8 at an average price of \$20 a pound is probably the general price level that can be expected in the near future.

With large demand and substantially increased price, it seems that the uranium industry should search for large tonnage, low-grade, easily mined uranium deposits, if this demand is to be satisfied.

Geologic evidence suggests that potentially economic concentrations of uranium are associated with certain types of granitic rocks. The uranium is disseminated in the rock and along fractures and shears, and may occur in the igneous rock or in the intruded rocks. It is suggested that these deposits be called "porphyry" uranium deposits, not because of a known intimate association with porphyritic rocks, but because they appear to have close historic, economic, and geologic similarities to porphyry copper deposits. Perhaps "porphyry" uranium deposits are the large low-grade deposits that should be sought.

Specifically excluded from this discussion are syenitic rocks and carbonatites. Many of these contain uranium and may be future sources of uranium ore. Examples are the rocks of the Bear Paw Mountains, Montana, U.S.A., and those of the Ilimaussaq massif of southern Greenland.

The purpose of this paper is to discuss the probability that "porphyry" uranium deposits do exist and can be found and mined.

ESTIMATED URANIUM REQUIREMENTS

The estimated uranium requirements to the year 2000, both domestic and worldwide, are so large that reserves and resources of high-grade low-cost uranium ore are inadequate, particularly if an 8-year future supply necessary to the utility industry is maintained.

Forecasts indicate that the United States \$8 per pound reserves from high-grade deposits will be exhausted in mid-1981, \$8 per pound reserves and potential in mid-1987, and \$15 per pound reserves and potential early in 1994 [4, fig. 8]. If the uranium mining industry maintains 8 years of reserves in the ground, then at present there are less than 8 years reserves at \$8 per pound; the \$8 per pound reserves and potential will be exhausted before 1980; and \$15 per pound reserves and potential will last until early 1986. World reasonably assured resources at \$10 per pound will be exhausted in mid-1984; and if 8 years reserves are maintained, they will be exhausted early in 1979 [5, fig. 2a]. It thus appears that in a few years, uranium at current prices will be in short supply.

The growth in the need for uranium for the next quarter century can be compared in many ways to the growth in the demand for copper that developed after 1900 when it became necessary to mine large low-grade deposits to meet the increasing demand for the growing electrical industry.

COPPER AND URANIUM CONCENTRATIONS IN GRANITIC ROCKS AND ORE DEPOSITS

Granitic rocks are estimated to contain 5 to 30 parts per million (ppm) copper and to average about 15 ppm [6]. A change in the grade of ore mined from 4.0 percent copper in 1900 to about 0.50 percent copper today, most of which comes from open-pit porphyry copper deposits, is an eightfold reduction in grade. Ore containing 0.50 percent copper (5 000 ppm) represents a geochemical concentration of about 300 times the average copper content of granitic rocks.

Granitic rocks contain about 4 ppm uranium [7]. From 1948 to 1972 the annual average grade of uranium ore mined in the United States ranged from a high of 0.323 percent U_3O_8 in 1950 to a low of 0.195 percent in 1968; the average for all ore mined during the same time interval is 0.235 percent U_3O_8 [8]. The range in grade represents geochemical concentrations of about 800 times to nearly 500 times the average uranium content of granitic rocks, and the average grade of all ore mined represents a geochemical concentration of nearly 600. Except for a very small amount that has been recovered as a byproduct of other mining, most uranium has been recovered from relatively high-grade sandstone-type deposits and some from vein deposits.

The geochemical concentrations of uranium ore being mined today are less than those of the 4 percent copper ore mined about the turn of the century. Without modern mining and extractive technology, however, it is probably safe to conjecture that minable uranium ores would have to contain about 1.0 percent U_3O_8 , approximately the same geochemical concentration as the copper ores 70 years ago. But geochemical concentration alone is not the sole consideration, for uranium is a higher priced commodity per unit weight than copper, and mathematical comparisons, therefore, should not be expected to be precisely the same. Even so, the amounts of geochemical concentrations are surprisingly alike.

A better approach might be to suggest that in the next quarter century there will be a reduction in the grade of uranium ore mined of about eightfold, for it is reasonable to assume that mining and extractive technology will continue to improve. If such a reduction is made, the average grade of uranium ore mined today, about 0.24 percent U_3O_8 , will drop to about 0.03 percent. This is a change from a geochemical concentration of about 600 to about 75.

Today many mines are mining ore that averages about 0.20 percent U_3O_8 , and most mills are including in their mill feed material that grades as little as 0.05 percent U_3O_8 . Also, at many mines the relatively small amount of material that contains 0.03 to 0.05 percent U_3O_8 is being stockpiled for processing at some future date, provided that this low-grade material has to be removed in the ordinary course of mining. These lower grades represent geochemical concentrations of 75 to 125 times the average uranium content of granitic rocks. The amount of this material associated with high-grade deposits is too small to supply the large amounts of uranium that are estimated to be needed in the not too distant future.

It thus remains necessary to identify the large low-grade uranium deposits that are amenable to large-scale inexpensive production methods. Such deposits would contain about 400 ppm uranium.

The geochemical behavior of uranium in magmatic differentiation perhaps is sufficiently well known to suggest the habitat in which "porphyry" uranium deposits containing about 400 ppm might be found.

URANIUM IN MAGMATIC DIFFERENTIATION

Uranium is a strongly lithophile element and is concentrated in the crust of the earth, particularly in the granitic rocks of the crust. A variation to this generalization, which will not be discussed here, is that uranium is also concentrated in potassium- and sodium-rich but calcium-poor alkalic rocks.

In a differentiating magma, uranium ions do not substitute for cations in the crystal lattices of common rock forming minerals because of ionic size, coordination requirements, or large electrical charges.

In the common granitic rock minerals, the feldspars, micas, and pyriboles, the crystal lattices could accommodate uranium ions, but uranium does not appear to substitute diadochically for cations in these minerals. All of the possible substitutions face the formidable difficulty of preserving local electrical balance in the crystal because of the high positive valences of uranium ions.

A consequence of non-substitution of uranium in common rock-forming minerals is that uranium becomes concentrated in the late magmatic fluids [9]. The uranium thus accumulated can either be expelled from the magma chamber, perhaps to form vein systems, or it can be retained within the magma where, upon cooling, it would be retained in the late crystallizing phases of the magma.

Several studies of the distribution of uranium in igneous rocks have been made [10, 11, 12, 13, and 14]. From these studies it is evident that uranium is concentrated in the late differentiates of a magma. Consequently, in a differentiated magmatic sequence, and provided that the uranium has not been expelled from the magma, it becomes possible to suggest the types of host rocks in which "porphyry" uranium deposits might be found. Suitable host rocks would be alaskite, leucocratic granite, graphic granite, myrmekite, biotite granite and biotite quartz monzonite that contain a complex ramifying network of aplitic dikes and pegmatitic seams and dikes consisting dominantly of quartz and potassium feldspar.

MINERALOGY AND DISTRIBUTION OF URANIUM

Uranium is incorporated into late crystallizing rocks in several different ways which can be conveniently grouped into three types of occurrence. First, uranium can form its own minerals; secondly, it can substitute diadochically in accessory minerals; and thirdly, it can occur, probably as molecular or ionic disseminations, occluded in crystals, in structural defects, in fluid inclusions and intergranular fluids, and adsorbed on crystal surfaces [15, 14].

The commonest uranium mineral in the suggested host rocks is uraninite which occurs in microscopic or submicroscopic crystals. This uraninite should contain thorium and rare earths in amounts similar to those contained in uraninite found in granitic pegmatites. The crystals occur as minute inclusions within mineral grains and between grains. Uranothorite is another expectable uranium mineral. Where the other necessary constituents are present, uranium can and does combine with them to form a wide variety of multiple oxides, collectively referred to as radioactive black minerals that are complex niobates, tantalates, and titanates and contain uranium,

thorium, and rare earths, e.g. eschynite-priorite, euxenite-polycrase, and fergusonite-formanite. The radioactive blacks commonly occur in pegmatites but they also occur as accessory minerals in some granitic rocks.

Uranium substitutes in the crystal lattices of several accessory minerals in granitic rocks. It substitutes in zircon, sphene, allanite, apatite, monazite, and xenotime; and it may also substitute isomorphically in epidote and garnet. It seems unlikely, however, that the uranium content reported for opaque minerals such as magnetite, ilmenite, and pyrite, can be in the crystal lattices of the minerals. If the type of host rock postulated here contained more than 300 ppm uranium, it is thought that there would be too much uranium present for all of it to be taken up solely by substitution in common accessory minerals because their total volume is so small.

In the third type of occurrence, molecular or ionic disseminations, uranium is not tightly held in granitic rocks or their constituent minerals. Many leaching experiments, among them those by Larsen and Gottfried [10], have shown that a large part of the uranium in granitic rocks is readily dissolved by weak acids in a short time. A large part of this easily soluble uranium is thought to occur as molecular or ionic disseminations, but it is not known how this uranium is held in the minerals and rocks. What portion of the easily soluble uranium is dissolved from metamict and easily soluble minerals such as uraninite is not known either. In leaching experiments, however, more uranium is dissolved than can be accounted for by the metamict and soluble uranium minerals that have been recognized in the samples. Leaching experiments also show that uranium that substitutes in accessory minerals is more tightly held and less easily soluble than other uranium in rocks [14].

CHARACTERISTICS OF "PORPHYRY" URANIUM DEPOSITS

The characteristics of the geologic model proposed here for a "porphyry" uranium deposit can be summarized as follows:

Host rocks: Biotite granite, biotite quartz monazite, alaskite, leucocratic granite, graphic granite, and myrmekite cut by aplite and pegmatite of similar composition.

Mineralogy: Primary uraninite, uranothorite, radioactive blacks, and ionic and molecular disseminations of uranium; secondary minerals near surface; uraninite contains amounts of thorium and rare earths similar to those found in uraninite in pegmatites; most uranium easily leachable; ore minerals disseminated and also fill and replace joints, shears, fractures, and openings; most ore minerals microscopic to submicroscopic in size.

Distribution: Most of the uranium contained in felsic and varietal minerals of the rock; very little uranium contained in accessory minerals; some ore in intruded rocks.

To the above tabulation might be added "unmetamorphosed rocks more favorable." So little is known about this possible type of deposit, however, that the characteristics listed are only those of a model and should not be confused with solid geologic fact.

It might be asked whether any examples of the suggested model are known to contain sufficient uranium to be considered ore deposits. Below are some examples of actual or potential "porphyry" uranium deposits.

POSSIBLE EXAMPLES OF "PORPHYRY" URANIUM DEPOSITS

Rössing, South West Africa

The type example of a "porphyry" uranium deposit is probably the Rössing deposit in South West Africa. The host rocks--alaskite, graphitic granite, and biotite granite--intrude metamorphic rocks and are cut by numerous alaskitic pegmatites. The principal ore mineral in unweathered rock is uraninite in grains a few microns to 0.3 mm in diameter that occurs as inclusions in quartz, feldspar, and biotite, and also as free grains. Betafite is also present and weathered outcrops contain secondary uranium minerals. Uraninite, betafite, and biotite from the host rock have all been dated provisionally as 510-40 million years old. The uranium minerals are easily leachable [16]. The deposit contains several hundred thousand tons of ore that averages about 0.04 percent U_3O_8 . Rössing is to start production in 1976 or 1977 [17], reportedly at 40,000 tons of ore per day.

Charlebois Lake area, Saskatchewan, Canada

In the Charlebois Lake area, biotite granite and biotite quartz monzonite intrude metamorphic rocks. Late magmatic myrmekitic intergrowths replace the potash feldspars. The granite and quartz monzonite are cut by light-colored fine-grained and coarse-grained pegmatites of granitic composition. The fine-grained pegmatite, descriptions of which suggest that it is very like alaskite, intimately intrudes schist to form migmatite (mixed rocks). Cubic uraninite crystals about 0.20 mm in diameter are closely associated with biotite, and the white fine-grained pegmatite contains disseminated, minute uraninite crystals [18]. Metallurgical tests showed that the uranium is easily leachable from Charlebois Lake samples [19]. When the Charlebois Lake area was explored in the early 1950's, high-grade ore was sought and six widely separated bodies were found that, in aggregate, contain at least 1 000 tons per vertical foot of material averaging about 0.20 percent U_3O_8 . "The amount of material . . . with an average grade of 0.08 percent uranium oxide is many times 1,000 tons per vertical foot" [18]. Might not the Charlebois Lake area be one in which to explore for a "porphyry" uranium deposit?

Crocker Well, South Australia, Australia

Another possible uranium "porphyry" is the Crocker Well deposit, South Australia, Australia. There, leucocratic biotite adamellite (quartz monzonite) intrudes metamorphic rocks and is intruded by alaskite, alaskite-pegmatite, and granitic pegmatite. The ore mineral is absite, a radioactive, black, complex uranium-thorium titanate of general composition $2UO_3 \cdot ThO_2 \cdot 7TiO_2 \cdot 5H_2O$ that contains 32 percent UO_3 . Adamellite is the host rock for all the important absite deposits and the absite occurs as a minor primary constituent of the adamellite. Absite also occurs as an accessory mineral in the alaskite and alaskite pegmatite [20]. The deposits originally investigated were absite-bearing sheared and brecciated zones that averaged between 1 and 1.5 pounds U_3O_8 per long ton. Drill indicated reserves in four of the areas ranged from 2 500 to 6 000 long tons per vertical foot. Because absite occurs as an accessory mineral in the host rocks and is concentrated in local structures, it appears that the Crocker Well area warrants close examination as a possible site for "porphyry" uranium deposits, particularly the Original Prospect where the breccia zone grade is about 1.5 pounds U_3O_8 per long ton.

Central Idaho, U.S.A.

Radioactive black minerals, principally euxenite, were mined from placers at Big Meadow in Bear Valley, Valley County, Idaho. The radioactive blacks occur as accessory minerals in quartz monzonite and quartz diorite which are cut by a network of aplite and pegmatite dikes and stringers. Euxenite is also found as an accessory mineral in the pegmatite dikes. Euhedral crystals and angular fragments of euxenite that range in size from 0.1 to 5.0 mm are found in the residual soil of the Bear Valley area. It is thought that the euxenite in the commercial placers in Bear Valley was derived from a 6-square-mile area to the south [21]. The drainage area tributary to Big Meadow might be a suitable place to explore for "porphyry" uranium deposits.

Northeastern Washington, U.S.A., and adjacent British Columbia, Canada

On the west flank of Mount Spokane, Spokane County, Washington, small quantities of meta-autunite and autunite have been mined. The host rocks are alaskite, graphic granite, and biotite quartz monzonite which are cut by numerous alaskitic and granitic pegmatite dikes and stringers. The ore minerals coat small joint, shear, and fracture surfaces, and coarse crystals of meta-autunite occur as fracture fillings in shears and in open spaces in the rocks [22]. Samarskite has been identified in a pegmatite and it also occurs as an accessory mineral in alaskite. The host rocks have been radiometrically dated and are thought to be about 50 million years old (Weissenborn, oral communication, 1974).

In Pend Oreille County at the Quartz Ridge and Lost Creek deposits, several miles north of Mount Spokane, a small amount of meta-autunite has been mined. The geologic setting and host rocks of these deposits are essentially identical to those on Mount Spokane.

There are no gangue minerals associated with the meta-autunite on Mount Spokane or at the Pend Oreille deposits; and there does not appear to be any wall rock alteration either. The meta-autunite is thought to have been deposited from ground water, but the source of the uranium is not known.

North of Grand Forks, British Columbia, at Cronus Minerals Limited's prospect, alaskite, graphic granite, and biotite granite cut by small granitic pegmatites occur in an area that has been mapped as part of the Shuswap Metamorphic Complex [23]. Euhedral cubic uraninite crystals occur in quartz and in biotite [24]. One grab sample assayed 1.00 percent U_3O_8 ; and other samples have assayed almost 0.60 percent U_3O_8 . At one place, biotite granite containing about 5 percent biotite gave about 2.5 times the reading on a scintillometer than the most radioactive biotite-rich area gave. The rocks at this prospect look very like the uranium-bearing rocks on Mount Spokane.

Many occurrences of radioactivity in pegmatitic rocks have been reported from the mountain range that lies west of the Columbia and Kettle Rivers, east of the town of Republic, Washington, and extends northward almost to Grand Forks, British Columbia. Radiometric dates of about 50 million years have been obtained from two biotite quartz monzonites in this area (John D. Obradovich, written communication, 1974).

The many uranium and radioactivity occurrences in biotite quartz monzonite, alaskite, and pegmatite in northeastern Washington suggest that this might be an area favorable for the occurrence of "porphyry" uranium

deposits. Moreover, the radiometric dates that have been determined suggest that these favorable host rocks may all be about the same age, and that there may have been a single period of intrusion, about 50 million years ago, during which uranium-rich rocks were emplaced.

COMMENTS ON EXPLORATION

Exploration for "porphyry" uranium deposits will be difficult and expensive just as it is for porphyry copper deposits. The actuality of a "porphyry" uranium mine, with the possible exception of Rössing, has yet to be demonstrated, but a knowledge of the possibility that such deposits may exist will aid in their discovery, if indeed they do exist.

Determination of grade will be difficult, and large bulk samples may be the only accurate method for determining grade. During mining, grade control probably will be difficult also.

Of the ore minerals that might occur in a uranium "porphyry," uraninite would be the most desirable because of its high concentration of uranium and its easy solubility in acid leaching.

In drilling low-grade uranium deposits, it may prove necessary to contain, recirculate, and sample drilling water. Uranium is easily soluble in water and could be leached from the core or chips and from the walls of the hole. If leaching of uranium does occur, there should be a progressive buildup of uranium in recirculated drill water. Such a buildup probably could be detected by analyzing the water, and perhaps even the amount of uranium leached might be estimated.

If Lyons' [11] interpretation of the mobility of uranium during metamorphism is correct, then unmetamorphosed rocks offer the best chance for discovery of a "porphyry." And because young rocks have had the least chance to be metamorphosed, they are the most favorable of the unmetamorphosed rocks. This should not be taken to mean, however, that old rocks should be ignored or that metamorphosed rocks should not be tested, because the fact is that the habitat of "porphyry" uranium deposits is not really known.

When a magma cools and crystallizes, the uranium in it can escape or it can be concentrated and retained in the late crystallizing rocks. A uranium "porphyry" is visualized as one in which the uranium has been concentrated and retained. Thorium and rare earths should also be retained. The presence of thorium and rare earths in the uraninite of a deposit might be a possible test for determining whether uranium has been retained in the magma and whether the chance for "porphyry" deposits is favorable. Here again a caveat is in order because so little is known about uranium "porphyries." A low-thorium, low-rare-earth uraninite "porphyry" deposit may mean only that the deposit does not fit the postulated model or that the model is no good.

As with porphyry copper deposits, "porphyry" uranium deposits will be easiest to find in arid climates; and they may contain secondarily enriched zones. In areas of abundant rainfall the uranium is flushed out; and the brilliantly colored, eye-catching secondary minerals do not have a chance to form.

The former positions of Africa and South America, as determined by current plate tectonic reconstructions, suggest that uranium deposits similar to Rössing should be sought in southernmost Brazil and adjacent Uruguay in granitic rocks about 500 million years old.

CONCLUSIONS

The economics of the electrical utilities industry indicate that most future large generating plants will use nuclear fuels. This use will create a large demand for uranium and will increase the price paid for U_3O_8 . At the prices anticipated, about triple the present prices, deposits containing about 0.04 percent U_3O_8 can become ore bodies.

Geologic evidence suggests that some late-differentiate granitic rocks, such as leucocratic granite, alaskite, biotite granite, and biotite quartz monzonite and their associated pegmatites, contain about 400 ppm uranium. Large bodies of this type can be mined by efficient modern mass-mining methods and thus become ore deposits. It is suggested that such ore deposits be called "porphyry" uranium deposits. Actual and potential examples of such deposits are known. "Porphyry" uranium deposits fill the gap between the relatively high-grade deposits mined today and the low-grade shales that contain 10 to 80 ppm uranium. "Porphyry" uranium deposits may well become the chief source of the world's future uranium supply.

The lead time necessary to find, explore, and develop a porphyry deposit, uranium or copper, is long. Uranium was first found at Rössing about 60 years ago, intensive prospecting started about 1955, recognition of its potential as a large low-grade deposit was in the late 1960s, and production is scheduled to begin in 1976 or 1977. Consequently, now is not too soon to start looking for other "porphyry" uranium deposits.

REFERENCES

- [1] Shaw, M., Landis, J. W., Laney, R. V., Rosenthal, M., Layman, W. H., 1970, Reactor development program, Nuclear Engineering International v. 15, no. 174, p. 899-904.
- [2] Olmsted, L. M., 1971, 17th steam station cost survey reveals steep rise for busbar energy, Electrical World v. 176, no. 9, p. 39-54.
- [3] Arthur D. Little, Inc., 1973, A study of base load alternatives for the Northeast Utilities System, A report to the Board of Trustees of Northeast Utilities, July 5, 1973, 106 p.
- [4] Nininger, R. D., 1973, Uranium reserves and requirements, in Nuclear Fuel Resources and Requirements, U.S. Atomic Energy Comm. Div. Production Raw Materials Management, Wash. 1243, p. 10-28.
- [5] Organization for Economic Cooperation and Development and International Atomic Energy Agency, 1973, Uranium, resources, production and demand, O.E.C.D. Publications, Paris, France, 140 p.
- [6] Cox, D. P., Schmidt, R. G., Vine, J. D., Kirkemo, Harold, Tourtelot, E. B., and Fleischer, Michael, 1973, Copper, in United States Mineral Resources, U.S. Geol. Survey Prof. Paper 820, p. 163-190.
- [7] Finch, W. I., Butler, A. P., Jr., Armstrong, F. C., and Weissenborn, A. E., 1973, Uranium, in Nuclear Fuels in United States Mineral Resources, Donald A. Brobst and Walden P. Pratt, eds., U.S. Geol. Survey Prof. Paper 820, p. 456-468.
- [8] United States Atomic Energy Commission, 1973, Statistical data of the uranium industry, U.S. Atomic Energy Comm. GJO-100(73), 65 p.

- [9] Larsen, E. S., Jr., Phair, George, Gottfried, David, and Smith, W. L., 1956, Uranium and magmatic differentiation, U.S. Geol. Survey Prof. Paper 300, p. 65-74.
- [10] Larsen, E. S., Jr., and Gottfried, David, 1961, Distribution of uranium in rocks and minerals of Mesozoic batholiths in western United States, U.S. Geol. Survey Bull. 1070-C, p. 63-103.
- [11] Lyons, J. B., 1964, Distribution of thorium and uranium in three early Paleozoic Plutonic Series of New Hampshire, U.S. Geol. Survey Bull. 1144-F, 43 p.
- [12] Malan, R. C., 1972, Summary report--Distribution of uranium and thorium in the Precambrian of the Western United States, U.S. Atomic Energy Comm., AEC-RD-12, 59 p.
- [13] Marjanemi, D. K., and Basler, A. L., 1972, Geochemical investigations of plutonic rocks in the western United States for the purpose of determining favorability for vein-type uranium deposits, U.S. Atomic Energy Comm., GJO-912-16, 134 p.
- [14] Leonova, L. L., and Tauson, L. V., 1958, The distribution of uranium in the minerals of Caldeonian granitoids of the Susamyr batholith (central Tien Shan), Geochemistry, no. 7, p. 815-826.
- [15] Neuerburg, G. J., 1956, Uranium in igneous rocks of the United States, U.S. Geol. Survey Prof. Paper 300, p. 55-64.
- [16] von Backström, J. W., 1970, The Rössing uranium deposit near Swakopmund, South West Africa, in Uranium Exploration Geology, Internat. Atomic Energy Agency, Vienna, Austria, p. 143-150.
- [17] Williams, R. N., 1974, Uranium, Canadian Mining Jour., v. 95, no. 2, p. 110-114.
- [18] Mawdsley, J. B., 1952, Uraninite-bearing deposits, Charlebois Lake area, northeastern Saskatchewan, Canadian Mining and Metallurgical Bulletin, v. 45, no. 482, p. 366-375.
- [19] Van Cleave, A. B., 1956, Beneficiation of low-grade pegmatitic uranium ores, Canadian Inst. Min. Metallurgy, v. 49, p. 827-834.
- [20] Campana, B., and King, D., 1958, Regional geology and mineral resources of the Olary Province, South Australia Dept. Mines Bull. 34, 133 p.
- [21] Mackin, J. H., and Schmidt, D. L., 1956, Uranium and thorium bearing minerals in placer deposits in Idaho, U.S. Geol. Survey Prof. Paper 300, p. 375-380.
- [22] Weissenborn, A. E., and Moen, W. S., 1974, Uranium in Washington, in Energy Resources of Washington, Wash. State Dept. Natural Resources Information Circular 50, p. 83-97.
- [23] Little, H. W., 1957, Kettle River, east half, Geol. Survey Canada Map 6-1957, Sheet 82E.
- [24] Hausen, D. M., and Odekirk, J., 1970, Mineralogic examination of uraniferous gneiss from property north of Grand Fork, British Columbia, Unpublished report Newmont Exploration Ltd., Metallurgical Dept., Danbury Conn., File: 209-1, 5 p.

DISCUSSION

D. S. ROBERTSON: I think the use of the word "potential" is improper in connection with ore reserves when "potential ore" is used as a basis for drawing supply curves and, indeed, as a basis for suggesting the future building of mills. The acceptance of this concept has contributed greatly to the problem we now face with ore reserves. If we contemplate the exploitation of low-grade ores, we must remember, too, that even large production units will yield relatively small amounts of product. A mill at Rössing, for example, handling 40 000 tons of ore per day, might be expected to yield only about 3000 tons of U_3O_8 per year — a mere drop in the bucket.

F. C. ARMSTRONG: I do not quite understand why Mr. Robertson feels that the drawing of these curves is "improper" or how he thinks they can contribute to the present problem. Surely, one must start from some point in attempting to make forecasts of future needs and supplies. The drawing of curves such as these assists us in examining a wide variety of information very carefully. And if 3000 tons of U_3O_8 per year are a drop in the bucket, they are at least a start in the right direction. The important point is that explorationists should start thinking of the possibility of "porphyry" uranium deposits.

W. BOURRET: I anticipate a number of problems that will almost certainly affect the exploitation of low-grade uranium ores. The uranium mines, unlike the copper porphyry ores, will not yield a high-grade sulphide concentrate by flotation methods and/or gravity concentration. Secondly, mass production methods require crushing and grinding to -100 mesh and sometimes even to -150 mesh. This would use large quantities of electric energy, which is becoming more and more costly. Finally, the success of "porphyry"-type operations requires years of lead time and large expenditures for drilling, testing, engineering and feasibility studies. I fear the uranium industry may not have the expertise necessary for this.

F. C. ARMSTRONG: A method of concentration that could be applied to uranium would obviously be a valuable contribution. It would probably work best for radioactive blacks; the uraninite in these rocks is microscopic or sub-microscopic, and it seems unlikely that concentration would work very well.

Admittedly the uranium industry lacks expertise in dealing with porphyry deposits, but at some time a start must be made. Moreover, many large copper mining companies are interested in uranium, and they might be best equipped to adapt copper porphyry techniques to uranium porphyries.

F. R. JOUBIN: I completely endorse the "uranium porphyry" concept outlined by Mr. Armstrong. The brutal force of economics will almost certainly drive us in that direction. Many of us, myself included, will eventually have to set aside our elegant theories and specialities and turn to the search for large low-grade uraniferous (and thorium-bearing) masses that can be mined on the open-pit system at low cost. This approach will have the advantage of encouraging full utilization of all by-product metals.

URANIUM OCCURRENCES IN BRAZIL

J.R. de ANDRADE RAMOS, M.O. FRAENKEL
Comissão Nacional de Energia Nuclear,
Rio de Janeiro,
Brazil

Abstract

URANIUM OCCURRENCES IN BRAZIL.

For the purpose of this paper, the authors have selected the most important uranium occurrences in Brazil and discussed them according to the following host-rock types: alkalic igneous, sedimentary, metaconglomerate and granitic rocks.

In the Poços de Caldas Plateau there are uranium-molybdenum deposits which contain a reserve of more than 5000 t of U_3O_8 . These zones are in addition to and separate from the caldasite occurrences often mentioned in the literature. The authors believe that these deposits are the result of concentration of uranium leached from metamict zircon crystals during hydrothermal alteration and weathering.

In the Paraná Basin a reserve of 2000 t of U_3O_8 is estimated in the sandstones of the lower part of the Rio Bonito Formation (Middle Permian). The authors believe that this deposit was formed in a lithostratigraphic unit protected from surface oxidation by two impermeable strata, a coal seam below and limestone bed at the top. Since Permian time, ground-water flow within this confined hydrologic system has leached uranium and reprecipitated it in favourable locations.

INTRODUCTION

This paper presents preliminary data on the genesis of Brazilian uranium deposits by gathering facts about uranium occurrences in Brazil and outlining ideas about the probable origin of these occurrences.

The main object of this study is to contribute data that can be compared with observations from uranium deposits in other countries, hoping that this Brazilian information will be useful in increasing knowledge of the genesis of these types of deposits. Besides mineralogical, geological and structural information, this paper also presents a collection of ideas of various authors concerning the formation of the uranium occurrences.

It is common knowledge that understanding the genesis of uranium deposits provides a frame of reference for prospecting and, consequently, facilitates the search for this economically important mineral, which is assuming a more important role each day, owing to the scarcity of traditional energy sources. The genetic speculations presented in this paper have always the objective of providing practical criteria for prospecting, which in this case encounters the problem of the vast and geologically little-known Brazilian territory.

The shortage of research laboratories makes it difficult for us to undertake as detailed scientific investigations of our uranium occurrences as we feel necessary.

The authors selected, from all the uranium occurrences in Brazil, those which seemed to them the most important at the present time. The

occurrences discussed have been grouped according to the following host-rock types:

- (1) Alkalic igneous rocks
- (2) Sedimentary rocks
- (3) Metaconglomerates
- (4) Granitic rocks

In each of the above-listed environments there are good possibilities of finding economic uranium deposits. Figure 1 shows the location of these uraniferous provinces.

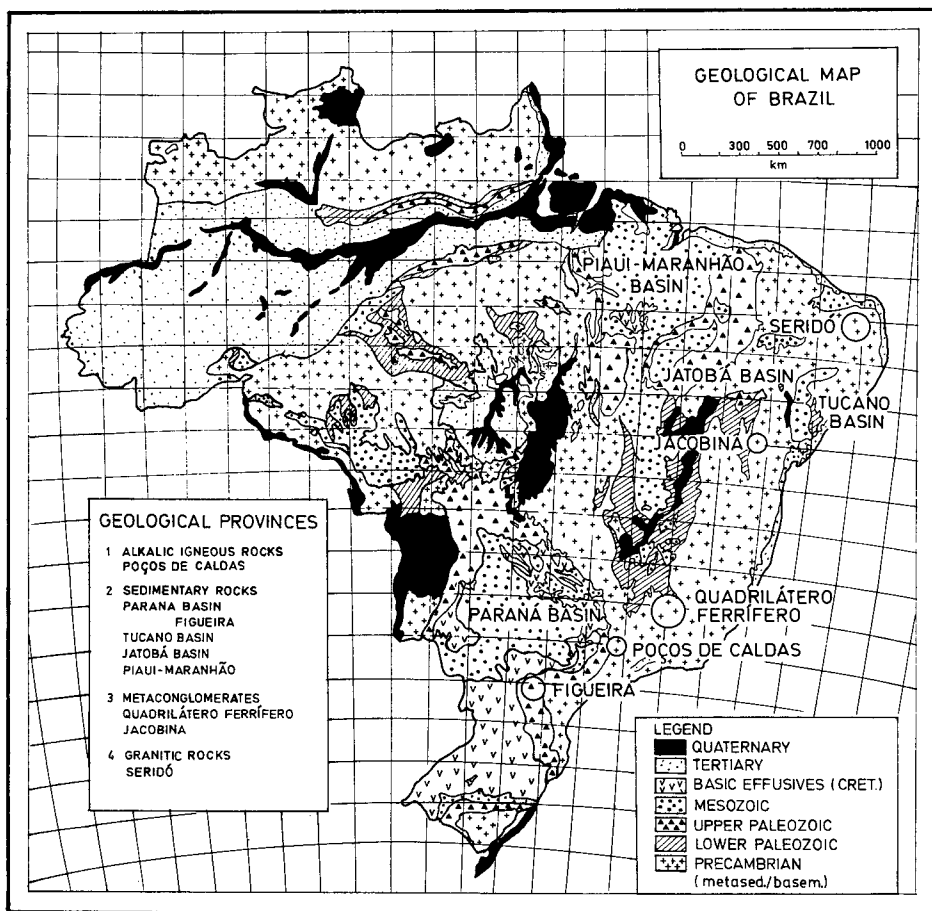


FIG. 1. Simplified geological map of Brazil, showing the main uranium occurrences.

1. ALKALIC IGNEOUS ROCKS

This type mainly includes the occurrences located in the alkalic pipe of Poços de Caldas (southwest of the State of Minas Gerais) which is situated in a SSE-NNW striking volcanic belt.

The age of the Poços de Caldas pipe as well as other similar volcanic features in Brazil is Upper Cretaceous (60 - 80 m. y.) (Ref. [1]).

This nepheline syenite pipe (foyaite, tinguaita and, in smaller quantities, phonolite) appears topographically in the form of a circular plateau, having a diameter of 30 km and altitudes ranging between 1000 and 1700 m above sea level. After the volcanism and consequent intrusions of the alkalic magma, two or more tectonic events followed by hydrothermal activity occurred in the interior of the massif. Parts of the host rocks, (gneiss of the Pre-Cambrian basement and Mesozoic sediments) were also affected.

One concludes that, from the Upper Cretaceous onwards, the area must have gone through successive movements that dislocated some sectors of the pipe. This tectonism left traces in the plateau, evident in the two contrasting forms of the present relief. One of them is characterized by an advanced phase of levelling and the other by a very irregular topography. This second form of relief is confined to a quadrant delimited by the two larger fault zones of the massif, with directions N 30° W and N 50° E. Their crossing in the centre of the plateau limits the above-mentioned quadrant located at the SE of the plateau. In this rejuvenated area the molybdo-uraniferous mineralizations of Agostinho and Cercado are located. These have been recently discovered and studied by de Oliveira and Utsumi [2]. This type of mineralization is quite different from the classic occurrences associated with caldasite (zircon and baddeleyite), known since the 1950s and often mentioned in the literature.

1.1. The Agostinho deposit

In the Agostinho deposit (Fig. 2) uranium appears as amorphous minerals disseminated in the tinguaitic breccia but also occurs in small quantities in the form of coffinite and uranothorianite. The occurrence of these minerals is associated with pyrite, fluorite and minerals of molybdenum and thorium. The average grades can be seen in Table I.

The uranium occurs in brecciated subvertical veins, with an average thickness of 2.5 m which cut tinguaitic rocks near the contact with foyaites. In this deposit 1100 t of U_3O_8 are measured and an additional 2400 t are inferred. These reserves assume a uranium price of between \$ 10 and \$ 15 per pound U_3O_8 .

1.2. The Cercado deposit

In the Cercado deposit (Fig. 2) the uraniferous mineralization occurs in tectonic breccia of hydrothermally altered tinguaita. The zones are subhorizontal, lenticular ore bodies with a thickness of up to 8 m. The minerals do not differ from those in the Agostinho deposit. However, the average grades are different, as can be seen in Table I.

In this ore, reserves of 2840 t of U_3O_8 are measured and an additional 3000 t are inferred (extraction cost of up to \$ 10 per pound of U_3O_8). The zirconium grade, in the form of silicate, is an important factor in the

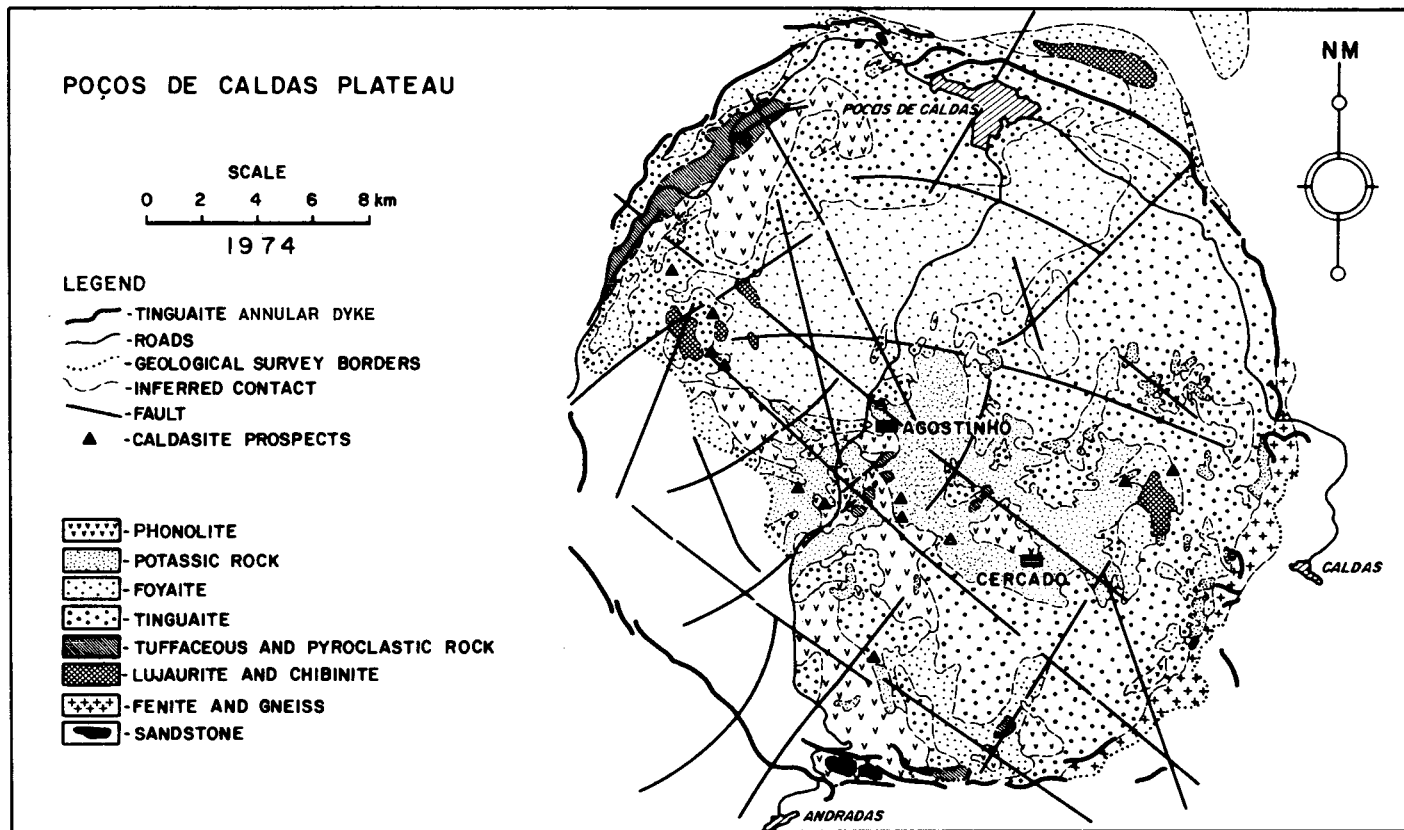


FIG.2. Simplified geological map of the Poços de Caldas Plateau. The Agostinho and Cercado deposits are in the rejuvenated quadrant.

TABLE I. AVERAGE GRADES IN THE CERCADO AND AGOSTINHO DEPOSITS

	AGOSTINHO	CERCADO
U ₃ O ₈ (%)	0.20	0.18
MoO ₃ (%)	0.60	0.25
ThO ₂ (%)	0.10	0.03
ZrO ₂ (%)	4.20	0.55

economic extraction of uranium since it is a highly refractory mineral. The zirconium grade in the Cercado deposit is about eight times lower than in the Agostinho deposit. For that reason, the extraction cost of uranium is about \$ 10 per pound for the Cercado ore and \$ 15 per pound for the Agostinho ore. Extraction of U₃O₈ from caldasite is not feasible, although its uranium grade is about 0.3%, much higher than in the deposits described above.

In the graph (Fig. 3) which represents chemical analyses of samples from more than a hundred holes drilled in the Cercado deposit, the relationship of the uranium grades with the grades of other associated elements in the ore is shown, plotted against depth.

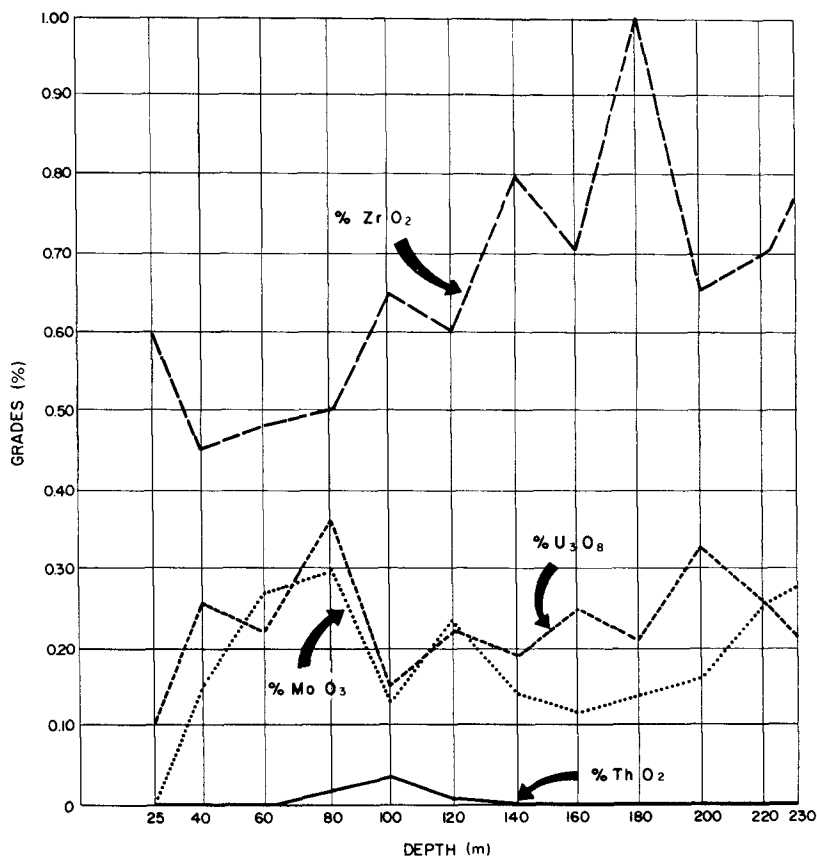
This graph illustrates the behaviour of U, Th, Mo, and Zr under the influence of hydrothermal alteration and weathering. Examination of the curves of grade variation indicates the following:

- (a) The lowest zirconium grades (averaging 0.35% of ZrO₂) are found in the weathering zone represented by soil and hydrothermally altered tinguaita. These rocks show intense leaching of mafic minerals and an abnormal enrichment of potassium which increases from 4% to 15% K₂O. The effects of hydrothermal action are emphasized by intense weathering. The highest uranium and molybdenum grades are concentrated in this zone at depths from 20 to 100 m. This zone represents the first level of enrichment. Locally the rocks are altered down to depths of 100 m.
- (b) From a depth of 100 m downwards, the molybdenum grades decrease considerably while those of uranium change very little. The percentages of zirconium increase progressively to 1% at 180 m below surface.
- (c) The thorium grades remain practically the same both in the altered zone and below.

Fujimori [3] concluded that the mineral responsible for the majority of uranium present is the metamict zircon, which also has molybdenum in its crystal structure.

Based on present knowledge, it is assumed that the destruction of the zircon crystals, already weakened by metamictization, would be accentuated by the action of the hydrothermal metamorphism and by weathering. Probably the metamict fluorite also has a role in the process by furnishing some uranium and perhaps by forming hydrofluoric acid during the hydrothermal alteration.

CERCADO-POÇOS DE CALDAS

FIG. 3. Grade variation of ThO₂, U₃O₈, MoO₃ and ZrO₂ with depth.

2. SEDIMENTARY ROCKS

The large Paleozoic intracratonic sedimentary basins and the small Mesozoic basins of the Brazilian northeast have been intensely prospected. Some good prospects were found. However, at the present time, appreciable uranium reserves have been defined only in the Paraná Basin in the south of Brazil.

Various occurrences associated with the clay and phosphatic matrix of sandstones deposited in Devonian coastal environments were found in the Piauí-Maranhão and Jatobá Basins, both located in the northeast of Brazil. This syngenetic origin mineralization is not of economic importance, owing to the irregularity and low uranium grade (200 to 300 ppm).

Anomalous uranium and vanadium values associated with organic material were found in the Tucano Basin, State of Bahia, in the lower part of the Sergi Formation (Cretaceous). Although there are black minerals underground and vanadates on the surface, no economic concentrations have yet been found. However, reinterpretation is now going on.

2.1. The Paraná Basin

The Paraná Basin, which is composed of Devonian to Cretaceous sediments located in Southern Brazil, has an area of approximately 1 200 000 km². About 80% of this area is covered by extensive Cretaceous basaltic lava flows or by overlying younger sediments which are not considered interesting for uranium prospecting.

The areas near the contact with granites and particularly the Permo-Carboniferous sediments are considered good locations for further prospecting.

An important uranium occurrence was located in the vicinity of Figueira, in the coal-producing region of Rio do Peixe. The coal field covers an area approximately 700 km² in the middle part of the southeast edge of the Paraná Basin (Fig. 4).

2.2. The Figueira area

During the Paleozoic and Mesozoic eras, this area underwent differential epeirogenic movements which formed the Ponta Grossa arch. These positive oscillatory movements began in the early Carboniferous and reached stability during the Cretaceous. The Devonian sediments, however, were deposited in an actively subsiding area while the Permo-Carboniferous sediments were deposited in a gently subsiding area. The dips of these sediments are approximately one degree to the northwest.

The Permo-Carboniferous in this area reaches a total thickness of approximately 900 m of which about 700 m are sediments of the Itararé Formation, composed chiefly of epi-tillites, sandstone and siltstone, all deposited in a predominantly glacial environment.

Above this formation 100-150 m of sediments of the Rio Bonito Formation were deposited (Middle Permian). This formation is mainly composed of sandstone, siltstone, dark grey shale and limestone which were deposited in fluvial, deltaic and coastal environments. The basal part of this formation contains the uranium mineralization.

2.3. The uraniferous formation

The Rio Bonito Formation is characterized by three rather different zones.

- (a) The basal zone, with a thickness ranging between 15 and 30 m, is composed of fine to coarse grey sandstone, grey siltstone and dark shale with coal beds. The sedimentary environments are fluvial, flood plain coastal swamps and epineritic.
- (b) The intermediate zone, which has a thickness of 80 m, is mainly formed by dark grey siltstone, with limestone intercalations and some sandy beds. The sedimentary environment is shallow marine.
- (c) The upper zone, with a thickness of about 20 m, is composed of extremely fine grained and laminated sandstone. The environment varies between epineritic and coastal.

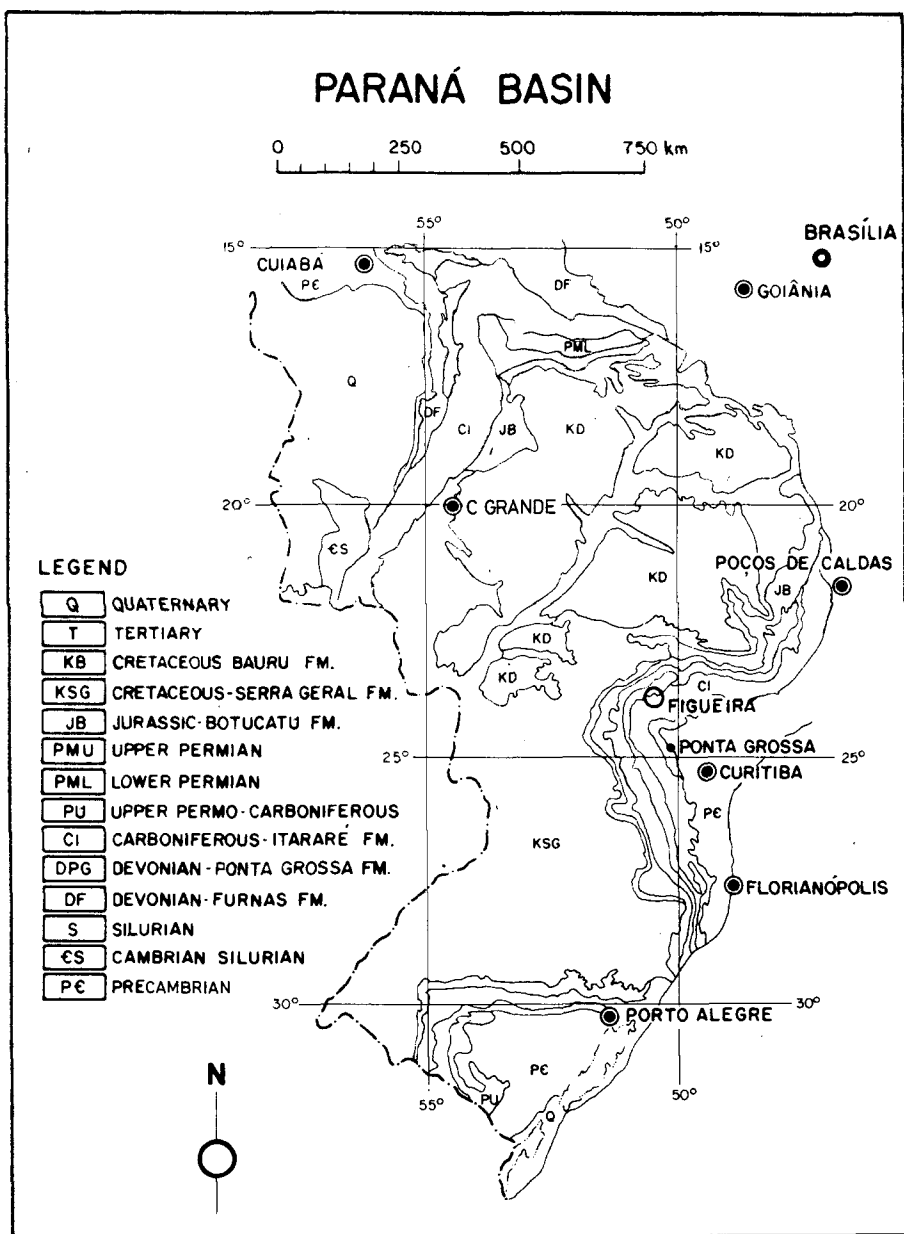


FIG.4. Simplified geological map of the Paraná Basin, locating the Figueira area. (FM = Formation).

Uranium occurs at the base of the Rio Bonito Formation as uraninite in sandstone occupying the interstices of the quartz grains. Uranium also occurs in the siltstone, dark shale and coal, in the form of organic complexes. It also appears as uranocircite as the result of a secondary process.

Molybdenum is also present in this formation, in the form of jordisite (amorphous MoS_2).

The paleogeography indicates a complex drainage system, with a general NW orientation.

In the relatively deeper axial parts of these channels, coarser clastic sediments with a high permeability were deposited. In the higher parts of the ancient meanders, the relative weakness of the currents resulted in deposition of fine-grained and homogeneous sandstone, siltstone and carbonaceous shales, which have a low permeability. In the intermediate zones there is an interfingering of the two types of sediments, which presents an ideal model for later remobilization and subsequent redeposition and concentration of uranium.

The Rio Bonito Formation is covered by 80 m of dark siltstone, deposited in a coastal environment (Palermo Formation, Upper Permian). Above the Palermo Formation are 30 m of pelitic sediments that were deposited in a deep lacustrine environment. These strata form the Irati Formation (Upper Permian). These two Permian formations are considered to be barren of uranium.

According to Saad [4], the uraniferous mineralization in the basal sediments of the Rio Bonito Formation has two origins:

- (a) The first, syngenetic, mainly observed in the central and eastern parts of the Figueira area (Fig. 5), in essentially pelitic sediments, deposited in swampy environments, rich in organic materials. The uranium grades found in these sediments (300 to 400 ppm) are not of economic importance at present.
- (b) The second, epigenetic, is found in the western part of the Figueira area, in zones drained by paleochannels, where psammitic predominated over pelitic sedimentation. This sedimentation, in a fluvial or fluviodeltaic environment, gave favourable conditions for mineralizing solutions to percolate through these permeable conduits.

2.4. The sequence of mineralization

The epigenetic uranium of the basal sediments of the Rio Bonito Formation would have followed a sequence of mobilization and precipitation phases which took place during and after the diagenesis of the host rocks.

These various phases have the following sequence:

- Phase I. Deposition of the lithostratigraphic Unit A (Fig. 6) in drainage zones above the top of the Itararé Formation, with simultaneous deposition of the uranium transported in solution. This unit presents gradually finer sediments, from bottom to top, covered by an impermeable bed of coal.
- Phase II. Establishment of a drainage system with the deposition of interfingering sandstone, siltstone, shale and organic material in several levels, which form Unit B. During this phase, part of the uranium initially deposited underwent remobilization and deposition in favourable sites near those drainage zones.

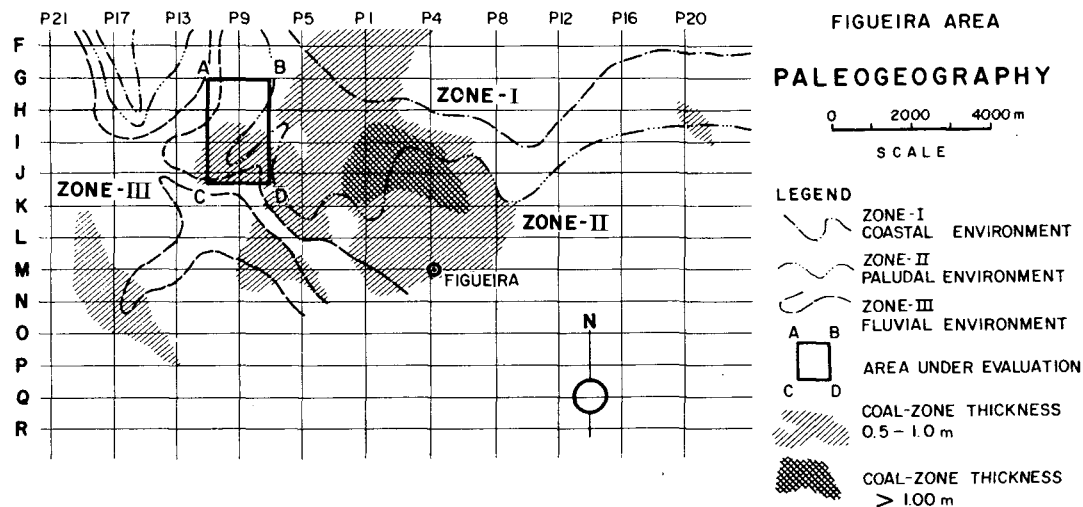


FIG. 5. Paleogeographic map showing the area ABCD under evaluation.

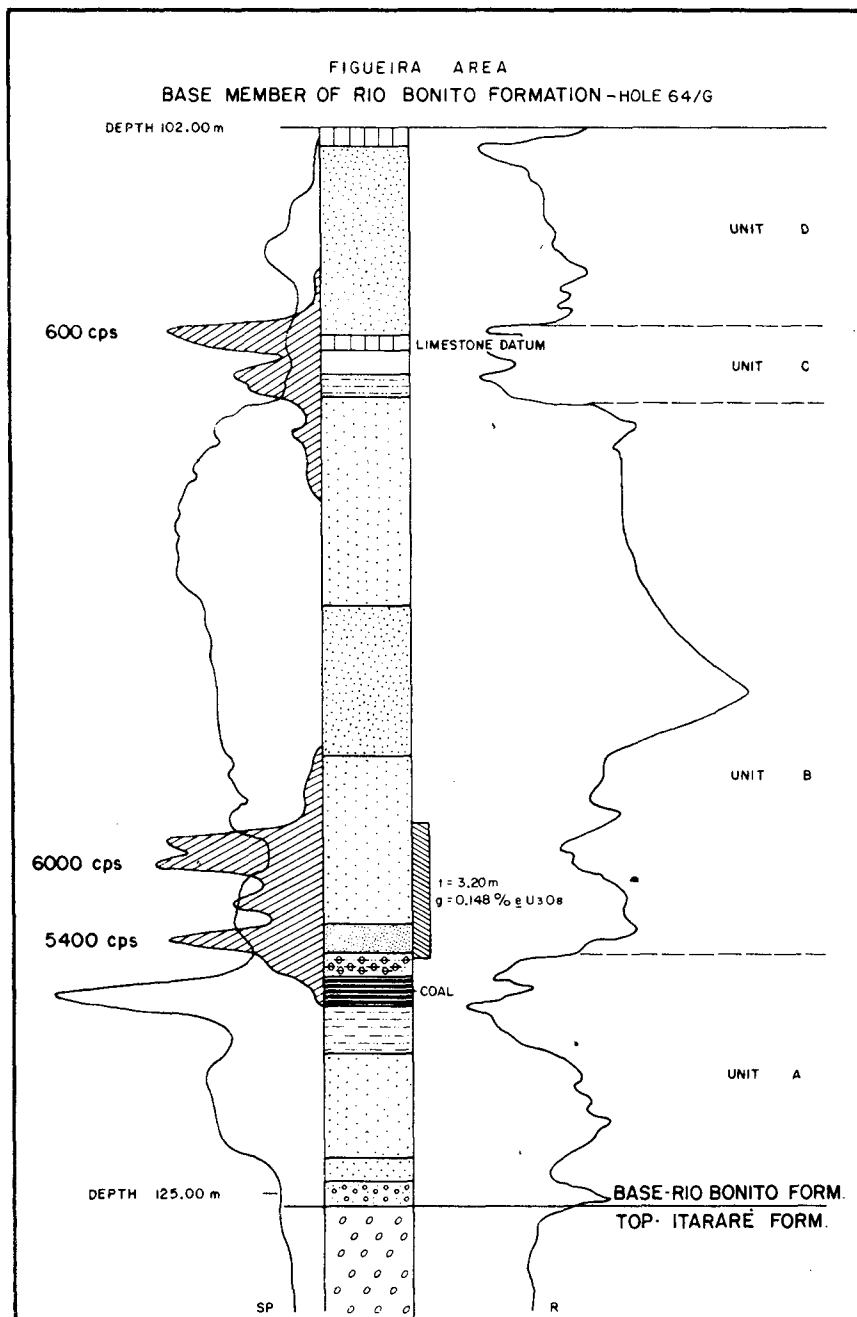


FIG. 6. A typical log of the mineralized zone at the basal part of Rio Bonito Formation showing the lithostratigraphic units. (cps = counts/s).

- Phase III. In this phase, the area was levelled, and the regional drainage arrived at its base level. This levelling caused a decrease in clastic and an increase in chemical sedimentation with the formation of the lithostratigraphic Unit C. This unit is composed of fine sediments and an impermeable limestone bed, spread throughout the area (a marker horizon for prospecting). Oxidation would have continued in this phase with remobilization of the previously deposited uranium.
- Phase IV. Since Unit B is practically sealed and protected from surface oxidation by Unit C, an increase in the hydrodynamic flow of the ground waters resulted. These waters were probably slightly alkaline and would have dissolved the uranium and redeposited it in reducing zones, with consequent development of the presently known ore bodies.
- Phase V. The enrichment process, started in Phase IV, continued throughout subsequent geological time during deposition of later sediments, when the ground water, confined between the two impermeable zones of units A and C, would have caused successive uranium remobilization and deposition.

The most favourable sites for uranium concentration are in the sandstone, located just above the coal seam that covers the lithostratigraphic Unit A, particularly when the beds are 10-12 m thick and intercalated between siltstone or carbonaceous shale.

The uranium of the area probably originated from reworked sediments of the Itararé Formation, which contain rock fragments of the crystalline basement with uranium grades above those considered normal for those rocks. This hypothesis is based on the fact that conglomerate with abnormal levels of radioactivity, containing pebbles of granitic, rhyolitic and tuffaceous rocks, were encountered at the top of the Itararé Formation.

Another argument favouring this hypothesis is the fact that various dikes of rhyolitic rocks, with thicknesses sometimes more than 10 m and with average uranium grades around 200 ppm, were noted at about 250 km south-east of Figueira, in the Carambei area. Such dikes are the remnants of a larger group of dikes emplaced in an area that has been eroded and whose detritus has formed part of the sediments of the Itararé Formation.

Correspondences between grades of Zn and As (less soluble elements) and also between grades of U and Mo (more soluble elements) were observed in the uranium deposition zones, which leads one to speculate about the existence of mineralizing cell fronts.

At present, a preliminary estimate of reserves in the Figueira area is 2000 t of U_3O_8 . The average grade for sandstone ore bodies averaging 1.3-m thick is 0.2% U_3O_8 . The ore bodies are at depths ranging between 130 and 190 m. In this type of occurrence it is reasonable to expect clusters of small mineralized bodies possibly rather close to each other.

There are indications of the existence of another area (NW of Figueira) with similar geological and paleogeographic characteristics. From what is now known of the Rio Bonito Formation, it is believed to be relatively easy to find similar sedimentary conditions.

3. METACONGLOMERATES

The Quadrilátero Ferrífero area is situated in the vicinity of Belo Horizonte, Minas Gerais. In this area, so called because of its large deposits of iron ore, uranium and gold occurrences in metaconglomerates were found.

The crystalline basement is composed of granitic gneiss and other similar coarse crystalline rocks. Mafic and ultramafic intrusions of various ages cut the rocks of the area.

According to Door [5], three series of Pre-Cambrian metasedimentary rocks reach a minimum accumulated thickness of 14 000 m. Some small areas of Tertiary continental sediments also occur.

The Pre-Cambrian metasedimentary section of the Quadrilátero Ferrífero is divided into

- (a) Rio das Velhas Series, mainly phyllites and schists affected by a first metamorphism 2800 m. y. ago.
- (b) Minas Series, superimposed with angular unconformity and subdivided by disconformities into four groups:

Tamanduá group: Quartzites and dolomites.

Caraça group: Quartzites and phyllites whose basal part is the Moeda Formation, which contains the uraniferous metaconglomerates.

Itabira group: This sequence contains rich iron and manganese deposits.

Piracicaba group: Quartzites, dolomites and phyllites.

The first known orogeny occurred after the time of the Rio das Velhas Series whose sediments were steeply folded. Granites, formed in a central uplift, as well as others situated west and south of the area, are the source of the coarse sediments of the Minas Series.

Later tectonic movements left the area folded and faulted, forming a curious pattern of synclines adjacent to a raised central block, known as the Rio das Velhas uplift.

In the area of the uraniferous occurrences the Moeda Formation is deposited directly on the basal group of the Rio das Velhas Series, which is known as the Nova Lima micaschists.

The Moeda Formation has a maximum thickness of 1150 m and is composed mainly of quartzite of varied grain size intercalated with conglomerate lenses and phyllite.

3.1. The uraniferous metaconglomerates

The uraniferous metaconglomerates are essentially oligomictic, made up of well-rounded quartz pebbles. In some places they are polymictic with phyllitic pebbles. They occur in restricted areas of the Moeda Formation, apparently coinciding with its widest sections. Detrital uraninite and pitchblende have been identified. The uraniferous mineralization occurs in association with pyrite which is present in the matrix and usually makes up

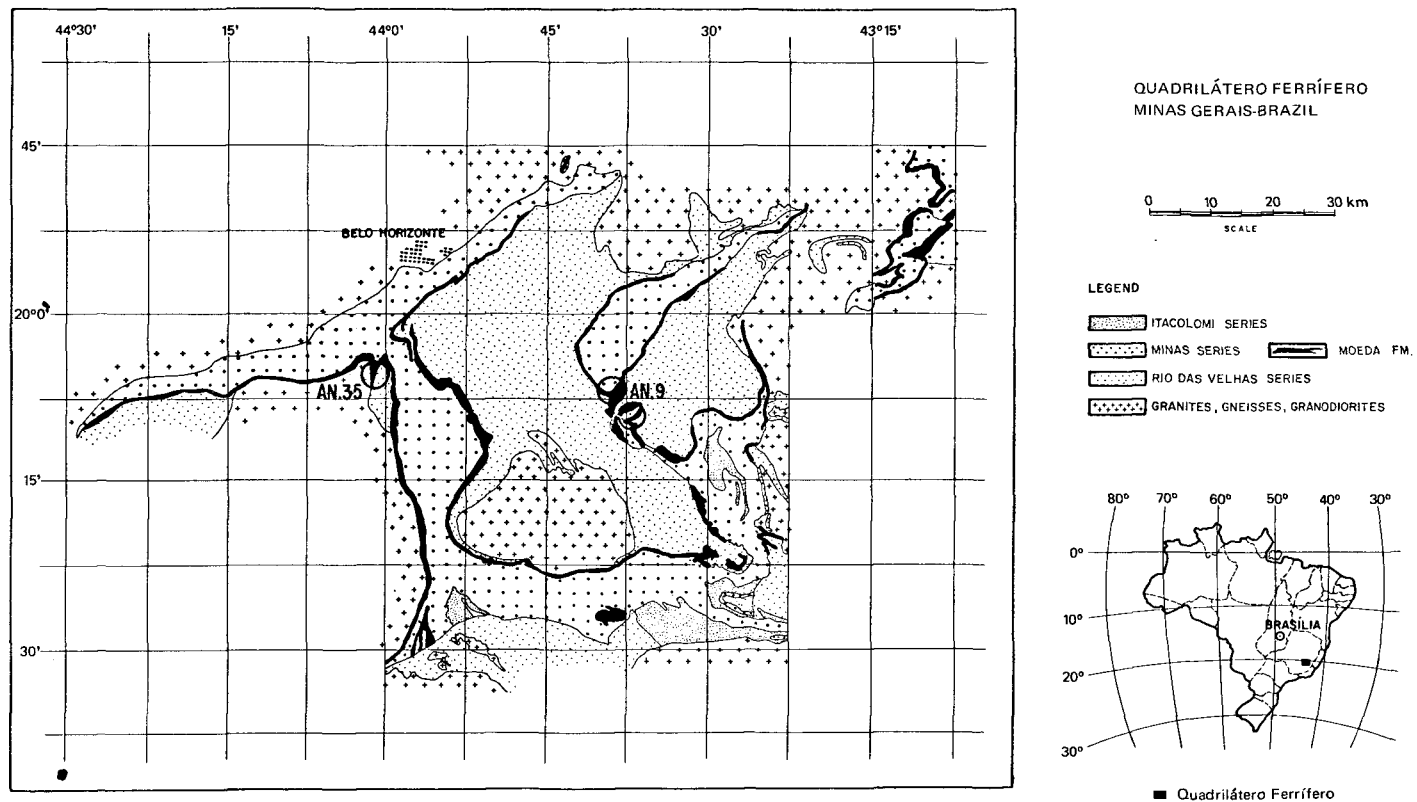


FIG. 7. Simplified geological map of the Quadrilátero Ferrífero area, showing the Moeda Formation and anomalies 9 and 35.

5-20% of the whole rock. Gold occurs together with uranium. Monazite, zircon, coffinite, pyrrhotite, chalcopyrite, rutile and xenotime are also present in the metaconglomerates.

According to mineralogical studies done in Canada, the highly radioactive coloured nodules taken from the pyritic matrix contain more uraninite than pitchblende. The radioactivity is explained by the presence of these minerals in amorphous hydrocarbons, similar to thucholite.

According to Robertson [6] and Villaça [7] these metaconglomerates are very similar to the Canadian and South African uraniferous conglomerates. They probably are of Aphebian age (i.e. lower Proterozoic). The ages are estimated to range from 2200 to 2500 m.y. They have the characteristics required for the deposition of uranium as a detrital mineral, being older than the oxygenation of the atmosphere, which was marked by the deposition of hematite (Fe^{3+}), represented in this area by the Itabira group itabirites. This hypothesis is also supported by the absence of traces of land flora which appeared from 2100 m.y. onwards.

It is believed that these metaconglomerates were deposited in a fluvial environment. Their characteristics, however, vary according to the local morphology at the time of deposition.

The paleogeography of the area is very difficult to interpret because of the superposition and intensity of the tectonic events which affected the Quadrilátero Ferrífero.

In anomaly 35 (Fig. 7), believed to be in the upstream part of a paleo-channel, the metaconglomerate is not well classified, showing many pebbles more than 8 cm in diameter. The conglomerates are split by many sand lenses.

In anomaly 9, situated 35 km southeast of anomaly 35, the metaconglomerate appears well classified, with pebbles generally measuring less than 4 cm. A further 30 km southeast, already in the vicinity of the ancient oceanic border, the metaconglomerate presents only a fine layer of pebbles, whose diameters are only up to 1 cm. In anomaly 9, the paleochannel contours are well defined. This is not the case in anomaly 35.

In anomaly 9, the accumulated thickness of the various metaconglomerate lenses is up to 100 m, while in anomaly 35 there is only one reef located near the base of the formation.

According to Bain [8], these facts correspond to deposition in a fluvial environment, varying from the piedmont environment (alluvial cones) upstream and passing through typical channel deposits, where the conglomerates are deposited by the "scour and fill" process, to the deltaic processes in coastal environment downstream.

3.2. Preliminary conclusions

The data obtained from drill holes in two or three anomalies, some of them drilled deeper than 500 m, i.e. well below the weathered levels, permit some preliminary conclusions.

- (a) There is a large volume of pyritic metaconglomerates, in good lithological conditions for deposition of detrital uranium and thorium. Uranium grades, however, are low.
- (b) The mineralized lenses have a maximum thickness of 1.5 m and do not have lateral continuity. The upstream mineralization (anomaly 35) is of

a higher grade than the downstream mineralization, but the volume of conglomerates is insufficient to form economic deposits at present prices.

- (c) There is no direct correlation between the amount of pyrite and the uranium mineralization, although it always occurs in pyritic levels. There is, however, a direct relation between uranium and titanium grades.
- (d) There are at least two ages or generations of pyrite. One, in masses up to 2 cm in diameter, occurs in the fine quartzites, metaconglomerates and even in the schists. Probably its origin is hydrothermal and more recent. The other, in smaller quantities, is represented by small crystals, which are finely distributed in the matrix. Their origin seems to be detrital. It follows the other heavy minerals.
- (e) There is not a direct relation between thorium and uranium grades, although both occur in almost all analysed samples, the relationship varying from hole to hole.
- (f) In the largest downstream occurrence (anomaly 9), the ratio $\text{ThO}_2/\text{U}_3\text{O}_8$ varies from 0.1 to 2.32, assuming an average value of 1.1. Considering that at the surface the ratio $\text{ThO}_2/\text{U}_3\text{O}_8$ is greater than 10, the existence of a strong uranium leaching is indicated.

As the $\text{ThO}_2/\text{U}_3\text{O}_8$ ratio varies from 0.1 to 2.32, i.e. by a factor of about 20, it can be concluded that such mineralization would be predominantly remobilized in areas richer in uranium. If it were syngenetic, i.e. mainly due to the detrital uranium and thorium minerals, uniformity in the ratio could be expected.

It can also be observed that where there is a 200 ppm uranium concentration, the $\text{ThO}_2/\text{U}_3\text{O}_8$ ratio is lower. In the upstream occurrence (anomaly 35) the values of the $\text{ThO}_2/\text{U}_3\text{O}_8$ ratio vary from 0.11 (minimum values) to 1.15 (maximum values), with the average values around 0.46. The average and maximum ratios correspond to half of the ratios found for the downstream occurrence.

- (g) Isopach maps show that the higher thorium and uranium grades do not coincide with the main axes of the paleodrainage.

3.3. Economic aspects

There is a large volume of pyritic conglomerates in the anomaly 9 area, deposited in favourable conditions for detrital uranium concentrations. Uranium content is not high enough for economical extraction at present energy prices.

Various levels, with an accumulated thickness of almost 100 m and with an average uranium grade higher than 10 ppm, show an intense uranium movement at the time of deposition. Considering that the phenomenon is not limited to this area, one can believe in the existence of a large uranium source during Aphebian time.

Gold was relatively little studied, but it is known to occur together with the uranium. Its average grade, in the 2.5 m of the basal conglomerate, is lower than 1 g/t, which is insufficient to change the economics of the occurrence.

In anomaly 35, the average gold grade is lower than 0.5 g/t.

These occurrences can be classified as geological reserves, that is, reserves at an extraction cost higher than \$ 20 per pound of extracted uranium. At current gold prices the minimum quantity of gold to make this mineralization economically feasible would be 2 g recoverable per ton.

Preliminary calculations related to the two areas with deep subsurface information indicate a geological reserve, i.e. an abnormal uranium accumulation, totalling about 5000 t of U_3O_8 in beds averaging 200 ppm and having an average thickness of 2.5 m.

3.4. Other occurrences in metaconglomerates

More recently, similar occurrences have been found in the Onça do Pitangui area, about 100 km west of Belo Horizonte, outside the Quadrilátero Ferrífero region. Here uranium occurs in similar conglomerates probably contemporaneous with those of the Moeda Formation. However, these show larger thorium and titanium concentrations and are stratigraphically located in the upper to middle part of the unit. No basal conglomerates were found. Probably the deposition conditions and sources of the sediments were a little different from those of the Moeda Formation.

These occurrences support the hypothesis that at the borders of the so-called São Francisco craton, (an extensive area which is the most stable of the Brazilian central region) the possibilities of finding economic uranium deposits in Pre-Cambrian metaconglomerates are promising.

In Serra de Jacobina, State of Bahia, on the other side of the geosyncline filled with the São Francisco craton debris, there are well-known uranium and gold mineralizations in lenticular quartz-pebble conglomerates of the Serra do Corrego Formation. These conglomerates are older than oxygenation of the atmosphere and also probably older than those from Moeda Formation. The average uranium grade of the Canavieiras Mine, at Serra de Jacobina, is 100 ppm. This would make uranium extraction possible only as a co-product of gold.

These occurrences represent only some of the many possible areas with Aphebian uraniferous and auriferous metaconglomerates within the borders of the São Francisco craton.

4. GRANITIC ROCKS

Recently, radiometric and geological reconnaissance work has shown several uraniferous occurrences in the Seridó geosyncline area, northeast Brazil. This area, well known because it includes the large Borborema scheelite province, must also be considered as a uranium province.

The Seridó geosyncline is formed by a Pre-Cambrian section of rocks called the Ceará Series which is stratigraphically subdivided into two groups:

- (a) Caicó group: Lower Pre-Cambrian age, discordantly overlying the Archean basement. The group includes migmatites, gneisses, meta-arkoses, para-amphibolites and limestones.
- (b) Seridó group: Upper Pre-Cambrian age, discordantly overlies the Caicó group. More strongly metamorphosed near the base, it includes quartzites, metaconglomerates, itabirites, gneisses, tactites, schists and phyllites.

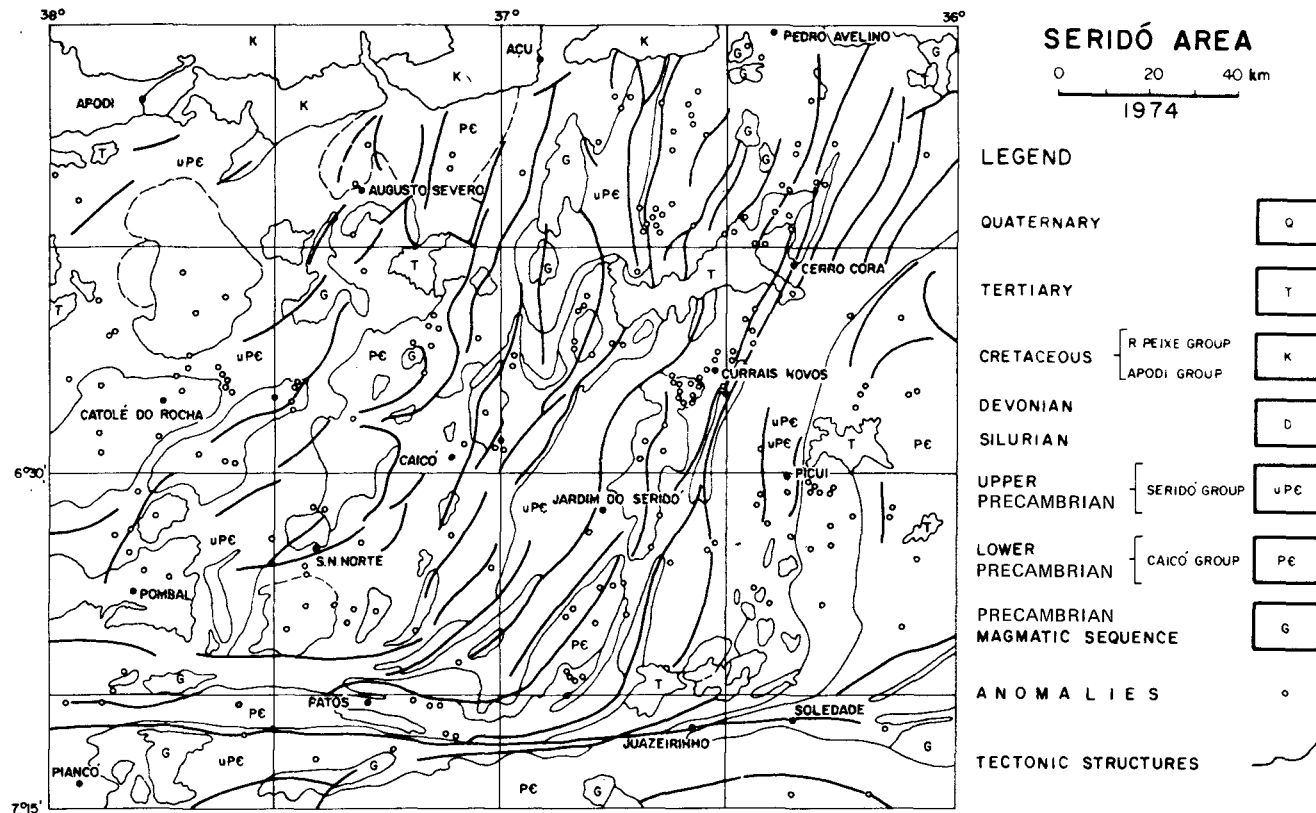


FIG. 8. Simplified geological map of the Seridó area, showing the relationship between tectonic structures and anomalies.

According to Ferreira [9], the Pre-Cambrian igneous sequence is represented by four types of granitic rocks. Besides these, basic and ultrabasic rocks up to 1800 m. y. old occur as dikes and sills. The four principal types of granitic rocks can be petrographically grouped as follows:

(a) Granodiorites of the "Conceição" type

These are grey granodiorites, with some orientation of the crystals, occurring in the form of elongated bodies which are almost concordant with the structural lineaments. These bodies are considered intrusive and synorogenic.

(b) Granites of the "Itaporanga" type

These are porphyritic, leucocratic granites, with abundant microcline crystals measuring up to 15 mm. Accessory minerals are biotite, hornblende and sometimes garnet. These granites are considered late orogenic.

(c) Granites of the "Itapetim" type

Equigranular, fine-grained granites, with a composition similar to the type (b), but without hornblende. They occur as dikes and are considered intrusive, late orogenic.

(d) Granites of the "Catingueira" type

Alkaline, leucocratic, fine-grained granites, with microcline, albite, quartz, biotite, titanite, zircon and magnetite. They occur as dikes, oriented according to the Patos lineament (EW). They are intrusive, with typical aureoles of contact metamorphism. Owing to the later reactivations of the Patos lineament faults, these dikes are brecciated and mylonitized.

Sandy sediments of Cretaceous and Tertiary ages occur in the Seridó region, but only in very restricted areas. Basalts and diabases related to the EW lineaments appear as sills and dikes penetrating the Cretaceous and Tertiary sediments. The dominant tectonic style is that of the linear foldings. Despite this predominance the area structure is marked by two strike slip faults: that of "Patos" and that of "Cariris Velhos", both with a general EW direction. These faults divide the Seridó region into three sections each with a different structural direction. The northern section with a general direction towards NNE-SSW; the central section with an EW direction and the southern section having axes and structural lines towards ENE-WSW.

4.1. Radiometric anomalies

In the Seridó geosyncline region, airborne radiometric surveys were undertaken over 29 000 linear km, covering an area of 126 000 km². More than 300 anomalies were found. An area situated between 5° 30' to 7° S and 36° to 38° W was selected as the most interesting. In this 36 000 km² area, 195 anomalies, 60% of the total, are located. In the same area a systematic airborne gamma-ray spectrometric survey was undertaken. Information from these surveys showed about 300 more radiometric uranium anomalies.

Of the 195 anomalies found by airborne survey, the majority (57%) occurs in granite and pegmatoid granite of the Pre-Cambrian igneous sequence. Thirty-four (17%) more interesting indications were selected on the basis of uranium grades. Of these, 65% are located in granite and

pegmatoid granite of the Itaporanga type. The location of the anomalies (Fig. 8) show an obvious relation to the local tectonic pattern. The anomalies in the northern and central part are located alongside the NNE-SSW structural lineations. The main anomaly pattern is spread according to this direction, in a 20-km band along a length of 80 km. Parallel to this band, both to the east and west, there is a smaller group of anomalies. It is interesting to note that near 7°S and 36° 30' W the anomaly pattern swings to an east-west direction, parallel to the large Patos lineament.

4.2. Uraniferous mineralization

According to Favali [10], the various types of uranium mineralization, found to correspond to the 34 selected anomalies, can be classified into two main categories:

- (a) Disseminated mineralization, mainly in granite and pegmatoid granite but also in biotite-schists, migmatite, meta-arkose, tactite, etc.
- (b) Vein-type mineralization, localized in fracture zones and without lithological control.

The disseminated uranium mineralization in the granite and pegmatoid granite is restricted to the intermediary lithological facies between the classic granitic and pegmatitic phases. This facies presents microcline and quartz as characteristic minerals, with subordinated plagioclase and biotite. Among the accessory minerals, the most important are titanite, magnetite, zircon, pyrite and molybdenite.

The primary uranium minerals are uraninite and uranothorianite, which are present in microscopic grains. Among the secondary minerals the most abundant is beta-uranophane. Meta-autunite, metatorbernite and francolite are also present. The presence of these secondary minerals, which predominate over the primary ones, is proved to a depth of 90 m. The average grades obtained in the disseminated mineralization in granites are approximately 400 ppm of U_3O_8 and 420 ppm of the ThO_2 .

In the pegmatoid granites the grades vary from 180 to 1800 ppm U_3O_8 , and the ThO_2 grades vary from 40 to 510 ppm.

The granitic and pegmatoid masses almost always occur on or near the anticlinal axes, and show synorogenic genetic relationships. It is known that in the evolution of geosynclines the granitic masses formed along the fold axes provide good conditions for uranium concentrations, particularly in the final phases of their differentiation. Therefore uranium in these rocks has a syngenetic origin but could also be emplaced in veins, when the structural conditions allowed.

The alteration of the primary minerals happened "in situ".

Uranium enrichments, probably epigenetic, were also found in the schists of the Seridó group.

Vein-type mineralization occurs in fractured zones with evidence of shearing in the vicinities of the major anticlinal axes. These axes are parallel to the general structure of the region and coincide with the long direction of the granite and migmatite bodies. Lithological control of the uranium mineralization was not observed. Petrographic-mineralogical studies show the interaction of various phases and degrees of metamorphic and hydrothermal processes.

Genetic interpretation of this type of occurrence is difficult. It is believed, however, that the uranium occurrences are related to the granitization processes. The veins have thicknesses ranging between 30 and 50 cm, and lengths of 400 to 800 m. The average grades obtained in the first drill holes are 0.15-0.30% U_3O_8 . Thorium is almost absent.

The primary minerals occur as pitchblende and uraninite, often associated with microscopic pyrite. The secondary minerals are uranophane, meta-autunite and kasolite.

Some veins can be classified as mesothermal polymetallic with significant amounts of Cu, Cr, Bi, Ag, and traces of Ni and Co. Other veins with well-crystallized autunite are considered to belong to the monometallic type.

Taking into consideration the large number of radiometric anomalies and other geological information, it is believed that in 1973 a new uraniferous province was found in the Seridó geosyncline region. Research is in its initial stage and does not yet permit conclusions concerning the presence of uranium deposits of economic importance.

REFERENCES

- [1] AMARAL, G., et al., Potassium-Argon Ages of Alkaline Rocks from Southern Brazil, *Geochronology Laboratory, University of São Paulo, Brazil; Geochim. Cosmochim. Acta* 31 (1967) 117.
- [2] OLIVEIRA, A.G., UTSUMI, O., *Informações e Características Gerais da Mineralização de Urânio no Setor C/09, Poços de Caldas, MG, CNEN Rep.*, Rio de Janeiro (1973), unpublished.
- [3] FUJIMORI, K., *Minerais Radioativos de Poços de Caldas, MG, CNEN Rep.*, Rio de Janeiro (1972), unpublished.
- [4] SAAD, S., A Mineralização Uranífera da Região de Figueira, PR, *Anais do XXVII Congresso Brasileiro de Geologia, Bol. n.º. 1, Soc. Bras. Geol., Núcleo Bahia, Salvador, Brazil* (1973) 36.
- [5] DOOR, J. V. N., *Physiographic, Stratigraphic and Structural Development of the Quadrilátero Ferrífero, Minas Gerais, Brazil, USGS Prof. Paper 641-A* (1969).
- [6] ROBERTSON, D. S., *Report on Studies in Brazil for Comissão Nacional de Energia Nuclear, CNEN Rep.* Rio de Janeiro (1973), unpublished.
- [7] VILLAÇA, J. N., FUZIKAWA, K., *Urânio no Quadrilátero Ferrífero, Anais do XXVII Congresso Brasileiro de Geologia, Bol. n.º. 1, Soc. Bras. Geol., Núcleo Bahia, Salvador, Brazil* (1973) 34.
- [8] BAIN, G. W., *Note on the Uraniferous Moeda Conglomerate Formation, Southward from Belo Horizonte, Brazil, CNEN Rep.* Rio de Janeiro (1972), unpublished.
- [9] FERREIRA, J. A. M., ALBUQUERQUE, J. P. T., *Sinopse da Geologia da Folha Seridó, Sudene, Divisão de Geologia, Série Geologia Regional n.º. 18, Recife, Brazil* (1969).
- [10] FAVALLI, J. C., *Mineralização Uranífera na Área do Geossinclinal do Seridó, Anais do XXVII Congresso Brasileiro de Geologia, Bol. n.º. 1, Soc. Bras. Geol., Núcleo Bahia, Salvador, Brazil* (1973) 48.

DISCUSSION

M. Y. MOGHAL: You mentioned that in the Agostinho and Cercado deposits the uranium is derived from metamict zircon, but apparently the fraction of zircon in the rocks is eight times greater at Agostinho than at Cercado. This being so, how do you account for the very similar grades of uranium in these two deposits? Do you think there is some additional source of the Cercado uranium, or is there some other explanation for the grade, such as local enrichment?

J. R. de ANDRADE RAMOS: We do not know exactly what the reason for this situation is. However, given the geological attitudes of the Agostinho and Cercado deposits – the former consists of vertical veins and the latter of

sub-horizontal lenses – the weathering mantle may have had a lot to do with the different percentages of zircon. Caldasite veins, which are also vertical, show grades of zirconium up to 70%. The Agostinho veins, which consist of brecciated material, are closer in genesis to caldasite veins than are the sub-horizontal bodies of the Cercado deposit. K. Fugimori is doing mineralogical studies on this subject at the University of São Paulo.

H. SØRENSEN: I understand that the new uranium deposits found in the alkaline rocks of the Poços de Caldas pipe were formed by reworking of the alkaline rocks in which they occur. What is the uranium content of the primary alkaline rocks, such as the tinguaita, and what are the uranium minerals in these rocks?

J. R. de ANDRADE RAMOS: Even though we have no accurate rock analyses available to us yet, we believe that the uranium content of the primary alkaline rocks is between 10 and 100 ppm of U_3O_8 . The uranium is contained mostly in zirconiferous minerals such as eudialyte, rosenbuschite, astrofilita, lavenite, encolite and zircon. Apatite, without being zirconiferous, is also uraniferous.

H. C. WHITESIDE: There is very deep weathering of the rocks in Brazil, which has given rise to a thick soil cover. Do you think there is enough residual radioactivity in these soils for normal scintillometric methods to pick up possible uraniferous ore bodies?

J. R. de ANDRADE RAMOS: The application of scintillometric methods is, of course, just the beginning of a continuous exploration process. These methods, even when they yield negative results, do not eliminate an area because a thick or even medium soil cover could naturally hide radioactive ore bodies. We do carry out extensive scintillometric surveys over our tropical weathered country because they give much quicker information than any other method and provide a guide for subsequent steps in uranium prospecting.

M. MOREAU: At Arlit in the Niger we have observed the presence of mobile zirconium which has perturbed the chemical treatment of the ore. Is it not possible that purely meteorological alteration of the zirconium-uranium minerals in Brazil might be partly responsible for the changes in the Zr/U ratio that you have observed in the altered portions of your deposits?

J. R. de ANDRADE RAMOS: Yes, purely meteorological alteration of the Zr/U ratio is undoubtedly one of the processes involved in the variations of uranium behaviour. Present knowledge indicates that the destruction of zircon crystals would be enhanced by the action of hydrothermal metamorphism and weathering. This is demonstrated by the fact that the upper forty metres of the Agostinho veins are much less refractory than the lower portions.

RELATION OF METALLOGENIC, TECTONIC AND
ZONING FACTORS TO THE ORIGIN
OF URANIUM DEPOSITS

Etude d'ensemble

ESSAI DE CLASSIFICATION METALLOTECTONIQUE DES GISEMENTS D'URANIUM

V. ZIEGLER

Commissariat à l'énergie atomique,
Châtillon, France

Abstract-Résumé

A POSSIBLE METALLOTECTONIC CLASSIFICATION OF URANIUM DEPOSITS.

The primary distribution of uranium and thorium is closely associated with the structural history of the sialic crust and hence with sialic magmatism. Accordingly, far from being distributed homogeneously, uranium should be associated preferentially with certain structural elements of the continental crust. Economic or subeconomic concentrations of uranium deriving for the most part from the primary distribution through hypogenic or supergenic remobilization should also be distributed in fairly close association with these structural elements. The author proposes a metallogenic classification in the form of a table in which the deposits are grouped according to both the metallogenic type to which they belong and to the main structural element with which they are associated; the relative ages of the minerals are also indicated. From this table, which is based on the principal known occurrences of uranium in the world, it is possible to see the main characteristics of the distribution of uranium deposits. The chief purpose of the table is to indicate the principles of a method for studying the distribution of uraniferous deposits. Drawn up for a particular region, with appropriate structural and metallogenic distinctions, such a table should make it possible to discern the far more detailed regional patterns which are called for in the search for deposits.

ESSAI DE CLASSIFICATION METALLOTECTONIQUE DES GISEMENTS D'URANIUM.

La répartition primaire de l'uranium et du thorium est étroitement associée à l'histoire structurale de la croûte sialique et par suite au magmatisme sialique. Il en résulte que, loin d'être réparti d'une manière homogène, l'uranium devrait s'associer préférentiellement à certains éléments structuraux de la croûte continentale. Les concentrations économiques ou sub-économiques d'uranium dérivant pour la plupart de ce stock primaire par remobilisations hypogènes ou supergènes, elles devraient également être distribuées en association plus ou moins étroite avec ces structures. Une classification métallogénique des gisements d'uranium est proposée sous la forme d'un tableau dans lequel les gisements sont classés à la fois suivant le type métallogénique auquel ils appartiennent et suivant l'élément structural majeur de l'écorce terrestre auquel ils s'associent. L'âge relatif de la minéralisation est également indiqué. Ce tableau, établi sur la base des principales occurrences uranifères connues dans le monde, permet de retrouver les caractéristiques principales de la répartition des gisements d'uranium. Sa présentation a pour objectif principal de proposer les principes d'une méthode d'étude de la répartition des gisements uranifères. Conçu à l'échelle d'une région donnée, avec des distinctions structurales et métallogéniques appropriées, un tel tableau devrait permettre de dégager des guides régionaux beaucoup plus fins pour la recherche des gisements.

INTRODUCTION

=====

Le rapport d'Août 1973 de l'OECD NEA/AIEA concernant les ressources, la production et la demande en uranium fait apparaître la nécessité de découvrir de nouvelles réserves d'uranium à une cadence passant graduellement d'ici à 1990 de 65 000 t U/an à 230 000 t U/an, c'est-à-dire que le potentiel total correspondant devrait augmenter de quelque 2 500 000 t U.

Il est probable que le potentiel uranifère, à mettre en évidence, se situe au moins en partie dans des gisements beaucoup plus difficiles à déceler ou à évaluer que ceux constituant les ressources déjà découvertes. Ces difficultés peuvent être d'ordre géographique, humain, mais surtout géologique.

Il en résulte qu'il se pose pour la recherche des gisements uranifères, des problèmes d'orientation beaucoup plus difficiles qu'auparavant, aussi bien au stade de la sélection des régions devant être soumises à des prospections, qu'à ceux des diverses phases de reconnaissance. La recherche d'un équilibre optimal entre l'effort à consentir dans une région et les chances de découvertes de minerais doit reposer sur des critères d'autant plus sûrs que la minéralisation recherchée est moins immédiatement perceptible.

Il est donc devenu urgent d'identifier des guides de la minéralisation plus puissants et plus fiables que dans le passé et ceci depuis le stade préliminaire de la sélection des régions dans lesquelles un programme de recherches a les meilleures chances de succès, jusqu'au stade de la détection et de l'étude d'un corps minéralisé individuel.

Comme le remarque la Notice d'Information de l'AIEA, concernant le présent Colloque, étant donné que l'essentiel des caractéristiques lithologiques et physiographiques de l'écorce terrestre dépendent en dernière analyse de processus de la tectonique globale, il en est sans doute de même de la répartition des gisements uranifères.

L'URANIUM DANS L'HISTOIRE STRUCTURALE DE LA CROÛTE TERRESTRE

=====

Déjà en 1970, au cours du Colloque précédent, la tendance à rechercher les critères de la répartition de l'uranium dans les événements essentiels de l'histoire structurale et à les relier aux éléments structuraux majeurs des continents était apparue avec les communications de S.H.U. BOWIE (7), de J.W. GABELMAN et dans une certaine mesure de A. GANGLOFF (21).

S.H.U. BOWIE arrivait à la conclusion que la majeure partie des réserves du monde occidental se répartissaient dans le domaine du Précambrien. Il en cherchait l'explication dans l'histoire précoce de la formation de la croûte terrestre, en se basant sur les travaux de C.R. ANHAEUSSER, et al. (2) et de A.E.G. ENGEL et al. (17). Selon ces auteurs en effet tous les éléments volatils, en particulier ceux constitutifs des granites, dont U, Th et K, auraient formé une fine croûte sialique primitive externe. L'histoire géologique ultérieure de ces éléments n'a été qu'une série de redistributions à la faveur de granitisations et de métamorphismes successifs. S.H.U. BOWIE en conclut que pratiquement tout le stock d'uranium présent dans la croûte terrestre est apparu dans cette phase précoce de l'histoire du globe et se trouve de ce fait associé actuellement aux boucliers précambriens et l'uranium n'apparaît dans les orogènes phanérozoïques que là où ils ont incorporé du socle précambrien.

De nombreux auteurs se sont intéressés à cette migration des lithophiles en général et de l'ensemble U-Th-K en particulier vers les parties supérieures du globe terrestre. Selon F. BIRCH (6) la Terre formée, il y a 5000 MA, par l'accrétion de météorites chondritiques, a hérité d'un stock initial d'U et Th à peine suffisant pour alimenter la croûte terrestre à elle seule. Après la séparation de la masse de fer du noyau central il y a quelque 4500 MA et la fusion de la phase silicatée, la fraction fusible de celle-ci a migré, entre

4500 et 3500 MA vers les zones externes pour former le manteau supérieur contenant tous les éléments radioactifs du globe. Dans certaines régions du globe la croûte continentale a atteint sa stabilité vers 3500 MA, mais ailleurs elle a poursuivi sa formation avec continuation de la concentration vers le haut des éléments radioactifs aux dépens du manteau supérieur. Ces éléments auraient été redistribués ultérieurement par érosion, transport latéral et remobilisation des sédiments.

Selon I.B. LAMBERT (35) les études faites sur le craton de YILGARN (Australie Occidentale) montrent que la presque totalité de U et Th est concentrée dans les 10 km superficiels du bouclier (zone des granites). Les teneurs respectives en ces éléments, très faibles à 40 km de profondeur, sont de moins de 1 ppm U et de quelques ppm Th à 10 km de profondeur. Elles augmentent brusquement dans ces 10 derniers kilomètres jusqu'à 3 ppm U et 20 ppm Th. Quant à K il passe de moins de 1 % à 40 km de profondeur à environ 2 % à 10 km puis à quelque 2,7 % dans ces 10 derniers kilomètres.

Cette tendance des éléments radioactifs à migrer vers les zones externes du globe n'implique pas nécessairement la formation d'une croûte sialique externe continue originelle. Cette dernière hypothèse a d'ailleurs été vivement controversée entre autres par A.Y. GLIKSON (24). Sur la base des travaux de certains chercheurs il souligne le caractère probablement peu différencié du manteau supérieur primitif qui de ce fait ne saurait donner par différenciation directe le sial primitif. La formation du sial implique la nécessité de différenciations répétées. Ce manteau archéen aurait été surmonté d'une croûte primitive de constitution comparable à la croûte océanique actuelle. La mise en place, dans cette dernière, des granites sodiques et des granodiorites (résultant de la fusion partielle de la croûte océanique dans les zones de subsidence) provoque la formation d'îles-continentes (protocontinents), à la manière de l'actuel Archipel des FIJI. Dans les espaces intermédiaires se forment des fosses de subsidence à remplissage de volcanites calco-alkalines et de sédiments, soumis ensuite à un métamorphisme de faible degré et à l'intrusion de granites potassiques. La coalescence de ces arcs insulaires et de ces zones de subsidence donne naissance aux noyaux cratoniques archéens. Ces noyaux s'entourent ensuite eux-mêmes de chaînes mobiles et les ensembles constitués par ces éléments forment ultérieurement les boucliers précambriens.

Une publication récente de A.E.G. ENGEL et D.L. KELM (18) montre une évolution dans le même sens de la compréhension de la géologie de l'Archéen. Cette ère aurait été en effet caractérisée par l'expansion des fonds océaniques associée à la migration d'arcs insulaires en évolution et à celle de fragments protocontinentaux. Elle aurait également été une période de mouvements complexes de dispersion-accrétion aboutissant à la constitution de mégacontinents.

Plus récemment encore C.J. TALBOT (57) a envisagé la genèse de la croûte sialique dans le cadre classique de la tectonique des plaques. C'est-à-dire que les processus tectoniques qu'il invoque pour l'Archéen sont semblables à ceux actuellement en cours, mais ils s'exercent sur une croûte terrestre différente, essentiellement formée de croûte océanique. Les petites différenciations sialiques originelles apparaissent suivant les bords d'accrétion des plaques (côté rides océaniques). Elles sont ensuite soumises à la dérive et en arrivant aux zones de subduction elles peuvent être entraînées dans le manteau et ensuite expulsées dans la plaque en formant les arcs insulaires. Ces arcs insulaires après une période de développement sont à leur tour entraînés vers les zones d'accrétion où ils sont éventuellement fragmentés et ensuite retournés vers de nouvelles zones de subduction. Ce processus continuellement répété conduit à la formation de nouveaux arcs insulaires et de cordillères qui à leur tour peuvent se fragmenter ou s'agglomérer avec d'autres accumulations sialiques de même nature. Partant du principe que ne peuvent entrer dans les zones de subduction que des

masses petites ou des fractions faibles du sial, restitué ensuite par différenciation, tout ce processus va dans le sens d'une croissance progressive et permanente de la masse sialique. Selon C.J. TALBOT l'Archéen prend fin avec l'avènement de la première orogénie de type himalayen, c'est-à-dire où deux masses sialiques suffisamment importantes pour arrêter la subduction s'affrontent donnant naissance aux chaînes mobiles (mobil belts). Les chaînes de roches vertes (greenstone belts) suturant les masses sialiques des noyaux cratoniques archéens représentent les océans archéens. D'ailleurs A.Y. GLIKSON (24) souligne de son côté la similitude géochimique des chaînes de roches vertes avec les tholéiites océaniques (pauvreté en U, Th et K en particulier). Elles introduisent donc une importante hétérogénéité dans la géochimie des noyaux cratoniques archéens.

Que nous adoptions le schéma de la croûte sialique primitive de C.R. ANHAËUSSER et al. (2) ultérieurement remaniée de manière à donner la succession des situations géologiques de l'histoire du globe ou les schémas mettant en jeu les processus de la tectonique des plaques dès le moment de la consolidation de la lithosphère primitive, on constate par l'extension des aires antérieures aux orogènes phanérozoïques qu'en fait la masse essentielle de la croûte sialique était individualisée à l'aube du Phanérozoïque. Si l'on tient compte de plus qu'une partie non négligeable du matériel impliqué dans les orogènes phanérozoïques dérive du remaniement des boucliers précambriens, on mesure l'apport relativement faible du sial au cours des orogénies phanérozoïques.

Pour faible qu'il soit, dans la mesure où ses caractéristiques géochimiques restent comparables à celles du sial précambrien, il pourrait cependant jouer un rôle non négligeable dans la distribution des gisements d'uranium.

Considérons le cas des gisements uranifères filoniens du Limousin et de Vendée en France situés dans des leucogranites mis en place il y a 300 MA dans la zone de cordillère hercynienne de l'Europe Occidentale. Ces granites peuvent représenter l'apport sialique dans la zone d'affrontement entre les boucliers fennoscandinave et africain au cours de l'orogénie hercynienne. Ces leucogranites se distinguent par une teneur fondamentale élevée en uranium de 15 à 20 ppm. Selon M. MOREAU et G. RANCHIN (45) ils auraient été soumis ultérieurement (les données géochronologiques suggèrent un décalage de l'ordre de 50 MA entre la mise en place des leucogranites et celle des minéralisations uranifères filoniennes) à l'action de fluides hydrothermaux riches en CO_2 qui seraient responsables de l'altération de ces granites et de la mobilisation consécutive de l'uranium.

Les conclusions de L. BURNOL (9) relatives à la formation des gisements uranifères du Limousin en diffèrent quelque peu par le fait que ce dernier auteur rattache la formation de ces gisements d'une façon plus étroite à l'évolution granitique et plus particulièrement au stade deutérique. Une étude géochimique très importante lui a montré que ces gisements uranifères, bien que ne s'intégrant pas dans une zonalité normale existant autour des massifs granitiques, se plaçaient cependant dans des zones limitées par les teneurs en Na variant de 2 à 2,3 %, en K allant de 4,5 à 5 % et en Be comprises entre 10 et 20 ppm.

Cependant M. MOREAU et G. RANCHIN (45) ont mis en doute le caractère juvénile de l'uranium de ces granites leucocrates. Ils observent un enrichissement en uranium de plus en plus marqué et localisé, par rapport à l'environnement métamorphique, depuis les granites à biotites jusqu'aux leucogranites. Cette dernière remarque concernant le caractère au moins partiellement hérité de l'uranium des leucogranites rappelle l'observation citée plus haut de S.H.U. BOWIE selon laquelle l'existence de gisements uranifères dans les chaînes phanérozoïques requiert la présence de vestiges précambriens.

Or dans la chaîne hercynienne européenne les provinces uranifères riches se trouvent précisément en relation avec les régions où l'on trouve des vestiges importants de fragments précambriens plus ou moins remaniés : Massif de Bohême, Massif Central Français.

Un autre type de gisement étroitement lié au magmatisme sialique, caractéristique des bords de saturation des plaques continentales est celui des gisements à uranium-molybdène dont on connaît dans le monde occidental un seul exemple typique d'une certaine importance (MARYSVALE, USA), alors qu'en URSS, il paraît fréquent, voire économiquement important. Les exemples évoqués s'associent à des orogènes phanérozoïques d'âges différents.

CLASSIFICATION METALLOTECTONIQUE DES GISEMENTS D'URANIUM PROPOSEE

=====

Le comportement de l'uranium paraissant ainsi étroitement lié à l'histoire structurale de la croûte sialique, il est logique de s'attendre à ce que les concentrations uranifères soient en dépendance plus ou moins étroite avec les éléments structuraux majeurs de celle-ci.

C'est ce que nous tentons de dégager à l'aide d'un tableau classant les gisements connus simultanément en fonction de leurs types métallogéniques et des éléments structuraux majeurs de l'écorce terrestre auxquels ils sont associés.

Les entrées horizontales se rapportent aux éléments structuraux. Ce sont d'abord les noyaux cratoniques archéens, que nous définissons comme les unités limitées à l'orogénie kénoréenne, donc d'un âge antérieur à 2500 MA. Viennent ensuite : l'ensemble des orogènes protérozoïques (postérieurs à 2500 MA) et les différents orogènes phanérozoïques.

Nous distinguons en outre dans chacune de ces structures les étages structuraux géosynclinaux, c'est-à-dire l'ensemble des terrains impliqués dans l'orogénie considérée, des formations de couverture constituées par l'ensemble des terrains discordants postérieurs, déformés uniquement par des accidents cassants ou des plis à grands rayons de courbure.

Les entrées verticales représentent les différents types de gisements uranifères exploitables dans les conditions actuelles ou des concentrations d'uranium considérables encore sub-économiques (phosphates marins ou schistes noirs) ou des types d'un intérêt scientifique particulier (pegmatites zonées, gisements de karsts).

Malgré toutes les imperfections que ce tableau peut comporter : son caractère sommaire, définition discutable de certaines subdivisions, position incorrecte ou contestable de certains gisements, appartenance simultanée possible de certains gisements à plus d'une position, etc..., il permet néanmoins de dégager un ensemble d'observations utiles à la définition des critères de répartition des concentrations uranifères.

TABLEAU. ESSAI DE CLASSIFICATION METALLOTECTONIQUE DES GISEMENTS D'URANIUM

Unités structurales	Eléments constitutifs des unités structurales		Gisements des conglomérats pyriteux (aurifères ou non)	Gisements dans ensembles grés-argileux continents	Gisements filoniens quasi monométalliques	Gisements finement disséminés à contrôle stratolite associés éventuellement à des filons	Gisements filoniens associés à des minéralisations polymétalliques	Gisements filoniens associés à la magnétite
			1	2	3	4	5	6
Noyaux cratoniques archéens (antérieurs à 2500 MA)	Bâti archéen (basement) (A)							
	Formations de couverture (B)		▲ Elliott Lake [40, 47] CDN ▲ Witwatersrand [27, 60] ZA	▲ Wyoming [26, 34] USA				
Chaînes plissées (mobile belts) protérozoïques	Etages géosynclinaux (C)				▲ Beaver lodge [5] CDN ▲ Nabarlek [38, 54] AUS ▲ Koongarra [54] AUS	▲ Singhbhum Belt [32] IND ▲ Ranger 1 [38, 54] AUS ▲ Koongarra [54] AUS	▲ Port-Radium [36] CDN ▲ ? Shinkolobwe [16] CGO	Krivoy Rog, SU Vastervik, S
	Formations de couverture (D)		▲ Jacobina [14] BR	▲ Niger [12, 58] (avec Mo)				
Orogènes du Paléozoïque inférieur (type calédonien)	Etages géosynclinaux (E)							
	Formations de couverture (F)							
Orogènes hercyniens ou autres du Paléozoïque supérieur	Zone géosynclinale (G)						▲ Jachymov Erzgebirge [48] CS et DDR (Ni-Co-Bi-Ag-Cu-Pb-Zn, As-Sb)	
	Zone de la Cordillère (H)				Massif Central français [22] Meseta ibérique [30]		▲ ? Pribram [48] CS (Pb-Zn-Ag)	

Gisements associés au molybdène et au volcanisme acide à intermédiaire	Gisements dans schistes épimétamorphiques péritholites	Gisements dans pegmatites et skarns	Gisements dans pegmatites zonées	Gisements à U et Th de complexes alcalins ou carbonatites liés aux rifts intra-continentaux	Gisements des calcrètes uranifères	Gisements dans schistes noirs	Gisements dans phosphates marins	Gisements dans karsts
7	8	9	10	11	12	13	14	15
			Ontario [40] CDN Tete [10] Mozambique	•Palabora [25] ZA				
					•Yeclirrie, AUS		• Cabinda [10] Angola	
		•Rossing [3] SWA •Bancroft [50] CDN •Mary Kathleen [28] AUS •Fort Dauphin [43] RM	•Plateau Central malgache [46]	•Ilimaussaq [53] (Groenland) •Pocos de Caldas, BR				
					•Désert de Nassib [3] SWA	•Schistes alunifères de Suède [56] Schistes de Chattanooga [13] USA		•Bakouma [21] RCA Le Vigan, F
♦ URSS [37, 51]								
♦ URSS [37, 51]								
	Portalegre [39] F Ciudad-Rodrigo, E							

TABLEAU (suite)

Unités structurales	Éléments constitutifs des unités structurales	Gisements des conglomérats pyriteux (aurifères ou non)	Gisements dans ensembles grés-argileux continentaux	Gisements filoniens quasi monométalliques	Gisements finements disséminés à contrôle stratotide associés éventuellement à des filons	Gisements filoniens associés à des minéralisations polymétalliques	Gisements filoniens associés à la magnétite
		1	2	3	4	5	6
Orogènes hercyniens ou autres du Paléozoïque supérieur	Formations de couverture (J)		•Hérault [21] F •Hamr [48] CS •Gulf Coast [8] USA				
	Etages géosynclinaux (J)		•Suleiman-Range PAK			•Isérables [29] CH (Pb-Cu-Sb) •Talmessi [4] IR (Ni-Co-Cu-Bi)	
Orogènes alpins	Fragments de socle hercynien (ou plus ancien) repris dans l'orogène (K)		•Trentin [23] I •Mts Messek [31] H •Spis basses Tatra [48] CS •Novazza [1] I (avec Zn)	Kalna, YU		•Macédoine [46] YU (Pb-Zn)	
	Etages géosynclinaux (L)					•Nombreuses occurrences avec: Pb-Zn-Ag; Cu-Ag; Ni-Co-Cu-As; pyrite aurifère	
Cordillères américaines (ensemble névado-laramien)	Fragments de socle précambrien (M) repris dans l'orogène		•Colorado [19] USA •Salta [55] RA •Malargue Mendoza [55] RA			•Front Range [52] USA (Pb-Zn-Cu, Mo)	

Types comportant des districts renfermant plus de 50 000 t U (en minerai économique)

Types comportant des districts renfermant plus de 200 000 t U (en minerai subéconomique)

Age de la première mise en place de la minéralisation (lorsque connu)

- ▼ Archéen
- ▲ Protérozoïque
- ◆ Paléozoïque inférieur
- Paléozoïque supérieur
- Cénozoïque
- Récent

N.B.: 1) Les chiffres entre parenthèses renvoient aux références bibliographiques en fin du texte.

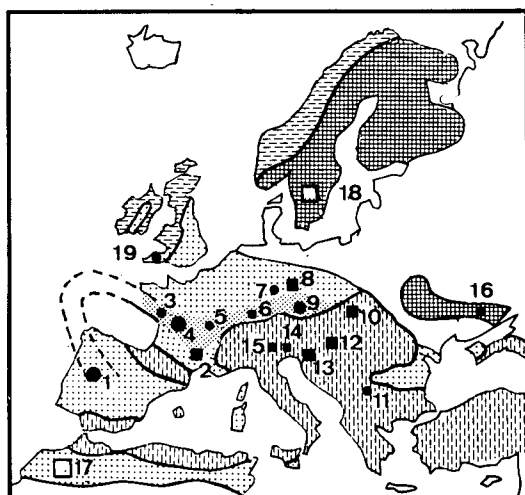
2) Les pays contenant les gisements sont désignés par les symboles de la Fédération internationale de l'Automobile.

Gisements associés au molybdène et au volcanisme acide à intermédiaire	Gisements dans schistes épimétamorphiques périthorlitiques	Gisements dans pegmatolites et skarns	Gisements dans pegmatites zonées	Gisements à U et Th de complexes alcalins ou carbonatites liés aux rifts intra-continentaux	Gisements des calcrètes uranifères	Gisements dans schistes noirs	Gisements dans phosphates marins	Gisements dans karsts
7	8	9	10	11	12	13	14	15
							• Maroc [49] • Floride [12] USA	
	• Spokane [58] USA • Austin [58] USA						• Phosphoria [42]	
• Marysvale [33] USA								

- Tendances générales de la répartition des concentrations uranifères

L'examen de notre tableau appelle les observations générales suivantes :

- Les concentrations d'uranium, dans leur ensemble, marquent une nette préférence à l'égard d'un nombre restreint d'éléments structuraux, et en fonction du type métallogénique auquel elles appartiennent, elles s'associent préférentiellement à l'un ou l'autre de ceux-ci. Ce qui confirme la dépendance étroite entre la répartition des concentrations uranifères et les unités structurales de la croûte terrestre.



Légende

- Domaine Précambrien
- Zone de la Cordillère Hercynienne
- Domaine Calédonien
- Domaine Alpin
- Domaine Hercynien

Gisements des phosphates marins et des schistes alu-
nifères

Gisements des formations de couvertures continentales

Gisements du groupe filonien (y compris schistes ibéri-
ques)

- 1. Meseta Ibérique; 2. Herault; 3. Vendée; 4. Limousin;
- 5. Forez; 6. St Hippolyte; 7. Erzgebirge; 8. Hamr;
- 9. Příbram; 10. Spis-Basses Tatras; 11. Macédoine;
- 12. MTS. Mecsek; 13. Zhirowski Vrh.; 14. Trentin; 15. Novazza;
- 16. Krivoy Rog; 17. Phosphates du Maroc; 18. Schistes de -
Suède; 19. Devon-Cornouaille.

FIG.1. Principaux gisements uranifères d'Europe.

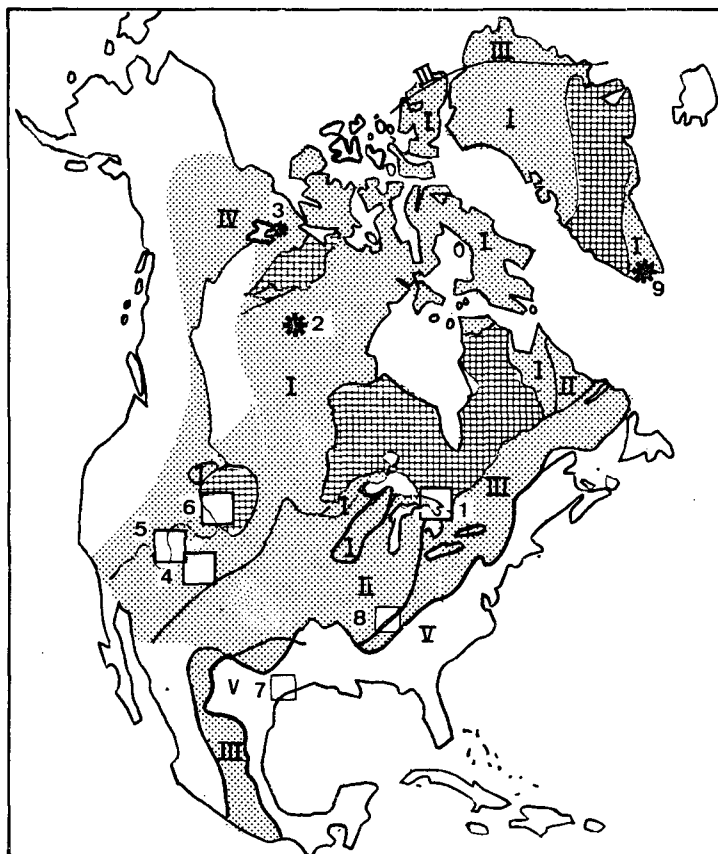


FIG.2. Carte schématique du socle précambrien de l'Amérique du Nord et emplacements des principaux districts uranifères (d'après P.B. King, 1969).

▨ Cratons archéens

▨ Domaine des orogènes protérozoïques:

I - orogène hudsonien; II - orogène elsonien; III - orogène de Grenville; IV - fosse beltienne

▨ Domaine des orogènes phanérozoïques

Districts uranifères principaux: 1 - Elliott Lake; 2 - Beaverlodge; 3 - Port-Radium; 4 - Ambrosia Lake; 5 - Plateaux du Colorado; 6 - Wyoming; 7 - Gulf Coast; 8 - Chattanooga; 9 - Illimaussaq

□ Districts à gisements uranifères contenus dans l'étape de couverture

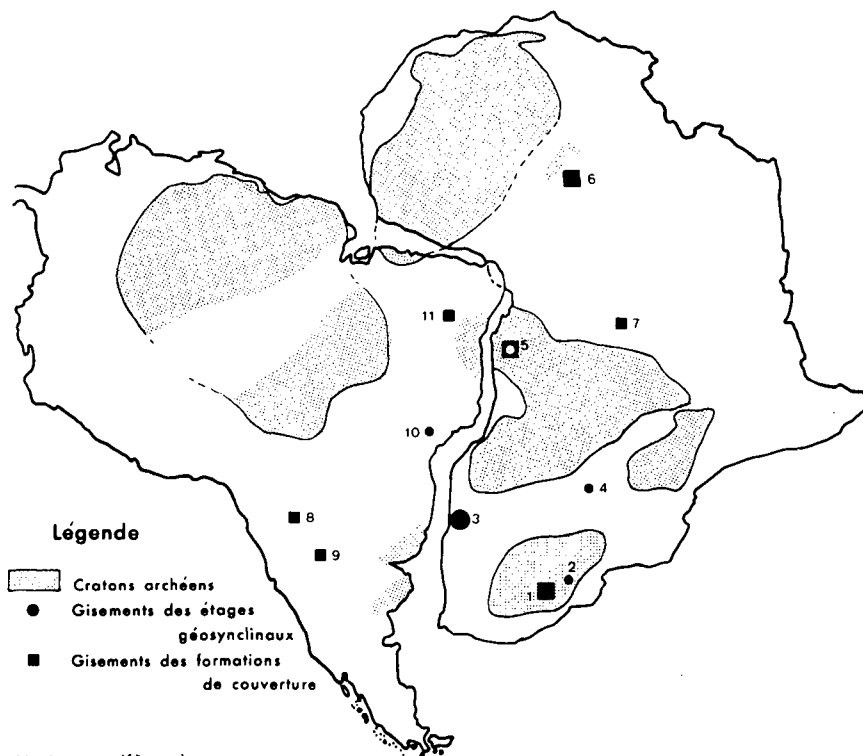
* Districts à gisements uranifères contenus dans l'étage géosynclinal ou le bâti archéen.

- En accord avec les conclusions de S.H.U. BOWIE, la majeure partie du potentiel uranifère mondial et en particulier presque tous les gisements ou districts uranifères contenant individuellement plus de 50 000 t U, de même que les gros ensembles de concentrations sub-économiques (schistes noirs, syénites néphéliniques) se situent dans les domaines précambriens. L'ensemble du Colorado, reposant sur un socle protérozoïque ancien pourrait dans une certaine mesure y être rattaché.

- . Cependant pratiquement aucune concentration valable n'apparaît à l'intérieur des noyaux cratoniques archéens, à l'exception de PALABORA (mais l'âge du complexe carbonatitique est lui-même protérozoïque). Il s'ensuit qu'à de rares exceptions près, les concentrations uranifères notables actuellement connues sont d'un âge inférieur à 2 500 MA.
- . Les étages géosynclinaux des orogènes protérozoïques constituent les sites privilégiés d'occurrences des gisements filoniens et apparentés (gisements disséminés à morphologie stratoïde, gisements des pegmatoïdes et des skarns...).
- . A l'exception des gisements urano-molybdénifères associés au magmatisme sialique d'URSS les orogènes du type calédonien paraissent particulièrement pauvres en concentrations uranifères.
- . Le domaine des orogènes de type hercynien se place au deuxième rang, par la fréquence des concentrations économiques d'uranium sinon par ses réserves. D'autant plus que les gisements économiques compris dans le domaine alpin d'Europe se situent en fait dans des fragments du socle hercynien. Les grands gisements de phosphates sédimentaires s'y trouvent également (fig. 1).
- . Exception faite des gisements de ces fragments hercyniens repris dans le domaine alpin, on ne connaît dans le monde occidental encore aucun gisement uranifère notable proprement alpin.
- . Dans le domaine des cordillères américaines, second par l'importance du potentiel uranifère qu'il contient, les concentrations uranifères notables sont associées aux fragments précambriens et sont essentiellement représentées par les ensembles grés-argileux continentaux des formations de couverture de ces fragments. Mais l'âge de cette couverture et des gisements qui s'y situent est typiquement cénozoïque. Il y a également des exemples de gisements filoniens associés à des minéralisations polymétalliques encaissées dans les fragments du socle précambrien lui-même, comme par exemple dans le Front Range (l'âge de ces minéralisations semble être en général cénozoïque aussi). De nombreuses autres occurrences uranifères filoniennes, jusqu'à présent représentant des concentrations modestes, associées à des paragenèses polymétalliques variées, sont encaissées dans des formations cordilleriennes indiscutables (fig. 2).
- . Une autre remarque importante se dégageant de l'examen du tableau et des figures est que la majeure partie du stock uranifère sous forme de concentrations économiques ou sub-économiques est contenue dans des formations de couverture, remarque faite déjà d'ailleurs par S.H.U. BOWIE (7).

- Remarques particulières à certains types de concentrations

- . Les gisements des couvertures à conglomérats pyriteux uranifères se limitent strictement aux cratons archéens ou à leur voisinage immédiat comme dans le cas de JACOBINA (fig. 3, ce gisement semble se situer en bordure du fragment brésilien du grand craton Congolais). Cette propriété est évidente si on leur admet une origine placérienne, auquel cas leur aire d'occurrence possible pourrait être limitée par l'isochrone 1700 MA, âge auquel l'atmosphère oxygénée semble s'être substituée à l'atmosphère carbonique.
- . Les gisements notables dans les ensembles grés-argileux continentaux se situent dans des couvertures de plateformes rigides ou encore de fragments de plateformes rigides repris dans des orogénies postérieures d'âges très variés. Ils



1. Witwatersrand ; 2. Palabora ; 3. Rössing ; 4. Shinkolobwe ;
5. Franceville ; 6. Niger ; 7. Bakouma ; 8. Salta ; 9. Malargue-Mendoza ;
10. Pocos de Caldas ; 11. Jacobina.

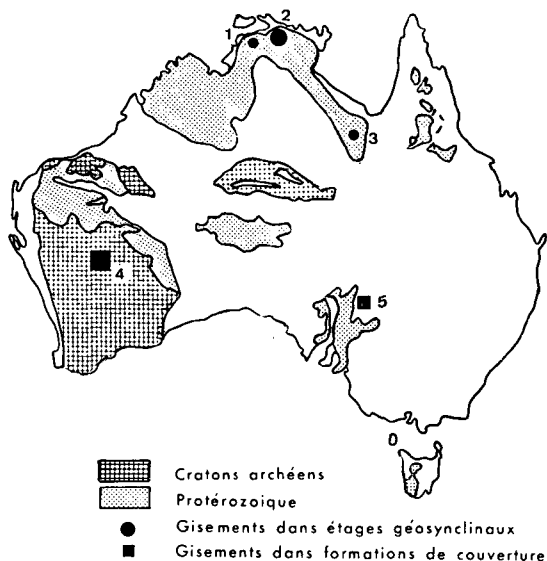
FIG.3. Districts uranifères d'Amérique du Sud et d'Afrique (carte d'après P.H. Hurley, 1968).

sont donc pratiquement indemnes de plissements, mais peuvent être affectés par des fracturations ou des basculements. L'âge de la minéralisation liée aux couvertures de tels fragments de socle peut être contemporain de celui du domaine orogénique où le gisement est situé (Cordillères Américaines) ou au contraire appartenir au cycle antérieur (Alpes Européennes).

De nombreux commentaires peuvent être faits en ce qui concerne les gisements filoniens et apparentés (colonnes 3 à 10). Nous nous limiterons à remarquer que :

- * Presque toutes les réserves exploitables du monde occidental entrant dans cette catégorie se situent dans les étages géosynclinaux protérozoïques et dans une moindre mesure hercyniens.
- * L'ubiquité, par rapport aux différents éléments structuraux, des minéralisations uranifères associées à des ensembles polymétalliques, n'est qu'apparente, car cette rubrique groupe artificiellement des associations d'éléments variables et des modes de liaison de l'uranium avec ces associations différents.

- * Nous avons distingué parmi les gisements filoniens le cas de l'association uranium-molybdène lié au volcanisme acide à intermédiaire, peu connu jusqu'à présent dans le monde occidental mais apparemment important en URSS. On pourrait s'attendre à rencontrer de tels gisements, associés à un magmatisme caractéristique des bords de poussée (leading edges) des plaques, dans les orogènes de tout âge. En particulier il nous semble qu'il pourrait apparaître dans certains secteurs des orogènes récents, comme c'est d'ailleurs le cas de MARYSVALE dans la Cordillère Nord-Américaine.
- . Il convient de réserver une place à part pour les gisements uranorifères des complexes alcalins et des carbonatites. Ils offrent en effet la particularité que leur répartition semble dépendre moins des grandes unités structurales distinguées dans notre tableau que d'un élément structural supplémentaire, surimposé : les rifts intracontinentaux plus ou moins avortés. Il est probable que leur apparition n'est pas indépendante de la nature de l'élément structural affecté par le rift, mais trop peu d'occurrences de ce type ont été décrites pour en tirer un enseignement. Dans les cas cités dans notre tableau les unités affectées sont archéennes ou protérozoïques. Quant à l'âge de la fracturation il semble variable : protérozoïque (ILLIMAUSSAQ, PALABORA), crétacé (POCOS de CALDAS).
- . La découverte récente du gisement de YEELIRRIE, succédant à celle des indices du désert de NASSIB, est un événement intéressant à plusieurs titres. Elle soulève en particulier la question : l'environnement précambrien, voire archéen est-il indispensable pour que les calcrètes puissent fournir des concentrations uranifères exploitables ? (fig. 4)



1. District de RUM JUNGLE; 2. Districts de South et EAST ALLIGATOR 3. Mary Kathleen
4. Yellirrie; 5. Lake Frome

FIG.4. Districts uranifères principaux d'Australie.

QUELQUES COMMENTAIRES ET CONCLUSIONS

Il semble donc se dégager des travaux de cette dernière décennie que le magmatisme sialique, agent générateur majeur de la croûte continentale, est responsable de la distribution primaire de l'uranium (et du thorium) dans la croûte terrestre. Il en résulte que cette répartition est hétérogène au sein de cette croûte et plus ou moins préférentiellement liée à certains éléments structuraux essentiels. Les concentrations économiques ou sub-économiques d'uranium directement associées à ce magmatisme, ou plus généralement dérivant des concentrations primaires résultantes, par remobilisations et reconcentrations sous l'effet de facteurs hypogènes ou supergènes, devraient logiquement se répartir également en association plus ou moins étroites avec certains de ces éléments structuraux.

C'est ce que nous avons cherché à dégager à l'aide de notre classification métallotectonique des gisements d'uranium. Une question qui se présente cependant, et qui a une grande importance dans l'établissement des critères de sélection des régions favorables, est de savoir si les produits du magmatisme sialique phanérozoïque, voire post-archéen, constituent des sources potentielles d'uranium aussi favorables que ceux du Précambrien (ou même de l'Archéen).

Ainsi l'hypothèse de S.H.U. BOWIE selon laquelle les chaînes phanérozoïques ne sont notablement uranifères que là où elles ont incorporé des vestiges précambriens, appliquée au cas des gisements du Colorado et même du Wyoming (qui en fait auraient pu dans notre tableau être classés ensemble) nous suggère certaines réflexions.

L'interprétation hypogéniste de la mise en place de ces gisements, retenue par cet auteur, confère effectivement une grande valeur en tant que critère de favorabilité à la nature précambrienne du socle constituant le fond des bassins uranifères considérés. Tandis qu'il semble perdre beaucoup en importance dans le cadre d'une hypothèse infiltrationniste. En effet les affleurements précambriens constituent une faible partie des masses magmatiques sialiques entourant le bassin et qui sont d'âge cénozoïque. Dans cette seconde hypothèse le critère favorable majeur devient la simple présence d'une grande masse de roches sialiques (caractère qui n'apparaît malheureusement pas dans notre tableau). Il faut toutefois remarquer que même ainsi le critère de S.H.U. BOWIE redeviendrait prépondérant si une partie au moins de l'uranium mobilisable des roches magmatiques sialiques cénozoïques était héritée du stock précambrien.

Il y a là un problème fort intéressant et que notre tableau fait ressortir, en ce sens qu'il montre qu'effectivement les minéralisations des formations de couverture aussi bien que les plus importantes minéralisations filoniennes uranifères (Marysvale, Front Range) des Cordillères Américaines par exemple, bien que d'âge cénozoïque, coïncident néanmoins avec la présence de fragments précambriens.

Nous voudrions ajouter quelques remarques au sujet du tableau présenté. Sa structure sommaire ne peut pas conduire à des conclusions originales et les propriétés que l'on a pu en déduire sont universellement connues. Cependant il les présente d'une façon cohérente et malgré son côté rudimentaire l'essentiel des grandes tendances de la répartition des gîtes uranifères s'en dégage.

Il nous semble que de tels tableaux pourraient être envisagés à des échelles régionales de l'importance d'un pays ou d'un ensemble de pays (Europe par exemple). En décomposant ces régions en éléments structuraux judicieusement

définis, il est probable que des tableaux conçus sur la base de ces principes puissent beaucoup aider à déceler les règles de répartition propres aux différents types de gisements que l'on trouve dans les régions considérées et de ce fait contribuer efficacement à la découverte des guides de prospection à l'échelle régionale.

REFERENCES¹

- [1] AGNOLO, M. d', TURCHI, A., Rapport SOMIREN (Italie), novembre 1963 (non publié).
- [2] ANHAEUSSER, C.R., et al., Geol. Soc. Amer. Bull. 80 11 (1969) 2175-220.
- [3] BACKSTRÖM, J.W. von, in Uranium Exploration Geology (C.R. Groupe d'étude Vienne, 1970), AIEA, Vienne (1970) 143-50.
- [4] BARIAND, P., et al., Geol. Surv. Iran, Rapport n° 7 (1965) 15-16.
- [5] BECK, L.S., Department of Mineral Resources, Province of Saskatchewan, Rapport n° 126 (1969).
- [6] BIRCH, F., Geol. Soc. Amer. Bull. 76 2 (1965) 133-34.
- [7] BOWIE, S.H.U., in Uranium Exploration Geology (C.R. Groupe d'étude Vienne, 1970), AIEA, Vienne (1970) 285-300.
- [8] BUNKER, C.M., MACKALLOR, J.A., US Geol. Surv. Prof. Pap. 765 (1973).
- [9] BURNOL, L., Thèse, Mémoire BRGM n° 85 (1973).
- [10] CAVACA, R., in 2^e Conf. int. util. énergie atom. fins pacif. (Actes Conf. Genève, 1964) 12, ONU, New York (1964) 177.
- [11] CATHCART, J.B., in Conf. int. util. énergie atom. fins pacif. (Actes Conf. Genève, 1955) 6, ONU, New York (1956) 514.
- [12] CHOUBERT, G., FAURE-MURET, A., Tectonique de l'Afrique, UNESCO, Paris (1971) 216-38.
- [13] CONANT, L.C., in Conf. int. util. énergie atom. fins pacif. (Actes Conf. Genève, 1955) 6, ONU, New York (1956) 435.
- [14] COX, D.P., Econ. Geol. 62 (1967) 773-80.
- [15] DAVIDSON, A., in Variations in Tectonic Styles in Canada, Geol. Assoc. Canada, Special paper 1 (1972) 382-433.
- [16] DERRIKS, J.J., VAES, J.F., in Conf. int. util. énergie atom. fins pacif. (Actes Conf. Genève, 1955) 6, ONU, New York (1956) 94.
- [17] ENGEL, A.E.G., et al., Geol. Soc. Amer. Bull. 76 7 (1965) 719-34.
- [18] ENGEL, A.E.G., KELM, D.L., Geol. Soc. Amer. Bull. 83 8 (1972) 2325-40.
- [19] FISHER, R.P., in Ore Deposits in the United States, 1933/1937 (Ridge, John D., Ed.) 1, Graton Sales Volume, The American Institute of Mining, Metallurgical and Petroleum Engineers, New York (1968) 736-46.
- [20] GABELMAN, J.W., in Uranium Exploration Geology (C.R. Groupe d'étude Vienne, 1970), AIEA, Vienne (1970) 315-30.
- [21] GANGLOFF, A., in Uranium Exploration Geology (C.R. Groupe d'étude Vienne, 1970), AIEA, Vienne (1970) 77-105.
- [22] GEFFROY, J., «Les gîtes uranifères dans le Massif Central», Géologie, géomorphologie et structure profonde du Massif Central français (C.R. Symp. J. Jung, Clermont-Ferrand, 1971), Plein Air Service, Clermont-Ferrand (1971) 541-79.
- [23] GIANNOTTI, G.P., TEDESCO, G., L'industria mineraria nel Trentino-Adige, Economica Trentina della CCIA di Trento, n°s 1-2 et 4-5 (1964).
- [24] GLIKSON, A.Y., Geol. Soc. Amer. Bull. 83 11 (1972) 3323-44.
- [25] HANEKOM, H.J., Geol. Surv. South Africa, Mémoire 54 (1965).
- [26] HARSHMAN, E.N., in Ore Deposits of the United States, 1933/1937 (Ridge, John D., Ed.) 1, Graton Sales Volume, The American Institute of Mining, Metallurgical and Petroleum Engineers, New York (1968) 815-32.
- [27] HAUGHTON, S.H., Geological History of South Africa, Geol. Soc. South Africa, Cape Town (1969).
- [28] HUGES, F.E., MUNRO, D.L., in Geology of Australian Ore Deposits (Proc. Eighth Commonwealth Mining and Metallurgical Congress) (McAndrew, J., Ed.) 1, Office of the Congress and the Australasian Institute of Mining and Metallurgy, Melbourne, Australia (1965) 256-63.

¹ Toutes les références ne sont pas mentionnées dans le texte.

- [29] HUGI, T., et al., Rapport inédit de la Société européenne de l'énergie atomique, C.R. Colloque de Grenoble sur la genèse des minéralisations uranifères des Alpes Occidentales, 1959, p. 85-89.
- [30] J.E.N., A provincia uranifera do Centro de Portugal, Lisbonne (1968).
- [31] KAROLY, V., VINCZE, J., A Mecseki uranerclelőhely kepzodesenek sajátosságai, Földatni közlöny, (Bull. Soc. Geol. Hongrie) 97 1 (1966) 39-59.
- [32] KAUL, I.K., Econ. Geol. 60 (1965) 1726-30.
- [33] KERR, P.F., et al., Geol. Soc. Amer., Special Paper 64 (1957).
- [34] KING, P.B., The tectonics of North America, US Geol. Surv. Prof. Pap. 628 (1969).
- [35] LAMBERT, I.B., Geol. Soc. Australia, Special Publication 3 (1971) 419-28.
- [36] LANG, A.H., et al., Geol. Surv. Canada, Econ. Geol. Ser. n°16 (1962) 186-93.
- [37] LEBREDEV-ZINOEV, A.A., MODNIKOV, I.S., Geologia Razvedka n° 5 (1971) 58-64.
- [38] LIDDY, J.S., Australian Mining (May 1972) 24-44.
- [39] LIMPO de FARIA, F., Comunicações dos Serviços Geológicas de Portugal 50 (1966) 9-50.
- [40] LITTLE, H.W., in Uranium Exploration Geology (C.R. Groupe d'étude Vienne, 1970), AIEA, Vienne (1970) 35-48.
- [41] McDOWELL, J.P., Ontario Department of Mines, Geological Circular n° 6 (1957).
- [42] McKELVEY, V.E., CARSWELL, L.D., in Conf. int. util. énergie atom. fins pacif. (Actes Conf. Genève, 1955) 6, ONU, New York (1956) 503.
- [43] MOREAU, M., Les gisements d'uranothorianite du Sud-Est de Madagascar et le problème de l'uranium et du thorium dans le métamorphisme, CEA (1958).
- [44] MOREAU, M., Rapport CEA-1685 (1960).
- [45] MOREAU, M., RANCHIN, G., in Les roches plutoniques dans leurs rapports avec les gîtes minéraux (Jubilé E. Raguin), Masson, Paris (1971) 77-100.
- [46] PANTIC, R., et al., in 2^e Conf. int. util. énergie atom. fins pacif. (Actes Conf. Genève, 1964) 12, ONU, New York (1964) 55.
- [47] PIENNAR, P.J., Geol. Surv. Canada Bull. 83 (1963).
- [48] RUZICKA, V., Department of Energy, Mines and Resources, Canada, Pap. 70-48 (1971).
- [49] SALVAN, H., in Géologie des gîtes minéraux marocains (C.R. 19^e Congr. Géol. Int.), Monographies régionales, 3^e sér., Maroc, n° 1 (1952) 283-320.
- [50] SATTERLY, J., HEWITT, D.F., Ontario Department of Mines, Geological Circular n° 2 (mars 1955).
- [51] SHTSHUROV, V.P., TIMOFEEV, E.V., Geol. Rud. mestorozhd. n° 4 (1965) 34-44.
- [52] SIMS, P.K., TOOKER, E.W., US Geol. Surv. Prof. Pap. 300 (1955) 105-11.
- [53] SOERENSEN, H., in Uranium Exploration Geology (C.R. Groupe d'étude Vienne, 1970), AIEA, Vienne (1970).
- [54] SOUTH, S.A., At. Energy Aust. 15 4 (1972) 15-30.
- [55] STIPANICIC, P.N., et al., Proc. 4th Inter-American Symp. on Peaceful Appl. Nucl. Energy 1, Organization of American States, Pan American Union, Washington, D.C., 541-E-6590 (1962) 313-33.
- [56] SVENKE, E., in Conf. int. util. énergie atom. fins pacif. (Actes Conf. Genève, 1955) 6, ONU, New York (1956) 198.
- [57] TALBOT, C.J., Philos. Trans. Roy. Soc. London, A 273 1235 (1972) 413-27.
- [58] THURLOW, E.E., US. Geol. Surv. Prof. Pap. 300 (1955) 85-89.
- [59] VALSARDIEU, C., Thèse, Faculté des Sciences de Nice (non publiée).
- [60] WHITESIDE, H.C.M., in Uranium Exploration Geology (C.R. Groupe d'étude Vienne, 1970), AIEA, Vienne (1970) 49-75.

LES CONDITIONS TECTONO-MAGMATIQUES DE LA FORMATION DES GISEMENTS D'URANIUM DE ROUMANIE

G. NITU

Ministère des mines, du pétrole et de la géologie,
Entreprise des métaux rares,
Bucarest, Roumanie

Présenté par T. Burtic

Abstract

THE TECTONOMAGMATIC CONDITIONS OF URANIUM DEPOSIT FORMATION IN ROMANIA.

The author analyses the age relationships between different tectonic, magmatic and mineralization phenomena, the position of uranium deposits in the geological evolution of different regions, the relationship between Laramian magmatism and tectonics, the paleotectonic conditions of deposit formation, and the types of deposit characteristic of certain geological conditions. On the basis of this analysis, the author tries to derive certain rules – or to formulate and in part justify a number of hypotheses – concerning the role of magmatic and tectonic activity in the formation of Romania's uranium deposits, the depth at which they occur, the relief at the time of their formation, the reasons for the diversity of deposit types and for the occurrence of deposits including solid asphalts (anthraxolites), and the possible origin of the metals and asphalts.

LES CONDITIONS TECTONO-MAGMATIQUES DE LA FORMATION DES GISEMENTS D'URANIUM DE ROUMANIE.

L'auteur analyse les rapports d'âge entre les différents phénomènes tectoniques, magmatiques et minéralisateurs, la position des gisements d'uranium dans l'évolution géologique des différentes régions, les rapports du magmatisme laramien (banatitique) avec la tectonique, les conditions paléotectoniques de la formation des gisements et les types de gisements caractéristiques de certaines conditions géologiques. A partir de cette analyse l'auteur essaie de définir certaines règles, ou de formuler et de justifier en partie quelques hypothèses concernant le rôle du magmatisme et de la tectonique de la formation des gisements d'uranium de Roumanie, la profondeur de leur formation, le caractère du relief pendant leur formation, les causes de la diversité des types de gisements et celles de l'apparition des gisements à bitumes solides (anthraxolites), ainsi que l'origine possible des métaux et des bitumes.

INTRODUCTION

Cet exposé se fonde sur les résultats des études conduites dans ce domaine par un grand nombre de géologues roumains. La plupart des conclusions présentées sont le fruit d'une activité collective à laquelle l'auteur a pris part lui aussi. L'attention sera attirée sur celles des considérations concernant le rapport des minéralisations avec la tectonique et le magmatisme qui constituent des conclusions ou des hypothèses ayant un caractère personnel plus marqué ou qui sont très discutables.

Les gisements d'uranium de la République socialiste de Roumanie sont concentrés dans trois régions différentes; dans chacune d'elles ils présentent des caractéristiques morphologiques et quelquefois même minéralogiques différentes de celles des gisements des autres régions. En même temps, chaque région présente des conditions tectoniques et magmatiques spécifiques.

Dans la première région, les gisements à minéralisation de pechblende révèlent une genèse hydrothermale assez évidente; leur formation peut être rapprochée de la présence de nombreuses intrusions de granitoïdes laramiques (banatites). Dans la seconde région, les gisements forment des lentilles concordantes dans des dépôts terrigènes du Permien, la minéralisation étant représentée par la pechblende dans des bitumes solides (anthraxolites). Le mode de formation des gisements est très controversé, diverses variantes de genèse exogène-épigénétique étant surtout invoquées. Enfin, dans une troisième région, les gisements constituent un type peu commun. La minéralisation, représentée par les mêmes anthraxolites avec pechblende que dans le cas précédent, forme des filons ayant certaines caractéristiques hydrothermales, dans des schistes cristallins.

GISEMENTS HYDROTHERMAUX LIES AUX BANATITES

La région où se trouvent ces gisements est caractérisée par une structure géologique particulièrement compliquée. On trouve des dépôts d'âges différents et charriés successivement, recouvrant un fond de schistes cristallins à couverture sédimentaire mésozoïque de prédominance calcaire et dolomitique, en partie terrigène, et dont la puissance atteint 1,5 à 2 km.

A la base on distingue une nappe formée de dépôts mésozoïques de composition lithologique similaire à celle de la couverture sédimentaire autochtone. Suit une nappe de formations paléozoïques, où des dépôts terrigènes, continentaux, du Permien présentent la dispersion la plus grande; ces dépôts ont une teinte rouge et une puissance de 1000 à 2000 m (conglomérats, grès feldspathiques, argiles, fréquemment intercalations de laves rhyolithiques, tuffs et tuffites). A la partie supérieure de la pile de formations charriées on trouve deux nappes comportant surtout des formations cristallines précambriennes. La puissance totale de l'allochtone peut dépasser 6000 m.

Tant la couverture sédimentaire de l'autochtone que les formations des nappes présentent des pendages monoclinaux de l'ordre de 10° à 20° et sont coupées par des failles verticales d'orientation différente. Les failles d'orientation NO-SE présentent le plus large développement, suivies par le système de failles OSO-ENE.

Tant au-dessus de l'autochtone qu'au-dessus des nappes se trouvent les formations terrigènes du Sénonien, nettement transgressives. Partout dans la région elles sont quasi horizontales.

L'édifice tout entier est traversé par un puissant complexe effusif-plutonique, dans lequel on peut distinguer une première série de manifestations à caractère volcanique (andésites, dacites, rhyolithes, tuffs), une seconde série intrusive, représentée par des amas, des pénétrations et quelquefois des corps plutoniques à proportions assez larges de diorites granitiques (quelquefois diorites, granites, granites alcalins), et une dernière série filonienne, représentée par des dykes et des sills, des lamprophyres, des porphyres andésitiques et des porphyres quartzifères.

Dans la littérature roumaine, la série volcanique a été quelquefois considérée comme reflétant une activité éruptive indépendante, ultérieure aux mouvements sous-hercyniens, les banatites étant donc représentées par la série intrusive, ultérieure aux mouvements laramiques [1].

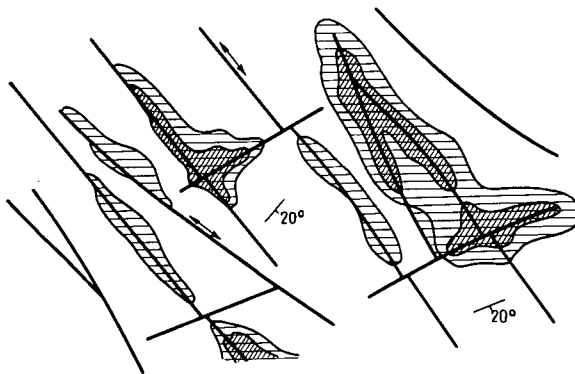


FIG.1. Position des corps de minerais, en rapport avec les failles, dans le cas d'un gisement de U, Cu, Co, Ni (plan).

Entre les phénomènes volcaniques et intrusifs on observe pourtant des interpénétrations; des manifestations volcaniques ont lieu, dans certains cas, après la consolidation des intrusions. Les deux séries - volcanique et intrusive - forment ensemble un seul complexe effusif-volcanique des banatites [2].

La tectonique disjonctive se forme en différentes phases, dont les premières sont contemporaines de la mise en place des nappes. Les plus nombreuses se présentent pendant le volcanisme sous-hercynien, d'autres interviennent avant et après la formation de la série intrusive, quelques failles, souvent importantes, apparaissent après le Sénonien et quelques ruptures sont de date récente.

Divers gisements de U, Mo, Bi, Cu, Pb, Zn, B se sont formés dans la région, en relation avec l'activité magmatique banatitique.

Les gisements d'uranium sont constitués pour la plupart par des corps en forme de lentilles concordantes, formées d'imprégnations et de concrétions métasomatiques, quelquefois de petites veines ou de petits filons.

On peut distinguer les types suivants de gisements:

- Des lentilles isométriques, à l'intersection de failles en grès du Permien fortement affectés par des transformations thermiques et hydrothermales (cornifications, diopsidisations, albitisations, amphibolisations, épidotisations, zéolitisations) où l'uranium est associé au cuivre et au molybdène.

- Des groupes de lentilles allongées dans la direction des failles orientées NO-SE et OSO-ENE (voir fig.1), se trouvant dans un horizon à lentilles de carbonates ou dans des zones avec schistosité accentuée à l'intérieur des schistes; les minéralisations d'uranium sont accompagnées de chloritisations, de séricitisations, de silicifications. On rencontre aussi, parallèles à ces minéralisations d'uranium, des bandes de pyrite (quelquefois à chalcoppyrite), de magnétite, des arséniures de cobalt et de nickel, quelquefois des bandes ou des nids de sulfures complexes, plus rarement des apparitions de bismuth.

– Des lentilles stratiformes de grès du Permien et du Werfénien de couleur grise, dans des paquets de grès rouges. La couleur grise est secondaire et due à un processus de décoloration. Les minéralisations d'uranium sont accompagnées de bandes de minéralisations complexes.

– Des lentilles concordantes dans des schistes séréciteux très écailleux, accompagnant des minéralisations de cuivre.

Dans la même région on rencontre aussi des gisements d'autres métaux:

- corps de molybdène et de bismuth minéraux à skarns grenatifères et wollastonitiques, formés le long d'un contact à forte inclinaison entre calcaires mésozoïques et cornéennes du Permien;
- corps en forme de piliers verticaux dans des dolomites mésozoïques présentant un noyau de minerai riche en cuivre et un anneau extérieur de bore minéral;
- corps lenticulaires concordants, quelquefois filons, dans des schistes cristallins à pyrite et pyrotine, ou à sulfures complexes (le zinc étant quelquefois prédominant, d'autres fois le plomb);
- rarement, corps de magnétite, dans des skarns sur calcaires cristallins.

POSITION DES GISEMENTS DANS L'EVOLUTION DES PHENOMENES TECTONIQUES ET MAGMATIQUES

L'étude de l'évolution géologique de la région montre que les gisements d'uranium et d'autres métaux y occupent une place bien déterminée.

Le système compliqué de charriages s'est formé pour la région considérée pendant la phase austrienne, lorsque les quatre nappes se sont mises en place en formant des blocs capturant à leur base les formations argileuses de l'Aptien, et ensuite celles de l'Albien. Nous supposons que la mise en place des nappes s'est produite comme un phénomène en quelque sorte passif, représentant l'effet éloigné et peut-être retardé de quelque autre effort de compression à l'extérieur de la région. Le processus a été accompagné de l'affaissement lent de la région, dont témoignent les faciès à grande profondeur des formations superposées.

Suit une période d'intense érosion, qui dure pendant tout le temps du Vraconien, du Cénomaniens et du Coniacien, déterminée non par des mouvements tectoniques de soulèvement, comme on le considère en général, mais par l'installation des nappes, dont la partie supérieure dépassait le niveau de la mer. La transgression qui suit n'est pas l'effet d'une nouvelle descente de la région, mais l'effet de la continuation lente du même mouvement descendant antérieur.

La série volcanique du complexe volcanique-intrusif apparaît pendant le Sénonien, en s'installant, parallèlement à la sédimentation, dans des dépressions. La série d'intrusions de granodiorites s'est mise en place à partir de la fin du Crétacé supérieur et a continué pendant le Paléocène, dans certains cas même jusqu'à l'Eocène inférieur, sur un fond de mouvements ascendants et d'une régression générale.

L'intrusion du complexe des banatites fixe définitivement la position des charriages et correspond au moment d'une cratonisation accentuée de la région. Ni les banatites, ni les dépôts sénoniens ne sont rompus par les plans anciens de chevauchement, qui n'ont plus été repris.

Au point de vue de la tectonique en plaques il faut admettre que cette cratonisation est en quelque sorte relative. La tectonique de la zone de

flysch des Monts Karpates nous montre que des déplacements horizontaux importants ont eu lieu aussi ultérieurement, après la formation des intrusions et des gisements, pendant tout le temps du Tertiaire, mais probablement au niveau de l'asténosphère.

En même temps, nous considérons qu'on ne peut pas démontrer l'existence d'un rapport causal local entre les mouvements sous-hercyniens et laramiques et l'activité magmatique d'âge correspondant. D'ailleurs, dans notre région, les mouvements de ces phases ont été beaucoup moins intenses que les mouvements austriques. Considérées sur l'ensemble du territoire roumain les intrusions de granodiorites coupent dans une mesure égale les structures austriques, sous-hercyniennes et laramiques et sont absentes en beaucoup de régions à intense activité tectonique laramique.

Les différentes phases des mouvements tectoniques (austrique, laramique, etc.) permettent d'ailleurs de constater l'effet de plissement produit par ces déplacements sur différents sédiments. Mais de tels mouvements ont eu lieu en permanence pendant le cycle alpin, où l'activité magmatique représente des épisodes plus rares. Il est probable que les déplacements verticaux des blocs sont beaucoup plus importants pour le déclenchement d'une certaine activité magmatique.

Il est bien possible que l'élévation du bloc ait été accompagnée ou même précédée d'un flux de matériau dans son asténosphère, ce qui aurait fait naître le fond thermique élevé favorable à l'apparition du magmatisme. Sur ce fond, qui se maintient même aujourd'hui, le magmatisme est apparu pendant les périodes où d'autres conditions (probablement fracture verticale) étaient remplies. Cette conception, quoique tenant compte des mécanismes généraux invoqués par les théories tectoniques en plaques, diffère sensiblement des tentatives visant à expliquer le magmatisme banatitique par simple subduction [3, 4].

La position des gisements dans l'évolution des phénomènes tectoniques est, en général, la même que celle du magmatisme. Mais des aspects intéressants apparaissent à l'analyse des rapports d'âge entre le magmatisme et les processus de minéralisation.

Les séries de roches intrusives filoniennes (dykes et sills de lamprophyres, porphyres andésitiques et porphyres quartzifères) sont probablement pour la plupart ultérieures et sont à rapprocher de la formation des massifs intrusifs plutoniques. On a rencontré des dykes coupant des intrusions granodioritiques et présentant des contacts nets avec elles, prouvant ainsi que le massif se trouvait à ce moment à un stade avancé de refroidissement.

La plupart des phénomènes de métamorphisme hydrothermal ou pyrometasomatique qui accompagnent les minéralisations sont ultérieurs et en rapport avec la série intrusive filonienne. On connaît de nombreux cas de kaolinisations, séricitisations, etc. qui ont eu lieu durant les contacts des dykes ou des sills. De même, dans beaucoup de cas, les minéralisations de molybdène, de complexes et quelquefois d'uranium présentes le long de quelques filons intrusifs sont évidemment plus jeunes que ceux-ci.

Dans certains cas, des failles verticales appartenant à un système affectant les dépôts sénoniens offrent des manifestations hydrothermales caractéristiques des minéralisations d'uranium.

Les investigations détaillées ont montré que dans le cadre des gisements d'uranium, les processus minéralisateurs sont précédés d'une partie

importante des phénomènes d'altération hydrothermale, qui ont d'ailleurs un rôle préparateur (albitisation, phénomènes de décoloration, etc.).

La succession établie des phénomènes magmatiques et minéralisateurs (intrusion des plutons des granodiorites — intrusion de la série filonienne — formation des altérations hydrothermales — formation des gisements, toutes séparées par des phénomènes de fracture) montre que l'origine des solutions minéralisatrices ne peut être cherchée que dans les plutons des granodiorites eux-mêmes, qui, à la date de formation des gisements, se trouvaient en cours de refroidissement et de consolidation. Les solutions minéralisatrices viennent probablement de profondeurs plus grandes, liées à des foyers magmatiques résiduels, à magmes ayant atteint un stade avancé de différenciation, dont quelques-uns, plus acides, sont fortement enrichis en substances volatiles. Ces conclusions [5] sont en concordance avec certaines données de la littérature concernant d'autres régions [6].

CAUSES DE LA DIVERSIFICATION DES TYPES DE GISEMENTS

Il est intéressant de remarquer le caractère très individuel des gisements de la région, qui sont différenciés tant par le complexe métallifère ou minéralogique que par les phénomènes de métamorphisme qui l'accompagnent.

Nous considérons que cette différenciation est le résultat de divers facteurs dont il est difficile de préciser l'importance relative. Le premier qui s'impose naturellement à notre attention est l'effet de la différenciation magmatique. Il est bien possible que celle-ci ait conduit à la constitution de chambres magmatiques spécialisées, qui ont été ensuite ouvertes par des failles à tour de rôle, les gisements pouvant présenter des âges en quelque sorte différents. Le rôle de la différenciation magmatique est tout de même difficile à démontrer et, pour le moment, nous ne pouvons offrir que l'argument indirect de l'existence d'une série variée de roches intrusives filoniennes étant elles-mêmes le résultat d'un processus de différenciation très avancé.

Il faut mentionner, bien sûr, l'influence du milieu (roches) où la minéralisation s'est localisée et qui peut être favorable à la précipitation de certaines minéralisations, et défavorable pour d'autres.

De même, le rôle du phénomène de filtration des solutions à travers différents paquets de roches est très important. Notre opinion est qu'en général, dans la localisation des gisements d'uranium en Roumanie, un rôle important est joué par différents horizons à perméabilité réduite, sous l'écran desquels les minéralisations forment des corps sous-horizontaux, concordants, à niveaux de schistosité remarquables [7]. Quelquefois, les corps de minerai d'uranium se trouvent immédiatement au-dessus des sills de diabase ou d'intercalations de gneiss. Les corps sous forme de piliers à minéralisations de cuivre et de bore s'appuient à la partie inférieure sur une plaque de cornéenne.

Un problème qui nous a préoccupés d'une manière toute spéciale est celui de la profondeur de formation des gisements et de son rôle dans la diversification des types de gisements. Contrairement aux opinions qui accordent de l'importance à la distance par rapport aux corps intrusifs [7], nous sommes arrivés à la conclusion qu'un rôle beaucoup plus important a été joué par la profondeur de formation des gisements.

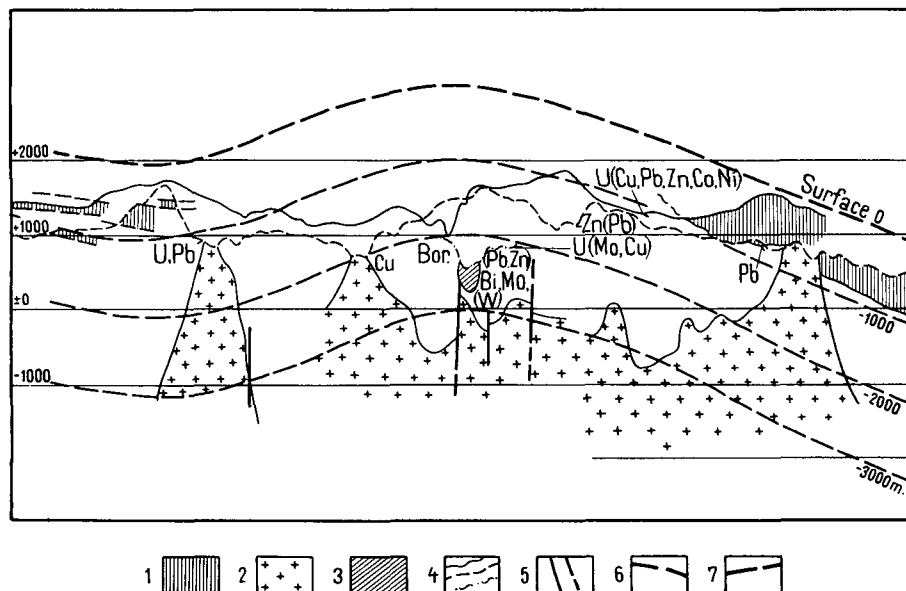


FIG. 2. Coupe schématique montrant la profondeur de formation des gisements d'uranium et d'autres métaux.

1 - Dépôts sénoniens; 2 - granodiorites; 3 - skarns; 4 - relief actuel dans diverses coupes; 5 - failles; 6 - position de la surface pendant la formation des gisements; 7 - niveaux de même profondeur par rapport à l'ancienne surface.

Nous avons entrepris quelques reconstitutions, en considérant comme horizon de repère les dépôts sénoniens, les derniers qui se sont formés avant l'intrusion des banatites (fig. 2). Nous en avons conclu que la partie supérieure des intrusions de granodiorites s'est élevée jusqu'à une profondeur de 3 km par rapport à l'ancienne surface, mais que beaucoup de leurs coupoles, différents amas représentant des masses plus élevées de plutons de profondeur, ont atteint une profondeur de moins de 1 km au-dessous de la surface.

Les gisements se sont formés sur une épaisseur atteignant 3 km, ce qui paraît être une règle générale dans de nombreuses régions [8].

On constate entre la profondeur de formation des gisements et le caractère de la minéralisation l'existence d'un rapport évident. Par exemple, les gisements de molybdène se sont formés à la profondeur de 2500 m environ, les gisements d'uranium à molybdène et cuivre (avec phénomènes de métamorphisme hydrothermal à haute température) à une profondeur de 2000 à 2200 m, ceux de cobalt et nickel (avec altérations hydrothermales à températures plus basses) à 1200 m environ, et les gisements de plomb, et même ceux d'uranium et de plomb, s'élèvent jusqu'à 500 m environ par rapport à l'ancienne surface. En même temps, la reconstitution met en évidence l'existence d'une certaine zonalité verticale régionale dans la disposition des gisements, phénomène plus rarement mentionné par la littérature géologique pour d'autres régions.

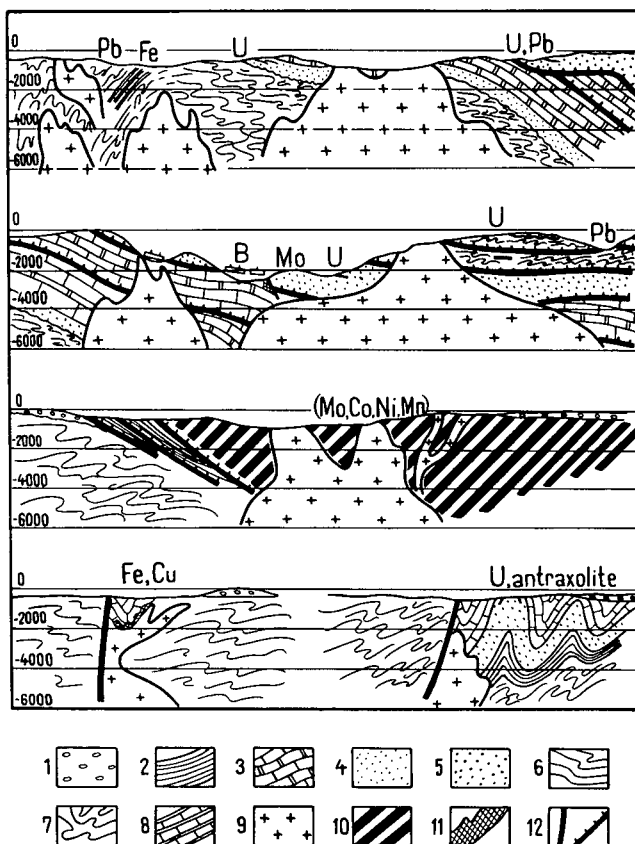


FIG. 3. Coupes illustrant le rôle des roches encaissantes et de l'assimilation dans la formation des gisements d'uranium.

1 - Dépôts terrigènes sénoniens; 2 - flysch crétacé inférieur; 3 - calcaires et dolomites mésozoïques; 4, 5, 6 - dépôts terrigènes (4 - werféniens, 5 - permien, 6 - carbonifères); 7 - schistes cristallins; 8 - calcaires cristallins; 9 - banatites; 10 - complexe ophiolitique; 11 - skarns; 12 - failles, chevauchements et charriages. Le niveau 0 représente la position horizontale de la surface pendant la formation des gisements.

Les gisements, au moins la plupart des intrusions de granodiorites, se sont formés au-dessous de la surface d'une région d'émergence: ce fait mis en évidence par nous apparaît très clair; il est aussi confirmé par quelques données de la littérature [9].

Le rôle des processus d'assimilation paraît assez convaincant, tout spécialement si nous considérons non seulement la région des gisements d'uranium, mais une superficie plus grande. Nous constatons au plan régional l'existence de relations très intéressantes entre la nature des roches assimilées et la métallogénèse causée par les banatites. Ainsi, il faut souligner que les gisements d'uranium sont associés à ces dernières seulement dans les zones où le magma en élévation a assimilé des

formations détritiques paléozoïques, surtout permienes. En fait, dans ces zones le complexe métallifère est le plus riche, des gisements de Mo, B, Cu, Pb, Zn étant aussi associés aux banatites. Dans les zones où les banatites assimilent seulement des schistes cristallins se trouvent des gisements de fer et de cuivre, quelquefois des complexes. Dans différentes régions où les roches transpercées sont représentées par le complexe ophiolitique (pour la plupart, des basaltes, diabases et gabbros à andésites, spilites et jaspes), les intrusions, quoique conservant une composition granodioritique, ne sont accompagnées que de minéralisations très sporadiques de Mo, Mn, Cu, Ni. Par contre, dans la zone des ophiolites, le magmatisme néogène est productif, surtout en gisements d'or.

GISEMENTS D'URANIUM DANS DES GRES DU PERMIEN

Le mémoire présenté par M. I. Corniciuc à ce Colloque [10] nous permet de nous arrêter sur certains aspects seulement.

Les gisements sont localisés dans le paquet supérieur (saxonien) d'une série paléozoïque terrigène continentale. A la base, les formations carbonifères et autuniennes sont caractérisées par une teinte grise; les formations autuniennes présentent de nombreux niveaux de schistes argileux bitumineux. Les formations saxonniennes sont représentées par une alternance rythmique de dépôts fluviatiles et lacustres, de nuance rouge (avec des niveaux gris provenant de certaines altérations secondaires) formés sous climat aride. Les dépôts du Jurassique et du Crétacé inférieur, à prépondérance calcaire, sont en transgression. Les dépôts sénoniens terrigènes forment des lambeaux rares. D'autres dépôts plus jeunes sont absents.

Toute la pile de dépôts sédimentaires, à l'exception des dépôts sénoniens, est serrée en des plis verticaux, par suite des mouvements austriques. La variation des puissances des dépôts aptiens et albiens prouve que les phénomènes de plissement ont commencé en même temps que la sédimentation. Les dépôts sénoniens s'étant formés après l'exondage et l'érosion provoqués par le plissement, ils restent quasi horizontaux.

Le long d'une puissante faille verticale qui sépare le complexe sédimentaire des schistes cristallins se sont introduits, probablement après le Sénonien, de nombreux corps de granodiorites banatitiques.

Les gisements d'uranium, représentés exclusivement par une minéralisation d'antraxolite à pechblende, forment des corps tubulaires et des lentilles allongées intercalées en concordance dans les dépôts saxonniens, le plus souvent dans les niveaux grossiers de nuance grise.

La genèse de ces gisements continue à provoquer de nombreuses discussions. La plupart des chercheurs considèrent qu'ils se sont formés par suite d'un processus exogène-épigénétique. On admet, entre autres variantes, que les bitumes solides résultent de la dégradation d'un gisement de pétrole (pendant la période triassique). L'uranium aurait pénétré ultérieurement dans les asphaltites, à partir soit de la surface, soit des dépôts inférieurs, ou du paquet minéralisé même par diffusion latérale. Il faut remarquer que les gisements sont fracturés par une intense tectonique disjonctive alpine, ce qui est considéré comme une preuve à l'appui de la formation des minéralisations dans le cycle tectonique hercynien.

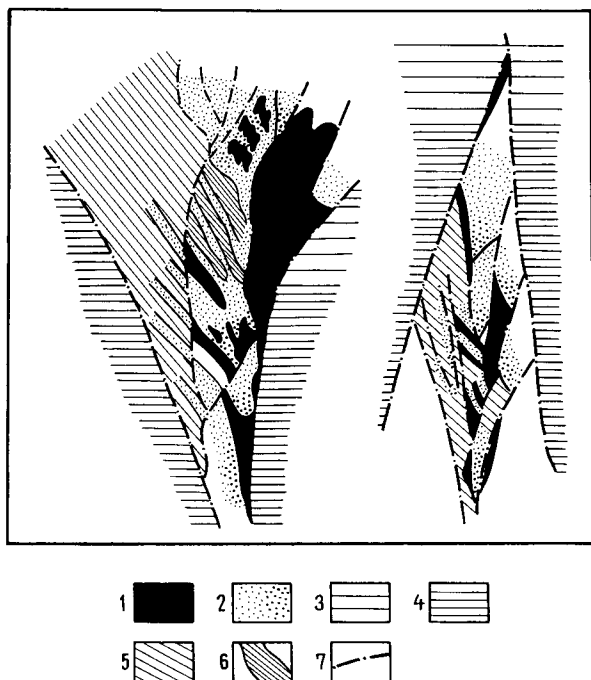


FIG. 4. Minéralisation d'uranium dans des grès permien (esquisses de détail).

1 - Anthraxolite, minéralisation compacte; 2 - imprégnation d'anthraxolite dans les grès; 3 - grès grossier massif; 4 - grès fin compact, 5 - grès fin schisteux; 6 - alévolites; 7 - failles.

Parmi ceux qui ont exprimé l'opinion qu'il existe une corrélation entre la formation des gisements et l'activité des banatites se trouve aussi l'auteur de ce mémoire.

Une analyse détaillée montre que la minéralisation, quoique antérieure par rapport à une certaine fracturation, est ultérieure à la formation de nombreuses failles appartenant toujours au cycle alpin. Quoique le rôle des facteurs lithologiques (dépôts de paléo-vallées) dans la localisation des minéralisations et dans la détermination de la forme des corps de minerai soit établi, quelques corps sont constitués par des bandes d'anthraxolite compacte, le long de décrochements parallèles à la stratification.

Dans certains cas la morphologie des zones minéralisées est strictement dépendante des structures de rupture, comme le montrent deux dessins exécutés par nous en 1964 (fig. 4). On peut observer la préférence de la minéralisation pour les angles entre les fractures et l'existence de petits filons d'anthraxolite massive. En même temps, l'existence de nombreux passages des grès stériles à l'anthraxolite massive est évidente, ce qui prouve le rôle du remplacement métasomatique des grès, y compris le quartz. D'ailleurs ce processus, qui suppose l'existence d'une solution très active, est très fréquent dans la région.

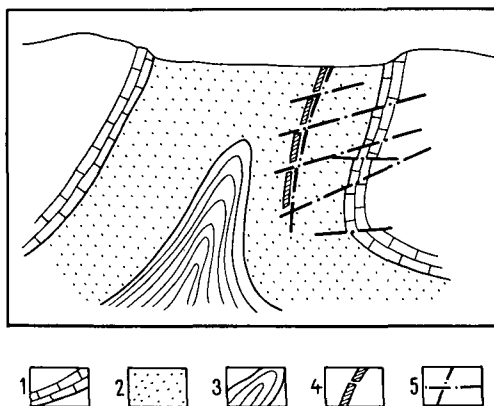


FIG. 5. Rapport entre les minéralisations d'uranium dans les grès permien et les structures disjonctives.

1 - Calcaires mésozoïques; 2 - grès saxoniens; 3 - argilites autuniennes; 4 - gisements d'uranium; 5 - failles.

Les décrochements et les failles légèrement diagonales sont apparus probablement vers la fin des processus de plissement, donc entre l'Albien et le Sénonien. Les structures qui fragmentent les gisements et qui présentent souvent de faibles inclinaisons (fig. 5) sont apparues plus tard, probablement pendant la phase laramique. Les deux systèmes de failles délimitent dans le temps la phase principale de formation des gisements, qui ont ainsi un âge proche de celui des banatites.

Nous mentionnerons aussi l'allongement vertical de beaucoup de gisements, l'absence de continuité entre les deux flancs de quelques plis, l'effilage graduel en chute de quelques-uns de ces gisements, l'existence de plusieurs corps parallèles dans les zones fortement tectonisées; ces faits suggèrent que la circulation des solutions minéralisatrices s'est produite après la mise en place des couches à la verticale.

Nous supposons aussi que les bitumes et, en partie, l'uranium, proviennent des dépôts carbonifères et autuniens.

Il convient de remarquer que dans une autre zone, où ces dépôts manquent à la base du Saxonien, les minéralisations sont représentées par des filons de pechblende avec d'importantes apparitions de bitumes.

L'homogénéité de la dispersion des grains de pechblende et le fait que l'anisotropie de l'antraxolite dépend de la présence de la pechblende suggèrent que tant les bitumes que l'uranium sont venus ensemble, les premiers sous forme gazeuse, polymérisant directement en hydrocarbures solides sous l'influence du rayonnement (ce point de vue gagne de plus en plus de terrain dans la littérature géologique). En admettant que les solutions hydrothermales liées aux banatites jouent un rôle dans la mobilisation des bitumes et de l'uranium, leur transport et leur dépôt, plusieurs des éléments géologiques reconnus dans la région considérée s'avèrent valables, dans ce cas aussi (formation des gisements dans la phase de cratonisation relative de la région, à faible profondeur, sous la surface d'une région émergée; instauration définitive - et contemporaine du magmatisme - des tendances tectoniques ascendantes, etc.).

GISEMENTS FILONIENS A ANTHRAXOLITE DE SCHISTES CRISTALLINS

Les minéralisations sont représentées quelquefois par des filons réguliers, d'autres fois par des corps filoniens à morphologie compliquée, par des nids ou par un réseau large et très capricieux de filons et de petits filons, disposés en un paquet de micaschistes à grenats et de gneiss, qui reste en position tectonique anormale au-dessus des schistes quartzitiques sériciteux, considérés comme plus jeunes. Malgré le désordre apparent, les minéralisations présentent une tendance claire à se disposer en conformité avec la schistosité, et c'est la raison pour laquelle elles présentent des pendages soit à prédominance verticale, soit relativement faibles, en fonction de la chute du paquet de micaschistes.

Les schistes cristallins se superposent à un paquet épais de plusieurs kilomètres de dépôts de flysch du Crétacé inférieur et sont couverts d'une plaque à puissance pouvant atteindre jusqu'à 1 km de dépôts terrigènes et carbonatiques mésozoïques, dont seuls des lambeaux isolés sont conservés à l'heure actuelle.

Quoique représentées par des anthraxolites à pechblende similaires à celles des dépôts du Permien, les minéralisations présentent un caractère hydrothermal évident: elles sont accompagnées de fortes zones de kaolinisation, carbonisation, silicification, quelquefois même hématitisation (fig. 6). Les carbonates sont bréchiformes et comportent des fragments de couleur et de composition différentes, en général cimentés par du calcite blanc. Les gisements ont une teneur très faible en pyrite, chalcoppyrite, marcassite et galène; la pénurie d'éléments parellites constitue un autre point de ressemblance avec les minéralisations du Permien.

L'aspect tout entier des minéralisations montre d'une manière convaincante qu'elles se sont formées dans les conditions d'une fragmentation tectonique ininterrompue. On rencontre souvent des blocs de carbonates ou des nids d'anthraxolite dans la masse d'argile, qui prouvent par leur forme qu'ils ont été brisés, déplacés et roulés.

D'autre part, le fait est évident que dans l'ensemble les minéralisations suivent le dessin d'un réseau compliqué de ruptures pré-existantes. Les cas de bifurcation des minéralisations sont fréquents, comme on le constate aussi dans la figure 6.

La nature hydrothermale du mécanisme de formation des gisements peut être acceptée, mais l'abondance des bitumes montre que les solutions ont eu, bien sûr, un caractère spécial. Il est bien possible que ces solutions aient été fortement enrichies en hydrocarbures gazeux et en dioxyde de carbone.

Dans les dépôts de flysch surmontés par les schistes cristallins on connaît l'existence de paquets de schistes bitumineux, souvent faiblement radioactifs. En même temps, le flysch est à prédominance carbonatique. Ces circonstances permettent de supposer que les bitumes, et peut-être aussi une partie de l'uranium et même les carbonates, ont leur origine dans les dépôts de flysch. A remarquer qu'en cette région on ne connaît pas d'intrusions acides, et les gisements d'uranium sont localisés seulement dans les zones où le cristallin se superpose au flysch.

L'âge des minéralisations a été controversé; l'opinion a été émise — et renforcée par quelques déterminations d'âge absolu — qu'elles pourraient être anciennes, éventuellement hercyniennes. Personnellement, nous sommes convaincus que leur âge est jeune, alpin.

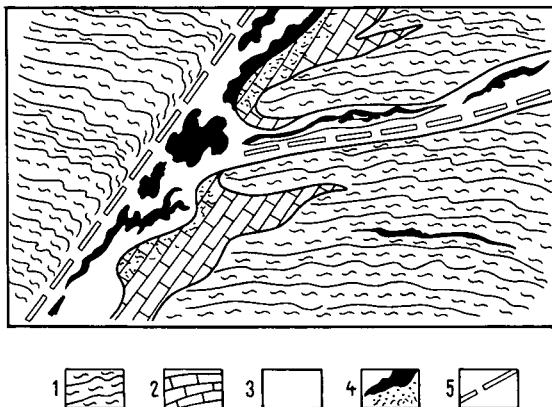


FIG. 6. Minéralisations d'anthraxolite uranifère dans des schistes cristallins (détail).

1 - Micaschistes; 2 - calcaires filoniens bréchiés; 3 - argile; 4 - anthraxolite uranifère massive, d'imprégnation et en veinules; 5 - failles.

Outre la relation spatiale évidente des minéralisations avec le contact des dépôts de flysch, il faut retenir aussi le fait que le réseau compliqué de ruptures suivi par les filons s'est formé selon toute probabilité pendant les mouvements alpins: depuis le Crétacé inférieur et pratiquement jusqu'à présent, le cristallin a avancé sans cesse vers le flysch. On peut même constater quelquefois que des failles du réseau considéré coupent les dépôts de flysch, et dans un certain cas le prolongement d'un accident tectonique minéralisé affecte des dépôts du Crétacé supérieur.

Nous supposons que la plaque de dépôts mésozoïques a joué pendant la formation des gisements le rôle d'un écran. Dans certains cas, de petits filons d'anthraxolite uranifère pénètrent dans les grès werféniens de la base du paquet sédimentaire. En même temps, au plan régional on constate que dans les zones où l'érosion a éliminé une couche plus puissante de schistes située au-dessous de sédiments mésozoïques, les minéralisations sont absentes.

CONCLUSIONS

Malgré leur diversité, dans la conception exposée les gisements d'uranium de Roumanie présentent au moins une particularité commune: leur âge alpin (à une approximation paléocène quelconque).

Dans chacune des trois séries, la formation des gisements a été précédée par des phénomènes propices à l'accumulation sédimentaire d'uranium en certains dépôts paléozoïques, quelquefois mésozoïques. L'uranium a été extrait de ces formations, transporté et déposé par des mécanismes différents: assimilation et différenciation magmatique, assimilation partielle, et surtout mobilisation par les solutions hydrothermales ou seulement mobilisation par les solutions venant d'une plus grande profondeur, sans liaison apparente avec une activité magmatique.

Avec la formation de gisements moins communs il peut y avoir passage progressif d'un mécanisme à l'autre. Outre l'uranium, des bitumes ou des carbonates ont été aussi mobilisés dans certains cas.

La formation des gisements a lieu après les importants déplacements horizontaux et les efforts de compression du Crétacé, pendant une période de calme tectonique relatif. Nous supposons que celui-ci a été un moment de relaxation des efforts tangentiels des flux de matériau dans l'asténosphère, avec l'exondage presque général du territoire et la montée vers la surface, par des lignes de fracture, d'un flux thermique et de substances volatiles favorisant l'apparition du magmatisme banatitique, mais aussi la mobilisation de substances en dehors des processus magmatiques.

REFERENCES

- [1] GIUȘCĂ, D., CIOFLICĂ, G., SAVU, M., Caracterizarea Provinciei Banatitice, An. Comit. Geol. XXXV, Bucarest (1966).
- [2] CIOFLICĂ, G., SAVU, M., BORCOȘ, M., STEFAN, A., ISTRATE, G., Symp. Volcanism and Metallogenesis (Guide), Bucarest, 1973.
- [3] RĂDULESCU, D.P., SĂNDULESCU, M., The Plate-Tectonics Concept and the Geological Structure of the Carpathians, Tectonophysics 16 (1973).
- [4] RĂDULESCU, D.P., Plate-Tectonics in Tertiary Volcanic Areas, An Example: The Carpathians, Symp. Volcanism and Metallogenesis, Bucarest, 1973.
- [5] NITU, G., Profondeur de formation et la zonalité verticale de quelques gisements d'uranium, Communication à la Session Scientifique 1967.
- [6] Geologiya gidrotermal'nyh uranovyh mestorozhdenij (Shcherbakov, D.I., Volfson, F.I., Eds), Nauka, Moscou (1966).
- [7] STOICOVICI, E., SĂLĂJAN, I., Contribuții la cunoașterea magmatismului banatitic, Studia Univ. Babeș-Bolyai, Serie Geol.-Miner., Fasc.2, Cluj (1970).
- [8] KUSHNAREV, I.P., Glubiny obrazovaniya endogennyh rudnyh mestorozhdenij, Nedra, Moscou (1969).
- [9] IVANOV, S., N. cul. Zakanomernosti razmeshcheniya poleznyh iskopaemyh IX Nauka, Moscou, (1970).
- [10] KORNICHUK, I., BURTIK, T., «Litologo-fatzial'nye usloviya lokalizatzii uranovyh rudoproyavlenij v permskih otlozheniyah v Sotzialisticheskoy Respublike Rumynii», ces comptes rendus, IAEA-SM-183/15.

REPORTS OF THE WORKING GROUPS

CHEMICAL AND PHYSICAL MECHANISMS IN THE FORMATION OF URANIUM MINERALIZATION, GEOCHRONOLOGY, ISOTOPE GEOLOGY AND MINERALOGY

CHEMICAL AND PHYSICAL MECHANISMS IN THE FORMATION OF URANIUM MINERALIZATION

An understanding of the chemical and physical mechanisms which permit uranium to be accumulated in solutions or melts, transported and precipitated, particularly at sufficient grades and tonnages to be of economic value, are fundamental to the discovery of new deposits, especially in the relatively unexplored parts of the earth's crust. Controls for uranium mineralization that can be recognized in the field or laboratory should be quantified and interpreted in the context of chemistry, physics, geochronology, mineralogy and isotope studies.

Mineralogy encompasses both chemical and physical parameters and can provide information not otherwise obtainable on the origin of a deposit. Such studies can also provide evidence on whether the present-time mineralization is original or has been subjected to remobilization during subsequent orogenic and/or metamorphic events.

It is not the intent of this report to compile a comprehensive list of chemical and physical mechanisms possibly important in the formation of uranium ore bodies. On the contrary, the Working Group has attempted to indicate only some of the more significant general topics which seem to warrant further study. The group solicits from the other Working Groups suggestions as to specific studies which, on the basis of well-documented observations on their particular types of deposits, deserve priority consideration.

Much has been published on the solution chemistry and transport of uranium, but the chemical and physical processes that result in uranium concentrations are less well understood. The Working Group suggests that this may be due in part to both insufficient factual data for many deposits and an inadequate interpretation of existing data in the context of chemical and physical mechanisms. It is thus important to obtain new data on environmental conditions that pertained throughout the period of uranium deposition.

To promote a broader familiarity with published chemical and physical data and mechanisms probably significant in the genesis of uranium deposits, the Working Group is considering the compilation of a selected bibliography.

Processes involved in the formation of economic uranium deposits probably include (a) incorporation of uranium in solution or melts, (b) transport to the site of deposition, (c) precipitation, (d) enrichment and (e) preservation. These processes are not necessarily in their order of occurrence, indeed some may occur more than once in the formation of particular types of deposits. A genetic understanding of an ore type, if it is to be useful in exploration, must identify which processes have operated

and in what order. It is in this identification that an understanding of chemical and physical mechanisms becomes useful. The following types of mechanisms are generally considered significant in the formation of uranium deposits.

1. Chemical

Solubility relations for the minerals of uranium deposits or functions of solution composition, pressure, temperature, oxidation potential etc. are important in their application to such problems as the formation and stability of complexes, the leaching of uranium from detrital minerals etc.

2. Physical

Conditions such as topography, climate, ground-water level, permeability of rock fracture and sediment, geothermal gradient etc. will affect the processes of ore formation.

3. Organic

Viable and non-viable organic material may affect the processes of ore formation by the dissolution, complexing, adsorption, reduction etc. of uranium and other elements.

There are unlimited studies which might be conducted on any or all of these mechanisms. However, it would be wise to concentrate first on those mechanisms that detailed investigations of actual deposits have shown to be of paramount importance.

With respect to the other topics assigned to this Working Group, we offer the following.

GEOCHRONOLOGY AND ISOTOPE GEOLOGY

Both radioisotope and stable isotope data can provide valuable information on ore genesis, particularly if this is tied closely to mineralogy. Having established the age (or ages) of mineralization by the study of radioisotopes and their decay products, changes in mineralogical composition of ore bodies can be correlated with other geological events. The methods outlined in the report¹ of Working Group 5 in 1970 are still pertinent, but to these should be added measurements of sulphur, oxygen, carbon, selenium and hydrogen isotopes. In the case of suspected recrystallization, $^{206}\text{Pb}/^{207}\text{Pb}$ ages should be obtained, if possible, since the model ages derived from galena and other sulphides should date the original emplacement of the mineral and are not affected by recrystallization.

¹ WORKING GROUP REPORT, "Group 5 - Age determinations", Uranium Exploration Geology (Proc. Panel Vienna, 1970), IAEA, Vienna (1970) 375.

MINERALOGY

The mineralogy of uranium deposits is fairly well known, but more work is required in a number of areas. The more important of these are:

- (a) Detailed information on the composition and stability of uraninite and the less well-crystallized variant, pitchblende².
- (b) The nature of urano-organic solids.
- (c) The genesis, distribution and alteration of brannerite.
- (d) The formation of authigenic minerals such as anatase, martite and magnetite in sedimentary environments.

The Working Group presents these suggestions on the understanding that they are merely a framework for discussion and require the continuous participation of the other Working Groups. The members feel that more frequent group meetings are necessary and that a balanced representation must be maintained from mining, educational and government organizations.

DISCUSSION

S. S. ADAMS: The bibliography we have in mind would be highly selective, referring to the literature which has a bearing on uranium chemistry. Obviously we will have to call on the assistance of many people to get the right papers in the right order.

J. E. FROST: Let me just emphasize that if we are interested in the chemistry of these solutions we must concern ourselves not only with uranium but with the other elements in solution as well. In many of our discussions I have had the impression that we were considering uranium out of context, so to speak.

H. H. ADLER: If you want to use information derived from oxygen, carbon and sulphur isotopes to get a better understanding of uranium geology, I am afraid you will not be able to limit yourselves to the isotope properties associated with the uranium deposits alone; if you did, no meaningful interpretation of the information available could be made. To make really good use of information on the sulphur isotope geology of uranium deposits, one would need a more or less complete knowledge of sulphur isotope composition and geology in all other types of ore and non-ore deposits; and to amass all that information oneself would be an enormous undertaking.

S. H. U. BOWIE: I quite agree. The fact of the matter is that we must rely on the sulphur-oxygen-hydrogen-carbon isotope data obtained by other people and published in the literature.

However, I am at present in charge of a laboratory recently set up to do just this kind of work. We can study all these isotope ratios (though we have not yet started on selenium), and we do not propose to limit ourselves to uranium deposits.

² Uraninite is the correct name for the species as a whole, but is used particularly for macrocrystalline examples, whether from pegmatites or hydrothermal veins. Ideally UO_2 , it is usually somewhat oxidized, UO_{2+x} , and may contain, in the case of pegmatitic occurrences, significant proportions of thorium and rare-earth elements. Pitchblende is a colloform, fine-grained variety, related to uraninite much as chalcedony is to quartz. It was already in a relatively highly oxidized state when formed and has only a small content of thorium and rare-earth elements. Both uraninite and pitchblende contain lead, which may be both original and the product of radioactive decay since the mineral crystallized.

REPORT OF WORKING GROUP II

SEDIMENTARY BASINS AND SANDSTONE-TYPE DEPOSITS

A. SANDSTONE-TYPE DEPOSITS

Sandstone-type uranium deposits are identified predominantly with sedimentary formations of detrital continental origin and are associated primarily with reducing environments in these rocks. The deposits can be classified on the basis of the depositional environment of the host rock into two principal types (Types I and II) and two types of lesser importance (Types III and IV).

Type I

These deposits are associated with fluviatile sediments, chiefly sandstones, in which ore distribution is controlled chemically by indigenous or introduced reductants in the form of carbonaceous matter of plant origin, hydrogen sulphide, pyrite, humate substances, bitumens and possibly other forms of organic matter. Ore occurs in peneconcordant and roll-type deposits which are represented by both static and mobilized or redistributed accumulations of uranium. This type is represented extensively by uranium deposits in the United States of America and by some occurrences in Permian sediments in Europe.

Type II

These deposits are associated with deltaic and littoral marginal marine sandstones in which the control of ore distribution is generally similar to Type I deposits. This type is represented by the deposits of Niger and Gabon (Franceville Basin) in Africa, Salta and Mendoza in Argentina, and the Gulf Coast of the USA. Proximity of uranium deposition to marine margins increases the likelihood of extending ore occurrences from fluvial into deltaic, tidal channel, beach and off-shore bar sands.

Type III

These are deposits in lacustrine rocks and may be subdivided further into (1) deposits associated with widespread limnic siltstone facies. Uranium of syngenetic origin is redistributed into ore concentrations through involvement of sedimentological, stratigraphic and tectonic factors; this type is represented by the deposit at Lodeve in France. (2) Deposits associated with lacustrine sediments in which uranium mineralization appears to have been epigenetically introduced; this type is represented by the deposit at Ningyo-toge, Japan.

Type IV

These are deposits in eolian sandstones. Although normally devoid of carbonaceous plant matter, deposits of reductants such as oil and hydrogen sulphide gas have been found in these rocks and may account for the presence of uranium which is usually associated with vanadium. Deposits of this type are found in the USA.

B. SEDIMENTARY CONTROLS

The following characteristics of depositional areas are identified with favourability for occurrences of Types I, II, III, and IV uranium deposits.

1. Large areas of crystalline rocks generally of silicic origin which border basin or foreland areas and through erosion produce a series of generally fluvial or deltaic arkosic sedimentary host rocks. Such land areas are presumed in many cases to have been rising intermittently during periods of deposition of the clastic host rocks and in the course of formation of the ore deposits.
2. A source of uranium either in bordering silicic crystalline and/or tuffaceous rocks, or within tuffaceous or other source material incorporated in the sedimentary host rocks.
3. Rapid burial of organic debris in the host sediments followed by a period of persistently high water tables preventing aerobic destruction of the organic matter.
4. Formation of H_2S and sporadically distributed pyrite from organic matter in the host rock and/or introduction of reductants such as H_2S , petroleum, humic acids, and bitumens, which are capable of reacting with uranium in solution to bring about its precipitation. Mobilization of bituminous substances from organic matter in the host rock is also of importance.
5. Persistence of gently dipping unfolded permeable strata during basin uplift providing for relatively slow introduction of substantial quantities of ground waters from basin margins and adjacent terrane.
6. Peneplanation, extensive erosion, or deep leaching of uranium source rocks adjacent to basin and foreland areas to provide for input of large quantities of uranium into waters moving into basin areas.
7. Sufficient interbedding and intercalation of mudstones with the sandstones to form confined aquifers which restrict water flow in the sandstones to rates that produce an optimum balance between destruction and preservation of the reducing environments that are present.
8. Subsequent partial alteration through oxidation or other mechanisms causing enrichment of uranium through redistribution.

9. Extensive areas of flat-lying lacustrine sediments representative of deposition under quiescent conditions.

The strong influence in this report of characteristics obviously related to deposits of the types found in the USA can be explained on two grounds. Firstly, these deposits make up a very large contribution to the uranium resources in sandstones, and secondly, with the exception of Messrs Gangloff and Barthels, there were unfortunately few representatives in the Working Group from other countries in which sandstone-type ore deposits are found.

C. CONSIDERATIONS CONCERNING FUTURE RESOURCES AND CONDITIONS OF ORE FORMATION

Sandstone-type deposits comprise 40% of the world's low-cost reserves of uranium and approximately two-thirds of the estimated additional potential. Based on currently available data on US resources, the additional amount of uranium that might be available at higher cost and lower grade may be two times as large as the low-cost material. Although this is an appreciable increase, it must be recognized that our knowledge of resources in sandstones diminishes rather than increases in proportion to the decrease in grade. It is problematic whether the USA will ever be able to rely on sandstone-type ores for its total requirements, and this appears to be even truer for the rest of the world. In the future, attention in the USA will undoubtedly be directed increasingly towards exploration and discovery of the other types of deposits which make up much of, and are today adding markedly to, total world resources.

Nevertheless, sandstone-type ores remain a prime target for exploration, and the development of useful techniques and concepts to aid in that effort is a very desirable and necessary goal. In this Symposium we are, however, more concerned with concepts than methods; therefore, the deliberations of this Working Group have been oriented accordingly.

A question of prime importance is whether there exist large quantities of uranium in sandstones in areas that have not yet been recognized as being potentially productive and cannot be recognized superficially by conventional radiometric exploration methods. During this Symposium a number of papers have been presented which directly or indirectly point to possibly fruitful areas of investigation that may lead to recognition of promising regions. Several of these have been noted and are offered here as examples of directions towards which future investigative efforts might be oriented.

1. Recognition of pathways of uranium migration
 - (a) Properties of hematite and limonite that are indicative of pyrite oxidation in contrast to properties associated with these minerals when derived from other sources by syngenetic, diagenetic, or epigenetic processes.
 - (b) Destruction or reconstitution of magnetite and ilmenite or other detrital minerals and their components, including reduction to

sulphides or removal by acid solutions and through organic complex formation, all of which may be related to processes of uranium ore formation.

- (c) Possible absorption of uranium by montmorillonite, zeolites, chlorite, and other micaceous or clay minerals in excess of background abundances especially in sediments where uranium has occurred in anomalous quantities in ground water.

2. Role of organic materials in uranium accretion

More specific identification of the role of petroleum and its derivatives, bitumens and humate substances in the formation of ore deposits.

This list of possible areas for investigation is obviously very abbreviated, and many additional possibilities can surely be suggested. The Chairman of Working Group II would welcome additional suggestions. Suggestions for collaborative research efforts would also be welcome where specific expertise or special laboratory procedures are needed and can be provided through collaboration. These will be noted by this Working Group in its deliberations regarding the need for research to improve knowledge of sandstone-type ore formation.

DISCUSSION

W. I. FINCH: Back in the mid-fifties, when I was working on a report on "sandstone-type" deposits, I was told to avoid that term, and to get around the difficulty I coined the expression "peneconcordant". At that time we did not fully understand the roll-type deposits in Wyoming; my original intention was to include both roll-type and tabular-type deposits. I still wonder whether "sandstone-type" is a satisfactory designation of these deposits.

Secondly, I disagree with your classification of deposits by the sedimentary environment they are found in; the classification is made to depend on an interpretation of the host rock, and I feel that some of the criteria for defining the environment of deposition have not yet been worked out. In southern Texas for example we find a very definite overlap between deposits in fluvial and near-shore environments. In such situations a classification in terms of environment becomes problematic.

H. H. ADLER: The statement that proximity of uranium deposition to marine margins increases the likelihood of ore occurrences extending from near-shore fluvial into deltaic-tidal and off-shore bar sand environments surely demonstrates a recognition of the fact that there is a gradation from fluvial into marginal marine and possibly marine-type environments.

As far as the term "sandstone-type" deposits is concerned, its use is, I think, a matter of convenience and convention. Whether it is strictly correct is hard to say, but the term "peneconcordant" surely has much greater limitations. I dare say that if we introduced some term other than "sandstone-type" now, we would confuse the literature for all future geologists.

G. R. UDAS: I think a positive statement to the effect that only marginal or fluviatile environments should be explored does more harm than good for geologists who cannot attend a symposium such as this. Surely it is better to leave the matter open and say that sandstones as such should be explored, provided the proper controls are present — though it would be perfectly proper to add that, in view of experience, preference should be given to fluviatile sandstone.

H. H. ADLER: I understand your point. What we have tried to say here, in brief summary, is that the uranium resources known to be present in sandstones today are found in fluviatile — or what my colleagues would refer to as marginal marine — deposits. I agree, however, that sandstones of any type, fluviatile, marginal marine, aeolian or marine, deserve attention as long as they satisfy the prerequisites for uranium precipitation. You may recall that I earlier stressed the occurrence of uranium in aeolian sandstones. This is not a common type of occurrence, but it serves to illustrate the importance of not limiting our thinking strictly to what we have experienced in the past.

G. R. UDAS: Very good; but I think it might be wise to shift the emphasis from the class of environment to the presence of appropriate controls.

J. E. FROST: I am very much in favour of the extra classification for marine sediments. At the same time, however, we must bear in mind that thousands and thousands of oil wells have been logged, and very little uranium has been found in marine sediments. Clearly a rather special type of environment is needed for uranium to be precipitated in these sandstones.

H. H. ADLER: We have discussed at length the question where marginal marine ends and marine begins, and not being a stratigrapher or a sedimentologist I am hardly qualified to give an answer. However, I would wager that a dozen stratigraphers and sedimentologists could not resolve the matter in a day's deliberation either. Evidently there are many conditions under which sediments were deposited in and around deltas and marine environments, and we have no very definite demarcation between the different sets of conditions. One can proceed from a delta system to an off-shore bar system and from there to a shelf system where sands persist; and these sands will gradually, through marine currents, move seaward into turbidite facies. I have seen turbidite facies that are both somewhat sandy and extremely fine-grained. I cannot say for sure whether they will yield uranium or not, but experience certainly suggests that we should not urge anyone who is interested in finding an economic uranium deposit to invest all his money in exploring turbidites or marine sandstones.

Incidentally, we have not created a special classification for marine sandstone. We merely say that the proximity of uranium to marine margins increases the likelihood of occurrences extending into deltaic sands and off-shore bars, because both a source and a permeable environment are available, and reductants could well have accumulated in the sands in such areas.

We know, of course, that large deltas are the most important areas of oil production, and there is admittedly little indication that uranium deposition is in any way controlled by oil deposits; there is no apparent correlation between the two. If such a relationship existed, it should be obvious. On the other hand, the history of the Entrada formation and the Navaho sandstone — both aeolian sandstones — warns us not to let our concepts

become too rigid. Here we are dealing with rock types not normally considered to be particularly favourable for mineralization, in which the only known reductants are related to petroleum formation or gas formation. Therefore we must conclude that uranium and vanadium deposition is in some way controlled, at least in these aeolian sandstones, by the environment created by petroleum or hydrogen sulphide gas. The magnitude of the deposition is hard to predict, but the concept exists and it would be foolish to ignore it.

F. R. JOUBIN: In your list of prerequisites for a favourable environment I see no reference to the preservation – not only preservation, but possibly also rejuvenation and even improvement – of pregnant sandstone basins existing particularly in the current coastal areas or near-marine category. I wonder whether the existence of a rising land mass might not be a prerequisite worth mentioning.

H. H. ADLER: Yes, we will be sure to include it.

A. DURANDAU: Might it not be a useful idea to classify the marine sandstone deposits in terms of the depth of the water layer beneath which the sandstone was deposited? The phosphatic deposits in Morocco, for example, are thought to have been deposited beneath a few metres of water. Would you call this a marine deposit or not?

H. H. ADLER: Yes, but marine phosphatic deposits have not normally been considered as falling within the category which it was our Working Group's task to define, namely sandstone-type deposits; nor have we included shales, siltstones and the syngenetic types of deposit that are formed more in marine than in continental conditions. Perhaps someone else could say where these are to be placed.

R. D. NININGER: At one time we considered having a special group for syngenetic sedimentary deposits, but we then decided that their economic importance was not great enough to justify it. I believe they will be covered in Mr. von Backström's report.

J. A. FERNANDEZ POLO: In general I agree with the conclusions of the Working Group. One difficulty I find, however, lies in the attempt to make a rigorous distinction between fluvial and deltaic sandstone deposits. In some countries the conditions of sedimentary formation were such that the sandstone basins suffered a revolution, as it were; as a consequence of both transgressive and regressive processes we find both fluvial and deltaic characteristics in a given zone, and a rigorous differentiation becomes very difficult.

H. H. ADLER: In this connection I might mention a paper which I wrote, in collaboration with Mr. Nininger, for the International Geologic Congress of India in 1964. We considered in a general way the development of the environment that precedes the formation of uranium deposits, basing our analysis on the work of several prominent stratigraphers and sedimentologists who had recognized that the sandstone environments most apt to retain organic material are those that evolve in rather humid and tropical climates. This insight is borne out by work done in the Wyoming Basin area. These were not desert-like terrains but actually tropical mountainous areas with torrential rains causing rapid non-chemical erosion of arkosic sediments from highland regions. In these circumstances the sediments retain their arkosic character, whereas if much chemical weathering occurs in the highlands one finds a development of micaceous sediments rather than arkosic, or of purely salicic rocks.

Under this theory, then, the preservation of feldspar indicates a rapid burial of sediments, and hence also of organic material. In these conditions the organic material which would normally be destroyed rapidly by aerobic processes tends to be preserved; a high water table is sustained, and this is in itself indicative of a wet climate.

Now, to go a step further, this system prevails not only in the area where the sediments originated but extends from that area through the savannah into the marginal coastal swamp. There is accordingly an extensive system of channels between the mountainous highland and the marine environment, reaching 50 or 100 miles or more in some places. On the other hand, there are areas in the world where the distance between the highland and the marine margins is very short; in these short intervals there is not the same opportunity for the formation of uranium ore deposits as in the much longer ones.

I realize there is a great deal of argument about the environment in which these arkosic sediments prevailed, and I do not wish to take part in it. It is a matter of fact, however, that the model I have outlined seems to fit the conditions in which we find uranium deposits in sandstones better than any other model that has been suggested.

A. M. GANGLOFF: I should think it would not be difficult to reconcile the different points of view that have been expressed here. Let me suggest the addition of a sentence in which we say something like: "One should not lose sight of the fact that, during the filling of sedimentary basins, there may well have been a progressive passage — progressive in time and in space — from one type of palaeogeographic landscape to another, that is to say from the purely continental to the purely marine extreme."

H. H. ADLER: That is an idea I tried to express earlier, though perhaps not so concisely and neatly. But I quite agree.

I. A. BREGER: The subject of organic material has come up in almost every paper this week; obviously it would be hard to overestimate its importance. Terms such as hydrocarbon, bitumen, anthraxolite and so on have been used, however, in what seems to me a rather insouciant fashion, without any real effort at specific identification through analytical work. At the risk of seeming fussy about terminology, I would remind you that inaccurate terminology has sometimes suggested trends for research that later on turned out to be useless. It might therefore be wise to use a general term such as "carbonaceous substances" except where the material in question has actually been identified by chemical analysis.

H. H. ADLER: A very good point. I think the reason for the deficiency is obvious: very little work has in fact been done — apart from what you did yourself during the early years of the uranium programme — to identify specifically the many different types of organic matter of interest, except in cases where their composition was easily recognizable. You may recall that the term asphaltite was commonly used some time ago. Now, to me the word asphalt suggests a derivative of a petroleum substance, not of a coal substance, so the term asphaltite was quite misleading except where oil was actually involved in the evolution of the material. Yet this term persisted in the literature for some time.

How we can overcome the deficiency without involving ourselves in a great deal of research, I do not know. Some of the terms used in our report have been used by your colleagues of the United States Geological Survey. Until more thorough analyses are performed, I have no alternative

to assuming that a person who discusses the details of a deposit is using his terminology in a reasonable way.

Another danger would lie in coining a new term for every variation of organic material, however slight, on the basis of its physical properties. That is decidedly something to be avoided.

R. D. NININGER: Let me encourage those who have comments on the report of Working Group II to write to the chairman. We must pass on now to the other reports.

URANIUM IN QUARTZ-PEBBLE CONGLOMERATES

Uranium-bearing, oligomictic, quartz-pebble conglomerates are epicontinental sediments laid down in Precambrian intracratonic basins. Most of these conglomerates are found in the sedimentary section prior to the development of the first limestones. None have been found of age younger than the first red beds and we believe that none younger will be found. We suggest that reports of young conglomerates of this type, such as a Cambrian conglomerate described in Soviet literature, are in error.

The deposition of uranium-bearing minerals in the known conglomerates appears closely related to sedimentary features. This is particularly true in the Witwatersrand and at Elliot Lake, where the presence of uranium in young, cross-cutting conglomerate beds clearly relates to scour of older beds.

Where the uraniferous mineral is structurally ordered thorium uraninite, we believe it to be of detrital origin. However, pitchblende occurs in some of the conglomerates and, in our opinion, this must have been deposited from solution even though the uranium has not moved far in dissolved form. In the main, such pitchblende is associated with carbonaceous material normally referred to as thucholite. The available evidence suggests that this material is of organic origin.

The conglomerates do not normally contain magnetite or ilmenite. On the other hand they always contain abundant pyrite. We are forced to believe that most pyrite originates by sulphidization of detrital magnetite and ilmenite. The sulphur originated from volcanogenic processes, active at the early stages of crustal evolution, which pertain to the time of deposition of the conglomerates. Some of the pyrite so formed may have entered the conglomerates in detrital form.

Conglomerates contained minerals ultimately formed by collection, concentration and distribution of detritus by major stream systems.

The formation of an economic deposit relates both to material available at source and to the degree to which the sorting and cleaning process produces a heavy mineral concentrate in the ultimate conglomerate. Known conglomerates differ widely in this regard so that uraniferous conglomerates may contain a variety of other valuable minerals. At present, gold is the significant example of this.

Age determinations suggest that the conglomerates form between about 2800 m.y. and 2200 m.y. As noted earlier, this is prior to the development of the first red beds of the sedimentary section. Prospection for such ores should utilize this as a working hypothesis.

In the opinion of the Working Group, those encountering conglomerates of this kind should prepare heavy mineral concentrates from reasonable rock volumes to facilitate study and understanding of the origin of uranium-bearing minerals and other heavy minerals in the rocks. Except for South Africa, where extensive work of this kind has been done, there is regrettably little data available. The Working Group recommends radiometric logging of all drill holes as the Rand-type thin conglomerates can easily be missed if core recovery is poor.

The Working Group feels it desirable to point out the importance of the conglomerate-type ores and to stress the need for more active interest in their prospection.

Conglomerate ores are potentially the largest source of uranium and presently comprise about 40% of the world's low-cost uranium reserves. These amounts are contained in two districts, each of which will be in production into the next century at rates which will be in excess of present capacity at Ambrosia Lake. No other deposit, or group of deposits, can provide this scale of production or security of supply.

Further, as cut-off grade drops, the deposits, being of more or less gradational character, can be expanded to suit the economics of the time.

The growing number of known, uraniferous conglomerates suggests that they are not as rare as once thought, even though time-bound. The Working Group is optimistic concerning the likelihood of finding more of them.

DISCUSSION

S. H. U. BOWIE: I am not quite sure what you mean when you say that the thucolite is of organic origin. Secondly, I think it is perhaps something of an understatement to say that "some of the material" is pitchblende. One is quite safe in asserting that the whole column of the Witwatersrand sediments contains pitchblende. The uranium-thorium ratio of that material is about 1:33 on average, as compared with the ratio of 1:4 that we normally find in thorian uraninite. I think this also applies to certain parts of the Blind River field, where one finds quite a lot of low thorium uraninite as well as the fairly high-thorium material which, I quite agree, could be of detrital origin.

D. S. ROBERTSON: There appear to be two possible origins for the material known as thucolite: one a deep source, the material being derived in gaseous form and presumably caught or polymerized by the uranium substance, and the other some very early form of life that degraded with time, leaving remnants which are now thucolite. The weight of the evidence convinced us that this was the ultimate source of most of the material.

The degree of emphasis to be accorded to pitchblende was one point on which we had some disagreement, so I must speak for myself and not for the group as a whole. It is my opinion that all the uranium in these deposits is ultimately of detrital origin. As you know, the Dominion Reef material is largely thorian uraninite. The bulk of the material in the Rand is well down-dip, and many years younger than it presumably was originally. The pitchblende at Eliot Lake, then, probably gives us an indication of what the material was on the Rand at one time, if we can put it that way. The bulk of the material at Eliot Lake and almost all the material known at Agnew Lake is in fact uraninite; there is really not so much pitchblende. Believing that Eliot Lake is in some ways like a primordial Rand, it is my opinion that the pitchblende on the Rand came from thorian uraninite. I think you understand me; whether you agree with me is another matter.

S. H. U. BOWIE: I understand well, but I most certainly do not agree.

D. S. ROBERTSON: It is interesting to note that the uranium of the Australian conglomerates - associated with small, round, glossy balls of thucolite - is in the form of pitchblende; at any rate the material is not

ordered, is not thorianiferous, and carries no rare earths. The material in Brazil, on the other hand — likewise found largely in rounded glossy balls of organic material — is largely uraninite; it is ordered and does carry thorium and rare earths. This is an interesting problem.

F. C. ARMSTRONG: Obviously, if you limit your purview to ancient conglomerates, you will put a fairly strict limit on exploration; and in doing so you tacitly imply that you really understand the origin of these deposits. On what grounds did you conclude that the deposits in the Soviet Union called Cambrian are in fact of older age? After hearing about these occurrences in the Soviet Union, I thought perhaps we might be well advised to examine some younger conglomerates.

D. S. ROBERTSON: The Soviet paper in question describes at some length other phenomena in the area, such as basic dikes and the like, with which uranium is associated. My initial impression that the material was equivalent to our basal Proterozoic material came through translation; we have since reviewed the descriptions in the paper and are agreed that the material is unlikely to be the kind of thing we originally had in mind.

W. BOURRET: As a member of this Working Group, I have been asked to speak briefly about the magnitude of the reserves in quartz-pebble conglomerates.

Most of you realize, I believe, that the Eliot Lake deposits have been very thoroughly studied. Some 40 shafts have been sunk in the Greater Eliot Lake region, many of which are of course under water now. For the drilling, many companies settled on a grid spacing of roughly 2000 ft, though some areas have been drilled on a 1000-ft grid. The fact that one can drill these conglomerates and obtain meaningful results for the whole interval of 1000 or 2000 ft between holes — and make a reasonable extrapolation for such large areas — speaks well for the continuity of the deposits and the reliability of the reserves. To my knowledge, the published figures for the Eliot Lake reserves are about 300 000 tons of contained U_3O_8 . Both Robertson and I think this is an extremely conservative figure, one that in fact represents the proven or semi-proven reserves. So, from the figure of between 300 000 and 400 000 tons of contained U_3O_8 , you can readily see that this is perhaps the largest known uranium deposit in the world.

The Witwatersrand deposits have also been very thoroughly studied, particularly for gold of course. Perhaps one of the most instructive ways of analysing the importance of the Rand deposits is to consider the ratio of uranium to gold. In many areas this ratio is roughly 10:1 to 15:1 by weight. Last year the Rand as a whole produced about 900 tons of gold. If we take a ratio of 10:1, this would represent an annual productive capacity of some 9000 tons of U_3O_8 — assuming that all the mines of the Rand produced uranium, which of course is not the case. In the Far West Rand the ratio of uranium to gold is even higher than 10:1.

With the change in the price of gold, I understand that uranium values are being restudied and recalculated. Only the companies themselves can produce a figure. For our part, it is important to remember that this sympathetic relationship of uranium to gold does exist and that the amount of uranium far outweighs the amount of gold.

W. G. HEARN: I want to mention a point that may not be widely enough recognized: what we mine for gold in these sedimentary piles are not only conglomerates, by any manner of means, but also very thin and often extremely insignificant carbon seams, as we call them, which are easily

missed in ordinary diamond drilling. Some of these are so insignificant that one must search a stope face very carefully to detect them at all. What one finds then amounts to a pencil line running down the stope face with a pebble every 10, 15 or 20 ft. Let me suggest, therefore, that the Working Group should refer to careful radiometric logging of boreholes rather than cores, because, in both visual inspection and in core recoveries, thin horizons of the carbon-seam type can easily be missed.

D. S. ROBERTSON: Thank you. The problem is that radiometric logging equipment for slim holes of the kind drilled in most places is not always readily available. Nevertheless, your point is an excellent one.

W. G. HEARN: We have done a great deal of this type of work in South Africa, logging ordinary B-sized holes to depths of 3000 to 3500 m.

R. C. HART: I have two comments, one about the tonnage of the Eliot Lake reserves and another about the age of uraniferous sediments. Firstly, the figures of 300 000 and even 400 000 tons of U_3O_8 seem to me to be unduly conservative for Eliot Lake; a realistic estimate would in my opinion be closer to 500 000 tons. Secondly, I have heard it suggested that uranium does not occur — or has not been found — in sediments post-dating the Lower Proterozoic. This is not true. It is a fact, though perhaps not a familiar one, that uranium does occur in sediments of much younger age, and this ought to be kept in mind when exploration targets are sought.

R. D. NININGER: Do these figures for the Eliot Lake reserves — 300 000 to 500 000 tons — include the potential? They are considerably higher than the official Canadian Government figure.

R. C. HART: They include the potential, and of course they also extend to prices in the \$15 range or thereabouts.

D. S. ROBERTSON: But let me emphasize that we are not using the word potential here in the sense in which it is used in the United States of America and by the IAEA. We are referring to material that is measurable, even if the points of measurement are somewhat dispersed.

R. D. NININGER: So in fact you are referring to inferred ore in the narrower sense?

D. S. ROBERTSON: Yes indeed.

R. H. DE VOTO: I am a little bit afraid that in defining our empirical data too narrowly we may be putting unduly strict limits on the search for new occurrences. We should use our geological acumen to get a thorough understanding of the processes that must have taken place in the deposits with which we are already familiar, and then use that information not to restrict our purview but to enlarge it. It has been pointed out, for example, that polymictic conglomerates may well bear placer uraninite in Archaean rocks; we should not limit our interest to the Lower Proterozoic. Similarly — harking back to the discussion that followed the report of Working Group II — I see no reason why the favourable environments that have been observed in fluvial non-marine sandstones should not be found in many deltaic and littoral formations as well. We should keep our minds open. We shall soon reach the stage where all the deposits that can be detected by means of airborne surveys will have been discovered; stratigraphers, sedimentologists, geochemists and geophysicists, working in close co-operation, will have to carry on from there. To sum up, then, I want to be sure that the Working Groups' recommendations open doors rather than close them.

D. S. ROBERTSON: Is that not exactly what we are doing? Exploration today is an exercise in the art of spending money and human talent wisely; the reserves of both are limited. The data we have amassed indicate that it would be foolish to look for uranium in marine sediments while there are parts of the world with attractive fluvial sediments that remain to be explored. Likewise, the available data do indicate — pace Mr. Bowie — that the kind of deposit I have been discussing is in fact limited in time. Why should we lavish time and effort on red conglomerates? There are a lot of oligomictic quartz-pebble conglomerates that are red; an immense amount of money and effort has gone into drilling and trenching them, and not one has yielded a jot of uranium. Thus our efforts must be bent towards narrowing down the types of places that merit closer examination. Of course we want to expand, but geographically, into environments as yet untested, not into environments that have been tested extensively and have been shown to be barren.

I shall add just one further remark while I have the floor: the fact that there was only one paper on conglomerates at this Symposium suggests a shocking lack of interest — shocking in view of the reserves contained by these rocks.

C. T. MEYERTONS: I understand there is a considerable difference between the grades of uranium in the South African and Canadian deposits, the Canadian being much higher in uranium and lower in gold. I suppose if the two metals can be extracted together economically, that is the main thing; but as our interest is primarily in uranium, I should think it would be very useful to have a good understanding of the source of the uranium contained in these conglomerates.

D. S. ROBERTSON: I quite agree.

H. C. WHITESIDE: Let me emphasize that the South African reserves are really dependent on the price of gold. This must be borne in mind when one is considering the aggregate reserves quoted for quartz-pebble conglomerates.

VEIN- AND SIMILAR-TYPE DEPOSITS

PART I: VEIN- AND SIMILAR-TYPE DEPOSITS

These sessions in Athens have illustrated quite clearly several inter-relationships both in time and genesis between vein and other types of deposits of uranium. In particular, the discussions on uranium in sediments have emphasized how uranium moving in solution to form roll and stratabound deposits need only accumulate in open fissures, breccias or along disconformities to form massive or vein-like deposits. This is well illustrated by the sedimentary deposits such as those of Lodève and Gabon where uranium is further concentrated in massive lodes in sedimentary and structural traps.

It was also pointed out that many sedimentary and vein deposits have a wide range of associated elements in common, notably selenium, vanadium, molybdenum, ferrous iron, cobalt, copper, beryllium, carbon and arsenic. Their rather ubiquitous distribution in both types of deposits leads the Working Group to suggest the possibility of similar ancestries. Furthermore, the concept that some uranium was carried through sediments in neutral to slightly alkaline oxidizing solutions with deposition against a reducing barrier can often be applied equally well to concentrations formed against structural barriers.

Thus there appears to be a rather thin line separating some deposits in sediments and those filling open spaces, and the Working Group suggests that these similarities, especially of uranium-bearing solutions and conditions of precipitation, deserve continuing study and analysis. In particular, geologists specializing in Precambrian vein uranium deposits would find it most beneficial to study deposits in young sedimentary sequences similar to those in the southwest United States of America. An understanding of these sedimentary processes from a chemical, physical and biochemical standpoint should shed some light on the possible Proterozoic processes. Of particular interest are the chlorite mica schists which form the host of many of the uranium deposits of the Northern Territory, Australia and Northern Saskatchewan, Canada, and which may well have been the immediate source of the uranium now concentrated in fractures.

The geochemical mechanisms which have governed the transport and deposition of uranium during Phanerozoic times have been well documented and provide considerable help in understanding earlier processes. In several papers during the Symposium, however, specific peculiarities were discussed of the geochemistry governing detrital uranium in Lower Proterozoic quartz-pebble conglomerates and the first appearance of uranium in Middle Proterozoic sediments and veins. The effect on uranium of progressive evolution in biochemical, tectonic and climatic events during early Precambrian eras is concisely considered in the appended discussion by M. Moreau of the Working Group. It is briefly synopsized in the following paragraphs.

Uranium appears to have acted in different ways during three major stages in the evolution of the early Precambrian. Initially, the Archaean period prior to 2800 to 2500 million years was characterized by an anoxic atmosphere and with no oxidation below the water table. Tetravalent uranium was mechanically transported as soon as meteoric water appeared on the continent.

The second stage appeared during the Lower Proterozoic from about 2500 to 2000 million years. Although the atmosphere was still without oxygen, in the photosynthesis zone at or below the water-continent interface algae were beginning to produce oxygen and organic material was being produced from the breakdown of CO_2 into carbon and oxygen. Thus for the first time, at this interface and admittedly in relatively minor amounts, hexavalent uranium was being dissolved in marine or lacustrine waters. Tetravalent uranium, however, was still being deposited in stream conglomerates such as at Elliot Lake and Witwatersrand.

During the third stage, roughly from 2000 to 500 million years, hexavalent uranium was dissolved below the water table and may have been chemically precipitated when brought into contact with organic matter. Atmospheric oxygen increased during the Phanerozoic period to its current maximum and, hence, uranium on the continent has been transported in hexavalent form in an oxidizing environment until precipitated as tetravalent uranium at an oxidization-reduction interface.

The Working Group concludes that continuing investigation of the nature of uranium-bearing solutions with respect to their position in geological history is of considerable importance in understanding the many mineralogical and lithological variations in uranium deposits.

New concepts in plate tectonics have provided many useful clues to the conditions under which vein and other uranium deposits are located and formed. While such studies are well documented for Tertiary movements and are of great assistance in understanding uranium deposits of the Hercynian, continuing investigation of Precambrian proto-continental movements is highly desirable. Several papers at the Symposium stressed the association of uranium with sedimentary and volcanic belts bordering or at the junctures of continental masses.

Recent studies have shown that some vein or massive deposits display variations in the ratio of ^{235}U to ^{238}U . In addition to its economic significance, this phenomenon, along with variations in the ratio of UO_2 to UO_3 , has a bearing on our understanding of the mechanisms which have affected and changed uranium deposits over the past 2500 million years. Clearly, many more detailed analyses of isotopic variations are required in order to assist the geologist in understanding and benefitting from these processes.

In a similar vein, several schools of geological thought have been considering the evidence of decrepitation studies of fluid inclusions concerning the temperature-pressure relations of uranium-bearing solutions which have filled cracks and fissures. Results to date indicate relatively low values of both temperature and pressure, but with ranges which are sufficiently broad to allow for several modes of transport.

Modern methods of age dating of host rocks, metamorphism and mineral deposition have greatly aided the field geologist in establishing the succession of events governing the original emplacement and subsequent remobilization and redeposition of uranium. They have also aided him in recognizing world-wide movements of uranium at specific periods in the earth's history.

The Working Group recommends continuing programmes of age dating with special emphasis being placed on selecting specimens with specific aims in mind.

The investigations of isotopic variations, fluid inclusions and age determinations are only a few of the many laboratory techniques which must be employed with increasing urgency to assist the field geologist.

The Working Group wishes to stress, however, the importance of solid responsible data collecting based on carefully documented field evidence. As was clearly emphasized by several speakers during the Symposium, the exploding demand for uranium has placed great pressure on mining companies to expand their staffs of exploration and exploitation geologists. To effectively use the relatively few professional people available to them, the private companies will have to rely heavily on laboratory assistance from reliable research institutes and government surveys in order to obtain the information they need to help them find new sources of uranium.

Note to Part II

A member of Working Group IV, Mr. M. Moreau of France, has prepared the following statement which the Working Group as a whole accepts and feels is a valuable contribution.

PART II: VEIN-TYPE URANIUM

In dealing with vein-type deposits it will be convenient to consider (a) the geochemical origin of the uranium, (b) the mechanisms of transport and (c) the site of deposition. The site of deposition is the easiest, because one need only replace the mineralization, as it were, within its structural and petrographic environment. The mechanisms of transport can be tackled by studying mineral parageneses and the fluid inclusions characteristic of different phases of mineralization.

The geochemical origin of the uranium is the most difficult. Geochemically speaking, uranium has undergone various processes of modification and concentration between the time of sedimentary or pedological deposition and the present time when the economic uranium found in fractures is being worked. Pedological alteration, sedimentation conditions, diagenesis, metamorphism, anatexis, transfer of uranium from silicate phases to fluid phases — all these things are important at some time in the history of an ore deposit.

1. GEOCHEMICAL ORIGIN OF URANIUM

Let us first consider the geochemical problem, as it is the most difficult. For this purpose it is important to distinguish the dissolving and pre-precipitation mechanisms which were operative in the Precambrian and Phanerozoic; the process was governed essentially by redox balances that varied over geological time, both in the atmosphere and hydrosphere.

Up to 1965 one considered only the Phanerozoic cycle, but in recent years numerous authors have sought to reconstruct the atmosphere since the beginning of the Earth. They suggest that oxygen first appeared in the atmosphere about 2200 million years ago, at the time of the first appearance of red-coloured horizons of the Paleo-Proterozoic (Huronian sediments in Canada).

However, the history of the uranium concentrations in the Proterozoic and the sedimentological character of the Proterozoic red beds suggest a different theory from the conventional one. This theory will be discussed below, although it diverts us for a moment from vein uranium.

1.1. Uranium and the Archaean (up to 2800-2600 million years)

The Archaean is characterized by a sial primarily composed of an alternation of greenstone bands (basic-granodioritic volcanic tuffs with slight metamorphism - greenschist facies) and migmatitic and granitic bands with dominant calco-sodic chemistry. Potassium, uranium and thorium are rare. It seems that throughout the Archaean these elements were not yet being extracted in any abundance from the only slightly differentiated upper mantle.

Then, starting from 2600 million years, the Kenoran orogeny produced the first large cratonizations of the Himalayan type with an extensive development of granitization and migmatization in the mobile belts and in the suture zones of the ancient microcratons, and the first large-scale extraction of potassium, uranium and thorium from the upper mantle took place. The uranium was then geochemically concentrated in the potassic granitoids and associated pegmatoids, in fairly close contact with the thorium and rare earths.

There are no known uranium-bearing veins emplaced during the Archaean. This could be due either to the degree of erosion attained by the Archaean cratons or (more likely) to the non-solubility even of tetravalent uranium under the physico-chemical conditions of the hydro-thermal fluids or meteoric waters.

1.2. Uranium during the Paleo-Proterozoic (Huronian)

Between 2500 and 2000 million years, the Kenoran chains were eroded. Since the bulk of the geochemical-stage uranium was concentrated in the potassic granitoids of the mobile belts, we see how important it is to study the sediments derived from them.

The atmosphere did not yet contain oxygen, but it did contain water and, above all, CO_2 of volcanic and magmatic origin in greater abundance than at present. The uranium therefore remained tetravalent on the continent and was transported to lower points below the water level as soon as the first possibilities for transport by watercourses and glaciers appeared. Below water level the sediments and uranium probably encountered slightly oxidizing conditions locally, when passing through the illuminated zone where the first marine organisms were living (algae and stromatolites).

There is at present some discussion on the genesis of the Elliot Lake brannerite. Considered to be of detrital origin by some investigators (for example Robertson), it stems according to others from a neoformation in

a reducing medium after dissolution of the uranium; and in fact, organic matter has been found within the brannerite crystals.

1.3. Uranium during the progressive development of marine life

Between 2000 and 1700 million years ago (late-Aphebian sedimentation in Canada), two factors helped to speed up the chemical processes: (i) the marine ferrous iron was largely oxidized and the oxygen produced by algal metabolism became available in the water, in the proximity of the organisms; and (ii) dissociation of CO_2 by marine algae produced a large quantity of organic matter which organized itself into progressively more complex compounds.

The dissolved uranium began to precipitate upon contact with the now abundant reducing media. During the Lower Proterozoic, the sediments deposited in the shelf zones were made up of iron-containing cherts with hematite, magnetite, stromatolitic magnesian limestones, quartz sandstones, and, finally, shales or argillites rich in organic matter (and in boron).

During metamorphism, these series yielded alternations of quartzite-chlorite schists or graphite mica schists associated with limestones or magnesian marbles characteristic of the uranium-bearing series. Here we recognize the typical sediments of the Tazin group in the western part of the Canadian Shield, or the Koolpin formation in Northern Australia.

It seems that in certain conditions of lagoonal confinement quite considerable concentrations of uranium were produced at that time. Indeed, the existence of the Oklo fossil reactor in Gabon, which operated 1700 million years ago in a sedimentary environment, proves that there must have been uranium concentrations of at least 20%.

Between 2200 and 1700 million years ago, on the periphery of the Archaean cratonized and granitized shields, there occurred remarkable pO_2 and pCO_2 conditions, both in the atmosphere and below water level, in connection with a certain stage of development of marine life. These conditions allowed, for the first time, dissolution of the geochemical stock of tetravalent uranium accumulated in the sedimentary series and in soils stemming from erosion and alterations of potassic granitoids.

2. MECHANISMS OF TRANSPORT

Subsequent orogeny, granitization, metamorphism and tectonic processes simply altered the geochemical uranium supply that had been introduced largely during the Lower Proterozoic.

In Canada, the first alteration occurred at the time of the Hudsonian orogeny (1700 million years); another far-reaching thermal event (the Grenville orogeny of 1000 million years ago) brought about a considerable change in the uranium, starting with the Aphebian or Huronian geochemical horizons.

In Western Europe — a permanent mobile belt zone up to the Alpine period — connections between vein mineralizations and the uraniferous source horizon have disappeared, as distinct from what happened in the Canadian and Australian Shields.

The mechanisms by which uranium is transported from a geochemical area are complex and still only poorly understood.

At high temperature ($>500^{\circ}\text{C}$), i. e. in the region of magmatism and volcanism, uranium is transported in the tetravalent or hexavalent state in the form of halides, accompanied by thorium and the rare earths. It is precipitated in the form of uraninite, or uranium-thorium-rare earth minerals (Rössing and Nilimaussaq pegmatoids, two-mica Limousin granite in France, and so on).

At temperatures below 400°C , according to Soviet and French studies, uranium is transported by CO_2 -rich fluids in the uranyl carbonate ion state and precipitated as pitchblende, which itself originates from partial reduction of a compound of the hexavalent uranium hydroxide type.

In the zones with high pitchblende concentrations in France, one always finds vein fluids with dominant CO_2 containing small amounts of hydrocarbons and sulphur compounds. Furthermore, the non-altered, banded pitchblende is always associated with iron sulphides (marcasite-pyrite).

The Soviets have shown that reducing fluids can nevertheless carry hexavalent uranium in the form of the uranyl carbonate ion. A drop in CO_2 pressure is then enough to precipitate uranium in the oxide form from such fluids. If a fluid contains only CO_2 and has an oxidizing reaction, however, simple separation of CO_2 does not permit the precipitation of tetravalent uranium. Furthermore, the host rock has to be a reducer (ferrous iron from basic dikes or amphibolite beds). Finally, it should be remembered that at low temperature ($<150^{\circ}\text{C}$) uranium can be solubilized in the tetravalent or hexavalent state by organometallic chelating complexes (C-N-O-H compound).

In conclusion, it seems that the differential action of the redox potential may explain, in a CO_2 environment, the more or less extensive migration of uranium in fractures, brecciated or episyenitic columns, stress release zones associated with folding, etc. Highly oxidizing fluids are the most likely to favour uranium transport over large distances (for example, the Ace and Fay veins at Beaverlodge in Canada, and certain hematite veins at Bois Noirs and in the Limousin and Vendée districts in France). On the other hand, reducing fluids would favour the formation of stratabound deposits, without hematite and invariably close to the geochemical source horizons (paleosurface — shelf zone, etc.). Examples in Canada are Cluff D, Rabbit Lake and the Lorado Mine.

Studies are under way in France on the fluids associated with vein mineralization.

3. SITE OF DEPOSITION

I shall not dwell on this problem because the literature contains many descriptions of uranium-bearing deposits. In the descriptions it is instructive to note the nature of the trap, whether structural or petrographic.

Mineral parageneses, more particularly the gangue sequence, the presence or absence of silica deposits, their development with depth — all these things provide valuable information which helps us to systematize the observations made elsewhere on fluid inclusions.

Finally, the regional context supplies us with interesting data on the type of deposit (association with volcanism and hypovolcanic magmatism at high temperature and low pressure, or, conversely, with deep magmatism at high pressure).

4. CONCLUSION

This brief study shows how many unresolved problems we face in dealing with uraniferous vein deposits. But it would be risky to consider vein deposits as a separate entity without bearing in mind the entire geochemical and paleogeographic context. In actual fact, veins are only one expression of the existence of a regional subjacent geochemical supply. From this supply all types of concentrations are possible, depending on the local geological history. That history is long, since it begins with the occurrence of the first extensive cratonizations 2600 and 2800 million years ago.

DISCUSSION

R. A. LAVERTY: The recycling of uranium described by Mr. Moreau must inevitably, in some cases, result not only in the production of veins but in the supply of some uranium-bearing solutions to the ground water. This may represent an addition to the sedimentary uranium deposits which are normally confined to orogenic belts. In other words, the uranium supplied to the ground water may be derived not just from erosion; some of the solutions may contain uranium that has escaped from veins.

J. C. ROWNTREE: According to my figures, about 20 to 30% of the new uranium reserves discovered during the last 15 years — representing about 200 000 tons of U_3O_8 — has been found in stratabound pitchblende deposits of the Lower Proterozoic. The new Alligator River field has about 160 000 tons of proven U_3O_8 in low-cost deposits that can be worked on the opencut system. Exploration might profitably be focussed on deposits of this type elsewhere, particularly in the United States of America.

E. E. N. SMITH: I would agree. We must hope that what has been found to date is merely a prologue, because we are going to have to find a tremendous amount of uranium.

R. D. NININGER: One cannot help wondering whether these recent discoveries in Australia and Canada are a one-time phenomenon or whether they mark the beginning of a long period of successful development of new vein-type deposits.

J. C. ROWNTREE: The East Alligator camp, with which I expect most of you are familiar, has four distinct deposits. The Ranger deposit contains 110 000 tons of U_3O_8 at about a 7 lb grade, material of simple mineralogy that can be worked on the opencut system. In this camp alone I should say that we are going to discover a lot more uranium during the next few years. There is even some potential for low-grade uranium occurrences of a more disseminated type in the same environment, and it seems quite obvious that such occurrences will make an important contribution to future uranium requirements.

D. OSTLE: Since our last meeting there has been a great resurgence of interest in vein-type deposits such as those at Alligator River; indeed, one may say that the new discoveries have put a rather different complexion on uranium exploration altogether. Possibly the fresh interest in vein-type deposits has not been adequately reflected in the attention they have received at this Symposium. I have the feeling, too, that we have not greatly enhanced or refined the criteria that we can offer to exploration geologists for practical searching purposes. Certainly if I were prospecting for vein-type uranium deposits at the moment, I would feel that there was a need for rather more precise data.

I have a number of fairly specific questions for some of you. We have heard about Mr. Smith's new interpretation of the geology of the deposits in northwest Canada; this, and the recent discovery of brines, marks a real advance in knowledge. However, I wonder whether this new knowledge — as opposed to his original tectonic criteria — would really modify Mr. Smith's approach to exploration in the area if uranium deposits were not already well known there.

Then I would like to ask Mr. Knipping whether he could not accept the conflicting age determination figures suggested by Mr. Little yesterday, simply on the assumption that the presence of the unconformity implies no more than a conditioning of the host rock, and that hypogene or epigenetic mineralization occurring in any one of a number of ways could have led to the formation of the deposit. This is an important question for the practical prospector of course, because acceptance of a purely supergene origin would obviously greatly enhance the significance of the unconformity as a guide.

Turning now to the discoveries in northern Australia, which have so remarkably underscored the importance of vein-type deposits, I wonder whether the broad conclusion that these deposits are due to a mobilization of uranium from the host rock takes us any further towards valid prospecting criteria than the structural guides that were available 20 years ago in the South Alligator River area. Mr. Adler asked yesterday whether there was any evidence of a mechanism for this very considerable migration of uranium, and, from my own admittedly limited knowledge of the area, I must confess that there appears to be no evidence of conditions comparable to those prevailing at Rabbit Lake. So I, too, find it difficult to envisage the physico-chemical process that could produce such massive, virtually monomineralic veins without leaving any trace of a metamorphic stage.

I would submit, therefore, that we are still some way from answering the question how uranium was transported and concentrated in these high-grade veins. Detailed, carefully controlled investigations such as those carried out at Rabbit Lake will have to be conducted on many other deposits. In the meantime, however, the prospector needs criteria which will enable him to identify the areas where this more detailed approach is justified. Part of the answer, as we well realize, must lie in geochemistry, and I feel sure that there is already a significant volume of geochemical information available that could be restudied with profit.

M. MOREAU: I should like to repeat what I said yesterday about the very good possibilities for uranium concentration in the Lower Proterozoic. We have plenty of evidence of this at Francevillien where there are sizeable deposits 1700 m.y. old with grades of several per cent, rising in fact as high as 20%. We know from the Oklo reactor that at the time of sedimentation — thus before any diagenesis or incipient metamorphism that

could have affected the series — this 20% concentration of uranium existed already. I think that, where there were concentrations of a few per cent or more in the sedimentary beds of the Lower Proterozoic — given appropriate carbonaceous or CO₂-rich fluids — the chances of obtaining fairly high grades of ore in neighbouring overlapping formations through remobilization would be quite good.

H. D. KNIPPING: I think there is no disagreement between Mr. Ostle, Mr. Little and myself. One's interpretation depends on the age of the unconformity in the Athabasca formation, and on this point we differ little if at all. What we do not agree about is the emplacement process.

E. E. N. SMITH: I think it is only fair to agree that we have developed our theories from what has been found in the past. In the early days I was probably as convinced a "hydrothermalist" as anyone else: to me it seemed that uranium must come from some mysterious depths. I have since changed my mind, however, and so have many others. The new ideas will probably help us in the future, but I should think, all the same, that the broad regional settings have by now been fairly well defined.

R. D. NININGER: It is certainly interesting to reflect on the progressive change in thinking, from the traditional hydrothermal concepts to present theories of the origin of vein-type deposits. Undoubtedly the Working Group should bear this evolution in mind.

OTHER URANIUM DEPOSITS

Under this heading are included uranium deposits which could not readily be classified according to certain well-defined types of uranium ore deposits established by the International Atomic Energy Agency at Montreal, Canada, in September 1972.

It will, however, be necessary to discover new uranium deposits in areas which lack well-established favourability criteria for uranium exploration. In favour of such an approach is the fact that no one rock type consistently appears as the preferred host for uranium mineralization; nor is this mineralization tied to any particular epoch or era or to any form, type or intensity of structural deformation.

There appears to be no doubt that there will be a dramatic rise in the demand for uranium and in prices over the next five to ten years; this will turn rocks containing small amounts of uranium into major uranium deposits.

"Other Uranium Deposits" makes provision for many diverse types of uranium mineralization of which the following would appear to hold the most potential for future uranium exploration.

ORTHOMAGMATIC AND ANATECTIC

The advent of nuclear reactors will be to the uranium-mining industry what the development of the electrical industry was to the copper-mining industry. A comparison between the histories of copper and uranium mining indicates that future activity should be directed towards the search for late-differentiate-type uranium deposits in granitic rocks. Large bodies of this type could be mined by efficient modern mass-mining methods and thus become ore deposits. It is suggested that such uranium ore deposits should be called porphyry uranium deposits inasmuch as it appears that they will have close historic, economic and geological similarities to the well-known porphyry copper deposits. Between 1900 and 1971 the average grade of copper ore mined in the United States of America dropped from 4.0% to 0.55%, almost an eightfold decrease in grade. If the average grade of uranium mined in the United States underwent a similar decrease in grade, then material containing 0.03% uranium (U_3O_8) would become ore, provided it were found in large quantities. Geological evidence suggests that concentrations of 300 to 500 ppm are indeed associated with certain types of late-differentiate granitic rocks.

Late differentiates of granitic magma that are considered suitable host rocks for porphyry uranium deposits are alaskite, leucogranite, biotite granite, biotite quartz monzonite, graphic granite and myrmekite, the last of which is cut by a network of aplitic and pegmatitic dykes and stringers of similar composition. Most of the uranium will be in the felsic and varietal minerals. This uranium is easily acid-soluble whereas that in accessory minerals is not.

Possible examples of porphyry uranium deposits are those at Rössing, South West Africa; at Charlebois Lake, Canada; at Crocker Well, Australia;

and in the Serido area of northeastern Brazil. Certain areas in central Idaho and in northeastern Washington, United States of America, may also contain porphyry uranium deposits.

In regionally metamorphosed regions, uranium mineralization may be associated with late-stage bodies of granitic rocks — in France, for instance, commonly with two-mica-granites. This mineralization appears to have been formed by hydrothermal reworking of the rocks along fracture zones.

Attention should also be directed towards the peralkaline rocks which are generally richer in uranium than other types of igneous rocks.

High concentrations of uranium may be built up in volcanic glasses rich in chlorine and in fluorine, and in peralkaline undersaturated plutonic rocks, especially agpaitic nepheline syenites which retain the volatile components of the magma. Such rocks may contain more than 100 ppm uranium and constitute potential low-grade resources. Concentrations of uranium are formed by the reworking of such volcanic and plutonic rocks and by processes of albitization, analcitization, etc. Poços de Caldas in Brazil, Ilimaussaq in Greenland and some deposits from Central Italy are typical examples. The last-named deposits are briefly described below as an example of deposits associated with alkaline rocks.

The volcanites of Central Italy are of Quaternary age, and outcrop in the Latium region over an area of more than 10 000 km². Petrographically they are potassium-rich trachytes and phonolites containing leucite, pyroxene and sanidine. They form pyroclastic flows and tuff zones. The unaltered rocks contain 20 to 50 ppm U, 120 to 340 ppm Th, and anomalous amounts of F, Rb, Be etc. Although phenocryst minerals make up 20% of the rock, the uranium is concentrated in the groundmass.

Uranium is present throughout the area and also occurs in the lake sediments derived from the erosion of the volcanic rocks. Other uranium occurrences are connected with supergenic processes which have affected the volcanics. Uranium is present in large quantities in meteoric waters which leach the volcanics, and is precipitated from ground water by H₂S which, together with CO₂, is a very common manifestation of the volcanic activity. Uranium is redistributed by strong leaching solutions formed by the rising gases.

Another type of uranium deposit of unusual occurrence associated with coarse-grained unzoned granites and syenites occurs in the Bancroft area of Canada and has provided about 4% of Canada's production to date. These deposits are red in colour and have an alkaline affinity. They are transgressing bodies that apparently resulted through differentiation during magmatism of ultrametamorphism in a plutonic environment. The ore minerals consist of uranothorite and somewhat less uraninite, and uranium mineralization is strongest where there is hematitization.

In addition to the Faraday deposit, a number of such deposits occur in the Bancroft area, ranging from 100 000 tons to a million and a half tons or more, at grades of 0.05 to 0.12% U₃O₈. Some are shallow deposits amenable to open pit mining that could form a group of contributors to a central custom treatment plant.

The presence of small amounts of uranium is a well-known associate of carbonatite intrusive complexes. Major reserves of metalliferous ores of great importance to the mining industry have been discovered in carbonatite-bearing complexes. The results from a nuclear-mineral

economic point of view have, however, been disappointing although minor concentrations of rare-earth minerals, associated with uranium, commonly occur in carbonatite.

Nevertheless, although the grade of uranium present in the carbonatite at Palabora in South Africa is only 0.004%, present day by-product uranium production is around 150 short tons per annum. For the existing open-pit mine, the reserves of uranium are estimated at 11 000 short tons U_3O_8 . For future underground mining operations reserves are estimated at roughly 1 000 short tons per 100-foot increase with depth. Grades of between 0.002 and 0.05% are present in carbonatite pipes in South Africa.

SUPERGENE

Recent surficial semi-consolidated material derived from areas where uranium is known to occur fills shallow depressions, basins, gulleys and old stream channels. This material also includes calcrete or caliche which, in some areas, may cover the underlying formations to considerable depths. Under suitable conditions, such deposits acted as traps for uranium deposited from ground waters which acted as carrier for uranium solvents.

In South West Africa such mineralized surficial rocks have experienced an arid climate over a considerable period of the Quaternary up to the present time, and have been above the permanent water table which is adjusted to a number of large dry rivers, such as the Swakop and Khan, which drain the plain.

In the Somali Tertiary basin in Central Somalia (northeast Africa), one finds caliche-sandstone-carnotite deposits, of probable economic importance, which derived their uranium from an area of Precambrian crystalline "basement" rocks nearby, in which a modest tonnage of marginal grade U_3O_8 has developed.

In the formation of uranium in calcrete, some type of control, e. g. dams, old stream beds, etc. is required to channel the uranium-bearing solutions over favourable host rocks in order to concentrate the uranium in commercial quantities. Source rocks for the uranium could be granite, tuff or some other intrusive which contains uranium in the ppm range.

REPORT OF WORKING GROUP VI

RELATION OF METALLOGENIC, TECTONIC AND ZONING FACTORS TO THE ORIGIN OF URANIUM DEPOSITS

To the best of the knowledge of the Working Group members, little new information on this aspect of the distribution of uranium concentrations has appeared in western literature since the 1970 Panel, where important statements were presented by J. W. Gabelman and S. H. U. Bowie and recorded in the Working Group report.¹ An attempt to augment the earlier report was therefore not merited and the group had to consider a means of providing some form of compilation which, on the basis of available information, could be of practical value to the uranium exploration geologist and which could also form the basis for continuously up-dating and disseminating information and ideas in this field of study, as they come to hand. Furthermore, considering the broad scope of the subject allotted to this Working Group, it was decided, at least for the first stage of the proposed exercise, to limit its target to an investigation of the relationships between uranium deposits and the main geostructural units of the earth.

The proposal, therefore, is that during the course of the next two years the Working Group shall compile a document in the form of a table, illustrating the geotectonic distribution of uranium, in the hope that this will eventually be of practical assistance at the initial planning stage of uranium reconnaissance programmes. In taking this course, the group recognizes and wishes to emphasize the importance and difficulty of this planning stage at which a commitment is made to a selected area of search. The Working Group proposes to use the classification table presented by Mr. V. Ziegler at this Symposium as the matrix for their task of establishing a more comprehensive metallotectonic classification into which all known deposits or enrichments, and all future discoveries, can be fitted. Once a basic classification has been agreed upon, the table can, of course, be used as a working document by any geologist wishing to augment it from his own experience and scientific standpoint, but the Working Group, by discussion among themselves and outside, will attempt to produce a classification conforming to a consensus of views.

As a first step, the individual members of the Working Group will carefully reconsider the structure of the table and will submit their suggestions for a significantly improved project document to the group chairman. The mineralized units which will have to be incorporated into such a classification will be carefully defined in order to make the table as homogeneous as possible. To facilitate the collection of data from authoritative sources, the group chairman has undertaken the design of a standard descriptive card which will be agreed upon by the group. It is proposed that copies of the card shall be submitted to geologists involved

¹ WORKING GROUP REPORT, Uranium Exploration Geology (Proc. Panel Vienna, 1970), IAEA, Vienna (1970) 363.

in uranium investigations covering the broadest possible spectrum of deposits. The group appreciates that the final usefulness of the classification table will depend largely on the co-operation of colleagues and kindly requests assistance by way of information from individual geologists and other Working Groups as the cards become available. Perhaps the Agency could agree to undertake the distribution and receipt of cards, while a similar role might be accepted by one individual in each country.

The geological exploration criteria prepared by the other Working Groups may be incorporated into the final classification, and the group believes that, provided there is constant revision as knowledge of geotectonic controls increases, the proposed document will be a valuable basis for many considerations regarding the distribution of uranium concentrations.

GENERAL CHAIRMAN AND SESSION CHAIRMEN

General Chairman	R.D. NININGER	United States of America
Session I	S.S. AUGUSTITHIS	Greece
Session II	A.G. DARNLEY	Canada
Session III	R.G. DODSON	Australia
Session IV	F.H. BARTHEL	Federal Republic of Germany
Session V	E. LUKACS	Yugoslavia
Session VI	G.R. UDAS	India
Session VII	A.M. GANGLOFF	France
Session VIII	J.R. DE ANDRADE RAMOS	Brazil
Session IX	R.D. NININGER	United States of America

SECRETARIAT

Scientific Secretary	J. CAMERON	Division of Nuclear Power and Reactors, IAEA
Administrative Secretary	G. SEILER	Division of External Relations, IAEA
Editor	F. MAUTNER MARKHOF	Division of Publications, IAEA
Records Officer	S. EDMINSTER	Division of Languages, IAEA

LIST OF PARTICIPANTS

ALBANIA

Dodona, A.P.	Entreprise Géophysique, Tirana
Langore, L.V.	Entreprise Géophysique, Tirana
Nasi, V.J.	Entreprise Géophysique, Tirana

AUSTRALIA

Cameron, E.	Western Mining Corporation, P.O. Box 71, Kalgoorlie, Western Australia 6430
Dodson, R.G.	Bureau of Mineral Deposits, P.O. Box 378, Canberra City, A.C.T.
McLaurin, A.N.	Geologist, Lisborne
Mosher, D.V.	Pancontinental Mining Ltd., 40 Clarence St., Sydney, N.S.W. 2000
Rowntree, J.C.	Pancontinental Mining Ltd., 40 Clarence St., Sydney, N.S.W. 2000
South, S.A.	Australian Atomic Energy Commission, 45 Beach Road, Coogee, N.S.W. 2034
Wilson, R.G.	C.R.A. Exploration Pty. Ltd., 140 Bourke St., Melbourne, Victoria 3001

AUSTRIA

Holzer, H.F.	Geologische Bundesanstalt, Rasumofskyg. 23, A-1031 Vienna
Müller, G.E.	Österreichische Studiengesellschaft für Atomenergie, Lenaugasse 10, A-1080 Vienna
Petraschek, W.	Montanistische Hochschule, A-8700 Leoben

BELGIUM

Collée, R.	Université de Liège, Place du XX août, Liège

Herbosch, A.

Université libre de Bruxelles,
Avenue F.D. Roosevelt, Brussels 1050

BOLIVIA

Doria-Medina, J.H.

Bolivian Atomic Energy Commission,
Box 4821, La Paz

BRAZIL

Andrade Ramos, J.R. de

Comissão Nacional de Energia Nuclear,
Av. General Severiano 90, Rio de Janeiro, GB

Fraenkel, M.O.

CNEN-DEM Rua Fonte da Saudade 247,
Lagoa, Rio de Janeiro

CANADA

Aitken, R.N.

BP Minerals Ltd.,
1980 Sherbrooke St. West, Montreal 109, Quebec

Darnley, A.G.

Geological Survey of Canada,
Dept. of Energy, Mines and Resources,
601 Booth St., Ottawa, Ontario, K1A 0E8

Delpierre, M.E.

Cominco Ltd.,
200 Granville Square, Vancouver, B.C.

Hart, R.C.

Rio Algom Mines Ltd.,
120 Adelaide St. West, Toronto, Ontario

Howe, A.C.A.

A.C.A. Howe International Ltd.,
826-159 Bay St., Toronto, Ontario M5J 1W5

Joubin, F.R.

Franc. R. Joubin and Assoc.,
170 Bloor St. West, Toronto 5, Ontario

Knipping, H.D.

Gulf Minerals Canada Ltd.,
10 King St. East, Toronto, Ontario M5C 1C3

Little, H.W.

Geological Survey of Canada,
601 Booth St., Ottawa, Ontario, K1A 0E8

Morton, R.D.

University of Alberta, Dept. of Geology,
Edmonton, Alberta T61 6T6

Robertson, D.S.

David S. Robertson and Associates Ltd.,
2000-65 Queen Street West, Toronto, Ontario

Sample, J.J.

American Smelting and Refining Company,
120 Broadway, New York, N.Y. 10005, USA

Sergiades, A.O.

Imperial Oil Ltd.,
111 St. Clair Ave. West, Toronto 7, Ontario

Smith, E.E.N.

Eldorado Nuclear Ltd.,
800 151 Slater St., Ottawa K1P 5H3

- Taylor, D.M. BP Minerals Ltd.,
1980 Sherbrooke St. West, Montreal 109, Quebec
- Williams, R.M. Department of Energy, Mines and Resources,
Mineral Development Sector,
Ottawa K1A 0E4

CHILE

- Mir Dupouy, J. Comisión Chilena de Energía Nuclear,
Av. Salvador 943, Santiago

CSSR

- Chlup, J. Československá komise pro atomovou energii,
Slezska 9, Prague 2, 12029
- Hrubý, J. Polytechna, Technical Co-operation Agency,
P.O. Box 834, Panská 6, Prague 1
- Oravec, J. Faculty of Natural Sciences, Comenius Univ.,
Department of Nuclear Physics,
Smeralova 2 A, Bratislava

DENMARK

- Nielsen, B.L. Geological Survey of Greenland,
Østervoldgade 10, DK-1350 Copenhagen K.
- Sørensen, H. Institut for Petrology,
Østervoldgade 5, DK-1350 Copenhagen K.

EGYPT, ARAB REPUBLIC OF

- El Hazeq, N.M.T. Atomic Energy Establishment,
Geology and Nuclear Raw Materials Department,
Cairo

FINLAND

- Peltoniemi, M.P. Geologinen Tutkimuslaitos, Geological Survey of Finland,
SF-02150 Otaniemi
- Sarikkola, R.K. Outokumpu Co., SF-02101 Tapiola

FRANCE

- Bernazeaud, J. Société nationale des pétroles d'Aquitaine (SNPA),
26. Avenue des Lilas, 64000 Pau
- Berthelin, J.R. Centre de pédologie-biologique du C.N.R.S.
(Centre national de la recherche scientifique),
B.P. N°5, F-54500 Vandœuvre-lès-Nancy

Gangloff, A.M.	C.E.A., B.P. N°4, F-92 Châtillon-sous-Bagneux
Gely, P.C.	Dong-Trieu, 5, rue Blanche, F-7509 Paris
Lehmann, J.-P.	Total, compagnie minière et nucléaire (Total Mining and Nuclear Company), 5, rue Michel-Ange, F-75781 Paris, Cédex 16
Moreau, M.	Commissariat à l'énergie atomique, F-92320 Châtillon
Poty, B.P.	Centre de recherches pétrographiques et géochimiques, C.O. N°1, F-54500 Vandœuvre-lès-Nancy
Soule de Lafont, D.	Rhône Progil, Quai Paul Doumer, F-92 Courbevoie
Ziegler, V.	C.E.A., DP-DRM, B.P. N°74, F-92320 Châtillon

GABON

Pfiffelmann, J.-P.	Compagnie des mines d'uranium de Franceville-Mounana

GERMANY, FEDERAL REPUBLIC OF

Barthel, F.H.	Bundesanstalt für Bodenforschung (Federal Geological Survey), P.O.B. 230153, D-3 Hanover 23
Bisewski, L.G.	C. Deilmann A.G., Postfach 75, D-4442 Bentheim
Dahlkamp, F.J.	Uranerzbergbau, Kölnstr. 367, D-53 Bonn
Fuchs, H.D.	Urangesellschaft, Westend Str.24, D-6 Frankfurt
Gehnes, P.	Bundesanstalt für Bodenforschung (Federal Geological Survey), Stilleweg 2, D-3 Hanover
Hauerstein, G.	Federal Ministry for Research and Technology, Stresemannstr. 2, Bad Godesberg, D-53 Bonn
Hentschel, H.E.	C. Deilmann A.G. Postfach 75, D-4442 Bentheim
Lieser, K.H.	Technische Hochschule, D-6100 Darmstadt
Möller-Arnsberg, O.	Entwicklungsgesellschaft für Technik und Wirtschaft, Grabmannstr.13, D-8 Munich
Nottmeyer, D.K.E.	Uranerzbergbau, Kölnstr.367, D-53 Bonn
Parekh, P.P.	Hahn-Meitner Institute for Nuclear Research, Nuclear Chemistry Division, Glienickestr.100, 1 Berlin 39

Wendt, I. Bundesanstalt für Bodenforschung (Federal Geological Survey),
Stilleweg 2, D-3 Hanover

Ziehr, H. Uranerzbergbau, Kölnstr.367, D-53 Bonn

GREECE

Anastopoulos, J.C. National Institute of Geological and Mining Research (NIGMR),
34 Veranzerou St., Athens 102

Angelikakis, J. National Institute of Geological and Mining Research (NIGMR),
34 Veranzerou St., Athens 102

Antoniadis, P. National Institute of Geological and Mining Research (NIGMR),
34 Veranzerou St., Athens 102

Augustithis, S.S. National Technical University, Department of Mineralogy,
Petrography, Geology,
42 October 28th Street, Athens

Baltatzis, E. University of Athens, Institute of Mineralogy and Petrology,
Panepistimiopolis, Ano Ilisia, Athens 621

Catsoulis, J. Ministry of Industry, Geochemistry Research Division,
11 Hercules Street, Athens

Cottis, T. National Institute of Geological and Mining Research (NIGMR),
34 Veranzerou St., Athens 102

Couvelos, C. National Institute of Geological and Mining Research (NIGMR),
34 Veranzerou St., Athens 102

Davis, Eleftheria Higher Agricultural School of Athens,
75 Iera Odos, Athens 301

Dimou, Eleftheria National Institute of Geological and Mining Research (NIGMR),
34 Veranzerou St., Athens 102

Drugas, J.E. National Institute of Geological and Mining Research (NIGMR),
34 Veranzerou St., Athens 102

Economou, Maria University of Athens, Institute of Mineralogy and Petrology,
Panepistimiopolis, Ano Ilisia, Athens 621

Galanos, D.A. Valaoritou 15, Athens 134

Georgiou, D.N. N.R.C. Democritos, Aghia Paraskevi, Attikis

Gikas, J.E. National Institute of Geological and Mining Research (NIGMR),
34 Veranzerou St., Athens 102

Grossou, Martha National Institute of Geological and Mining Research (NIGMR),
34 Veranzerou St., Athens 102

Hadjiyiannis, G. National Institute of Geological and Mining Research (NIGMR),
34 Veranzerou St., Athens 102

Haralambous, A.D.	National Institute of Geological and Mining Research (NIGMR), 34 Veranzerou St., Athens 102
Hilakos, P.G.	National Institute of Geological and Mining Research (NIGMR), 34 Veranzerou St., Athens 102
Ioannidis, K.	National Institute of Geological and Mining Research (NIGMR), 34 Veranzerou St., Athens 102
Kalogeropoulou, S.E.	University of Athens, Institute of Ore Deposits, Panepistimiopolis, Ano Ilisia, Athens 621
Kanaris, J.	National Institute of Geological and Mining Research (NIGMR), 34 Veranzerou St., Athens 102
Katsavos, A.	National Institute of Geological and Mining Research (NIGMR), 34 Veranzerou St., Athens 102
Kirgotis, T.	N.R.C. Democritos, Aghia Paraskevi, Attikis
Kotopoulou, Eleftheria	N.R.C. Democritos, Aghia Paraskevi, Attikis
Koukoulas, C.	National Institute of Geological and Mining Research (NIGMR), 34 Veranzerou St., Athens 102
Laskou, Magdalen	University of Athens, Institute of Mineralogy and Petrology, Panepistimiopolis, Ano Ilisia, Athens 621
Lutat, U.R.	Bauxites Parnasse Mining Co., 21A Amerikis Str., Athens 135
Mack, E.G.	Bauxites Parnasse Mining Co., 21A Amerikis St., Athens 135
Marakis, G.	University of Athens, Institute of Mineralogy and Petrology, Panepistimiopolis, Ano Ilisia, Athens 621
Marinos, G.	University of Athens, Dept. of Geology, Roosevelt Ave.46, Athens
Marinos, P.	National Technical University, Athens 147
Markoulis, M.T.	National Institute of Geological and Mining Research (NIGMR), 34 Veranzerou St., Athens 102
Mercouriadis, A.N.	National Institute of Geological and Mining Research (NIGMR), 34 Veranzerou St., Athens 102
Mitropoulos, P.	University of Athens, Institute of Mineralogy and Petrology, Panepistimiopolis, Ano Ilisia, Athens 621
Mitsaki, V.	National Institute of Geological and Mining Research (NIGMR), 34 Veranzerou St., Athens 102
Nathanael, E.	National Institute of Geological and Mining Research (NIGMR), 34 Veranzerou St., Athens 102

Nicolaou, M.	Hellenic Chemical Products and Fertilizers Co. Ltd., 20 Amalias Avenue, Athens 118
Papadakis, A.	University of Thessaloniki, Mineralogical Institute, Thessaloniki
Papadopoulos, G.	National Institute of Geological and Mining Research (NIGMR), 34 Veranzerou St., Athens 102
Papageorgakis, J.	National Technical Union, Athens 147
Papageorgiou, Helen N.	Efpolinos Ltd., Lekka 23-25, Athens
Papaioannou, C.G.	National Institute of Geological and Mining Research (NIGMR), 34 Veranzerou St., Athens 102
Papastamatakis, A.	National Institute of Geological and Mining Research (NIGMR), 34 Veranzerou St., Athens 102
Papazeti, Helen	National Institute of Geological and Mining Research (NIGMR), 34 Veranzerou St., Athens 102
Pavlopoulos, A.	Higher Agricultural School of Athens, Institute of Mineralogy and Geology, Iera Odos 75, Athens 301
Pergamalis, F.	N.R.C. Democritos, Aghia Paraskevi, Attikis
Pournis, S.	N.R.C. Democritos, Aghia Paraskevi, Attikis
Profi-Moussouros, Stella	University of Athens, Institute of Mineralogy and Petrology, Panepistimiopolis, Ano Ilisia, Athens 621
Sideris, C.G.	University of Athens, Institute of Mineralogy and Petrology, Panepistimiopolis, Ano Ilisia, Athens 621
Sideris, G.	N.R.C. Democritos, Aghia Paraskevi, Attikis
Spathi, Catherine	Bauxites Parnasse Mining Co., 21A Amerikis St., Athens 135
Stavropodis, J.D.	N.R.C. Democritos, Aghia Paraskevi, Attikis
Tataris, A.	National Institute of Geological and Mining Research (NIGMR), 34 Veranzerou St., Athens 102
Teissie, J.J.	S.M.G., 20 Amalias St., Athens
Tsagalidis, A.C.	Higher Agricultural School of Athens, Iera Odos 75, Athens 301
Tsamantoyridis, P.	National Institute of Geological and Mining Research (NIGMR), 34 Veranzerou St., Athens 102
Vidalaki, Irene	Univeristy of Athens, Mineralogy Laboratory, Athens
Vrahamis, S.C.	N.R.C. Democritos, Aghia Paraskevi, Attikis

Young, D.J.

Bethlehem Steel Corp.,
701 E. Third Street,
Bethlehem, Pa., USA

Zafiriadis, A.

Bauxites Parnasse Mining Co.,
21A Amerikis St., Athens 135

HUNGARY

Barabas, A.

Mecsek Ore Enterprises,
Dandár út 19, 39-ES, 7633 Pécs

INDIA

Udas, G.R.

Atomic Minerals Division,
West Block 7, R.K. Puram, New Delhi-22

IRAN

Zereshki, A.

C.N.U.T., B.P. 2989 Teheran

IRAQ

Al-Ani, K.H.

Nuclear Research Institute, Tuwaitha, Baghdad

Al-Dabbagh, S.M.A.

Nuclear Research Institute, Tuwaitha, Baghdad

ISRAEL

Shiloni, Y.

Geological Survey of Israel,
30 Malchei Israel, Jerusalem

ITALY

Arietti, A.

AGIP, S. Donato Milanese, Milan

D'Agnolo, M.

AGIP, S. Donato Milanese, Milan

Dall'Aglio, M.

CNEN-Laboratorio Geominerario,
CSN- Casaccia,
S. Maria di Galeria, I-0060 Rome

Turchi, A.

AGIP, S. Donato Milanese, Milan

JAPAN

Hirono, S.

Power Reactor and Nuclear Fuel Development Corporation,
Akasaka 1-9-13, Minato-ku, Tokyo 107

Kashiwagi, T.

Mitsubishi Metal Corporation,
No.5-2, Ohte-Machi 1-chome, Chiyoda-ku, Tokyo 100

Katayama, N.

Power Reactor and Nuclear Fuel Development Corporation,
Akasaka 1-9-13, Minato-ku, Tokyo 107

LIBYA

Aburkes, M.G.

M.G. Aburkes Industrial Research Centre,
P.O. Box 3633, Tripoli

MEXICO

Constantino Herrera, S.

Instituto Nacional de Energía Nuclear,
Insurgentes Sur 1180, 4°Piso, Mexico 12 D.F.

Rodríguez Torres, R.

Instituto Nacional de Energía Nuclear,
Insurgentes Sur 1180, 4°Piso, Mexico 12 D.F.

Soto, E.R.

Instituto Nacional de Energía Nuclear,
Insurgentes Sur 1180, 4°Piso, Mexico 12 D.F.

MOROCCO

Barrakad, S.C.

BRPM, 27 Charii Moulay, El Hassan

Bouchta, R.

Bureau de recherches et de participations minières,
B.P. 99, Rabat

Idir, E.H.

Ministère des mines et de la géologie, Rabat

NETHERLANDS

Blaser, R.

Koninklijke/Shell Exploratie en Produktie Laboratorium,
Shell Research V.B.,
Postbus 60, Rijswijk

Brinck, J.

IRC-Brinck International Resources Consultants B.V.,
Postbox 471, Alkmaar

Coelewij, P.A.

Billiton International Metals B.V.,
Louis Couperusplein 19, The Hague

PAKISTAN

Moghal, M.Y.

Atomic Energy Mineral Centre,
P.O. Box 658, Ferozepur Road, Lahore

POLAND

Bielikowski, K.

L'Autorité d'énergie atomique de Pologne,
Pałac Kultury i Nauki, Warsaw 00-110

ROMANIA

Burtic, T.	State Committee for Nuclear Energy, Bucharest
Corniciuc, I.	Ministry of Mining, Dionitie Lupo 68, Bucharest

SOUTH AFRICA

Backström, J.W. von	Atomic Energy Board, Private Bag X256, Pretoria
Harris, T.J.	United States Steel Int. N.Y., Inc., P.O. Box 31346, Braamfontein, Johannesburg
Hearn, M.G.	Chamber of Mines, Main Street, Johannesburg
Whiteside, H.C.	Consulting Geologist, 32 Sandown Village, Maude St., Sandton, Transvaal 2001

SPAIN

Fernández Polo, J.A.	Junta de Energía Nuclear, Avda Complutense 22, Madrid
Martín-Delgado Tamayo, J.	Junta de Energía Nuclear, Ciudad Universitaria, Madrid

SWEDEN

Lundberg, B.R.	Geological Survey of Sweden, S-10405 Stockholm 50

SWITZERLAND

Gryksa, H.P.	Nuclear Assurance Corp., Mainaustr.8, CH-800 Zurich

TURKEY

Çetintürk, İ.	Commission de l'énergie atomique de Turquie, Institut d'études et de recherches minières, Ankara
Kaplan, J.	Commission de l'énergie atomique de Turquie, Institut d'études et de recherches minières, Ankara
Uz, S.	Commission de l'énergie atomique de Turquie, Institut d'études et de recherches minières, Ankara

UNITED KINGDOM

Bowie, S.H.U.	Institute of Geological Sciences, 64/78 Gray's Inn Road, London WC1X 8NG

Chater, A.M.	British Petroleum Co. Ltd., Moor Lane, London EC2Y 9B4
Doran, M.B.	C.E.G.B., Berkeley Nuclear Labs., Berkeley, Glos.
Marsh, R.D.	British Nuclear Fuels Ltd., Risley, Warrington, Cheshire WA3 6AT
Millman, A.P.	University College Cardiff, Mineral Exploitation Department, Newport Road, Cardiff
Ostle, D.	Institute of Geological Sciences, 64/78 Gray's Inn Road, London WC1X 8NG
Wilson, R.A.M.	Charter Consolidated Ltd., 7 Rolls Building, Fetter Lane, London

UNITED STATES OF AMERICA

Adams, S.S.	The Anaconda Co., Uranium Division, 1849 West North Temple, Salt Lake City, Utah
Adler, H.H.	US Atomic Energy Commission, Washington, D.C. 20545
Anzalone, S.	American Smelting and Refining Co., 504-535 Thurlow St., Vancouver, B.C., Canada
Armstrong, F.C.	US Geological Survey, 656 US Court House, W.920 Riverside Av., Spokane, Wash. 99203
Ary, T.S.	Union Carbide Exploration, 270 Park Ave., New York, N.Y. 10017
Bourret, W.	Utah International Inc., 550 California St., San Francisco, Calif. 94104
Breger, I.A.	US Geological Survey, Washington, D.C. 20244
Collins, C.J.	Rocky Mountain Energy Co., 508 North Fenway St., Casper, Wyo. 82601
Dahl, A.R.	Exxon Co., USA, Minerals Department, P.O. Box 120, Denver, Colo. 80201
Danchin, P.D.	Union Carbide Exploration, 270 Park Ave., New York, N.Y. 10017
De Voto, R.H.	Colorado School of Mines, Golden, Colo. 80401
Donald, N.H., Jr.	St. Joe Minerals Corp., 250 Park Ave., New York, N.Y. 10580

Ellsworth, P.C.	Kerr-McGee Corp., Kerr-McGee Center, Oklahoma City, Okla. 73104
Enyart, G.	Michael P. Grace, P.O. Box 100, Grants, N. Mex. 87020
Faulkner, R.L.	Consultant, 8624 Beech Tree Road, Bethesda, Md.
Finch, W.I.	US Geological Survey, Federal Center Bldg.25, Lakewood, Colo. 80225
Fowler, F.E., Jr.	Mount Sopris Instruments Co., P.O. Box 449, Delta, Colo.
Frost, J.E.	Esso Eastern Inc., P.O. Box 1415, Houston, Tex.
Fruchey, R.A.	Amax Uranium Corp., P.O. Box 311, Riverton, Wyo. 82501
Granger, H.C.	US Geological Survey, Federal Center, Lakewood, Colo. 80225
Greider, R.	Chevron Oil Co., Minerals Staff, 225 Bush St., San Francisco, Calif. 94104
Harshman, E.N.	US Geological Survey, Denver Federal Center, Denver, Colo. 80226
Heiny, L.W.	Continental Oil Co., 1755 Glenarm Pl., Denver, Colo. 80202
Hermann, J.A.	Kerr-McGee Corp., Kerr-McGee Center, Oklahoma City, Okla. 73104
Laverty, R.A.	Westinghouse Electric Corp., 55 W. Fifth Ave., Denver, Colo. 80204
Marrall, G.E.	Minerals Exploration Co., P.O. Box 2674, Casper, Wyo. 82601
Mathez, Muriel	Exxon Corp., 1251 Ave. of Americas, New York, N.Y.
Maxwell, R.D.	Continental Oil Co., 220 Young St., Kenedy, Tex. 78119
Meyertons, C.T.	Esso Eastern Inc., P.O. Box 1415, Houston, Tex. 77001
Nininger, R.D.	US Atomic Energy Commission, Washington, D.C. 20545
Rackley, R.I.	Amax Uranium Corp., 207 Goodstein Bldg., Casper, Wyo. 82601
Rapaport, I.	4 Conners Exploration Co., P.O. Box 116, Grants, N. Mex.

Riddell, P.A.	Getty Oil Development Co. Ltd., 275 Alfred St., North Sydney, N.S.W. 2060, Australia
Tremaïne, J.W.	United States Steel Corp., 600 Grant St., Pittsburgh, Pa. 15230
Wyllie, R.	World Mining, 123A Chaussée de Charleroi, Brussels, Belgium

URUGUAY

Bossi, J.	Faculty of Chemistry, Gral Flores Avenue 2124, Montevideo

VENEZUELA

Pasquali, J.	Ministerio de Minas e Hidrocarburos Torre Norte, Piso 19, Centro Simón Bolívar, Caracas

YUGOSLAVIA

Florjančič, A.P.	Geološki Zavod (Geological Survey), Dimičeve 16, 64000 Ljubljana
Lukacs, E.	Geološki Zavod (Geological Survey), Dimičeve 16, 64000 Ljubljana
Markov, C.	Institute for Geological and Mining Exploration and Investigation of Nuclear and other Mineral Raw Materials, Rovinjska 12, Belgrade
Radusinović, D.	Institute for Geological and Mining Exploration and Investigation of Nuclear and other Mineral Raw Materials, Rovinjska 12, Belgrade
Ristić, M.	Institute of Geological and Mining Exploration and Investigation of Nuclear and other Mineral Raw Materials, Rovinjska 12, Belgrade

FORATOM

Mitterpergher, M.	C.N.E.N., Viale Regina Margherita 125, Rome, Italy

IAEA

Armour-Brown, A.	Uranium Exploration Project, N.R.C. Democritos, Aghia Paraskevi, Attikis, Greece
Durandau, A.	IAEA Expert, Casier ONU, Rabat-Chellah, Morocco
King, J.W.	UNDP, PK 407, Ankara, Turkey

Olsen, H.	Uranium Exploration Project, N.R.C. Democritos, Aghia Paraskevi, Attikis, Greece
Simov, S.D.	International Atomic Energy Agency, P.O. Box 590, A-1011 Vienna, Austria
Smith, A.Y.	Uranium Exploration Project, N.R.C. Democritos, Aghia Paraskevi, Attikis, Greece

WORKING GROUPS

Working Group I: CHEMICAL AND PHYSICAL MECHANISMS IN THE FORMATION OF URANIUM MINERALIZATION, GEOCHRONOLOGY, ISOTOPE GEOLOGY AND MINERALOGY

Chairman: S. H. U. Bowie (United Kingdom)

Members: S. S. Adams (United States of America)
J. R. Berthelin (France)
M. Dall'Aglio (Italy)
H. C. Granger (United States of America)
I. Wendt (Federal Republic of Germany)
J. Pasquali (Venezuela)

Working Group II: SEDIMENTARY BASINS AND SANDSTONE-TYPE DEPOSITS

Chairman: H. H. Adler (United States of America)

Members: F. Barthel (Federal Republic of Germany)
A. M. Gangloff (France)
E. N. Harshman (United States of America)
L. W. Heiny (United States of America)
J. W. King (IAEA)
R. I. Rackley (United States of America)

Working Group III: URANIUM IN QUARTZ-PEBBLE CONGLOMERATES

Chairman: D. S. Robertson (Canada)

Members: J. R. de Andrade Ramos (Brazil)
W. Bourret (United States of America)
H. W. Little (Canada)
H. C. Whiteside (South Africa)

Working Group IV: VEIN- AND SIMILAR-TYPE DEPOSITS

Chairman: E. E. N. Smith (Canada)

Members: R. G. Dodson (Australia)
H. D. Knipping (Canada)
B. R. Lundberg (Sweden)
M. Moreau (France)
B. L. Nielsen (Denmark)
B. P. Poty (France)
J. C. Rowntree (Australia)

Working Group V: OTHER URANIUM DEPOSITS

Chairman: J. W. von Backström (South Africa)

Members: F. C. Armstrong (United States of America)
T. S. Ary (United States of America)
M. O. Fraenkel (Brazil)
F. R. Joubin (Canada)
R. A. Lavery (United States of America)
H. W. Little (Canada)
M. Mittempergher (Italy)
H. Sørensen (Denmark)

Working Group VI: RELATION OF METALLOGENIC, TECTONIC AND ZONING FACTORS TO THE ORIGIN OF URANIUM DEPOSITS

Chairman: V. Ziegler (France)

Members: J. W. Brinck (Netherlands)
D. Ostle (United Kingdom)
J. A. Fernández Polo (Spain)
S. A. South (Australia)

AUTHOR INDEX

Numbers underlined refer to the first page of a paper.

Other page numbers refer to discussion comments.

- Abdel Monem, A.A.: 467
 Adams, S.S.: 70, 219, 252, 312, 356, 401, 417, 478, 582, 697
 Adler, H.H.: 47, 86, 141, 168, 252, 272, 288, 328, 339, 478, 567, 592, 697, 702
 Andrade Ramos, J.R., de: 511, 637, 657
 Anzalone, S.: 182, 528
 Armstrong, F.C.: 218, 402, 625, 635, 709
 Ary, T.S.: 168, 424
 Augustithis, S.S.: 61, 70, 135, 182
 Backström, J.W., von: 135, 419, 423, 605, 621
 Barthel, F.H.: 277, 288
 Basham, I.R.: 405
 Bernazeaud, J.: 217
 Berthelin, J.R.: 73, 86, 137, 253
 Bhurat, M.C.: 89
 Blaser, R.: 123, 136, 167, 329, 491
 Bohse, H.: 49
 Bossi, J.: 583, 592
 Bourret, W.: 340, 635, 709
 Bowie, S.H.U.: 183, 217, 253, 273, 297, 356, 402, 417, 452, 623, 697, 708
 Breger, I.A.: 99, 123, 136, 217, 252, 329, 705
 Brinck, J.W.: 21
 Burtic, T.: 343
 Cameron, J.: 48, 328, 400, 621
 Çetintürk, İ.: 453
 Constantino Herrera, S.: 417, 465, 491
 Corniciuc, I.: 343, 355
 Cuney, M.: 569
 Curtis, H.S.: 219
 Dahl, A.R.: 201, 217
 Dahlkamp, F.J.: 568
 Dall'Aglio, M.: 33, 47, 87
 Darnley, A.G.: 70, 88, 218, 272, 327
 De Voto, R.H.: 183, 216, 355, 380, 424, 548, 568, 710
 Dodson, R.G.: 18, 87, 423, 510, 551, 567
 Dommergues, Y.: 73
 Durandau, A.: 312, 328, 424, 704
 Dwivedy, K.K.: 89
 El Hazeq, N.M.T.: 467, 477
 Ellsworth, P.C.: 217, 452
 El Shazly, E.M.: 467
 Erkan, E.: 291
 Fernández Polo, J.A.: 135, 401, 477, 479, 601, 704
 Finch, W.I.: 702
 Florjančič, A.P.: 313, 356
 Fraenkel, M.O.: 637
 Frost, J.E.: 48, 621, 697, 703
 Fuchs, H.D.: 98, 182, 620
 Gangloff, A.M.: 402, 705
 Gragnani, R.: 33
 Granger, H.C.: 185
 Hafen, P.L.: 219
 Hagmaier, J.L.: 201
 Harshman, E.N.: 169, 182, 401
 Hart, R.C.: 710
 Hearn, W.G.: 709
 Herbosch, A.: 136, 359, 38, 478
 Hirono, S.: 437
 Hrubý, J.: 357
 Jayaram, K.M.V.: 89
 Joubin, F.R.: 400, 510, 529, 635, 704
 Kaplan, H.: 453, 465

- Katayama, N.: 437, 452, 478
 Khawasik, S.M.: 467
 King, J.W.: 329, 401
 Knipping, H.D.: 87, 529, 531,
 548, 581, 721
 Kubo, S.: 437
 Kulshrestha, S.G.: 89
 Kunzendorf, H.: 49
 Lavery, R.A.: 719
 Leroy, J.: 569
 Little, H.W.: 271, 528, 548
 Locardi, E.: 33
 Løvborg, L.: 49
 Lukacs, E.: 313, 327
 Magne, R.: 73
 Mahadevan, T.M.: 425
 Markov, C.: 331
 Martín Calvo, M.: 125
 Martín-Delgado Tamayo, J.: 479,
 491
 Meyertons, C.T.: 340, 510, 711
 Mittempergher, M.: 289, 299,
 312, 329
 Moghal, M.Y.: 383, 401, 436,
 657
 Moreau, M.: 380, 568, 581,
 658, 720
 Morsi, M.A.: 467
 Morton, R.D.: 182, 255, 271, 527
 Mostafa, M.E.M.: 467
 Mposkos, E.: 61
 Needham, R.S.: 551
 Neuwirth, K.: 291
 Nininger, R.D.: 3, 18, 704, 710,
 719
 Nitu, G.: 679
 Ostle, D.: 719
 Page, R.W.: 551
 Pasquali, J.: 48, 70, 123, 136,
 217, 273, 424, 491
 Petrascheck, W.E.: 291, 298,
 328, 465, 478
 Poty, B.P.: 288, 528, 569, 581,
 592
 Rackley, R.I.: 401, 418
 Radusinović, D.: 593, 601
 Rice, C.M.: 405
 Ristić, M.: 331, 339
 Robertson, D.S.: 87, 452, 495,
 512, 635, 708
 Rodríguez Torres, R.: 252
 Rose-Hansen, J.: 49
 Rowntree, J.C.: 271, 719
 Sergiades, A.O.: 528
 Smart, P.G.: 551
 Smith, E.E.N.: 515, 528, 719
 Sørensen, H.: 49, 658
 South, S.A.: 18
 Steenfelt, A.: 49
 Udas, G.R.: 18, 98, 137, 400,
 418, 425, 436, 510, 703
 Uz, S.: 453
 Vgenopoulos, A.: 61
 Warren, C.G.: 185
 Watchman, A.L.: 551
 Wendt, I.: 218
 Whiteside, H.C.: 423, 658, 711
 Wilkes, P.G.: 551
 Wilson, R.G.: 272
 Wyllie, R.: 402
 Zayed, Z.M.: 467
 Zereshki, A.: 88, 328
 Ziegler, V.: 661

TRANSLITERATION INDEX

Буртик, Т.
Корничук, И.

Burtic, T.
Corniciuc, I.

**CONVERSION TABLE:
FACTORS FOR CONVERTING UNITS TO SI SYSTEM EQUIVALENTS***

SI base units are the metre (m), kilogram (kg), second (s), ampere (A), kelvin (K), candela (cd) and mole (mol).
[For further information, see International Standards ISO 1000 (1973), and ISO 31/0 (1974) and its several parts]

<i>Multiply</i>	<i>by</i>	<i>to obtain</i>
Mass		
pound mass (avoirdupois)	1 lbm = 4.536×10^{-1}	kg
ounce mass (avoirdupois)	1 ozm = 2.835×10^1	g
ton (long) (= 2240 lbm)	1 ton = 1.016×10^3	kg
ton (short) (= 2000 lbm)	1 short ton = 9.072×10^2	kg
tonne (= metric ton)	1 t = 1.00×10^3	kg
Length		
statute mile	1 mile = 1.609×10^0	km
yard	1 yd = 9.144×10^{-1}	m
foot	1 ft = 3.048×10^{-1}	m
inch	1 in = 2.54×10^{-2}	m
mil (= 10^{-3} in)	1 mil = 2.54×10^{-2}	mm
Area		
hectare	1 ha = 1.00×10^4	m ²
(statute mile) ²	1 mile ² = 2.590×10^0	km ²
acre	1 acre = 4.047×10^3	m ²
yard ²	1 yd ² = 8.361×10^{-1}	m ²
foot ²	1 ft ² = 9.290×10^{-2}	m ²
inch ²	1 in ² = 6.452×10^2	mm ²
Volume		
yard ³	1 yd ³ = 7.646×10^{-1}	m ³
foot ³	1 ft ³ = 2.832×10^{-2}	m ³
inch ³	1 in ³ = 1.639×10^{-4}	mm ³
gallon (Brit. or Imp.)	1 gal (Brit) = 4.546×10^{-3}	m ³
gallon (US liquid)	1 gal (US) = 3.785×10^{-3}	m ³
litre	1 l = 1.00×10^{-3}	m ³
Force		
dyne	1 dyn = 1.00×10^{-5}	N
kilogram force	1 kgf = 9.807×10^0	N
poundal	1 pdl = 1.383×10^{-1}	N
pound force (avoirdupois)	1 lbf = 4.448×10^0	N
ounce force (avoirdupois)	1 ozf = 2.780×10^{-1}	N
Power		
British thermal unit/second	1 Btu/s = 1.054×10^3	W
calorie/second	1 cal/s = 4.184×10^0	W
foot-pound force/second	1 ft·lbf/s = 1.356×10^0	W
horsepower (electric)	1 hp = 7.46×10^2	W
horsepower (metric) (= ps)	1 ps = 7.355×10^2	W
horsepower (550 ft·lbf/s)	1 hp = 7.457×10^2	W

* Factors are given exactly or to a maximum of 4 significant figures

<i>Multiply</i>	<i>by</i>	<i>to obtain</i>
<i>Density</i>		
pound mass/inch ³	1 lbm/in ³ = 2.768 × 10 ⁴	kg/m ³
pound mass/foot ³	1 lbm/ft ³ = 1.602 × 10 ¹	kg/m ³
<i>Energy</i>		
British thermal unit	1 Btu = 1.054 × 10 ³	J
calorie	1 cal = 4.184 × 10 ⁰	J
electron-volt	1 eV ≈ 1.602 × 10 ⁻¹⁹	J
erg	1 erg = 1.00 × 10 ⁻⁷	J
foot-pound force	1 ft·lbf = 1.356 × 10 ⁰	J
kilowatt-hour	1 kW·h = 3.60 × 10 ⁶	J
<i>Pressure</i>		
newtons/metre ²	1 N/m ² = 1.00	Pa
atmosphere ^a	1 atm = 1.013 × 10 ⁵	Pa
bar	1 bar = 1.00 × 10 ⁵	Pa
centimetres of mercury (0°C)	1 cmHg = 1.333 × 10 ³	Pa
dyne/centimetre ²	1 dyn/cm ² = 1.00 × 10 ⁻¹	Pa
feet of water (4°C)	1 ftH ₂ O = 2.989 × 10 ³	Pa
inches of mercury (0°C)	1 inHg = 3.386 × 10 ³	Pa
inches of water (4°C)	1 inH ₂ O = 2.491 × 10 ²	Pa
kilogram force/centimetre ²	1 kgf/cm ² = 9.807 × 10 ⁴	Pa
pound force/foot ²	1 lbf/ft ² = 4.788 × 10 ¹	Pa
pound force/inch ² (= psi) ^b	1 lbf/in ² = 6.895 × 10 ³	Pa
torr (0°C) (= mmHg)	1 torr = 1.333 × 10 ²	Pa
<i>Velocity, acceleration</i>		
inch/second	1 in/s = 2.54 × 10 ¹	mm/s
foot/second (= fps)	1 ft/s = 3.048 × 10 ⁻¹	m/s
foot/minute	1 ft/min = 5.08 × 10 ⁻³	m/s
mile/hour (= mph)	1 mile/h = $\begin{cases} 4.470 \times 10^{-1} \\ 1.609 \times 10^0 \end{cases}$	$\begin{cases} \text{m/s} \\ \text{km/h} \end{cases}$
knot	1 knot = 1.852 × 10 ⁰	km/h
free fall, standard (= g)	= 9.807 × 10 ⁰	m/s ²
foot/second ²	1 ft/s ² = 3.048 × 10 ⁻¹	m/s ²
<i>Temperature, thermal conductivity, energy/area·time</i>		
Fahrenheit, degrees — 32	°F — 32	°C
Rankine	°R	K
1 Btu·in/ft ² ·s·°F	$\begin{matrix} \frac{5}{9} \\ = 5.189 \times 10^2 \end{matrix}$	W/m·K
1 Btu/ft·s·°F	= 6.226 × 10 ¹	W/m·K
1 cal/cm·s·°C	= 4.184 × 10 ²	W/m·K
1 Btu/ft ² ·s	= 1.135 × 10 ⁴	W/m ²
1 cal/cm ² ·min	= 6.973 × 10 ²	W/m ²
<i>Miscellaneous</i>		
foot ³ /second	1 ft ³ /s = 2.832 × 10 ⁻²	m ³ /s
foot ³ /minute	1 ft ³ /min = 4.719 × 10 ⁻⁴	m ³ /s
rad	rad = 1.00 × 10 ⁻²	J/kg
roentgen	R = 2.580 × 10 ⁻⁴	C/kg
curie	Ci = 3.70 × 10 ¹⁰	disintegration/s

^a atm abs: atmospheres absolute;
atm (g): atmospheres gauge.

^b lbf/in² (g) (= psig): gauge pressure;
lbf/in² abs (= psia): absolute pressure.

HOW TO ORDER IAEA PUBLICATIONS



Exclusive sales agents for IAEA publications, to whom all orders and inquiries should be addressed, have been appointed in the following countries:

UNITED KINGDOM	Her Majesty's Stationery Office, P.O. Box 569, London SE 1 9NH
UNITED STATES OF AMERICA	UNIPUB, Inc., P.O. Box 433, Murray Hill Station, New York, N.Y. 10016



In the following countries IAEA publications may be purchased from the sales agents or booksellers listed or through your major local booksellers. Payment can be made in local currency or with UNESCO coupons.

ARGENTINA	Comisión Nacional de Energía Atómica, Avenida del Libertador 8250, Buenos Aires
AUSTRALIA	Hunter Publications, 58 A Gipps Street, Collingwood, Victoria 3066
BELGIUM	Office International de Librairie, 30, avenue Marnix, B-1050 Brussels
CANADA	Information Canada, 171 Slater Street, Ottawa, Ont. K 1 A 0S 9
C.S.S.R.	S.N.T.L., Spálená 51, CS-11000 Prague
FRANCE	Alfa, Publishers, Hurbanovo námestie 6, CS-80000 Bratislava
	Office International de Documentation et Librairie, 48, rue Gay-Lussac, F-75005 Paris
HUNGARY	Kultura, Hungarian Trading Company for Books and Newspapers, P.O. Box 149, H-1011 Budapest 62
INDIA	Oxford Book and Stationery Comp., 17, Park Street, Calcutta 16
ISRAEL	Heiliger and Co., 3, Nathan Strauss Str., Jerusalem
ITALY	Libreria Scientifica, Dott. de Biasio Lucio "aeiou", Via Meravigli 16, I-20123 Milan
JAPAN	Maruzen Company, Ltd., P.O.Box 5050, 100-31 Tokyo International
NETHERLANDS	Marinus Nijhoff N.V., Lange Voorhout 9-11, P.O. Box 269, The Hague
PAKISTAN	Mirza Book Agency, 65, The Mall, P.O.Box 729, Lahore-3
POLAND	Ars Polona, Centrala Handlu Zagranicznego, Krakowskie Przedmiescie 7, Warsaw
ROMANIA	Cartimex, 3-5 13 Decembrie Street, P.O.Box 134-135, Bucarest
SOUTH AFRICA	Van Schaik's Bookstore, P.O.Box 724, Pretoria
	Universitas Books (Pty) Ltd., P.O.Box 1557, Pretoria
SPAIN	Nautrónica, S.A., Pérez Ayuso 16, Madrid-2
SWEDEN	C.E. Fritzes Kungl. Hovbokhandel, Fredsgatan 2, S-10307 Stockholm
U.S.S.R.	Mezhdunarodnaya Kniga, Smolenskaya-Sennaya 32-34, Moscow G-200
YUGOSLAVIA	Jugoslovenska Knjiga, Terazije 27, YU-11000 Belgrade



Orders from countries where sales agents have not yet been appointed and requests for information should be addressed directly to:



Publishing Section,
International Atomic Energy Agency,
Kärntner Ring 11, P.O.Box 590, A-1011 Vienna, Austria

INTERNATIONAL
ATOMIC ENERGY AGENCY
VIENNA, 1974

PRICE: US \$38.00
Austrian Schillings 710,-
(£16.40; F.Fr. 180; DM 100,-)

SUBJECT GROUP: IV
Chemistry, Geology and Raw Materials/
Geology