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**GEOLOGY**
**Paper: Sedimentology and Petroleum Geology**
**Module: Maturation of Kerogen: Biogenic and Thermal Effects**

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**GEOLOGY**

**Paper: Sedimentology and Petroleum Geology**

**Module: Maturation of Kerogen: Biogenic and Thermal Effects**

## 1. Learning outcomes

After studying this module you shall be able to:

- understand types of organic matter, their transformation to kerogen and classification of kerogen on the basis of H:C ratio
- Learn about different stages of transformation of organic matter, causative agents (biogenic and thermal) behind transformation, relative role/s of agents at different transformation stages.
- Know about different parameters and indices those are in use to assess maturity of sediment and criteria followed to categorize any sediment body as an effective source rock.

## 2. Introduction

Potential hydrocarbon (oil and gas) source beds are formed dominantly by thermal maturation of organic matters present within sediment under the combined effects of thermal kinetic energy and geologic time as sediments undergo burial. In diagenesis, biogenic decay and abiogenic reactions suffered by organic matters release methane, CO<sub>2</sub>, water and leave a complex hydrocarbon compound within sediments that is referred to as 'Kerogen', made up of carbon, hydrogen and oxygen with minor amounts of nitrogen and sulfur. It is differentiated from 'Bitumen' by its insolubility in normal organic solvents like carbon disulfide. The transformation of organic matter to kerogen takes place right from shallow burial (with near surface temperature) up to a depth of 1km and ~50°C temperature. In a steadily subsiding sedimentary basin, the transformation (maturation) of organic matter to kerogen and its subsequent maturation to oil and gas happens under three different stages of burial viz. diagenesis, catagenesis and metagenesis (Tissot, 1977).

*Maturation* is a combination of complex processes through which complex biological molecules, created by living organisms, are first converted into simple bio-molecule and finally cooked to give petroleum. In the early stages of alteration, termed as diagenesis, an intermediate form of organic matter, called kerogen, is formed. Dehydration (release of  $H_2O$ ) and Decarboxylation (release of  $CO_2$ ) are the two main reactions at this stage, dominantly under the influence of bacterial action. The Eh - PH condition at the sediment-water interface principally guides bacterial action on organic matters. While free sulfur is released from sulfate ion with removal of oxygen under the action of *Desulfovibrio* bacteria in reduced condition below water table, oxydation of free sulfur by the bacteria *Thiobacillus* in an oxygenated condition result in formation of sulfate ions.

In general, bacterial action at first oxidise organic matters and release water, carbon dioxide, nitrates and phosphates. Reduction reactions follow, which turn nitrates into nitrites and sulfates into hydrogen sulfide and ammonia. Organic matters are diverse and complex in constitution and made up of proteins, carbohydrates, lipids and lignin with proteins being most unstable and lignin most stable. Microbial enzymes decompose these compounds and form biomonomers e.g proteins transform to amino acids, carbohydrates to sugar and lipids to glycerol and fatty acid. Cellulose gets converted to methane and  $CO_2$ . In fact, methane ( $CH_4$ ) constitutes a major product of bacterial decay. All these changes happen in top few meters of the sediment column and further with increase in depth temperature increases and chemical reactions start dominating over bacterial action.

Net outcome of all diagenetic reactions is the reduction of oxygen content within organic matters keeping carbon: hydrogen ratio intact. As burial continues in deep subsurface at *catagenetic* stage, fluid phase is released from kerogen (oil and then gas), which further decrease the H: C

ratio in the kerogen. A fluid phase high in hydrogen is released and a residue rich in carbon results. In still higher temperature condition at the *metagenetic* stage, almost near metamorphism, the last hydrocarbon i.e methane is released leaving behind extremely carbon-rich graphite residue. Although this represents the general pathway through which organic matter and kerogen matures, examples are available where thermally immature Cambrian source beds (about 500 million years old) are exposed in outcrop in southern Sweden, and gas-generating, over-mature Tertiary source beds belonging to Miocene shales encountered along the west flank of the Red Sea in Ethiopia. While in the first case the time elapsed for the Cambrian shales provide the required compensation for the thermal effect, the high thermal gradient in the southern Red Sea, similar to the high gradients found today, is identified as the causative reason in the second case.

The hypotheses about thermal maturation histories of potential source beds must be used carefully. In geochemical modeling of hydrocarbon source rock, geologists widen their range of input data and use data from the fields of coal petrography, such as vitrinite reflection data, or coloration of spores or chitinous microfossils, if they are available. Detailed chemical analyses of oils and source beds for specific compounds also add to our understanding of the thermal histories of rocks and basins. A reliable interpretation of source bed maturation is possible only after all data are collected and processed.

### 3. Organic matters and Kerogen types

Depending on terrestrial (plant) or aquatic (plant and animal) origin, organic matters are broadly classified as humic and sapropelic in character. Humic organic matters are largely carbohydrate-lignin in composition with protein in subordinate amount, relatively rich in carbon and nitrogen and



poor in hydrogen. Thermal alteration of humic organic matter results in humic acids, rich in oxygen and poor in hydrogen. These organic matters are gas-prone and poor in liquid, volatile product yield. In contrast, sapropelic organic matters are of aquatic (marine and lacustrine) derivation, made up of structureless vegetable slime, polymerized lipid and protein (Fig. 1). Spores, pollens, cuticles, alginites etc. with high hydrogen content constitute this organic matter and thermal alternation release liquid, volatile products e.g oil from these organic matters. Differentiation between the two types of organic matters can be done taking into consideration their H:C contents: H:C content in humic organic matters is less than 0.8, in mixed humic and sapropelic organic matter the ratio is between 0.8 and 1.0 and in sapropelic organic matters it is above 1.0. At diagenetic stage organic matters transform under bacterial attack into a thermally reactive organic complex i.e kerogen with release of methane, CO<sub>2</sub> and H<sub>2</sub>O.

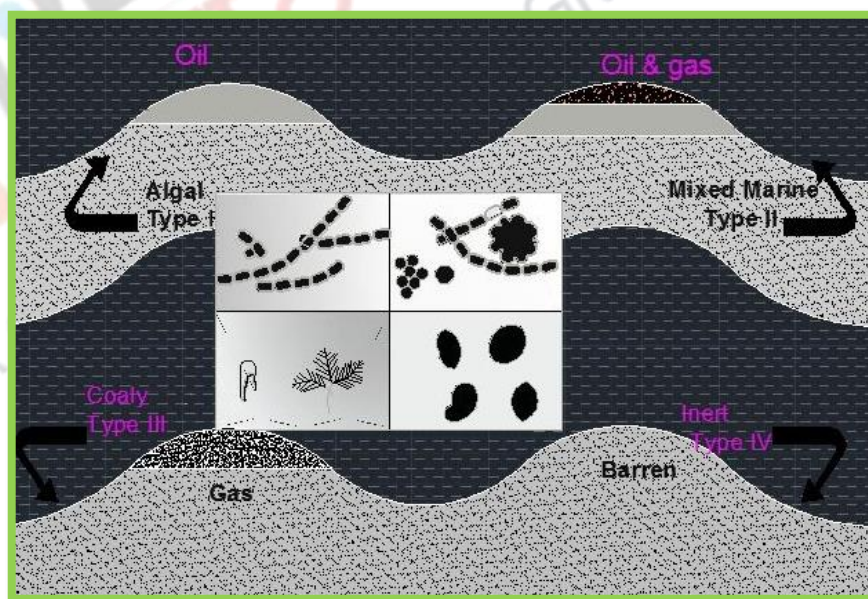


Fig. 1. Different types of organic matters; Algal (Type I), Spores, pollens mixed marine (Type II), terrestrial woody (Type III) and Inert, barren (Type IV).

Microscopically, kerogen can be seen as yellow-orange to brown-black particles or amorphous material. Since kerogens originate from different kinds of living organisms with different kinds and proportions of biological molecules, their chemical compositions vary widely and result in formation of hydrocarbons of different types and amounts. Geologists have found it convenient to group kerogens into four fundamentally different classes ranging between Type I and Type IV.

Type I kerogen is derived from sapropelic organic matters, principally constituted of high-grade algal remains, lacustrine, with high H:C ratio i.e 1.6 - 1.8 and on maturation yields crude oil. It represents the most petroleum generating kerogen type. Type II kerogen consists mostly of amorphous material, both continental and aquatic in origin and derived from the bacterial and mechanical breakdown of a mixture of marine, one-celled plants and animals. Algal tissues, spores, pollens also contribute. This kerogen type has H:C ratio about 1.4 and oil-prone but yields more natural gas than Type I. Type III kerogen (H:C ratio 1.0 or less) is derived from humic organic matters of terrestrial, woody origin from higher land plants and sometimes known as coaly kerogen, equivalent to vitrinite macerals in coal. The humic material in Type III kerogen has a low capacity to form oil and yields mostly natural gas. Type IV kerogen (H: C ratio 0.4 or less) consists mostly of inert particles that have been highly oxidized, recycled and altered before burial, like charcoal. It is the rarest kerogen type and has practically no ability to generate either oil or gas (Fig. 2).

The chemistry of crude oil can also be linked to kerogen type and original organic matter. Usually land-derived, non-marine organic matter deposited near continental drainage areas (Type III coaly kerogen) will form mostly gas, but any oil formed will be low sulfur, paraffinic to paraffinic-naphthenic crude oils. Marine organic matter, particularly protein-rich types derived from marine animals (Type I or Type II mixed marine kerogen) tends to yield high sulfur aromatic-intermediate crude.

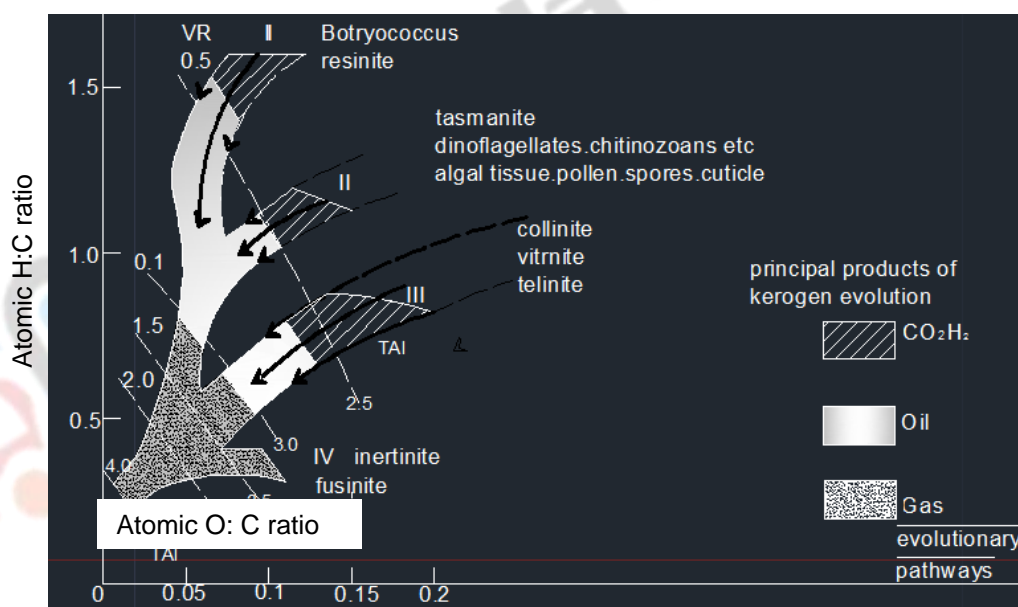


Fig. 2 Evolution pathway of different kerogen types with increase in temperature. Dashed while lines represent maturation indices at different stages of transformation. values on the left of dashed lines represent Vitrinite reflectance (VR) and to the right Thermal Alteration Index (TAI) (modified after North, 1995).

#### 4. Agents of transformation:



Biological transformation of organic matter to kerogen and chemical transformation of thermally reactive kerogen give rise to the generation of petroleum. Bacterial processes remain mostly effective in initial break down of organic matters, while cooking of transformed organic matter i.e kerogen is guided by chemical processes. A combination of negative redox potential and alkaline Ph condition i.e between 7.5 and 8.4 favours liberation of petroleum. In isolated bottom condition where generation of  $H_2S$  turns bottom condition acidic with Ph lower than 7, hydrocarbons are retained in kerogen and not liberated. Both temperature and pressure increases as organic matters get buried. Transformation of organic matters is independent of pressure, in fact high pressure may counter rate of decomposition. In contrast, temperature plays pivotal role in organic matter transformation; higher molecular weight organic matters transform into simpler compounds by thermal cracking. Generation of petroleum is a rate-controlled, thermocatalytic process. In addition to temperature, time spent by organic matter at different temperatures also plays a key role. Since thermal decomposition of organic matter is a temperature-dependant chemical reaction, the rate of transformation reaction is guided by Arrhenius equation i.e  $k = Ae^{-E_a/RT}$ ; where  $k$  is rate constant,  $A$  is pre-exponential factor dependant on temperature,  $E_a$  is activation energy of reaction,  $R$  is universal gas constant and  $T$  is temperature in Kelvin. According to this equation, reaction rate doubles in every  $10^\circ C$  increase in temperature. Since generation of petroleum is a chemically reactive process, the amount of petroleum generated will vary linearly with time and exponentially with temperature.

### ***Temperature and Time***

Petroleum is generated when kerogen is subjected to the increased temperatures that accompany sediment burial (Fig. 3)

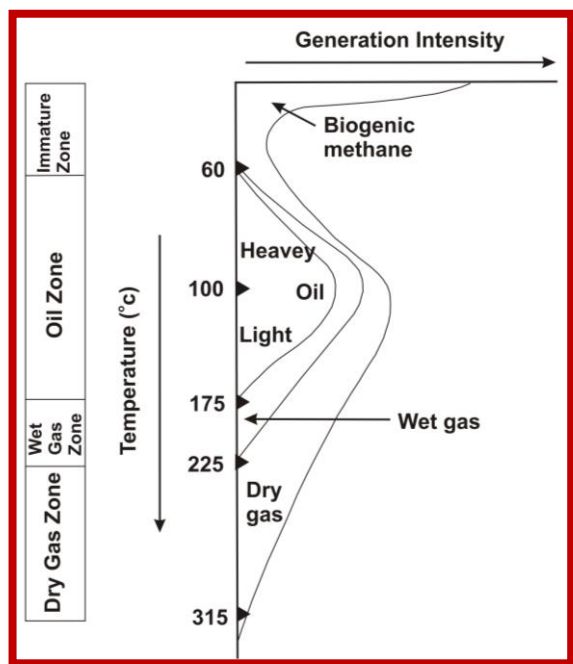


Fig. 3 Various transformation products with increase in temperature and burial. Principle oil producing zone is termed as 'Oil Window' (redrawn after North, 1995).

The alteration of kerogen to petroleum is similar to other thermal cracking reactions. Large kerogen molecules decompose upon heating, to yield smaller molecules of petroleum. These reactions usually require temperatures greater than 60 °C. At lower temperatures, during early diagenesis, natural gas, (called biogenic methane or marsh gas) is generated through the action of microorganisms that live near the earth's surface. Vast quantities of biogenic methane are probably generated, but most of this will not encounter a trap and will be lost to the atmosphere.

The temperature range between about 60°C and 175°C is commonly called the *oil window*. This is the principle zone of oil formation. It begins at burial depths of 1 to 2 km and ends at depths of 3 to 4 km in most areas, depending on factors such as the geothermal gradient. The first oil generated

is heavy and tends to be richest in aromatic and N-S-O compounds. As burial and temperature increases, oil becomes lighter and more paraffinic. At temperatures much above 175°C, the generation of liquid petroleum ceases and gas formation becomes dominant. When formation temperatures exceeds 225°C, most kerogen has used up its petroleum-generating capacity. Source rocks become overmature. However, some methane can still be created, even at these very high temperatures, by the breakdown of the larger, heavier molecules of previously generated crude oil.

Along with a series of chemical reactions, time also play a major role in the conversion of kerogen to petroleum. Young, Tertiary-age rocks need to be deeply buried or have high geothermal gradients in order to generate significant amounts of petroleum. Although generation, migration and entrapment have been documented in rocks as young as 1.0 to 1.5 million years old, major petroleum accumulations have not been found in rocks younger than 10 million years (Halbouty et al., 1970). On the other hand, some old Paleozoic and Mesozoic source rocks might not have been buried very deeply i.e buried only up to the uppermost level of the oil window but have still generated petroleum because of the time factor. However, in most petroleum occurrences, temperature appears to be a more significant factor than time.

#### **5. Tracking maturation history of kerogen using organic-geochemical and optical paleo-thermometers:**

The chemical law of kinetics, expressed in the Arrhenius equation, states that rate of any chemical reaction is related with temperature and time. It is estimated that the reaction rate doubles with every 10°C increase in temperature. Two commonly used indices for maturation study are Time-Temperature index (TTI) and Level of Organic Maturation (LOM). While TTI

integrates temperature increase with time spent in each temperature interval, for an incremental increase of 10°C, in course of sediment burial, the LOM scale is framed with the consideration that reaction rate doubles in every 10°C increase in temperature. In LOM scale oil generation occurs between 7 and 13 and prominent gas generation records values between 13 and 18.

With increase in depth and temperature kerogens undergo progressive carbonization with reduction in H:C content. In fact, the thermal maturation results in release of a fluid product, rich in hydrogen, industrially known as oil and gas leaving behind a residue very high in carbon. Hence, hydrogen content or carbon content of a source rock is considered a good proxy for its degree of maturation. Since hydrogen content of sediments may also include hydrogen contained within pore waters or in combination with clay minerals, the carbon (C) ratio is considered a good indicator for degree of maturation. The carbon ratio of coal is defined by

$$\text{C ratio (\%)} = \left( \frac{\text{dry, ash-free fixed carbon}}{\text{fixed carbon} + \text{volatile carbon}} \right) \times 100.$$

The fixed and volatile carbon values in the equation are determined by pyrolysis, for that matter by carrying out proximate analysis in case of coal.

For sediments other than coal viz. shales, we seek resort to some other parameters such as Hydrogen Index (HI) and estimation of volatilized (retortable) carbon. Organic acids, a major constituent of organic matters, react with potash (KOH) to result potash products. This reaction is named as saponification. In course of progressive maturation of kerogen, saponifiable components of organic matters get changed to non-saponifiable products;

degree of this transformation from saponifiable to non-saponifiable product is referred to as HI

$$HI = (\text{non-saponifiable compound} / \text{saponifiable compound}) \times 100$$

Sediments with HI = 100 indicates complete conversion and thus overmatured, i.e all saponifiable compounds transformed into non-saponifiable compounds. Commonly, sediments with HI above 90 are considered as suitable for prolific oil generation and indices less than 40 are indicative of immature recently deposited organic matters without any significant maturation. Another index for maturation estimation is the ratio between retortable carbon (carbon that can be volatilized at 500°C in an inert atmosphere) and Total Organic carbon (TOC). Total organic carbon of any sample is measured first by removing inorganic carbon present in form of carbonates by acid treatment and then by measuring the CO<sub>2</sub> combustion product of the sample at about 1000°C. Hydrocarbon source sediments yield values between 0.4 and 0.5, at cases even higher i.e 0.6 or more. Non-productive/barren shales give values 0.1 or less. What these parameters actually measure is the volatile content present within any sample. With progressive maturation as volatiles are lost, accordingly the H: C content of organic matters also reduces. However, for peak hydrocarbon generation from organic matters elemental carbon in organic matter should not be more than 80-85% and hydrogen content should not be less than 7%, preferably it should be above 10% by weight. It is suggested that the quantity of hydrocarbon generated from any sample generally maintain a linear relationship with the organic matter content of that sample, which is termed as 'oil quantity factor' for a sample.

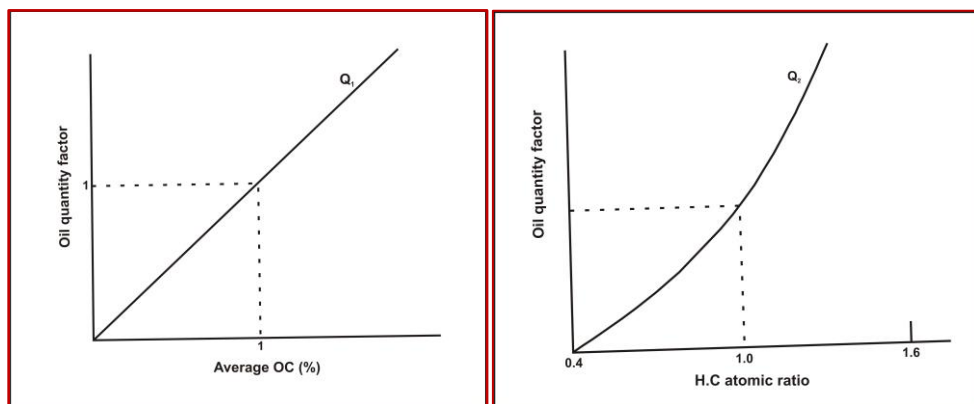


Fig. 4 Quantity of oil generated with respect to organic carbon content and H:C atomic ratio of organic matter (after North, 1995).

Amount of volatilized carbon in organic matters is identified by pyrolysis. In Pyrolysis organic matter is heated in a stream of helium in an inert atmosphere. Temperature is gradually raised in a controlled manner at a carefully measured rate in Rock-Eval pyrolyser and expelled volatiles are recorded in a hydrogen flame ionization detector. At 200-300°C temperature free hydrocarbons present in sample get volatilized. This is referred to as the  $S_1$  peak in pyrolysis curve (Fig. 5). With increase in temperature hydrocarbons are expelled from kerogen, which is designated as  $S_2$  ( $T_{max}$ ) in the pyrolysis curve. On further heating up to a temperature around 390°C, expulsion of  $CO_2$  is marked in the pyrolysis curve as  $S_3$ . Pyrolysis continues up to 800 – 900°C. The readings i.e  $S_1$ ,  $S_2$  and  $S_3$  are used for estimation of source rock maturation. The ratio  $S_1 / (S_1 + S_2)$ , also referred to as *production index*, is used to estimate the amount of hydrocarbon generated with respect to the total amount of hydrocarbon capable of being generated from the organic matter. The ratio  $S_2 / (S_1 + S_2)$ , referred to as *hydrogen index*, correlates directly with the H:C content of organic matters. The area of  $S_3$  denotes  $CO_2$  derived from organic matter and the ratio i.e  $S_3 / (S_1 + S_2)$  i.e the *oxygen index* correlates with O:C atomic ratio within the organic matter.



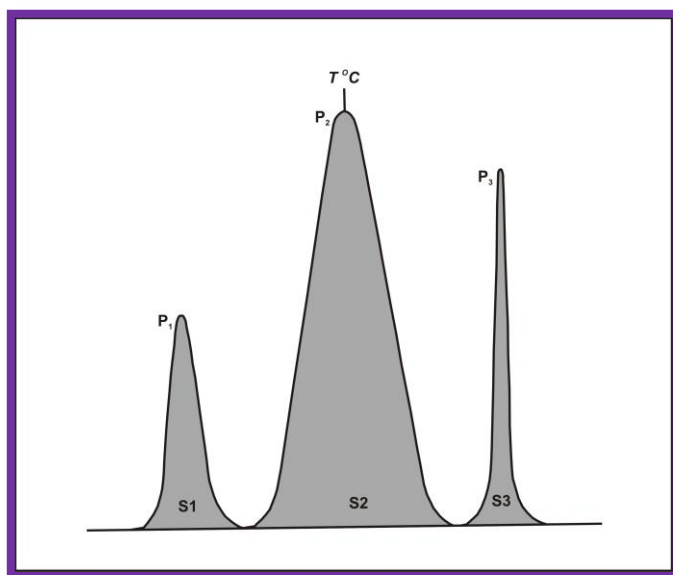


Fig. 5 Rock Eval pyrolysis data of rock sample. Note three prominent peaks S<sub>1</sub>, S<sub>2</sub> and S<sub>3</sub> (after North, 1995)

Another method in use for maturation study is Gas chromatography. With increase in burial depth of organic matter and temperature there is more evolution of *n*-alkanes. A correlation is established between changing pattern of chromatograph and distribution of *n*-alkanes. In immature source rocks *n*-alkanes show a broad 'whaleback' with a bimodal distribution of unresolved components. With increase in temperature and maturation of organic matter the whaleback submerges and the unresolved components define a single peak. Broad low 'whaleback' devoid of spike denotes degraded oil (Fig. 6).

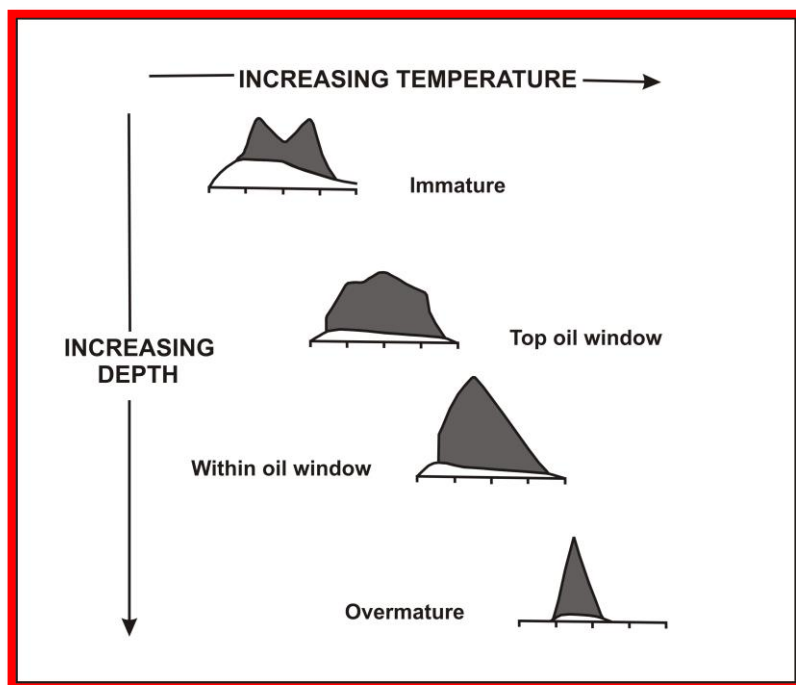


Fig. 6 Gas chromatograph patterns for *n-alkanes* undergone maturation with increasing temperature and burial. While broad whaleback with bimodal unresolved component distribution signify sediment immaturity, submerged whaleback with single peak mode bear indication for over maturity.

#### **Optical (biological) thermometers:**

Spore Coloration Index (SCI) and Vitrinite Reflectance (VR) are the two most useful paleothermometers in source rock maturation study. During thermal maturation dispersed organic matters including spores within sediments change colour from yellow and brown to black. The change in colour depends not only on rise of temperature but also on the duration of time through which the organic matter sustains that temperature i.e the geothermal history. The changes that happen in organic matter is time-dependant, unidirectional, progressive and irreversible. Keeping this in view, a ten point spore coloration Index (SCI) scale has been devised. Organic

matters of animal origin are also used for the purpose provided they are chitinous or carbonaceous e.g conodonts display a comparable progressive color change i.e pale yellow through brown to black and finally crystal clear.

Vitrinite reflectance ( $R_o$ ; expressed in percentage) in oil immersion with the use of reflectance microscope has been in regular use in source rock maturation study. Vitrinite, a maceral, records maturation in its reflectance value, which is dependent both on time and temperature. Measurement of  $R_o$  values of representative samples with different fixed carbon contents allowed reconstruction of maturation gradient curve, the gradient of which is dependent on geothermal gradient and sedimentation rate. However, before applying this method care must be taken to ensure its correct identification. Also application of this method is not possible in pre-Carboniferous rocks.

Taking into consideration both SCI and VR, an empirical relationship is established between hydrocarbon generation and these paleo-thermometers. Crude oil generation is noticed between  $R_o$  values 1.5 and 3.0, which matches with spore colour dark yellow to dark brown.  $R_o$  values between 0.6 and 1.5 indicates immaturity and correlates with light yellow colour of spore, whereas  $R_o$  value above 3.0 suggests essential graphitic condition of organic matter without any hydrocarbon when spore colour turns into black (Fig. 7). These values, however, only give idea about degree to maturation and temperature attainment; no way are these values indicative of hydrocarbon generation propensity of organic matters. Hydrocarbon generation capacity of organic matter depends on its type (humic/ sapropelic/ mixture of both), subject to proper cooking with regulated time-temperature effect.

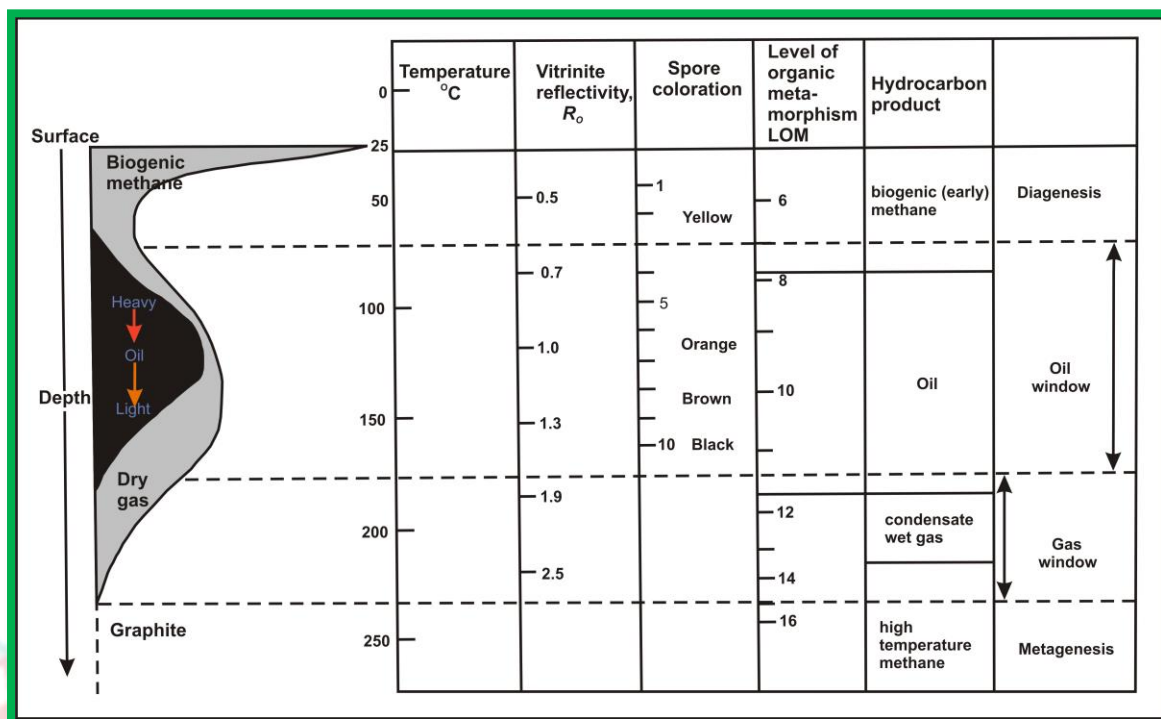


Fig. 7 Correlation between temperature and organic maturation indices viz. VR, SCI, LOM and respective maturation products at different stages (modified after Selley and Sonenberg, 2014)

## 6. Parameters of effective oil source rock (after North, 1985)

For becoming an effective oil source rock sediment should have

1. Total Organic Carbon (TOC) should be 0.4 % or more
2. Elemental Carbon content between 75 and 90%. Lower than 75 and higher than 90 values are indicative of immature state and over mature state, respectively.

3. Bitumen to Toc ratio should exceed 0.05
4. Kerogen should be sapropelic and oil prone.
5. VR should be between 0.6 and 1.3 and SCI between dark yellow to dark brown
6. H:C ratio should be  $\geq 0.69$

## 7. Summary

Depending on mode of origin (terrestrial/marine; vascular plant/algal/spore/pollen etc.), organic matters are classified as humic and sapropelic in character and further classified under four types i.e Type I - IV on the basis of their H:C contents. Along with host sediments, organic matters undergo burial as they come under the influence of biogenic and chemical transformations. At shallow depth of burial i.e the diagenetic stage organic matters transform into thermally-reactive complex hydrocarbon compounds referred to as 'Kerogen', made up of carbon, hydrogen and oxygen with minor amounts of nitrogen and sulfur. Dehydration and Decarboxylation are the two most important reactions at this stage. Net outcome of all diagenetic reactions is the reduction of oxygen content of organic matters keeping carbon: hydrogen ratio intact. Subsequent burial expose kerogen to high temperatures and prompt thermal cracking of complex organic compounds into biomonomers. Formation of oil from suitable organic matters is best noted between temperature  $60^{\circ}$  and  $135^{\circ}\text{C}$ , conventionally referred to as the 'Oil Window'. At temperature  $\geq 150^{\circ}\text{C}$  thermal cracking of hydrocarbon starts with formation of methane. Beside temperature, the other important factor responsible for maturation is age of sediment. A balanced combination of temperature and time can result in proper cooking of organic matter and yield hydrocarbon.

A number of chemical and biological (optical) parameters and indices are devised in order to study maturation of sediments and their contained organic matters. Amongst these, Vitrinite Reflectance (VR), Spore coloration Index (SCI), Hydrogen Index (HI) and Production Index (PI) are some of widely used maturation indices. However, it may be noticed that all these parameters and indices only talk about thermal maturity of sediment but in no way indicator of hydrocarbon potentiality. Hydrocarbon potentiality depends on type of organic matter and total concentration (TOC) within sediment.

#### **Suggested Readings:**

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