Bioinorganic Chemistry

M.Sc. III SEM

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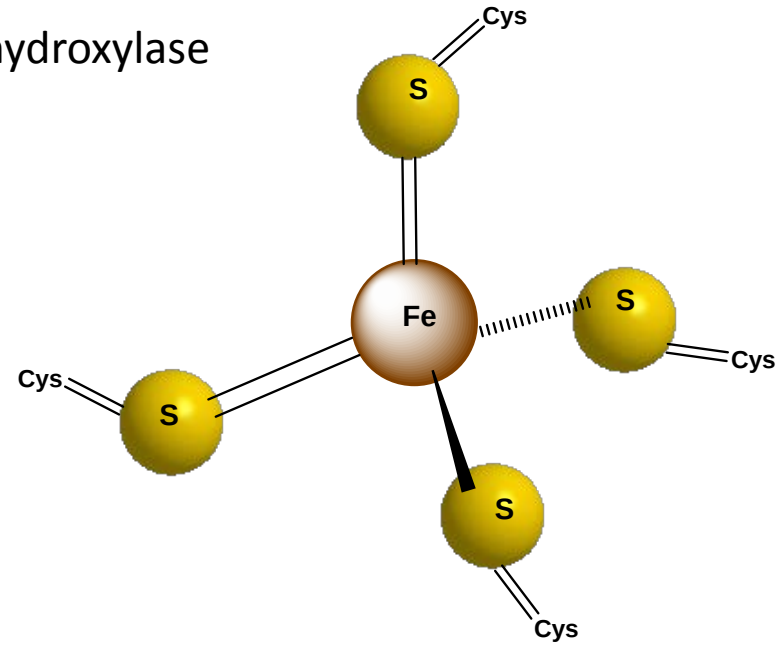
Iron-Sulfur Proteins

- Nonheme proteins containing Fe-S clusters
- Involved in electron transfer reactions (redox reaction)
- All types of Fe-S proteins participate in one electron transfers irrespective to the number of iron atoms
- almost all Fe centres are tetrahedrally coordinated to sulfur atoms
- Present in anaerobic and aerobic bacteria, algae, fungi, higher plants and animals
- Classified into two types (1) Rubredoxin (Rd) and (2) Ferredoxin (Fd)

Rubredoxin

- Singel iron atoms tetrahydrally coordinated by four sulfur atoms $(Cys\text{-}S)_4Fe$
- Do not have acid labile sulfide
- Ligands are cysteines which provide four thiolate donors
- Iron atom in rubredoxin exhibits +2 and +3 oxidation states
- Molecular weight around 6000 with 54 amino acid residues
- Oxidized form is red and reduced form is colorless
- It receives electron from NADH and turns to Fe(II) and rexoidized to Fe(III) after releasing electron to hydroxylase

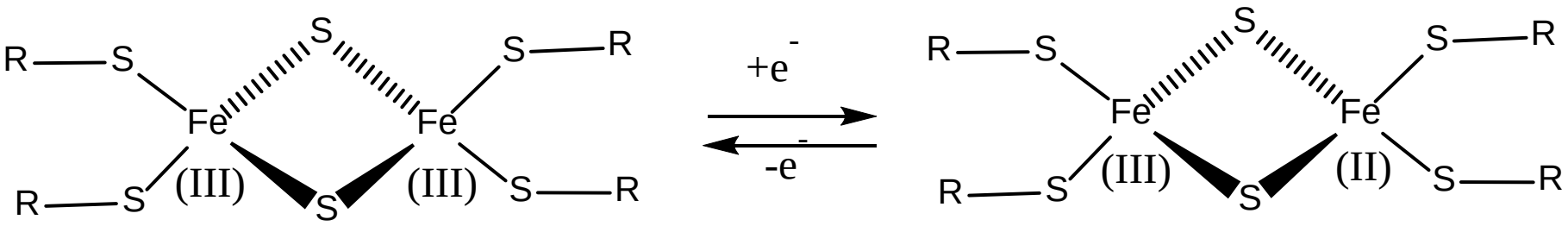


Ferredoxins

2Fe-2S and 4Fe-4S are most common ferredoxins

2Fe-2S

- $[Fe_2S_2(S\text{-}Cys)_4]^{2-}$ cluster
- The two Fe(III) sites are antiferromagnetically coupled and resulting in diamagnetic cluster
- Donate electrons to Cyt P-450 monooygenase and Cyt P-450 camphormonooxygenase



Fd_{ox} Fd_{red}

Ferredoxins

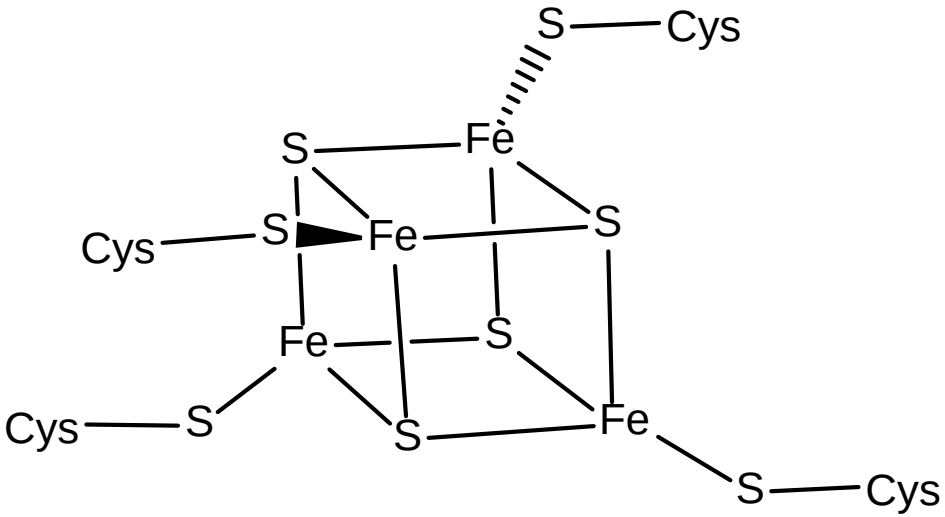
4Fe-4S

Subdevided into Low potential and High potential (HiPIP) ferredoxins

In Low potential ferredoxin [$2Fe^{3+}$, $2Fe^{2+}$] or [$1Fe^{3+}$, $3Fe^{2+}$]

In High potential ferredoxin [$3Fe^{3+}$, $1Fe^{2+}$] or [$2Fe^{3+}$, $2Fe^{2+}$]

- **Play an important role in biological nitrogen fixation.**



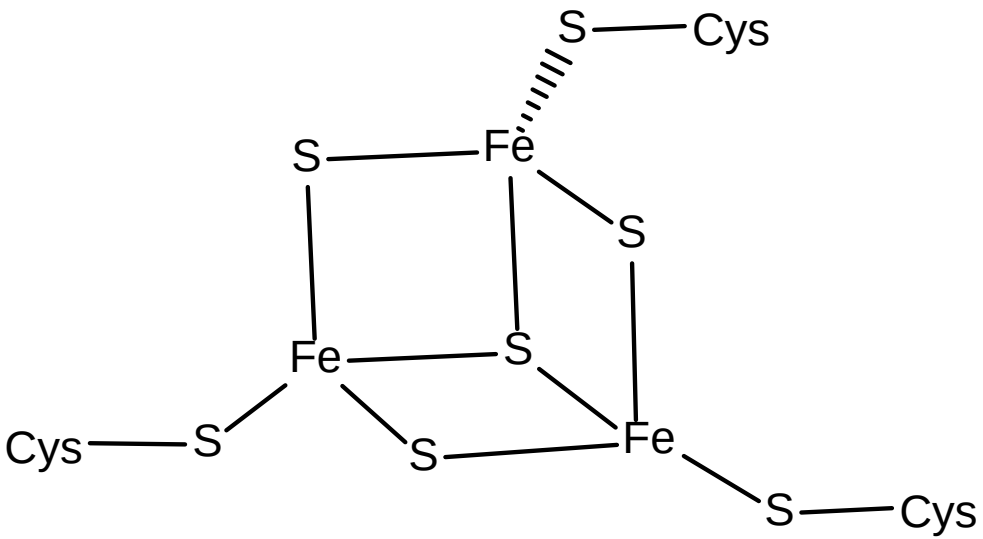
$Fe_4S_4^{3+}$ $\overset{+e^-}{\rightleftharpoons}$ $Fe_4S_4^{2+}$ $\overset{+e^-}{\rightleftharpoons}$ $Fe_4S_4^{+}$

$[Fe(III)_3Fe(II)]$ $[Fe(III)_2Fe(II)_2]$ $[Fe(III)Fe(II)_3]$

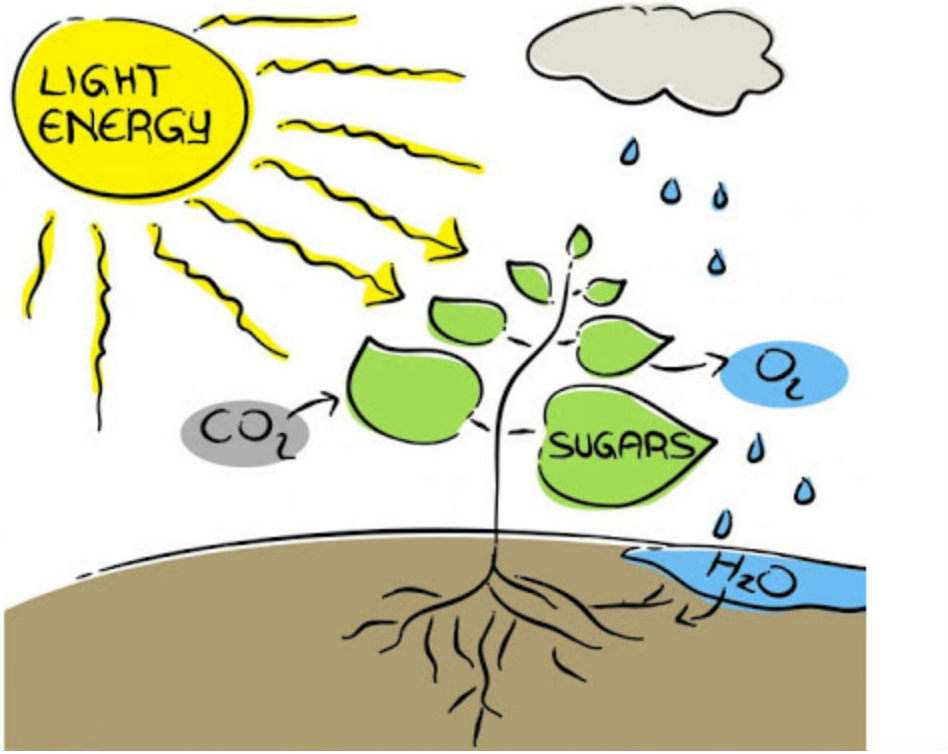
oxidized HiPIP reduced HiPIP

Ferredoxins

3Fe-4S



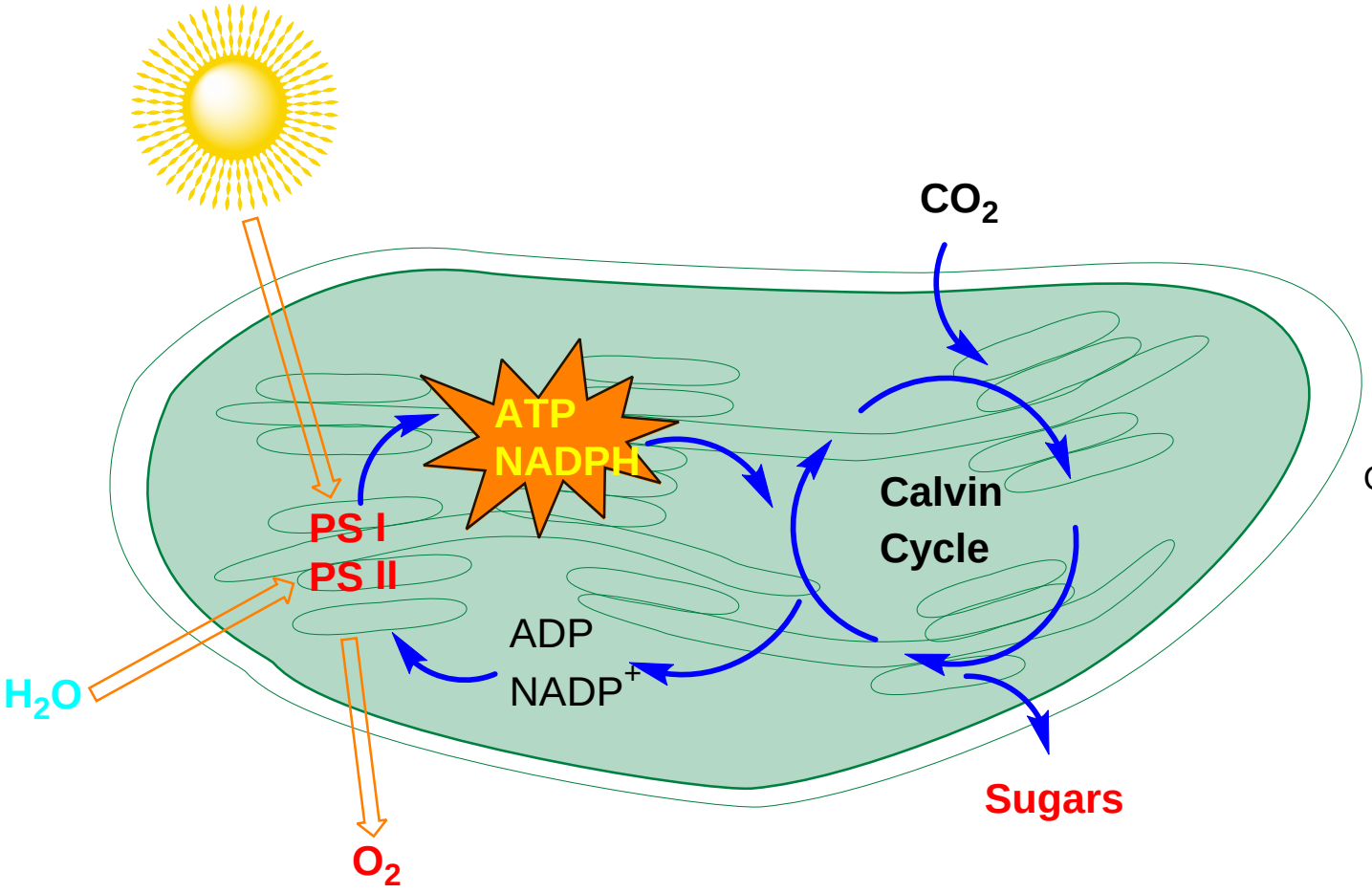
Photosynthesis

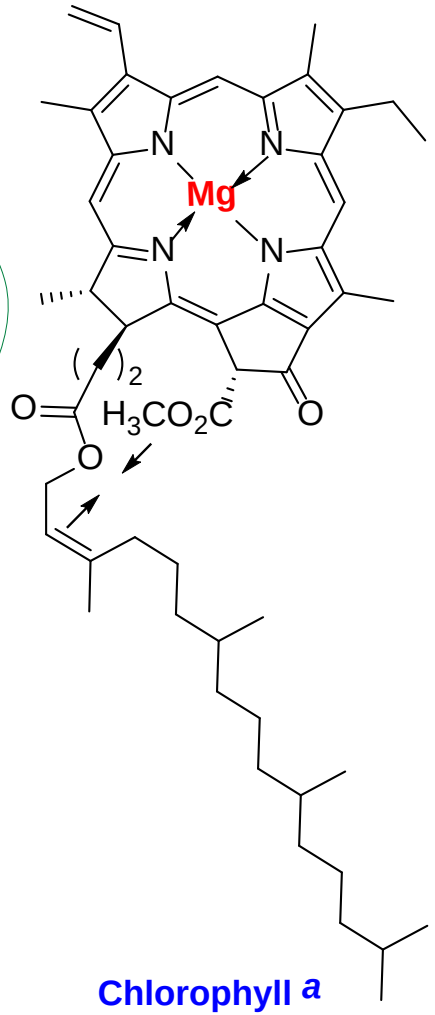


$$nCO_2 + nH_2O \xrightarrow[\text{Chlorophyll}]{\text{Light}} (CH_2O)_n + nO_2$$

Image source: *Credit Shutterstock, Earth Times*

Photosynthesis: Chlorophyll



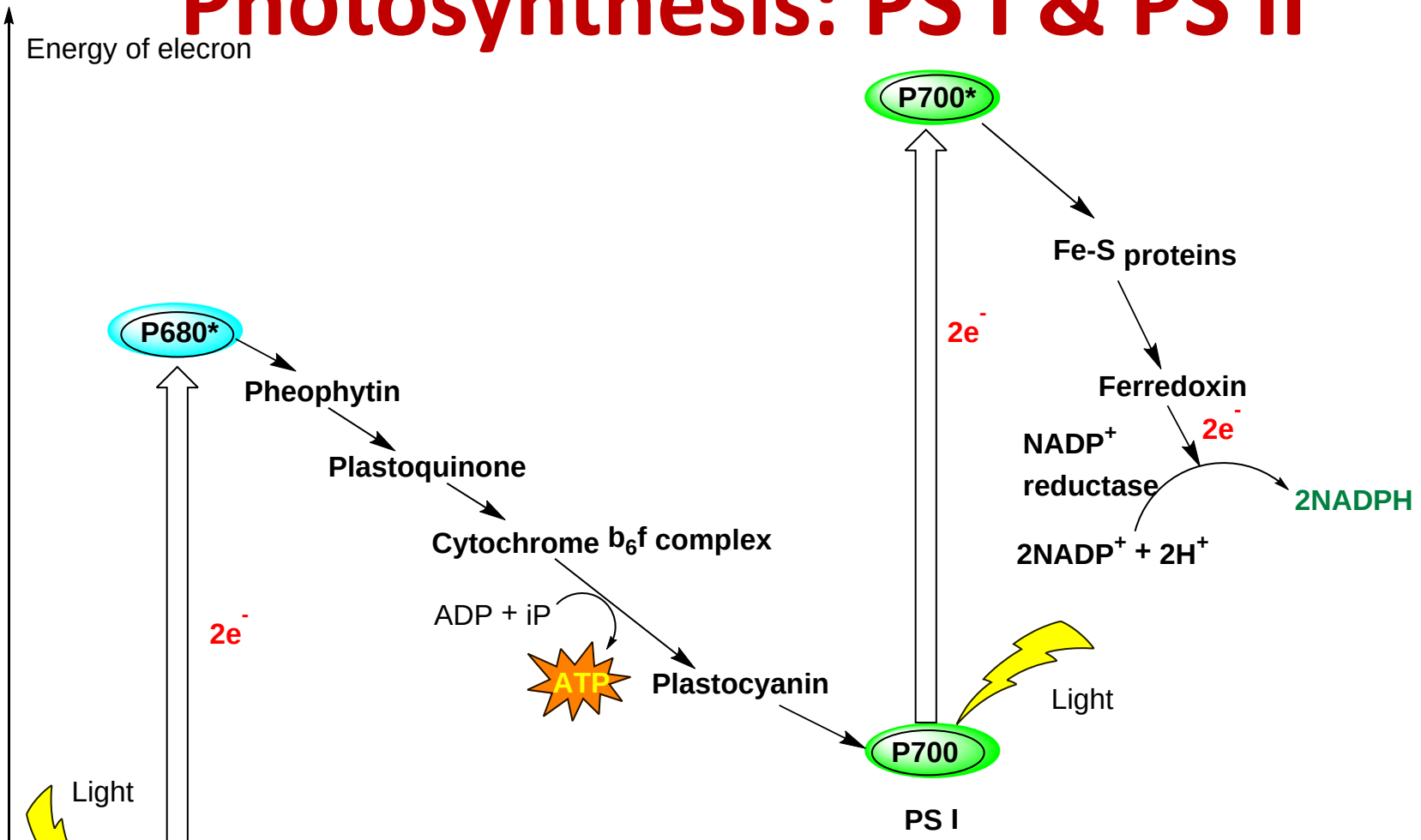


Chlorophyll *a*

PS I : contains about 200 molecules of Chl. A and 50 carotenoid pigments, absorption at 700 nm

PS II : contains Chl. a, Chl. B and othe rassociated pigments, absorption at 680 nm

Photosynthesis: PS I & PS II



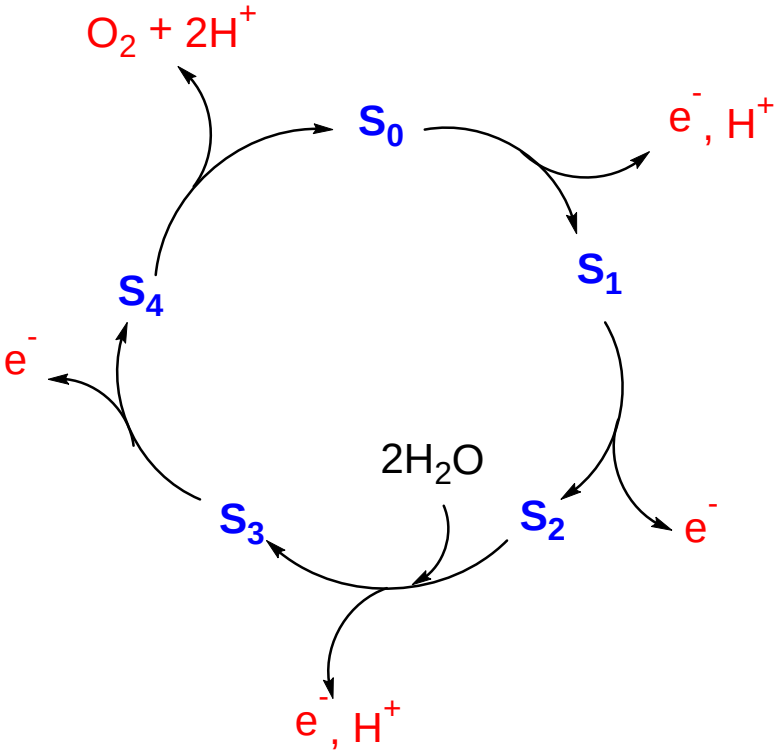
The net reaction is

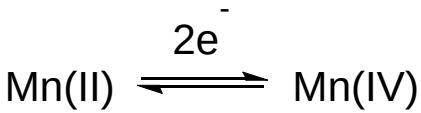
$2H_2O + 2NADP^+ \xrightarrow{8\ photons} 2NADPH + 2H^+ + O_2$

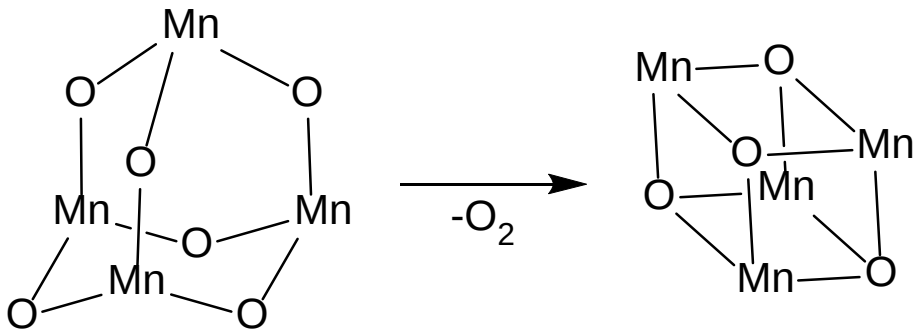
$2H2O(l) \longrightarrow 4H+(aq) + O2(g) + 4e^-$

The Pathway of electron transfer from H_2O to NADP+ in two Photosystems for green plants

Photosynthesis







S_4 Adamantane form S_0 Cubane form

Proposal for the cyclic four steps of oxidation that release O_2 in PS II