Chemistry 2211a

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Section 5

Magnesium

..such a wonderful metal - could it be less exciting than zinc? Seems hard to beat zinc. But then, consider its physiological chemistry in mammals – and especially "us". wow.. and now in plants.
OK exciting is a very good word to describe Mg's role in biology…

11/14/2017 8:21:00 AM 2211a-2017-5-Mg-R17-jkL.docx **Rev- 17-Nov11-14-iJ-jkL**

Mg in Man….Between 270 and 400 mg/kg body weight in man, which provides a mass of about 24 g in the 70 kg man. About 90% is in bone and muscle.

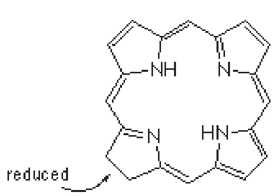
1. A very low 1% is extracellular giving a value of 1.7 meq/l serum (meq?).
2. Daily intake of the order 4 mg/kg body-weight/day - US recommended level is 300-500 mg/day per 70 kg man. Very fast excretion - inefficient absorption. Crops with large amounts of Mg: potatoes; tomatoes - good sources: nuts, cereals, seafood, meat. Green vegetables; chocolate;
3. Deficiency is rare in adults: because Mg is in most foods (but possible after GI tract surgery) and other diseases and conditions can lead to Mg deficiency - alcoholism, burns, renal disease, cirrhosis of the liver, cardiovascular disorders.
4. Mg deficiency can result in disastrous consequences - seizures, coma, death. It is proposed that Mg deficiency in the brain can lead to alteration of cell membrane permeability to ATP transfer reactions so that energy-dependent pumps - Na,K-ATPase - fail to work properly. Cell death occurs as well as accumulation of toxins in the brain. Clinical indicators relate to CNS and muscular tremors - results in convulsions
5. Excess leads to anesthesia - ie a coma-like condition.
6. However, Mg deficiency in ruminants is common – 'grass staggers' because their digestion system can bind the Mg and not absorb it
7. The role of Mg in mammals is widespread and includes not only a role in activating many enzymes, particularly phosphorylation Ca/Mg-ATPases, but also stabilizing RNA and DNA and interactions with other metals and their functions, both beneficial (eg Na, K and Ca) and harmful (Be and Ni). Mg also seems to reduce kidney stone formation (see Ca). Also, heart disease in hard-water areas (eg London, UK) much less than in soft-water areas (Glasgow, UK) attributed to Mg-deficiency as there is no Mg in the water..
8. As a result its concentration is tightly regulated (The TRPM7 is implicated in the regulation of magnesium homeostasis….TRPM7 is a nonselective channel that is inhibited by high Mg^{2+}) ..
9. but we will now look more closely at what happened long ago ….

Biology - role in biological molecules - Mg

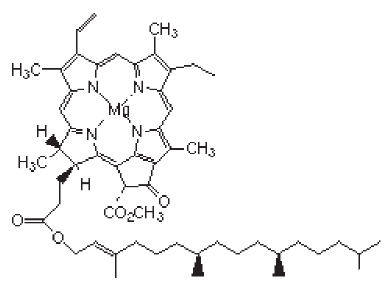
- **PLANTS: Incorporation into a porphyrin to form chlorophyll.**
- Photosynthesis contributed to atmospheric oxygen from cyanobacteria.
- As an aside - once the upper atmosphere was oxygen rich, so UV light formed ozone that then protected the earth's surface from the damaging effects of UV wavelengths allowing cellular growth to take place on the earth's surface.
- Chlorophyll absorbs red wavelengths rather than the higher energy UV wavelengths so was unaffected by the reduction in light with wavelengths less than 350 nm.

Chlorophyll

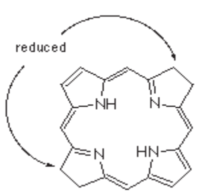
- Aerobic photosynthesis - uses a Mg-porphyrin with a phytol chain - located in a chloroplast (lots of figs coming).
- Several different chlorophylls found - referred to by letters, a, b, etc. and band maxima of the lowest energy Q band absorption, 670, 680,700, – see spectrum..
- Chl a is the first step in the light gathering reaction and is located in the photosynthetic reaction centre.
- **The peripheral ring substitution means that chlorophylls are nonsymmetrical** so the lowest energy $S_0 \rightarrow S_1$ transition is pushed down in energy to those wavelengths available 1.8 billion years ago – that is just below 700 nm (higher in energy at 680 nm for PSII and at 700 nm for PSI). Qu – What is this energy gap equal to? If $c=3.0\times10^{8}$ m/s and Plank's Constant (h) per photon is – 6.626×10^{-34} Js or 4.135×10^{-15} eV s (in case we want to think about this in terms of AA batteries). N_A – $6.023 \times 10^{+23}$ for a mole of photons.
- **There are two light reactions:** PSII makes O_2 and $4H^+$ from $2H_2O$ (via the Oxygen Evolving Complex), and electrons for PSI that then makes NADPH. The protons from PSII drive the formation of ATP from ADP in a separate reaction and location. The dark reaction uses NADPH and ATP to make glucose from CO_2 and H_2O. So it all starts with the chlorophyll ring and the solar spectrum, next ….



Chlorin

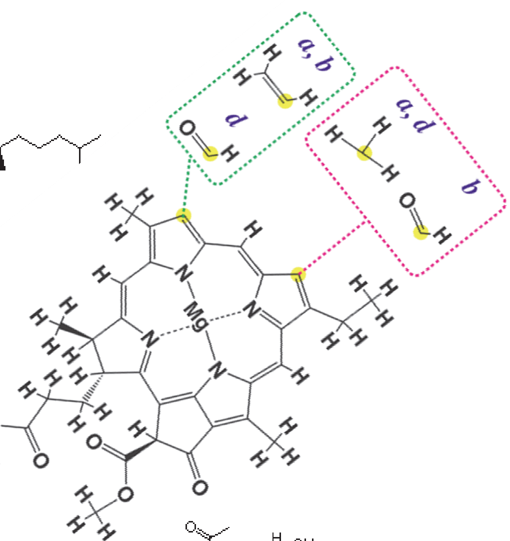


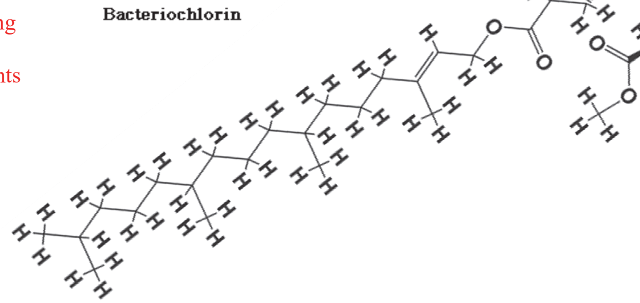
Chlorophyll a

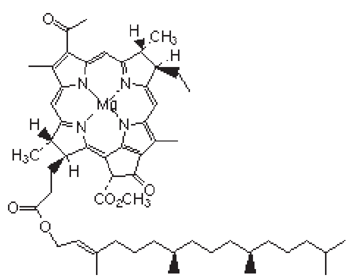


Bacteriochlorin

The chlorin or bacteriolchlorin ring can be found with different substituents …

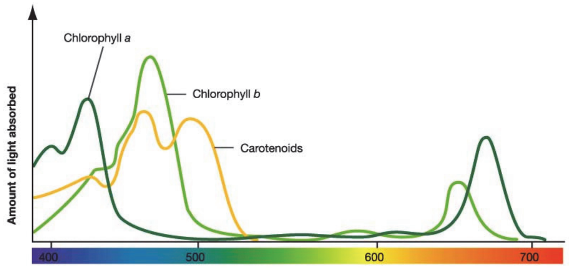


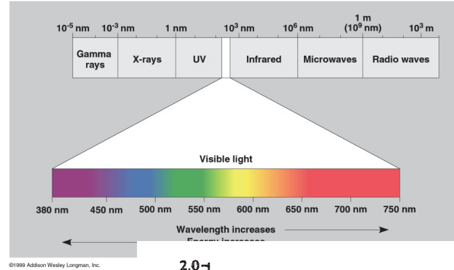




Bacteriochlorophyll a

- Photosynthetically active radiation.. 400 to 800 nm





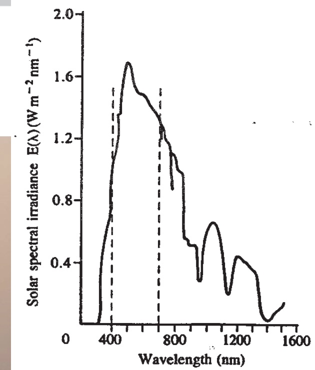
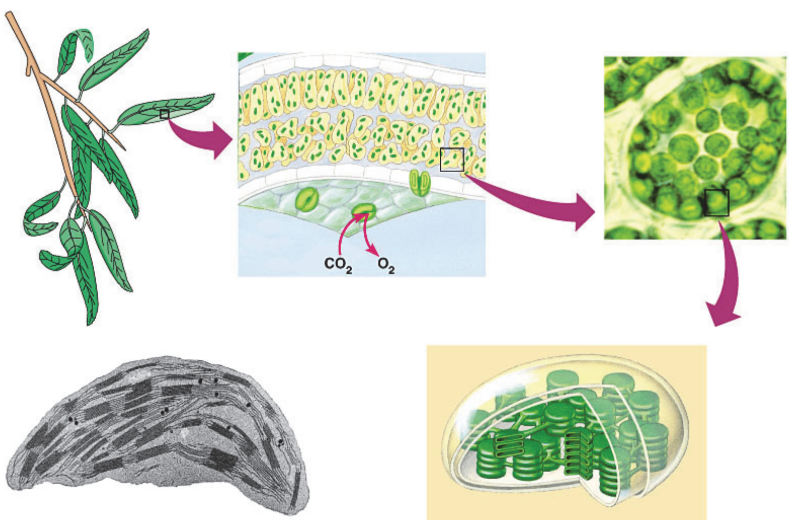


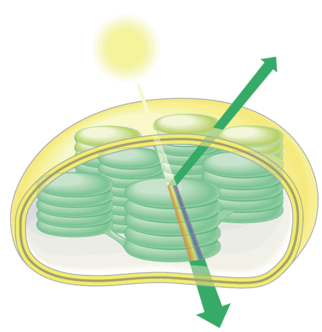
Figure 18·2
Distribution of solar radiation at the earth's surface. Radiant energy reaching the surface of the earth spans the visible region of the electromagnetic spectrum (400–700 nm) and extends into the infrared region (700–1 000 000 nm). More than half of this radiant energy (52%) lies in the infrared region; 43% lies in the visible region. Most of the ultraviolet radiation from the sun is absorbed by the ozone layer of the earth's upper atmosphere. Thus, only about 5% of the solar radiation reaching the surface of the earth lies in the ultraviolet region (approximately 10–400 nm) of the electromagnetic spectrum. (Illustrator: Mike Webb.) [Adapted from Bolton, J. R. Solar fuels. *Science* 202:705-711; 1978.]

- The location and structure of chloroplasts



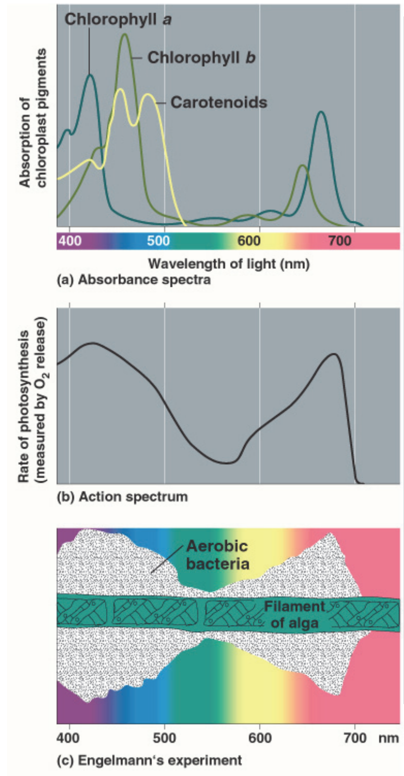
The leaf… structure showing pores to allow gases in and out called a MESOPHYLL cell- contains the chloroplasts

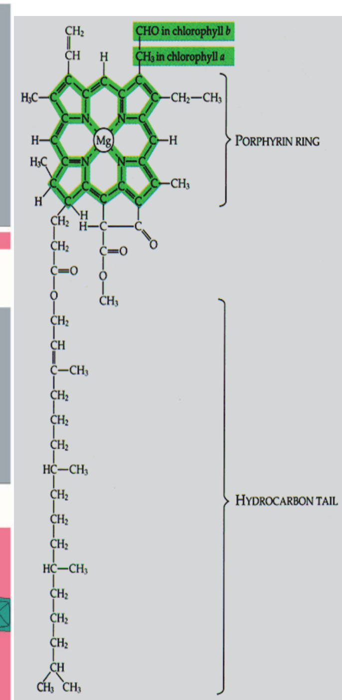
The chloroplast contains the stacks of THYLAKOIDS the stacks are called GRANUM (or GRANA for many) ..then there is the THYLAKOID which has the MEMBRANE – and the LUMEN and the STROMA outside – ah – no exploded view of the thylakoid yet,…



Engelmann's experiment to prove the action spectrum was really very elegant:

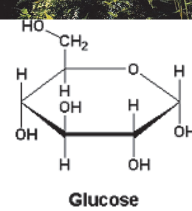
- he added the oxygen requiring bacteria B. termo to a microscope slide containing strands of the green photosynthetic algae Cladophora
- and irradiated the chloroplasts in selected regions with different coloured light.
- he counted the numbers of O_2-seeking B. termo bacteria (several species actually) that had moved to regions high in oxygen. This proved that the photosynthetic activity was wavelength dependent.
- oxygen from the chloroplast photosynthesis – this was in 1881.

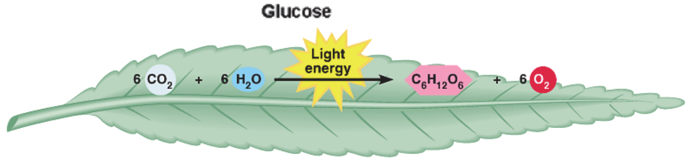




• Light is central to the life of a plant

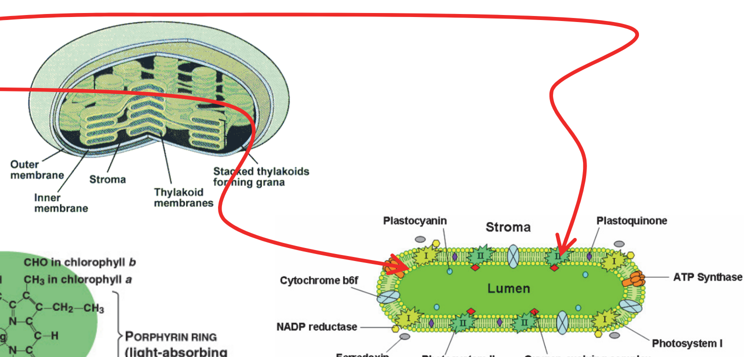
- Photosynthesis is the most important chemical process on earth
  - It provides food for virtually all organisms
- Plant cells convert light into chemical signals that affect a plant's lif cycle
  - Plants that get adequate light are often bushy, with deep green leaves
  - Without enough light, plants become tall and spindly with small pale leaves
- Too much sunlight can damage a plant
  - Chloroplasts, carotenoids and **anthocyanin** help to prevent such damage
- Photosynthesis is the process by which phototrophic organisms** use light energy to make sugar and dioxygen from carbon dioxide and water

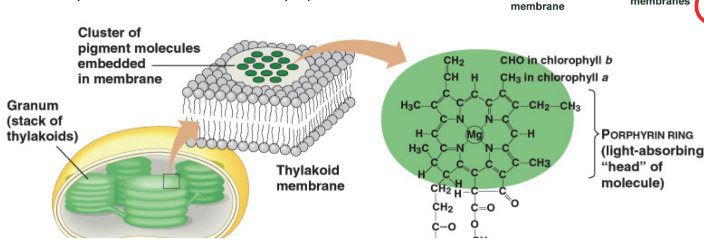




*** organisms that make their own food using photosynthesis and just CO_2, and water to form complex molecules.

- Photosynthesis fixes tons of CO_2 per year, used as energy for virtually all organisms
- 2 phases (i) 2 light-dependent reactions PSII and light-independent or DARK reaction cycle (Calvin C
- In most plants, photosynthesis occurs primarily in chloroplasts
- A chloroplast contains: stroma (a thick fluid like t for moving chemicals about) and grana (stacks of t
- The thylakoids contain chlorophyll embedded into
-



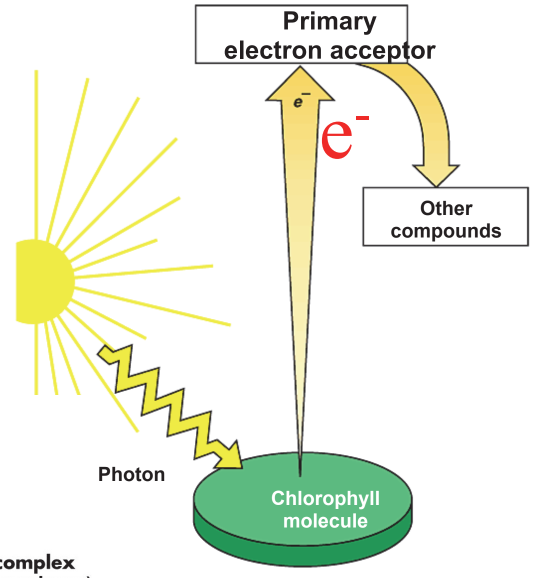


Excitation of chlorophyll in a chloroplast

There are many antenna or light harvesting chlorophylls with absorption maxima slightly higher in energy than the Reaction Centre chlorophyll (lower in λ - near 680 nm in PSII and 700 nm in PSI).

After initial excitation into PS II, the electron 'lost' to the 'electron-acceptors' is replaced by the electrons from oxidation of water – the O^{2-} in water becomes 1/2 O_2 – ie loses 2 electrons = oxidation step.

Photons **absorbed** between 400 and 700 nm can run photosynthesis. But all are used at energy equivalent of just a red 680-700 nm photon. (Why? Remember the energy level diagram from INSTR unit).



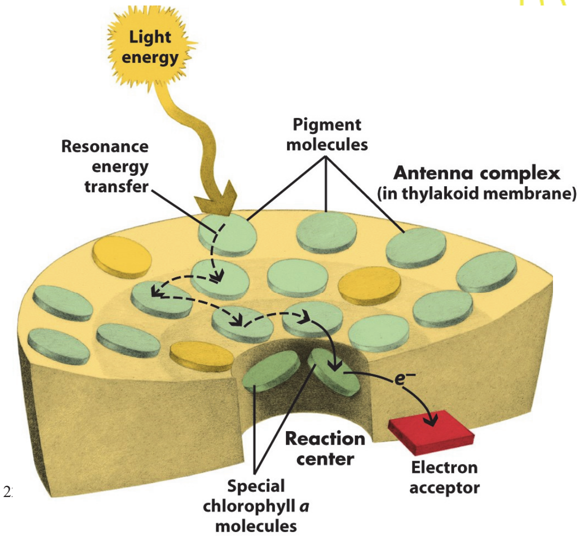
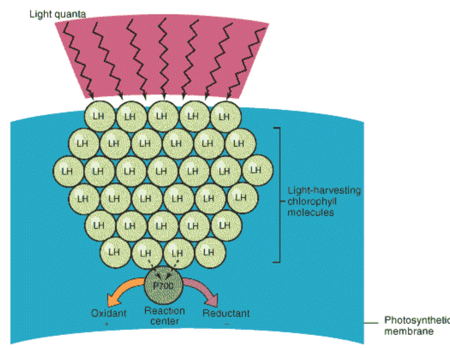
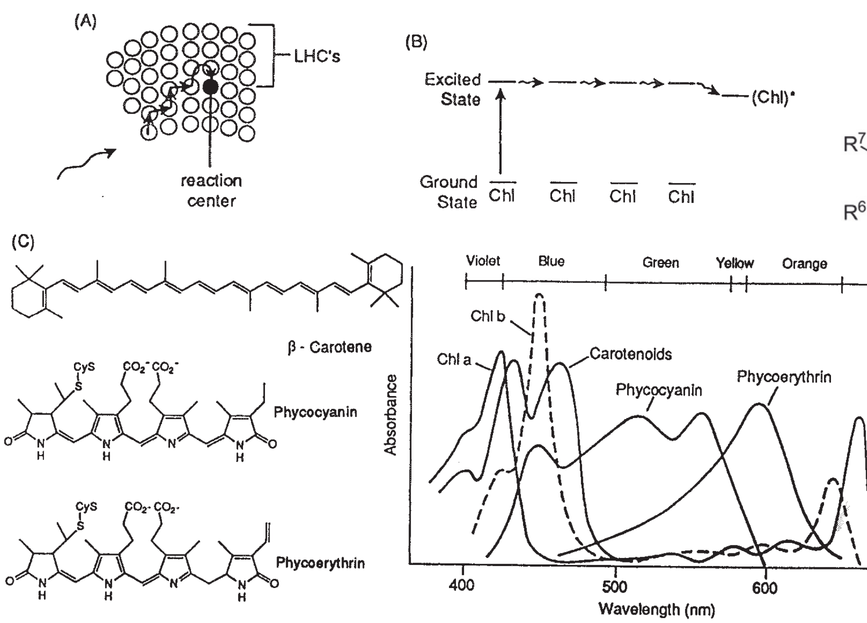
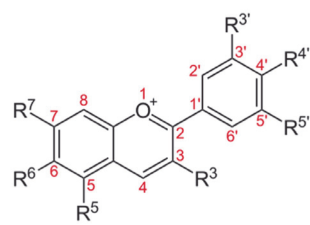


Figure 7-10
Biology of Plants, Seventh Edition







Anthocyanidins - red - blue in colour - pH dep R's -H and -OH commonly) - >500 combinations - with R's = anthocyanins

think apples; pansies; fall leaf colours; peaches; blackcurrants; red cabbage

Figure 5.19 General features of a photosynthetic apparatus. (A) Light is captured by light-harvesting complexes (LHC). These are transmembrane polypeptides that contain a variety of chromophores (chlorophylls, carotenes, or other pigments, according to the photosynthetic system) that together absorb light over the entire range of the visible spectrum. Light absorption may be tuned by small changes in chromophore structure [e.g., note the difference in absorption spectrum for chlorophylls *a* and *b* in (C)]. (B) Energy is transferred to the reaction center by a mechanism known as exciton coupling where the energy stored in the excited state of one chromophore is used to promote the excitation of another. Eventually this energy is trapped by a special chromophoric unit (typically a special chlorophyll or bacteriochlorophyll complex) in the reaction center, from which a rapid charge separation occurs (see Figure 5.20). (C) Ancillary pigments and their absorption spectra. See Figure 5.11 for chlorophyll structures.

In summary

Photosynthesis can be broadly separated into:

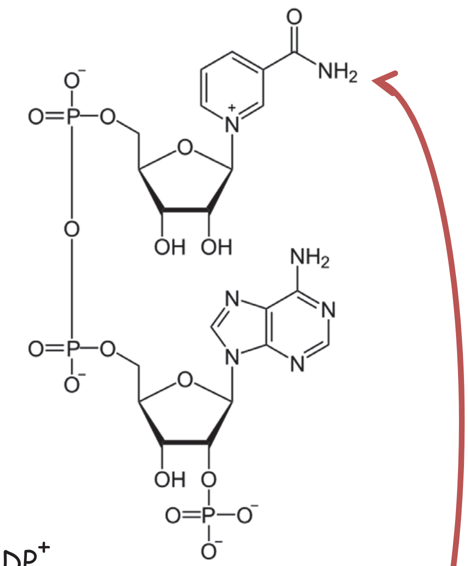
- light reactions - light dependent
- dark reactions - light independent

Light reactions are involved in:

- the oxidation of water to oxygen
- reduction of NADP+ to NADPH and ATP
- occur in thylakoid membranes

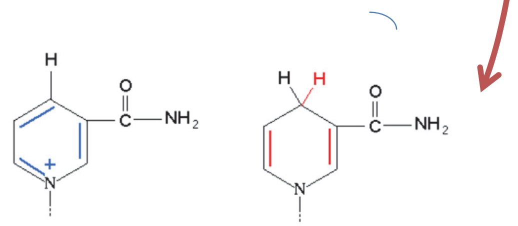
Dark reactions :

- use NADPH and ATP to fix CO_2 into CH_2O
- occur in stroma matrix of chloroplasts



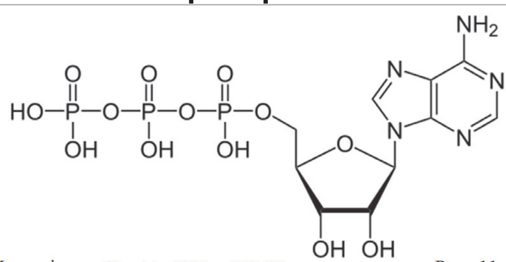
NADP$^+$

Nicotinamide adenine dinucleotide phosphate



nicotinamide   nicotinamide with extra H

Adenosine triphosphate



What comes next:

1) Overview of the 2 stage light-reaction and then the dark-reaction
- light excites an electron from a chlorophyll in PSII – leaves behind a positive charge; P^+_{680}
- light excites an electron from a chlorophyll in PSI – leaves behind a positive charge; P^+_{700}
- electron from PSII – neutralizes the PSI chlorophyll: $P_{700}^+ + e \rightarrow P_{700}$
- electrons from $2H_2O \rightarrow O_2 + 4H^+ + 4e$ – neutralize the $P_{680}^+ + e \rightarrow P_{680}$
- we find three electron chaperones - …

2) …(Chl)2* + Pheo →·(Chl)2+ + ·Pheo- (charge separation) (Pheo=Chl-no Mg^{2+})
then 2·Pheo- + 2H+ + QB →2Pheo + QBH2 (quinone reduction)
– PQ –plastoquinone - simply an aromatic organic ring that can add e and H+ - floats the electron to the Cytochrome Complex that is embedded in the membrane
– Pc – plastocyanin - a beautiful molecule that holds a single Cu atom as if in fingers – picks up an electron and gives it to the PSI chlorophylls
and there is - Fd – ferredoxin – 2 Fe's that flip Fe(II) to Fe(III) and back!

3) …and two energy related molecules, NADPH and ATP - structures above.

4) ….and finally, glucose is made (actually not directly…) in the Calvin Cycle.

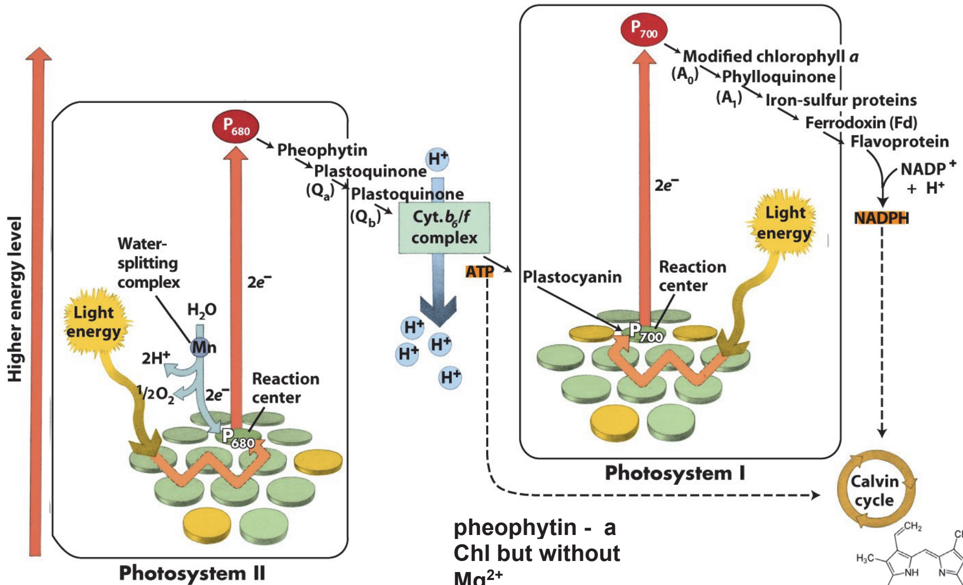


Figure 7-11
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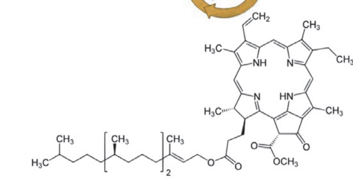
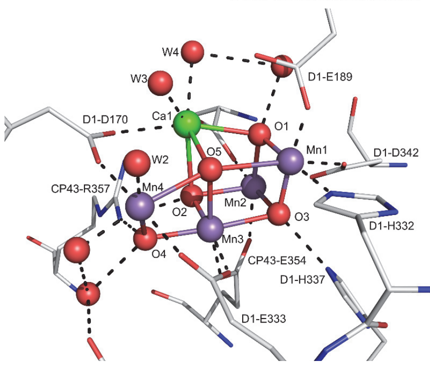
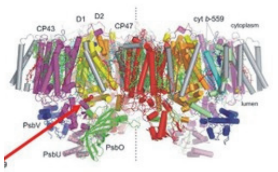
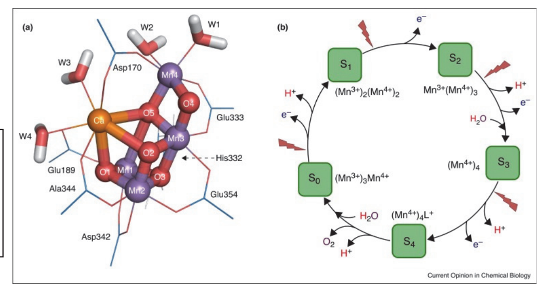
pheophytin - a Chl but without Mg^{2+}



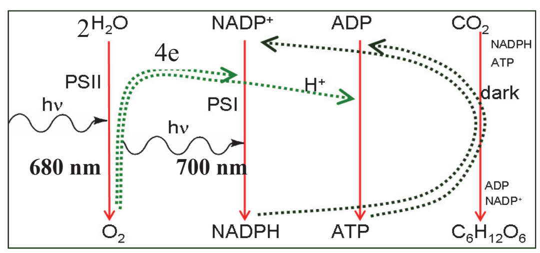




Oxygen Evolving Complex- OEC
Involves 4 Mn (3xIII->3xIV) (red) and 1 Ca (green) – amazing!



The electronic system looks like this:



PS II supplies the electrons for PS I.
PS I then reduces (adds electrons & H+ to) $NADP^+$, to make NADPH, which is used making sugar in the Calvin-dark reaction (see below).

NADPH = Nicotinamide adenine dinucleotide phosphate – see RHS →

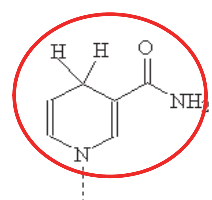
H^+ from both PSII and Cytochrome Complex (inside the membrane) drive the independent ADP → ATP reaction for the Calvin CO_2 trapping chemistry.

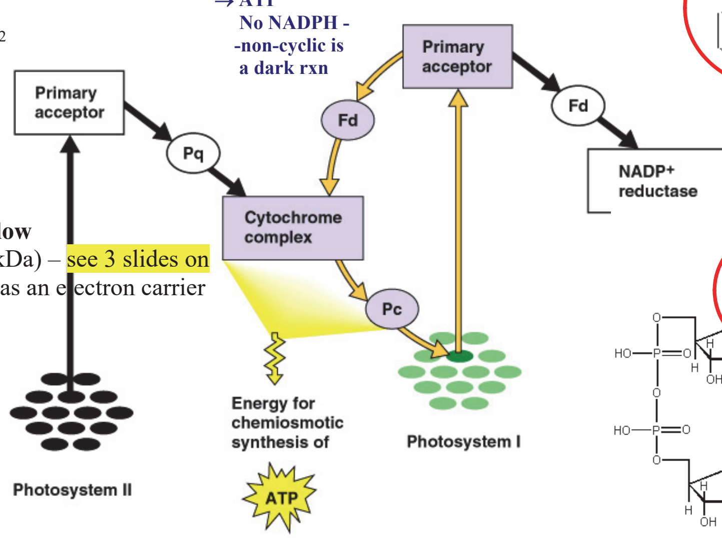
pheophytin →

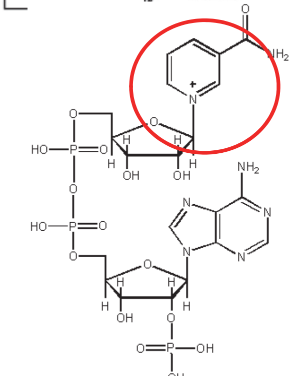
Fd: chloroplast-type Fe_2S_2 $(CYS)_2$ **ferredoxin** that function as an electron carrier
The Fe flips 2+ to 3+
See next slide for more details.

Plastoquinone –PQ-
PQ +2H+ + 2e → PQH_2 – see below
Pc = Plastocyanin a small (10.5 kDa) – see 3 slides on Cu-containing protein which acts as an electron carrier between the cytochrome b_6f and photosystem I (PS1) complexes in the photosynthetic electron-transfer chain.
Cu flips 1+ to 2+ and back
See 2 slides on for more details.

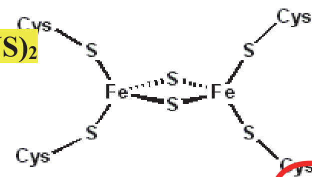
Cyclic phosphorylation → ATP
No NADPH - -non-cyclic is a dark rxn







Fd: chloroplast-type Fe_2S_2 $(CYS)_2$



ferredoxins that function as electron carriers
Fe is coordinated by 2 CYS and 2 S atoms!
The Fe flips 2+ to 3+

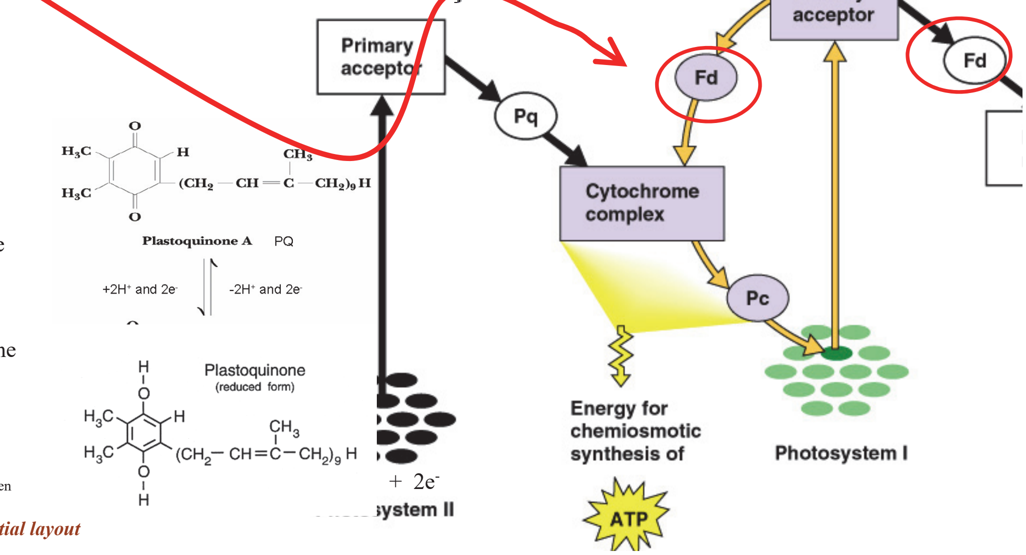
$PQ + 2H^+ + 2e \rightarrow PQH_2$

$2H^+_{stroma} + 2e^- + PQ \longrightarrow PQH_2$

PQH2 diffuses across the thylakoid membrane to deliver the 2e to the cytochrome complex.
It then diffuses back to the PSII chlorophyll

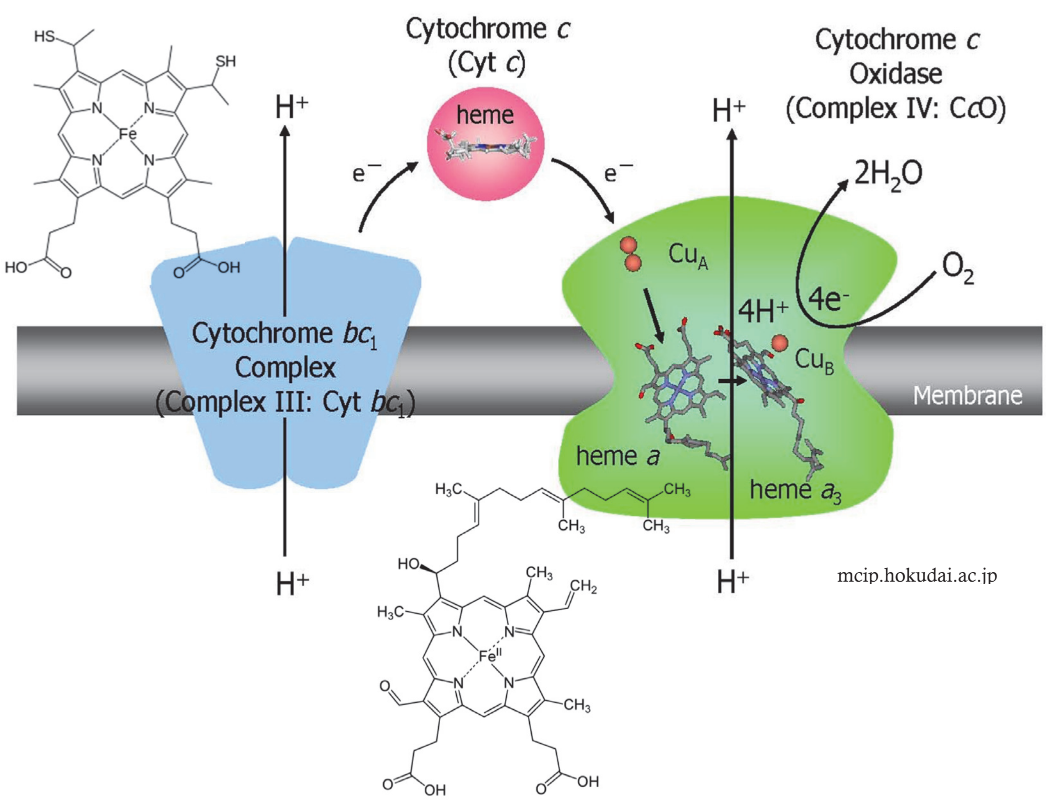
$PQH2 \longrightarrow PQ + 2H^+_{lumen}$

See several slides on for spatial layout



Ca/4Mn complex– water to O_2 Cytochrome – Fe heme Fd: Fe(II)/(III)
Mg - chlorophyll

Pc: Plastocyanin: Cu(I)/(II)

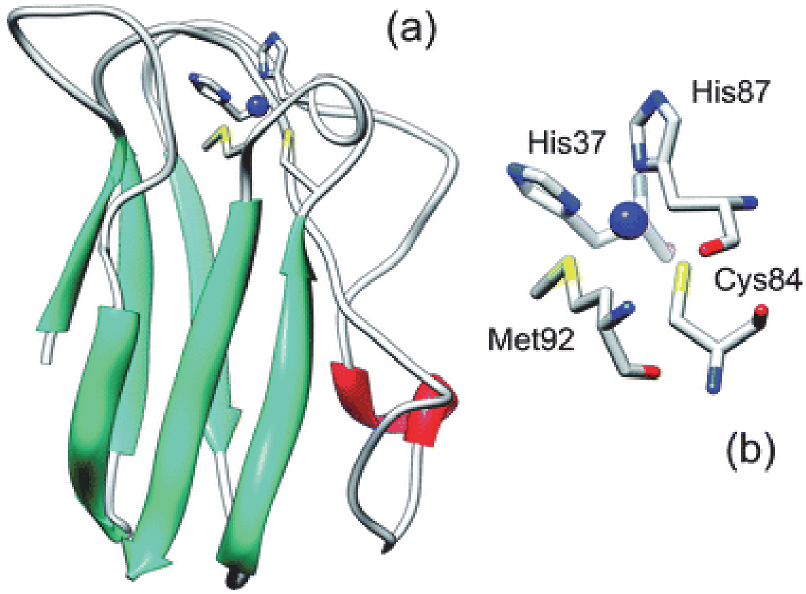


Pc = Plastocyanin a small (10.5 kDa) Cu-containing protein which acts as an electron carrier between the cytochrome b_6f and photosystem 1 (PS1) complexes in the photosynthetic electron-transfer chain.

Pc belongs to the group of: type 1 blue copper proteins, which are characterized by a strong blue color (which copper ox state is this from? Why?)

2^0 and 3^0 structure is dominated by?

An excellent example of a β barrel.



The copper(II) d^9 ion near the top is coordinated in an approx. tetrahedral symmetry by His-37, Cys-84, His-87 and Met-92

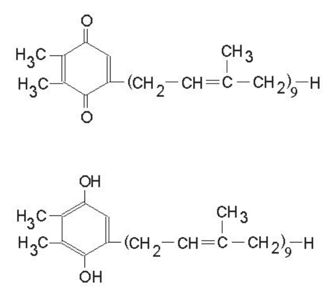
(N, SH, N, CSC)

Cu flips 1+ to 2+ and back

$Cu^{2+}Pc + e^- \rightarrow Cu^{+}Pc$

Why does this work? The Cu(II) is not really stable as Tetrahedral BUT the Cu(I) is also not Tetrahedral enough to be stable. Think of squeezing a pea pod – and ejecting the electron from Cu(I) making Cu(II)… a redox enzyme

The whole of the Light Reaction sequence is arranged like this - see next 3 pages for different views…..

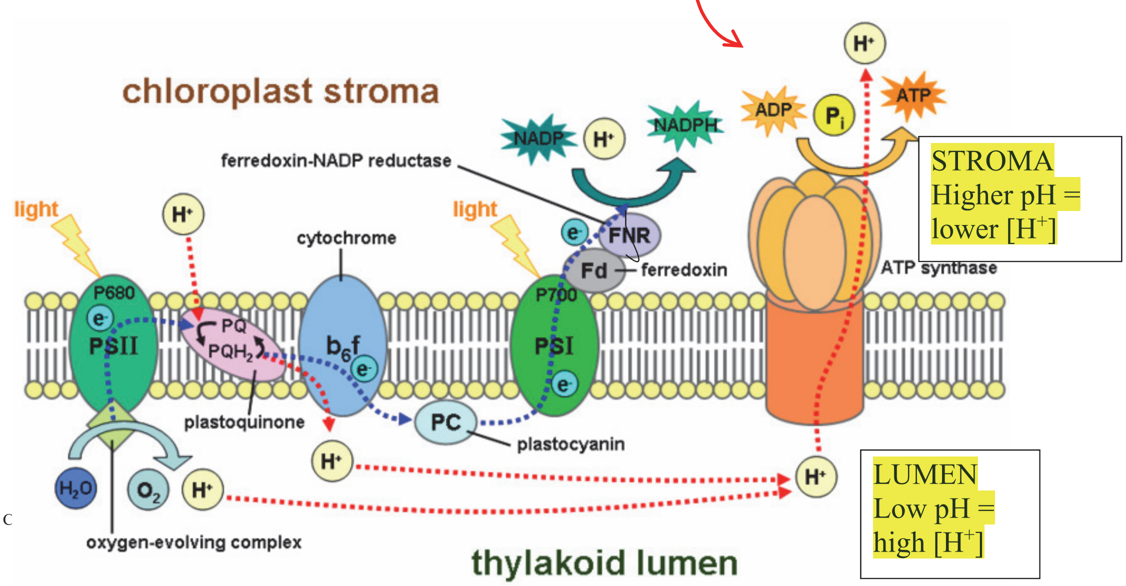


The H^+ flow from the high side (inside) at low pH to the low concn side (higher pH) drives ATP formation

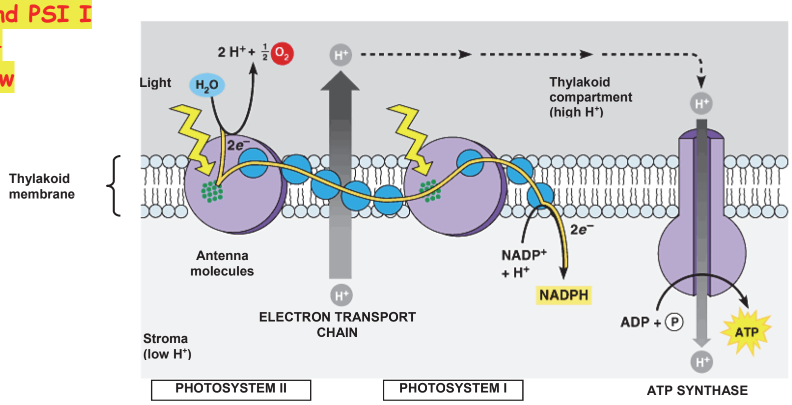
- Stroma pH = 8.2. Lumen pH = 6 in the light (but in the dark they are both around pH 7). – rest is for interest only PQ + H2 → PQH2 the reduced form – holding 2e- .

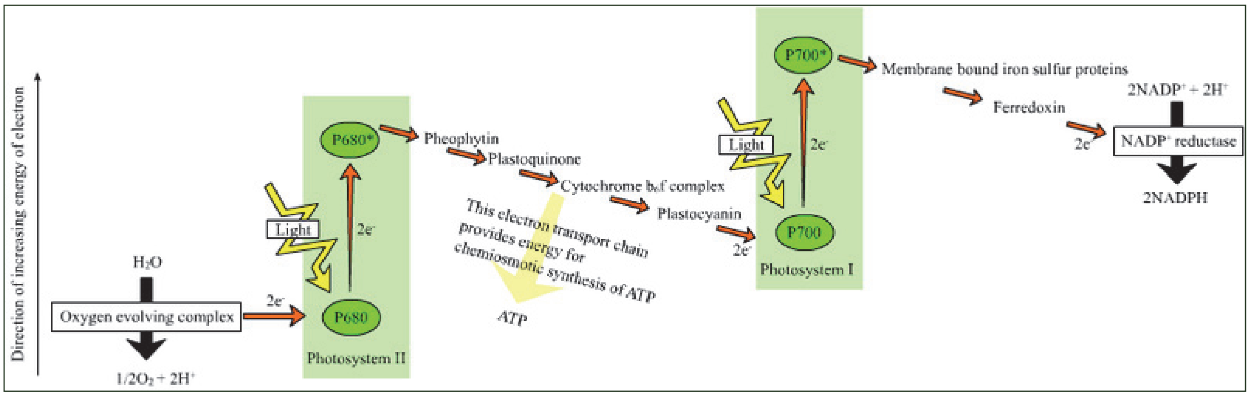
PQ = plastoquinone --

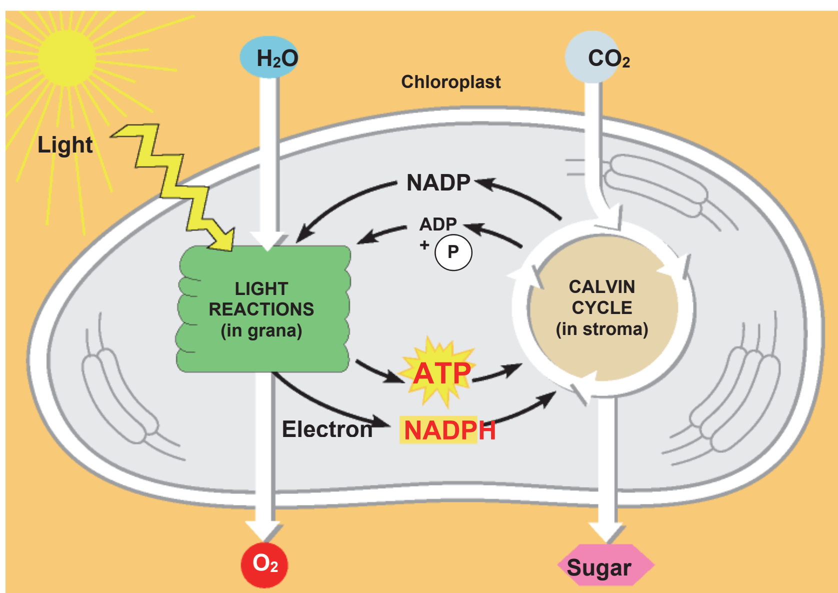
- C=O the quinone part - reduced = C-OH



where PSII and PSI I are located – different view







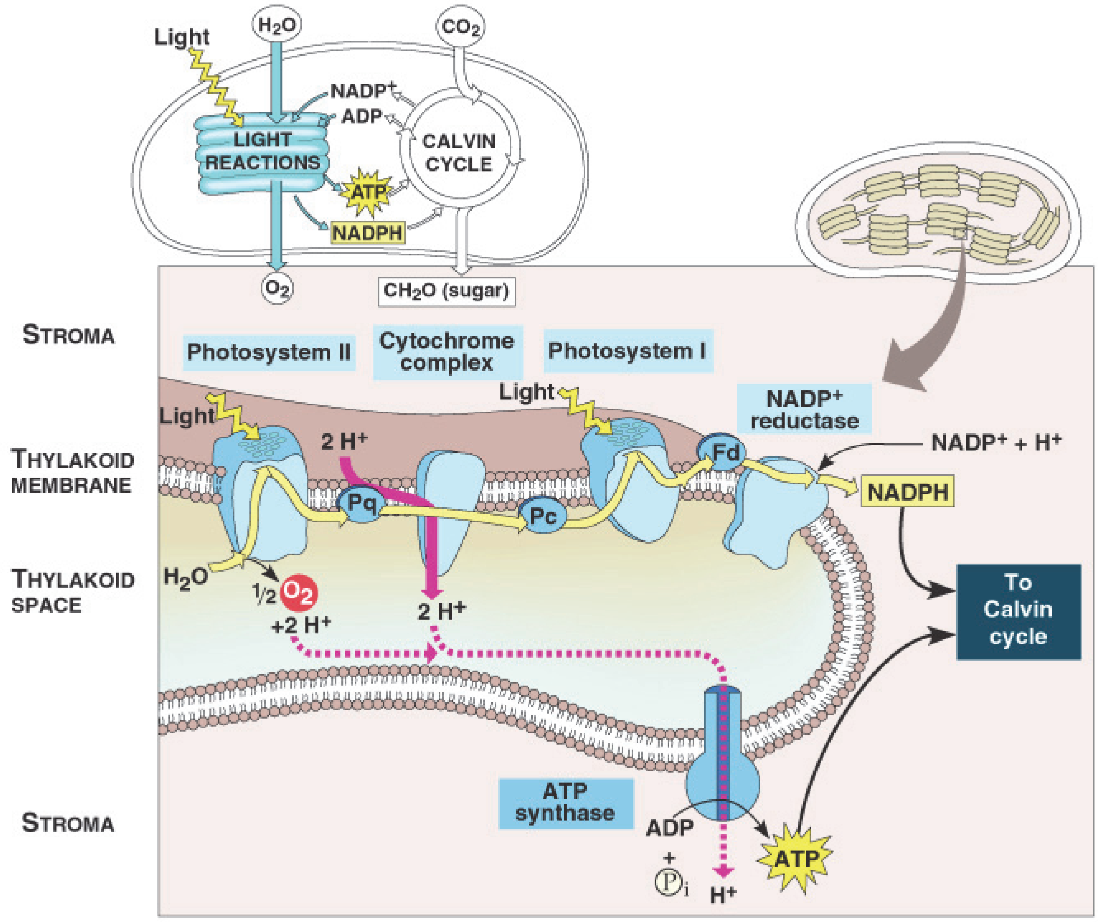
To complete the process of photosynthesis CO_2 must be fixed to make carbohydrates: = light-independent Calvin cycle

- The H^+ gradient from PSII across the membrane (=potential energy) ADP → ATP in ATPsynthase

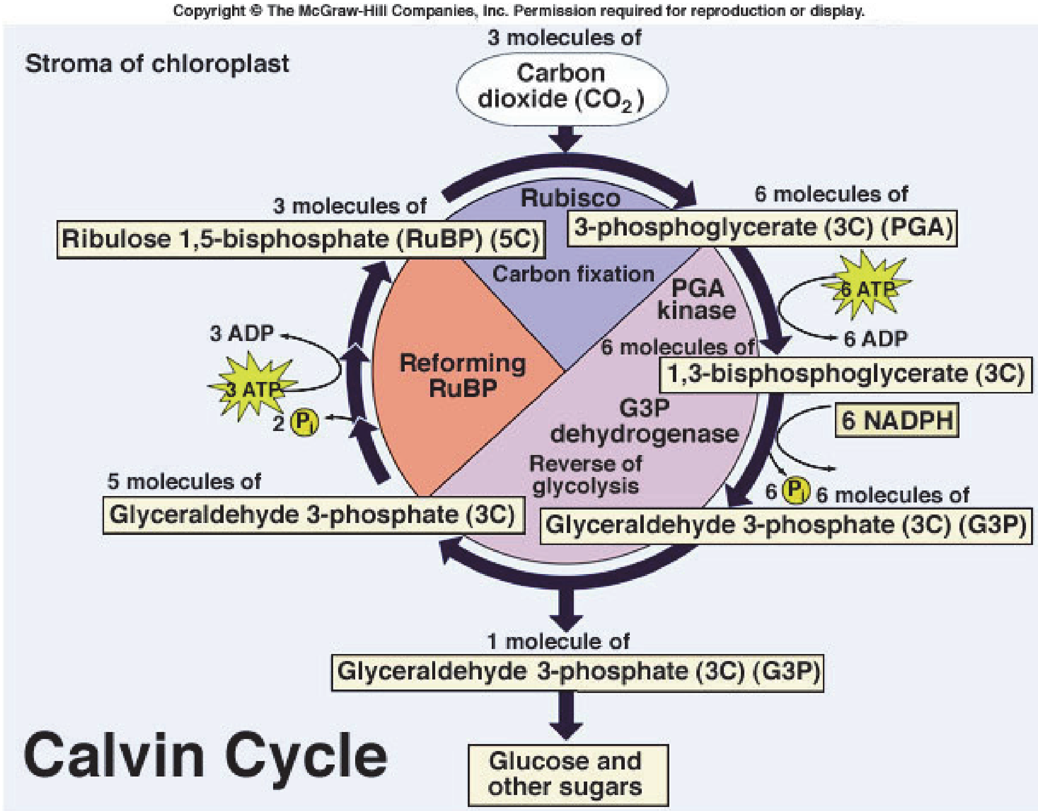
The Calvin cycle (does not run in the dark - just doesn't need light) - called the Carbon Reaction Pathway now - assembles sugar molecules from CO_2 using the energy-carrying products of the light reactions – ATP and NADPH, thus storing energy in a stable form and producing basic building blocks for synthesis of all other organic molecules. The cycle uses the free energy of cleavage of ~P bonds of ATP, and reducing power of NADPH, to fix and reduce CO_2 to form carbohydrate. Enzymes and intermediates of the Calvin Cycle are located in the chloroplast stroma,.

Ribulose Bisphosphate Carboxylase (RuBP Carboxylase or RuBisCO) catalyzes CO_2 fixation:

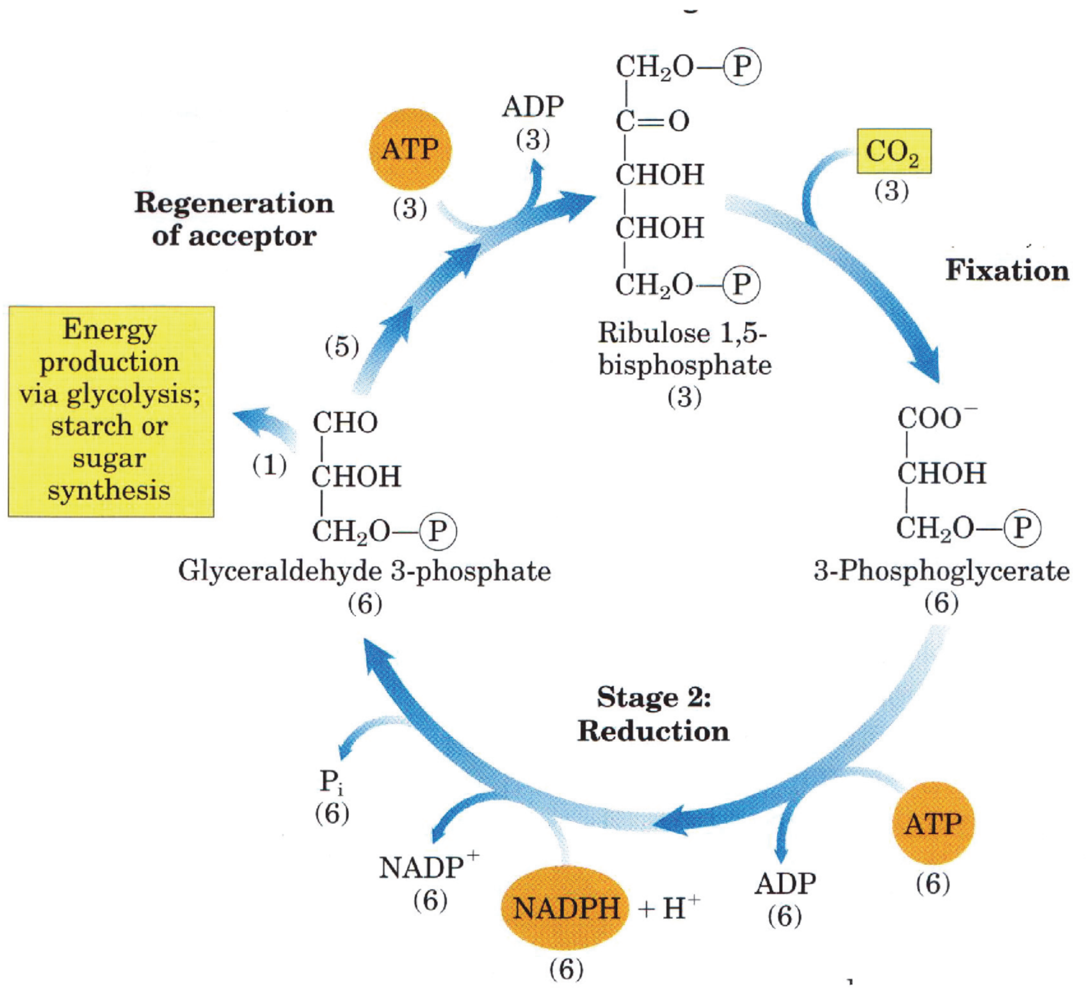
ribulose-1,5-bisphosphate + CO_2 →→→ 2 3-phosphoglycerate



Magnes



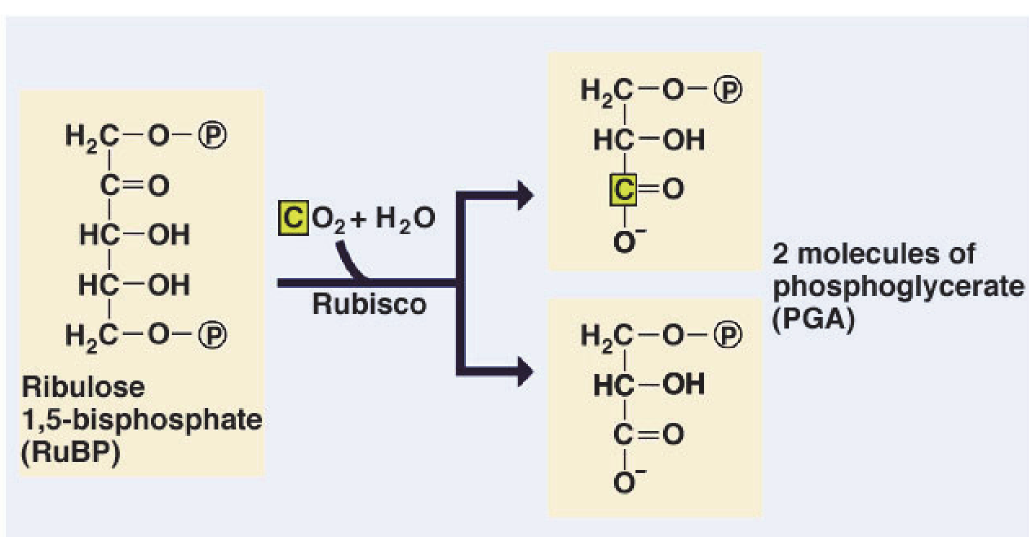
This is the summary - see the next slide for the cycle - then broken down into steps and finally 'what is RuBisCo? The key to it all



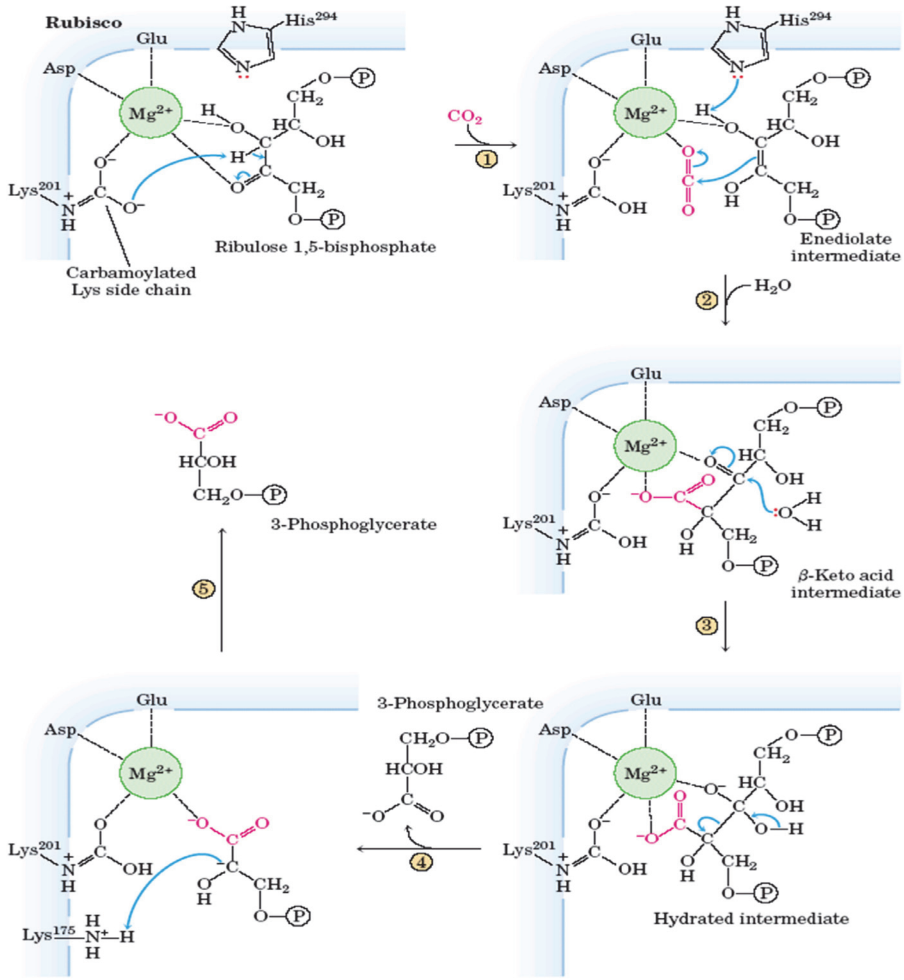
Magnes

Chem 2211a

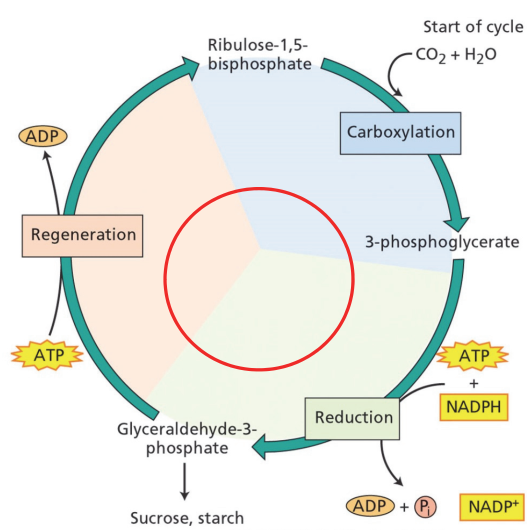
First Step in Carbon Fixation



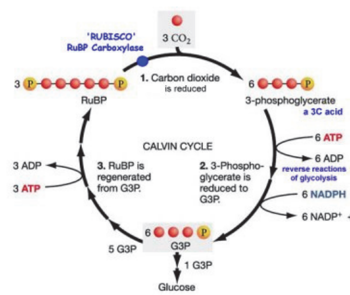
Mg is required to activate RuBisCo



Returning to the Calvin cycle



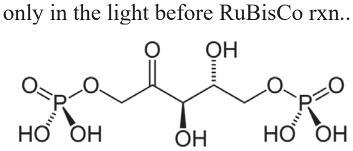
PLANT PHYSIOLOGY, Third Edition, Figure 8.2 © 2002 Sinauer Associates, Inc.



Biochemistry Note: the "-ose" suffix in "triose phosphate" means this is a sugar; "tri" means there are three carbon atoms; "phosphate" means there is an attached P.

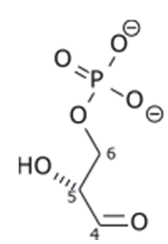
ribulose biphosphate carboxylase
Rubisco is uniquely regulated by a separate protein called rubisco activase - see next page..

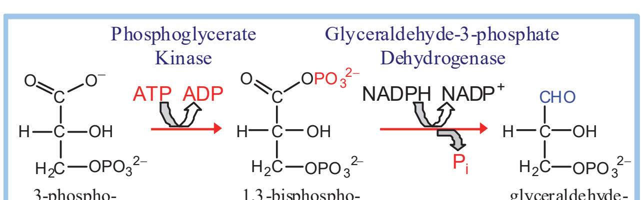
ribulose biphosphate (RuBP) is formed only in the light before RuBisCo rxn..



-- this is the 1st step in the CO_2 fixing rxn.

This is a triose phosphate





3-phospho-glycerate (a three-carbon compound) or D-glyceraldehyde 3-phosphate (G3P) the carbohydrate products of the Calvin Cycle are three-carbon sugar phosphate molecules, or "triose phosphates," specifically, glyceraldehyde-3-phosphate.

Hexose (six carbon) sugars are not a product of the Calvin cycle

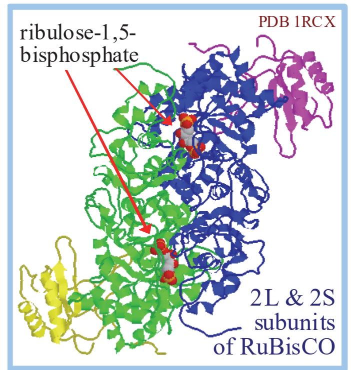
RuBP Carboxylase in plants is a complex (L8S8) of:

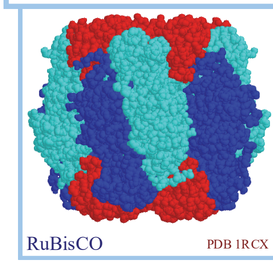
- **8 large catalytic subunits** (**L**, 477 residues, blue, cyan)
- **8 small subunits** (**S**, 123 residues, shown in red).

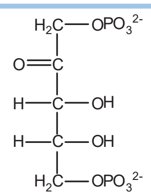
Some bacteria contain only the large subunit, with the smallest functional unit being a homodimer, **L2**.
Roles of the small subunits have not been clearly defined. There is some evidence that interactions between large & small subunits may regulate catalysis.
Large subunits within RuBisCO are arranged as **antiparallel dimers**, with the N-terminal domain of one monomer adjacent to the C-terminal domain of the other.

Each **active site** is at an **interface** between monomers within a dimer, explaining the minimal requirement for a dimeric structure.

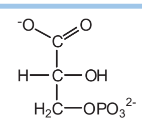
The substrate binding site is at the mouth of an ab-barrel domain of the large subunit.
Most active site residues are polar, including some charged amino acids (e.g., Thr, Asn, Glu, Lys).



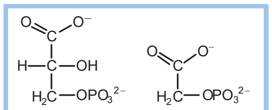




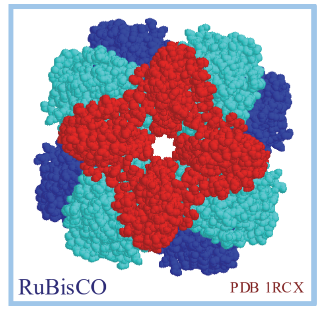
Ribulose-1,5-bisphosphate (RuBP)



3-Phosphoglycerate (3PG)

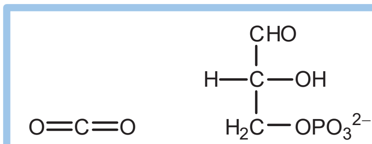


3-phospho-glycerate phosphoglycolate



Summary of Calvin Cycle

3 CO_2 + 9 ATP + 6 NADPH ◊
glyceraldehyde-3-P + 9 ADP + 8 Pi + 6 NADP+



carbon dioxide — glyceraldehyde-3-phosphate

Glyceraldehyde-3-P may be converted to **other CHO**:

- metabolites (e.g., fructose-6-P, glucose-1-P)
- energy stores (e.g., sucrose, starch)
- cell wall constituents (e.g., cellulose).
- fatty acods
- amino acids, etc etc

Regulators prevents the Calvin Cycle from being **active in the dark**, when it might function in a **futile cycle** with the Glycolysis & Pentose Phosphate Pathway, wasting ATP & NADPH.

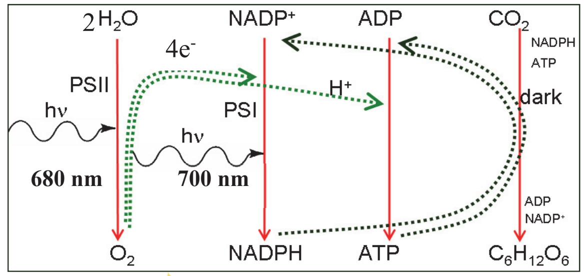
Light-activated e- transfer is linked to **pumping of H^+** into thylakoid disks. pH in the stroma increases to about 8.

Alkaline pH activates stroma Calvin Cycle enzymes RuBP Carboxylase, Fructose-1,6-Bisphosphatase & Sedoheptulose Bisphosphatase.

The light-activated H^+ shift is countered by **Mg^{2+}** release from thylakoids **to stroma**. RuBisCO Carboxylase (in stroma) requires Mg^{2+} binding to the carbamate at the active site.

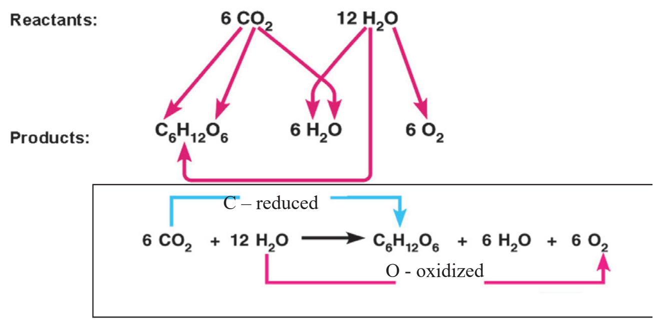
The whole process in terms of the chemistry

The PSII Mn-complex makes O_2 from $2H_2O$ BUT what is most important releases $4e^-$ and $4H^+$ - these electrons replace those lost when light excites the ground state (S_0) electron to the excited state (S_1) at 680* nm in PSII. The PSII electrons replace those lost in PSI.
In PSI light excites the ground state (S_0) electron to the excited state (S_1) at 700* nm and when the electron drops down it makes NADPH – reduced by the electrons that started from the water and H^+ from the stroma (not from the H_2O)
(*Depends on exact species of plant)
The Calvin Cycle – makes glucose from CO_2 –
The overall reaction of all steps is:
Of course the oxygen is oxidized from O^{2-} to O^0
2-electron oxidation – two O`s to make O_2 = 4 e.
The C is reduced from the 4+ in CO_2 to Zero on average in glucose
Does this work out correctly?



$$6\ CO_2 + 12\ H_2O \xrightarrow{\text{Light}} C_6H_{12}O_6 + 6\ H_2O + 6\ O_2$$

$$6\ CO_2 + 12\ H_2O \xrightarrow{\text{Light}} C_6H_{12}O_6 + 6\ H_2O + 6\ O_2$$

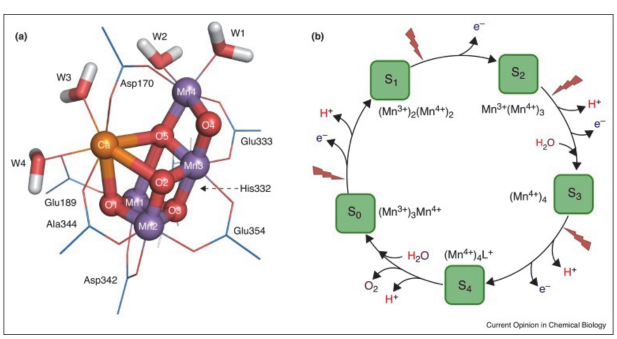


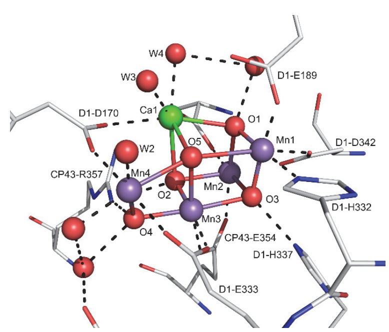
Photosynthetic Reaction Center

A refresher on the oxygen evolving complex because its presence changed the world for ever – the Great Oxidation Event – anaerobic to aerobic.

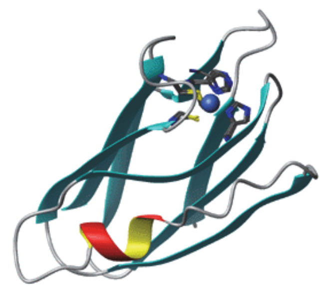
"So a date and a culprit can be fixed for what scientists refer to as the Great Oxidation Event, but mysteries remain. What occurred 2.45 billion years ago that enabled cyanobacteria to take over? What were oxygen levels at that time? Why did it take another one billion years—dubbed the "boring billion" by scientists—for oxygen levels to rise high enough to enable the evolution of animals?"

https://www.scientificamerican.com/article/origin-of-oxygen-in-atmosphere/

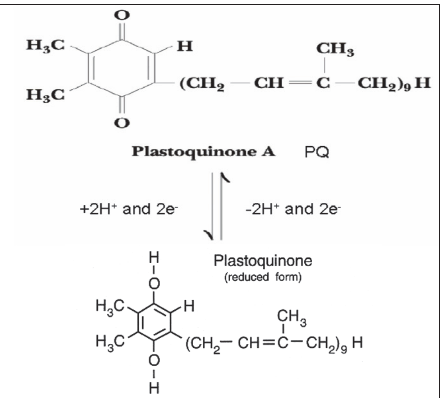




Interesting reading below--- (not examined – just for interest)
http://www.chm.bris.ac.uk/motm/oec/motm.htm

	Key points from this unit
1	24 g in the 70 kg man. About 90% is in bone and muscle (meq?). Meaning? Deficiency is rare in adults - alcoholism, burns, renal disease, cirrhosis of the liver, cardiovascular disorders. Mg deficiency can result in disastrous consequences - seizures, coma, death Excess leads to anesthesia - ie a coma-like condition
2	The role of Mg in mammals is widespread and includes not only a role in activating many enzymes, particularly phosphorylation Ca/Mg-ATPases, Also, heart disease in hard-water areas (eg London, UK) much less than in soft-water areas (Glasgow, UK).
3	Conversion of solar energy into a synthetic organic driving force – once the first reaction occurred; there was no going back – why not?
4	All photons absorbed between 400 and 700 nm can run photosynthesis. But all are used at energy equivalent of a red 660 nm photon. (Why? Remember the energy level diagram).
5	Plastocyanin (Pc) is a small (10.5 kDa) Cu-containing protein which acts as an electron carrier between the cytochrome b_6f and photosystem 1 (PS1) complexes in the photosynthetic electron-transfer chain. Pc belongs to the group of so called type 1 copper proteins which are characterized by a strong blue color. 2^0 and 3^0 structure is? β pleated sheet. The copper(II) d^9 ion near the top is coordinated in an approx. tetrahedral symmetry by His-37, Cys-84, His-87 and Met-92.(N, SH, N, CSC)Cu flips 1+ to 2+ and back $Cu^{2+}Pc + e^- \rightarrow Cu^{+}Pc$ - 

	Why does this work - what colour do you predict Pc is when reduced? http://www.nmrfam.wisc.edu/~volkman/research/plast.html
6	The scheme below summarizes the overall reaction catalyzed by PSII LIGHT/Chlorophyll PSII $2H_2O + 2PQ \rightarrow O_2 + 2PQ(2H)$ or PQH_2
	PSI: Photosystem I the primary electron donor is P700. Accepts electrons from a bound (PC) plastocyanin. Reduces (Fd) ferredoxin, an Fe/S (this time Fe_4S_4) protein. NADP+ is reduced to NADPH from ferredoxin by ferredoxin-NADP+ oxidoreductase.
	The chemical balance summary is very important **Light driven reactions:** 12 NADP+ + 18 ADP + 18 P + 6 H^+ + 48 $h\nu$ (photons) $\rightarrow \rightarrow$ $6O_2$ + 12 NADPH + 18 ATP + $6H_2O$
	The Calvin reaction is: $6CO_2$ + 12NADPH + 18ATP + $12H_2O \rightarrow\rightarrow\rightarrow\rightarrow$ $C_6H_{12}O_6$ + 12NADP+ + 18ADP + 18Pi + $6H^+$ notice imbalance of NADP and ATP 12:18.

7	Overall: $6H2O + 6CO_2 + 48\ h\nu \rightarrow C_6H_{12}O_6 + 6O_2$ Plastoquinone PQ is: (PQ is not plastoCYANIN!) PQ molecule and reaction 
8	Why are the structural components in the leaf so important to photosynthesis?
9	At what point do we have: H_2O split to evolve O_2. and NADPH synthesized?
10	$ADP + P_i \rightarrow ATP + H_2O$ (is an endergonic reaction (why obviously?) - needs energy from the proton gradient). Where is the proton gradient coming from? The H^+ set up a gradient – that gradient = a voltage – a driving force across the membrane.
11	Nicotinamide adenine dinucleotide (NAD) consists of two ribose rings, one with adenine attached to its 1' carbon atom and the other with nicotinamide at this position; these two sugar-heterocycle moieties are joined together by a bridge of two phosphate groups through the 5' carbons. In $NADP^+$, the ribose ring attached to the adenine has an additional phosphate group at the 2' position.