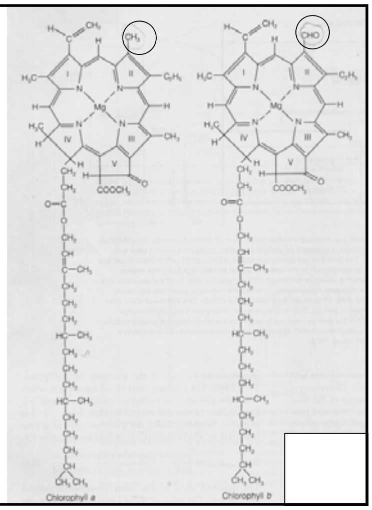
Let's take a closer look, from small to large spatial scales…

A. Chlorophyll Molecules

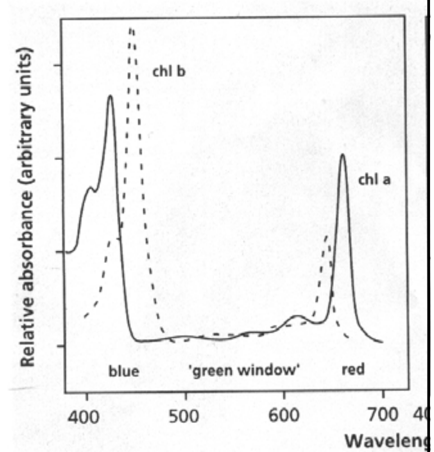
- at least 10 different types of chlorophylls, a and b are the most common and the only kind found in land plants.
- hydrocarbon tail anchors chl to photosynthetic membrane.
- ring structure is where photons are absorbed



Absorption spectra are similar, and explain why leaves are green.

Note: all blue photons absorbed are quickly translated into the 'red' excited state of Chl (the remaining energy is lost as heat).

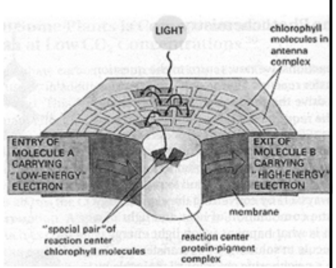
Thus, red photons exclusively power photosynthesis.



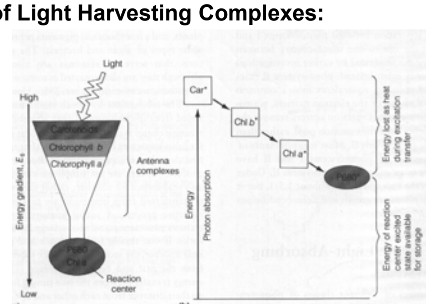
Let's take a closer look…

B. Organization of chlorophylls – antenna, or light harvesting complexes

- Hundreds of chlorphyll molecules per reaction center
- Reaction center also made of chlorophyll (a 'special pair', embedded in a membrane-spanning protein
- Highly schematic (only bacterial antenna complexes resolved so far)



A fascinating factiod regarding Chl a, Chl b, and the function of Light Harvesting Complexes:



-**recall Chl b (a) absorbs maximally at 650 (670) nm**
-**Thus, excitation energy can transfer easily from Chl b to a, but not from Chl a to b (the extra energy lost as heat).**
- **More Chl b on the outer portions of the LHC effectively funnels energy directionally to the reaction center.**

The fate of photonically-excited chlorophyll:

Three things can happen:

1. Energy funneled to the reaction center, used for photosynthesis ('good' outcome)

2. Chlorophyll returns to ground state and loses energy as heat ('bad')

3. Chlorophyll re-emits a photon (flourescence). Also no good for photosynthesis – indicates a backup in electron flow – acceptors saturated, indicative of stress.

Question: How can a chlorophyll give up energy as 'heat'?

Quantum Yield:

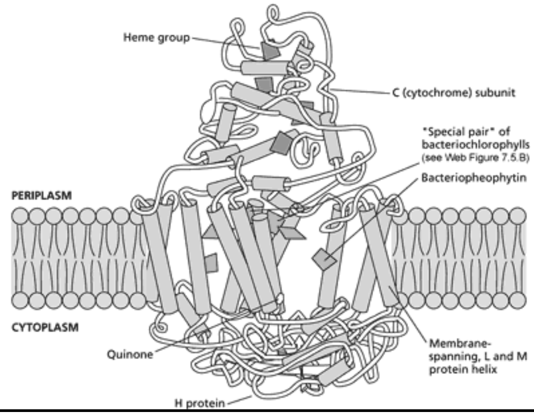
The ratio of photons making it through to photochemistry to total absorbed photons.

Any guesses?

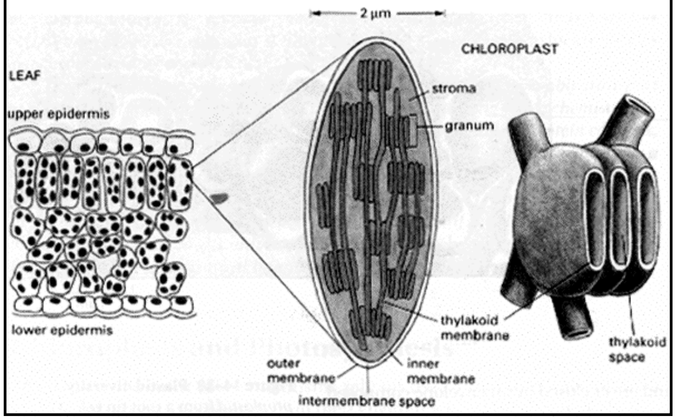
In functional chloroplasts, about 0.95 for photochemistry (in dim light)! The other 0.05 is flouresced, and almost none is lost as heat.

Bottom line: Photosynthetic photon harvesting is extremely efficient!

Reaction centers are bound in a phospholipid membrane. Details of a bacterial reaction center (won a Nobel prize '88)



Antenna and reaction centers are embedded in thylakoid membranes, which are stacked (grana) and unstacked, inside Chloroplasts, which are inside leaf mesophyll cells.



Going a bit deeper…

Antenna complexes and reaction centers together are called a "Photosystem"

There are 2 photosystems – PSI and PSII - that play a coordinated role with each other in converting light into chemical energy.

Let's look at features and coordination of PSI and PSII …

PSI and PSII are concentrated in different areas –
Not entirely clear why
But indicates loose stoichiometric linkage.

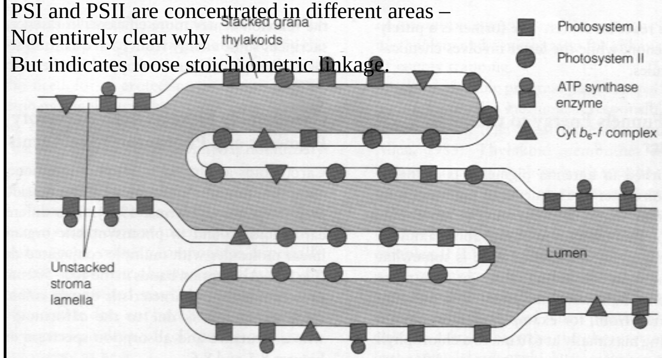
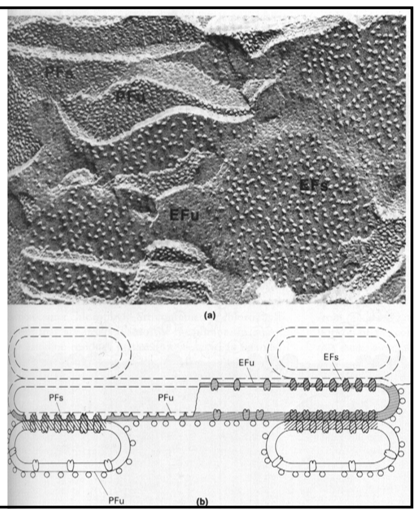


FIGURE 8.20. Organization of the protein complexes of the thylakoid membrane. Photosystem II is located predominantly in the stacked regions of the thylakoid membrane, while photosystem I and the ATP synthesizing enzyme are found in the unstacked regions, protruding into the stroma. Cytochrome b_6-f complexes are evenly distributed. This lateral separation of the two photosystems requires that electrons and protons produced by photosystem II be transported a considerable distance before they can be acted on by photosystem I and the ATP coupling enzyme.

SEM imagery allows us to see individual protein complexes (including photosystems I and II) spanning thylakoid membranes!



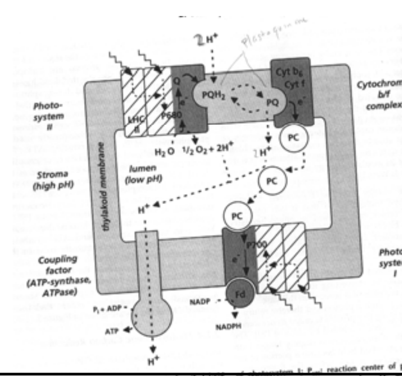
The two photosystems play distinct roles, along with other membrane bound and free proteins, to convert light to chemical energy.

PSII splits water:
H20 -> ½ O2 + 2e- + 2H+

Both the H+ and e- end up generating chemical energy.

H+ builds up (acidifies) the lumen, building a proton gradient across the membrane. This gradient drives ATP synthesis.

Electrons are transferred through several protein electron acceptor/donors to PSI, which, using light, transfers electrons from PC to Fd, to NADPH.



Taking stock…

- We have just covered the major features of the *light* reactions of photosynthesis.

-major processes included

- **-Light absorption and funneling**
- **-Splitting of water, liberating protons and electrons**
- **-Protons, electrons fuel the generation of energy rich molecules ATP and NADPH.**

-Next: How this ATP and NADPH is used in dark reactions to build energy rich carbon compounds.

Photosynthetic Carbon Reduction

a.k.a. the Dark Reactions
a.k.a. the Calvin Cycle

Photosynthetic Carbon Reduction

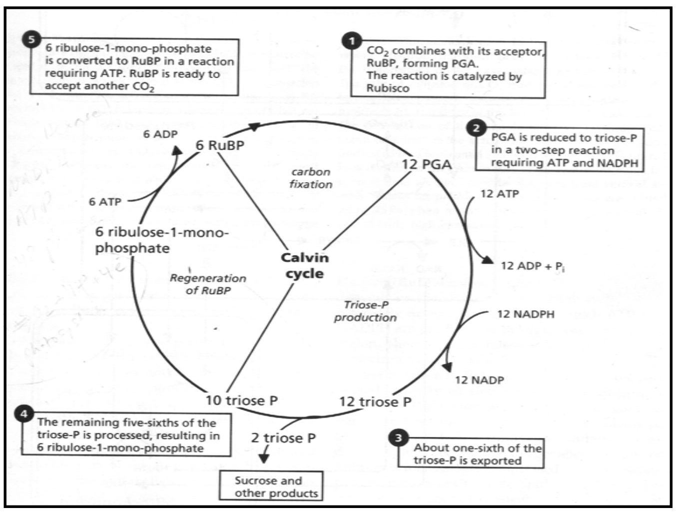
Three major steps:

1. *Fix*, or chemically bind, CO2, to an acceptor molecule (RuBP), forming a new intermediate molecule (PGA)

2. *Produce* sugar from PGA, using ATP, NADPH from the light reactions

3. *Regenerate* RuBP, from some of the sugar produced in step 2. Export the rest of the sugar.

Let's take a look at each step in sequence…



Carboxylation

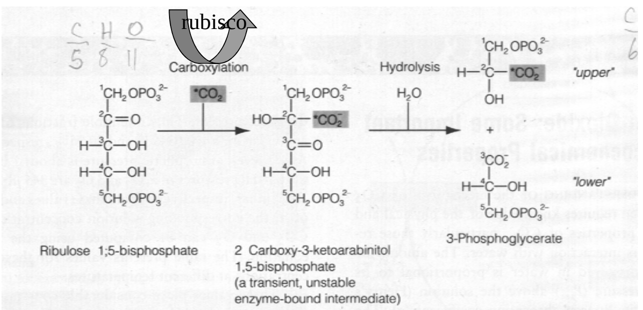
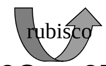


FIGURE 9.3. The carboxylation of ribulose 1,5-bisphosphate, catalyzed by Rubisco, proceeds in two stages, carboxylation and hydrolysis. Carboxylation involves the addition of CO_2 to carbon 2 (C-2) of ribulose 1,5-bisphosphate to form the unstable, enzyme-bound intermediate, 2-carboxy-3-ketoarabinitol 1,5-bisphosphate, which undergoes hydrolysis to yield two molecules of the stable product, 3-phosphoglycerate. The two molecules of 3-phosphoglycerate, "upper" and "lower," are distinguished by the fact that the "upper" molecule contains the newly incorporated carbon dioxide, designated as $*CO_2$.

As long as Rubp and Rubisco are around (which are expensive to make), the carboxylation reaction is very favorable (proceeds in the forward direction).



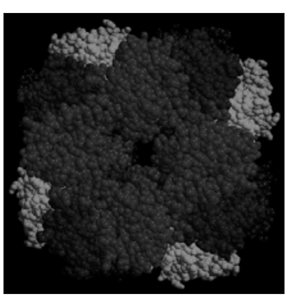
Rubp + CO2 +H2O -> 2PGA ΔG = -52 kJ/mol

Compare to RT = 2.5 kJ/mol and H-bonds = 10-40 kJ/mol

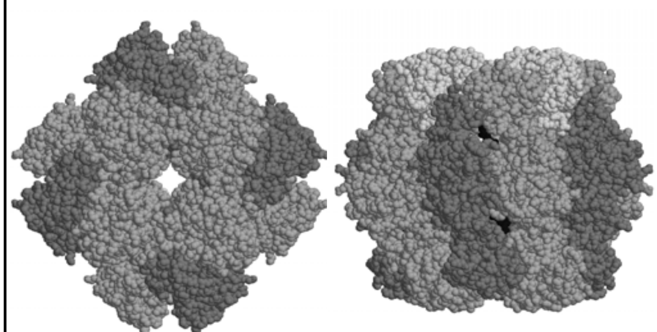
This is an important energetic 'ratchet' so that the Calvin cycle doesn't 'leak' backward.

Rubisco: Ribulose bisphosphate carboxylase oxygenase:

An amazing story behind this molecule…



The Story of Photosynthesis and Rubisco:



What is Rubisco?

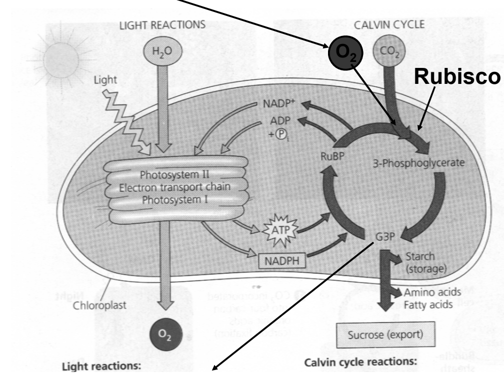
•Ribulose bisphosphate carboxylase oxygenase.

•A large macromolecule (56 kg/mol) found in leaf chloroplasts

•The most abundant single enzyme on earth (20 kg for every person on earth).

•Key catalyst for the Photosynthesis: $CO2 + H2O \rightarrow CH2O + O2$

Rubisco 'fixes' CO2 AND O2. No apparent use for O2!

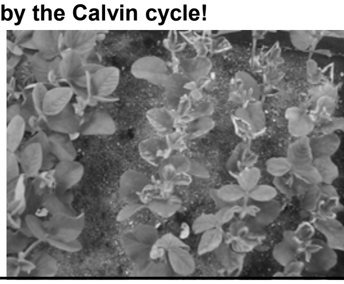


This is called C3 photosynthesis (3 carbon sugar)

Calvin cycle processing of O2 not only doesn't produce energy (ATP); it consumes large amounts of energy to get rid of waste products of O2 fixation (photorespiration)

This is a substantial cost to all plants.

In Soybeans, photorespiration consumes up to 50% of the carbon fixed by the Calvin cycle!



This really didn't matter when photosynthesis evolved

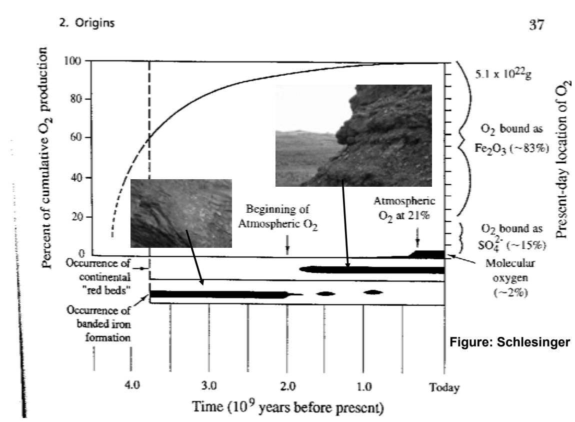
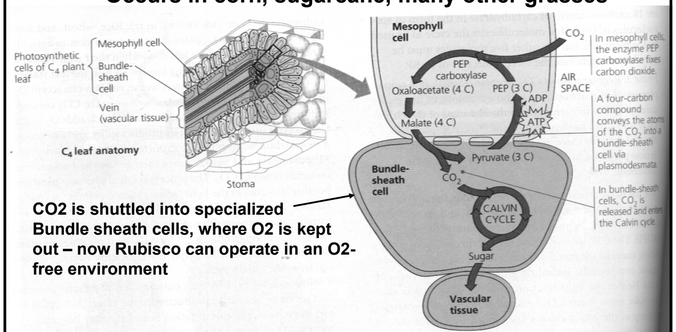


Figure: Schlesinger

But it became a problem with the rise of atmospheric O2

Evolution's answer: C4 photosynthesis – the ultimate 'gated community' in plants. CO2 sequestered, O2 kept out.

Occurs in corn, sugarcane, many other grasses



CO2 is shuttled into specialized Bundle sheath cells, where O2 is kept out – now Rubisco can operate in an O2-free environment

Important principle: Evolution doesn't start over; it build on previous (sometimes non-optimal) plans.

Fun C4 factoids:

- **C4 evolved 20-30 million years ago in response to low global CO2 levels.**
- **It evolved independently over 45 times in 19 angiosperm families! Convergent Evolution.**
- **C4 has energetic costs as well as benefits, and was (is) found mostly in dry areas. Why dry areas? Plants must close stomates to conserve water, but this makes CO2 even more scarce in photosynthesizing cells, and O2 a greater burden.**
- **If CO2 continues to rise, C3 plants may gain a competitive advantage over C4.**

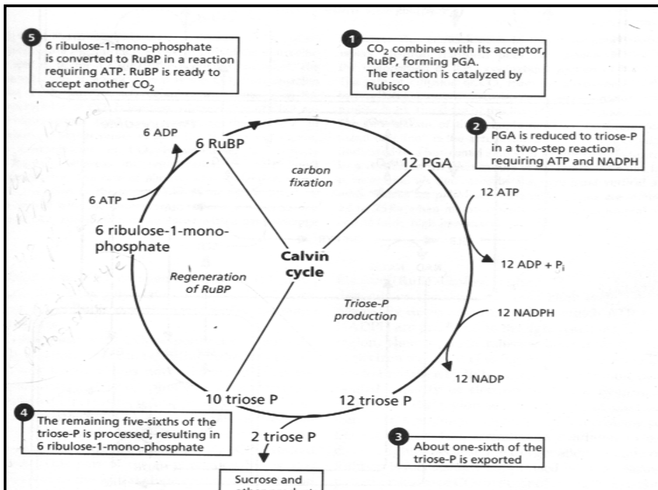
The moral of the story:

Collectively, plants altered their own environments detrimentally, with 'unanticipated' effects.

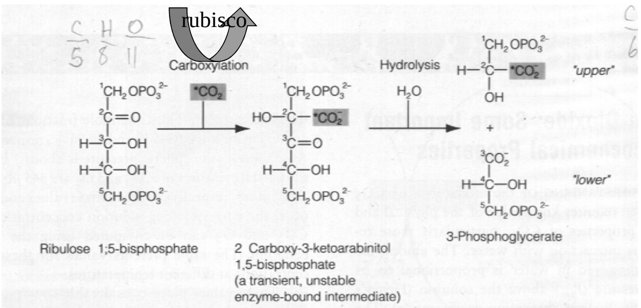
A couple other points:

On the other hand, they created a hospitable environment for aerobic heterotrophs (like us)!

O_2 in earth's atmosphere has been used as a criticism of the Gaia Hypothesis



Carboxylation



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Triose – Phosphate (3-carbon sugar) production:

2. *3-Phosphoglycerate kinase*
   3-phosphoglycerate + ATP → 1,3-bisphosphoglycerate + ADP

3. *NADP:glyceraldehyde-3-phosphate dehydrogenase*
   1,3-bisphosphoglycerate + NADPH + H^+ → glyceraldehyde 3-phosphate + $NADP^+$ + $HOPO_3^{2-}$

6-C sugars easily made from

Key point: We are starting to use ATP and NADPH. (PGA + ATP + NADPH -> Triose-P)