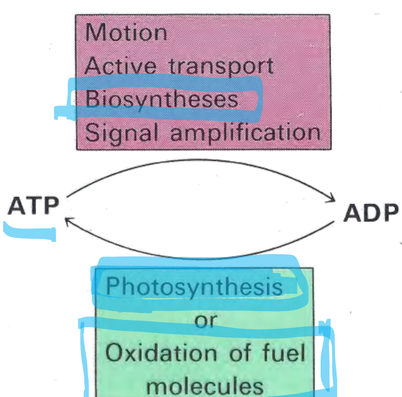
ANABOLISM I
Carbohydrates

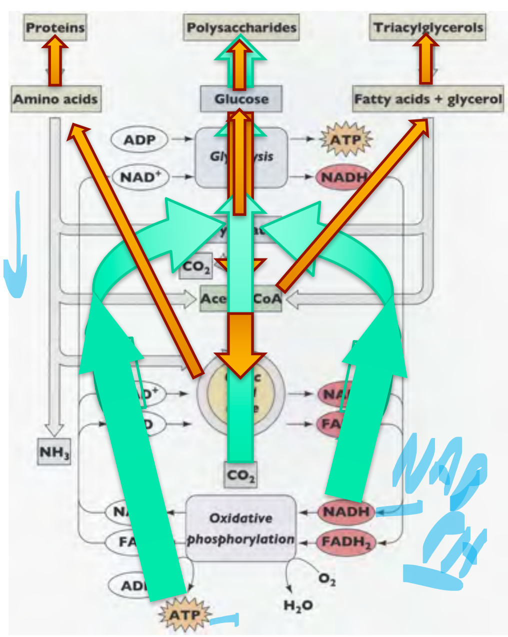
Photosynthesis and Carbohydrate Synthesis in Plants

Introduction to Anabolic Pathways

So far, we were mainly concerned with ***CATABOLISM***: how to extract energy from biomolecules.

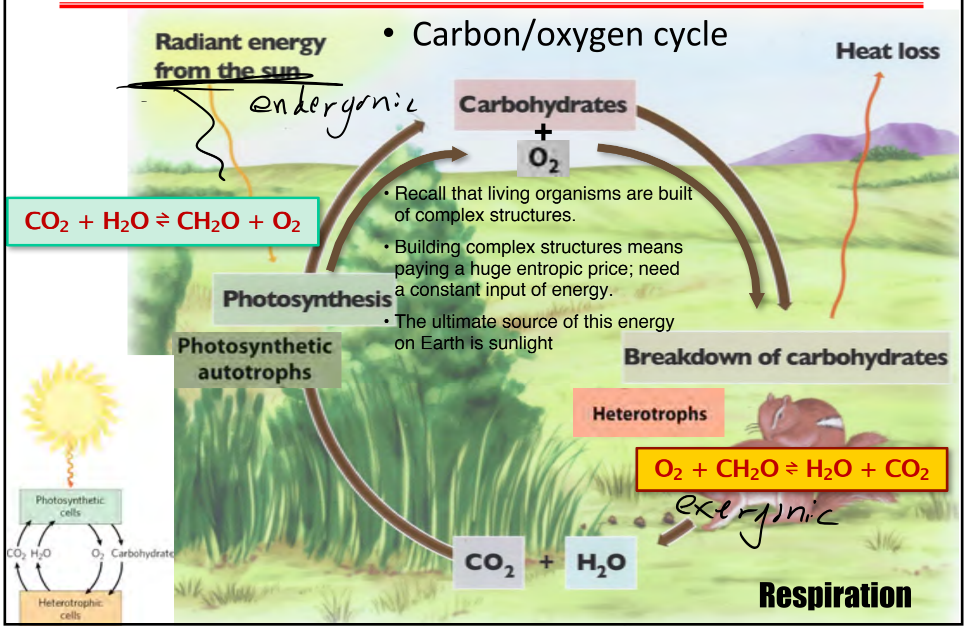
The rest of the semester we'll be concerned with ***ANABOLISM***: how to build biomolecules.





Photosynthesis

Metabolism



- Carbon/oxygen cycle
  - Recall that living organisms are built of complex structures.
  - Building complex structures means paying a huge entropic price; need a constant input of energy.
  - The ultimate source of this energy on Earth is sunlight

Photosynthesis

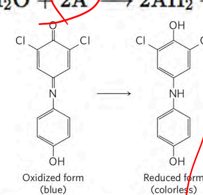
Key topics:

- Photosynthetic electron transfer and photophosphorylation
- CO_2 assimilation in photosynthetic organisms
- Photorespiration in C_3 plants
- Avoiding photorespiration in C_4 plants

Kornberg
Lecture 03.17.17
(33:00-36:17) 3 min

Key experiments:

$$2H_2O + 2A \xrightarrow{\text{light}} 2AH_2 + O_2.$$



❖ Light caused O_2 (Hill reaction)

∴light causes electron flow, and O2 evolution did not involve any CO_2.

❖ Light caused reduction of NADPH (Ochoa reaction)

$$2H_2O + 2NADP^+ \xrightarrow{\text{light}} 2NADPH + 2H^+ + O_2.$$

∴light causes electron flow to NADPH (=A)

….The lack of involvement of CO_2 in light caused oxygen production was definitively shown in 1941

Photosynthesis

$CO_2 + H_2O \rightleftharpoons CH_2O + O_2$

Use heavy isotope of oxygen (^{18}O) to "label" the oxygen separately in CO_2 and H_2O, then test the O_2 that is produced.

HYPOTHESIS▶ The oxygen released by photosynthesis comes from water rather than CO_2.

Photosynthesis

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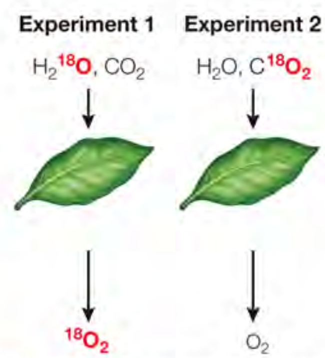
METHOD

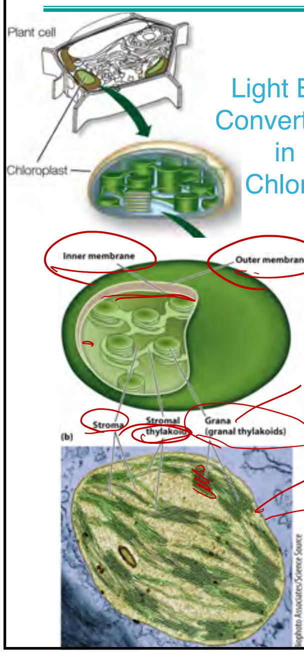
RESULTS



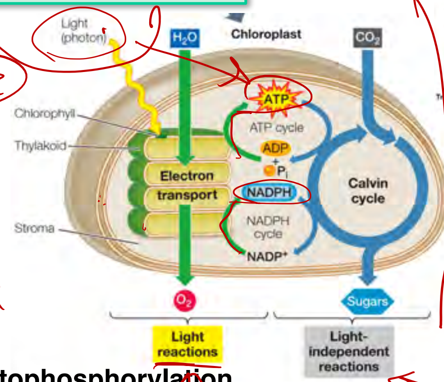
CONCLUSION▶ Water is the source of the oxygen atoms in the O_2 produced by photosynthesis.

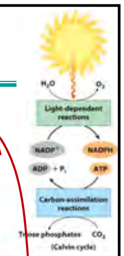
Photosynthesis

$CO_2 + H_2O \rightleftharpoons CH_2O + O_2$



Light Energy is Converted to ATP in Plant Chloroplasts





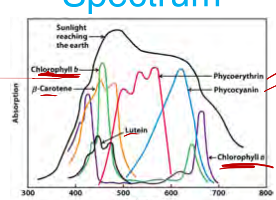
Photophosphorylation

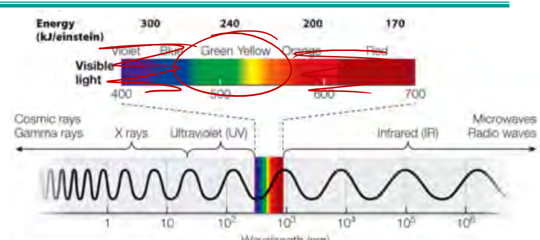
$2H_2O \rightleftharpoons O_2 + 4e^- + 4H^+$ ($2NADPH + 2H^+$)

$4e^- + 4H^+ + CO_2 \rightleftharpoons CH_2O + H_2O$

Photosynthesis

The Electromagnetic Spectrum





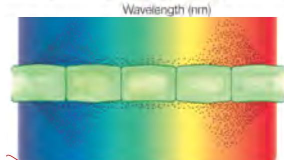
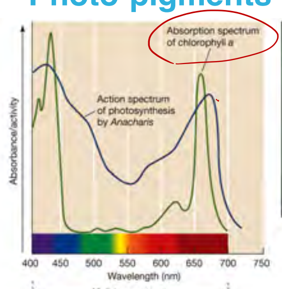
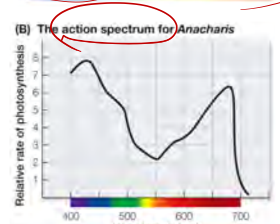


Photo-pigments





Photosynthesis

- If Light Energy is Converted to ATP, how much light is needed?
- What is the energy in ONE photon of light?
  - There is enough Light Energy to make >5 ATP
  - How do you convert photons to chemical energy?
  - You go through electrons….
  - So we have to do re-dox (ox-phos in reverse!

Max Planck was a physicist who initiated the particle theory of light; its not just electromagnetic waves. Einstein developed the concept of a photon, or a quanta of light. Thus, quantum mechanics was born.

Electromagnetic **energy** could be emitted only in quantized form, in other words, the energy could only be a multiple of an elementary unit:

$$E = h\nu \quad \nu = c/\lambda$$
$$= h \cdot c/\lambda$$

where h is Planck's constant, also known as Planck's action quantum, and ν is the frequency of the radiation. Note that the units of energy are represented by $h\nu$ and not simply by ν. So, the energy comes in units and not just a spectrum or continuum.

Energy of one mole of photons (1 einstein):

h = Planck's constant (6.626×10^{-34} J•s)

$c = 3 \times 10^{8}$ m/s

$\lambda = 700 \times 10^{-9}$ m

$E = 2.84 \times 10^{-19}$ J/photon $\times$ 6.022×10^{23} photons/einstein

$E = 17.1 \times 10^{4}$ J/einstein

E = 171 kJ/einstein

E = 41 kcal/mole of photons

E = +1.8 V/mole of photons

Photosynthesis

- If we have to do re-dox, what is it that must be done?

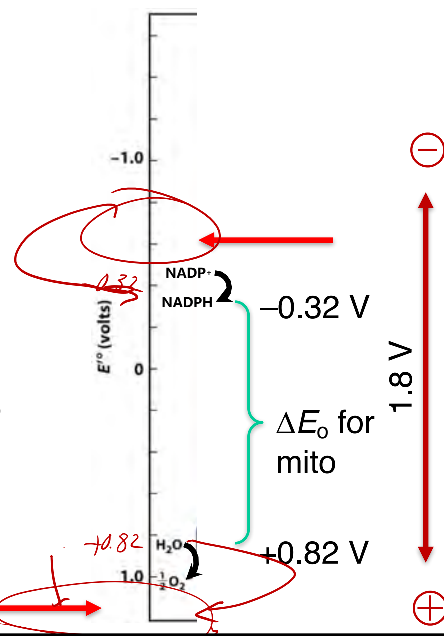
$$CO_2 + H_2O \rightleftharpoons CH_2O + O_2$$

Because we know that oxygen comes from the water, using the energy from the light, and we know that NADPH is the reductant…..we have a problem!

We need an electron acceptor with E_o more positive than water

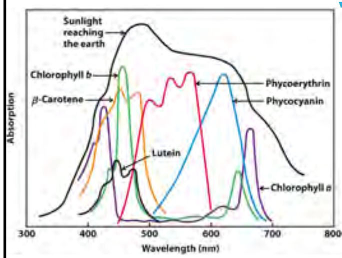
We need an electron donor with E_o more negative than NADPH

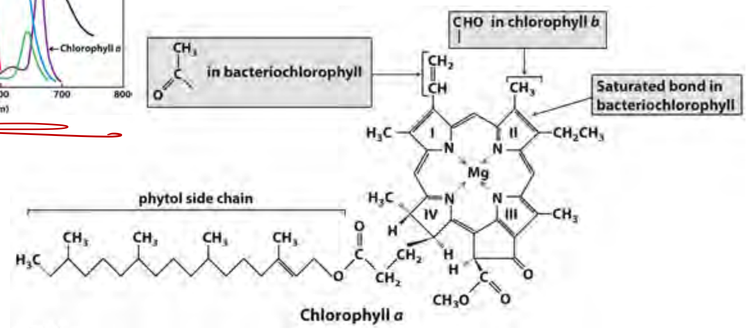
- First thing is to absorb the light. What does this?

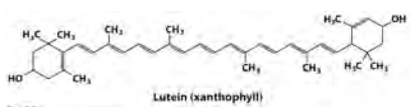


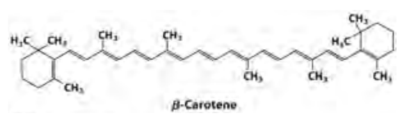
Photosynthesis

Various Pigments Harvest the Light Energy



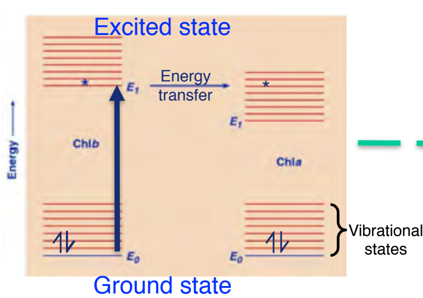


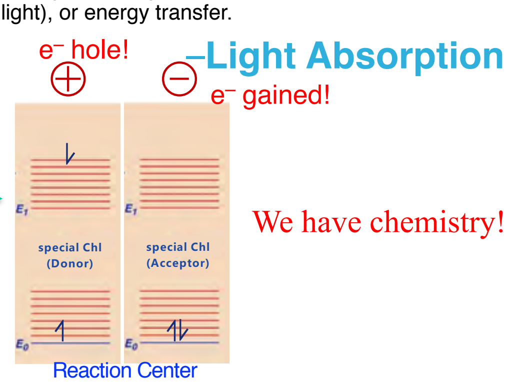




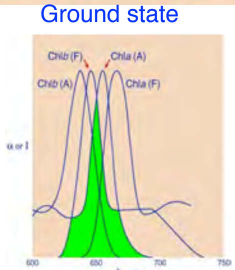
Photosynthesis

The excited state has several choices for dissipating the energy:
internal conversion (heat), fluorescence (emit light), or energy transfer.
Which occurs depends on several factors:





We have chemistry!

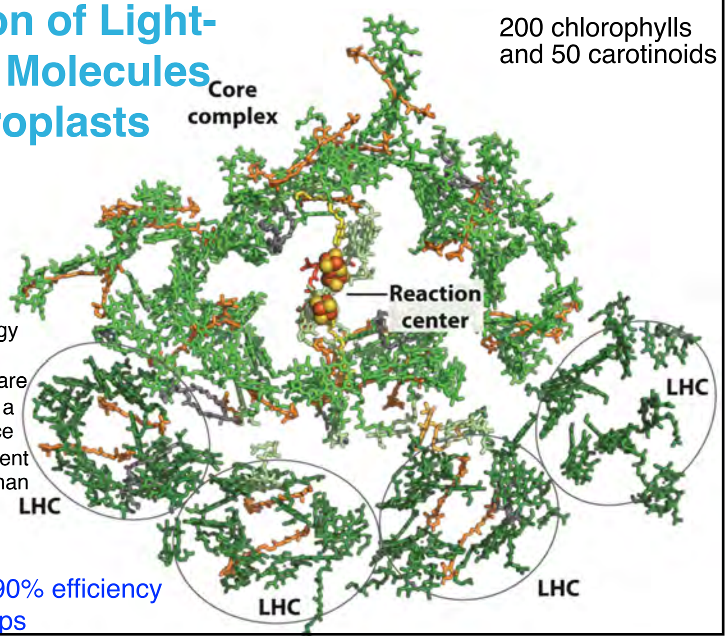


(1) The overlap of the fluorescence band of the donor and the absorption band of the acceptor (Förster's overlap integral).
(2) The distance between the two molecules; essentially a dipole-dipole interaction obeying Columb's law proportional to r^6. They have to be close.
(3) The orientation of the dipoles of the donor and the acceptor molecules.

Photosynthesis

Organization of Light-Absorbing Molecules in Chloroplasts

200 chlorophylls and 50 carotinoids

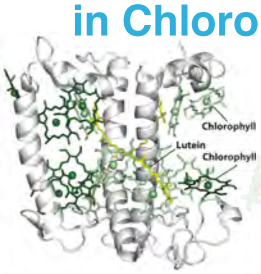


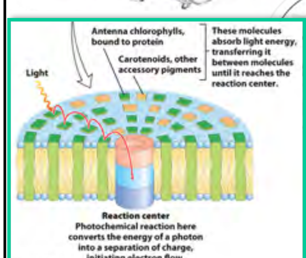
The probability of energy transfer is ~50% when the "critical distances" are of the order of 50 Å. In a chloroplast, the distance between different pigment molecules much less than 50 Å, so that the probability of energy transfer is high.

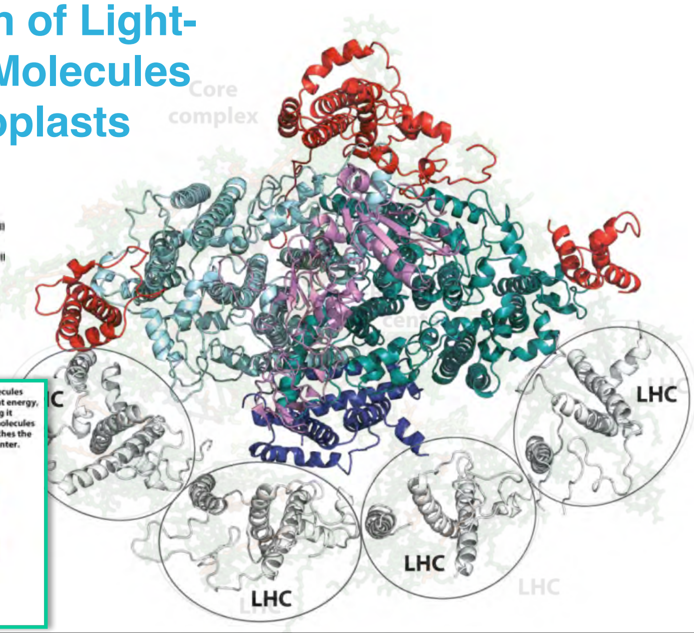
It is actually >90% efficiency and fast <100 ps

Photosynthesis

Organization of Light-Absorbing Molecules in Chloroplasts

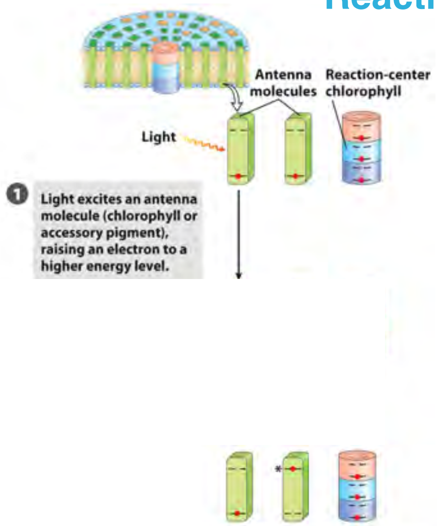






Photosynthesis

Harvested Light causes charge separation in the Reaction Center



Photosynthesis

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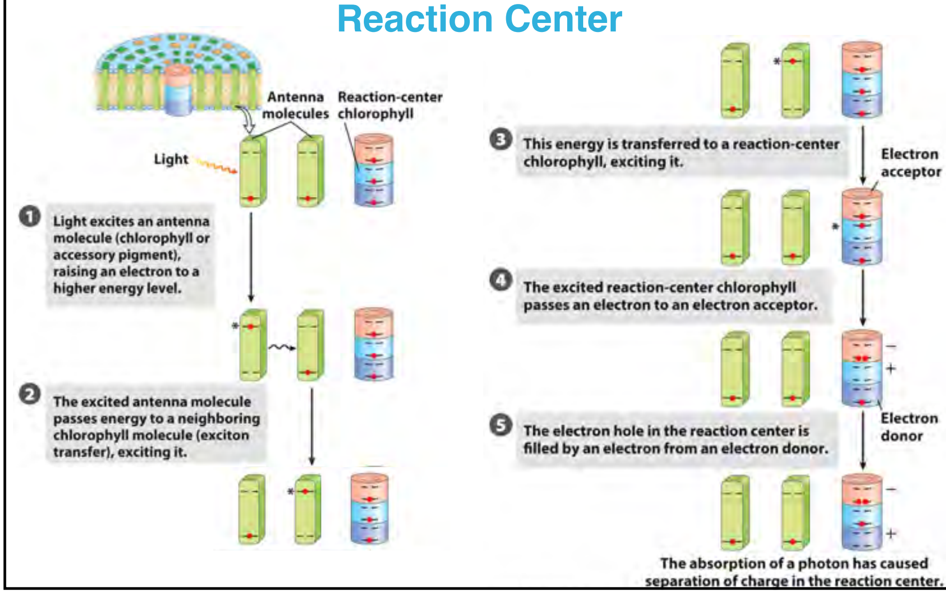

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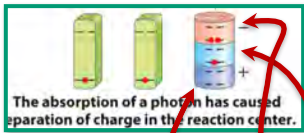
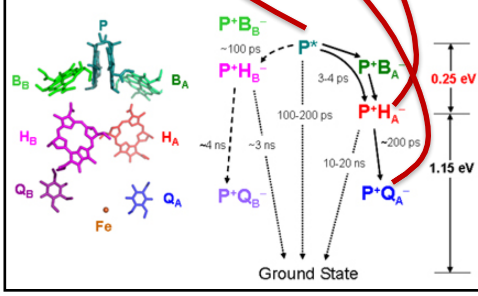
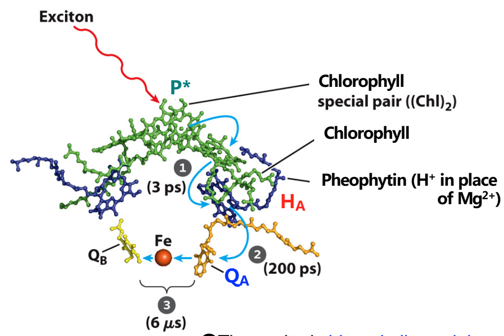


All these distances are ~10 Å





−1.45 V

+0.045 V

ΔE_o for PSII≈1.5 V

❶The excited chlorophyll special pair passes an electron through a chlorophyll monomer to pheophytin (very very fast).

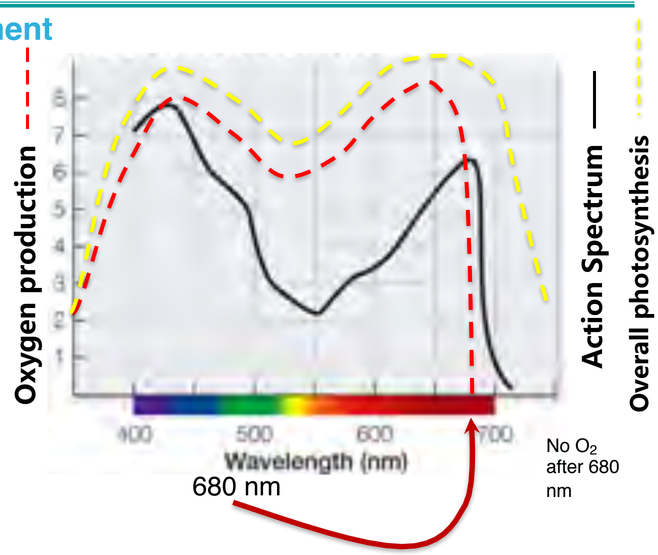
❷from which the electron moves rapidly to the tightly bound menaquinone, Q_A.

❸This quinone passes electrons much more slowly to the diffusible ubiquinone, Q_B, through the non-heme Fe.

Photosynthesis

Red-Drop Experiment

Keep yellow light on. Give flashes of higher and higher wavelengths



No O_2 after 680 nm

Conclusion is that there are two photosystems:

PS I (P700) &

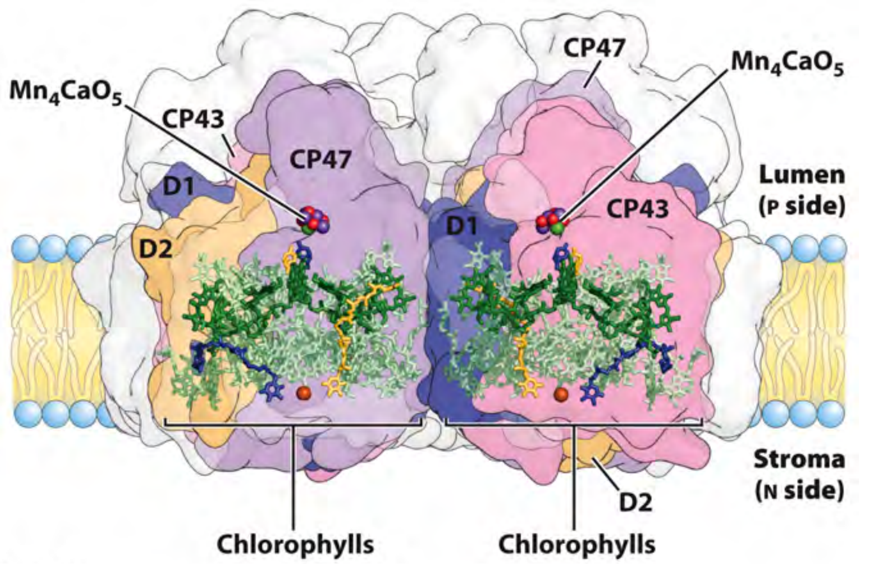
PS II (P680)

AND, PS II is responsible for O_2 production

∴ below 680 nm there is photosynthesis system that generates oxygen

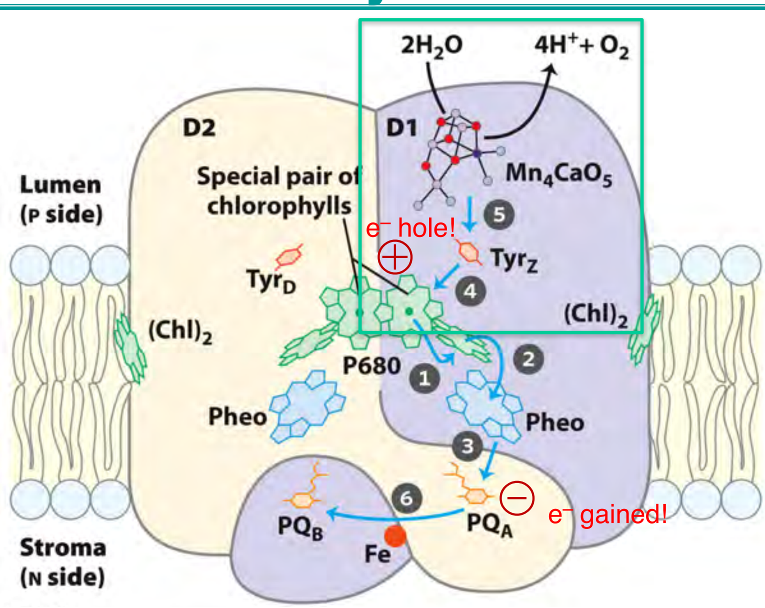
But, above 680 nm there must be another photosystem because the overall photosynthesis still goes on.

Photosynthesis



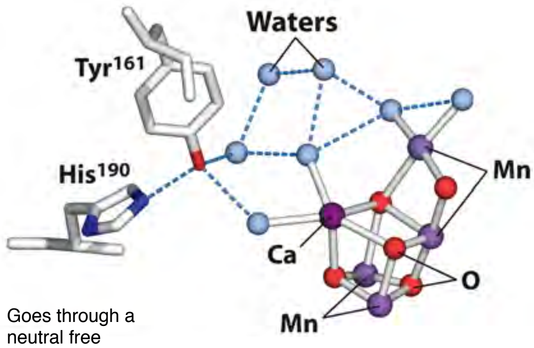
Photosystem II (P680)

Photosynthesis



Photosystem II Evolves Oxygen from Water

Photosynthesis



Goes through a neutral free radical: Y-O• + H•

The water-splitting complex offers single electrons to photosystem II to fill the hole after charge separation. After four electrons are freed from two waters, a single O_2 is released.
Overall reaction:

$2H_2O \rightleftharpoons O_2 + 4e^- + 4H^+$