OUTLINE:

Introduction and review
Transport
Glycogenolysis
Glycolysis
Other sugars
Pasteur: Anaerobic vs Aerobic

Exam-1 material

Fermentations
Pyruvate
Krebs' Cycle
Oxidative Phosphorylation
- Electron transport
- Chemiosmotic theory: Phosphorylation

Exam-2 material

Fat Catabolism
Fatty acid Catabolism
- Mobilization from tissues (mostly adipose)
- Activation of fatty acids
- Transport; carnitine
- Oxidation: b-oxidation, 4 steps:
  - Saturated FA
  - Unsaturated FA
  - Odd-chain FA
  - Ketone Bodies

Protein Catabolism
- Digestion, lysosome, Ubiquitin-Proteosome

Amino-Acid Degradation
- Dealing with the nitrogen
  - Urea Cycle
- Dealing with the carbon
  - Seven Families
    - One-carbon (1-C) metabolism; THF, SAM
    - PLP uses
- Convergence with Fatty acid-odd chain

Nucleic Acid and Nucleotide Degradation
- Nucleic Acids
- Nucleotides
  - Salvage pathway
  - Degradation of purines
  - Degradation of pyrimidines

Exam-3 material

ANABOLISM I: Carbohydrates

PHOTOSYNTHESIS:

- Overview of Photosynthesis
- Key experiments:
- Light Reactions
  - energy in a photon
  - pigments
  - HOW
  - Light absorbing complexes–"red-drop expt"
    - Reaction center
    - Photosystems (PS)
      - PSII – oxygen from water splitting
      - PSI – NADPH
- Proton Motive Force – ATP
- Carbon Assimilation – Calvin Cycle
  - Stage One – **Rubisco**
  - Stage Two – making sugar
  - Stage Three – remaking Ru $1,5P_2$
- Overview and regulation
- Calvin cycle connections to biosynthesis
- C4 versus C3 plants
- Kornberg cycle – glyoxylate

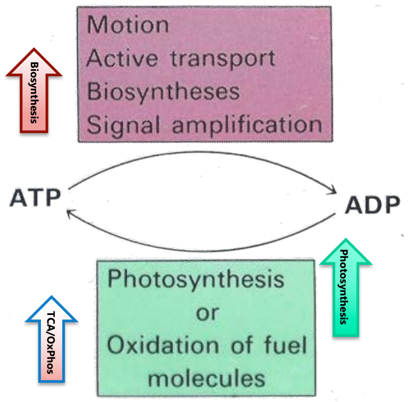
ANABOLISM I
Carbohydrates

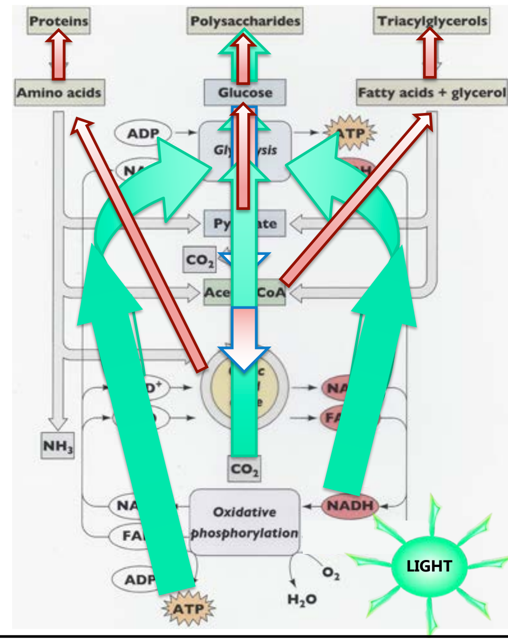
Photosynthesis and Carbohydrate Synthesis in Plants

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.

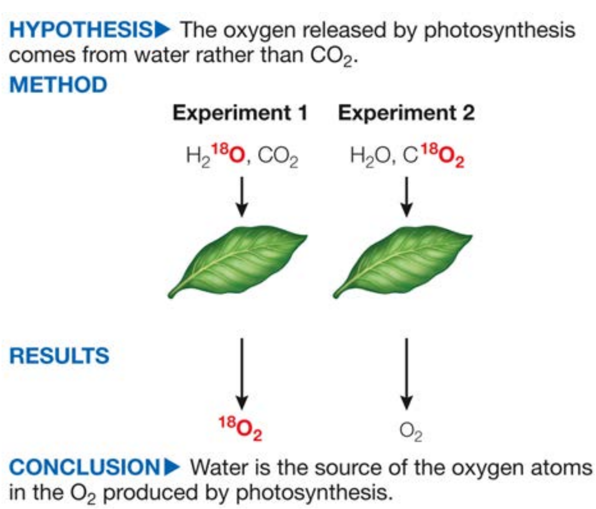




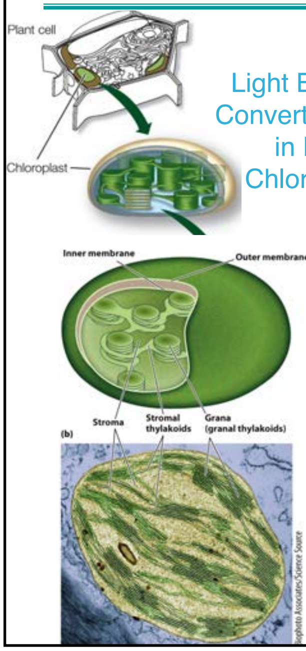
Photosynthesis

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

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.

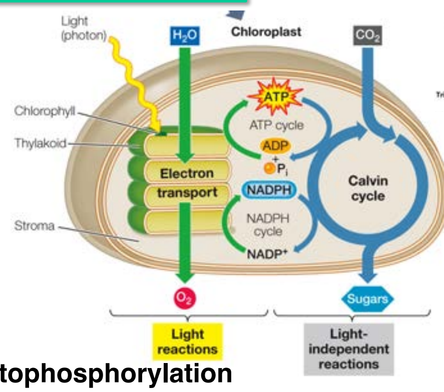


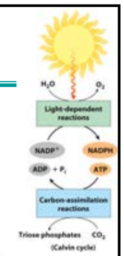
Photosynthesis



$CO_2 + H_2O \rightleftharpoons CH_2O + O_2$

Light Energy is Converted to ATP in Plant Chloroplasts





Photophosphorylation

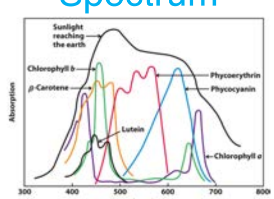
$2H_2O \rightleftharpoons O_2 + 4e^- + 4H^+$ $(2NADPH + 2H^+)$

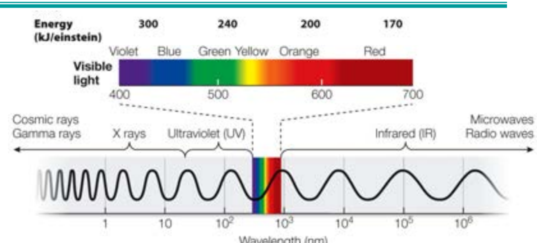
$4e^- + 4H^+ + CO_2 \rightleftharpoons CH_2O + H_2O$

Both of these half-reactions are VERY unfavorable!!

Photosynthesis

The Electromagnetic Spectrum





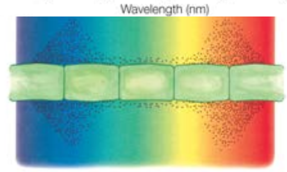
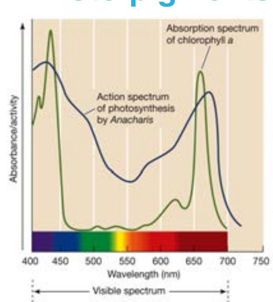
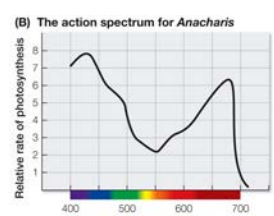


Photo-pigments





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!

1928: Walther Nernst, Albert Einstein, Max Planck, Robert Millikan, and Max Laue

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:

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

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 × 6.022×10^{23} photons/einstein

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

E = 171 kJ/einstein

E = 41 kcal per mole of photons….In terms of volts:

E = +1.8 volts per mole of photons

Photosynthesis

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

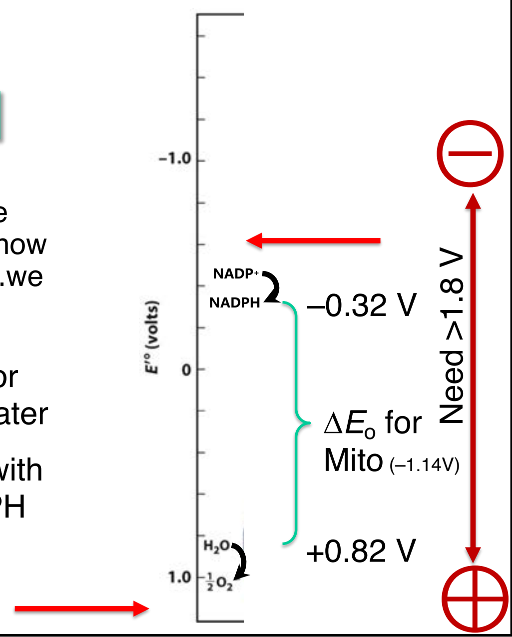
$$CO_2 + H_2O \rightleftharpoons CH_2O + O_2$$

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

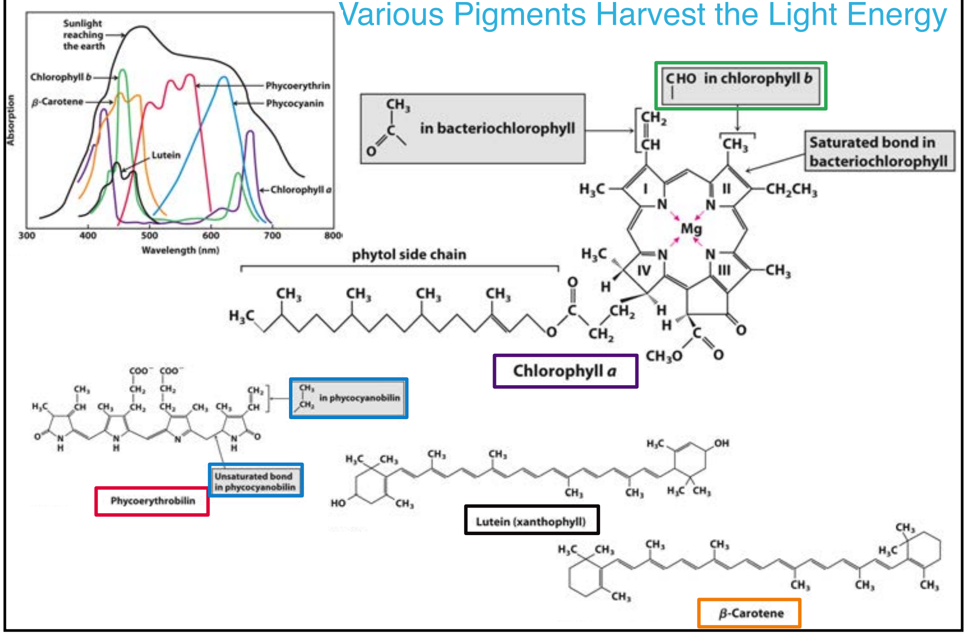
We need an electron donor with E_o more negative than NADPH

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



Photosynthesis

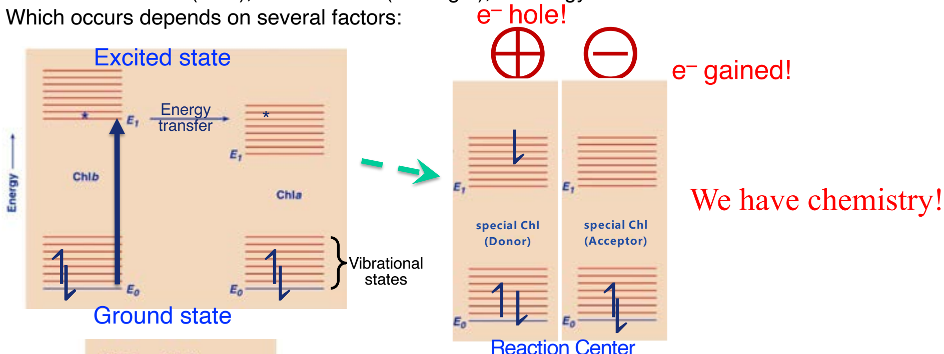
Various Pigments Harvest the Light Energy

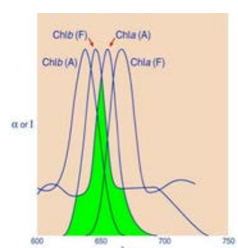


Photosynthesis

–Light Absorption

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:



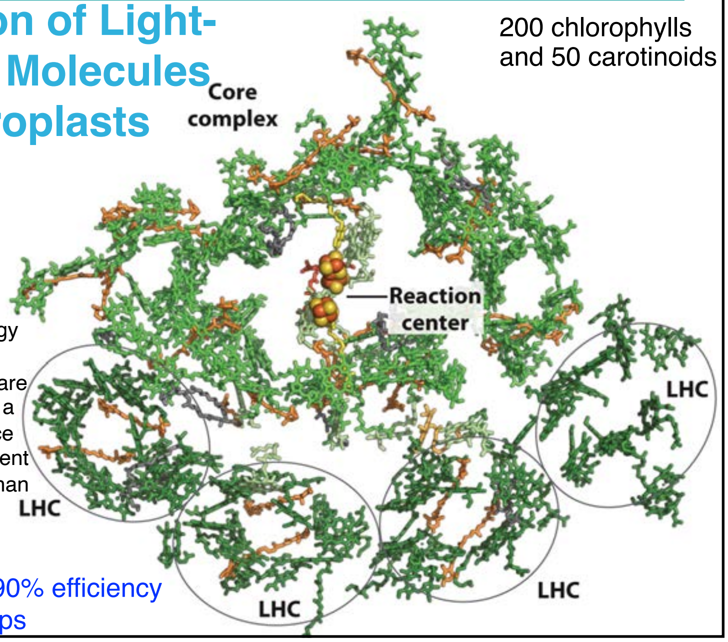


(1) The overlap of the fluorescence band of the donor and the absorption band of the acceptor (Förster's overlap integral).
(2) The distance between the two molecules; essentially a dipole-dipole interaction obeying Coulomb's law proportional to r^{6}. They have to be close.
(3) The orientation of the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

Photosynthesis

Organization of Light-Absorbing Molecules in Chloroplasts

200 chlorophylls and 50 carotinoids

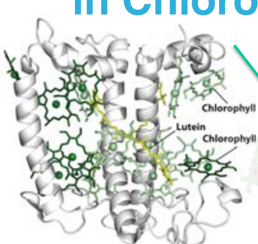


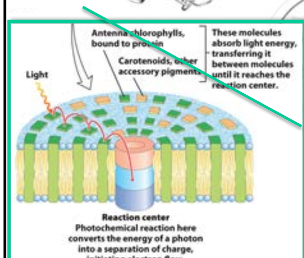
The probability of energy transfer is ~50% when the "critical distances" are of the order of 50 Å. In a chloroplast, the distance between different pigment molecules much less than 50 Å, so that the probability of energy transfer is high.

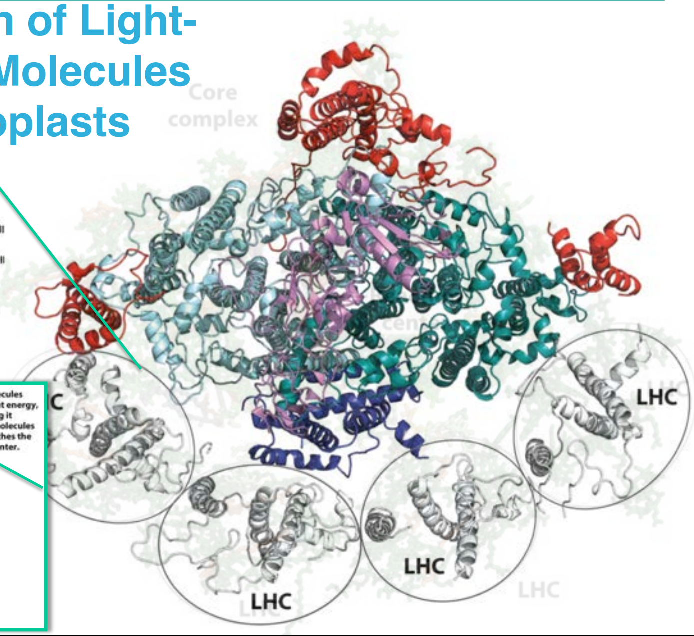
It is actually >90% efficiency and fast <100 ps

Photosynthesis

Organization of Light-Absorbing Molecules in Chloroplasts

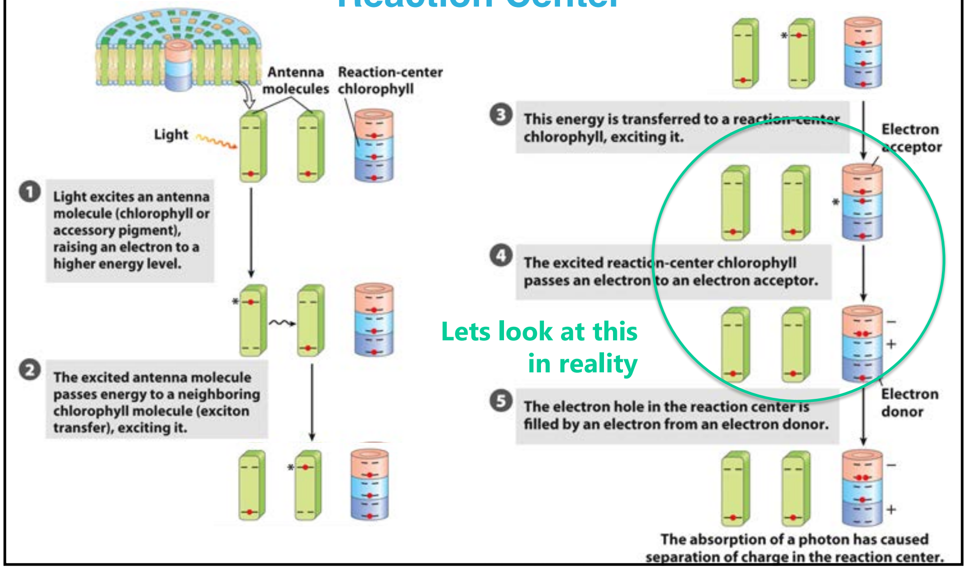






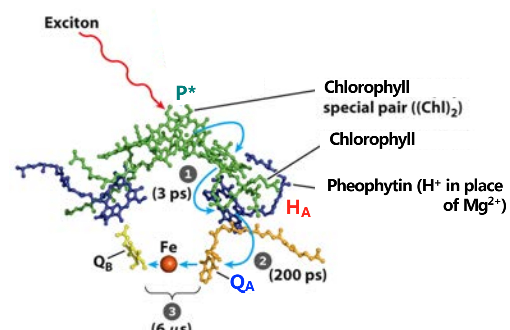
Photosynthesis

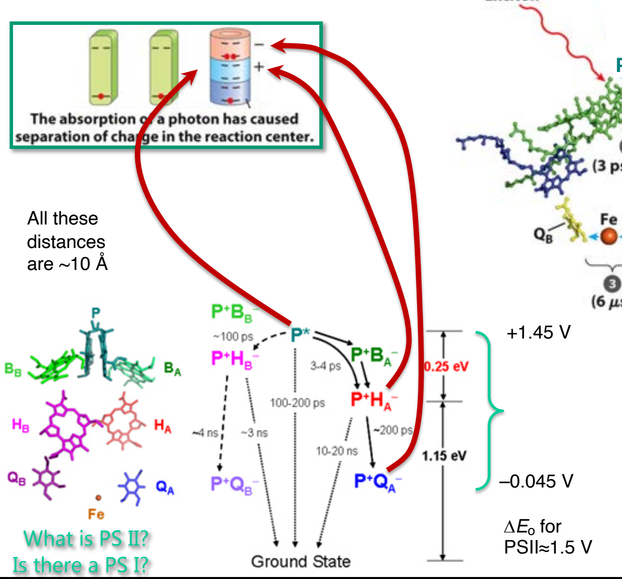
Harvested Light causes charge separation in the Reaction Center



Photosynthesis

Harvested Light causes charge separation in the Reaction Center





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.

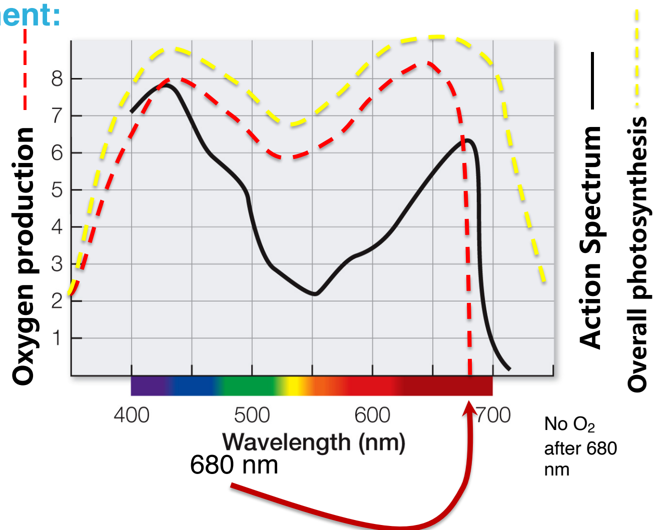
Photosynthesis

RED-DROP Experiment

How do we know there were two PSs?

Red-Drop Experiment:

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



Conclusion is that there are two photosystems:

PS I (P700) &

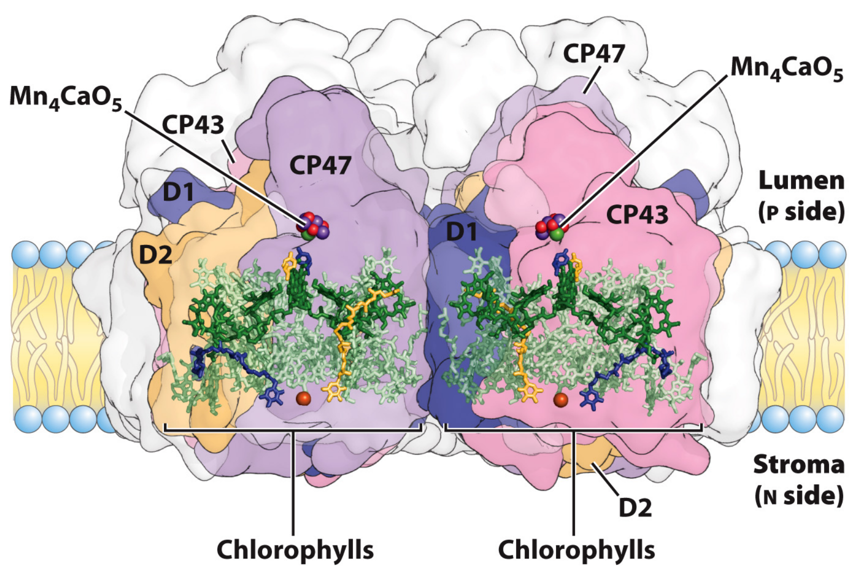
PS II (P680)

AND, PS II is responsible for O_2 production

∴ below 680 nm there is photosynthesis system that generates oxygen

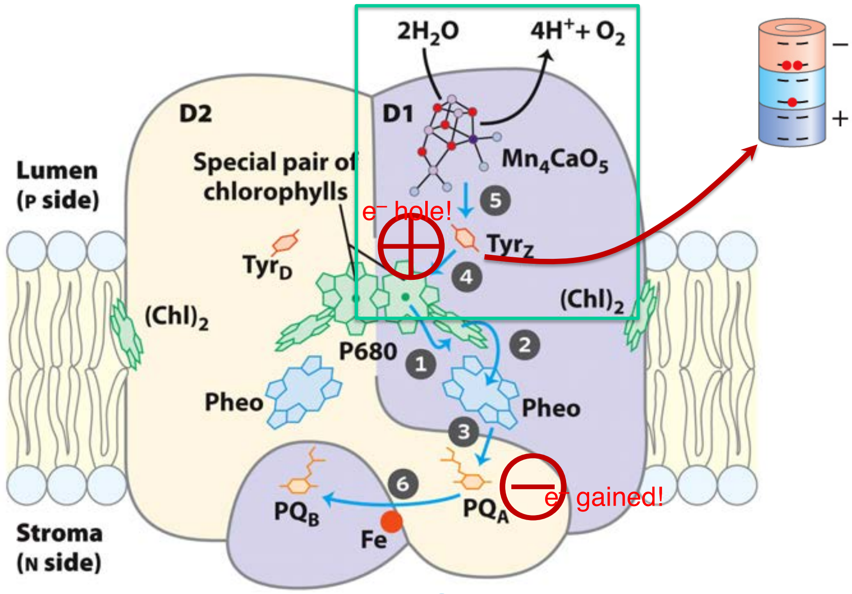
But, above 680 nm there must be another photosystem because the overall photosynthesis still goes on.

Photosynthesis



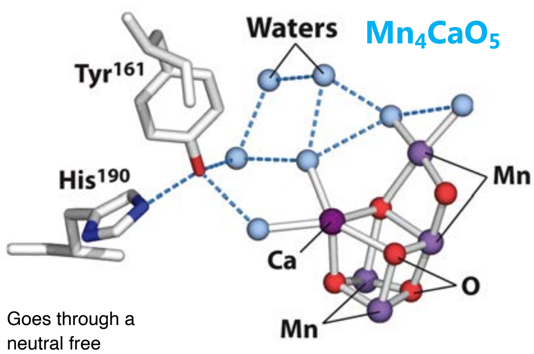
Photosystem II (P680)

Photosynthesis



Photosystem II Evolves Oxygen from Water

Photosynthesis



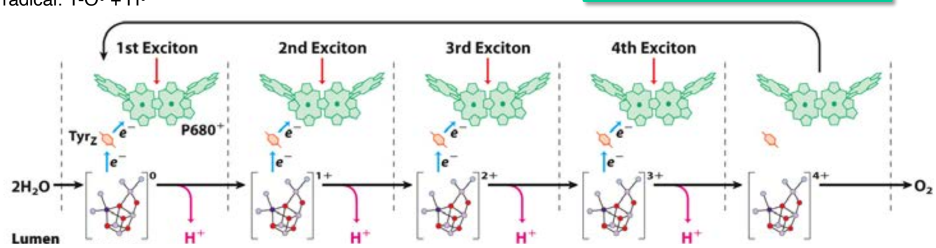
The water-splitting complex offers single electrons to photosystem II to fill the hole after charge separation.

After four electrons are freed from two waters, a single O_2 is released.

Overall reaction:

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

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

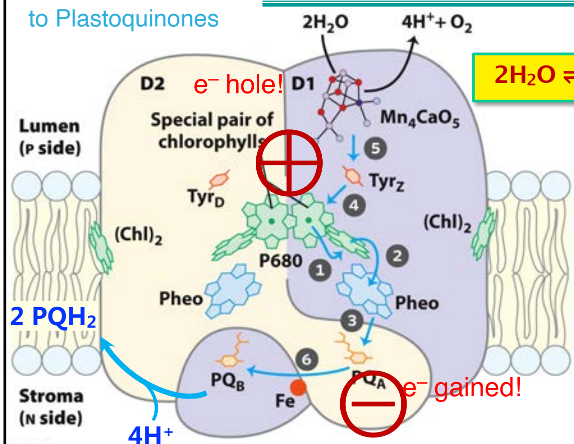


Photosynthesis

Photosystem II Transfers Electrons to Plastoquinones

[NOTE on what side of the thylakoid membrane is the water splitting machine……

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

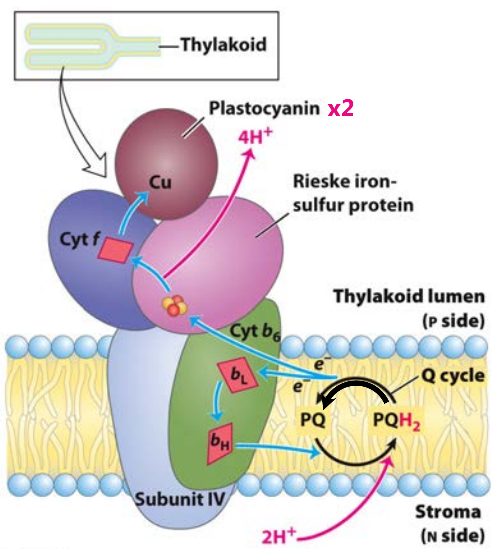


Recall that the ΔE_o is enough to provide an electron hole deep enough to dissociate water (E'_o +1.45V), but not a reductant with the ability to reduce $NADP^+$ (PQ, like CoQ, likes e– more than NADH).

Plastoquinones are structurally and functionally similar to ubiquinones (CoQ) found in the mitochondria.

These lipid-soluble small molecules transport two electrons to the cytochrome b_6f complex.

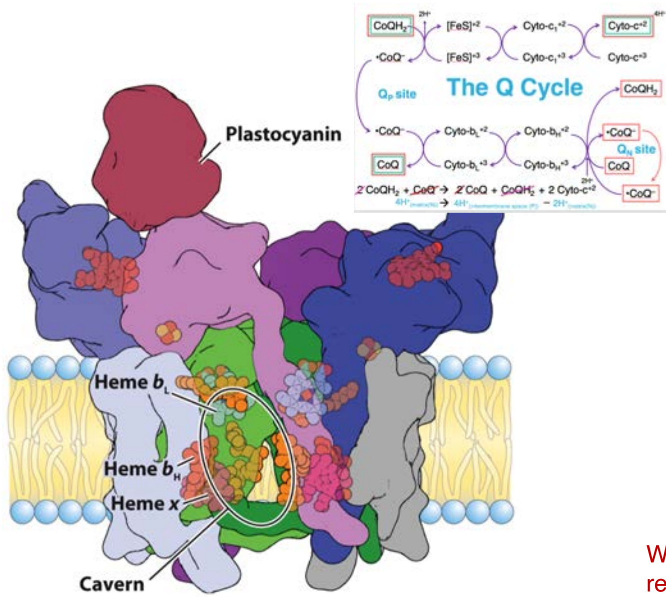
Photosynthesis

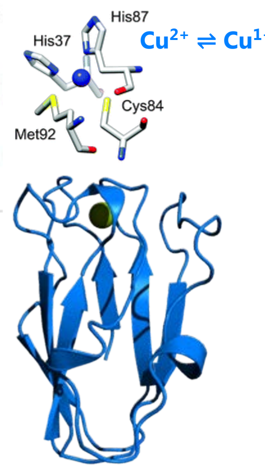


- Structurally and functionally similar to Complex III in the electron-transport chain
- Protons are removed from plastoquinones (PQH_2) as plastoquinones are oxidized (PQ).
- The PQ cycle is similar to the Q cycle in the ETC.
- Electrons are funneled to plastocyanin, a single electron carrier, which carries the electron to PS-I.

Cytochrome b_6f Complex Translocates Protons into the Lumen

Photosynthesis



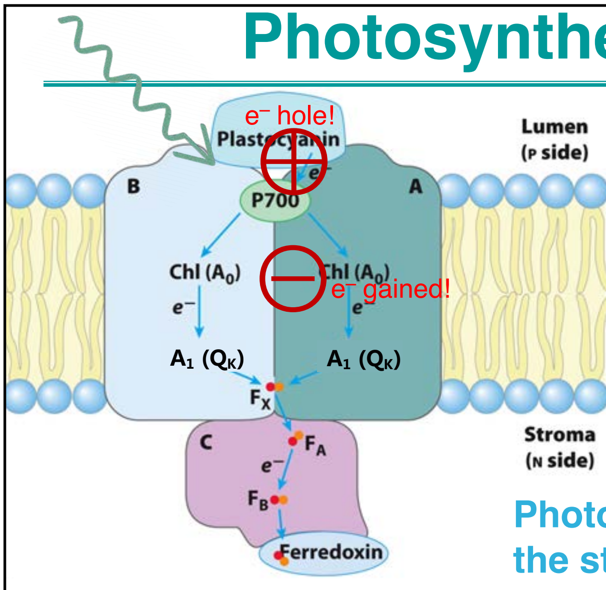


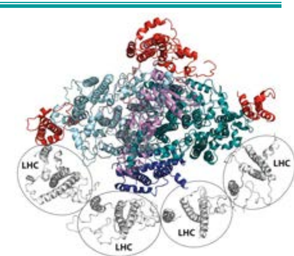
Plastocyanin
(E'_o is +0.37)

What do we do with all the reduced Plastocyanin?

Cytochrome b_6f Complex Translocates Protons into the Lumen

Photosynthesis





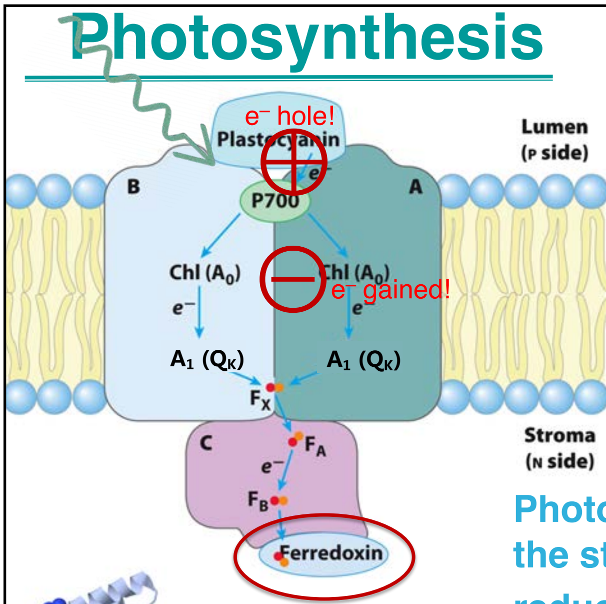
PQ_A	Plastoquinone	PSII
PQ_B	Second quinone	PSII
A_0	Electron acceptor chlorophyll	PSI
A_1	Phylloquinone	PSI

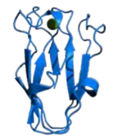
Photosystem I creates the strongest biological reductant known: A_0^-

(E'_o is ~⁻1.4)

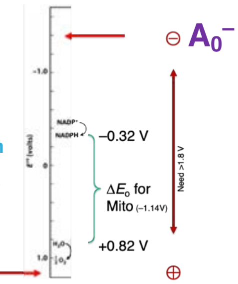
Photosystem I (P700)

Photosynthesis





Plastocyanin
(E'_o is +0.37)



Shuttling the electron quickly out:

PQ_A	Plastoquinone	PSII
PQ_B	Second quinone	PSII
A_0	Electron acceptor chlorophyll	PSI
A_1	Phylloquinone	PSI

Photosystem I creates the strongest biological reductant known: A_0^-
(E'_o is ~⁻1.4)

Ferredoxin
(E'_o is –0.4)

Photosystem I (P700)

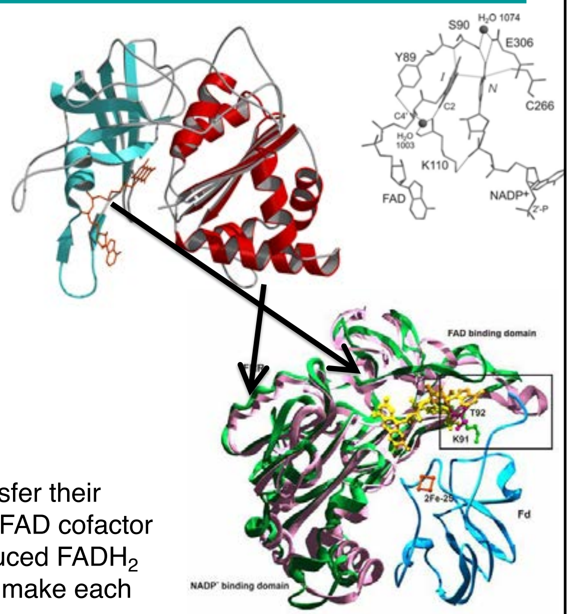
Photosynthesis

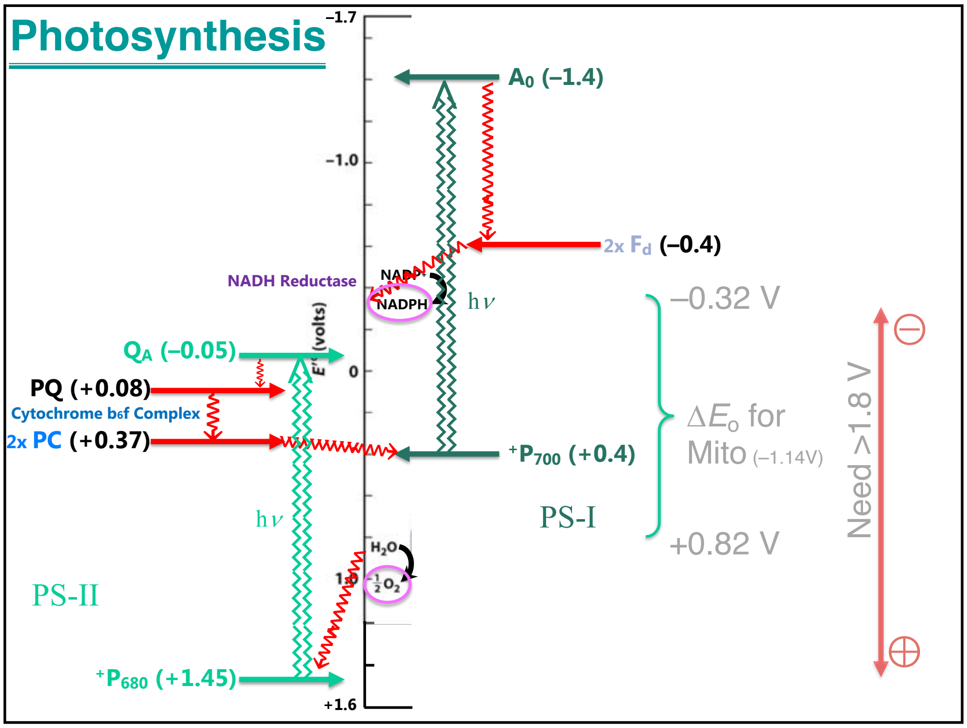
NADPH is produced by the NADPH Reductase in the Stroma

Photosystem I created reduced ferrodoxin (F_d)

(E'_o is –0.4)

F_d is a 1-e⁻ carrier, so 2 F_d transfer their electrons, one at a time, to the FAD cofactor in the reductase. The fully reduced $FADH_2$ then transfers 2e⁻ to $NADP^+$ to make each NADPH.




Photosynthesis
−1.7
A0 (−1.4)
−1.0
2x Fd (−0.4)
NADH Reductase
NADP+
NADPH
hν
−0.32 V
QA (−0.05)
E°′ (volts)
0
PQ (+0.08)
Cytochrome b6f Complex
2x PC (+0.37)
+P700 (+0.4)
ΔEo for
Mito (−1.14V)
Need >1.8 V
⊖
hν
PS-I
+0.82 V
H2O
1.0
½ O2
PS-II
⊕
+P680 (+1.45)
+1.6