植物生理

光合作用 photosynthesis

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Definition

- Physiology

  principle for life

- Plant

  A life that is

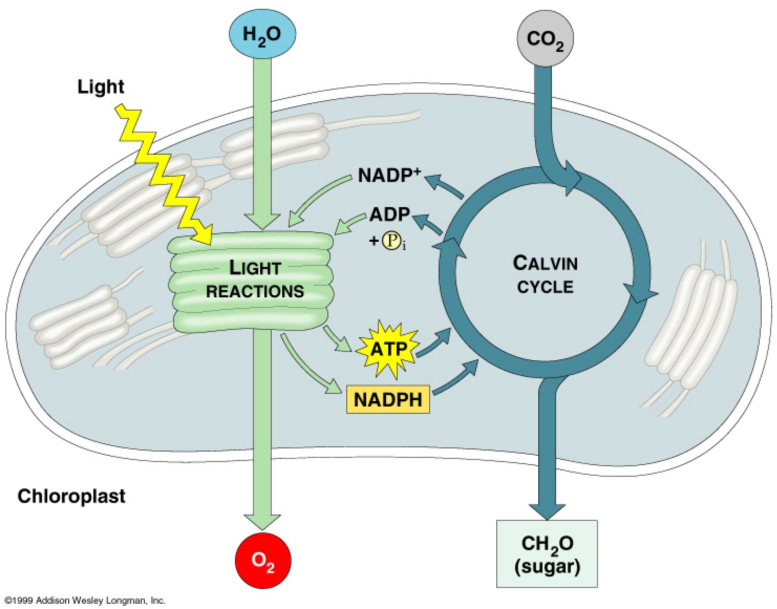
  Autotrophic

  Photosynthesis

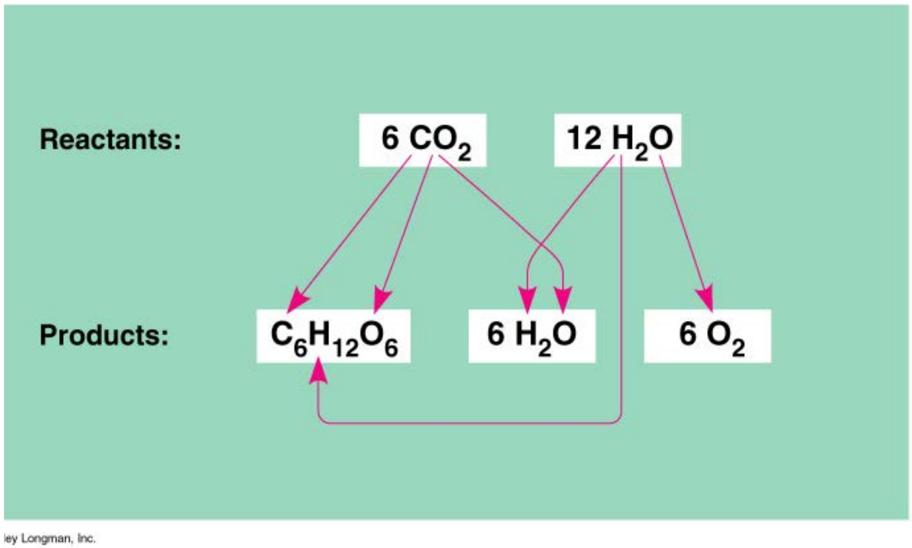
  Cell wall

Overview of Photosynthesis

- Process by which chloroplast bearing organisms transform solar light energy into chemical bond energy
- 2 metabolic pathways involved
  - **Light reactions**: convert solar energy into cellular energy
  - **Calvin Cycle**: reduce CO_2 to CH_2O



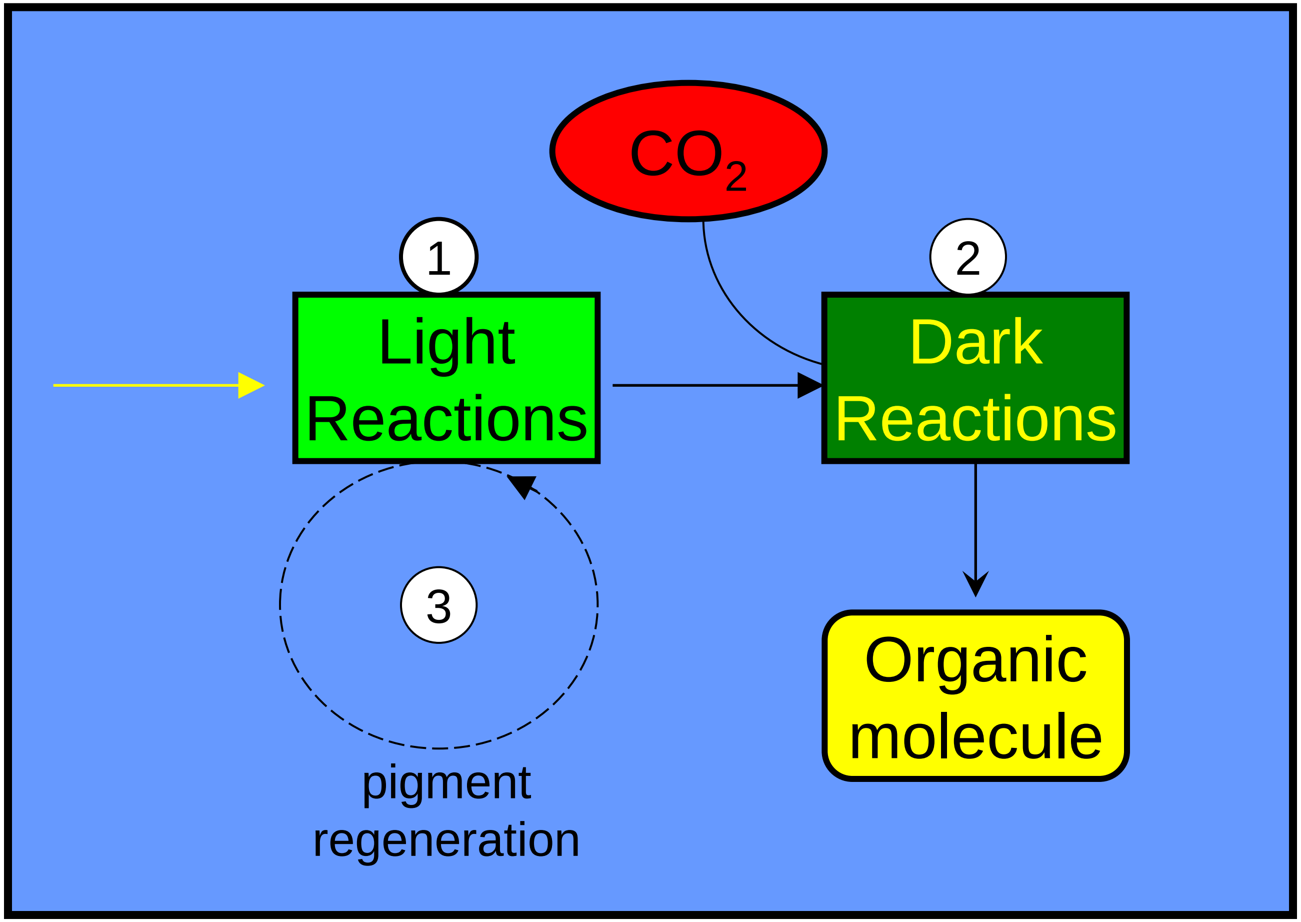
Photosynthesis Equation

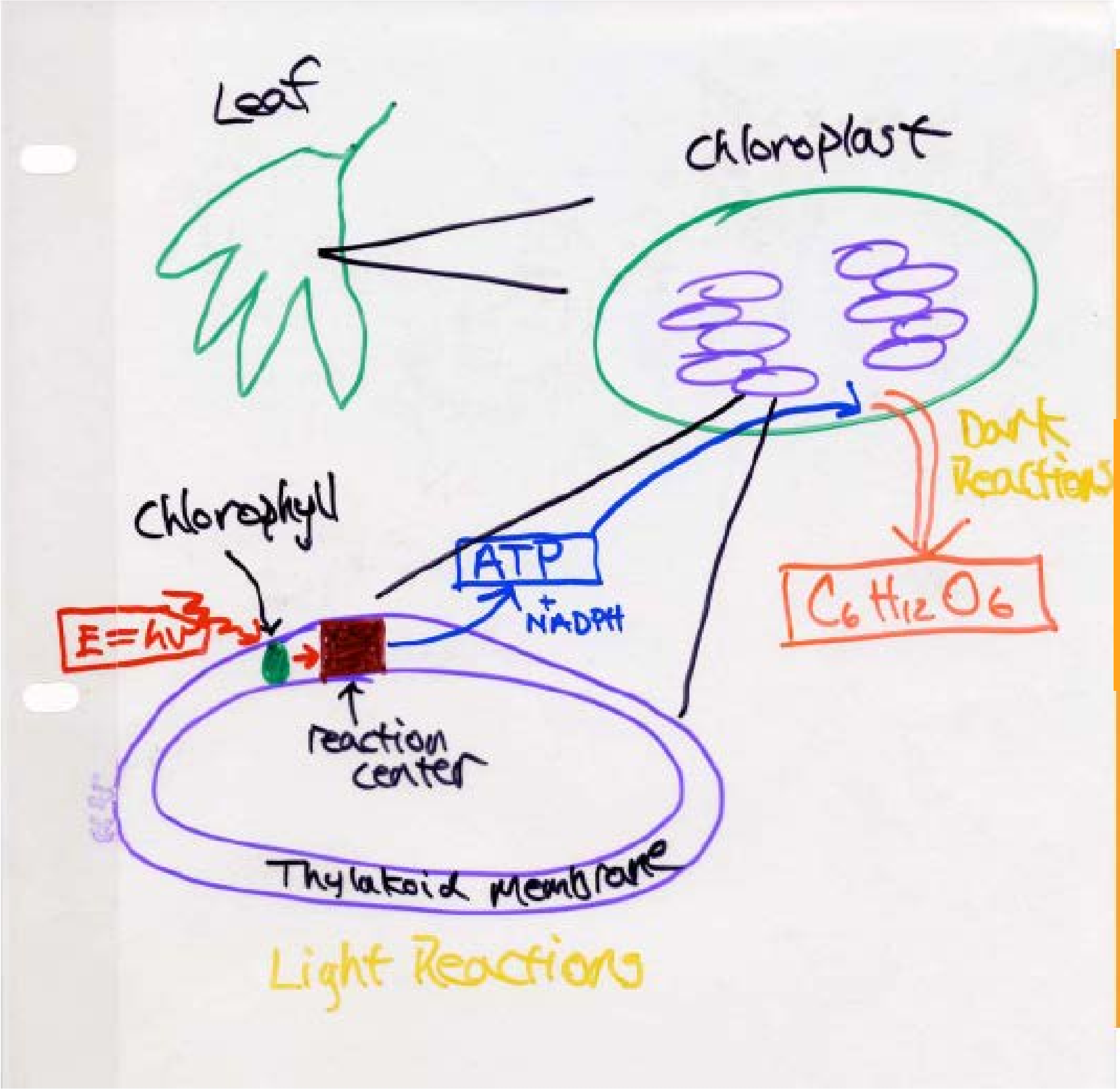


1 mole of CO_2 consumed as 1 mole of O_2 produced

- Photosynthesis
  $6CO_2 + 6H_20 + \text{light} \rightarrow C_6H_{12}0_6 + 6O_2$
- Reduction of carbon dioxide into carbohydrate via the oxidation of energy carriers (ATP, NADPH)
- Light reactions energize the carriers
- Calvin Cycle produces PGAL (phosphoglyceraldehyde)

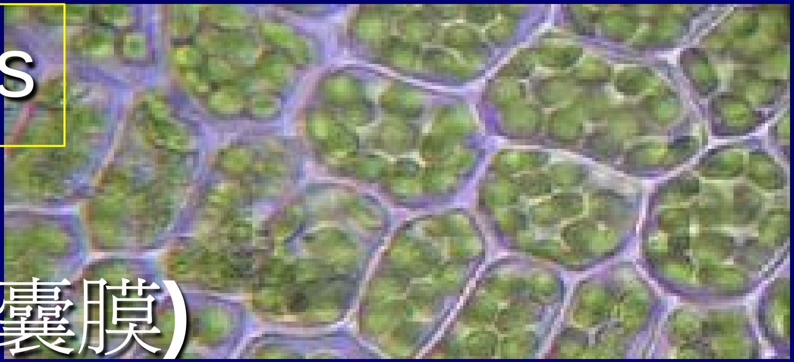
3 Steps of Photosynthesis



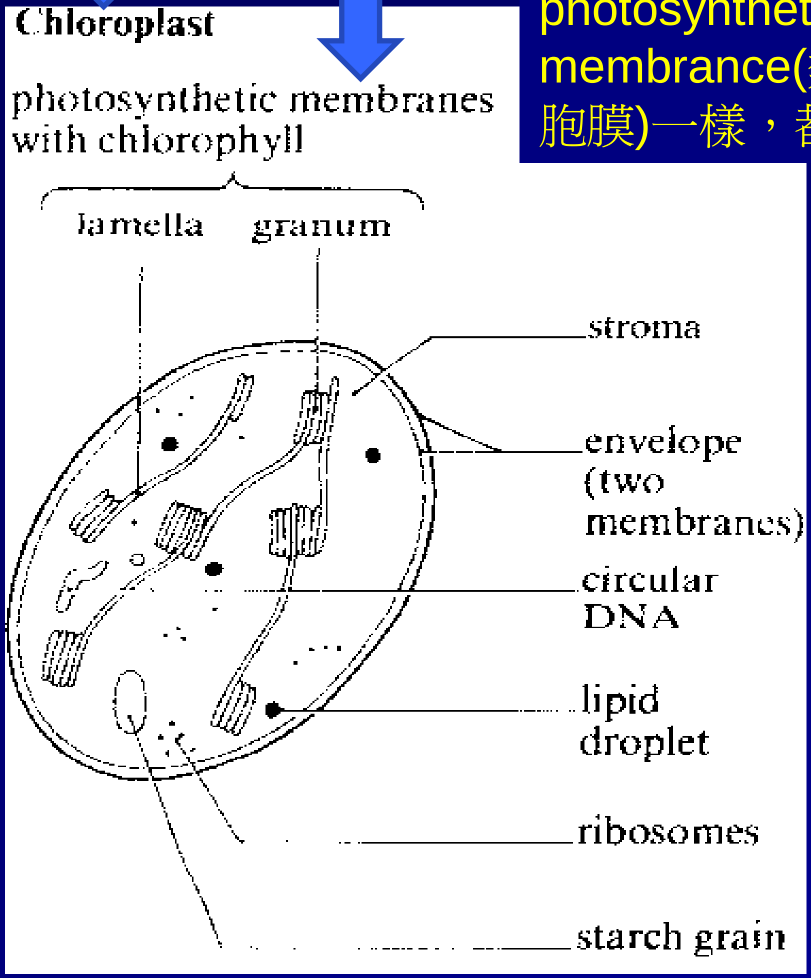


Schematic Photosynthesis Process

The site for photosynthesis



Chloroplast (葉綠體)
thylakoid membrane (類囊膜)



photosynthetic pigment(光合色素)是嵌在**thylakoid** membrance(類囊膜)上的，類囊膜和plasma membrance(細胞膜)一樣，都是磷脂雙層(phospholipids bilayers

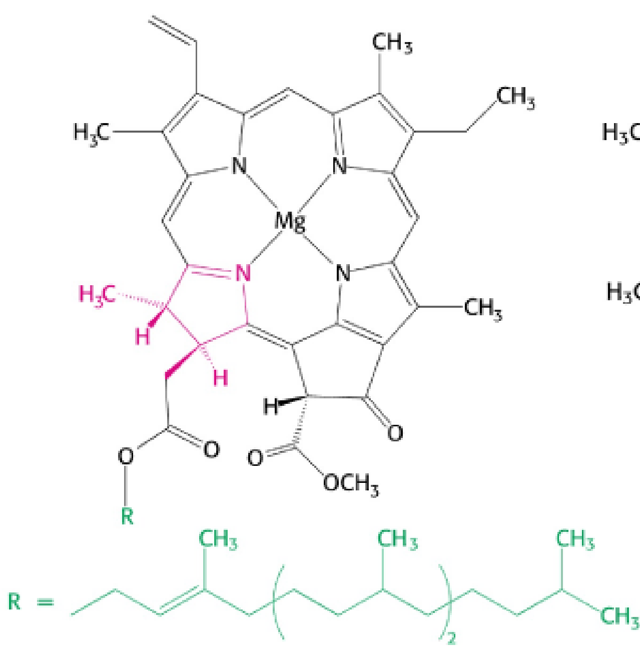
Each plastid creates multiple copies of the circular 75-250 kilo bases plastid genome. The number of genome copies per plastid is flexible, ranging from more than 1000 in rapidly dividing cells, which generally contain few plastids, to 100 or fewer in mature cells, where plastid divisions has given rise to a large number of plastids.

The **plastid genome** contains about **100 genes** encoding ribosomal and transfer ribonucleic acids (rRNAs and tRNAs) as well as proteins involved in photosynthesis and plastid gene transcription and translation.

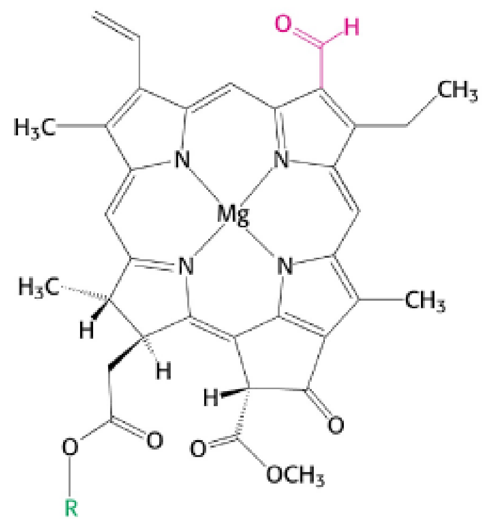
Chlorophylls are the primary light gathering pigments

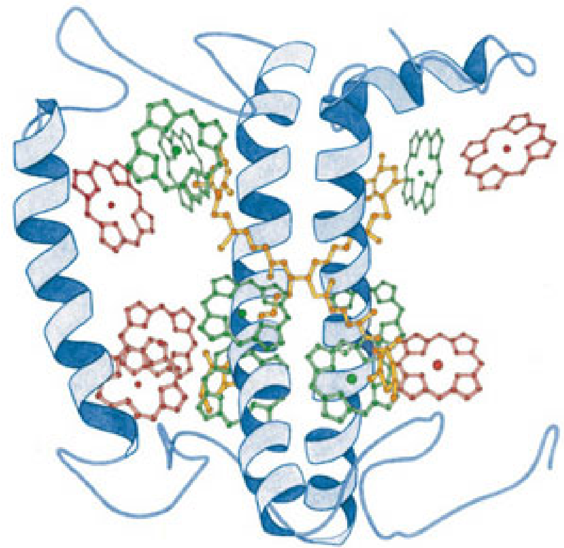
They have a heterocyclic ring system that constitutes an extended polyene structure, which typically has strong absorption in visible light.

Chlorophyll *a*

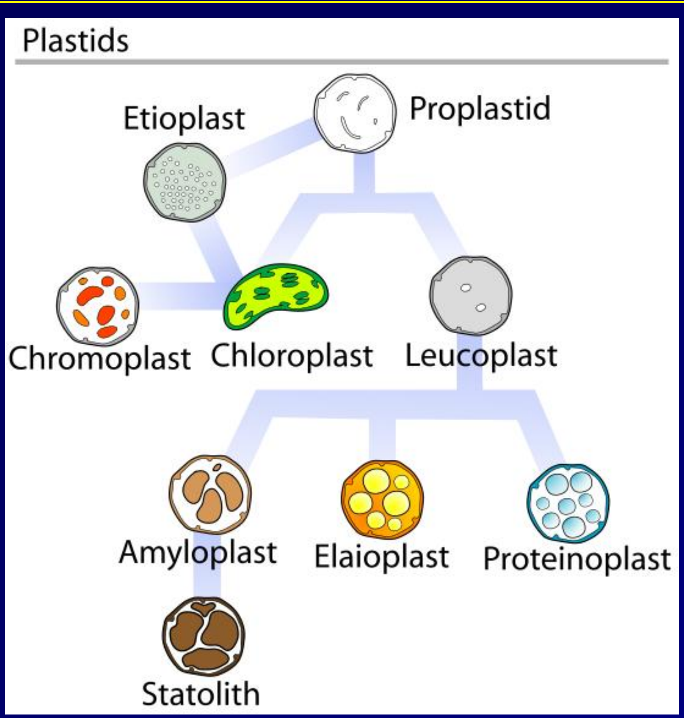


Chlorophyll *b*





Plastid differentiation



Plastids in algae
In algae, the term leucoplast (leukoplast) is used for all unpigmented plastids. Their function differ from the leukoplasts in plants. **Etioplast, amyloplast and chromoplast are plant-specific and do not occur in algae**. Algal plastids may also differ from plant plastids in that they contain pyrenoids.

All plastids are derived from proplastids (formerly "eoplasts", eo-: dawn, early), which are present in the meristematic regions of the plant. Proplastids and young chloroplasts commonly divide, but more mature chloroplasts also have this capacity. In plants, plastids may differentiate into several forms, depending upon which function they need to play in the cell. Undifferentiated plastids (proplastids) may develop into any of the following plastids:

⇒ Chloroplasts: for photosynthesis; see also etioplasts, the predecessors of chloroplasts

⇒ Chromoplasts: for pigment synthesis and storage

⇒ Leucoplasts: for monoterpene synthesis; leucoplasts sometimes differentiate into more specialized plastids:

⇒ Amyloplasts: for starch storage

⇒ Statoliths: for detecting gravity

⇒ Elaioplasts: for storing fat (不同於油滴)

⇒ Proteinoplasts: for storing and modifying protein

Plastid development

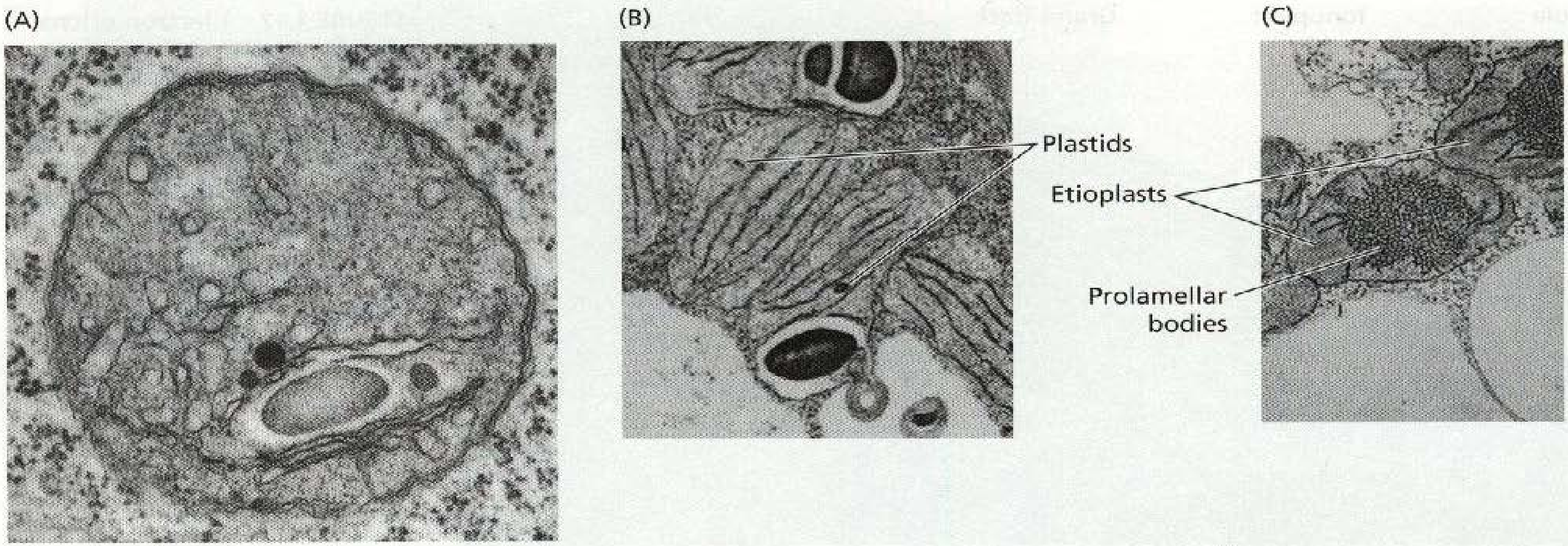
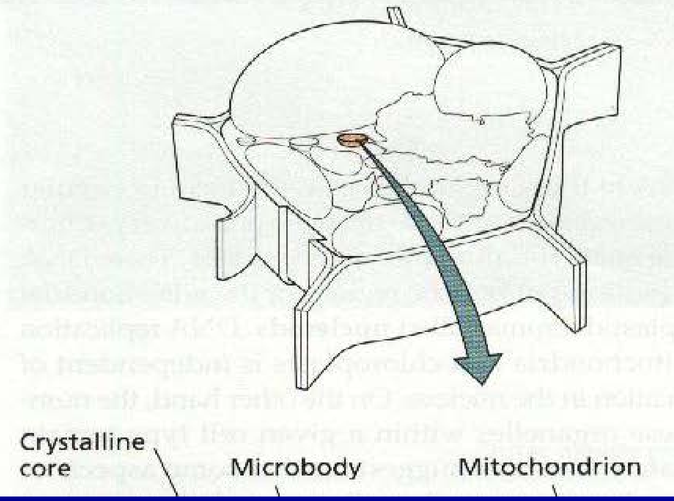


FIGURE 1.18 Electron micrographs illustrating several stages of plastid development. (A) A higher-magnification view of a proplastid from the root apical meristem of the broad bean (*Vicia faba*). The internal membrane system is rudimentary, and grana are absent. (47,000×) (B) A mesophyll cell of a young oat leaf at an early stage of differentiation in the light. The plastids are developing grana stacks. (C) A cell from a young oat leaf from a seedling grown in the dark. The plastids have developed as etioplasts, with elaborate semicrystalline lattices of membrane tubules called prolamellar bodies. When exposed to light, the etioplast can convert to a chloroplast by the disassembly of the prolamellar body and the formation of grana stacks. (7,200×) (From Gunning and Steer 1996.)



Chromoplast 番茄果實爲例

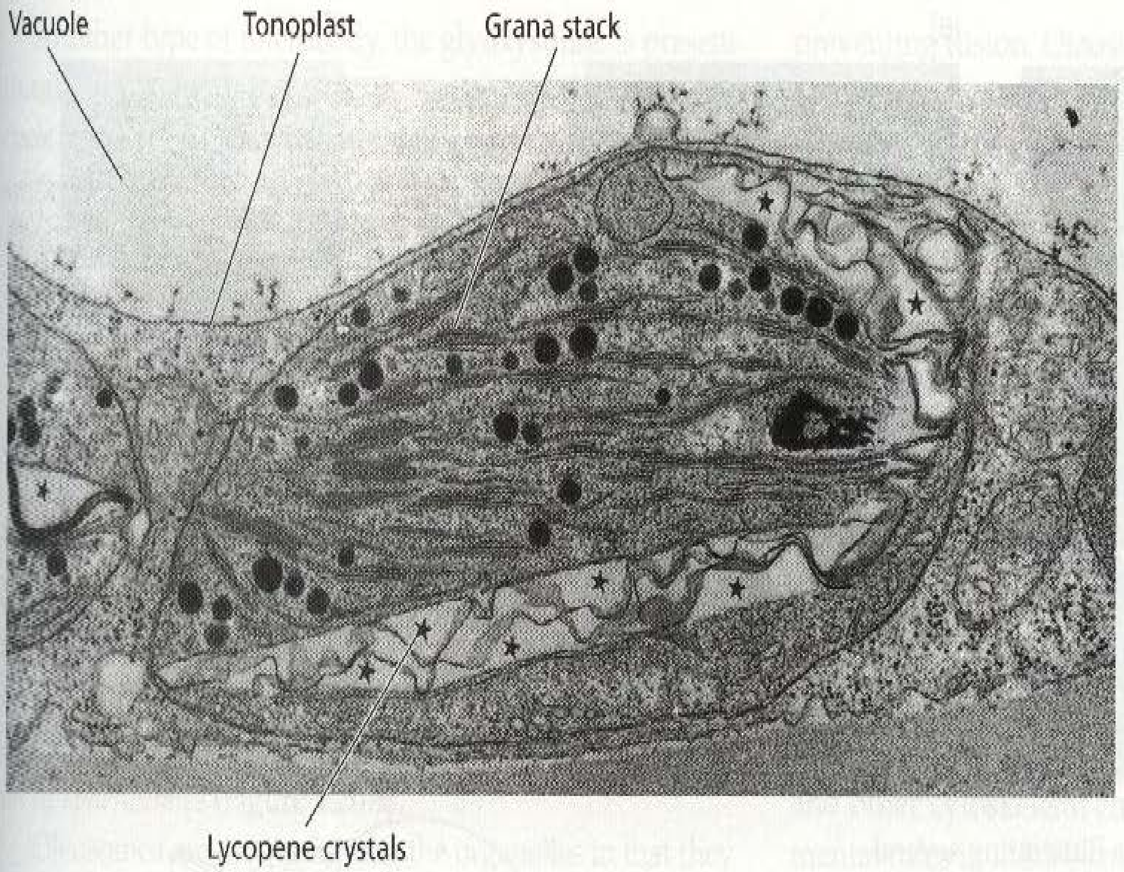
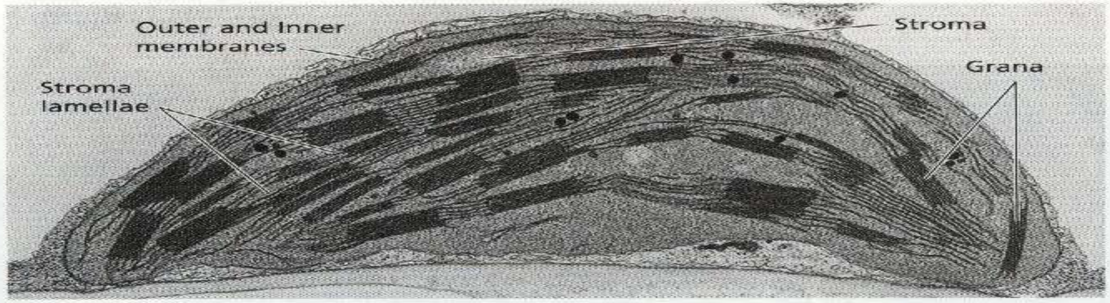
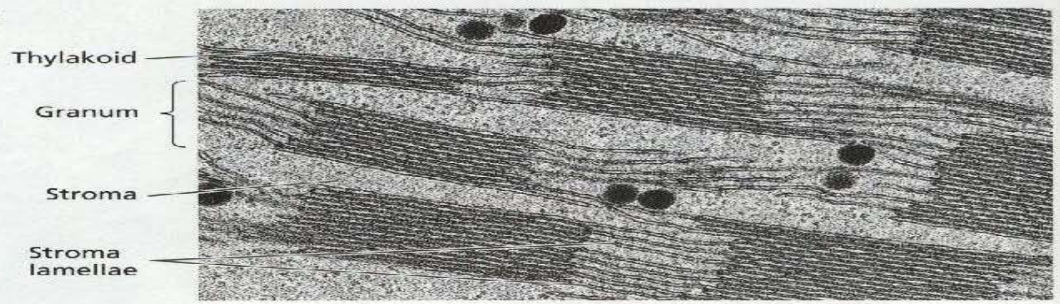


FIGURE 1.17 Electron micrograph of a chromoplast from tomato (*Lycopersicon esculentum*) fruit at an early stage in the transition from chloroplast to chromoplast. Small grana stacks are still visible. Crystals of the carotenoid lycopene are indicated by the stars. (27,000×) (From Gunning and Steer 1996.)

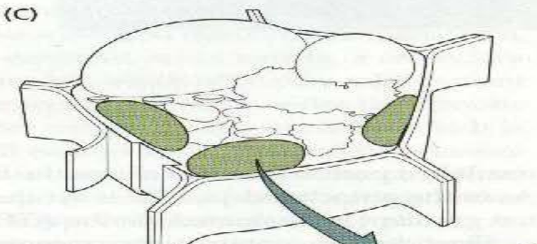
(A)



(B)



(C)



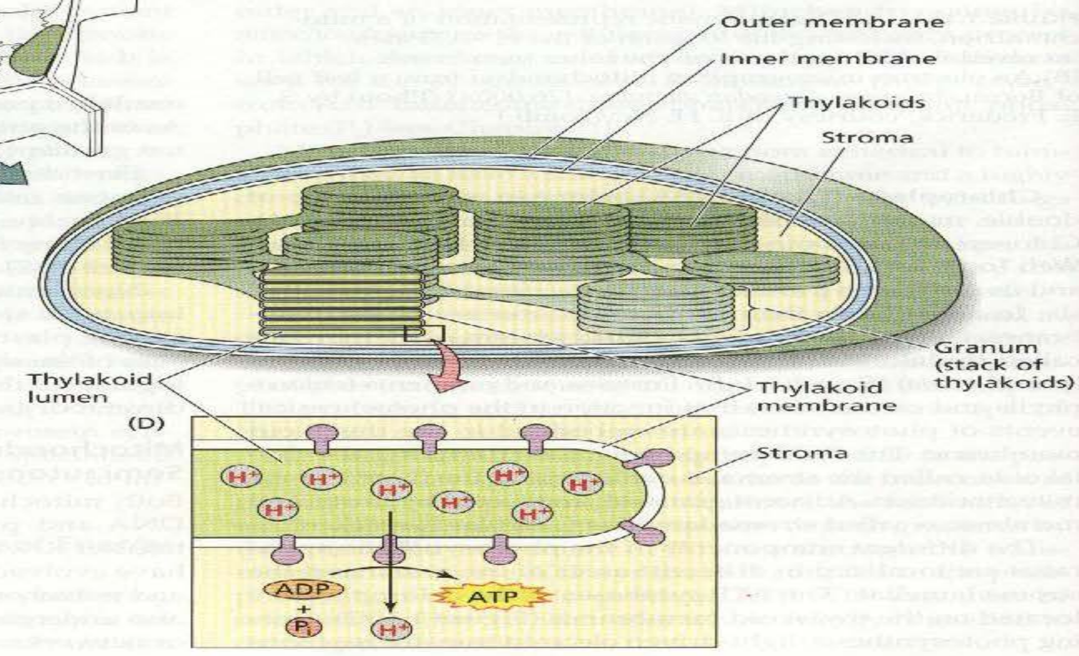
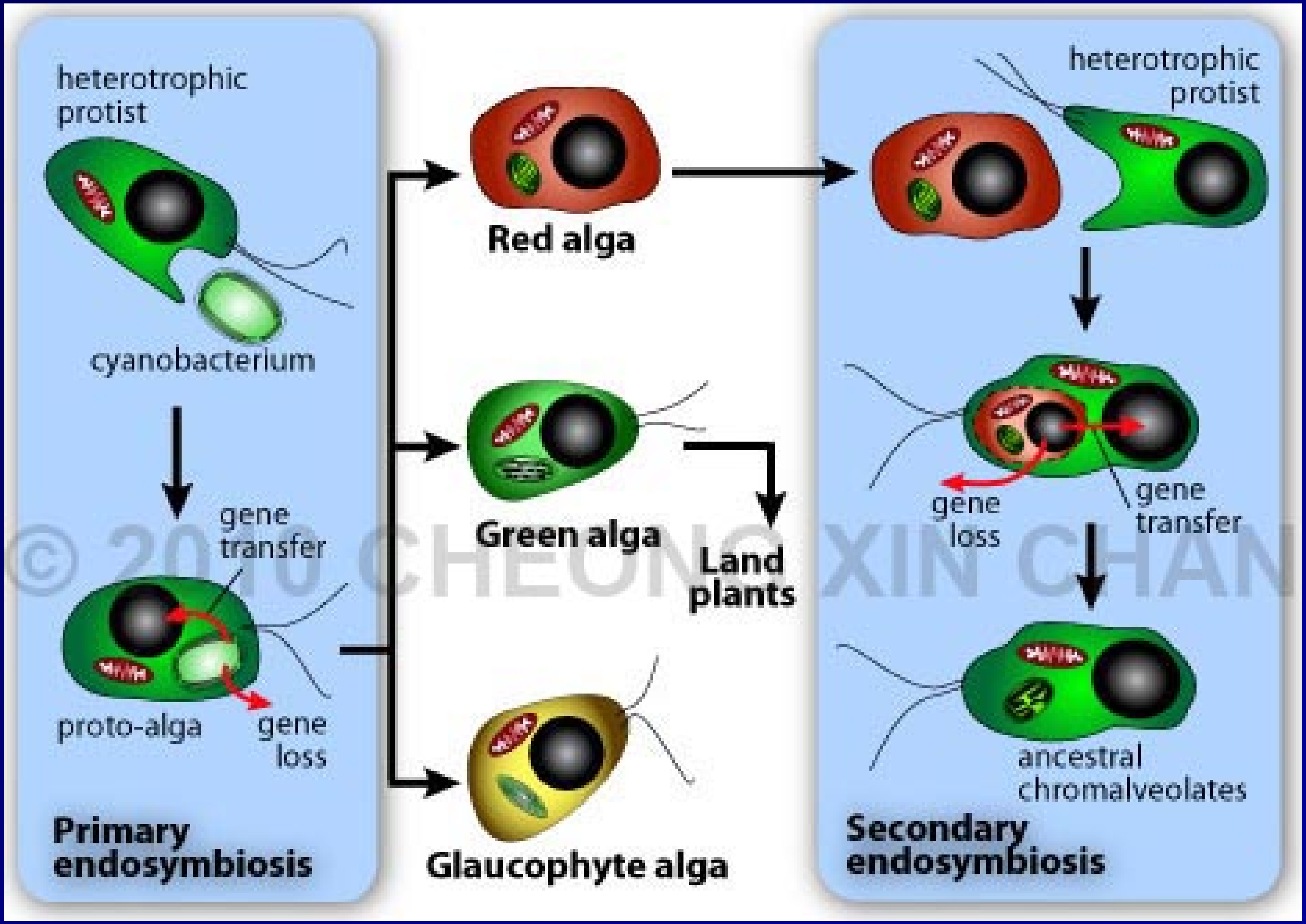


FIGURE 1.16 (A) Electron micrograph of a chloroplast from a leaf of timothy grass, *Phleum pratense*. (18,000×) (B) The same preparation at higher magnification. (52,000×) (C) A three-dimensional view of grana stacks and stroma lamellae, showing the complexity of the organization. (D) Diagrammatic representation of a chloroplast, showing the location of the H+-ATPases on the thylakoid membranes. (Micrographs by W. P. Wergin, courtesy of E. H. Newcomb.)

Plastid origin and **algal** evolution

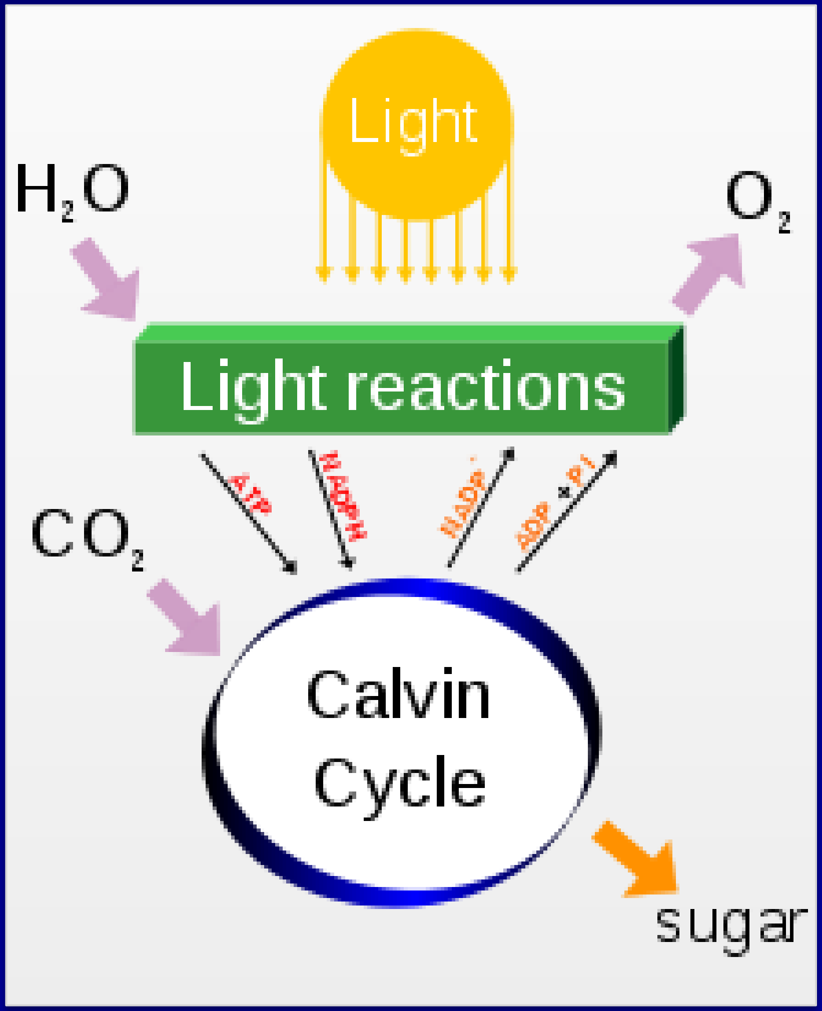


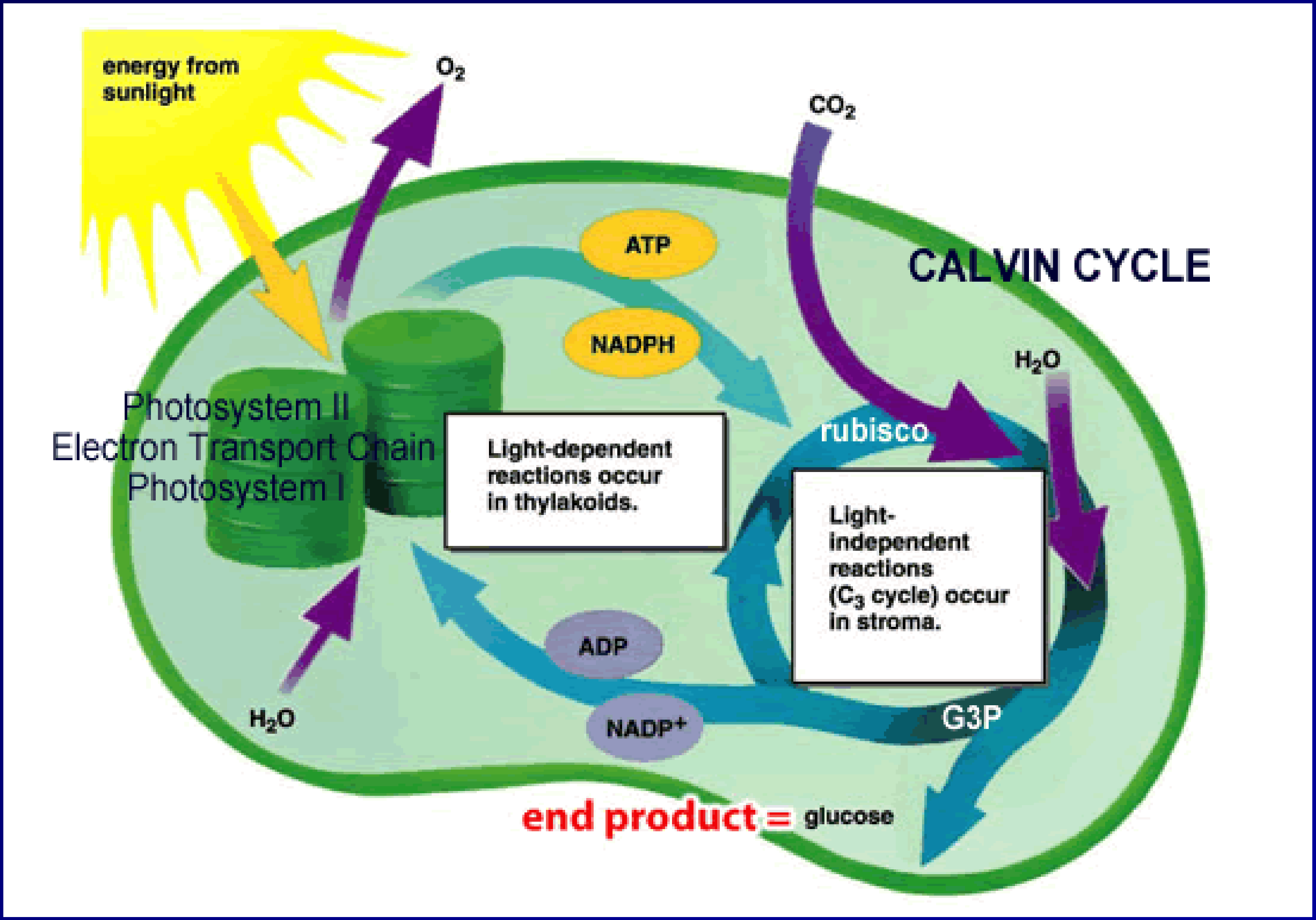
Hedges, S. Blair et al. (2004) "A molecular timescale of eukaryote evolution and the rise of complex multicellular life" BMC Evolutionary Biology 4:2

Photosynthesis

$2n\ CO_2 + 2n\ H_2O + \text{photons} \rightarrow 2(CH_2O)n + 2n\ O_2$

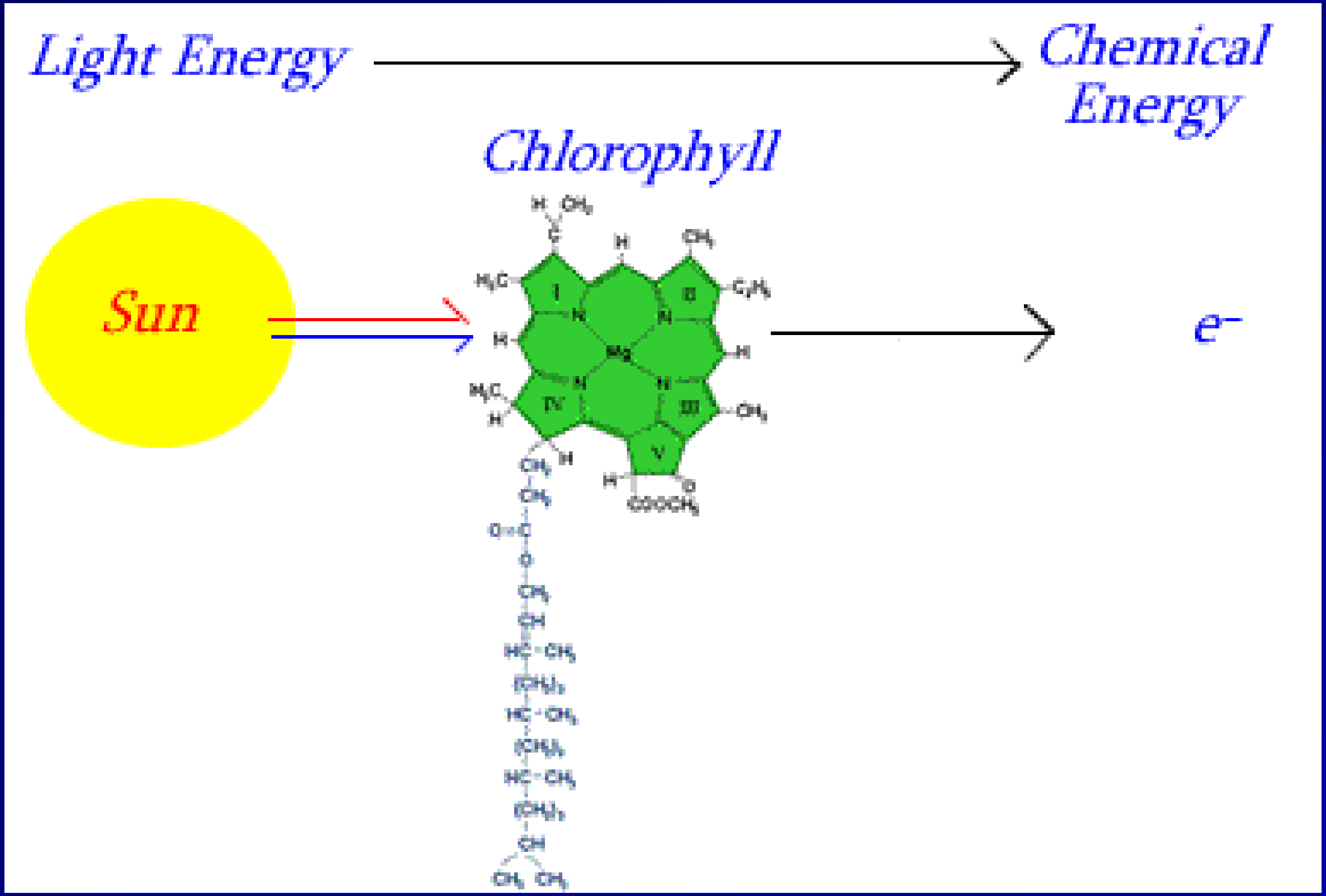
- photochemical processes
- enzymatic processes



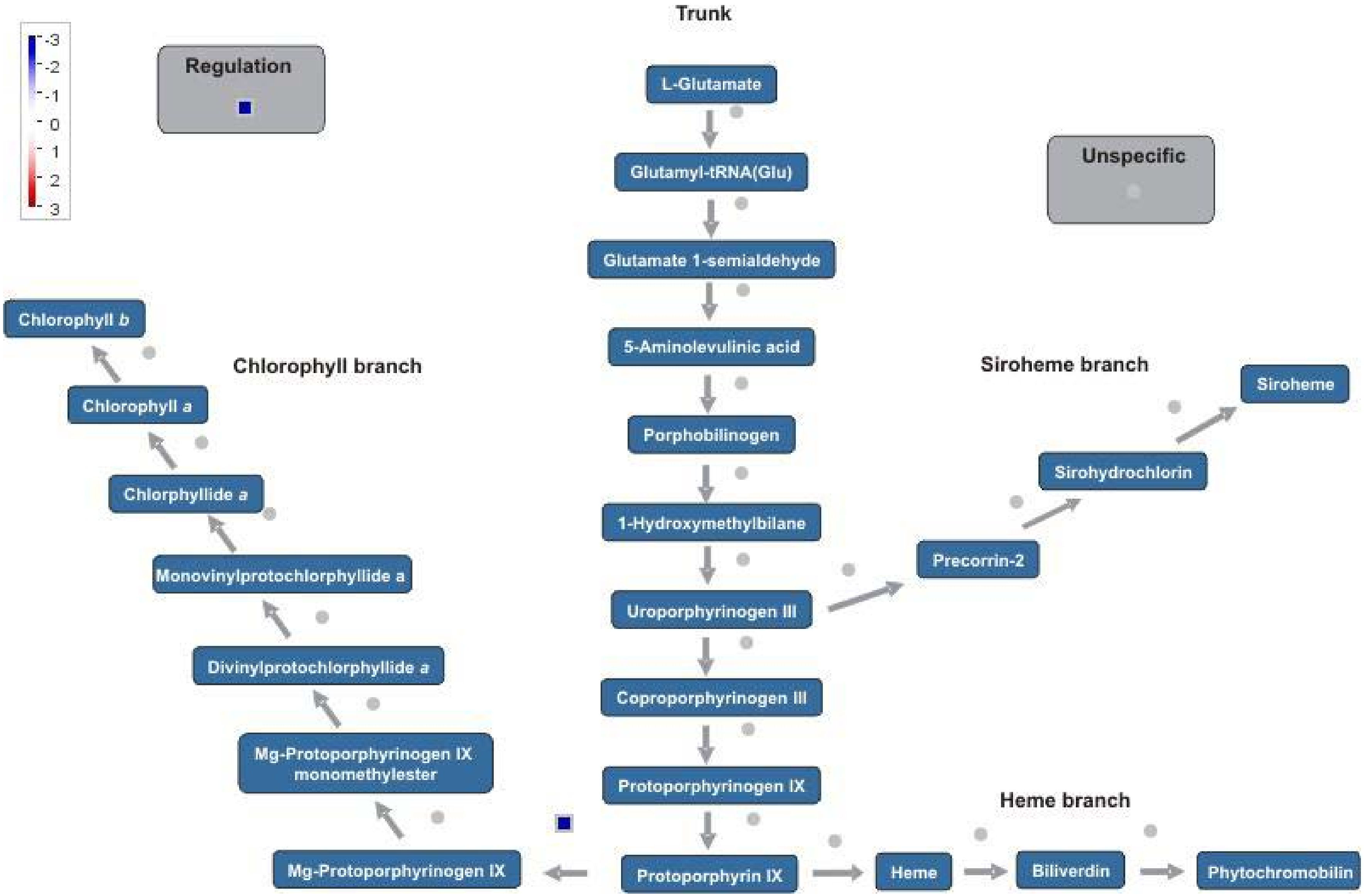


energy from sunlight
O_2
CO_2
ATP
NADPH
CALVIN CYCLE
H_2O
Photosystem II
Electron Transport Chain
Photosystem I
Light-dependent reactions occur in thylakoids.
rubisco
Light-independent reactions (C_3 cycle) occur in stroma.
ADP
H_2O
$NADP^+$
G3P
end product = glucose

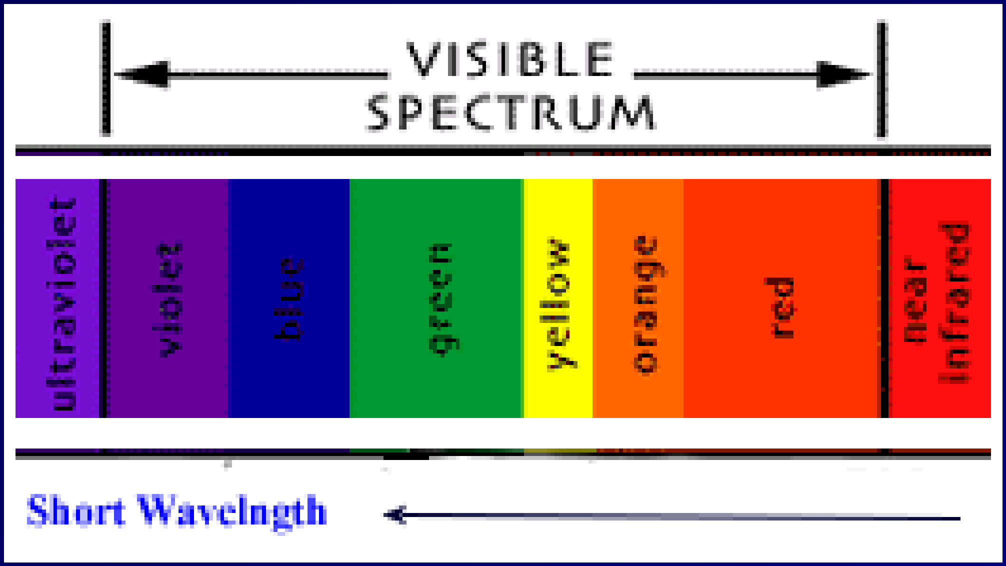
the conversion of light energy into chemical energy

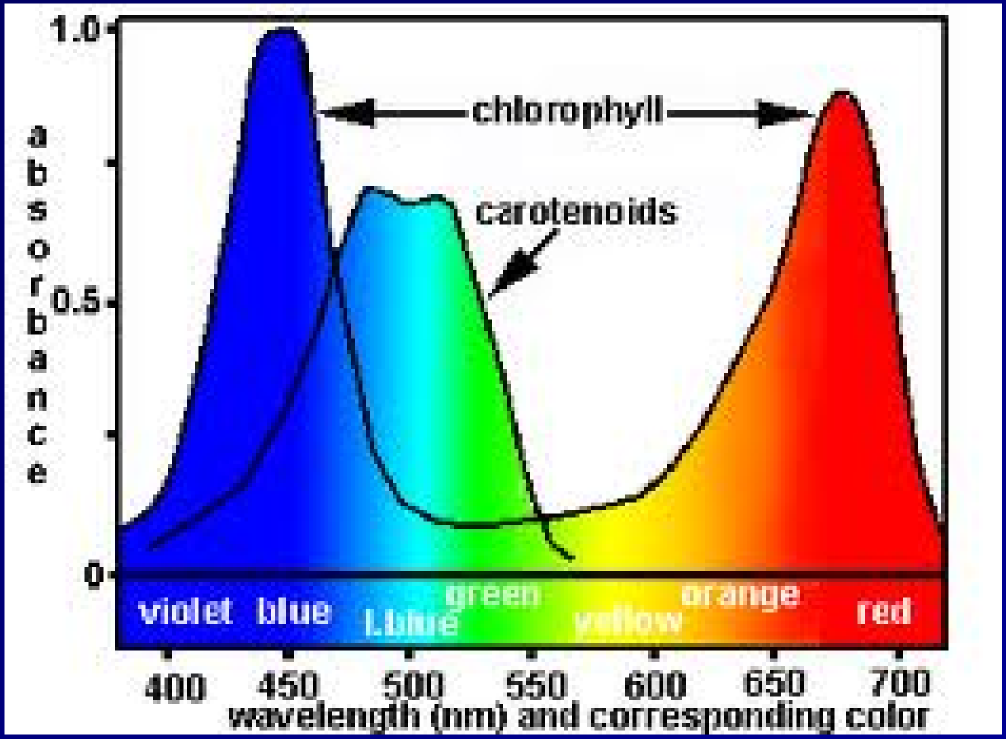


tetrapyrrole



Sun Radiation





Chlorophyll is the main photosynthetic pigment

Photosynthetically active radiation, often abbreviated **PAR**, designates the spectral range (wave band) of solar radiation from 400 to 700 nanometers that photosynthetic organisms are able to use in the process of photosynthesis.

Pigment for photosynthesis

- Essential pigments

  chlorophyll: 2, 3

- Accessory pigments

  carotenoid: 5

  phycobiliprotein: 4

Bacteriochlorophyll: 1

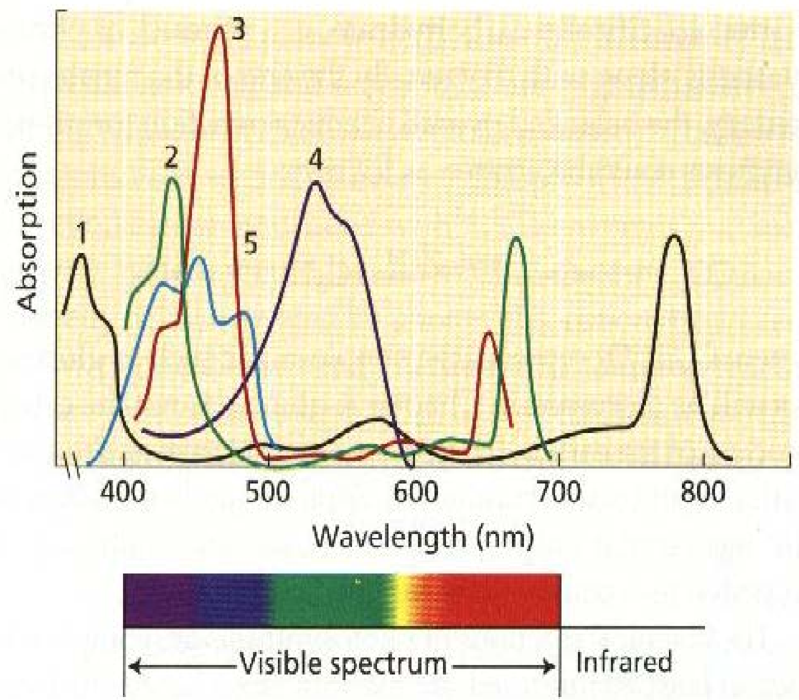


FIGURE 7.7 Absorption spectra of some photosynthetic pigments. Curve 1, bacteriochlorophyll *a*; curve 2, chlorophyll *a*; curve 3, chlorophyll *b*; curve 4, phycoerythrobilin; curve 5, β-carotene. The absorption spectra shown are for pure pigments dissolved in nonpolar solvents, except for curve 4, which represents an aqueous buffer of phycoerythrin, a protein from cyanobacteria that contains a phycoerythrobilin chromophore covalently attached to the peptide chain. In many cases the spectra of photosynthetic pigments in vivo are substantially affected by the environment of the pigments in the photosynthetic membrane. (After Avers 1985.)

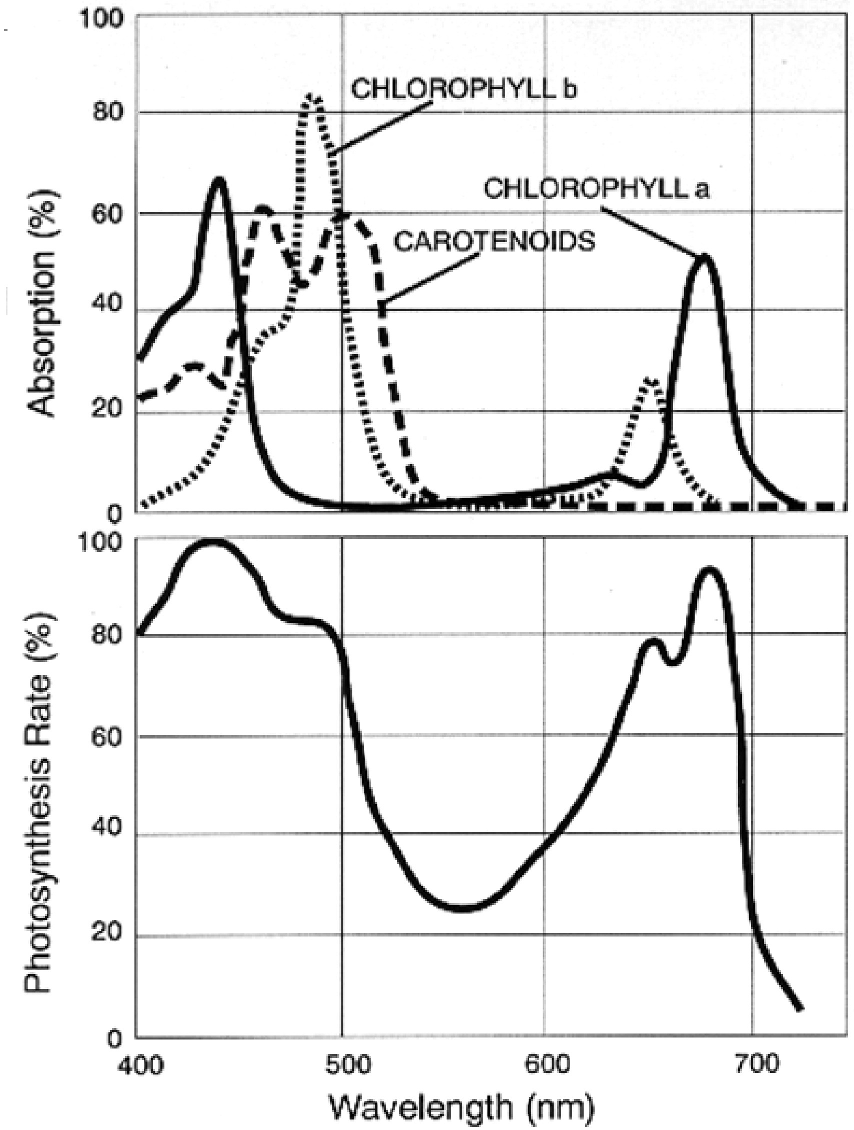
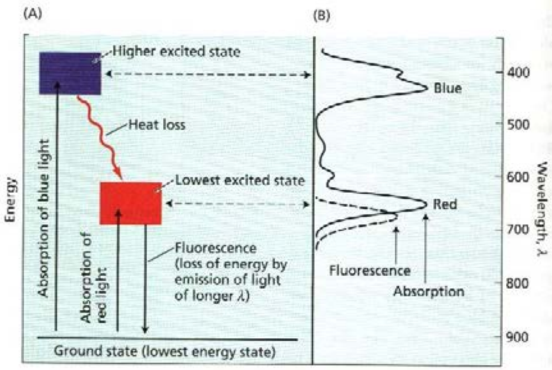
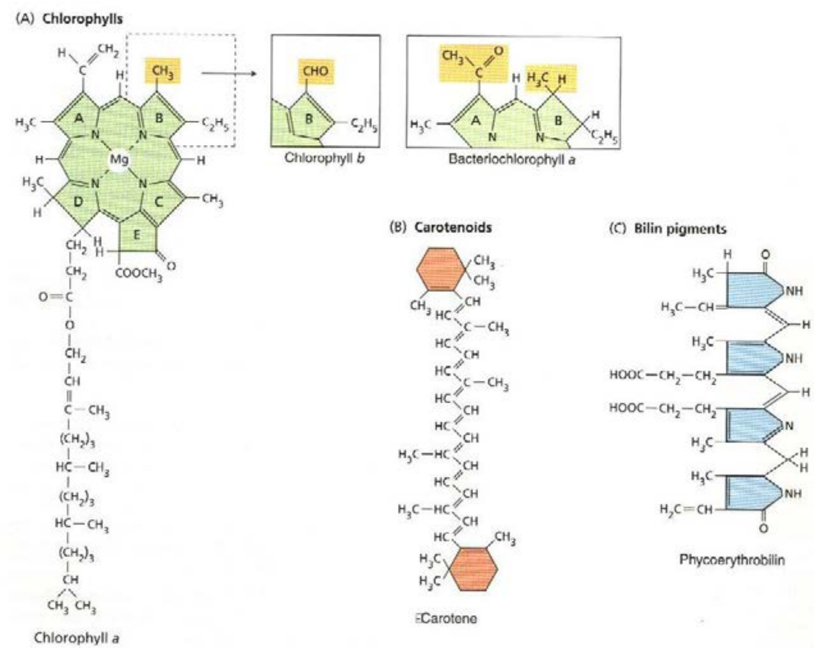
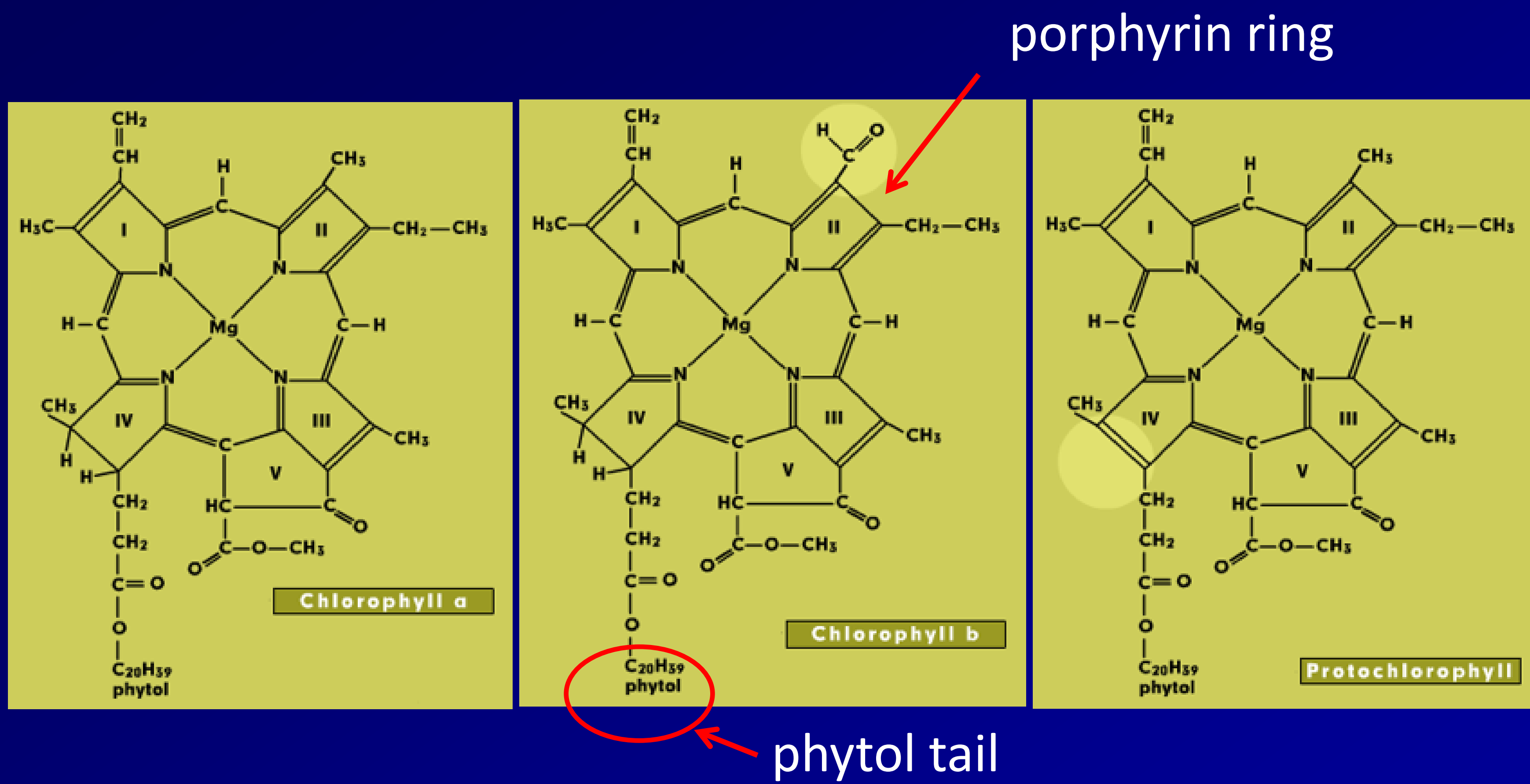


FIGURE 7.5 Light absorption and emission by chlorophyll. (A) Energy level diagram. Absorption or emission of light is indicated by vertical lines that connect the ground state with excited electron states. The blue and red absorption bands of chlorophyll (which absorb blue and red photons, respectively) correspond to the upward vertical arrows, signifying that energy absorbed from light causes the molecule to change from the ground state to an excited state. The downward-pointing arrow indicates fluorescence, in which the molecule goes from the lowest excited state to the ground state while re-emitting energy as a photon. (B) Spectra of absorption and fluorescence. The long-wavelength (red) absorption band of chlorophyll corresponds to light that has the energy required to cause the transition from the ground state to the first excited state. The short-wavelength (blue) absorption band corresponds to a transition to a higher excited state.

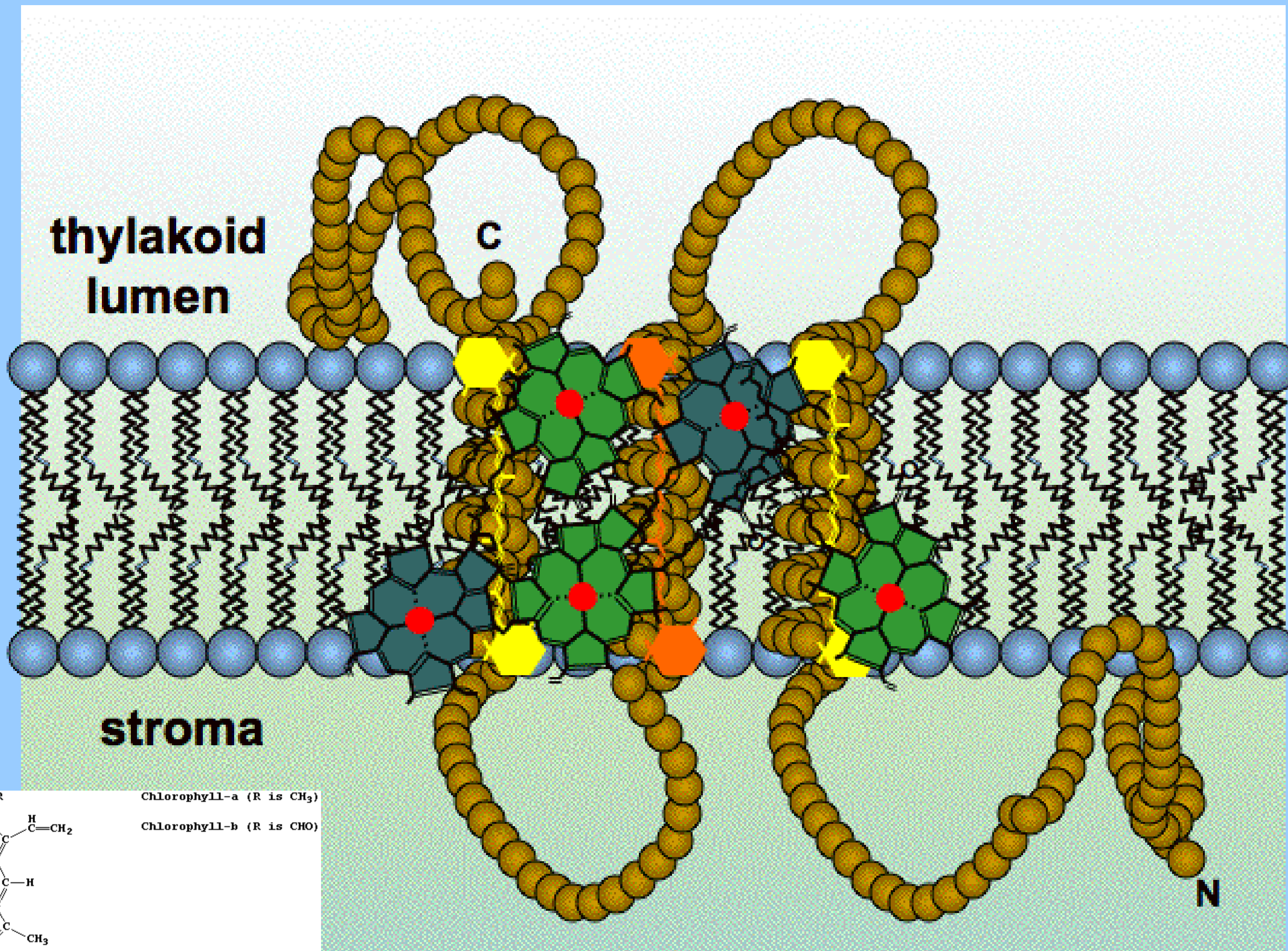


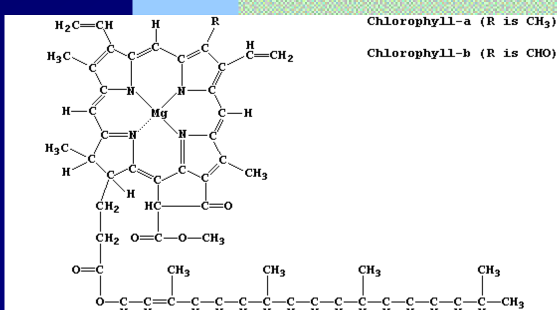




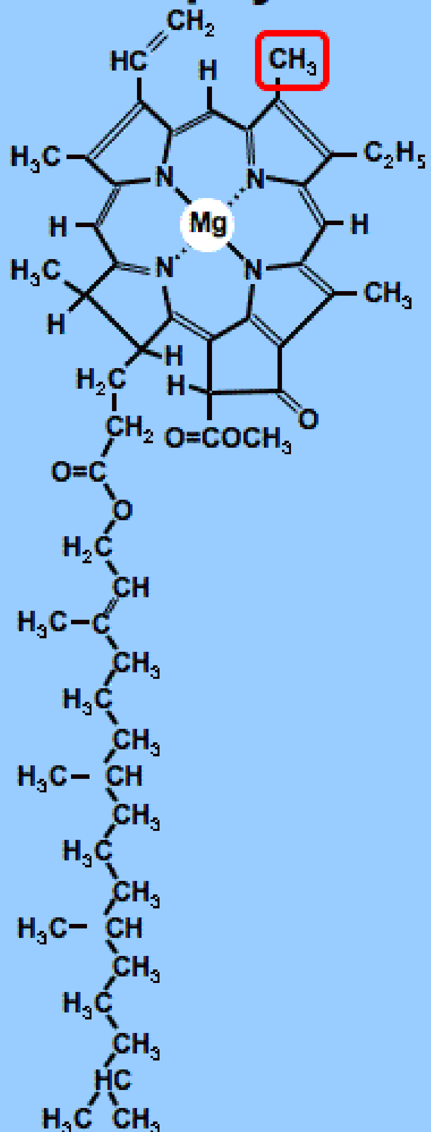
Chlorophylls consist of a light-absorbing with a magnesium atom at the center and a long phytol tail that anchors the molecule in a membrane (Figure 1). They absorb light in the blue and red parts of the spectrum, but the green wavelengths are transmitted or reflected.

Photosynthetic pigments are associated with membrane proteins

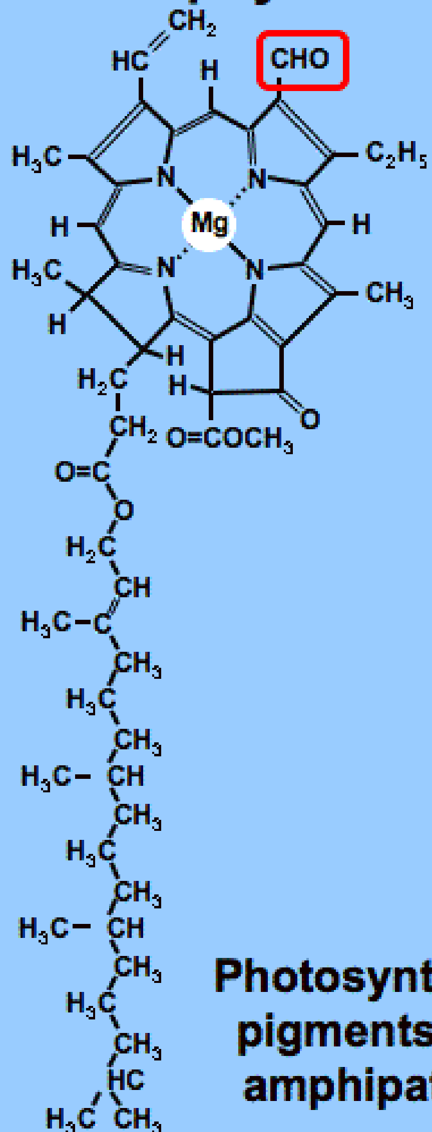




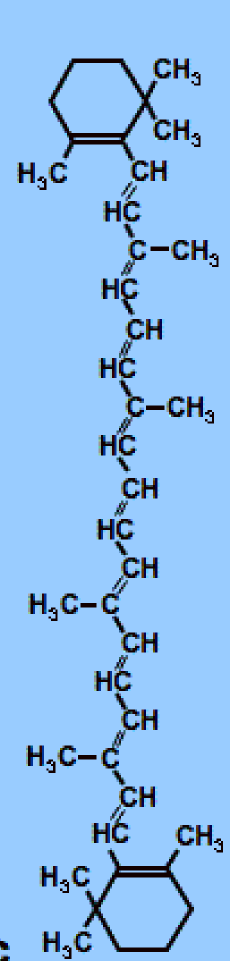
Chlorophyll a



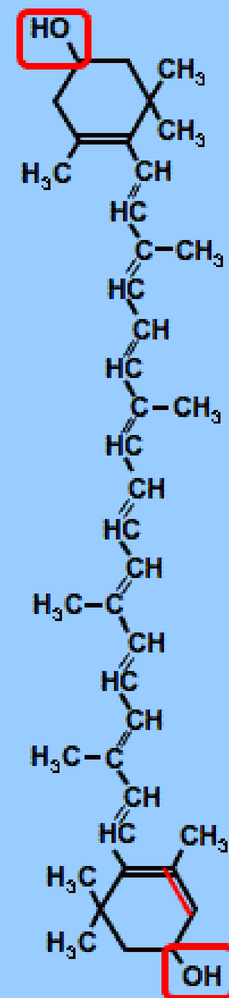
Chlorophyll b



ß-Carotene

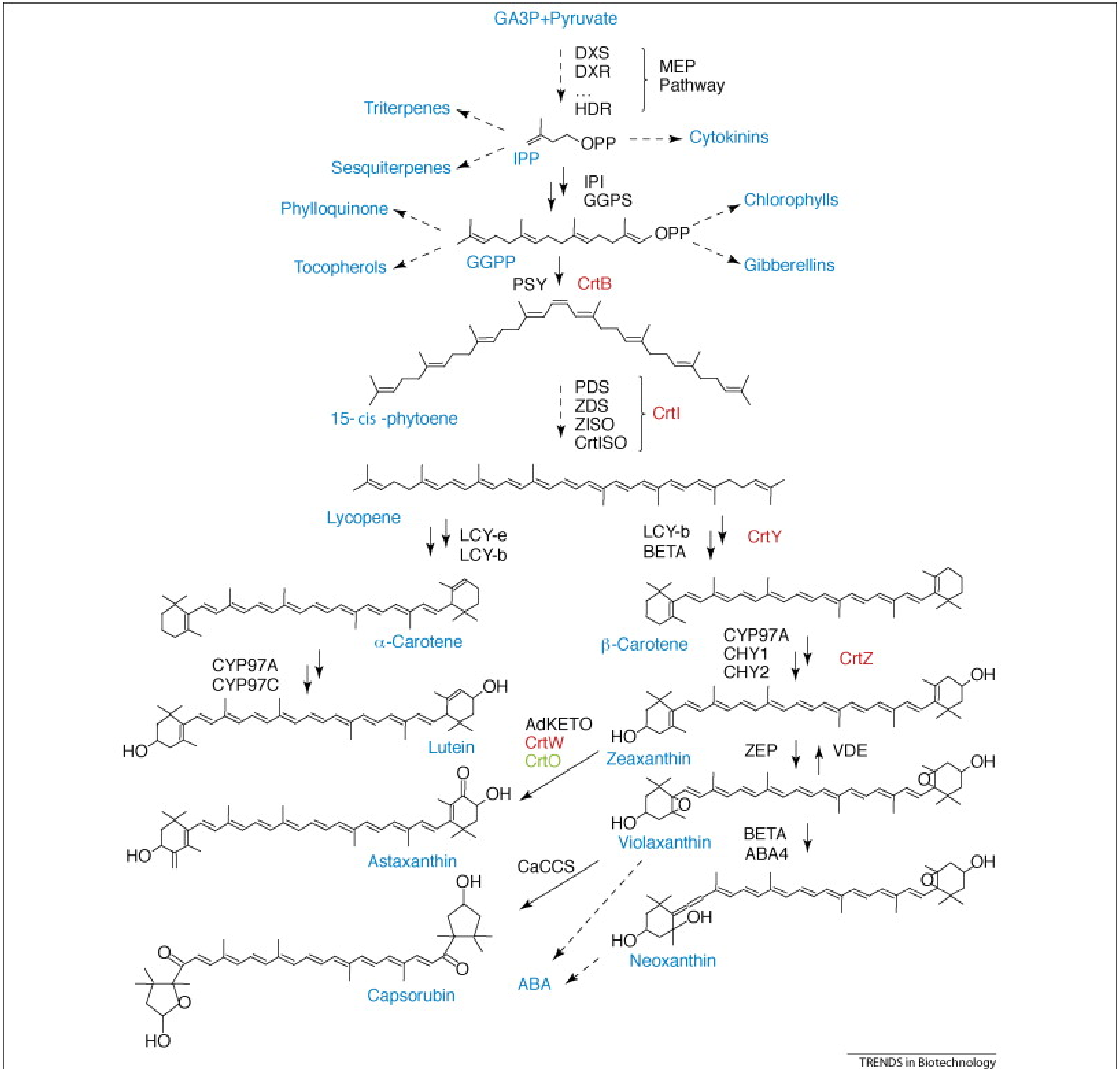


Zeaxanthin

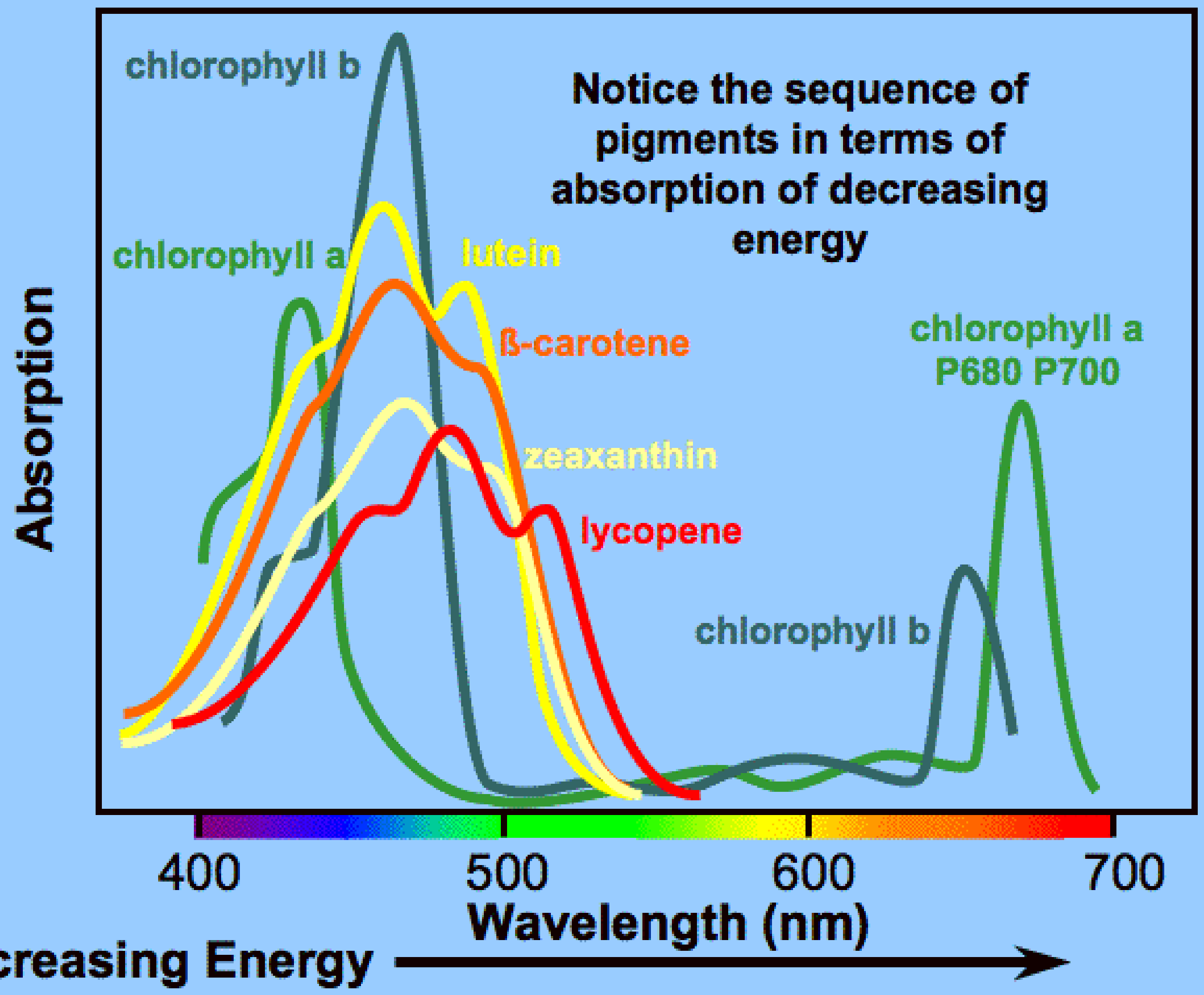


Lutein

Photosynthetic pigments are amphipathic


GA3P+Pyruvate
DXS
DXR
...
HDR
MEP
Pathway
Triterpenes
Sesquiterpenes
OPP
IPP
Cytokinins
IPI
GGPS
Phylloquinone
Tocopherols
OPP
GGPP
Chlorophylls
Gibberellins
PSY
CrtB
15- cis -phytoene
PDS
ZDS
ZISO
CrtISO
CrtI
Lycopene
LCY-e
LCY-b
LCY-b
BETA
CrtY
α-Carotene
β-Carotene
CYP97A
CYP97C
CYP97A
CHY1
CHY2
CrtZ
OH
HO
Lutein
AdKETO
CrtW
CrtO
HO
Zeaxanthin
ZEP
VDE
O
OH
Astaxanthin
HO
Violaxanthin
BETA
ABA4
CaCCS
Neoxanthin
Capsorubin
ABA
TRENDS in Biotechnology

The photosynthetic pigments absorb much of the spectrum



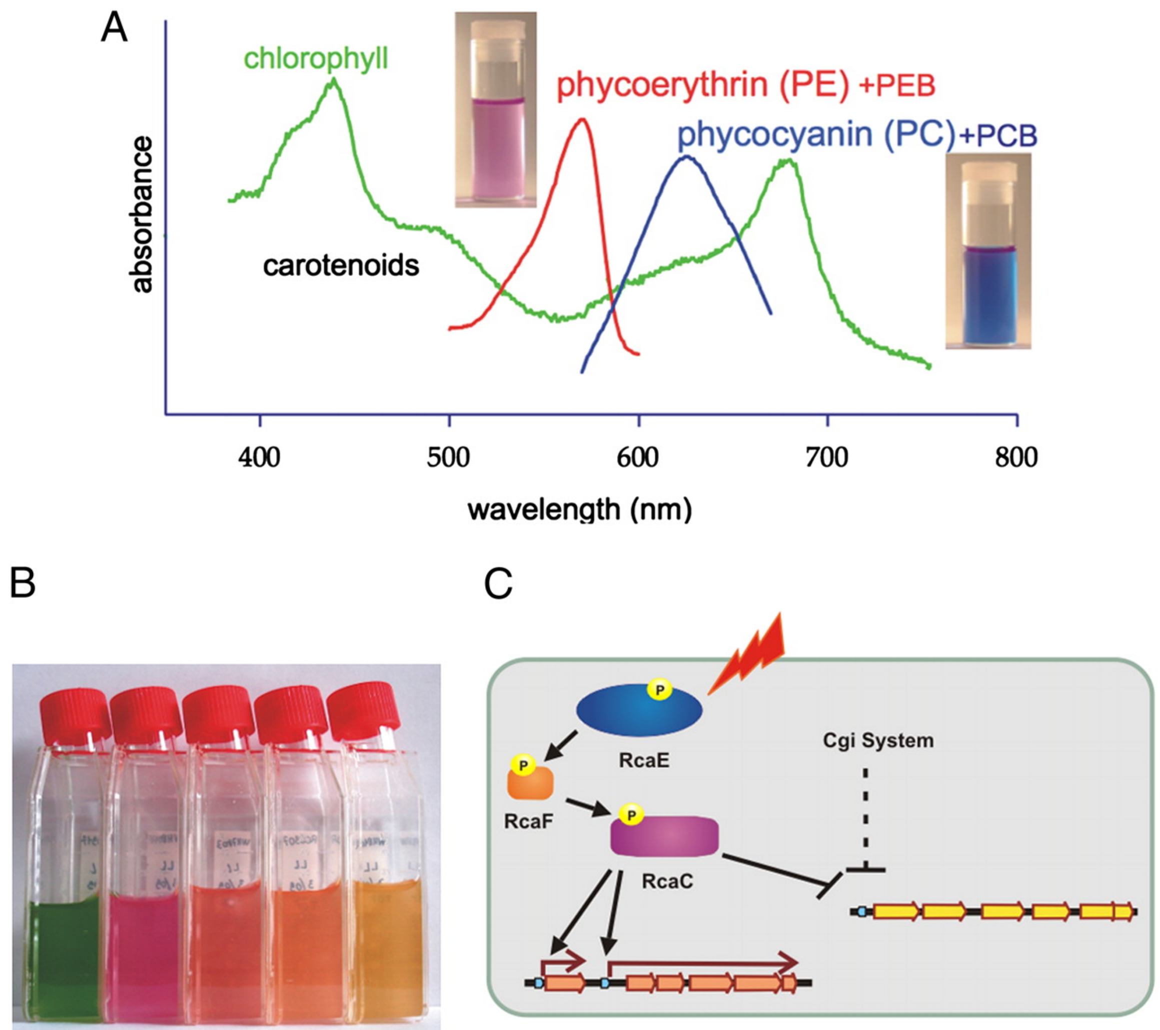
A change in chlorophyll to light quality change

TABLE 1. CHLOROPHYLL CONTENT OF HYDRILLA AND VALLISNERIA AS A FUNCTION OF WATER DEPTH.[a]

Species	Depth (m)	Chlorophyll Content (mg/g fr wt) a	b	total	Chlorophyll a/b Ratio
Hydrilla	0.0	0.7835 d	0.4420 c	1.2252 d	1.77 cd
	0.5	0.3787 c	0.2408 b	0.6194 c	1.57 b
	1.0	0.2887 b	0.1784 a	0.4667 b	1.54 b
	1.5	0.1736 a	0.1508 a	0.3253 a	1.15 a
Vallisneria	0.0	0.5296 c	0.3012 c	0.8270 c	1.96 cd
	0.5	0.5011 c	0.2392 b	0.7402 bc	2.09 d
	1.0	0.4062 b	0.2262 b	0.6323 b	1.94 cd
	1.5	0.0842 a	0.0411 a	0.1227 a	2.00 d

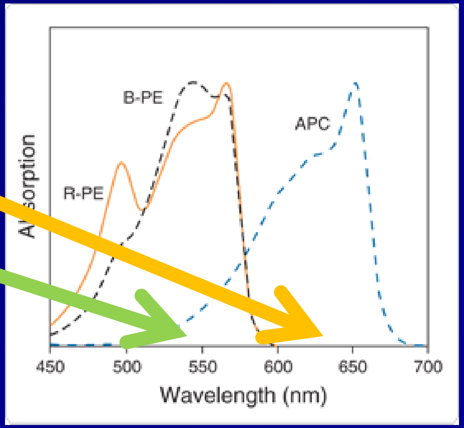
[a] Values in a column followed by the same letter are not significantly different at the 5% level as determined by Duncan's Multiple Range Test. Each value is the mean of four replications.

Phycobiliproteins, bilin variation, and group III CA regulation.



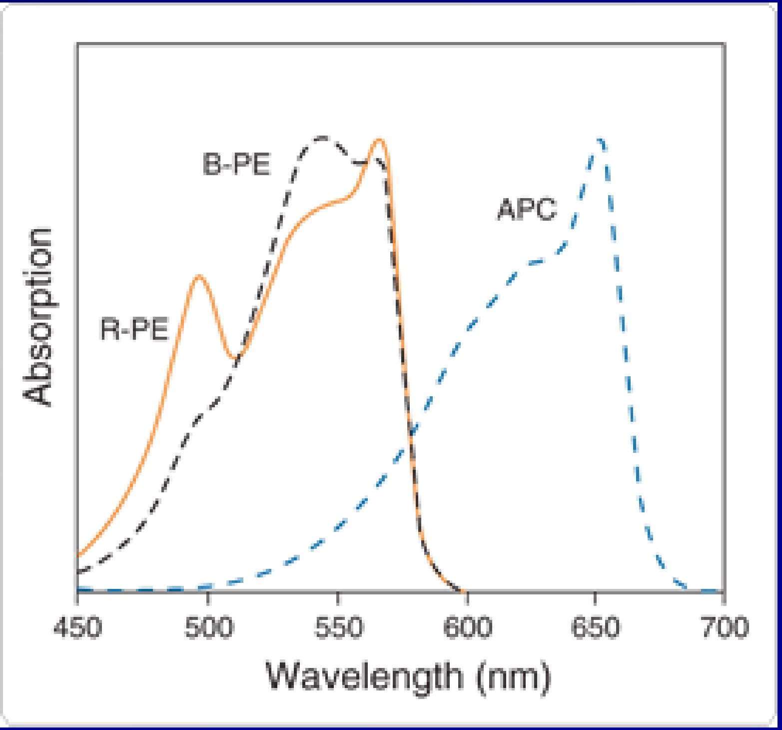
Kehoe D M PNAS 2010;107:9029-9030

- Phycobilins occur only in three groups of algae: cyanobacteria (blue-green algae), Rhodophyta (red algae), and Cryptophyceae (cryptophytes), and are largely responsible for their distinctive colors, including blue-green, red, and yellow.
- Five different phycobilins have been identified to date.
- Phycocyanobilin – 吸橘光
- Phycoerythrobilin – 吸綠光
- phycourobilin
- phycobiliviolin
- A fifth phycobilin, which absorbs deep-red light (697 nm)



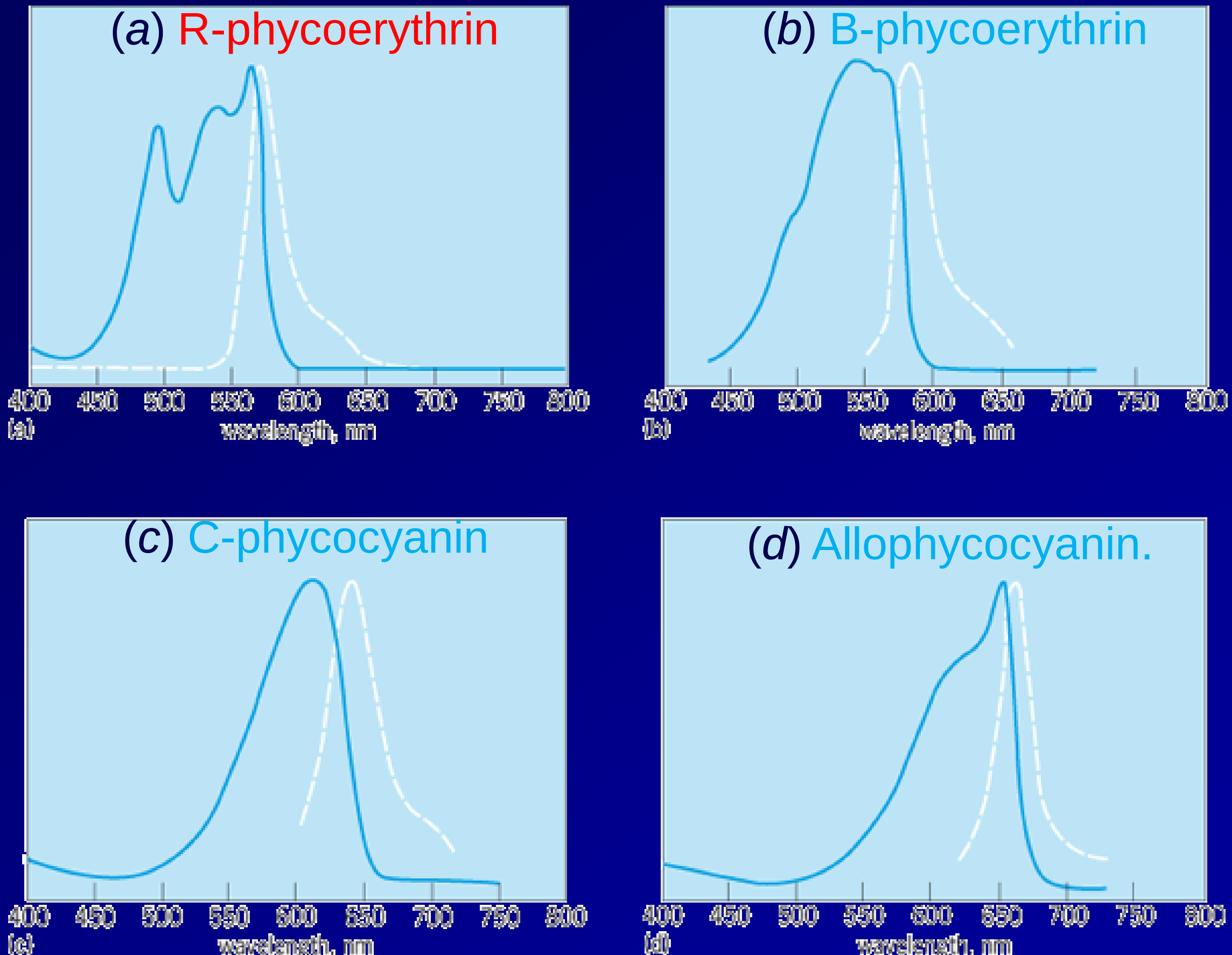
Todd M. Kana, "Phycobilin," in AccessScience, ©McGraw-Hill Companies, 2008, http://www.accessscience.com

- The two most common are phycocyanobilin [structure (1)], a blue pigment, and phycoerythrobilin (2), a red pigment.
- phycocyanobilin absorbs light maximally in the orange (620-nanometer) portion
- Phycoerythrobilin absorbs green (550-nm) portion



Todd M. Kana, "Phycobilin," in AccessScience, ©McGraw-Hill Companies, 2008, http://www.accessscience.com

Absorption spectra (colored lines) and fluorescence emission spectra (white lines) for several isolated phycobiliproteins. (*After M. N. Kronick*, *The use of phycobiliproteins as fluorescent labels in immunoassay*, *J. Immunol. Meth*., *92*:*1–13*, *1986*)



- A blue-green light (495-nm) absorbing pigment, phycourobilin, is found in some cyanobacteria and red algae.
- A yellow light (575-nm) absorbing pigment, phycobiliviolin (also called cryptoviolin), is apparently found in all cryptophytes, but in only a few cyanobacteria.
- A fifth phycobilin, which absorbs deep-red light (697 nm), has been identified spectrally in some cryptophytes, but its chemical properties are unknown

Some phycobiliproteins and their characteristics*

Phycobiliprotein	Distribution	Wavelength of absorption peaks in visible light spectrum, nm	Wavelength of maximum fluorescence emission, nm	Presence of phycobilins		
				α subunit	β subunit	γ subunit
Allophycocyanin	Cyanobacteria, Rhodophyta	650	660	1 phycocyanobilin	1 phycocyanobilin	
Allophycocyanin B	Cyanobacteria, Rhodophyta	671, 618	680	1 phycocyanobilin	1 phycocyanobilin	
C-phycocyanin	Cyanobacteria, Rhodophyta	620	637	1 phycocyanobilin	2 phycocyanobilin	
R-phycocyanin	Rhodophyta	617, 555	636	1 phycocyanobilin	1 phycocyanobilin 1 phycoerythrobilin	
Phycoerythrocyanin	Cyanobacteria	568, 590	619	1 phycobiliviolin	2 phycocyanobilin	
Phycocyanin 645	Crytophyceae	645, 585	660	1 697†	2 phycocyanobilin 1 phycobiliviolin	
C-phycoerythrin	Cyanobacteria	565, 540	577	2 phycoerythrobilin	4 phycoerythrobilin	
R-phycoerythrin‡	Rhodophyta	568, 545, 498	578	2 phycoerythrobilin	2 phycoerythrobilin, 1 phycourobilin	1 phycoerythrobilin, 3 phycourobilin
B-phycoerythrin	Rhodophyta	545, 563, 498	575	2 phycoerythrobilin	3–4 phycoerythrobilin	2 phycoerythrobilin, 2 phycourobilin
b-Phycoerythrin	Rhodophyta	545, 563	570	2 phycoerythrobilin	4 phycoerythrobilin	
Phycoerythrin 555	Cryptophyceae	545	585	? phycoerythrobilin	? phycoerythrobilin	

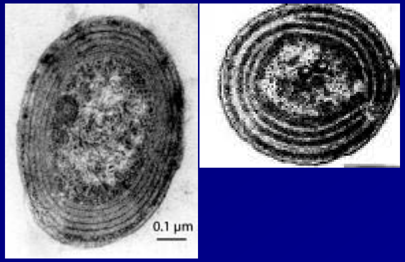
*Not included are two known phycoerythrins and phycocyanins from cryptophytes, as well as several phycoerythrins from marine cyanobacteria, which contain unusually high amounts of phycourobilin.

†Unidentified chromophore with peak absorption at 697 nm.

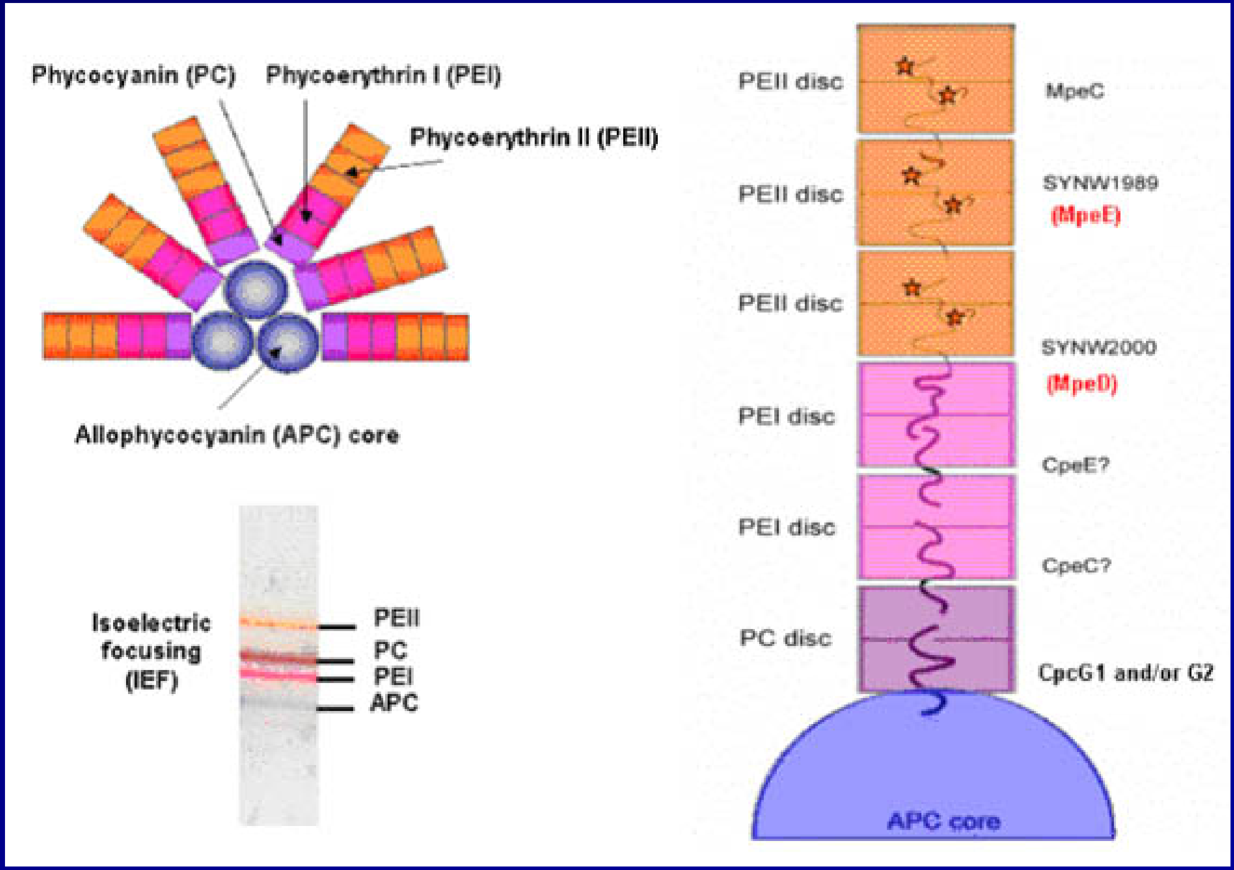
‡Variable phycobilin composition.

Phycobiliprotein in cyanobacteria

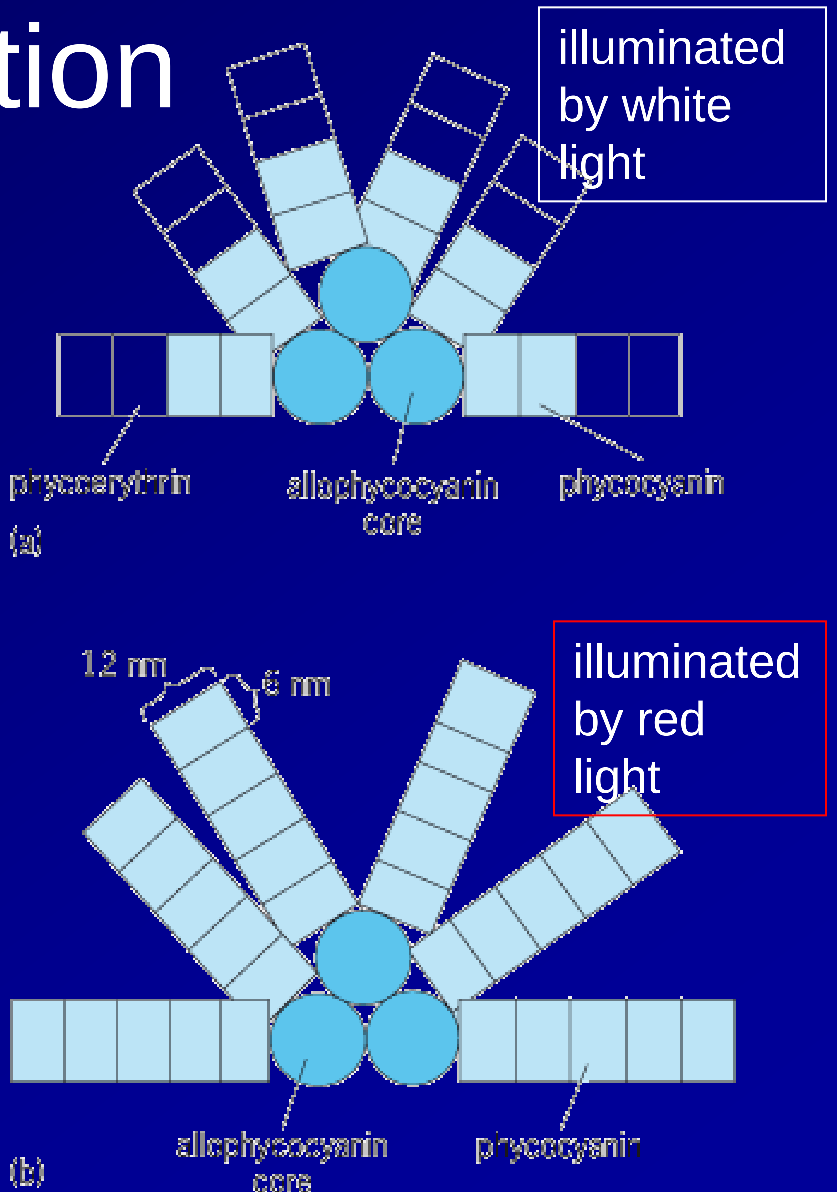
In oceanic waters, cyanobacteria comprise only two main genera: ***Synechococcus*** and ***Prochlorococcus***.



These antennae (called "**phycobilisomes**" in ***Synechococcus***) are composed of pigment-proteins complexes arranged in such a way to capture light with a high efficiency. Pigments that are bound to antenna systems may have very different colours (such as green, blue, pink or orange) and this will determine the wavelengths of the solar spectrum that cells can efficiently harvest in the oceanic waters.

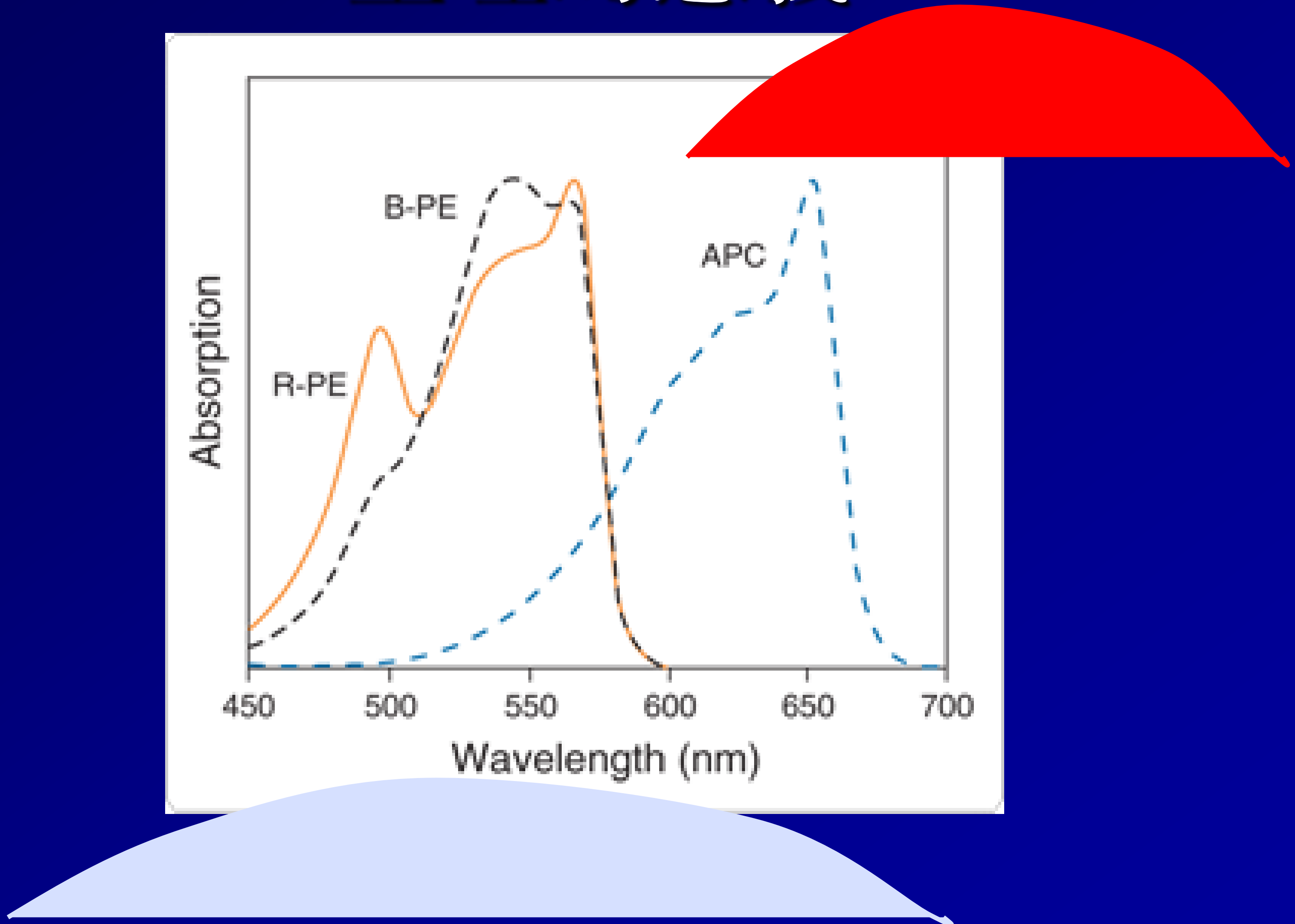


complementary chromatic adaptation



Structure of a hemidiscoidal phycobilisome of *Tolypothrix tenuis* under different light conditions. (*a*) When illuminated by white light, the phycobilisome contains phycoerythrin, phycocyanin, and allophycocyanin. Energy absorbed by phycoerythrin is transferred to phycocyanin and allophycocyanin. The allophycocyanin core proteins are attached, via a linker protein, to the photosynthetic membrane, which is not shown. (*b*) When illuminated by red light, the phycobilisome undergoes complementary chromatic adaptation, in which phycoerythrin is no longer produced but additional phycocyanin is produced. (*After R. MacColl and D. Guard-Friar, Phycobiliproteins, CRC*

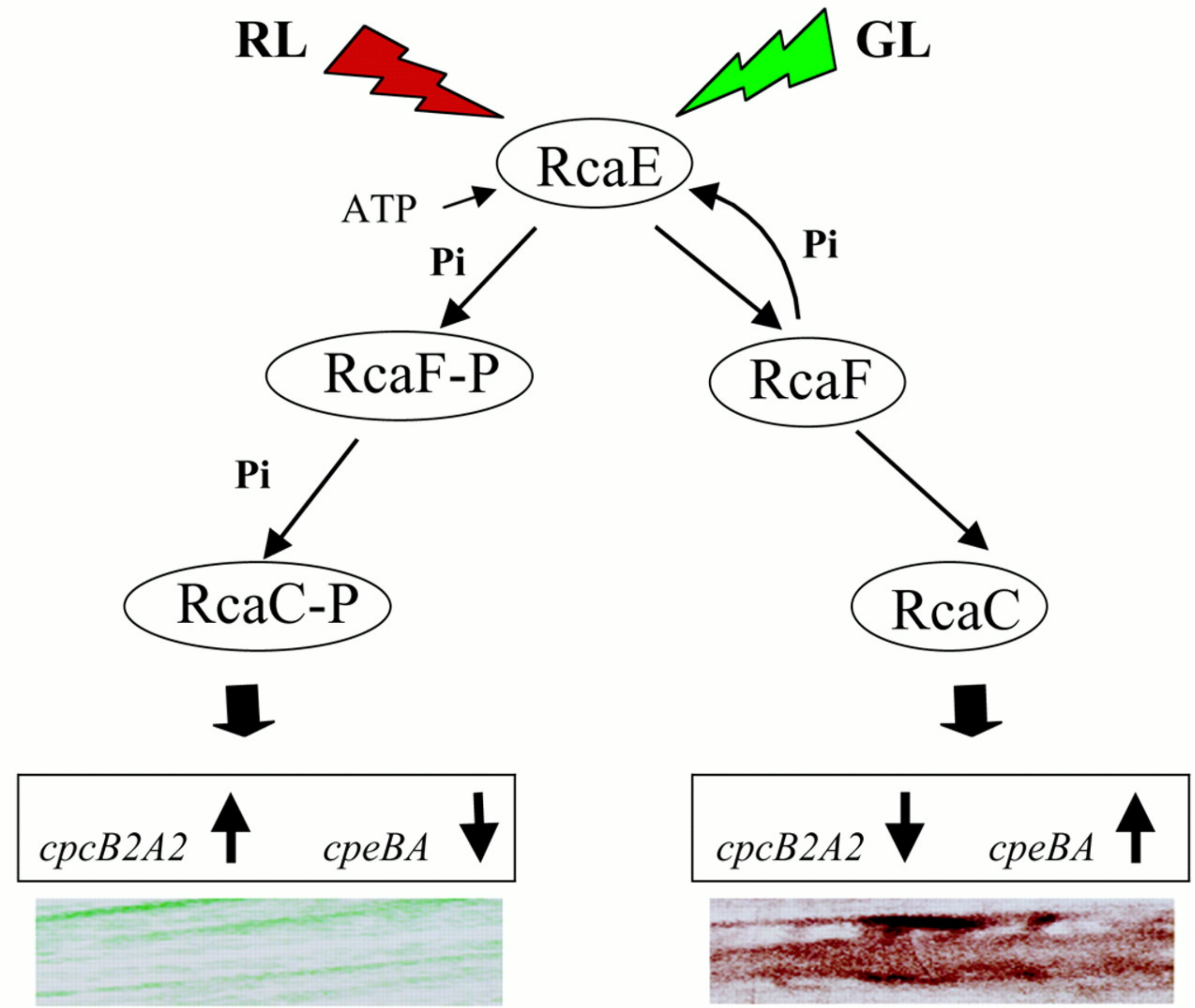
藻類? 變色龍? Why?
生理的意義



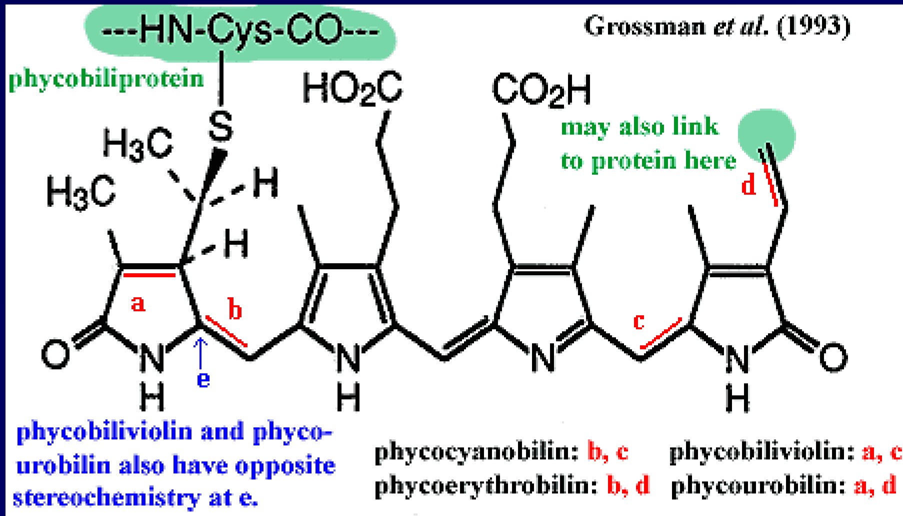
Physiology

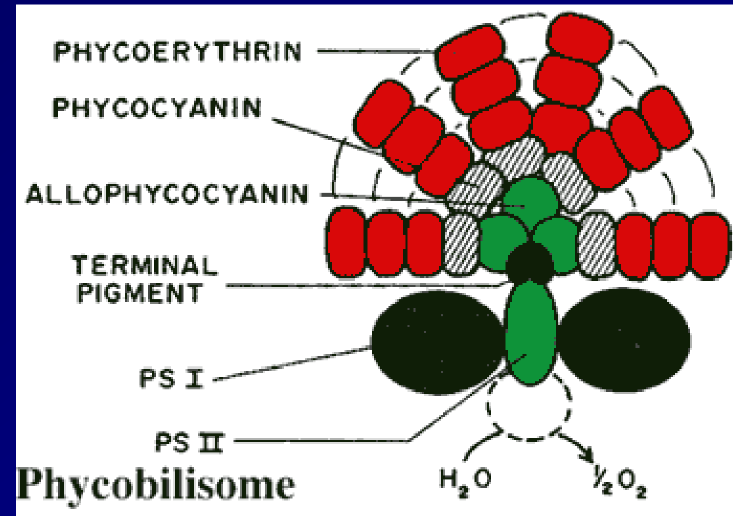
- Several environmental factors can influence the phycobiliprotein content. Algal cells grown under low light intensity may have up to 20 times more phycobiliprotein than those grown under high light intensity. This response increases the ability of the alga to absorb light when it is in limited supply. Some cyanobacteria and red algae are also influenced by the color of the growth light and exhibit a phenomenon called complementary chromatic adaptation. For example, when the cyanobacterium *Tolypothrix tenuis* is grown under red light, it produces red-light-absorbing phycocyanin as its accessory pigment. However, when grown under green light, it produces green-light-absorbing phycoerythrin along with small amounts of phycocyanin .
- This response is controlled by an unidentified photoreversible pigment in a manner similar to the action of phytochrome, but with absorption maxima near 545 and 645 nm.
- This process is regulated at the level of deoxyribonucleic acid (DNA) transcription.

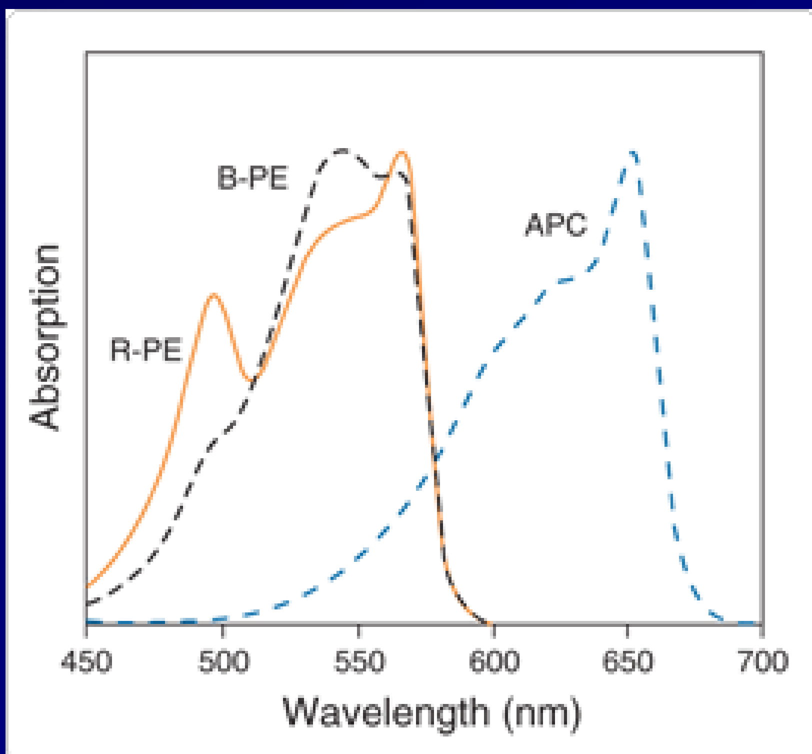
Phosphorelay regulation of CCA. Theleft side depicts RL-stimulated phosphorylation of components of the signal transduction pathway, activation ofcpcB2A2, and suppression of cpeBA.

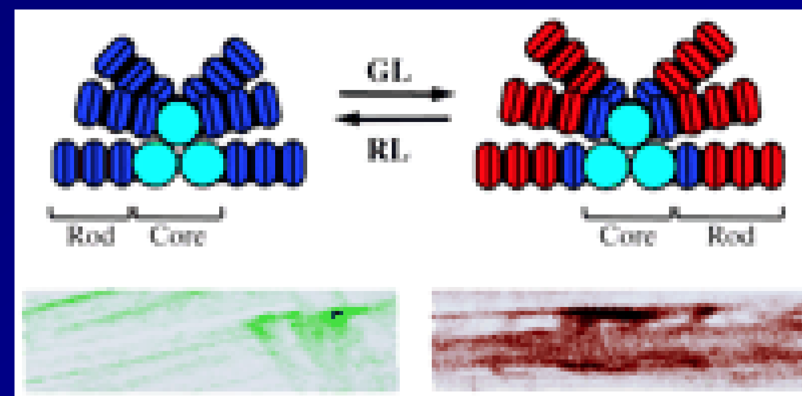


Grossman A R et al. J. Biol. Chem. 2001;276:11449-11452









complementary chromatic adaptation (CCA)

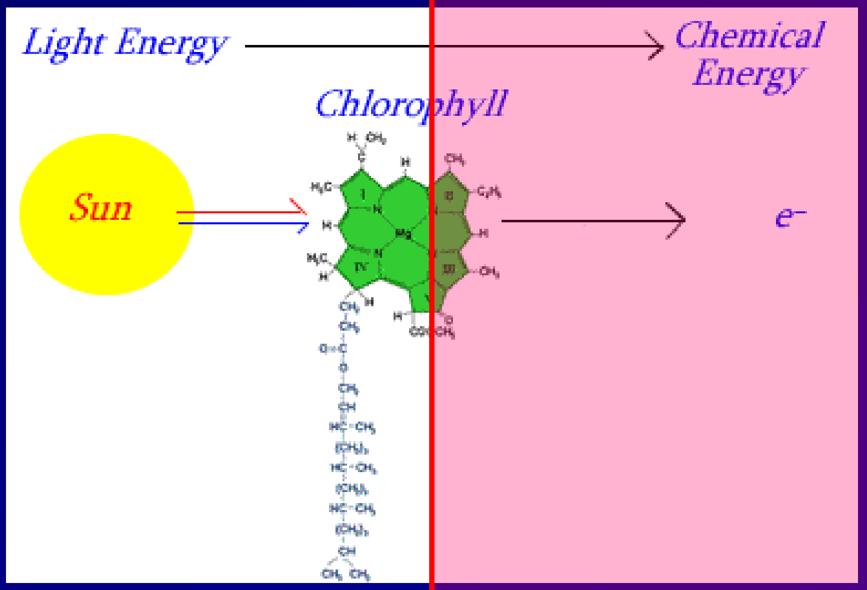
The Journal of Biological Chemistry, 276, 11449-11452 (2001)

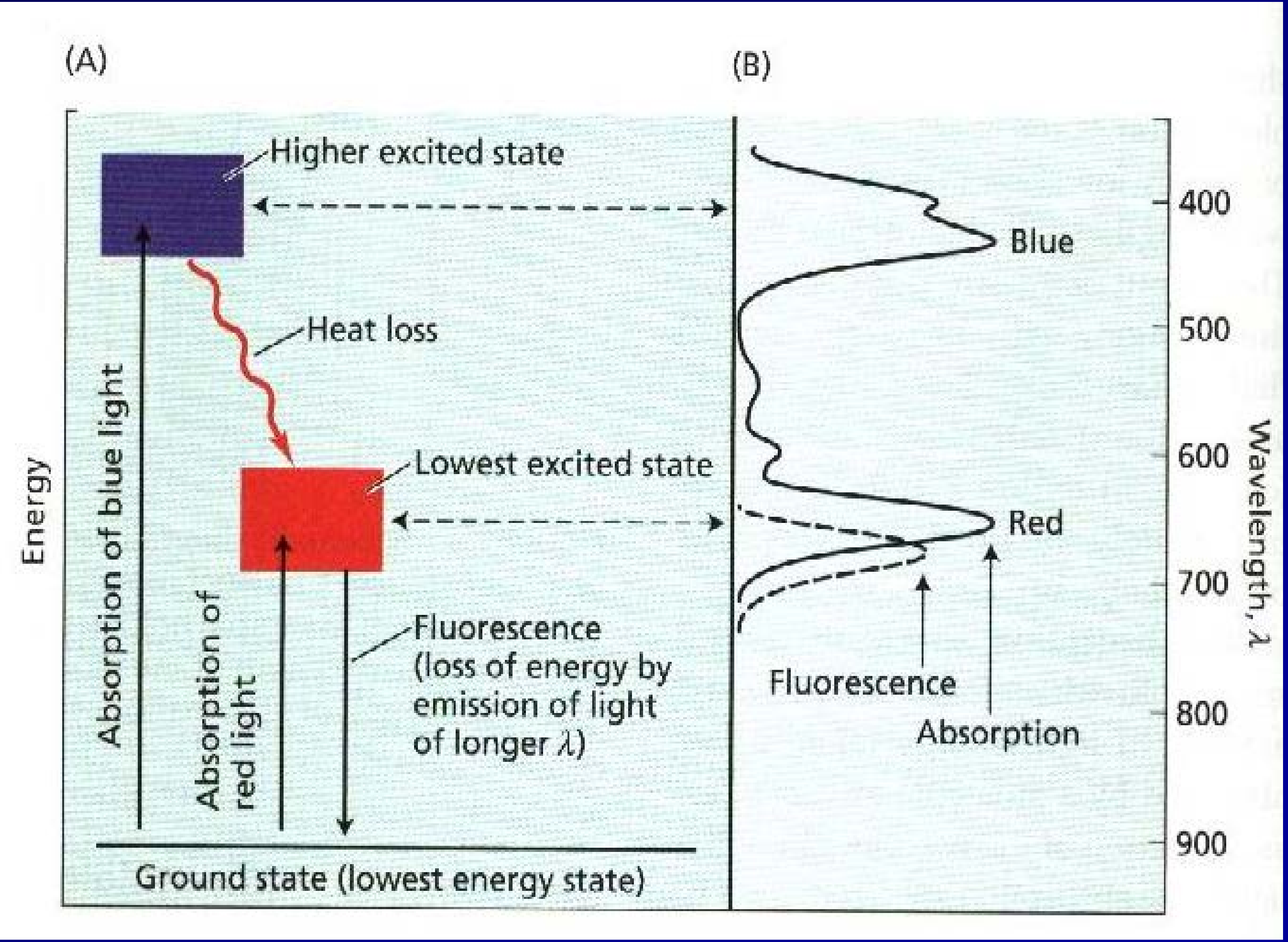
Regulation of phycobiliprotein concentration

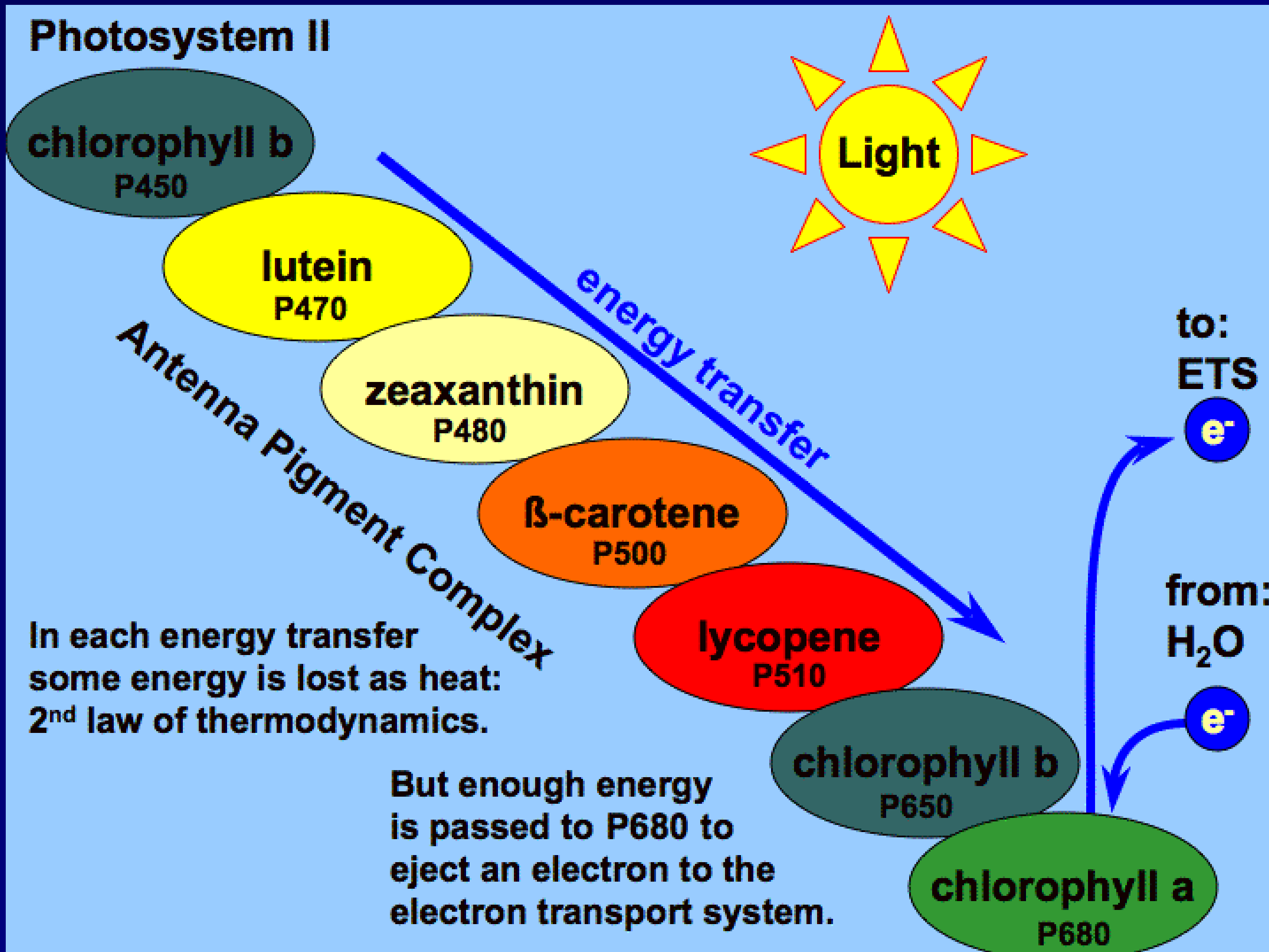
- Excdept light quality and intensity, phycobiliprotein concentration also depends on the availability of nutrients, including nitrogen, carbon dioxide, phosphorus, sulfur, and iron. Nutrient starvation generally causes a loss of phycobiliprotein, with the rod proteins of the phycobilisomes being lost more rapidly than the core proteins.
- In cyanobacteria, this reduction is due to specific proteolytic degradation of biliprotein present in the cell and repression of synthesis of new biliprotein.

Light reaction

- 2 pigment system: photosystem Ⅱ (PS Ⅱ) and photosystem Ⅰ (PS Ⅰ)
  - light harvesting pigment-protein complex(LHPC); antenna pigment; reaction center(chlorophyll-a-protein complex, PS Ⅱ:P680; PS Ⅰ:P700)
  - xanthophylls play a role in the removal of excess energy (xanthophylls cycle)
- non-cyclic electron transport: NADP+ is reduced to NADPH and generate ATP, and O_2 gas
- cyclic electron transport: ATP
- absorbed radiation energy
  - fluorescent and phosphorescent light and heat

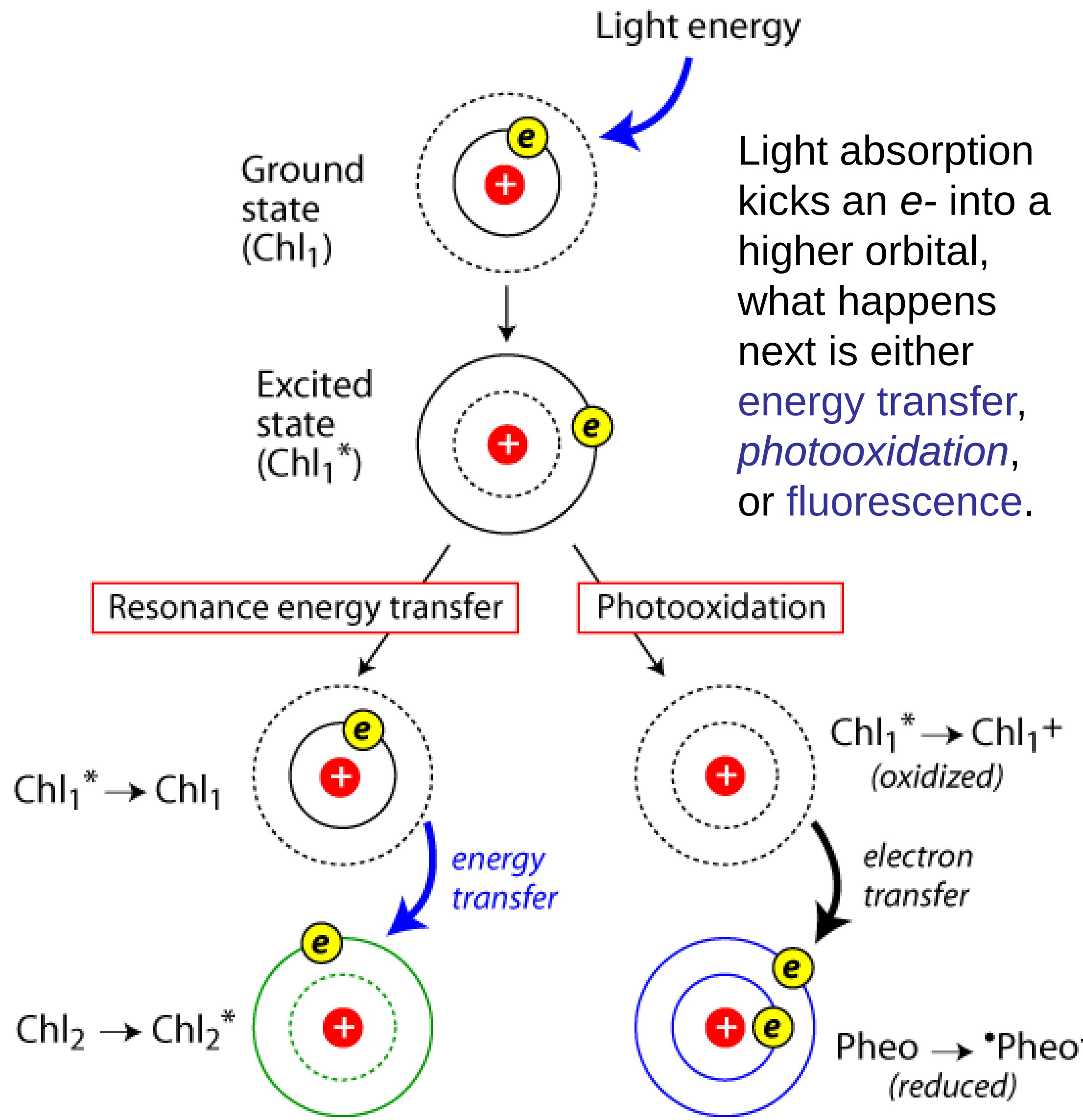



(A)
(B)
Higher excited state
Heat loss
Lowest excited state
Energy
Absorption of blue light
Absorption of red light
Fluorescence (loss of energy by emission of light of longer λ)
Ground state (lowest energy state)
Blue
Red
Fluorescence
Absorption
400
500
600
700
800
900
Wavelength, λ


Photosystem II
chlorophyll b
P450
lutein
P470
zeaxanthin
P480
ß-carotene
P500
lycopene
P510
chlorophyll b
P650
chlorophyll a
P680
Light
energy transfer
Antenna Pigment Complex
to:
ETS
e^-
from:
H_2O
e^-
In each energy transfer
some energy is lost as heat:
2nd law of thermodynamics.
But enough energy
is passed to P680 to
eject an electron to the
electron transport system.

Light harvesting involves **resonance energy transfer**, whereas, **photooxidation** involves **e- transfer** from chlorophyll to the electron acceptor called **pheophytin** which becomes negatively charge as denoted by •Pheo-.

Importantly, the oxidized chlorophyll molecule (now positively charged, Chl^{+}) returns to the ground state by accepting an electron through a coupled redox reaction involving the oxidation of H_2O.



Light absorption kicks an *e*- into a higher orbital, what happens next is either energy transfer, *photooxidation*, or fluorescence.

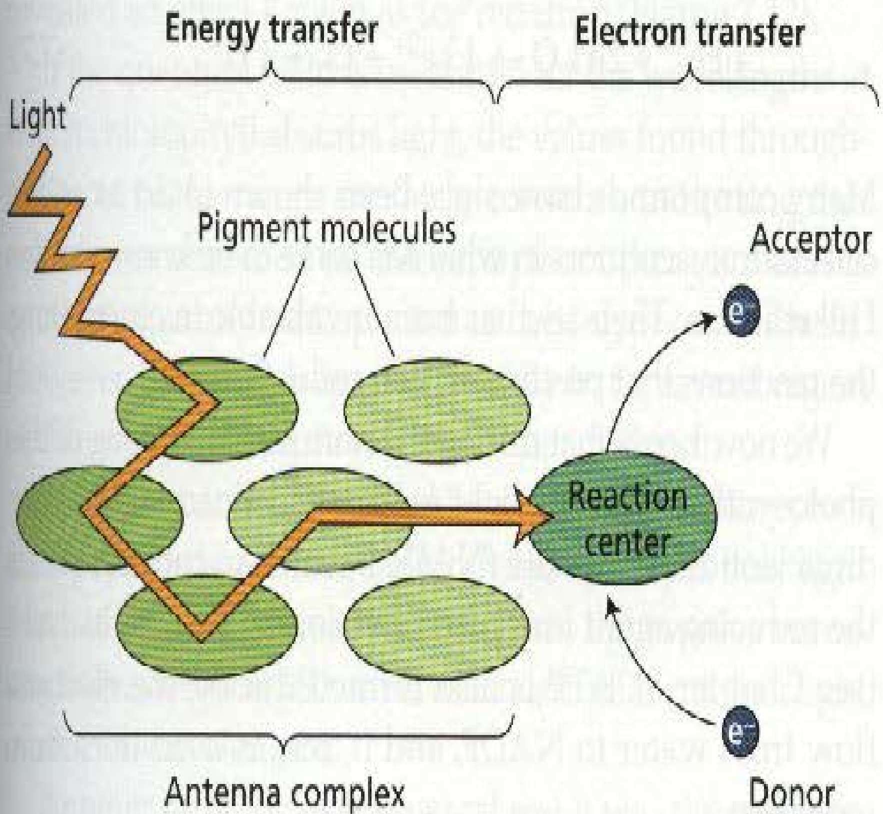


FIGURE 7.10 Basic concept of energy transfer during photosynthesis. Many pigments together serve as an antenna, collecting light and transferring its energy to the reaction center, where chemical reactions store some of the energy by transferring electrons from a chlorophyll pigment to an electron acceptor molecule. An electron donor then reduces the chlorophyll again. The transfer of energy in the antenna is a purely physical phenomenon and involves no chemical changes.

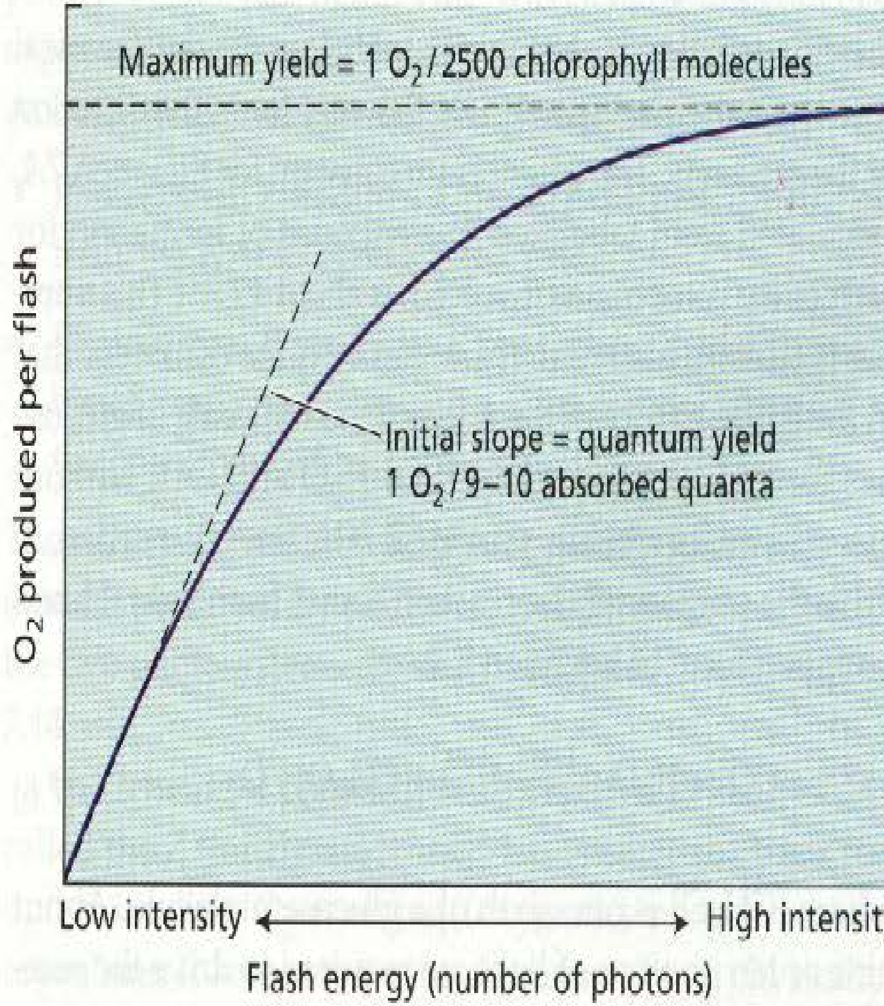
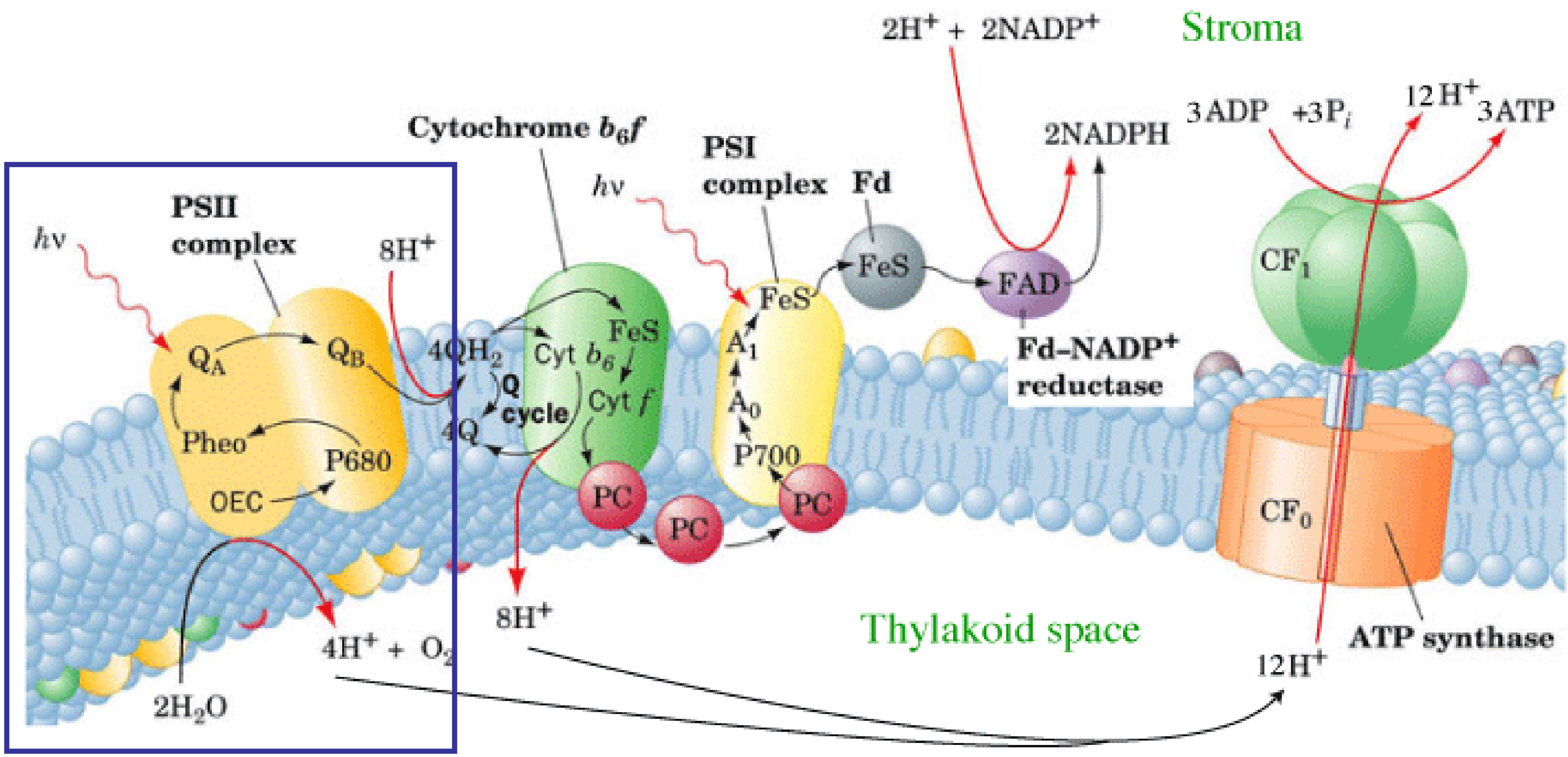


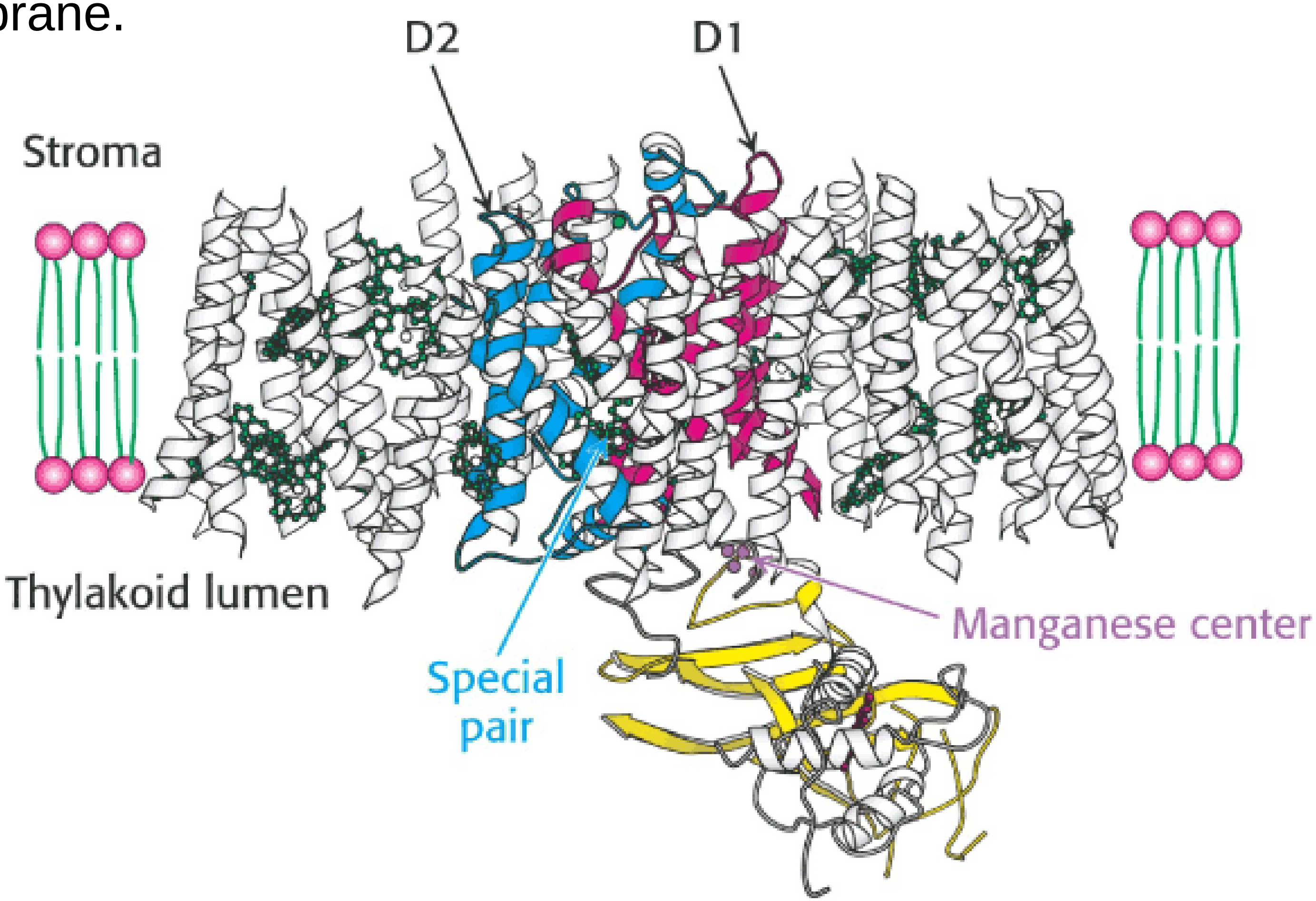
FIGURE 7.11 Relationship of oxygen production to flash energy, the first evidence for the interaction between the antenna pigments and the reaction center. At saturating energies, the maximum amount of O_2 produced is 1 molecule per 2500 chlorophyll molecules.

Now all we have to do is follow the photons, electrons, and protons starting with PSII



Photosystem II (PSII)

Photosystem II contains chlorophylls a and b and absorbs light at 680nm. This is a large protein complex that is located in the thylakoid membrane.



PSII

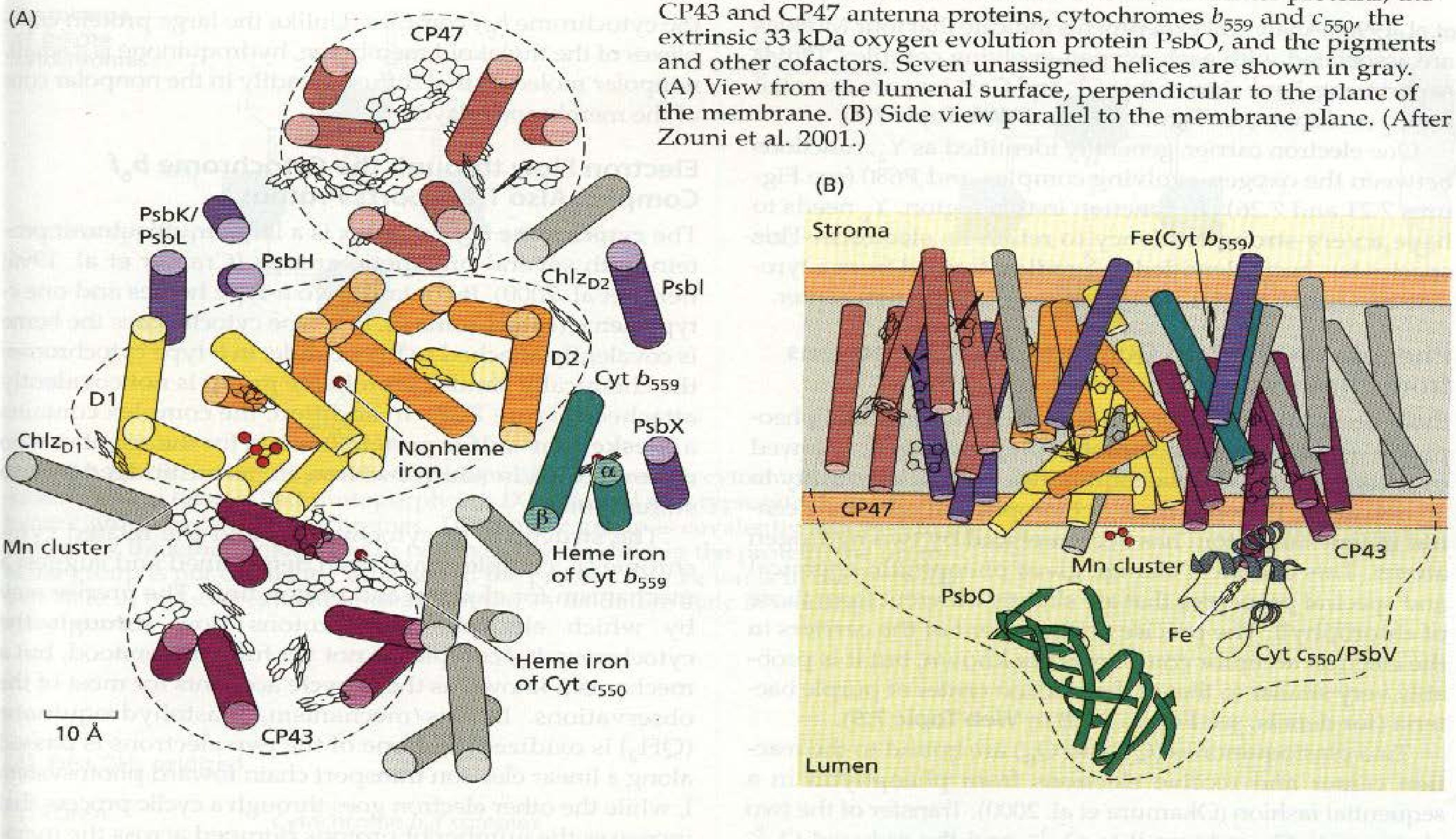
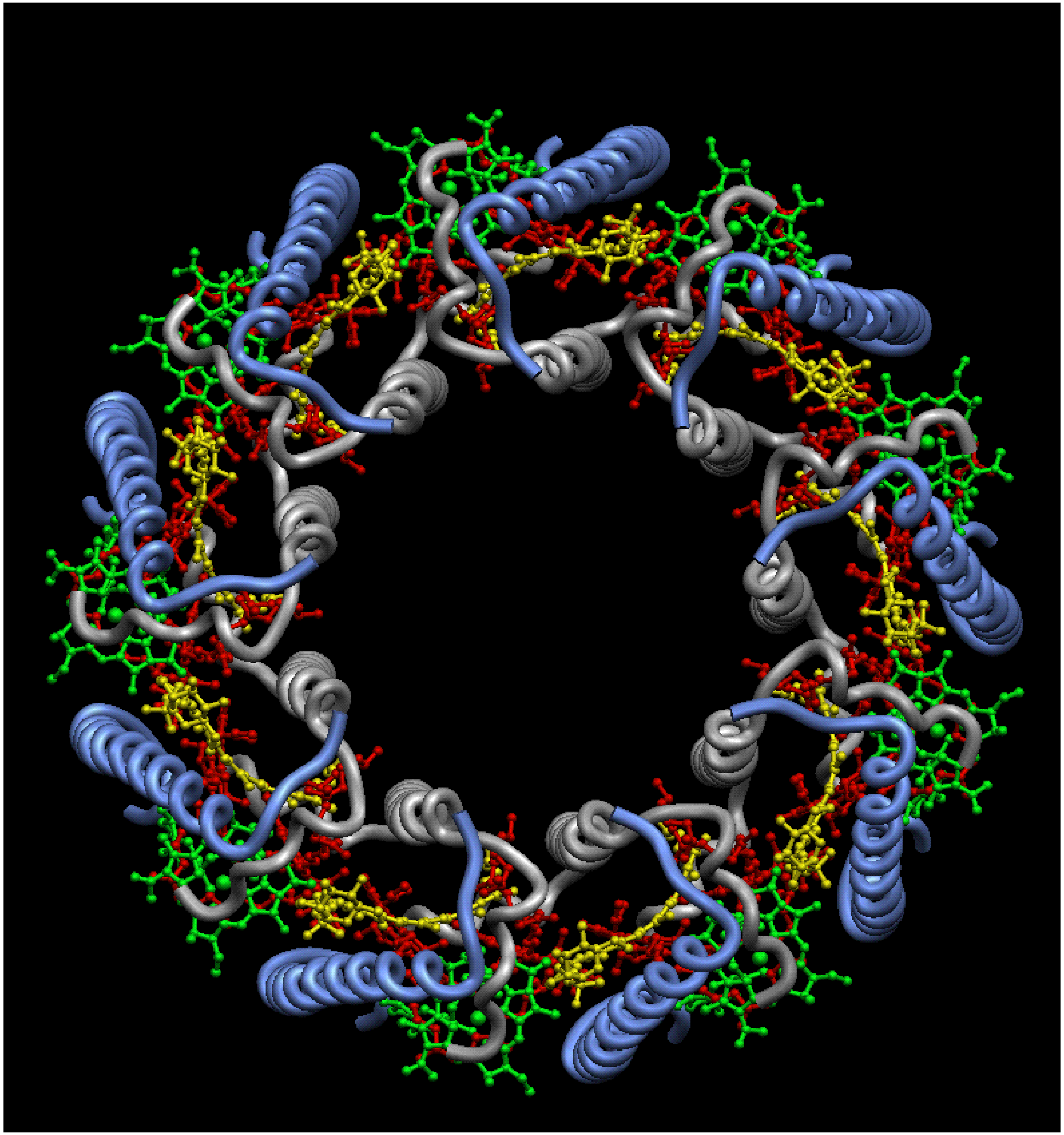
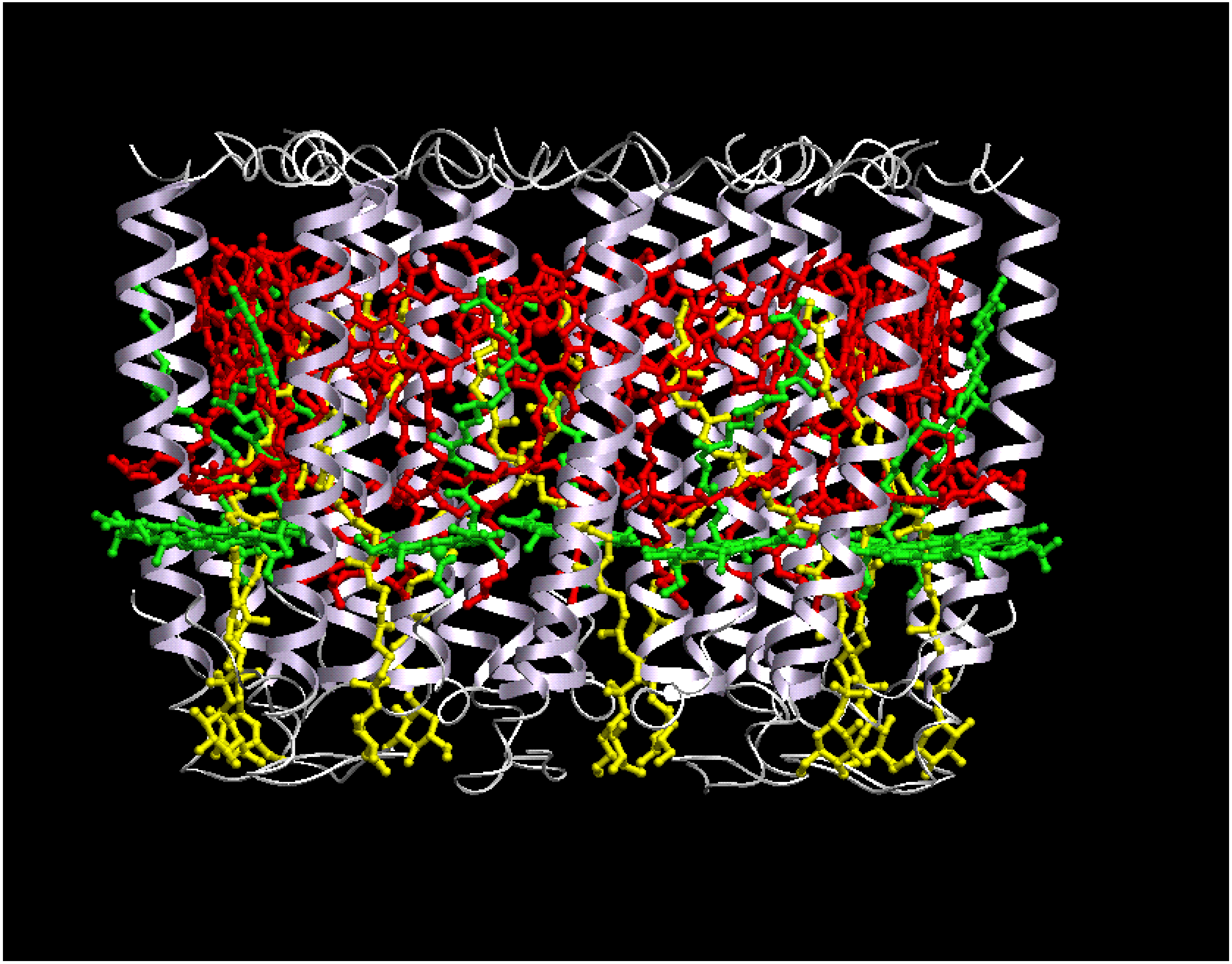


FIGURE 7.25 Structure of the photosystem II reaction center from the cyanobacterium *Synechococcus elongatus*, resolved at 3.8 Å. The structure includes the D1 and D1 core reaction center proteins, the CP43 and CP47 antenna proteins, cytochromes b_{559} and c_{550}, the extrinsic 33 kDa oxygen evolution protein PsbO, and the pigments and other cofactors. Seven unassigned helices are shown in gray. (A) View from the lumenal surface, perpendicular to the plane of the membrane. (B) Side view parallel to the membrane plane. (After Zouni et al. 2001.)

LH2 FROM *Rs. acidophhilus*



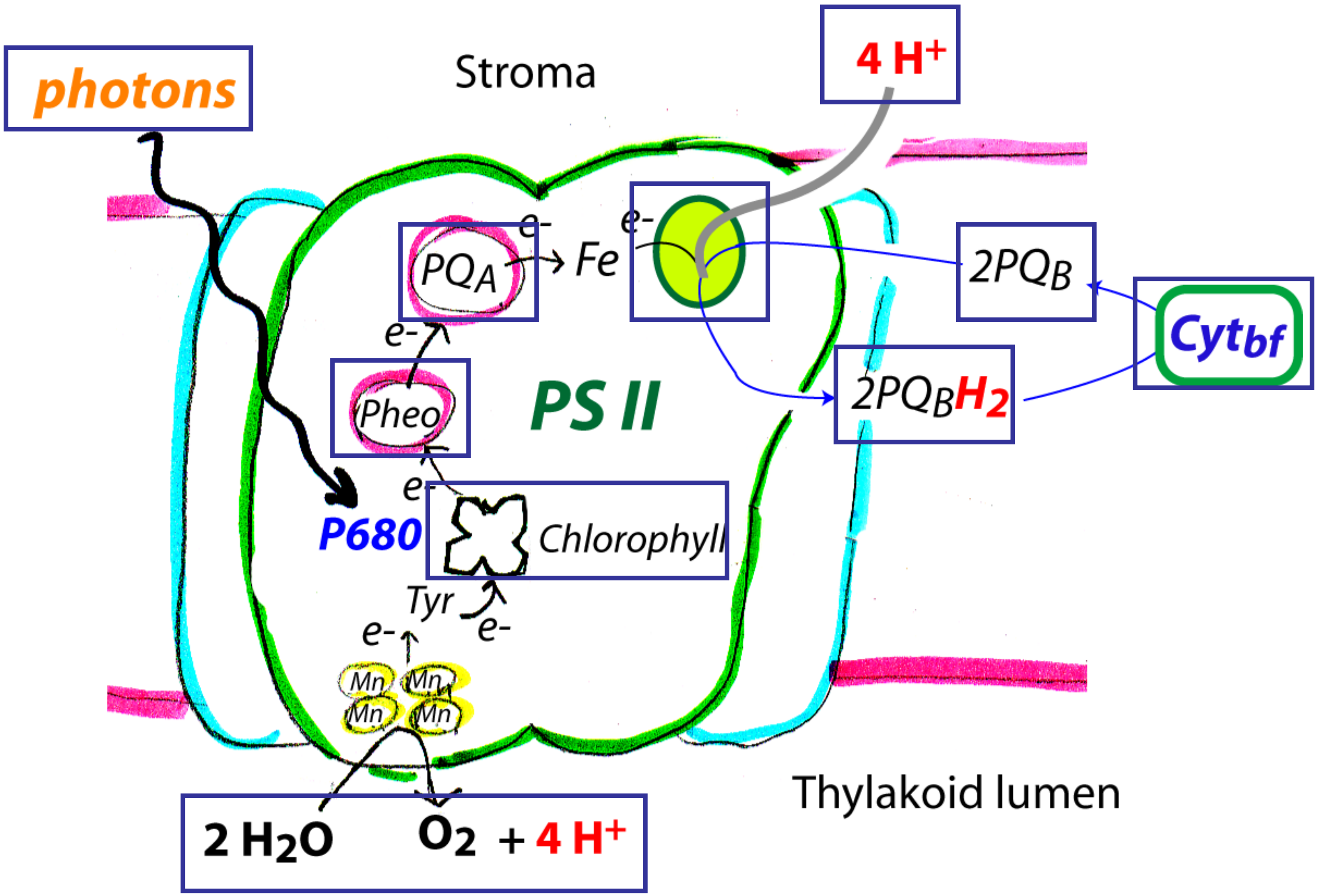


LHC-II

- MOST ABUNDANT MEMBRANE PROTEIN IN CHLOROPLASTS OF GREEN PLANTS
- A TRANSMEMBRANE PROTEIN
- BINDS
  - ~ 7 CHLOROPHYLL a MOLECULES
  - ~ 5 CHLOROPHYLL b MOLECULES
  - TWO CAROTENOIDS

- COMPRISES ABOUT 50% OF ALL CHLOROPHYLL IN BIOSPHERE

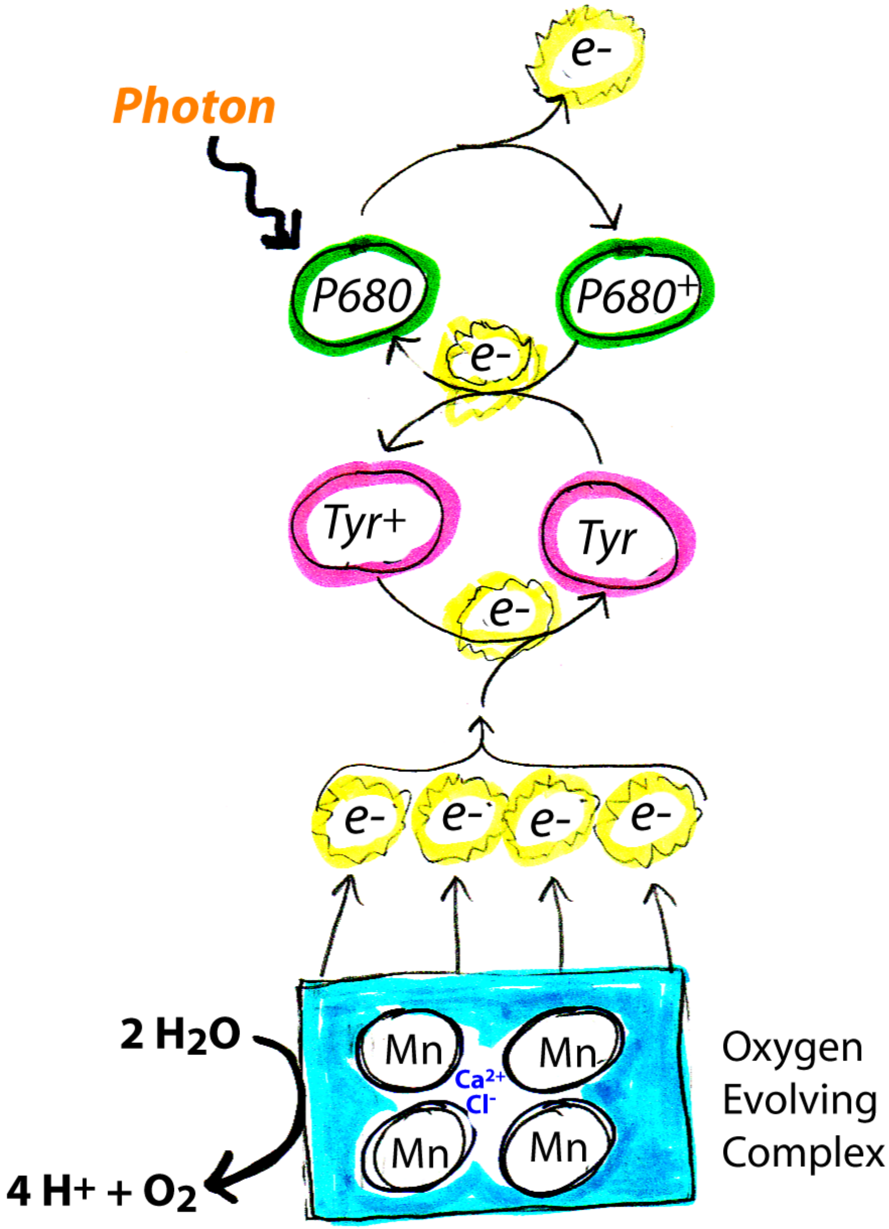
Functional organization of the PSII complex



The electron that was transferred from the P680 chlorophyll reaction center needs to be replaced, this replacement electron comes from the oxidation of H_2O within the oxygen evolving complex.

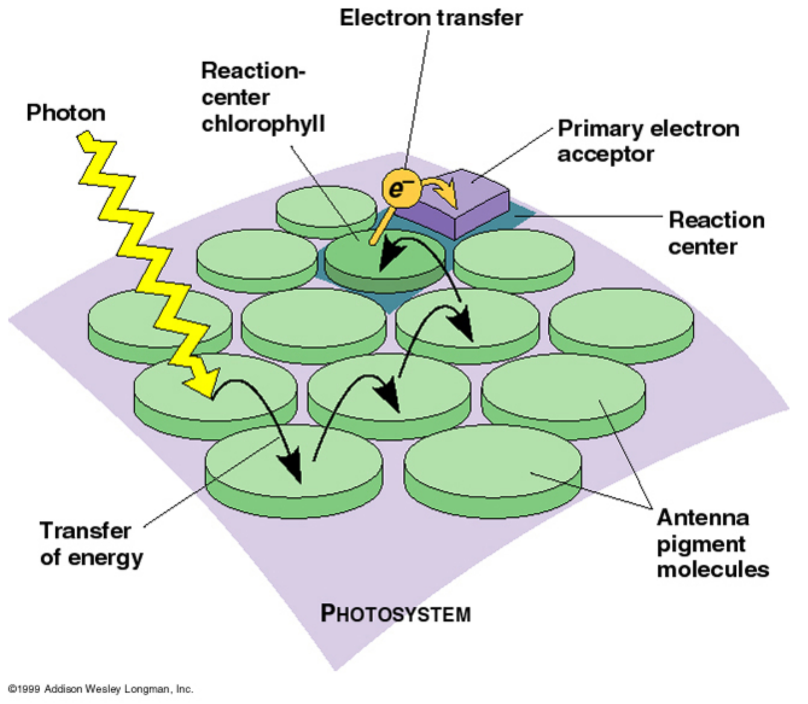
The tricky part is that the oxidation of H_2O releases 4 *e*-, however, photooxidation only transfers one *e*- at a time to pheophytin.

Therefore, the Mn atoms must be able to “store” electrons and release them one at a time.



What Next?

- At the reaction center are 2 molecules
  - Chlorophyll *a*
  - Primary electron acceptor
- The reaction-center chlorophyll is oxidized as the excited electron is removed through the reduction of the primary electron acceptor
- Photosystem I and II



electron transport

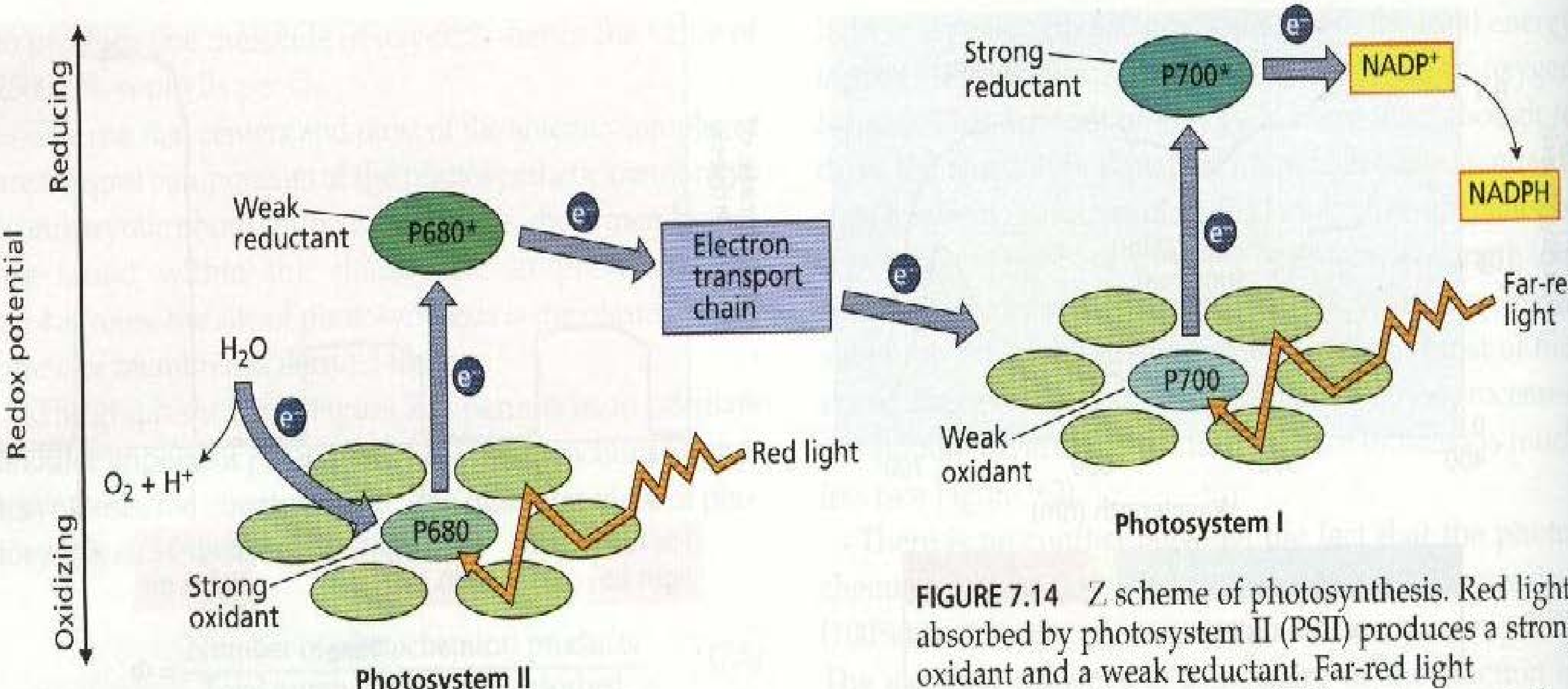
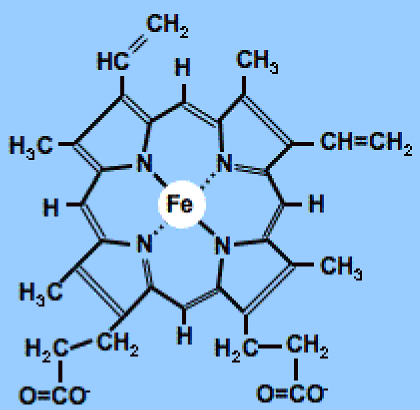


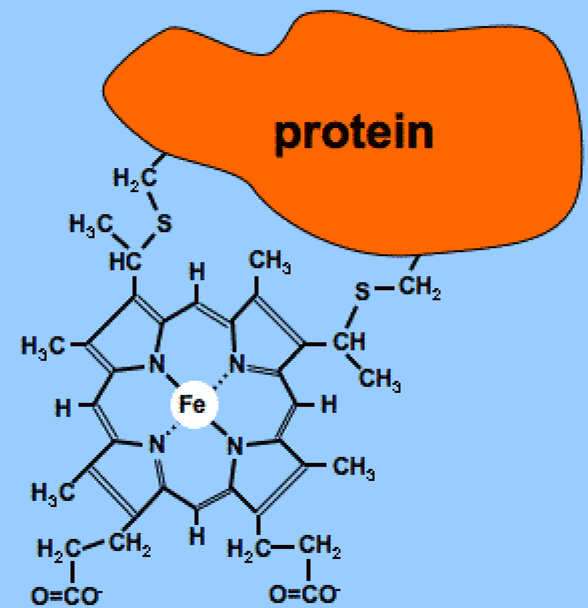
FIGURE 7.14 Z scheme of photosynthesis. Red light absorbed by photosystem II (PSII) produces a strong oxidant and a weak reductant. Far-red light absorbed by photosystem I (PSI) produces a weak oxidant and a strong reductant. The strong oxidant generated by PSII oxidizes water, while the strong reductant produced by PSI reduces $NADP^+$. This scheme is basic to an understanding of photosynthetic electron transport. P680 and P700 refer to the wavelengths of maximum absorption of the reaction center chlorophylls in PSII and PSI, respectively.

Cytochromes include a heme group and a membrane protein

protoheme of cytochrome-b



heme of cytochrome-c

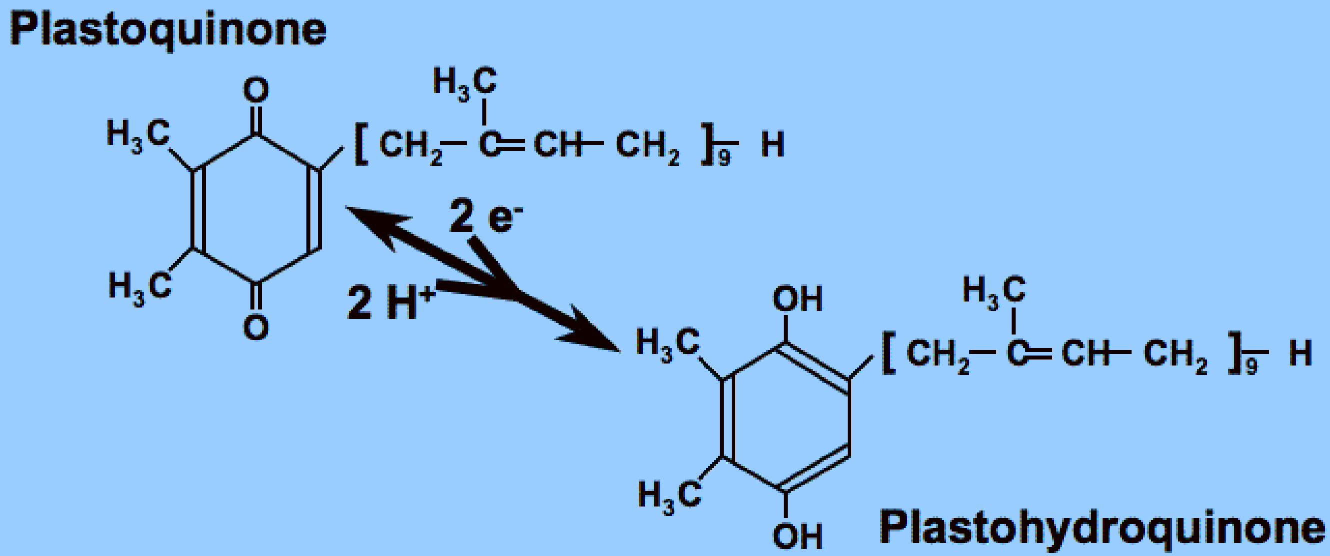


Cytochrome [Fe^{3+}] + e^- ⟷ Cytochrome [Fe^{2+}]

-ic -ous

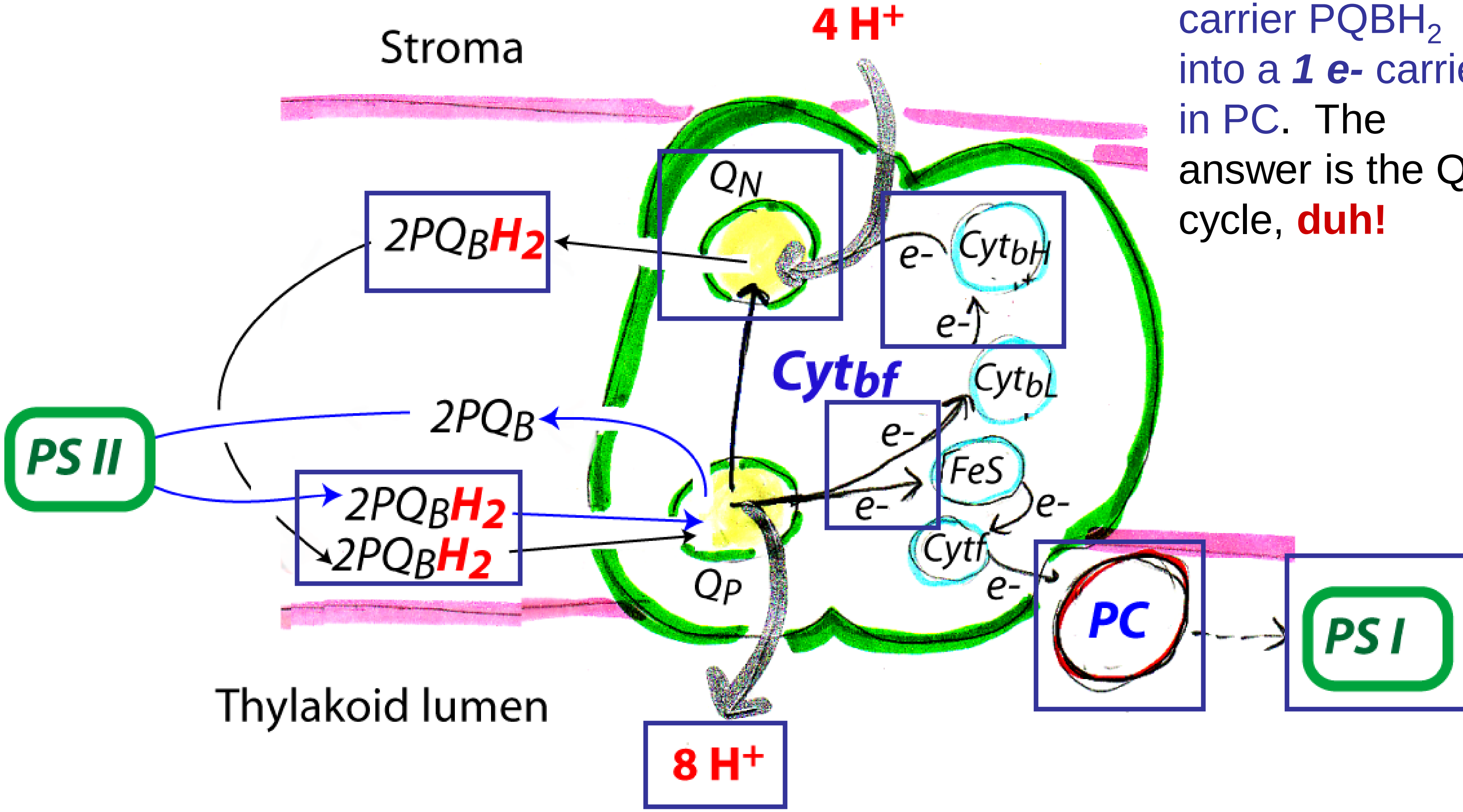
Plastocyanin [Cu^{2+}] + e^- ⟷ Plastocyanin [Cu^{1+}]

Plastoquinone is a shuttle for protons across the thylakoid membrane

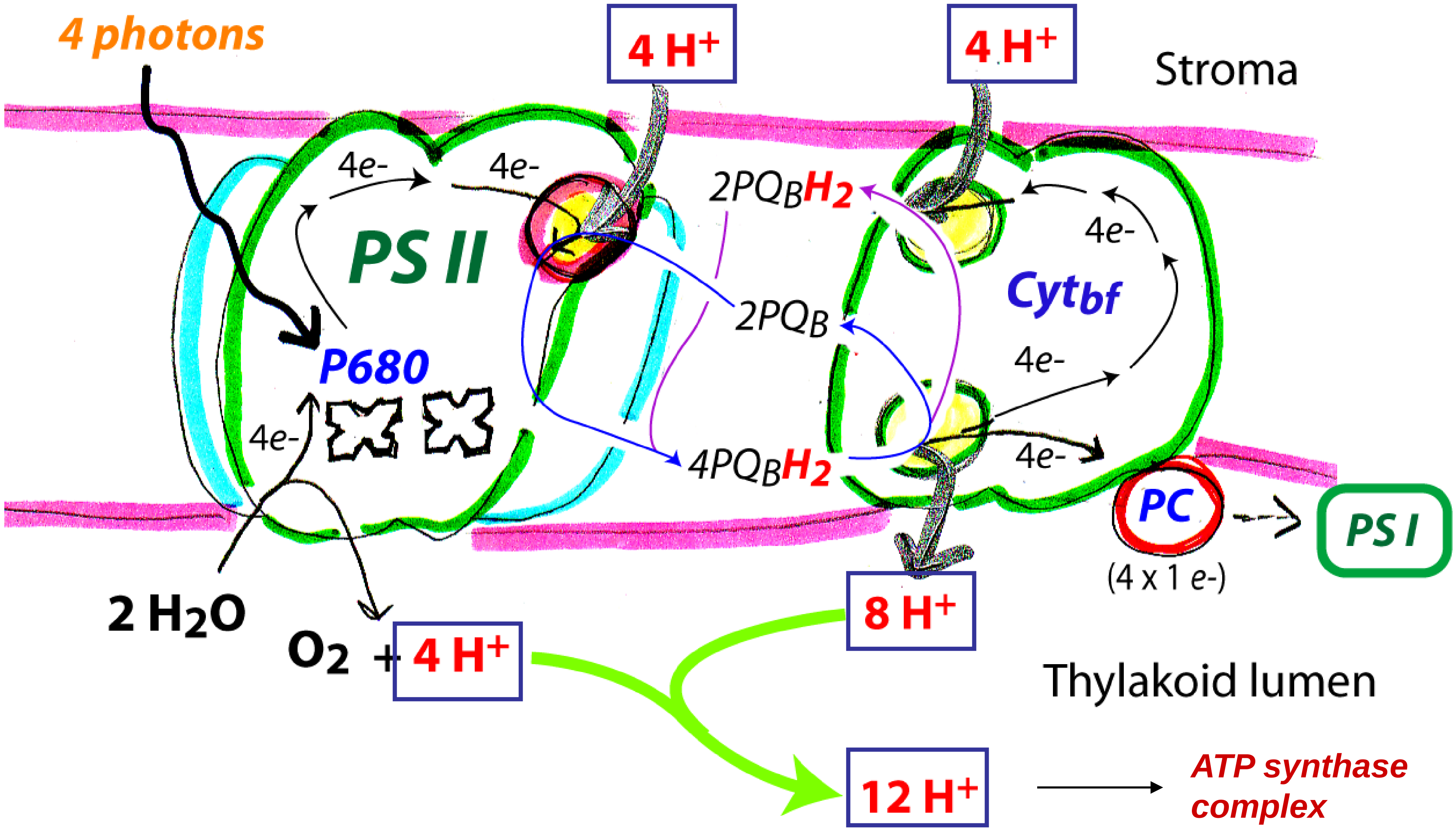


Functional organization of the cytochrome b_6f complex

The same deal here as in **complex III of ETS**, we need to convert the ***2 e-*** carrier $PQBH_2$ into a ***1 e-*** carrier in PC. The answer is the Q cycle, **duh!**

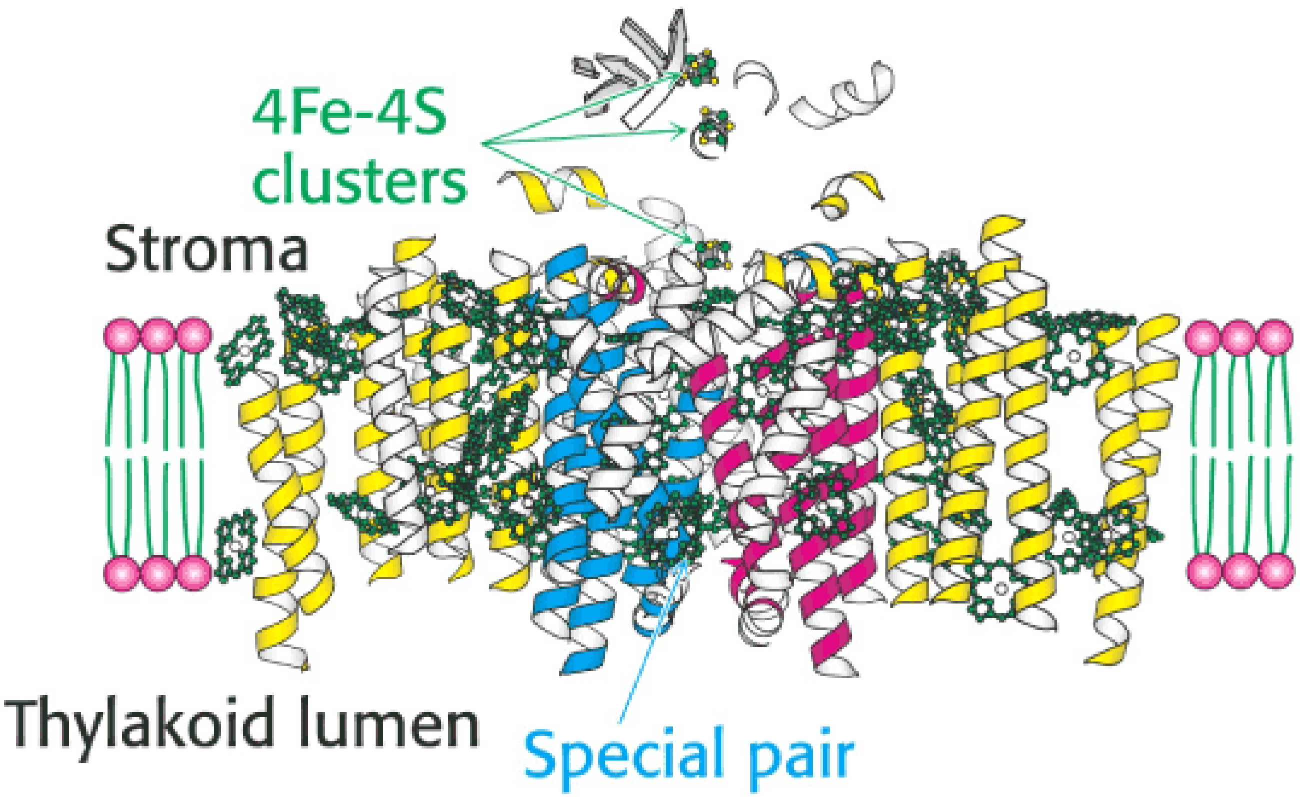


The light-driven Q cycle is responsible for translocation of 8 H^+ from the stroma to the lumen



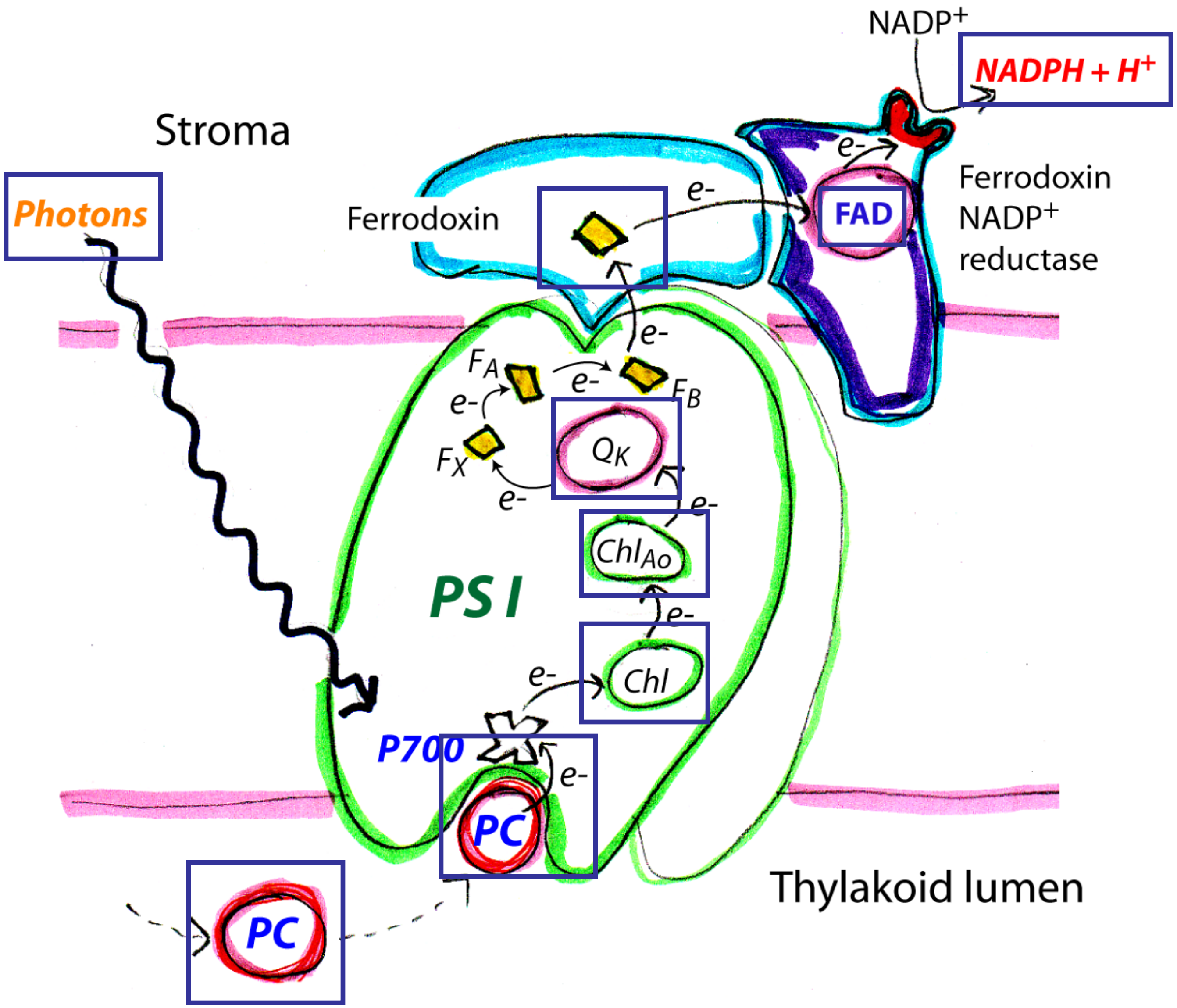
Photosystem I (PSI)

The final stage of photosynthesis: the absorption of light energy by PS I is at a maximum of 700 nm. Again 4 photons are absorbed, but in this case, the energy is used to generate reduced ferredoxin, which is a powerful reductant.



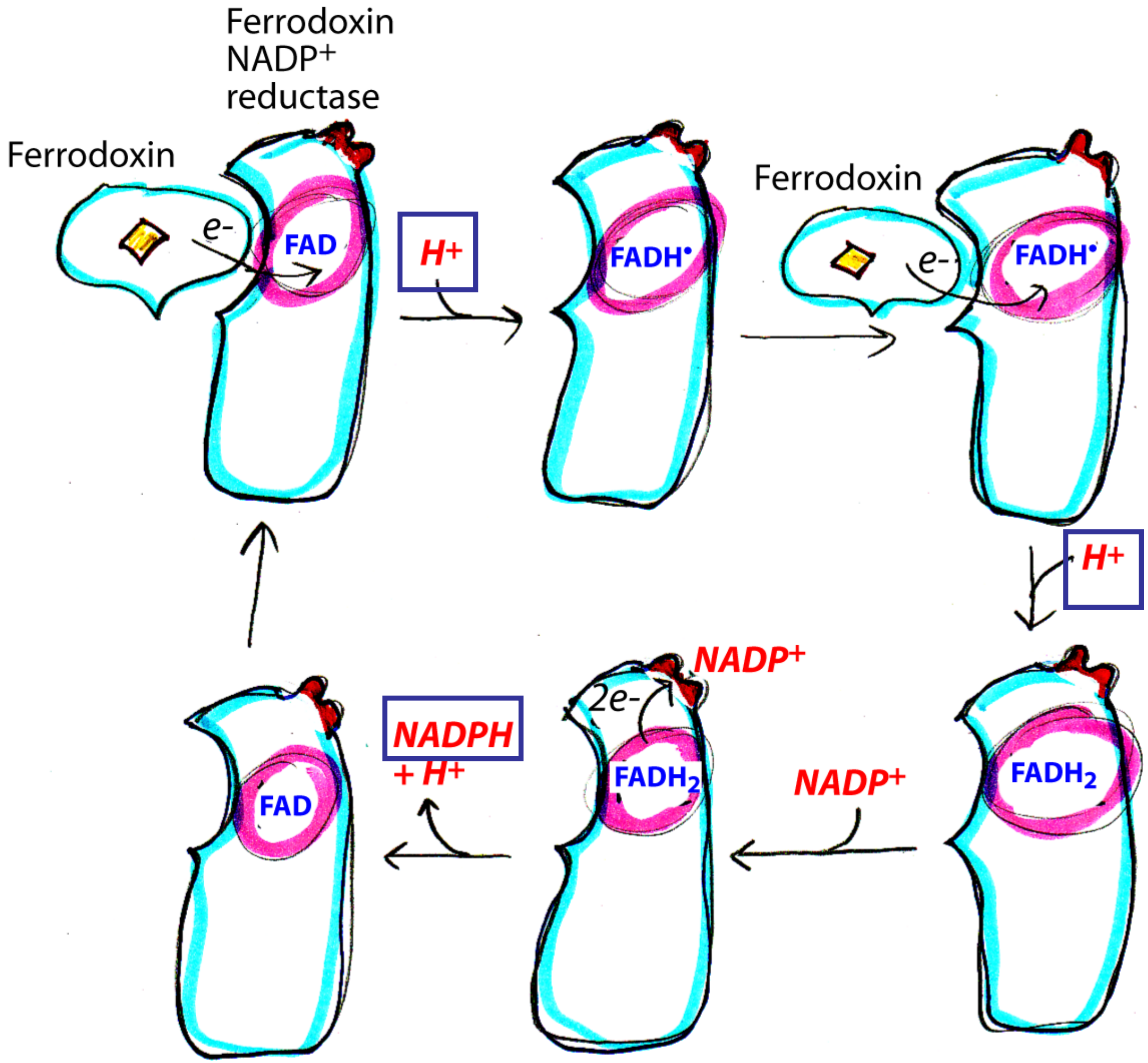
Structure of PS I complex showing Fe-S clusters

Functional organization of the PSI complex

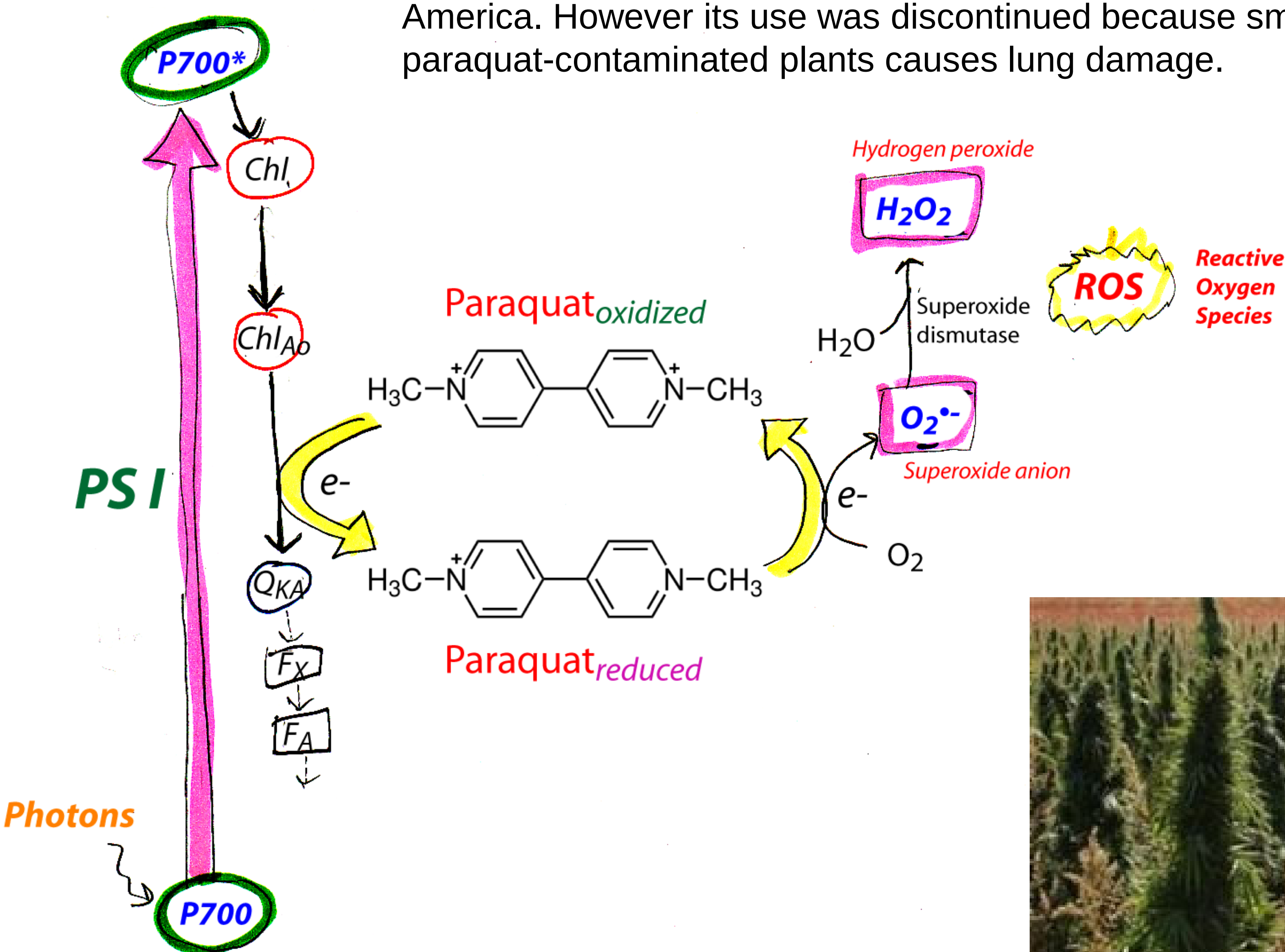


Ferrodoxin NADP$^+$ reductase plays a crucial role in converting redox energy into a useable form for the Calvin Cycle by generating NADPH.

Since *e*- arrive in PSI one at a time, the FAD coenzyme must store on *e*- in a semiquinone chemical structure.



Paraquat was once used extensively as an aerial herbicide to destroy illegal fields of marijuana and coca plants in North and South America. However its use was discontinued because smoking paraquat-contaminated plants causes lung damage.



Energy input at both the PSII and PSI reaction centers

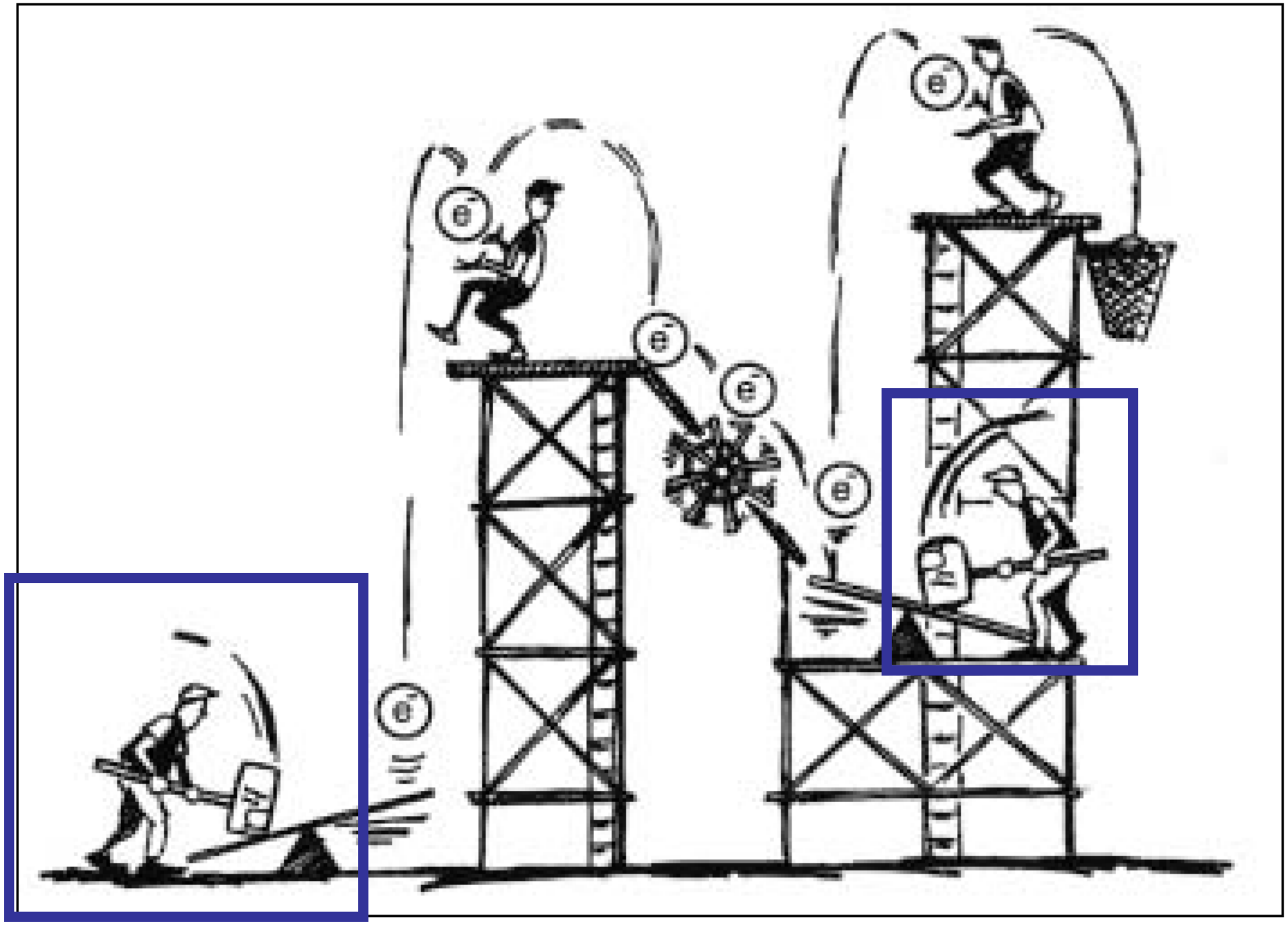


Fig. 2. Cartoon representation of Z-scheme, courtesy of Richard Walker [6,17]. Now available in animated form (http://www.alegba.demon.co.uk/CARTOON.AVI) [18].

Electron Flow

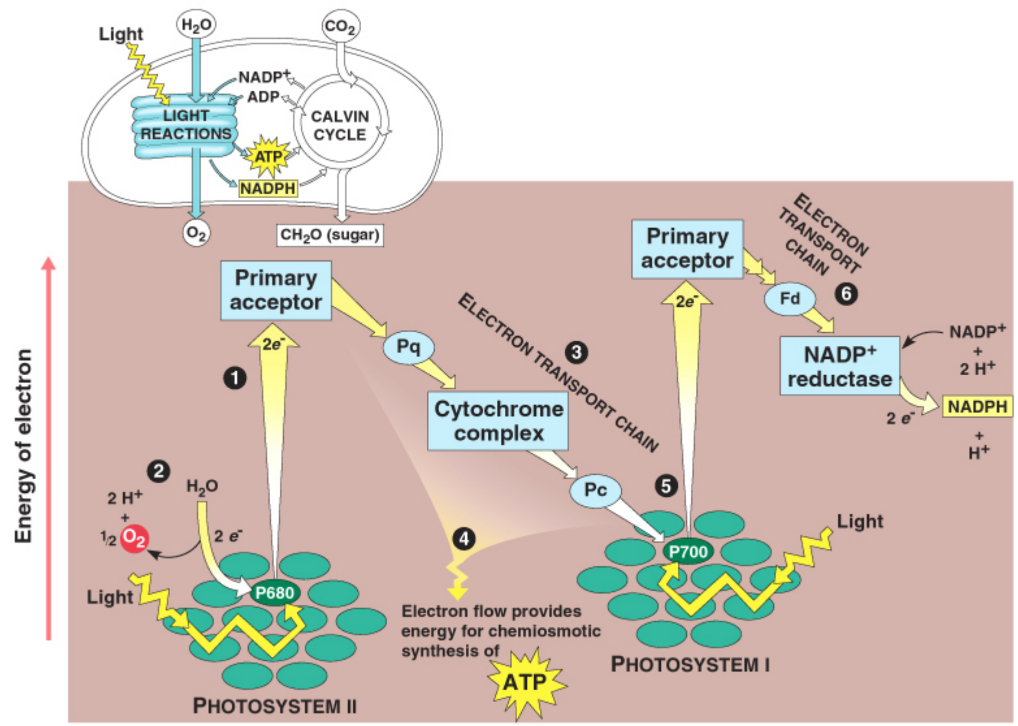
- Two routes for the path of electrons stored in the primary electron acceptors
- Both pathways
  - begin with the capturing of photon energy
  - utilize an electron transport chain with cytochromes for chemiosmosis
- **Noncyclic** electron flow
  - uses both photosystem II and I
  - electrons from photosystem II are **removed** and replaced by electrons donated from water
  - synthesizes ATP and NADPH
  - electron donation converts water into O_2 and $2H^+$
- **Cyclic** electron flow
  - Uses photosystem I only
  - electrons from photosystem I are **recycled**
  - synthesizes ATP only

Noncyclic Electron Flow

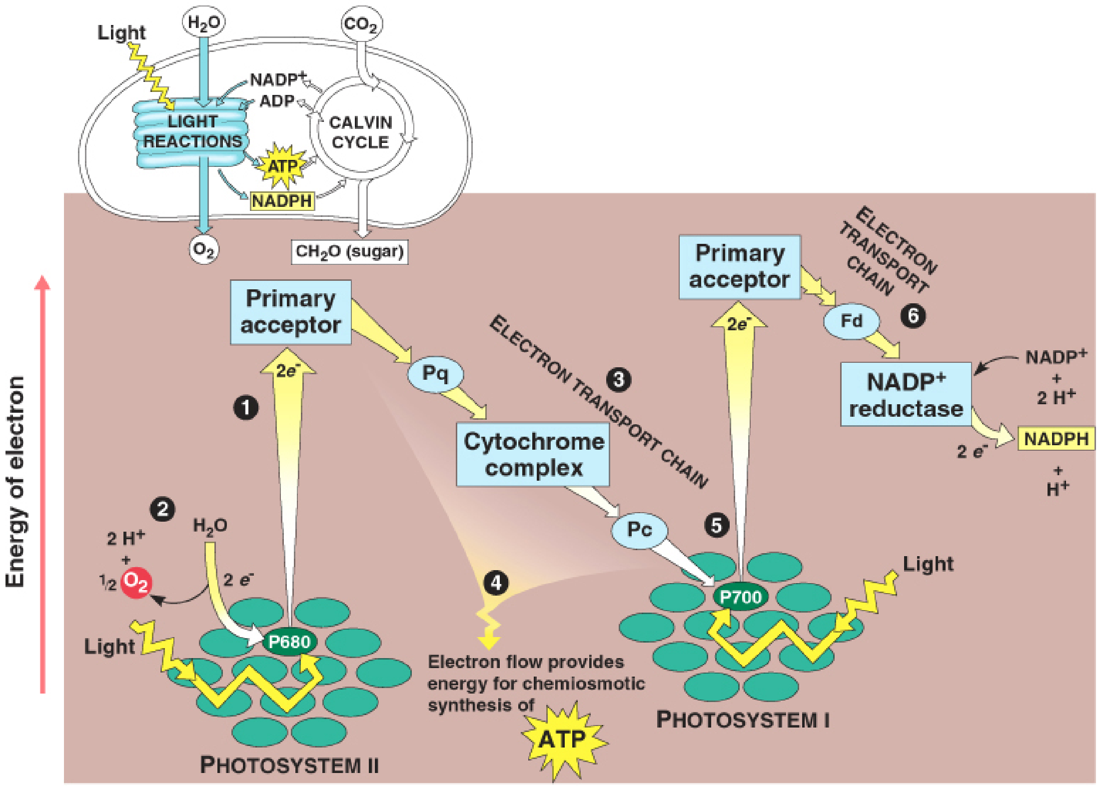
1 Electron at reaction-center energized

2 H2O split via enzyme catalysed reaction forming $2H^+$, $2e^-$, and O_2. Electrons move to fill orbital vacated by removed electron

3,4 Each excited electron is passed along an electron transport chain fueling the chemiosmotic synthesis of ATP



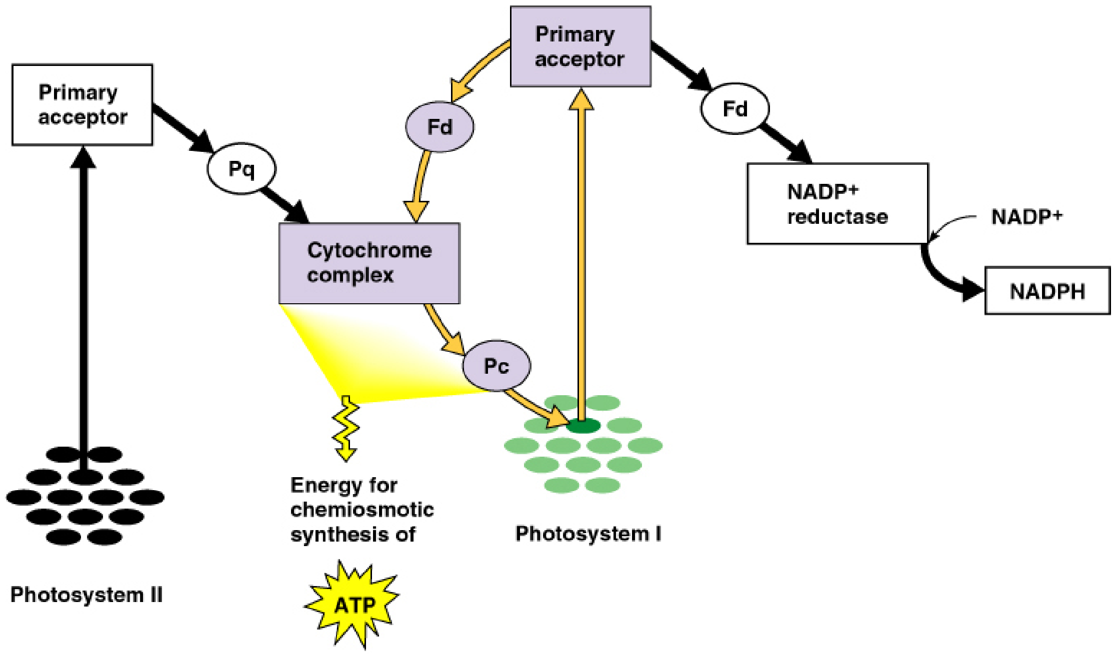
Noncyclic Electron Flow



5 The electron is now lower in energy and enters photosystem I where it is re-energized

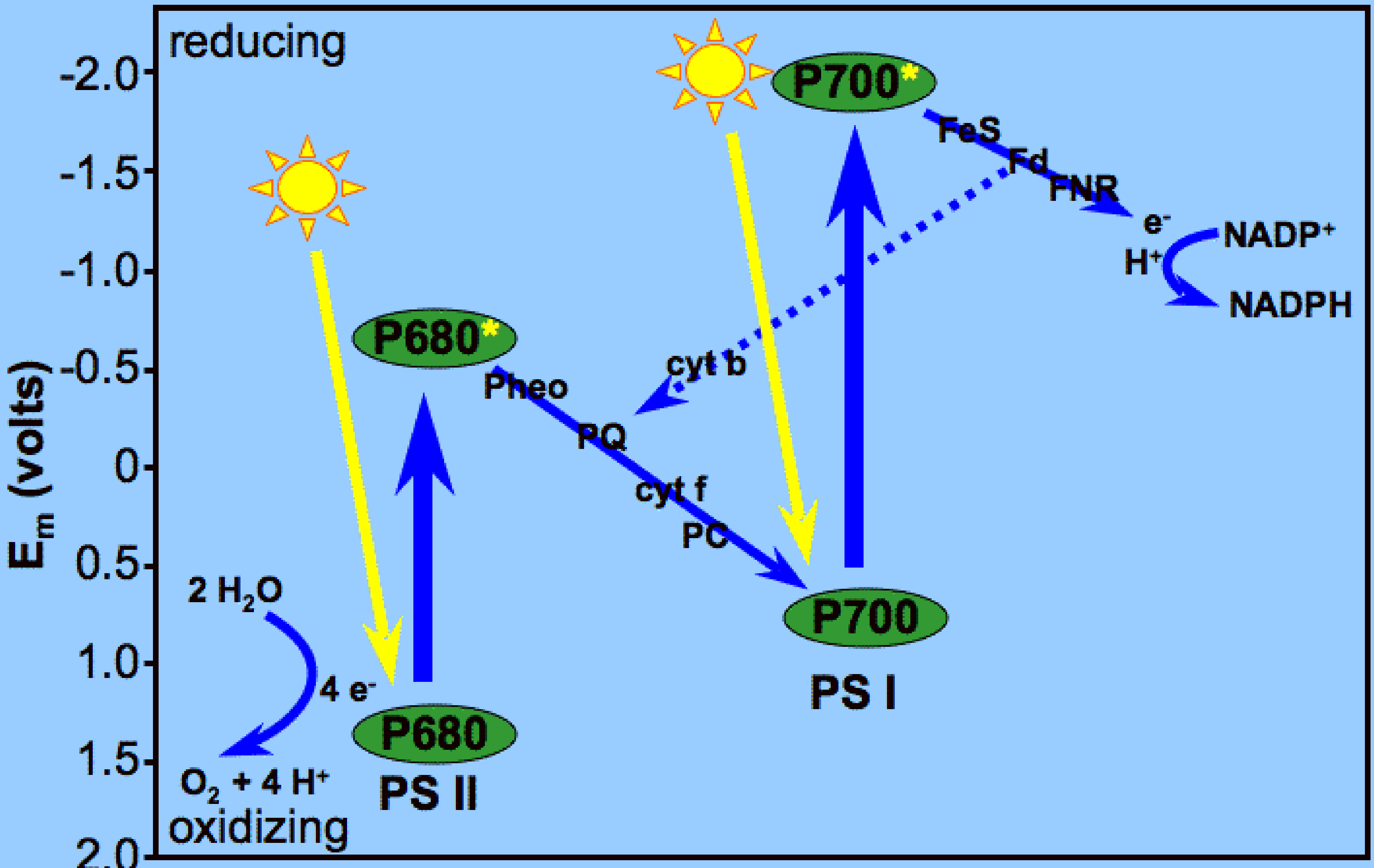
6 This electron is then passed to a different electron transport system that includes the iron containing protein ferridoxin. The enzyme $NADP^+$ reductase assists in the oxidation of ferridoxin and subsequent reduction of $NADP^+$ to NADPH

Cyclic Electron Flow



- Electron in Photosystem I is excited and transferred to ferredoxin that shuttles the electron to the cytochrome complex.
- The electron then travels down the electron chain and re-enters photosystem I

The Z-scheme of the Light Reactions: An Energy Diagram



Redox mechanism

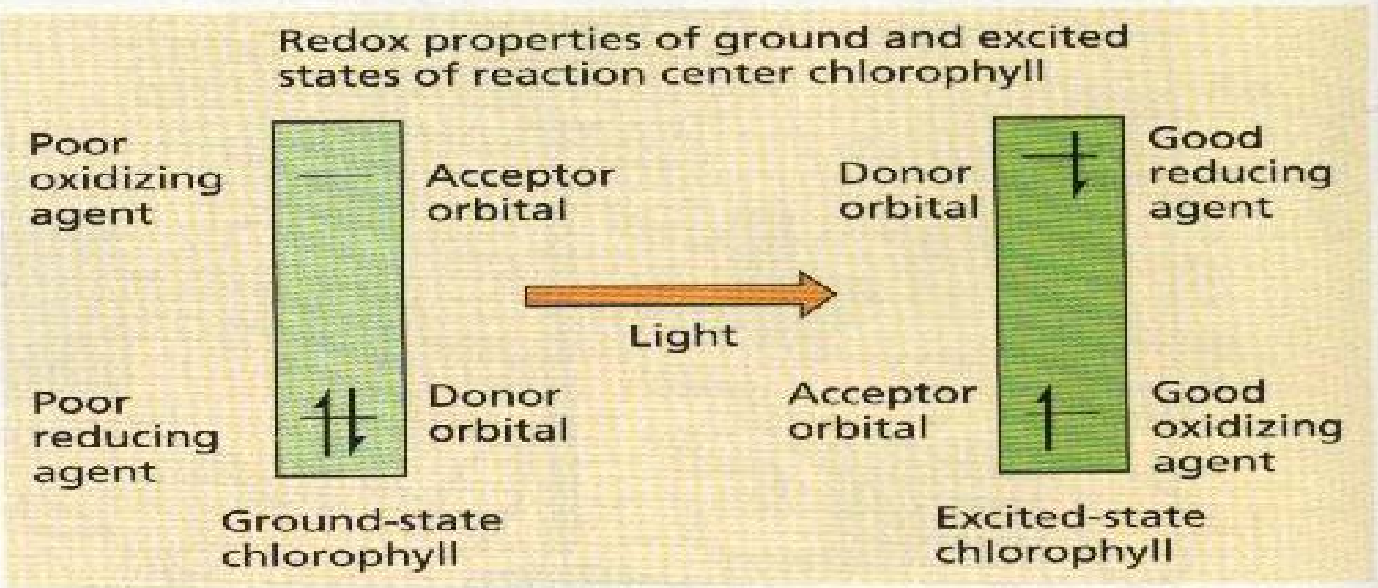
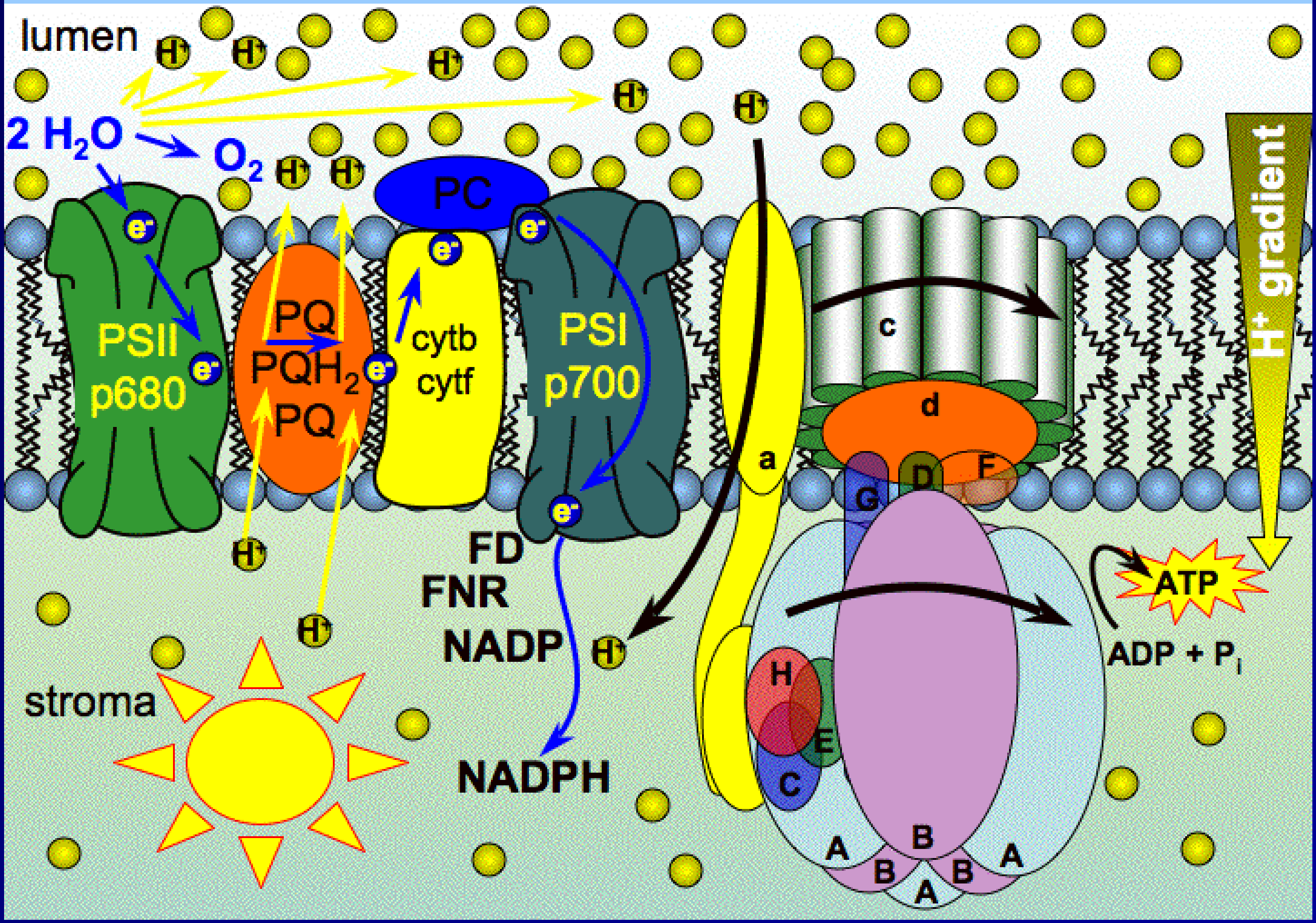
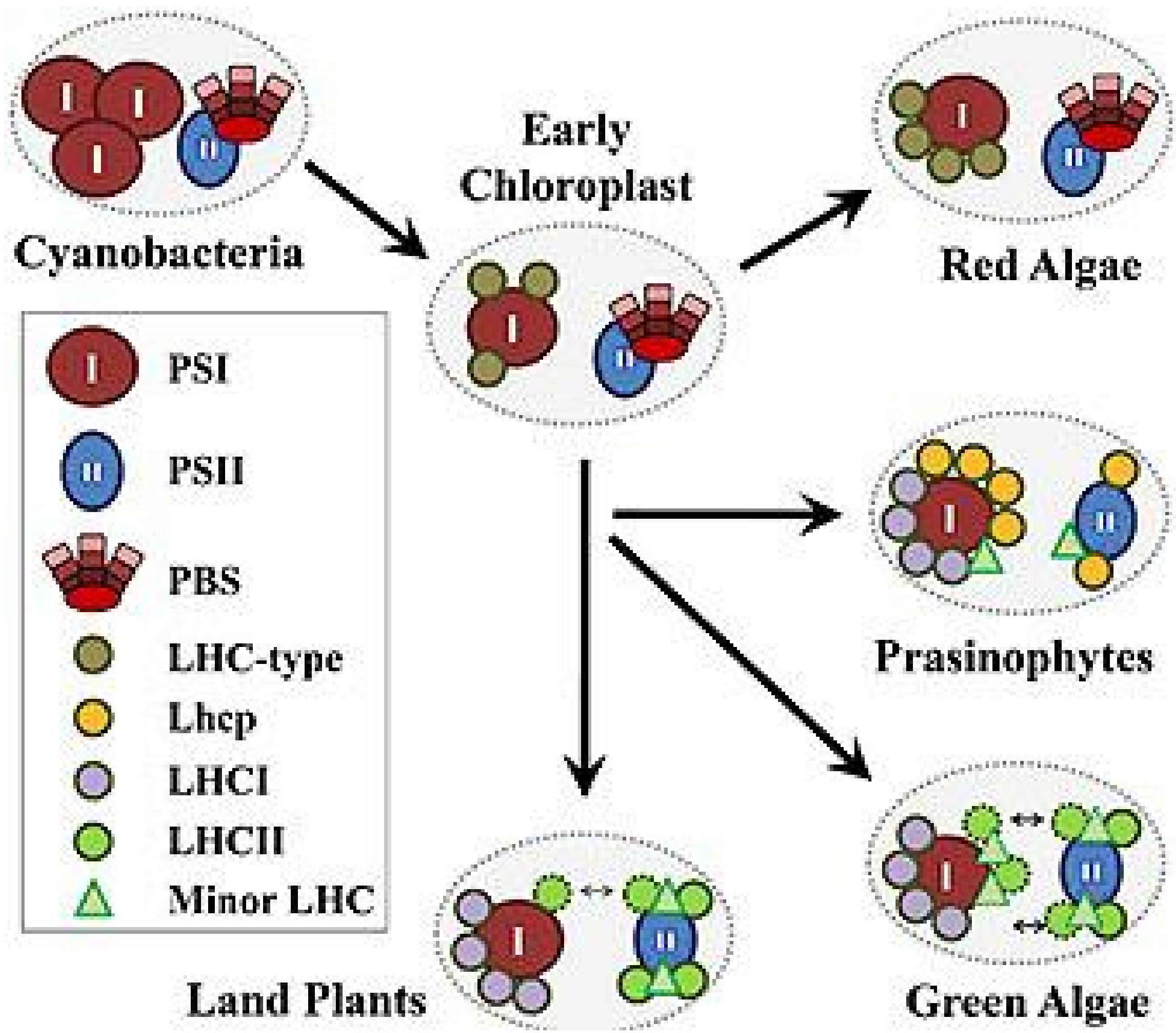


FIGURE 7.23 Orbital occupation diagram for the ground and excited states of reaction center chlorophyll. In the ground state the molecule is a poor reducing agent (loses electrons from a low-energy orbital) and a poor oxidizing agent (accepts electrons only into a high-energy orbital). In the excited state the situation is reversed, and an electron can be lost from the high-energy orbital, making the molecule an extremely powerful reducing agent. This is the reason for the extremely negative excited-state redox potential shown by P680* and P700* in Figure 7.21. The excited state can also act as a strong oxidant by accepting an electron into the lower-energy orbital, although this pathway is not significant in reaction centers. (After Blankenship and Prince 1985.)

Thylakoid structure and location of the Light Reactions

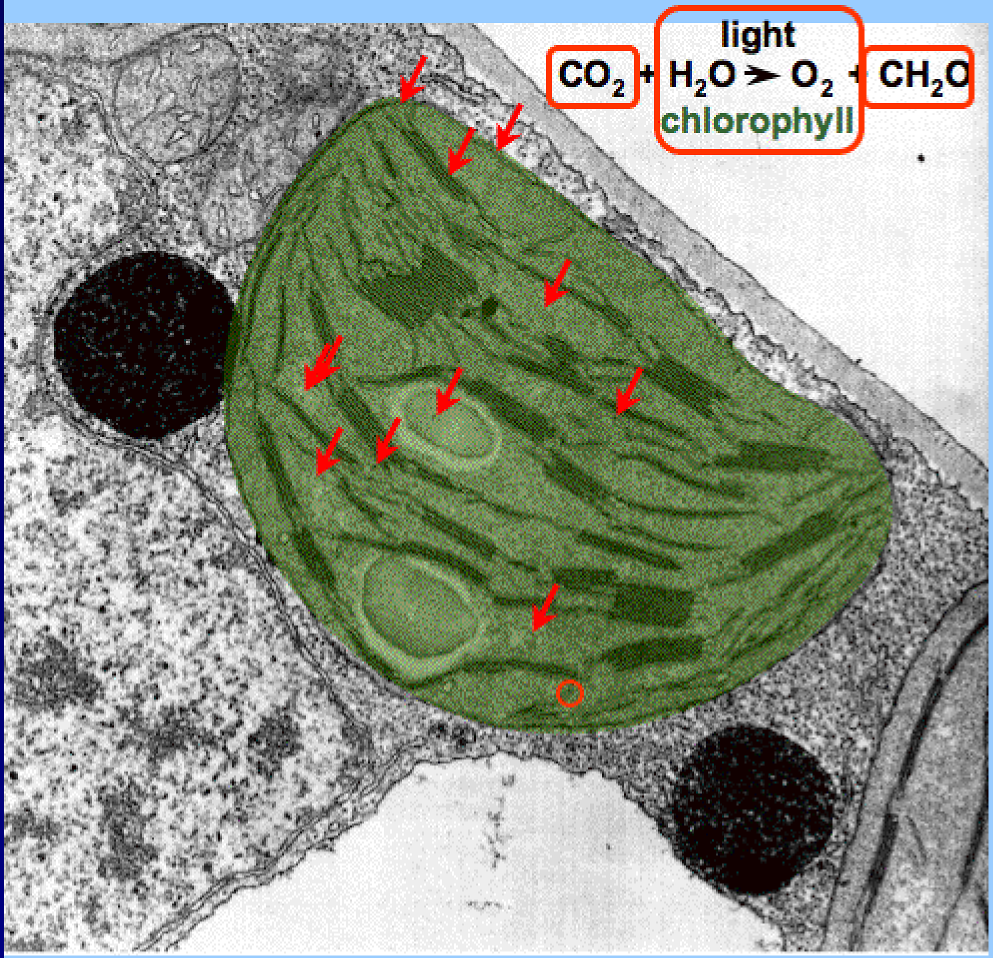




請看文章7.9. 補充資料 PSII PSI 演化假說

Major LhcII 是可以移動到PSI =state 2
綠藻保有此類的能力較高等植物大，綠藻
Minor LhcI 也會移動

TEM of a Plant Cell



Chloroplast

double outer membrane

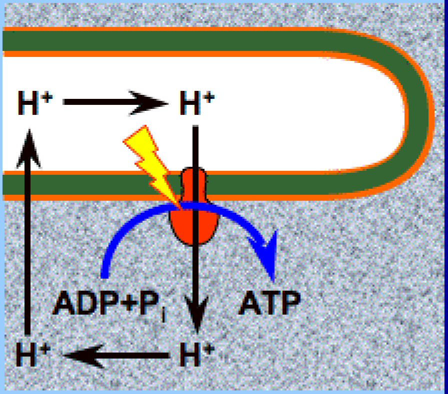
thylakoid

stroma

starch grain

DNA circles

70S ribosomes



http://faculty.uca.edu/~johnc/Chloroplast_and_microbodies.jpg

Components of e$^-$ transport

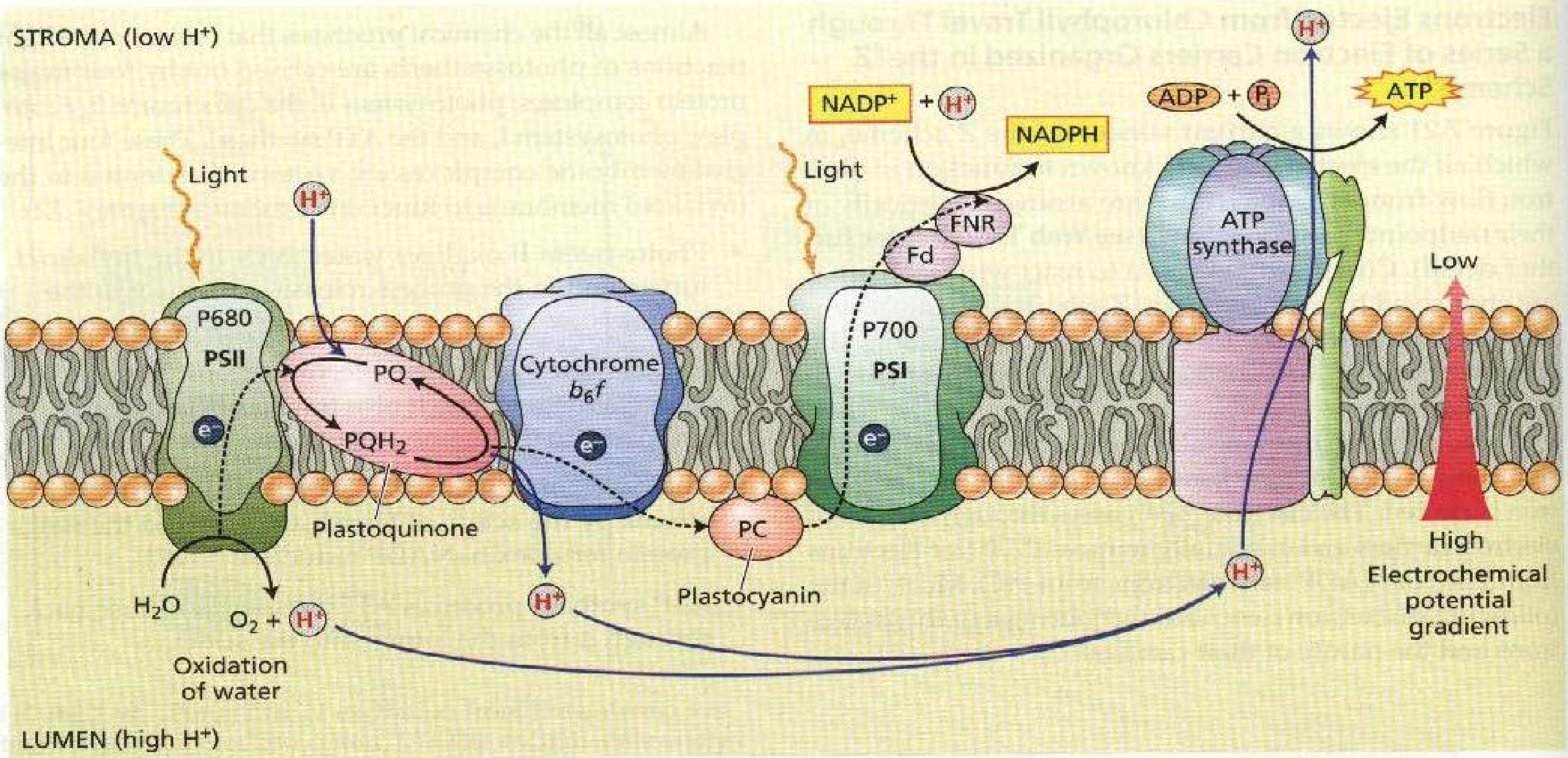
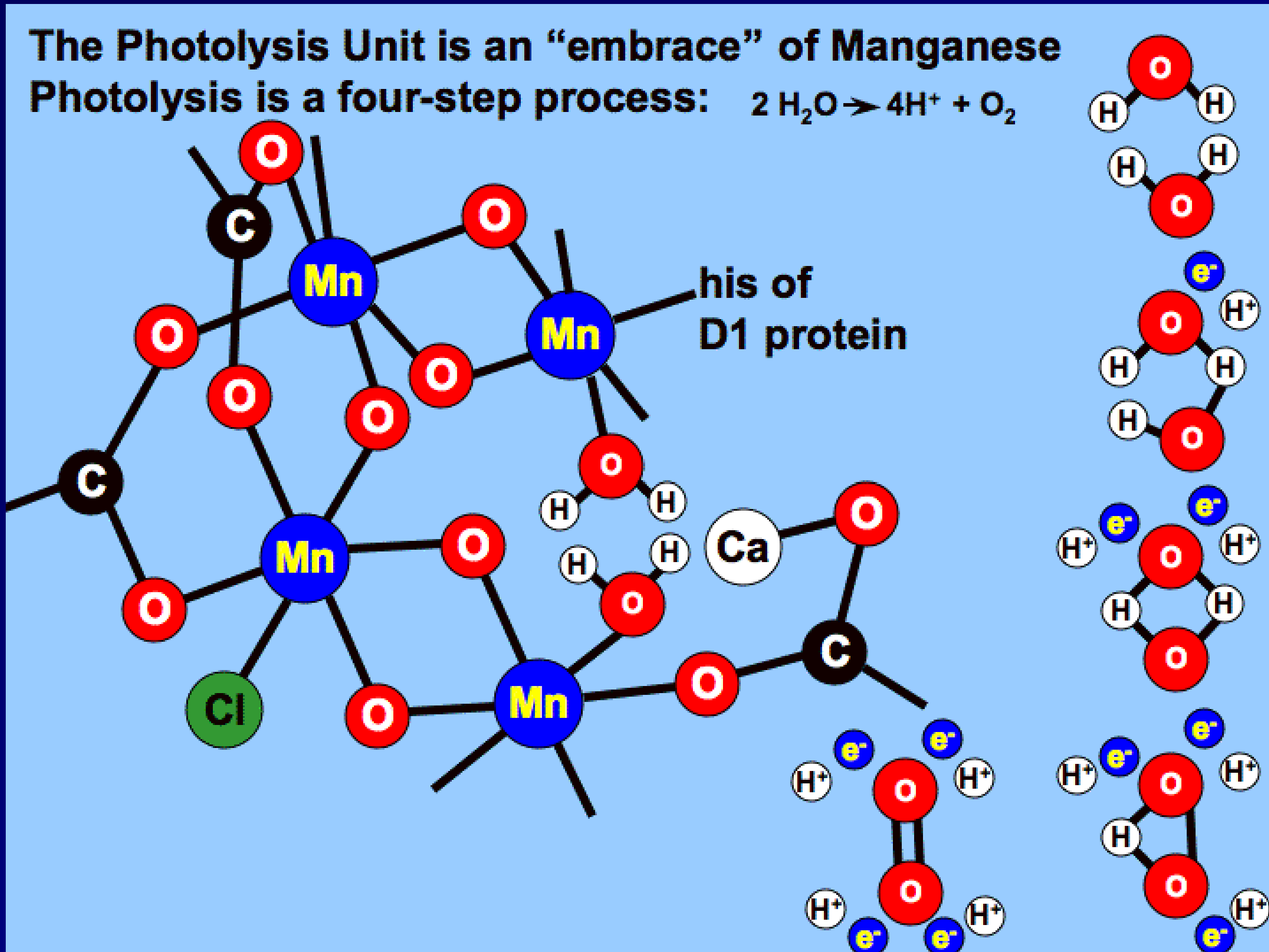


FIGURE 7.22 The transfer of electrons and protons in the thylakoid membrane is carried out vectorially by four protein complexes. Water is oxidized and protons are released in the lumen by PSII. PSI reduces $NADP^+$ to NADPH in the stroma, via the action of ferredoxin (Fd) and the flavoprotein ferredoxin–NADP reductase (FNR). Protons are also transported into the lumen by the action of the cytochrome b_6f complex and contribute to the electrochemical proton gradient. These protons must then diffuse to the ATP synthase enzyme, where their diffusion down the electrochemical potential gradient is used to synthesize ATP in the stroma. Reduced plastoquinone (PQH_2) and plastocyanin transfer electrons to cytochrome b_6f and to PSI, respectively. Dashed lines represent electron transfer; solid lines represent proton movement.


The Photolysis Unit is an “embrace” of Manganese
Photolysis is a four-step process: $2\ H_2O \rightarrow 4H^+ + O_2$
his of
D1 protein
Mn
Mn
Mn
Mn
Ca
Cl
C
C
C
O
H
H^+
e^-

PSI

the complex. Another similar sequence of electron flow fully reduces the plastoquinone, which picks up protons from the stromal side of the membrane and is released from the b_6f complex as plastohydroquinone.

The net result of two turnovers of the complex is that two electrons are transferred to P700, two plastohydroquinones are oxidized to the quinone form, and one oxidized plastoquinone is reduced to the hydroquinone form. In addition, four protons are transferred from the stromal to the lumenal side of the membrane.

By this mechanism, electron flow connecting the acceptor side of the PSII reaction center to the donor side of the PSI reaction center also gives rise to an electrochemical potential across the membrane, due in part to H^+ concentration differences on the two sides of the membrane. This electrochemical potential is used to power the synthesis of ATP. The cyclic electron flow through the cytochrome *b* and plastoquinone increases the number of protons pumped per electron beyond what could be achieved in a strictly linear sequence.

Plastoquinone and Plastocyanin Carry Electrons between Photosystems II and I

The location of the two photosystems at different sites on the thylakoid membranes (see Figure 7.18) requires that at least one component be capable of moving along or within the membrane in order to deliver electrons produced by photosystem II to photosystem I. The cytochrome b_6f complex is distributed equally between the grana and the stroma regions of the membranes, but its large size makes it unlikely that it is the mobile carrier. Instead, plastoquinone or plastocyanin or possibly both are thought to serve as mobile carriers to connect the two photosystems.

Plastocyanin is a small (10.5 kDa), water-soluble, copper-containing protein that transfers electrons between the cytochrome b_6f complex and P700. This protein is found in the lumenal space (see Figure 7.29). In certain green algae and cyanobacteria, a *c*-type cytochrome is sometimes found instead of plastocyanin; which of these two proteins is synthesized depends on the amount of copper available to the organism.

The Photosystem I Reaction Center Reduces NADP+

The PSI reaction center complex is a large multisubunit complex (Figure 7.30) (Jordan et al. 2001). In contrast to PSII, a core antenna consisting of about 100 chlorophylls is a part of the PSI reaction center, P700. The core antenna and P700 are bound to two proteins, PsaA and PsaB, with molecular masses in the range of 66 to 70 kDa (Brettel 1997; Chitnis 2001; see also **Web Topic 7.8**).

The antenna pigments form a bowl surrounding the electron transfer cofactors, which are in the center of the complex. In

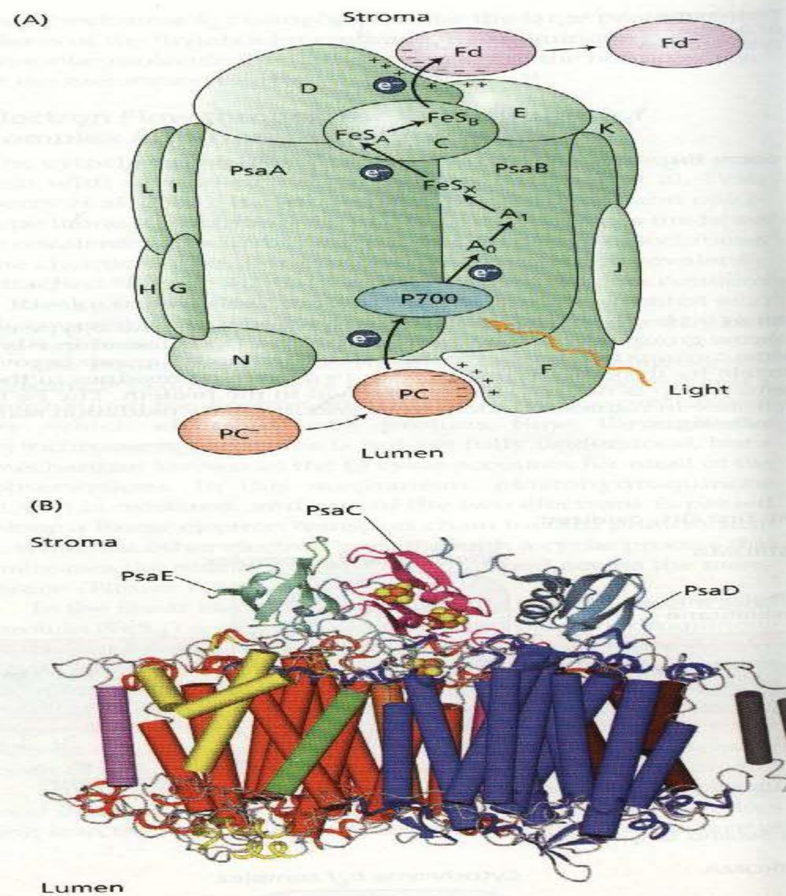
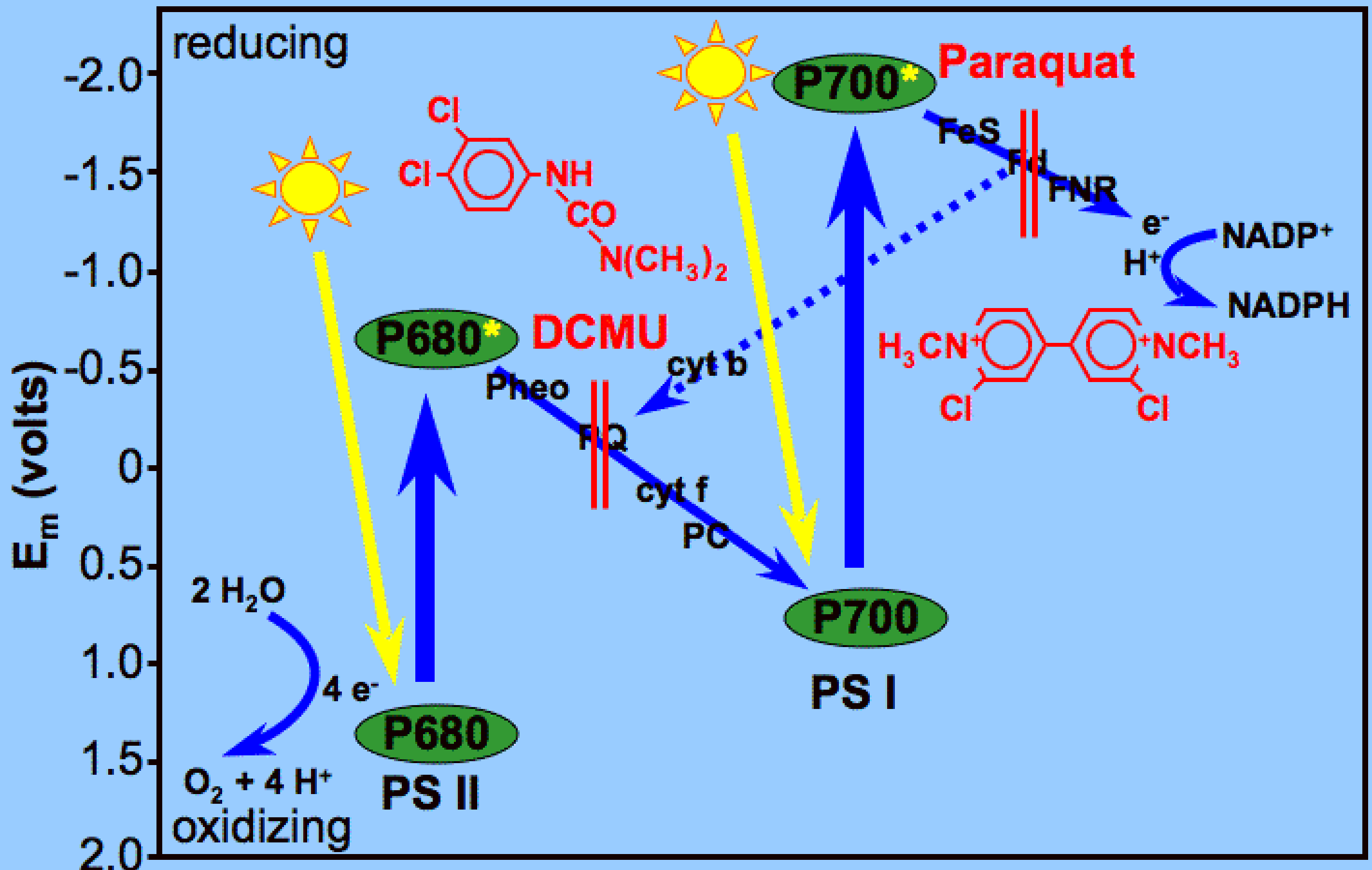


FIGURE 7.30 Structure of photosystem I. (A) Structural model of the PSI reaction center. Components of the PSI reaction center are organized around two major proteins, PsaA and PsaB. Minor proteins PsaC to PsaN are labelled C to N. Electrons are transferred from plastocyanin (PC) to P700 (see Figures 7.21 and 7.22) and then to a chlorophyll molecule, A_0, to phylloquinone, A_1, to the FeS_X, FeS_A, and FeS_B Fe–S centers, and finally to the soluble iron–sulfur protein, ferrodoxin (Fd). (B) Side view of one monomer of PSI from the cyanobacterium *Synechococcus elongatus*, at 2.5 Å resolution. The stromal side of the membrane is at the top, and the lumen side is at the bottom of the figure. Transmembrane α-helices of PsaA and PsaB are shown as blue and red cylinders, respectively. (A after Buchanan et al. 2000; B from Jordan et al. 2001.)

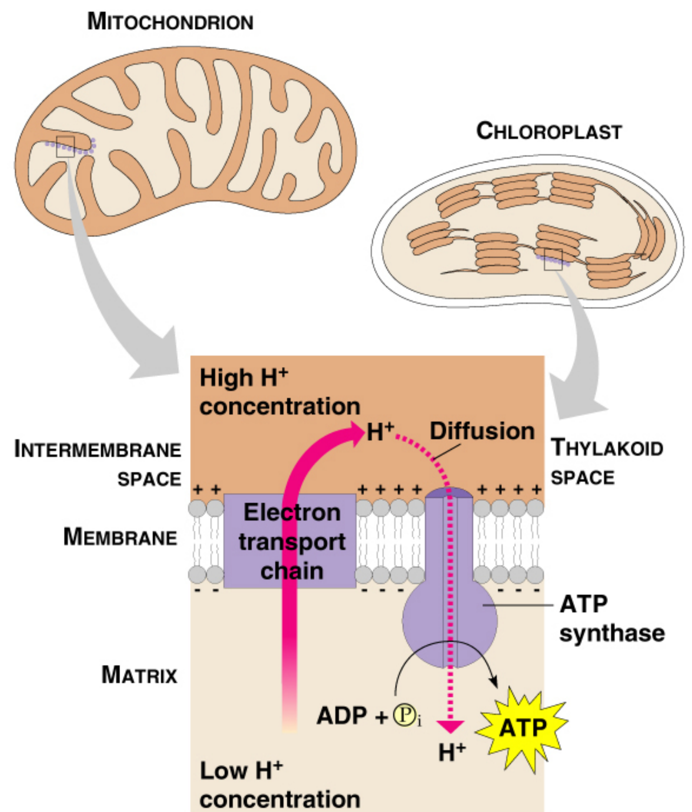
The Z-scheme of the Light Reactions: An Energy Diagram



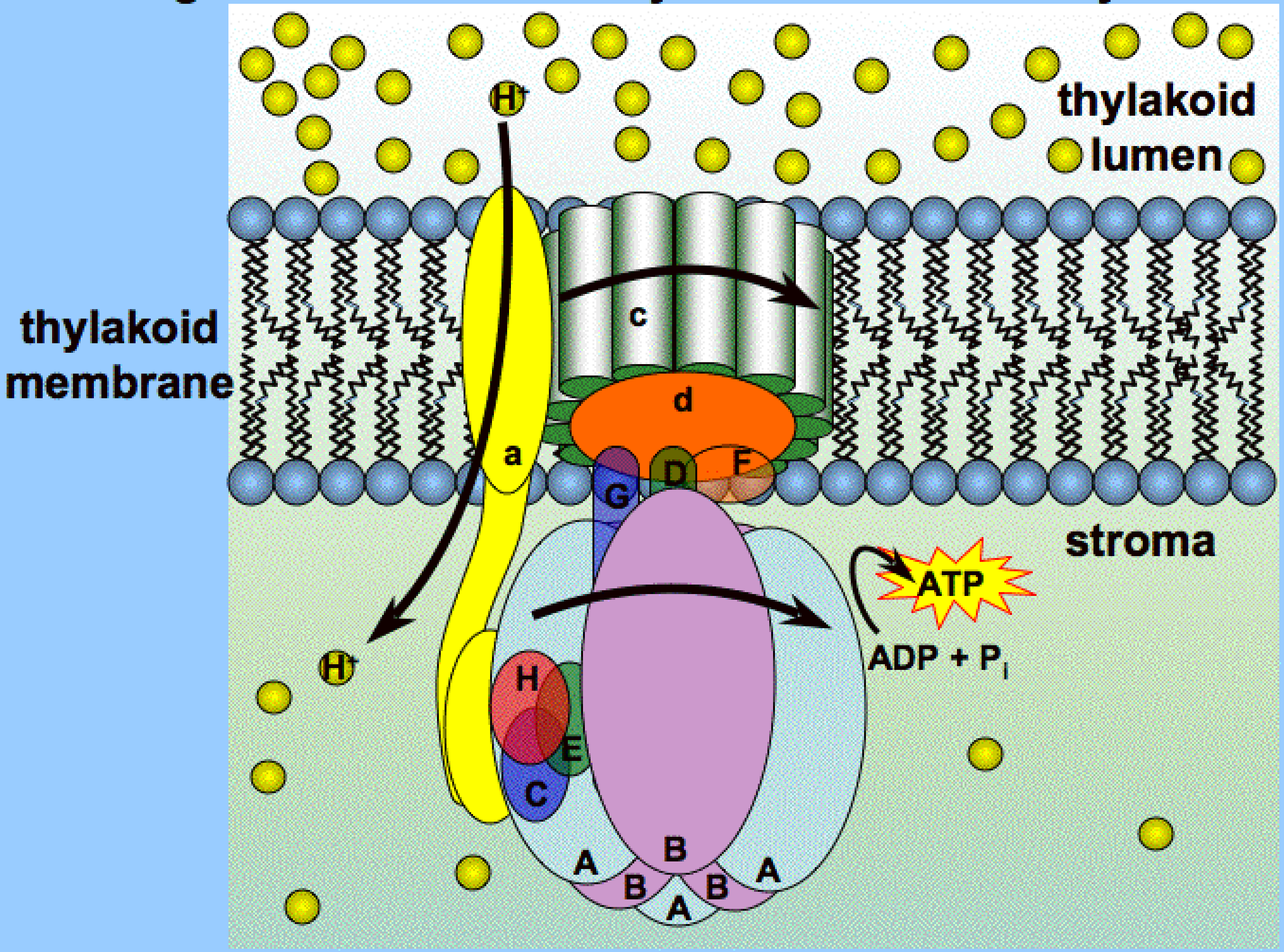
ATP generation Chemiosmosis in 2 Organelles

- Both the Mitochondria and Chloroplast generate ATP via a proton motive force resulting from an electrochemical inbalance across a membrane
- Both utilize an electron transport chain primarily composed of cytochromes to pump H^+ across a membrane.
- Both use a similar ATP synthase complex

- Source of "fuel" for the process differs
- Location of the H^+ "reservoir" differs



The H+ gradient across the thylakoid drives ATP synthesis



Generation of ATP

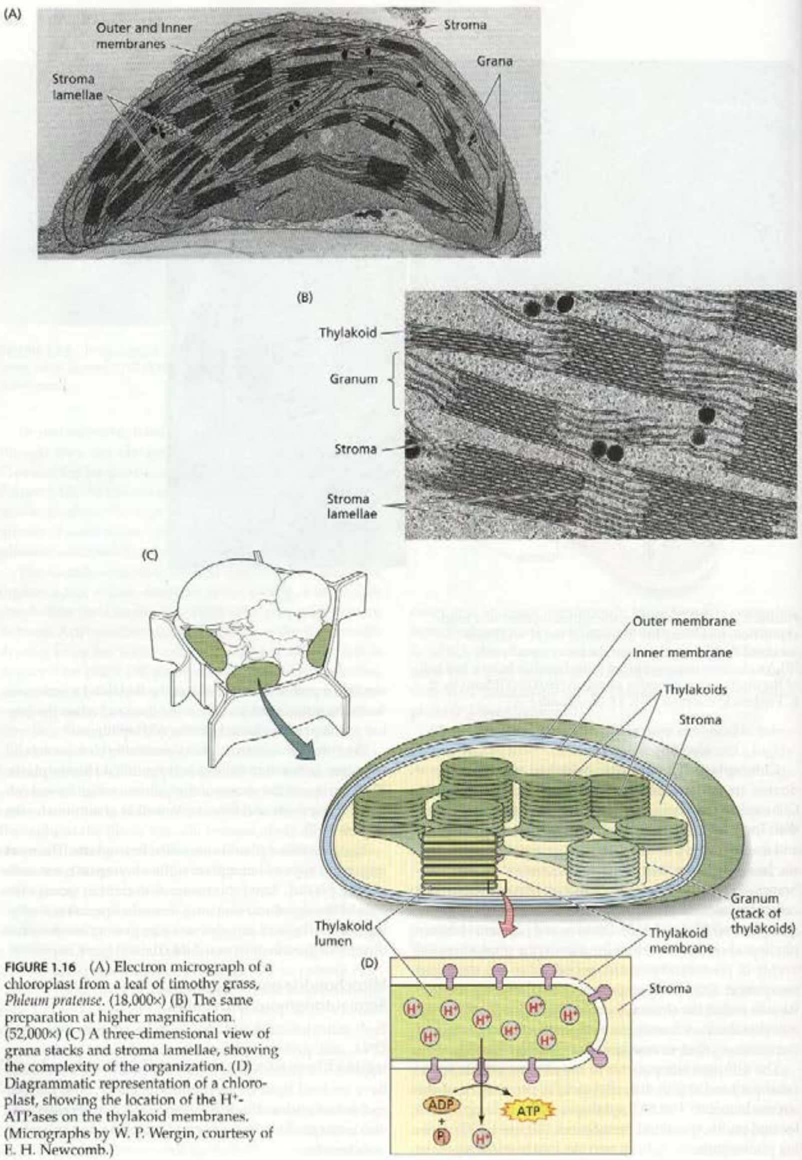


FIGURE 1.16 (A) Electron micrograph of a chloroplast from a leaf of timothy grass, *Phleum pratense*. (18,000×) (B) The same preparation at higher magnification. (52,000×) (C) A three-dimensional view of grana stacks and stroma lamellae, showing the complexity of the organization. (D) Diagrammatic representation of a chloroplast, showing the location of the H^+-ATPases on the thylakoid membranes. (Micrographs by W. P. Wergin, courtesy of E. H. Newcomb.)

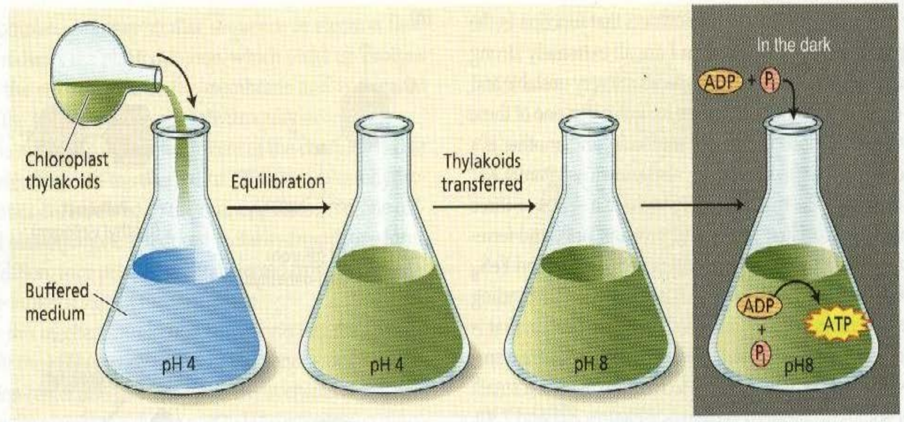


FIGURE 7.32 Summary of the experiment carried out by Jagendorf and coworkers. Isolated chloroplast thylakoids kept previously at pH 8 were equilibrated in an acid medium at pH 4. The thylakoids were then transferred to a buffer at pH 8 that contained ADP and P_i. The proton gradient generated by this manipulation provided a driving force for ATP synthesis in the absence of light. This experiment verified a prediction of the chemiosmotic theory stating that a chemical potential across a membrane can provide energy for ATP synthesis.

Chemo-osmotic theory

ATP (Adenosine triphosphate)

- ATP ATP is a nucleotide that performs many essential roles in the cell.
  It is the major energy currency of the cell, providing the energy for most of the energy-consuming activities of the cell.
  It is one of the monomers used in the synthesis of RNA and, after conversion to deoxyATP (dATP), DNA.
  It regulates many biochemical pathways.

- Energy
  When the third phosphate group of ATP is removed by hydrolysis, a substantial amount of free energy is released.
  The exact amount depends on the conditions, but we shall use a value of 7.3 kcal per mole.
  $ATP + H_2O \rightarrow ADP + P_i$
  ADP is adenosine diphosphate. Pi is inorganic phosphate.

- Synthesis of ATP
  $ADP + P_i \rightarrow ATP + H_2O$
  requires energy: 7.3 kcal/mole
  occurs in the cytosol by glycolysis
  occurs in mitochondria by cellular respiration
  occurs in chloroplasts by photosynthesis

- Consumption of ATP
  Most anabolic reactions in the cell are powered by ATP.
  Examples:
  - assembly of amino acids into proteins
  - assembly of nucleotides into DNA and RNA
  - synthesis of polysaccharides
  - synthesis of fats
  - active transport of molecules and ions
  - beating of cilia and flagella

NADP

•Nicotinamide adenine dinucleotide (NAD) & its relative nicotinamide adenine dinucleotide phosphate (NADP) are two of the most important coenzymes in the cell. NADP is simply NAD with a third phosphate group attached as shown at the Bottom
of the figure.

•Because of the positive charge on the nitrogen atom in the nicotinamide ring (upper right), the oxidized forms of these important redox reagents are often depicted as NAD+ and NADP+ respectively.

•In cells, most oxidations are accomplished by the removal of hydrogen atoms. Both of these coenzymes play crucial roles in this. Each molecule of NAD+ (or NADP+) can acquire two electrons; that is, be reduced by two electrons. However, only one proton
accompanies the reduction. The other proton produced as two hydrogen atoms are removed from the molecule being oxidized is liberated into the surrounding medium.

•For NAD, the reaction is thus:

$$NAD^+ + 2H \rightarrow NADH + H^+$$

•NAD participates in many redox reactions in cells, including those
in glycolysis and most of those
I n the citric acid cycle of cellular respiration.

•NADP is the reducing agent
- produced by the light reactions of photosynthesis
- consumed in the Calvin cycle of photosynthesis and
- used in many other anabolic reactions in both plants and animals.

•Under the conditions existing in a normal cell, the hydrogen atoms shown in red are dissociated from these acidic substances.

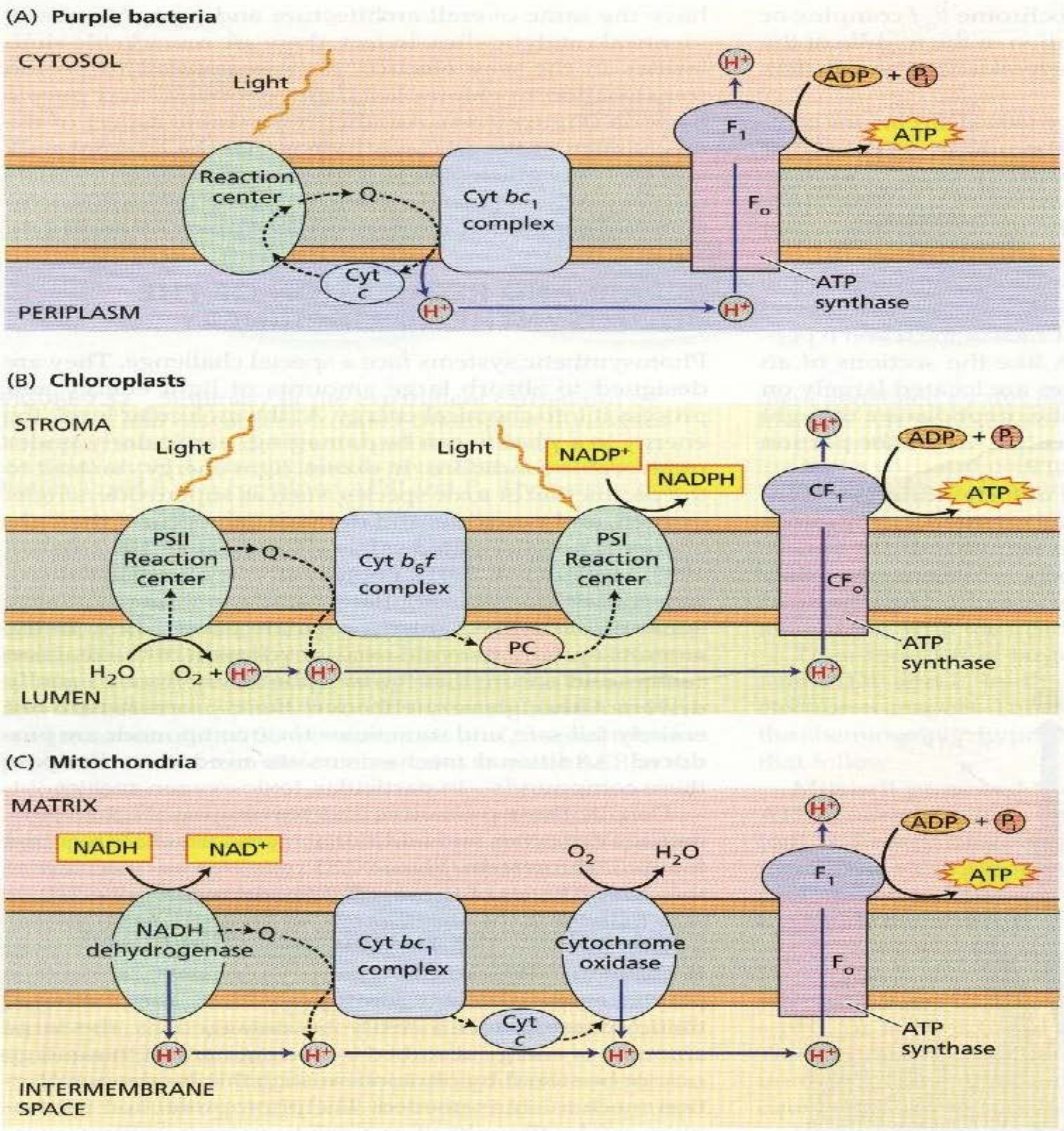
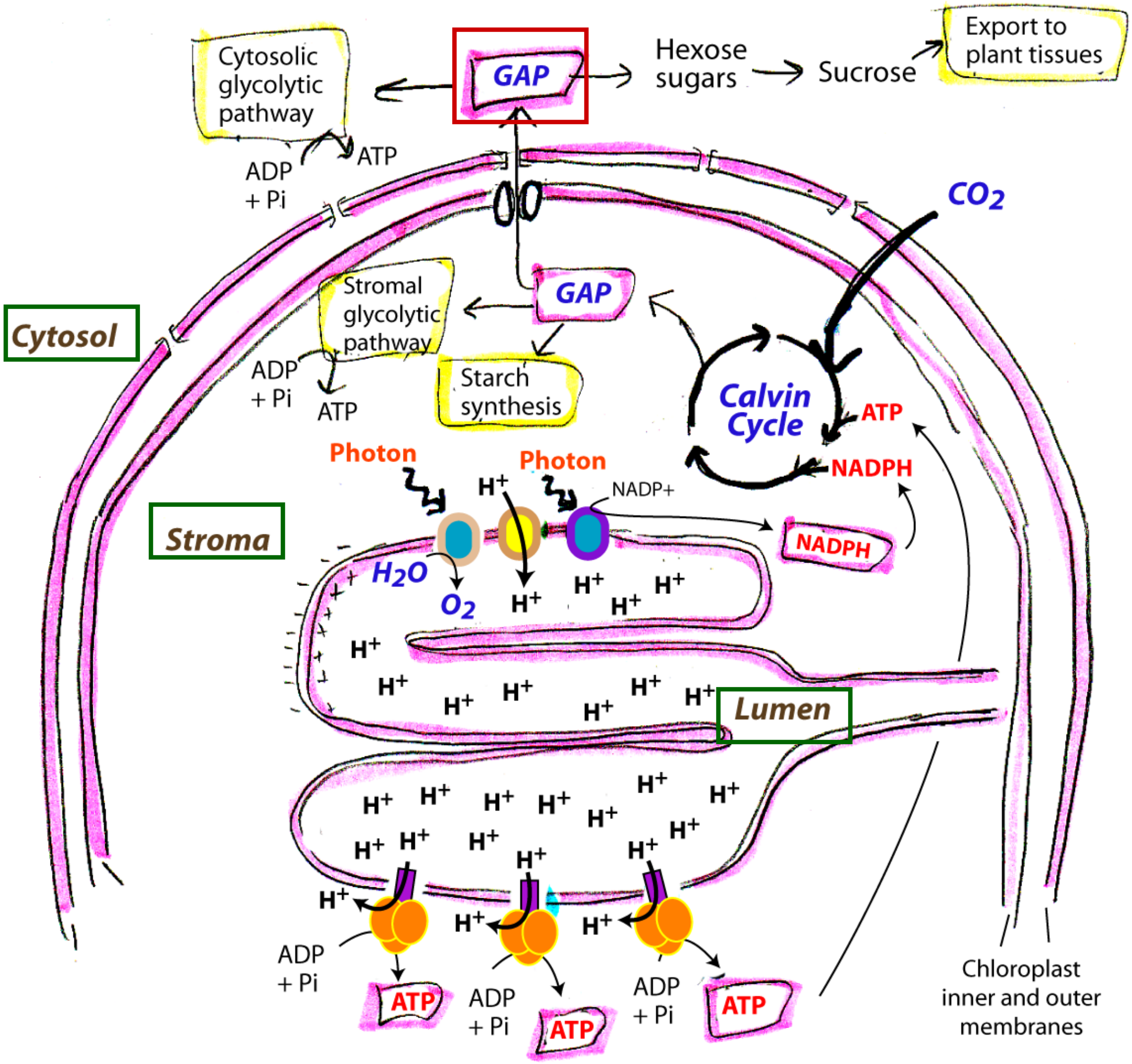


FIGURE 7.34 Similarities of photosynthetic and respiratory electron flow in bacteria, chloroplasts, and mitochondria. In all three, electron flow is coupled to proton translocation, creating a transmembrane proton motive force (Δp). The energy in the proton motive force is then used for the synthesis of ATP by ATP synthase. (A) A reaction center (RC) in purple photosynthetic bacteria carries out cyclic electron flow, generating a proton potential by the action of the cytochrome bc_1 complex. (B) Chloroplasts carry out noncyclic electron flow, oxidizing water and reducing $NADP^+$. Protons are produced by the oxidation of water and by the oxidation of PQH_2 (Q) by the cytochrome b_6f complex. (C) Mitochondria oxidize NADH to NAD^+ and reduce oxygen to water. Protons are pumped by the enzyme NADH dehydrogenase, the cytochrome bc_1 complex, and cytochrome oxidase. The ATP synthases in the three systems are very similar in structure.

Pay attention to the compartmentalization inside and outside of the chloroplast.

The product of the carbon fixation is **glyceraldehyde-3P (GAP)** which is converted to hexose sugars for use as chemical energy at night.



What pathway has GAP as a central intermediate, does this make sense here?

C fixation

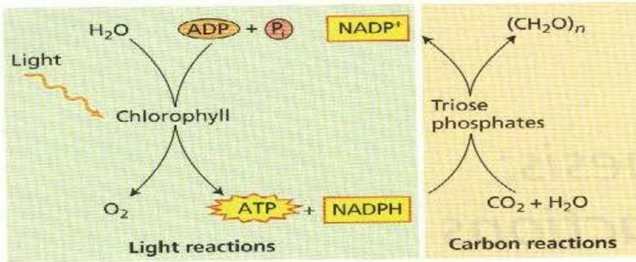


FIGURE 8.1 The light and carbon reactions of photosynthesis. Light is required for the generation of ATP and NADPH. The ATP and NADPH are consumed by the carbon reactions, which reduce CO_2 to carbohydrate (triose phosphates).

ciency of photosynthesis. This chapter will also describe biochemical mechanisms for concentrating carbon dioxide that allow plants to mitigate the impact of photorespiration: CO_2 pumps, C_4 metabolism, and crassulacean acid metabolism (CAM). We will close the chapter with a consideration of the synthesis of sucrose and starch.

THE CALVIN CYCLE

All photosynthetic eukaryotes, from the most primitive alga to the most advanced angiosperm, reduce CO_2 to carbohydrate via the same basic mechanism: the photosynthetic carbon reduction cycle originally described for C_3 species (the **Calvin cycle**, or **reductive pentose phosphate [RPP] cycle**). Other metabolic pathways associated with the photosynthetic fixation of CO_2, such as the C_4 photosynthetic carbon assimilation cycle and the photorespiratory carbon oxidation cycle, are either auxiliary to or dependent on the basic Calvin cycle.

In this section we will examine how CO_2 is fixed by the Calvin cycle through the use of ATP and NADPH generated by the light reactions (Figure 8.1), and how the Calvin cycle is regulated.

The Calvin Cycle Has Three Stages: Carboxylation, Reduction, and Regeneration

The Calvin cycle was elucidated as a result of a series of elegant experiments by Melvin Calvin and his colleagues in the 1950s, for which a Nobel Prize was awarded in 1961 (see **Web Topic 8.1**). In the Calvin cycle, CO_2 and water from the environment are enzymatically combined with a five-carbon acceptor molecule to generate two molecules of a three-carbon intermediate. This intermediate (3-phosphoglycerate) is reduced to carbohydrate by use of the ATP and NADPH generated photochemically. The cycle is completed by regeneration of the five-carbon acceptor (ribulose-1,5-bisphosphate, abbreviated RuBP).

The Calvin cycle proceeds in three stages (Figure 8.2):

1. *Carboxylation* of the CO_2 acceptor ribulose-1,5-bisphosphate, forming two molecules of 3-phosphoglycerate, the first stable intermediate of the Calvin cycle
2. *Reduction* of 3-phosphoglycerate, forming gyceraldehyde-3-phosphate, a carbohydrate
3. *Regeneration* of the CO_2 acceptor ribulose-1,5-bisphosphate from glyceraldehyde-3-phosphate

The carbon in CO_2 is the most oxidized form found in nature (+4). The carbon of the first stable intermediate, 3-phosphoglycerate, is more reduced (+3), and it is further reduced in the glyceraldehyde-3-phosphate product (+1). Overall, the early reactions of the Calvin cycle complete the reduction of atmospheric carbon and, in so doing, facilitate its incorporation into organic compounds.

The Carboxylation of Ribulose Bisphosphate Is Catalyzed by the Enzyme Rubisco

CO_2 enters the Calvin cycle by reacting with ribulose-1,5-bisphosphate to yield two molecules of 3-phosphoglycerate (Figure 8.3 and Table 8.1), a reaction catalyzed by the chloroplast enzyme ribulose bisphosphate carboxylase/oxygenase, referred to as **rubisco** (see **Web Topic 8.2**). As indi-

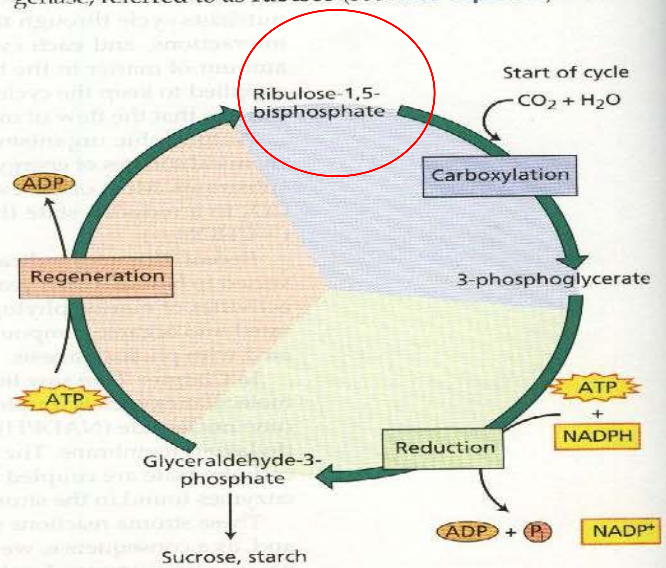
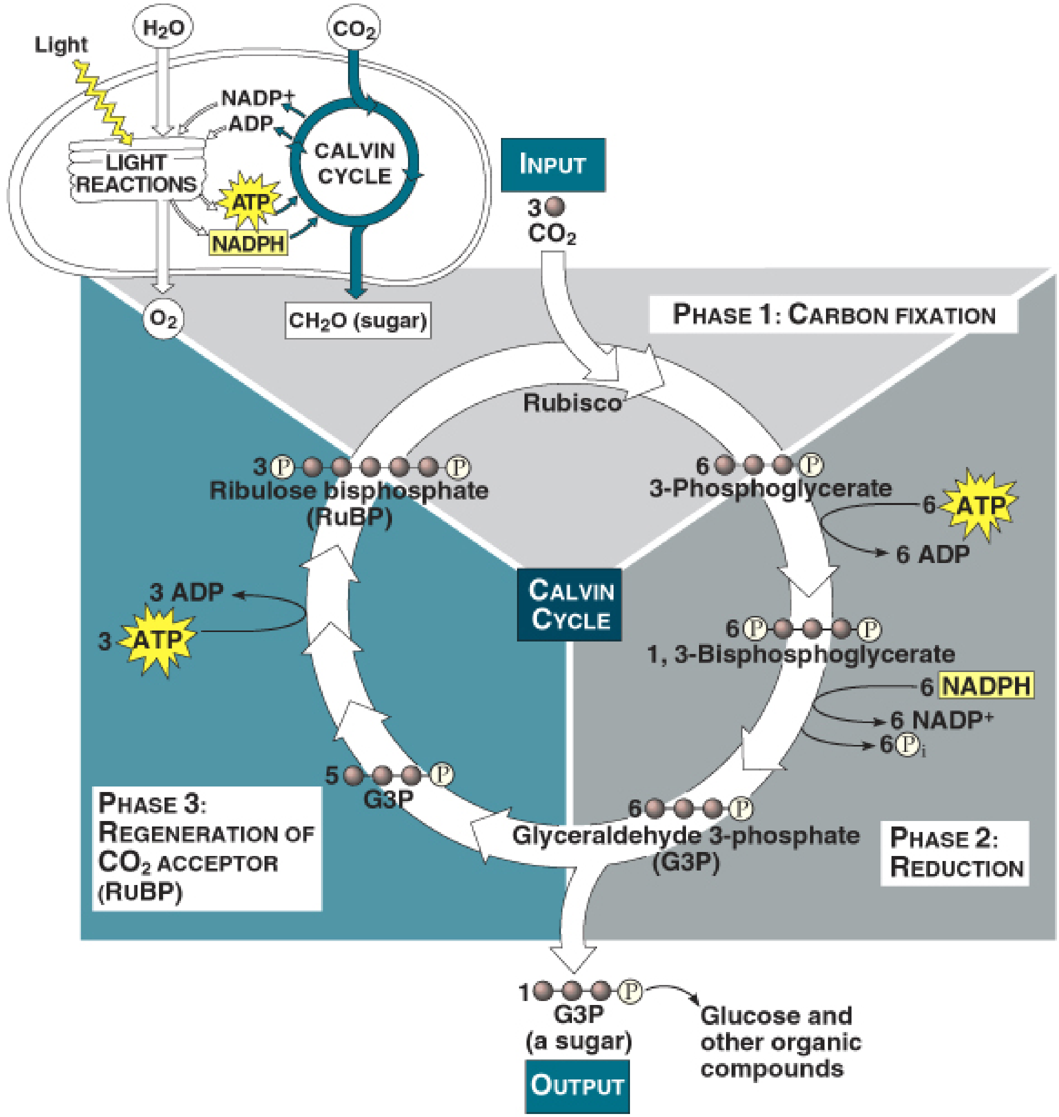


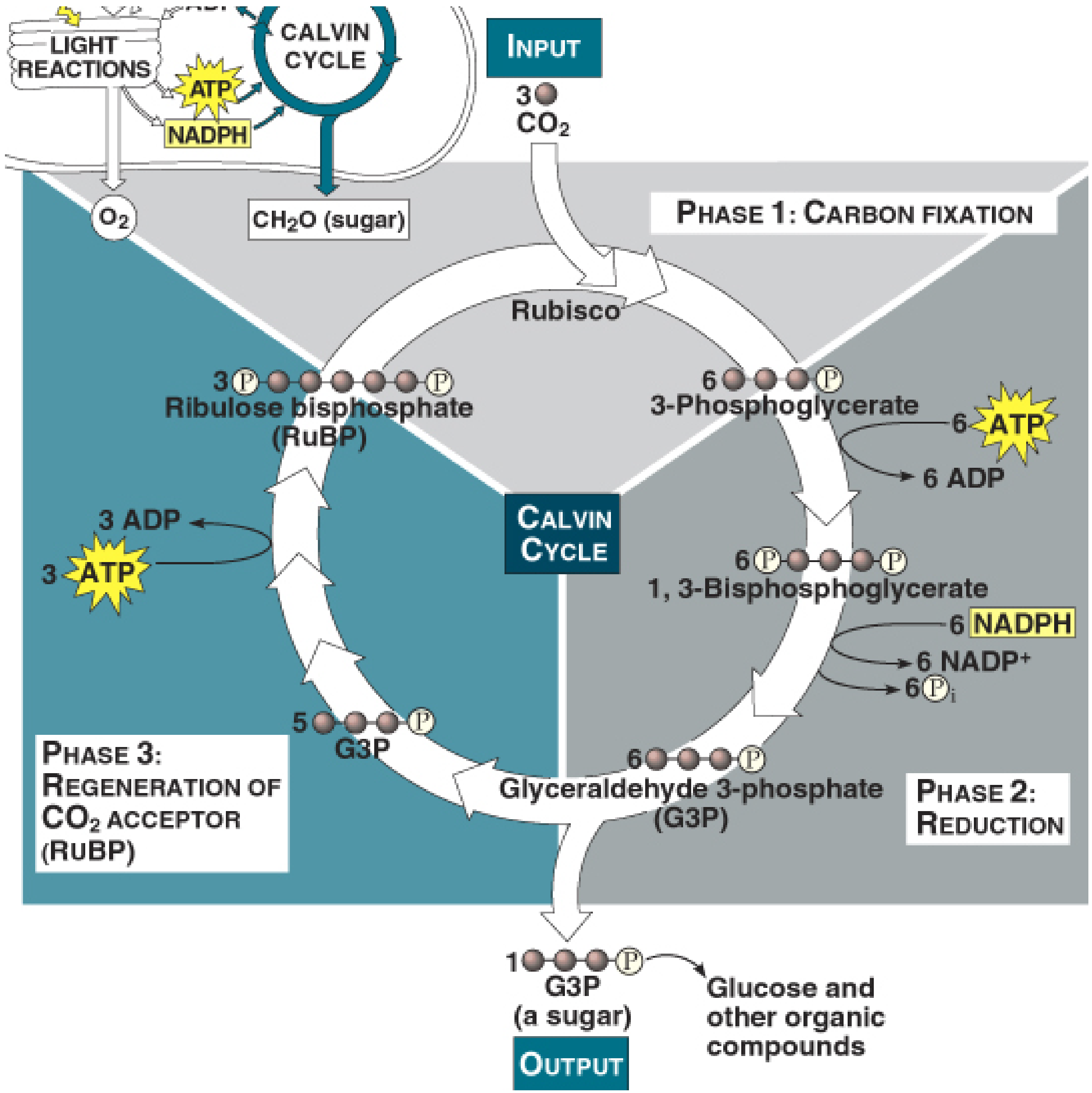
FIGURE 8.2 The Calvin cycle proceeds in three stages: (1) carboxylation, during which CO_2 is covalently linked to a carbon skeleton; (2) reduction, during which carbohydrate is formed at the expense of the photochemically derived ATP and reducing equivalents in the form of NADPH; and (3) regeneration, during which the CO_2 acceptor ribulose-1,5-bisphosphate re-forms.

Calvin Cycle

- Starts with CO_2 and produces Glyceraldehyde 3-phosphate
- Three turns of Calvin cycle generates one molecule of product
- Three phases to the process
  - Carbon Fixation
  - Reduction of CO2
  - Regeneration of RuBP

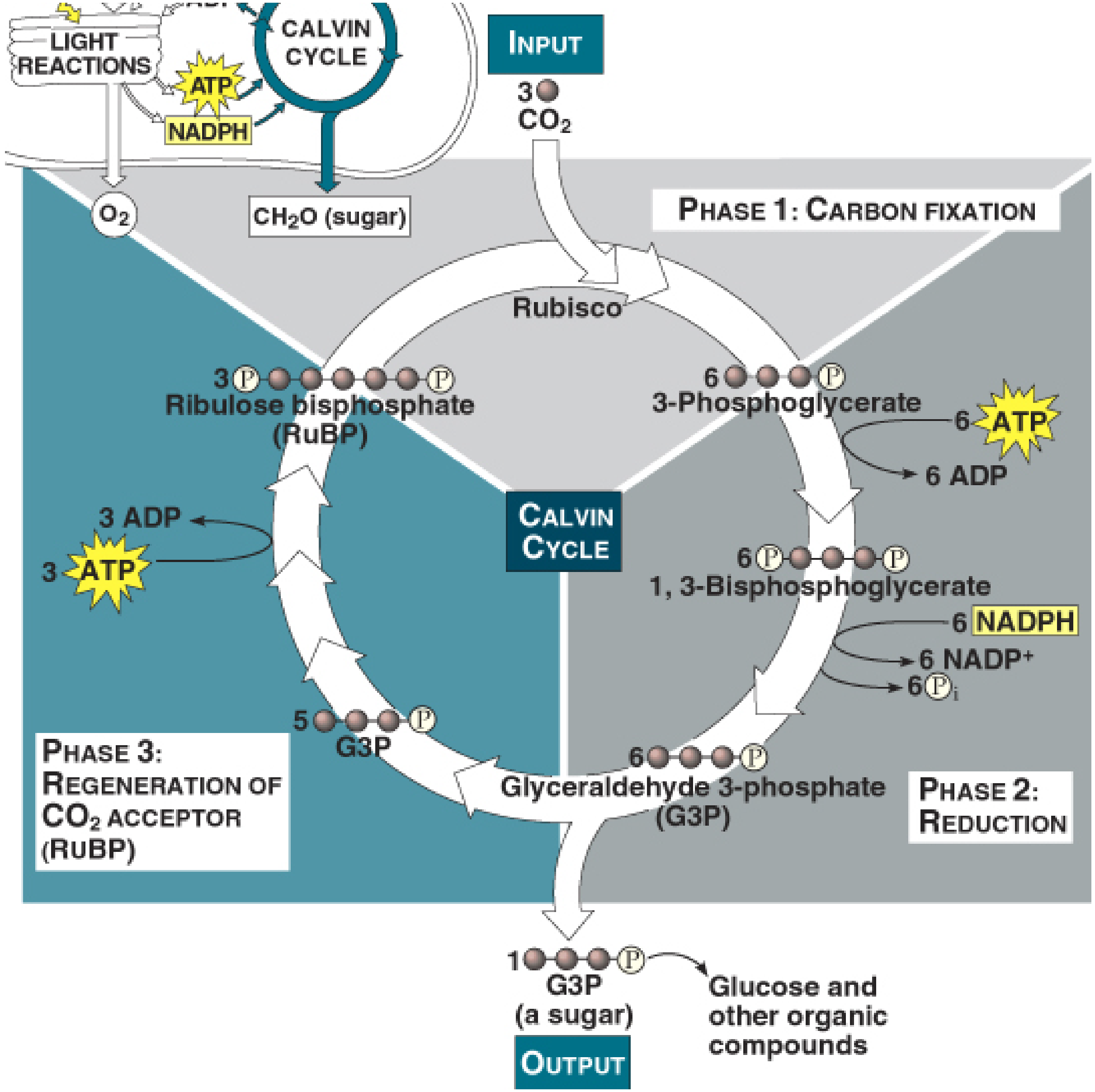


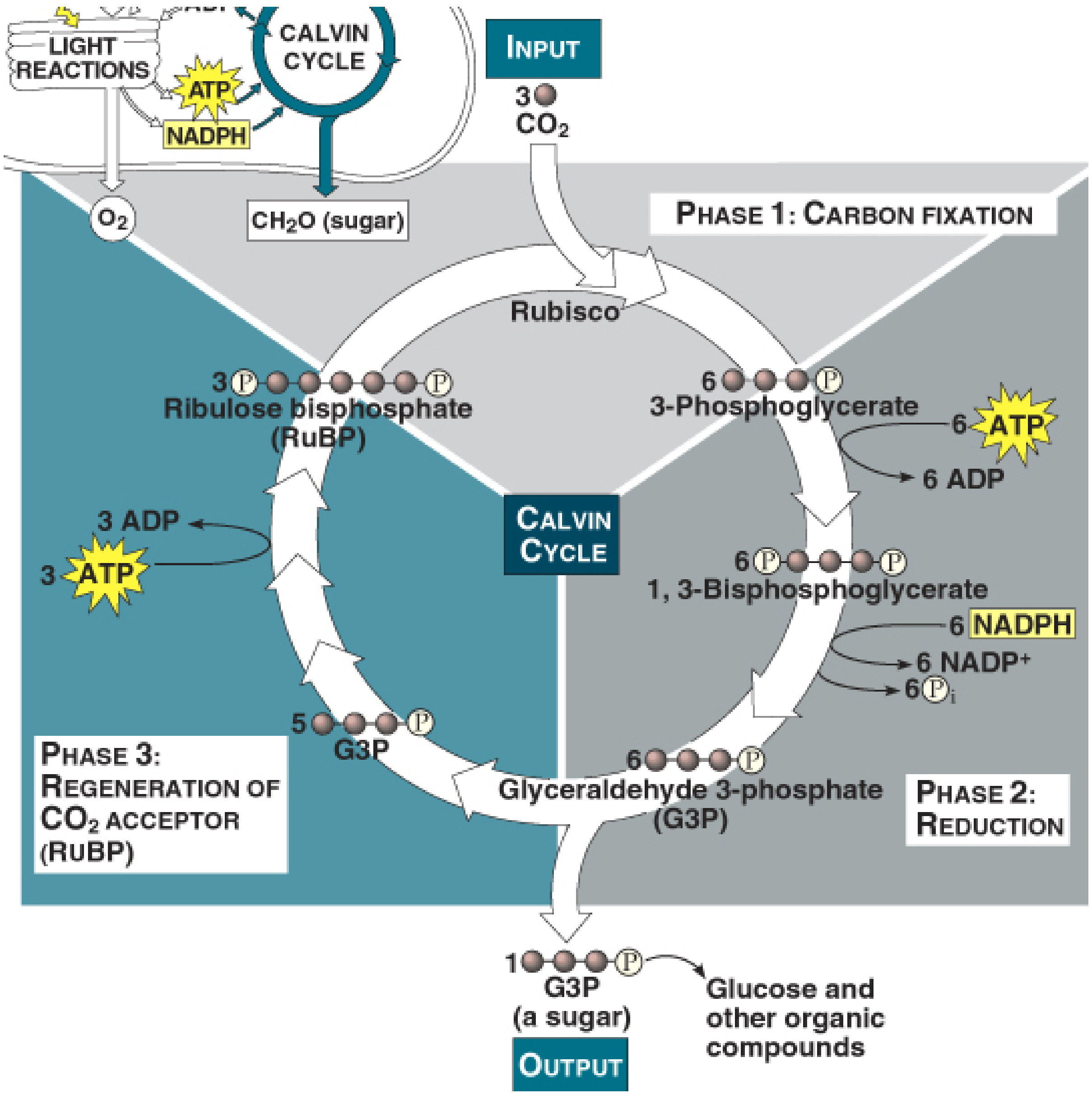
1 A molecule of CO_2 is converted from its inorganic form to an organic molecule (fixation) through the attachment to a 5C sugar (ribulose bisphosphate or RuBP).
  - Catalysed by the enzyme RuBP carboxylase (Rubisco).
- The formed 6C sugar immediately cleaves into 3-phosphoglycerate



2 Each 3-phosphoglycerate molecule receives an additional phosphate group forming 1,3-Bisphosphoglycerate (ATP phosphorylation)

- NADPH is oxidized and the electrons transferred to 1,3-Bisphosphoglycerate cleaving the molecule as it is reduced forming Glyceraldehyde 3-phosphate



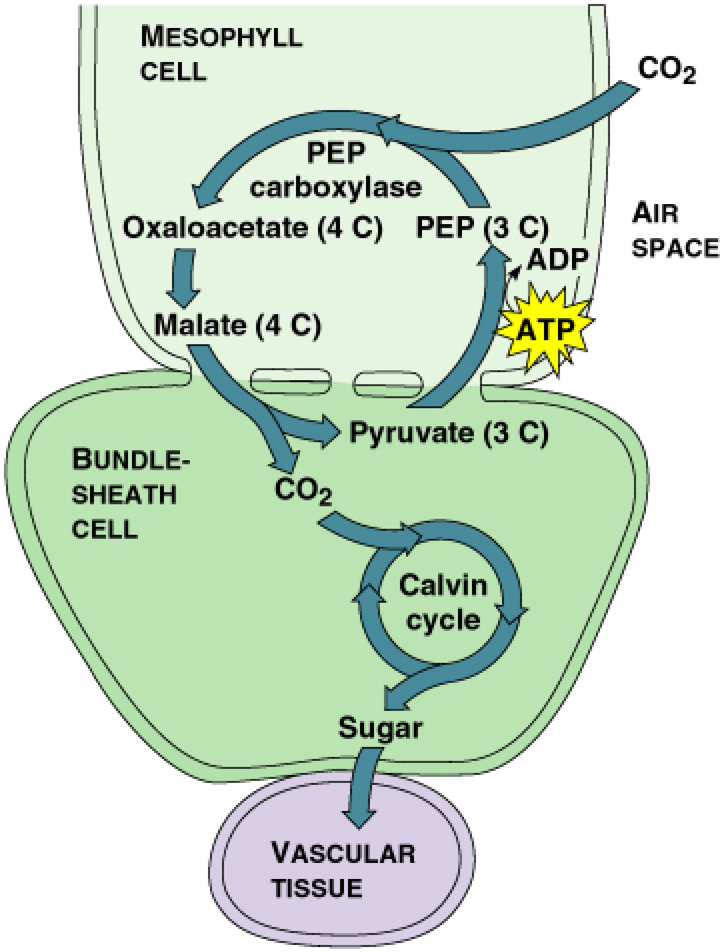


3 The final phase of the cycle is to regenerate RuBP

- Glyceraldehyde 3-phosphate is converted to RuBP through a series of reactions that involve the phosphorylation of the molecule by ATP

Variations Anyone?

- In hot/arid regions plants may run short of CO_2 as a result of water conservation mechanisms
- **C_4 Photosynthesis**
  CO_2 may be captured by conversion of PEP (Phosphoenolpyruvate) into oxaloacetate and ultimately malate that is exported to cells where the Calvin cycle is active
- **CAM Photosynthesis**
  CO_2 may be captured as inorganic acids that my liberate CO_2 during times of reduced availability



(b) The C_4 pathway

C2 cycle: photorespiration

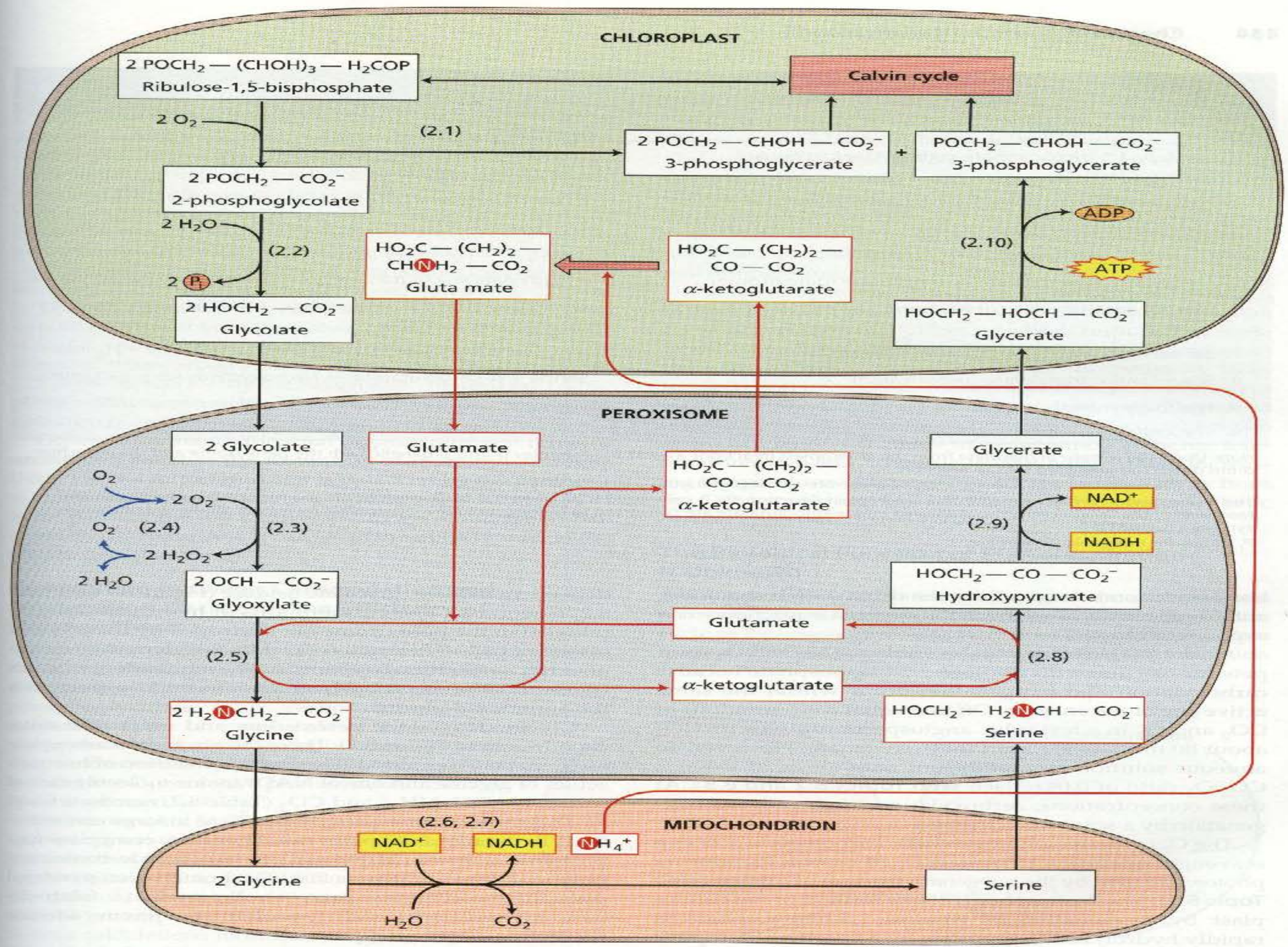


FIGURE 8.7 The main reactions of the photorespiratory cycle. Operation of the C_2 oxidative photosynthetic cycle involves the cooperative interaction among three organelles: chloroplasts, mitochondria, and peroxisomes. Two molecules of glycolate (four carbons) transported from the chloroplast into the peroxisome are converted to glycine, which in turn is exported to the mitochondrion and transformed to serine (three carbons) with the concurrent release of carbon dioxide (one carbon). Serine is transported to the peroxisome and transformed to glycerate. The latter flows to the chloroplast where it is phosphorylated to 3-phosphoglycerate and incorporated into the Calvin cycle. Inorganic nitrogen (ammonia) released by the mitochondrion is captured by the chloroplast for the incorporation into amino acids by using appropiate skeletons (α-ketoglutarate). The heavy arrow in red marks the assimilation of ammonia into glutamate catalyzed by glutamine synthetase. In addition, the uptake of oxygen in the peroxisome supports a short oxygen cycle coupled to oxidative reactions. The flow of carbon, nitrogen and oxygen are indicated in black, red and blue, respectively. See Table 8.2 for a description of each numbered reaction.

Thank You!