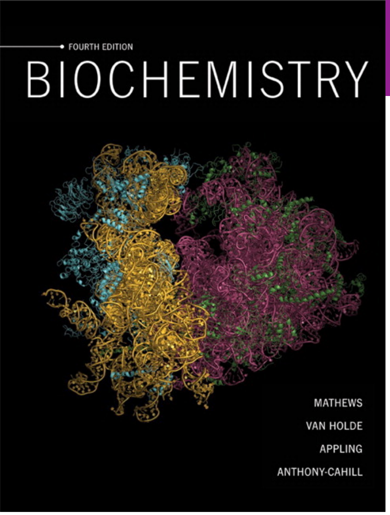


Chapter 16

Photosynthesis

長庚大學醫學院生物化學科
吳嘉霖 老師
分機:5159

The Basic Processes of Photosynthesis

Photosynthesis:

- Provides carbohydrates for energy production
- Fixes CO_2
- The major source of atmospheric O_2

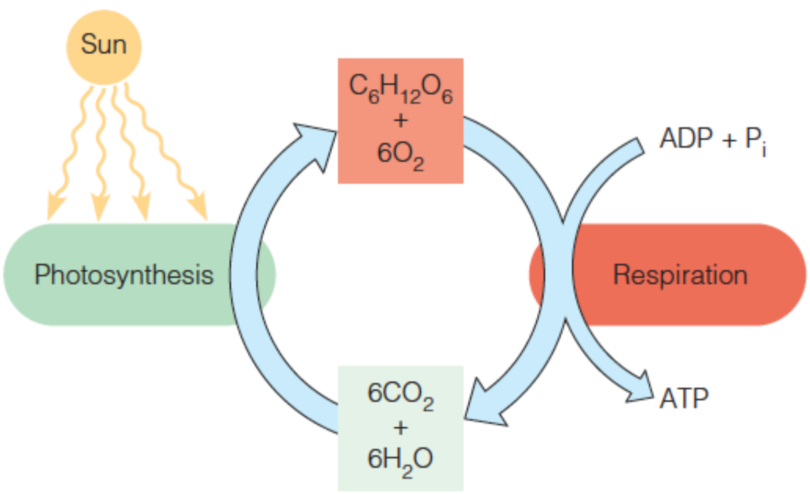
The Basic Processes of Photosynthesis

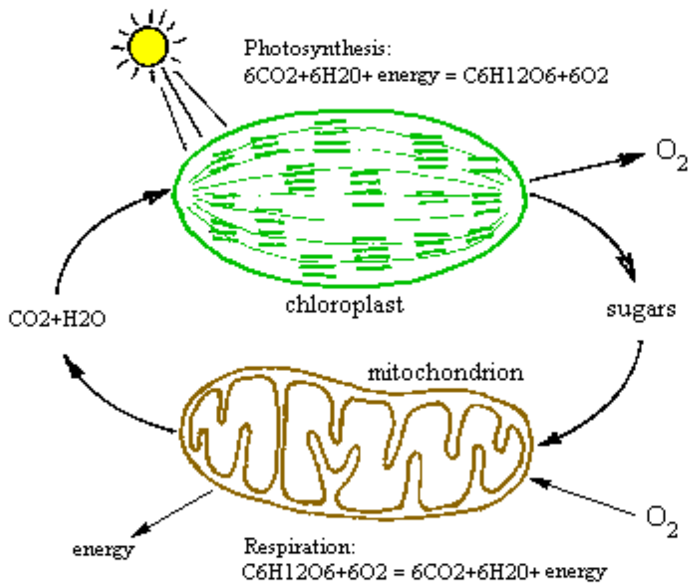
The carbon cycle in nature:

•**Carbon dioxide** and **water** are combined through photosynthesis to form carbohydrates.

•In both photosynthetic and nonphotosynthetic organisms these carbohydrates can be reoxidized to regenerate CO_2 and H_2O.

•Part of the energy obtained from both photosynthesis and fuel oxidation is captured in ATP.





The Basic Processes of Photosynthesis

- Photosynthesis requires a reductant, usually H_2O, to reduce CO_2 to the carbohydrate level.

$$CO_2 + H_2O \xrightarrow{\text{Light energy}} [CH_2O] + O_2$$

$$CO_2 + 2H_2A \xrightarrow{\text{Light energy}} [CH_2O] + H_2O + 2A$$

The Basic Processes of Photosynthesis

$$CO_2 + 2H_2O \xrightarrow{\text{Light energy}} [CH_2O] + H_2O + O_2$$

Table 16.1 Examples of some photosynthetic reactions

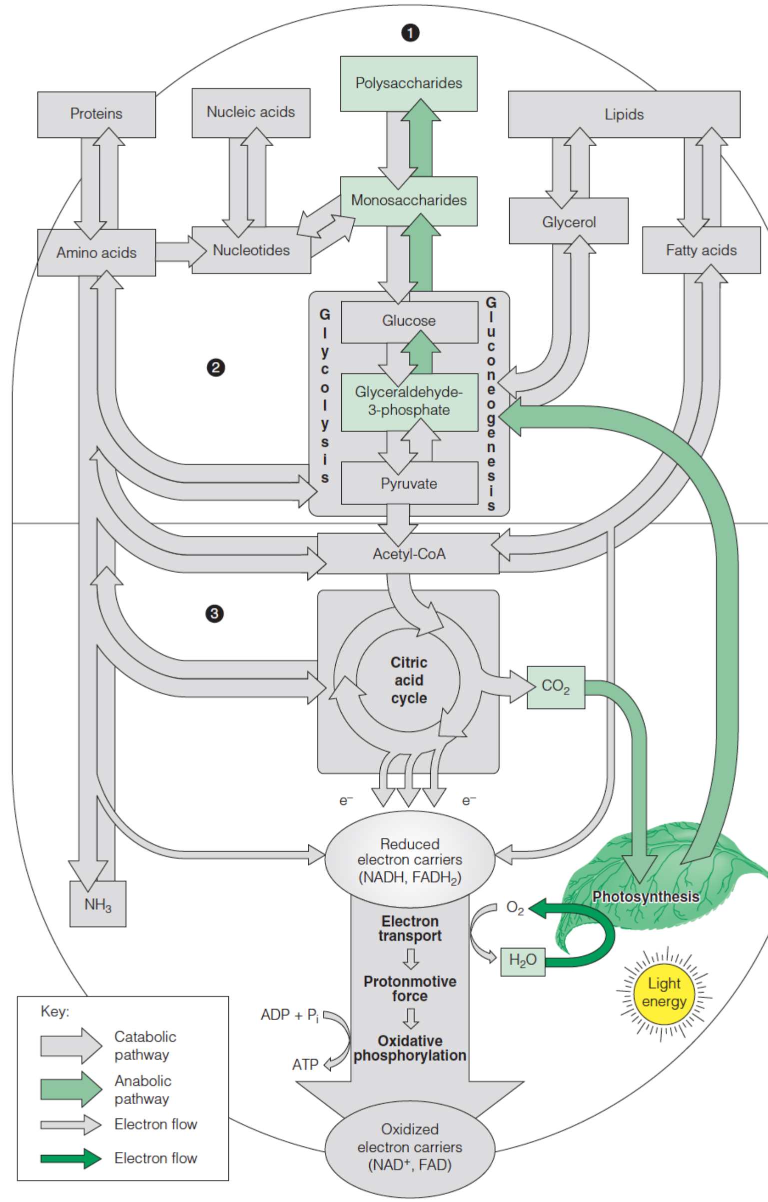
Organisms	Reductant	Carbon Assimilation Reaction
Plants, algae, cyanobacteria	H_2O	$CO_2 + 2H_2O \rightarrow [CH_2O] + H_2O + O_2$
Green sulfur bacteria	H_2S	$CO_2 + 2H_2S \rightarrow [CH_2O] + H_2O + 2S$
Purple bacteria	$[HSO_3^-]$	$CO_2 + H_2O + 2[HSO_{3-}] \rightarrow [CH_2O] + 2[HSO_4^-]$
Nonsulfur photosynthetic bacteria	H_2 or many other reductants such as lactate	$CO_2 + 2H_2 \rightarrow [CH_2O] + H_2O$ $CO_2 + 2(HC{-}OH) \rightarrow [CH_2O] + H_2O + 2(C{\equiv}O)$ $CO_2 + 2\underbrace{\left(\begin{array}{c} CH_3 \\ \vert \\ HC{-}OH \\ \vert \\ COO^- \end{array}\right)}_{\text{Lactate}} \longrightarrow [CH_2O] + H_2O + 2\underbrace{\left(\begin{array}{c} CH_3 \\ \vert \\ C{=}O \\ \vert \\ COO^- \end{array}\right)}_{\text{Pyruvate}}$

The Basic Processes of Photosynthesis

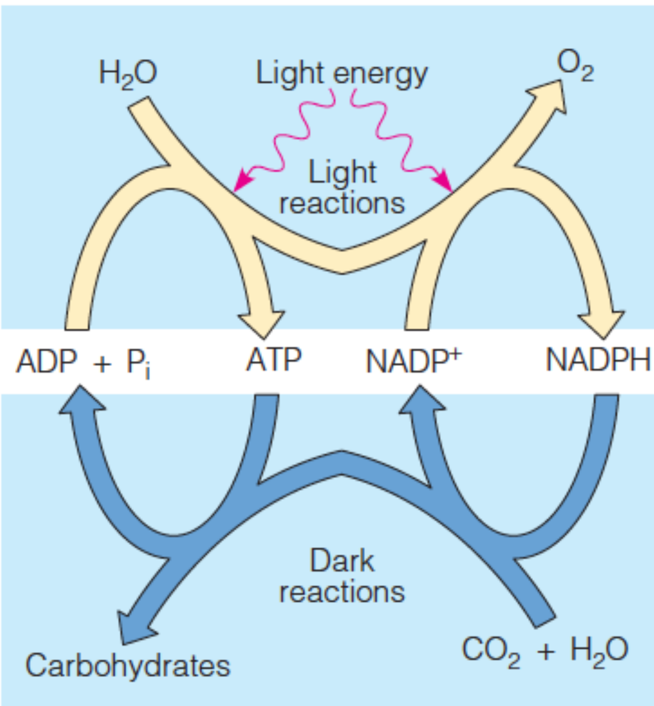
The role of photosynthesis in metabolism:

•The major biosynthetic pathways leading from carbon dioxide and water to polysaccharides are highlighted in green.

•Oxygen derived from the water is released as a by-product of photosynthesis.



The Basic Processes of Photosynthesis



The two subprocesses of photosynthesis:

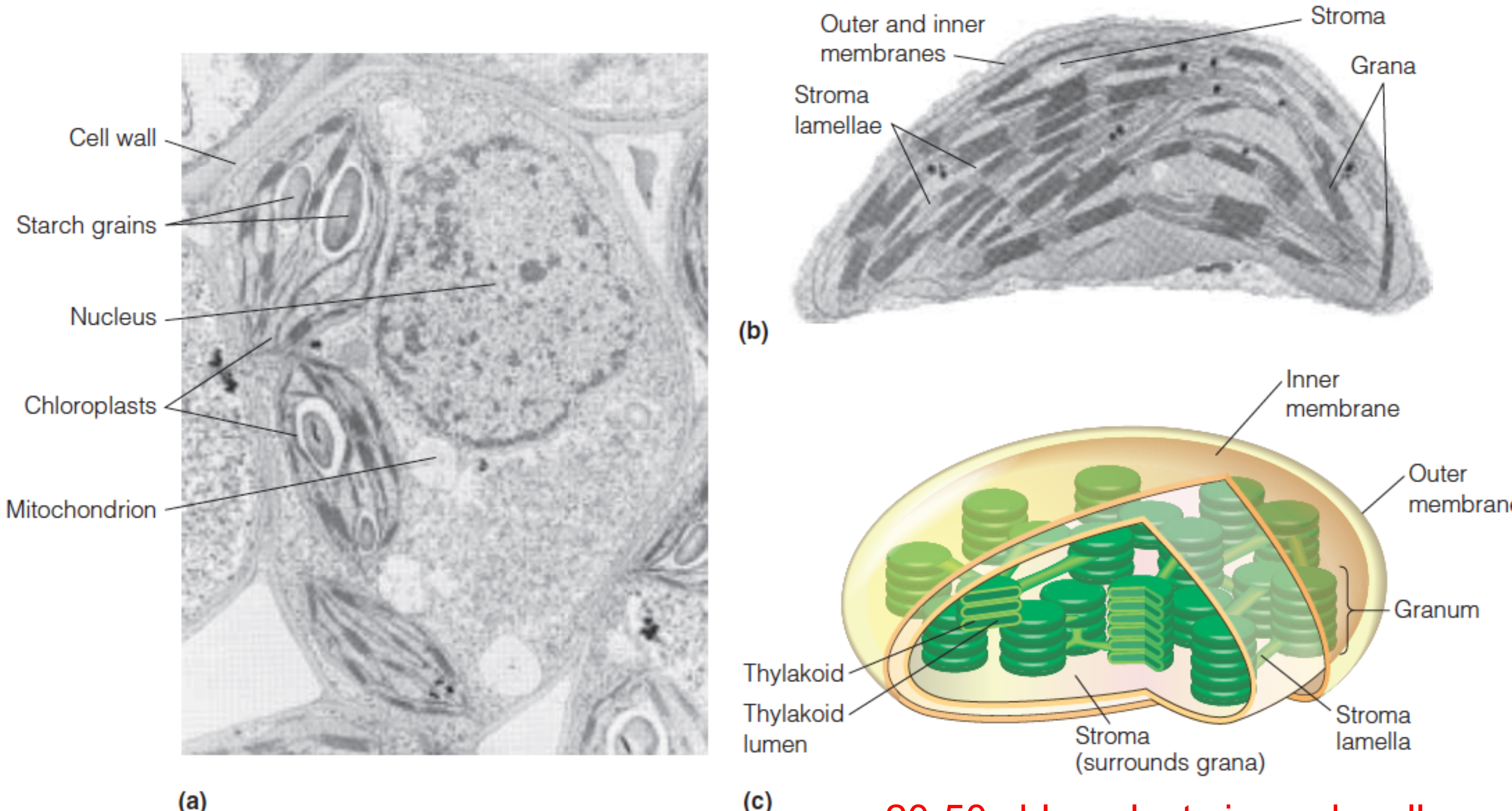
•The overall process of photosynthesis is divided into ***light reactions*** and ***dark reactions***.

•The ***light reactions***, which require visible light as an energy source, produce reducing power (in the form of NADPH), ATP, and O_2.

•The NADPH and ATP drive the so-called ***dark reactions***, which occur in both the presence and the absence of light and fix CO_2 into carbohydrates.

The Chloroplast

Chloroplasts (葉綠體) are the photosynthetic organelles of green plants and algae.



20-50 chloroplasts in each cell

a) Several chloroplasts are shown in a cross section of a cell from a *Coleus leaf.*
b) Enlarged view of a single chloroplast from a leaf of timothy grass.
c) Schematic rendering of a chloroplast.

The Chloroplast

A photosynthetic prokaryote:

•This electron micrograph of a thin section of the cyanobacterium *Anabaena azollae* shows the folded membranes, which resemble the thylakoids of eukaryotic chloroplasts.

•**Absorption of light** and the **light reactions** occur in the **chloroplast membranes**.

•The **dark reactions** occur in the **stroma**.

The Light Reactions

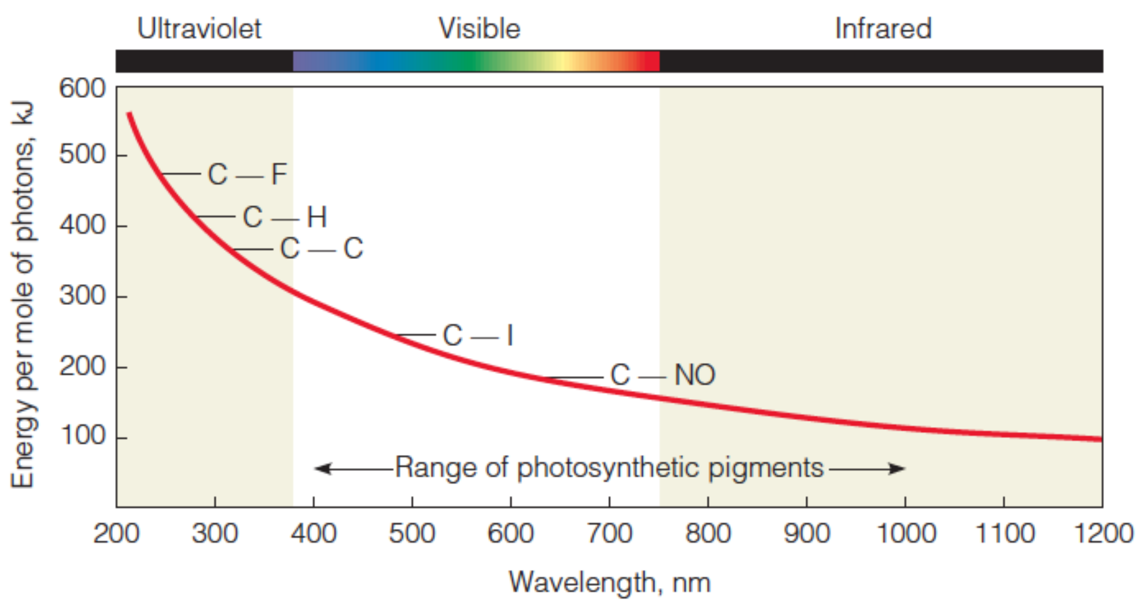
The energy of photons:

•The graph shows energy per mole of photons as a function of wavelength, compared with energies of several chemical bonds.

•Light in the ultraviolet range has enough energy to break many chemical bonds directly.

•Visible light can break some weak bonds.

•Light in the long-wavelength portion of infrared region of the spectrum causes only heat-producing molecular vibrations.



The Light Reactions

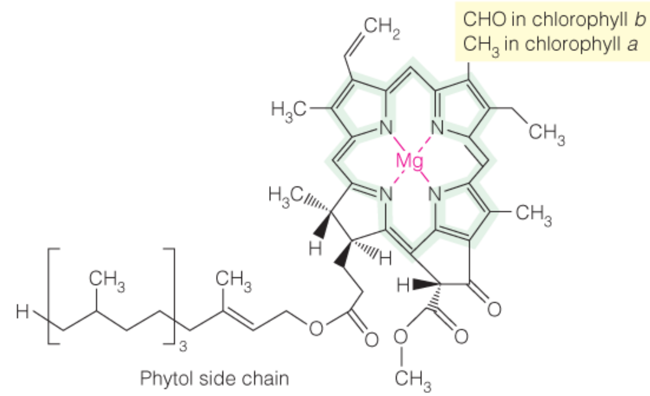
Some photosynthetic Pigments (Chromophores):

•**Chlorophylls *a*** and **b** are the most abundant plant and algal pigments, whereas ***β*-carotene** and **phycocyanin** are examples of accessory pigments.

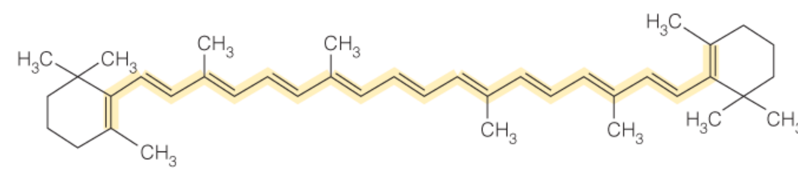
•Phycocyanin and the related phycoerythrin are open-chain tetrapyrroles that are covalently attached to **phycobiloproteins** via a sulfhydryl group, and they are abundant in aquatic photosynthetic organisms.

•These pigments absorb strongly in the 500–600 nm range, wavelengths that can efficiently pass through water.

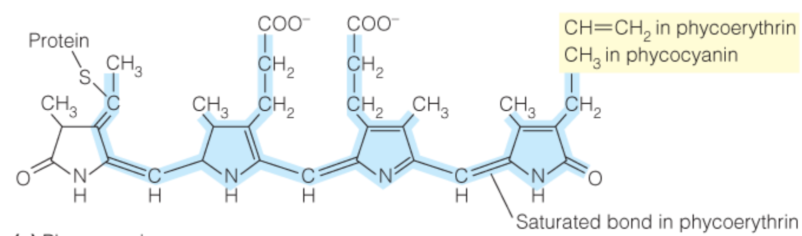
•There are also bacteriochlorophylls, which differ slightly in structure.



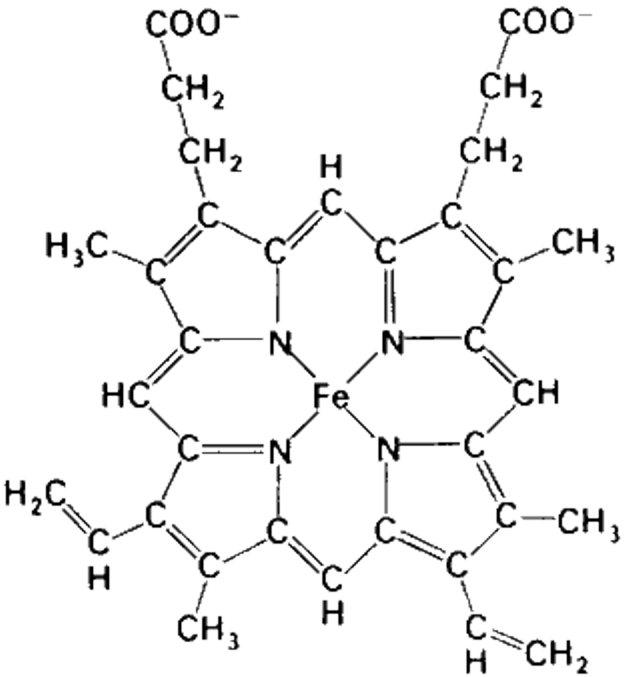
(a) Chlorophylls *a* and *b*



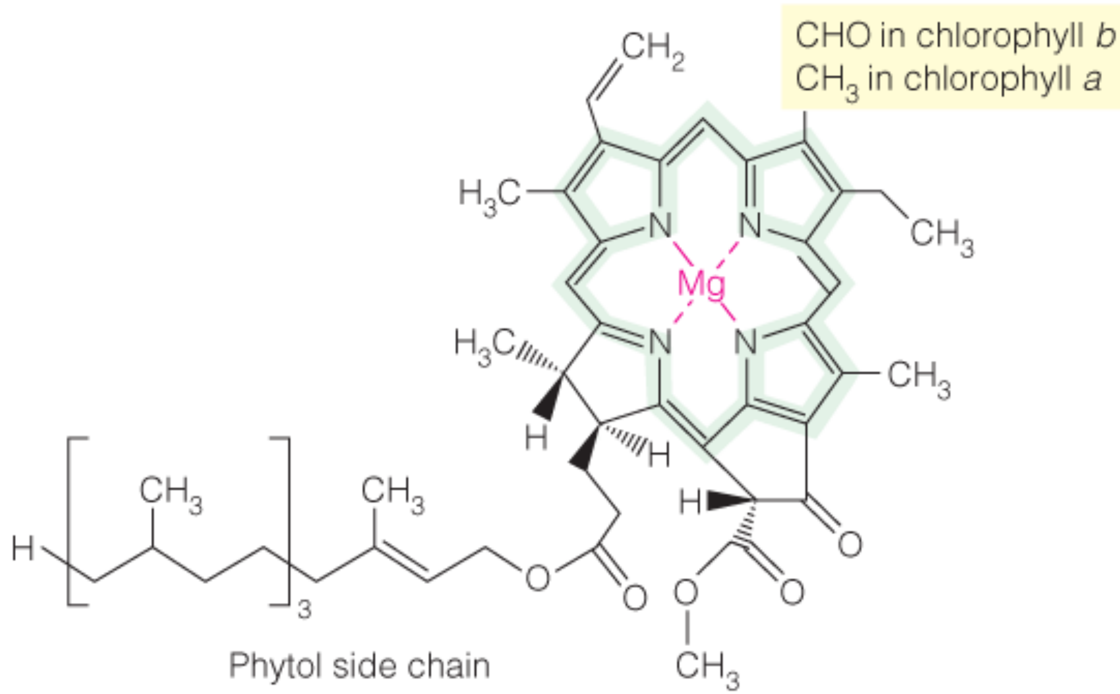
(b) *β*-Carotene



(c) Phycocyanin



Heme
(Fe-protoporphyrin IX)



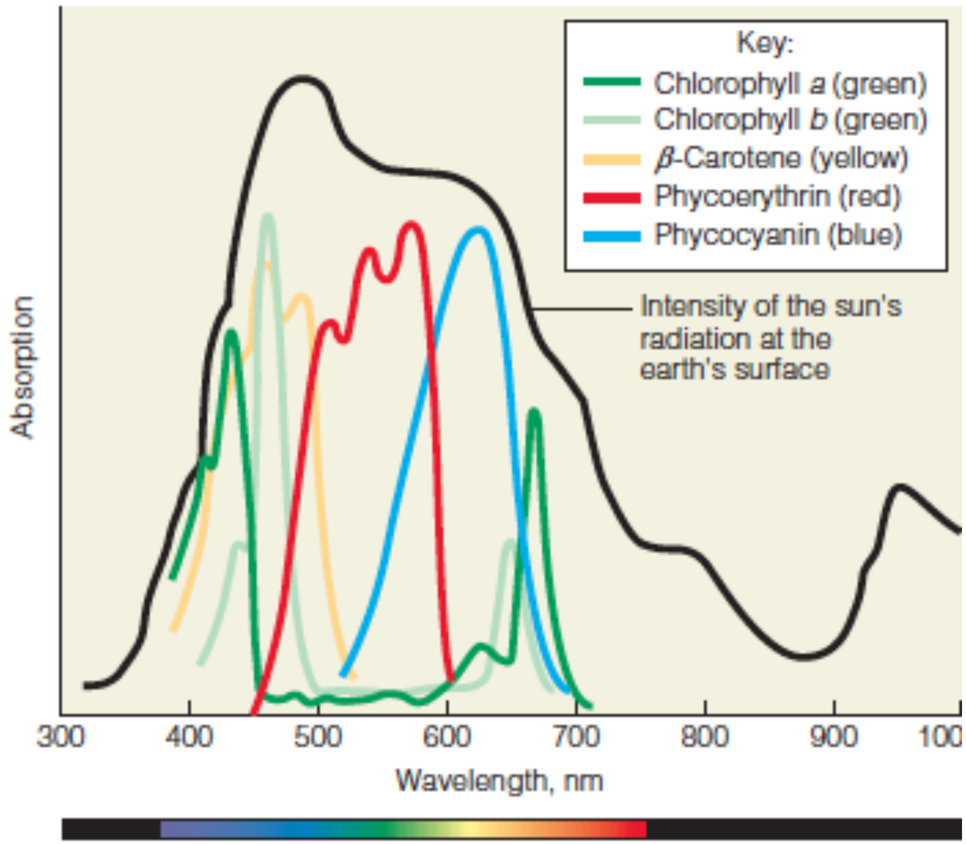
(a) Chlorophylls *a* and *b*

Myoglobin(肌紅蛋白)
Hemoglobin(血紅蛋白)
Cytochrome(細胞色素)

The Light Reactions

Absorption spectra and light energy:

•The absorption spectra of various plant pigments are compared with the spectral distribution of the sunlight that reaches the earth's surface.

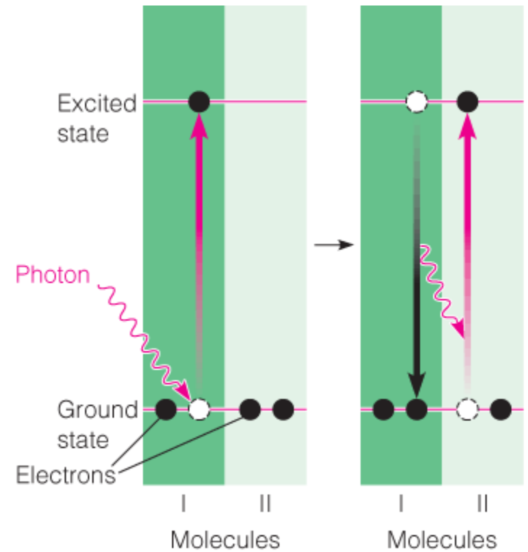


The Light Reactions

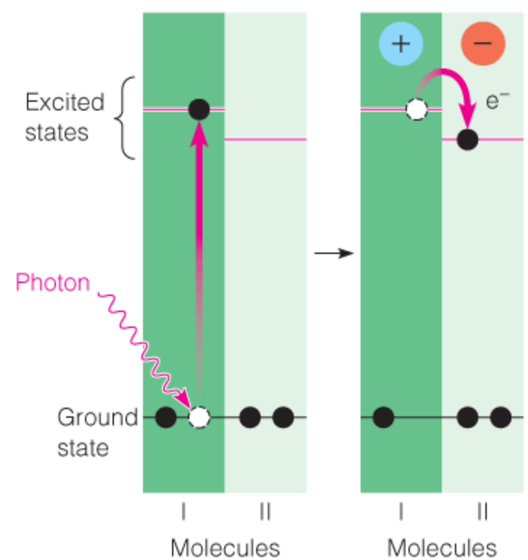
Two modes of energy transfer following photoexcitation:

a)In ***resonance transfer*** molecule I transfers its excitation energy to an identical molecule II, which rises to its higher energy state as molecule I falls back to the ground state. Resonance transfer is extraordinarily fast.

b)In ***electron transfer*** an excited electron in molecule I is transferred to the slightly lower excited state of molecule II, making molecule I a cation and molecule II an anion.

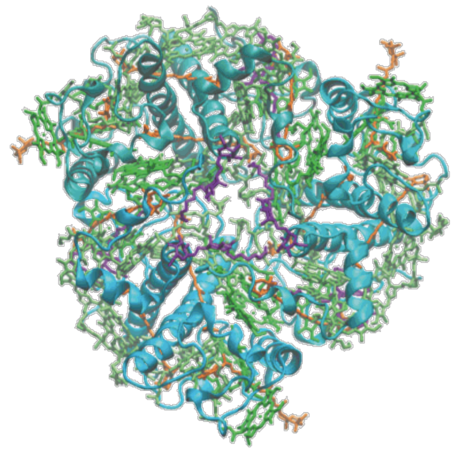


(a) Resonance transfer

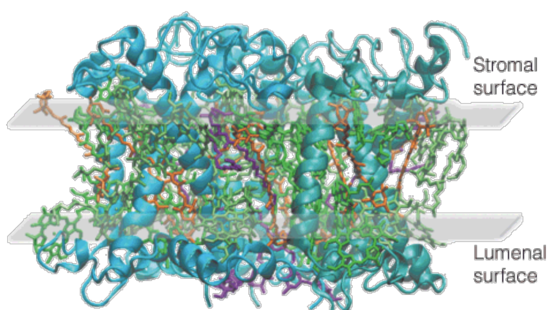


(b) Electron transfer

The Light Reactions



(a)



(b)

- Most chlorophyll molecules are used as antennae to catch photons and pass their energy on to reaction centers.

- Three-dimensional structure of the trimeric light-harvesting complex II of plants.

- The X-ray structure of the pea LHCII shows that the protein exists as a **homotrimer** buried in the thylakoid membrane.

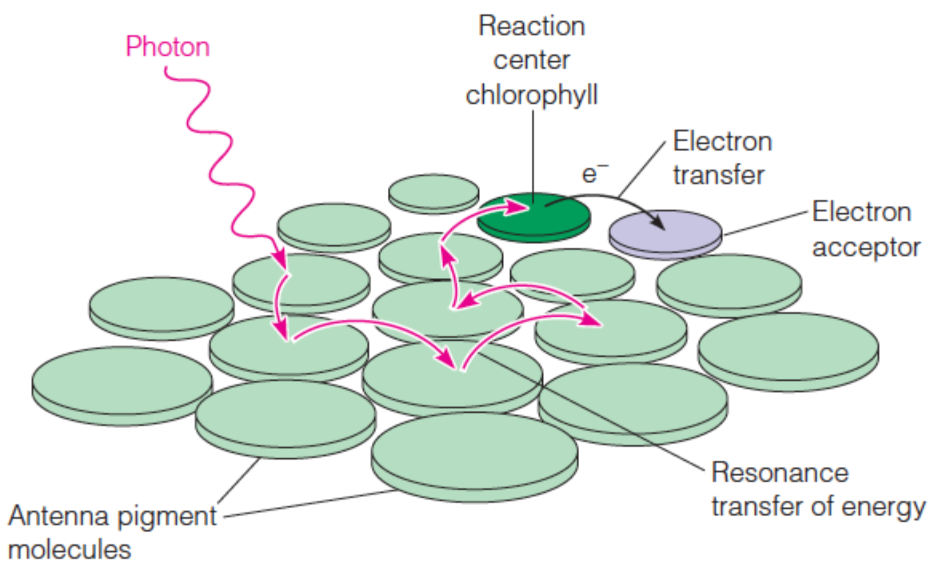
- Each trimer contains 24 chlorophyll *a* molecules, 18 chlorophyll *b* molecules, and 12 carotenoids (luteins and xanthophylls), all serving as antenna molecules.

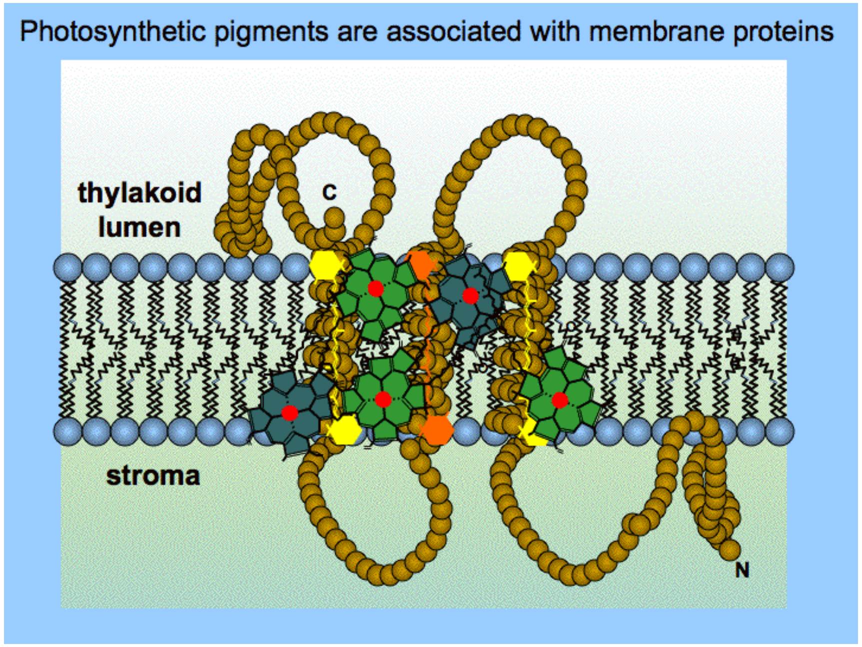
The Light Reactions

Resonance transfer of energy in a light-harvesting complex:

•The excitation energy originating in a photon of light wanders from one antenna molecule to another until it reaches a **reaction center**.

•There an electron is transferred to a primary electron acceptor molecule, and the energy is trapped.





The Light Reactions

- **Two photosystems**, linked in series, are involved in the photosynthetic light reactions in algae, cyanobacteria, and higher plants.

- In each of the two photosystems, the primary step is transfer of a light-excited electron from a reaction center (P680 or P700) into an **electron transport chain**.

- The ultimate **source of the electrons** is the **water** molecules producing O_2.

- The final destination of the electrons is the molecule of **NADP$^+$**, which is thereby reduced to **NADPH**.

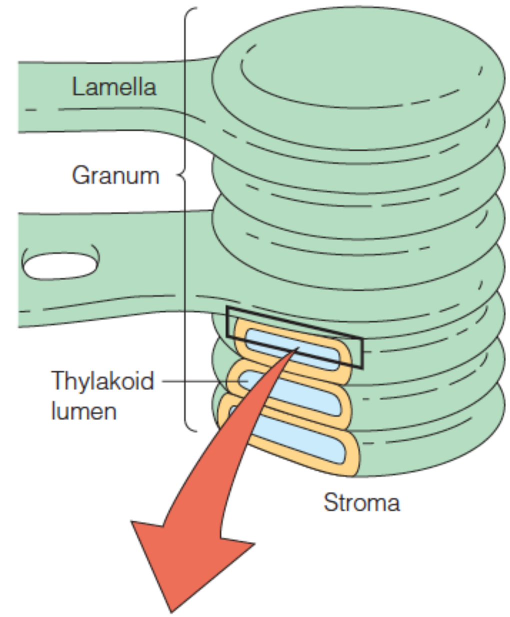
The Light Reactions

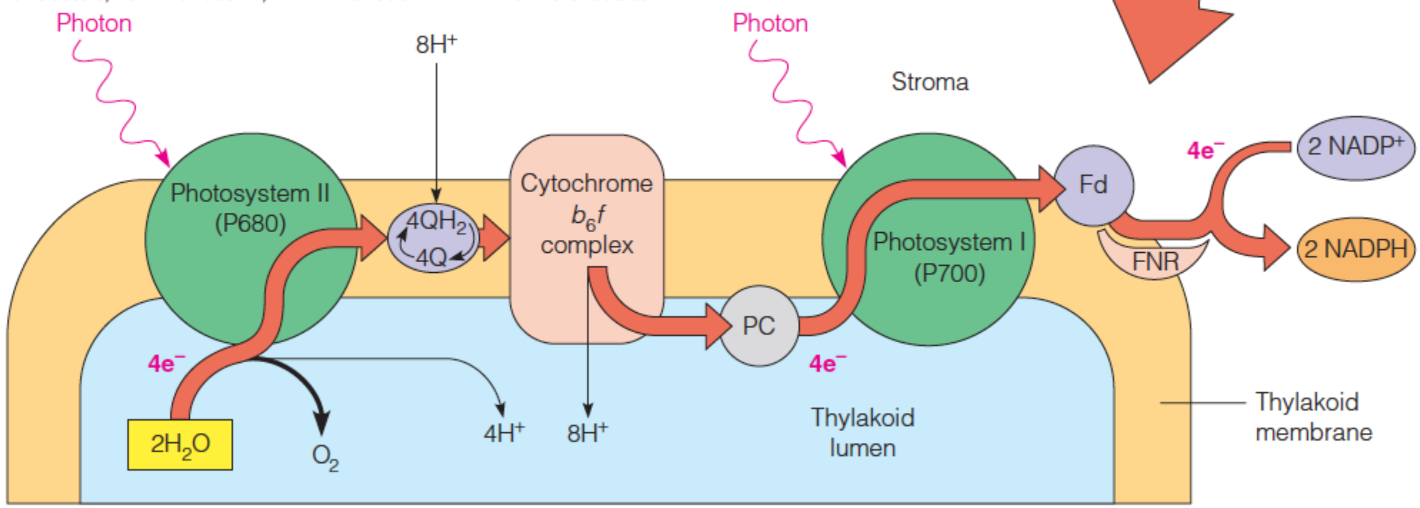
- At two stages in the electron transport process, **protons** are released into the **thylakoid lumen**.
- Some of the protons come from the H_2O that is broken down, some come from the stroma.
- This **transfer of protons** into the lumen produces a **pH gradient** across the thylakoid membrane.
- Thus, ATP and reducing power in the form of NADPH are the products of the light reactions.
- These compounds are exactly what is needed to drive the syntheses carried out in the dark reactions.

The Light Reactions

FIGURE 16.12

The two-photosystem light reactions. In the two-photosystem mode of photosynthesis, the light reactions are carried out by two photosystems linked in series. **(a)** A schematic view of the path of electrons through the two photosystems. The two systems and the cytochrome complex are embedded in the thylakoid membrane. Electrons taken from water in photosystem II are transferred to photosystem I via plastoquinones (Q), the cytochrome b_6f complex, and plastocyanin (PC). In photosystem I the electrons are excited by light again, for transfer via a series of intermediates to ferredoxin. Reduced ferredoxin reduces $NADP^+$. **(b)** Energetics of the two-photosystem light reactions. In each of the two reaction centers, P680 and P700, electrons are raised to an excited state by absorption of photons. In each photosystem the excited electrons are passed through an electron transport chain, which drives the pumping of protons into the thylakoid lumen. The two-photosystem mode has historically been called the Z-scheme because of the pattern of energy changes shown here, but N-scheme would be more accurate. The estimate of eight protons pumped by the cytochrome b_6f complex is based on the Q cycle translocating two protons for each electron transported. **Key:** OEC = oxygen-evolving complex; Y_Z = donor to P680; P680 = photosystem II reaction center chlorophyll; Ph = pheophytin acceptor; Q_A, Q_B = protein-bound plastoquinones; QH_2 = plastoquinol (reduced plastoquinone) in membrane; Cyt b_6f = cytochrome b_6f complex; PC = plastocyanin; P700 = photosystem I reaction center chlorophyll; A_0 = chlorophyll acceptor; A_1 = protein-bound phylloquinone; F_A, F_B, F_X = iron–sulfur clusters; Fd = ferredoxin; FNR = ferredoxin:$NADP^+$ oxidoreductase.





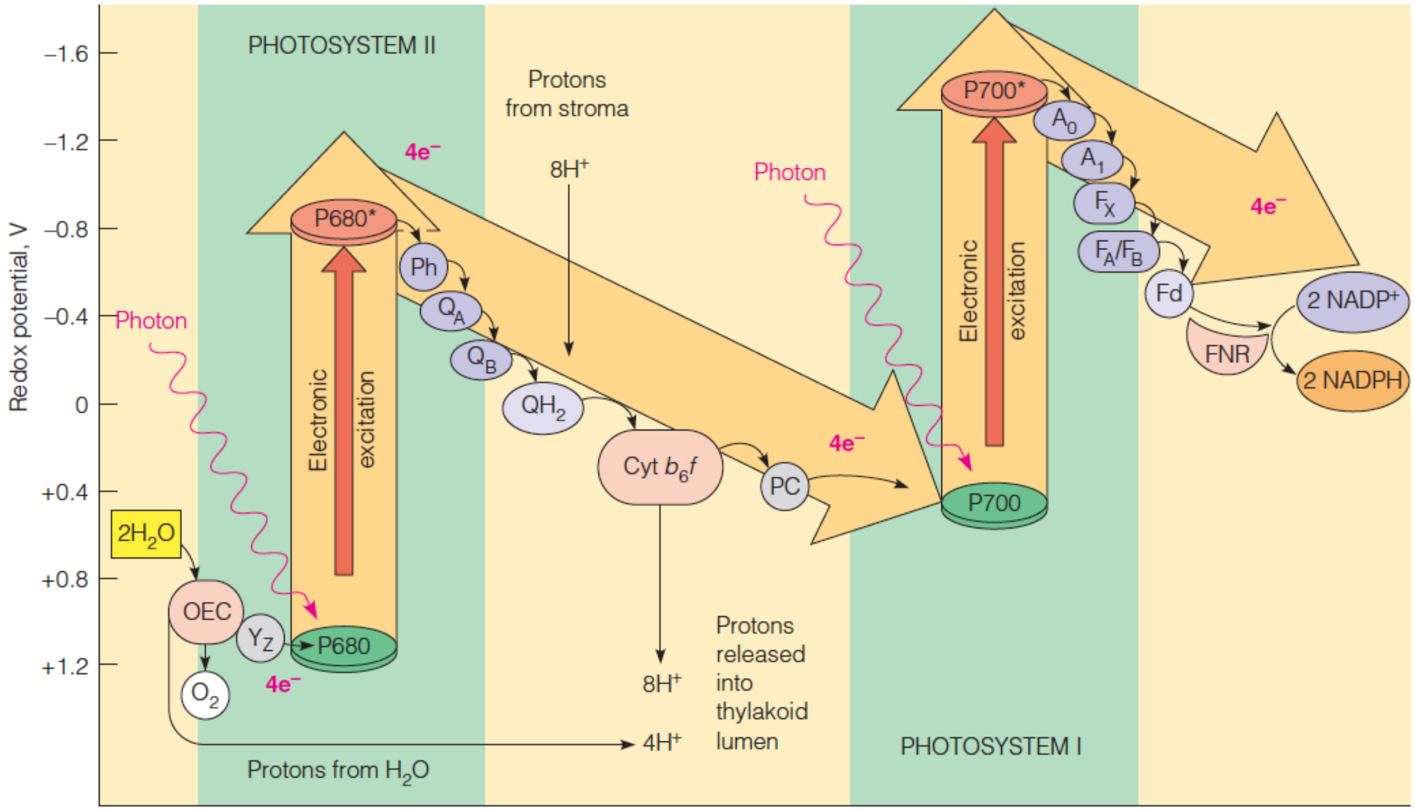
(a)

P680: photosystem II reaction center chlorophyll
P700: photosystem II reaction center chlorophyll

Q: plastoquinones
PC: plastocyanin
Fd: ferredoxin
FNR: ferredoxin:$NADP^+$ oxidoredutase

The Light Reactions

Energetics of the two-photosystem light reactions:



(b)

Ph: Pheophytin acceptor

Q_A, Q_B: protein-bound plastoquinones

A_0: chlorophyll acceptor

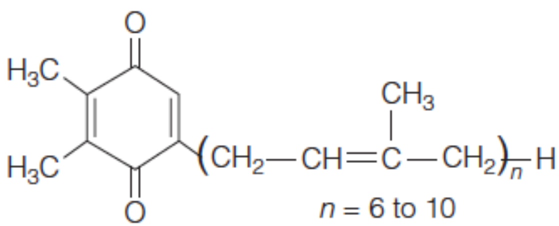
A_1:protein-bound plastoquinones

F_A, F_B, F_X: iron-sulfer clusters

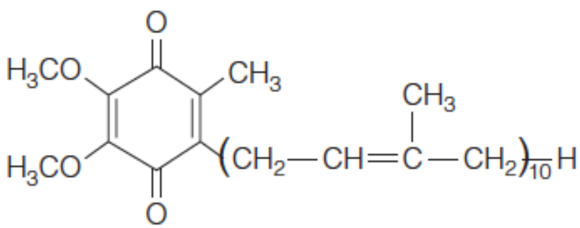
Q_A, Q_B: protein-bound plastoquinones

The Light Reactions

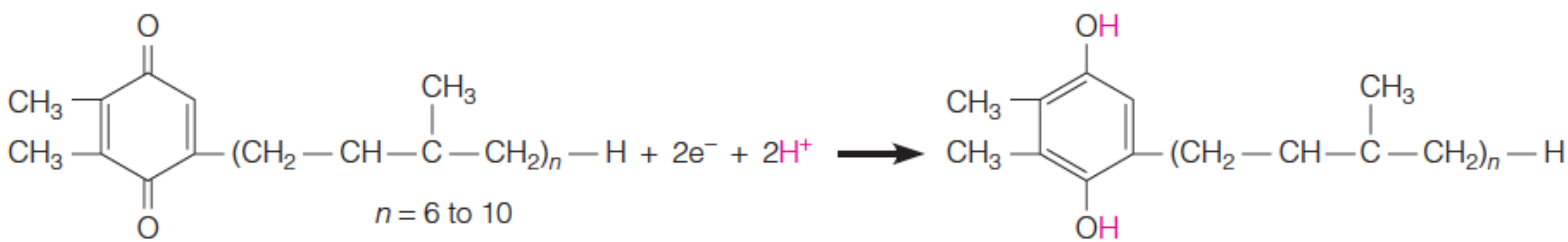
Structure and reactivity of plastoquinone:



Plastoquinone



Ubiquinone (Coenzyme Q_{10})



Plastoquinone **Plastoquinol**

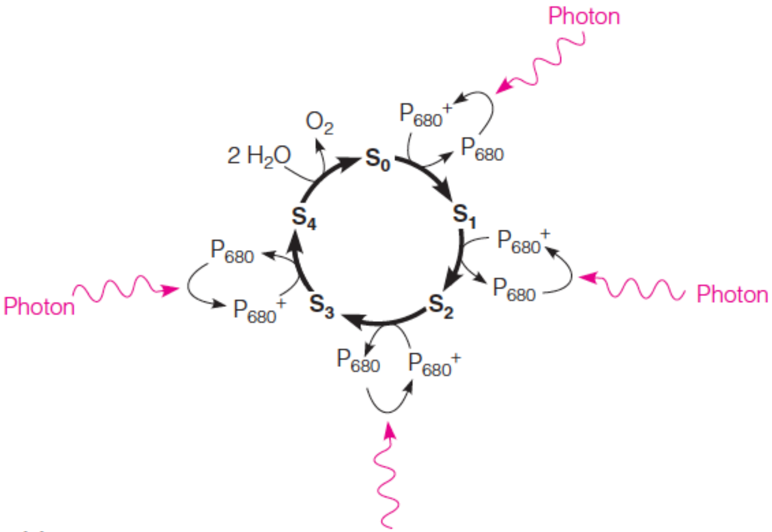
The Light Reactions

A model for the catalytic function of the oxygen evolving complex (OEC) cluster in PSII:

•S_0 - S_4 represent the different oxidation states that the ligated metal cluster cycles through as e^- and H^+ are abstracted from the H_2O molecules.

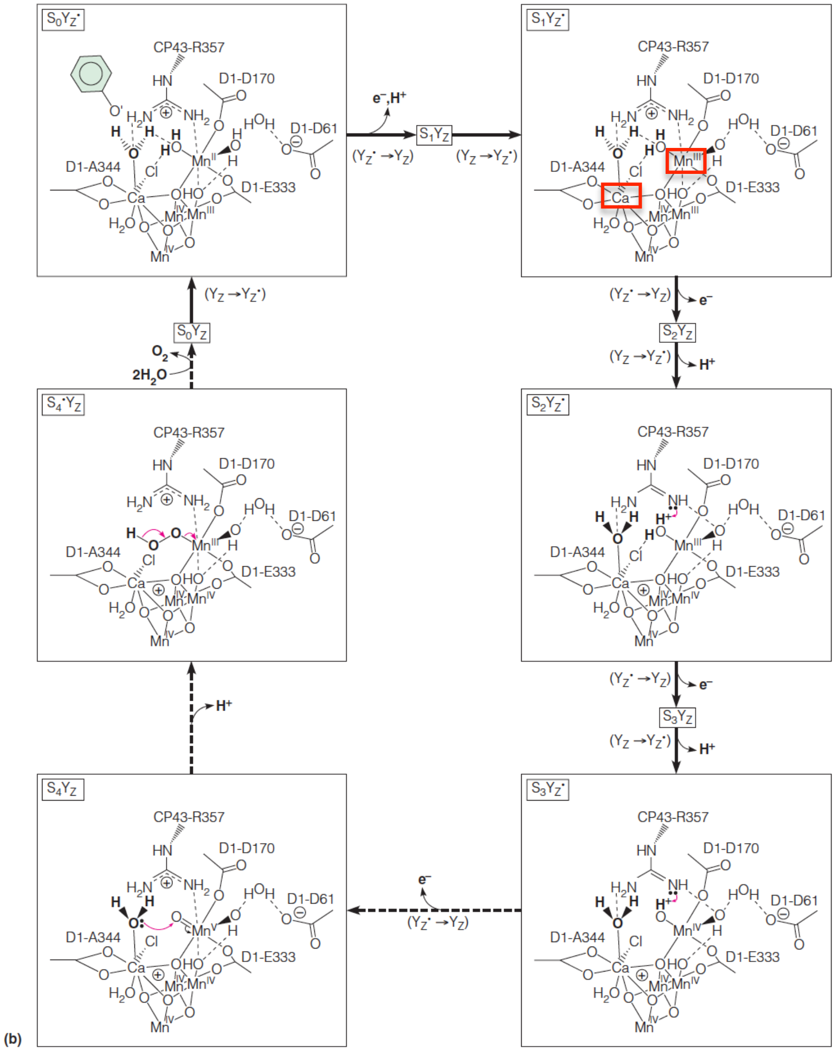
•In the first four transitions, light energy is used to oxidize P_{680} to $P_{680}{}^+$, which in turn oxidizes the metal-oxo cluster of the OEC.

•The transition is light-independent and releases H_2O. Thus, four photons are required to oxidize two H_2O to one O_2.



(a)

The Light Reactions



- In this proposed mechanism, Y_Z represents the redox-active tyrosine residue of the D1 subunit; the oxidized form of Y_Z is the neutral, deprotonated radical species, Y_Z.

- The two H_2O molecules are bound in the S_0Y_Z state by the Ca^{2+} ion and the “dangler” Mn^{III} ion.

- Each transition passes through an intermediate S_nY_Z , in which the oxidized tyrosine is poised to oxidize the metal cluster of the OEC, but for clarity, the tyrosine radical is shown only once.

- In this model, only two of the **Mn ions** change their oxidation states.

- The $S_4 \rightarrow S_4$’ transition is the crucial O-O bond-forming step and involves the attack by a calcium-bound water upon the electrophilic Mn^V=O oxo group. O_2 is released, and two new H_2O are bound to initiate another cycle.

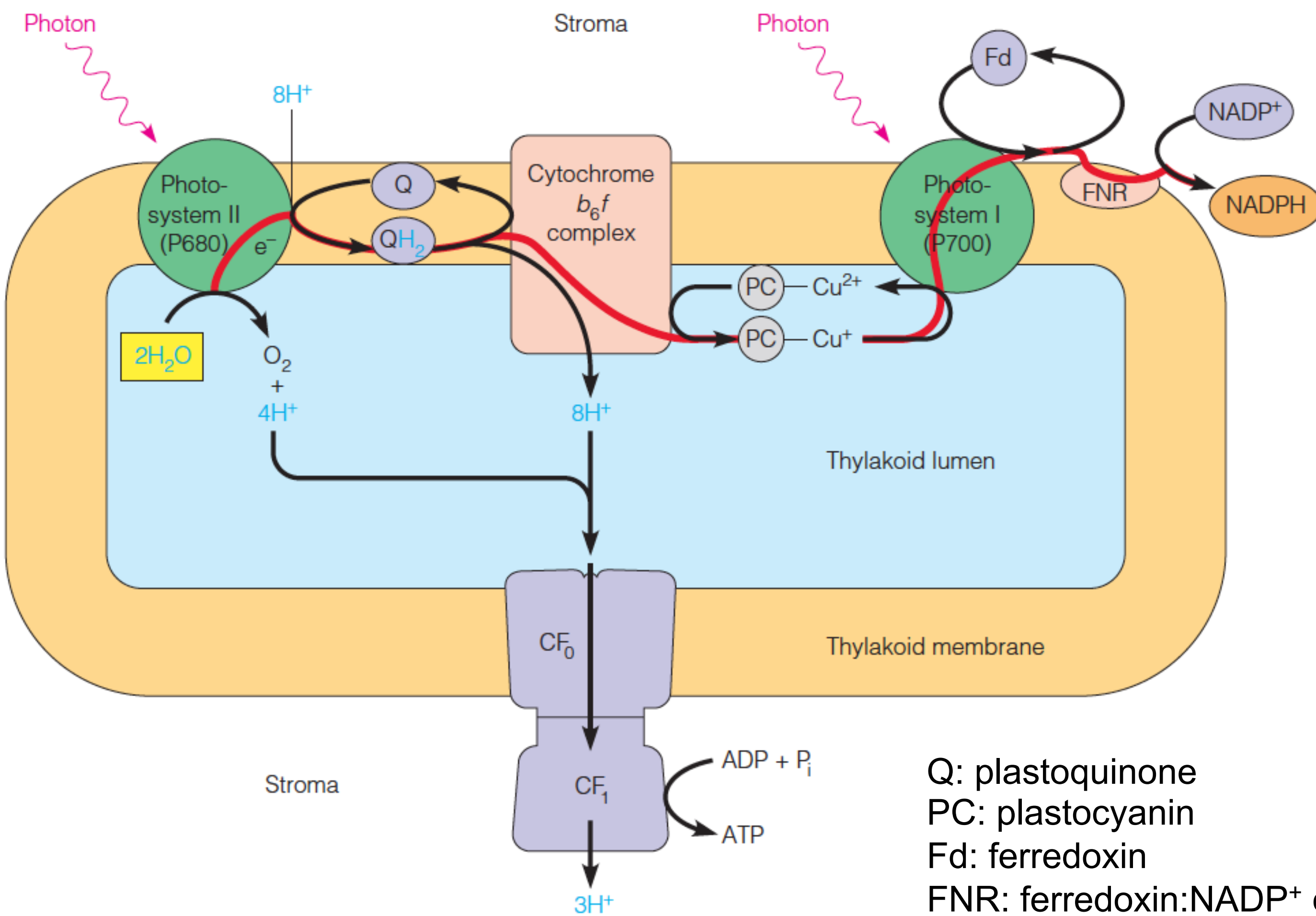
The Light Reactions

- The system has in effect stripped four electrons from the four hydrogen atoms in two water molecules.
- The oxygen produced diffuses out of the chloroplast.
- The four protons that are produced from the two water molecules are released into the thylakoid lumen, helping to generate a pH difference between the lumen and stroma.
- We may summarize the reaction carried out by photosystem II as follows:

$$2H_2O \xrightarrow{4h\nu} 4H^+ + 4e^- + O_2$$

The Light Reactions

Summary view of the light reactions as they occur in the thylakoid:



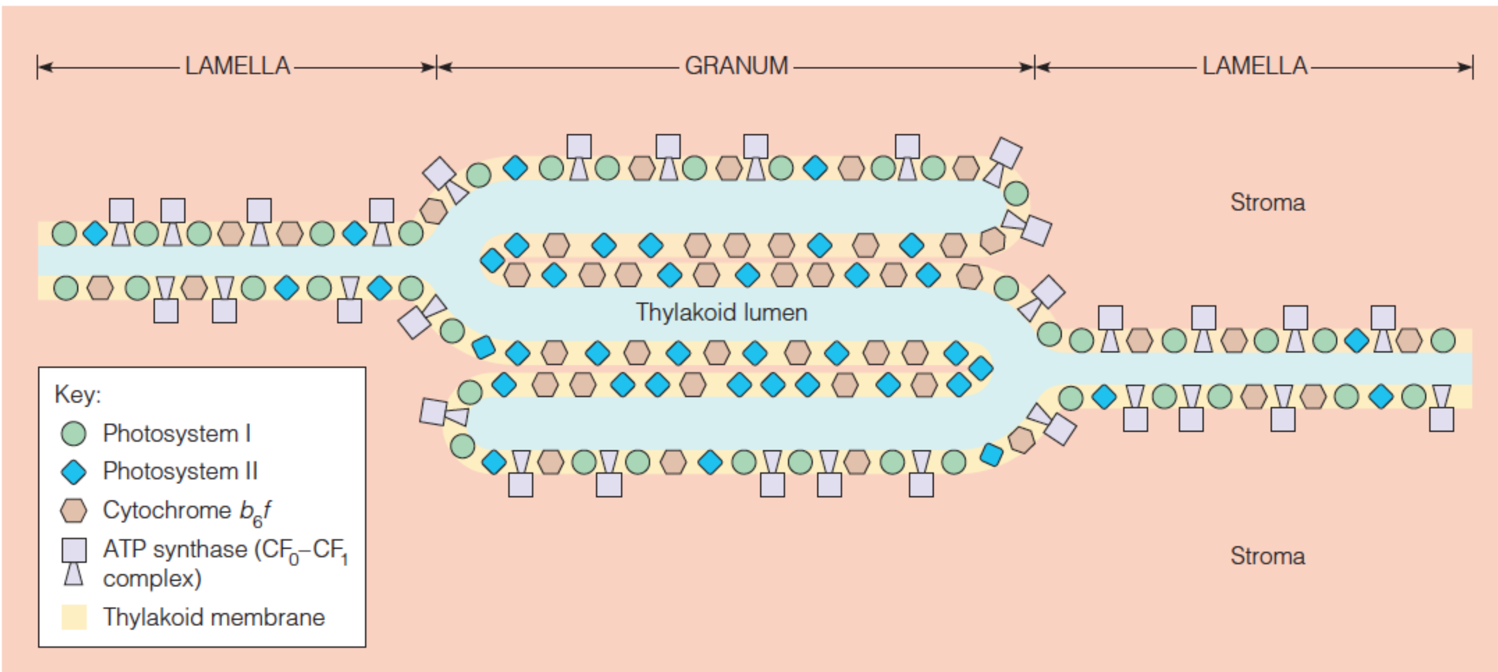
Q: plastoquinone
PC: plastocyanin
Fd: ferredoxin
FNR: ferredoxin:NADP$^+$ oxidoredutase
CF_0-CF_1: ATP synthase complex

The Light Reactions

Arrangement of components of the two photosystems on the thylakoid membrane:

•The membrane layers in **the interior of the granum are rich in photosystem II**.

•The stroma lamellae and the **top and bottom surfaces of the granum are rich in photosystem I** and **ATP synthase** particles, allowing NADP reduction and ATP generation to occur at or near these stroma-facing surfaces.

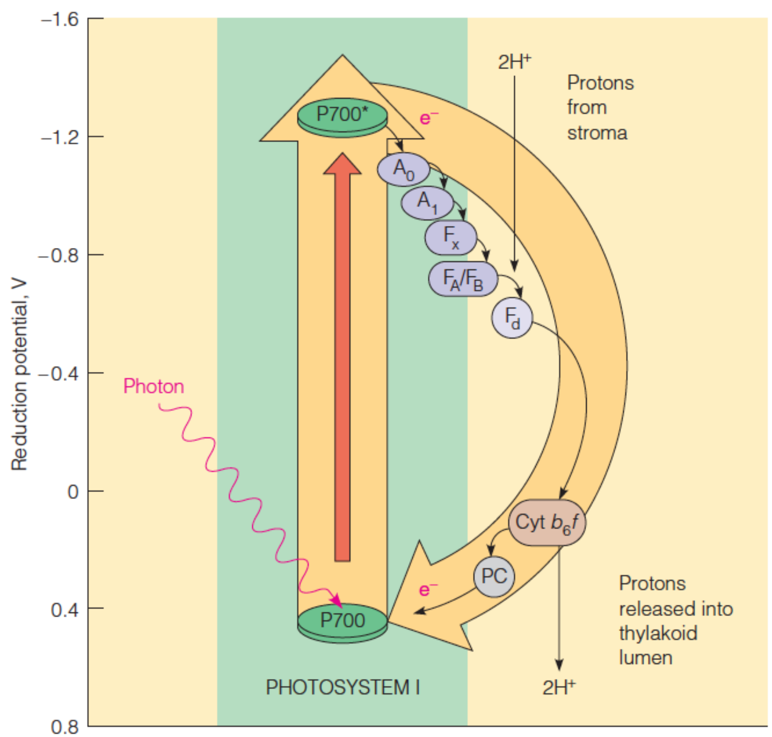


The Light Reactions

Cyclic electron flow:

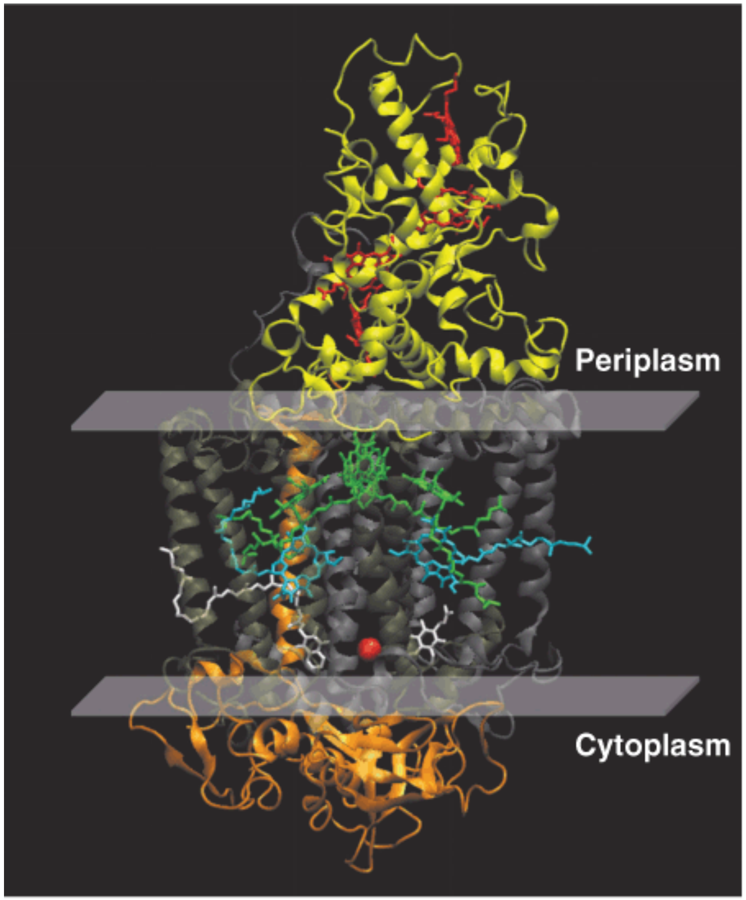
•When **levels of $NADP^+$ are low** and levels of **NADPH are high**, electrons from the P700 center are returned to it via the cytochrome b_6f complex.

•There is **no $NADP^+$ reduction**, but **protons are pumped across the membrane** and therefore ATP is generated.



The Light Reactions

Model of a purple bacterial reaction center complex:



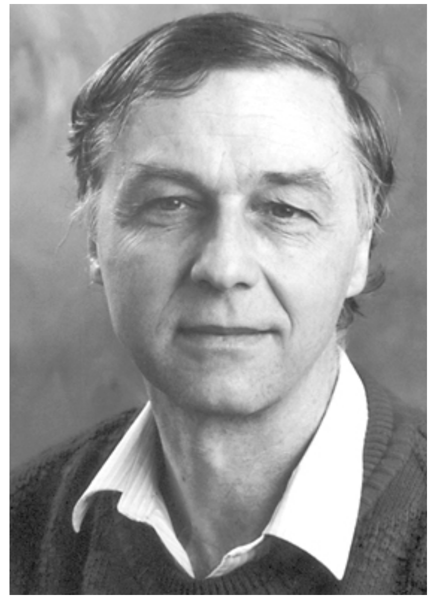
Cytochrome(yellow)
4 heme groups (red)

4 bacteriochlorophylls (green)
2 bacteriophenophytins (cyan)
2 quinones, Q_A & Q_B (white)
1 iron atom (red)

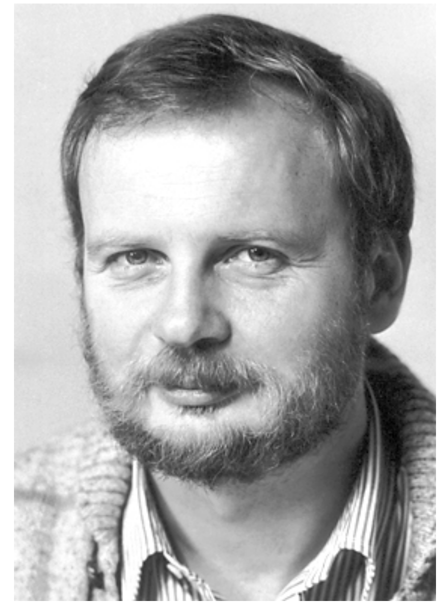
Subunit H (orange)

The Nobel Prize in Chemistry 1988

Johann Deisenhofer



Robert Huber



Hartmut Michel

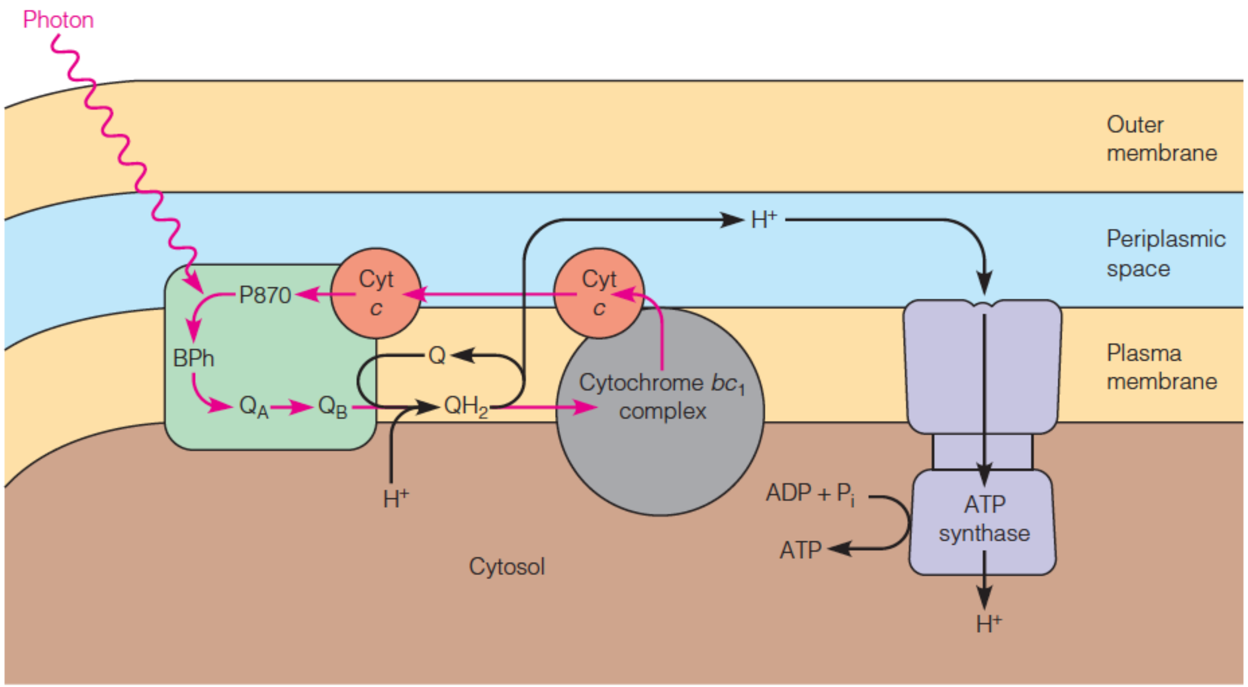
"for the determination of the three-dimensional structure of a photosynthetic reaction center".

The Light Reactions

Postulated mechanism for purple bacterial photosynthesis:

•This process somewhat resembles the photosystem II reactions in the thylakoid, with a reaction center and a membrane-bound cytochrome complex.

•However, there is only one kind of reaction center, water is not split, and electron flow is cyclic.



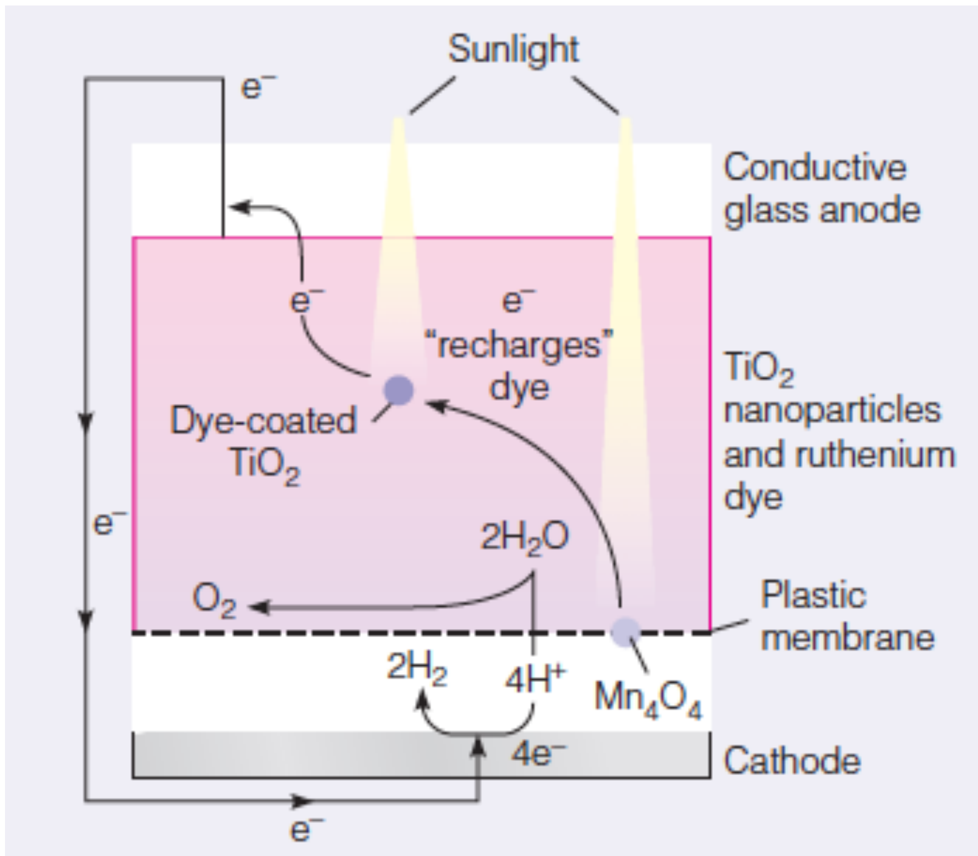
BPh: bacteriophenophytin

Q_A & Q_B: Quinones

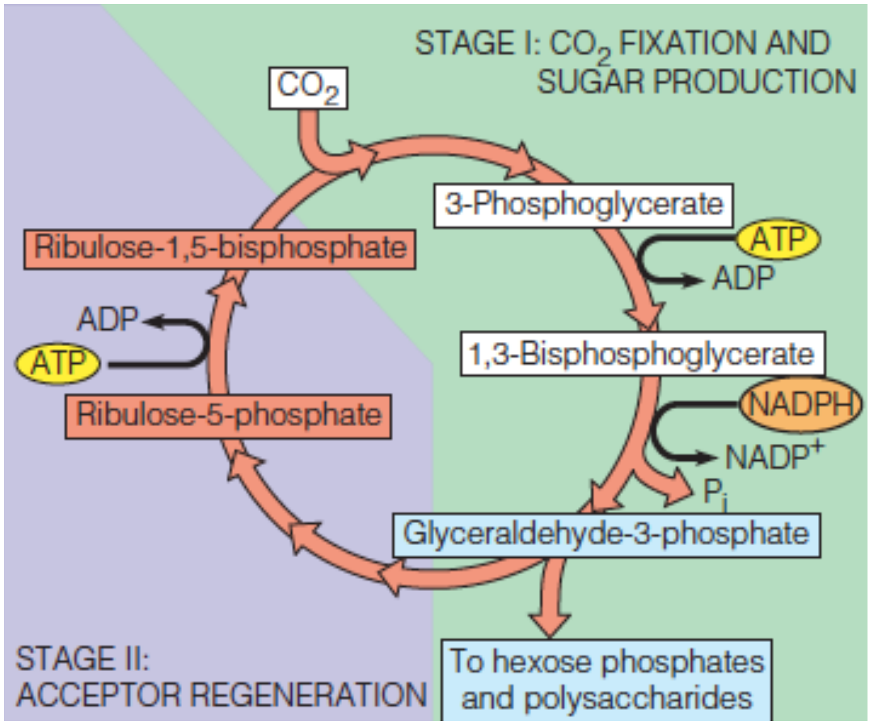
The Light Reactions

Artificial photosynthesis:

•In this solar cell, absorbed light energy drives the splitting of water into oxygen and protons, forming H_2 fuel.



The Dark Reactions: The Calvin Cycle



Schematic view of the Calvin cycle:

Stage I - **CO_2 is fixed** and **glyceraldehyde-3-phosphate (GAP)** is produced.

- Part of this GAP is used to make hexose phosphates and eventually polysaccharides.

Stage II - another fraction of the GAP is used to generate the acceptor molecule, **ribulose-1,5-BP**.

The Dark Reactions: The Calvin Cycle

Stage I: Carbon Dioxide Fixation and Sugar Production

•CO_2 is incorporated into glyceraldehyde-3-phosphate (GAP).

•The acceptor molecule for CO_2 is ***ribulose-1,5-bisphosphate*** **(*RuBP*).**

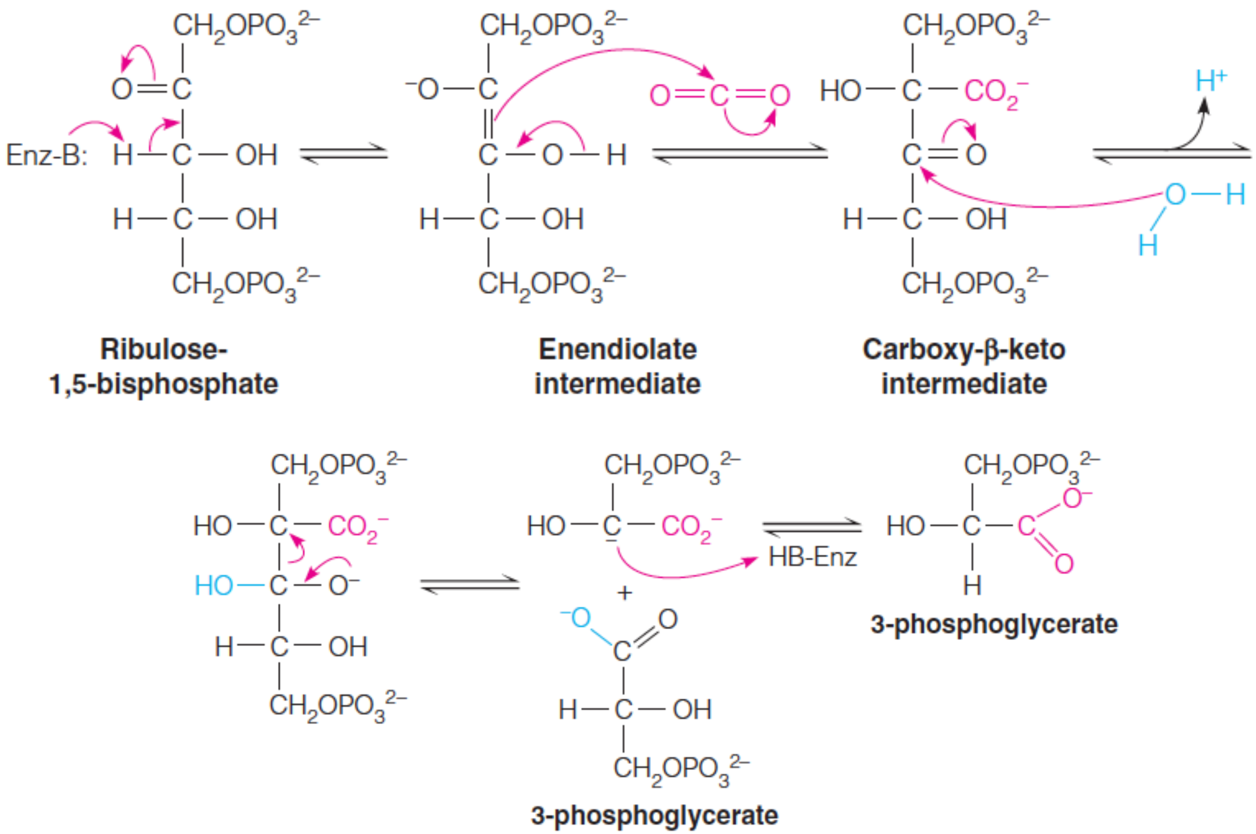
•CO_2 from the air diffuses into the stroma of the chloroplast, where it is added at the carbonyl carbon of RuBP.

•The reaction is catalyzed by the enzyme ***ribulose-1,5-bisphosphate carboxylase,*** also known as ribulose-1,5-bisphosphate carboxylase/ oxygenase (or ***rubisco***).

•This enzyme is one of the most important in the biosphere and certainly the most abundant. It makes up about 15% of all chloroplast proteins, and there are an estimated 40 million tons of it in the world—about 20 pounds for every living person.

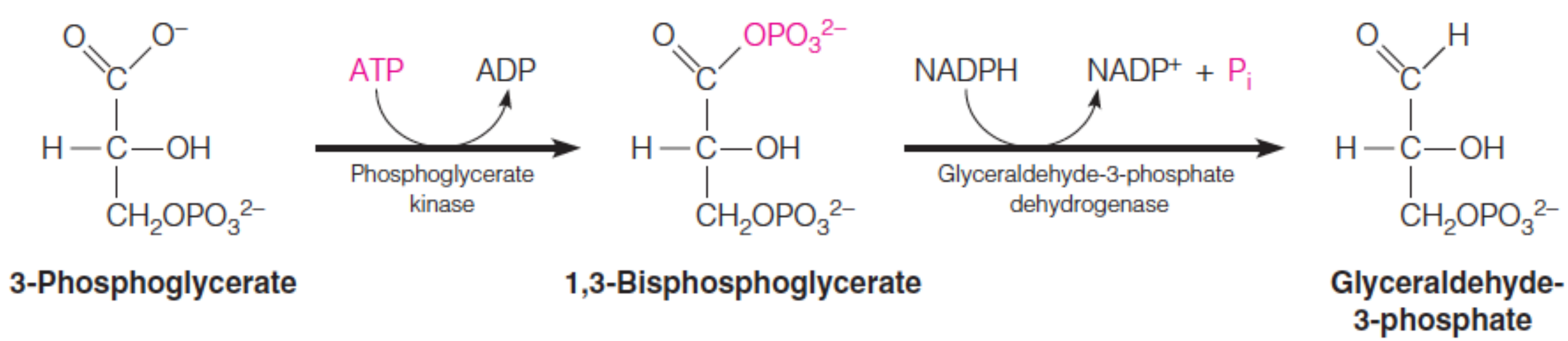
The Dark Reactions: The Calvin Cycle

- The carboxylase reaction is a complex series of steps in which the actual acceptor is proposed to be the five-carbon enediolate intermediate:

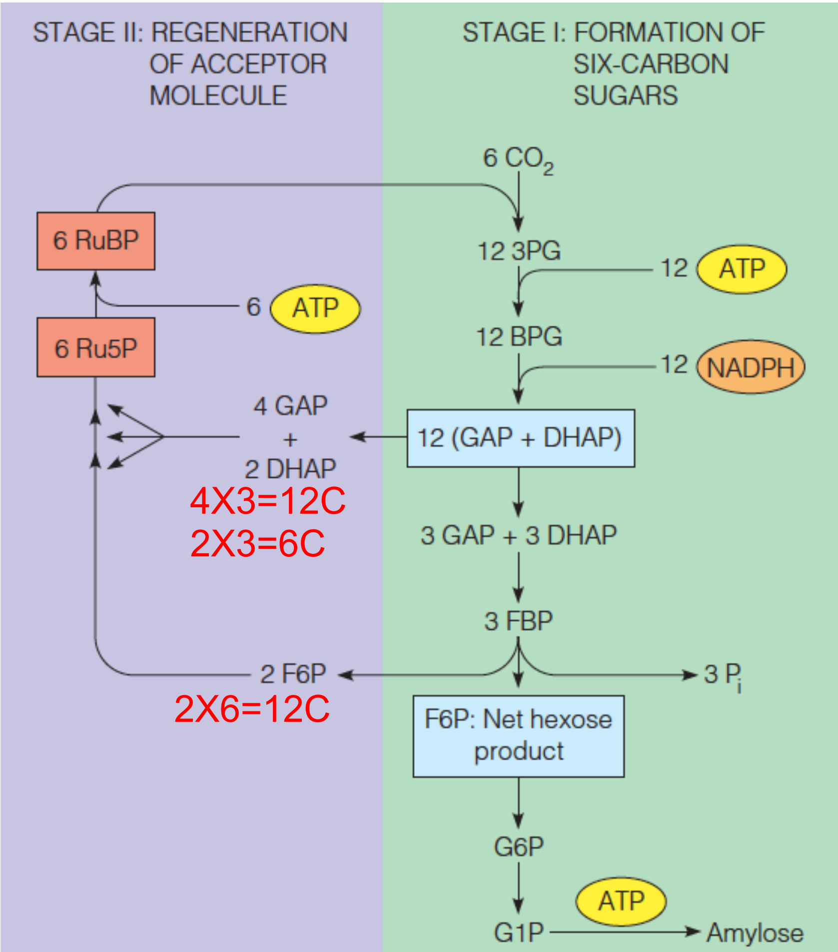


The Dark Reactions: The Calvin Cycle

- Each molecule of 3PG is phosphorylated by ATP, in a reaction catalyzed by ***phosphoglycerate kinase***.
- The 1,3-bisphosphoglycerate so produced is then reduced to glyceraldehyde-3-phosphate (GAP), with accompanying loss of one phosphate.
- The reducing agent is NADPH, produced in the light reaction, and the reaction is catalyzed by the enzyme ***glyceraldehyde-3-phosphate dehydrogenase***:



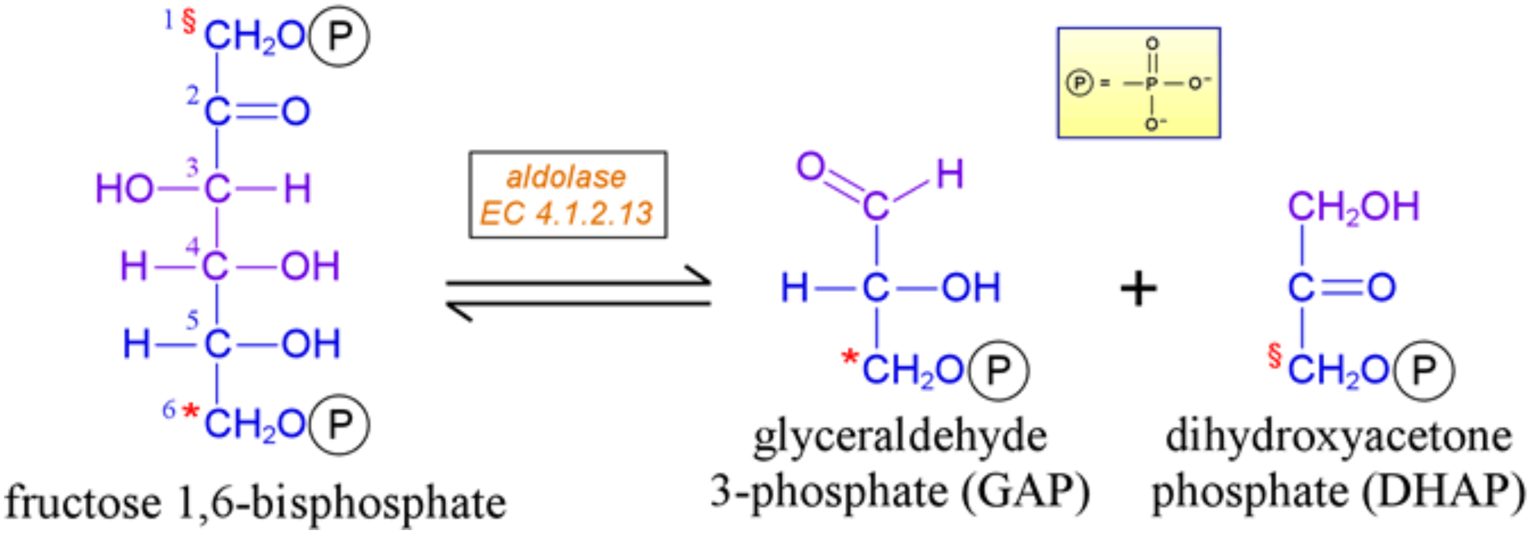
The Dark Reactions: The Calvin Cycle

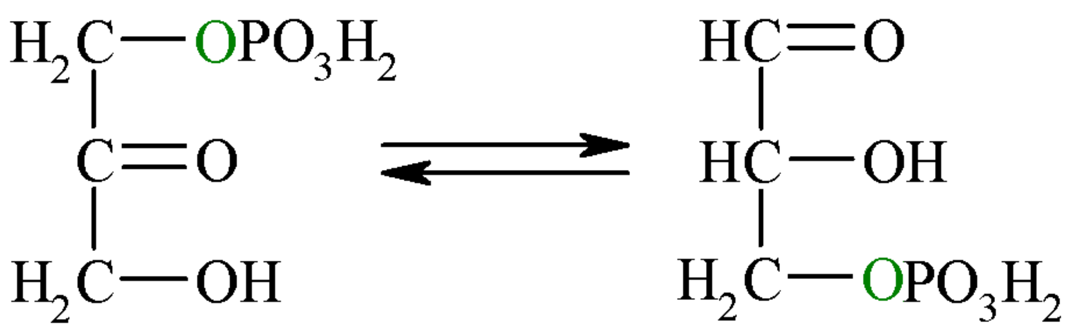


Stoichiometry of the Calvin cycle:

- In six turns of the Calvin cycle, 6 CO_2 molecules will have entered and bound to 6 RuBP to yield 12 GAP.
- Because GAP is in isomeric equilibrium with DHAP, the 12 GAP may be considered an interconvertible stock of 12 (GAP-DHAP).
- Of these, 6 are used to make 3 FBP, of which *one* constitutes the net hexose product of the 6 turns.
- The other 2 FBPs are used, together with the 6 remaining molecules of (GAP-DHAP), to form 6 Ru5P, which are then phosphorylated to regenerate the required 6 RuBP.

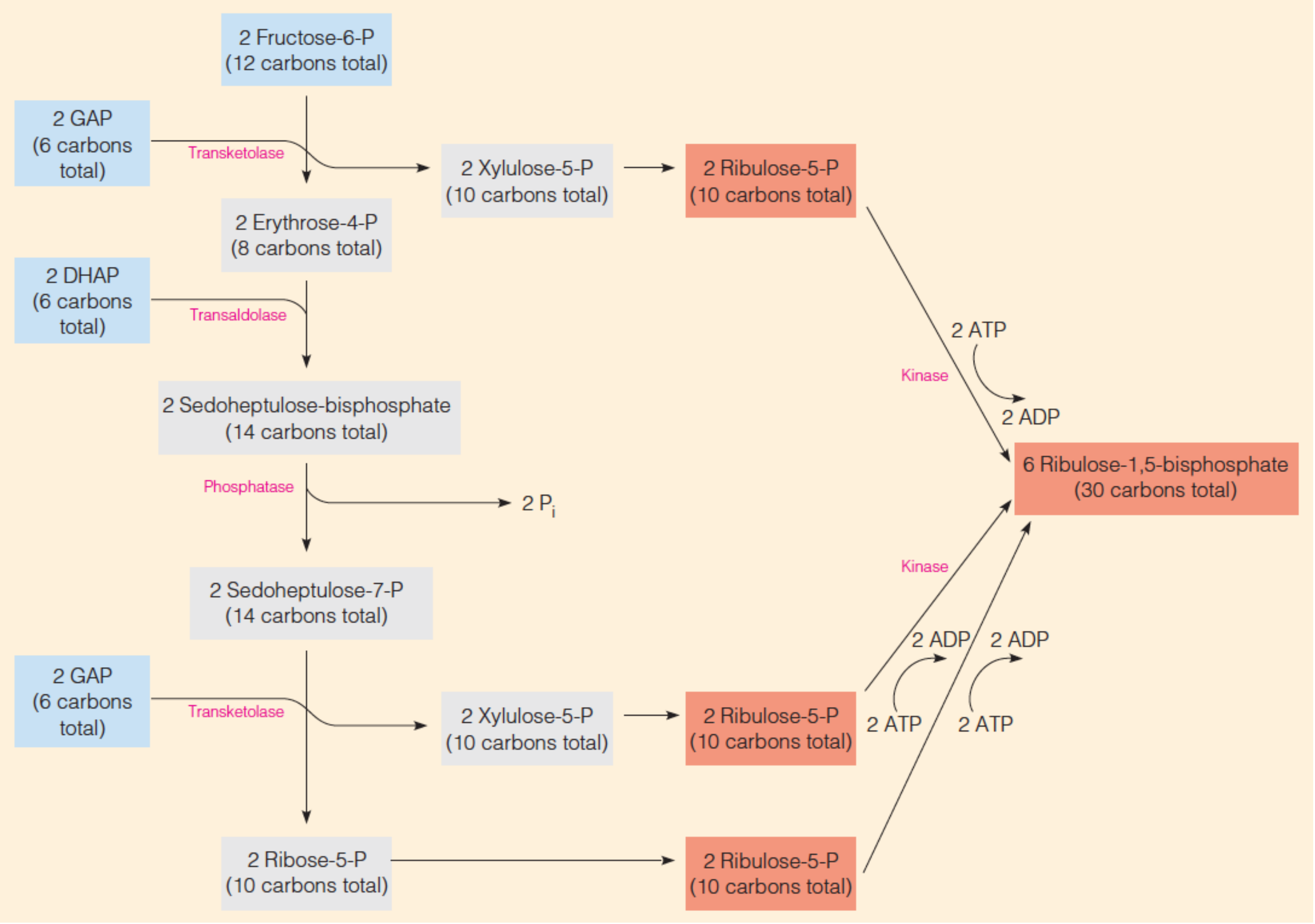
The Dark Reactions: The Calvin Cycle





The Dark Reactions: The Calvin Cycle

Regeneration phase of the Calvin cycle:



* Note the similarity of this pathway to parts of the pentose phosphate pathway running in reverse

Stage II: Regeneration of the Acceptor

•The reactions we have considered to this point can account for the introduction of one carbon into one molecule of hexose, with subsequent **formation of oligosaccharides or polysaccharides.**

•To complete the Calvin cycle, it is necessary to **regenerate enough RuBP to keep the cycle going**.

•This means we will need to regenerate 6 moles of RuBP for every 6 moles of CO_2 taken up.

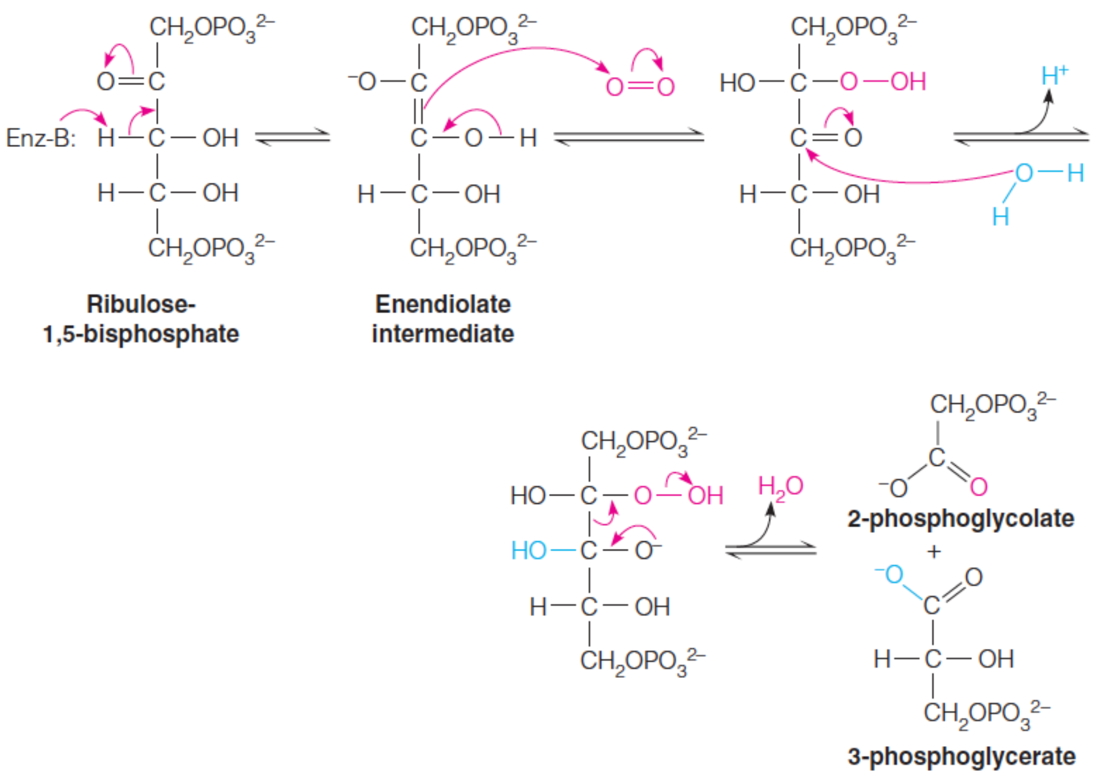
•This is accomplished by the set of reactions, which constitute the ***regenerative phase*** of the cycle.

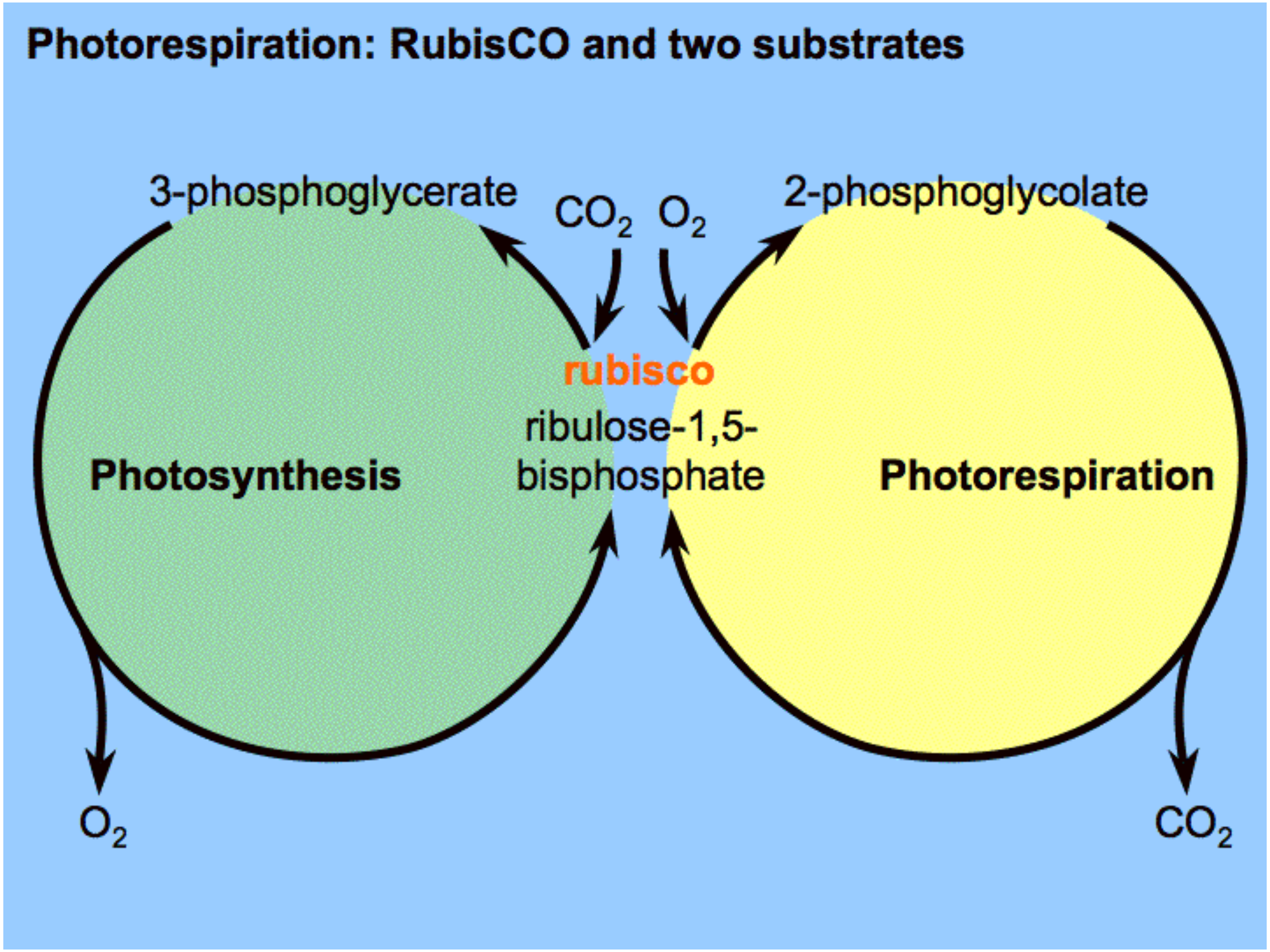
•Note that the ***input molecules*** in this somewhat complex reaction pathway are as follows:

> Two molecules of DHAP and four molecules of GAP, from the six GAP that were diverted to the regeneration pathway.
>
> Two of the three molecules of fructose-6-phosphate (F6P) that were produced from the remaining three GAP and three DHAP.

Photorespiration

- Ribulose bisphosphate carboxylase/oxygenase (**rubisco**) is a peculiar enzyme.
- Under normal environmental conditions, it can behave as an ***oxygenase*** as well as a ***carboxylase***.
- In the oxygenase reaction, it is proposed that the enediolate intermediate nucleophilically attacks O_2 instead of CO_2.




Photorespiration: RubisCO and two substrates
3-phosphoglycerate
CO_2
O_2
2-phosphoglycolate
rubisco
ribulose-1,5-
bisphosphate
Photosynthesis
Photorespiration
O_2
CO_2

Photorespiration

Photorespiration的反應是在葉肉細胞的過氧化體(peroxisomes)中進行。

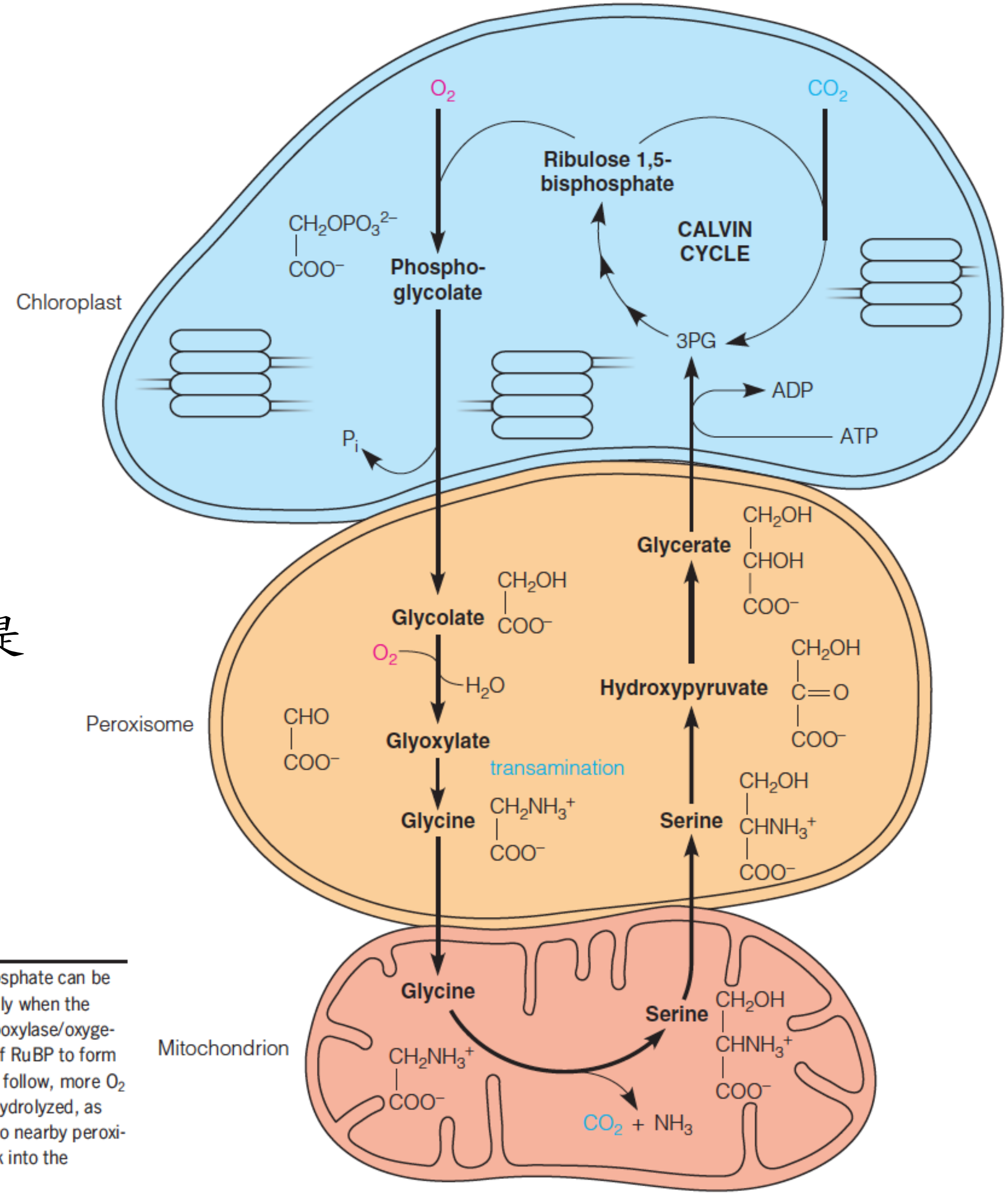
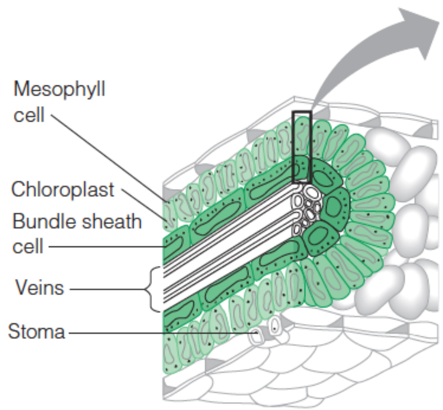


FIGURE 16.28

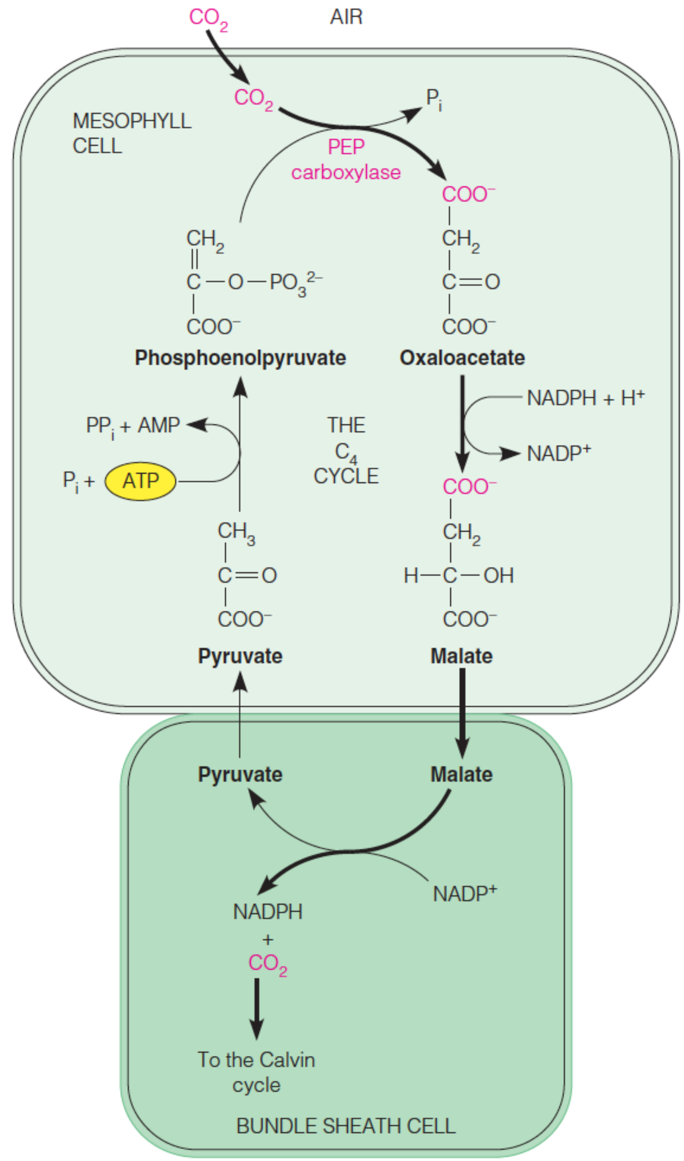
Photorespiration. Ribulose-1,5-bisphosphate can be diverted from the Calvin cycle, especially when the concentration of CO_2 is low. RuBP carboxylase/oxygenase (rubisco) catalyzes the oxidation of RuBP to form phosphoglycolate. In the reactions that follow, more O_2 is used, CO_2 is generated, and ATP is hydrolyzed, as metabolites pass from the chloroplast to nearby peroxisomes and mitochondria and then back into the chloroplast.

C_4 Cycle

玉米或熱帶植物有一種四碳的化合物途徑，稱為C_4 cycle，首先發生於葉肉細胞(mesophyll cells)內。



(a)



(b)

FIGURE 16.29

Reactions of the C_4 cycle. (a) In C_4 plants the mesophyll cells (light green) trap CO_2 in C_4 intermediates. The C_4 compounds are then delivered to the bundle sheath cells (dark green), where most of the Calvin cycle photosynthesis takes place (C_3). **(b)** CO_2 is transported from mesophyll cells to the bundle sheath cells by coupling it to phosphoenolpyruvate, forming oxaloacetate. Oxaloacetate is then reduced to malate, which is passed to the bundle sheath cells and decarboxylated. The pyruvate product is returned to the mesophyll cells, where it is phosphorylated to regenerate phosphoenolpyruvate.

PEP:phosphoenolpyruvate

Evolution of Photosynthesis

Proposed evolution of oxygenic photosynthesis: