Chapter 15 - Photosynthesis

- **Photosynthesis**: a process that converts atmospheric CO_2 and H_2O to carbohydrates
- Solar energy is captured in chemical form as **ATP** and **NADPH**
- ATP and NADPH are used to convert CO_2 to hexose phosphates
- **Phototrophs**: photosynthetic organisms (some bacteria, algae, higher plants)

15.1 Photosynthesis Consists of Two Major Processes

- Net reaction of photosynthesis is:

$$CO_2 + H_2O \longrightarrow (CH_2O) + O_2$$

- The oxidation of water is driven by solar energy
- Electrons from this oxidation pass through an electron-transport chain (which resembles the mitochondrial ETC)

The light reactions

Light reactions (light-dependent reactions)

- H^+ derived from H_2O is used in the chemiosmotic synthesis of ATP
- Hydride ion ($H:^-$) from H_2O reduces $NADP^+$ to NADPH
- Release of O_2 from splitting $2H_2O$ molecules

The dark reactions

Dark reactions (light-independent or carbon-fixation reactions)

- Reduction of gaseous CO_2 to carbohydrate
- Requires energy of NADPH and ATP

Sum of light and dark reactions

- Both processes can occur simultaneously

In the presence of light:

$$H_2O + ADP + P_i + NADPH \longrightarrow O_2 + ATP + NADPH + H^+$$

Reactions which can occur in the dark:

$$\underline{CO_2 + ATP + NADPH + H^+ \longrightarrow (CH_2O) + ADP + P_i + NADP^+}$$

$$\text{Sum: } CO_2 + H_2O \longrightarrow (CH_2O) + O_2$$

15.2 The Chloroplast

- **Chloroplasts**: specialized organelles in algae and plants where photosynthesis occurs
- **Thylakoid membrane**: highly folded continuous membrane network, site of the light-dependent reactions that produce NADPH and ATP

Chloroplast (continued)

- **Stroma**: aqueous matrix of the chloroplast which surrounds the thylakoid membrane
- **Lumen**: aqueous space within the thylakoid membrane

Fig 15.1 (a) Structure of the chloroplast

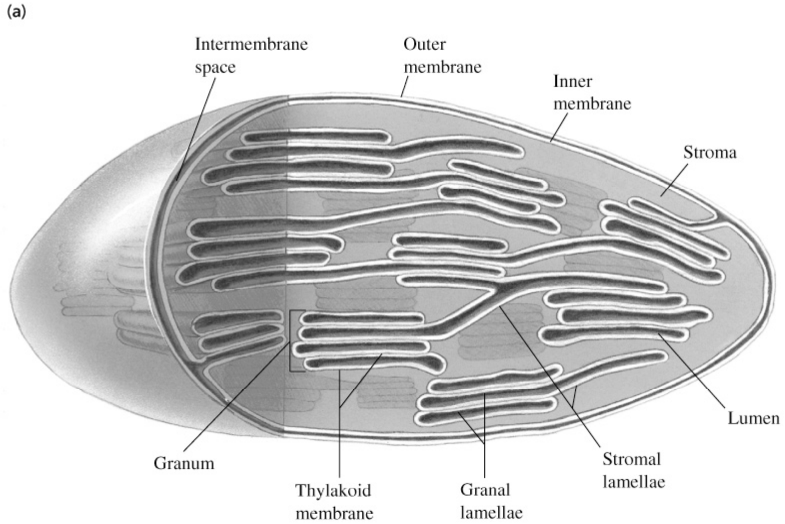
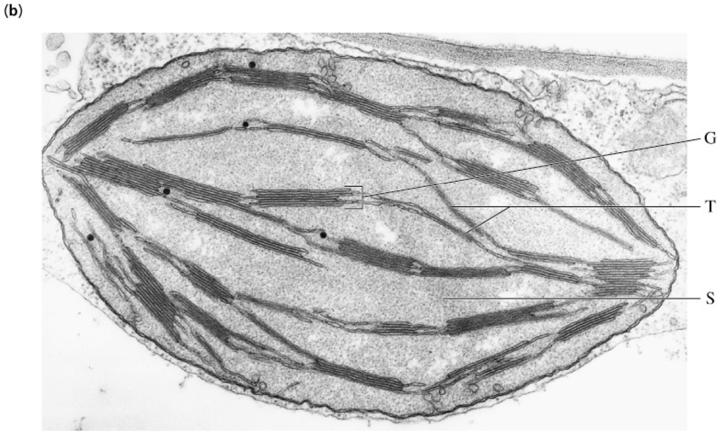


Fig 15.1 (b)

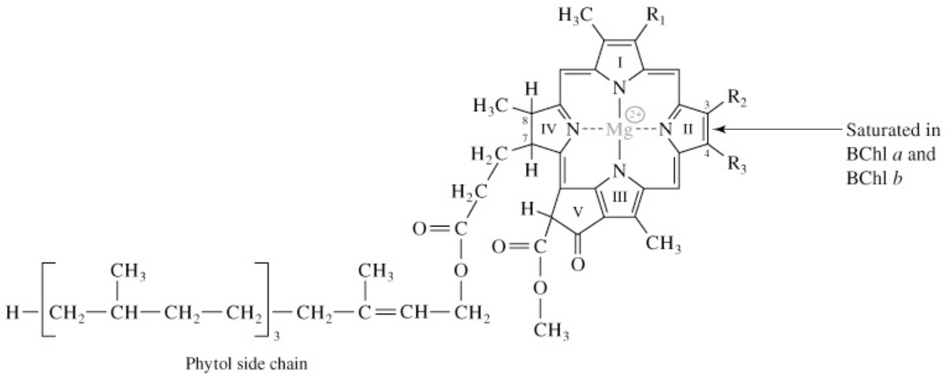


15.3 Chlorophyll and Other Pigments Capture Light

A. Light-Capturing Pigments

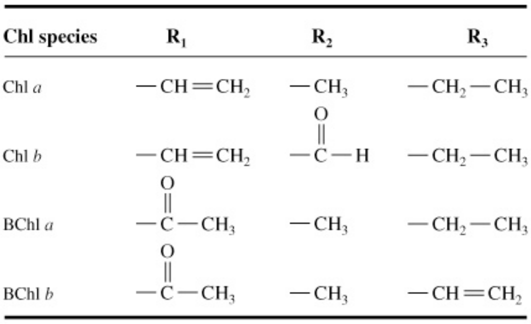
- **Chlorophylls** - usually most abundant and most important pigments in light harvesting
- Contain tetrapyrrole ring (chlorin) similar to heme, but contains Mg^{2+}
- Chlorophylls *a* (Chl *a*) and *b* (Chl *b*) in plants
- Bacteriochlorophylls *a* (BChl *a*) and *b* (BChl b) are major pigments in bacteria

Fig 15.2 Structures of Chlorophyll and bacteriochlorophyll



(Chlorophyll species, R_1, R_2, R_3 table next slide)

Fig 15.2 (continued)



Chl species	R_1	R_2	R_3
Chl *a*	$-\mathrm{CH}=\mathrm{CH}_2$	$-\mathrm{CH}_3$	$-\mathrm{CH}_2-\mathrm{CH}_3$
Chl *b*	$-\mathrm{CH}=\mathrm{CH}_2$	$-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{H}$	$-\mathrm{CH}_2-\mathrm{CH}_3$
BChl *a*	$-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{CH}_3$	$-\mathrm{CH}_3$	$-\mathrm{CH}_2-\mathrm{CH}_3$
BChl *b*	$-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{CH}_3$	$-\mathrm{CH}_3$	$-\mathrm{CH}=\mathrm{CH}_2$

Fig 15.3 Absorption spectra of photosynthetic pigments

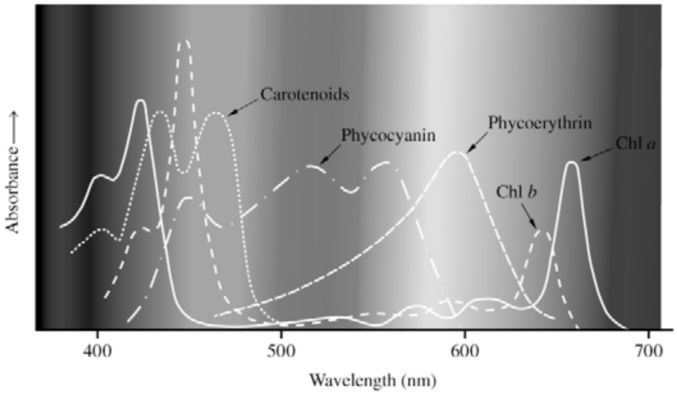
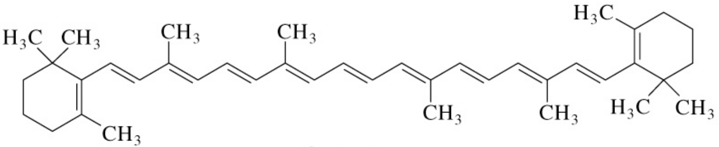
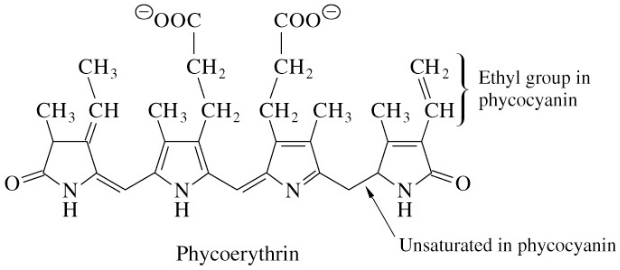


Fig 15.4 Accessory pigments



β-Carotene



Phycoerythrin

B. Photosystems

Photosystems I (PSI) and II (PSII):

- Functional units of photosynthesis in plants
- Contain many proteins and pigments embedded in the thylakoid membrane
- These two electron-transfer complexes operate in series, connected by cytochrome *bf* complex
- Electrons are conducted from H_2O to $NADP^+$

Table 15.1

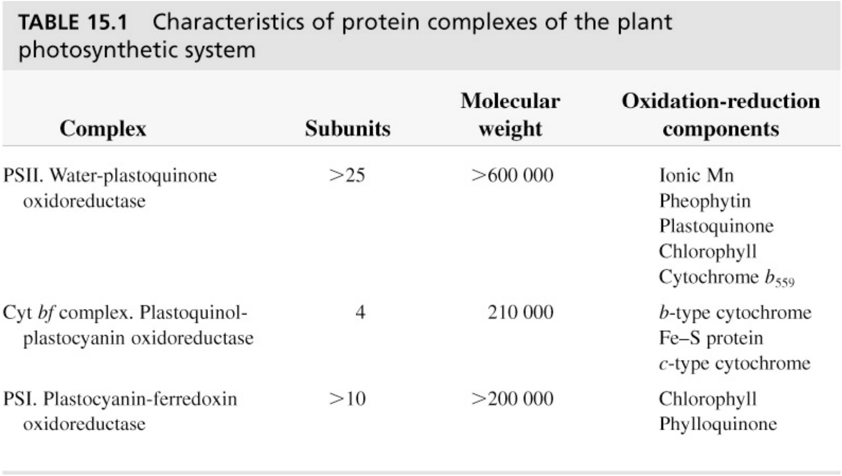


TABLE 15.1 Characteristics of protein complexes of the plant photosynthetic system

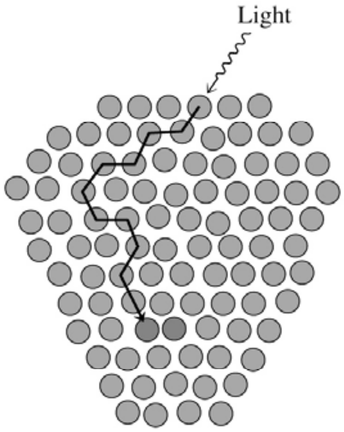
Complex	Subunits	Molecular weight	Oxidation-reduction components
PSII. Water-plastoquinone oxidoreductase	>25	>600 000	Ionic Mn Pheophytin Plastoquinone Chlorophyll Cytochrome b_{559}
Cyt *bf* complex. Plastoquinol-plastocyanin oxidoreductase	4	210 000	*b*-type cytochrome Fe–S protein *c*-type cytochrome
PSI. Plastocyanin-ferredoxin oxidoreductase	>10	>200 000	Chlorophyll Phylloquinone

Reaction centers of the photosystems

- PSI and PSII each contain a **reaction center** (site of the photochemical reaction)
- **Special pair**: two chlorophylls in each reaction center that are energized by light
- In PSI special pair is: **P700** (absorb light maximally at 700nm)
- In PSII the special pair is: **P680** (absorb light maximally at 680nm)

Fig 15.5 Light energy transfer from antenna pigments to special-pair chlorophylls

- Light can be captured by antenna pigments (green) and transferred among themselves until reaching the special-pair chlorophyll molecules (red) in the reaction center of a photosystem



15.4 Electron Transport in Photosynthesis

- Fig 15.6 Distribution of photosynthetic components

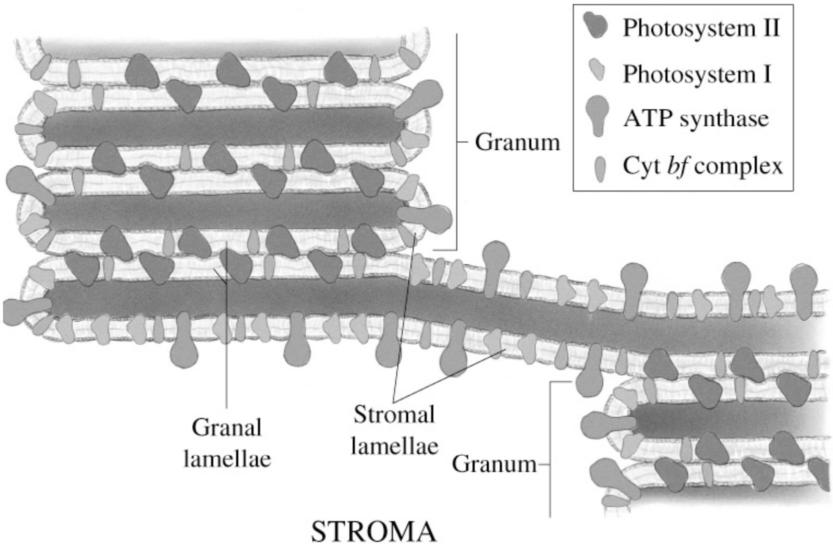
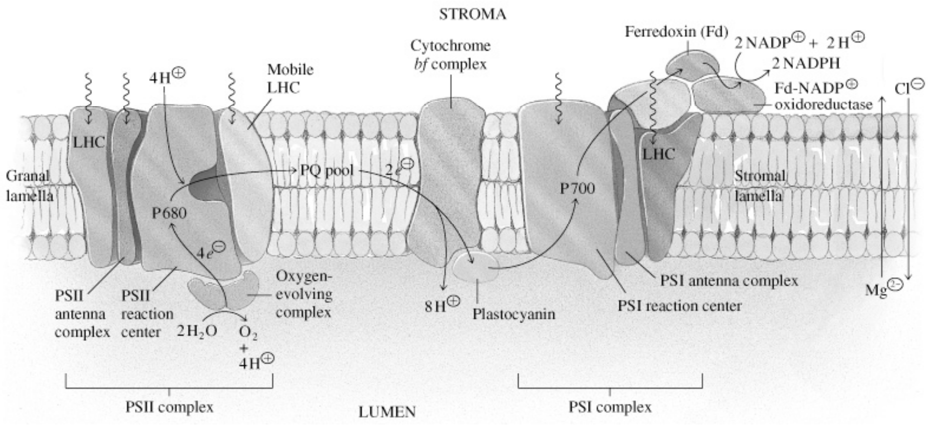


Fig 15.7 Light capture, electron transport and proton translocation in photosynthesis

- Light is captured by antenna complexes
- Light energy drives the transport of electrons from PSII through cytochrome *bf* complex to PSI and ferridoxin and then to NADPH
- The proton gradient generated is used to drive ATP production
- For 2 H_2O oxidized to O_2, 2 $NADP^+$ are reduced to 2 NADPH

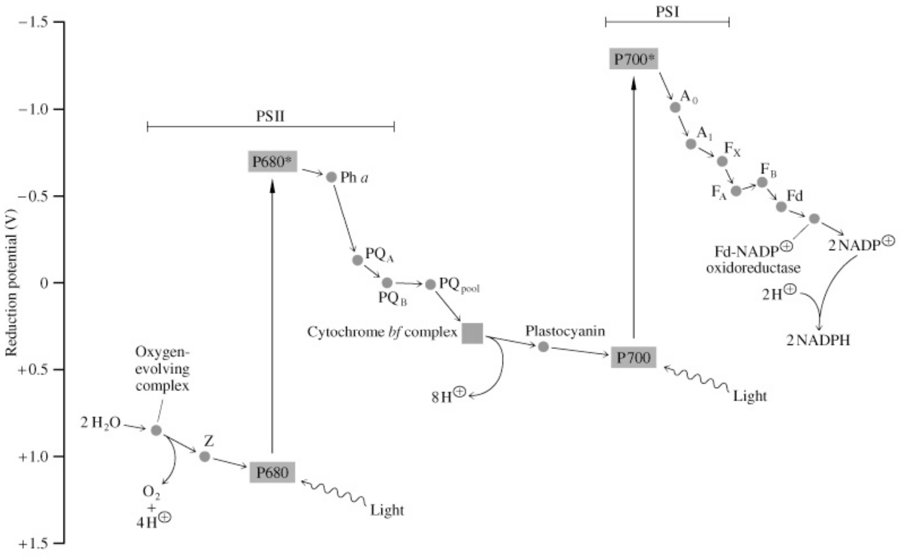
Figure 15.7 Diagram of photosynthesis membrane systems



The Z-scheme

- **Z-scheme**: path of electron flow and reduction potentials of the components in photosynthesis
- Absorption of light energy converts P680 and P700 (poor reducing agents) to excited molecules (good reducing agents)
- Light energy drives the electron flow uphill
- $NADP^+$ is ultimately reduced to NADPH

Fig. 15.8 Diagram of the Z-scheme



A. Electron Transport From PSII through Cytochrome *bf*

- Electrons for transport are obtained from the oxidation of water
- Catalyzed by the oxygen-evolving complex (water-splitting enzyme) of PSII

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

Fig 15.9 Reduction, excitation and oxidation of P680

- P680 special-pair pigment of PSII
- $P680^+$ is reduced by e^- derived from oxidation of H_2O
- Light energizes to P680*, increasing its reducing power

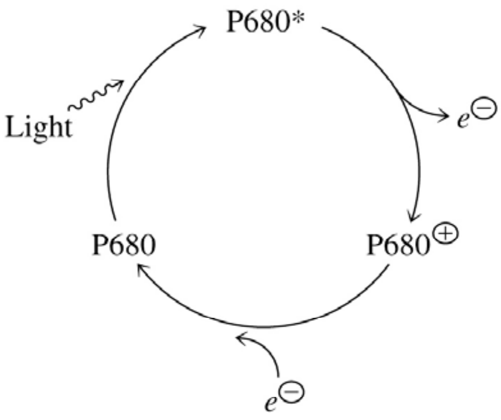


Fig 15.10

- Reduction of plastoquinone to plastoquinol

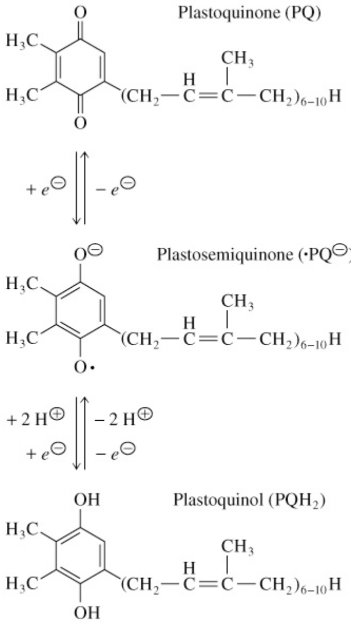
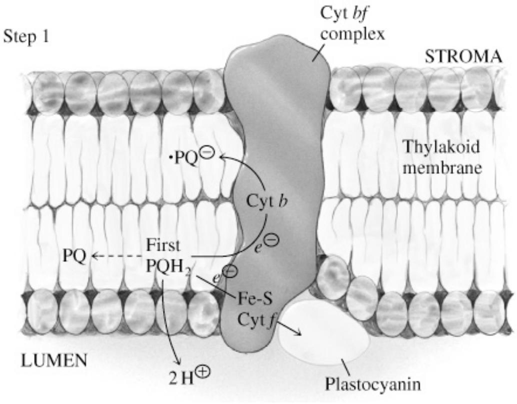
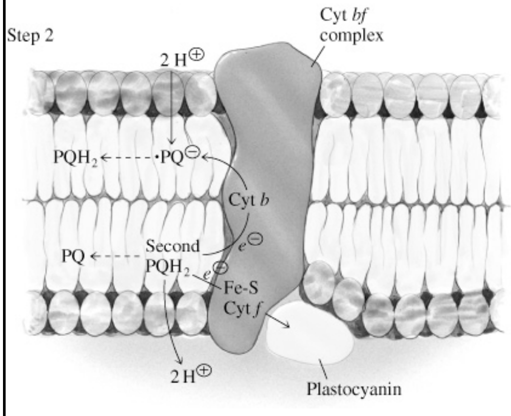


Fig 15.11 Photosynthetic Q cycle (Step 1)



In the first step, PQH_2 is oxidized at a site adjacent to cytochrome *f*, and the two protons from oxidized PQ are released into the lumen. One of the electrons from PQH_2 oxidation is funneled through cytochrome *f* and reduces plastocyanin. The second electron converts a molecule of PQ to $\cdot PQ^{\ominus}$ at a site away from the PQH_2 oxidation site.

Photosynthetic Q cycle (Step 2)



In the second step, a second molecule of PQH_2 is oxidized. Once again, two protons are released into the lumen, one electron reduces plastocyanin, and the other electron (plus two stromal protons) converts the $\cdot PQ^{\ominus}$ from Step 1 to PQH_2. The fully reduced PQH_2 is then released into the plastoquinone pool. Since the cytochrome *bf* complex can accept only electrons and not protons from PQH_2, Q cycling by plastoquinone and the cytochrome *bf* complex contributes to the proton concentration gradient. Each complete Q cycle results in the net oxidation of one molecule of PQH_2 to one molecule of PQ and the translocation of four protons to the lumen.

B. PSI and Beyond

- Reduced P700 is excited to P700* (the strongest reducing agent in the chain) by light absorbed by the PSI antenna complex
- P700* donates an electron through a series of acceptors to ferredoxin (Fd)
- Reduction of $NADP^+$ ($E^{o'} = -0.32$ V) by Fd ($E^{o'} = -0.43$ V) is catalyzed by ferredoxin-$NADP^+$ oxidoreductase on the stromal membrane side

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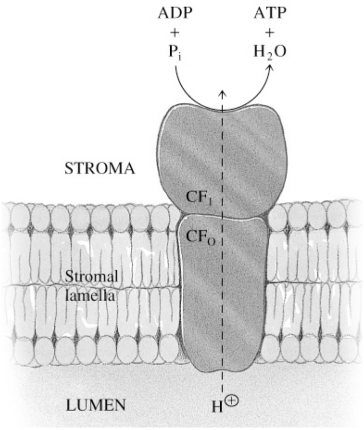
15.5 Photophosphorylation and Cyclic Electron Flow

- **Photophosphorylation**: synthesis of ATP which is dependant upon light energy
- **Chloroplast ATP synthase** consists of two major particles: **CF_o** and **CF_1**
- CF_o spans the membrane, forms a pore for H^+
- CF_1 protrudes into the stroma and catalyzes ATP synthesis from ADP and P_i

Fig 15.12 Orientation of chloroplast ATP Synthase

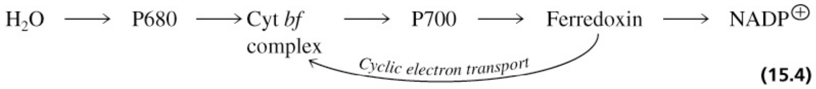


Cyclic photophosphorylation

- For $4e^-$ transferred to 2 NADPH, 2 ATP are produced from the proton gradient
- However, for each CO_2 reduced to (CH_2O) in carbohydrate synthesis, 2 NADPH and 3 ATP are required
- Cyclic electron transport yields ATP but not NADPH, thus balancing the need for 3 ATP for every 2 NADPH

Cyclic electron flow pathway

- Ferridoxin donates e$^-$ not to NADP$^{+,}$ but back to the PQ pool via a specialized cytochrome
- Cyclic flow increases the protonmotive force and increases ATP production, but no NADP$^+$ is produced



(15.4)

15.6 The Dark Reactions

- Reductive conversion of CO_2 into carbohydrates
- Process is powered by ATP and NADPH (formed during the light reactions of photosynthesis)

Dark Reactions (continued)

- Occur in chloroplast stroma by the **reductive pentose phosphate cycle** (**RPP cycle**):

  (1) Fixation of atmospheric CO_2

  (2) Reduction of CO_2 to carbohydrate

  (3) Regeneration of the molecule that accepts CO_2

15.7 Ribulose 1,5-*Bis*phosphate Carboxylase-Oxygenase (Rubisco)

- Gaseous CO_2 and the 5-carbon sugar ribulose 1,5-*bis*phosphate form two molecules of 3-phosphoglycerate
- Reaction is metabolically irreversible
- Rubisco makes up about 50% of the soluble protein in plant leaves, and is one of the most abundant enzymes in nature

Fig 15.13 Stereo view of Rubisco

- L_8S_8 structure of spinach Rubisco

(a) top, (b) side views

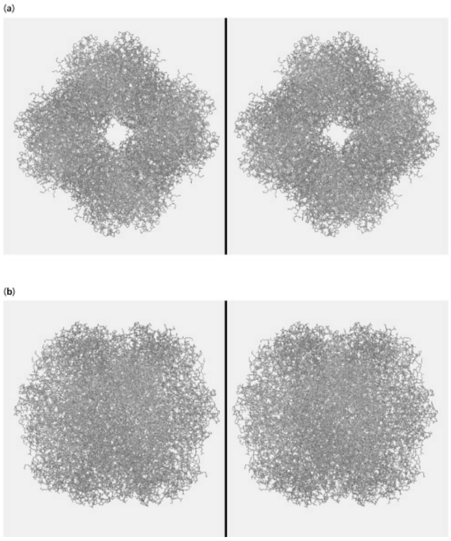


Fig 15.14 Mechanism of Rubisco

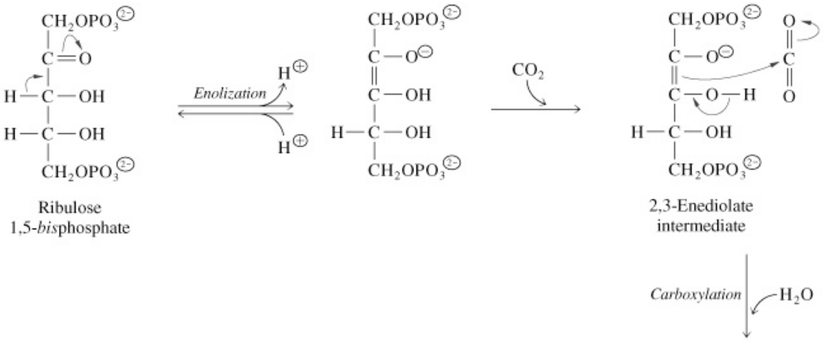
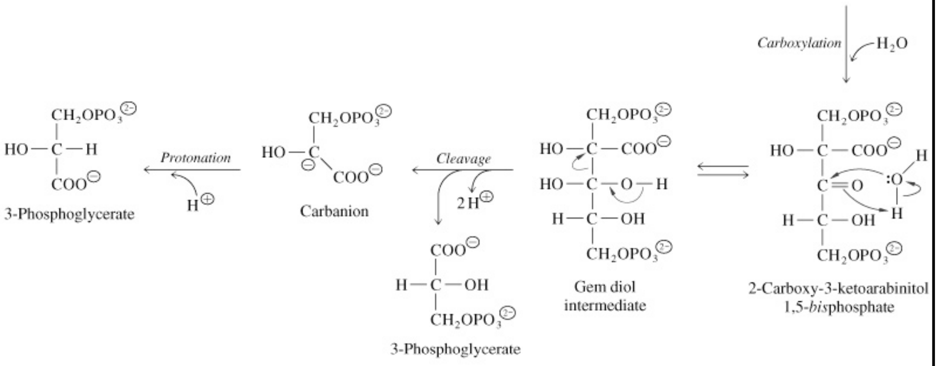


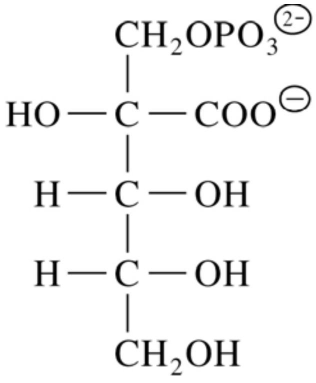
Fig 15.14 (continued)



Active and inactive forms of Rubisco

- Rubisco cycles between an active form (in the light) and an inactive form (in the dark)
- Activation requires light, CO_2, Mg^{2+} and correct stromal pH
- At night 2-carboxyarabinitol 1-phosphate (synthesized in plants) inhibits Rubisco

Fig 15.15 2-Carboxyarabinitol 1-phosphate



15.8 The RPP Cycle

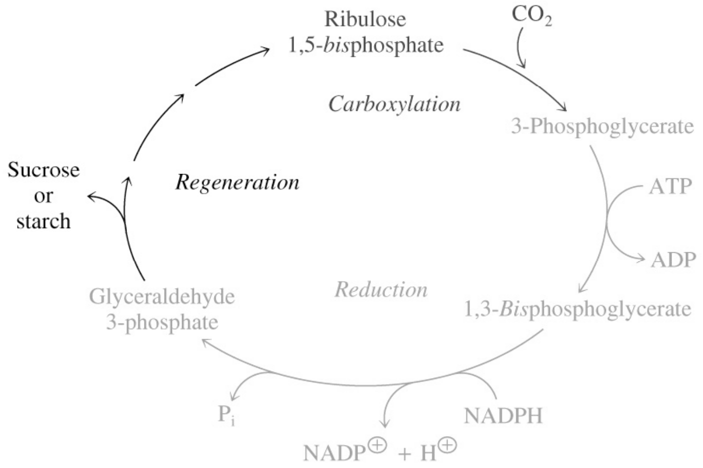
- The RPP cycle has 3 stages:

  (1) Carboxylation (catalyzed by Rubisco)

  (2) Reduction (3-phosphoglycerate converted to glyceraldehyde 3-phosphate (G3P))

  (3) Regeneration (most of the G3P is converted to ribulose 1,5-*bis*phosphate)

Fig 15.16 Summary of the RPP cycle



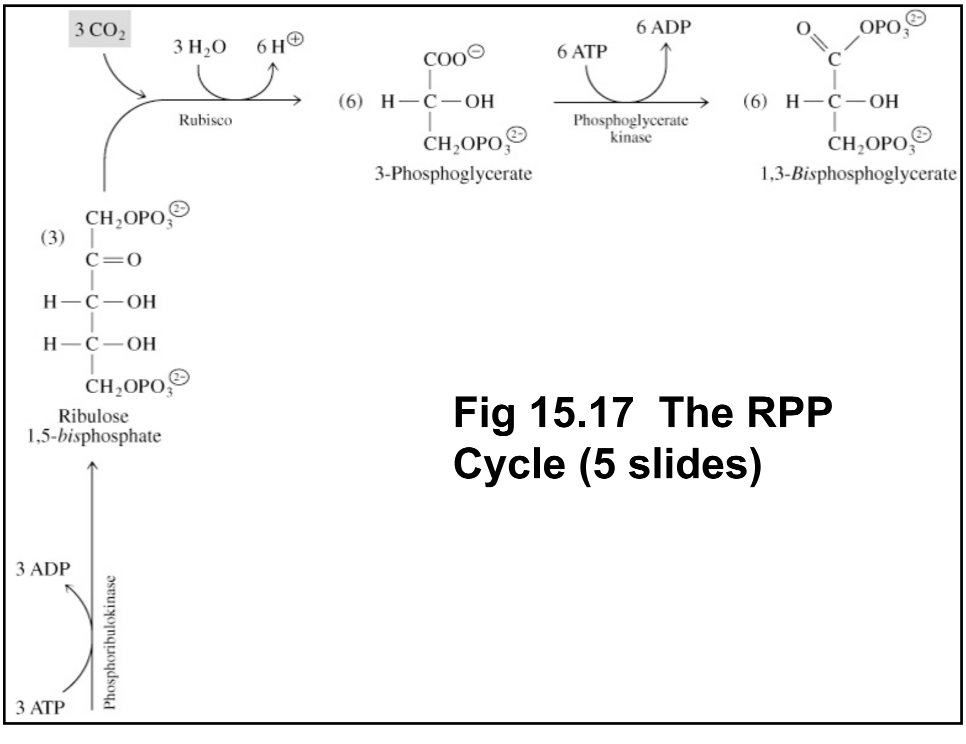
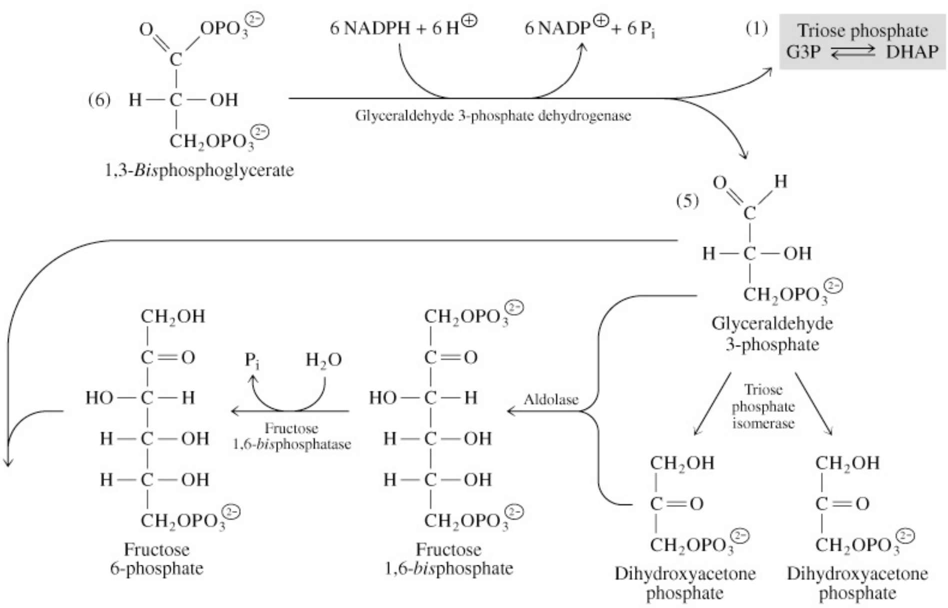
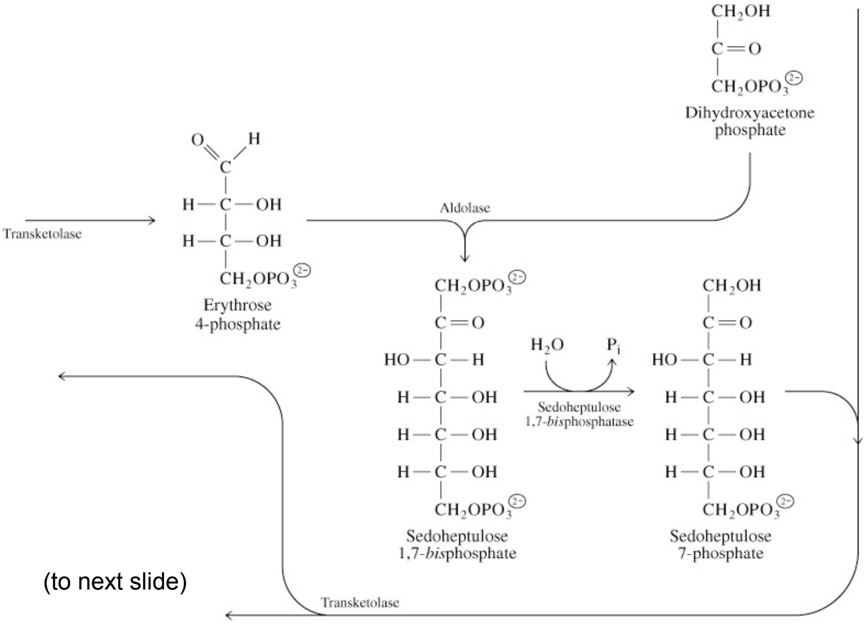


Fig 15.17 The RPP Cycle (5 slides)





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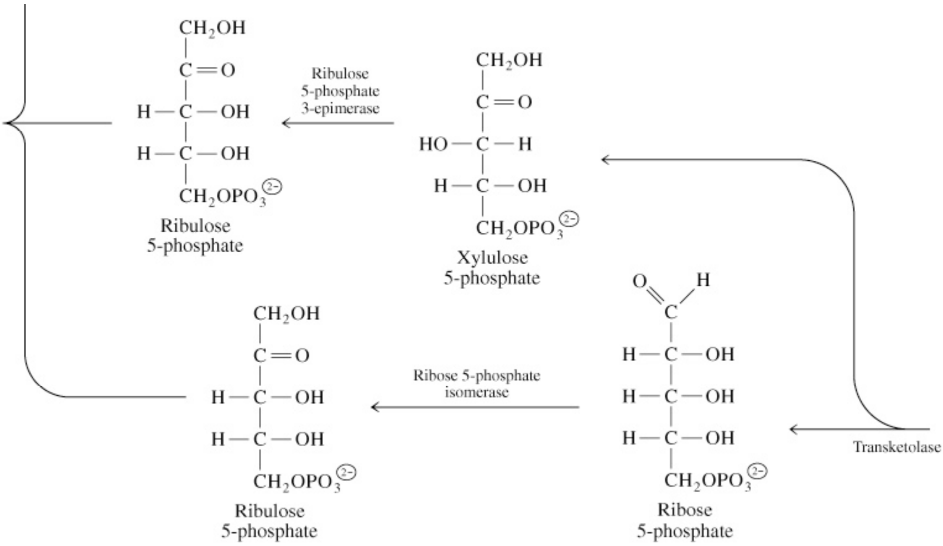
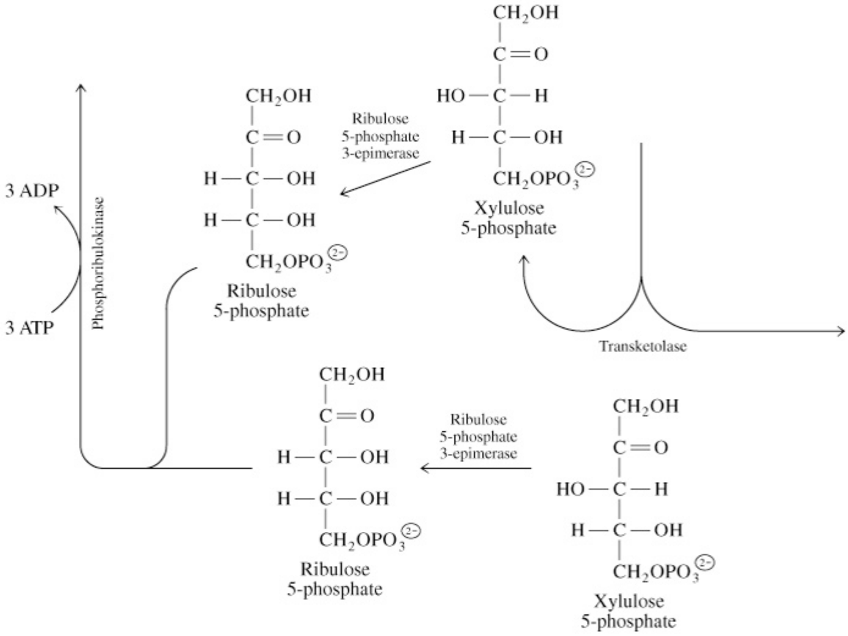

Ribulose 5-phosphate
Ribulose 5-phosphate 3-epimerase
Xylulose 5-phosphate
Ribulose 5-phosphate
Ribose 5-phosphate isomerase
Ribose 5-phosphate
Transketolase


Xylulose 5-phosphate
Ribulose 5-phosphate 3-epimerase
Ribulose 5-phosphate
3 ADP
3 ATP
Phosphoribulokinase
Transketolase
Ribulose 5-phosphate
Ribulose 5-phosphate 3-epimerase
Xylulose 5-phosphate

Net equation for the RPP cycle

$3\ CO_2 + 9\ ATP + 6\ NADPH + 5\ H_2O \longrightarrow$

$9\ ADP + 8\ P_i + 6\ NADP^+ +$ *Triose phosphate

*(G3P or DHAP)

Regulation of the RPP cycle

Night

- Oxidation of surface-exposed -SH groups on some RPP enzymes inactivates them, preventing CO_2 assimilation
- Catabolism of starch via glycolysis and the citric acid cycle provides energy

Regulation of the RPP cycle (daytime)

Daytime

- Thioredoxin (protein coenzyme) is reduced by photosynthetic electron transport
- Reduced thioredoxin reduces disulfides to -SH, thereby activating some RPP enzymes
- Stromal Mg^{2+} and pH increase as protons are translocated into the lumen, thereby activating fructose 1,6-*bis*phosphate and sedoheptulose 1,7-*bis*phosphatase

15.9 Oxygenation of Ribulose 1,5-Bisphosphate

- Rubisco can also use O_2 to catalyze an oxygenation reaction ("**photorespiration**"), which competes with the carboxylation reaction
- Normally carboxylation is 3-4 times greater than oxygenation
- Photorespiration consumes NADH, ATP and yields products including glyoxylate, serine, glycine and CO_2

Fig 15.18 Oxygenation of ribulose 1,5-*bis*phosphate catalyzed by Rubisco