Chapter 15 - Photosynthesis

• **Photosynthesis**: a process that converts atmospheric CO₂ and H₂O to carbohydrates

• Solar energy is captured in chemical form as **ATP** and **NADPH**

• ATP and NADPH are used to convert CO₂ to hexose phosphates

• **Phototrophs**: photosynthetic organisms (some bacteria, algae, higher plants)

15.1 Photosynthesis Consists of Two Major Processes

• Net reaction of photosynthesis is:

  \[ \text{CO}_2 + \text{H}_2\text{O} \rightarrow (\text{CH}_2\text{O}) + \text{O}_2 \]

• 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 H₂O is used in the chemiosmotic synthesis of ATP
• Hydride ion (H⁻) from H₂O reduces NADP⁺ to NADPH
• Release of O₂ from splitting 2H₂O molecules

The dark reactions

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

• Reduction of gaseous CO₂ to carbohydrate
• Requires energy of NADPH and ATP
Sum of light and dark reactions

- Both processes can occur simultaneously

In the presence of light:

\[ \text{H}_2\text{O} + \text{ADP} + \text{P}_i + \text{NADPH} \rightarrow \text{O}_2 + \text{ATP} + \text{NADPH} + \text{H}^+ \]

Reactions which can occur in the dark:

\[ \text{CO}_2 + \text{ATP} + \text{NADPH} + \text{H}^+ \rightarrow (\text{CH}_2\text{O}) + \text{ADP} + \text{P}_i + \text{NADP}^+ \]

Sum:

\[ \text{CO}_2 + \text{H}_2\text{O} \rightarrow (\text{CH}_2\text{O}) + \text{O}_2 \]

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
15.3 Chlorophyll and Other Pigments Capture Light

A. Light-Capturing Pigments

• Chlorophylls - usually most abundant and most important pigments in light harvesting

• Contain tetapyrrole 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

![Chemical structures of Chlorophyll and bacteriochlorophyll](image)

(Chlorophyll species, R₁, R₂, R₃ table next slide)

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Fig 15.2 (continued)

<table>
<thead>
<tr>
<th>Chl species</th>
<th>R₁</th>
<th>R₂</th>
<th>R₃</th>
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<td>Chl α</td>
<td>—CH = CH₂</td>
<td>—CH₁</td>
<td>—CH₂ —CH₃</td>
</tr>
<tr>
<td>Chl b</td>
<td>—CH = CH₂</td>
<td>—C —H</td>
<td>—CH₂ —CH₃</td>
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<tr>
<td>BCHl α</td>
<td>—C —CH₃</td>
<td>—CH₁</td>
<td>—CH₂ —CH₃</td>
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<tr>
<td>BCHl b</td>
<td>—C —CH₃</td>
<td>—CH₁</td>
<td>—CH = CH₂</td>
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</table>
Fig 15.3 Absorption spectra of photosynthetic pigments

Fig 15.4 Accessory pigments
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 $b_{6}$ complex
- Electrons are conducted from $H_{2}O$ to NADP$^+$

### Table 15.1

<table>
<thead>
<tr>
<th>Complex</th>
<th>Subunits</th>
<th>Molecular weight</th>
<th>Oxidation-reduction components</th>
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<tr>
<td>PSII Water-plastoquinone oxidoreductase</td>
<td>&gt;25</td>
<td>&gt;600 000</td>
<td>Ionic Mn</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Pheophytin</td>
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<td></td>
<td></td>
<td></td>
<td>Plastoquinone</td>
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<td></td>
<td></td>
<td></td>
<td>Chlorophyll</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cytochrome $b_{6}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyt $b_{6}$ complex, Plastoquinol-plastocyanin oxidoreductase</td>
<td>4</td>
<td>210 000</td>
<td>$b$-type cytochrome</td>
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<td></td>
<td></td>
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<td>Fe-S protein</td>
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<td></td>
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<td></td>
<td>$c$-type cytochrome</td>
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<tr>
<td>PSI, Plastocyanin-ferredoxin oxidoreductase</td>
<td>&gt;10</td>
<td>&gt;200 000</td>
<td>Chlorophyll</td>
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<tr>
<td></td>
<td></td>
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<td>Phylloquinone</td>
</tr>
</tbody>
</table>
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)

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**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
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
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.

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$
**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\(_2\)O
- 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 $b$, 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 $\cdot$PQH$_2$ 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 $\cdot$PQH$_2$ from Step 1 to PQH$_2$. The fully reduced PQH$_2$ is then released into the plastoquinone pool. Since the cytochrome $b/f$ complex can accept only electrons and not protons from PQH$_2$, $Q$ cycling by plastoquinone and the cytochrome $b/f$ 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⁺ (E⁰' = -0.32 V) by Fd (E⁰'= -0.43 V) is catalyzed by ferredoxin-NADP⁺ oxidoreductase on the stromal membrane side

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: CF₀ and CF₁
- CF₀ spans the membrane, forms a pore for H⁺
- CF₁ protrudes into the stroma and catalyzes ATP synthesis from ADP and Pᵢ
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 CO₂ reduced to (CH₂O) 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

\[ \text{H}_2\text{O} \rightarrow \text{P}680 \rightarrow \text{Cyt bf complex} \rightarrow \text{P}700 \rightarrow \text{Ferridoxin} \rightarrow \text{NADP}^{\ominus} \]  
(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-Bisphosphate Carboxylase-Oxygenase (Rubisco)

• Gaseous CO$_2$ and the 5-carbon sugar ribulose 1,5-bisphosphate 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

[Diagram of the mechanism of Rubisco]

Ribulose 1,5-bisphosphate

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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
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-bisphosphate)
Fig 15.16 Summary of the RPP cycle

Fig 15.17 The RPP Cycle (5 slides)
(1) Triose phosphate

6 NADPH + 6 H⁺ ➔ 6 NADP⁺ + 6 P_i

Glyceraldehyde 3-phosphate dehydrogenase

(5) Glyceraldehyde 3-phosphate

CH₂OPO₄²⁻

H - C - O - H

CH₂OH

C = O

HCOO⁻

H₂O

Fructose 6-phosphate

Fructose 1,6-bisphosphatase

(6) 1,3-Bisphosphoglycerate

O - C - OPO₄²⁻

H - C - O - H

CH₂OPO₄²⁻

H₂O

(fructose 1,6-bisphosphate)

Dihydroxyacetone phosphate

Dihydroxyacetone phosphate isomerase

CH₂OH

C = O

CH₂OPO₄²⁻

H - C - O - H

CH₂OH

C = O

(to next slide)

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Net equation for the RPP cycle

$$3 \text{ CO}_2 + 9 \text{ ATP} + 6 \text{ NADPH} + 5 \text{ H}_2\text{O} \rightarrow 9 \text{ ADP} + 8 \text{ P}_i + 6 \text{ NADP}^+ + \ast \text{Triose phosphate}$$

$\ast (\text{G3P or DHAP})$

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-bisphosphate and sedoheptulose 1,7-bisphosphatase

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-bisphosphate catalyzed by Rubisco

\[
\begin{align*}
\text{Ribulose} & \quad \text{Ribulose} \\
\text{1,5-bisphosphate} & \quad \text{1,5-bisphosphate} \\
\text{CH}_2\text{OPO}_3^{\ominus} & \quad \text{CH}_2\text{OPO}_3^{\ominus} \\
\text{C} & \quad \text{C} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{O} & \quad \text{O} \\
\text{O}_2 & \quad 2\text{H}^{\ominus} \\
\rightarrow & \\
\text{2-Phosphoglycolate} & + \\
\text{3-Phosphoglycerate} & \\
\text{CH}_2\text{OPO}_3^{\ominus} & \quad \text{CH}_2\text{OPO}_3^{\ominus} \\
\text{COO}^{\ominus} & \quad \text{COO}^{\ominus} \\
\text{H} & \quad \text{H} \\
\text{C} & \quad \text{C} \\
\text{OH} & \quad \text{OH}
\end{align*}
\]