Photosynthesis

- The process that plants, algae and prokaryotes perform by using light energy to synthesize organic compounds is called **photosynthesis**. This is a biological oxidation-reduction (redox) process.

- It compasses a complex series of reactions:
  - light absorption
    - energy conversion
      - electron transfer
        - multistep enzymatic pathway that converts carbon dioxide and water into carbohydrates.

What is photosynthesis?

- In eukaryotes, photosynthesis occurs in **chloroplast**, which is a specialized plastid. Chloroplasts from higher plants are surrounded by a double-membrane system that consists of an outer and inner envelope. It also contains an internal membrane system, which is called **thylakoid membrane**. Some thylakods (**granal thylakoids**) are organized into grana (stacks of apressed membranes) and others (**stromal thylakoids**) are unstacked and therefore exposed to the surrounding fluid membrane (the **chloroplast stroma**).The thylakoid membranes are interconnected and enclose an internal space which is called the **lumen**.

THE PHOTOSYNTHETIC PROCESS:

Photosynthesis takes place in three stages:

- (1) capturing energy from sunlight;
- (2) using the energy to make ATP (Adenosine triphosphate) and reducing power in the form of a compound called NADPH (Nicotinamide Adenosine Dinucleotide Phosphate); and
- (3) using the ATP and NADPH to power the synthesis of organic molecules from CO_2 in the air (carbon fixation).

In other words, light reactions produce O_2, ATP and NADPH and carbon-linked reactions (Calvin cycle or carbon reduction cycle) reduces CO_2 to carbohydrate and consume the ATP and NADPH produced in the light reactions.

- The first two stages take place in the presence of light and are commonly called the light reactions. The third stage, the formation of organic molecules from atmospheric CO_2, is called the Calvin cycle. **As long as ATP and NADPH are available, the Calvin cycle may occur in the absence of light.**

- The following simple equation summarizes the overall process of photosynthesis:

$$\underset{\text{carbon dioxide}}{6\ CO_2} + \underset{\text{water}}{12\ H_2O} + \text{light} \longrightarrow \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{water}}{6\ H_2O} + \underset{\text{oxygen}}{6\ O_2}$$

- Inside the Chloroplast The internal membranes of chloroplasts are organized into sacs called **thylakoids,** and often numerous thylakoids are stacked on one another in columns called **grana**. The thylakoid membranes house the photosynthetic pigments for capturing light energy and the machinery to make ATP.

- Surrounding the thylakoid membrane system is a semiliquid substance called **stroma.** The stroma houses the enzymes needed to assemble carbon molecules. In the membranes of thylakoids, photosynthetic pigments are clustered together to form a photosystem.

- Each pigment molecule within the photosystem is capable of capturing **photons**, which are packets of energy. A lattice of proteins holds the pigments in close contact with one another. When light of a proper wavelength strikes a pigment molecule in the photosystem, the resulting excitation passes from one chlorophyll molecule to another.
- The excited electron is not transferred physically—it is the energy that passes from one molecule to another.

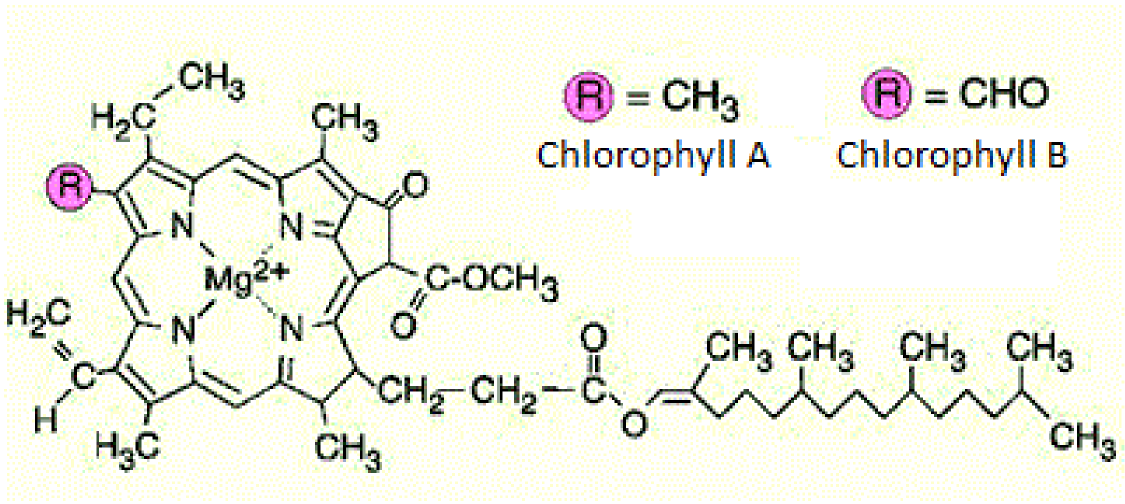
Photosystem I and II

- Thylakoid membranes contain the multiprotein photosynthetic complexes: **photosystem I and II** (PSI and PSII). These include the reaction centers responsible for converting light energy into chemical bond energy. These reaction centers are a part of a photosynthetic electron transfer chain which moves electrons from water in the thylakoid lumen to soluble redox-active compounds in the stroma (e.g. $NADP^+$).

- Eventually the energy arrives at a key chlorophyll molecule that is touching a membrane-bound protein. The energy is transferred as an excited electron to that protein, which passes it on to a series of other membrane proteins that put the energy to work making ATP and NADPH and building organic molecules. The photosystem thus acts as a large antenna, gathering the light harvested by many individual pigment molecules.

Chlorophylls and Carotenoids

- For light energy to be used by any system, the light first must be absorbed. And molecules that absorb light are called pigments.
- Chlorophylls absorb photons by means of an excitation process analogous to the photoelectric effect. These pigments contain a complex ring structure, called a porphyrin ring, with alternating single and double bonds. At the centre of the ring is a magnesium atom. Photons absorbed by the pigment molecule excite electrons in the ring, which are then channelled away through the alternating carbon-bond system. Several small side groups attached to the outside of the ring alter the absorption properties of the molecule in different kinds of chlorophyll.
- The precise absorption spectrum is also influenced by the local microenvironment created by the association of chlorophyll with specific proteins.

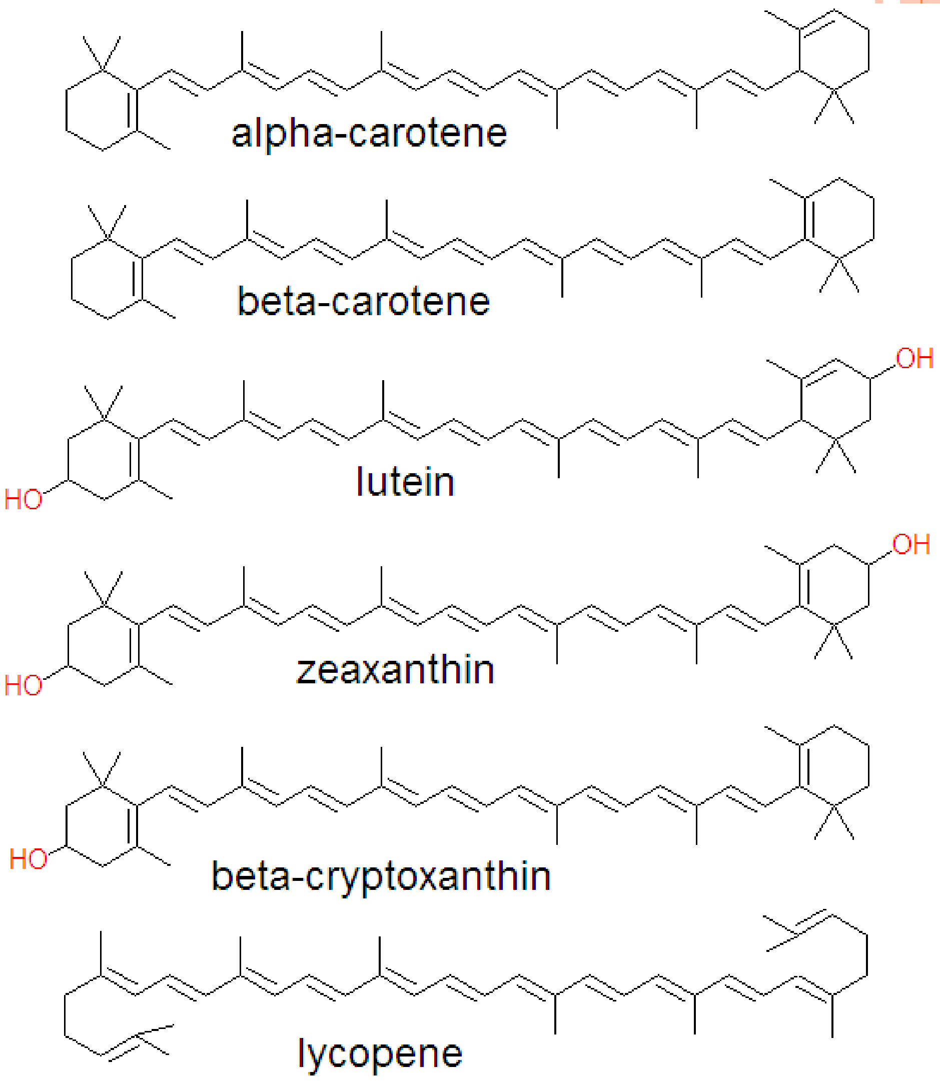


Chlorophyll a is bluish-green colored and chlorophyll b is yellowish-green colored. In nature, chlorophyll a is found **3 times more** than chlorophyll b.

- All plants, algae, and cyanobacteria use chlorophyll a as their primary pigments. It is reasonable to ask why these photosynthetic organisms do not use a pigment like retinal (the pigment in our eyes), which has a broad absorption spectrum that covers the range of 500 to 600 nanometers. The most likely hypothesis involves photoefficiency. Although retinal absorbs a broad range of wavelengths, it does so with relatively low efficiency. Chlorophyll, in contrast, absorbs in only two narrow bands, but does so with high efficiency. Therefore, plants and most other photosynthetic organisms achieve far higher overall photon capture rates with chlorophyll than with other pigments.

- Carotenoids consist of carbon rings linked to chains with alternating single and double bonds. They can absorb photons with a wide range of energies, although they are not always highly efficient in transferring this energy. Carotenoids assist in photosynthesis by capturing energy from light of wavelengths that are not efficiently absorbed by chlorophylls.

- A typical carotenoid is β-carotene, whose two carbon rings are connected by a chain of 18 carbon atoms with alternating single and double bonds. Splitting a molecule of β-carotene into equal halves produces two molecules of vitamin A.
- Oxidation of vitamin A produces retinal, the pigment* used in vertebrate vision. This explains why carrots, which are rich in β-carotene, enhance vision. The wavelengths absorbed by a particular pigment depend on the available energy levels to which light-excited electrons can be boosted in the pigment.



*A pigment is a molecule that absorbs light.

How Photosystems Convert Light to Chemical Energy

- Bacteria Use a Single Photosystem Photosynthetic pigment arrays are thought to have evolved more than 3 billion years ago in bacteria similar to the sulphur bacteria studied by van Niel.

1. **Electron is joined with a proton to make hydrogen.** In these bacteria, the absorption of a photon of light at a peak absorption of 870 nanometers (near infrared, not visible to the human eye) by the photosystem results in the transmission of an energetic electron along an electron transport chain, eventually combining with a proton to form a hydrogen atom. In the sulphur bacteria, the proton is extracted from hydrogen sulphide, leaving elemental sulphur as a by-product. In bacteria that evolved later, as well as in plants and algae, the proton comes from water, producing oxygen as a by-product.

2. Electron is recycled to chlorophyll

- The ejection of an electron from the bacterial reaction centre leaves it short one electron. Before the photosystem of the sulphur bacteria can function again, an electron must be returned. These bacteria channel the electron back to the pigment through an electron transport; the electron's passage drives a proton pump that promotes the chemiosmotic synthesis of ATP.
- One molecule of ATP is produced for every three electrons that follow this path. Viewed overall, the path of the electron is thus a circle. Chemists therefore call the electron transfer process leading to ATP formation cyclic photophosphorylation.
- Note, however, that the electron that left the P870 reaction centre was a high-energy electron, boosted by the absorption of a photon of light, while the electron that returns has only as much energy as it had before the photon was absorbed.
- The difference in the energy of that electron is the photosynthetic payoff, the energy that drives the proton pump.

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- For more than a billion years, cyclic photophosphorylation was the only form of photosynthetic light reaction that organisms used. However, its major limitation is that it is geared only toward energy production, not toward biosynthesis. Most photosynthetic organisms incorporate atmospheric carbon dioxide into carbohydrates. Because the carbohydrate molecules are more reduced (have more hydrogen atoms) than carbon dioxide, a source of reducing power (that is, hydrogens) must be provided. Cyclic photophosphorylation does not do this. The hydrogen atoms extracted from H_2S are used as a source of protons, and are not available to join to carbon. Thus bacteria that are restricted to this process must scavenge hydrogens from other sources, an inefficient undertaking.

Why Plants Use Two Photosystems

- After the appearance of sulphur bacteria, other kinds of bacteria developed an improved version of the photosystem that overcame the limitation of cyclic photophosphorylation in a neat and simple way: a second, more powerful photosystem using another arrangement of chlorophyll a was combined with the original.

- In this second photosystem, called photosystem II, molecules of chlorophyll a are arranged with a different geometry, so that more shorter wavelength, higher energy photons are absorbed than in the ancestral photosystem, which is called photosystem I.
- As in the ancestral photosystem, energy is transmitted from one pigment molecule to another within the antenna complex of these photosystems until it reaches the reaction center, a particular pigment molecule positioned near a strong membrane-bound electron acceptor.

- In photosystem II, the absorption peak (that is, the wavelength of light most strongly absorbed) of the pigments is approximately 680 nanometers; therefore, the reaction center pigment is called P680.
- The absorption peak of photosystem I pigments in plants is 700 nanometers, so its reaction center pigment is called P700. Working together, the two photosystems carry out a noncyclic electron transfer.

- When the rate of photosynthesis is measured using two light beams of different wavelengths (one red and the other far-red), the rate was greater than the sum of the rates using individual beams of red and far-red light. This surprising result, called the enhancement effect, can be explained by a mechanism involving two photosystems acting in series (that is, one after the other), one of which absorbs preferentially in the red, the other in the far-red.

How the Two Photosystems of Plants Work Together

- Plants use the two photosystems discussed earlier in series, first one and then the other, to produce both ATP and NADPH. This two-stage process is called noncyclic photophosphorylation, because the path of the electrons is not a circle—the electrons ejected from the photosystems do not return to it, but rather end up in NADPH. The photosystems are replenished instead with electrons obtained by splitting water. Photosystem II acts first. High-energy electrons generated by photosystem II are used to synthesize ATP and then passed to photosystem I to drive the production of NADPH. For every pair of electrons obtained from water, one molecule of NADPH and slightly more than one molecule of ATP are produced.

Photosystem II

- The reaction centre of photosystem II, called P680, closely resembles the reaction centre of purple bacteria. It consists of more than 10 transmembrane protein subunits. The light-harvesting antenna complex consists of some 250 molecules of chlorophyll a and accessory pigments bound to several protein chains. In photosystem II, the oxygen atoms of two water molecules bind to a cluster of manganese atoms which are embedded within an enzyme and bound to the reaction centre. In a way that is poorly understood, this enzyme splits water, removing electrons one at a time to fill the holes left in the reaction centre by departure of light-energized electrons. As soon as four electrons have been removed from the two water molecules, O_2 is released.

The Path to Photosystem I

- The primary electron acceptor for the light-energized electrons leaving photosystem II is a quinone molecule, as it was in the bacterial photosystem described earlier. The reduced quinone which results (plastoquinone, symbolized as Q) is a strong electron donor; it passes the excited electron to a proton pump called the b6-f complex embedded within the thylakoid membrane (figure 10.15). This complex closely resembles the bc1 complex in the respiratory electron transport chain of mitochondria discussed in chapter 9. Arrival of the energetic electron causes the b6-f complex to pump a proton into the thylakoid space. A small copper-containing protein called plastocyanin (symbolized pC) then carries the electron to photosystem I.

Making ATP: Chemiosmosis

- Each thylakoid is a closed compartment into which protons are pumped from the stroma by the b6-f complex. The splitting of water also produces added protons that contribute to the gradient.
- The thylakoid membrane is impermeable to protons, so protons cross back out almost exclusively via the channels provided by ATP synthases. These channels protrude like knobs on the external surface of the thylakoid membrane.

- When a photon of light strikes a pigment molecule in photosystem II, it excites an electron. This electron is coupled to a proton stripped from water by an enzyme and is passed along a chain of membrane-bound cytochrome electron carriers. When water is split, oxygen is released from the cell, and the hydrogen ions remain in the thylakoid space. At the proton pump (b6-f complex), the energy supplied by the photon is used to transport a proton across the membrane into the thylakoid.
- The concentration of hydrogen ions within the thylakoid thus increases further. When photosystem I absorbs another photon of light, its pigment passes a second high-energy electron to a reduction complex, which generates NADPH. the thylakoid through the ATP synthase channel, ADP is phosphorylated to ATP and released into the stroma, the fluid matrix inside the chloroplast.The stroma contains the enzymes that catalyze the reactions of carbon fixation.

Photosystem I

- The reaction centre of photosystem I, called P700, is a transmembrane complex consisting of at least 13 protein subunits. Energy is fed to it by an antenna complex consisting of 130 chlorophyll a and accessory pigment molecules. Photosystem I accepts an electron from plastocyanin into the hole created by the exit of a light-energized electron.

- This arriving electron has by no means lost all of its light-excited energy; almost half remains. Thus, the absorption of a photon of light energy by photosystem I boosts the electron leaving the reaction center to a very high energy level. Unlike photosystem II and the bacterial photosystem, photosystem I does not rely on quinones as electron acceptors. Instead, it passes electrons to an iron-sulphur protein called ferredoxin (Fd).

Making NADPH

- Photosystem I passes electrons to ferredoxin on the stromal side of the membrane (outside the thylakoid). The reduced ferredoxin carries a very-high potential electron.
- Two of them, from two molecules of reduced ferredoxin, are then donated to a molecule of $NADP^+$ to form NADPH. The reaction is catalyzed by the membrane-bound enzyme NADP reductase.

- Since the reaction occurs on the stromal side of the membrane and involves the uptake of a proton in forming NADPH, it contributes further to the proton gradient established during photosynthetic electron transport.