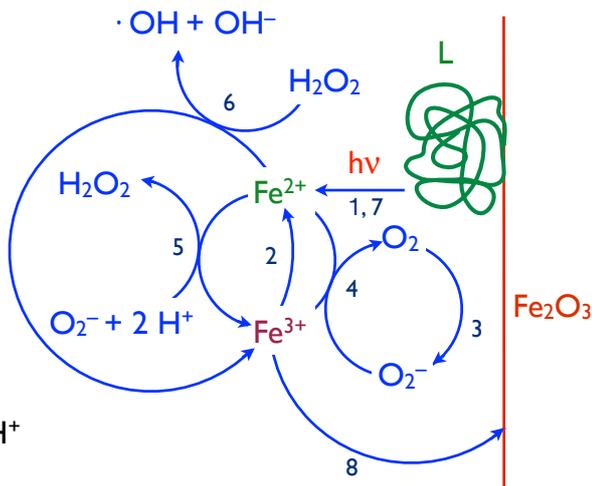


6.2 Photochemistry of waters and soils

Iron photochemical cycle

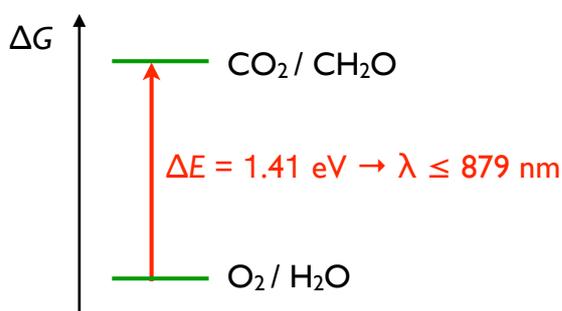
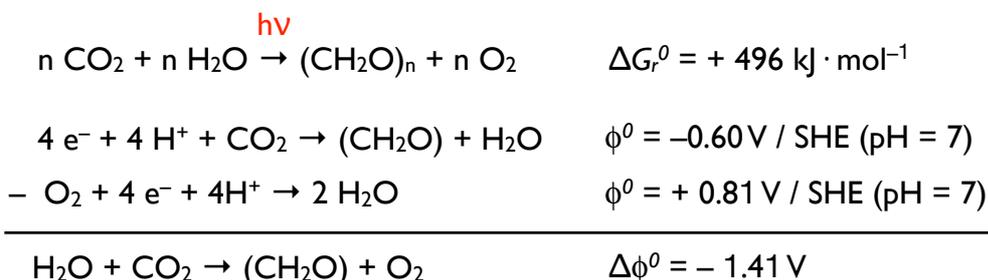
Iron (III) oxide Fe_2O_3 (hematite) and Fe^{3+} complexes formed with natural ligands, such as oxalates and humic acids, strongly absorb visible light. They are at the origin of numerous natural photo-oxidation reactions in atmospheric waters (fogs, clouds) and in ground waters (water tables, rivers, acid lakes, seas).

- 1) $\text{Fe}_2\text{O}_3 \xrightarrow{\text{L, hv, H}_2\text{O}} \text{Fe}^{2+} + \cdot\text{OH} + \text{H}^+$
- 2) $\text{Fe}^{3+} \xrightarrow{\text{L, hv}} \text{Fe}^{2+}$
- 3) $\text{Fe}_2\text{O}_3 (\text{e}^-_{\text{cb}}) \longrightarrow \text{O}_2^{\cdot-} / \text{HO}_2$
- 4) $\text{Fe}^{3+} + \text{O}_2^{\cdot-} \longrightarrow \text{Fe}^{3+} + \text{O}_2$
- 5) $\text{Fe}^{3+} + \text{O}_2^{\cdot-} \xrightarrow{2 \text{H}^+} \text{Fe}^{3+} + \text{H}_2\text{O}_2$
- 6) $\text{H}_2\text{O}_2 + \text{Fe}^{2+} \xrightarrow{\text{Fenton}} \text{Fe}^{3+} + 2 \cdot\text{OH}$
- 7) $\text{Fe}^{3+} + \text{H}_2\text{O} \xrightarrow{\text{L, hv}} \text{Fe}^{2+} + \cdot\text{OH} + \text{H}^+$
- 8) $\text{Fe}^{3+} + \text{OH}^- \longrightarrow \text{Fe}_2\text{O}_3 + \text{H}^+$



Thermodynamics

The photosynthesis reaction occurring in cyanobacteria, algae, and superior plants can be summarized as follows:

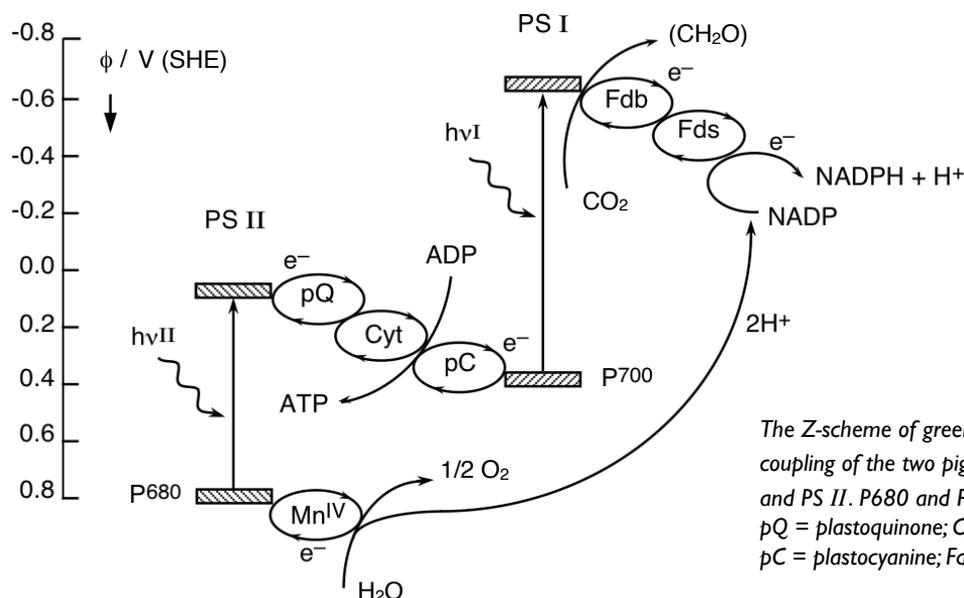


In principle, a single photon in the vis/NIR domain with $\lambda \leq 879 \text{ nm}$ should be able to drive the overall reaction. However, simultaneous oxidation of water to O_2 and reduction of CO_2 to the carbohydrate unit (CH_2O) requires the exchange of four electrons. Hence, the process has to take place within several steps.

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Calvin cycle

Using quantum yield measurement, it was inferred that 8 photons are necessary for the conversion of each CO_2 molecule. Melvin Calvin (Nobel laureate 1961) showed that the mechanism consists of two consecutive steps occurring within two different photosystems (PS II, PS I).



The Z-scheme of green plants photosynthesis: coupling of the two pigment systems, PS I and PS II. P680 and P700 = chlorophyll; pQ = plastoquinone; Cyt = cytochrome; pC = plastocyanine; Fd = ferredoxine.

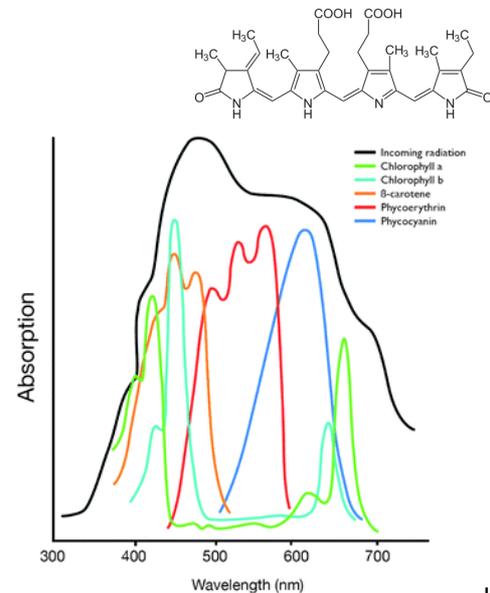
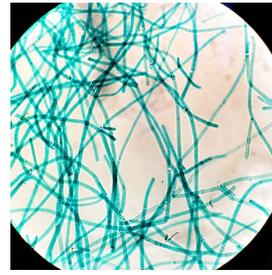
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Cyanobacteria

Photosynthetic cyanobacteria (also wrongly called «blue-green algae») get their colour from the bluish pigment phycocyanin, which they use to capture light for photosynthesis.

Many cyanobacteria are able to reduce nitrogen and carbon dioxide under aerobic conditions. The water-oxidizing photosynthesis is accomplished by coupling the activity of photosystems II and I (Z-scheme, see next slide). In anaerobic conditions, they are also able to use only PS I with electron donors other than water (H_2S , thiosulphate, or even H_2) just like purple photosynthetic bacteria.

Cyanobacteria created the conditions in the planet's early atmosphere that directed the evolution of aerobic metabolism. They are still important contributors to global carbon and nitrogen budgets.

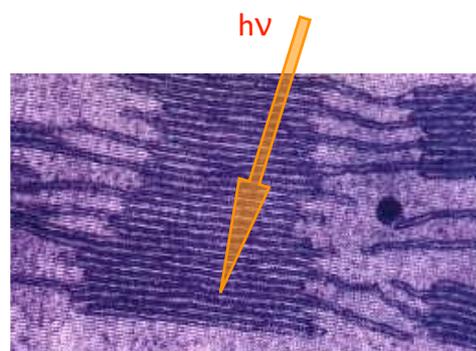
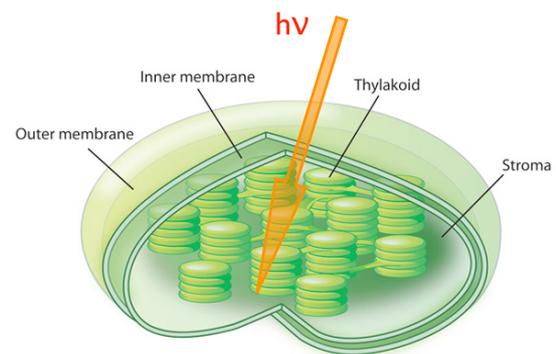


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Green algae and plants

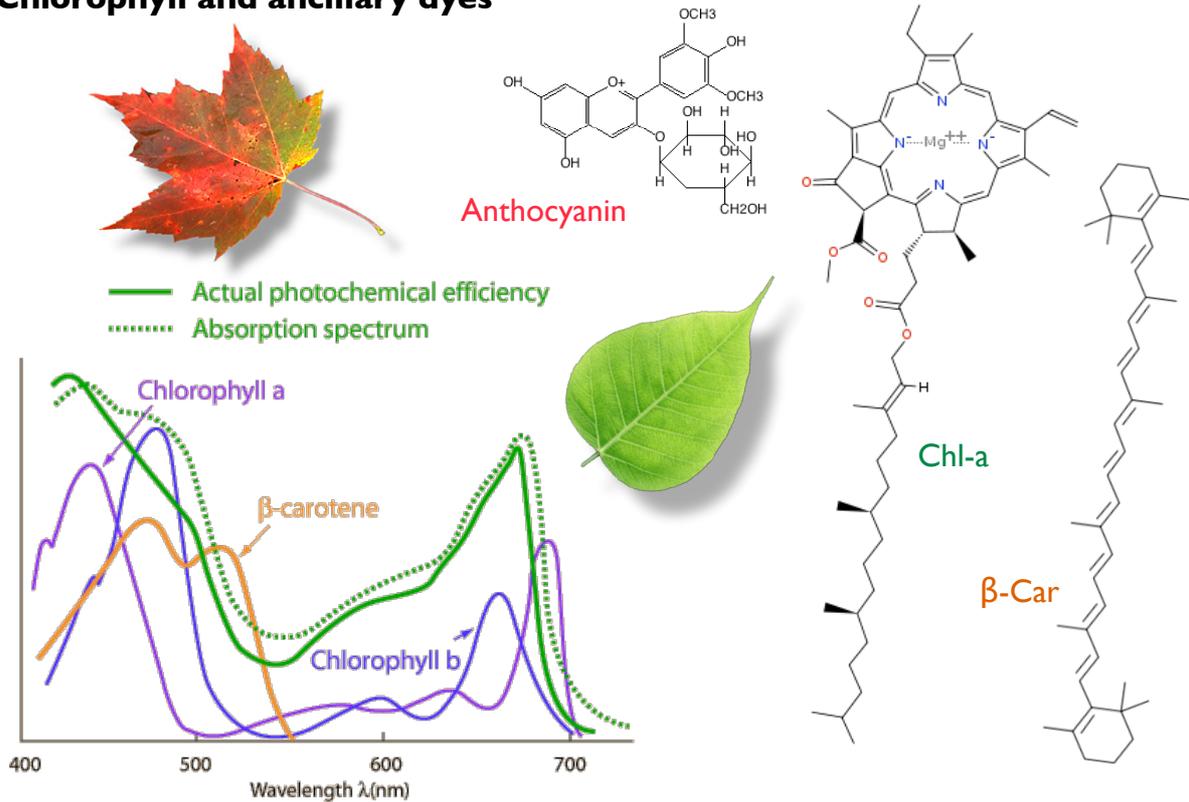
Photosynthesis operates by fixing CO_2 through a cycle of reactions called the Calvin cycle. To convert 6 moles of CO_2 to one mole of glucose $C_6H_{12}O_6$, the cycle uses 18 moles of ATP, converting it to ADP. Reductive equivalents are provided by NADPH. 12 moles of NADPH are needed for every mole of sugar made. Light provides the necessary energy to generate ATP from ADP and NADPH from NADP.

In green plants, the photosynthetic apparatus is located in chloroplasts. These organelles contain stacks of flattened disks, called thylakoids. The thylakoids membrane contain the light-harvesting complex, including pigments such as chlorophyll, as well as the electron transport chains used in photosynthesis.



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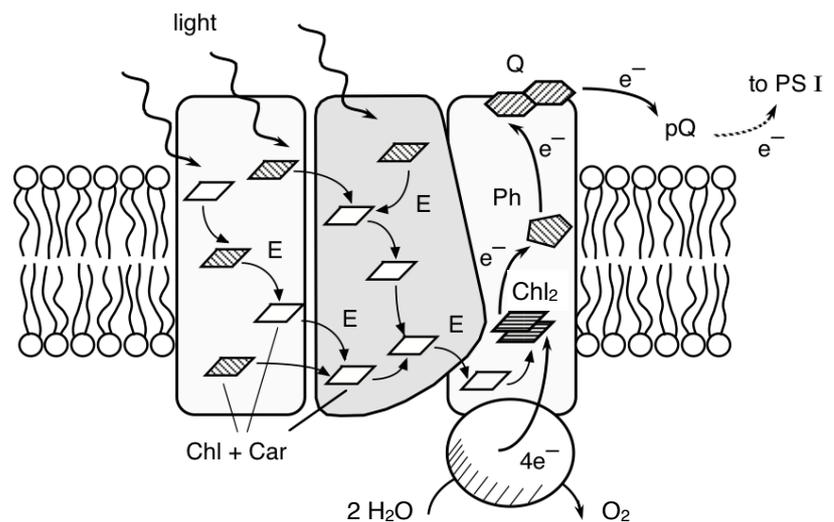
Chlorophyll and ancillary dyes



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Electron transport chain

Excitation energy is harvested by chlorophyll (Chl) and carotenoids (Car) molecules and transferred from one molecule to the next through Förster energy transfer until it is trapped on a chlorophyll dimer (Chl_2). This antenna effect allows to efficiently funnel excitation energy to a reaction center.



In photosystem II, vectorial electron transfer across the membrane takes place from excited Chl_2^* to plastoquinone (pQ) via pheophytine (Ph) and quinone (Q) electron mediators. A well-defined chromophore arrangement in a rigid protein matrix, combined with optimised energetics of the different electron carriers, allows a highly efficient charge-separation process. The individual molecular reactions at room temperature are well described by conventional electron-transfer (Marcus) theory.

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Energy conversion efficiency

Why is chlorophyll green and not black ? Early in Earth's history, the oceans were dominated by purple cyanobacteria that create energy from the sun in a process analogous to photosynthesis (but completely differently at the chemical level). As algae came along, they would have found a beneficial niche by utilizing the unused red and blue wavelengths.

Most green plants operate with photosynthesis efficiencies of a few percent. The top energy conversion efficiency reported under natural growing conditions for a plant is with winter-evening primrose at 8 %. Sugarcane has registered 7 %, eucalyptus tree 5 %. The intensively cultivated agricultural plants, such as corn, average about 3 % in photosynthetic efficiency, and most crops range from 1-4 %. This is also typical of algae.

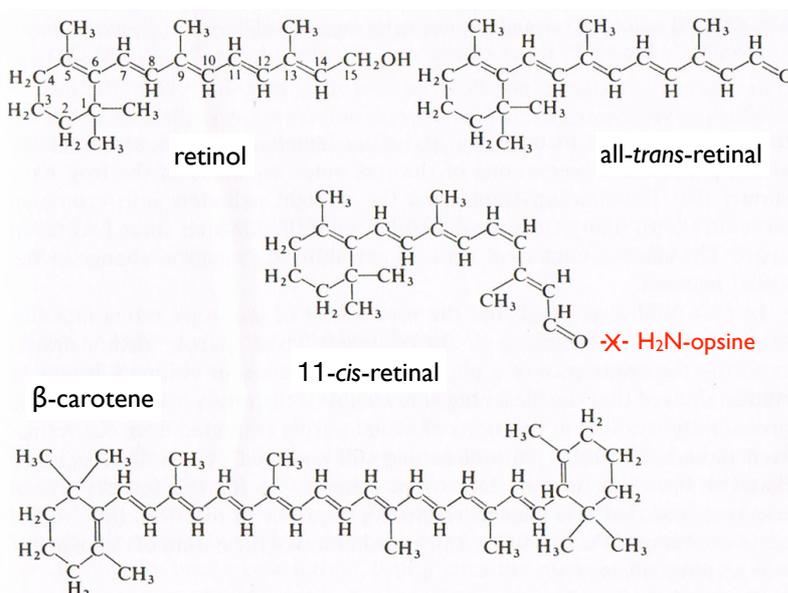


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6.4 Mechanism of vision

Retinal

Among vertebrates, photosensitive pigments responsible for vision contain the retinal chromophore, also found in the photosynthetic apparatus of cyanobacteria. Retinal is a metabolic product of the oxidation of retinol and β -carotene (vitamin A1).

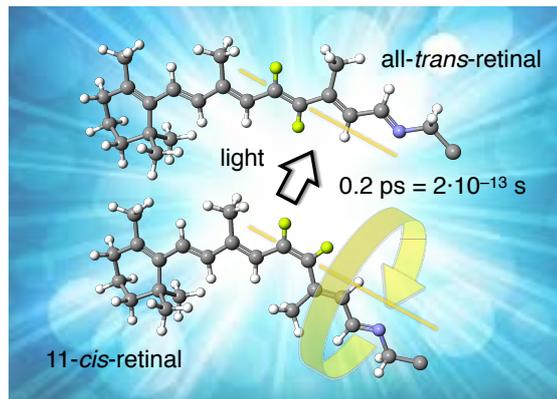
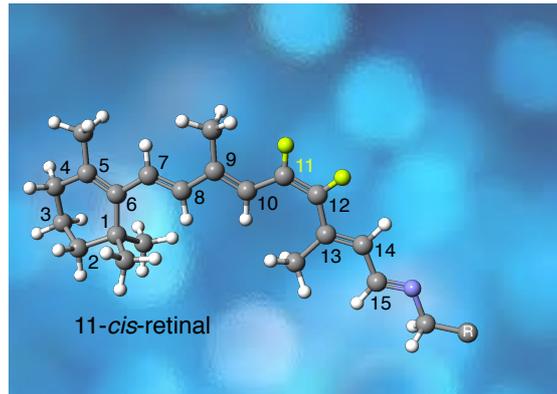
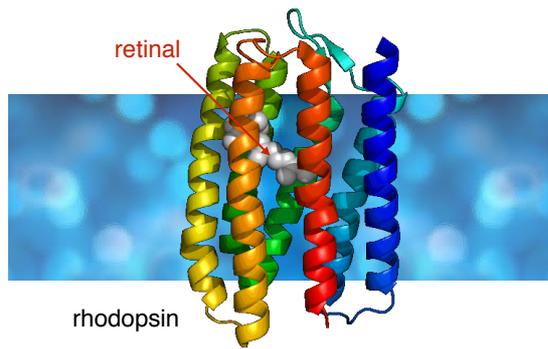


11-cis retinal is associated to a protein, opsin, to form rhodopsin, whose structural and optical properties depend upon the chemical bond formed with the chromophore.

Cis-trans photoisomerization of retinal causes the cleavage of the chromophore-protein bond and a folding of the protein to yield the bathorhodopsin structure within a few tens of picoseconds.

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Retinal photoisomerization

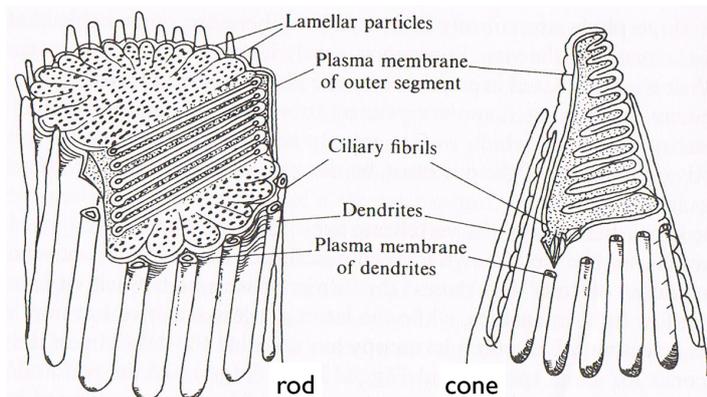
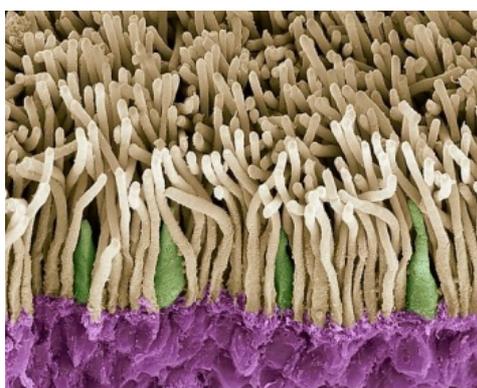


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Rods and cones

The receptors of the retina consist of "rods" and "cones". Rods possess high light sensitivity and are used for night- and peripheral vision. Cones are a thousand times less sensitive but have a faster response and may carry colour-selectivity. They are concentrated in the central part of the retina (fovea).

A number of lamellae are formed by the infolding of plasma membranes, and these lamellae are the carriers of the visual pigments.



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Rods and cones

Cones are divided into three types. S cones are sensitive to blue light and M cones to the yellow and green spectral domains. L cones are sensitive to red light and, in a lesser extend, also to the blue. Human vision is thus essentially trichromatic.

"Color-blind" people (8 % of men) usually miss one of the three cone types. Some studies suggest that a part of humans (up to 50% of women and 8% of men) actually possess 4 types of cones (tetrachromacy) and are thus able to distinguish color shades that other cannot.

