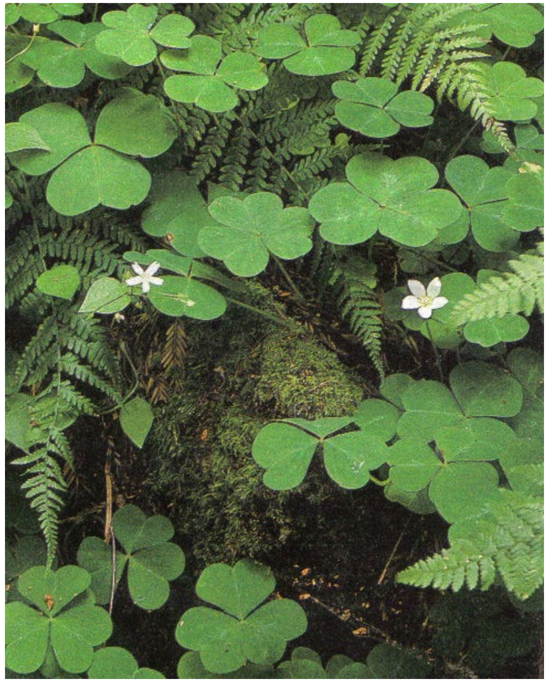
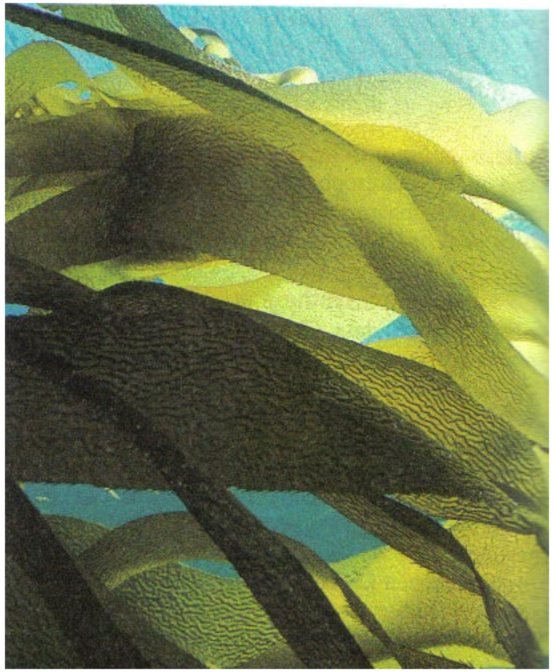
Photosynthesis

Directly of indirectly, photosynthesis furnishes food for nearly all living creatures. Every living being needs organic molecules to produce carbon rich compounds and energy. It can gain these organic compounds by two ways: autotrophic or heterotrophic feeding. Plants are autotrophic, since they use CO_2 from the air, as well as water and mineral salts from the soil. Additionally they also need light to synthesize carbohydrates, lipids, proteins and other organic substances. Heterotrophic living beings can not produce energy and essential carbohydrates from CO_2. Therefore they rely on eating plants or animals.

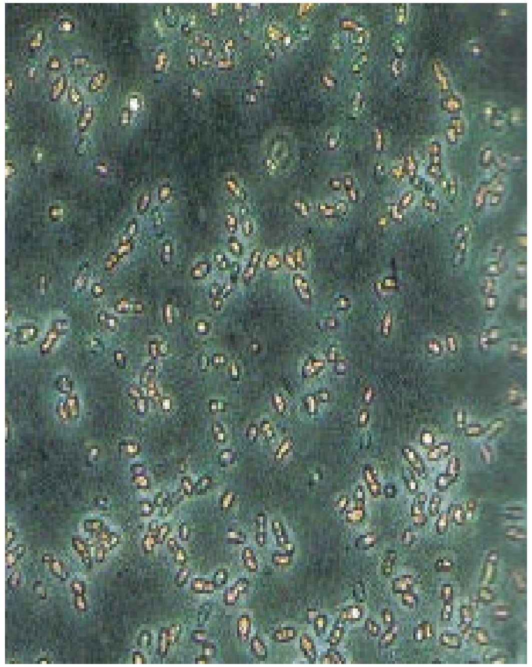
Below are a few examples of autotrophs:



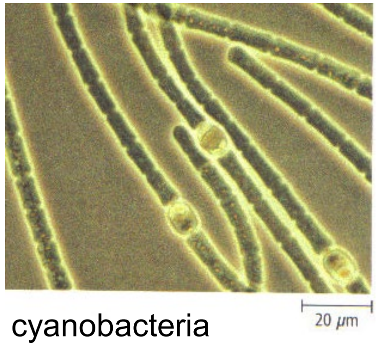
plants



algeas



sulfurbacteria



cyanobacteria

unicellular organisms

Evolution of living organisms over geological time

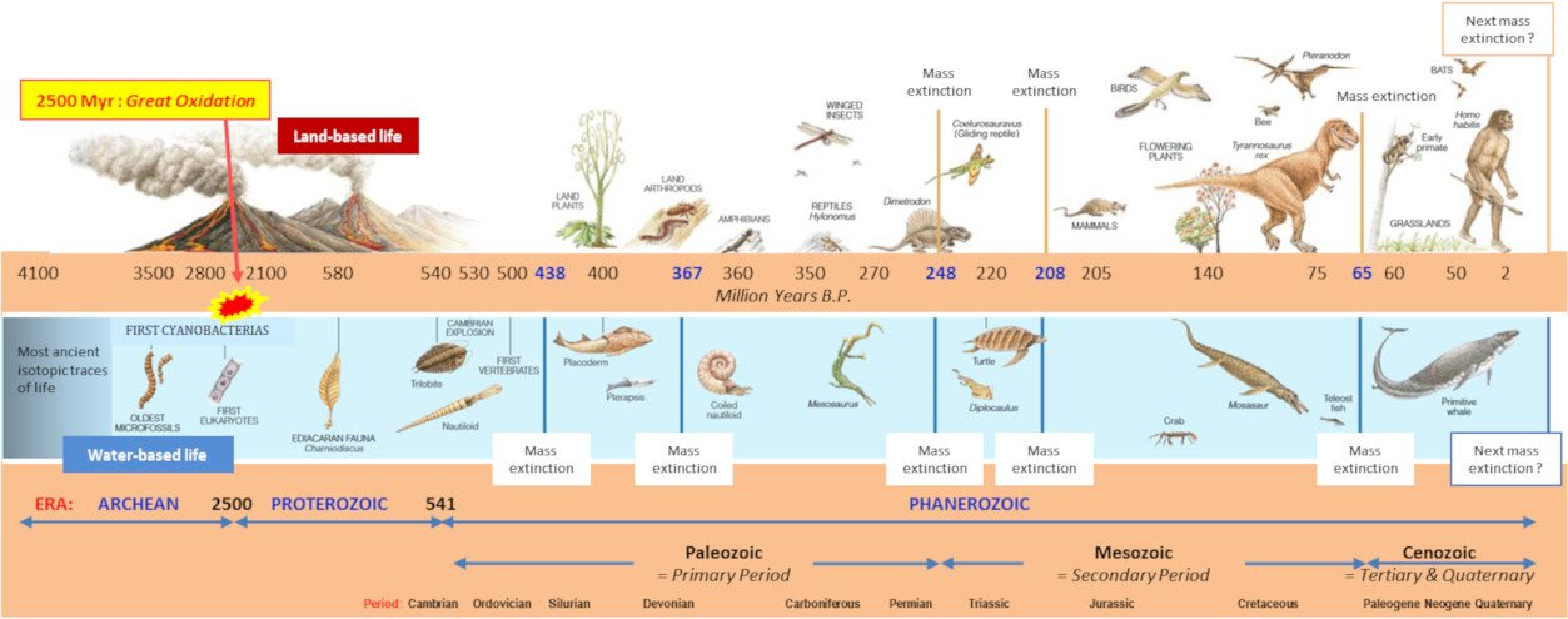


Diagram adapted from a drawing by Tomo Narashima originally published in “Scientific American” (October 1994) and included in “Pour la Science” (December 1994)

Abundance of fossil fuels

How can we be so sure about the abundance of fossil fuels? Aren’t there some hidden reserves that we have not found yet?
Based on a simple model we can indeed estimate the total resources of carbohydrates fuels. It is assumed that before the event of organic life on earth, there was no elementary carbon, nor was there gaseous oxygen. After creation of the universe, high temperatures lead to the formation of CO2, carbides, oxides etc. There is strong evidence that the early atmosphere contained only small concentrations of oxygen due to numerous oxygen sinks (carbon material and metals, especially iron). 3.5 billion old rocks show ferrous Fe^{2+} which would have reacted with oxygen to form ferric Fe^{3+} , so the presence of Fe^{2+} indicates that at some point in early atmosphere, the oxygen content was very low. Therefore substantial amounts of atmospheric oxygen O2 on earth comes from photosynthesis together with the occurrence of life on our planet, about 4 billion years ago with a massive increase in atmospheric oxygen about 500 mio years ago (plants).

$$n\,(H_2O + CO_2) \rightarrow n\,CH_2O + n\,O_2$$

With one mole of O_2 we would also obtain one mole of carbohydrates in the form of CH_2O. Now , if we know the total mass of gaseous oxygen in the atmosphere and the earth crust, we could obtain an estimated value of the total mass of carbohydrates.

Let us first calculate the mass of the air in the atmosphere, assuming an ideal gas. The barometric formula tells us the dependence of air pressure *p* on height *h* over the ground:

$$p = p_0 e^{-\frac{m_{air} g h}{k_B T}}$$

where p_o is the pressure at sea level (1bar), m_{air} is the mass of an air molecule, k_B is the Boltzmann factor and *T* is the temperature.

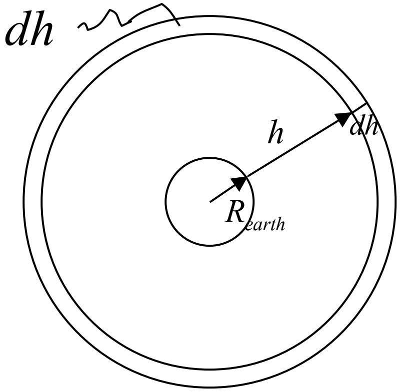
Now the total mass of the atmosphere can be calculated by integrating from zero to infinity:

$$M_{tot} = \int_0^\infty \rho(h)\, dV = \int_0^\infty \frac{p(h) m_{Air}}{k_B T} 4\pi (R_{earth} + h)^2 dh =$$

$$\frac{m_{Air} 4\pi p_0}{k_B T} \int_0^\infty e^{-\frac{m_{Air} g h}{k_B T}} (R_{earth} + h)^2 dh \approx \frac{R_{earth}{}^2 p_0 4\pi}{g} \approx$$

$$\approx \frac{(6.4 \cdot 10^6)^2 \cdot 10^5 4\pi}{9.81} = 5.2 \cdot 10^{18} kg$$

$$dV(h) = 4\pi (R_{earth} + h)^2 dh$$



Air contains 20% of oxygen and so $m_{O2} = 10^{18}$kg.

The amount of oxygen in the atmosphere must have accumulated over the past 500 million years and amounts to only 2.3% oxygen produced in all these years. The major part of oxygen coming from photosynthesis is chemically bound as iron oxides (~83%). Therefore the total mass of oxygen produced

$$m_{O2,total} = \frac{m_{O2,atmos}}{2.3} 100 = 4.83 \cdot 10^{19}\text{kg}$$

Using the molecular weight ratio between O_2 and carbon, we can estimate the total mass of carbon :

$\frac{M_C}{M_{O2}} = \frac{12}{32}$ and assuming 1 mol of C for 1 mol of O_2 we get: $m_C = \frac{12}{32} m_{O2} = 1.8 \cdot 10^{19}\text{kg}$

Now 1kg of hydrocarbon corresponds to about 10 kWh of energy (e.g. the combustion enthalpy of iso-octane is -5461 kJ/mol, MW = 114.23 g/mol → 1kg corresponds to 47807 kJ = 13.3 kWh)

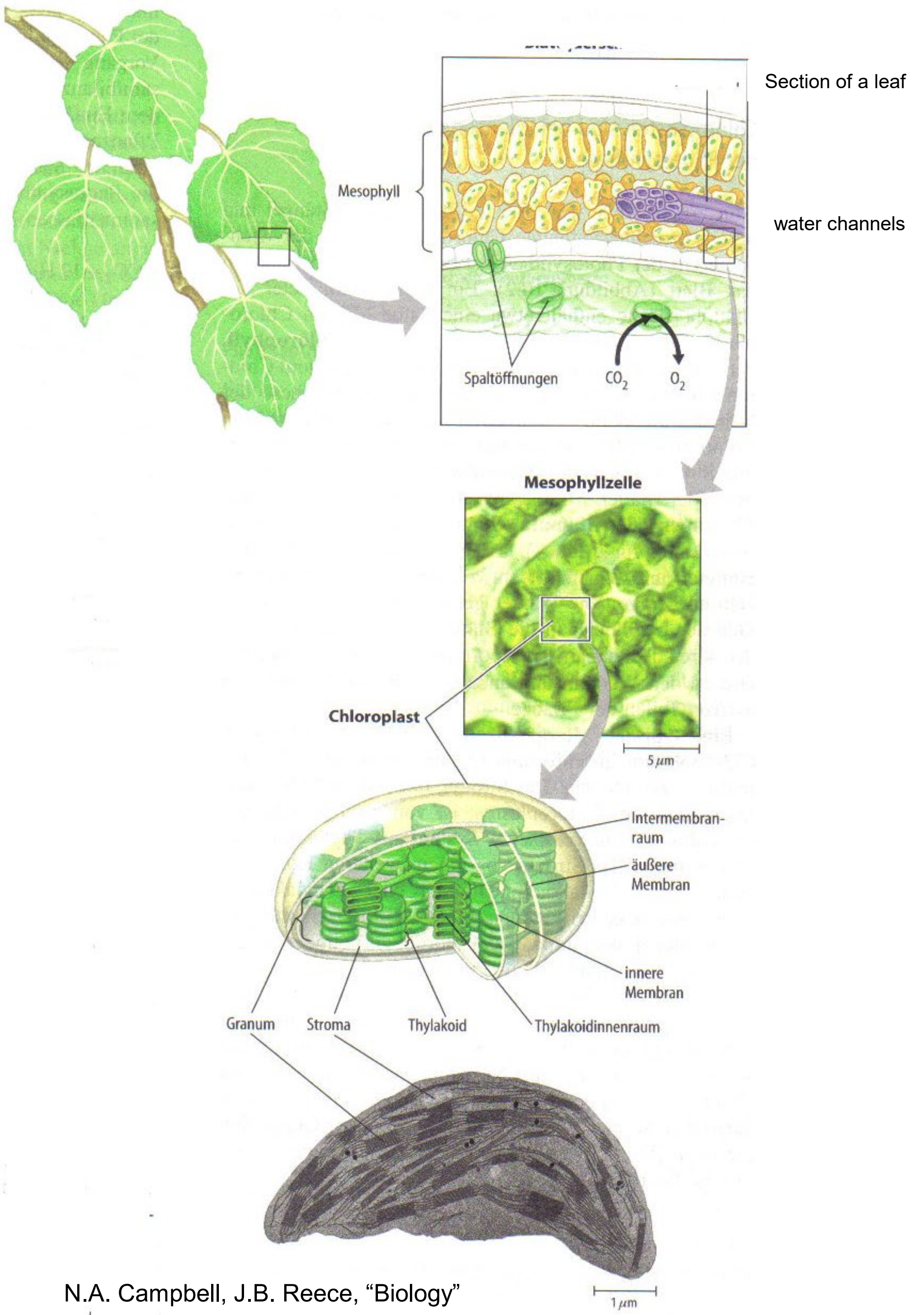
→Totally we would have an **amount of carbon reserves of about $1.8 \cdot 10^{20}$ kWh!**

Today, the consumption of fossil fuels is $>10^{14}$ kWh/year so the amount of hydrocarbons remaining seems to be immense. Nevertheless, only a small part of the hydrocarbons can be exploited technically and economically. The exploitable fossil reserves are estimated to correspond to only about 10^{16} kWh, which would leave us a few 100 years before we run out of them, if consumption goes ahead as now.

The location of photosynthetic activity

The largest photosynthetic activity occurs in leaves. They are green because of the green pigment, chlorophyll, that is located in the chloroplasts. One square millimeter contains about half a million chloroplasts. One mesophyll cell contains about 40 chloroplasts. A viscous liquid is contained inside the chloroplasts (stroma) and is surrounded by a double membrane. The green chlorophyll pigment is located in the so called thylakoids, which are packed together in small packages called grana. Chlorophyll is actually located inside the thylakoid membrane, which is a double membrane.

In order to bring together the necessary educts and in order to release the photosynthetic products exchange channels with the exterior and interior of the plant are required. CO_2 enters from the apertures in the leaf called stomata, This is also where oxygen is released.

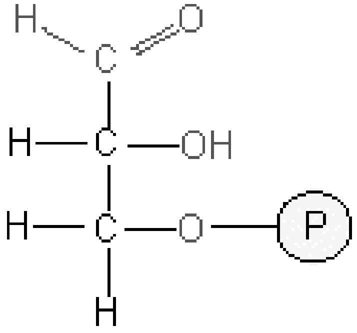


N.A. Campbell, J.B. Reece, “Biology”

Reaction equations

$$6\,CO_2 + 12H_2O \xrightarrow{h\nu} C_6H_{12}O_6 + 6O_2 + 6H_2O$$

The carbohydrate $C_6H_{12}O_6$ is glucose. The primary product of photo-synthesis is not sugar with only three carbon atoms, namely glyceraldehyde-3-phosphate or G3P.

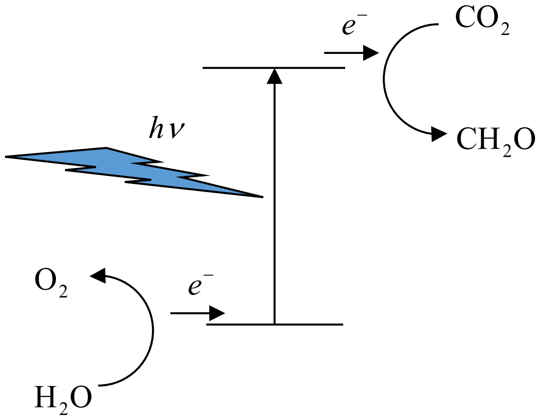


G3P

In a simplified way:

$$CO_2 + H_2O \xrightarrow{h\nu} CH_2O \;\; + O_2 \qquad \Delta G^0 = 478\,\mathrm{kJ/mol}\,CO_2$$

(ΔG^0 = 4.96 eV)



The direct fission of water by light is not feasible since it would involve photons with a wavelength smaller than 250 nm.

If one looks at the half reactions, one can see that 4 electrons are necessary to reduce a molecule of CO_2 and to oxidize a molecule of water to produce oxygen.

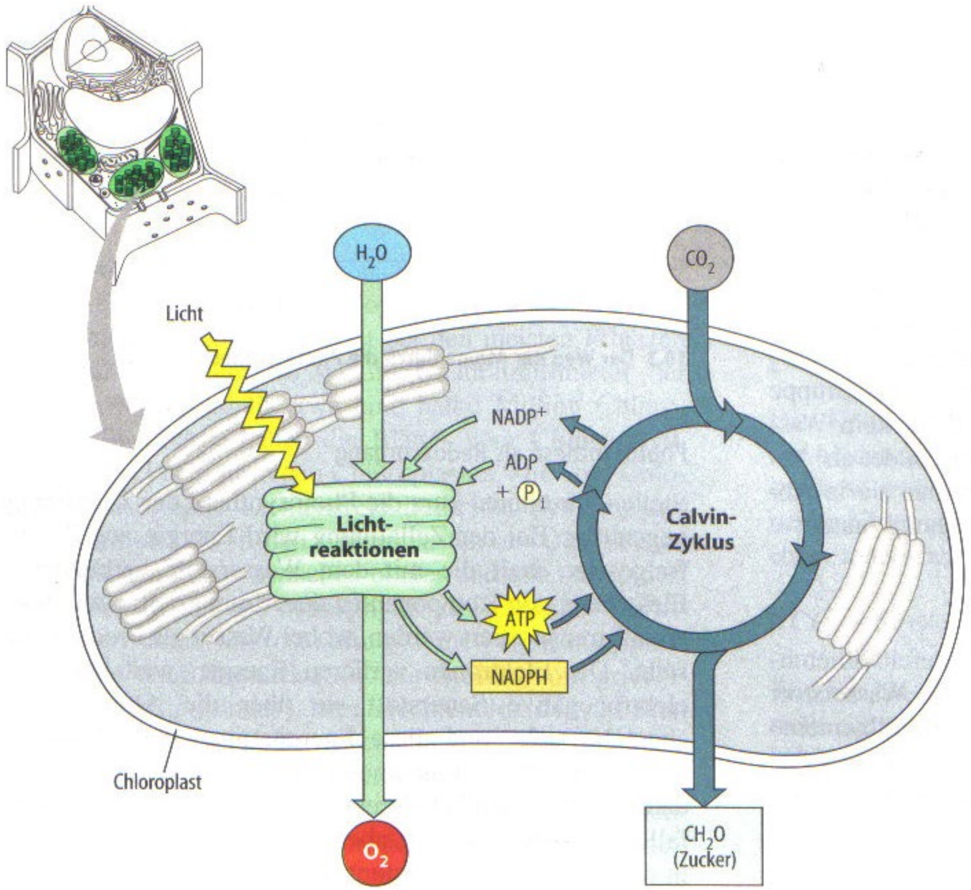
$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$$
$$4H^+ + 4e^- + CO_2 \longrightarrow CH_2O + H_2O$$

If the process could be split up into four 1 electron reactions, then each photoinduced process would require and average energy of 472 $kJmol^{-1}$ / 4 = 118 $kJmol^{-1}$, i.e. a photon wavelength of at least 1000 nm.

Measurement of the photosynthesis quantum yield has shown that actually 8 photons are necessary for the conversion of each CO_2 molecules, suggesting a two step mechanism.

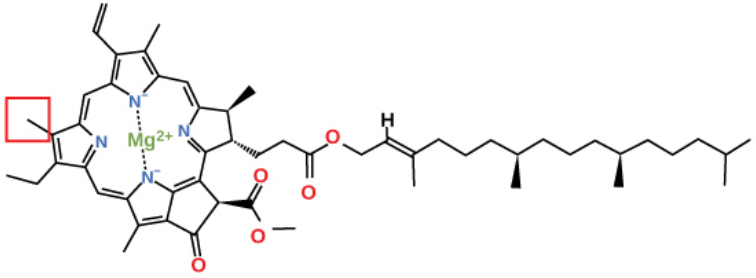
The two main processes in photosynthesis

Calvin earned the Nobel price for elucidating the photosynthesis mechanism and the carbon cycle associated to it. Unlike the simple equations above might suggest, photosynthesis is not just a single process, but consists of two processes each containing numerous reaction steps. These two major processes are termed photo-reactions and Calvin cycle, respectively.

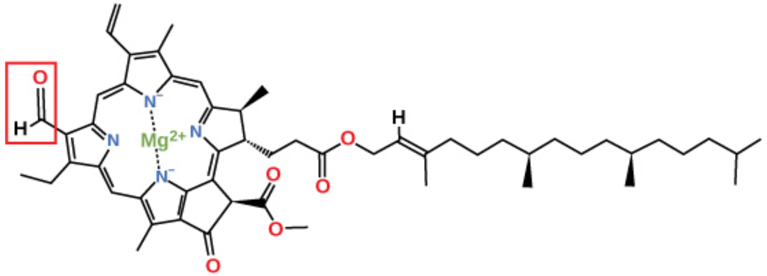


The main absorbing chromophores

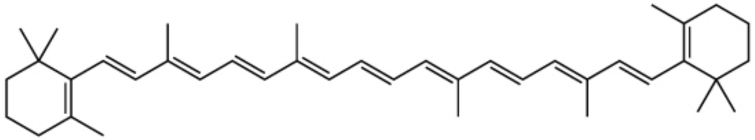
The molecules absorbing solar photons are situated in the thylakoid membrane. As we know by looking at leaves, the relevant dyes absorb in the blue and red spectral domain thus allowing green light to be transmitted and reflected. The active dyes are chlorophyll a and chlorophyll b. Additionally there are carotenoids with a larger variety of colors that extend the photosensitivity of the leaves.



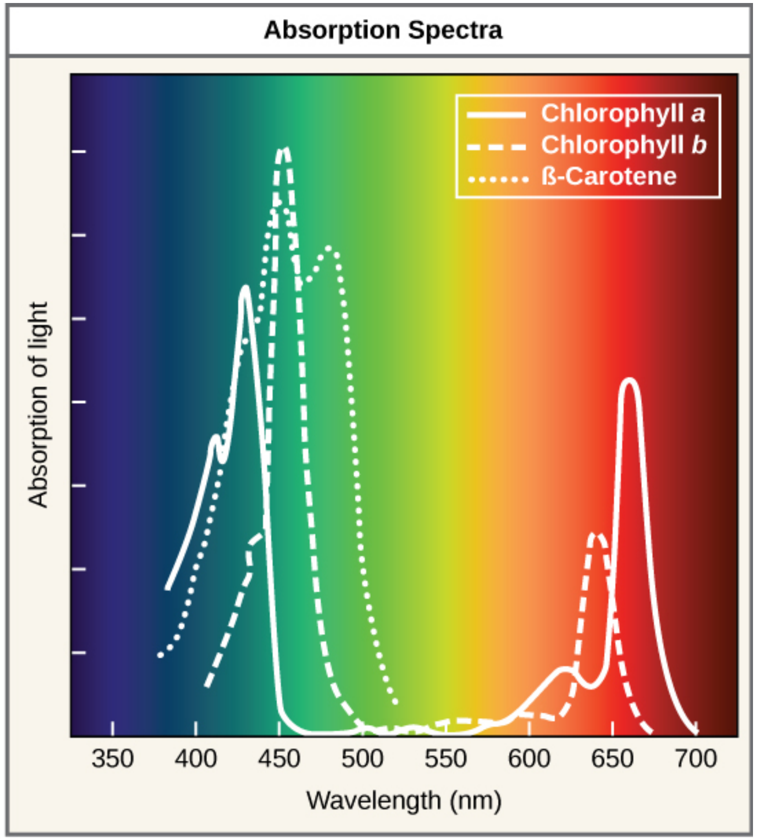
Chlorophyll a



Chlorophyll b



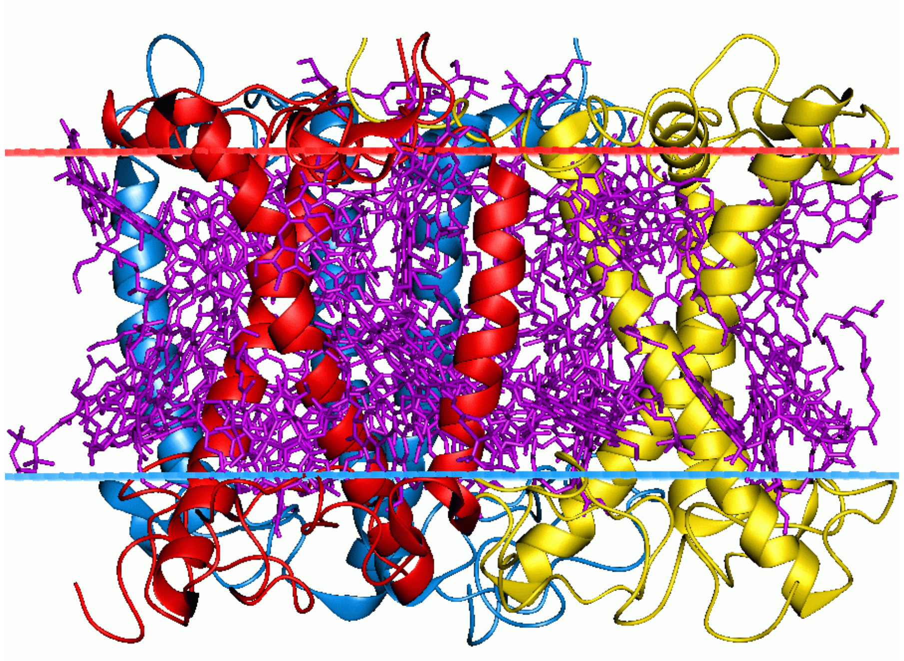
β-Carotene

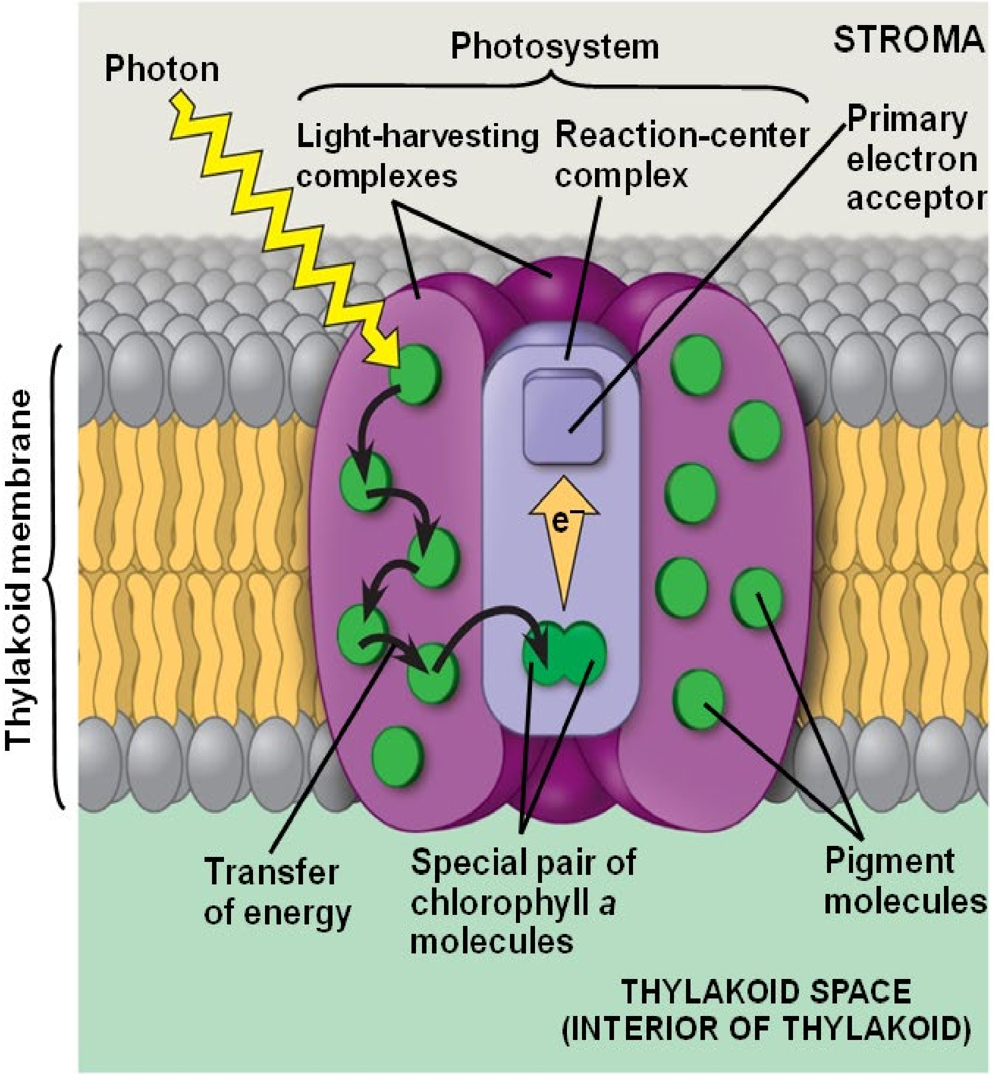


(d)

The light harvesting complex

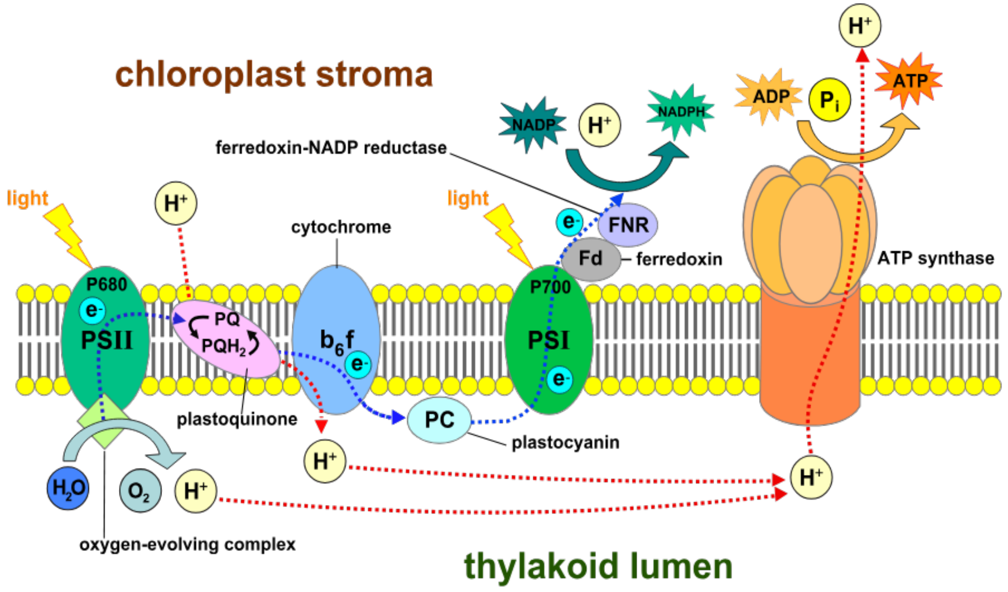
About 250 to 300 chlorophyll molecules are incorporated in each photosystem. Energy is transferred via Förster resonance energy transfer (FRET) from molecule to molecule until it reaches the special dimer where the energy is trapped and electron transfer occurs to the primary electron acceptor. The quantum efficiency of photochemical quenching is close to 100% at low light intensity and decreases to 70% at high light intensity.





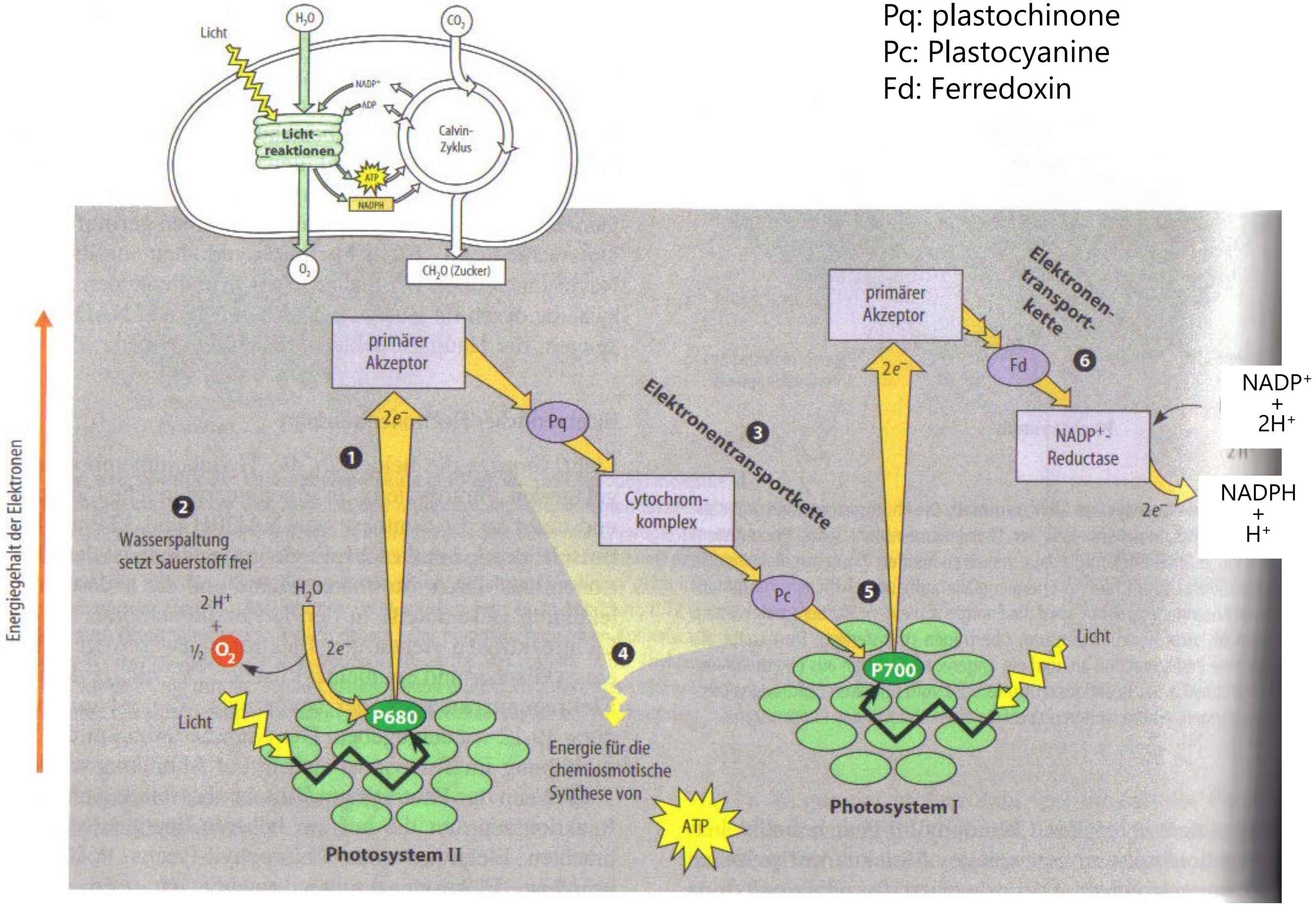
The so called "Z-scheme "

Both photosystem I and photosystem II are composed of the same dyes, mainly chlorophyll-a molecules. Nevertheless, the binding to different proteins makes that their absorption is slightly different. The reaction centre of photosystem I has an absorption maximum at 700 nm while the one of photosystem II is at 680 nm. This also lead to the name P680 and P700.

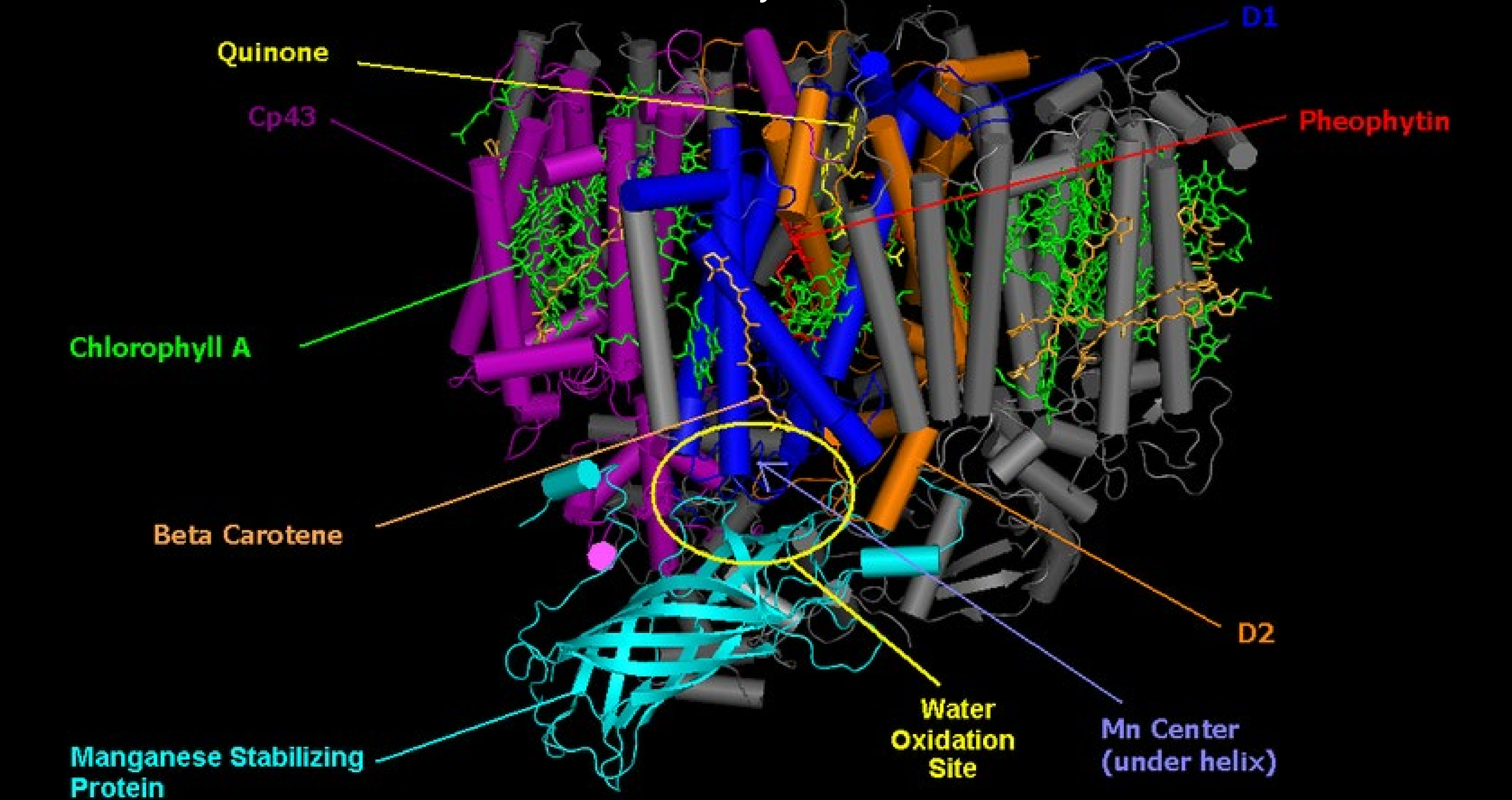


Legend:

Pq: plastochinone
Pc: Plastocyanine
Fd: Ferredoxin



Photosystem II



The overall yield of photosynthesis

We can analyze the energy conversion yield of water and CO_2 to GP3 and oxygen. Furthermore we can use the assumption that the photochemical quantum yield is close to 100% (low light-intensity). $\eta_{spectrum} = 50\%$ is the fraction of photons from the sun absorbed by chlorophyll etc. in the leaf (range of 400 nm to 700 nm). Regarding the number (=8) photons absorbed photons (average wavelength of 550 nm) to drive the reaction, the energy yield for the reaction can be calculated as follows:

$$\eta_{energy} = \frac{reaction\ free\ energy}{photonic\ energy} = \frac{4.96\ eV}{8 \cdot 2.25\ eV} = 27.5\%$$

Finally, 30% are lost due to incomplete foilage, reflection, scattering etc. giving $\eta_{loss} = 70\%$. For the total energy conversion yield one obtains:

$$\eta_{tot} = \eta_{spectrum} \cdot \eta_{energy} \cdot \eta_{loss} = 9.5\%$$

Considering recycling of hydrocarbons and photorespiration during the night $\eta_{resp} = 60\%$ the total efficiency would drop to 5.8 %.

This is considerably lower than todays PV modules ($\eta_{PCE} = 18\%$) even considering that fuel would be generated with electricity (e.g. H_2 using an electrolyzer with $\eta_{electrolyzer} = 80\%$. For H_2 to liquid fuel, conversion efficiency would be 50 %.)

A few more numbers

Experimentally we define the photobiological conversion yield by using the weight of dry biomass produced and the solar irradiation during growth.

Maize: 3.4%
Wheat: 1.7%
Peas: 1.9%
Rice: 1.4%
Sugar cane: 2.8% (D. O. Hall, FEBS letters, Volume 64, number 1, D. O. HALL)

Despite these seemingly low numbers:

- The yearly energy production due to photosynthesis amounts to 10 times the global human primary energy consumption in 2025 (i.e. $1.8 \cdot 10^{14}$ kWh/year).

- The yearly production of carbohydrates due to photosynthesis amounts to $160 \cdot 10^{9}$ tons. No other chemical process on earth is nearly that productive. For example, the production of polymers from crude oil amounts to 445 mio. tons (2025)