12

The Evolution of Photosynthesis and its Environmental Impact

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Abstract. Photosynthesis in plants is a very complicated process, utilizing two photosystems in series to carry out the very energy-demanding process of oxidizing water to molecular oxygen and reducing carbon dioxide to organic compounds. The first photosynthetic organisms, living more than 3.4, perhaps even 3.8 Ga, i.e. American billion (10^9) years ago, carried out a simpler process, without oxygen production and with only one photosystem. A great variety of such one-photosystem photosynthesizers are living even today, and by comparing them, and from chemical fossils, researchers are trying to piece together a picture of the course of the earliest evolution of photosynthesis. Chlorophyll *a* probably preceded bacteriochlorophyll *a* as a main pigment for conversion of light into life energy. The process of carbon dioxide assimilation, today taking place mainly in conjunction with photosynthesis, is even older than photosynthesis itself. Oxygenic photosynthesis, i.e. photosynthetic production of molecular oxygen, first appeared in ancestors of present-day cyanobacteria more than 2.7, perhaps already 3.7 Ga ago. Cyanobacteria entered into close association with other organisms more than 1.2 Ga ago, and chloroplasts in green algae and green plants as well as those in algae on the "red" line of evolution (red algae, cryptophytes, diatoms, brown algae, yellow-green algae and others) stem from a single early event of endosymbiotic uptake of a cyanobacterium into a heterotrophic organism. Only ecologically unimportant exceptions from this rule have been found. The chloroplasts on the "red line", excepting those of red algae, stem from a single event of secondary endosymbiosis, in which a red alga was taken up into another organism. There are also examples of tertiary (third level) endosymbiotic events. Thylakoids in land plants are partially appressed and forming grana, while those of, e.g., red algae do not have this structure, and this difference can be explained by the different spectra of ambient light. At the end of the chapter a brief review is given of the evolution of the assimilation of carbon dioxide, the adaptation to terrestrial life, and the impact of photosynthesis on the terrestrial environment.

12.1 Introduction

The Earth began to form about 4.6 Ga (gigayears, billion years) ago. Thirty million years later a core had formed (Yin, Jacobsen, Yamashita, Blicher-Toft *et al.* 2002;

Kleine, Münker, Mezger and Palmer 2002), and 4.4 Ga ago there was a continental crust and an ocean (Wilde, Valley Peck *et al.* 2001). Between 4.2 and 3.7 Ga ago the Earth was subjected to ”the late heavy bombardment” (Gomes, Levison, Tsiganis, and Morbidelli, 2005 and literature cited there), which is by many thought to have wiped out any life that might have existed at that time. The first organisms emerging after that cataclysm were not able to carry out photosynthesis. Probably they got their metabolic energy by reducing carbon dioxide to methane, using hydrogen as reductant. But photosynthetic life is also very ancient, probably at least 3.4 Ga (Tice and Lowe 2004, 2006). The first photosynthesis differed from the process taking place in plants now, but there are some common features, and a direct line evolution from these first forms.

12.2 A Short Review of Plant Photosynthesis

Plant photosynthesis consists mainly of an oxidation of water to molecular oxygen, and a reduction of carbon dioxide to organic matter, primarily carbohydrate. It takes place in the chloroplasts, with one set of reactions in the pigment-rich thylakoid membranes, and with another set of reactions in the stroma, a solution of enzymes between the membranes (Figs. 12.1 and 12.2).

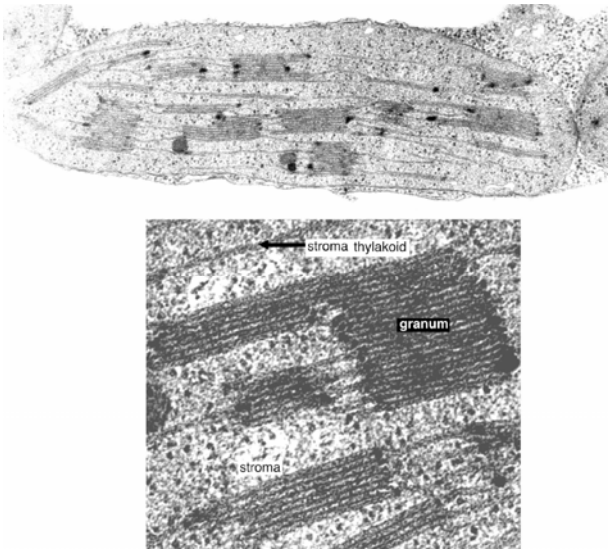

Fig. 12. 1. Chloroplast from tobacco plant (top), and detail at higher magnification (below) showing details of grana and thylakoids. The stroma thylakoids (stroma lamellae) run through the stroma between the grana. Courtesy Professor Claes Weibull, Lund University.

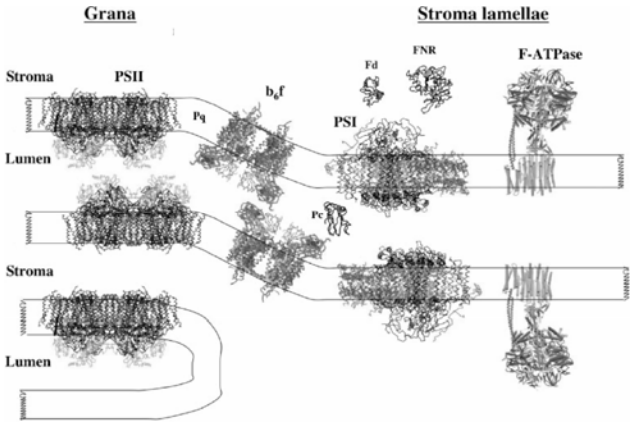

Fig. 12. 2. The arrangement of molecules participating in photosynthesis in a green plant. Of the large protein complexes photosystem II (PSII) is located predominantly in the grana lamellae (the parts of the thylakoid memebranes forming grana) and photosystem I (PSI) and F-ATPase mainly in the stroma lamellae, but the photosystems are mobile. Electrons taken from water by PSII are transferred to the cytochrome b6f complex via plastoquinone (Pq), and from there to PSI via plastocyanin (Pc). Electrons from PSI go via ferredoxin (Fd) and ferredoxin-NADP reductase (FNR) to NADP. The resulting NADPH is used as a reductant in carbon dioxide assimilation, which takes place in the stroma. Coupled to the electron transport is a translocation of protons from the stroma to the lumen. Protons flowing back to the stroma via the F-ATPase drive the synthesis of ATP, which is also used in carbon dioxide assimilation. Variations of this scheme occur, and algae on the red line of evolution differ in several respects (see sections 12.7 and 12.8). From Nelson and Ben-Shem (2002).

In the thylakoid membranes the following takes place: The light is absorbed in chlorophyll *a*, and also in other pigment molecules. The absorbed energy is transferred to a reaction center. Among other prosthetic groups this contains chlorophyll *a*. There are two kinds of reaction center-containing pigment-protein complexes, called photosystem I (PSI) and photosystem II (PSII), see Figs. 12.2 and 12.3. They can be regarded as light-powered ”electron pumps” connected in series by another protein complex (the cytochrome bf complex) and two smaller, mobile molecules, plastoquinone and plastocyanin. The ”electron pumps” lift electrons from an energy-poor state in water to an energy-rich state in a substance called ferredoxin. What remains of the water from which electrons have been removed is free oxygen (molecular oxygen, O_2) and hydrogen ions (protons). The protons also gain energy by being pumped into the interior of the thylakoids where they attain a higher concentration than they had before. This energy is then used to produce energy-rich phosphate, ATP. In the stroma, reduced ferredoxin and ATP and protons are used to re-

duce carbon dioxide to carbohydrate. This is a very short description of the essential steps of photosynthesis. For details the reader is referred to Ke (2001); Blankenship (2002); Golbeck (2006, for PS I) and Wydrzynski and Satoh (2005, for PS II).

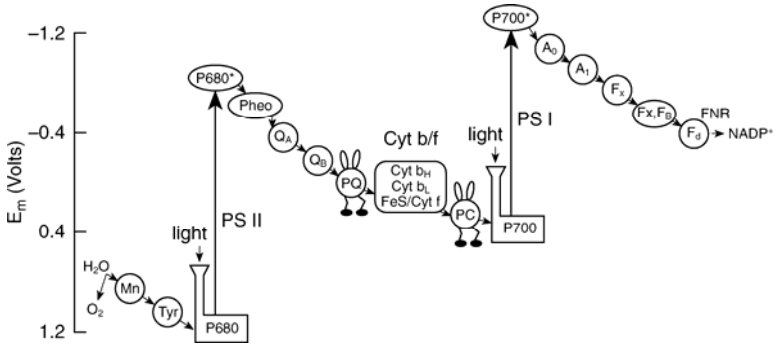

Fig. 12. 3. Cartoon of the electron transport in plant photosynthesis, the so-called Z-scheme. Light is collected by antenna pigments, symbolized as funnels and conducted to the reaction center pigments (P680 in PS II and P700 in PS I, in both cases chlorophyll *a*). Electrons are "sucked" from water via manganese atoms in the water-splitting enzyme and tyrosine residues in a PS II peptide. The photosystems "lift" the electrons to a higher energy (more negative redox potential). They leave the reaction center chlorophylls, which temporarely become positively charged, and flow over a chain of electron carriers. Of these Pheo (pheophytin), Q_A and Q_B (quinones) as well as A_0, A_1, F_x and F_A, F_B (iron-sulfur centers) are membrane bound, while PQ is plastoquinone diffusing in the membrane lipid, PC a small protein (plastocyanin) diffusing in the aqueous lumen space, and F_d (ferredoxin) and $NADP^+$ diffuse in the stroma. FNR stands for the enzyme ferredoxin-$NADP^+$ reductase. The feet and rabbit ears on PQ and PC symbolize their mobility. Between them is the large cytochrom b_6/f complex with several electron carriers. When $NADP^+$ takes up 2 electrons and one proton it becomes NADPH, which is used for carbon dioxide reduction. From Govindjee (2000).

12.3 The Domains of Life

The living world is nowadays subdivided into three "domains" or main organismal groups, i.e. Archaea (formerly called archaebacteria), Bacteria (eubacteria, or just bacteria), and Eukarya (eukaryotes, which comprise all organisms known 200 years ago, and many others, plants, fungi, animals, and people). Photosynthesis has arisen only in the domain Bacteria. That plants, too, can carry out photosynthesis is because the precursors of plant cells have combined with bacteria. More about this later. For the story of the discovery of Archaea, see Woese (2005).

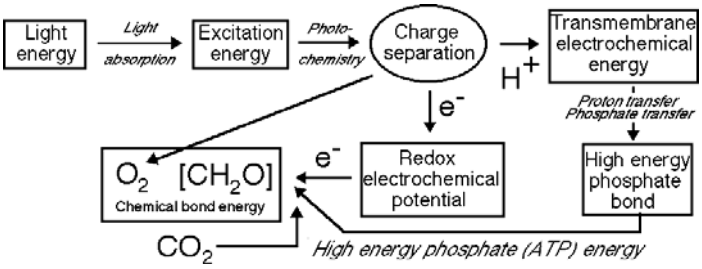

Fig. 12.4. Energy transformations in photosynthesis. Light energy absorbed by antenna pigments is transferred to reaction centers where charge separation takes place. The positive charges are transferred to water, which splits into hydrogen ions (H^+) and molecular oxygen (O_2). The non-equilibrium distribution of hydrogen ion results in energy trapped in ATP, while the energy gained by electrons make it possible for them to act as reductants for carbon dioxide, aided by the energy from ATP.

12.4 Predecessors of the First Photosynthetic Organisms

As was already mentioned, plant photosynthesis can be divided into two processes: (1) oxidation of water and transport of electrons and protons in the thylakoids, with ensuing synthesis of ATP, and (2) the reduction of carbon dioxide, taking place in the stroma. Of these, the reduction of carbon dioxide is a much more ancient process than the oxidation of water. We have already mentioned one type of light-independent carbon dioxide reduction, namely the reduction to methane with hydrogen as reductant. Also other light-independent forms of carbon dioxide reduction are more ancient than that driven by the thylakoids. The reduction taking place in the stroma of plant chloroplasts has evolved from one of these early light-independent processes. Plants use the enzyme rubisco (ribulose-1,5-bisphosphate carboxylase/oxygenase) to bind carbon dioxide, and also some non-photosynthetic bacteria use this enzyme. One type of such bacteria which have recently received much attention is bacteria living at deep sea hydrothermal vents, where hydrogen sulfide emerges. They get their energy by oxidizing the hydrogen sulfide with molecular oxygen, O_2. The first chemoautotrophs could not do that, since there was no free oxygen present. But they could get energy by reducing carbon dioxide with hydrogen, and later there emerged many other kinds of chemoautotrophs.

Rubisco has similarities to other enzymes with other functions in bacteria which do not fix carbon dioxide, such as 2,3-diketo-5-methylthiopentyl-1-phosphate enolase in *Bacillus subtilis* (Ashida, Saito, Kojima *et al.* 2003; Ashida, Danchin, Yokota *et al.* 2005), and may have evolved from a protein involved in sulfur metabolism.

When the first photosynthetic organisms appeared they could thus inherit many useful biochemical components from predecessors. This does not hold only for those soluble components present in the stroma in plant chloroplasts, but also many of the electron transporters in the thylakoid membranes. Such components are the iron-sulfur proteins (of which there are several kinds in the thylakoids; in addition the soluble ferredoxin belongs to the iron-sulfur proteins). Iron-sulfur proteins are thought to have ancestry back to life's beginning, and their active center is derived from inorganic iron sulfide. Eck and Dayhoff (1966) thought that the protein part of ferredoxin had evolved from a peptide with only four amino acids. Other types of electron transporters in the thylakoids with very ancient orgins are quinones and cytochromes. The most important of the thylakoid pigments, chlorophyll, is derived from the same biosynthetic pathway that leads to heme, the central part of cytochromes. Complex porphyrin-like molecules having a ring composed of four smaller, five-membered rings, similar to those forming parts of heme and chlorophyll, are thought to have arisen before the emergence of life, and could have been one of the raw materials for life.

Cytochromes can be traced back to the "last common ancestor" of all extant organisms. This organism lived before there was any photosynthesis, and PSI and PSII are possibly descendents of cytochrome *b* (Xiong and Bauer 2002). There are similarities in structure between the cytochrome b6f containing complex that mediates electron transfer between the photosystems and the photosystems themselves. The cytochrome complex also contains one molecule of chlorophyll *a* per monomer (Bald, Kruip, Boekema, and Rögner 1992; Huang, Everly, R. M. Cheng *et al*. 1994; Pierre *et al.* 1997; Stroebel *et al.* 2003; Kurisi *et al.* 2003; Dashdori *et al.* 2005). Cytochromes *b* from various sources, as well as other heme compounds, can be photoreduced (Pierre, Bazin, Debey and Santus 1982; Asard, Saito, Kojima *et al*. 1989; Gu, Li, Sage, and Champion 1993; Rubinstein 1993, Zhang *et al.* 2005).

12.5 The First Photosynthesis

The first photosynthetic organisms did not have two photosystems in series, as plants do, but only one. They could not oxidize water to molecular oxygen. Thus far the researchers agree, but no further. Extant photosynthesizing bacteria can, with regard to photosystems, be divided into three main groups. One is cyanobacteria (it used to be referred to as blue-green algae), which have two photosystems (PSI and PSII) connected in series and are able to evolve oxygen, and we shall return to them. Another group consists of green sulfur bacteria plus heliobacteria, which have a photosystem resembling PSI in plants and cyanobacteria, The third group consists of purple bacteria plus green nonsulfur bacteria, which have a photosystem resembling photosystem II in plants and cyanobacteria, but it has no water-oxidizing part. All photosystems, PSI-like as well as PSII-like have important similarities that there is no doubt that they all derive from the same ancestral photosystem.

Where is the origin of this first photosynthesizer? Some years ago Nisbet, Cann, and VanDover (1995) suggested that the ability to photosynthesize would have evolved from an orientation (phototaxis) system in bacteria living deep in the sea near hydrothermal vents, and which were able to perceive the heat radiation from the vents. Björn (1995) showed that in any case it would not have been possible to drive photosynthesis by the heat radiation from those vents. But since then White, Chave, Reynolds *et al.* (2000, 2002a,b) have shown that the vents radiate not only heat radiation, but also another kind of light which probably originates from oxidation of sulfide (Tapley *et al*. 1999). Even if White, Chave, and Reynolds (2002a) arrived at the conclusion that the light is too weak to sustain autotrophy, Beatty, Overmann, Lince *et al.* (2005) have later shown that photoautotrophic bacteria are really present in the vicinity of the vents. The hypothesis of Nisbet, Cann, and VanDover (1995) is therefore still worth persuing further. One has to remember that chemiluminescence from sulfide oxidation probably has a prerequisite of molecular oxygen , but it is possible that also other kinds of light emission could have resulted in such an environment with steep temperature and chemical gradients.

Hirabayashi, Ishii, Takaichi *et al*. (2004) have cultivated a photosynthetic bacterium, *Chlorobium phaeobacteroides*, in very weak light (less than 3 micromol photons m^{-2} s^{-1} of photosynthetically active radiation). Raven, Kübler and Beardall (2000) arrived by theoretical considerations at the opinion that a photosynthetic organism might be able to live from as little as 4 nmol photons m^{-2} s-^{1} (0.004 micromol photons m^{-2} s^{-1}) as a daily average.

The most ancient type of photosynthesis of which we have undisputable preserved traces is a 3.416 Ga old chert in South Africa (Tice and Lowe 2004, 2006), but the carbon istotope composition in 3.8 Ga old graphite in Greenland has been attributed to photosynthesis (Olson 2006). These organisms seem to have used molecular hydrogen as reductant. Later other forms developed, which used other reductants, such as divalent iron or hydrogen sulfide. Old morphological fossils attributed to photosynthetic organisms have been described by Awramik (1992) and others.

Green sulfur bacteria and heliobacteria, which have the same type of PSI-like photosystem reaction center, are not closely related in other respects. Neither all the bacteria having PSII-like photosystems are closely related. *Chloroflexus auranticus* with a photosystem of type II has about the same pigment complement as *Chlorobium tepidum* with a photosystem of type I, and both bacteria are regarded as being rather closely related. These ”inconsistensies” are explainable by ”horizontal” or ”lateral” gene transfer, meaning that a gene can be transferred from one unrelated organism to another (Raymond and Blankenship 2003; Raymond, Siefert, Staples and Blankenship 2003). During the enormous time spans of bacterial evolution, there have been sufficient occasions for transfer of all the genes required for construction of a photosystem. But it could also be that the group to which *Chloroflexus* and *Chlorobium* belong is the group in which the differentiation between photosystems of type I and type II has taken place during evolution.

12.6 Appearance of Oxygenic Photosynthesis

With the exception of cyanobacteria with PSII, bacteria lack the water oxidizing (oxygen evolving) part, even if they otherwise possess a photosystem of type II. The type II photosystems of these bacteria differ also in some other respects from PSII of plants. Plant PSII reaction center has 6 losely interacting pigment molecules in place of the arrangement with a tightly coupled "special pair" of (bacterio)chlorophyll molecules in the bacteria. The arrangement with a tightly coupled pair of (bacterio) chlorophyll molecules gives a lower-lying first excited state than what a single molecule would have. As long as the energy quanta for the electron transport need not be very great, this is an advantage in that it provides an efficient sink for the excitations in the pigment antenna. For the oxidation of water there is a need for larger quanta, and this is probably the reason there is a different pigment arrangement in the reaction center of oxygenic PSII (Rutherford and Faller 2002). It is well-known that dimerization causes a shift to longer wavelength for the long-wavelength peak in the absorption spectrum, i.e. a lowering of the energy for the lowest-lying excited state.

Dismukes *et al*. (2001) have come up with an apparently well founded theory for how the water oxidizing system could have evolved via a bicarbonate-oxidizing and oxygen-evolving intermediate stage. The interesting finding of Warburg, Krippahl, and Jetschma (1965) that oxygen evolution is stimulated by carbon dioxide was the first indication of this. Clausen, Junge, Dau and Haumann (2005) and Clausen, Beckmann, Junge and Messinger (2005) have shown that *free* carbon dioxide is not an intermediate in the oxygen evolution of plants. Bicarbonate has been shown to function on both the electron acceptor and donor sides of PS II (review by van Rensen, Xu and Govindjee 1999). Further, in the crystal structure of PS II, Ferreira, Iverson, Maghlaoui *et al.* (2004) have modeled one bicarbonate anion near the non-heme iron on the acceptor side, and another on the electron donor side.

There are different opinions about how the evolution has taken place of organisms with only one photosystem to cyanobacteria, algae and terrestrial plants with two photosystems in series. One can imagine that, from the first photosynthetic organism there has taken place an evolution along two lines, in both cases still with a single photosystem. One line has led to bacteria having photosystems of type I, the other one to bacteria with photosystems of type II. The two kinds of bacteria have then entered into symbiosis which has become more and more intimate, until the result was an integrated organism, which evolved into the first cyanobacterium. Another possibility is that gene transfer has taken place from one organism to another without complete fusion of the two lines of evolution. A third possibility is suggested by Allen (2005) and will be further described below.

Much of the views of how the early evolution of photosynthesis has taken place is based on comparisons between extant organisms. But there is also geological evidence to rely on. The morphological fossils do not give much guidance, except that the occurrence of heterocyst-like structures strengthen the view that both cyanobacteria and an oxygen-containing atmosphere are of great antiquitiy (Tomitani. A., Knoll, A.H., Cavanaugh, C.M, and Ohno 2006). But there are also chemical and

physical fossils, even if their interpretation is often debated. The substance 2-α-methyl hopane is regarded as a reliable signature of the presence of cyanobacteria (Summons *et al.* 1999), and it has been found in 2.7 Ga old rocks (Brocks *et al.* 2003). However, similar compounds have also been traced to anaerobic bacteria. The ratio between the amounts of the carbon isotopes ^{13}C and ^{12}C in organic compounds has also played a part in the discussions. Sometimes a certain ratio has been seen as a sign that the carbon has been assimilated by the enzyme rubisco, or been seen as a signature of a certain kind of assimilating organism. Banded iron formations (BIFs) have been interpreted in different ways. Nowadays it is thought that the formation of at least some of them has been mediated by photosynthetic bacteria which have oxidized divalent to trivalent iron, instead of oxidizing water as plants do (Kappler *et al.* 2005).

Already the type of photosynthesis carried out by cyanobacteria needs a very complicated machinery with cooperation between two photosystems in series and an enzyme which manages to collect four oxidation equivalents for the very difficult oxidation of water. Most researchers think that this has required a very long evolution, during a vast expanse of time, from the first primitive bacterial photosynthesis. Contrary to this view, Rosing and Frei (2004) have arrived at the conclusion that such photosynthesis took place already 3.7 Ga ago. This opinion rests on the ratio between thorium and uranium in the old sediments. Under reducing conditions both elements are insoluble, and therefore the ratio between their concentrations should not change during sedimentation. But in fact, the ratio between the concentrations has changed, so some kind of fractionation must have taken place. This can happen in the presence of oxygen, when uranium is oxidized to soluble uranyl complexes. Thorium, on the contrary, remains insoluble under such conditions. More recently there have been several objections to even regard deposits of such age as showing traces of any kind of life (e.g., Brasier, Green, Lindsay *et al.* 2005; Moorbath 2005), and other explanations have been afforded for the thorium/uranium fractionation.

Small amounts of hydrogen peroxide could have formed abiotically in the Archaean age by action of ultraviolet radiation on pyrite and there have been speculations that oxygenic photosynthesis evolved as a protective decomposition of hydrogen peroxide (Borda, Elsetinow, Schoonen and Strongin 2001). However, the structure of the oxygen evolving complex, which has no similarity to other manganese hydrogen peroxide, does not support such a theory.

The structure of the oxygen-evolving complex (Yano, Kern, Sauer *et al.* 2006) has similarities to some manganese minerals, and probably inherited its structure from these (Sauer and Yachandra 2002). Photochemical oxidation of manganese driven by ultraviolet radiation may have taken place early in the Earth's history, and could have been the starting point for the evolution of the oxygen-evolving mechanism in oxygenic photosynthesis (Anbar and Holland 1992; Allen and Martin 2007). Related to this is the finding that UV inhibition of PSII in present-day organisms is partly caused by UV absorption by manganese (Hakala, Tuominen, Keränen *et al.* 2005; Hakala, Rantamäki, Puputti *et al.* 2006).

According to a theory presented by Allen (2005) and further elaborated by Allen and Martin (2007) organisms having two photosystems are older than oxygenic photosynthesis. The ancestral photosystem was probably more similar to PSI than to PSII (Baymann, Brugna, Mühlenhoff and Nitschke 2001; Mulkidianian, Koonin, Makarova *et al.* 2006). After gene duplication a PSII-like photosystem evolved within the same organism, but still without oxygen evolution (Fig. 12.5). The evolution pressure for the change in properties of the new photosystem could have been changing environmental conditions, in particular changing redox conditions. Because of the variability of the environment it would have been adventageous for the organism to keep both photosystems, and a regulatory switch evolved which made it possible for the organism to transcribe the gene most appropriate for the moment. With increasing scarcity of other electron donors, the PSII-like system evolved towards a state where it could connect to a manganese compound that was already able to be photooxidized by ultraviolet radiation, but could from now on be oxidized through PSII by light of longer wavelength. The mechanism for switching between transcription of one or the other photosystem gene then became superfluous and disappeared. The first cyanobacterium had evolved.

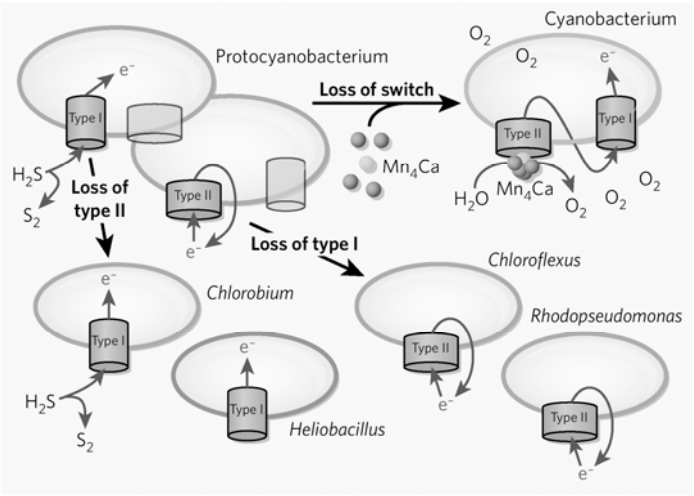

Fig. 12. 5. An early photosynthesizer having two photosystems and a switch to select expression of the gene for one or the other (upper left) could, during evolution, lose one or the other of the genes and turn into one of several types of non-oxygenic photosynthetic bacteria (either as *Chlorobium* or *Heliobacillus* with type I photosystem or as *Chloroflexus* or *Rhodopseudomonas* with type II photosystem). Alternatively it could, under appropriate environmental conditions, lose the switch and evolve into an organism constitutively equipped with two photosystems, and then evolve into a cyanobacterium with oxygenic photosynthesis. From Allen and Martin (2007). Reprinted by permission from Macmillan Publishers Ltd: Nature 445, 610-612, copyright 2007.

Once the cyanobacteria emerged and started to produce free oxygen, several hundred million years elapsed before oxygen started to accumulate in the atmosphere. The reason for this was that there was so much of reducing substances (divalent iron, reduced sulfur, probably also methane) that had to be oxidized first, and reproduction of cyanobacteria might also have been hampered by ultraviolet radiation and other environmental conditions. It took an even longer time before the deep strata of the ocean became oxidized, and this led to chemical problems which delayed full oxygenation (see below). But once the oxygen started to accumulate, many life forms were poisoned by the oxygen. Never before or after has any other form of life dominated the planet so completely for such a long time as cyanobacteria did, about a billion years. In some ways the cyanobacteria are still very important, not the least in an altered form, as the chloroplasts in plants and algae.

12.7 From Cyanobacteria to Chloroplasts

" Let us imagine a palm tree, growing peacefully near a spring, and a lion hiding in the bush nearby, all of its muscles taut, with blood thirsty eyes, prepared to jump upon an antelope and to strangle it. The symbiotic theory, and it alone, lays bare the deepest mysteries of this scene, unravels and illuminates the fundamental principle that could bring forth two such utterly different entities as a palm tree and a lion. The palm behaves so peacefully, so passively, because it is a symbiosis, because it contains a plethora of little workers, green slaves (chromatophores) that work for it and nourish it. The lion must nourish itself. Let us imagine each cell of the lion filled with chromatophores, and I have no doubt that it would immediately lie down peacefully next to the palm, feeling full, or needing at most some water with mineral salts."

(Constantin Sergeevich Mereschkowsky (1905) Über Natur und Ursprung der Chromatophoren im Pflanzenreiche. Biol. Centralbl. **25**: 593–604; Annotated English translation by W. Martin and K.V. Kowallik (1999) Eur. J. Phycol. 34, 287–295)

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The theory that chloroplasts are derived from cyanobacteria, which were long ago taken up by non-photosynthetic organisms is more than one hundred years old. Complete proof that it is correct has been obtained from molecular biology. By comparisons of DNA sequences the cyanobacterial ancestry of chloroplasts has been established, just as it is now certain that mitochondria are descendents of another bacterial clade.

Among chloroplasts there are two developmental lines, the "green line" (in green algae and plants) and the "red line" (in red algae and most other algae). Even if some researchers still believe that these two lines start with two separate endosymbiotic events, the contrary view prevails. This means that all chloroplasts are derived from one original chloroplast, which has appeared when a cyanobacterium entered another cell. It is a little surprising that it is so, since we have so many other examples of very intimate symbiotic relationships between a number of algae and a number of other organisms. A very recent appearance of a new type of chloroplast has also been

observed: Marin, Nowack. and Melkonian (2005) have found an amoeba containing a plastid with a different cyanobacterial origin. This does not detract from the fact that the chloroplasts of all major organismal groups derive from a single endosymbiotic event. The chloroplasts of green algae, glaucophytes, land plants and red algae are directly derived in such a way, while other chloroplasts on the red line are derived by secondary endosymbiosis, in which red algae were taken up by non-photosynthetic organisms. The chloroplasts of some groups, especially some dinoflagellates, have an even more complicated evolutionary history (e.g., Stoebe *et al.* 2003).

Many cyanobacteria have red phycoerythrin and blue phycocyanin (and a small amount of another blue protein, allophycocyanin) as light collecting pigments. They are assembled into complexes known as phycobilisomes, which are located on the external side of the thylakoid membranes which house the photosystems (PSI and PSII). (The most primitive cyanobacteria do not have any thylakoids, but carry out photosynthesis by their outer cell membrane, but they do have phycobilisomes; Gutiérrez-Cirlos *et al.* 2006.) Red algae have the same pigment arrangement. One type of cyanobacterium, sometimes referred to as prochlorophytes (after *Prochloron*, the genus first discovered), have, instead of phycocyanin and phycoerythrin , chlorophyll *a* and chlorophyll *b*, as green algae and plants do. It was once thought that the green and the red evolutionary lines each stemmed from two different types of cyanobacteria. Later a cyanobacterium (*Prochlorococcus marinus*) was discovered which is equipped with both sets of light-collecting pigments (Hess 1996). Most researchers therefore now believe that the first chloroplast was derived from a cyanobacterium having both phycobilisomes and chlorophyll b. In each of the developmental lines, one of the pigment sets would have been lost later. The common origin of the chloroplasts on both lines is strengthened by the fact that the protein import machinery is of the same kind. These import systems must have evolved in connection with the genesis of chloroplasts, or later, because they would not be required as long as the cyanobacteria were independent with all required proteins made by themselves. The nuclear genes on both developmental lines are in general so similar that there cannot have occured endosymbiosis in quite different organisms.

Fossils of red algae have been found which date back 1.2 Ga (Butterfield 2000, Fig. 12.6). These are the oldest organisms for which one has been able to infer sexuality. Other algae on the red line, for instance cryptophytes, diatoms, brown algae and yellow-green algae, have evolved by uptake of red algae into a non-photosynthetic organism, and also this event is thought to have taken place only once (Petersen, Teich, Brinkmann and Cerff, 2006). One reason to believe that these different algal chloroplasts have resulted from a single secondary endosymbiotic event is the surprising fact that they all have the same type of phosphoribulokinase (an enzyme of the Calvin-Benson-Bassham cycle) as organisms on the green line of chloroplast evolution, a type which is very different from the type present in red algae. The most probable interpretation of this is that soon after the secondary endosymbiotic event a lateral gene transfer from the green line has taken place, and the phosphoribulokinase from the red alga has been lost. Another indication that the

secondary plastids on the red line are monophyletic is that they all share a type of glyceraldehyde-3-phosphate dehydrogenase (another enzyme in the Calvin-Benson-Bassham cycle), which does not occur in any other organisms (not in cyanobacteria, not in red algae, and not in organisms on the green evolutionary line) (reviewed by Petersen, Teich, Brinkmann and Cerff 2006). In contrast, secondary plastids have evolved several times on the green line (e.g., Rogers, Gilson, Su *et al.* (2007).

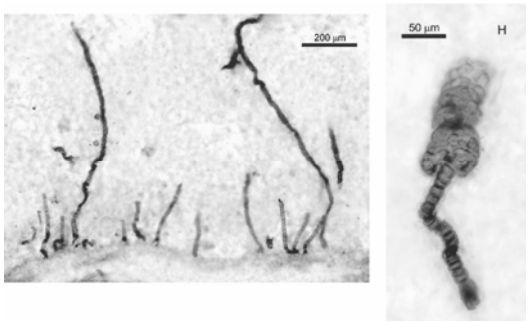

Fig. 12.6. 1200 Ma old fossils of the red alga *Bangiomorpha pubescens*. From Butterfield (2000).

The copper protein plastocyanin is lacking in chloroplasts on the whole red line of evolution (and also in some cyanobacteria). The electrons from the cytochrome b6f complex are instead carried to PSI by a small soluble cytochrome, cytochrome c_6 (Raven 1999). Many green algae and cyanobacteria can switch to using cytochrome c_6 when deficient in copper. An analogues cytochrome (cytochrome c_2) is used by photosynthetic purple bacteria (Hu *et al.* 2002). Plastocyanin has probably evolved long after the emergence of oxygenic photosynthesis, as copper was tied up in insoluble sulfide during a period of the Earth's history (see below). On the other hand, iron is less accessible now than it was before the oxygenation of the atmosphere.

12.8 Evolution of Photosynthetic Pigments and Chloroplast Structure

Forms of chlorophyll typical for extant photosynthetic bacteria, which do not evolve oxygen, are collectively referred to as bacteriochlorophyll. Chlorophyll *a* is a biochemical precursor to these chlorophyll forms. For this reason, Granick (1957) postulated that bacteria with bacteriochlorophyll as photosynthetic pigment have evolved from those who have chlorophyll *a*. But those present-day bacteria which have bacteriochlorophyll (and only one photosystem) seem to be more primitive and carrying out a simpler kind of photosynthesis than cyanobacteria, which are the only

extant bacteria with chlorophyll *a*. The solution to this apparent paradox could be that there had existed now extinct non-oxygenic organisms having only one photosystem, with chlorophyll *a*.

The reasons that chlorophyll is a suitable pigment for photosynthesis are discussed in Chapter 9, Section 9.2, and by Kiang *et al.* (2007) from a spectral perspective, and by Mauzerall (1976) from a chemical perspective.

When two different photosystems started to evolve in the same organism (a primitive predecessor of present-day cyanobacteria) the spectra of the pigment molecules in their reaction center of PSI began to differ from the spectra of the pigment molecules in the PSII reaction center. This has to do with the different functions of the two photosystems. In PSII the difficult oxidation of water requires big energy quanta, and this sets an upper wavelength limit for the chlorophyll molecules involved. The reduction of ferredoxin by PSI does not require so big energy quanta, and in order to best make use also of longer wavelength light the chlorophyll in PSI acquired a longer wavelength spectrum than that in PSII. The molecules are in both cases molecules of chlorophyll *a* (except in some cyanobacteria, such as *Acaryochloris*, where it is chlorophyll *d*), but the spectra differ due to different environments around the molecules.

When the cyanobacteria had turned into chloroplasts, the further evolution along the "green" path (green algae and plants) came to differ from that along the "red" path (red algae, diatoms, brown algae etc.). Already the cyanobacteria were equipped with very sophisticated light-collecting antennae in the form of phycobilisomes. These can be regarded as a kind of energy transformers, which collect all kinds of light and adapt the size of the energy quanta so they fit the energy levels of chlorophyll. The red algae inherited these structures rather unchanged. Cryptophytes have the same kinds of red and blue pigments arranged in a slightly different way. But why have these equisite light transformers disappeared from the rest of the "red" line, and never appeared on the line leading to land plants?

We probably have a correct explanation for this now, but it is a bit involved and not quite easy to understand. We shall recount here in essence the explanation given by Anderson (1999). This has to do with the different light environments to which the organisms have adapted. In order not to make it too complicated, we shall limit ourselves to a comparison between red algae and land plants. Red algae live in water, often deeper than other algae. The light reaching them has been filtered through water, which absorbs long-wavelength light more strongly than other visible (and photosynthetically active) light. Therefore an energy deficiency in PSI relative to PSII could easily develop, if extra energy could not be added in addition to the light energy absorbed by PSI. This extra energy comes by "spillover" from PSII. Spillover of energy is possible, because the energy quanta collected in PSII are larger than what is needed to "lift" electrons in PSI, and because the two photosystems are intermingled among one another in red algae (as in cyanobacteria). Contrary to this, PSI cannot lose energy to PSII, because it cannot take up the small energy quanta from PSI. Red algae collect energy mainly via their phycobilisomes, and this energy can be used both by PS II and by PS I, so they can go "in step".

For land plants the situation is different. The first land plants were small beech organisms living without competition from larger plants, exposed to full sunlight; also their forerunners, the green algae, lived in very exposed habitats. Their problem was not lack of light energy, and thus they did not have much use for phycobilisomes. With time plants grew larger and more numerous. The average chloroplast became more and more shaded, filtered by other chloroplasts. From the perspective of an individual chloroplast it did not matter much whether the chloroplasts shading it were located in other plants, or in other leaves on the same plant, or even in the same leaf. The light hitting the chloroplast became, during the evolution of plants and ecosystems, more and more depleted in short-wave light, while the long-wave light, on the long-wave edge of the chlorophyll absorption spectrum was not attenuated to the same extent. The spectral situation was opposite that for chloroplasts in red algae. Now the imbalance between the photosystems could not be adjusted by spillover, since the energy quanta of the most exposed photosystem (PSI) were too small. Therefore PSI and PSII had to be separated to prevent spillover, otherwise PSII would be even more depleted. Evolution has succeeded in this by development of grana in the chloroplasts of land plants (see Figs 12.1 and 12.2). Grana are regions in the chloroplasts where the thylakoid membranes are closely stacked on top of one another and are enriched in PSII. The stacking of membranes, and absence of PSI gives room for larger pigment antennae, not in the form of phycobilisomes, but in the form of protein bound chlorophyll *a* and chlorophyll *b*. PSI is located in the more sparsely distributed membranes between the grana. There it is in good contact with stroma between the membranes, and this is advantageous, because PSI delivers reduction equivalents via ferredoxin to NADP, which are then used for the reduction of carbon dioxide in the stroma.

The structure of the chloroplasts, and in particular the proximity of membranes to one other, is not static, but constantly adjusted to available light. During evolution more and more sophisticated regulation systems have appeared, and also various mechanisms for protection against too strong light. One of the most important of these mechanisms is the so-called xanthophyll cycle, giving protection against strong light while allowing efficient use of weak light. Remarkably, it exists in essentially the same form, although exploiting different kinds of xanthophylls, both in the “red” and the “green” line of evolution. It is left for future research to find out whether this is an example of convergent evolution or due to common descent. The reader is referred to Demmig-Adams, Adams III, and Mattoo (2006) for details about the topic of photoprotection.

Yoshi (2006) has traced the evolution of carotenoids on the "green line". The most primitive living algae on this line have carotenoids which absorb maximally in the violet part of the spectrum, while more modern types have carotenoids with absorption peaks at longer wavelengths. Yoshi speculates that this may reflect the ultraviolet radiation conditions under which the algae have evolved. Those algae living long ago, before a protecting ozone layer had developed (and preserved as "living fossils" today) would have had to live at a depth where they were protected from

ultraviolet radiation, and where only short-wave photosynthetically active radiation would penetrate. The modern types would have evolved near the surface in a light regime containing also light between the chlorophyll absorption peaks, where long-wave absorbing carotenoids are efficient antenna pigments. A difficulty with Yoshi's interpretation is that an ozone layer most likely evolved already long before the appearance of eukaryotic algae.

12.9 Many Different Systems for the Assimilation of Carbon Dioxide Have Been Tried in the Course of Evolution

Assimilation of carbon dioxide is not necessarily coupled to photosynthesis. The ability to take up carbon dioxide and assimilate the carbon to organic substance is older than the ability to photosynthesize. It takes place in both archaea and bacteria. The ability has either evolved before the two domains separated in evolution, or one of the organismal groups has acquired it from the other one by horizontal (lateral) gene transfer. Since many enzymes are involved the former possibility is the most likely one.

Apart from the first two ones, the enzymes in Table 12.1 and their assimilation pathways (Fig. 12.7) are present only in bacteria and archaea. But the typical carbon binding enzyme of plants, rubisco, occurs also in some archaea, even though the whole Calvin-Benson-Bassham cycle has not been demonstrated in them.

Table 12.1. Pathways and enzymes for CO_2 assimilation (CoA = coenzyme A)

CO_2 binding enzyme	Pathway for CO_2 assimilation
Ribulose-1,5-bisphosphate-carboxylase-oxygenase (RuBisCO, rubisco)	Calvin-Benson-Bassham cycle
Phosphoenol pyruvate carboxylase (PEPC)	C4- and CAM cycles
Formate dehydrogenase	Acetyl-CoA pathway
Carbon monoxide dehydrogenase	Acetyl-CoA pathway
Pyruvate:ferredoxin oxidoreductase	Arnon-Buchanan cycle (reductive TCA cycle)
2-oxoglutarate: ferredoxin oxidoreductase	Arnon-Buchanan cycle
Isocitrate dehydrogenase	Arnon-Buchanan cycle
Pyruvate carboxylase	Arnon-Buchanan cycle
Acetyl-CoA carboxylase	3-hydroxypropionate cycle
Propionyl-CoA carboxylase	3-hydroxypropionate cycle

The first alternative to the Calvin-Benson-Bassham cycle detected was a cycle discovered by Evans, Buchanan and Arnon (1966), see also Buchanan and Arnon 1990). The acetyl-CoA pathway is present in some acetate-forming bacteria, some sulfate-reducing bacteria and some hydrogen-oxidizing archaea. The 3-hydroxypropionate pathway is present in green nonsulfur bacteria and some hydrogen oxidizing bacteria and some sulfur-reducing archaea. Thus every type of carbon

dioxide assimilation occurs in taxonomically quite different types of microorganisms. Selesi (2005) has detected a large set of rubisco types in soil microorganisms, of which only a minor part is derived from photosynthetic organisms.

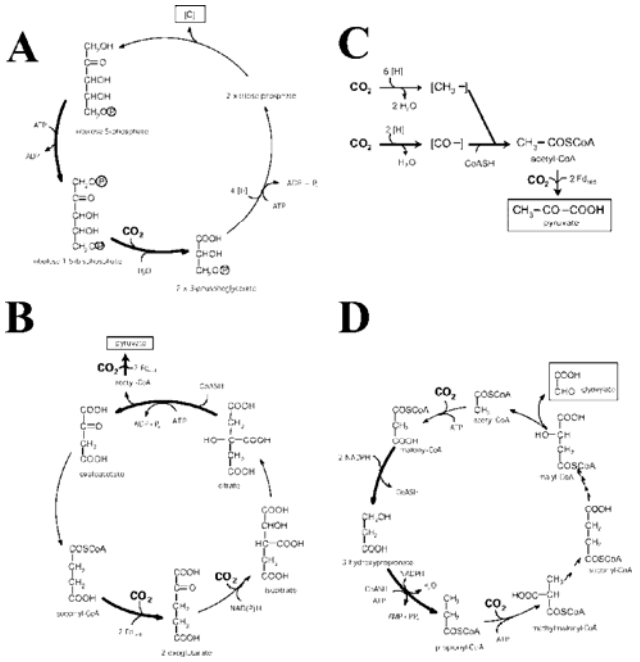

Fig. 12.7. Metabolic cycles for assimilation of carbon dioxide present in various prokaryotes. A. The Calvin-Benson-Bassham cycle, B. The reductive TCA cycle (Arnon-Buchanan cycle), C. The reductive acetyl-CoA pathway, and D. The 3-hydroxpropionate cycle. Of these only the Calvin-Benson-Bassham cycle is present in photosynthetic eukaryotes (cyanobacteria, algae and plants). [C] stands for assimilated carbon, [H] for reduction equivalents, Fd_{red} for reduced ferredoxin, P och P in a circle for phosphate groups, [CH_3-] for enzyme bound methyl group, and [CO-] for enzyme bound carbon monoxide. From Hügler *et al*. (2003).

It is clear that rubisco is a very ancient enzyme, and it was "designed" under conditions quite different from the present ones. The most important differences are that oxygen was absent from the primordial environment, and the concentration of carbon dioxide was much higher than in the contemporary environment. Therefore the properties of rubisco are not optimal for the present environment. It works slowly. It binds carbon dioxide only weakly (has a low affinity, and a high Michaelis constant for carbon dioxide). This was not a problem as long as the concentration of carbon dioxide was very high. It can react with oxygen instead of carbon dioxide, and when

this happens a product, phosphoglycolic acid, is formed, which the organism has no real use for, and which can even act as a poison if not taken care of in a proper way. This substance was not formed when oxygen was absent from the environment. When it is formed in algae living in water it can be excreted to the environment, but for land plants it is an expensive affair to take care of it, and for this a special metabolic cycle had to be invented: the photorespiratory cycle.

To compensate for the bad properties of rubisco, different photosynthesizers have evolved different strategies. A common one is to produce large amounts of the enzyme to compensate for its slowness, and this has made it the most ubiquitous protein molecule on earth. Various systems for concentrating carbon dioxide at the enzyme surface have also evolved, so carbon dioxide can compete efficiently with oxygen for the common binding site. The methods used by cyanobacteria and algae have been described by Badger and Price (2003); Giordano, Beardall, J. and Raven (2006); Keeley and Rundel (2002). Here we shall limit ourselves to the so-called C4-metabolism and to CAM.

12.10 C4 Metabolism

About half of this planet's photosynthetic production takes place on land, and the other half in water. According to Sage (2004) the mere 3% of the terrestrial plants having C4 metabolism carry out about half of the production on land. C4 photosynthesis has evolved at least 45 times (Sage 2004). From this we can understand that there has been a very strong evolution pressure towards this kind of metabolism. An important component in this evolution pressure has been the decrease in carbon dioxide pressure that took place between 30 and 40 Ma ago. Another component has been the drying of the environment that was an even more recent event (Osborne and Beerling 2006). C4 metabolism (Fig. 12.8) became a significant component of the carbon cycle as recently as 10 Ma ago.

In C4 metabolism carbon dioxide is not initially bound to rubisco, as the case is in C3 plants. Instead bicarbonate ions (formed from carbon dioxide and water with the aid of the enzyme carbonic anhydrase) are bound by the enzyme phospho-enol-pyruvate carboxylase (PEPC, see Table 1) and united with phospho-enol-pyruvate (PEP) to form malate. Malate has 4 carbon atoms, hence the designation C4 metabolism. In C3 metabolism the first formed assimilate product is 3-phosphoglyceric acid, which has 3 carbon atoms. C4 metabolism is more efficient at a low concentration of carbon dioxide, because PEPC binds bicarbonate very tightly, and because oxygen cannot compete with this. It is also more efficient under dry conditions, since plants then can conserve water by keeping their stomata only slightly open. This causes a lowering of the inner carbon dioxide concentration in the plants, but this does not interfere with its uptake in C4 plants. It is also more efficient than C3 metabolism at high temperatures. In C3 plants the so-called photorespiration, caused by oxygen competition for rubisco binding, makes carbon dioxide uptake inefficient at high temperatures. Under other conditions, C4 metabolism is less efficient than C3 me-

tabolism, because it uses up more ATP (5 molecules per molecule of CO_2 assimilated, compared to 3 for C3 plants).

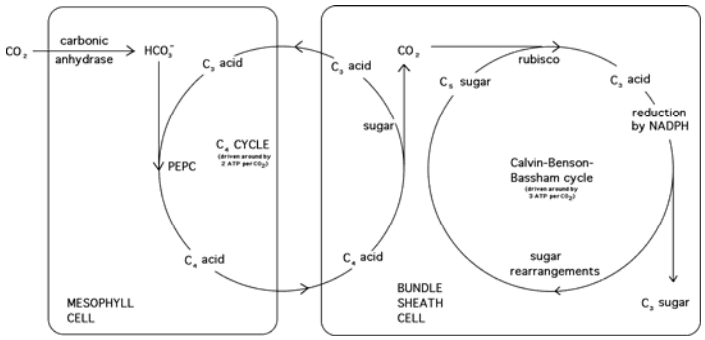

Fig. 12.8. Carbon dioxide assimilation in C4 plants. The first cycle concentrates carbon dioxide at the rubisco, and the assimilation itself proceeds as in C3 plants.

One fascinating fact with C4 metabolism is that it has evolved within a relatively short time, and independently within many groups of plants. C4 metabolism occurs primarily among seed plants, but has been found also elsewhere, even among diatoms (Reinfelder, Kraepiel and Morel 2000; Reinfelder, Milligan and Morel 2004).

Since the oxygen concentration during the Carboniferous (370-300 Ma ago) was even higher, and the carbon dioxide concentration even lower than today (Fig. 12.9), one would have expected the C4 metabolism to have evolved already then. But the plant fossils from that time for which the isotopic composition of the carbon has been investigated, all carry a C3-like signature, $\delta^{13}C \approx -20‰$ (Beerling, Lake, Berner, *et al.* 2002; Bocherens, Friis, E.M., Mariotti, A. and Pedersen 2002).

One enigmatic circumstance is that CAM plants were present earlier; why do we then have only C3 type discrimination? Perhaps CAM plants did not contribute much to biomass production? The corresponding value for C4 plants is about -13‰. There is some suspicion that some C4 plants could have evolved already then, but not become very common (Osborne *et al.* 2006). A possible reason that more C4 plants did not evolve during this period, is that the temperature was low.

C4 plants have evolved at least 45 times in 19 families of higher plants. It is now present in about 7500 species of seed plants (3% of the species of terrestrial plants), of which 4500 are grasses, 1500 sedges and 1200 dicots (Sage 2005). C4 plants occur primarily in warm and dry countries and among epiphytes, and a number of evolution centers for C4 metabolism can be distinguished.

We refer to Andrew Benson (pp. 793–813) and James A. Bassham (pp. 815–832) for the stories behind the discovery of the Calvin-Benson-Bassham pathway, and to M. D. Hatch (pp. 875–880) for C4 metabolism in Govindjee *et al.* (2005).

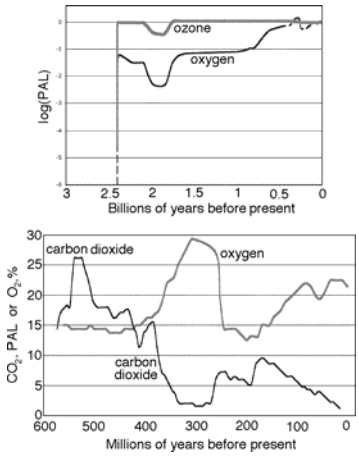

Fig. 12.9. The evolution of the Earth's atmosphere. Top panel: Ozone and oxygen, on a logarithmic scale, as fraction of present atmospheric leve, during the past 3 billion years. Bottom panel: oxygen (%) and carbon dioxide (in relation to present atmospheric level) on a linear scale during the last 570 million years. Based on Beerling, Lake, Berner *et al.* (2002); Berner (2006); Canfield (2005); Falkowski, Katz, Milligan *et al.* (2005); Huey and Ward (2005); Segura, Krelove, Kasting *et al*. (2003) and other sources.

12.11 CAM (Crassulacean Acid Metabolism)

Another way of using PEPC to complement the assimilation by rubisco is shown by plants possessing crassulacean acid metabolism (CAM). As the name implies, this kind of metabolism was first found in the family Crassulaceae. CAM plants have the ability to take up carbon dioxide during the night when the stomata are open, and bind it to PEP with the help of PEPC. The photosynthesis proper, using light to process the assimilate in the Calvin-Benson-Bassham cycle, is carried out during the day, when the stomata are closed. By keeping stomata open only during the night the plants conserve water.

CAM is more ancient than is C4 metabolism, and its has been driven by water stress (Keeley and Rundel 2002). It is known only to exist in vascular plants, and it is present in species of clubmosses, ferns, the strange gymnosperm *Welwitschia mirabilis*, the cycad *Dioon edule*, monocots and dicots. Among the latter the following families deserve to be mentioned: Aizoaceae, Cactaceae, Portulaceae, Crassulaceae, Euphorbiaceae, Asclepiadaceae, and Asteraceae, and among monocots Bromeliaceae and Orchidaceae. Just as C4 metabolism, CAM has evolved several times within various plant groups when need has arisen due to water deficiency, mainly among desert plants and plants living on stones or as epiphytes (on other plants, Keeley and

Rundel 2002). However, there are also aquatic CAM plants, and the reason for this is not clear. Among the aquatic plants the large and primitive genus *Isoëtes* deserves special mention. All of its members seem to be CAM plants (although only about one third of the ca. 125 species have been investigated). Since this genus existed already during the early Triassic, more than 200 million years ago, it must be assumed that CAM existed already then (Keeley and Rundel 2002). Dekker and de Wit (2006) give further evidence for the early evolution of CAM. See C.C. Black and C. Barry Osmond (pp. 881-893) in Govindjee, Beatty, Gest, and Allen (2005) for the stories on the discovery of CAM.

12.12 Evolution of ATP-Synthesizing Enzymes

The use of proton gradients for synthesis of adenosine triphosphate (ATP) occurs in all three domains of life, Archaea, Bacteria, and Eukarya, and also the last common ancestor of all organisms must have made use of this. The ancestry of the ATP-synthesizing enzyme of chloroplasts, the F-ATPase, has been described by Zhaxybayeva, Lapierre and Gogarten (2005). This enzyme consists of several subunits, and corresponding subunits show similarities across the domain borders.

12.13 The Journey Onto Land

Some kind of photosynthetic organisms are thought to have been present on land as early as 1.2 Ga ago, based on carbon isotope ratios, i.e. ^{13}C depletion (literature cited by Horydski and Knauth 1994). These organisms were probably cyanobacteria forming crusts as can still be found in deserts. The oldest lichen-like fossils containing what has been interpreted as cyanobacteria are about 600 Ma old (Yuan *et al.* 2005). Stronger evidence, both morphological (Taylor *et al.* 2004) and chemical (Jahren 2003) for lichens, is found from the early Devonian, ca 400 Ma ago. However, based on the ”molecular clock”, Heckman, Geiser, Eidell *et al.* (2001) estimate that terrestrial fungi existed prior to 900 Ma ago, and these first terrestrial fungi might well have been living in lichen-like associations. While land plants now account for about half of the planet’s photosynthesis, the contribution of these early pioneers was likely almost negligible compared to that of the ocean.

The great change came with the evolution of the embryophytes. Their closest relatives are the Charales (stoneworts), a kind of green algae (Karol, McCourt, Cimino and Delwiche 2001). Spores that are suspected to stem from liverwort-like plants have been found that are from the mid-Ordovician, 475 Ma ago (Wellman *et al.* 2003), but bryophyte fossils that can be identified with more certainty are younger, from late Silurian, 425 Ma ago. ”Molecular clock” evidence points to a much earlier separation of the terrestrial-plant line from the algal line of evolution (Heckman, Geiser, Eidell *et al.* 2001).

In the early Devonian (ca 410 Ma ago) plants had evolved that had leaves and roots (*Eophyllophyton bellum,* Hao, Beck, and Wang 2003). The leaves seem to have been adapted to a dry climate and high carbon dioxide concentration. In the late Devonian (370 million years ago), as the atmospheric concentration of carbon dioxide fell (Fig. 12.9), larger leaves evolved, which were more efficient in collecting both carbon dioxide and light (Beerling, Lake, Berner *et al.* 2001).

In the terrestrial environment, the weight of the plant body cannot be supported by buoyancy as in the water. To be able to stretch toward the light among competitors, plants had to improve their rigidity. An important means for this was to strengthen the cell walls with lignin. Such strengthening was also required for the water conduits to withstand the pressure difference. Lignin synthesis requires molecular oxygen, and could thus not commence until the oxygen concentration had risen to a sufficient level. Lignin synthesis builds on the phenylpropanoid pathway, which can be traced back to the characeans: Flavonoids have been found in *Nitella* (Markham and Porter 1969). The "molecular clock" indicates that the line leading to terrestrial plants diverged from the charophytes about 1 Ga ago (Heckman *et al.* 2001), so this pathway can be assumed to have at least this age.

Throughout their evolution land plants maintained a close association with fungi. A majority of extant plants have mycorrhiza, and many have endophytic fungi also in the shoots, and, of course, fungi on the leaf surfaces. The combination of rooted plants and mycorhizal fungi increased the weathering of the continental rocks enormously. This, in turn, meant a postive feedback on photosynthesis by providing more nutrients, also for marine organisms.

Aquatic organisms need not be protected against desiccating evaporation, but when plants colonized land it was necessary for them to conserve water, and they developed cuticle and cutinized external cell walls, and sometimes wax coatings. All this is an obstacle to gas exchange, and so the sophisticated gas valves evolved which go under the name stomata. Stomata are adjustable openings which are regulated in a very complicated way for the optimal balance between loss of water and access to carbon dioxide. Water and carbon dioxide conditions are sensed directly in the leaf for short term regulation, but water availability is sensed also in the roots, and hormonal signals (in the form of abscisic acid) sent to the stomata for long term regulation. In addition several light-sensing systems affect the stomatal aperture.

But in addition to regulation of the individual stomata, there is also a developmental regulation to achieve an optimal number and size of stomata. The higher the atmospheric concentration of carbon dioxide, the more sparsely do stomata develop on the leaf surface. This provides a method for estimating past carbon dioxide concentrations by studying the stomatal density on fossilized leaves (McElwain 1998; McElwain, Mayle and Beerling 2002; Haworth *et al.* 2005).

After having adapted to the terrestrial environment some plants returned to the water, and had to cope with new problems (Rascio 2002). It was not simply a reversal of the adaptation to dry land (some researchers think that our modern charophytes have also made a transient visit to terra firma). On land, plants had become larger and needed to develop aerenchyma (air conducting tissue) to provide all parts with

sufficient oxygen. If roots or rhizomes were to be maintained in anoxic muddy bottoms, their oxygen requirement was of special importance, and in some cases diffusive oxygen transport did not suffice. Also the provision with carbon dioxide could be a problem, and this explains the evolution of various mechanisms for its concentration, including a kind of C4 metabolism.

12.14 Impact of Photosynthesis on the Biospheric Environment

When we think about how photosynthesis has affected our environment, we may first remember that it has produced the oxygen we breathe, and (directly or indirectly) the food we eat. But the impact of photosynthesis is much wider. The oxygen produced by photosynthesis has also given rise to the ozone layer, which protects the biosphere from the ultraviolet-B radiation from the sun (Chapter 19). The fossil fuel, which we have now become too dependent on, has been produced by photosynthesis in times past. The sequestration of carbon from the atmosphere has given us a human-friendly climate, which unfortunately we are now destroying. But perhaps the process of photosynthesis, as an environmental-friendly way of energy transformation, can help us to draw up a blue-print for a solution to the conflict between our hunger for energy and the necessity to maintain an environment that can sustain humanity.

But we must not fall into the trap of believing that photosynthesis has always resulted in a good environment for the inhabitants of our planet. The free oxygen is still a hazard for our own cells, and even for the chloroplasts producing oxygen.

Photosynthesis has not always had a friendly, Gaia-like influence on inhabitants of the Earth. When oxygen first started to accumulate, it almost certainly killed off a large part of the terrestrial population by direct poisoning. It was even a hurdle to the producers themselves. Many of the cyanobacteria (as many other bacteria as well as archaea) carry out nitrogen fixation by means of nitrogenase. Nitrogenase is extremely sensitive to oxygen and easily inhibited by it, and organisms had to invent various methods for protecting the nitrogen fixing enzyme from oxygen. Some of the filamentous forms developed special cells (heterocysts) for a special kind of photosynthesis, which fixes nitrogen using PSI only, and does not fix carbon dioxide or evolve oxygen. From morphological fossils it has been deduced that this arrangement is 1.5 Ga old. No convincing fossil of heterocysts themselves has been found, so this opinion (Golubic and Seong-Joo 1999) rests on the presence of akinetes, a kind of resting cell. In modern cyanobacteria there is a strict correlation between occurence of heterocysts and of akinetes.

Before cyanobacteria evolved, the oxygen content of the atmosphere was below 10^{-5} of the present. The initial effects of photosynthetic oxygen production on climate were disastrous. Before the oxygenation of the atmosphere the earth was kept comfortably warm (too warm for the human taste) by not only a high atmospheric content of carbon dioxide, but also by another greenhouse gas, methane. When oxygen arrived, methane was first oxidized to carbon dioxide by an emerging new group

of microorganisms. Then also the concentration of carbon dioxide was drastically lowered by cyanobacterial assimilation. This led to a sharp temperature decrease and a glaciation which lasted for about 70 million years, between 2.32 and 2.22 Ga ago. Since traces from this time of glaciation (the Makganyene glaciation) are found near the ancient equator, some scientists believe that the whole globe became covered with ice and snow during at least part of this time. There was what has been called a "snowball earth" (Kirschvink *et al*. 2000; Kopp, Kirschwink, Hilburn, and Nash 2005). The ice cover prevented silicate weathering, a process that consumes carbon dioxide, and continuing volcanism increased the carbon dioxide content again and eventually put an end to the long ice age. In the meantime the hydrothermal vents at the bottom of the sea had spewed out nutrients at a rate which could not under the icy conditions be matched by consumption. Therefore, many cyanobacterial nutrients were abundant at the end of the glaciation, but probably not all.

Contributing to the severity of this glaciation may have been that the Sun emitted less energy than it does today (e.g., Gough 1981, Fig. 12.10), but all scientists today do not believe in this "faint young Sun" theory. Neither is the "snowball" scenario unquestionable. An alternative explanation for glaciation in the equatorial region is that the "tilt" (the inclination) of the Earth's axis was greater in the past (Williams, Kasting and Frakes 1998, but cf. Levrard and Laskar 2003).

One way of constraining the timing of the oxygenation of the atmosphere comes from studies of the isotopic sulfur composition of pyrite. Most chemical and physical processes lead to a fractionation of isotopes of elements which depends on atomic weight. Photochemical processes can lead to deviations from this, i.e. to mass-independent fractionation. As long as the atmosphere remains reducing, hydrogen sulfide emitted from volcanoes remains in the atmosphere long enough for photochemical processes to imprint their special signature on the pyrite that is eventually formed. In pyrites which, by use of osmium isotope ratios could be accurately dated to 2316±7 Ma, the sulfur isotope ratio indicates an oxidizing atmosphere; thus this is taken as a minimum age for the oxic atmosphere (Hannah, Bekker, Stein *et al.* 2005). The oxygen concentration at that time was, of course, much lower than today.

The protein complexes involved in the electron transport chain in the thylakoids contain several atoms of several metals. In addition to the magnesium atoms of chlorophyll, there are in PS I twelve Fe, in the cytochrome b_6f complex six Fe, and in PSII two Fe, four Mn and one Ca. (The electron transfer chain in addition contains soluble metal proteins: iron containing ferredoxin and either copper containing plastocyanin or iron containing cytochrome c_6.) These metals can sometimes be difficult to obtain, depending on, for instance, redox potential and presence of hydrogen sulfide. PSI contains more iron than the other complexes, and Strzepek and Harrison (2004) have noted that diatoms adapted to coastal regions, where iron is more available, have a higher PSII/PSI ratio (around 9) compared to diatoms adapted to oceanic regions (around 3), where available iron is often a limiting factor for growth. Presumably the PSI of oceanic diatoms have larger light-collecting pigment antennae to compensate for the lower number of reaction centers. Furthermore, only the coastal diatoms have cytochrome c_6, another iron-containing protein. For historical accounts

on the structure and function of PSI, see Petra Fromme and Paul Mathis (pp. 311-326) and Horst Witt (pp. 237-259) in Govindjee, Beatty, Gest and Allen (2005).

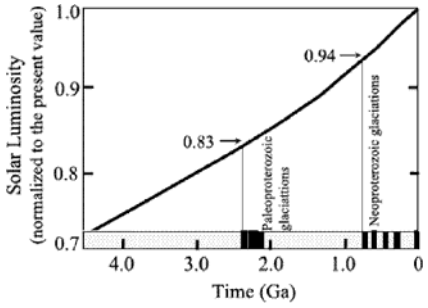

Fig. 12.10. The relative power radiated by the Sun during Earth history, and the timing of glaciations. From Tajika (2003), based on Gough (1981). Not all scientists (see Sackmann and Boothroyd 2003) believe in this "faint young Sun" scenario, the main argument being the documented presence of liquid water on Mars ≈ 3.8 Ga (gigayears) ago.

During a period after the emergence of cyanobacteria and oxygen evolving photosynthesis, the concentration of hydrogen sulfide rose in the depth of the ocean, and this made iron hard to get at (Canfield 1998). One can imagine that the cyanobacteria present at that time adapted their photosynthetic machinery to economize with iron. The closest present-day analog to this ancient ocean is the Black Sea. According to Anbar and Knoll (2002) sulfidic condition in the deep sea prevailed most of the time between 2500 and 543 Ma ago, although the ocean surface where photosynthesis could take place was oxygenated. Still, the sulfidic depth caused a deficiency of several important metals, such as iron and, even more so, molybdenum. This caused a pressure for evolution of molybdenum-free nitrogenases (using vanadium and iron). According to Canfield, Poulton and Narbonne (2007) the increase of deep ocean oxygen over a critical point spurred the rapid evolution of animal life.

15 Conclusion

Photosynthesis is a very ancient process on our planet. It has had profound impacts on the biosphere, the chemical composition of the Earth's surface and the Earth's atmosphere, and on climate, including the radiation climate. It is difficult to imagine what this planet would have been like had photosynthesis (and especially the oxygenic variant) not evolved. In any case we would not have been here to find out.

References

Allen, J.F. (2005) A redox switch hypothesis for the origin of two light reactions in photosynthesis. FEBS Lett. 579, 963-968.

Allen, J.F. and Martin W. (2007) Out of thin air. Nature 445, 61-612.

Anbar, A.D. and Holland, H.D. (1992) The photochemistry of manganese and the origin of banded iron formations. Geochim. Cosmochim. Acta 56, 2595-2603.

Anbar, A.D. and Knoll, A.H. (2002) Proterozoic ocean chemistry and evolution: a bioinorganic bridge. Science 297, 1137–1142.

Anderson, J.M. (1999) Insights into the consequences of grana stacking of thylakoid membranes in vascular plants: a personal perspective. Aust. J. Plant Physiol. 26, 625–639.

Asard, H., Venken, M., Caubergs, R., Reijnders, W., Oltmann, F.L. and De Greef, J.A. (1989) b-Type cytochromes in higher plant plasma membranes. Plant Physiol. 90,1077–1083.

Ashida, H., Saito, Y., Kojima, C., Kobayashi, K., Ogasawara, N., Yokota, A. (2003) A functional link between RuBisCO-like protein of *Bacillus* and photosynthetic RuBisCO. Science 302, 287–290.

Ashida, H., Danchin, A., Yokota, A. (2005) Was photosynthetic RuBisCO recruited by acquisitive evolution from RuBisCO-like proteins involved in sulfur metabolism? Res. Microbiol. 156, 611–618.

Awramik, S. M. (1992) The oldest records of photosynthesis. Photosynthesis Res. 33, 75–89.

Badger, M.R. and Price, G.D. (2003) CO_2-concentrating mechanisms in cyanobacteria: molecular components, their diversity and evolution. J. Exp. Bot. 54, 609–622.

Bald, D., Kruip, J., Boekema, E.J. and Rögner, M. (1992) Structural investigations on cyt b_6 f complex and PS I complex from the cyanobacterium *Synechocystis* PCC6803. In: N. Murata (Ed.) *Photosynthesis: from Light to Biosphere*, Part I. Kluwer Academic Publishers, Dordrecht, The Netherlands, pp. 629–633.

Baymann, F., M. Brugna, M., Muhlenhoff, U. and Nitschke, W. (2001) Daddy, where did (PS)I come from? Biochim. Biophys. Acta 1507, 291–310.

Bhattcharaya, D., Yoon, H.S. and Hackett, J.D. (2003) Photosynthetic eukaryotes unite: endosymbiosis connects dots. BioEssays 26, 50–60.

Beatty, J.T., Overmann, J., Lince, M.T., Manske, A.K.. Lang, A.S., Blankenship, R.E., Van Dover, C.L., Martinson,T.A. and Plumley, G.F. (2005) An obligately photosynthetic bacterial anaerobe from a deep-sea hydrothermal vent. Proc. Natl. Acad. Sci. USA 102, 9306–9310.

Beerling, D.J. Lake, J.A., Berner, R.A., Hickey, J.J., Taylor, D.W. and Royer, D.L. (2002) Carbon isotope evidence implying high O_2/CO_2 ratios in the Permo-Carboniferous atmosphere. Geochim. Cosmochim. Acta, 66, 3757–3767.

Benson, A.A. and Calvin, M. (1950) Carbon dioxide fixation by green plants. Annu. Rev. Plant Physiol. 1, 25–40.

Berman-Frank, I., Lundgren, P. and Falkowski, P. (2003) Nitrogen fixation and oxygen evolution in cyanobacteria. Res. Microbiol. 154, 157–164.

Berner, R.A. (2006) GEOCARBSULF: A combined model for Phanerozoic atmospheric O_2 and CO_2. Geochim. Cosmochim. Acta 70, 5653-5664.

Björn, G.S. and Björn, L.O. (1982) Prochloron — sidospår eller felande länk? Svensk Bot. Tidskr. 76, 43–45.

Björn, L.O. (1995) Origins of photosynthesis Nature 376, 25–26.

Björn, L.O., Ekelund, N.G.A. (2005) Dinoflagellater — hopplock från livets smörgåsbord. Svensk Bot. Tidskr. 99, 7–16.

Blankenslip, R.E. (1992) Origin and early evolution of photosynthesis. Photosynthesis Res.

33, 91–111.
Blankenship, R.E. (2002) *Molecular Mechanisms of Photosynthesis*. Blackwell Science.
Blankenslip, R.E. and Hartman, H. (1998) The origin and evolution of oxygenic photosynthesis. Trends in Biochem. Sci. 23, 94–97.
Bocherens, H., Friis, E.M., Mariotti, A. and Pedersen, K.R. (1993) Carbon isotopic abundances in Mesozoic and Cenozoic fossil plants – Paleoecological implications. Lethaia 26, 347–358.
Borda, M.J., Elsetinow, A.R., Schoonen, M.A. and Strongin, D.R. (2001) Pyrite-induced hydrogen peroxide formation as a driving force in the evolution of photosynthetic organisms on an early Earth. Astrobiology 1, 283–288.
Brasier, M.D., Green, O,R., Lindsay, J.F., McLoughlin, N., Steele, A. and Stoakes, C. (2005) Precambrian Res. 140, 55–102.
Brocks, J.J., Buick, R., Summons, R.E. and Logan, G.A. (2003) A reconstruction of Archean biological diversity based on molecular fossils from the 2.78 to 2.45 billion-year-old Mount Bruce Supergroups, Hamersley Basin, Western Australia. Beochim. Cosmochim. Acta 67, 4321-4335.
Buchanan, B. B. and D. I. Arnon. (1990) A reverse Krebs cycle in photosynthesis: consensus at last. Photosynth. Res. 24,47–53.
Butterfield, N.J. (2000) *Bangiomorpha pubescens* n. gen., n. sp.: implications for the evolution of sex, multicellularity, and the Mesoproterozoic/Neoproterozoic radiation of eukaryotes. Paleobiology 26, 386–404.
Canfield, D.E. (1998) A new model for proterozoic ocean chemistry. Nature 396, 450-453.
Canfield, D.E. (2005) The early history of atmospheric oxygen: Homage to R.M. Garrels. Annu. Rev. Earth Planet. Sci. 33, 1-36.
Canfield, D.E., Poulton, S.W. and Narbonne, G.M. (2007) Late Neo-Proterozoic deep-ocean oxygenation and the rise of animal life. Science 315, 92-95.
Clausen, J., Beckmann, K., Junge, W. and Messinger, J. (2005) Evidence that bicarbonate is not the substrate in photosynthetic oxygen evolution. Plant Physiol. 139, 1444–1450.
Clausen. J., Junge. W., Dau H. and Haumann, M. (2005) Photosynthetic water oxidation at high O_2 backpressure monitored by delayed chlorophyll fluorescence. Biochemistry 44, 12775–12779.
Dashdori, N., Zhang, H., Kim, H., Yan, J., Cramer, W.A. and Savikhin, S. (2005) The single chlorophyll a molecule in the cytochrome b6 f complex, unusual optical properties protect the complex against singlet oxygen. Biophys. J. 88 , 4178–4187.
Decker, J.E. and de Wit, M.J. (2006) Carbon isotope evidence for CAM photosynthesis in the Mesozoic. Terra Nova 18, 9–17.
Demmig-Adams, B., Adams III, W.W. and Mattoo, A. (eds) (2006) *Photoprotection, Photoinhibition, Gene Regulation, and Environment*. Advances in Photosynthesis and Respiration Series (Govindjee, series ed.), vol. 21. Springer.
Dismukes, G.C., Klimo, V.V. Baranov, S.V., Kozlov, Yu.N., DasGupta, J. and Tyryshkin, A. (2001) The origin of atmospheric oxygen on Earth: The innovation of oxygenic photosynthesis. Proc. Natl. Acad. Sci. USA 98, 2170–2175.
Eck, R.V. and Dayhoff, M.O. (1966) Evolution of the structure of ferredoxin based on living relics of primitive amino acid sequences. Science (N.S.) 152, 363–366.
Evans, M. C., Buchanan, B.B. and Arnon, D.I. (1966) A new ferredoxin dependent carbon reduction cycle in a photosynthetic bacterium. Proc. Natl. Acad. Sci. USA 55, 928–934.
Falkowski. P.G., Katz, M.E., Milligan, A.J., Fennel, K., Cramer, B.S., Aubry, M.P., Berner, R.A., Novacek, M.J. and Zapol, W.M. (2005) The rise of oxygen over the past 205 million

years and the evolution of large placental mammals. Science 309, 2202-2204.
Fennel, K., Follows, M. and Falkowski, P.G. (2005) The co-evolution of the nitrogen, carbon and oxygen cycles in the Proterozoic ocean. Am. J. Sci. 305, 526–545.
Ferreira, K.N., Iverson, T.M., Maghlaoui, K., Barber, J. and Iwata, S. (2004) Architecture of the photosynthetic oxygen-evolving center. Nature 303, 1831–1837.
Fukuyama, K., (2004) Structure and function of plant-type ferredoxins. Photosynthesis Res. 81, 289–301.
Giordano, M., Beardall, J. and Raven, J.A. (2005) CO_2 concentrating mechanisms in algae: Mechanisms, environmental modulation, and evolution. Annu. Rev. Plant Physiol. 56, 99–131.
Golbeck, John H. (ed.) (2006) *Photosystem I: The Light-Driven Plastocyanin: Ferredoxin Oxidoreductase*. Advances in Photosynthesis and Respiration Series, vol. 24 (Govindjee, series ed.). Springer, New York.
Golubic, S. and Seong-Joo, L. (1999) Early cyanobacterial fossil record: preservation, palaeoenvironments and identification. Eur. J. Phycol. 34, 339–348.
Gomes, R., Levison, H.F., Tsiganis, K. and Morbidelli, A. (2005) Origin of the cataclysmic Late Heavy Bombardment period of the terrestrial planets. Nature 435, 466–469.
Govindjee (2000) Milestones in photosynthesis research. In: Yunus, M., Pathre, U. and Mohanty, P. (eds.) Probing Photosynthesis: Mechanisms, Regulation And Adaptation, Taylor & Francis, London, pp. 9-39.
Govindjee, Beatty, J.T., Gest, H., Allen, J.F. (eds) (2005) *Discoveries in Photosynthesis*. Advances in Photosynthesis and Respiration Series, vol. 20 (Govindjee, series editor). Springer, New York.
Granick, S. (1957) Speculations on the origins and evolution of photosynthesis. Ann. NY Acad. Sci. 69, 292–308.
Gu, Y., Li, P., Sage, J.T. and Champion, P.M. (1993) Photoreduction of heme proteins: spectroscopic studies and cross-section measurements. J. Am. Chem. Soc. 115, 4993–5004.
Gutiérrez-Cirlos, E.B., Pérez-Gómez, B., Krogmann, D.W. and Gómez-Lojero, C. (2006) The phycocyanin-associated rod linker proteins of the phycobilisome of *Gloeobacter violaceus* PCC 7421 contain unusually located rod-capping domains. Biochim. Biophys. Acta 1757, 130–134.
Hakala, M., Tuominen, I., Keränen, M., Tyystjärvi, T. and Tyystjärvi, E. (2005) Evidence for the role of the oxygen-evolving manganese complex in photoinhibition of Photosystem II. Biochim. Biophys. Acta 1706, 68-80.
Hakala, M., Rantamäki, S., Puputti, E.-M., Tyystjärvi, T. and Tyystjärvi, E. (2006) Photoinhibition of manganese enzymes: insights into the mechanism of photosystem II photoinhibition. J. Exp. Bot. 57, 1809-1816.
Hannah, J.L., Bekker, A., Stein, H.J., Markey, R.J. and Holland, H.D. (2004) Primitive Os and 2316 Ma age for marine shale: implications for Paleoproterozoic glacial events and the rise of atmospheric oxygen. Earth Planetary Sci. Lett. 225, 43–52.
Hao, S.G., Beck, C.B. and Wang, D.M. (2003) Structure of the earliest leaves: Adaptations to high concentrations of atmospheric CO_2. Intern. J. Plant Sci. 164, 71-75.
Haworth, M., Hesselbo, S.P., McElwain, J.C., Robinson, S.A. and Brunt, J. (2005) Mid-Cretaceous pCO_2 based on stomata of the exinct conifer *Pseudofrenelopsis* (Cheirolepidiaceae). Geology 33, 749–752.
Heckman, D.S., Geiser, D.M., Eidell, B.R., Stauffer, R.L., Kardos, N.L. and Hedges, S.B. (2001) Molecular evidence for the early colonization of land by fungi and plants. Science 293, 1129–1133.
Hess, W.R., Partensky, F., van der Staay, G.W.M., Garcia Fernandez, J.M., Borner, T. and

Vaulot, D. (1996) Coexistence of phycoerythrin and a chlorophyll a/b antenna in a marine prokaryote. Proc. Natl Acad. Sci. USA 93, 11126-11130.

Hirabayashi, H., Ishii, T., Takaichi, S., Inoue, K. and Uehara, K (2004) The Role of Carotenoids in the Photoadaptation of the Brown-colored Sulfur Bacterium *Chlorobium phaeobacteroides*. Photochem. Photobiol. 79, 280–285.

Hu, X., Ritz, T., Damjanovic, A., Felix Autenrieth, F. and Schulten, K. (2002) Photosynthetic apparatus of purple bacteria. Quart. Revs Biophys. 35, 1–62.

Huang, D., Everly, R. M. Cheng, R.H., Heymann, J.B., Schagger, H., Sled, V., Ohnishi, T., Baker, T.S. and Cramer, W.A. (1994) Characterization of the chloroplast cytochrome b_6 f complex as a structural and functional dimer. Biochemistry. 33, 4401–4409.

Huey, R.B. and Ward, P.D. (2005) Hypoxia, global warming, and terrestrial Late Permian extinctions. Science 308, 398-401.

Hügler, M., Hüber, H., Stetter, K.O. and Fuchs, G. (2003) Autotrophic CO2 fixation pathways in archaea (Crenarchaeota). Arch. Microbiol. 179, 160-173.

Jahren, A.H., Porter, S. and Kuglitsch, J.J. (2003) Lichen metabolism identified in Early Devonian terrestrial organisms. Geology 31,99–102.

Kappler, A., Pasquero, C., Konhauser, K.O. and Newman, D.K. (2005) Deposition of banded iron formtions by anoxygnic phototrophic Fe(II)-oxidizing bacteria. Geology 33, 865-868.

Karol, K.G., McCourt, R.M., Cimino, M.T. and Delwiche, C.F. (2001) The closest living relatives of land plants. Science 294, 2351–2353.

Ke, B. (2001) Photosynthesis: Photobiochemistry and Photobiophysics. In: Govindjee (Series Editor): *Advances in Photosynthesis and Respiration*, Volume 10. Springer, Dordrecht.

Keeley, J.E. and Rundel, P.W. (2003) Evolution of CAM and C4 carbon-concentrating mechanisms. Int. J. Plant Sci. 164 (3 Suppl.), S55–S77.

Kirschvink, J.L., Gaidos, E.J., Bertani, L.E., Beukes, N.J., Gutzmer, J., Maepa, L.N. and Steinberger, R.E. (2000) Paleoproterozoic snowball Earth: Extreme climatic and geochemica global change and its biological consquences. Proc. Natl. Acad. Sci. USA 97, 1400–1405.

Kiang, N.Y., Siefert, J., Govindjee and Blankenship, R.E. (2007) Spectral signatures of photosynthesis. I. Review of Earth organisms. Astrobiology 7, 222-274.

Kleine, T., Münker, C., Mezger, K. and Palmer, H. (2002) Rapid accretion and early core formation on asteroids and the terrestrial planets from Hf–W chronometry. *Nature* 952–955.

Kopp, R.E., Kirschwink, J-L., Hilburn, I.A. and Nash, C.Z. (2005) the Paleoproterozoic snowball Earth: A climate disaster triggered by the evolution of oxygenic photosynthesis. Proc. Natl. Acad. Sci. USA 102, 11131–11136.

Krapez, B., Barley, M.A. and Pickard, A.L. (2003) Hydrothermal and resedimented origins of the precursor sediments to banded iron formation: sedimentological evidence from the Early Palaeoproterozoic Brockman Supersequence of Western Australia. Sedimentology 50, 979–1011.

Kurisu, G., Zhang, H., Smith, J.L. and Cramer, W.A. (2003) Structure of the cytochrome b_6 f complex of oxygenic photosynthesis: tuning the cavity. Science 302, 1009–1014.

Lenton, T. (2001) The role of land plants, phosphorus weathering and fire in the rise and regulation of atmospheric oxygen. Global Change Biology 7, 613–629.

Levrard, B. and Laskar, J. (2003) Climate friction and the Earth's obliquity. Geophys. J. 154, 970–990.

Marg, B.-L., Schweimer, K., Sticht, H. and Oesterhelt, D. (2005) A two-helix extra domain mediates the halophilic character of a plant-type ferredoxin from halophilic archaea. Bio-

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chemistry 44, 29–39.
Marin, B., Nowack, E.C.M. and Melkonian, M. (2005) A plastid in the making: evidence for a second primary endosymbiosis. Protist *156,* 425–432.
Markham, K.R. and Porter, LJ. 1969. Flavonoids in the green algae (Chlorophyta). Phytochemistry 8, 1777–1781.
Mauzerall, D. (1976) Chlorophyll and photosynthesis. Phil. Trans. Roy. Soc. Lond. B 273, 287-294.
McElwain, J.C. (1998) Do fossil plants signal palaeatmospheric CO_2 concentration in teh geological past? Royal Soc. London Phil. Transact. B 353, 83–96.
McElwain, J.C., Mitchell, F.J.G. and Jones, M.B (1995) Relationship of stomatal density and index of *Salix cinerea* to atmospheric carbon dioxide concentrations in the Holcene. The Holocene 5, 539–570.
McElwain, J.C., Mayle, F.E. and Beerling, D.J. (2002) Stomatal evidence for a decline in atmospheric CO_2 concentration during the Younger Dryas stadial: a comparison with Antarctic ice core records. J. Quaternary Sci. 17, 21–29.
Mercer-Smith, J.A. and Mauzerall, D. (1981) Molecular hydrogen production by uroporphyrin and coproporhyrin: A model for the origin of photosynthetic function. Photochem. Photobiol. 34, 407–10.
Moorbath, S. (2005) Palaebiology: Dating the earliest life. Nature 434, 155.
Mulkidjanian, A.Y., Koonin, E.V., Makarova, K.S., Mekhedov S.L., Sorokin, A., Wolf, Y.I, Dufresne, A., Partensky, F., Burd, H., Kaznadzey, D., Haselkorn, R. and Galperin, M.Y. (2006) The cyanobacterial genome core and the origin of photosynthesis. Proc. Natl Acad. Sci. USA 103, 13126-13131.
Nelson, N. and Ben-Shem, A. (2005) The structure of photosystem I and evolution of photosynthesis. BioEssays 27, 914-922.
Nisbet, E. G., Cann, J. R. and VanDover, C. L. (1995) Origins of photosynthesis. Nature (London*)* 373, 479–480.
Olson, J.M. (2006) Photosynthesis in the Archean era. Photosynthesis Res. 88, 109-117.
Osborne, C.P. and Beerling, D.J. (2006) Nature's green revolution: the remarkable evolutionary rise of C4 plants. Phil. Transact. Roy. Soc. B. – Biol. Sci. 361, 173–194.
Petersen, J., Teich, R., Brinkmann, H. and Cerff, R. (2006) A ”green” phosphoribulokinase in complex algae with red plastids: Evidence fro a single secondary endosymbiosis leading to haptophytes, cryptophytes, heterokonts, and dinoflagellates. J. Molecular Evolution 23, 1109-1118.
Pierre, J., Bazin, M., Debey, P. and Santus, R. (1982) One-electron photo-reduction of bacterial cytochrome P450 by ultraviolet light. 1. Steady-state measurements. Europ. J. Biochem. 124, 533–537.
Pierre, Y., Breyton, C., Lemoine, Y., Robert, B., Vernotte, C. and Popot, J.-L. (1997) On the presence and role of a molecule of chlorophyll *a* in the cytochrome b_6 f complex. J. Biol. Chem. 272, 21901–21908.
Raven, J.A., Kübler, J.E. and Beardall, J. (2000) Put out the light and then put out the light. J. Mar. Biol. Ass. U.K. 80, 1–25.
Raymond, J. and Blankenship, R.E. (2003) Horizontal gene transfer in eukaryotic algal evolution. Proc. Natl Acad. Sci. USA 100, 7419-7420.
Raymond, J., Zhaxybayeva, O., Gogarten, J.P. and Blankenship, R.E. (2003) Evolution of photosynthetic prokaryotes: a maximum-likelihood mapping approach. Royal Soc. London Phil. Transact. B 358, 223–230.
Raymond, J., Siefert, J.L., Staples, C.R. and Blankenship, R.E. (2003) The natural history of nitrogen fixation. Mol. Biol. Evol. 21, 541–554.

Reinfelder, J.R., Kraepiel, A.M.L., and Morel, F.M.M. (2000) Unicellular C4 photosynthesis in a marine diatom. Nature 407, 996–99

Reinfelder, J.R., Milligan, A.J. and Morel F.M.M. (2004) The role of C4 photosynthesis in carbon accumulation and fixation in a marine diatom. Plant Physiol. 135, 2106–11.

Rogers, M.B., Gilson, P.R., Su, V., McFadden, G.I. and Keeling, P.J. (2007) The complete chloroplast genome of the chlorarachniophyte *Bigelowiella natans*: Evidence for independent origins of Chlorarachniophyte and Euglenid secondary endosymbionts. Mol. Biol. Evol. 24, 54–62.

Rosing, M.T. and Frei, R. (2004) U-rich Archaean sea-floor sediments from Greenland — indications of >3700 Ma oxygenic photosynthesis. Earth and Planetary Science Letters 217, 237–244.

Rubinstein, B. (1993) Plasma membrane redox processes: components and role in plant processes. Annu. Rev. Plant Physiol. Plant Mol. Biol. 44, 131–55.

Rutherford, A.W. and Faller, P. (2003) Photosystem II: evolutionary perspectives. Phil. Trans. Roy. Soc. London B 358, 254-253.

Sage, R.F. (2004) The evolution of C4 photosynthesis. New Phytologist 161, 341–370.

Sauer, K and Yachandra, V.K. (2002) A possible evolutionary origin for the Mn-4 cluster of the photosynthetic water oxidation complex from natural MnO2 precipitates in the early ocean. Proc. Natl Acad. Sci. USA 99, 8631-8636.

Segura, A., Krelove, K., Kasting, JF., Sommerlatt, D., Meadows, V., Crisp, D., Cohen, M. and Mlawer, E. (2003) Ozone concentrations and ultraviolet fluxes on earth-like planets around other stars. Astrobiology 3, 689-708.

Selesi, D., Schmid, M. and Hartmann, A. (2005) Diversity of green-like and red-like ribulose-1,5-bisphosphate carboxylase/oxygenase large-subunit genes (*cbbL*) in differently managed agricultural soils. Appl. Environm. Microbiol. 71, 175–184.

Staehelin LA (1986) Chloroplast structure and supramolecular organization of photosynthetic membranes. In: Staehelin LA and Arntzen CJ (eds) *Photosynthesis III: Photosynthetic Membranes and Light-Harvesting Systems*, Vol 19, pp 1–84. Springer-Verlag, Berlin.

Stoebe, B. and Maier, U.-G. (2002) One, two, three: nature's tool box for building plastids. Protoplasma 219, 123–130.

Stroebel, D., Choquet, Y., Popot, J.-L. and Picot, D. (2003) An atypical haem in the cytochrome b_6 f complex. Nature. 426, 413–418.

Strzepek, R.F. and Harrison, P.J. (2004) Photosynthetic architecture differs in coastal and oceanic diatoms. Nature 431, 689–692.

Summons, R.E., Jahnke, L.L., Hope, J.M. and Logan, G.A. (1999) 2-methylhopanoids as biomarkers for cyanobacterial oxygenic photosynthesis. Nature 400, 554-557.

Svensson, P., Bläsing, O.E. and Westhoff, P. (2003) Evolution of C4 phosphoenolpyruvate carboxylase. Arch. Biochem. Biophys. 414, 180–188.

Tajika, E. (2003) _Faint young Sun and the carbon cycle: implication for the Proterozoic global glaciations. Earth Planetary Sci. Lett. 214, 443-453.

Tapley, D.W., Buettner, G.R. and Shick, J.M. (1999) Free Radicals and Chemiluminescence as Products of the Spontaneous Oxidation of Sulfide in Seawater, and Their Biological Implications. Biol. Bull. 196, 52–56.

Tice, M.M. and Lowe, D.R. (2004) Photosynthetic microbial mats in the 3,416 Myr-old ocean. Nature 431, 549–552.

Tice, M.M. and Lowe, D.R. (2006) Hydrogen-based carbon fixation in the earlies known photosynthetic organisms. Geology 34, 37–40.

Tomitani. A., Knoll, A.H., Cavanaugh, C.M, and Ohno, T. (2006) The evolutionary diversifi-

cation of cyanobacteria: Molecular-phylogenetic and paleontological perspectives. Proc. Natl Acad. Sci. USA 103, 5442-5447.

Van Rensen, J.J.S., Xu, C. and Govindjee (1999) Role of bicarbonate in Photosystem II, the water –plastoquinone oxido-reductase of plant photosynthesis. Physiol. Plant. 105, 585-592.

Warburg, O., Krippahl, G. and Jetschma, C. (1965) Widerlegung der Photolyse des Wassers und Beweis der Photolyse der Kohlensäure nach Versuchen mit lebender *Chlorella* und den Hill-Reagentien Nitrat und $K_3Fe(Cn)_6$. Z. Naturforsch. B B20, 993–996.

White, S.N., Chave, A.D., Reynolds, G.T., Gaidos, E.J., Tyson, J.A. and Van Dover, C.L. (2000) Variations in ambient light emission from black smokers and flange pools on the Juan de Fuca Ridge. Geophys. Res. Lett. 27, 1151–1154.

White, S.N., Chave, A.D. and Reynolds, G.T. (2002) Investigations of ambient light emission at deep-sea hydrothermal vents. J. Geophys. Res. – Solid Earth 107 (B1), Art. No. 2001.

White SN, Chave AD, Reynolds GT, Van Dover CL. (2002) Ambient light emission from hydrothermal vents on the. Mid-Atlantic Ridge. Geophys. Res. Lett. 29, Art. No. 1744.

Wilde, S.A., Valley, J.W., Peck, W.H. and Graham, C.M. (2001) Evidence from detrital zircons for the existence of continental crust and oceans on the Earth 4.4 Gyr ago. Nature 409, 175–178.

Williams, D.M., Kasting, J.F. and Frakes LA (1998) Low-latitude glaciation and rapid changes in the Earth's obliquity explained by obliquity-oblateness feedback. Nature 396, 453–455.

Witt, H.T. (2005) Photosystem II: Structural elements, the first 3D crystal structure and functional implications. In: Wydrzynski, T.J. and Satoh, K. (eds) *Photosystem II, the light-driven water:plastoquinone oxidoreductase* Advances in Photosynthesis and Respiration Series (Govindjee, series ed.), vol. 22. Springer, Dordrecht, pp 425-447.

Woese, C.R. (2005) The archaeal concept and the world it lives in: a retrospective. In: Govindjee, Beatty, J.T., Gest, H. and Allen, J.F. (eds) *Discoveries in Photosynthesis*. Advances in Photosynthesis and Respiration (Govindjee, series ed.), vol 20. Springer, Dordrecht, pp 1109-1120

Xiong, J. and Bauer, C.E. (2002) A cytochrome *b* origin of photosynthetic reaction centers: an evolutionary link betweeen respiration and photosynthesis. J. Mol. Biol. 322, 1025–1037.

Xiong, J. and Bauer, C.E. (2002) Complex evolution of photosynthesis. Annu. Rev. Plant Biology 53, 503–521.

Yano, J., Kern, J,, Sauer, K., Latimer, M.J., Pushkar, Y., Biesiadka, J., Loll, B., Saenger, W., Messinger, J., Zouni, A. and Yachandra, V.K. (2006) Where water Is oxidized to dioxygen: Structure of the photosynthetic Mn_4Ca cluster. Science 314, 821-825.

Yin, Q., Jacobsen, S.B., Yamashita, K., Blichert-Toft, J., Télouk, P. and Albarède, F. (2002) A short timescale for terrestrial planet formation from Hf-W chronometry of meteorites. Nature 418, 949–952.

Yoshi, Y. (2006) Diversity and evolution of photosynthetic antenna systems in green plants. Phycolog. Res. 54, 220–229.

Zhang, B.P., Janicke, M.T., Woodruff, W.H. and Bailey, J.A. (2005) Photoreduction of a heme peptide encapsulated in nanostructured materials. J. Phys. Chem. B. 109, 19547–19549.

Zhaxybayeva, O., Lapierre, P. and Gogarten, J.P. (2005) Ancient gene duplications and the root(s) of the tree of life. Protoplasma 227, 53-64.

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