The Evolution of Photosynthesis and Its Environmental Impact

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Lars Olof Björn and Govindjee

16.1 Introduction

The earth began to form about 4.6 Ga (gigayears, billion years) ago. Thirty million years later a core had formed (Yin et al. 2002; Kleine et al. 2002), and as early as 4.4 Ga ago, there may have been a continental crust and an ocean (Wilde et al. 2001). Land probably started to emerge from the ocean 3.4 Ga ago (Flament 2013). Between 4.2 and 3.7 Ga ago, the earth was subjected to "the late heavy bombardment" (Gomes et al. 2005), which is by many thought to have wiped out any life that might have existed at that time. The oldest known fossils are 3.34 Ga old (Fliegel et al. 2010). The first organisms emerging after that cataclysm may not have been able to carry out photosynthesis, but relied on conversion of energy for their life processes by reducing carbon dioxide to methane, using hydrogen as reductant (see Thauer et al. 2008 for further information). Photosynthetic life is likely as ancient as the currently earliest fossils, probably at least 3.3–3.4 Ga (Blankenship 1992; Tice and Lowe 2004, 2006; Westall et al. 2011). The earliest photosynthesis differed from the process taking place in plants now, but there are likely to be some features that may be traced all the way back to the earliest form of photosynthesis.

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16.2 A Brief Review of Oxygenic Photosynthesis

Oxygenic photosynthesis consists of the oxidation of water to molecular oxygen and reduction of carbon dioxide to organic matter, primarily carbohydrate. It takes place in chloroplasts, with one set of reactions in the pigment-rich thylakoid membranes and another set of reactions in the stroma (Figs. 16.1 and 16.2).

In the thylakoid membranes the following takes place: Light is absorbed by chlorophyll *a* and other pigment molecules. The absorbed energy is transferred to reaction centers (RC). There are two kinds of reaction center-containing pigment-protein complexes, photosystem I (PSI) and photosystem II (PSII) (see Figs. 16.3 and 16.4). They can be regarded as light-powered "electron pumps" that move electrons between electron carriers, and thereby chemically stabilize the energy, originally contained in absorbed photons. These pumps are connected in series by another protein complex (the cytochrome b/f complex) and two smaller, mobile electron carriers, plastoquinone, and plastocyanin. The "electron pumps" lift electrons from an energy-poor state in water to an energy-rich state in NADPH. What remains of the two water molecules from which electrons have been removed is free oxygen (molecular oxygen, O_2) and hydrogen ions (protons). As a consequence of the electron transfer process, protons are pumped from the stroma into the interior of the thylakoids. This proton concentration difference between the inside of the thylakoid and the outside (stroma) is then used to produce energy-rich phosphate, ATP by the ATP synthase. The process outlined above is, in essence, the chemiosmotic theory of Peter Mitchell for which he received the Nobel Prize in 1978. In the stroma, reduced ferredoxin and ATP and protons are used to reduce carbon dioxide to carbohydrate. This is a very brief description of the essential steps of oxygenic photosynthesis. For further details on the photosynthetic

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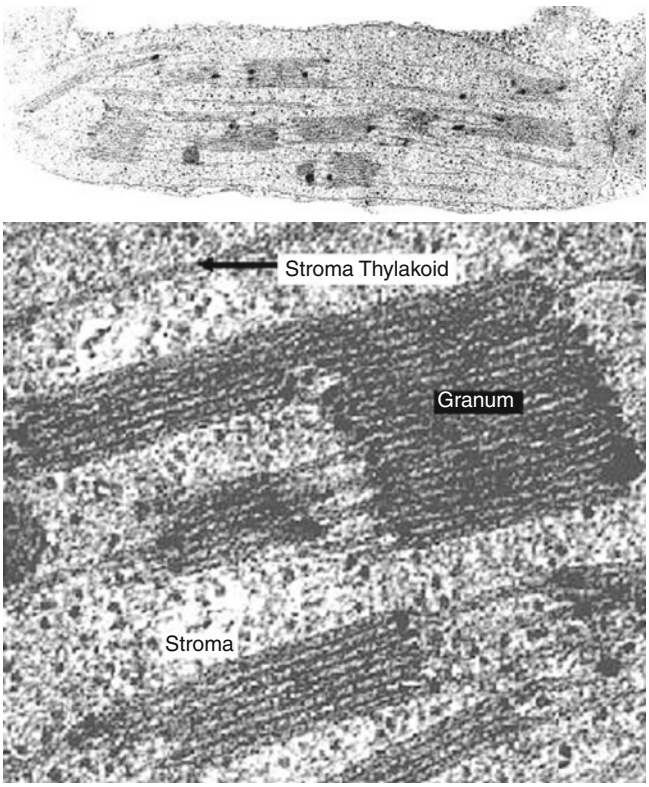

Fig. 16.1 An electron micrograph of a section of a chloroplast from tobacco leaf (*top*) and the same at a higher magnification (*bottom*) showing details of grana and thylakoids. The stroma thylakoids (*stroma lamellae*) run through the stroma between the grana (Courtesy of Professor Claes Weibull, Lund University)

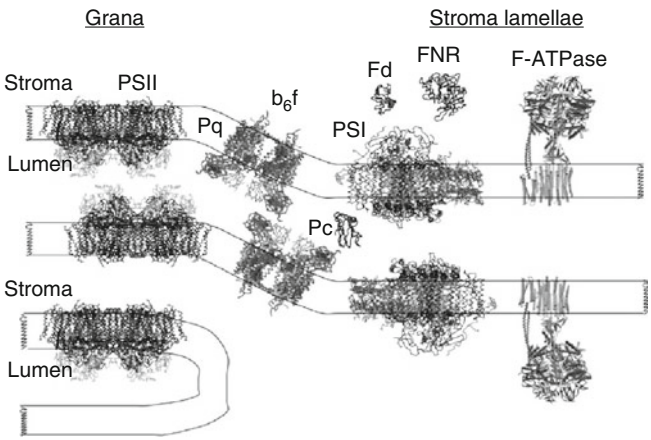

Fig. 16.2 Arrangement of molecules participating in photosynthesis in a green plant. Of the large protein complexes, photosystem II (*PSII*) is located predominantly in the grana lamellae (parts of thylakoid membranes forming grana) and photosystem I (*PSI*) and F-ATPase (ATP synthase) mainly in the stroma lamellae. In PSII, electrons are transferred from water to the cytochrome b6f complex via plastoquinone (*Pq*), and from there, they are transferred 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 of the thylakoid membrane. Protons flowing back to the stroma via the ATP synthase drive the synthesis of ATP, which is also used in carbon dioxide assimilation. Variations of this scheme occur, and cyanobacteria and algae on the red line of evolution differ in several respects (see Sects. 16.7 and 16.8) (From Nelson and Ben-Shem 2002)

process, see Ke (2001), Blankenship (2014), Nelson and Ben-Shem (2005), Golbeck (2006) for PSI, and Wydrzynski and Satoh (2005) and Rutherford and Faller (2003) for PSII. Oxygenic photosynthesis is carried out by plants, algae and cyanobacteria. In contrast, a large number of photosynthetic bacteria carry out anoxygenic photosynthesis where water is not oxidized, and oxygen is not evolved (see Section 16.5; for details, and chapters in Blankenship et al. 1995, and Hunter et al. 2009).

16.3 The Domains of Life

The living world is subdivided into three "domains" or main organismal groups, i.e., Archaea (formerly called archaebacteria), Bacteria (eubacteria, or just bacteria), and Eukarya (eukaryotes) (Woese 2005).

Photosynthesis is only found in the domain Bacteria (as such or when they became parts of certain Eukarya). That plants can carry out photosynthesis is because the precursors of plant cells had combined with a photosynthetic bacterium in endosymbiotic events (see Sect. 16.8)

16.4 Predecessors of the First Photosynthetic Organisms

As already mentioned, oxygenic 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) reduction of carbon dioxide, taking place in the stroma. Of these, the reduction of carbon dioxide may be a much more ancient process than the oxidation of water. One type of light-independent carbon dioxide reduction is its reduction to methane with hydrogen as a reductant. Light-independent reduction of carbon dioxide in early organisms may be more ancient than that driven by the thylakoids (Battistuzzi et al. 2004). It is possible that one of these early light-independent carbon reduction pathways is the ancestor of the carbon fixation taking place in the stroma of chloroplasts. Plants use the enzyme RuBisCO (ribulose-1, 5-bisphosphate carboxylase/oxygenase) to bind carbon dioxide; further, some nonphotosynthetic bacteria also use this enzyme.

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

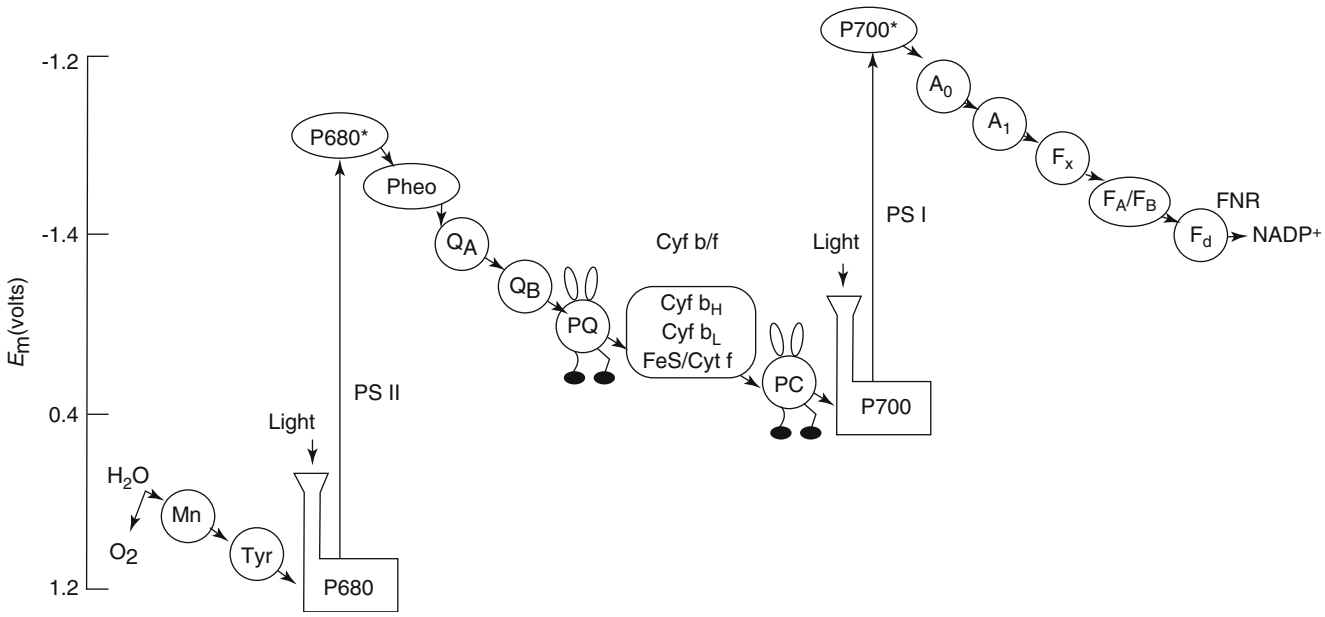

Fig. 16.3 Drawing of electron transport (the so-called Z-scheme) in oxygenic photosynthesis in plants, algae, and cyanobacteria. Light is collected by antennas pigments, symbolized as funnels and transferred to reaction center pigments (P680 in PS II and P700 in PS I, in both cases chlorophyll a). Electrons are "sucked" from water via the manganese complex (made up of 4 Mn and 1 Ca) in the water-splitting enzyme and a specific tyrosine residue in a PS II peptide. Using energy from light, photosystems "lift" the electrons to a higher energy (more negative redox potential). They leave the reaction center chlorophylls, which temporarily become positively charged, and flow over a chain of electron carriers. Of these, Pheo (pheophytin), Q_A and Q_B (both quinones), as well as A_0 (chlorophyll), A_1 (vitamin K), F_x and F_A, and F_B (iron–sulfur centers) are membrane bound, while PQ is plastoquinone that diffuses in the membrane lipid, PC is plastocyanin, a small copper protein that diffuses in the aqueous lumen space, and Fd (ferredoxin) and $NADP^+$ (nicotinamide dinucleotide phosphate) diffuse in the stroma. FNR stands for the enzyme ferredoxin-$NADP^+$ reductase. The feet and rabbit ears on PQ and PC symbolize that they are mobile. Between them is the large cytochrome b6/f complex with several electron carriers. When $NADP^+$ takes up two electrons and one proton, it becomes NADPH, which is used for carbon dioxide reduction (From Govindjee 2000). What is missing in the diagram is a bicarbonate ion, bound on a non-heme iron, between Q^A and Q^B, nd required for the reduction of Q^B. An account of the research that has led to the Z-scheme is given by Govindjee and Björn (2012)

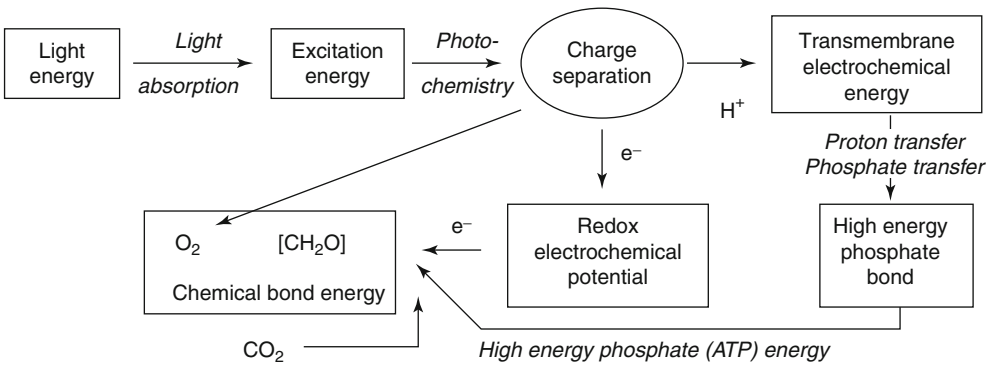

Fig. 16.4 Energy transformation in photosynthesis. Light energy absorbed by antennas pigments is transferred to reaction centers where charge separation takes place. The positive charges are transferred to water, which splits into hydrogen ions (H^+) and molecular oxygen (O_2). The nonequilibrium distribution of hydrogen ions ultimately results in energy trapped in ATP, while the energy gained by the nicotinamide adenine dinucleotide ($NADP^+$) as it is reduced to NADPH makes it possible for it to act as a reductant for carbon dioxide, aided by the energy from ATP

Bacillus subtilis (Ashida et al. 2003, 2005), and it may have evolved from a protein involved in sulfur metabolism.

When the first photosynthetic organisms appeared, they inherited many useful biochemical components from their nonphotosynthetic predecessors, including soluble components present in the chloroplast stroma and the electron transporters in the thylakoid membranes.

Iron–sulfur proteins are thought to have an ancestry that reaches back to life's beginnings, with their active centers being derived from inorganic iron sulfide. Eck and Dayhoff

(1966) suggested that the protein part of ferredoxin has evolved from a peptide with only four amino acids. Other types of electron transporters in the thylakoids with very ancient origins are quinones and cytochromes. According to one view (Schoepp-Cothenet et al. 2013) the last universal common ancestor (LUCA) was equipped with quinones and cytochromes, but reasons for a different view have also been presented (Sousa et al. 2013b; Xiong and Bauer 2002). The most important of the thylakoid pigments, chlorophyll *a*, is derived from the same biosynthetic pathway that leads to heme, the central part of cytochromes. During chlorophyll biosynthesis, there are steps that convert protochlorophyllide to chlorophyllide; interestingly, the genes for the enzyme reducing protochlorophyllide to chlorophyllide *a* in the dark (DPOR) is thought to have been derived from genes for another enzyme, nitrogenase, which is used by organisms to fix N_2 (Armstrong 1998; Chew et al. 2007).

Photosystems I and II are possibly descendants of cytochrome *b*, as structural similarities between the cytochrome b6/f-and photosystems have been presented by Xiong and Bauer (2002); further, the cytochrome complex also contains one molecule of chlorophyll *a* per monomer (Baldet al. 1992; Huang et al. 1994; Pierre et al. 1997; Stroebel et al. 2003; Kurisu et al. 2003; Dashdori et al. 2005). Another line of evidence for an ancient relationship between cytochromes and reaction centers comes from the finding that cytochromes *b* from various sources, as well as other heme compounds, can be photoreduced using light absorbed in the heme (Pierre et al. 1982; Asard et al. 1989; Gu et al. 1993; Rubinstein 1993; Zhang et al. 2005; Löwenich et al. 2008).

16.5 The First Photosynthesis

The first photosynthetic organisms did not have two types of photosystems in series, as the present-day cyanobacteria, algae, and plants do, but contained a single type of photosystem. The very first photosynthetic organisms could not oxidize water to molecular oxygen—thus far, the researchers agree, but not further. Extant photosynthesizing bacteria can, with regard to photosystems, be divided into three main groups. (1) Cyanobacteria (formerly referred to as blue-green algae) with two photosystems (PSI and PSII) connected in series, and evolving oxygen; we shall return to them later; (2) green sulfur bacteria, heliobacteria, and acidobacteria, with only a single photosystem resembling PSI of plants and cyanobacteria; (3 purple bacteria and filamentous anoxygenic phototrophs (also known as green non-sulfur bacteria), also with single photosystem resembling the PSII core in plants and cyanobacteria, but without water oxidizing machinery (see Hu et al. 2002). All photosystems, PSI-like as well as PSII-like, have important similarities so that there is no doubt that they all derive from the same ancestral photosystem.

Where is the origin of this first photosynthesizer? Nisbet et al. (1995) suggested that the ability to photosynthesize would have evolved from a system involved in orientation (e.g., phototaxis) in bacteria living deep in the sea near hydrothermal vents, which were able to sense heat radiation from the vents. Björn (1995) suggested that it would not have been possible to drive photosynthesis by the heat radiation from those vents. However, Beatty et al. (2005) showed that photoautotrophic bacteria are present in the vicinity of thermal vents. White et al. (2000, 2002a, b) have shown that the vents radiate not only heat radiation but also visible light which probably originates from oxidation of sulfide (Tapley et al. 1999).

Hirabayashi et al. (2004) have cultivated a photosynthetic bacterium, *Chlorobium phaeobacteroides*, in very weak light (less than 3 μmol photons m^{-2} s^{-1} of photosynthetically active radiation). After theoretical considerations, Raven et al. (2000) suggested that a photosynthetic organism might be able to live even with a daily average of only 4 nmol photons m^{-2} s^{-1}.

The most ancient evidence for photosynthesis, accepted by a majority of scientists, is found in a 3.416-Ga-old chert in South Africa (Tice and Lowe 2004, 2006). Even more ancient evidence for photosynthesis is present in the carbon isotope composition of a 3.8-Ga-old graphite in Greenland (Olson 2006). The organisms performing this ancient photosynthesis may have used molecular hydrogen as a reductant. Later, electron donors such as divalent iron (Fru et al. 2013) or hydrogen sulfide were utilized. Fossils attributed to photosynthetic organisms based on morphological features have been described by Awramik (1992) and Fru et al. (2013).

Green sulfur bacteria, heliobacteria, and photosynthetic acidobacteria, which have the same type of PSI-like photosynthetic reaction center, are not closely related, as judged by other characteristics. Nor all the bacteria having PSII-like photosystems are closely related. *Chloroflexus aurantiacus*, with a photosystem of type II, has about the same pigment complement as *Chlorobium tepidum* with a photosystem of type I. These apparent "inconsistencies" 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 et al. 2003a, b). During the enormous time span of bacterial evolution, there must have been sufficient occasion for transfer of all the genes required for the formation of photosystems.

Although anoxygenic photosynthesis is thought by most to have preceded the more complicated oxygenic photosynthesis (see Björn and Govindjee 2009), there has been disagreement about whether the use of chlorophyll *a* as light-harvesting and reaction-center pigment, as is the case in most extant oxygenic organisms, or some version of bacteriochlorophyll came first. Granick (1957) reasoned that, since chlorophyll *a* precedes bacteriochlorophyll in the biosynthetic pathway of modern organisms, chloro-

phyll *a*-based photosynthesis must have preceded bacteriochlorophyll-based photosynthesis in evolution. Olson and Pierson (1987) further speculated that the first photosynthesis was mediated by a pigment, a couple of steps further back in the biosynthetic path, namely, protoporphyrin IX. The absorption coefficient of this compound at its long-wavelength absorption maximum is 7,000 M^{-1} cm^{-1} (in ethyl ether), as compared to 22,000 for protochlorophyll and 90,000 for chlorophyll *a*. Therefore it seems that the additional steps within the prolongation of the biosynthetic path way brought with it considerable improvement in absorption power. The addition of the a light-harvesting antennas to the reaction center led to more photosynthesis and, thus, growth, since more photons could be harvested (see Sect. 1.18).

Further, Olson and Pierson (1987) drew up a scheme, in which a reaction center of type 1 evolved before type 2. In a primitive organism with this single reaction center and only one type of photoreaction, a gene duplication took place which led to an organism with both type 1 and type 2 reaction centers, as in the present-day cyanobacteria. Bacteria having only type 2 reaction centers then evolved by deletion of the genes for type 1 reaction centers. With increase in sequenced bacterial genomes, it has become possible to test these ideas. Mulkidjanian and Galperin (2013) arrived at largely the same evolutionary scenario as did Olson and Pierson (1987) (Fig. 16.5), but with additional details.

A final step in the evolution of anoxygenic photosynthesis would have been the replacement of chlorophyll *a* with various forms of bacteriochlorophyll. Gupta (2013) provides evidence that genes in the terminal steps of bacteriochlorophyll (or more specifically bacteriochlorophyll *a*) synthesis are derived from the corresponding genes for chlorophyll *a* synthesis.

Chlorine reductase is found in anoxygenic photosynthetic bacteria, but not in cyanobacteria. Gupta (2013) points out that conserved insertions or deletions in the NifH, BchX, and BchL proteins provide evidence that BchX homologues originated prior to the BchL homologues and that a conserved indel in the BchL protein provides evidence that BchL homologues from Heliobacteriaceae are primitive in comparison to sequences from other phototrophs. Several researchers (including Radhey S. Gupta) have come to the conclusion that photosynthesis originated in Heliobacteriaceae; further, they find it likely that either Chloroflexi or Cyanobacteria were the earliest recipients of the genes for photosynthesis from Heliobacteriaceae. The latter might well also be a common ancestor for both Chloroflexi and Cyanobacteria. This view differs from that of Mulkidjanian et al. (2006) and Mulkidjanian and Galperin (2013), who regard photosynthesis to have originated in a hypothetical Procyanobacteria, which would have given rise to all other photosynthetic bacteria.

The scheme of Mulkidjanian and Galperin (2013) is largely in agreement with the one by Olson and Pierson (1987) focusing on the evolution of photosynthetic pigments. Olson and Pierson find it likely that the first photosynthesis pigment was protoporphyrin IX, the precursor of protochlorophyllide. The primitive reaction center would in addition have contained FeS as primary electron acceptor. A quinone could have been added later and allowed proton transport across a membrane. They assume that cytochrome would have been added later.

16.6 Photoheterotrophy in the Ocean: Light Harvesting on the Loose

16.6.1 Energy-Harvesting Systems on the Run I: Proteorhodopsin

As mentioned above, it has been difficult to define how the evolution of photosynthesis has taken place among organisms; this is because of the widespread horizontal transfer of photosynthesis genes. Two fundamentally different photoconverters are present in today's organisms. One type uses rhodopsin as the light absorbing pigment to mediate proton translocation across a membrane. The other type uses chlorophylls to convert light energy into redox energy, which is stored in electron carriers, the mean theme of this chapter.

Microbial rhodopsin was first known from halorhodopsin in *Halobacterium*. A variant of this rhodopsin, known as proteorhodopsin, is found not only among α- (Stingl et al. 2007), β-, and γ-proteobacteria, such as the classical organoheterotroph *Vibrio campbellii* (Wang et al. 2012), but also among Bacteriodetes (Gómez-Consarnau et al. 2007, 2011, González et al. 2008; Riedel et al. 2010), Archaea (Frigaard et al. 2006), and eukaryotes (Janke et al. 2013). Although proteorhodopsin is related to halorhodopsin and other "microbial" (type I) rhodopsins, it forms a very distinct clade (McCarren and DeLong 2007; Fig. 16.6).

We have little doubt that viruses harboring proteorhodopsin genes have contributed to their widespread distribution (Yutin and Koonin 2012). The proteorhodopsin-containing organisms are not able to carry out carbon dioxide assimilation, but the light-driven proton translocation across a membrane provides them, via a membrane-bound ATP-synthase, with ATP. This kind of light harvesting has been found in many taxa, despite the lower absorption cross section of proteorhodopsin as compared to absorption cross sections of (bacterio-)chlorophyll-based photosystems (Bryant and Frigaard 2006). It has been experimentally shown that rhodopsins can help bacteria grow in a low organic carbon environment to gather carbon compounds from their environment and, thus, increase growth (Gómez-Consarnau et al. 2007; Steindler et al. 2011).

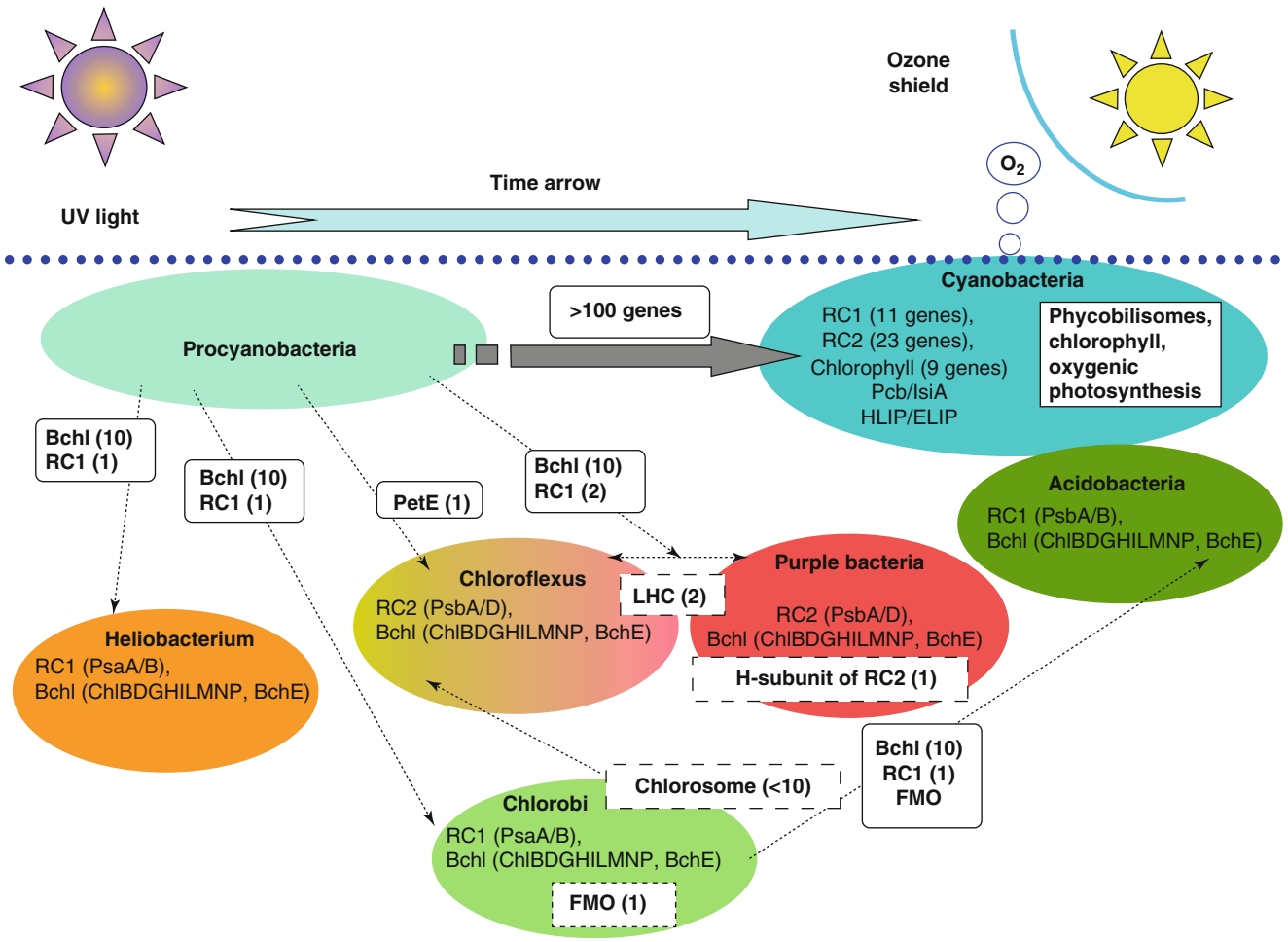

Fig. 16.5 Evolution of bacterial reaction centers according to Mulkidjanian and Galperin (2013). Gupta (2013) arrived at a slightly different relationship, with primitive photosynthesis having arisen in Heliobacteriaceae and from there spreading first to either Cyanobacteria or Chloroflexi. He regards Chlorobi as descendents of Chloroflexi, despite the differences in the reaction center type they have *BChl*, bacteriochlorophyll; *Chl*, chlorophyll; *ELIP*, early light-stress protein; *FMO*, Fenna-Matthews-Olson complex; *IsiA*, a photoprotective protein; *LHC*, light-harvesting complex: *HLIP*, high light-induced protein; *Pcb*, prochlorophyte chlorophyll binding protein; *Psa* and *Psb*, reaction center polypeptides; *RC*, reaction center; (Copyright 2013 © National Academy of Sciences USA; reproduced with permission)

16.6.2 Energy-Harvesting Systems on the Run II: Roseobacter

The other "photoconverter on the run" that deserves special mention is the chlorophyll-based photoconverter found in aerobic anoxygenic type of photosynthesis common within the "Roseobacter clade," which has many genera and is exclusively marine or hypersaline, with isolates which require salt and/or are tolerant to it (Wagner and Bibl 2006). Like the proteorhodopsin system, it produces ATP, but there is only transitory photoreduction in the system. Holert et al. (2011) have shown that in *Dinoroseobacter shibae*, light-driven reactions contribute to chemiosmotic energy conservation. The genes for this kind of "photosynthesis" are transmitted between bacteria by plasmids (Petersen et al. 2012, 2013; Yutin and Koonin 2012). Not all members of the *Roseobacter* clade carry out light harvesting, but those who do are found in many marine habitats, both as free-living bacteria and as symbionts in dinoflagellates, and other organisms (Allgaier et al. 2003).

Kirchman and Hanson (2013) have compared the energy economy of organisms for harvesting energy, those that use proteorhodopsin, with those that use a chlorophyll-type photosystem, as in the *Roseobacter* (Fig. 16.7); further, Kirshman and Hansen found that the *Roseobacter* system is more efficient, even after they had taken into account the lower maintenance cost for the proteorhodopsin system. This is simply because *Roseobacter* has a large antennas system per reaction center. A higher ratio of light-harvesting pigments to protein gives a better energy-gathering capability with respect to the maintenance cost.

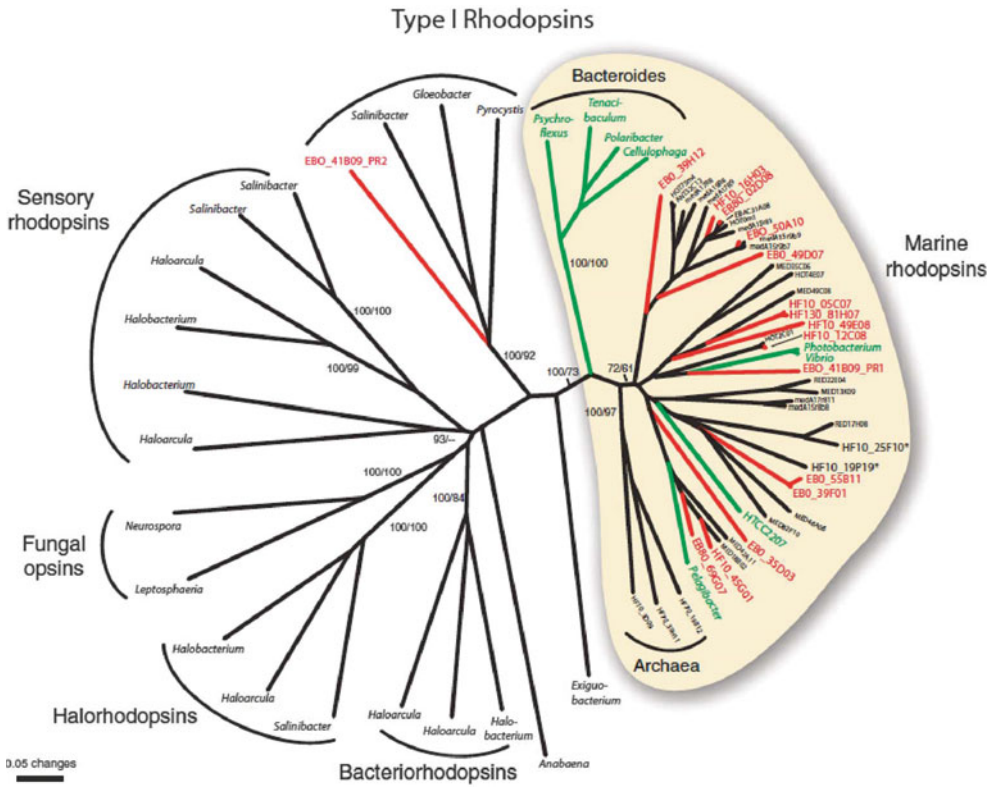

Fig. 16.6 Phylogenetic relationship among "microbial" (type I) rhodopsins. What is designated above as "marine rhodopsins" is what is usually referred to as proteorhodopsins (from McCarren and DeLong 2007)

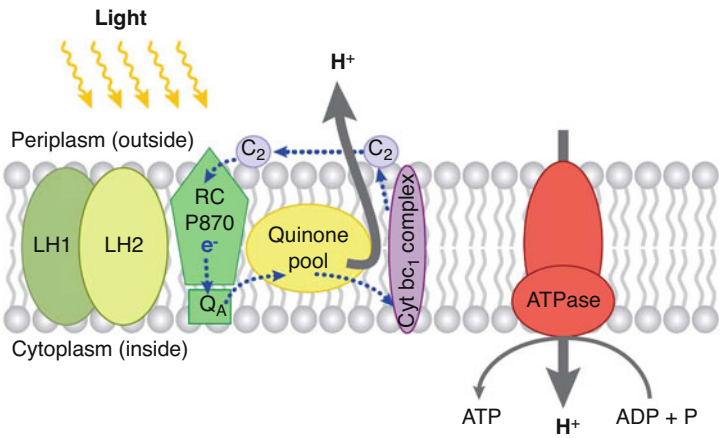

Fig. 16.7 The energy harvesting system of Roseobacter and related bacteria (from Wagner-Döbler and Bibl 2006)

16.7 Appearance of Oxygenic Photosynthesis

In contrast to cyanobacteria that have PSII, anoxygenic photosynthetic bacteria lack the water-oxidizing (oxygen-evolving) complex, even if they possess a photosystem of type II. The type II photosystem of these bacteria differs also in some other respects from the PSII of plants, algae, and cyanobacteria. The oxygenic PSII-type reaction center contains six separated pigment molecules instead of the "special pair"-type chlorophyll molecules, arranged as a tightly coupled pair in most anoxygenic autotrophs and in PSI. The "special pair" arrangement gives a lower-lying first excited state than a single molecule would have. As long as not very large quanta are needed for the electron transfer, this is an advantage since it allows the use of a wider part of the daylight spectrum. For the stepwise oxidation of water, more energy is required than for the electron transport processes mediated by most anoxygenic photosystems. Rutherford and Faller (2003) postulated that this is the main reason for the special chlorophyll characteristics of PSII

compared to special pair bacteriochlorophyll arrangement found in anoxygenic photosystems.

Dismukes et al. (2001) have speculated on how the water-oxidizing system could have evolved via a bicarbonate-oxidizing and oxygen-evolving intermediate stage. The interesting finding of Warburg et al. (1965) that oxygen evolution is stimulated by carbon dioxide may have been the first indication of this concept. Clausen et al. (2005a, b) have shown that *free* carbon dioxide is not an intermediate in oxygen evolution. Bicarbonate has been shown to function on both the electron acceptor and donor sides of PS II (see reviews by Van Rensen et al. 1999; Shevela et al. 2012). Further, in the crystal structure of PS II, Ferreira et al. (2004) have modeled one bicarbonate anion near the nonheme iron on the acceptor side and another one on the electron donor side. However, Umena et al. (2011) do not see any bound bicarbonate on the donor side. This does not mean that there is no effect of bicarbonate on the donor side of PSII; it may be involved in protonation reactions during water oxidation, without it being bound on that side (see Shevela et al. 2013).

Johnson et al. (2013) provide geologic indications that manganese may have served as an electron donor for photosynthesis before a system for its re-reduction by water evolved. By isotopic analysis of drill cores, they established that the oxidative branch of the Mn cycle predates rise of oxygen. Blankenship and Hartman (1998) point to hydrogen peroxide as a possible reductant before water.

There are different opinions about how organisms evolved from having one photosystem to two photosystems as in cyanobacteria, algae, and plants. One can imagine that from the first photosynthetic organism evolution took place along two lines, but with a single photosystem in each case. One line led to bacteria having photosystems of type I and the other to bacteria with type II photosystem. The two kinds of bacteria then entered into a symbiosis, which became more and more intimate, until the result was an integrated organism, which evolved into the first cyanobacterium. (We note, however, that this is not enough without the origin of the oxygen evolving complex, which by itself remains quite a mystery.) Another possibility is that gene transfer took place from one organism to another without complete fusion of the two lines of evolution. There is also a third possibility that was suggested by Allen (2005); we describe it below.

Much of the evidence for the views of how the early evolution of photosynthesis took place is based on comparison between extant organisms. But there is also reliable geological evidence for it. Morphological features of bacteria preserved in fossils do not give much guidance in clarifying the nature of the first photosynthetic bacteria, except that the occurrence of heterocyst-like structures strengthens the view that both cyanobacteria and an oxygen-containing atmosphere are of great antiquity (Tomitani et al. 2006). There are also chemical and physical characteristics of fossils to support this view, even if their interpretation is often debated. Perhaps, 2-α-methyl hopane is a reliable signature of the presence of cyanobacteria (Summons et al. 1999); it has been indeed found in 2.7-Ga-old rocks (Brocks et al. 2003). However, similar compounds have also been traced to be related to anaerobic bacteria (Härtner et al. 2005) and, in particular, those carrying out photosynthesis with Fe^{2+} as electron donor (Eickhoff et al. 2013). One opinion is that the oldest proof for the existence of cyanobacteria dates to about 2.15 Ga ago (Hofmann 1976; Tomitani et al. 2006; Rasmussen et al. 2008), but oxygen production had taken place earlier than that (Crowe et al. 2013). Sometimes a certain carbon isotope ratio has been seen as a sign that the carbon has been assimilated by RuBisCO or to indicate the existence of a certain kind of assimilating organism. Farquhar et al. (2011) provide a thorough and critical discussion of various proxies for the oxygenation of the oceans and the atmosphere during the Great Oxygenation Event (2.45–2.32 Ga ago) and the first oxygenic photosynthesis taking place about 200 Ma before that. Anbar et al. (2007) present evidence for "a whiff of oxygen" 2.501 ± 0.008 Ga ago. Crowe et al. (2013) argue for at least transient oxygenation already about 3 Ga ago.

Banded iron formations (BIFs) have been interpreted in many different ways (see Krapež et al. 2003, for further information). 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 cyanobacteria do (Kappler et al. 2005).

The type of photosynthesis carried out by cyanobacteria requires a very complicated machinery with cooperation between the two photosystems in series and an enzyme which collects four oxidation equivalents for the 4-step oxidation of water. Many researchers believe that the evolution of this complex machinery from the first primitive chlorophyll-based photoconverter(s) required a vast expanse of time. 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 observation of changing ratios between thorium and uranium in 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, and, thus, 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. Thus, a changed ratio is taken as evidence for the presence of oxygen 3.7 Ga ago. However, objections have been voiced for interpreting geological features in terms of the involvement of biological activity (e.g., Brasier et al. 2005; Moorbath 2005).

Small amount of hydrogen peroxide could have formed abiotically in the Archaean age by the action of ultraviolet radiation on pyrite, and there have been speculations that

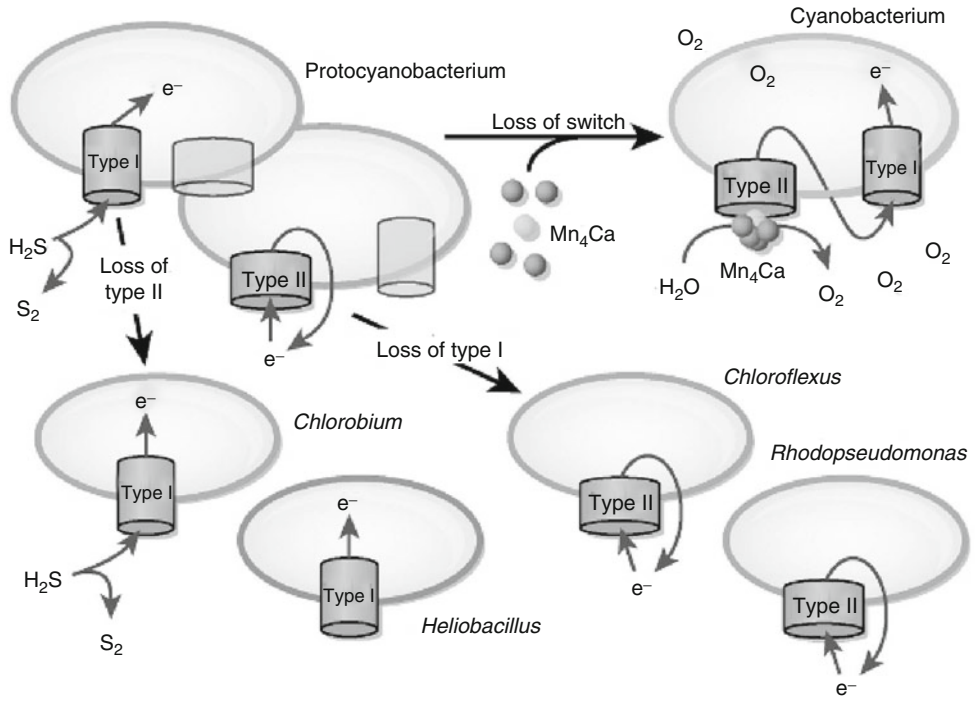

Fig. 16.8 An early photosynthesizer having two photosystems and a switch to select expression of the gene for one or the other (*upper left*) could, during evolution, lose one or the other of the genes and turn into one of several types of nonoxygenic photosynthetic bacteria (either as *Chlorobium* or *Heliobacillus* with a type I photosystem or as *Chloroflexus* or *Rhodopseudomonas* with a 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)

oxygenic photosynthesis evolved from a pathway for detoxification of hydrogen peroxide (Borda et al. 2001) (see also Blankenship and Hartman 1998 and references therein; Rutherford and Nitschke 1996; Bader 1994; Samuilov et al. 2001 concerning the possibility of peroxide as an electron donor). In our opinion, the structure of the oxygen-evolving complex, which has little similarity to other manganese-containing hydrogen peroxide utilizing enzymes with known structure, does not support such a theory.

The structure of the oxygen-evolving complex (Yano et al. 2006; Umena et al. 2011) has similarities to some manganese minerals; it is possible that it may have inherited its structure from these compounds (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 inhibits PSII in present-day organisms partly by UV absorption by manganese (Hakala et al. 2005, 2006).

According to a hypothesis of Allen (2005) and elaborated by Allen and Martin (2007) and Sousa et al. (2013a, b), organisms having two types of photosystems are older than oxygenic photosynthesis. Arguments have been made that the ancestral photosystem was probably more similar to PSI than to PSII (Baymann et al. 2001; Mulkidjanian et al. 2006). After gene duplication of this PSI-like photosystem, a PSII-like photosystem evolved within the same organism that had no oxygen evolution capability (Fig. 16.8). The evolution pressure for the change in properties of the new, PSII-like, photosystem could have been the changing environmental conditions, in particular changing redox conditions. Because of the variability of the environment, it would have been advantageous for the organism to keep genes for both photosystems, and a regulatory switch must have evolved that made it possible for the organism to transcribe the gene that was most appropriate for the changed environment. One scenario for the acquisition of oxygen-evolving capacity is that the PSII-like system evolved toward 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 wavelengths. The mechanism for switching between transcription of one or the other photosystem gene then became superfluous and disappeared. The first cyanobacterium had evolved.

Evolution of a bacterial type 2 photosystem required, in addition to the addition of an oxygen evolving center, also an adaptation that would protect the system from the damaging effects of oxygen. The two parts of the originally homodimeric photosystem became gradually more differentiated. The electron transfer chain became concentrated on one of

the monomers, and mechanisms developed for rapid exchange of the easily damaged peptide that supported it.

Once the cyanobacteria emerged and started to produce oxygen, several hundred million years elapsed before oxygen started to accumulate in the atmosphere. The earliest evidence that water was used as the hydrogen source in photosynthesis is found in 2.97-Ga (billion years)-old South African rocks (Crowe et al. 2013), while the so-called Great Oxidation Event (GOE) took place 2.45–3.32 Ga ago (Bekker et al. 2004; Kump 2008; Sessions et al. 2009). There are several explanations for the lag in oxygenation of the atmosphere. One is that that there were many reducing substances (hydrogen, divalent iron, reduced sulfur, probably also methane) that had to be oxidized first (Zahnle et al. 2013). Holland (2009) points to a probable change in volcanic gases that would have favored oxygen accumulation at this time and reproduction of cyanobacteria might also have been hampered by ultraviolet radiation, since no protection by ozone would have existed before oxygenation of the atmosphere. A prerequisite for oxygen accumulation was prevention, by burial, of reoxidation of assimilated carbon (Karhu and Holland 1996; Fennel et al. 2005). From time to time reoxidation seems to have occurred (Kump et al. 2011) resulting in fluctuations in the oxygen content (Canfield et al. 2013; Partin et al. 2013). 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, it poisoned many life-forms. 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. This domination is also due to the offspring of cyanobacteria that are present as chloroplasts in plants and algae.

16.8 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) in 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

The theory that chloroplasts are derived from cyanobacteria, which were long ago taken up by nonphotosynthetic organisms, is more than 100 years old. However, the overwhelming support that this theory is correct has been obtained from molecular biology. By comparison of DNA sequences, the cyanobacterial ancestry of chloroplasts has been established, just as it is now certain that mitochondria are descendants of another bacterial clade.

Among chloroplasts, there are, in addition to a couple of smaller branches, two main developmental lines. According to Rogers et al. (2007) we have the "green line" (in green algae and plants) and the "red line" (in red algae and most other algae). Even if some researchers still remain open to the idea that these two lines started with two separate endosymbiotic events, the following view prevails: All chloroplasts are derived from one cyanobacterium that was incorporated in one eukaryotic 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. For example, a new type of chloroplast that is the result of a more recent endosymbiotic event has been observed: Marin et al. (2005) have found an amoeba containing a plastid with a different cyanobacterial origin; see also Rogers et al. (2007). However, this does not detract from the fact that chloroplasts of all major groups had been derived 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 in the red line are derived by secondary endosymbiosis, in which certain organisms engulfed red algae. Chloroplasts of some groups, especially some dinoflagellates, have an even more complicated evolutionary history (see, e.g., Stoebe and Maier 2002; Bhattcharaya et al. 2003).

Many cyanobacteria have phycoerythrin (red) and phycocyanin (blue), and a small amount of another protein, allophycocyanin (also blue) 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 two 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, referred to as prochlorophytes (after *Prochloron*, the genus first discovered), does not use phycocyanin and phycoerythrin as its main light-harvesting system–sometimes not at all, but instead chlorophyll *a* and chlorophyll *b*, as green algae and plants do.

It was once thought that the green and the red evolutionary lines each arose from two different types of cyanobacteria. Later, a cyanobacterium (*Prochlorococcus marinus*) was discovered which utilizes chlorophyll *a* and chlorophyll *b*,

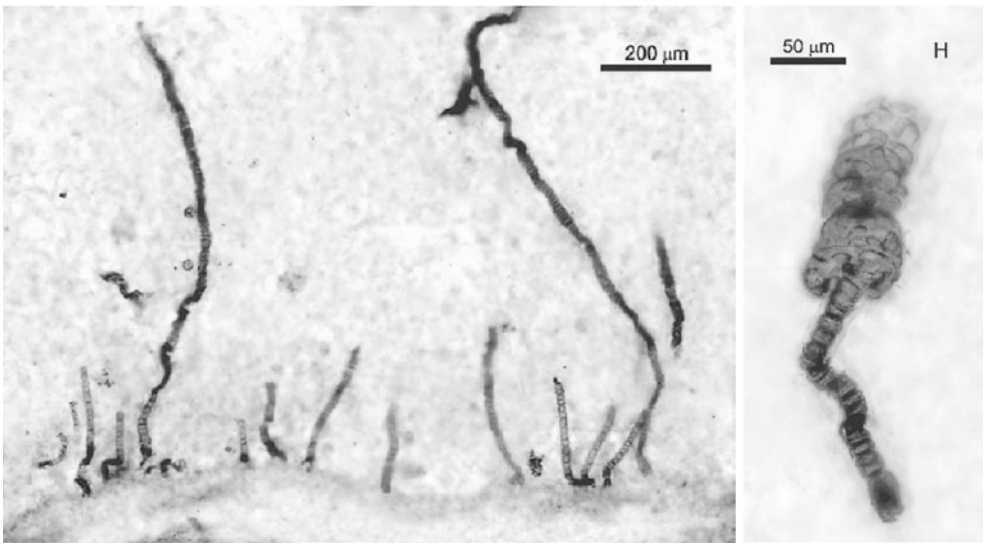

Fig. 16.9 1,200-Ma-old fossils of the red alga Bangiomorpha pubescens (from Butterfield 2000)

and phycobilins for light harvesting (Hess et al. 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 in both lines is strengthened by the fact that the protein import machinery is very similar. These import systems must have evolved during early stages of interfacing the incorporated cyanobacteria with its host, Also genes transferred from the cyanobacteria to the nucleus of their host on the "red line" and "green line" are in general so similar that it is difficult to argue that they are the consequence of endosymbiosis in very different organisms.

Fossils of red algae have been found which date back to 1.2 Ga (Butterfield 2000; Fig. 16.9). 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 nonphotosynthetic organism (or possibly already photosynthetic organism that had lost its original photosystems), and also this may have taken place only once. 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–cycle) as organisms on the green line of chloroplast evolution, a type very different from the type present in red algae (Petersen et al. 2006). The most probable interpretation of this is that soon after the secondary endosymbiotic event, a lateral gene transfer from the green line took place, and the phosphoribulokinase from the red alga was lost. In a later publication, some of the same authors present evidence that cryptophytes, haptophytes, and stramenopiles have acquired their chloroplasts through separate secondary symbiotic events (Baurain et al. 2010).

Plastocyanin, a copper protein that is an electron carrier in the chloroplast, is missing in chloroplasts of the entire red line of evolution (and also in some cyanobacteria); here, electrons from cytochrome b6/f complex are, instead, carried to PSI by a small soluble cytochrome, cytochrome c6 (Raven et al. 1999). The use of plastocyanin as an electron carrier was probably established after the emergence of oxygenic photosynthesis, as copper may have been tied up in insoluble sulfide during a period of Earth's history (see below). On the other hand, iron is less accessible now than it was before the oxygenation of the atmosphere.

16.9 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 (Chew and Bryant 2007; Masuda and Fujita 2008). For this reason, Granick (1957) postulated that bacteria, with bacteriochlorophyll as photosynthetic pigment, have evolved from those which had chlorophyll *a*. But those present-day bacteria which have bacteriochlorophyll (and only one photosystem) seem to be more primitive and carry 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 nonoxygenic organisms having only one photosystem, with chlorophyll *a*.

The reasons that chlorophyll is a suitable pigment for photosynthesis are discussed in Chap. 9, Sect. 9.2 and by Kiang et al. (2007) from a spectral perspective, and by Mauzerall (1976) from a chemical perspective, while Björn et al. (2009a) have traced the possible reasons for the uniqueness of Chl *a* for its use in the primary photochemistry. This is due to its physicochemical properties as affected by its protein environment; Chl *a* in vivo is capable of generating a radical cation or a radical anion or remaining completely redox silent, all depending on the protein environment. Many authors, e.g., Björn et al. (2009b) have speculated about what kind of photosynthesis might take place on other planets.

When cyanobacteria had turned into chloroplasts, further evolution along the "green" line (green algae and plants) began to differ from that along the "red" line (red algae, diatoms, and brown algae). We know that cyanobacteria were, and are, equipped with very sophisticated light-collecting antennas in the form of phycobilisomes. These can be regarded as a kind of energy transformer, which collects all kinds of light and adapts the excitation energy so the quanta correspond to 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 exquisite light transformers disappeared from the rest of the "red" line and never appeared on the line leading to land plants?

We probably have a good explanation for this now. We shall recount here in essence an explanation given by Anderson (1999) that relies on different light environments to which the organisms have adapted. In order to streamline our discussion, 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, a deficiency in photons absorbed by PSI relative to PSII could easily develop. To avoid this, it is suggested that some excitation energy is transferred from PSII to PSI. Red algae collect energy mainly via their phycobilisomes, and this energy can be used both by PS II and by PS I.

For land plants, the situation is different. The first land plants were small beach organisms living without competition from larger plants, exposed to full sunlight; their forerunners, the green algae, lived in very exposed habitats. Therefore, the challenge for the first land plants was not lack of light energy, and thus, they did not have much use for phycobilisomes. With time, plants developed a complex light-harvesting system, and the chloroplast became more and more shaded by other chloroplasts. The light hitting the chloroplast became, during the evolution of plants and ecosystems, more and more depleted in shortwave light, while the long-wave light (the long-wave edge of the chlorophyll absorption spectrum) was not attenuated to the same extent. The spectral situation was opposite to that for chloroplasts found in red algae. Now the imbalance between the photosystems could not be adjusted by energy transfer from PSII to PSI, since PSII had enough energy for its own needs only. Rather PSI and PSII had to be separated to prevent excess energy transfer from PSII to PSI; otherwise, PSII would be even more depleted of energy. Evolution has succeeded in this by the development of grana in the chloroplasts of land plants (see Figs. 16.1 and 16.2).

Grana are regions in the chloroplasts where thylakoid membranes are closely stacked on top of one another and are enriched in PSII. The stacking of membranes and the absence of PSI gives room for larger pigment antennas, not in the form of phycobilisomes, but in the form of chlorophyll *a* and chlorophyll *b*-containing light-harvesting complexes located within the thylakoid membrane. PSI is located in the less stacked membrane regions. This is advantageous because PSI delivers reducing equivalents via ferredoxin to NADP, which is then used for the reduction of carbon dioxide in the stroma.

The structure of chloroplasts, and in particular the proximity of membranes to one other, is not static, but it constantly adjusts to the available light. During evolution more and more sophisticated regulation systems have appeared, as have various mechanisms for protection against excess light (Demmig-Adams et al. 2006). 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 while exploiting different kinds of xanthophylls, both in the "red" and the "green" line of evolution. It is left for future researchers to find out whether this is an example of convergent evolution or due to common descent. The reader is referred to Demmig-Adams, Adams, and Mattoo (Eds) (2006) and Demmig-Adams, Garab, Adams, and Govindjee (Eds) (2014) 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 that absorb maximally in the violet part of the spectrum, while more modern types have carotenoids with absorption peaks at longer wavelengths. Y. Yoshi speculates that this may reflect the high ultraviolet radiation conditions under which the algae have evolved. Those ancient algae living 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. The spectrum of light is filtered by water to enhance the shortwave part of photosynthetically active radiation. More modern algae would have evolved near the water surface, in a light regime that is enriched with longer wavelength photons. A difficulty with Yoshi's interpretation is that an ozone layer most likely evolved long before the appearance of eukaryotic algae.

16.10 Many 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 carbon into organic substance is older than the ability to photosynthesize. It takes place in both Archaea and Bacteria. This ability has evolved either before the two domains had separated or one of these groups of organisms has acquired it from the other group by horizontal (lateral) gene transfer. Since many enzymes are involved, the former possibility is the most likely one.

Apart from the first two enzymes, enzymes listed in Table 16.1 and their assimilation pathways (Fig. 16.10) are present only in Bacteria and Archaea. But the typical carbon-binding enzyme of plants, algae and cyanobacteria, RuBisCO, occurs also in some Archaea, even though the complete Calvin–Benson cycle has not been demonstrated in them.

The first alternative to the Calvin–Benson cycle detected was a cycle discovered by Evans et al. (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, 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 et al. (2005) have detected a large set of RuBisCO types in soil microorganisms, of which only a minor part is derived from photosynthetic organisms.

It is clear that RuBisCO is a very ancient enzyme, which 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 binds carbon dioxide only weakly (i.e., it 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. RuBisCO reacts also with oxygen, in addition to carbon dioxide, and when this happens, a product, phosphoglycolic acid, is formed. There are indications that the ability to metabolize phosphoglycolic acid evolved very early, even before oxygen had accumulated outside the cyanobacterial cell (Eisenhut et al. 2008).

To compensate for the poor 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 in proximity to the RuBisCO have also evolved, so carbon dioxide can compete efficiently with oxygen for the common binding site. There is also the view that photorespiration is essential for plants that have evolved it. Carbon concentrating mechanisms of cyanobacteria and algae have been described by Badger and Price (2003); Giordano et al. (2005); and Keeley and Rundel (2003). Here we shall limit ourselves to alternative pathways that rely on a spatial and temporal separation of light energy conversion and carbon fixation that provide advantages, the so-called C4 metabolism and CAM.

Table 16.1 Pathways and Enzymes for CO_2 Assimilation

CO_2-binding enzyme	Pathway for CO_2 assimilation
Ribulose-1,5-bisphosphate-carboxylase-oxygenase (RuBisCO, rubisco)	Calvin–Benson 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

16.11 C4 Metabolism

About half of this planet's photosynthetic production takes place on land and the other half in water (Geider et al. 2001; Falkowski and Raven 2007) According to Sage (2004) the mere 3 % of the terrestrial plants having C4 metabolism carry out about half of CO_2 fixation on land. C4 metabolism is present in about 7,500 species of seed plants (3 % of the species of terrestrial plants), of which 4,500 are grasses, 1,500 sedges, and 1,200 dicots (Sage 2005). C4 plants occur primarily in warm and dry countries and among epiphytes. It is well-known that C4 metabolism has evolved many times in different locations.

C4 plants have evolved at least 45 times in 19 families of higher plants (Sage 2004). From this we understand that there has been a very strong evolution pressure toward 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 (Retallack 2002). Another component has been the drying of the environment that was an even more recent event (Osborne and Beerling 2006; Strömberg and McInerney 2011). C4 metabolism (Fig. 16.11) 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 is the case in C3 plants. Instead bicarbonate ions (formed from carbon dioxide and water with the aid of

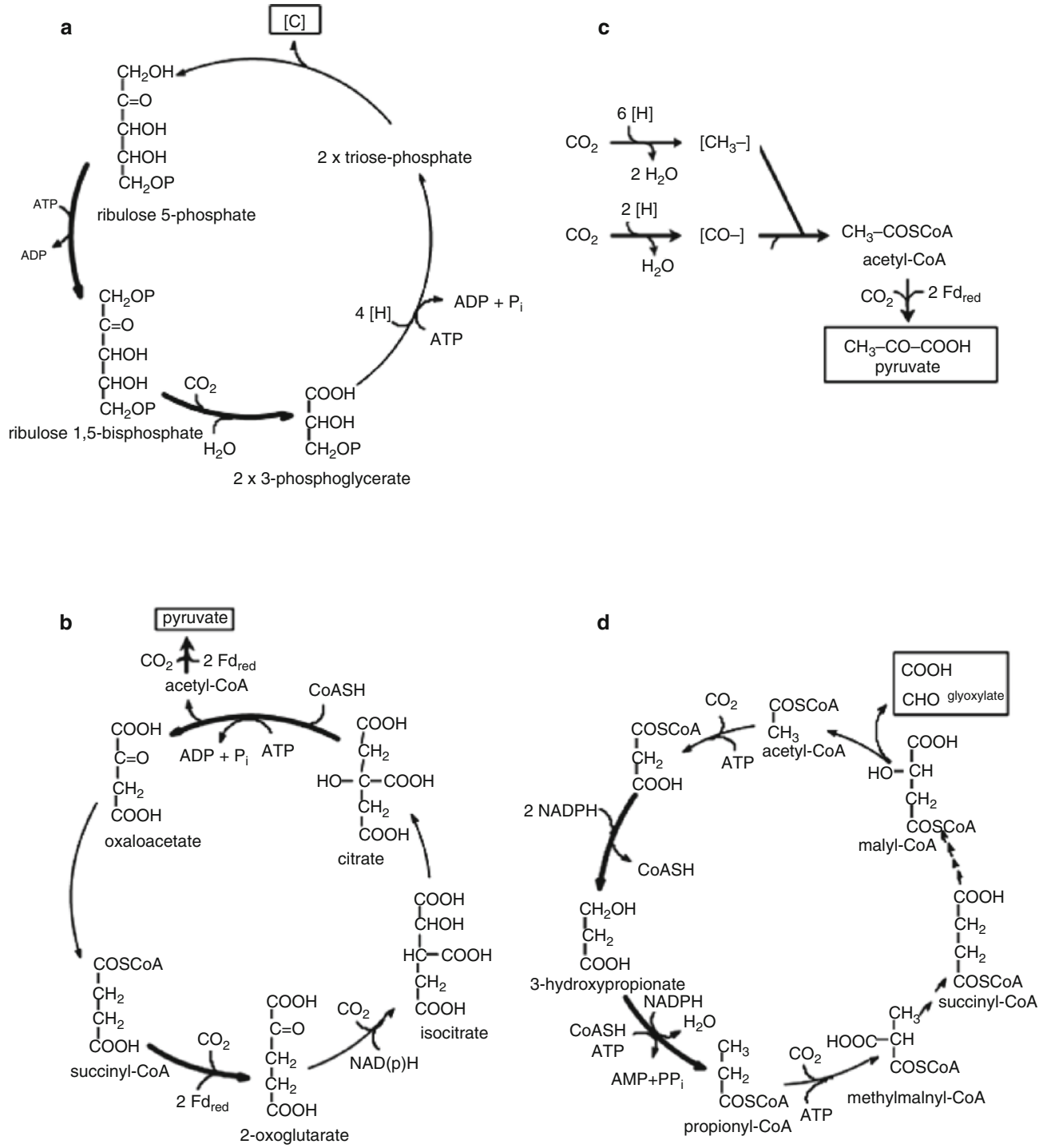

Fig. 16.10 Metabolic cycles for assimilation of carbon dioxide present in various prokaryotes: (**a**) the Calvin–Benson cycle, (**b**) the reductive TCA (TriCarboxylic Acid) cycle (Arnon–Buchanan cycle), (**c**) the reductive acetyl-CoA pathway, and (**d**) the 3-hydroxpropionate cycle. Of these only the Calvin–Benson cycle is present in photosynthetic eukaryotes (cyanobacteria, algae, and plants). C: assimilated carbon, [H]: reducing equivalents, Fdred: reduced ferredoxin, P or P in a circle: phosphate groups, CH_3–: enzyme-bound methyl group, CO–: enzyme-bound carbon monoxide (from Hügler et al. 2003)

the enzyme carbonic anhydrase) is bound by the enzyme phosphoenolpyruvate carboxylase (PEPC; see Table 16.1 and Fig. 16.11) and when it combines with phosphoenol-pyruvate (PEP) malate is formed. Malate has four carbon atoms, hence the designation C4 metabolism. In C3 metabolism, the first stable product is 3-phosphoglyceric acid, which has three carbon atoms. C4 metabolism is more efficient at a low concentrations of carbon dioxide, because

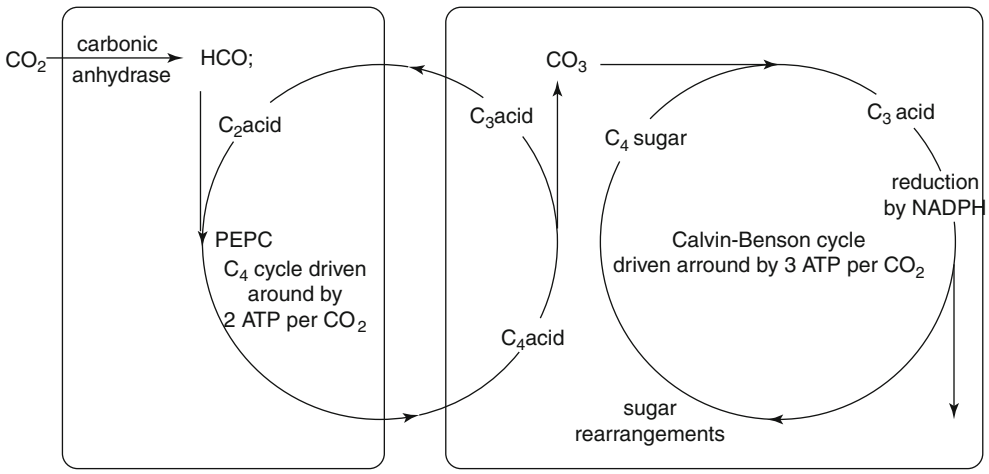

Fig. 16.11 Carbon dioxide assimilation in C4 plants. The first cycle (see the *left box*) concentrates carbon dioxide at the rubisco, and the assimilation itself proceeds as in C3 plants (see the *right box*)

PEPC binds bicarbonate very tightly and lowers the relative binding of oxygen.

C4 carbon fixation is also more efficient under dry conditions since plants 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 can be compensated by the increased CO_2 utilization efficiency of C4 metabolism. C4 metabolism is also more efficient than C3 metabolism at high temperatures. In C3 plants, photorespiration, due to competition by oxygen for RuBisCO makes carbon dioxide uptake inefficient at high temperatures. Under other conditions, like low light, C4 metabolism is less efficient than C3 metabolism, because it uses up more ATP (5 molecules per molecule of CO_2 assimilated, compared to 3 for C3 plants).

One fascinating fact about 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 et al. 2000, 2004).

Since 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 by then. But all the plant fossils from that time for which the isotopic composition of the carbon has been investigated have a C3-like signature, $\partial^{13}C \approx -20$ ‰ (Beerling et al. 2002; Bocherens et al. 1993).

One enigmatic circumstance is that CAM plants which also use PEPC (phosphoenol pyruvate carboxylase, discussed below) were present earlier. So why do we have only C3-type isotope discrimination from that time? Perhaps CAM plants did not contribute much to biomass production. The corresponding $\partial^{13}C$ value for C4 plants is about −13 ‰ (e.g., Hattersley 1982). There is some suspicion that some C4 plants could have evolved during the Carboniferous, but remained low in number (Osborne and Beerling 2006). A possible reason that more C4 plants did not evolve during this period is that the temperature was low.

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 pathway and to M. D. Hatch (pp. 875–880) for C4 metabolism (Govindjee et al. 2005). For further details on C4 photosynthesis, see Raghavendra and Sage (2011).

16.12 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 binding it to PEP with the help of PEPC. The carbon fixation by the Calvin–Benson cycle is carried out during the day, when the stomata are closed. By keeping stomata open only during the night, CAM plants conserve water.

CAM is more ancient than C4 metabolism, and it has been driven by water stress (Keeley and Rundel 2003). It is known only to exist in vascular plants, and it is present in species of clubmosses, ferns, the unusual gymnosperm *Welwitschia mirabilis*, the cycad *Dioon edule*, some monocots, and some dicots. Among the dicots, the following families, among others have CAM: Aizoaceae, Cactaceae, Portulaceae, Crassulaceae, Euphorbiaceae, Asclepiadaceae, and Asteraceae. Among the monocots, we have Bromeliaceae and Orchidaceae. Like C4 metabolism, CAM has evolved several times within various plant groups as an adaptation to water deficiency, mainly among desert plants and plants living on stones or as epiphytes on other plants (see Keeley and Rundel 2003). However, there

are also aquatic CAM plants, but the reason for this is not clear. Among 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 approximate 125 species have been investigated). Since this genus existed already during the early Triassic, more than 200 Ma ago, it must be assumed that CAM existed then (Keeley and Rundel 2003). Dekker and de Wit (2006) have provided further evidence for the early evolution of CAM. See Black and Osmond (pp. 881–893) in Govindjee et al. (2005) for the description of the discovery of CAM.

16.13 Evolution of ATP-Synthesizing Enzymes

The use of proton gradients for the synthesis of ATP occurs in all three domains of life—Archaea, Bacteria, and Eukarya—and the last common ancestor of all organisms is likely to have made use of this. The ancestry of the ATP-synthesizing enzyme of chloroplasts, F-ATPase, has been described by Zhaxybayeva et al. (2005). This enzyme consists of several subunits that are conserved across Bacteria and Archaea.

16.14 The Journey onto Land

Photosynthetic organisms are thought to have been present on land as early as 1.2 Ga ago, based on carbon isotope ratios (see Horodyski 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, approximately 400 Ma ago. However, based on the "molecular clock," Heckman et al. (2001) estimated 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 perhaps almost negligible compared to that of the ocean.

A great increase in the amount of photosynthetic production came with the evolution of the embryophytes. Their closest relatives are the Charales (stoneworts), a type of green algae (Karol et al. 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 et al. 2001). In the early Devonian (approximately 410 Ma ago) plants (e.g., *Eophyllophyton bellum*) had evolved that had leaves and roots (Hao et al. 2003). Their leaves seem to have been adapted to a dry climate and high carbon dioxide concentration. In the late Devonian (370 Ma ago), as the atmospheric concentration of carbon dioxide fell (Fig. 16.13), larger leaves, megaphylls, evolved, which were more efficient in collecting both carbon dioxide and light, as well as in transpiration of water vapor (Beerling et al. 2001 Mercer-Smith and Mauzerall 1981).

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 mycorrhizal fungi increased the weathering of the continental rocks enormously. This, in turn, meant a positive feedback on photosynthesis by providing more nutrients, also for marine organisms.

Aquatic organisms do not require protection from desiccating evaporation, but when plants colonized land, protection mechanisms were necessary for them to conserve water. Therefore, land plants developed cuticle and cutinized external cell walls and sometimes wax coatings. All this is an obstacle to gas exchange, and so sophisticated gas valves evolved which we refer to as stomata. Stomata are adjustable openings, which are regulated to allow an optimal balance between the 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. In addition to regulation of the individual stomata, there is also a developmental regulation to achieve an optimal number and size distribution of stomata. The higher the atmospheric concentration of carbon dioxide, the more sparsely stomata develop on the leaf surface. Studying the stomata density on fossil leaves provides a method for

estimating past carbon dioxide concentrations (McElwain 1998; McElwain et al. 1995, 2002; Haworth et al. 2005).

After having adapted to the terrestrial environment, some plants returned to water and had to cope with new challenges (Rascio 2002). It was not simply a reversal of the adaptation to dry land; some researchers believe that our modern charophytes have also made a transient visit to terra firma. On the land, plants had become larger and needed to develop aerenchyma (air-conducting tissue) to provide all living cells with sufficient oxygen. If roots or rhizomes were to be maintained in anoxic muddy ground, diffusive oxygen transport may not be sufficient. 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.

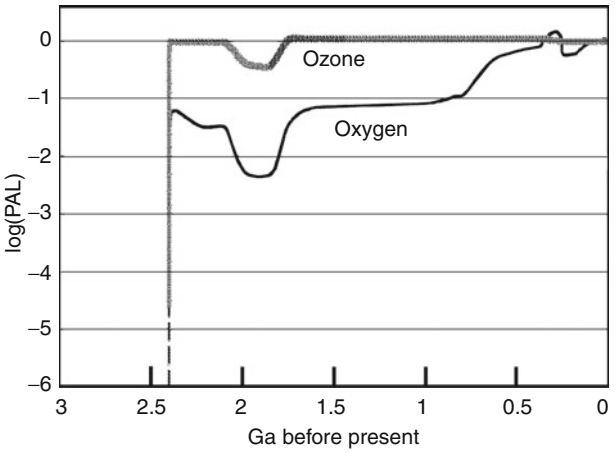

Fig. 16.12 Evolution of the earth's atmosphere. Ozone and oxygen, on a logarithmic scale, as fraction of the present atmospheric level (PAL), during the past three billion years (based on Beerling et al. 2002; Berner 2006; Canfield 2005; Falkowski et al. 2005; Huey and Ward 2005; Segura et al. 2003, and other sources)

16.15 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 UV-B radiation from the sun (Chap. 22). Fossil fuel, on which we have now become dependent, 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 photosynthesis, as an environmental-friendly way of energy transformation, can help us to draw up a blueprint for a solution to the conflict between our hunger for energy and the necessity to maintain an environment that can sustain humanity.

However, we must be aware that photosynthesis has not always resulted in a good environment for the inhabitants of our planet. Free oxygen is still a hazard for our own cells and even for the chloroplasts that produce it.

Photosynthesis has not always had a friendly, Gaia-like (Lovelock 1979) influence on inhabitants of the earth. When oxygen first started to accumulate, it almost certainly killed off a large part of the earth's 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 using nitrogenase. Nitrogenase is extremely sensitive to oxygen and easily inhibited by it, and organisms had to invent various methods for protecting nitrogen-fixing enzymes from oxygen. Some of the filamentous cyanobacterial forms developed special cells (heterocysts) and compartmentalized photosystems to fix nitrogen. Heterocysts contain only PSI and do not fix carbon dioxide or contain oxygen-producing PSII and therefore provide an oxygen-free environment. From morphological fossils it has been deduced that this arrangement is 1.5 Ga old. No ancient and convincing fossil of heterocysts themselves has been found, so the existence of ancient heterocysts (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 the occurrence of heterocysts and akinetes.

Before cyanobacteria evolved, the oxygen content of the atmosphere was less than 10^{-5} times the present value (Fig. 16.12). 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 humans) not only by 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 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 100 Ma, between 2.3 and 2.2 Ga ago (Liang et al. 2006). 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. During this "Snowball Earth" (Kirschvink et al. 2000) an ice cover prevented silicate weathering, a process that consumes carbon dioxide; see Kopp et al. (2005). Gradually volcanism increased the carbon dioxide content and this 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 be matched by its consumption by organisms under the ice surface. Therefore, many nutrients were abundant at the end of the glaciation, but probably not all. See also Sekin et al. (2011)

for the relation between glaciation/deglaciation and oxygen production Hannah et al. (2004) and Canfield et al. (2013).

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. 16.14), but not all scientists 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 et al. 1998; but see Levrard and Laskar 2003).

One way of constraining the timing of 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 2,316 ± 7 Ma ago, the sulfur isotope ratio indicates an oxidizing atmosphere; thus, this is taken as a minimum age for the oxic atmosphere (Hannah et al. 2004; Bekker and Holland 2012). The oxygen concentration at that time was, of course, much lower than today.

Campbell and Allen (2008) have pointed out that the oxygen content of the atmosphere has risen in steps, and every step has been associated with the formation of supercontinents. The explanation for this is that in connection with the collision between the continents, new mountains emerged and erosion increased and consequently also the input of nutrients to the sea (Lenton 2001). This increased not only photosynthesis and the production of molecular oxygen but also the burial under sediments of oxidizable material (organic carbon and pyrite), so that the newly formed oxygen was not consumed again (Fennel et al. 2005). It has been suggested that the last large increase of atmospheric oxygen, from 10 % of the present to above the present level during the Carboniferous and Permian, around 300 Ma ago (Figs. 16.13 and 16.14), is due to the emergence and spread of land plants and burial of the produced organic material in swamps.

The protein complexes involved in the electron transport chain in the thylakoids contain a variety of metals. In addition to the magnesium atoms of chlorophyll, there are 12 Fe in PSI, six Fe in the cytochrome b6/f complex, and two Fe, four Mn, and one Ca in PSII. The electron transfer chain contains additional soluble metal-containing 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, the redox potential of the environment and the presence of hydrogen sulfide. PSI contains more iron than the other

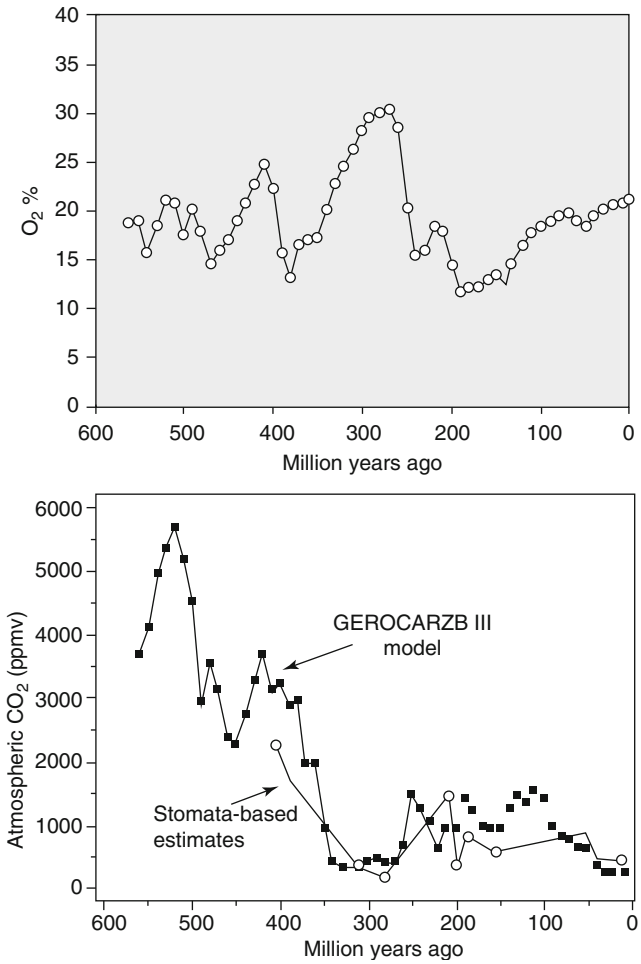

Fig. 16.13 Atmospheric changes over the Phanerozoic. *Upper panel*: The atmospheric oxygen content in percent according to the GEOCARBSULF model (redrawn from Berner 2006). *Lower panel*: The carbon dioxide content according to the GEOCARBSULF model compared to estimates based on stomata from various sources. In general the carbon dioxide decreases when the oxygen content increases

complexes, and Strzepek and Harrison (2004) have noted that diatoms adapted to coastal regions, where iron is more available, have a lower PSII/PSI ratio (around 3) compared to diatoms adapted to oceanic regions (around 9), where available iron is often a limiting factor for growth. Presumably the PSI of oceanic diatoms have larger light-collecting pigment antennas to compensate for the lower number of reaction centers. Furthermore, the coastal diatom *Thalassiosira weissflogii* uses cytochrome c_6 (Inda et al. 1999; Strzepek and Harrison 2004), another iron-containing protein, while the marine diatom *Thalassiosira oceanica* uses plastocyanin for electron transfer to PSI (Peers and Price 2006). Many cyanobacteria and eukaryotic algae still retain their capacity to synthesize both plastocyanin and cytochrome c_6 to adapt their metabolism to changing aqueous environments (Hervás et al. 2003). For historical accounts on the structure and function of PSI, see Fromme

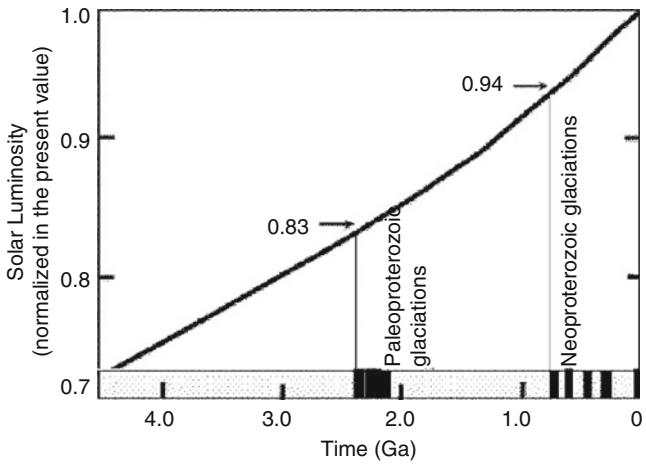

Fig. 16.14 The relative power radiated by the sun during earth history, and the timing of glaciations (From Tajika 2003, based on Gough 1981.) Not all scientists (see Sackmann and Boothroyd 2003) believe in this "faint young sun" scenario, the main argument being the documented presence of liquid water on Mars ≈3.8 Ga (gigayears) ago

and Mathis (pp. 311–326) and Witt (pp. 237–259) in Govindjee et al. (2005).

During a period after the emergence of cyanobacteria and oxygen-evolving photosynthesis, hydrogen sulfide was available only in the depths of the oceans (Canfield 1998). One can imagine that the cyanobacteria present at that time adapted their photosynthetic machinery to economize with iron, because much of this metal was tied up as sulfide. The closest present-day analog to this ancient ocean is the Black Sea. According to Anbar and Knoll (2002), sulfidic conditions in the deep sea prevailed most of the time between 2,500 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. Lack of molybdenum may have been the cause for the evolution of molybdenum-free nitrogenases (using vanadium and iron, Berman-Frank et al. 2003). According to Canfield et al. (2007) the increase of deep ocean oxygen over a critical point spurred the rapid evolution of animal life.

Conclusions

Photosynthesis is a very ancient process on our planet. It has had profound impact on the biosphere, the chemical composition of Earth's surface and Earth's atmosphere, and on climate, including radiation in the environment. 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.

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