Evolution of Photosynthesis

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Abstract

Energy conversion of sunlight by photosynthetic organisms has changed Earth and life on it. Photosynthesis arose early in Earth's history, and the earliest forms of photosynthetic life were almost certainly anoxygenic (non-oxygen evolving). The invention of oxygenic photosynthesis and the subsequent rise of atmospheric oxygen approximately 2.4 billion years ago revolutionized the energetic and enzymatic fundamentals of life. The repercussions of this revolution are manifested in novel biosynthetic pathways of photosynthetic cofactors and the modification of electron carriers, pigments, and existing and alternative modes of photosynthetic carbon fixation. The evolutionary history of photosynthetic organisms is further complicated by lateral gene transfer that involved photosynthetic components as well as by endosymbiotic events. An expanding wealth of genetic information, together with biochemical, biophysical, and physiological data, reveals a mosaic of photosynthetic features. In combination, these data provide an increasingly robust framework to formulate and evaluate hypotheses concerning the origin and evolution of photosynthesis.

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INTRODUCTION

Our planet is alive and photosynthesis powers it. This is evident by the spectral signature of our planet (96), which is colored by the pigments engaged in harvesting sunlight. An atmosphere in which large amounts of complex organic molecules and high concentrations of oxygen coexist (106) is another sign that the entire planet is bustling with life. Over billions of years, photosynthetic organisms have transformed our planet and the life on it (30). The interdependence of photosynthesis and the development of our planet and the life it harbors make the study of the evolutionary development of photosynthesis an exciting endeavor that connects experimental data and theoretical concepts across scientific disciplines.

The Energetics of Present Life

Life requires a constant flux of energy to persist and proliferate. The energy gradient that maintains our biosphere is provided by photosynthesis. Photosynthetic organisms stabilize the fleeting energy contained in a photon by breaking and creating chemical bonds against the chemical equilibrium. Our present atmosphere composition, with more than 20% O_2, provides the basis of the energy gradient that sustains life close to the Earth's surface (147). The dominant group of photosynthetic organisms generates O_2 through the decomposition of water. The electrons liberated in this process can be used to reduce inorganic carbon to form organic molecules to build cellular components. This stored redox energy can be released by oxidizing the generated molecules, thereby recombining electrons with O_2 and protons to generate water. This process is the basis of energy generation by oxygen-dependent respiration. Photosynthesis and oxygen-dependent respiration complete a water-oxygen cycle (46). Before water was adopted as the main electron source, photosynthetic organisms may have utilized hydrogen, ferrous iron, and hydrogen sulfide in place of oxygen as an electron source for redox cycling (**Table 1**), and even today many types of anoxygenic (non-oxygen-evolving) photosynthetic organisms utilize these electron donors instead of water. The continued utilization of oxygen, sulfur, and iron, in combination with the incorporation of inorganic carbon, left

signatures for tracing the early evolution of life and metabolic processes such as photosynthesis through geological times (74).

Energetics of the Early Period in Life History

Virtually all oxygen in our atmosphere has been produced by oxygenic photosynthetic organisms. However, for long periods in the history of our planet and life, oxygen may not have been present in the atmosphere to an appreciable extent (80). The ancient atmosphere was composed of methane, carbon dioxide, and nitrogen. The organisms that lived then did not rely on the oxygen–water cycle but were linked to other molecules in a strictly anaerobic biochemistry. When O_2 appeared in the atmosphere approximately 2.4 Gya, it fundamentally altered the redox balance on Earth, and organisms were either forced to adapt to oxygen, retreat to anaerobic ecological niches, or become extinct. Evolving ways to tolerate O_2 and eventually to utilize the tremendous amount of energy available when O_2 is used as a terminal oxidant, organisms greatly expanded their repertoire of metabolic processes (29, 152).

The Quest for Carbon

The ability to create organic molecules by incorporating inorganic carbon is critical to carbon-based life forms. Creatures that can do it without using organic molecules produced by others are endowed with the title "autotroph." Different pathways for the incorporation of carbon exist (171) (**Table 1**). Some organisms grow autotrophically on methane that is oxidized to generate energy as well as to provide the carbon for incorporation into cellular metabolism (173) by aerobic and oxygen-independent respiration (145). In contrast to CH_4 incorporation, where getting rid of electrons is the tricky part, the incorporation of CO_2 requires electrons. Electron donors in the environment are the staple electron source for chemoautotrophic organisms, and electrons boosted by light-driven reaction centers (RCs) provide electrons for photoautotrophic organisms, including green sulfur bacteria, most purple bacteria, cyanobacteria, and photosynthetic eukaryotes. In contrast, photoheterotrophic organisms, including some types of purple bacteria, acidobacteria, heliobacteria, and some photosynthetic Archaea, utilize light energy to generate a protonmotive force and phosphoanhydride bonds but require organic molecules as a carbon source. A schematic of different modes of light-driven energy conversion is given in **Figure 1**.

Table 1 Redox midpoint potentials of electron donor and electron carrier redox couples

Reductant	Redox couple	Redox midpoint potential at pH 7 [V]
Hydrogen[a]	$H_2/2H^+$	−0.420
Sulfide[a]	H_2S/S^0	−0.240
Ferrous iron[b,c]	$Fe^{2+}/Fe(OH)_3$	0.150
Hydrogen peroxide[a]	H_2O_2/O_2	0.270
Water[a]	$H_2O/1/2\ O_2$	0.815
Ferredoxin (red)[a]	Fd (red)/Fd (ox)	−0.430
NADPH[a]	NADPH/NADP	−0.320
Menaquinol[d]	MQ (red)/MQ (ox)	−0.070
Ubiquinol[d]	UQ (red)/UQ (ox)	0.100
Plastoquinol[d]	PQ (red)/PQ (ox)	0.100
Rieske FeS cluster[c]	RFeS (red)/RFeS (ox)	0.100–0.270

[a]See Reference 121.
[b]See Reference 118.
[c]At 10 μM L^{-1}.
[d]See Reference 160.

Proton and Electron Transport

The flow of electrons—from electron donor to electron acceptor—is channeled by protein complexes that always contain metallo-organic cofactors. Although dissipating this energy gradient can store energy by generating or breaking chemical bonds, another mechanism for capturing energy is ubiquitous throughout the tree of life. Membrane-bound complexes couple the transfer of electrons across the membrane to the generation of an ion gradient and transmembrane electrical potential. The

Gya: giga (1×10^9) years ago

Autotroph: an organism that can produce all carbon-containing molecules from small, inorganic molecules utilizing chemical energy gradients (chemoautotroph) or light energy (photoautotroph)

RC: reaction center

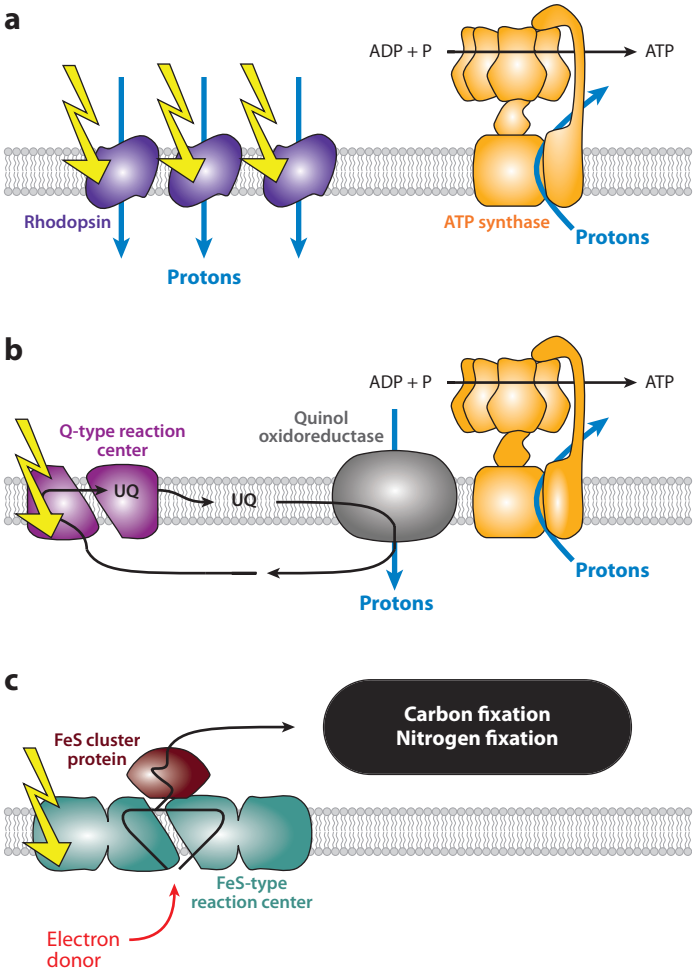


Figure 1

Modes of electron transport. Proton translocation and ATP generation by rhodopsin photoconverters (*a*) and a quinone-type reaction center (Q-type RC) participating in cyclic electron transport (*b*). Reductant generation for carbon and nitrogen fixation by FeS-type RCs during linear electron transport (*c*). Proton translocation is indicated by white arrows. Electron transport is indicated by solid lines and arrows. Photon absorption is indicated by yellow lightning bolts.

Q-type RC: reaction center in which the last electron acceptor is a quinone

FeS-type RC: reaction center in which the last electron acceptor is an iron sulfur cluster

electrochemical gradient established in this manner is utilized by ATP synthases (119, 120) to generate phosphoanhydride bonds stored in ATP, the universal currency for transferring energy within cells. This chemiosmotic mechanism was likely present in the last common ancestor and has been carried forward to the three presently persisting domains of life, Bacteria, Archaea, and Eukarya (97).

Distribution of Photosystems and Rhodopsins

Photosynthetic organisms are able to engage the chemiosmotic machinery by directly translocating protons (rhodopsins) or electrons (photosynthetic RCs) across a membrane. The RCs donate electrons to either quinones (Q-type RCs) or an FeS cluster (FeS-type). Anoxygenic Q-type RCs participate in a cyclic electron transport that generates a proton gradient for ATP generation. FeS-type RCs provide electrons for cyclic electron transport or for the incorporation of oxidized C, S, and N-containing molecules. Whereas the rhodopsin contributes substantially to energy generation only in Archaea, chlorophyll-containing RCs have been identified only in Bacteria (15) and their endosymbiotic progeny. Oxygen-producing cyanobacteria combined with an early eukaryotic organism in a process called endosymbiosis to give rise to all photosynthetic eukaryotes. These oxygenic organisms utilize a Q-type and an FeS-type RC in series to generate ATP and electron-reducing equivalents that drive carbon fixation.

This Review

The evolution of photosynthesis spans billions of years and interfaces with the emergence of life and the geology and atmosphere of our planet. Although in some ways daunting, this complex interdependence provides a fantastic framework to cross-check our hypotheses for how photosynthesis emerged and developed. In addition, we can query live witnesses in that organisms alive today are the winning designs that carry metabolic innovations from the dawn of life within their genomes, including how to live on light and air.

GEOLOGICAL EVIDENCE FOR PHOTOSYNTHESIS

It has been proposed that meteorites may have provided large amounts of organic molecules that constituted the ingredients of the

primordial soup, postulated as a cradle of life (70, 135). Indeed, the chemical analysis of meteorites shows substantial amounts of organic materials (4, 35). Once this abiotic source of organic carbon was used up, carbon-based life forms must have incorporated inorganic carbon, as indicated by a change in carbon isotope ratio. The existence of inorganic carbon fixation, however, is not necessarily an indication of photosynthesis, because energy gradients provided by geological features can also drive metabolism in the absence of light (105).

Carbon in Ancient Rocks

A great amount of progress in the understanding of the emergence of life and photosynthesis has resulted from advances in the analysis of ancient rocks. Earth may have started to cool down by 4.4 Gya to allow for rock formation (179). Early life may reach as far back as the oldest rocks we know, but metamorphic events that may have changed ancient rocks add uncertainty in tracing life back this far. Carbon signatures that point to established life have been found in Greenland rocks dating to 3.8 Gya (109, 157). If correct, then the emergence of life would coincide with or come relatively soon after the end of the "late heavy bombardment" by asteroids, 4.1–3.8 Gya. Numerical models suggest that throughout this infernal stage, places on Earth suitable for harboring microbial life may have existed (1). However, the demonstration that carbon signatures thought to indicate biological carbon fixation can be produced by abiotic processes (115) has triggered a careful reevaluation of carbon isotope–based evidence of early life and photosynthesis.

Oxygen

Oxygen is considered a solid indicator for cyanobacterial-type photosynthesis. The ability of organisms to carry out oxygenic photosynthesis may have preceded the accumulation of oxygen in the atmosphere by hundreds of millions of years (26). The reasons for this putative delay in accumulation of oxygen are not clear and may include both biological and geological aspects. The ability to evolve oxygen may have been very inefficient at first, with organisms only slowly developing the needed defenses against oxygen. There may also have been dissolved buffers present that prevented oxygen from escaping into the atmosphere. One prominent buffer is ferrous iron, which combines with oxygen to form magnetite, hematite, and siderite. The resulting large banded iron formations (BIFs) occur in the geologic record as early as 3.7 Gya and largely stopped forming after oxygen accumulated in the atmosphere (80) (**Figure 2**). An alternative mechanism for the formation of BIF is anoxygenic photosynthesis that utilizes ferrous iron as an electron donor (132). Evidence for the increase of oxygen in the atmosphere comes from the nitrogen–oxygen redox cycle, which seems to have been established by 2.7 Gya (59); the chromium signatures consistent with the presence of oxygen by 2.8 Gya (51); and the sulfur fractionation data consistent with oxygen accumulation by 2.5 (28) to 2.45 (48) Gya.

Mya: mega (1×10^6) years ago

The accumulation of oxygen occurred in two phases (80). A gradual increase in atmospheric oxygen to 1–2% occurred between 2.4 and 2.0 Gya. After this "great oxygenation event" (80), oxygen levels may have been stable until 850 Mya; levels then rose to the ~20% observed in today's atmosphere, with a likely peak of 30–35% in the Carboniferous era (80). The second rise has been linked to the emergence of photosynthetic eukaryotes and the increased photosynthetic productivity of algae and lichens colonizing land masses, which accelerated the degradation of rocks, thereby releasing fertilizing minerals 800 Mya. A high oxygen concentration in the Carboniferous (360–300 Mya), as revealed in insect gigantism (73), seems to coincide with the emergence of vascular plants and with increased carbon burial (12). The oxygenation of the upper oceans follows a pattern that parallels that of the atmosphere, whereas the deep oceans may have been oxygenated only as recently as 580–550 Mya (92).

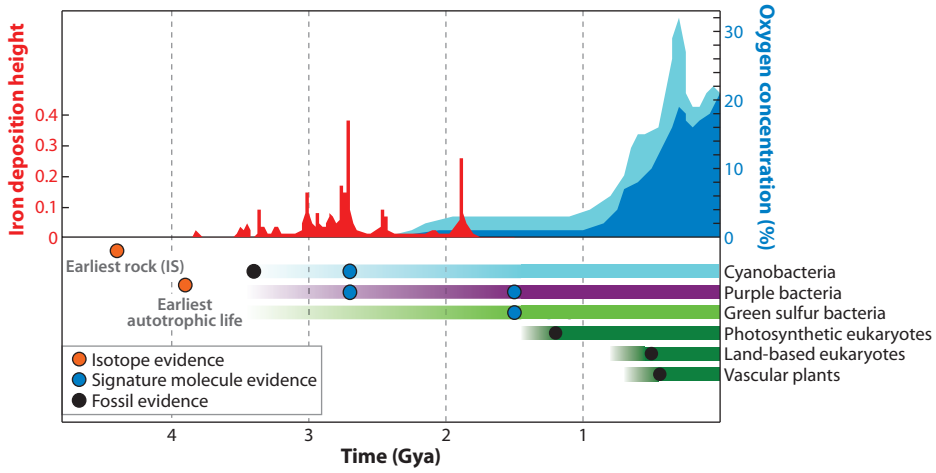


Figure 2

Evolution of life and photosynthesis in geological context, highlighting the emergence of groups of photosynthetic organisms. Minimum and maximum estimates for oxygen concentration are indicated by dark blue and light blue areas, respectively. Oxygen concentration data from Reference 80; banded iron formations data from Reference 87.

Fossil Record

The mineralized imprints of organisms provide another measure for the occurrence of life. The fossil record covers the diversification of vascular plants (418–407 Mya) (58) and the earlier eukaryotic land colonizers that left characteristic spores (~470 Mya) (62). Fossils of photosynthetic eukaryotes occur at 1.2 Gya (27). The fossil record of cyanobacteria, however, has recently been a major source of controversy. Fossils occurring in rocks from 3.5 Gya have been grouped into clades, some of which are thought to resemble modern cyanobacterial forms (161). However, recent doubts have been voiced concerning the undisturbed geology of the location (20), the suitability of environmental conditions for bacterial life, and the fossils themselves (143). Although the existence of layered microbial associations as early as 3.50 Gya has been reported (reviewed in Reference 162), uncertainties about the biotic origin of some of the earliest fossils have arisen (67, 162). Recently, layered structures that carry organic globule structures similar to modern stromatolites dating back to 2.72 Gya have been described (101).

Chemical Indicators

A number of different organic molecules derived from distinctive cellular components have been used as biomarkers for specific organism groups. Oxygen-producing photosynthesis enabled the synthesis of biological molecules whose biogenesis is oxygen-dependent. Methyl-substituted hopanoids (168) were thought to provide a first biological marker for an emerging oxygen-dependent biosynthetic pathway 2.7 Gya. However, these molecules have also been recently identified in anaerobic purple bacteria (146, 177), thereby removing them as a reliable biomarker for oxygenic photosynthesis. Molecules thought to indicate the presence of green sulfur bacteria (chlorobactene and isorenieratene) and of purple bacteria (okenone) (22) have been reported to have existed as far back as 1.64 Gya.

Genetic Evidence

The presence of oxygen triggered a revolution in cellular metabolism (21, 152). The recent finding that oxygen can be generated from nitric oxide (45) indicates that oxygen-dependent

pathways may have been operational before the emergence of oxygenic photosynthesis. However, it is unlikely that this process is capable of generating large quantities of oxygen due to the requirement for high-energy molecular precursors.

MECHANISMS OF EVOLUTION

Molecular Evolution

Evolution occurs on a molecular level through changes in DNA that create novel proteins offering novel metabolic opportunities. Within an organism, gene (84) or genome duplication (140) may provide a "sand box" for molecular innovation. RC evolution (see below) is certainly a case of gene duplication in which a single gene coding for a homodimeric protein is duplicated to derive heterodimeric RCs. Gene fusion and splitting are also the likely mechanisms behind the fused RC center core and antennas (see below). Lateral gene transfer enables the transfer of metabolic capabilities between organisms (148) and is a likely mechanism underlying the presently observed mosaic of photosynthetic light-harvesting complexes (LHCs) within different groups of photosynthetic organisms. Some genomes contain compact clusters that include genes coding for RCs and the synthesis of photosynthetic pigments (85) that may serve as a vehicle for transfer of photosynthetic capabilities between organisms. Lateral gene transfer between Bacteria (164) and Archaea and Bacteria (52) may account for the present distribution of rhodopsins.

Establishing Metabolic Networks

Several concepts have been developed to account for mechanisms that establish metabolic networks and new metabolic capabilities with direct relevance to photosynthesis. Using chlorophyll biosynthesis from hemes as an example, Granick (61) proposed that biosynthetic pathways recapitulate their evolution, hypothesizing that the intermediate compounds of the modern biosynthetic pathways were the final products of early pathways, and thus the evolution of the pathway can be traced from the beginning to the end. This contrasts with the retrograde hypothesis (81), which posits that present biosynthetic pathways are set up in the reverse order to their evolutionary history and occurred through gene duplications. An example of this retrograde relationship may be present in proteins involved in nitrogen fixation (NifD, K, E, and N) that show relatedness to one another (47). The Granick and retrograde hypotheses are not mutually exclusive. Because the retrograde hypothesis is a consequence of the depletion of "base" molecules present in the primordial soup, molecules that follow the Granick hypothesis may be more derived. For example, heme biosynthesis is conserved throughout Archaea and Bacteria and may involve ancient pathways formed according to the retrograde hypothesis, whereas chlorophyll biosynthesis is more derived and may largely follow the Granick model. Enzymes that act in one metabolic pathway may be recruited to other pathways to perform similar reactions on related substrates (89). An interesting case for a nonspecific enzyme that may have originally modified two places on a symmetrical substrate but later specialized after a gene duplication event is present in chlorophyll biosynthesis (see section entitled The Earliest Chlorophyll).

EVOLUTION OF COFACTORS

Electron transport, proton translocation, and light harvesting are essential functions of photosynthetic systems. Specific protein complexes and molecules are utilized to mediate these functions. Electron transport appears to be composed of an ancient "kit" of components (6) that can be combined and adapted to new functions.

Iron Sulfur Cluster

FeS clusters (90) mediate electron transport in photosynthesis and respiration, including ferredoxins (4Fe-4S, 3Fe-4S, 2Fe-2S) and Rieske FeS clusters. FeS clusters span a wide range

of redox potentials from greater than +500 to less than −500 mV versus normal hydrogen electrode (49).

The use of FeS clusters in electron transport may go back to the very beginning of the emergence of life (71, 97). In fact, simple FeS clusters form spontaneously from ferrous iron and sulfide in reducing conditions, while assembly machineries for their biosynthesis are found in modern organisms (50, 103). FeS clusters are found universally in Bacteria and Archaea, but it is notable that there is a preference for their use by organisms operating in anaerobic conditions and methanogens, almost certainly owing to their general instability to oxygen exposure.

Where FeS clusters are utilized in organisms, they are buried in proteins to keep oxygen at a distance from the catalytic site. Could oxygen sensitivity be a reason for the lack of FeS clusters in the oxygen-producing Q-type RC (PSII) and for the spatial separation (38) between PSI and PSII in photosynthetic organisms? A look at the redox midpoint potentials of electron transport cofactors of PSI and PSII (**Figure 7**) may suggest that, energetically, oxygen and NADPH production may be accomplished by a single RC.

Rieske iron sulfur cluster. Rieske FeS clusters are employed in cytochrome bc_1 and b_6f complexes of the photosynthetic electron transport chain (**Figure 9**). Deducing the evolution of the Rieske protein provides a valuable case study for the limits of unguided, sequence-based alignments (100), illustrating a typical problem of many cofactor-containing photosynthetic proteins. The functional domain of the Rieske FeS cluster is almost invariable. Available structural information reveals that a part of the protein is evolutionarily constrained through interactions with cytochrome *b*, whereas other parts have little evolutionary constraint, the consequence of which is frequent insertion and deletion of amino acids. Deriving phylogenetic data is extremely difficult in small electron transfer proteins like type I monoheme cytochromes, copper proteins, thioredoxins, and ferredoxins because the available information in short sequences is often insufficient to lead to robust phylogenies.

Hemes

Hemes share part of the biosynthetic pathway with chlorophylls (7). Tetrapyrroles serve as electron carriers in all domains of life. Heme-carrying proteins were postulated to have been present in the last common ancestor of Bacteria and Archaea (6, 21, 97). Some methanogens, however, lack cytochromes and quinones entirely (172).

Quinones

Membrane-bound quinones are nearly ubiquitous in Archaea, Bacteria, and Eukarya. Only a few methanogenic Archaea and obligate fermentative organisms do not have the ability to synthesize quinones (128).

Quinone diversity and flexibility. Different quinones have been adapted to mediate electron transport by complexes shared between photosynthetic and respiratory electron transport. Several lines of evidence suggest that menaquinone (MQ) is the "original" quinone. Only cyanobacteria and their progeny have plastoquinone (PQ), and the α,β,γ-proteobacteria have mainly adopted ubiquinone (UQ) (160) (**Figure 3**). Reduced MQ is quickly oxidized by oxygen. The oxygen sensitivity and change in midpoint redox potential of the electron transport chain when oxygen is utilized as an electron acceptor triggered a series of adaptations.

MQs (−70 mV) possess a more negative (by ~170 mV) redox midpoint potential than UQs and PQs (+100 mV). A more positive potential quinone pool is critical for bridging the redox potentials from anaerobic legacy metabolism to oxygen. Changes in utilized quinones are an interesting evolutionary marker for investigating the evolution of photosynthesis and respiration because a change in the utilized quinone has consequences for all complexes interacting with the quinone pool (43). Some

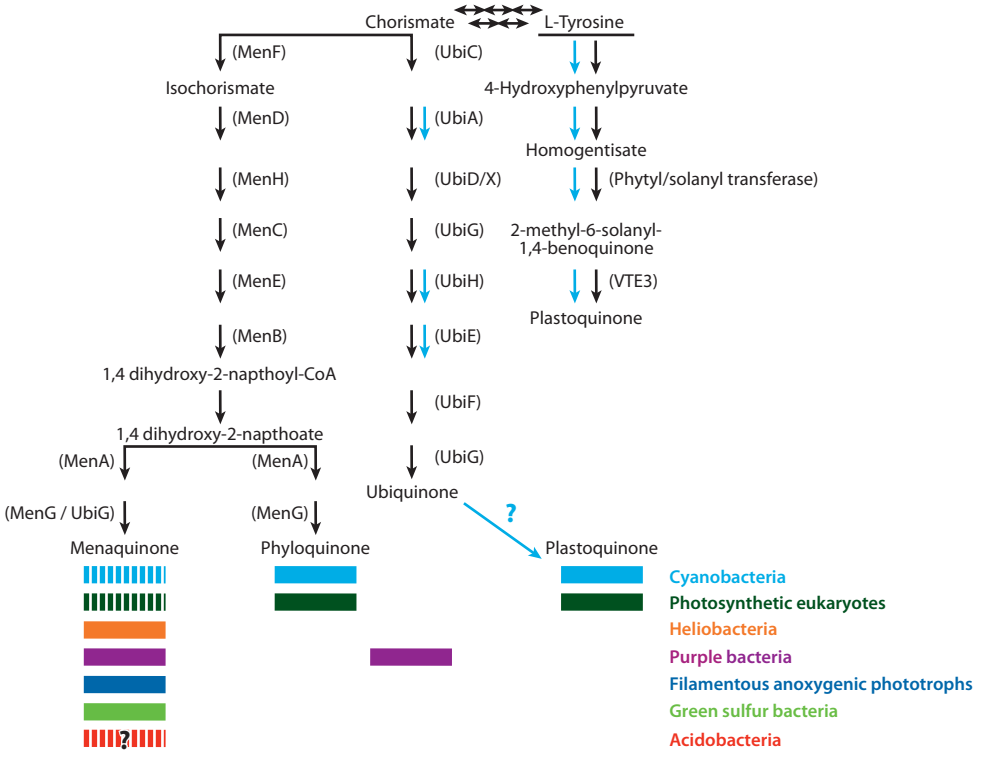


Figure 3

Quinone biosynthesis in photosynthetic organisms. The FeS-type reaction center (RC) of the early branching cyanobacterium *Gloeobacter violaceus* contains menaquinone, whereas all other known cyanobacteria contain phylloquinone. Plastoquinone (PQ) synthesis in cyanobacteria (*cyan arrows*) uses a synthesis pathway found in plants as well but also uses an alternative pathway that may utilize proteins with homology to ubiquinone (UQ) synthesis, UbiA, UbiH, and UbiE, which are found in cyanobacterial genomes. The type of quinone in the RC of photosynthetic acidobacteria has been tentatively identified as a menaquinone (MQ), which is present in other acidobacteria. Quinones that are universally present in an organism group are indicated by solid bars, whereas quinones that are not present in all organisms of a group are indicated by broken bars.

γ-proteobacteria possess the ability to switch between MQ and UQ. The switch from the aerobic use of UQ to the anaerobic use of MQ is observed in the nonphotosynthetic model *Escherichia coli* (174), with different protein complexes having preference for one or the other of the quinones. This flexibility, however, seems to come at a price in that *E. coli* abandoned the cytochrome bc_1 complex and its quinone oxidation and reduction sites. It has been suggested that ancestors of the α,β,γ-proteobacteria may have possessed two cytochrome bc_1 complexes optimized for operating with either UQ or MQ (43). The ancient MQ is used as the standard RC and acceptor pool quinone by Q-type RCs (filamentous anoxygenic phototrophs) and the RC acceptor A_1 in FeS-type RCs (green sulfur bacteria, heliobacteria) that perform photosynthesis only in anaerobic conditions, whereas other quinones are utilized by organisms that can carry out photosynthesis under aerobic or microaerobic conditions.

Quinones in quinone-type reaction centers. The Q-type RCs contain two quinones as electron acceptors. The first, called Q_A, acts as a single-electron acceptor, and the second, Q_B, accepts two electrons before leaving the

RC to become part of the quinone pool. PQ is the Photosystem II RC quinone and pool quinone utilized by all oxygen-producing organisms. Interestingly, the RCs of some purple bacteria contain either one MQ (Q_A) and one UQ (Q_B) (*Rhodopseudomonas viridis*) (37) or two UQs (*Rhodobacter sphaeroides*) (44). This is consistent with the flexibility of utilizing MQ or UQ observed in α,β,γ-proteobacteria. Filamentous anoxygenic phototrophs use MQ as both Q_A and Q_B.

Quinones in iron sulfur-type reaction centers. Almost all known cyanobacteria and their plastid progeny use phylloquinone as a membrane-bound one-electron acceptor (A_1) in Photosystem I. Phylloquinone and MQ have an identical naphthoquinone head group but different side chains and are synthesized by homologous biosynthetic pathways, and as a consequence, respective enzymes are often annotated as their MQ homologs. The early, branching cyanobacterial "living fossil" *Gloeobacter violaceus*, a primitive, unicellular red algae (*Cyanidium caldarium*), and a centric diatom (*Chaetoceros gracilis*) use MQ in the FeS-type RC (129) instead of phylloquinone, which is by far dominant in cyanobacteria and eukaryotic photosynthetic organisms. This distribution may point to (*a*) the presence of MQ in cyanobacteria that gave rise to eukaryotic cells and the move to phylloquinone in prokaryotic and eukaryotic oxygenic organisms at different occasions, (*b*) the presence of both MQ and phylloquinone pathways in the ancestor of all photosynthetic eukaryotes, or (*c*) independent lateral gene transfer events. The ability to utilize different quinones as an A_1 has been demonstrated in mutants deficient in phylloquinone. These mutants readily incorporate PQ and nonnative quinones into the A_1 site, leading to only slightly impaired FeS-type RCs (91).

Quinones as modulator of excitation energy transfer. Another potential function of quinones is energy dissipation. Oxidized quinones interact with excited chlorophylls (53, 79), and it is possible that this quinone-mediated excitation quenching has been adapted by photosynthetic organisms to regulate the amount of excitation that reaches the RCs. This has been well documented in the chlorosome complexes of green sulfur bacteria (18). However, in photosynthetic eukaryotes, this function has been assumed by carotenoids in the nonphotochemical quenching mechanism.

Quinone biosynthesis. The present distribution of UQ (in proteobacteria) and PQ (in cyanobacteria and plastids) may identify them as separate inventions. However, the biosynthesis of PQ is well understood only in plants. Genetic deletion of either of two essential steps in plant PQ synthesis, the gene for 2-methyl-6-phytyl-1, 4-benzoquinone/2-methyl-6-solanyl-1-4-benzoquonone methyl transferase and the gene for 4-hydroxyphenylpyruvate dioxygenase (36), does not lead to complete loss of PQ synthesis in *Synechocystis* sp. PCC 6803 as it does in plants. Intriguingly, all known cyanobacterial genomes include genes homologous to those genes involved in UQ synthesis (UbiA, Ubi/X, UbiE, and often UbiH) that do not, however, add up to an entire UQ pathway (**Figure 3**). Given the chemical relatedness (both are benzoquinones), it may be that UQ and PQ synthesis share a common core of enzymes and have a common ancestry but that plastids implemented a modified version that also accomplishes PQ synthesis.

Chlorophylls

Chlorophylls (66) are the defining feature for charge-separating RCs. In addition to the charge-separation machinery, chlorophylls also provide the principal antenna pigments in all RC-containing organisms (63), with the exception of some cyanobacteria in which bilins associated with phycobilisomes provide the characteristic color.

Chlorophyll diversity. In contrast to the open-chain tetrapyrrole bilins, all chlorophylls

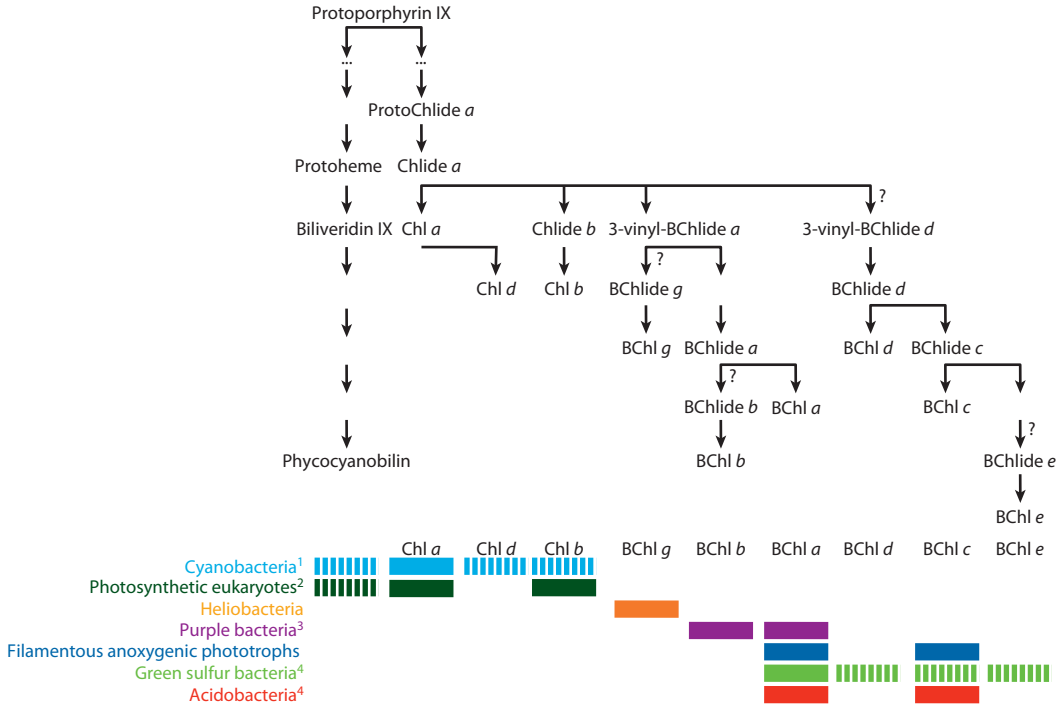


Figure 4

Chlorophyll (Chl) and bacteriochlorophyll (BChl) biosynthesis and distribution showing biosynthesis pathways for phycobilins, Chls, and BChls. Hypothetical enzymes are indicated by a question mark. The presence of tetrapyrroles in different groups of photosynthetic organisms is shown. Chls and BChls that are universally present in an organism group are indicated by solid bars, whereas Chls and BChls that are not present in all organisms of a group are indicated by broken bars. 1. All cyanobacteria synthesize Chl *a*. Chl *d* is synthesized by acaryochlorophytes. Chl *b* is synthesized by prochlorophytes. Phycobilins are synthesized by most cyanobacteria. 2. Photosynthetic eukaryotes synthesize Chl *a*/*b*. Glaucophytes and rhodophytes synthesize phycobilins. Several algae also synthesize Chl *c*. 3. Purple bacteria synthesize either BChl *a* or *b*. 4. Green sulfur bacteria synthesize BChl *a* and either one or combinations of BChl *c*/*d*/*e* as the main light-harvesting pigment located in the chlorosomes. 5. The only known photosynthetic acidobacterium contains BChl *a*/*c*. BChl *c* is the main light-harvesting pigment located in the chlorosomes.

are circularized terapyrroles with a central magnesium. The biogensis of chlorophylls (32) is of interest in understanding the evolution of photosynthesis because knowing the "original" chlorophyll may help in reconstructing the evolution of photosynthetic machinery in different organisms. Following the Granick hypothesis (see section entitled Establishing Metabolic Networks), the two obvious candidates for this ancient chlorophyll are Chl *a* and the bacteriochlorophyll BChl *a* (**Figure 4**). A strict Granick hypothesis would argue for Chl *a* as a very primitive type of chlorophyll. However, Chl *a* is found only in cyanobacteria and their eukaryotic progeny, which possess the most derived RC complexes (see section entitled Reaction Centers). Most other groups of bacteria contain BChl *a* (green sulfur bacteria, purple bacteria, filamentous anoxygenic phototrophs, acidobacteria), at least in their charge-separating core, with the exception of heliobacteria (BChl *g*) and a subgroup of cyanobacteria (acaryophytes) that contain Chl *d*. It is also the case that some of these organisms contain trace quantities of Chl *a* derivatives that function in the electron transfer chain in the RCs but not in the antenna system, so that they must retain the ability to synthesize them, although not in large quantities. Can this confusing distribution of pigments be

BChl: bacteriochlorophyll

understood, and does it tell us anything about the evolution of photosynthesis? Almost certainly, more symmetric porphyrins preceded chlorophylls as photosynthetic pigments in early photosynthetic organisms (114). These were replaced in favor of the present group of pigments, which have stronger absorption, especially in the red region of the spectrum.

The earliest chlorophyll. One suggestion is that BChl *a* is structurally closer to the early chlorophyll, at least in terms of the reduction level of the ring system. The near final step in the biosynthesis of Chls and BChls involves the reduction of the double bond in ring D between C17 and C18 in both Chl *a* and BChl *a*. In BChl *a* biosynthesis, a second double bond reduction takes place between C7 and C8 in ring B. These reductions are mediated by the light-independent protochlorophyllide oxidoreductase enzyme complexes BChLNB (for the C17–18 reduction) and BchXYZ (for the C7–8 reduction). These enzyme complexes are homologous and have clearly been derived from an ancestral enzyme complex via gene duplication (153). This ancestral enzyme may have catalyzed both the reduction of ring D as well as the reduction of ring B. A gene duplication event then allowed for the evolution of two separate, specific enzymes that are present in contemporary organisms, and the loss of the *bchXYZ* genes in oxygenic organisms resulted in organisms that can reduce only the C17–18 double bond in ring D, leading to Chl *a*. This proposal could be tested using the technique of reconstruction of ancient enzymes (57, 72), in which the ancestral enzyme is produced and its substrate specificity examined.

The Chl *d* in acaryochlorophytes has recently been shown to be derived from Chl *a* (159). However, the biosynthetic pathway of BChl *g* remains an interesting topic for several reasons. The genome of *Heliobacterium modesticaldum* appears to have both *bchLNB* and *bchXYZ* genes (156), suggesting that a compound similar to BChl *a* (probably the C3-vinyl BChl *a*) is synthesized as an intermediate for generating BChl *g*. However, the enzyme catalyzing the conversion of BChl *a* to BChl *g* remains elusive. Interestingly, BChl *g* readily isomerizes to yield Chl *a*. The suggestion has been made that the oxygen-sensitive BChl *g* may be the ancestor of Chl *a* found in all oxygenic organisms (129).

Oxygen-dependent chlorophyll biogenesis steps. The presence of oxygen allowed the development of novel reaction pathways that include Chl biosynthesis. Three of the enzymes involved in chlorophyll biosynthesis are different in aerobic and anaerobic phototrophs. The anaerobic versions of the enzymes are presumed to be the original ones and were replaced at some point with aerobic enzymes that take advantage of the extra energy available when O_2 is used as the oxidant (149). In some cases, facultative organisms contain both copies of the enzymes, whereas strict anaerobes contain only the anaerobic versions and aerobes have the aerobic versions. Although in anaerobic conditions BchE incorporates oxygen from water into ring E at the $C13^2$ position, oxygen is the substrate utilized by AcsF. Some purple bacteria that contain both BchE and AcsF can switch between these proteins depending on the availability of oxygen (136). So the present biosynthetic pathway for chlorophyll is a mosaic with some steps catalyzed by enzymes retained from the anaerobic past and some that have more recently been replaced by distinct gene products that utilize O_2. This means that care must be used in interpreting evolutionary scenarios based on chlorophyll biosynthetic pathways, as the pathways may have changed over the course of evolution, rendering direct comparisons across wide groups of taxa problematic.

Light niches. What could have prompted the diversity of pigments? One aspect is certainly the availability of light niches that can be exploited by an alternative pigment. This is certainly the case for the chlorophyll *d*–containing acaryophytes (169) and the organisms utilizing the newly discovered chlorophyll *f* (31) that have a shifted absorption spectrum to other photosynthetic organisms they compete with.

An interesting hypothesis may be that the absorption spectra of chlorophylls follow a sequence that is determined by the evolution for light niche adaptations. It is hoped that biochemical analysis of Chl and BChl biosynthetic pathways, together with their distribution, will allow for a retrospective evolutionary scenario for the evolution of chlorophyll biosynthesis (98).

EVOLUTION OF PROTEIN COMPLEXES

Rhodopsins

Compared with the much more complicated chlorophyll-containing RC complexes, rhodopsins appear to be an amazingly simple way of harvesting light energy. Rhodopsins are proteins that are composed of seven transmembrane helices (TMH) and catalyze the light-driven translocation of ions across the membrane. One chromophore, the carotenoid retinal, undergoes light-induced isomerization. This conformational change is utilized to translocate protons (bacteriorhodopsin in Archaea and proteorhodopsin in proteobacteria) or chloride (halorhodopsin in Archaea).

Rhodopsin distribution. Rhodopsins display a broad, yet patchy distribution in Archaea, thought to be the result of lateral gene transfer and gene loss (164). This distribution of rhodopsins raises the question of whether they were present as photoconverters in the last common ancestor of Archaea (86) or in the last common ancestor of Bacteria and Archaea, or alternatively, whether they spread by horizontal gene transfer (164).

The first rhodopsins in Bacteria were identified in oceanic proteobacteria (10). Expression of these proteorhodopsins in *E. coli* generates a transmembrane potential, indicating a role as ion pump (175). It has been shown that a rhodopsin-generated proton gradient stimulates growth in members of the Bacteroidetes (Flavobacteria) (60) and enhances survival in γ-proteobacteria (*Vibrio*) (39). The structural simplicity and potential utility make rhodopsins a "protein without borders" as it concerns vertical and lateral gene transfer, even between Archaea and Bacteria (52).

Rhodopsin autotrophy? Presently, there is no evidence for light-driven, autotrophic life that is dependent on rhodopsins as photoconverters. There is, however, no obvious fundamental reason why this is not a possibility, given an electron source and mechanisms to convert the rhodopsin-dependent proton gradient into a redox gradient, which can be used to reduce CO_2 (23). However, it is not clear that rhodopsins could achieve the coverage of the solar spectrum that chlorophylls exhibit, and it appears unlikely that a large and efficient antenna system can be coupled to these systems, although xanthorhodopsin contains a single carotenoid antenna pigment, which transfers excitation to retinal pigment with 40% efficiency (5). This is in stark contrast to hundreds or thousands of chromophores that can be connected with one chlorophyll-based RC through antennas (see section entitled Light-Harvesting Complexes). This may be the root reason that chlorophyll RCs and rhodopsin-based photoconverters do not seem to be functional within a single organism at the same time.

Reaction Centers

Photosynthetic RCs represent some of the most complicated known membrane protein assemblies. For example, the FeS-type RC of photosynthetic eukaryotes is composed of more than 13 subunits and 193 cofactors (3), and the Q-type RC (PSII) contains more than 20 protein subunits housing more than 50 cofactors (69). How could such complex proteins evolve (150)? Structural, functional, and genetic studies help us to address this question. These data and the ever increasing number of discovered organisms and RCs reveal patterns that can be used to derive the evolutionary history of RCs.

The defining component of an RC, the charge-separation machinery, is located within a dimeric protein consisting of 5 TMH per

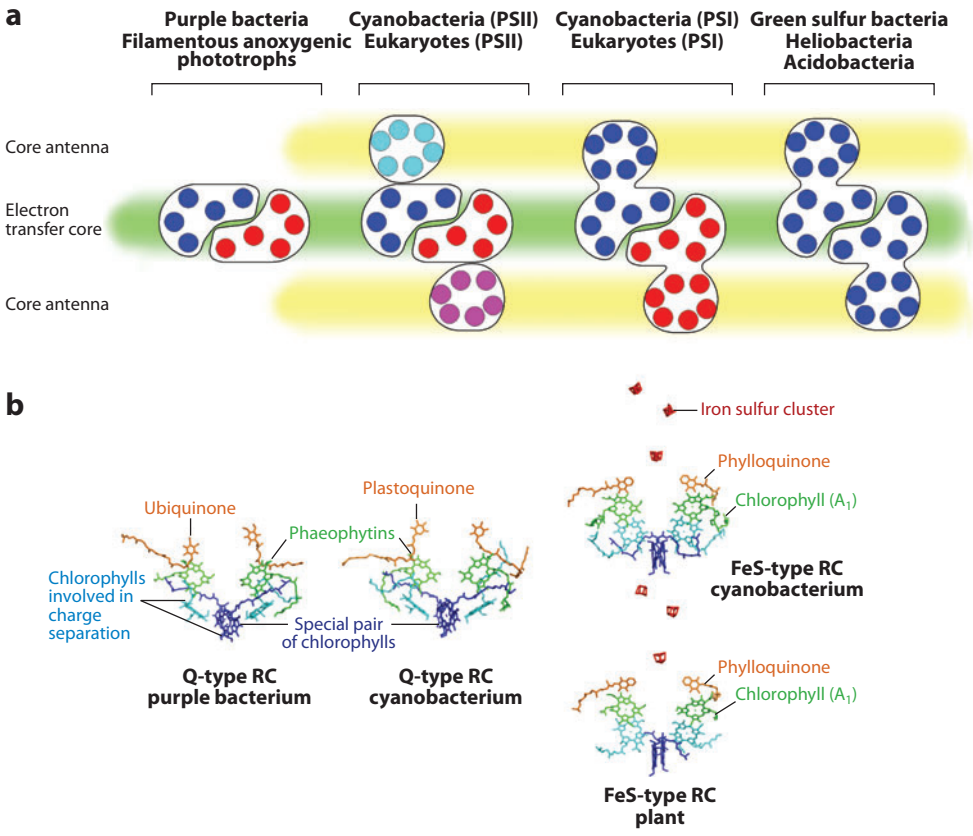


Figure 5

(*a*) Schematic diagram indicating the transmembrane helical composition of photosynthetic reaction centers (RCs). Purple bacteria and filamentous anoxygenic phototrophs possess a heterodimeric (L, M) quinone (Q)-type RC. The Q-type RC (PSII) of cyanobacteria and photosynthetic eukaryotes consists of a heterodimeric electron transfer core (D1, D2) and two homologous subunits (CP47, CP43) that act as a core antenna. The FeS-type RC (PSI) of cyanobacteria and higher plants is heterodimeric. Heliobacteria and green sulfur bacteria possess a homodimeric FeS-type RC. The core antennas of heliobacteria, green sulfur bacteria, and PSI are homologous to the separately encoded core antennas of PSII of oxygenic eukaryotes and cyanobacteria. Transmembrane helices (TMH) (*circles*) are encoded by separate genes shown in different colors. (*b*) Arrangement of electron transport cofactors involved in the charge separation and stabilization of Q-type and FeS-type RCs. The data were obtained from solved crystal structures: Q-type purple bacterium RC (*Rhodobacter sphaeroides*, PDB 1aij), Q-type cyanobacterium RC (*Thermosynechococcus elongatus*, PDB 1s5l), FeS-type cyanobacterium RC (*Thermosynechococcus elongatus*, PDB1jb0), FeS-type plant RC (*Pisum sativum*, PDB 2o01). The special set of chlorophylls involved in charge separation is shown in blue and cyan (special pair). Tetrapyrroles are phaeophytins in Q-type RCs and chlorophylls (A_1) in FeS-type RCs and are shown in green. Ubiquinone (UQ) (in purple bacterium), plastoquinones (PQ) (Q-type RC of cyanobacteria), and phylloquinone (FeS-type RC of cyanobacteria and plants) are shown in orange. The FeS clusters of the FeS-type RCs are shown in red. Adapted from Reference 78.

dimer (**Figure 5**). Each half of the dimer contains an identical (or nearly identical) set of cofactors. Four Chls (two per dimer) are arranged in close proximity to form the "special set" that upon excitation expels an electron. This electron is donated to another tetrapyrrole and then to a quinone. There is very little variation between the orientations of these

cofactors in all available RC crystal structures (**Figure 5**). If the electron is transferred from the first electron-accepting quinone to a second quinone, the RC is classified as a Q-type RC (often called Type 2 RCs), whereas FeS-type RCs (often called Type 1 RCs) transfer electrons from quinone to a series of FeS clusters. In some FeS-type RCs, specifically the RCs of the green sulfur bacteria and heliobacteria, it is not clear whether the electron resides on the quinone at all or passes from the tetrapyrroles directly to the FeS clusters.

Quinone-type reaction centers. The electron transport pathway in the Q-type RCs utilizes only one branch of the electron transport chain and then passes the electron from one quinone (Q_A) to the quinone of the other chain (Q_B). The interquinone electron transfer direction is roughly parallel to the plane of the membrane. This functional preference imposes a heterodimeric structure on the Q-type RCs of cyanobacteria and photosynthetic eukaryotes and in purple bacteria and filamentous anoxygenic phototrophs. The RCs of purple bacteria and filamentous anoxygenic phototrophs consist of a dimeric 5 TMH domain. In addition, the Q-type RC in the cyanobacterial lineage also requires the presence of two related 6 TMH complexes, CP43 and CP47, which house additional pigments as a core antenna. These 6 TMH complexes are related to the part of the RC that forms the core antenna in FeS-type RC.

Iron sulfur-type reaction centers. In contrast to the cyanobacterial Q-type RCs in which 5 TMH and 6 TMH are separate proteins, all known FeS-type RCs are 11 TMH dimers in which the 5 TMH electron transport core and the 6 TMH core antennae are contained in a single protein. The FeS-type RCs are homodimeric; that is, the dimer is formed from two identical 11 TMH proteins in green sulfur bacteria, acidobacteria, and heliobacteria. In cyanobacteria, however, the FeS-type RCs are heterodimeric, although there appears to be little functional difference between the two electron transport branches that exist within the heterodimer (125). There are good reasons to postulate that the "original" RC (UrRC) was a homodimer and that the heterodimeric forms were derived via gene duplication and divergence events. However, it is presently not clear whether that dimer was composed of two 11 TMH proteins or two 5 TMH proteins, or whether it was an FeS-type or a Q-type RC or possibly something in between, sometimes humorously called a Type 1.5 RC (16).

UrRC: the last common ancestor of all present chlorophyll-based reaction centers, the "original" RC

11 versus 5 transmembrane helices. Was the UrRC an 11 or a 5 TMH protein? A key aspect when considering this question is the origin of the Q-type RCs in the purple and filamentous anaerobic phototrophs and cyanobacteria. The RCs of purple bacteria and filamentous anoxygenic bacteria are very similar, and there is some evidence that suggests that filamentous anoxygenic bacteria obtained them though lateral gene transfer from purple bacteria (68), therefore, we treat them together in this review as purple RCs.

Did the purple RCs and cyanobacterial RCs emerge from a single gene duplication event, or did gene duplication events in several photosynthetic clades result in the same overall design? Phylogenetic and structural analyses (155) (**Figure 6**) point to two independent gene duplication events, one giving rise to the heterodimeric purple RCs and the other to the heterodimeric cyanobacterial RC. This independent origin of two 5 TMH RCs argues that the UrRC was a 5 TMH RC, given that a coincidental split of a hypothetical 11 TMH (and loss of the 6 TMH) RC in purple bacteria and cyanobacteria appears unlikely. However, a convergent evolution of a 5 TMH core, owing to the use of mobile quinones as electron acceptor, from an 11 TMH UrRC cannot be excluded.

Quinone-type versus iron sulfur-type reaction centers. FeS-type RCs are physically, if not functionally, homodimeric, and a homodimeric configuration can be assumed to

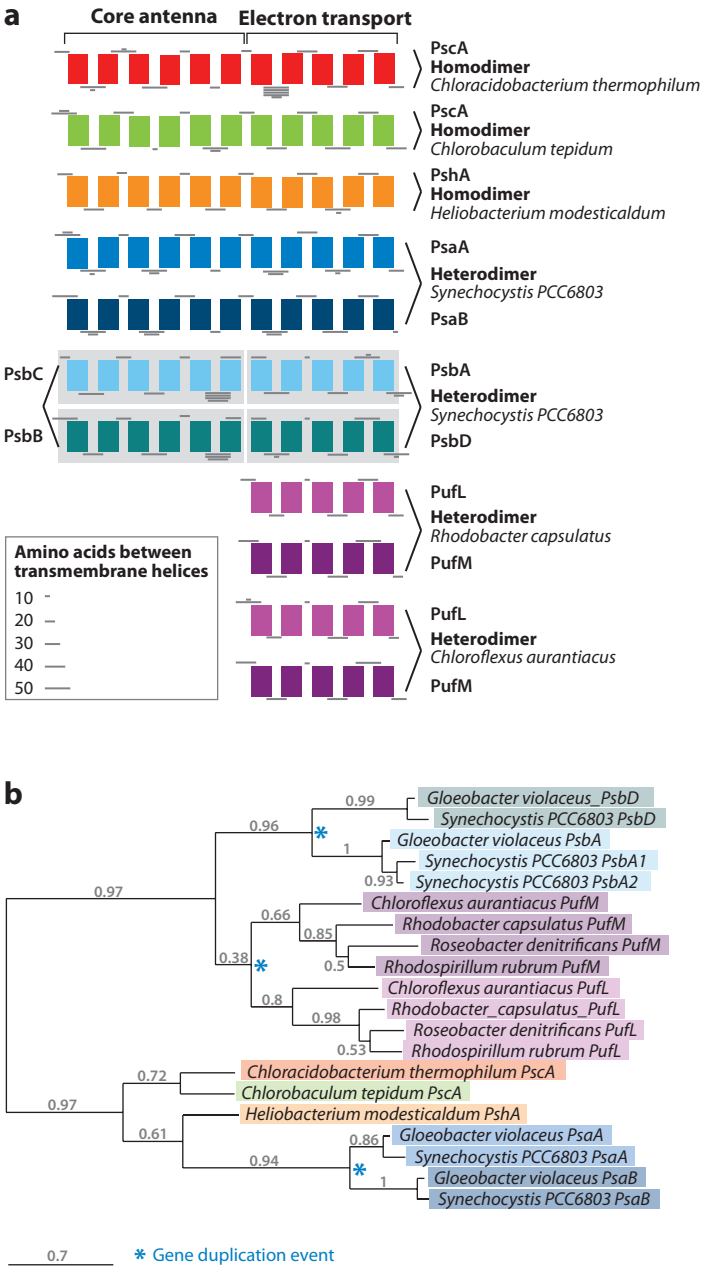


Figure 6

Topology of transmembrane helices (TMH) in photosynthetic organisms and a phylogenetic tree of electron transport TMH. (*a*) Diagram indicating protein topography of reaction centers (RCs) in selected organisms. (*b*) Phylogenetic tree of the five TMH that constitute the RC electron transfer domain of selected photosynthetic organisms. Colors correspond to organism group representatives in (*a*).

be the original form. Therefore, the argument could be made that FeS-type RCs represent the ancestral form. However, there are several considerations that point to the opposite Q-type UrRC. For one, the two FeS-cluster complexes that are the defining part of all FeS-type RCs are housed in subunits not found in Q-type RCs. Some of the FeS-cluster proteins may have different evolutionary origins, as the green sulfur PscD and the cyanobacterial PsaD appear not to be closely related. Furthermore, the quinones in green sulfur bacteria and heliobacteria do not appear to have a function (discussed in Reference 75), giving these quinones a potential status as vestigial cofactors.

Viral reaction center relatives. A recent report identified the presence of genes encoding PSI subunits in cyanobacterial phages (165). One special feature of the encoded genes is that two subunits, PsaJ and PsaF, are fused, in contrast to separate subunits in cyanobacteria. Genes that code for one of the PSII core proteins (D1) have also been found in viral genomes (108) and are expressed during viral infections (105). It has been hypothesized that RC-coding genes allow the maintenance of photosynthetic energy generation that can be utilized to drive viral replication (105, 108). The presence of RC encoding genes in viral genomes demonstrates the potential for lateral gene transfer of photosynthetic genes between different bacteria.

Electron donors. The complexity and high energies involved in extraction of electrons from water results in the integration of the electron-donating enzyme, termed the oxygen-evolving center (OEC), into the Q-type RC of cyanobacteria and photosynthetic eukaryotes. An evolutionary scenario for the generation of the OEC has been proposed (17, 151), based in part on similarities between the Mn-containing OEC and the Mn catalases (141). This RC may have first utilized hydrogen peroxide as an electron source. Today, no peroxide-oxidizing RC is known, but a peroxide species may be a possible intermediate during the catalysis of water oxidation (33). Other electron sources used

in photosynthesis are extracted by complexes that are not associated with the RC but are supplied to the RC via mobile electron carriers like cytochrome.

Electron sources other than water were utilized throughout bacterial evolution (40) and are also utilized by present photosynthetic bacteria. Hydrogen is an easily accessible electron donor that is fed into the PQ pool by hydrogenases. The machinery involved in oxidation of ferrous iron is common to many bacteria, including purple bacteria (178) and green sulfur bacteria (76), but appears not to be biochemically defined at the moment. Sulfide oxidation is mediated by a sulfide quinone oxidoreductase (64) in green sulfur bacteria, purple bacteria, and some cyanobacteria. These electron donors (hydrogen, sulfide, ferrous iron, hydrogen peroxide, water) possess increasingly positive redox midpoint potentials (**Table 2**) that may have been exploited by photosynthetic organisms during the evolution of photosynthesis (132).

Fusion versus selective loss. The presence of FeS- and Q-type RCs within cyanobacteria (**Figure 7**) poses the question of how these two types of RCs became established within a single organism. Two proposals have been made to account for the coexistence of the two types of RCs within a single organism (**Figure 8**). The fusion model (14, 113) proposes that FeS- and Q-type RCs developed in different organisms and that a bacterium that ultimately gave rise to the cyanobacterial line received a complementary RC in addition to the RC it already had through lateral gene transfer. The selective loss model (130, 133, 134) suggests that two types of RCs were present early on in a single photosynthetic organism and that all photosynthetic clades, with the exception of cyanobacteria, lost either the FeS- (purple bacteria, filamentous anoxygenic phototrophs) or the Q-type RC (heliobacteria, green sulfur bacteria, acidobacteria). A related proposal suggests that both types of RCs developed within a single organism through gene duplication events but were expressed under different

Table 2 Known autotrophic pathways

Nomenclature[a]	Calvin-Benson cycle	Reductive citric acid cycle	Reductive acetyl-CoA pathway>	3-Hydroxypropionate/ malyl-CoA cycle	3-Hydroxypropionate/ 4-hydroxybutyrate cycle	
Organisms	Cyanobacteria Purple bacteria	Green sulfur bacteria —	Strictly anaerobic Bacteria Strictly anaerobic Archaea	Chloroflexi	Aerobic Archaea	Anaerobic Archaea
Carboxylation product	3-Phosphoglycerate	Pyruvate Oxaloacetate 2-Oxoglutarate Isocitrate	Acetyl-CoA Formate Pyruvate	Malonyl-CoA (S)-methylmalonyl-CoA	Malonyl-CoA (S)-methylmalonyl-CoA	Pyruvate Oxaloacetate 2-Oxoglutarate Isocitrate
Main carboxylase	RubisCO	Pyruvate synthase Phosphoenolpyruvate (PEP) carboxylase 2-Oxoglutarate synthase Isocitrate dehydrogenase	CO dehydrogenase Acetyl-CoA synthase Formate dehydrogenase Pyruvate synthase	Acetyl-CoA carboxylase Propionyl-CoA carboxylase	Acetyl-CoA carboxylase Propionyl-CoA carboxylase	Pyruvate synthase PEP carboxylase

[a]See Reference 171.
[b]See Reference 182.

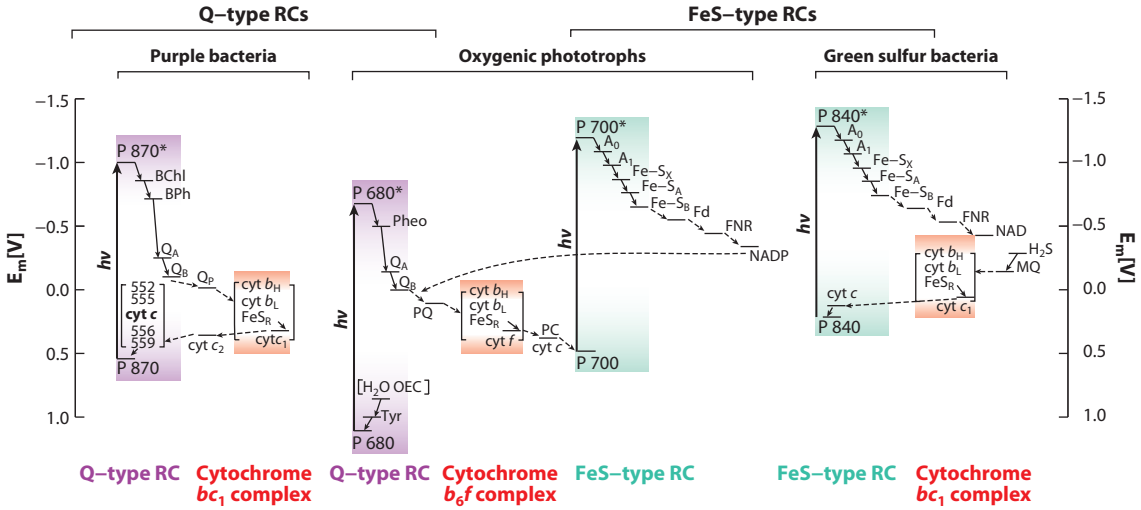


Figure 7

Overview of reaction center (RC) types and photosynthetic electron transport chains of purple bacteria, oxygenic phototrophs, and green sulfur bacteria. The redox midpoint potential (E_m) at physiological conditions for the cofactors is indicated. Protein complexes are shown as shaded blocks. RCs are classified as Q- or FeS type, depending on whether quinones or a series of FeS clusters are the final electron acceptors. Absorption of a photon with energy $h\nu$ (h, Planck's constant; ν, wavelength frequency) by RC pigments causes the transition from the ground state (P) to the excited state (P*). The peak absorption wavelength is indicated for each type of RC. The cytochrome (cyt) bc_1 and b_6f complexes, together with their Rieske FeS clusters (FeS_R), both receive electrons from RCs (*dashed arrows*) and are incorporated into the schemes to indicate linear and cyclic electron transport. Different species of cyt are indicated by lowercase italic letters: the subscripts L and H refer to low-potential and high-potential forms of cyt *b*, respectively. In the purple bacterial RC, four different forms of cyt *c* are indicated by their absorption maxima. Bacteriochlorophyll (BChl) and bacteriopheophytin (BPh) are early electron acceptors in purple bacteria, and pheophytin (Pheo) is the first electron acceptor from P680* in oxygenic phototrophs. Q_A and Q_B are primary and secondary quinone electron acceptors, respectively. In purple bacteria, the pool of membrane-associated quinone acceptors is referred to as Q_p, and in oxygenic phototrophs this is designated as the plastoquinone (PQ) pool. In the green sulfur bacteria, a membrane-associated pool of menaquinone (MQ) is present that is oxidized by the cyt bc_1 complex. In oxygenic phototrophs, the oxygen-evolving center (OEC) catalyzes water oxidation and donates electrons via a conserved tyrosine (Tyr) to the P680 RC. Electrons are transferred between the cyt b_6f complex and the P700 RC by either a *c*-type cyt or a plastocyanin (PC). In the FeS-type RCs of oxygenic phototrophs and green sulfur bacteria, the primary electron acceptors are A_0, a (bacterio)chlorophyll, and A_1, an electron-accepting quinone species. FeS_X, FeS_A, and FeS_B are RC-associated FeS clusters that transfer electrons to NADP or NAD via ferredoxin (Fd) and a ferredoxin-NAD(P) oxidoreductase (FNR).

conditions and then selectively lost in different clades, with the exception of cyanobacteria (2).

ATP Synthases

All through the tree of life, ATP synthases are instrumental in converting the chemiosmotic gradient, which is due to ions of different concentrations separated by a membrane, into energy that can readily be utilized to drive biochemical reactions. The ubiquitous distribution of ATP synthases and ATPases has prompted the suggestion that they were present in the last common ancestor of Archaea and Bacteria (97). This amazing machine is composed of an ion-conducting membrane-embedded component, an ATP catalytic site, and a stalk connecting the membrane and catalytic domain may have been in place when both rhodopsin and the Chl-type photoconverter started generating ion gradients. Whether ATP synthases and ATPases were present in the earliest cells is problematic, as primitive membranes were likely to have been very leaky, so that a chemiosmotic gradient could not be maintained (65). This suggests that the chemiosmotic mechanism was not present in the earliest cells but was added prior to the last common ancestor of all extant life.

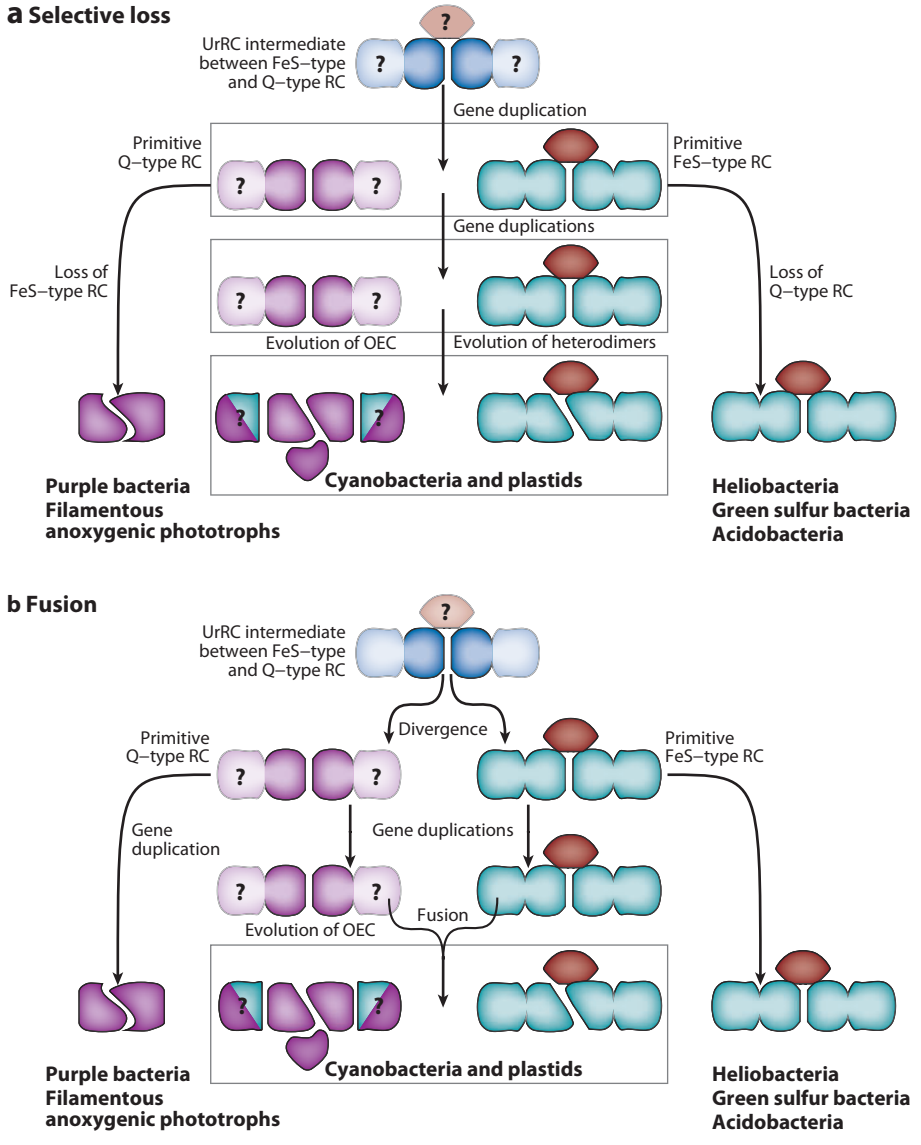


Figure 8

Schematic diagram illustrating the selective loss (*a*) and fusion (*b*) hypotheses for the evolutionary development of photosynthetic reaction centers (RCs). The core protein subunits of the various RCs are distinguished by color. Homodimeric complexes have two identical subunits, whereas heterodimeric complexes have two similar, yet distinct subunits. The gene duplication, divergence, and loss events that led to existing organisms are indicated. Cells containing two types of RCs are shown enclosed within a box. Time is read from the top to the bottom of the diagram, with the primordial homodimeric RC at the top and the six known groups of phototrophic prokaryotes, as well as the eukaryotic chloroplast, at the bottom. Abbreviations: OEC, oxygen-evolving center; RC, reaction center; UrRC, original reaction center; Q type, quinone type.

Although ATP synthases are complex machines, the presence of two distinct functional components within ATP synthases (an ion-conducting membrane component and an ATP catalytic site) have prompted speculation about how they could have been combined. There is homology between ATPases and hexameric DNA helicases (139). Furthermore, a protein excretion system, T3SS, has been identified that appears to combine aspects of ATP synthase (124) and the flagellar motor of bacteria (137). This observation prompted a hypothesis that the ATP synthase membrane domain originated as a membrane channel that together with the catalytic head functioned first as an RNA translocase and later as a protein translocase (similar to T3SS). Combining membrane and head subunit with a stalk then resulted in the ATP synthase (124).

Light-Harvesting Complexes

LHCs occur in an amazing abundance and variation of structure and cofactors (63). Light-harvesting antenna systems increase the absorption cross-section of RC chlorophylls located in the electron transport core. The known classes of antenna systems represent an extraordinary diversity of protein structure, utilization of pigments, interaction with the RCs, and cellular location. This lack of any recognizable similarity among different classes of light-harvesting systems strongly suggests that they have arisen multiple times during the course of the evolution of photosynthetic organisms, probably as adaptations to different light environments.

Reaction center core antenna family. In FeS-type RCs, the absorption cross-section of the RC core is extended by the core antenna that is fused with the electron transfer core. In cyanobacterial Q-type RCs, this core antenna is split from the electron transfer core (see the section entitled Reaction Centers). The separated protein complex, CP43, has been adapted as Q-type RC light-harvesting systems in prochlorophytes (Pcb) and, under stress conditions, in an FeS-type RC light-harvesting system in cyanobacteria (isiA). IsiA forms a ring that completely encloses the FeS-type RC (13, 19)

Eukaryotic light-harvesting complex family. A probably unrelated line of membrane-bound LHCs consists of members of a 3 TMH superfamily that includes CAP (chlorophyll *a/b* proteins in chlorophytes), FCP (fucoxanthin chlorophyll *a/c* proteins in diatoms and phaeophytes), as well as chlorophyll *a-containing* LHCs in some rhodophytes (62). This distribution suggests that the Ur-chloroplast that gave rise to LHC and FCP already contained a 3 TMH light-harvesting protein associated with FeS-type RC, a hypothesis corroborated by the association of LHCs with the PSI in rhodophytes (180). Recent biochemical studies of early, branching chlorophytes (170) are in line with an ancestral association of LHCs with PSI that was extended to PSII to varying degrees in the chlorophytes, with green algae and plants possessing LHCs that can shuttle between PSI and PSII (93).

An evolutionary scenario posits that the three-membrane helix antenna protein family is the result of two consecutive gene duplication-fusion events that started from HLIP-type 1 TMH proteins, giving rise to a 4 TMH PsbS-like protein (102). The present LHCs subsequently lost one helix. This scheme has been extended to also include the 6 TMH Pcb/IsiA protein family (56).

Bacterial light-harvesting family. A third group of membrane-embedded light-harvesting systems that appears to be evolutionarily distinct from those mentioned thus far are the 1 TMH light harvesting (LH) antenna complexes of purple bacteria (34) and filamentous anoxygenic phototrophs (18). LHCs consist of two related, yet distinct 1 TMH proteins that together house two BChl molecules and a carotenoid. Approximately 16 of these LH1 subunits form a large ring that completely encloses the Q-type RC (LH1 ring), and smaller rings consisting of 8–9 LH2 subunits can be located adjacent to

the LH1 ring. Each LH2 subunit complex contains three BChl molecules and one carotenoid The small size of these proteins makes phylogenetic analysis difficult owing to the lack of a robust signal, although it appears that all the LHCs have a single common origin.

Chlorosomes. Chlorosome antenna complexes found in green sulfur bacteria, filamentous anoxygenic prokaryotes, and chloroacidobacteria are different from all other light-harvesting systems, in that most pigments are not bound to proteins. Instead, more than 100,000 molecules (122) of bacteriochlorophyll *c,d,e* form undulating laminar sheets (144) or rod-shaped aggregates (54) in the presence of carotenoids and quinone. These aggregates are enclosed by a unilayer membrane toward the cytosolic side and a protein array called the baseplate toward the cytoplasmic membrane-embedded RCs. In acidobacteria and green sulfur bacteria, the baseplate channels excitation energy to the RC via an FMO-protein [a separate protein family (131)]; in filamentous anoxygenic phototrophs, LHCs connect the RC to the baseplate. The use of chlorosomes as the main light-harvesting system in very basal branches of photosynthetic life appeared as a surprise because the BChls *c,d,e* that assemble in chlorosomes appear to be very derived (**Figure 4**). On the other hand, the overall design of chlorosomes is very simple and may lend itself to easy transfer between organisms (77).

Phycobiliproteins. Most rhodophytes, cyanobacteria, and glaucophytes possess proteins (phycobiliproteins) that bind open-chain tetrapyrroles, called bilins (63). Phycobiliproteins form cylindrical structures that can aggregate into fans or domes, funneling light energy to the Q-type RC. Although the primary endosymbiont probably contained phycobilins, they have been lost in several eukaryotic photosynthetic organisms and have been largely replaced by LHC-type light-harvesting complexes.

Lumenal light-harvesting systems. The peridinin chlorophyll protein (PCP) is an independent invention of dinoflagellates, employing the carotenoid peridinin in a light-harvesting system enclosed in the lumen of the thylakoids (107). Lumen-located light-harvesting proteins, which are derived from phycobiliproteins, are also found in cryptophytes (176).

What prompted the evolution of such a variety of light-harvesting systems? As with the evolution of pigments, a driving force is certainly niche adaptation for the light environment, available metabolic constraints, and evolutionary history that can lead to the creation of new opportunities, or to LHCs in this case. Extramembranous light-harvesting systems may have an advantage because less membrane lipid has to be synthesized, and the diffusion pathways of mobile electron carriers like quinones and cytochromes can be minimized. However, it could also be argued that well-adapted membrane proteins may aide in restricting and directing mobile cofactors. At first sight, chlorosomes may appear to be very resource efficient because there is no need for additional proteins. However, the low-light niches occupied by green sulfur bacteria and filamentous anoxygenic phototrophs require the synthesis of hundreds of thousands of BChl. Furthermore, the chlorosomes of green sulfur bacteria and filamentous anoxygenic bacteria are incompatible with the presence oxygen, restricting their use. The exclusion of oxygen may have been a driving force for the use of membrane- and protein-embedded light-harvesting systems.

Quinol-Acceptor Oxidoreductase

Electrons generated by Q-type RCs are transferred into a membrane-bound quinone pool (see above). Oxidation of these quinones provides enough energy to translocate several protons across the membrane.

Cytochrome *bc* complex family. A protein conserved across Bacteria and Archaea is the

cytochrome bc_1 complex (163). The central complex (cytochrome *b*) with features most consistent with the common ancestor of all *bc*-type complexes found today is that found in proteobacteria, including purple bacteria and the mitochondria of eukaryotes, in which it is called Complex III. This protein complex consists of eight TMH that house two hemes catalyzing the oxidation of quinones. Two quinone-binding pockets act in concert with a Rieske protein (a 2 histidine–2 cysteine–2 iron–4 sulfur cluster) to translocate two protons across the membrane for each oxidized quinone. The Rieske iron-sulfur protein is flexible and orchestrates the donation of one electron per oxidized quinone to a cytochrome c_1; the second electron stripped from the quinone is donated to an oxidized quinone waiting in the second binding pocket via the two *b*-type hemes. Each quinone oxidized leads to one electron being transferred to cytochrome c_1 and two H^+ deposited in the luminal or periplasmic space, hence the proton-to-electron ratio of two. The reduced cytochrome c_1 then donates electrons to other electron carriers (a cytochrome in most organisms).

The original eight-transmembrane design has undergone modifications indicative of a succession, with stages represented by green sulfur bacteria, heliobacteria, and cyanobacteria (126). In green sulfur bacteria, the cytochrome *b* subunit is reduced to a 7 TMH, whereas heliobacteria and cyanobacteria contain a split cytochrome *b* complex composed of a 4 TMH (cytochrome b_6) and a 3 TMH (complex IV) that contains an additional heme c_i (42, 167). In cyanobacteria, instead of the cytochrome c_1, the system uses a cytochrome *f* to interface with either mobile cytochromes or plastocyanin. The structure and sequence of cytochrome *f* and cytochrome c_1 are very different from each other, with cytochrome *f* having a largely beta-sheet secondary structure unlike any other known cytochrome (reviewed in Reference 9). The evolutionary origin of cytochrome *f* remains a mystery.

Alternative complex III. Not all photosynthetic organisms utilize a cytochrome bc_1 type complex or derivative thereof for the oxidation of the quinone pool. The filamentous anoxygenic phototrophs exemplified by *Chloroflexus aurantiacus* utilize a fundamentally different type of Quinol-acceptor oxidoreductase that appears to replace the bc_1 complex in many other organisms (55, 181), including the only known photosynthetic acidobacterium (25).

EVOLUTION OF ORGANISM GROUPS

Evolution of Photosynthetic Bacteria

The process of chlorophyll-based photosynthesis almost certainly originated within the bacterial domain, as all known representatives (except eukaryotes, see below) are found in that domain. Cyanobacteria, purple bacteria, and green sulfur bacteria were classified before 1900, whereas the most recent group of photosynthetic organisms has only recently been discovered (24). We now know six broad groups (phyla) that include Chl-containing organisms. These are cyanobacteria, purple bacteria, green sulfur bacteria, filamentous anoxygenic phototrophs, heliobacteria and acidobacteria. There is a very patchy distribution of bacterial groups that is most likely due to a combination of vertical inheritance of the main metabolic capabilities that is complemented by lateral gene transfer events of photosynthetic components (154). The evolutionary diversity of bacterial species is largely covered by section on the RC, bc_1/b_6f complex, light harvesting, and cofactor evolution. A diagram that points out major features of these different classes is included (**Figure 9**).

Evolution of Photosynthetic Eukaryotes

Endosymbiosis. Schimper (158), Meyer (117), and Mereschkowsky (111, 115) were the first to suggest that the chloroplasts in algae

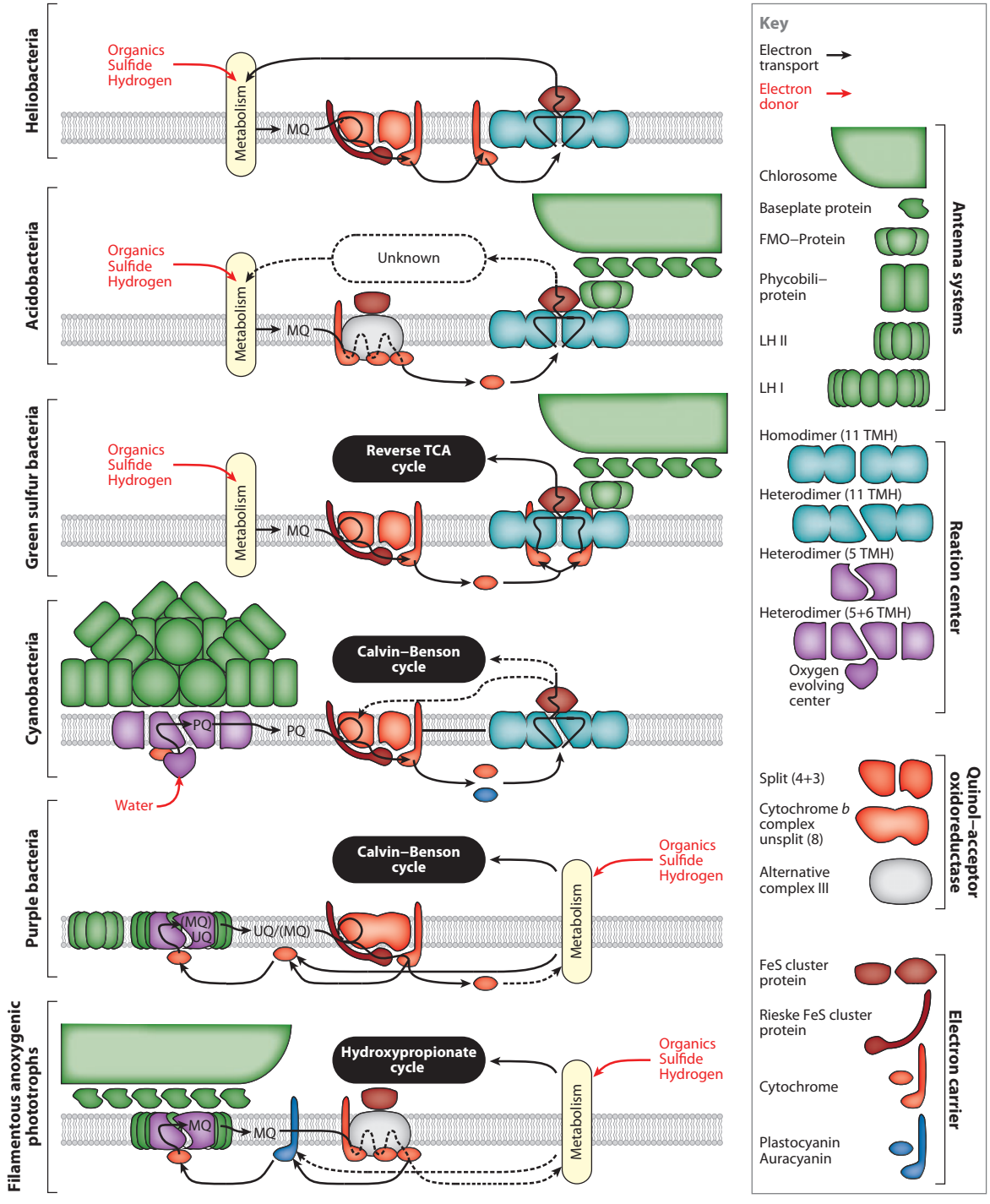


Figure 9

Photosynthetic machinery and electron transport of photosynthetic bacteria, including a description of photosynthetic complexes. Abbreviations: LH, light harvesting; MQ, menaquinone; PQ, plastoquinone; TCA, tricarboxylic acid; TMH, transmembrane helix(ces); UQ, ubiquinone.

and plants are derived from cyanobacteria. The arrival of electron microscopy and molecular biology provided a wealth of evidence that endosymbiosis gave rise to photosynthetic eukaryotes (110). From an initial and most likely loose coupling of metabolic functions between the two partners, a complete integration has taken place that includes the transfer of most of the genetic information of the cyanobacterium to the eukaryotic host, so that 18% of the nuclear genome of the reference plant *Arabidopsis thaliana* shows signs of cyanobacterial origin (112).

So far we know of three distinct ancient lines of photosynthetic eukaryotes: glaucophytes, rhodophytes, and chlorophytes. There remains uncertainty over whether these groups are the result of single (138) or possibly separate (82, 99) ancient, endosymbiotic events occurring possibly more than 1 Gya (41). Each photosynthetic group carries evidence of its cyanobacterial origin to various degrees. All are oxygenic phototrophs with an electron transport chain characteristic of cyanobacteria, including a cytochrome b_6f complex. One line (glaucophytes) still retains a cyanobacterial peptidoglycan cell wall (142) and carboxysomes within the host cell. Green algae and its progeny lost the cyanobacterial phycobilisome light-harvesting system, whereas red algae (rhodpohytes) and glaucophytes retained it.

Why only oxygen-producers have been recruited as photosynthetic endosymbiotic partners is another critical question about endosymbiosis. Surely, fixed carbon provided by a green sulfur bacterium would be a valuable resource in the right environment. Chemosynthetic endosymbiotic relationships are likely to exist in black smoker environments (166) that may also house green sulfur bacteria (8).

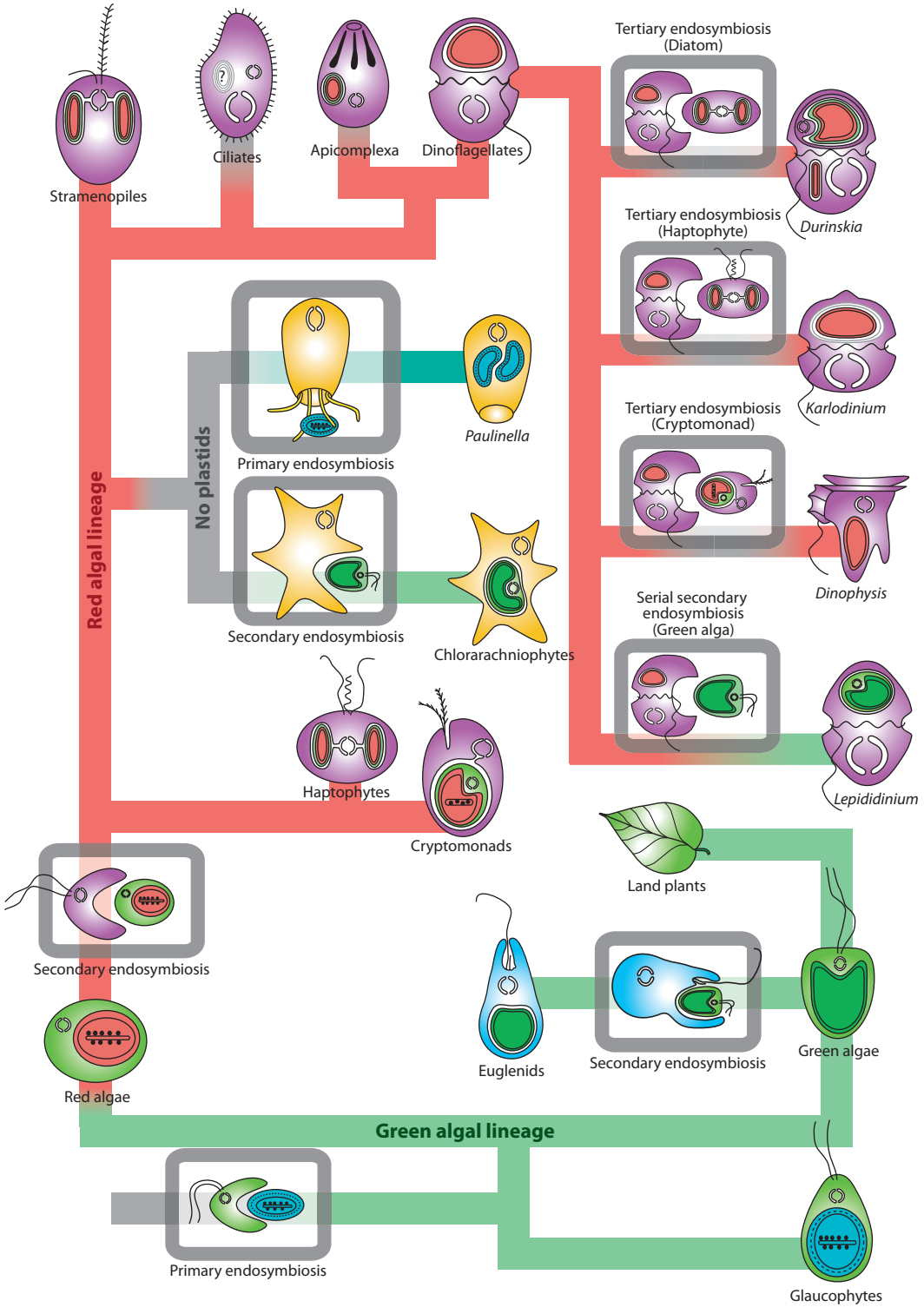
Multiple endosymbiotic events. Current thinking [summarized by Keeling (95)] (**Figure 10**) states that much of the diversity found in algae is due to secondary and tertiary endosymbiotic events, in which a photosynthetic eukaryote was incorporated into another eukaryote. A secondary symbiosis is assumed to have given rise to euglenoids (derived from a chlorophyte eukaryote) as well as to cryptomonads, haptophytes, stramenopiles, ciliates, apicomplexans, and dinoflagellates (all of which are derived from a rhodophyte).

A serial secondary endosymbiosis of green algae is thought to result in *Lepidodinum*. Tertiary endosymbiosis gave rise to *Durinskia* (incorporating a dinoflagellate-type organism), *Karlodinum* (incorporating a haptophyte-type organism), and algae belonging to the genus *Dinophysis* (incorporating a cryptophyte-type organism).

Recent endosymbiotic event. Excitement has been generated by the discovery of a more recent endosymbiotic event that gave rise to *Paulinella chromatophora* and close relatives

Figure 10

Schematic view of plastid evolution in the history of eukaryotes. The various endosymbiotic events that gave rise to the current diversity and distribution of plastids involve divergences and reticulations whose complexity has come to resemble an electronic circuit diagram. Endosymbiosis events are boxed, and the lines are colored to distinguish lineages with no plastid (*grey*), plastids from the green algal lineage (*green*), or the red algal lineage (*red*). At the bottom is the single primary endosymbiosis leading to three lineages (glaucophytes, red algae, and green algae). On the lower right, a discrete secondary endosymbiotic event within the euglenids led to their plastid. On the lower left, a red alga was taken up in the ancestor of chromalveolates. From this ancestor, haptophytes and cryptomonads (as well as their nonphotosynthetic relatives like katablepharids and telonemids) first diverged. After the divergence of the rhizarian lineage, the plastid appears to have been lost, but in two subgroups of Rhizaria, photosynthesis was regained: the chlorarachniophytes by secondary endosymbiosis with a green alga and the *Paulinella* by taking up a cyanobacterium (many other rhizarian lineages remain nonphotosynthetic). At the top left, the stramenopiles diverged from alveolates, where plastids were lost in ciliates and predominantly became nonphotosynthetic in the apicomplexan lineage. At the top right, four different events of plastid replacement are shown in dinoflagellates, involving a diatom, haptophyte, cryptomonad (three cases of tertiary endosymbiosis), and green alga (a serial secondary endosymbiosis). Most of the lineages shown have many members or relatives that are nonphotosynthetic, but these have not all been shown for the sake of clarity. Figure and caption reproduced with permission by The Royal Society from Reference 95 (figure 2).



(127). Evidence for a late endosymbiotic event that gave rise to this "chromatophore" termed cyan-colored endosymbiont is seen in how closely related they are to living *Prochlorococcus/Synechococcus* of the α-cyanobacteria clade (compared with the relatedness of plastids to the β-cyanobacterial clade) and that there are very few photosynthetic members of an otherwise nonphotosynthetic group of Cercozoan amoebae.

Photosynthesis lost. The ancestors of some human parasites that include *Plasmodium falciparum* and *Toxoplasma gondii* were once photosynthetic, indicated by the presence of a rudimentary chloroplast, the apicoplast. A missing link between these apicomplexans and their photosynthetic past has recently emerged. The alga *Chromera velia* (123) is closely related to apicomplexans but contains a fully functional chloroplast. Genetic analysis of this alga supports a direct linear descent of apicomplexans, dinoflagellates, and *Chromera velia*–related algae from a single red algal ancestor (88).

PERSPECTIVE

Genomic information is a rich resource that contains the life story of photosynthesis in a multilayer, encrypted form. To unlock this story, however, requires the context provided by complementary data from other disciplines. Genomic data can be the basis of tantalizing ideas and correlations, but experimental follow-up is required. Together, these data give us an inventory of today's living world so that we can proceed in exploring the past.

Billions of years of trial and error are contained within each organism that we have the privilege to investigate today. Looking at this diversity, we can be sure that all the failures have been weeded out and we are "face to culture flask" with the organisms that stood the test of time. We have to resist the temptation to classify features as either primitive or more advanced. Understanding the evolutionary constraints imposed on bioenergetic systems is not only an intellectual pursuit but may be a key to unlock our energy future.

SUMMARY POINTS

1. A multidisciplinary approach is revealing the main aspects of the evolution of photosynthesis.
2. Geologic evidence points to carbon fixation as having occurred very early in Earth's history.
3. Photosynthetically produced oxygen induced geological features and changed cellular physiology fundamentally.
4. Photosynthetic bacteria are the result of a complex evolution involving lateral gene transfer of photosynthetic components.
5. It is not quite certain whether the evolution of glaucophytes, rhodophytes, and chlorophytes is the result of a single endosymbiotic event.

FUTURE ISSUES

1. Was the last common ancestor photosynthetic?
2. Was the first type of RC a Q-type RC, an FeS-type RC, or a bifunctional RC?

3. Did the evolution of the RCs required for oxygenic photosynthesis take place in a single cell?
4. Are there undiscovered types of photosynthesis and photosynthetic organisms present on Earth?
5. What are the evolutionary origin and history of photosynthetic components?

DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

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