Evolution of Oxygenic Photosynthesis

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Abstract

The origin of oxygenic photosynthesis was the most important metabolic innovation in Earth history. It allowed life to generate energy and reducing power directly from sunlight and water, freeing it from the limited resources of geochemically derived reductants. This greatly increased global primary productivity and restructured ecosystems. The release of O_2 as an end product of water oxidation led to the rise of oxygen, which dramatically altered the redox state of Earth's atmosphere and oceans and permanently changed all major biogeochemical cycles. Furthermore, the biological availability of O_2 allowed for the evolution of aerobic respiration and novel biosynthetic pathways, facilitating much of the richness we associate with modern biology, including complex multicellularity. Here we critically review and synthesize information from the geological and biological records for the origin and evolution of oxygenic photosynthesis. Data from both of these archives illustrate that this metabolism first appeared in early Paleoproterozoic time and, despite its biogeochemical prominence, is a relatively late invention in the context of our planet's history.

INTRODUCTION

Chlorophyll: chlorin pigments found in all oxygenic and some anoxygenic phototrophs that absorb photons to provide the energy needed for photochemistry

Anoxygenic phototroph: a phototrophic organism that uses electron donors other than water

Oxygenic photosynthesis is an evolutionary singularity—it evolved once in the ancestors of modern Cyanobacteria. Understanding its origin and evolution is a grand-challenge problem in geobiology that requires integrating insights from multiple disparate scientific fields, including comparative biology, genomics, biochemistry, ecology, geology, geochemistry, and paleontology. Each of these approaches views the problem through a different lens, providing perspectives that have individual strengths and weaknesses. Biological studies, on the one hand, allow access to molecular diversity, illuminate mechanistic details, and enable rigorous hypothesis testing. However, they can ordinate evolutionary events only in relative time, and they are blind to extinction because they rely on extant organisms. Geology and geochemistry, on the other hand, provide an empirical historical record of phototrophic and photosynthetic processes, enabling absolute timing of key events. However, these approaches are limited by challenges associated with accurately reading ancient chemistry from sedimentary rocks and can paint metabolic and ecological processes only in broad and coarse brushstrokes. Because the geological and biological records present different perspectives of the same history, their integration should provide a consistent view. This logic frames our pedagogy here. We begin with an overview of the mechanisms and diversity of chlorophyll-based phototrophy. We then discuss insights into the origin and evolution of oxygenic photosynthesis gained from the geological and biological records, focusing on geological evidence for O_2 and the discovery of deep-branching nonphototrophic Cyanobacteria. We end by discussing an emerging testable hypothesis consistent with available data: Oxygenic photosynthesis may have evolved via an Mn-oxidizing intermediate in ancestral Cyanobacteria, near in time to the rise of oxygen.

PHOTOTROPHY'S MOLECULAR MECHANICS

Phototrophy is the process by which organisms convert the energy carried in photons into electrochemical energy useful to cells (Blankenship 2014, Overmann & Garcia-Pichel 2013). There are two types of phototrophy known: chlorophyll-based chlorophototrophy and rhodopsin-based phototrophy (Bryant & Frigaard 2006). Here we focus exclusively on chlorophototrophy because it was single-handedly responsible for the greatest environmental transition in Earth history—the rise of oxygen. In addition to generating energy from sunlight, photosynthetic organisms fix either CO_2 or bicarbonate into biomass. Anoxygenic phototrophs derive the electrons needed for energy generation from reduced inorganic and organic compounds, such as Fe^{2+}, H_2, S^0, HS^-, $S_2O_3^{2-}$, NO_2^-, AsO_3^{3-}, and various organic central metabolism intermediates. In contrast, oxygenic photosynthesis uses electrons originating from water, generating O_2 as product: $nCO_2 + H_2O + \text{light} \rightarrow (CH_2O)_n + O_2$. This reaction conceals substantial biochemical complexity. It is useful to decompose the net reaction into separate components consisting of those directly involved in photochemistry and those involved in carbon fixation, given that not all phototrophs fix inorganic carbon and, moreover, that these distinct processes have different evolutionary histories. Here we focus on the light reactions because they are the key components that perform photochemistry coupled to water oxidation. A brief discussion of the carbon fixation reactions can be found in the sidebar Carbon Fixation.

Photochemical Reactions

Phototrophy is powered by reaction centers (called photosystems in Cyanobacteria), molecular machines that transduce light energy into chemical energy. When a reaction center absorbs a photon of light, or receives an exciton of energy from neighboring light-gathering antennae, it undergoes a charge separation event (Blankenship 2014) (**Figure 1**). This allows the reaction

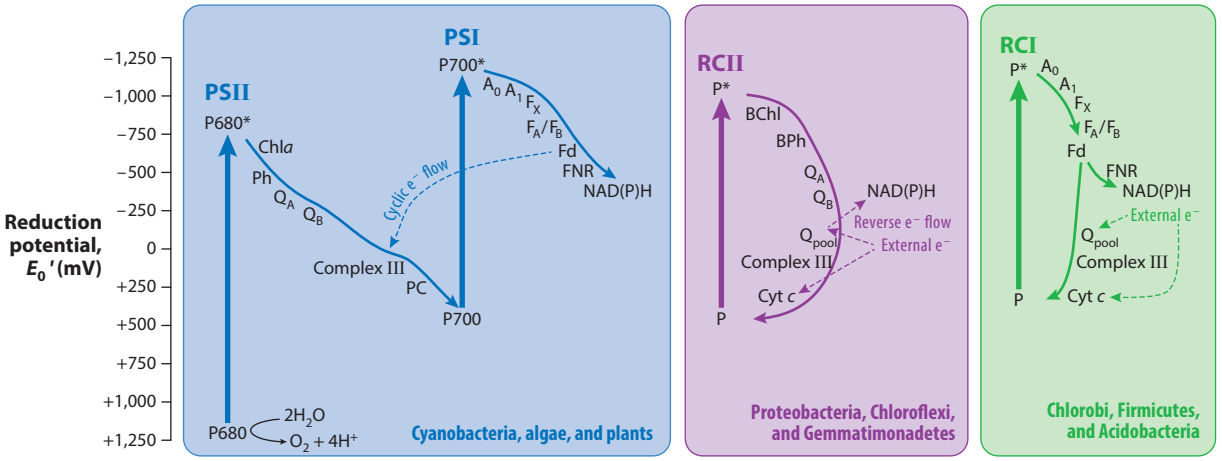
CARBON FIXATION

Cyanobacteria use the reducing power and energy derived from photochemistry to fix carbon using the Calvin-Benson-Bassham (CBB) cycle (sometimes called the reductive pentose phosphate cycle). The core carboxylation enzyme of this pathway is ribulose 1,5-bisphosphate carboxylase oxygenase—more commonly known as RuBisCO. RuBisCO is the most abundant protein on the planet (Ellis 1979) and is responsible for the largest CO_2 flux in the carbon cycle. Surprisingly, RuBisCO can also function as an oxygenase, leading to a process called photorespiration, which manifests in a counterproductive loss of CO_2 and energy. Despite this it has been hypothesized that RuBisCO has been optimized for the difficult task of distinguishing CO_2 from O_2, while still maintaining reasonable catalytic efficiency (Tcherkez et al. 2006). Photorespiration may be an inevitable consequence of operating the Calvin cycle in oxygen-producing organisms, and it likely played a role in cyanobacterial evolution (Bauwe et al. 2012). The evolutionary history of the CBB cycle is not well understood (Tabita et al. 2007). It is not unique to the phylum Cyanobacteria but is found in a number of other groups, including Proteobacteria and Actinobacteria (Grostern & Alvarez-Cohen 2013). Interestingly it is absent in currently known members of Melainabacteria, nonphototrophic close relatives of oxygenic Cyanobacteria. RuBisCO appears to have evolved from an ancient enolase involved in the microbial methionine salvage pathway (Ashida et al. 2005). But when and how this protein appeared in the ancestors of Cyanobacteria is poorly constrained. Indeed, one might ask why evolution would choose such an enzyme for a metabolism that also makes O_2. Other photoautotrophs utilize different carbon fixation pathways—for example, the reverse tricarboxylic acid cycle (rTCA) in members of the phylum Chlorobi and the 3-hydroxypropionate (3HP) bicycle of in members of Chloroflexi—that are more efficient and do not have oxygenase activity (Berg 2011). Why not use one of these for oxygenic photosynthesis? The main reason is that these pathways demand proteins and cofactors that are highly oxygen sensitive and are therefore incompatible with aerobic metabolisms like those in Cyanobacteria, though this does not appear to be true for all of them (Bar-Even et al. 2012). So it remains an open question to what degree RuBisCO and the CBB cycle in oxygenic photosynthesis reflect a historical accident versus the best tools for a difficult metabolic job.

center to simultaneously generate a lower-redox-potential electron donor (either a quinol or an iron-sulfur cluster) and a higher-redox-potential electron acceptor (P^+) in different parts of the protein. The lower-potential electron is removed from the reaction center to do useful work, such as energy conservation or carbon fixation. The hole at P^+ is then filled by an electron, returning the reaction center to the ground state and completing the reaction cycle.

The reaction centers are classified by their terminal electron acceptors into two types: type 1 reaction centers [reaction center I (RCI) and photosystem I (PSI)] and type 2 reaction centers [reaction center II (RCII) and photosystem II (PSII)] (Blankenship 2014). RCIs reduce ferredoxin as the terminal electron acceptor, whereas RCIIs reduce quinones. All anoxygenic phototrophs use one reaction center for phototrophy, either RCI or RCII (**Figure 1**). To conserve energy they use a complex III to generate a proton motive force from the low-potential electrons produced by the reaction center. There are two known types of complex III: cytochrome *bc* complexes (Kramer et al. 2008) and alternative complex III (ACIII) (Refojo et al. 2013). These unrelated proteins perform the same function—the transfer of electrons from a membrane-bound two-electron carrier (quinol) to a soluble one-electron carrier protein (cytochrome *c*, cupredoxin, or iron-sulfur protein). The cytochrome *bc* complexes perform electron bifurcation (known as the Q cycle), which maximizes energy conservation ($2H^+$ per e^- transferred). The ACIIIs were recently discovered, and little is known about their energy conservation (Yanyushin et al. 2005). Anoxygenic phototrophs predominately perform cyclic electron transfer (Blankenship 2014), in which electrons excited by the

Proton motive force: the potential energy stored in the electrochemical proton gradient across an energized biological membrane



Cyanobacteria and chloroplasts
Q = PQ
Complex III = Cyt b_6f
A_0 = Chl*a*
A_1 = phyloquinone

Proteobacteria
P870/P870* = BChl*a*
Q = MQ/UQ
Complex III = Cyt bc_1

Chloroflexi
P865/P865* = BChl*a*
Q = MQ
Complex III = ACIII
Cyt *c* = auracyanin

Gemmatimonadetes
P/P* = BChl*a*
Q = MQ
Complex III = ACIII, Cyt bc_1

Chlorobi
P840/P840* = BChl*a*
A_0 = Chl*a*
A_1 = MQ
Q = MQ
Complex III = Cyt bc_1

Firmicutes
P800/P800* = BChl*g*
A_0 = Chl*a*–OH
A_1 = MQ
Q = MQ
Complex III = Cyt bc_1

Acidobacteria
P840/P840* = BChl*a*
A_0 = Chl*a*
A_1 = MQ
Q = MQ
Complex III = ACIII, Cyt bc_1

ACIII Alternative complex III
(B)Chl (Bacterio)chlorophyll
Cyt Cytochrome
Fd Ferredoxin
FNR Ferredoxin–$NADP^+$ reductase
F_A/F_B $2Fe_4$-S_4
F_X Fe_4-S_4
MQ Menaquinone
P Chlorophyll special pair
PC Plastocyanin
Ph Pheophytin
PQ Plastoquinone
Q Quinone
UQ Ubiquinone

Figure 1

Comparative energetics of oxygenic and anoxygenic phototrophy. Note the reversed scale. Large negative values indicate strong reductants, whereas large positive values indicate strong oxidants. Arrows illustrate the photoexcitation of electrons by the different reaction centers, and the lengths of the arrows reflect the energies of the excitons. Key novel evolutionary attributes that distinguish this oxygenic photosynthesis from anoxygenic phototrophy are the two photosystems coupled in series, the high-potential photooxidants produced by photosystem II (PSII) and the water-oxidizing complex of PSII that enables the splitting of water. All reaction centers oxidize small single-electron-carrier proteins like cytochrome *c*, except PSII, which directly oxidizes Mn^{2+} and water. Thus reaction center I (RCI), reaction center II (RCII), and photosystem I (PSI) produce oxidants that are <500 mV and would be unable to oxidize high-potential electron donors such as H_2O and Mn^{2+}. The highest-potential electron donor for extant anoxygenic phototrophs is nitrite (430 mV).

reaction center run through a complex III (conserving energy) and return to the reaction center via a soluble protein carrier to reduce the oxidized P^+ (**Figure 1**). If there were no loss of electrons during this process, anoxygenic phototrophs could cycle their electrons indefinitely. However, some of the electrons are funneled into other cellular processes in noncyclic flow (such as carbon fixation in photoautotrophs) and must be replaced by external electron donors. As mentioned above, a wide variety of compounds can be used as electron donors for anoxygenic phototrophy. Depending on which substrate is used, electrons can enter the electron transport chain at the level of either quinones or protein carrier pools. In this regard, anoxygenic photosynthesis has plug-and-play logic: If there exists a biochemical means of getting electrons from an external donor into either

of these pools, then chances are an organism in nature has figured out how to use it as an electron donor for photosynthesis. For photoautotrophic growth fixing CO_2, organisms with an RCI can readily generate NADH with electrons from ferredoxin. However, those with an RCII need to use reverse electron transfer, consuming energy from the proton motive force, to generate NADH.

Reverse electron transfer: uses the proton motive force to drive electron transfer reactions in energetically unfavorable directions

Oxygenic photosynthesis in Cyanobacteria is substantially more complex. They have assembled both types of reaction centers (PSI and PSII) together in series, allowing them to span the energy difference from water to ferredoxin, while conserving substantial energy along the way (**Figure 1**). The path that electrons take during oxygenic photosynthesis is outlined in **Figure 2**. Starting at PSII when chlorophyll P680 is excited, an electron is rapidly transferred to plastoquinone Q_B. This process generates $P680^+$, the most oxidizing chemical species in all of biology (with a redox potential of >1,250 mV) (Rappaport & Diner 2008) (**Figure 1**). The electron hole at $P680^+$ is filled by an electron from a nearby redox-active tyrosine (Y_Z), which in turn is reduced by an electron from the water-oxidizing complex, a tetramanganese-bearing bioinorganic cluster that is able to harvest electrons from water (more on this below). After another photocycle, fully reduced plastoquinol Q_B is released into the membrane, where it is funneled through complex III to plastocyanin, conserving energy. Next, the electron flows to PSI (to chlorophyll $P700^+$), where it replaces the electron removed by a photon-driven charge separation event similar to the one that occurs in PSII. In PSI the electrons are transferred to an iron-sulfur cluster, where

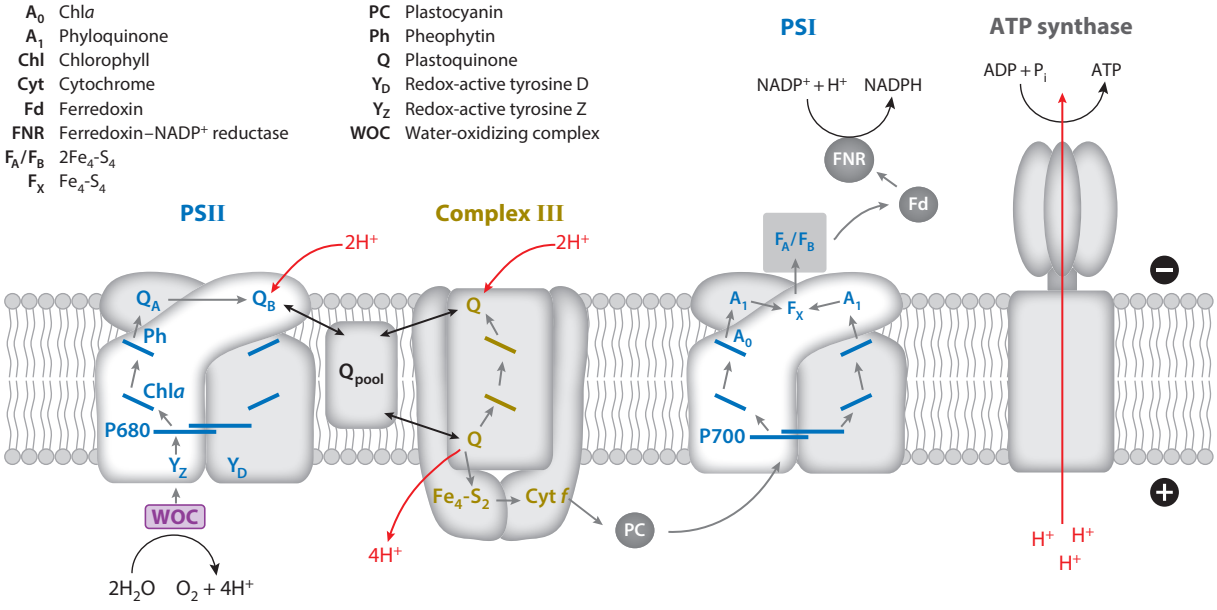


Figure 2

Membrane cross section showing electron transport and energy conservation of oxygenic photosynthesis. Gray arrows mark the path of electron flow. Red arrows show proton translocation. The electrons derived from water flow through photosystem II (PSII) and into the membrane-soluble quinol pool. From there they flow into complex III (in Cyanobacteria this is cytochrome b_6f) and participate in the Q cycle—a series of oxidation-reduction reactions that shuttle extra protons across the membrane. Electrons then travel from complex III to plastocyanin (a small soluble single-electron carrier) and are delivered to photosystem I (PSI), where they arrive at ferredoxin. Ferredoxin–$NADP^+$ reductase places them subsequently onto NADPH, which can then be used for carbon fixation, biosynthesis, and aerobic respiration (not shown). Both protons from water splitting and protons translocated across the membrane during electron transport flow back through ATP synthase, generating ATP.

they are donated to a ferredoxin protein, and ultimately to $NAD(P)^+$ for use in carbon fixation (**Figures 1** and **2**).

The Water-Oxidizing Complex

All reaction centers do single-electron photooxidation reactions, but PSII in Cyanobacteria, algae, and plants is unique because it is capable of the four-electron chemistry required for water oxidation: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$. The photochemistry of reaction centers is fundamentally a single-electron process. Consequently, the most basic aspect to understanding the origin of oxygenic photosynthesis was solving the evolutionary problem of how to adapt a molecular machine that does single-electron chemistry for a task that requires it do four. An elegant solution is provided by the water-oxidizing complex (WOC) of PSII—the sole water oxidation catalyst in biology.

The WOC is a bioinorganic, high-valent tetramanganese cluster bound to the business end of PSII, comprising an Mn_3CaO_4 distorted cubane structure bound to a fourth Mn by oxo-bridges (McEvoy & Brudvig 2006, Yano & Yachandra 2014). The WOC serves as a redox capacitor that links the native single-electron photochemistry of the reaction center to accomplish the oxidation of two water molecules to produce O_2 through four successive photooxidation reactions of PSII (referred to as the S cycle) (**Figure 3**).

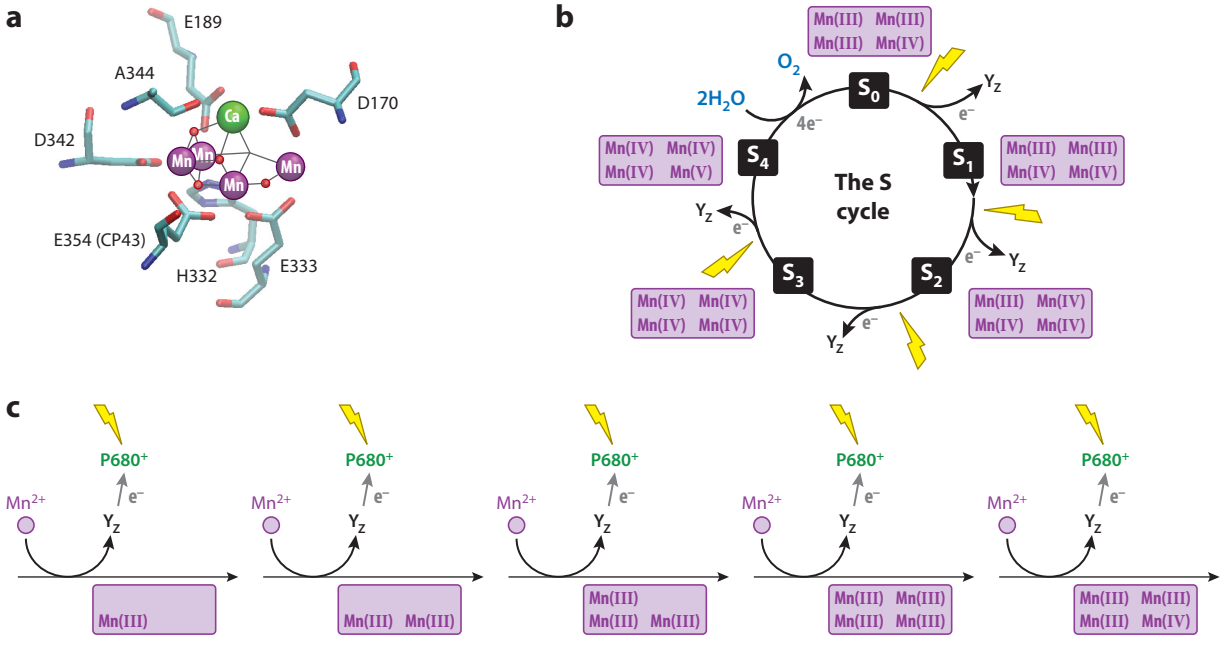


Figure 3

(*a*) The structure of the water-oxidizing complex (WOC) of photosystem II (PSII) (Umena et al. 2011). Ligands provided by the protein complex are shown; note the role of CP43. (*b*) The S cycle of the WOC enables PSII to oxidize two waters and form O_2 through four successive reaction photocycles. (*c*) Photoassembly of the WOC demands just Mn^{2+} and light, with the ligands to stabilize the cluster provided by the protein complex. This biochemistry illustrates that water oxidation begins with manganese oxidation and powers the hypothesis that Mn(II) once played a key role as an electron donor for anoxygenic photosynthesis prior to the evolution of oxygenic photosynthesis.

How did the WOC arise? It was recognized long ago that during the evolution of PSII, transitional states must have existed that exhibited physiologically useful catalysis but did not split water (Olson 1970). Several ideas have looked elsewhere in biology for different Mn-bearing proteins that might have been integrated and adapted to form the WOC. For example, it was proposed that a binuclear Mn-catalase domain that received electrons from a peroxide donor might have been an intermediate step in the evolution of PSII (Blankenship & Hartman 1998). However, additional sequence and structural data have not supported this idea (Cardona 2015). Though exaptation is a common mode of innovation in biology, comparison with the known protein world illustrates that the WOC evolved ex nihilo (Fischer et al. 2015).

Important insights into WOC evolution can be gleaned from the photoassembly process of how it is made (Fischer et al. 2015). Photoassembly of the WOC requires only Mn^{2+} and light to form the high-valent WOC (Tamura & Cheniae 1987). Over the course of five photocycles, five electrons are donated from four Mn(II) atoms to produce the basal S_0 oxidation state of the WOC, which with subsequent photocycles begins to evolve O_2 (**Figure 3**). Thus all biological water splitting begins with manganese oxidation, with those electrons derived from Mn indistinguishable from those later derived from water. This also provides a powerful and attractive class of evolutionary hypotheses for the origin of the WOC, wherein Mn(II) played a role as an electron donor for phototrophy prior to oxygenic photosynthesis (Allen & Martin 2007; Cardona et al. 2015; Dismukes et al. 2001; Fischer et al. 2015; Johnson et al. 2013a,b; Zubay 2000).

GEOLOGICAL EVIDENCE FOR THE EVOLUTION OF OXYGENIC PHOTOSYNTHESIS

Phototrophy is extremely old; consequently, it is remarkable that we can derive inferences about its evolutionary history from observations of the geological record (**Figure 4**). The primary challenge in interpreting this record is determining how information related to ancient biology is captured and stored in sedimentary rocks. These inferences are often subtle and indirect, and need to be critically assessed. For metabolic innovations that occurred early in Earth history, the difficulties increase primarily because the quality of the sedimentary record degrades as a function of time due to tectonics and crustal recycling. With older and older rocks, postdepositional processes such as metasomatism and/or metamorphism can significantly alter, or even erase, the archive recorded in these ancient rocks. That said, there are a number of invaluable constraints on the evolution of oxygenic photosynthesis that can be gleaned from signals captured in very ancient sedimentary rocks.

The Archean Sedimentary Record

A range of observations from the Archean (>2.5 Ga) sedimentary record support the hypothesis that anoxygenic phototrophy evolved early in Earth history. The earliest good evidence for phototrophy is found in the 3.416 Ga Buck Reef Chert from the Barberton Greenstone Belt, South Africa. Tice & Lowe (2004, 2006) observed water depth–dependent production of organic matter in the silicified remains of benthic microbial mats. Because the depth of intact mats was restricted to the photic zone, this observation suggests that the mats were largely composed of phototrophic and/or photosynthetic microbes. Furthermore, based on the local absence of ferric iron minerals (despite the presence of Fe^{2+} in the water column), it was argued that these phototrophs were anoxygenic and used H_2 as an electron donor for carbon fixation—though from this data alone, it is difficult to completely rule out other electron donors, such as soluble organic molecules and a range of sulfur species. Similar logic has been applied to Archean and early Paleoproterozoic iron formations, where the discovery of extant photoferrotrophy (Widdel et al. 1993) gave a substantial boost to the idea that early iron oxidation was catalyzed by anoxygenic photosynthesis prior to

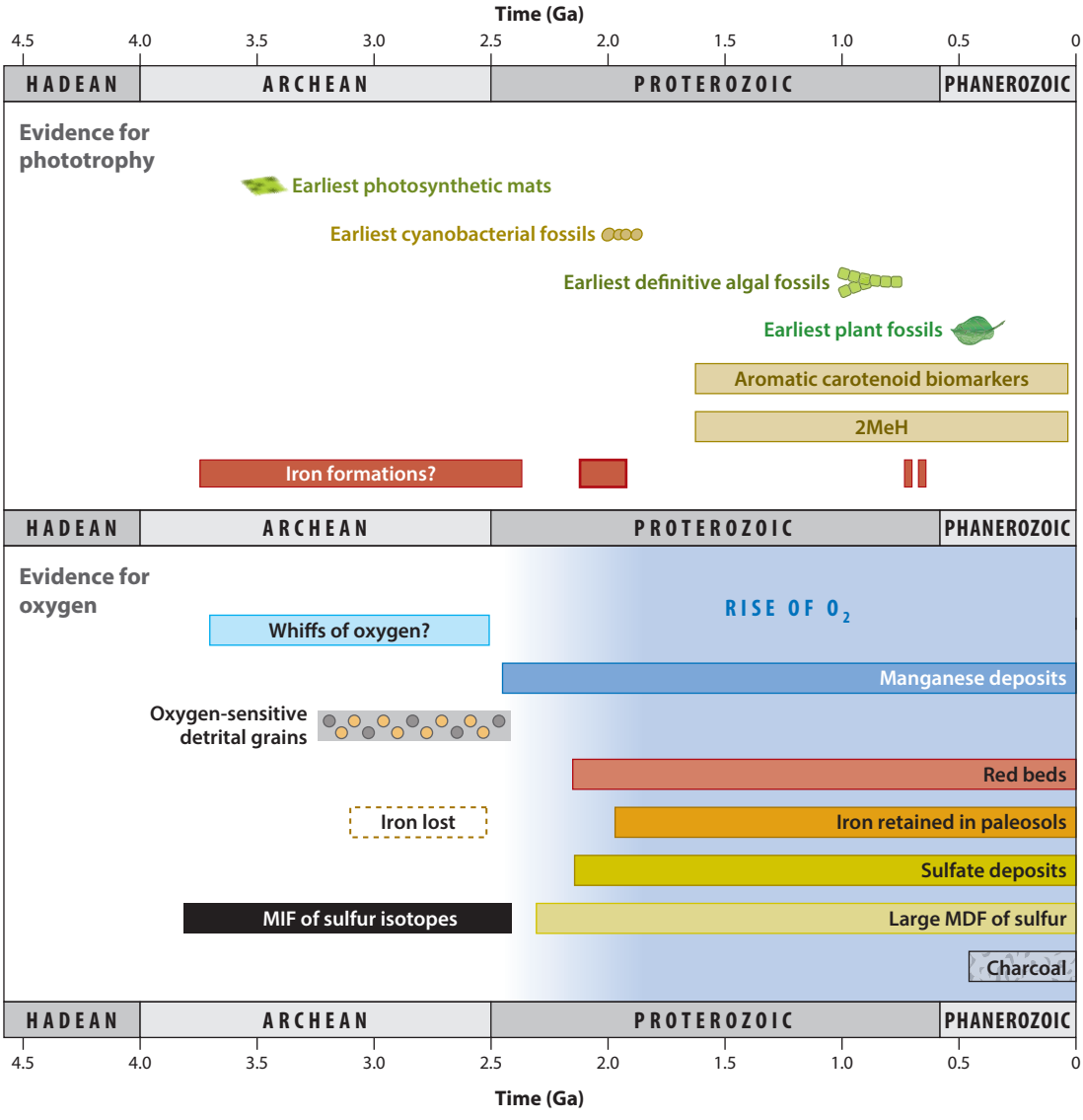


Figure 4

Geological constraints on the evolution of phototrophy and Cyanobacteria including data from the body and molecular fossil (lipid biomarker) records, and constraints on the rise of oxygen from a variety of sedimentological and geochemical observations. Although anoxygenic photosynthetic mats appear to be quite ancient, the oldest direct fossil evidence for Cyanobacteria consists of microfossils in carbonate strata at ~1.9 Ga. The rise of oxygen—marked in part by the loss of redox-sensitive detrital grains and mass-independent fractionation of sulfur isotopes and the appearance of red beds, hematite-bearing paleosols, and sulfate deposits—provides a minimum age for the evolution of oxygenic photosynthesis at ~2.35 Ga. Note also that the Mn deposits do not appear until just before the rise of oxygen. This pattern supports the hypothesis that Mn(II) was a substrate for phototrophy prior to the evolution of oxygenic photosynthesis. Abbreviations: MDF, mass-dependent fractionation; MIF, mass-independent fractionation.

the rise of oxygen (Bekker et al. 2010, Fischer & Knoll 2009, Garrels et al. 1973, Hartman 1984, Kappler et al. 2005, Walker 1987). Iron is the most abundant source of electrons available on our planet (Walker & Brimblecombe 1985) and may have fueled the biosphere prior to the rise of oxygen (Fischer & Knoll 2009, Walker 1987). Photoferrotrophy has also been extended to explain Fe isotope ratio data from the iron formations (albeit highly metamorphosed) from the 3.7–3.8 Ga Isua Supracrustal Belt, Greenland (Czaja et al. 2013). All of these Archean observations can be reasonably explained by the presence of phototrophs that used single reactions centers and electrons from ferrous iron, H_2, organic compounds, and possibly other inorganic electron donors.

What is the earliest geological evidence for the presence of Cyanobacteria? Observations of stromatolites, carbon isotope ratios, and microfossils in some of the oldest sedimentary rocks were initially proposed to be evidence for Cyanobacteria (**Figure 4**). However, it is now recognized that these are not diagnostic for Cyanobacteria (Knoll 2003, Schopf 2006). Early stromatolites have strong crystal precipitation modes of growth (Allwood et al. 2009, Grotzinger & Knoll 1999), and the role of phototrophic biology in the origin of stromatolites still endures as an unanswered question in geobiology (Bosak et al. 2013, Shepard & Sumner 2010), making stromatolites equivocal records at best for Cyanobacteria. Carbon isotope ratios can diagnose only carboxylation metabolisms, and RuBisCO (the key enzyme that imparts a large kinetic isotope effect into the Calvin cycle; see the sidebar Carbon Fixation) is shared among a diverse suite of organisms including many that are not phototrophic (Tabita et al. 2007). Finally, interpretation of early putative microfossil structures from some of the earliest sedimentary rocks (Schopf & Packer 1987) has been controversial, and the continuing debate is not whether these structures represent Cyanobacteria, but rather whether they are the remains of microorganisms (Brasier et al. 2002, 2005; Knoll 2003; Marshall et al. 2011).

The oldest body fossils reasonably interpreted as Cyanobacteria are from ~1.9 Ga strata in the Belcher Islands, Canada (Hofmann 1976) (**Figure 4**). Yet oxygenic photosynthesis must be older than this, because it is thought to be responsible for the O_2 fluxes during the rise of oxygen around 2.35 Ga (Bekker et al. 2004, Rasmussen et al. 2013). A large part of this discordance is due to the general lack of a robust Archean fossil record, coupled with classic paleontological challenges made acute by the limits of fossilization, the scarcity of characters diagnostic for microorganisms (Knoll & Golubic 1992), and the identification and interpretation of stem-group organisms (Marshall & Valentine 2010).

Without a good body fossil record, early efforts to study the Archean molecular fossil record were met with great enthusiasm. The detection of 2α-methylhopane biomarkers in samples throughout the Late Archean sedimentary record (2.7 to 2.5 Ga) suggested that Cyanobacteria were ecologically and environmentally widespread long before the rise of oxygen (Brocks et al. 1999, Eigenbrode et al. 2008, Summons et al. 1999, Waldbauer et al. 2009). But the syngeneity of these hydrocarbons has since been called into question (Brocks 2011, Rasmussen et al. 2008), and recently it was demonstrated that these molecules were sourced from younger contaminants (French et al. 2015). Independently, genomic and environmental data have shown that the precursor lipids to 2α-methylhopane (2β-methylhopanoids) are not specific to Cyanobacteria, but are produced by several other bacterial groups (Alphaproteobacteria, Acidobacteria, and possibly others). Therefore they are not diagnostic for phototrophic Cyanobacteria (Doughty et al. 2009, Ricci et al. 2013, Welander et al. 2010), and may have actually evolved after the rise of oxygen (Ricci et al. 2015). The major challenges with all lipid biomarker studies arise due to the thermal maturity of the sedimentary organic matter and the biological specificity of the lipid structures. This is particularly problematic in the Archean record because the rocks are more altered, and the added evolutionary time makes it harder to interpret molecular fossils with confidence (Brocks & Summons 2004, Fischer & Pearson 2007). Black shales of the 1.64 Ga Barney Creek Formation in

the McArthur Basin of northern Australia currently contain the oldest syngenetic lipid biomarkers (Brocks et al. 2005, Brocks & Schaeffer 2008). This assemblage contains 2α-methylhopanes but is particularly notable for its high relative abundance of aromatic carotenoids (e.g., isorenieratane, okenane, chlorobactane)—geological derivatives of pigments commonly associated with phototrophic members of the phyla Proteobacteria and Chlorobi (**Figure 4**).

It is important to note that the absence of an Archean cyanobacterial record is not due to the lack of effort. The Archean sedimentary record contains the lithologies and paleoenvironments, such as chert nodules and shallow-water carbonate platforms, that in Proterozoic strata readily yield fossil cyanobacteria (Green et al. 1987, Hofmann 1976, Knoll & Golubic 1992, Schopf 1968, Zhang & Golubic 1987). Chert—a lithology favored by paleontologists for cellular permineralization—is famously abundant in the Archean strata (Buick 1990, Stefurak et al. 2014), and authigenic carbonate cements were widespread across a range of paleoenvironments on Archean carbonate platforms (Grotzinger 1989, Sumner & Grotzinger 2004). In addition, compared to other microbes, some Cyanobacteria have a reasonably good fossil record due to their typically large sizes, durable construction (sheaths), and biomineralization (Golubic & Seong-Joo 1999, Riding 1982). Despite all of these factors that should support an earlier microfossil record, cyanobacterial microfossils do not appear until Proterozoic time. It is possible that in Archean basins these authigenic lithologies had subtly different environmental conditions that were somehow unsuited to cyanobacterial fossilization (Fischer & Knoll 2009), but a simpler explanation is that photosynthetic Cyanobacteria were not present in Archean shallow water environments (Brasier et al. 2002, 2005). Unfortunately, at this time the body and molecular fossil records do not provide much detailed insight into the origins of Cyanobacteria.

Molecular Oxygen as a Proxy for Cyanobacteria

How can we evaluate the evolutionary origins of oxygenic photosynthetic Cyanobacteria in the absence of a robust early fossil record? An alternative approach to the problem relies on finding geochemical evidence for the product of their unique metabolism: oxygen (Farquhar et al. 2011, Lyons et al. 2014).

A wide range of geological observations provide strong evidence for the rise of oxygen during early Paleoproterozoic time (**Figure 4**). Redox-sensitive detrital grains, the distribution of sedimentary iron formations, fluvial and nearshore marine red beds, the behavior of iron in paleosols (ancient soil horizons), and gypsum (calcium sulfate salt) deposits all show secular trends that illustrate a first-order and irreversible oxygenation of Earth surface environments early in the Paleoproterozoic (Beukes et al. 2002; Cameron 1982; Cloud 1968; Fischer & Knoll 2009; Frimmel 2005; Grandstaff 1980; Holland 1984; Prasad & Roscoe 1996; Pufahl & Hiatt 2012; Roscoe 1969, 1973; Rye & Holland 1998; El Tabakh et al. 1999; Utsunomiya et al. 2003). Many of these observations were originally made by geologists decades ago, but they are just as important and useful today. These records are powerful because they capture major changes in mass fluxes of abundant redox-active elements such as iron and sulfur, and we have a good understanding of their mechanics. For example, by the 1950s it was already recognized that early Precambrian sandstones and conglomerates were distinct from younger rocks because they contained common redox-sensitive detrital grains, such as pyrite, uraninite, and siderite. These minerals rapidly decompose in the presence of oxygen (Grandstaff 1976, Williamson & Rimstidt 1994), implying that weathering and sediment transport took place in environments that contained much less O_2 in the distant past (Grandstaff 1980, Holland 1984, Liebenberg 1955, Prasad & Roscoe 1996, Ramdohr 1958, Rasmussen & Buick 1999). This presents a simple and straightforward O_2 proxy because these textures are easy to observe using light and electron microscopy and can be used

to place quantitative constraints on environmental O_2 levels given an understanding of sediment provenance and transport processes; recent studies show that redox-sensitive detrital grains can be sensitive to very small amounts of O_2 (10^{-5} atm), constraining the rise of oxygen to after ~2.4 Ga (Johnson et al. 2014).

Recently, more subtle and sophisticated geochemical proxies have joined in the search for molecular oxygen. The most important of these was the discovery of mass-independent fractionation (MIF) of multiple sulfur isotopes in Archean and early Paleoproterozoic rocks (Farquhar et al. 2000). Rocks older than 2.35 Ga contain large deviations from expected mass fractionation laws, but all younger rocks do not (Farquhar & Wing 2003). The origin of this unique isotopic signal is thought to arise from atmospheric photochemistry involving SO_2 (Farquhar et al. 2000). Although the mechanics of the process and subsequent cycling are not well understood (Paris et al. 2014, Ueno et al. 2009, Whitehill et al. 2013), it can be rationalized why this proxy is very sensitive to environmental oxygen—this relates to the strongly oxidizing nature of the atmosphere with even a little oxygen (~1 ppm, Pavlov & Kasting 2002) and abbreviation of the sulfur cycle when O_2 is scarce (Halevy 2013, Zahnle et al. 2006). Importantly, multiple sulfur isotope studies from a range of sedimentary basins globally showed that MIF yields the same secular trends as the geological observations described above. In addition, because MIF evaluates signals preserved in a common mineral, pyrite, this proxy can be applied to nearly every marine rock, though pyrite in these old rocks tends to have a complex history of mineralization (Fischer et al. 2014). This enables the detection of stratigraphic trends with sufficient resolution to help tighten constraints on the timing for the rise of oxygen (Guo et al. 2009). Although the timing of this MIF transition still remains somewhat uncertain due to incompleteness of the stratigraphic record and limited high-quality geochronology, the current constraints place the rise of oxygen—and thus significant phototrophic O_2 fluxes—somewhere between 2.4 and 2.35 Ga (Bekker et al. 2004; Guo et al. 2009; Hoffman 2013; Johnson et al. 2013a, 2014; Papineau et al. 2007; Rasmussen et al. 2013).

Oxygenic photosynthesis in Cyanobacteria is widely considered to be responsible for the rise of oxygen, which formally places a firm constraint on the minimum age of oxygenic photosynthesis (and thus stem-group photosynthetic Cyanobacteria). Indeed the rise of oxygen can be easily explained if it records the proximal origin of oxygenic photosynthesis between 2.4 and 2.35 Ga (Fischer 2008). This is consistent with the body and molecular fossil records described above. Such a scenario is also consistent with recent constraints from comparative biology (developed below): that oxygenic photosynthesis is a derived feature of the Cyanobacteria phylum, and that coupled photosystems evolved relatively late in Earth history, long after the evolution of anoxygenic phototrophy.

However, a substantial and important debate exists over whether the rise of oxygen stems directly from the evolution of Cyanobacteria at ~2.35 Ga (e.g., Kopp et al. 2005, Ward et al. 2015b) or whether instead oxygenic Cyanobacteria originated several hundred million to more than a billion years earlier in Earth history (Lyons et al. 2014). The latter notion is fueled by observations of redox-sensitive trace elements such as Mo, Re, Cr, and U in some Archean samples, which suggest that the history of O_2 on the early Earth was not so straightforward (Lyons et al. 2014). These developing geochemical redox proxies have been interpreted to reflect spatially, or temporally, local to regional pulses of photosynthetically derived O_2 that cycled as a trace gas in the environment—leading to the apt term whiffs of oxygen (Anbar et al. 2007) (**Figure 4**). Recent studies have interpreted oxygenation based on strata dating to nearly 3 Ga (Crowe et al. 2013, Planavsky et al. 2014), but arguments for oxygenic photosynthesis on the basis of trace element data have been made for some of the oldest (meta)sedimentary rocks on Earth, older than 3.7 Ga (Rosing & Frei 2004). These interpretations remain controversial because the geochemical cycles of these elements are not well understood over a range of timescales including the modern (e.g.,

Helz et al. 2011, Morford et al. 2012, Nägler et al. 2011), and they appear in conflict with other redox proxies (like MIF, paleosols, and redox-sensitive detrital grains) in the same basin and in some cases the same lithologies (Frimmel 2005, Grandstaff 1980, Guy et al. 2012, Papineau & Mojzsis 2006). Furthermore, we do not have a strong understanding of the mineral phases that control these trace element distributions within rocks (e.g., Dahl et al. 2013, Havig et al. 2015, Helz et al. 2011, Morford et al. 2012), or how they were affected by the various postdepositional metamorphic and metasomatic processes common to all Archean sedimentary basins (Fischer et al. 2014, Pufahl & Hiatt 2012). Despite these open questions, use of these trace element proxies is a rapidly growing pursuit in geochemistry, and understanding their mechanics in modern and ancient environments is an important avenue of ongoing research.

Oxygenic phototroph: a phototrophic organism that uses water as an electron donor for photosynthesis, producing dioxygen as a product

Using the presence of O_2 (perhaps in trace amounts) as a proxy for oxygenic Cyanobacteria has been a fruitful approach for the field. However, this approach is a double-edged sword, because it demands that we labor under the implicit assumption that there were no meaningful nonphototrophic sources of oxygen on the early Earth. Indeed a few independent biotic sources of oxygen have been described: nitric oxide dismutation (Ettwig et al. 2010), peroxide decomposition by catalase (Loew 1900), and chlorite dismutation (Coates & Achenbach 2004). Abiotic sources are also possible: atmospheric photochemistry of O-bearing species (Haqq-Misra et al. 2011, Lu et al. 2014) and photochemistry of water ice (Liang et al. 2006) and solid mineral phases (Borda et al. 2001). Our knowledge of the evolutionary history of these metabolisms and the relative importance of these processes on the Archean Earth remains limited. Consequently, using O_2 as a proxy for oxygenic photosynthesis remains an imperfect approach because it opens the door for false-positive detections, particularly at trace concentrations (see the sidebar Oxygen on Mars). What concentrations and fluxes characterize these nonphototrophic processes? How much O_2 is required to robustly indicate the presence of oxygenic phototrophy? These important questions remain unanswered.

OXYGEN ON MARS

The sedimentary record of Mars provides a natural framework for comparison with the early Earth. From a range of geological and geochemical observations by independent orbiter and rover missions it is clear that Mars surface environments were warmer, wetter, and more oxidizing in the past (Bibring et al. 2006, Christensen et al. 2001, DiBiase et al. 2013, Grotzinger 2014, Grotzinger et al. 2015, Hecht et al. 2009, Hurowitz et al. 2010, Leshin et al. 2013, McLennan et al. 2005). Mass anomalies in the O isotopic composition of authigenic carbonate cements from Mars that are nearly four billion years old support the hypothesis that Mars's ancient atmosphere was notably oxygenated (Farquhar et al. 1998, Halevy et al. 2011, Shaheen et al. 2015). The habitable paleoenvironments discovered by investigation of the sedimentary rocks exposed at the base of Mt. Sharp in Gale Crater (Grotzinger 2014, Grotzinger et al. 2015) contained Mn- and oxychlorine-rich phases that document the importance of an early O_2 cycle. From the perspective of comparative planetology, these observations contrast strongly with the early Earth, which did not develop manganese enrichments until after the rise of oxygen (Johnson et al. 2013a, Kirschvink et al. 2000)—though an important exception to this is described in the main text. It is likely that these martian strata record fluxes of O_2 (and other oxidants created from O_2) sourced from photochemical processes (Lu et al. 2014, Zahnle et al. 2008). These deposits would pass naive tests for the presence of oxygenic phototrophy, and therefore Cyanobacteria, if they were from Earth. Although it is incorrect to infer that oxygenic phototrophy was present on early Mars, comparison of the geological records of these terrestrial neighbors sharpens the challenges that come along with using O_2 as a biomarker for oxygenic phototrophy not just on Earth, but on terrestrial planets more broadly.

In summary, the geological record supports the following conclusions related to the evolution of oxygenic photosynthesis (**Figure 4**): (*a*) Anoxygenic phototrophy is an old process that was present on the Archean Earth, (*b*) the oldest direct evidence for Cyanobacteria is 1.9 Ga microfossils, and (*c*) the oldest certain evidence for O_2 produced by Cyanobacteria is the rise of oxygen at ~2.35 Ga.

Lateral gene transfer: transmission of genetic material in a nonvertically inherited manner (i.e., not through progeny); also known as horizontal gene transfer

EVOLUTIONARY INSIGHTS FROM COMPARATIVE BIOLOGY

While the geological record provides temporal constraints on the evolution of oxygenic photosynthesis, recent advances in comparative biology—driven in large part by genome sequencing—are starting to shed light on the molecular details.

There are three classes of evolutionary hypotheses to explain the distribution of phototrophy and the origin of two photosystems in Cyanobacteria: the selective loss model, the Cyanobacteria origin model, and the fusion model. In the selective loss model, an ancestral phototroph evolved that contained both type I and type II reaction centers (Cardona 2015, Hohmann-Marriott & Blankenship 2011). All other phototrophs are proposed to have evolved from this ancestor, with anoxygenic phototrophs selectively losing one or the other of the reaction centers, while Cyanobacteria retained both. This model implies that phototrophy is (largely) vertically inherited, and that nonphototrophs that evolved from the common phototrophic ancestor lost both reaction centers. The Cyanobacteria origin model proposes that ancestral Cyanobacteria invented phototrophy and that the ancestral reaction center diverged into type I and type II reaction centers within this clade (Mulkidjanian et al. 2006, Sousa et al. 2013). Later, other clades acquired either an RCI or RCII via lateral gene transfer. Because there is evidence for phototrophy in early Archean time, this model predicts that phototrophic Cyanobacteria are exceptionally old. The fusion model proposes that after the origin of reaction centers they evolved independently in different lineages, and that ancestral Cyanobacteria then acquired one or both reaction centers via lateral gene transfer (Hohmann-Marriott & Blankenship 2011). In some versions of this model, Cyanobacteria evolved from phototrophic ancestors and acquired a second reaction center; in others, Cyanobacteria evolved from nonphototrophic ancestors by acquiring both reaction centers.

The molecular record provides a way to test these hypotheses. We first describe the evolutionary relationships between the different phototrophic clades, with attention given to the role of lateral gene transfer in the extant distribution of phototrophy. Next we discuss what the shared biochemical components of phototrophy can tell us about its evolution. We end by synthesizing a testable hypothesis that describes the emergence of Cyanobacteria from anoxygenic phototrophic ancestors—drawing on the key role that manganese played in this history.

Diversity of Extant Phototrophs

Organisms capable of oxygenic photosynthesis evolved from anoxygenic ancestors. In addition to Cyanobacteria there are currently six known bacterial phyla that contain phototrophic members: Proteobacteria, Chloroflexi, Chlorobi, Firmicutes, Acidobacteria, and Gemmatimonadetes. We provide a brief overview of each of these clades, focusing on the distribution of phototrophy within them and the specific molecular components they use for phototrophic electron transfer (**Figure 1**). Then, by mapping these properties onto the tree of life, we can glean useful insights into the evolution of phototrophy.

The phylum Proteobacteria (Madigan & Jung 2008), commonly delineated into the classes Alpha-, Beta-, and Gammaproteobacteria, comprises an extremely diverse group of microbes that are prevalent in many environments on modern Earth, with various members performing a broad range of fermentation reactions in addition to aerobic and anaerobic respiration and anoxygenic

Bacteriochlorophyll: chlorin pigments in anoxygenic phototrophs that absorb photons to provide the energy for photochemistry

phototrophy. Phototrophy is sparsely distributed throughout the phylum, and it is common for strains closely related to phototrophs to be nonphototrophic. All known phototrophic members utilize an electron transfer chain consisting of an RCII, bacteriochlorophyll *a* or *b*, and a cytochrome bc_1 complex. Most use high-potential ubiquinone (100 mV) as a membrane-soluble electron shuttle; however, one strain has been described that can utilize low-potential menaquinones (−75 mV) (Schoepp-Cothenet et al. 2009). The photoautotrophic members use the RuBisCO-based Calvin-Benson-Bassham pathway for carbon fixation. Genes for phototrophy, excluding those encoding complex III, are found colocalized into photosynthetic gene clusters (PGC). The PGC genes are not evolutionarily congruent with the core genome in many proteobacterial clades, suggesting that lateral gene transfer played a major role in the distribution of phototrophy within the Proteobacteria (Swingley et al. 2008).

Chloroflexi were originally described as a phototrophic clade of gliding filamentous bacteria (Overmann 2008), but recent discoveries have added substantial metabolic diversity to the phylum (Hemp et al. 2015, Hug et al. 2013, Ward et al. 2015a). The vast majority of Chloroflexi species are nonphototrophic, with most phototrophic members now relegated to the late-branching Chloroflexales order. Members of Chloroflexales are facultative photoheterotrophs, with many also being able to perform aerobic and anaerobic respiration. Recently a phototrophic member of the distantly related Anaerolineae class was described from a hot spring in Yellowstone National Park (Klatt et al. 2011), highlighting the possibility that the diversity of phototrophic Chloroflexi species will expand in the future. Phototrophic members of Chloroflexi utilize an electron transfer chain composed of an RCII, bacteriochlorophyll *a* or *c*, and menaquinone (Bryant & Liu 2013). Notably, they vary in which complex III they use for energy conservation. The genome of *Chloroflexus aurantiacus* does not encode a cytochrome *bc* complex (Yanyushin et al. 2005), but this strain was shown to use an ACIII for phototrophic growth. Interestingly other phototrophic members of Chloroflexi encode for either an ACIII or a cytochrome *bc* complex, whereas a few have both. Further biochemical and physiological characterization will be required to understand this redundancy.

Chlorobi were also originally described as a solely phototrophic clade of strict anaerobes (Bryant & Liu 2013; Davenport et al. 2010; Imhoff 2014a,b), but again new discoveries have expanded the metabolic diversity of this phylum. Recently two early-branching taxa, *Thermochlorobacter aerophilum* (Liu et al. 2012b) and *Chlorobium* sp. GBChlB (Stamps et al. 2014), have been discovered that are aerobic photoheterotrophs, suggesting that the anaerobic and phototrophic members of the Chlorobi may have aerobic ancestors. In addition, two nonphototrophic strains of Chlorobi, *Ignavibacterium album* (Iino et al. 2010, Liu et al. 2012a) and *Melioribacter roseus* (Podosokorskaya et al. 2012), have been isolated and characterized as facultative anaerobes. These microbes branch basal to the phototrophic Chlorobi taxa, suggesting that the phylum was not ancestrally phototrophic. The phototrophic Chlorobi members utilize an electron transfer chain consisting of an RCI, various chlorophylls (bacteriochlorophylls *a*, *c*, *d*, and *e* and chlorophyll *a*), a cytochrome *bc* complex, and menaquinone, and they fix carbon using the reverse tricarboxylic acid cycle.

Heliobacteria are a small clade of photoheterotrophic clostridia within the Firmicutes phylum (Heinnickel & Golbeck 2007, Sattley & Blankenship 2010). During phototrophy, members of this clade use an electron transfer chain composed of an RCI, bacteriochlorophyll *g*, a cytochrome *bc* complex, and menaquinone (Sattley et al. 2008). Oddly, they do not contain any peripheral antennae proteins for light gathering. As for the Proteobacteria, the genes for phototrophy (including complex III) are encoded in a PSG, suggesting lateral gene transfer played a role in their evolution.

The Acidobacteria are metabolically diverse and common in many environments, especially soils. In 2007 a phototrophic acidobacterium, *Chloroacidobacterium thermophilum*, was isolated

from Yellowstone National Park (Bryant et al. 2007). Genomic and physiological characterization showed that it is a photoheterotroph capable of various metabolisms, including aerobic respiration (Garcia Costas et al. 2012a, Tank & Bryant 2015). This organism uses an RCI with three chlorophylls (bacteriochlorophyll *a*, chlorophyll *a*, and zinc-bacteriochlorophyll), and menaquinone (Garcia Costas et al. 2012b). It encodes both a cytochrome *bc* complex and an ACIII, likely using the cytochrome *bc* complex during phototrophy.

Little is known about the Gemmatimonadetes phylum, though recently a phototrophic member, *Gemmatimonas* sp. AP64, was isolated from a fresh water lake in China (Zeng et al. 2014). Its phototrophy genes are located in a PGC very similar to those in phototrophic Proteobacteria. Phylogenetic analysis verified that the PGC was acquired from the Proteobacteria via lateral gene transfer, providing the first indisputable evidence for interphylum lateral gene transfer of phototrophy. *Gemmatimonas* sp. AP64 uses an electron transfer chain composed of an RCII, bacteriochlorophyll *a*, and menaquinone. It also encodes both types of complex III, a cytochrome *bc* complex and ACIII.

All known phototrophic Cyanobacteria perform oxygenic photosynthesis, with the exception of two phylogenetically derived algal symbionts (Nakayama et al. 2014, Tripp et al. 2010). Their electron transfer chains are highlighted in **Figure 2**. Notably, phototrophic Cyanobacteria also generate energy from aerobic respiration using a low-affinity O_2 reductase and consume nearly as much O_2 as they produce.

Chlorin: a heterocyclic aromatic ring with a core consisting of three pyrroles and one pyrroline coupled through four =CH– linkages

Heterodimer: a complex formed by two different protein molecules

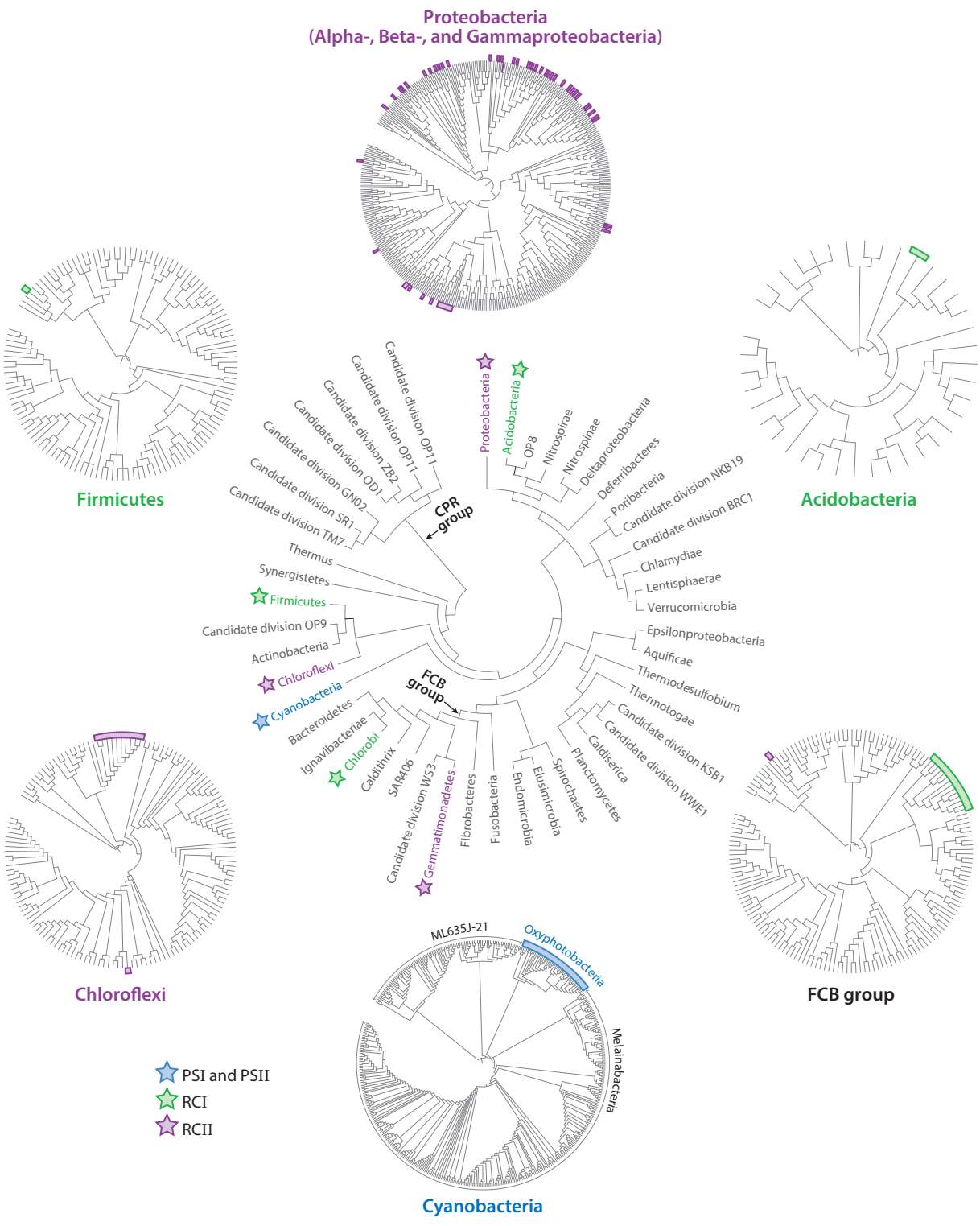
Homodimer: a complex formed by two identical protein molecules

Evolutionary Relationships of Phototrophs

While chlorophototrophy occurs in bacteria and eukaryotes, it is clear that eukaryotes acquired phototrophy through endosymbiosis, and interestingly, no chlorophototrophic Archaea have been described to date, suggesting that chlorophyll-based photosynthesis arose within the Bacteria. Evolutionary relationships between major well-known bacterial phyla illustrate that there is no single vertically inherited history of phototrophy (**Figure 5**). The seven bacterial phyla with phototrophic members are variably scattered throughout the tree. Although it is common to observe somewhat different phylogenetic relationships between bacterial phyla depending on the character sets (genes, proteins, or concatenated genes and proteins) and evolutionary models used, more and more commonalities are observed with growing genomic data (Rinke et al. 2013). It is important to note that no character can align phototrophy into a single monophyletic clade (i.e., a phototrophy superphylum) independent of the presence or absence of proteins used for phototrophy.

Mapping the biochemical features of phototrophy (types of reaction centers, complex IIIs, and chlorin biosynthesis) onto the tree does not yield a consistent pattern of evolution. Members of Proteobacteria, Chloroflexi, and Gemmatimonadetes have RCIIs, whereas members of Chlorobi, Firmicutes, and Heliobacteria have RCIs—members of Cyanobacteria use PSI and PSII (**Figures 1** and **5**). Chlorobi and Gemmatimonadetes both belong to the Fibrobacteres-Chlorobi-Bacteroidetes (FCB) superphylum, but they use different types of reaction centers. The closest phototrophic relatives of the Proteobacteria are the Acidobacteria; however, the latter use RCI instead of RCII. Furthermore, despite the large evolutionary distance that separates the phyla Chloroflexi and Proteobacteria, members of both use similar heterodimeric RCIIs that share a common homodimeric ancestor, different from the homodimeric ancestor of PSII (**Figure 5**). Chlorosomes are found in some phototrophic members of Chloroflexi (Grouzdev et al. 2015), Chlorobi, and Acidobacteria, but their origin is unknown, and lateral gene transfer is responsible in some part for their distribution (Frigaard & Bryant 2006).

Analyses of the distribution of phototrophy within each of the phyla reveals additional complexity that indicates lateral gene transfer is an important mode of evolution for the modern



distribution of phototrophy (Raymond et al. 2002) (**Figure 5**). Phototrophy is unevenly dispersed throughout the Proteobacteria phylum, and phototrophic members tend to have their phototrophic genes organized into PGCs—superoperons that facilitate lateral gene transfer. There is no evidence that the Proteobacteria were ancestrally phototrophic, and the phylogeny of these PGCs shows that lateral gene transfer is common in this clade (Igarashi et al. 2001, Nagashima & Nagashima 2013). Furthermore, proteobacterial PGCs have been found on plasmids (Kalhoefer et al. 2011, Petersen et al. 2012), important vectors of gene transfer. Phototrophs in the FCB superphylum do not share an immediate phototrophic ancestor, with several nonphototrophic clades branching between them. The phylum Chlorobi contains a monophyletic clade of phototrophs; however, the basal members of this phylum are not phototrophic (Liu et al. 2012a). The phototrophic Gemmatimonadetes species use a PGC that was acquired from phototrophic Proteobacteria via lateral gene transfer (Zeng et al. 2014). The Chloroflexi show a similar pattern to the FCB group; the basal clades are nonphototrophic, with two small clades of phototrophs separated by many nonphototrophic clades. In addition the phototrophic members of Firmicutes and Acidobacteria have derived positions with diverse nonphototrophic relatives. Importantly, the same relationships are seen with the discovery of deep-branching nonphototrophic members of Cyanobacteria, which suggests this phylum was not ancestrally phototrophic (more on this below).

Altogether these observations cannot be explained by the presence of anoxygenic phototrophy in an ancient ancestor followed by massive gene losses, making the selective loss hypothesis unlikely. It is clear that lateral gene transfer has been an important vector in the history of photosynthesis. All currently known anoxygenic phototrophic groups appear to be derived within the phyla in which they occur. Interestingly and perhaps more speculatively, all extant anoxygenic phototrophs appear to be derived within groups that have basal members with aerobic metabolism. This observation suggests the hypothesis that it is relatively easy for (facultative) aerobes to adapt for phototrophy because of the modular nature of the high-potential redox modules of aerobic (and denitrifying) electron transport chains; it also carries the potential implication that much of the extant diversity of phototrophs postdates the Paleoproterozoic rise of oxygen. This idea is supported by current data from the molecular fossil record for phototrophic members of Proteobacteria and Chlorobi (Brocks et al. 2005).

There is no evidence that any phylum was ancestrally phototrophic. All currently known phototrophic groups appear to be derived late within the phyla in which they occur, supporting this view. This provides additional support for the fusion model of the evolution of oxygenic photosynthesis.

Figure 5

Evolutionary trees of the diversity of phototrophs from RpoB, a useful phylogenetic marker protein from a subunit of the bacterial RNA polymerase. The central cladogram illustrates the relationships between select bacterial phyla; generally similar relationships are observed from 16S rDNA and concatenated protein analyses. Stars mark the seven phyla currently known to have phototrophic members, with each star colored according the reaction center type. A separate phylogeny is shown for each of these clades, with colored outer bands that reflect the distribution of phototrophic members. These relationships highlight that even within phyla, phototrophy remains variably distributed and/or evolutionarily derived. The same is true for the Cyanobacteria phylum (shown here from 16S rDNA data), in which oxygenic photosynthesis sits nested within several nonphotosynthetic classes, including the Melainabacteria and ML635J-21 clades. These relationships show that lateral gene transfer played an important role in the distribution of phototrophy observed today. Furthermore, though the photosystems themselves are very old, their distribution in extant groups is comparatively young. No phylum is currently known that was inarguably phototrophic from its inception. Abbreviations: CPR, candidate phyla radiation; FCB, Fibrobacteres-Chlorobi-Bacteroidetes; PS, photosystem; RC, reaction center.

Nonphototrophic Cyanobacteria

A major breakthrough for understanding the evolution of oxygenic photosynthesis was the recent discovery of deep-branching nonphototrophic Cyanobacteria. It was previously thought that the Cyanobacteria phylum was strictly composed of oxygenic phototrophs. If true, this would make Cyanobacteria unique among Bacteria for their relative lack of metabolic diversity; all other major bacterial phyla studied to date contain members with diverse metabolisms. It has also been shown that although phototrophic Cyanobacteria may be morphologically diverse, they have little phylogenetic diversity compared to many other bacterial phyla (Dojka et al. 2000, Shih et al. 2013).

Early 16S rDNA gene surveys from a wide variety of environments (Ley et al. 2005) highlighted a large number of uncharacterized microbes that cluster robustly with Cyanobacteria in phylogenetic trees. Intriguingly, the majority of these sequences were observed in samples from aphotic environments, such as animal guts, anaerobic digesters, subsurface aquifers, soils, and deep marine sediments. Recently genomes from a number of these organisms were observed in metagenomic data sets (Di Rienzi et al. 2013, Johnson et al. 2013b, Soo et al. 2014, van der Lelie et al. 2012) and one cultured isolate (Soo et al. 2015). Importantly, none contain genes for phototrophy. Analyses of their genomes provide strong evidence that they are indeed members of the Cyanobacteria phylum, and based on this, an updated classification has been proposed (Soo et al. 2014) in which there are now three classes within Cyanobacteria: Oxyphotobacteria, Melainabacteria, and ML635J-21 (**Figure 5**). Members of Oxyphotobacteria are oxygenic phototrophs. Melainabacteria is a nonphototrophic sister clade to Oxyphotobacteria that consists of multiple orders: Caenarcaniphilales, Gastranaerophilales, Obscuribacterales, and Vampirovibrionales. To date members of Caenarcaniphilales and Gastranaerophilales are strict fermenters, whereas members of Obscuribacterales and Vampirovibrionales have broader metabolic capabilities, including aerobic respiration. ML635J-21 is the deepest-branching clade within the phylum Cyanobacteria, though there is little genomic information currently available for this class. The fact that the majority of these sequences were observed in aphotic environments supports the idea that Cyanobacteria were ancestrally nonphototrophic, with the implication that lateral gene transfer was an important vector for the evolution of oxygenic photosynthesis in this group. This is consistent with the fusion hypothesis.

Diversity and Evolution of Chlorins

Prior to the advent of molecular sequencing, phototrophic bacteria were classified based on their pigment profiles (Van Niel 1944). Chlorins (chlorophyll and bacteriochlorophyll) are the only pigments found in all chlorophototrophs, and they play central roles in both light gathering and photochemistry. Therefore substantial effort has been placed on understanding the evolution of photosynthesis from the perspective of their biosynthesis.

A long-standing hypothesis for the evolution of chlorins relies on the conjecture—termed the Granick hypothesis—that biosynthetic pathways in extant organisms recapitulate their evolution (Granick 1957). In the chlorin biosynthesis pathway, chlorophyllide *a* is a precursor to bacteriochlorophyll (Chew & Bryant 2007); therefore, the Granick hypothesis predicts that chlorophyll evolutionarily preceded bacteriochlorophyll. An alternative hypothesis was also proposed based on the observation that all anoxygenic phototrophs utilize bacteriochlorophyll. Because anoxygenic phototrophy preceded oxygenic photosynthesis, it followed that bacteriochlorophyll must have preceded chlorophyll in an evolutionary sense. An early phylogenetic study of chlorin biosynthesis

genes to test these hypotheses suggested that bacteriochlorophyll *a* was the primordial chlorin, and that photosynthesis originated within the Proteobacteria phylum (Xiong et al. 2000). However, conflicting results were recovered with similar phylogenetic analyses of chlorin biosynthesis genes (Green & Gantt 2000, Mix et al. 2005, Raymond et al. 2002, Sousa et al. 2013).

In order to use chlorin biosynthesis genes to infer the evolution of phototrophy, three criteria must be met: (*a*) The genes studied must retain a phylogenetic signal over long time intervals, (*b*) they must not have been subject to lateral gene transfer independent of reaction center genes, and (*c*) valid outgroups need to be identified to root the phylogenetic trees. Many chlorin biosynthesis genes do not satisfy these criteria. The majority of these are small soluble proteins with localized active sites, whose sequences can more rapidly saturate under evolutionary drift, losing phylogenetic information. This is reflected by poorly resolved trees of many chlorin biosynthesis genes (Lockhart et al. 1996). Then there are many examples of lateral gene transfer of chlorin biosynthesis genes (Sousa et al. 2013). Cyanobacteria, for example, use a protochlorophyllide reductase derived from Proteobacteria (Bryant et al. 2011), and some Proteobacteria use a light-dependent protochlorophyllide oxidoreductase (Kaschner et al. 2014) derived from Cyanobacteria—demonstrating that homologous replacement is not only possible but might be common. Additionally, phylogenetic trees are typically rooted using *nif* genes (encoding subunits of the nitrogenase complex), but this introduces a degree of logical uncertainty because it is possible that nitrogen fixation evolved after the rise of oxygen and relatively late in Earth history (Boyd & Peters 2013); indeed, the converse challenge is true for nitrogen fixation.

The Granick hypothesis has received support from a wide range of additional observations (Bryant & Liu 2013), in addition to the current understanding of the core biosynthetic pathways (Chew & Bryant 2007). Organisms with RCI use chlorophyll *a* in their reaction centers (**Figure 6**); indeed, all phototrophic organisms synthesize chlorophyll *a*, although in members of Proteobacteria and Chloroflexi these are intermediates in the production of bacteriochlorophylls (Bryant & Liu 2013). Therefore, it is reasonable to infer that ancestral reaction centers functioned with chlorophyll *a*, or closely related derivatives. It likely that light gathering has always had some degree of evolutionary pressure to diversify chlorin biosynthesis pathways and produce molecules that absorb light of different wavelengths (Kiang et al. 2007)—meeting an ecological challenge ever present in light-stratified environments. Finally, pigment biosynthesis would receive an important evolutionary overhaul for both oxygenic and anoxygenic phototrophs after the rise of oxygen, as aerobes replaced parts of their pathways with aerotolerant enzymes (Raymond & Blankenship 2004), and anaerobes would need new modifications to scavenge light from their deeper positions with greater redox stratification of the environment (Chew & Bryant 2007). Ultimately, light-gathering strategies are highly diverse, and this aspect of phototrophic biology appears to be evolutionarily plastic, dictated more by environment and ecology than by history.

Evolution of Reaction Centers

All reaction centers are related to one another, and they are among the most evolutionarily conserved proteins in nature (Shi et al. 2005). Consequently, their evolutionary relationships provide valuable insights into both the evolution of phototrophy and the origin of oxygenic photosynthesis.

Early hypotheses suggested a common origin of reaction centers from observations of the cofactors present and their spectroscopy (Blankenship 1992, Nitschke & Rutherford 1991), and from (albeit limited) sequence data (Beanland 1990, Moënne-Loccoz et al. 1990). This hypothesis was confirmed with the solution of crystal structures that showed the five transmembrane helices are nearly identically placed in type I and type II reaction centers (Cardona 2015, Sadekar et al.

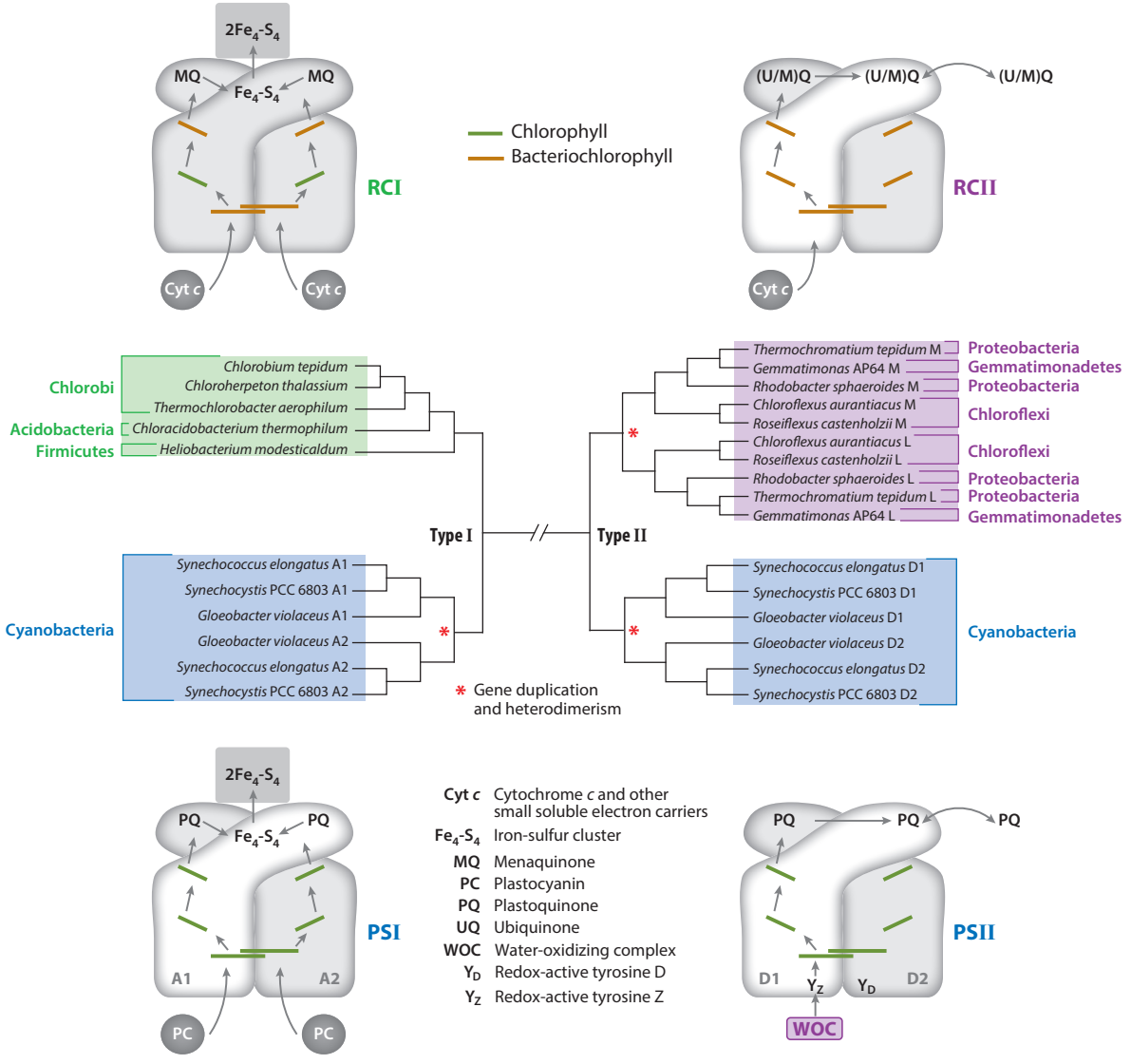


Figure 6

Evolutionary relationships between photochemical reaction centers constructed from a combination of maximum likelihood analyses of protein sequence alignments of the core dimeric reaction center peptides and observations of crystal structures. Gene duplication events illustrate that reaction center II (RCII) and photosystem II (PSII) evolved independently from an ancestral homodimer type II reaction center. The scale break between type I and type II clades conceals a substantial evolutionary distance that indicates they diverged from one another long ago. This provides the inference that the coupled photosystems of oxygenic photosynthesis constitute a relatively recent invention compared to anoxygenic phototrophy.

2006, Schubert et al. 1998). Substantial amounts of genomic, metagenomic, and structural data now provide strong support for a single origin of all phototrophic reaction centers, whose diversity was subsequently expanded by evolutionary divergence and multiple gene duplication events.

The core of the reaction center is composed of a pair of integral membrane proteins that contain all of the redox-active cofactors (chlorophylls, pheophytins, quinones, etc.) required to perform

charge separation (Rutherford & Faller 2003). Type I (RCI and PSI) and type II (RCII and PSII) reaction centers share a highly conserved structural core of five transmembrane helices (Sadekar et al. 2006, Schubert et al. 1998). In some reaction centers the core pair of integral membrane proteins is composed of homodimers (RCIs), whereas in others it consists of heterodimers (RCIIs, PSIs, and PSIIs). In addition to the shared core, the type I reaction centers also have a six-transmembrane-helix antenna protein fused to their N terminus. This antenna domain is related to the CP41 and CP43 antenna proteins associated with PSII in Cyanobacteria. Evolutionary analysis suggests that the CP41 and CP43 proteins were derived from the antenna component of PSI (Mix et al. 2005).

The evolutionary relationships between the different reaction centers and photosystems are presented in **Figure 6**. Type I and Type II reaction centers form two clades divided by a prodigious evolutionary distance. Despite their common origin and although they fold to essentially the same structures and place their cofactors in the same configurations (Sadekar et al. 2006), the degree of identity in protein sequence alignments between the two reaction center types is very low (typically less than 10%). The differences between RCIs and RCIIs place them into what is colloquially known as the twilight zone in molecular evolution (Doolittle 1986). When taxa diverge from one another, so too do their nucleotide and protein sequences. Through neutral drift and functional degeneracies they accumulate differences—the more time apart, the more differences accumulate. And eventually it can be hard to recognize common ancestry from sequence data alone. So much time has passed since the divergence of type I and type II reaction centers that little sequence identity unites them today.

Phylogenetic data illustrate that gene duplication and subsequent paralogous evolution to produce heterodimeric reaction centers has taken place at least three independent times (marked in **Figure 6**). The D1 and D2 subunits of the PSII heterodimer are more similar to each other than either is to the L and M subunits of the RCI heterodimer (Beanland 1990). This is also true for the A1 and A2 subunits of PSI, which record a third independent gene duplication event followed by heterodimerism. RCI remains the only extant homodimeric reaction center. An important aspect to heterodimerism in PSI appears to be related to tuning electron transfer to cope with the presence of molecular oxygen (Rutherford et al. 2012). Similar logic suggests that this could also be an evolutionary factor for RCII (semiquinones can reduce O_2 to O_2^-) that if correct implies that RCII and PSI heterodimers evolved after the rise of oxygen. These duplications also illustrate that the root (and ancestor) to this protein family sits somewhere on a branch between the two types of reaction centers. A number of hypotheses have been proposed for how the ancestral reaction center originated; comparison of features common to all extant reaction centers suggests that it was a homodimer composed of five transmembrane helices that reduced quinones, perhaps functionally similar to type II reaction centers. The ancestral type I reaction center had to acquire two features: an antenna domain fusion and the ability to donate electrons to iron-sulfur proteins. The order of these events remains uncertain. Nonetheless, the gene duplication events polarize and ordinate the evolutionary path taken for oxygenic photosynthesis (Cardona 2015, Sadekar et al. 2006).

These observations highlight that oxygenic photosynthesis evolved by combination of ancestral homodimeric type I and type II reaction centers to produce coupled photosystems linked together in an electron transport series (Mix et al. 2005). To explain the impressive evolutionary distance, this must have occurred long after type I and type II reaction centers diverged from each other. This aspect of comparative biology strongly implies that anoxygenic photosynthesis preceded oxygenic photosynthesis by a substantial amount of time—a scenario supported by observations from the geological record. These observations also provide the insight that photosynthesis is truly old, even if the clades that perform it today are not.

WORKING HYPOTHESIS FOR THE EVOLUTION OF OXYGENIC PHOTOSYNTHESIS

We now synthesize an updated hypothesis for the evolution of oxygenic photosynthesis that integrates the key constraints described above from the biological and geological records (**Figure 7**).

Manganese-Oxidizing Phototrophy as a Precursor to Oxygenic Photosynthesis

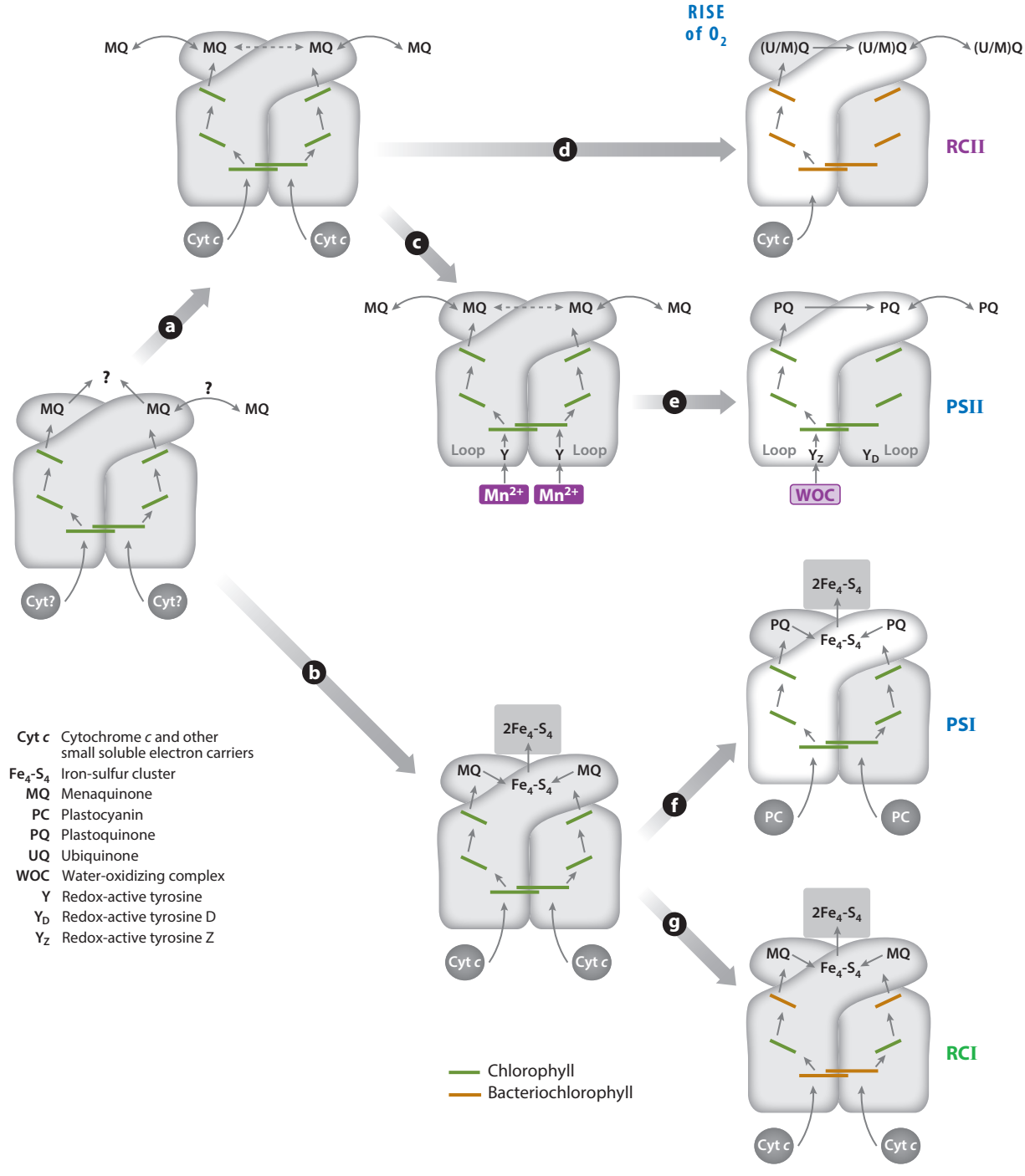
The transition from anoxygenic phototrophy to oxygenic photosynthesis required three key innovations: (*a*) a high-potential photosystem (≫820 mV) capable of oxidizing water, (*b*) a bioinorganic complex to catalyze the four-electron oxidation reaction of water to O_2, and (*c*) the coupling of two reaction centers in series that span the energy required to reduce ferredoxin with water. The evolution of a high-potential reaction center necessarily preceded the origin of oxygenic phototrophy, because a strong oxidant capable of removing electrons from water is required for the function of the WOC (Cardona et al. 2015, Rutherford & Faller 2003). This strongly suggests some type of high-potential anoxygenic phototrophy was a direct precursor to oxygenic phototrophy.

Analysis of type II reaction centers demonstrates that they shared a common ancestor that was homodimeric and likely oxidized low-potential donors; therefore, high-potential phototrophy is a derived feature of the PSII lineage. Sequence and structural analyses of PSII strongly suggest that the ancestral PSII possessed three key features: It was homodimeric, contained a redox active tyrosine (similar to Y_Z and Y_D), and had a C-terminal loop extension (Fischer et al. 2015, Grotjohann et al. 2004, Rutherford & Faller 2003). The presence of a redox-active tyrosine (800 to 1,200 mV) in the ancestral PSII implies that it generated substantially high potentials. The loop extension in the ancestral PSII homodimer places a critical constraint on possible electron donors. All known RCIIs receive electrons indirectly, oxidizing their substrates (Fe^{2+}, H_2, S^0, NO_2^-, etc.) in separate protein complexes, commonly located in the periplasm or inner membrane. The electrons are then transferred to RCII via soluble single-electron carriers. The ancestral PSII would have been unable to accept electrons from these carriers because the C-terminal loop extension would sterically block their approach (Fischer et al. 2015). This suggests that the electron donor for ancestral PSII must have been a small molecule oxidized directly by the reaction center.

These two important constraints on ancestral PSII—that it was high potential and catalyzed direct substrate oxidation—severely limit its possible electron donors. When donors that require complex multi-electron transfer reactions, produce toxic intermediates, or have redox potentials greater than Y_D/Y_Z are excluded, the only remaining plausible electron donor is Mn^{2+}. Manganese requires a high-potential reaction center for oxidation (600 to 920 mV) and is the only known

Figure 7

Conceptual framework for the evolution of oxygenic photosynthesis from the perspective of reaction centers proteins that honors data from both the comparative biological and geological records. (*a*,*b*) It is uncertain whether the immediate last common ancestor delivered electrons to iron-sulfur clusters or exchangeable quinones, but these differences were established with the evolutionary divergence to produce the type I reaction center (RCI) and type II reaction center (RCII). (*c*) Evolution of homodimeric RCII capable of high-potential photosynthesis (≫800 mV) marked by redox-active tyrosines. This high-potential homodimer also acquired two loop extensions from the C terminus that precluded the ability to receive electrons from standard protein donors such as cytochrome *c* but was capable of Mn(II) oxidation. (*d*) Gene duplication and evolution of the RCII heterodimer, perhaps in response to the rise of oxygen: incorporation of bacteriochlorophylls and the higher-potential ubiquinone. (*e*) Evolution of coupled photosystems and the ligand field to stabilize the water-oxidizing complex, including gene duplication and heterodimeric evolution of photosystem II (PSII). Incorporation of higher-potential plastoquinone. (*f*) Gene duplication and evolution of photosystem I (PSI) heterodimer to cope with O_2. Evolution of plastocyanin to transmit electrons from the b_6f complex. (*g*) Evolution of bacteriochlorophylls for light gathering in redox-stratified environments.



Cyt *c*	Cytochrome *c* and other small soluble electron carriers
Fe_4-S_4	Iron-sulfur cluster
MQ	Menaquinone
PC	Plastocyanin
PQ	Plastoquinone
UQ	Ubiquinone
WOC	Water-oxidizing complex
Y	Redox-active tyrosine
Y_D	Redox-active tyrosine D
Y_Z	Redox-active tyrosine Z

electron donor other than water that is capable of direct electron donation to reaction centers. In fact, all extant PSIIs catalyze the direct oxidation of Mn^{2+} during the photoassembly of the WOC (Tamura & Cheniae 1987), and the electrons donated during this process are indistinguishable from those donated by water during subsequent photochemical reaction cycles (**Figure 3**). It is important to note that, apart from Cyanobacteria, no phototrophs are currently known that use Mn(II) as an electron donor for photosynthesis. It is possible that they remain extant in nature, as metagenomic studies illustrate that we have just scratched the surface on microbial metabolic diversity. Typical enrichment conditions for Mn phototrophs may have been prohibitively selective, for example, with the use of strong PSII inhibitors such as 3-(3,4-dichlorophenyl)-1,1-dimethylurea (DCMU). It is also useful to consider that such a physiology might be long extinct, and so it is important that the proposal that Mn-oxidizing phototrophy was the direct precursor to oxygenic photosynthesis receives support from the geological record.

Geological Record of Manganese Oxidation

The secular distribution of manganese deposits in the geological record lends important insights into the evolution of oxygenic photosynthesis. Manganese is the third most common transition metal in the crust, where it substitutes for iron in a diversity of igneous minerals, exclusively as Mn(II). Chemical weathering of crustal silicates therefore liberates a large flux of soluble Mn^{2+} to the oceans, where it can accumulate if it remains reduced. Once oxidized to Mn(III) or Mn(IV), manganese rapidly hydrolyzes and precipitates as insoluble oxides that can accumulate in sediments (Calvert & Pedersen 1996, Morgan 2005). However, to oxidize Mn^{2+}, high-potential oxidants are required ($\gg$500 mV)—far higher than needed for the oxidation of ferrous iron or sulfur compounds. In addition, manganese oxidation is kinetically limited [and for many oxidation reactions thermodynamically inhibited (Luther 2010)] and typically very slow in the absence of biological catalysis compared to iron oxidation (Morgan 2005). This makes the Mn cycle uniquely sensitive to high-potential oxidants, such as O_2 or its derivatives. Reconstruction of the ancient Mn cycle, coupled with estimates of ancient O_2 concentrations, can also be used to test the hypothesis that Mn-oxidizing phototrophy preceded the evolution of oxygenic photosynthesis. If this hypothesis is correct, manganese oxidation should predate the evolution of oxygenic photosynthesis and rise of oxygen, occurring instead in photic paleoenvironments that were effectively devoid of free oxygen (Johnson et al. 2013a).

Why did biology choose manganese for phototrophic water oxidation? Certainly its bioinorganic chemistry is well suited to the task (Armstrong 2008, Brudvig 2008), but the geological record provides an important complementary reason. A substantial body of work on the geochemistry of Precambrian carbonates shows that both shallow and deep seawater in Archean marine basins contained high levels of Mn^{2+} (Beukes 1987, Fischer & Knoll 2009, Ronov & Migdisov 1971, Sumner 1997, Sumner & Grotzinger 2004, Veizer 1978, Veizer et al. 1989). A range of observations, coupled with theoretical calculations, suggest that anoxygenic photoautotrophs living in surface seawater during Archean time would have been electron limited (Fischer & Knoll 2009, Kappler et al. 2005, Kharecha et al. 2005). The abundance of Mn^{2+} in seawater would have provided a novel metabolic opportunity for electron-limited phototrophs; however, in order to oxidize Mn(II), they would need to have high-potential reaction centers. From this perspective, this solution to an electron-limited ecosystem could have placed ancient Cyanobacteria on an evolutionary path ending in water oxidation (Johnson et al. 2013a).

Recently, authigenic Mn deposits that occur before the rise of oxygen were discovered in the 2.415 Ga Koegas Subgroup in South Africa (Fischer et al. 2015; Johnson et al. 2013a,b, 2014; Schröder et al. 2011). The strata that contain these deposits are composed of nearshore marine

deltaic deposits that episodically accumulated Mn-rich iron formation during intervals of lobe-switching on the delta. Abundant detrital pyrite and uraninite (Johnson et al. 2014) and widespread MIF of multiple sulfur isotopes (Johnson et al. 2013a) were also observed in these stratigraphic sections. These results independently confirmed that environmental O_2 levels remained several orders of magnitude lower than could be explained by the observed sedimentary Mn enrichments (Johnson et al. 2013a,b). Taken together, these lines of ecosystem-scale geological and geochemical evidence suggest that Mn^{2+} was oxidized by anoxygenic phototrophs prior to the evolution of oxygenic photosynthesis and rise of oxygen (Johnson et al. 2013a). (**Figure 7*c*,*e***). Several sedimentary successions of broadly similar Paleoproterozoic age deposited on different continents (Sekine et al. 2011, Williford et al. 2011) provide limited additional support for this hypothesis, though the processes of Mn mineralization are currently unclear and the geochronological constraints with respect to the rise of oxygen remain only coarsely bounded (Fischer et al. 2015).

Evolution of Water Oxidation and Modern Cyanobacteria

Although the concept of Mn phototrophy as a high-potential evolutionary intermediate during the development of oxygenic photosynthesis receives substantial support from both biological and geological records, whether and how direct phototrophic Mn oxidation may have led to efficient water splitting remain open questions. Again there are some important constraints that can be leveraged from comparative structural biology.

How did Cyanobacteria come to use coupled photosystems? An organism that performed Mn-oxidizing phototrophy with an ancestral version of PSII would have an interesting problem. It would be able to reduce the quinone pool with electrons from Mn, but it would be unable to perform cyclic electron transfer because the presence of the loop extension would block the ability of soluble electron carriers to reduce the oxidized photosystem. Without a sink for electrons from the quinone pool, the cell would quickly become completely overreduced and unable to perform further phototrophy. This dilemma could be solved if there were a second photosystem present that could receive electrons from soluble electron carriers. Importantly, the WOC is ligated by a residue from CP43, a subunit derived from PSI (Mix et al. 2005, Zhang et al. 2007) (**Figure 3*a***). This necessitates that ancestral versions of both PSI and PSII were present in Cyanobacteria before the origin of the WOC and provides additional support for coupled photosystems prior to water oxidation. Thus one can infer that ancestral Cyanobacteria capable of Mn(II) oxidation had two photosystems.

A homodimeric Mn-oxidizing reaction center would have performed electron transfer on both sides of the complex, making it highly unlikely that it was able to oxidize water, which would require the coordination of eight electron transfers (Fischer et al. 2015). It is therefore probable that gene duplication and heterodimerization of PSII enabled the evolution of the WOC (**Figure 7**). By retaining the oxidized Mn bound to the protein on the D1 side, the protein gained the ability to oxidize water—a limitless electron donor. Details of how this might have occurred remain unclear. Once the WOC evolved, electron transfer was optimized on the D1 side, and the D2 side took on other roles (Rutherford et al. 2004).

After the origin of oxygenic photosynthesis, stem-group Oxyphotobacteria increased phototrophic efficiency by modifying key components of the electron transfer chain. The redox potential of the quinone pool was increased by switching from menaquinone to plastoquinone, plastocyanin replaced cytochrome *c* as an electron carrier from complex III to PSI, and the evolution of aerobic respiration helped to maintain the redox balance of the cell. Furthermore, PSI duplicated from a homodimeric ancestor into a heterodimer to help minimize the risk caused by charge separation and photochemistry in the presence of O_2 (Rutherford et al. 2012). These

incremental changes occurred before the radiation of crown-group Oxyphotobacteria, and the acquisition of chloroplasts by plants and algae, because all extant oxygenic phototrophs now include these modifications (Shih & Matzke 2013).

POSTSCRIPT

The evolution of oxygenic photosynthesis by Cyanobacteria put in place the biochemical machinery for carbon fixation driven by water oxidation. After its origin, this metabolism became the core engine of the carbon cycle and generated an atmosphere with free oxygen. Despite our knowledge that the residence time of oxygen in the atmosphere is measured in hundreds of years (Bender et al. 1994, Field et al. 1998, Severinghaus et al. 2009), the geological record shows that O_2 levels have been dynamically maintained on our planet for more than two billion years (**Figure 3**). The rise of oxygen was irreversible. This metabolic invention so profoundly transformed the energetics of Earth surface ecosystems that there was no going back to a solely anaerobic world.

Here we focused on what we understand about the evolution of photochemistry from the complementary perspectives of comparative biology and the geological record. But the story of oxygenic photosynthesis does not end with the Cyanobacteria. Endosymbiosis and the development of plastids—organelles derived from engulfing Cyanobacteria (Mereschkowsky 1905)—provided an important vector for acquiring and distributing photosynthesis in eukaryotes (Delwiche 1999, Keeling 2010). Photosynthetic eukaryotes began to play a role in marine ecosystems toward the end of Proterozoic time (Butterfield et al. 1990, Knoll et al. 2006) but would come to have major impact on marine ecology and biogeochemistry in Phanerozoic oceans (Falkowski et al. 2004, Knoll et al. 2007). The evolution of land plants in Paleozoic time would require clever anatomical and biochemical solutions to take photosynthesis—a fundamentally aquatic process—and adapt it for life on land. And C4 photosynthesis would emerge dozens of times independently in the past 10 million years in both terrestrial (Cerling et al. 1997, Sage et al. 2012) and marine ecosystems (Reinfelder et al. 2000) to cope with a changing climate and the growing scarcity of CO_2 in the atmosphere. Each of these events has rich history to be uncovered.

SUMMARY POINTS

1. Phylogenetic relationships reveal that there is no single conserved evolutionary history among the known phototrophic organisms, which are scattered throughout seven different bacterial phyla: Proteobacteria, Chloroflexi, Chlorobi, Firmicutes, Acidobacteria, Gemmatimonadetes, and Cyanobacteria. Phototrophy appears to be a derived trait in each of the extant clades in which it occurs—Cyanobacteria are no exception. Lateral transfer appears to be an important process in the extant distribution of phototrophy. There has been substantial debate about which modern clade invented photosynthesis, but the best answer from current data appears to be none of them.
2. Evolutionary relationships for the reaction center proteins—independent of the organisms that host them—provide a constraint that can ordinate anoxygenic photosynthesis and oxygenic photosynthesis in relative time. Because oxygenic photosynthesis evolved from a fusion of a homodimeric type I reaction center and a homodimeric type II reaction center, and given the evolutionary distance between these proteins, one can securely intuit that anoxygenic photosynthesis must be very old, whereas oxygenic photosynthesis is relatively young.

3. The WOC of PSII is the core biochemical innovation that enabled phototrophic water splitting. Photoassembly of the WOC motivates the hypothesis that Mn(II) was an electron donor to PSII prior to the evolution of oxygenic photosynthesis. This hypothesis is strongly supported by the structural biology and biochemistry of PSII in Cyanobacteria and receives additional support from a growing body of geological and geochemical evidence from the Archean and Paleoproterozoic sedimentary records that demonstrates that the oxidative branch of the Mn cycle switched on prior to the rise of oxygen.
4. Independent insights from comparative biology, modern biochemistry, and genomic and metagenomic data all imply that oxygenic photosynthesis is a relatively late metabolic invention from the perspective of Earth history. This view is supported by a wide range of data from the geological record, including the body and molecular fossil records and sedimentological and geochemical observations of the Paleoproterozoic rise of oxygen—currently constrained to between 2.4 and 2.35 Ga. Interpretations of whiffs of oxygen from trace element proxies contrast with this, arguing instead that Cyanobacteria and phototrophic O_2 fluxes were prevalent in certain environments on the Archean Earth.

FUTURE ISSUES

1. All ideas about the evolution of oxygenic photosynthesis rely fundamentally on interpretive frameworks developed from what we know about the physiologies and evolutionary relationships of extant microorganisms. Breakthroughs in environmental and single-cell sequencing technologies are rapidly transforming the landscape for microbial evolution. It stands to reason that many phototrophs remain to be discovered. Will these efforts uncover phototrophic Archaea, or organisms with homodimeric type II reaction centers?
2. Recent discoveries of nonphotosynthetic close relatives to the oxygenic Cyanobacteria provide fresh insight into the evolution of this phylum. By studying these organisms we have an opportunity to evaluate the possible metabolic and physiological characteristics of ancestral Cyanobacteria before they developed oxygenic photosynthesis.
3. There is still much that we do not know regarding the timing of the emergence of oxygenic photosynthesis and how it relates to the rise of oxygen. High-precision geochronologic constraints remain meager; renewed efforts are required. And can we better evaluate the quality of redox proxy data generated from Precambrian samples? Deeper understanding of the mechanics of these proxies, and how they might be affected by postdepositional processes that are unavoidable in rocks of this age, may help reconcile the discordant behavior of different redox proxies and test ideas like the whiffs of oxygen.
4. Finally, is it acceptable to use O_2 to document the evolution of Cyanobacteria, and what do we sacrifice to do so? At what levels is O_2 unique for oxygenic photosynthesis? Not only are answers to these questions important for understanding the evolution of oxygenic photosynthesis and the oxygen cycle on Earth, but insights into these questions will also play a role in future assessments of life on planets outside our Solar System.

DISCLOSURE STATEMENT

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