Minireview

The role of biology in planetary evolution: cyanobacterial primary production in low-oxygen Proterozoic oceans

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Summary

Understanding the role of biology in planetary evolution remains an outstanding challenge to geobiologists. Progress towards unravelling this puzzle for Earth is hindered by the scarcity of well-preserved rocks from the Archean (4.0 to 2.5 Gyr ago) and Proterozoic (2.5 to 0.5 Gyr ago) Eons. In addition, the microscopic life that dominated Earth’s biota for most of its history left a poor fossil record, consisting primarily of lithified microbial mats, rare microbial body fossils and membrane-derived hydrocarbon molecules that are still challenging to interpret. However, it is clear from the sulfur isotope record and other geochemical proxies that the production of oxygen or oxidizing power radically changed Earth’s surface and atmosphere during the Proterozoic, pushing it away from the more reducing conditions prevalent during the Archean. In addition to ancient rocks, our reconstruction of Earth’s redox evolution is informed by our knowledge of biogeochemical cycles catalysed by extant biota. The emergence of oxygenic photosynthesis in ancient cyanobacteria represents one of the most impressive microbial innovations in Earth’s history, and oxygenic photosynthesis is the largest source of O2 in the atmosphere today. Thus the study of microbial metabolisms and evolution provides an important link between extant biota and the clues from the geologic record. Here, we consider the physiology of cyanobacteria (the only microorganisms capable of oxygenic photosynthesis), their co-occurrence with anoxygenic phototrophs in a variety of environments and their persistence in low-oxygen environments, including in water columns as well as mats, throughout much of Earth’s history. We examine insights gained from both the rock record and cyanobacteria presently living in early Earth analogue ecosystems and synthesize current knowledge of these ancient microbial mediators in planetary redox evolution. Our analysis supports the hypothesis that anoxygenic photosynthesis, including the activity of metabolically versatile cyanobacteria, played an important role in delaying the oxygenation of Earth’s surface ocean during the Proterozoic Eon.

Introduction

Understanding the evolution of the Earth’s surface chemistry is one of the most exciting challenges in modern geoscience. The prevailing view is that the early Earth was oxygen-poor in comparison with that of today, with mildly reducing conditions characterized by a N2/CO2 atmosphere and trace amounts of CH4 during the Archean Eon. Also during this time, Earth’s surface was sunlit, but the sun’s brightness may have been ∼70% than what it is today because of a higher ratio of hydrogen to helium in its core (Sagan and Mullen, 1972; Kasting, 2010). Despite an Archean sun that was 20–30% less bright than today, there is abundant evidence that the oceans of early Earth were liquid. The Great Oxidation Event (GOE), the first permanent rise of oxygen in the atmosphere, occurred sometime between 2.4 and 2.1 Gyr ago (Lyons et al., 2014). Although there is considerable uncertainty about atmospheric oxygen concentrations during the Proterozoic, oxygen levels after the abrupt increase (the GOE) were less than the present atmospheric level (PAL). Current estimates range from 0.1% to 10% PAL (Fig. 1).
photochemical reactions were occurring (Pavlov and
required very low-oxygen levels in the atmosphere where
The preservation of these signals in the rock record
mass-independent fractionations of gas-phase sulfur
wavelength photochemical reactions were responsible for
the oxidation of Mn requires high-potential oxidants –
multi-subunit protein complex containing a Mn 4CaO5
cluster that uses light energy to oxidize two molecules of
water to molecular oxygen during the light-dependent
reactions of oxygenic photosynthesis.
Feedbacks that would act to stabilize low-oxygen con-
ditions in the Proterozoic for 1–2 billion years have proven
more difficult to envision, highlighting an important gap in
our understanding of ancient biogeochemical cycling. A
plausible scenario invokes significant contributions to
primary production by anoxygenic phototrophs (Eqs 2–4)
(Johnston et al., 2009), including metabolically versatile
cyanobacteria capable of performing anoxygenic photo-
synthesis. In this scenario, the activity of anoxygenic pho-
tosynthesis in Earth’s oceans, where conditions of mildly
oxic water at the surface and euxinia below were common
in continental shelf areas, afforded the generation of organic
matter via oxidation of reduced S (Eq. 2) with no
O2 production. The resulting positive feedback would stall
the accumulation of O2 at levels much lower than those
observed today, consistent with redox-sensitive proxies in

(Kump, 2008; Planavsky et al., 2014a). Existing evidence
strongly suggests that oxygen levels did not rise to the
present level for 2 Gyr after the GOE (Canfield, 2005).
The final rise of oxygen to present levels ∼0.5 Gyr ago
ended the nearly complete dominance of prokaryotes and
ushered in a new era characterized by an abundance of
multicellular life (Knoll, 2003).

The disappearance of mass-independent sulfur isotope
fractionation in mineral sulfides and sulfates provides the
most convincing evidence of the rise in oxygen ∼2.5 Gyr
ago (Farquhar et al., 2000; Bekker et al., 2004). Short
wavelength photochemical reactions were responsible for
mass-independent fractionations of gas-phase sulfur
compounds released from volcanoes during the Archean.
The preservation of these signals in the rock record
required very low-oxygen levels in the atmosphere where
photochemical reactions were occurring (Pavlov and
Kasting, 2002), and thus the disappearance of this signal
in rocks dating to ∼2.5 Gyr indicates that oxygen was
present in the atmosphere. A peak in the deposition of
banded iron formations is also observed around this time
(Isley, 1995), as well as the appearance of rusty red soils
(indicative of oxidized iron) (Holland, 2006) and the
disappearance of sedimentary detrital grains made from
easily oxidized minerals such as pyrite and uraninite
(Canfield, 2005). Cyanobacteria are the only microorgan-
isms capable of oxygenic photosynthesis and presumably
provided the first large-scale biotic source of oxygen on
early Earth, although oxygen produced biologically by
nitrite-driven anaerobic methane oxidation by oxygenic
bacteria could have also contributed to the GOE (Ettwig
et al., 2010). There is still some debate regarding the
timing of the emergence of oxygenic photosynthesis rela-
tive to intra-aerobic denitrification. Nevertheless, the evo-
lution of oxygenic photosynthesis in ancient
cyanobacteria, aided by geological changes such as
increased subaerial volcanism [which delivers oxidized
gases (H2O, CO2, SO2) in contrast to submarine volcan-
ism, which releases more reducing gases (H2, CO, CH4,
H2S) (Kump and Barley, 2007)], a decrease in the average
pressure of volcanic degassing (Gaillard et al., 2011) and
stabilization of the continents (Barley et al., 2005), trans-
formed Earth, ultimately providing conditions that ushered
in complex multicellular life forms.

The deep oceans most likely remained anoxic until ∼0.5
Gya when oxygen levels in the atmosphere rose to near
present levels. The prevailing view is that during this time,
the deep ocean was oxygen-poorest and iron-rich (Shen
et al., 2003; Planavsky et al., 2011) or sulfidic (euxinic)
(Meyer and Kump, 2008), particularly in restricted basins
and along productive margins (Scott et al., 2008; Lyons
et al., 2009; Poulton et al., 2010; Planavsky et al., 2011;
Poulton and Canfield, 2011). Euxinic conditions would
have been destabilized by increasing oxygen in the
atmosphere due to oxygenic photosynthesis (Eq. 1 below)
and the geologic trends discussed above. In fact, multiple
feedbacks that would act to destabilize Proterozoic-like
(sulfidic, low-oxygen) conditions in the world’s oceans
have been identified (Lyons and Gill, 2010). Nonetheless,
there is evidence in Proterozoic rocks for persistently
low-oxygen levels. The apparent loss of manganese (Mn)
from some mid-Proterozoic soils (palaeosols) and Cr iso-
topes ratios indicate limited terrestrial Mn oxidation
(Catling and Buick, 2006; Frei et al., 2009; Lyons et al.,
2014). Mn is particularly useful as a redox proxy because
the oxidation of Mn requires high-potential oxidants –
namely O2 or photosystem II (Kopp et al., 2005; Clement
et al., 2009; Johnson et al., 2014). Photosystem II is a
multi-subunit protein complex containing a Mn3CaO5
cluster that uses light energy to oxidize two molecules of
water to molecular oxygen during the light-dependent
reactions of oxygenic photosynthesis.

Fig. 1. Levels of atmospheric oxygen throughout Earth’s history.
The black line represents the ‘classical, two-step view’ of the
evolution of atmospheric oxygen over time (Kump, 2006), ignoring
proposed ‘whiffs’ in the Archean (Anbar et al., 2007) and the
proposed dynamic ‘Great Oxygen Transition’ (Lyons et al., 2014).
The grey boxes indicate the range of oxygen concentrations
compatible with currently accepted proxies. (Modified with
permission from Kump, 2008).
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In particular, we discuss the physiology of known methanotrophs, which play a key role in the regulation of atmospheric methane. Methane is primarily produced through fermentation and methanogenesis (Eq. 5) and hydrogenotrophic methanogenesis (Eq. 6). This input of methane to the atmosphere is countered by methane oxidation. Aerobic methanotrophs oxidize methane (Eq. 7) using monooxygenase enzymes requiring molecular O₂, whereas anaerobic methanotrophs (ANME) (Knittel and Boetius, 2009) catalyse the oxidation of methane using sulfate (Eq. 8) (Knittel and Boetius, 2009). A third, recently discovered route for the oxidation of methane occurs via nitrite-driven anaerobic methane oxidation (Eq. 9) (Ettwig et al., 2010); however, the contribution of this process to methane oxidation on a global scale is not known. Oxygen levels in the atmosphere are dictated by this balance between methane production and oxidation, in addition to the oxygen flux from the surface oceans due to net burial of organic carbon produced by oxygenic photosynthesis (Eq. 1).

\[
\begin{align*}
\text{CO}_2 + \text{H}_2\text{O} + \text{hv} & \rightarrow \text{CH}_2\text{O} + \text{O}_2 & (1) \\
\text{CO}_2 + \text{S}_{\text{red}} + \text{hv} & \rightarrow \text{CH}_2\text{O} + \text{S}_{\text{aq}} & (2) \\
\text{CO}_2 + 4\text{H}_2 + \text{hv} & \rightarrow \text{CH}_2\text{O} + 8\text{H}^+ & (3) \\
\text{HCO}_3^- + 4\text{Fe}^{2+} + 10\text{H}_2\text{O} + \text{hv} & \rightarrow \text{CH}_2\text{O} + 4\text{Fe(OH)}_3 + 7\text{H}^+ & (4) \\
2\text{CH}_2\text{O} & \rightarrow 4\text{H}_2 + \text{CO}_2 & (5) \\
4\text{H}_2 + \text{CO}_2 & \rightarrow 4\text{H}_2\text{O} & (6) \\
\text{CH}_4 + 2\text{O}_2 & \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} & (7) \\
\text{CH}_4 + \text{SO}_4^{2-} & \rightarrow \text{HCO}_3^- + \text{HS}^- + \text{H}_2\text{O} & (8) \\
3\text{CH}_4 + 8\text{NO}_2^- + 8\text{H}^+ & \rightarrow 3\text{CO}_2 + 4\text{N}_2 + 10\text{H}_2\text{O} & (9)
\end{align*}
\]

Below we consider in more detail the idea that organic matter burial in the absence of oxygen production delayed the accumulation of oxygen in Earth’s atmosphere. In particular, we discuss the physiology of known modern cyanobacteria and propose that metabolically versatile ( facultatively anoxygenic) cyanobacteria contributed to the protracted delay in the rise of oxygen after the initial GOE at the start of the Proterozoic Eon.

Sources and Sinks for O₂

There are four known biological reactions that produce oxygen – oxygenic photosynthesis, perchlorate or chlorate reduction, detoxification of reactive oxygen species such as superoxide (O₂⁻), hydrogen peroxide (H₂O₂) or the hydroxyl radical (OH), and nitrite-driven anaerobic methane oxidation (Ettwig et al., 2010). Oxygen can also be produced abiotically by photodissociation of H₂O and the subsequent escape of hydrogen gas to space. However, the rate of oxygen production through water photodissociation is low (Walker, 1977; Kasting and Walker, 1981). Therefore, accumulation of oxygen to appreciable levels required the emergence of at least one biological pathway.

Water-splitting photosynthesis is most commonly invoked as the only quantitatively important source of free oxygen on Earth’s surface. It is possible that oxygen production from intra-aerobic denitrification – nitrite-driven anaerobic methane oxidation – could have played a role in the production of oxygen during the Archean, when methane was more abundant in the atmosphere (Pavlov et al., 2000; Ettwig et al., 2010). However it seems likely that intra-aerobic detoxification evolved after oxygenic photosynthesis, as oxygenation began to increase the availability of nitrogen oxides that can be used as electron acceptors. Nitrate-dependent methane oxidation is a recent discovery and the contributions of this process to oxygen production and methane oxidation are still very poorly constrained. Regardless, oxygen production from nitrite should be considered in models that address the role of biology in planetary evolution.

In contrast, it is generally accepted that detoxification of reactive oxygen species evolved only after oxygenic photosynthesis, with the first mechanisms of defence based on physical barriers (Bilinski, 1991) rather than enzymatic conversion. Today, perchlorate occurs naturally but rarely in the environment. Elevated concentrations are found in the Chilean saltpetre deposits or attributed to anthropogenic contamination (Rao et al., 2010). Perchlorate can be generated in the atmosphere but only in trace amounts by the oxidation of chlorine species through pathways involving ozone or its photochemical products (Catling et al., 2010). Thus, oxygen resulting from perchlorate or chlorate reduction would have only played a role following the development of the ozone layer and even then, would only represent a small fraction of the oxygen budget.

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Geochemical data including redox-sensitive proxies support the hypothesis that biological oxygen production evolved before the GOE. O₂-consuming reactions coupled with volcanism and continent formation buffered the oxygen additions from oxygenic photosynthesis and maintained low levels of O₂ in the atmosphere throughout the Archean. Today, almost all primary production is carried out by oxygenic phototrophs (plants, algae, cyanobacteria), and oxygen levels are therefore determined by the balance between organic carbon burial and a diminished supply of reductants from the deep Earth via volcanic activity and metamorphism (Holland, 1978; 1984). Thus, for oxygen to accumulate in the atmosphere, the sedimentary carbon burial rate had to exceed the rate of O₂ consumption by reductants supplied to the atmosphere and ocean by geologic processes. The accumulation of oxygen may have been aided by other processes such as hydrogen escape to the atmosphere (Catling et al., 2001). During the Archean, reducing conditions were sufficient to scavenge free oxygen. Free oxygen would have been rapidly consumed by reduced metamorphic and submarine volcanism releasing reduced forms of hydrogen, carbon, sulfur and iron (Catling, 2014). As a result, oxidizing the Earth’s atmosphere and oceans required oxidizing large reservoirs of reductants including reduced iron. Following this initial rapid rise and perhaps overshoot (Lyons et al., 2014), atmospheric oxygen concentrations remained well below current levels throughout much of the Proterozoic. The cause of the protracted delay in the oxygenation of Earth’s surface is the subject of debate, and almost certainly involves feedbacks between Earth’s biota and elemental cycles – specifically the dominant primary producers and carbon cycle – as is true for modern biogeochemical systems.

**Phototrophy**

The ability to harvest light and convert it to chemical energy represents one of the most elegant and complex biological innovations to date – and notably it connected biology directly to the primary source of energy for Earth, namely the sun (Sleep and Bird, 2008). Phototrophs convert light energy to chemical energy employing either photochemical reaction centres (RCs) containing (bacterio)chlorophylls or rhodopsins. Rhodopsins (retinal binding proteins; bacteriorhodopsin, proteorhodopsin and xanthorhodopsin) are involved in light–energy conversion by direct transduction of photons into proton motive force but do not mediate electron transfer reactions. During photosynthesis, both electrons and ATP are required. Therefore organisms containing rhodopsins can produce ATP using light (phototrophy) but cannot carry out photosynthesis (Bryant and Frigaard, 2006). The genetic capacity to produce rhodopsins is widespread in marine environments (Venter et al., 2004) and occurs in the genomes of diverse prokaryotes as well as several multicellular organisms (i.e. fungi, green algae), although the exact functions are not always known (Bryant and Frigaard, 2006). Regardless of the function, phototrophy employing rhodopsins appears to be a trait that can easily be horizontally transferred because it requires the acquisition of only two genes, bacteriorhodopsin and β-carotene oxygenase, if an organism can already synthesize the common pigment β-carotene.

Unlike rhodopsin-based phototrophy, chlorophyll-based phototrophy (chlorophototrophy) probably has not been spread as promiscuously by horizontal gene transfer, although there is excellent evidence that Gemmatimonas aurantiaca T-27 acquired an intact photosynthesis gene cluster from a purple sulfur bacterium (Zeng et al., 2014). This is probably due in part to the number of genes required to assemble the more complex but also more efficient chlorophyll-based photosystems. All chlorophotrophic organisms use photochemical RCs containing (bacterio) chlorophylls (BChls or Chls) to capture solar energy and convert it into chemical energy (Bryant and Frigaard, 2006; Gomez Maqueo Chew and Bryant, 2007). Photosynthetic prokaryotes are currently found within seven bacterial phyla (Acidobacteria, Chlorobi, Chloroflexi, Cyanobacteria, Gemmatimonadetes, Proteobacteria and Firmicutes) (Fig. 2).

**Chlorophototrophs**

Cyanobacteria are the only chlorophototrophic bacteria that perform oxygenic photosynthesis, photo-oxidizing water and evolving oxygen via two RCs, Photosystem (PS) I and PS II. PS I acts as an oxidoreductase, transferring electrons from cytochrome c₆ or plastocyanin to the electron carriers ferredoxin or flavodoxin. It produces a weak oxidant and a strong reductant in doing so. PS II catalyses the light-dependent oxidation of water and reduction of plastoquinone by making a strong oxidant and weak reductant. In this chlorophyll a-based system, blue and red lights are efficiently harvested. In oxygenic photosynthesis water serves as the electron donor and dioxygen is released as a by-product. Anoxygenic phototrophs employ one RC, which may be either type 1 or type 2, but do not evolve oxygen and generally absorb light in the blue and near-infrared regions of the solar spectrum. Anoxygenic photosynthesis relies on a supply of reducing equivalents from reduced sulfur compounds, organic acids, hydrogen, nitrite or Fe(II) to drive CO₂ reduction.

**Niches of extant prokaryotic phototrophs**

The co-occurrence of cyanobacteria and anoxygenic phototrophs is common in eutrophic lakes, phototrophic
microbial mats, hot springs and hypersaline lagoons where sufficient fluxes of reduced compounds are available to support anoxygenic photosynthesis. The ability to harvest light and tolerance to oxygen are most often cited as the key factors governing occurrence of phototrophs in ecological niches along stratified water columns and mats. For instance, green and purple sulfur bacteria (GSB and PSB) are found in most sunlit, sulfidic environments, where PSB are generally found at more shallow depths in the water column or mats (Overmann and Garcia-Pichel, 2006; Meyer et al., 2011). GSB have lower light requirements and are generally less tolerant to oxygen. In addition, GSB have higher affinity for sulfide than PSB, conferring a competitive advantage over PSB when reduced sulfur compounds are limiting (Van Gemerden and Garcia-Pichel, 2006; Meyer et al., 2011). GSB have lower light requirements and are generally less tolerant to oxygen. In addition, GSB have higher affinity for sulfide than PSB, conferring a competitive advantage over PSB when reduced sulfur compounds are limiting (Van Gemerden and Garcia-Pichel, 2006; Meyer et al., 2011). GSB have lower light requirements and are generally less tolerant to oxygen. In addition, GSB have higher affinity for sulfide than PSB, conferring a competitive advantage over PSB when reduced sulfur compounds are limiting (Van Gemerden and Garcia-Pichel, 2006; Meyer et al., 2011).

Extant members of the phylum Cyanobacteria are metabolically diverse and include species that can perform anoxygenic photosynthesis in the presence of high sulfide (Cohen et al., 1975a,b) in environments where sulfide is present in the photic zone (Jørgensen et al., 1983; 1986). Some cyanobacteria can also use hydrogen as an electron donor (Cohen et al., 1986), perform sulfide-dependent nitrogen fixation (Belkin et al., 1982), and/or grow phototrophically (Kenyon et al., 1972; Rippka et al., 1979). This phenotypic diversity enables cyanobacteria to tolerate a variety of environmental extremes, and results in their ability to occupy niches in almost any environment where light is available, including many in which they are important primary producers. For example, benthic cyanobacterial mats in Solar Lake, Sinai, a hypersaline pond, undergo drastic yearly changes in temperature, salinity, oxygen, light and H2S. Cyanobacterial mats in Solar Lake are dominated by metabolically diverse cyanobacteria such as Oscillatoriopsis species that are capable of anoxygenic photosynthesis and phototaxis (Cohen et al., 1975a; Krumbien et al., 1977). Similarly, Phormidium species survive freezing and desiccation in Antarctica (Taton et al., 2003) and persist in the low O2 conditions in the Middle Island Sinkhole of Lake Huron (Voorhies et al., 2012).

In some extant environments such as photic zones where oxygen and sulfide coexist, the ecological niches of anoxygenic phototrophs and cyanobacteria can overlap (Klatt et al., 2011; 2013). For instance, in some stratified lakes, the oxic/anoxic interface is shallow and supports dense layers of anoxygenic phototrophs. These conditions mimic those thought to be present in areas of the Proterozoic oceans, especially along continental shelf margins. In these systems today, anoxygenic photosynthesis can be the main source of primary production (Van Gemerden and Mas, 1995).

**Facultatively anoxygenic photosynthesis among cyanobacteria**

Despite their crucial role in the oxygenation of Earth’s surface and atmosphere, cyanobacteria persisted under low oxygen and/or sulfidic conditions throughout much of Earth’s history. Because PS II can be inhibited by sulfide, taxonomically diverse extant cyanobacteria display a wide range of sulfide tolerances. The species most sensitive to sulfide are typically planktonic cyanobacteria, which occupy sulfide-free environments in the modern oceans.
However cyanobacteria are often observed in the surface layers of stratified ( euxinic) lakes, where they may be exposed to sulfide (Melak and Kilham, 1974; Cohen et al., 1975a; 1986). In species that inhabit sulfide-rich environments, PS II often displays higher tolerance to sulfide to maintain oxygenic photosynthesis. In sunlit environments where sulfide is present, some cyanobacteria can use sulfide as the electron donor to PS I in the absence of oxygen generation (Cohen et al., 1975a,b; Padan, 1979; Padan and Cohen 1982; Castenholz et al., 1990; 1991), enabling PS II-independent photoassimilation of CO2 with the same efficiency as oxygenic photosynthesis (Oren et al., 1977; Oren and Padan, 1978).

Biochemical characterizations suggest that cyanobacteria employ a sulfide-quinone oxidoreductase (Sqr) to oxidize sulfide, providing electrons to PS I. Some anoxygenic phototrophs such as members of the phyla the Chioroflexi and Chiorobi also employ Sqr to oxidize sulfide for anoxygenic photosynthesis. Members of the Chlorobi (GSB) oxidize elemental sulfur and sulfide to sulfate, and several strains also oxidize thiosulfate. Sulfide is the preferred substrate and GSB typically have a high affinity for sulfide (Brune, 1995; Frigaard and Bryant, 2008). In pure cultures, GSB typically oxidize sulfide to elemental sulfur, which is deposited extracellularly, until sulfide is depleted, then these organisms oxidize extracellular elemental sulfur to sulfate (Frigaard and Bryant, 2008). Other anoxygenic phototrophs, including some GSB and PSB, have evolved the thiosulfate-oxidizing Sox enzyme complex to oxidize reduced sulfur compounds (Frigaard and Dahl, 2008). Using the Sox system, GSB and PSB oxidize thiosulfate, producing polysulfide and sulfate. Other reduced substrates such as H2 and Fe(II) often serve as electron donors for anoxygenic photosynthesis. However, members of the phylum Cyanobacteria are not known to utilize substrates other than sulfide for PS II-independent photosynthesis. Stoichiometric oxidation of sulfide to thiosulfate has been observed in pure cultures of Microcoleus chthonoplastes strain 11 (de Wit and van Gemerden, 1987), whereas other anoxygenic Cyanobacteria (i.e. Oscillatoria spp.) oxidize sulfide to elemental sulfur that accumulates extracellularly (Cohen et al., 1975a,b; Castenholz and Utikilen, 1984). Oxidation of thiosulfate (requiring the Sox pathway) has not been demonstrated in cyanobacteria.

Examples of characterized cyanobacteria capable of anoxygenic photosynthesis are relatively rare. A number of Oscillatoria spp. have been isolated from sulfidic environments, and most of the cyanobacteria capable of performing anoxygenic photosynthesis appear to belong to this genus (Cohen et al., 1975a,b; Jørgensen et al., 1986; de Wit and van Gemerden, 1987; Castenholz et al., 1991; Voorhies et al., 2012). However, the Oscillatoria spp. are paraphyletic. In addition, the biochemical underpinnings of electron flow to PS I via sulfide-quinone oxidoreductase in anoxygenic photosynthesis by cyanobacteria is not well studied, and thus the evolutionary history of anoxygenic photosynthesis by cyanobacteria is still rather mysterious. Anoxygenic photosynthetic cyanobacteria studied to date have low affinity for sulfide compared with PSB and GSB; this suggests that cyanobacteria should not be competitive where these phototrophic groups coexist and sulfide is limiting (de Wit and van Gemerden, 1987; Castenholz et al., 1990; 1991). More recent observations suggest that the light-independent enzyme kinetics of Sqr control the rates of anoxygenic photosynthesis in cyanobacteria when the sulfide concentration is low. In contrast, at higher levels of sulfide, light intensity dictates the upper limit of anoxygenic photosynthesis rates (Klatt et al., 2015). These observations are further complicated by our lack of understanding of the mechanism of sulfide inhibition of PS II, and underscore the need for further characterization of anoxygenic photosynthetic activity in modern cyanobacteria.

Geochemical proxies for the emergence of oxygenic photosynthesis

Cyanobacteria are the only prokaryotes capable of producing O2 (via oxygenic photosynthesis) and were presumably the earliest organisms to do so, yet there is no consensus on the timing of the emergence of this metabolism. Current estimates span almost one third of Earth’s history – from 3.7 to 2.3 Gyr. Definitive organic biomarkers for cyanobacteria during this time are lacking, leaving geochemical proxies in the form of isotopes or trace metals as the best evidence for O2 in the atmosphere before the GOE. Interpretation of these geologic signatures remains challenging due to the fact that at least three other biological pathways are known to produce oxygen, one of which may have emerged before the phylum Cyanobacteria. The presence of banded iron formations before the GOE strongly suggests local oxygen production through biological means because abiotic oxidation of iron is slow in the absence of oxygen and because UV-induced Fe oxidation has not been demonstrated in seawater. Fe(II) oxidation can be catalysed by chemosautotrophs in microaerophilic environments (Canfield, 2005 and references therein) or by anoxygenic phototrophs (Widdel et al., 1993). Given that oxygen could have been produced under anoxic conditions from nitrite via intra-aerobic denitrification (Ettwig et al., 2010), both chemosautotrophic Fe(II) oxidation and photoferrotrophy could account for the presence of banded iron formations before the GOE (Konhauser et al., 2002; Kappler et al., 2005; Crowe et al., 2008).

In addition to the disappearance of mass-independent fractionation of sulfur isotopes (Farquhar et al., 2000; Bekker et al., 2004), post-GOE marine sediments
acquired with drill cores rich in redox-sensitive trace metals such as Mo have been cited as evidence for O₂ in the atmosphere, implying oxidative weathering of sulfide minerals in the continental crust. For instance, the enrichment of Mo and Re in organic-rich shales dated to 2.5 Gyr lead to the idea that ‘whiffs’ of O₂ accumulation occurred before the GOE (Anbar et al., 2007). Recent studies exploiting Mo isotopes as proxies for manganese oxides date oxygen production to ~3 Gyr (Planavsky et al., 2014b). In this study, large isotopic shifts are constrained to a thin horizon, which the authors interpret as localized oxygen production and consumption in an otherwise reducing environment. Similarly, Cr isotopes and redox-sensitive metals in rocks from the Pongola Supergroup in South Africa indicate the presence of atmospheric oxygen ~3 Gyr (Crowe et al., 2013). Other evidence bolstering the accumulation of atmospheric oxygen around 2.5 Gyr include the persistence of redox-sensitive uraninite, pyrite, and siderite detrital grains in Archean sedimentary rocks (Rasmussen and Buick, 1999), increased iron in paleosols (Rye and Holland, 1998), and the enrichment of Cr and U in iron-rich sedimentary rocks (Konhauser et al., 2011; Partin et al., 2013).

Shales rich in organic matter dating to the Archean are common. These deposits of organic carbon are isotopically indistinguishable from modern deposits deposited in similar environments (Lyons et al., 2014). Given the mildly reducing atmosphere and anoxic oceans present at the time, the deposition of large amounts of organic matter due to biological activity in Archean sediments is difficult to interpret. Sulfide-dependent anoxygenic photosynthesis is difficult to maintain in the absence of an external source of organic carbon (for sulfide production via SRB) (Overmann et al., 1996; Hamilton et al., 2014). Furthermore, the Archean oceans were low in sulfate, which did not accumulate until oxidative weathering of sulfides on the continents increased sulfate fluxes to the ocean. In the absence of sulfate and sufficient organic carbon, biological sulfate reduction sufficient to fuel significant primary productivity via anoxygenic photosynthesis does not seem likely. Further evidence against a total organic carbon (TOC) pool driven by H₂S-based primary productivity is that organic-rich Archean shales appear to have originated in Fe²⁺-rich waters (Reinhard et al., 2009). Alternative electron donors such as ferrous iron (Fe²⁺) or hydrogen (H₂) may have been less abundant than H₂O, the electron donor for oxygenic photosynthesis, but could nonetheless have fuelled significant anaerobic primary production (anoxygenic photosynthesis) in the Archean.

Biomarkers for oxygenic photosynthesis

Microbial life leaves a poor fossil record and much of the geological record for life is recorded in microbially influenced sedimentary structures. Throughout the Proterozoic, the fossil record of photosynthetic microbial communities is robust – stromatolitic carbonates (laminated, lithified sedimentary structures) identified along continental margins in Proterozoic rocks have been attributed to cyanobacteria (Walter, 1976). If these structures are well preserved, relationships between microbial community and environmental characteristics can be discerned (Awramik and Semikhatov, 1979; Seong-Joo and Golubic, 1999; Knoll et al., 2013). However, microbial fossils older than ~2.5 Gyr are both rare and potentially obscured by multiple generations of geologic events, and linking them to specific metabolisms or taxonomic groups remains difficult. Furthermore, the biogenicity of stromatolites and microbially induced sedimentary structures dating to the Archean are still controversial (Bosak et al., 2013) and these structures rarely contain definitive microbial body fossils (Mackey et al., 2015). In addition, recent analyses indicate that previously sampled Archean sedimentary rocks host biomarker contaminants accumulated during sample collection and processing and overmature hydrocarbons (French et al., 2015). Thus, previously reported Archean biomarkers do not provide good evidence for the rise of oxygenic phototrophs prior to the GOE (French et al., 2015). Regardless, cyanobacteria today are key primary producers in laminated mats that also host anoxygenic phototrophs, sulfate-reducing organisms and methanogenic archaea. These modern microbial mats provide model systems for interpreting Archean and Proterozoic stromatolites. These structures are common in hypersaline and alkaline environments as well as at geothermal and other groundwater springs. The morphology of stromatolites and laminated mat structures is influenced by both environmental characteristics and microbial processes and thus these modern analogues inform the processes and microbial taxa that created the ancient structures. There are numerous examples of modern analogues of actively forming or recently formed stromatolitic structures such as those in Lake Joyce and Lake Fryxell, Antarctica (Mackey et al., 2015; Sumner et al., 2015), alkaline salt lakes (Arp et al., 1999) and marine environments (Reid et al., 2000; Visscher et al., 2000; Burns et al., 2004; Pagès et al., 2014) as well as 2000-year-old structures in Lagoa Salgada, Brazil, (Birgel et al., 2015). Examples of modern stromatolites and mats in low-oxygen environments including riverbed, lacustrine, estuarine, and benthic sediments are of particular interest because these environments may have served as oxygen oases before the GOE (Lalonde and Konhauser, 2015; Sumner et al., 2015). Furthermore, examples of well-preserved mats and stromatolites from the Mesoproterozoic (Knoll et al., 2013), the Jurassic (Heffer et al., 1993) and Early Triassic (Heindel et al., 2015) are consistent with the presence of
layered mats containing both oxygenic and anoxygenic phototrophs in saline, low-oxygen marine environments thought to be prevalent on early Earth.

In addition to stromatolitic structures, biomarkers for cyanobacteria and other phototrophs include lipids, carotenoids and chlorophylls, and the recovery of these fossil hydrocarbons have been used to infer phototrophic community structure (Brocks et al., 2005). For instance, the caroteneoid pigment okeneone is preserved as the hydrocarbon fossil equivalent okenane. Some members of the Chromatiaceae, anoxygenic phototrophic PSB, make okeneone (Vogl and Bryant, 2012), and thus okenane has been used as biomarker for PSB. Similarly, some GSB synthesize isorenieratene (some of the BCHl e-producing species) or chlorobactene (BCHl c/d-producing spp.) (Maresca et al., 2008), which are preserved as isorenieratane and chlorobactane, respectively, upon diagenesis. Other hydrocarbons that are typical breakdown products of aromatic carotenoids have been identified as biomarkers of photosynthesis (Brocks and Summons, 2004) although many organisms that do not harvest sunlight for growth also produce carotenoids. For cyanobacteria, 2-methylbacteriohopanepolysols were originally thought to be synthesized exclusively by cyanobacteria (Summons et al., 1999). The hopanoid hydrocarbon backbone and methylation at the C-2 position is preserved upon diagenesis. Recent studies indicate that organisms from several clades make these lipids, including some anoxygenic phototrophs (Rashby et al., 2007; Welander et al., 2010), and they are not synthesized in the most abundant modern cyanobacteria (Talbot et al., 2008). Components of cyanobacterial lipids, specifically mid-chain branched monomethylalkanes, have been used to infer the presence of cyanobacteria (Shiea et al., 1990; Schirmer et al., 2010). The production of mid-chain branched monomethylalkanes is nearly universal among cyanobacteria and the major product is 7-methyleneptadecane. There are examples of other organisms that produce 7-methyleneptadecane although those organisms employ a different biosynthetic pathway. The biosynthesis of 7-methyleneptadecane in cyanobacteria proceeds through a pathway that to date has only been observed in members of the cyanobacterial clade (Coates et al., 2014) and requires the presence of molecular oxygen (Li et al., 2011; 2012). Methylated heptadecanes have been recovered from a variety of environments including freshwater microbial mats of calcifying cyanobacteria (Thiel et al., 1997), hot spring cyanobacterial mats (Shiea et al., 1990), microbial carbonates (Arp et al., 1999), carbonate samples from the Late Jurassic (Hefter et al., 1993) and stromatolitic carbonate rocks that have been inhabited by cyanobacteria since the Cenozoic Eon (Hoshino and George, 2015). Thus, mid-chain branched monomethylalkanes could be promising biomarkers for ancient cyanobacteria.

**Phylogenetic reconstructions dating the emergence of oxygenic photosynthesis**

The increasing availability of genomic sequence data, coupled to the study of model organisms, is greatly enhancing our ability to examine the phylogenetic relatedness of extant life and can aid in the elucidation of the timescale of the evolution of life. In the absence of concrete fossil evidence for the earliest life forms, intense debate has led to diverse hypotheses regarding the timing, form and physiological capabilities of the first forms of life. A common hypothesis invokes a thermophilic origin with subsequent spread and diversification of physiological strategies including photosynthesis. Some reconstructions suggest that the emergence of photosynthesis occurred early in the evolution of life (~3.6 Gya) although the time estimate is very broad (2.80–3.63 Gya) (Battistuzzi et al., 2004). These estimates are consistent with geological evidence for life that indicates that Earth has been inhabited for at least 3.8 Gya. However, the early emergence – 3.6 Gya – of photosynthesis requires high rates of evolution and innovation. Evidence for a rapid increase in genetic innovation from 3.3 to 2.8 Gya emerges from the analysis of O2-binding gene families during this ‘Archean Expansion’ (David and Alm, 2011) – consistent with a stable source of oxygen, even if restricted to local environments (Anbar et al., 2007; Olson et al., 2013). However, multiple lines of phylogenetic evidence suggest that the less complex anoxygenic mode of photosynthesis evolved before oxygenic photosynthesis (Blankenship, 2001; Xiong and Bauer, 2002; Sadekar et al., 2006; Bryant and Liu, 2013). Debate remains regarding the nature and phylogenetic affiliation of the first anoxygenic phototrophs. Molecular evolution studies support geochemo- and organic biomarker data, which date the emergence of oxygenic photosynthesis to ~2.5 to 2.8 Gya (Rye and Holland, 1998; Brocks et al., 1999; Des Marias, 2000; Hedges et al., 2001; Xiong and Bauer, 2002) (Fig. 1). Unfortunately, phylogenetic reconstructions are often constrained using absolute dates derived from studies of biomarkers, isotopic signatures or geochemical proxies recorded in the rock record. These data are further confounded by evidence for lateral gene transfer between phototrophic bacteria (Raymond et al., 2002). As such, building an independent and robust phylogenetic record of the emergence of chlorophotrophy remains a difficult challenge, evidenced for example by the growing controversy regarding the interpretation of Archean biomarker records (Rasmussen et al., 2008; Brocks, 2011; French et al., 2015). Regardless, the majority of geologic, isotopic
and phylogenetic analyses indicate that oxygenic photosynthesis emerged before the GOE.

Proterozoic oceans

Models of Earth's surface oceans throughout the Proterozoic range from fully oxic to euxinic to ferruginous (anoxic and rich in reduced iron). Ferruginous conditions are likely to have prevailed in the open oceans throughout most of Earth's history, whereas continental shelf margins were most likely euxinic and host to the majority of marine primary production (Lyons et al., 2014). Today, biological sulfate reduction serves as the main pathway for the anaerobic mineralization of organic matter on continental margins (Jørgensen, 1982), and presumably, these regions would have had the highest organic matter loading during the ancient past. If Proterozoic oceans were mostly ferruginous, it is plausible that primary productivity driven by Fe$^{2+}$-dependent anoxygenic photosynthesis could have been widespread in the open ocean. However, appreciable amounts of oxidized iron from this time are not apparent in the geologic record, and it has been hypothesized that upwelling Fe(II) would react with oxygen, producing reactive oxygen species that are toxic to phototrophs (Shkolnick et al., 2009). Indeed, laboratory experiments on Synechococcus sp. PCC 7002 and geochemical modelling indicate that Fe(II) toxicity would have limited primary productivity in zones of Fe$^{2+}$ upwelling (Swanner et al., 2015). In addition, examples of extant anoxygenic phototrophs that utilize Fe$^{2+}$ for CO$_2$ photoassimilation are rare compared with those that prefer reduced forms of sulfur (Fig. 2). One notable example is Rhodopseudomonas palustris strain TIE-1, a purple non-sulfur bacterium that grows photo-autotrophically by oxidizing Fe$^{2+}$ or H$_2$ (Jiao et al., 2005). TIE-1 synthesizes 2-methyl hopanoids and a significant variation in methylation at the C-2 position was observed between electron donors – an observation that may be relevant to interpreting biosignatures in the sedimentary record (Eickhoff et al., 2013). In any case, Fe$^{2+}$ as an electron donor for anoxygenic photosynthesis in cyanobacteria has not been demonstrated among extant organisms. The distribution and activity of terrestrial cyanobacteria during this time also remains poorly defined. Based on currently available evidence, the major sources of primary productivity on early Earth appear to have been marine, especially at ocean margins and in restricted basins where euxinic conditions were prevalent (Lyons et al., 2014 and references therein). Some models indicate that areas experiencing vigorous vertical mixing or strong upwelling could have hosted high productivity, potentially resulting in mild oxygenation even before the GOE (Olson et al., 2013).

Although vertical redox stratification is the most often cited condition of Proterozoic oceans, many current conceptual models overlook lateral mixing, which could have important consequences, especially in the photic zone. Assuming that sulfide-rich deep-water upwelling would deliver sulfide to the surface oceans, the flux of which could exceed the downward mixing of oxygen (Meyer and Kump, 2008). In the absence of ample wind-mixing, sulfide would reach the surface in areas where the upward sulfide flux exceeds wind-mixed oxygen flux (Kump et al., 2005). This flux of sulfide to the photic zone would have been sufficient to support anoxygenic photosynthesis.

Proterozoic cyanobacteria

Although an important role for cyanobacteria in the rise of oxygen on early Earth is not disputed, the cause of the ~2 billion year period following the GOE during which atmospheric levels of oxygen remained far below those observed today remains poorly understood. Extant cyanobacteria occupy diverse habitats, some of which are sulfide rich; however, given the large differences in energetics between oxygenic and anoxygenic chlorophotrophs and the ubiquity of H$_2$O as an electron donor, a scenario selecting for abundant PS II-independent CO$_2$ photoassimilation by Proterozoic marine cyanobacteria seems unlikely. Assuming the relatively simple model of Sqr-catalysed sulfide oxidation providing electrons for PS I-dependent photosynthesis, Sqr-containing cyanobacteria could presumably utilize either H$_2$O or H$_2$S in sulfide-rich photic zones such as those present at continental margins throughout much of Earth’s history. Modern anoxygenic photosynthetic cyanobacteria oxidize sulfide to S(0) or polysulfide as the end-product (Cohen et al., 1975a,b). In the model of Earth’s middle age that was sustained by anoxygenic photosynthesis (Johnston et al., 2009), S(0) production by Proterozoic primary producers is involved in a second feedback loop that results in pyrite precipitation and burial, a necessary step for balancing sulfide concentrations. According to the model, organic matter-associated S(0) or polysulfide (formed through the reaction of S(0) with sulfide in the water column) is exported to the sediments and, with H$_2$S and Fe$^{2+}$, forms pyrite. It is worth noting that ancient cyanobacteria performing anoxygenic photosynthesis in a sulfidic water column could have also contributed polysulfide, similar to extant cyanobacteria, and thus played a role in preventing runaway sulfide production. In fact, pyrite formation involving iron(II) and polysulfide is one of only three established mechanisms for pyrite formation (Rickard, 1975; Luther, 1991; Rickard and Luther, 2007).
Although examples are rare, observations of cyanobacteria performing both oxygenic and anoxygenic photosynthesis simultaneously have been documented (de Wit and Gemerden, 1987; Klatt et al., 2015). In extant cyanobacteria, a 2-h induction time is observed before sulfide-dependent anoxygenic photosynthesis unless sulfide is provided during the previous diel cycle (Klatt et al., 2015). It is plausible that early in the evolution and fine-tuning of PS II and oxygen production, both processes occurred in parallel. Considering that PS I and PS II have different absorption spectra (Oren et al., 1977) and that oxygenic photosynthesis requires both photosystems, the spectral quality of light reaching the photic zone would impact the efficiency of these processes. Indeed, in a cyanobacterium performing both oxygenic and anoxygenic photosynthesises simultaneously, rates of anoxygenic photosynthesis are governed by light and H₂S concentration and are not affected by oxygenic photosynthesis (Klatt et al., 2015). In phototrophic mat systems, cyanobacteria switch between oxygenic and anoxygenic photosynthesis on a daily cycle, consuming sulfide in the early morning when this substrate is more abundant. In Proterozoic oceans, niche overlap and niche separation of phototrophs could have been similar to those observed in stratified water columns today. A simplified model of the Proterozoic water column would consist of oxygenic cyanobacteria in the upper layers with anoxygenic phototrophs (including cyanobacteria) occupying the sulfide-rich lower layer of the photic zone (Fig. 3). Other sulfur-oxidizing strategies (i.e. Sox, sulfur storage) such as those present in PSB and GSB could also be ancient relics of Proterozoic oceans. For instance, thiosulfate concentrations would have increased in waters where oxygen and sulfide are present and fluctuating sulfide concentrations could have provided the selective pressure to store elemental sulfur. Versatile cyanobacteria would have consumed some of the sulfide, enabling evolution and fine-tuning of oxygenic photosynthesis in the upper oxic layers. These organisms would have produced some oxygen, providing selective pressure for anoxygenic phototrophs to adapt to varying sulfide concentrations as well as to retreat to deeper regions of the water column. This metabolic versatility would provide cyanobacteria a selective advantage over oxygen-sensitive phototrophs, especially given that surface oceans were most likely heterogeneous with respect to redox gradients (Olson et al., 2013). These characteristics are especially apparent in GSB, which are very sensitive to oxygen, produce strong reductants through carbon fixation via the reverse TCA cycle and occupy the lowest light niches of extant phototrophs (Frigaard and Bryant, 2008).

A further complication in our picture of primary productivity in early Earth oceans emerges from evidence that fixed sources of nitrogen (ammonia, nitrate) may have been limiting, especially in surface waters. Nitrogen fixation, the biologically mediated reduction of N₂ to ammonia, would have been a major source of fixed N for primary producers within the photic zone. Nitrogen fixation has a significant biological cost – the process is energetically demanding, requiring 16 ATP to reduce one mole of N₂, and the enzymatic machinery is oxygen sensitive. Among extant organisms, only a small subset of microorganisms is known to catalyse dinitrogen reduction. These organisms include some cyanobacteria and anoxygenic phototrophs, and some methanogenic archaea. To date, nitrogen fixation has not been observed in eukaryotes. In the nitrogen-poor Proterozoic oceans, a steady supply of ATP would be required for use in N₂ fixation among phototrophic diazotrophs. This supply could come from photosynthetic activity or fermentation. An intriguing possibility is that ancient cyanobacteria exploited energy production using PS I alone or PS I and PS II together to fuel both primary productivity and nitrogen fixation. The genome of a globally distributed, uncultivated marine cyanobacteria, UCYN-A, lacks genes encoding photosystem II and carbon fixation, indicating it cannot perform oxygenic photosynthesis; however, the organism appears to use photosystems I to fuel a light-dependent fermentative metabolism and fix nitrogen (Zehr et al., 2008; Tripp et al., 2010). In Geitlerinema sp. PCC 9228...
(formerly *Oscillatoria limnetica*), a typical photoautotrophic cyanobacterium, rates of N2 fixation are elevated in the presence of sulfide (Belkin *et al*., 1982), although the mechanism of this rate enhancement is not understood. Regardless, even limited characterization of extant cyanobacteria supports the hypothesis that ancient ancestors of these organisms could have contributed significantly to primary productivity in the absence of oxygen production, even if sources of fixed nitrogen were limiting.

**Concluding remarks and future perspectives**

Understanding the role of photosynthesis in the rise of oxygen on Earth is a challenging task. Our current knowledge of anoxygenic photosynthesis strongly suggests that these organisms, including cyanobacteria, played a role in delaying the rise of oxygen in Earth’s atmosphere after the GOE. Recent investigations of sunlit environments where sulfide and oxygen coexist have revealed metabolically versatile cyanobacteria capable of both oxygenic and anoxygenic photosynthesis (Voorhies *et al*., 2012; Hamilton *et al*., 2013; Klatt *et al*., 2015). These extant organisms and ecosystems are our best models for interrogating the environmental and ecological controls on primary productivity and oxygen production in Earth’s past. A better understanding of the metabolic diversity, physiology, ecology and evolutionary history of cyanobacteria in these ancient analogue environments is needed. Omics approaches well within our technical grasp have the potential to reveal the identity and evolutionary origin of methanogenesis, phototrophy, and the colonization of land. A better understanding of the metabolic diversity, physiology, ecology and evolutionary history of cyanobacteria in these ancient analogue environments is needed. Omics approaches well within our technical grasp have the potential to reveal the identity and evolutionary history of genes and regulatory mechanisms that ancient ancestors of these organisms could have contributed significantly to primary productivity in the absence of oxygen production, even if sources of fixed nitrogen were limiting.

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