

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 Eon, 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)

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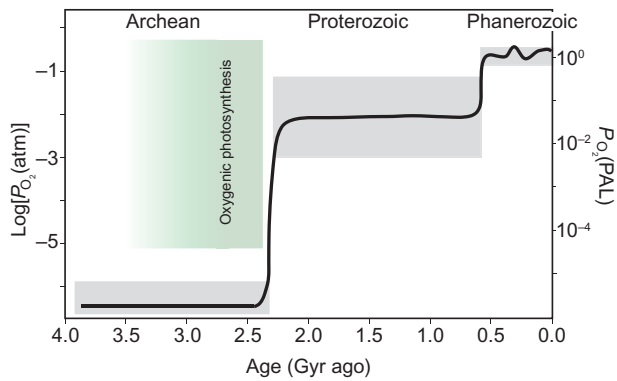


Fig. 1. Levels of atmospheric oxygen throughout Earth's history. The black line represents the 'classical, two-step view' of the evolution of atmospheric oxygen over time (Kump, 2008), ignoring proposed 'whiffs' in the Archean (Anbar *et al.*, 2007) and the proposed dynamic 'Great Oxygen Transition' (Lyons *et al.*, 2014). The grey boxes indicate the range of oxygen concentrations compatible with currently accepted proxies. (Modified with permission from Kump, 2008).

(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).

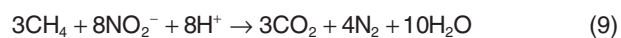
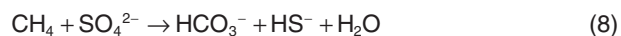
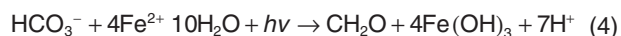
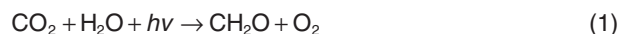
The disappearance of mass-independent sulfur isotope fractionation in mineral sulfides and sulfates provides the most convincing evidence of the rise in oxygen ~2.5 Gyr ago (Farquhar *et al.*, 2000; Bekker *et al.*, 2004). Short wavelength photochemical reactions were responsible for mass-independent 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 microorganisms 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 relative 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 (H_2O , CO_2 , SO_2) in contrast to submarine volcanism, which releases more reducing gases (H_2 , CO , CH_4 , H_2S) (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), transformed 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-poor 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 isotopes 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 O_2 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 Mn_4CaO_5 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 conditions 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 photosynthesis. In this scenario, the activity of anoxygenic photosynthesis 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 O_2 production. The resulting positive feedback would stall the accumulation of O_2 at levels much lower than those observed today, consistent with redox-sensitive proxies in

the rock record. The maintenance of euxinic conditions in this scenario relies on phototrophic sulfide oxidation as the main source of electrons for organic matter fixation. A second idea perhaps complementary to the scenario above considers the total flux of reductants and oxidants to the atmosphere (Goldblatt *et al.*, 2006). In this conceptual model, concentrations of atmospheric methane resulting from anaerobic respiration are controlled by the balance between input (methane) and loss of reductants – due to hydrogen escape to space (Goldblatt *et al.*, 2006). Today, fluxes of methane are regulated by aerobic methanotrophic bacteria, the methanogenic archaea, and the anaerobic methanotrophic archaea (ANME) (Knittel and Boetius, 2009). The main inputs of methane to the atmosphere are anaerobic respiration of organic matter by acetoclastic methanogens (represented by the contributions of both fermentation and methanogenesis in 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) 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).



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 denitrification 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.

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 *c*₆ 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 euxinic lakes, phototrophic

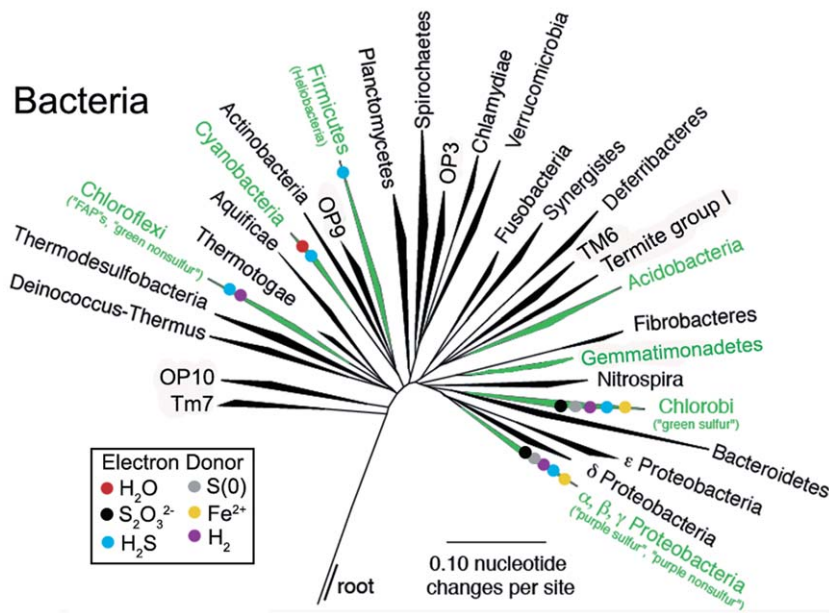


Fig. 2. 16S rRNA tree highlighting lineages with chlorophototrophic members. Green branches represent phyla that contain chlorophototrophs. Electron donors for photosynthetic growth are indicated by filled circles.

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 Gernerden, 1984; Pringault *et al.*, 1999). In contrast, a combination of sulfide and temperature appears to inhibit photosynthesis in alkaline hot springs above $\sim 70^{\circ}\text{C}$ (Cox *et al.*, 2011; Boyd *et al.*, 2012).

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 photoheterotrophically (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 *Oscillatoria* 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 Gernerden 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 *Chloroflexi* and *Chlorobi* also employ Sqr to oxidize sulfide for anoxygenic photosynthesis. Members of the *Chlorobiales* (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 Utkilen, 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 chemoautotrophs 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 chemoautotrophic Fe(II) oxidation and photoferrotothrophy 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 influ-

enced 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 (Hefter *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 carotenoid pigment okenone is preserved as the hydrocarbon fossil equivalent okenane. Some members of the *Chromatiaceae*, anoxygenic phototrophic PSB, make okenone (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-methylbacteriohopanepolyols 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-methylheptadecane. There are examples of other organisms that produce 7-methylheptadecane although those organisms employ a different biosynthetic pathway. The biosynthesis of 7-methylheptadecane 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 geochemical 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 Maris, 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 chlorophototrophy 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 Fe²⁺-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 (Scholnick *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 Fe²⁺ upwelling (Swanner *et al.*, 2015). In addition, examples of extant anoxygenic phototrophs that utilize Fe²⁺ for CO₂ photoassimilation are rare compared with those that prefer reduced forms of sulfur (Fig. 2). One notable example is *Rhodospseudomonas palustris* strain TIE-1, a purple non-sulfur bacterium that grows photoautotrophically by oxidizing Fe²⁺ or H₂ (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, Fe²⁺ 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 chlorophototrophs and the ubiquity of H₂O as an electron donor, a scenario selecting for abundant PS II-independent CO₂ 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 H₂O or H₂S 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 H₂S and Fe²⁺, 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).

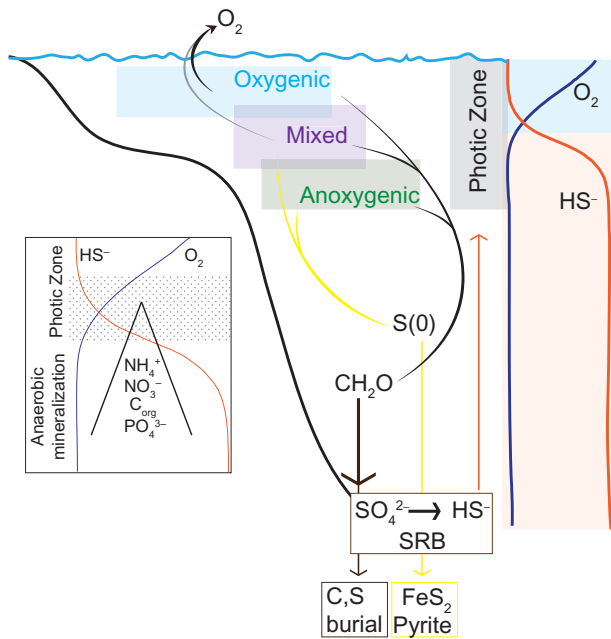


Fig. 3. A schematic model of marine primary productivity in the photic zone of euxinic regions of Proterozoic oceans. Inset demonstrates the consumption of nutrients (fixed nitrogen, organic carbon and phosphate) through the deep waters and into the photic zone, leading to nutrient-poor surface waters. SRB, sulfate-reducing bacteria.

Although examples are rare, observations of cyanobacteria performing both oxygenic and anoxygenic photosynthesis simultaneously have been documented (de Wit and Gernerden, 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 photosyntheses simultaneously, rates of anoxygenic photosynthesis are governed by light and H_2S 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 N_2 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 N_2 , 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 N_2 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 photoautotrophs 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 history of genes and regulatory mechanisms that control flows of carbon, nitrogen, sulfur and oxygen, and may provide new insights into organic, isotopic and geochemical biosignatures of cyanobacterial life that can serve to inform our interpretation of the rock record.

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References

Anbar, A.D., Duan, Y., Lyons, T.W., Arnold, G.L., Kendall, B., Creaser, R.A., *et al.* (2007) A whiff of oxygen before the Great Oxidation Event? *Science* **317**: 1903–1906. doi:10.1126/science.1140325.

Arp, G., Reimer, A., and Reitner, J. (1999) Calcification in cyanobacterial biofilms of alkaline salt lakes. *Eur J Phycol* **34**: 393–403. doi:10.1080/09670269910001736452.

Awramik, S.M., and Semikhatov, M.A. (1979) The relationship between morphology, microstructure and microbiota in Gunflint stromatolites. *Can J Earth Sci* **16**: 484–495.

Barley, M.E., Bekker, A., and Krapez, B. (2005) Late Archean to Early Paleoproterozoic global tectonics, environmental change and the rise of atmospheric oxygen. *Earth Planet Sci Lett* **238**: 156–171. doi:10.1016/j.epsl.2005.06.062.

Battistuzzi, F.U., Feijao, A., and Hedges, S.B. (2004) A genomic timescale of prokaryote evolution: insights into the origin of methanogenesis, phototrophy, and the colonization of land. *BMC Evol Biol* **4**: 44. doi:10.1186/1471-2148-4-44.

Bekker, A., Holland, H.D., Wang, P.-L., Rumble, D., III, Stein, H.J., Hannah, J.L., *et al.* (2004) Dating the rise of atmospheric oxygen. *Nature* **427**: 117–120. doi:10.1038/nature02260.

Belkin, S., Arielli, B., and Padan, E. (1982) Sulfide-dependent electron transport in *Oscillatoria limnetica*. *Israel J Bot* **31**: 199–200. doi:10.1080/0021213X.1982.10676943.

Bilinski, T. (1991) Oxygen toxicity and microbial evolution. *Biosystems* **24**: 305–312.

Birgel, D., Meister, P., Lundberg, R., Horath, T.D., Bontognali, T.R.R., Bahnuk, A.M., *et al.* (2015) Methanogenesis produces strong ¹³C enrichment in stromatolites of Lagoa Salgada, Brazil: a modern analogue for Palaeo/Neoproterozoic stromatolites? *Geobiology* **13**: 245–266. doi:10.1111/gbi.12130.

Blankenship, R.E. (2001) Molecular evidence for the early evolution of photosynthesis. *Trends Plant Sci* **6**: 4–6. doi:10.1016/S1360-1385(00)01831-8.

Bosak, T., Knoll, A.H., and Petroff, A.P. (2013) The meaning of stromatolites. *Annu Rev Earth Planet Sci* **41**: 21–44. doi:10.1146/annurev-earth-042711-105327.

Boyd, E.S., Fecteau, K.M., Havig, J.R., Shock, E.L., and Peters, J.W. (2012) Modeling the habitat range of phototrophs in Yellowstone National Park: toward the development of a comprehensive fitness landscape. *Front Microbiol* **3**: 221. doi:10.3389/fmicb.2012.00221.

Brocks, J.J. (2011) Millimeter-scale concentration gradients of hydrocarbons in Archean shales: live-oil escape or fingerprint of contamination? *Geochim Cosmochim Acta* **75**: 3196–3213. doi:10.1016/j.gca.2011.03.014.

Brocks, J.J., and Summons, R.E. (2004) *Treatise on Geochemistry*, Vol. 8. (Biogeochemistry). Schlesinger, W.H. (ed.). Oxford: Elsevier, pp. 63–115.

Brocks, J.J., Logan, G.A., Buick, R., and Summons, R.E. (1999) Archean molecular fossils and the early rise of eukaryotes. *Science* **285**: 1033–1036. doi:10.1126/science.285.5430.1033.

Brocks, J.J., Love, G.D., Summons, R.E., Knoll, A.H., Logan, G.A., and Bowden, S.A. (2005) Biomarker evidence for green and purple sulphur bacteria in a stratified Palaeoproterozoic sea. *Nature* **437**: 866–870. doi:10.1038/nature04068.

Brune, D.C. (1995) Sulfur compounds as photosynthetic electron donors. In *Anoxygenic Photosynthetic Bacteria*. Blankenship, R.E., Madigan, M.T., and Bauer, C.E. (eds). Netherlands: Springer, pp. 847–870.

Bryant, D.A., and Frigaard, N.-U. (2006) Prokaryotic photosynthesis and phototrophy illuminated. *Trends Microbiol* **14**: 488–496. doi:10.1016/j.tim.2006.09.001.

- Bryant, D.A., and Liu, Z. (2013) Green bacteria: Insights into green bacterial evolution through genomic analyses. In *Advances in Botanical Research*. Beatty, J.T. (ed.). Oxford, UK: Elsevier, pp. 99–150.
- Burns, B.P., Goh, F., Allen, M.A., and Neilan, B.A. (2004) Microbial diversity of extant stromatolites in the hypersaline marine environment of Shark Bay, Australia. *Environ Microbiol* **6**: 1096–1101. doi:10.1111/j.1462-2920.2004.00651.x.
- Canfield, D.E. (2005) The early history of atmospheric oxygen: homage to Robert A. Garrels *Annu Rev Earth Planet Sci* **33**: 1–36. doi:10.1146/annurev.earth.33.092203.122711.
- Castenholz, R.W., and Utkilen, H.C. (1984) Physiology of sulfide tolerance in a thermophilic *Oscillatoria*. *Arch Microbiol* **138**: 299–305.
- Castenholz, R.W., Bauld, J., and Jørgensen, B.B. (1990) Anoxygenic microbial mats of hot springs: thermophilic *Chlorobium* sp. *FEMS Microbiol Ecol* **74**: 325–336. doi:http://dx.doi.org/10.1111/j.1574-6968.1990.tb04079.x.
- Castenholz, R.W., Jørgensen, B.B., D'Amelio, E., and Bauld, J. (1991) Photosynthetic and behavioral versatility of the cyanobacterium *Oscillatoria boryana* in a sulfide-rich microbial mat. *FEMS Microbiol Lett* **86**: 43–57. doi: http://dx.doi.org/10.1111/j.1574-6968.1991.tb04794.x.
- Catling, D.C., Zahnle, K.J., and McKay, C.P. (2001) Biogenic methane, hydrogen escape, and the irreversible oxidation of early Earth. *Nature* **293**: 839–843. doi:10.1126/science.1061976.
- Catling, D.C., and Buick, R. (2006) Oxygen and life in the Precambrian. *Geobiology* **4**: 225–226. doi:10.1111/j.1472-4669.2006.00088.x.
- Catling, D.C., Claire, M.W., Zahnle, K.J., Quinn, R.C., Clark, B.C., Hecht, M.H., and Kounaves, S. (2010) Atmospheric origins of perchlorate on Mars and in the Atacama. *J Geophys Res* **115**: E00E11. doi:10.1029/2009JE003425; 2010.
- Catling, D.C. (2014) The great oxidation event transition. In *Treatise on Geochemistry*. Turekian, K.K., and Holland H.D. (eds). Amsterdam: Elsevier, pp. 177–195.
- Clement, B.G., Luther, G.W.I.I.I., and Tebo, B.M. (2009) Rapid, oxygen-dependent microbial Mn(II) oxidation kinetics at sub-micromolar oxygen concentrations in the Black Sea suboxic zone. *Geochim Cosmochim Acta* **73**: 1878–1889. doi:10.1016/j.gca.2008.12.023.
- Coates, R., Podell, S., Korobeynikov, A., Lapidus, A., Pevzner, P., Sherman, D., et al. (2014) Characterization of cyanobacterial hydrocarbon composition and distribution of biosynthetic pathways. *PLoS ONE* **9**: e85140. doi:10.1371/journal.pone.0085140.
- Cohen, Y., Jørgensen, B.B., Padan, E., and Shilo, M. (1975a) Sulphide-dependent anoxygenic photosynthesis in the cyanobacterium *Oscillatoria limnetica*. *Nature* **257**: 489–492. doi:10.1038/257489a0.
- Cohen, Y., Padan, E., and Shilo, M. (1975b) Facultative anoxygenic photosynthesis in the cyanobacterium *Oscillatoria limnetica*. *J Bacteriol* **123**: 855–861.
- Cohen, Y., Jørgensen, B.B., Revsbech, N.P., and Poplawski, R. (1986) Adaptation to hydrogen sulfide of oxygenic and anoxygenic photosynthesis among *Cyanobacteria*. *Appl Environ Microbiol* **51**: 398–407. doi:10.1016/0378-1097(87)90036-X.
- Cox, A., Shock, E.L., and Havig, J.R. (2011) The transition to microbial photosynthesis in hot spring ecosystems. *Chem Geol* **280**: 344–351. doi:10.1016/j.chemgeo.2010.11.022.
- Crowe, S.A., Jones, C., Katsev, S., Magen, C., O'Neill, A.H., Sturm, A., et al. (2008) Photoferrotrophs thrive in an Archean ocean analogue. *Proc Natl Acad Sci USA* **105**: 15938–15943. doi:10.1073/pnas.0805313105.
- Crowe, S.A., Døssing, L.N., Beukes, N.J., Bau, M., Kruger, S.J., Frei, R., and Canfield, D.E. (2013) Atmospheric oxygenation three billion years ago. *Nature* **501**: 535–538. doi:10.1038/nature12426.
- David, A., and Alm, E. (2011) Rapid evolutionary innovation during an Archean genetic expansion. *Nature* **469**: 93–96. doi:10.1038/nature09649.
- Des Marais, D. (2000) When did photosynthesis emerge on Earth? *Science* **289**: 1703–1705. doi:10.1126/science.289.5485.1703.
- Eickhoff, M., Birgel, D., Talbot, H.M., Peckmann, J., and Kappler, A. (2013) Oxidation of Fe(II) leads to increased C-2 methylation of pentacyclic triterpenoids in the anoxygenic phototrophic bacterium *Rhodospseudomonas palustris* strain TIE-1. *Geobiology* **11**: 268–278. doi:10.1111/gbi.12033.
- Ettwig, K.F., Butler, M.K., Le Paslier, D.L., Pelletier, E., Mangenot, S., Kuypers, M.M.M., et al. (2010) Nitrite-driven anaerobic methane oxidation by oxygenic bacteria. *Nature* **464**: 543–548. doi:10.1038/nature08883.
- Farquhar, J., Bao, H., and Thiemens, M. (2000) Atmospheric influence of Earth's earliest sulfur cycle. *Science* **289**: 756–758. doi:10.1126/science.289.5480.756.
- Frei, R., Gaucher, C., Poulton, S.W., and Canfield, D.E. (2009) Fluctuations in Precambrian atmospheric oxygenation recorded by chromium isotopes. *Nature* **461**: 250–253. doi:10.1038/nature08266.
- French, K.F., Hallman, C., Hope, J.M., Schoon, P.L., Zumberge, J.A., Hoshino, Y., et al. (2015) Reappraisal of hydrocarbon biomarkers in Archean rocks. *Proc Natl Acad Sci USA* **112**: 5915–5920. doi:10.1073/pnas.1419563112.
- Frigaard, N.-U., and Bryant, D.A. (2006) Genomic and evolutionary perspectives on sulfur metabolism in green sulfur bacteria. In *Microbial Sulfur Metabolism*. Dahl, C., and Friedrich, C.G. (eds). Berlin, Germany: Springer-Verlag, pp. 60–76.
- Frigaard, N.-U., and Bryant, D.A. (2008). Genomics insights into the sulfur metabolism of phototrophic green sulfur bacteria. In *Advances in Photosynthesis and Respiration*. Hell, R., Dahl, C., Knaff, D.B., and Leustek, T. (eds). Heidelberg: Springer, pp. 337–355.
- Frigaard, N.-U., and Dahl, C. (2008) Sulfur metabolism in phototrophic sulfur bacteria. *Adv Microb Physiol* **54**: 103–200. doi:10.1016/S0065-2911(08)00002-7.
- Gaillard, F., Scaillet, B., and Arndt, N.T. (2011) Atmospheric oxygenation caused by a change in volcanic degassing pressure. *Nature* **478**: 229–232. doi:10.1038/nature10460.
- Goldblatt, C., Lenton, T.M., and Watson, A.J. (2006) Bistability of atmospheric oxygen and the Great Oxidation. *Nature* **443**: 683–686. doi:10.1038/nature05169.

- Gomez Maqueo Chew, A., and Bryant, D.A. (2007) Chlorophyll biosynthesis in bacteria: the origins of structural and functional diversity. *Annu Rev Microbiol* **61**: 113–129. doi:10.1146/annurev.micro.61.080706.093242.
- Hamilton, T.L., Bird, L.M., Freeman, K.H., and Macalady, J.L. (2013) 2-Methyl hopanoid production and anoxygenic photosynthesis: a model early earth cyanobacteria isolated from a proterozoic ocean analog. *Mineral Mag* **77**: 1249.
- Hamilton, T.L., Bovee, R.J., Thiel, V., Sattin, S.R., Mohr, W., Schaperdoth, I., et al. (2014) Coupled reductive and oxidative sulfur cycling in the phototrophic plate of a meromictic lake. *Geobiology* **12**: 451–468. doi:10.1111/gbi.12092.
- Hedges, S.B., Chen, H., Kumar, S., Wang, D.Y.C., Thompson, A.S., and Watanabe, H. (2001) A genomic timescale for the origin of eukaryotes. *Evol Biol* **1**: 4. doi:10.1186/1471-2148-1-4.
- Hefter, J., Thiel, V., Jenisch, A., Galling, U., Kempe, S., and Michaelis, W. (1993) Biomarker indications for microbial contribution to recent and rate Jurassic carbonate deposits. *Facies* **29**: 93–106.
- Heindel, K., Richo, S., Birgel, D., Brandner, R., Klügel, A., Krystyn, L., et al. (2015) Biogeochemical formation of calyx-shaped carbonate crystal fans in the subsurface of the Early Triassic seafloor. *Gondwana Res* **27**: 840–861. doi:10.1016/j.gr.2013.11.004.
- Holland, H.D. (2006) The oxygenation of the atmosphere and oceans. *Phil Trans R Soc B* **361**: 903–915. doi:10.1098/rstb.2006.1838.
- Holland, H.D. (1978) *The Chemical Evolution of the Atmosphere and Oceans*. Hoboken, NJ, USA: John Wiley & Sons Inc.
- Holland, H.D. (1984) *The Chemical Evolution of the Atmosphere and Oceans. Princeton Series in Geochemistry*. Princeton, NJ, USA: Princeton University Press.
- Hoshino, Y., and George, S.C. (2015) Cyanobacterial inhabitation on Archean rock surfaces in the Pilbara Craton, Western Australia. *Astrobiology* **15**: 559–574. doi:10.1089/ast.2014.1275.
- Isley, A.E. (1995) Hydrothermal plumes and the delivery of iron to banded iron formation. *J Geol* **103**: 169–185.
- Jiao, Y.Y.Q., Kappler, A., Croal, L.R., and Newman, D.K. (2005) Isolation and characterization of a genetically tractable photoautotrophic Fe(II)-oxidizing bacterium, *Rhodospseudomonas palustris* strain TIE-1. *Appl Environ Microbiol* **71**: 4487–4496. doi:10.1128/AEM.71.8.4487-4496.2005.
- Johnson, J.E., Webb, S.E., Thomas, K., Ono, S., Kirschvink, J.L., and Fischer, W.W. (2014) Manganese-oxidizing photosynthesis before the rise of cyanobacteria. *Proc Natl Acad Sci USA* **110**: 11238–11243. doi:10.1073/pnas.1305530110.
- Johnston, D.T., Wolfe-Simon, F., Pearson, A., and Knoll, A.H. (2009) Anoxygenic photosynthesis modulated Proterozoic oxygen and sustained Earth's middle age. *Proc Natl Acad Sci USA* **106**: 16925–16929. doi:10.1073/pnas.0909248106.
- Jørgensen, B.B. (1982) Mineralization of organic matter in the sea bed—the role of sulphate reduction. *Nature* **296**: 643–645. doi: 10.1038/296643a0.
- Jørgensen, B.B., Revsbech, N.P., and Cohen, Y. (1983) Photosynthesis and structure of benthic microbial mats: microelectrode and SEM studies of four cyanobacterial communities. *Limn Oceanogr* **28**: 1075–1093.
- Jørgensen, B.B., Cohen, Y., and Revsbech, N.P. (1986) Transition from anoxygenic to oxygenic photosynthesis in a *Microcoleus chthonoplastes* cyanobacterial mat. *Appl Environ Microbiol* **51**: 408–417.
- Kappler, A., Pasquero, C., Konhauser, K.O., and Newman, D.K. (2005) Deposition of banded iron formations by anoxygenic phototrophic Fe(II)-oxidizing bacteria. *Geology* **33**: 865–868. doi:10.1130/G21658.1.
- Kasting, J.F. (2010) Early Earth: faint young sun redux. *Nature* **464**: 687–689. doi:10.1038/464687a.
- Kasting, J.F., and Walker, J.C.G. (1981) Limits on oxygen concentration in the prebiological atmosphere and the rate of abiotic fixation of nitrogen. *J Geophys Res* **86**: 9776–9782.
- Kenyon, C.N., Rippka, R., and Stanier, R.Y. (1972) Fatty acid composition and physiological properties of some filamentous blue-green algae. *Arch Microbiol* **83**: 216–236.
- Klatt, C.G., Wood, J.M., Rusch, D.B., Bateson, M.M., Hamamura, N., Heidelberg, J.F., et al. (2011) Community ecology of hot spring cyanobacterial mats: predominant populations and their functional potential. *ISME J* **5**: 1262–1278. doi:10.1038/ismej.2011.73.
- Klatt, C.G., Inskeep, W.P., Herrgard, M.J., Jay, Z.J., Rusch, D.B., Tringer, S.G., et al. (2013) Community structure and function in high-temperature chlorophototrophic microbial mats inhabiting diverse geothermal environments. *Front Microbiol* **4**: 106. doi:10.3389/fmicb.2013.00106.
- Klatt, J.M., Al-Najjar, M.A.A., Yilmaz, P., Lavik, G., de Beer, D., and Polerecky, L. (2015) Anoxygenic photosynthesis controls oxygenic photosynthesis in cyanobacterium from a sulfidic spring. *Appl Environ Microbiol*. doi:10.1128/AEM.03579-14.
- Knittel, K., and Boetius, A. (2009) Anaerobic oxidation of methane: progress with an unknown process. *Annu Rev Microbiol* **63**: 311–334. doi:10.1146/annurev.micro.61.080706.093130.
- Knoll, A.H. (2003) *Life on a Young Planet: The First Three Billion Years of Evolution on Earth*. Princeton, NJ, USA: Princeton University Press.
- Knoll, A.H., Wörmle, S., and Kah, L.C. (2013) Covariance of microfossil assemblages and microbialite textures across an upper Mesoproterozoic carbonate platform. *Palaios* **28**: 453–470. doi:10.2110/palo.2013.p13-005r.
- Konhauser, K.O., Hamade, T., Raiswell, R., Morris, R.C., Ferris, F.G., Southam, G., and Canfield, D.E. (2002) Could bacteria have formed the Precambrian banded iron formations? *Geology* **30**: 1079–1082. doi:10.1130/0091-7613(2002)030<1079:CBHFTP>2.0.CO;2.
- Konhauser, K.O., Lalonde, S.V., Planavsky, N.J., Pecoits, E., Lyons, T.W., Mojzsis, S.J., et al. (2011) Aerobic bacterial pyrite oxidation and acid rock drainage during the Great Oxidation Event. *Nature* **478**: 369–373. doi:10.1038/nature10511.
- Kopp, R.E., Kirschvink, J.L., Hilburn, I.A., and Nash, C.Z. (2005) The Paleoproterozoic snowball Earth: a climate disaster triggered by the evolution of oxygenic photosynthesis. *Proc Natl Acad Sci USA* **102**: 11131–11136. doi:10.1073/pnas.0504878102.

- Krumbien, W.E., Cohen, Y., and Shilo, M. (1977) Solar Lake (Sinai). 4. Stromatolitic cyanobacterial mats. *Limn Oceanogr* **22**: 635–656.
- Kump, L.R. (2008) The rise of atmospheric oxygen. *Nature* **451**: 277–278. doi:10.1038/nature06587.
- Kump, L.R., Pavlov, A., and Arthur, M.A. (2005) Massive release of hydrogen sulfide to the surface ocean and atmosphere during intervals of oceanic anoxia. *Geology* **33**: 397–400. doi:10.1130/G21295.1.
- Kump, L.R., and Barley, M.E. (2007) Increased subaerial volcanism and the rise of atmospheric oxygen 2.5 billion years ago. *Nature* **448**: 1033–1036. doi:10.1038/nature06058.
- Lalonde S.V., and Konhauser, K.O. (2015) Benthic perspective on Earth's oldest evidence for oxygenic photosynthesis. *Proc Natl Acad Sci USA* **112**: 995–1000. doi: 10.1073/pnas.1415718112.
- Li, N., Nørgaard, H., Warui, D., Booker, S., Krebs, C., and Bollinger, J. (2011) Conversion of fatty aldehydes to alka(e)nes and formate by a cyanobacterial aldehyde decarbonylase: cryptic redox by an unusual dimetal oxygenase. *J Am Chem Soc* **133**: 6158–6161. doi:10.1021/ja2013517.
- Li, N., Chang, W.-C., Warui, D., Booker, S., Krebs, C., and Bollinger, J. (2012) Evidence for only oxygenative cleavage of aldehydes to alk(a)e)nes and formate by cyanobacterial aldehyde decarbonylases. *Biochemistry* **51**: 7908–7916. doi:10.1021/bi300912n.
- Luther, G.W. (1991) Pyrite synthesis via polysulfide compounds. *Geochim Cosmochim Acta* **55**: 2839–2849. doi:10.1016/0016-7037(91)90449-F.
- Lyons, T.W., and Gill, B.C. (2010) Ancient sulfur cycling and oxygenation of the early biosphere. *Elements* **6**: 93–99. doi:10.2113/gselements.6.2.93.
- Lyons, T.W., Anbar, A.D., Severmann, S., Scott, C., and Gill, B.C. (2009) Tracking euxinia in the ancient ocean: a multiproxy perspective and Proterozoic case study. *Annu Rev Earth Planet Sci* **37**: 507–534. doi:10.1146/annurev.earth.36.031207.124233.
- Lyons, T.W., Reinhard, C.T., and Planavsky, N.J. (2014) The rise of oxygen in Earth's early ocean and atmosphere. *Nature* **506**: 307–315. doi:10.1038/nature13068.
- Mackey, T.J., Sumner, D.Y., Hawes, I., Jungblut, A.D., and Andersen, D.T. (2015) Growth of modern branched columnar stromatolites in Lake Joyce, Antarctica. *Geobiology* **13**: 373–390. doi:10.1111/gbi.12138.
- Maresca, J.A., Graham, J.E., and Bryant, D.A. (2008) The biochemical basis for structural diversity in the carotenoids of chlorophototrophic bacteria. *Photosynth Res* **97**: 121–140. doi:10.1007/s11120-008-9312-3.
- Melak, J.M., and Kilham, P. (1974) Photosynthetic rates of phytoplankton in East African alkaline, saline lakes. *Limnol Oceanogr* **19**: 743–755.
- Meyer, K.M., and Kump, L.R. (2008) Oceanic euxinia in Earth history: causes and consequences. *Annu Rev Earth Planet Sci* **36**: 251–288. doi:10.1146/annurev.earth.36.031207.124256.
- Meyer, K.M., Macalady, J.L., Fulton, J.M., Kump, L.R., Schaperdoth, I., and Freeman, K.H. (2011) Carotenoid biomarkers as an imperfect reflection of the anoxygenic phototrophic community in meromictic Fayetteville Green Lake. *Geobiology* **9**: 321–329. doi:10.1111/j.1472-4669.2011.00285.x.
- Olson, S.L., Kump, L.R., and Kasting, J.F. (2013) Quantifying the areal extent and dissolved oxygen concentrations of Archean oxygen oases. *Chem Geol* **362**: 35–43. doi:10.1016/j.chemgeo.2013.08.012.
- Oren, A., and Padan, E. (1978) Induction of anaerobic photoautotrophic growth in the cyanobacterium *Oscillatoria limnetica*. *J Bacteriol* **133**: 558–563.
- Oren, A., Padan, E., and Avron, M. (1977) Quantum yields for oxygenic and anoxygenic photosynthesis in the cyanobacterium *Oscillatoria limnetica*. *Proc Natl Acad Sci USA* **74**: 2152–2156.
- Overmann, J., and Garcia-Pichel, F. (2006) The Phototrophic Way of Life. In *Ecophysiology and Biochemistry, The Prokaryotes*, Vol. 2. Dworkin, M., Falkow, S., Rosenberg, E., Schleifer, K.H., and Stackebrandt, E. (eds). Heidelberg, Germany: Springer, pp. 32–85.
- Overmann, J., Beatty, J.T., Krouse, H.R., and Hall, K.J. (1996) The sulfur cycle in the chemocline of a meromictic salt lake. *Limn Oceanogr* **41**: 147–156.
- Padan, E. (1979) Facultative anoxygenic photosynthesis in Cyanobacteria. *Ann Rev Plant Physiol* **30**: 27–40.
- Padan, E., and Cohen, Y. (1982) Anoxygenic photosynthesis. In *The biology of cyanobacteria*. Carr, N.C., and Whitton, B.A. (eds). Oxford: Blackwell Scientific, pp. 215–235.
- Pagès, A., Grice, K., Vacher, M., Welsh, D.T., Teasdale, P.R., Bennett, W.W., and Greenwood, P. (2014) Characterizing microbial communities and processes in a modern stromatolite (Shark Bay) using lipid biomarkers and two-dimensional distributions of porewater solute. *Env Microbiol* **16**: 2458–2474. doi:10.1111/1462-2920.12378.
- Partin, C.A., Lalonde, S.V., Planavsky, N.J., Bekker, A., Rouxel, O.J., Lyons, T.W., and Konhauser, K.O. (2013) Uranium in iron formations and the rise of atmospheric oxygen. *Chem Geol* **362**: 82–90. doi:10.1016/j.chemgeo.2013.09.005.
- Pavlov, A.A., and Kasting, J.F. (2002) Mass-independent fractionation of sulfur isotopes in Archean sediments: strong evidence for an anoxic Archean atmosphere. *Astrobiology* **2**: 27–41. doi:10.1089/153110702753621321.
- Pavlov, A.A., Kasting, J.F., Brown, L.L., Rages, K.A., and Freedman, R. (2000) Greenhouse warming by CH₄ in the atmosphere of early Earth. *J Geophys Res Planets* **105**: 11981–11990. doi:10.1029/1999JE001134.
- Planavsky, N.J., McGoldrick, P., Scott, C.T., Li, C., Reinhard, C.T., Kelly, A.E., et al. (2011) Widespread iron-rich conditions in the mid-Proterozoic ocean. *Nature* **477**: 448–452. doi:10.1038/nature10327.
- Planavsky, N.J., Reinhard, C.T., Wand, X., Thomson, D., McGoldrick, P., Rainbird, R.H., et al. (2014a) Low mid-Proterozoic atmospheric oxygen levels and the delayed rise of animals. *Science* **346**: 536–638. doi:10.1126/science.1258410.
- Planavsky, N.J., Asael, D., Hofmann, A., Reinhard, C.T., Lalonde, S.V., Knudsen, A., et al. (2014b) Evidence for oxygenic photosynthesis half a billion years before the Great Oxidation Event. *Nat Geo* **7**: 283–286. doi:10.1038/ngeo2122.

- Poulton, S.W., and Canfield, D.E. (2011) Ferruginous conditions: a dominant feature of the ocean through Earth's history. *Elements* **7**: 107–112. doi:10.2113/gselements.7.2.107.
- Poulton, S.W., Fralick, P.W., and Canfield, D.E. (2010) Spatial variability in oceanic redox structure 1.8 billion years ago. *Nature Geosci* **3**: 486–490. doi:10.1038/ngeo889.
- Pringault, O., de Wit, R., and Kühl, M. (1999) A microsensor study of the interaction between purple sulfur and green sulfur bacteria in experimental benthic gradients. *Microb Ecol* **37**: 173–184. doi:10.1007/s002489900141.
- Rao, B., Anderson, T.A., Redder, A., and Jackson, A.W. (2010) Perchlorate formation by ozone oxidation of aqueous chlorine/oxy-chlorine species: role of Cl_xO_y radicals. *Environ Sci Technol* **44**: 2961–2967. doi:10.1021/es903065f.
- Rashby, S.E., Sessions, A.L., Summons, R.E., and Newman, D.K. (2007) Biosynthesis of 2-methylbacteriohopanepolyols by an anoxygenic phototroph. *Proc Natl Acad Sci USA* **104**: 15099–15104. doi:10.1073/pnas.0704912104.
- Rasmussen, B., and Buick, R. (1999) Redox state of the Archean atmosphere: evidence from detrital heavy minerals in ca. 3250–2750 Ma sandstones from the Pilbara Craton, Australia. *Geology* **27**: 115–118. doi:10.1130/0091-7613(1999)027<0115:RSOTAA>2.3.CO;2.
- Rasmussen, B., Fletcher, I.R., Brocks, J.J., and Kilburn, M.R. (2008) Reassessing the first appearance of eukaryotes and *Cyanobacteria*. *Nature* **455**: 1101–1104. doi:10.1038/nature07381.
- Raymond, J., Zhaxybayeva, O., Gogarten, J.P., Gerdes, S.Y., and Blankenship, R.E. (2002) Whole-genome analysis of photosynthetic prokaryotes. *Science* **298**: 1616–1620. doi:10.1126/science.1075558.
- Reid, R.P., Visscher, P.T., Decho, A., Stolz, J.K., Bebout, B.M., Dupraz, C., *et al.* (2000) The role of microbes in accretion, lamination and early lithification of modern marine stromatolites. *Nature* **406**: 989–992. doi:10.1038/35023158.
- Reinhard, C.T., Raiswell, R., Scott, C., Anbar, A.D., and Lyons, T.W. (2009) A late Archean sulfidic sea stimulated by early oxidative weathering of the continents. *Science* **326**: 713–716. doi:10.1126/science.1176711.
- Rickard, D. (1975) Kinetics and mechanisms of pyrite formation at low temperatures. *Am J Sci* **275**: 636–652.
- Rickard, D., and Luther, G.W. (2007) Chemistry of iron sulfides. *Chem Rev* **107**: 514–562. doi:10.1021/cr0503658.
- Rippka, R., Deruelles, J., Waterbury, J., Herdman, M., and Stanier, R.Y. (1979) Generic assignment, strain histories and properties of pure cultures of *Cyanobacteria*. *J Gen Microbiol* **111**: 1–61.
- Rye, R., and Holland, H.D. (1998) Paleosols and the evolution of atmospheric oxygen: a critical review. *Am J Sci* **298**: 671–672.
- Sadekar, S., Raymond, J., and Blankenship, R.E. (2006) Conservation of distantly related membrane proteins: photosynthetic reaction centers share a common structural core. *Mol Biol Evol* **23**: 2001–2007. doi: 10.1093/molbev/msl079.
- Sagan, C., and Mullen, G. (1972) Earth and Mars: evolution of atmospheres and surface temperatures. *Science* **177**: 52–56.
- Schirmer, A., Rude, M.A., Li, X., Popova, E., and del Cardayre, S.B. (2010) Microbial biosynthesis of alkanes. *Science* **329**: 559–562. doi:10.1126/science.1187936.
- Scott, C., Lyons, T.W., Bekker, A., Shen, Y., Poulton, S.W., Chu, X., and Anbar, A.D. (2008) Tracing the stepwise oxygenation of the Proterozoic ocean. *Nature* **452**: 456–459. doi:10.1038/nature06811.
- Seong-Joo, L., and Golubic, S. (1999) Microfossil populations in the context of synsedimentary micrite deposition and acicular carbonate precipitation: Mesoproterozoic Gaoyuzhuang Formation, China. *Precambrian Res* **96**: 183–208. doi:10.1016/S0301-9268(99)00004-2.
- Shcolnick, S., Summerfield, T.C., Reytman, L., Sherman, L.A., and Keren, N. (2009) The mechanism of iron homeostasis in the unicellular cyanobacterium *Synechocystis* sp. PCC 6803 and its relationship to oxidative stress. *Plant Physiol* **150**: 2045–2056. doi:10.1104/pp.109.141853.
- Shen, Y., Knoll, A.H., and Watler, M.R. (2003) Evidence for low sulphate and anoxia in a mid-Proterozoic marine basin. *Nature* **423**: 632–635.
- Shiea, J., Brassell, S.C., and Ward, D.M. (1990) Mid-chain branched mono- and dimethyl alkanes in hot spring cyanobacterial mats: a direct biogenic source for branched alkanes in ancient sediments? *Org Geochem* **15**: 223–231. doi:10.1016/0146-6380(90)90001-G.
- Sleep, N.M., and Bird, D.K. (2008) Evolutionary ecology during the rise of dioxygen in the Earth's atmosphere. *Philos Trans R Soc Lond B Biol Sci* **363**: 2651–2664. doi:10.1098/rstb.2008.0018.
- Summons, R.E., Jahnke, L.L., Hope, J.M., and Logan, G.A. (1999) 2-Methylhopanoids: molecular fossils for *Cyanobacteria* recording a geological history of oxygenic photosynthesis. *Nature* **400**: 554–557. doi:10.1038/23005.
- Sumner, D.Y., Hawes, I., Mackey, T.J., Jungblut, A.D., and Doran, P.T. (2015) Antarctic microbial mats: a modern analog for Archean lacustrine oxygen oases. *Geology* **43**: 887–890. doi:10.1130/G36966.1.
- Swanner, E.D., Mloszewska, A.M., Cirpka, O.A., Schoenbery, R., Konhauser, K.O., and Kappler, A. (2015) Modulation of oxygen production in Archaean oceans by episodes of Fe(II) toxicity. *Nat Geo* **8**: 126–130. doi:10.1038/ngeo2327.
- Talbot, H.M., Summons, R.E., Jahnke, L.L., Cockell, C.S., Rohmer, M., and Farrimond, P. (2008) Cyanobacterial bacteriohopanepolyol signatures from cultures and natural environmental settings. *Org Geochem* **39**: 232–263. doi:10.1016/j.orggeochem.2007.08.006.
- Taton, A., Grubisic, S., Brambilla, E., de Wit, R., and Wilmotte, A. (2003) Cyanobacterial diversity in natural and artificial microbial mats of Lake Fryxell (McMurdo Dry Valleys, Antarctica): a morphological and molecular approach. *Appl Environ Microbiol* **69**: 5157–5169. doi:10.1128/AEM.69.9.5157-5169.2003.
- Thiel, V., Merz-Preiß, M., Reitner, J., and Michaelis, W. (1997) Biomarker studies on microbial carbonates: extractable lipids of a calcifying cyanobacterial mat (Everglades, USA). *Facies* **36**: 163–172.

- Tripp, H.J., Bench, S.R., Turk, K.A., Fosters, R.A., Desany, B.A., Niazi, F., *et al.* (2010) Metabolic streamlining in an open-ocean nitrogen-fixing cyanobacterium. *Nature* **464**: 90–94. doi:10.1038/nature08786.
- Van Gernerden, H. (1984) The sulfide affinity of phototrophic bacteria in relation to the location of elemental sulfur. *Arch Microbiol* **139**: 289–294.
- Van Gernerden, H., and Mas, J. (1995) Ecology of Phototrophic Sulfur Bacteria. In *Anoxygenic Photosynthetic Bacteria*. Blankenship, R.E., Madigan, M.T., Bauer, C.E. (eds). Netherlands: Springer, pp 49–85.
- Venter, J.C., Remington, K., Heidelberg, J.F., Halpern, A.L., Rusch, D., Eisen, J.A., *et al.* (2004) Environmental genome shotgun sequencing of the Sargasso Sea. *Science* **340**: 66–74. doi:10.1126/science.1093857.
- Visscher, P.T., Reid, R.P., and Bebout, B.M. (2000) Microscale observations of sulfate reduction: correlation of microbial activity with lithified micritic laminae in modern marine stromatolites. *Geology* **28**: 919–922. doi:10.1130/0091-7613(2000)28<919:MOOSRC>2.0.CO;2.
- Vogl, K., and Bryant, D.A. (2012) Biosynthesis of the biomarker okenone: χ -ring formation. *Geobiology* **10**: 205–215. doi:10.1111/j.1472-4669.2011.00297.x.
- Voorhies, A.A., Biddanda, B.A., Kendall, S.T., Jain, S., Marcus, D.N., Nold, S.C., *et al.* (2012) Cyanobacterial life at low O₂: community genomics and function reveal metabolic versatility and extremely low diversity in a Great Lakes sinkhole mat. *Geobiology* **10**: 250–267. doi:10.1111/j.1472-4669.2012.00322.x.
- Walker, J.C.G. (1977) *Evolution of the Atmosphere*. New York, NY, USA: Macmillan Publishing Company.
- Walter, M.R. (1976) *Stromatolites*. New York, NY, USA: Elsevier.
- Welander, P.V., Coleman, M.L., Sessions, A.L., Summons, R.E., and Newman, D.K. (2010) Identification of a methylase required for 2-methylhopanoid production and implications for the interpretation of sedimentary hopanes. *Proc Natl Acad Sci USA* **107**: 8537–8542. doi:10.1073/pnas.0912949107.
- Widdel, F., Schnell, S., Heising, S., Ehrenreich, A., Assmus, B., and Schink, B. (1993) Ferrous iron oxidation by anoxygenic phototrophic bacteria. *Nature* **362**: 834–836. doi:10.1038/362834a0.
- de Wit, R., and Van Gernerden, H. (1987) Oxidation of sulfide to thiosulfate by *Microcoleus chthonoplastes*. *FEMS Microbiol Ecol* **45**: 7–13. doi:10.1016/0378-1097(87)90036-X.
- Xiong, J., and Bauer, C.E. (2002) Complex evolution of photosynthesis. *Annu Rev Plant Biol* **53**: 503–521. doi:10.1146/annurev.arplant.53.100301.135212.
- Zehr, J.P., Bench, S.R., Carter, B.J., Hewson, I., Niazi, F., Shi, T., *et al.* (2008) Globally distributed uncultivated oceanic N₂-fixing cyanobacteria lack oxygenic photosystem II. **322**: 1110–1112. doi: 10.1126/science.1165340.
- Zeng, Y., Feng, F., Medová, H., Dean, J., and Koblížek, M. (2014) Functional type 2 photosynthetic reaction centers found in the rare bacterial phylum *Gemmatimonadetes*. *Proc Natl Acad Sci USA* **111**: 7795–7800. doi: 10.1073/pnas.1400295111.