ANNUAL REVIEWS

Annual Review of Earth and Planetary Sciences

Controls on O_2 Production in Cyanobacterial Mats and Implications for Earth's Oxygenation

Gregory J. Dick, Sharon L. Grim, and Judith M. Klatt

Department of Earth and Environmental Sciences, University of Michigan, Ann Arbor, Michigan 48103, USA; email: gdick@umich.edu

Annu. Rev. Earth Planet. Sci. 2018. 46:123–47

First published as a Review in Advance on March 12, 2018

The *Annual Review of Earth and Planetary Sciences* is online at earth.annualreviews.org

https://doi.org/10.1146/annurev-earth-082517-010035

Keywords

cyanobacteria, sulfide, oxygenation, anoxygenic photosynthesis, microbial mat, Proterozoic

Abstract

Cyanobacterial mats are widely assumed to have been globally significant hot spots of biogeochemistry and evolution during the Archean and Proterozoic, but little is known about their quantitative contributions to global primary productivity or Earth's oxygenation. Modern systems show that mat biogeochemistry is the outcome of concerted activities and intimate interactions between various microbial metabolisms. Emerging knowledge of the regulation of oxygenic and sulfide-driven anoxygenic photosynthesis by versatile cyanobacteria, and their interactions with sulfur-oxidizing bacteria and sulfate-reducing bacteria, highlights how ecological and geochemical processes can control O_2 production in cyanobacterial mats in unexpected ways. This review explores such biological controls on O_2 production. We argue that the intertwined effects of light availability, redox geochemistry, regulation and competition of microbial metabolisms, and biogeochemical feedbacks result in emergent properties of cyanobacterial mat communities that are all critical yet largely overlooked mechanisms to potentially explain the protracted nature of Earth's oxygenation.

1. INTRODUCTION

Anoxygenic photosynthesis (AP): photosynthesis in which no O_2 is produced; alternatives to water, such as hydrogen sulfide, are used as electron donor

Redox proxies: information from sedimentary rocks (e.g., trace element and isotopic data) providing insights into chemistry and redox conditions of ancient environments

The evolution of Earth's surface geochemistry was tightly coupled to the evolution of O_2-producing photosynthesis by cyanobacteria. This remarkable metabolism is the dominant source of free O_2 at Earth's surface. It transformed Earth into a planet with an O_2-rich surface capable of supporting plants and animals. The Great Oxidation Event (GOE) at 2.3–2.4 Ga is well marked in the rock record by multiple lines of evidence (Lyons et al. 2014). However, what was once viewed as a relatively simple story has deepened into an intriguing puzzle due to mounting evidence that the rise of O_2 was far more complex than a single event. First, transient and/or local pulses of O_2 may date as far back as 3.0 Ga or earlier. If this is true, then why did it take at least a half-billion years between the innovation of oxygenic photosynthesis and the GOE? Second, following the GOE, atmospheric O_2 remained low for nearly two billion years. If cyanobacteria had already risen to prominence, why did it take approximately another two billion years to reach a second oxygenation event that finally brought atmospheric O_2 into the ballpark of modern levels? Calculations suggest that O_2 produced from oxygenic photosynthesis should rapidly overwhelm reducing buffers (Ward et al. 2016). This review focuses on underexplored biological controls on O_2 production—in particular, interactions between microbial metabolisms and with geochemistry in microbial mats that lead to emergent properties of O_2 production. Before digging into these mechanisms we briefly review current evidence on the origins of oxygenic photosynthesis and the biological and geological controls on O_2 production.

1.1. The Origin and Nature of Early Oxygenic Phototrophs

The origin of oxygenic cyanobacteria is key to understanding the pattern of Earth's oxygenation. Unfortunately, the fossil record is not conclusive (Butterfield 2015, Fischer et al. 2016a, Schirrmeister et al. 2016), and molecular biomarkers (Brocks et al. 1999) are now considered unreliable (French et al. 2015). Perhaps more confounding is the link between microfossils and metabolism. Anoxygenic photosynthesis (AP) evolved before oxygenic photosynthesis (OP) (Hohmann-Marriott & Blankenship 2011), and the direct ancestors of cyanobacteria may have been anoxygenic (Fischer et al. 2016a, Johnson et al. 2013) or lacked photosynthetic machinery altogether, acquiring it later via lateral transfer (Soo et al. 2017). It is unclear whether microfossil morphology and/or biomarkers can differentiate oxygenic cyanobacteria from nonphotosynthetic or anoxygenic cyanobacteria. The genomic record has also been interrogated in attempts to resolve cyanobacterial origins, but the lack of anchoring microfossils and biomarkers for calibration of molecular clocks and assignment of absolute ages makes for substantial uncertainty (Butterfield 2015, Schirrmeister et al. 2016).

In the absence of definitive fossil, biomarker, or molecular clock evidence, the most compelling constraints on the origins of OP come from the appearance of free O_2 itself (Lyons et al. 2014, though see Fischer et al. 2016a for caveats). The GOE at 2.3–2.4 Ga is clearly marked, and redox proxies (Robbins et al. 2016) indicate whiffs of O_2 at 2.5–3.0 and even 3.7 Ga (Anbar et al. 2007, Crowe et al. 2013, Planavsky et al. 2014a, Rosing & Frei 2004). Though they are widely employed, much remains to be learned about these geochemical proxies (Robbins et al. 2016), and their interpretation with regard to free O_2 is met with some skepticism (Fischer et al. 2016a). Indeed, a late origin of OP (i.e., at the GOE) remains a viable interpretation (Fischer et al. 2016a, Johnson et al. 2013, Shih et al. 2017, Soo et al. 2017).

1.2. Geological and Geochemical Controls on Oxygenation

Numerous geological and geochemical mechanisms have been proposed to explain both the lag between purported whiffs of O_2 and the GOE and why atmospheric and ocean O_2 levels remained low

through much of the Proterozoic (Planavsky et al. 2014b). Concentrations of O_2 are the result of the balance between its sources and sinks; oxygenation could result from an increase in the strength of the sources of O_2 and/or a decrease in the strength of the sinks. Photosynthesis is a net source of O_2 only when the produced organic carbon (or its reducing equivalents) is buried rather than being consumed by O_2 (Canfield 2005, Falkowski & Isozaki 2008). Reducing chemicals in Earth's oceans and atmosphere buffered O_2 accumulation; O_2 first had to consume them before it could accumulate (Anbar et al. 2007, Canfield 2005, Holland 2006, Konhauser et al. 2011, Ward et al. 2016). Loss and/or decreased production of these reductants could be achieved through atmospheric, geological, or biological mechanisms, or some combination thereof (Canfield 2005, Catling et al. 2001, Daines et al. 2017, Gaillard et al. 2011, Konhauser et al. 2009, Kump & Barley 2007).

Euxinia: a condition in which a natural water body has elevated levels of free hydrogen sulfide

Benthic: used here to refer to habitats in which microbes attach to surfaces such as sediments, soils, and rocks

1.3. The Case for Biology's Role in Protracted Oxygenation

Environmental controls on rates of photosynthesis have long been invoked to explain the timing and pattern of Earth's oxygenation. Nutrients can limit photosynthesis, and availabilities of nitrogen (Anbar & Knoll 2002, Godfrey & Falkowski 2009, Olson et al. 2016), phosphorus (Michiels et al. 2017), and trace metals (Anbar & Knoll 2002) have all been implicated in limiting primary production, and thus O_2 production, in Precambrian oceans. Conversely, increased nutrient fluxes stimulated primary production and oxygenation (Konhauser et al. 2011, Planavsky et al. 2010). Although lack of evidence for sufficiently increased carbon burial has cast doubt on increased production explaining the GOE (Lyons et al. 2014), new models suggest that this mechanism merits further scrutiny (Daines et al. 2017).

The control of OP itself has not received as much attention. In the simplest sense, O_2 production should be proportional to the abundance and activity of O_2-producing cyanobacteria. Organisms newly armed with this metabolism may have been inefficient at first, with limited fitness and/or restricted niches. Johnston et al. (2009) reignited a more sophisticated line of inquiry by showing that the proportional contribution of sulfide-driven AP to overall photosynthesis could have limited O_2 production. Further, only a modest contribution from AP is needed to drive biogeochemical feedbacks that sustain euxinia and low-O_2 conditions. "Competition" between OP and AP may be between different microbes specializing in each of these metabolic modes or within metabolically versatile cyanobacteria capable of switching between the two. These insights emphasize that we must consider the ecology and physiology of early cyanobacteria, both in terms of how they interacted with their environment and competed with other phototrophic groups and in terms of how they regulated their photosynthetic modes (and hence O_2 production) at a cellular level. Johnston et al. framed their argument in terms of the water column while recognizing that it applied to benthic mats as well. Indeed, there are good reasons to expect that this hypothesis is even better suited to cyanobacterial mats: (*a*) Nearly all cyanobacteria known to be capable of AP with sulfide as the electron donor are mat-formers; (*b*) mats are highly productive ecosystems, densely packed into just a few vertical millimeters, where intense metabolic interactions take place, including feedbacks between cyanobacteria and sulfate-reducing bacteria; and (*c*) benthic microbial mats likely played a much greater role in global primary production in the Archean and Proterozoic than they do today. Before delving into the dynamics of these mat communities that shape O_2 budgets we piece together a picture of early phototrophic communities and the environments they inhabited.

2. THE HABITAT AND NATURE OF PRECAMBRIAN PHOTOTROPHS

The nature and spatial distribution of photosynthesis through most of Earth's history were very different than today. Primary production in the modern world is dominated by OP (**Figure 1**);

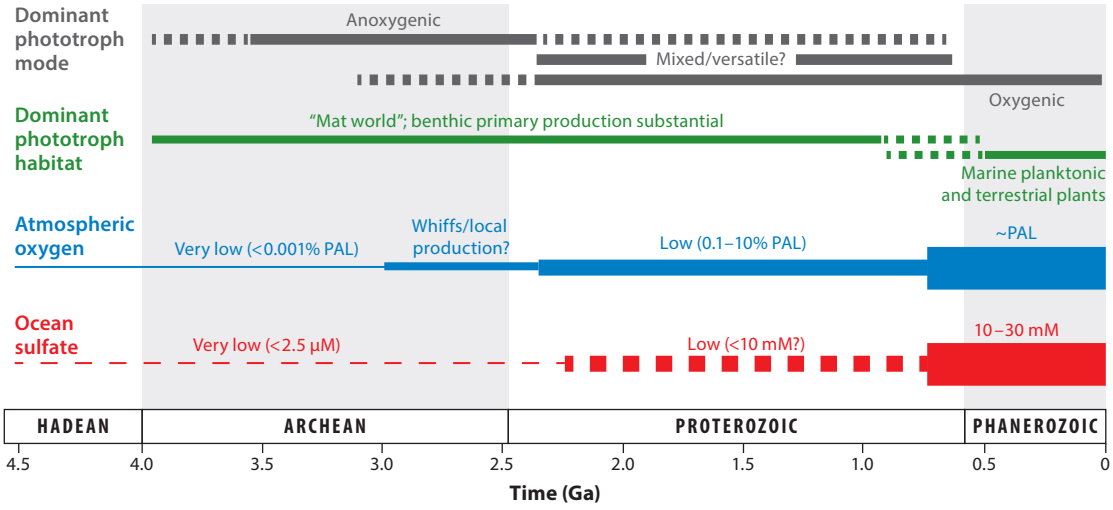


Figure 1

Schematic illustration of estimated phototrophy characteristics, atmospheric oxygen concentrations, and ocean sulfate concentrations through geologic time. Broken lines indicate especially large uncertainty. Estimates of oxygen concentrations are from Lyons et al. (2014); estimates of sulfate concentrations are from Fike et al. (2015), and from Crowe et al. (2014b) as described by Fike et al. (2015). Estimates of Precambrian sulfate concentrations carry substantial uncertainty. Abbreviation: PAL, present atmospheric levels.

about half is contributed by planktonic microbial cells in the water column of the oceans and half by terrestrial vegetation (Duursma & Boisson 1994). In contrast, as the evolutionary precursor to OP (Fischer et al. 2016a, Hohmann-Marriott & Blankenship 2011), AP played a substantial role in primary production in the Archean and perhaps through much of the Proterozoic (**Figure 1**), and benthic habitats likely contributed much more to global budgets of primary production. Although an important role for microbial mat ecosystems is often assumed, their quantitative contribution to global primary production has not been well constrained. Here we critically review knowledge (and knowledge gaps) on the nature of ancient phototrophic ecosystems, with a focus on the benthic realm.

2.1. Geochemistry of Phototrophic Habitats in Precambrian Oceans

Availability of electron donors for AP (e.g., H_2S, H_2, or Fe^{2+}) likely limited global primary production before the advent of OP (Kharecha et al. 2005). The predominant electron donor was likely Fe^{2+}, which was available in plentiful supply in ferruginous oceans (Lyons et al. 2014). Even under the highly reducing conditions of the Archean, ferrophototrophy and other forms of AP could have depleted electron donors, resulting in stratified oceans in which primary production was limited by transport of reduced compounds (**Figure 2**). In upwelling regions where Fe^{2+} was supplied to sunlit depths, photoferrotrophy likely flourished, whereas the remaining photic zone of the open oceans hosted AP driven by sulfur and H_2 supplied from the atmosphere (Kharecha et al. 2005).

As electron donors for AP were depleted in zones of localized high primary production (including mats), the evolutionary pressure to use water, the least (energetically) desirable yet most available electron donor, would have increased. This innovation of H_2O-based OP provided a tremendous competitive advantage and likely resulted in spatially and/or temporally restricted pockets where O_2 accumulated (Anbar et al. 2007, Cloud 1965, Olson et al. 2013) and early aerobic life evolved (Gingras et al. 2011).

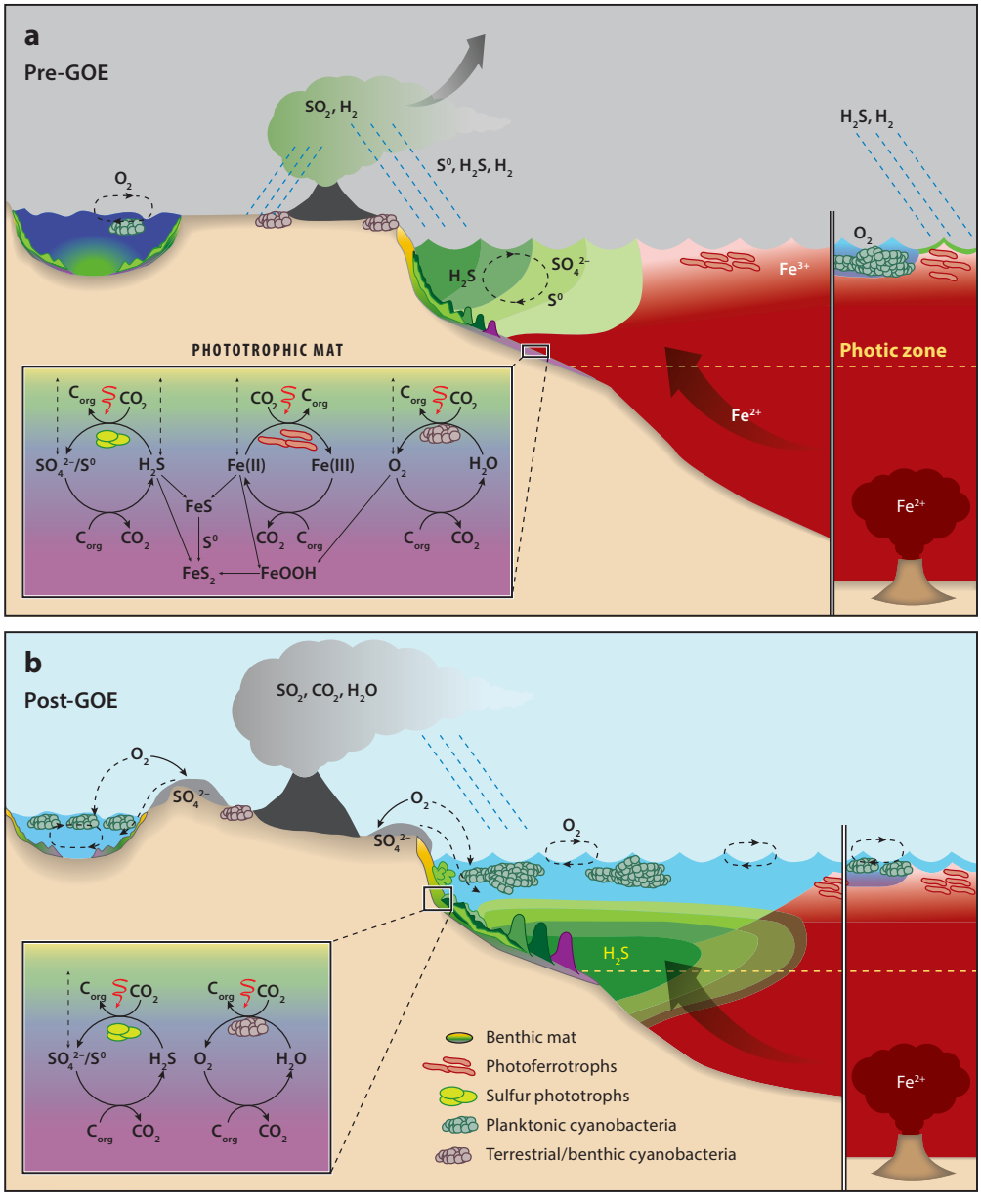


Figure 2

Examples of potential habitats for sulfide-driven anoxygenic photosynthetic mats in pre- and post-GOE settings. Geochemical profiles are based on Lyons et al. (2012); note that geochemical conditions (*blue*, O_2; *green*, H_2S; *red*, Fe^{2+}; *pink*, Fe^{3+}) in the oceans were variable both spatially and temporally at these times, and these illustrations represent two snapshots of many plausible scenarios. (*a*) Pre-GOE: ferruginous oceans, local O_2 production, and local pockets of euxinia of varying extent. The mat inset illustrates the main phototrophic processes and corresponding respiratory and abiotic reactions, as well as how they could be linked to sustain active sulfur cycling and sulfide-driven anoxygenic photosynthesis beneath a ferruginous water column. (*b*) Post-GOE: stratified oceans under a low-O_2 atmosphere with pockets of euxinia growing due to oxidative weathering. The mat inset illustrates how sediment-driven sulfate reduction could fuel sulfide-driven anoxygenic photosynthesis under a low-O_2 water column. At both times the relative importance of each mat process varied within the mats and with external conditions such as water column depth and redox. Abbreviations: GOE, Great Oxidation Event; C_{org}, organic carbon.

Pelagic: occurring in the water column of the open ocean

Initial pulses of oxygen caused a series of geochemical cascades that changed the landscape of electron donors and acceptors available for metabolism, increased concentrations of sulfate and sulfide in Proterozoic oceans, and shifted respiratory processes toward sulfate reduction (Canfield 1998, Konhauser et al. 2011). Although earlier models with euxinic seas throughout the Proterozoic (Canfield 1998) have now been revised toward predominantly ferruginous conditions in the open oceans, evidence points toward spatial and temporal heterogeneity, with sulfur cycling and sulfidic conditions likely restricted to highly productive coastal environments (Lyons et al. 2014) (**Figure 2**). Evidence for sulfide in the photic zone can be found through much of the Proterozoic (Boyle et al. 2013, Brocks et al. 2005, Hardisty et al. 2017, Sahoo et al. 2016).

An important conclusion from the above is that post-GOE oceans still had abundant electron donors for AP despite global atmospheric oxygenation (Johnston et al. 2009) (**Figure 1**). While we can paint a broad picture of diverse forms of phototrophy in Proterozoic and Archean oceans, little is known about the particular organisms of these times. Anoxygenic bacteria that used pigments similar to those in today's green and purple sulfur bacteria inhabited the water column of the mid-Proterozoic (Brocks et al. 2005). Cyanobacteria were likely important members of the phytoplankton, but the relatively recent evolution of dominant modern planktonic cyanobacteria (Neoproterozoic) and eukaryotic algae (Mesozoic) (Katz et al. 2007, Sanchez-Baracaldo et al. 2014) emphasizes that the dominant types were different than those of today and raises the possibility that benthic microbial mats played a greater role.

2.2. Benthic Photosynthetic Habitats

Benthic ecosystems form the interface between water column and sediment and are hot spots for interactions between various physical, chemical, biological, and geological agents (McCave 1976). Photosynthetic microbial mats are driven by light energy, and they are incredibly dense and productive; benthic OP exceeds pelagic OP 1,000–10,000-fold on a per-volume basis (Lalonde & Konhauser 2015 and references therein). This energy is then exploited by other metabolisms. Due to the directionality of incoming sunlight, mass transfer phenomena, and thermodynamics, mats are often vertically stratified, with metabolisms positioned according to their energy yield, efficiency, and kinetics. Unless there is an external supply of electron donor for AP, modern phototrophic microbial mats are ultimately driven by OP. Organic material from oxygenic phototrophs is used in fermentation or consumed by aerobic and anaerobic respiratory processes such as sulfate reduction, liberating H_2S as an electron donor.

The benthic habitat also includes the terrestrial realm, where biological soil crusts may have colonized exposed land surface (Lalonde & Konhauser 2015). Before the evolution of OP, terrestrial primary production was likely more limited in electron donor than coastal primary production, because it relied on atmospheric exchange to obtain electron donors (H_2S, H_2) for photosynthesis (Kharecha et al. 2005). Thus shallow waters in the photic zone were likely the globally most relevant hot spots for benthic primary production prior to OP, consistent with fossil evidence (Grotzinger & Knoll 1999; Tice & Lowe 2004, 2006).

The widespread distribution of microbial mats in the Archean and Proterozoic is reflected in the geological record of microbialites, including stromatolites (Bosak et al. 2013, Grotzinger & Knoll 1999, Stal 2002, Walter et al. 1992). While often interpreted as cyanobacterial mats, anoxygenic phototrophs also accrete stromatolites (Bosak et al. 2007), and the link between stromatolites and cyanobacteria remains an active area of inquiry (Bosak et al. 2013, Fischer et al. 2016a). Indeed, through at least the mid-Proterozoic, these coastal mat ecosystems likely intersected at an oxic–anoxic interface with dynamic redox conditions, including electron donors for AP, such as sulfide (Hardisty et al. 2017).

Nutrients likely limited primary production in the Archean and Proterozoic water column to a greater extent than today (Anbar & Knoll 2002, Godfrey & Falkowski 2009, Michiels et al. 2017). In contrast, mats efficiently retain, recycle, and ultimately concentrate nutrients from the water column into the benthic environment (Des Marais 1998, Hawes et al. 2013, Nold et al. 2013). Thus, nutrient availability favored benthic over water column habitats and likely was not the primary control on mat global distribution and productivity (Des Marais 1998). Rather, the main constraint may have been the area of sea floor exposed to sufficient light. Here we encounter enormous uncertainty. The continents started to form perhaps by 4 Ga (Hastie et al. 2016) and certainly by 3 Ga, and they emerged significantly above sea level at 2.7–2.5 Ga (Dhuime et al. 2015, Lee et al. 2016).

The Archean benthic habitat likely covered enough area for production of O_2 sufficient to generate observed signals of oxidative weathering prior to the GOE (Lalonde & Konhauser 2015). However, constraints on rates of O_2 production such as direct inhibition and competition from other metabolisms are often ignored. Sulfide availability is a chief concern due to its inhibition of OP, sustainment of AP, and strong control on the overall biogeochemistry of microbial mats (Canfield & Des Marais 1993; Jørgensen et al. 1986, 1979). Indeed, despite newly recognized spatial and temporal restrictions on the extent of euxinia in Proterozoic oceans (Reinhard et al. 2013), evidence for sulfur cycling in phototrophic mats dates back to the Archean (Meyer et al. 2017). Highly productive photoferrotrophy and/or OP could have fueled sulfate-reducing bacteria and initiated active sulfide cycling in mat microenvironments, even underneath a ferruginous water column (**Figure 2**). On the other end of the redox spectrum, even in today's largely oxic world, benthic microbial mats are exposed to fluxes of sulfide from sediments on a daily basis. Under a lower-O_2 atmosphere such sulfide exposure would have been even more prevalent, underscoring the critical need to understand the effect of sulfide on cyanobacterial photosynthesis.

3. THE EFFECT OF SULFIDE ON CYANOBACTERIAL PHOTOSYNTHESIS

How did sulfide affect cyanobacterial photosynthesis in Archean and Proterozoic mats? To address questions about physiological responses and adaptations we must turn to modern biology. However, we still have woefully incomplete knowledge of modern microorganisms and metabolisms, with new phyla and processes still being discovered at an astonishing rate. Of the studied cyanobacteria, most are highly sensitive to sulfide, because it directly inhibits OP. Yet cyanobacteria adapted to reducing redox conditions can tolerate sulfide or even use it as the preferred electron donor, switching from OP to sulfide-oxidizing AP (Cohen et al. 1986, Jørgensen et al. 1986, Bühring et al. 2011). Cohen et al. (1986) described four basic responses of cyanobacterial photosynthesis to sulfide: (*a*) complete inhibition, (*b*) continued OP, (*c*) simultaneous OP and AP, and (*d*) switching between OP and AP (Cohen et al. 1986). They recognized that this scheme is an oversimplification and that in reality there is a spectrum of cyanobacterial adaptations to sulfide. Below we highlight how new insights into the interplay between light and H_2S and the timescale of their physiological effects require a more complex scheme for explaining the tremendous variation of sulfide physiologies among cyanobacteria.

3.1. Sulfide Inhibition, Tolerance, and Detoxification

Sulfide directly inhibits the water-splitting reaction of photosystem II (PSII) (Oren et al. 1979). While the exact mechanism is unknown, current models indicate interference with an intermediate of the oxygen-evolving complex (Hamilton et al. 2018, Klatt et al. 2015b). The reversibility and

temporal dynamics of this inhibition are variable and in some cases dependent on light level (Cohen et al. 1986, Hamilton et al. 2018, Klatt et al. 2015b). Sulfide also inhibits other enzymes involved in photosynthesis and associated processes (Hamilton et al. 2018, Miller & Bebout 2004).

Given the potentially lethal effects of sulfide on photosynthesis, cyanobacteria have adapted diverse strategies to cope with it. Some cyanobacteria inhabiting sulfidic environments increase tolerance by synthesizing a more resistant form of PSII (Garcia-Pichel & Castenholz 1990). The level of resistance is highly variable among species (Miller & Bebout 2004), and while the mechanism is not resolved, it may be encoded by one of several *psbA* genes expressed under certain light and/or redox conditions (Grim & Dick 2016). In some cases H_2S can even enhance the rates of OP if concentrations are below a species-specific threshold (Cohen et al. 1986; Klatt et al. 2015a,b).

3.2. Sulfide-Based Anoxygenic Photosynthesis by Cyanobacteria

The ultimate cyanobacterial adaptation to sulfide is the use of H_2S as an electron donor for AP. AP by cyanobacteria was first reported in a culture of *Geitlerinema* sp. PCC9228 (formerly *Oscillatoria limnetica* Solar Lake) (Cohen et al. 1975a). It is supported by three main lines of evidence: (*a*) light-driven stoichiometric coupling of H_2S oxidation to CO_2 fixation (de Wit & van Gemerden 1987, Klatt et al. 2015a, van Gemerden 1993) (**Figure 3**), (*b*) stoichiometric production of an intermediately reduced sulfur compound (S^0 or thiosulfate) (Cohen et al. 1975a, de Wit & van Gemerden 1987), and (*c*) anaerobic photoautotrophic growth in the presence of DCMU, an inhibitor of OP (Oren & Padan 1978). Microsensor-based approaches added another dimension to studying cyanobacterial AP by allowing estimates of rates (Castenholz et al. 1991, Jørgensen & Des Marais 1986) and even affinities (de Wit & van Gemerden 1987, Klatt et al. 2016a) in situ.

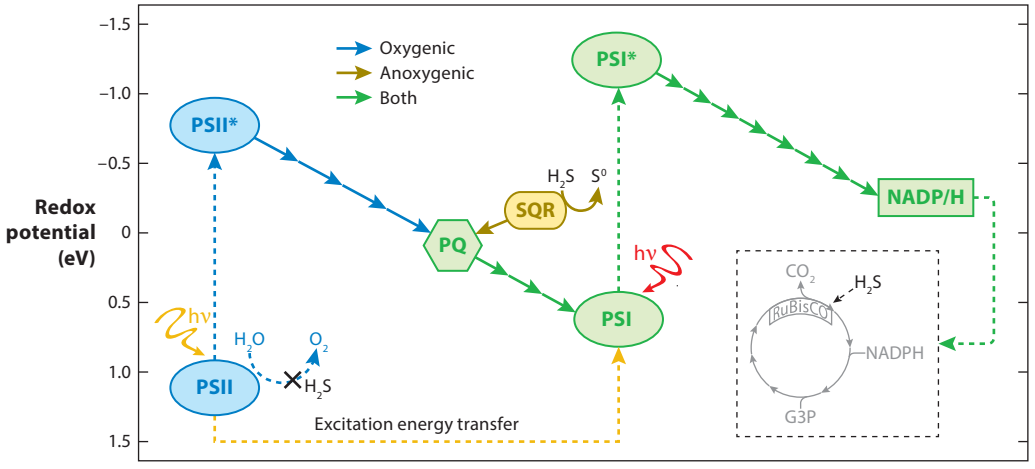


Figure 3

Simplified schematic of oxygenic (*blue arrows*) and anoxygenic (*dark yellow arrows*) electron transport reactions in cyanobacteria. Green arrows indicate reactions shared by both photosynthetic modes. Namely, the oxygenic and anoxygenic electron transport chains intersect in the PQ pool, with PSII and SQR reducing PQ, respectively. Other main sites of interaction of H_2S with photosynthetic reactions are indicated in black: H_2S inhibits oxygenic photosynthesis directly at the oxygen-evolving complex at the donor site of PSII. Also, H_2S can enhance and inhibit CO_2 fixation in the Calvin cycle, possibly due to interaction with RuBisCO. During anoxygenic photosynthesis, state transition and corresponding excitation energy transfer between PSII and PSI are promoted. Figure modified from Klatt et al. (2015a). Abbreviations: G3P, glyceraldehyde 3-phosphate; PQ, plastoquinone; PSI, photosystem I; PSII, photosystem II; SQR, sulfide quinone reductase.

Cyanobacteria in microbial mats transition from AP to OP and back over diel light cycles (Castenholz et al. 1991, de Beer et al 2017, Jørgensen et al. 1986, Klatt et al. 2016b)—a critical adaptation to mats, where H_2S and O_2 concentrations often fluctuate. H_2S concentration has long been considered a key determinant of the partitioning between OP and AP, both because of its toxicity toward OP and because it drives AP. The concentration of H_2S at which AP kicks in is species dependent, but may be below 1 μM (Hamilton et al. 2018; Klatt et al. 2015a, 2016b). AP can entirely replace OP at H_2S concentrations as low as 1 μM, and some cyanobacteria conduct AP at H_2S concentrations of >10 mM (Klatt et al. 2015a).

Diel: a regular daily cycle over a 24-h period

Cyanobacterial AP occurs through photosystem I (PSI) (**Figure 3**). H_2S is oxidized by sulfide quinone reductase (SQR), which passes electrons to PSI via the plastoquinone (PQ) pool. Because PSI has a different absorption spectrum than PSII, the spectral quality of light influences the balance of AP and OP (Oren et al. 1977). The mechanisms underlying the regulation of OP and AP are not yet clear, especially in the context of the diversity of responses to sulfide. However, an emerging theme is that the balance of OP and AP can be determined by simple biochemical affinities and kinetics. OP and AP electron transport chains intersect in the PQ pool, and electrons derived from H_2O and H_2S therefore compete for this pool (**Figure 3**). The apparent affinities of the immediate electron donors for oxidized PQ in OP (PSII) and in AP (SQR) determine the relative contributions of both photosynthetic processes to the overall electron transport rate. Theoretically, with no changes in the transcriptome or proteome, cyanobacteria can seamlessly switch between AP and OP, a key advantage in the dynamic redox environment of microbial mats (Klatt et al. 2015a). OP can have low rates or can even be completely absent in the presence of sulfide, even though PSII is not inhibited.

3.3. Light and Temporal Dynamics Shape the Cyanobacterial Response to Sulfide

The kinetic competition between AP and OP for shared components of the electron transport chain implies that light intensity influences the switch between these two photosynthetic modes. Coregulation of AP and OP by light and H_2S has been observed in two versatile cyanobacteria (Klatt et al. 2015a, 2016a) in which light determines critical thresholds of H_2S concentrations below which simultaneous OP and AP is possible and at which rates of AP and OP are equal. Light intensity also determines the upper limit of AP rates (Hamilton et al. 2018; Klatt et al. 2015a, 2016a). These effects can be explained by a model in which H_2S oxidation rates are influenced by availability of oxidized PQ, which is governed by light energy harvested in PSI (Hamilton et al. 2018; Klatt et al. 2015a, 2016a).

The interplay between light and sulfide also involves temporal dynamics. AP in some cyanobacteria is inducible, requiring exposure to both H_2S and light (Garcia-Pichel & Castenholz 1990, Oren & Padan 1978). There can also be a delay between depletion of H_2S and recovery of OP, and this rate of recovery can be governed by light (Hamilton et al. 2018). Similarly, recovery after anoxia can be boosted by H_2S (Klatt et al. 2015b). In some cyanobacteria, OP can be sustained for only a limited irradiance-dependent time frame (Klatt et al. 2015b). Hence, temporal dynamics are a crucial component of adaption to the diurnally fluctuating redox conditions in mats and may play an underappreciated role in overall O_2 production rates (see below).

4. MODERN ANALOGS OF PRECAMBRIAN CYANOBACTERIAL MATS REVEAL ECOLOGICAL CONTROLS ON O_2 PRODUCTION

Studies of modern microbial mats are crucial to uncovering the history of photosynthesis and its interplay with geochemistry. Given the rapid response, small size, and diffusion-controlled

transport mechanisms of mats, their biogeochemistry is readily studied and modeled (Des Marais 2003). Mats enable studies of interactions and feedbacks among microbial groups and better parameterization of models of ancient ecosystems (de Wit et al. 1995, Herman & Kump 2005), leading to testable hypotheses on how biogeochemical cycles operated in the past.

What qualifies contemporary ecosystems as analogs of ancient phototrophic ecosystems relevant to Earth's oxygenation? To return to a world dominated by microbial mats we need to visit extreme environments where plants (mat competitors) and animals (mat grazers) are largely excluded due to their lower tolerance of extreme temperature, salt, acidity, or sulfide. Terrestrial and shallow marine hydrothermal systems, hypersaline environments, intertidal mats, and redox-stratified lakes and marine basins have all served as valuable analogs of mat systems and water columns and have been reviewed extensively (Camacho et al. 2017, Fike et al. 2008, Pierson et al. 1992). Concerning O_2 production, however, the key differences between modern and ancient mats are redox environment and photosynthetic mode; whereas the vast majority of modern phototrophic communities exist under oxic conditions and conduct OP, Archean and Proterozoic benthic environments were marked by lower O_2 and greater exposure to reducing compounds that could fuel AP, such as H_2S.

Several modern environments, including springs, sinkholes, and perennially ice-covered lakes, have been recently used to study O_2 production under low-O_2, sulfidic, and low-sulfate conditions likely characteristic of shallow aquatic mat habitats of the Archean and Proterozoic. Among these, the sulfidic Frasassi springs in mid-central Italy (Klatt et al. 2016b, Macalady et al. 2006, Montanari et al. 2002); the Middle Island Sinkhole in Michigan, USA (Kinsman-Costello et al. 2017, Ruberg et al. 2008, Voorhies et al. 2012); the Little Salt Spring sinkhole in Florida, USA (Clausen et al. 1979, de Beer et al. 2017, Hamilton et al. 2018); and Lake Fryxell, a ~20-m-deep meromictic ice-covered lake in Antarctica (Sumner et al. 2015), provide particularly valuable natural laboratories for studying versatile cyanobacteria as well as broader interactions and competition between chemosynthetic and photosynthetic metabolisms and groups. Most prominently, cyanobacterial mats in all these systems thrive under low-O_2 and/or sulfidic conditions and display light-dependent elevated O_2 concentrations within the mats compared to surrounding water column. Thus, they serve as valuable analogs of oxygen oases that likely occurred in mats after the evolution of OP but before widespread oxygenation.

Studies of these analogs reveal that even when external light and nutrients are plentiful, internal biological and geochemical processes may limit photosynthetic production of O_2. H_2S exerts key controls because it inhibits OP and serves as the primary electron donor for the two key competitive metabolisms, AP and chemosynthesis. Light availability also mediates competition due to the obvious advantage provided to phototrophs over chemotrophs, but also due to its modulation of the rates of OP and AP. Various interactions between microbial groups, both competitive and cooperative, add complexity to the controls on O_2 budgets (**Figure 4**). The effect of competition and feedbacks between AP and OP in the water column has been explored previously (Johnston et al. 2009); here we add chemosynthesis to the mix and focus on benthic microbial mat communities, where biogeochemical interactions and feedbacks are concentrated.

4.1. Competition Between Oxygenic and Anoxygenic Phototrophs

The primary drivers of the distribution of obligate anoxygenic and oxygenic phototrophs in microbial mats are temperature, light availability, and sulfide concentration (Boyd et al. 2012). In microbial mats underlying an oxic water column, the main source of sulfide is often located within deeper, nonphotosynthetic layers of the mat or in underlying sediments. If light is limiting in

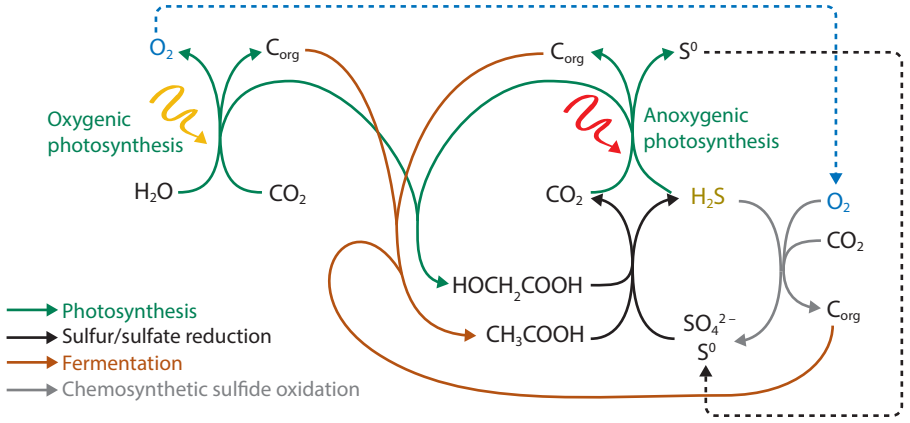


Figure 4

Metabolic interactions based on carbon and sulfur cycling in cyanobacterial mats. Acetate (CH_3COOH) is shown as a representative product of fermentation. Glycolate ($HOCH_2COOH$) is representative of small organics released during high productivity. Abbreviation: C_{org}, organic carbon.

such a system, anoxygenic phototrophs must position themselves according to the potential tradeoff between obtaining light from above and electron donor (e.g., H_2S) from below. In contrast, oxygenic phototrophs are not limited by electron donor (water) in aqueous environments, and cyanobacteria are therefore free to occupy the upper, high-light portion of the mat. Extant obligate anoxygenic phototrophs occupy a distinct niche in terms of light absorption spectra that is well tuned to the local light environment underneath oxygenic phototrophs; these two groups do not directly compete for light, so niche differentiation allows their coexistence (Gause 1934, Stomp et al. 2007).

The situation may be different when nutrients limit primary production in microbial mats (Al-Thani et al. 2014, Pinckney et al. 1995). In this scenario the direction of supply can be a critical determinant for the outcome of competition. If the limiting nutrient is supplied externally or by remineralization within aerobic mat layers, then the outcome may be comparable to light limitation, and OP is favored over AP. However, if anaerobic remineralization is the main supply of limiting nutrient, then anoxygenic phototrophs establish a nutrient "gauntlet," thus tempering OP because of their advanced light-utilization efficiency (Johnston et al. 2009). This concept may not fully apply if bioavailable nitrogen limits productivity, because N_2-fixing cyanobacteria would be favored unless limited by trace metal availability (Anbar & Knoll 2002, though see Olson et al. 2016 for potential physiological constraints). Some cyanobacteria preferentially couple sulfide-driven AP to nitrogen assimilation rather than carbon fixation (Klatt et al. 2015a, Padan & Cohen 1982, Villbrandt & Stal 1996) and are thus well suited to sulfidic, nitrogen-limited settings.

The niches of cyanobacteria and obligate anoxygenic phototrophs can overlap if the cyanobacteria are photosynthetically versatile and can switch between OP and sulfide-driven AP, invoking competition for H_2S. Both the affinity for and toxicity of H_2S must be considered. Based on studies of *Microcoleus chthonoplastes* (de Wit & van Gemerden 1987), AP cyanobacteria are commonly assumed to have low affinity for sulfide compared with AP specialists, suggesting that they should not be competitive at low H_2S concentrations (Camacho et al. 1991, de Wit & van Gemerden 1987, Hamilton et al. 2016, Overmann & Garcia-Pichel 2013, Stal 2002). However, the range of affinities for H_2S in cyanobacteria is enormous, with K_m values ranging from <10 μM (Klatt

et al. 2015a, 2016a) to nearly 1 mM (de Wit & van Gemerden 1987), so the outcome of their sulfide-based competition with anoxygenic bacteria varies depending on the species.

Sulfuretum: microbially mediated cycling of sulfur between reduced and oxidized forms

Given the potentially overlapping niches of versatile anoxygenic phototrophic cyanobacteria and AP specialists, what are the advantages of versatility? The advantage over obligate AP is clear: Versatile cyanobacteria can switch to water once H_2S is depleted, so there is no limitation of electron donor. But why is versatility better than obligate OP? The answer is not obvious; neither strategy is limited by the supply of electron donor, and oxygenic phototrophs have evolved strategies to tolerate sulfide. Five main hypotheses concerning the advantage of photosynthetic versatility in cyanobacteria have been put forward: (*a*) Rapid removal of H_2S is for detoxification (de Wit & van Gemerden 1987, Jørgensen et al. 1986, Stal 2002); (*b*) AP is energetically more favorable than OP when excitation energy transfer between PSI and PSII occurs or if the photosystem stoichiometry is adjusted (Klatt et al. 2015a,b); (*c*) AP helps cyanobacteria to directly outcompete obligate anoxygenic phototrophs by rapid H_2S removal (Stal 2002); (*d*) the transition from AP to OP helps cyanobacteria regulate internal redox balance and enhances competitiveness for nutrients when NO_3^- assimilation and N_2 fixation are coupled to AP (Klatt et al. 2015a); or (*e*) simultaneous OP and AP induce a negative feedback effect on H_2S production and thus temper total AP (Klatt 2015). These hypotheses are not mutually exclusive. That cyanobacteria conduct AP suggests that there is a strong advantage to versatility in mats, where redox swings dramatically between sulfidic and oxic on diel cycles.

Diel fluctuations in light, O_2, and H_2S have important effects on mat structure and the balance between AP and OP. A common pattern is for AP to predominate in the morning, when H_2S is available in the photic zone, followed by a transition to OP upon light-driven H_2S depletion (de Beer et al. 2017, Jørgensen et al. 1986, Klatt et al. 2016b, van Gemerden 1993) (**Figure 5**). When light levels again decline in the evening, OP declines, the H_2S chemocline rises into the photic zone, and photosynthesis transitions back to AP. Especially under low-light conditions, this promotion of AP and inhibition of OP in the morning and evening can dramatically shrink the window of oxygen production; at Little Salt Spring, net OP was limited to 4 h/day (de Beer et al. 2017). Intriguingly, the length of the OP window was widened in mats where solid-phase Fe(III) accumulated, perhaps due to abiotic oxidation of Fe^{2+} by O_2, thus shielding cyanobacteria from H_2S. These results highlight how diel light dynamics, interacting microbial metabolisms, and geochemistry can conspire to shape O_2 budgets.

In defining the ecological role of cyanobacterial AP, feedback effects must also be considered. In addition to consuming sulfide by AP, cyanobacteria also modulate the sulfur cycle by feeding sulfate-reducing bacteria, which manipulates their microenvironment by providing organic carbon to kick off the sulfuretum (de Wit et al. 1995). Further, the type of organic carbon (exopolysaccharides, glycolate, fermentation products, and substrates from death and cell lysis) and the timing and location of its release vary according to patterns of cyanobacterial vertical migration in the mat. For example, *Microcoleus* spp. position themselves in the sulfide gradient in the dark and in light (Richardson & Castenholz 1989), determining the location, timing, and type of organic carbon available. This means that the cyanobacteria can shape the magnitude and location of H_2S production, which, as described above, influences the mode of phototrophy (AP versus OP) and their competition with other phototrophs and lithotrophs. The close coupling between versatile cyanobacteria and local production of sulfide by sulfate-reducing bacteria is evident at Little Salt Spring (de Beer et al. 2017, Hamilton et al. 2018). Overall, the above discussion shows that the competition between cyanobacteria and obligate anoxygenic bacteria has many dimensions, and indeed there are others not detailed here, such as superior cyanobacterial strategies for dealing with photooxidative stress (Asada 1996, Beatty 2002, Fischer et al. 2016b, Glaeser et al. 2011, Oh & Kaplan 2001).

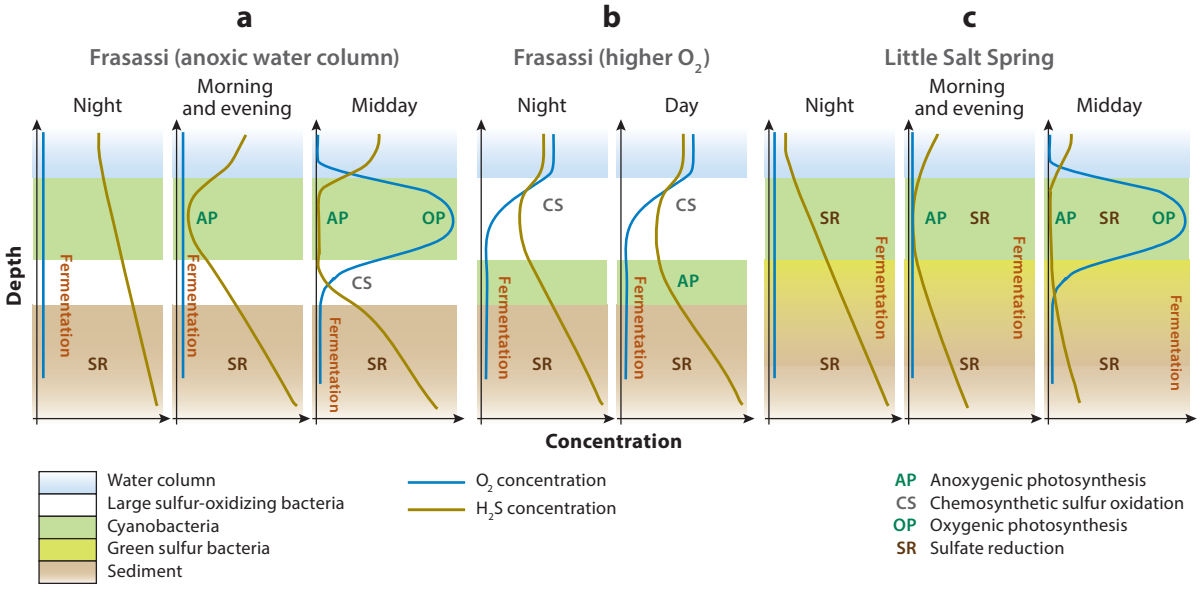


Figure 5

Diel dynamics shape O_2 budgets in cyanobacterial mats. Layered schematics show estimated localization of processes over a diel cycle. (*a*) A mat from the Frasassi springs in mid-central Italy that forms underneath an anoxic sulfidic water column. Temporal and spatial arrangements of processes behave as expected. (*b*) A mat from Frasassi where light, O_2, and H_2S are all supplied from above, allowing sulfur-oxidizing bacteria to compete for the uppermost position. (*c*) Processes in mats at Little Salt Spring in Florida, USA, where green sulfur bacteria are abundant. Concomitant activity of green sulfur bacteria and cyanobacteria leads to the depletion of sulfide in the photosynthetically active layers—and, mysteriously, also below. Locally produced sulfide still fuels cyanobacterial anoxygenic photosynthesis until the inhibitory effects of H_2S on oxygenic photosynthesis are overcome. Oxygenic photosynthesis can occur earlier during the day in mats that retain Fe pockets, which shield cyanobacteria from toxic H_2S (not shown). Total sulfide (here, H_2S) and O_2 depth profiles are estimated based on microsensor measurements in cyanobacterial isolates and mats at Little Salt Spring (de Beer et al. 2017, Hamilton et al. 2018) and in the Frasassi cyanobacterial mats (Klatt et al. 2016b).

4.2. Competition Between Phototrophs and Chemolithotrophs in Microbial Mats

Chemotrophic sulfur-oxidizing bacteria can also compete with both obligate anoxygenic bacteria and versatile cyanobacteria. Again, light availability and depth of the O_2–H_2S interface are primary determinants of competitive outcomes (Jørgensen & Des Marais 1986, Klatt & Polerecky 2015, Visscher 1992). In microbial mats underlying an oxic water column, where the main source of sulfide is often located within deeper layers of the mat, sulfur-oxidizing bacteria need to adjust their position in opposing gradients of sulfide and electron acceptor (O_2 or NO_3^-). The relative depths of the O_2–H_2S interface and the light–H_2S interface are thus crucial for the competition between obligate anoxygenic phototrophs and chemolithotrophs. Because oxygenic phototrophs are not faced with the dilemma of opposing gradients and because cyanobacteria and chemolithotrophs rely on entirely different forms of energy, competition is not expected. However, studies of the Frasassi sulfidic springs show that these two functional groups can compete for the uppermost position of the mat—with unexpected outcomes.

The Frasassi sulfidic springs illustrate how O_2 availability can mediate competition between versatile cyanobacteria and sulfur-oxidizing bacteria within microbial mats (**Figure 5**). Under low-O_2 conditions (<5 μM O_2), photosynthetic mats are dominated by versatile cyanobacteria that switch between AP and OP over diel cycles (Klatt et al. 2016b). Aerobic sulfide oxidation

by sulfur-oxidizing bacteria is entirely dependent on O_2 produced by cyanobacteria. In contrast, at higher O_2 (>45 μM), mats are driven by chemosynthesis rather than photosynthesis, even in the presence of full sunlight (Klatt et al. 2016b). Here the sulfur-oxidizing bacteria profit from a continuous supply of both H_2S and O_2 from the water column and form a dense reflective layer that allows only a small fraction of light to reach the cyanobacteria underneath, which perform AP rather than OP. Interestingly, this state is not optimized energetically; more energy would be available to the community if the cyanobacteria were on top to take full advantage of the sunlight. These results emphasize the importance of chemosynthesis as a competitor of photosynthesis and highlight how bacterial behavior, in this case migration, can fundamentally reduce the productivity and O_2 budget of ecosystems. They also suggest that the first pulses of O_2 may have promoted chemosynthesis and induced negative feedback effects on OP.

In summary, both beneficial and competitive interactions between microbes have consequences for the net O_2 budget of microbial mats. Obligate anoxygenic phototrophs, obligate oxygenic phototrophs, and versatile cyanobacteria have different effects on net O_2 budgets, and chemolithotrophs can play an important role. Thus, the composition of microbial mat communities, in terms of the different functional guilds and the diversity of physiologies within them, and their relative coverage of global mat habitat, is expected to influence global O_2 budgets. Critical to piecing together the evolutionary and ecological history of these organisms through time is the development of signatures that can be used to trace them through records left in rock and genome sequences.

5. MOLECULAR MECHANISMS AND EVOLUTIONARY HISTORY OF ANOXYGENIC PHOTOSYNTHESIS IN CYANOBACTERIA

Genes, transcripts, and proteins can serve as molecular signatures for tracking metabolic processes on timescales ranging from minutes to eons (Dick & Lam 2015). In modern systems these molecules may be detected more readily than the cryptic biogeochemical processes they catalyze (Canfield et al. 2010). Whole genomes also represent a record for inferring the timing and nature of metabolic evolution through Earth's history (Soo et al. 2017). Hence, we have much to learn from studying the genes and enzymes that underpin cyanobacterial adaptations to sulfide, including sulfide-driven AP.

SQR is a key enzyme both for sulfide-driven AP and for sulfide tolerance in cyanobacteria. It is a membrane-bound protein that oxidizes sulfide and transfers electrons to quinones in the electron transport chain (Bronstein et al. 2000) (**Figure 3**). Genes encoding SQR are present in organisms in all three domains of life, including cyanobacteria, obligate anoxygenic bacteria, and lithotrophs (Gregersen et al. 2011, Marcia et al. 2010, Theissen et al. 2003). Experimental and structural studies provide functional context for the *sqr* phylogeny; the different clades of the SQR enzyme display key biochemical differences, such as affinity for sulfide, that underpin important physiological diversity. In addition to its role in anoxygenic phototrophy, SQR also catalyzes sulfide oxidation during chemolithotrophy (Theissen et al. 2003), detoxification of sulfide (Marcia et al. 2009) and metals (Nagy et al. 2014, vande Weghe & Ow 1999), and signal transduction (Wang 2002). In eukaryotes, SQR activity in mitochondria is linked to sulfide consumption and detoxification and to ATP synthesis (Theissen et al. 2003).

5.1. Phylogenetic Distribution and Evolutionary History of Cyanobacterial Sulfide Physiology and Sulfide Quinone Reductase

Cyanobacterial sulfide adaptations are not linked to phylogeny of core genes such as 16S rRNA; they are distributed throughout the cyanobacterial phylum and vary among closely related strains

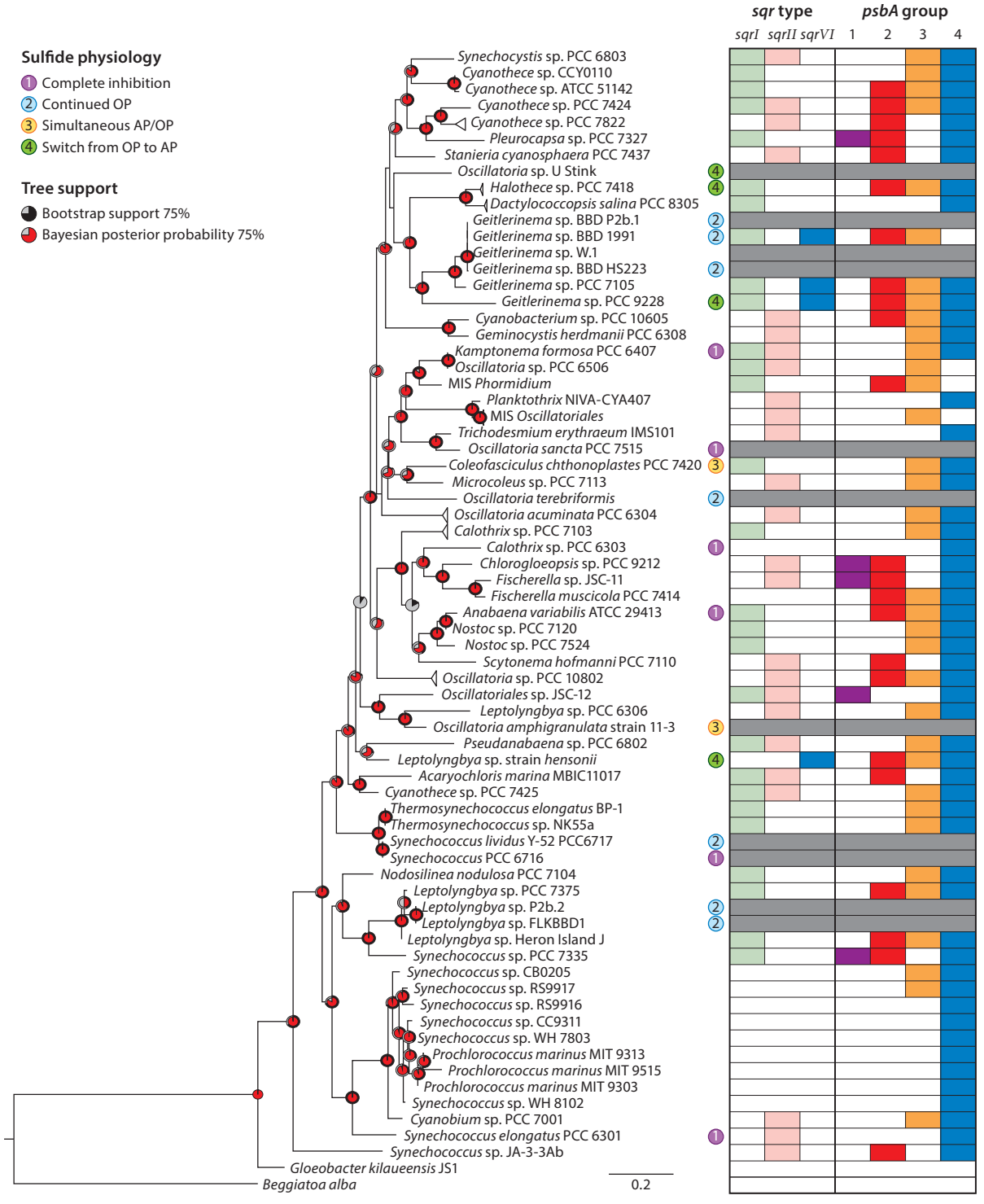
(Miller & Bebout 2004) (**Figure 6**). Genome sequences provide new windows into the genetic basis of this pattern; *sqr* is present in over 40 cyanobacterial genomes but absent in the remaining ~90% of publicly available cyanobacterial genomes (Grim & Dick 2016). However, while many cyanobacteria use SQR for light-dependent sulfide oxidation, this does not necessarily imply coupling to carbon fixation or that *sqr* encodes AP. In some cyanobacteria *sqr* is thought to encode sulfide tolerance (Den Uyl et al. 2016, Miller & Bebout 2004); thus, verification of sulfide-based AP requires physiological evidence.

Three of the six *sqr* clades (Marcia et al. 2010) are found in cyanobacteria (Grim & Dick 2016, Shahak & Hauska 2008). Like the sulfide phenotypes, *sqr* genes are scattered throughout the cyanobacterial phylogeny, but the presence of the different types of *sqr* is not obviously related to observed phenotype (**Figure 6**). Type I *sqr* genes are specific to cyanobacteria (Grim & Dick 2016), have high affinity for sulfide and exposure-dependent expression and are used in sulfur-dependent AP in several model organisms, including *Geitlerinema* sp. PCC 9228, *Halothece* spp., and *Synechocystis* spp. (Bronstein et al. 2000, Gregersen et al. 2011, Nagy et al. 2014). Instead of or in addition to type I, cyanobacteria may possess type II *sqr* genes, which have low affinity for sulfide and are related to *sqr* genes from eukaryotes that are involved in sulfide detoxification (Nagy et al. 2014). Both type I and type II *sqr* genes are found in natural systems with anoxygenic cyanobacteria (Cole et al. 2014, Grim & Dick 2016, Voorhies et al. 2012). Recently, type VI *sqr* genes were identified in cyanobacterial genomes, but their presence in cyanobacteria is rare and their function unknown (Grim & Dick 2016). Type VI *sqr* genes in sulfur-oxidizing bacteria and noncyanobacterial anoxygenic phototrophs are expressed at elevated sulfide concentrations (>4 mM) (Chan et al. 2009).

The phylogenetic distribution of *sqr* genes (Theissen et al. 2003) and their presence on plasmids and within transposable elements (Nagy et al. 2014) have been interpreted as evidence for horizontal gene transfer. However, *sqr* genes are absent from the picocyanobacteria, indicating some phylogenetic cohesiveness (**Figure 6**). Cyanobacterial AP has been hypothesized to be a relic from ancestral cyanobacteria that predated OP (Oren et al. 1977, Padan 1979) or an intermediate state during the evolution of OP (Hamilton et al. 2016). An early study of the phylogenetic distribution of *sqr* in cyanobacteria concluded that it is a derived rather than ancestral characteristic (Sanchez-Baracaldo et al. 2005), but details of the evolutionary history of *sqr* and AP in cyanobacteria and how that history relates to geologic time and the geochemical evolution of the photic zone remain unclear. The growing availability of genome sequences, together with new phylogenomic methods, makes this a promising area for future research.

5.2. Molecular Regulation of Anoxygenic Photosynthesis in Cyanobacteria

In addition to biochemical kinetics (see Section 3.2), regulation of gene and/or protein expression may also play a role in transitions between AP and OP. Some cyanobacteria perform AP immediately upon exposure to sulfide (Garcia-Pichel & Castenholz 1990, Hamilton et al. 2018), while others require up to 4 h for synthesis of SQR (Arieli et al. 1991, Garcia-Pichel & Castenholz 1990, Oren & Padan 1978). A transcriptional regulator in the *sqr* operon (Bronstein et al. 2000) is related to the *arsR* family of transcriptional regulators, which are typically involved in arsenic resistance (Nagy et al. 2014). In cyanobacteria the *arsR*-like gene is commonly found in association with *sqr* (Grim & Dick 2016). In *Synechocystis* sp. 6803 it represses *sqr* expression until exposure to sulfide or arsenite (Nagy et al. 2014). Taken together, these observations suggest that the key gene for sulfide tolerance and AP is regulated at the transcriptional level in some if not all cyanobacteria.



(Caption appears on following page)

Figure 6 (*Figure appears on preceding page*)

Phylogenetic tree of cyanobacterial 16S rRNA genes compared to phylogeny and distribution of *sqr* and *psbA* and to sulfide physiologies. Sequences from 69 cyanobacterial taxa and *Beggiatoa alba* (outgroup) were aligned in mothur 1.34.0 to the SILVA full-length rRNA database (release 119) and trimmed to consensus length. Aligned sequences were analyzed in RAxML 8.1.15 with the GTRGAMMAI algorithm and bootstrapped 1,000 times. The resulting tree was visualized in FigTree 1.4.2 and edited in Adobe Illustrator. For Bayesian analysis, MrBayes 3.2 was used with the GTRGAMMAI model. Two Metropolis-coupled Markov chain Monte Carlo trees, each with four chains (three heated, one cold), were compared every 1,000 generations, starting with a random tree and continuing for 10,000,000 generations, until the standard deviation of split frequencies was below 0.01. Bootstrap values (from RAxML; *black circle graphs*) and Bayesian posterior probabilities (from MrBayes; *red circle graphs*) are reported for consensus nodes. Translated *psbA* and *sqr* genes (amino acid sequences) were aligned with Clustal Omega 1.2.0 (Sievers et al. 2011) and analyzed with the PROTGAMMAGTR algorithm in RAxML, with the same parameters as above. Phylogenetic group categories are after Cardona et al. (2015) and Marcia et al. (2010). Sulfide physiologies are (①) complete inhibition, (②) continued OP, (③) simultaneous OP and AP, and (④) switching between OP and AP (Cohen et al. 1986). White shading indicates gene absence, and gray shading indicates lack of genomic data. Abbreviations: AP, anoxygenic photosynthesis; OP, oxygenic photosynthesis.

5.3. The Potential Role of Additional Proteins in Sulfide Tolerance and Versatile Anoxygenic/Oxygenic Photosynthesis

The lack of strong correlation between *sqr* genes and sulfide phenotype (**Figure 6**) implies involvement of additional proteins and/or diverse regulatory mechanisms. This notion is supported by results from Hamilton et al. (2018) that suggest a second sulfur-oxidizing enzyme is needed to fit observations to the current biochemical model. Additionally, given that sulfide-tolerant cyanobacteria produce sulfide-resistant PSII complexes and that sulfide inhibition of OP occurs on the water-oxidizing side of PSII (Miller & Bebout 2004), the D1 protein is a strong candidate to influence sulfide response phenotype. Encoded by the *psbA* gene, four different types of D1 proteins enable cyanobacteria to efficiently manage O_2 production in order to optimize photosynthesis, minimize oxidative stress, and facilitate O_2-sensitive processes such as nitrogen fixation (Aro et al. 1993, Blankenship 2002, Sicora et al. 2009). They are characterized by their water-oxidizing capability and conditions of expression: (*a*) "Super-rogue" versions are synthesized during exposure to far-red light and do not oxidize water; (*b*) anaerobic "rogue" variants with uncertain capacity for water oxidation are expressed in the dark, with nitrogenase activity, and during heterotrophic growth; (*c*) microaerobic functional forms are expressed under low oxygen concentrations; and (*d*) regular/high-light D1 and related photoprotective versions synthesized under high-light and oxic conditions (Cardona et al. 2015). Substitution of alternative D1 subunits into PSII may confer tolerance to sulfide and/or serve as a placeholder during PSI-based AP (Grim & Dick 2016), but this remains to be demonstrated.

A third mechanism for regulating AP and OP is to manage the ratio of PSII to PSI. Long-term exposure to H_2S alters the stoichiometry of PSII and PSI in cyanobacteria (Garcia-Pichel & Castenholz 1990) and plants (Dooley et al. 2013). While this may be suitable for long-term adaptations, short-term responses are likely best mediated by either kinetic mechanisms or targeted substitution of proteins such as D1 described above. Finally, while oxidation of sulfide via SQR and extracellular accumulation of elemental sulfur remain the paradigm for AP in cyanobacteria (Castenholz & Utkilen 1984, Cohen et al. 1975a, Cohen et al. 1975b), evidence for stoichiometric oxidation of sulfide to thiosulfate (de Wit & van Gemerden 1987, Utkilen 1976) suggests the existence of alternative yet unidentified pathways for AP in cyanobacteria. More widespread development of genetic systems (Bronstein et al. 2000) is critical to advance this field.

CONCLUSIONS AND OUTLOOK

Although cyanobacterial mats shaped ecology and geochemistry through much of Earth's long low-O_2 history, scarce knowledge on their functioning under these conditions constrains our

ability to build an understanding of the biological and geochemical evolution of the biosphere. Studies of modern analogs and organisms detailed here highlight how microbial metabolism and behavior can lead to unexpected biogeochemical outcomes, especially those that limit O_2 production. Competition among oxygenic and anoxygenic phototrophs and chemolithotrophs fundamentally affects net O_2 production in mats and is shaped by the magnitude, direction, and continuity of external supply of electron donor, nutrients, and light and by biological responses that create feedbacks on all three of these factors. Microbial mats are hot spots of intense biological activity and biogeochemical cycling with geochemical microenvironments that are not easily measured in modern mats, much less proxies used to infer ancient conditions.

An overlay of current understanding of the biology of O_2 production in mats and geochemistry of ancient mat habitats reveals gaps and opportunities for advances. Inhibition of OP and onset of AP can occur at sulfide concentrations as low as 1 μM (Hamilton et al. 2018; Klatt et al. 2015a, 2016a). Although progress in tracing the redox geochemistry of Archean and Proterozoic oceans points toward more ferruginous and less euxinic conditions than recognized previously (Lyons et al. 2014, Sperling et al. 2015), evidence for active sulfur cycling, including sulfide in coastal environments, remains strong (Boyle et al. 2013, Godfrey et al. 2013, Li et al. 2010, Poulton et al. 2004, Poulton et al. 2010), and current proxies cannot rule out sulfide concentrations in the low micromolar range in mat habitats at the sediment–water interface. The case for sulfide's potential importance in modulating photosynthetic mode is further supported by evidence for sulfide-driven AP in modern ferruginous systems (Crowe et al. 2014a). Defining how the key tipping points—light, nutrients, and redox geochemistry—that govern the balance of OP, AP, and chemosynthesis project onto our views of the geochemistry of mat habitats at various points through Earth history is a grand challenge. An understanding of how positive feedbacks between sulfide-driven AP and sulfate reduction (Johnston et al. 2009) operate within cyanobacterial mats (Canfield & Des Marais 1991) is critical to assess the plausibility of sustaining euxinia in cyanobacterial mats in otherwise ferruginous and/or oxic oceans.

The emergence of light intensity as a key control on the balance of OP and AP raises the potential for a host of new influences on Earth's oxygenation. Solar output, water depth and clarity, and atmospheric transparency all become important considerations. Migratory behavior of sulfur-oxidizing bacteria strengthens lags in O_2 production associated with the daily transition between AP and OP; combined with the importance of cyanobacterial movement in navigating the chemocline, this underscores the central but little-explored role of motility in governing mat metabolism and O_2 budgets. The innovation of highly motile filamentous morphologies of both cyanobacteria and sulfur-oxidizing bacteria was thus critical to the mat lifestyle and provides a target for paleontological and phylogenetic studies to constrain evolutionary timing. Likewise, advances in molecular understanding of sulfide-driven AP may present new opportunities to put a timeline on the evolution of this metabolism in cyanobacteria. Here we must unravel the complicated evolutionary history of later transfer of *sqr* genes and keep our eyes and minds open for other forms of AP that may have served a similar predecessor or transitional role in cyanobacteria (e.g., Johnson et al. 2013).

Growing knowledge of the ecophysiological and biogeochemical functioning of microbial mats has not yet been integrated into understanding how they affected the geochemistry of Earth's surface. Models that quantify mat biogeochemical process and their geochemical outputs (e.g., de Wit et al. 1995, Herman & Kump 2005) are poised to do so. Coupling these with larger-scale models (e.g., Olson et al. 2013) to study various regimes—tectonic (mat habitat defined by area and distribution of continents and shelves), astronomical (solar luminosity), oceanographic (nutrient and redox geochemistry, water clarity), and atmospheric (O_2 concentration, transparency)—holds

great promise for exploring various plausible scenarios for how microbial mats shaped the trajectory of Earth's oxygenation.

DISCLOSURE STATEMENT

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

ACKNOWLEDGMENTS

We are grateful to Sean Crowe, David Fike, Ann Pearson, Hannah Marchant, and Arjun Chennu for thoughtful input and/or feedback. This work was supported by grant EAR 1637066 from the National Science Foundation Geobiology Low-Temperature Geochemistry program.

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Annual Review
of Earth and
Planetary Sciences
Volume 46, 2018

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Errata

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