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Review Article

How did the evolution of oxygenic photosynthesis influence the temporal and spatial development of the microbial iron cycle on ancient Earth?

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ABSTRACT

Iron is the most abundant redox active metal on Earth and thus provides one of the most important records of the redox state of Earth's ancient atmosphere, oceans and landmasses over geological time. The most dramatic shifts in the Earth's iron cycle occurred during the oxidation of Earth's atmosphere. However, tracking the spatial and temporal development of the iron cycle is complicated by uncertainties about both the timing and location of the evolution of oxygenic photosynthesis, and by the myriad of microbial processes that act to cycle iron between redox states. In this review, we piece together the geological evidence to assess where and when oxygenic photosynthesis likely evolved, and attempt to evaluate the influence of this innovation on the microbial iron cycle.

1. Introduction

The question of how oxygenic photosynthesis impacted the Archean (4.0–2.5 Ga) iron cycle should have a rather straightforward answer because the reaction of reduced (ferrous) iron with oxygen is rapid at circumneutral pH. Accordingly, as oxygen became available with the evolution of oxygenic photosynthesis, oxidized (ferric) iron should have precipitated out of seawater as an Fe(III) (oxyhydr)oxide mineral phase. However, the question is complicated by uncertainties in terms of when and where cyanobacteria first evolved and how this influenced the evolution and activity of iron-metabolizing bacteria, i.e. microaerophilic, nitrate-reducing and phototrophic Fe(II)-oxidizers as well as Fe(III)-reducers. Dating the onset of oxygenic photosynthesis has become a point of significant contention because there is no consensus on the timing of the evolution of cyanobacteria; putative evidence permits a possible range from as early as 3.8 Ga to as late as 2.4 Ga. The question regarding where cyanobacteria evolved first is also becoming more contentious, with cyanobacterial evolution having been proposed both on land as benthic mats and in the oceans as plankton. Furthermore, both questions are not trivial for the development of iron-metabolizing bacteria as the evolution of early cyanobacteria and the resulting oxygenation of the Earth's atmosphere and oceans would have significantly altered the biogeochemical iron cycle. Below, we summarize the evidence regarding the timing and location of cyanobacterial evolution, and present a hypothesis that attempts to place our current understanding of iron cycling on the early Earth within the context of cyanobacterial evolution and expansion.

2. When and where did cyanobacteria evolve?

There are a variety of studies based on geological, geochemical and biological evidence attempting to constrain the timing of the evolution of oxygenic photosynthesis. As a result, there is a wide range of interpretations of the rock record and a lack of consensus on both when and where oxygenic photosynthesis evolved. In this section, we present a chronological review of the key geological and geochemical evidence used to infer either an early (Archean) or late (Palaeoproterozoic) timing for the emergence of cyanobacteria. Against this geological backdrop, we discuss the genetic evidence which points to either scenario. We then review current literature which aims to determine the location of cyanobacterial evolution and the expansion of cyanobacteria in the Earth system.

2.1. Geological evidence for an Archean evolution for cyanobacteria

Numerous studies have provided evidence that suggests cyanobacteria could be as ancient as the oldest sedimentary rocks on Earth. Rosing et al. [1] reported elevated uranium (U)/thorium (Th) ratios in

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pelagic shales from the 3.8–3.7 Gyr Isua supracrustal belt in southwest Greenland. Those authors interpreted the high U/Th ratio as reflecting the presence of oxidizing (O_2-rich) fluids which facilitated the preferential transport of U to the site of sedimentation where it was ultimately scavenged by planktonic biomass. However, other workers have suggested that this U(VI) might not require O_2 [2]. The same rocks were also previously described as having up to 0.4 wt% reduced carbon with $\delta^{13}C$ values as low as −25.6‰ [3] – evidence seemingly pointing to biological carbon fixation. However, the biogenicity of such isotopic signatures in similar geologic settings has been questioned and instead Fischer-Tropsch-type synthesis of organic compounds has been invoked to explain highly negative $\delta^{13}C$ values [4–7]. Iron formations (IF), from another location at Isua, were subsequently shown to contain positively fractionated chromium (Cr) isotopes, relative to the crust, suggesting oxidative chemical weathering involving the presence of atmospheric O_2 as an intermediate [8]. At the 3.8 Gyr Nuvvuagittuq belt in Quebec, Canada, putative "microfossils" were recently described from ferruginous cherts that were interpreted as marine hydrothermal precipitates [9]. The "microfossils" occur as micrometer-sized hematite tubes and filaments that are reminiscent of modern O_2-dependent, microaerophilic Fe(II)-oxidizing bacteria found in Fe(II)-rich modern environments. Importantly, extant Fe(II)-oxidizing bacteria generally use O_2 as the electron acceptor, so by extension, if the "microfossils" are as advertised, then aerobic metabolisms must already have evolved by 3.8 Gyr.

More compelling is the geochemical evidence of oxygen oases at 3.3–3.0 Ga. Satkoski et al. [10] measured U enrichment and positive $\delta^{56}Fe$ values in shallow-water sediment compared to deep-water sediments in the 3.25 Ga Manzimnyama IF of the Fig Tree Group in South Africa. The authors suggested that a discrete redox boundary between deep and shallow waters existed at this time. They proposed that deep-water iron-rich IF samples were oxidized in water where O_2 contents were lower than shallow-water iron-poor IF samples that were precipitated entirely above the redoxcline where O_2 contents were uniformly elevated. In marine shales from the 3.2 Gyr old Soanesville Group in northwestern Australia, nitrogen (N) isotope values of the kerogen within the shales were interpreted as being derived from biological nitrogen fixation, most probably using molybdenum (Mo)-based nitrogenase [11]. Given that Mo is sourced from oxidative weathering of Mo-bearing sulfide minerals in crustal rocks, the use of a Mo-based enzyme suggests Mo availability (and by extension some oxidative weathering because Mo is more mobile under oxidizing conditions) already occurred at that time. Interestingly, the Gorge Creek Group that immediately overlies the Soanesville Group contains shales that are hundreds of meters thick, hundreds of kilometers in aerial extent, deficient in sulfur and iron, and with up to 10 wt% total organic carbon (TOC). Buick [12] speculated that only oxygenic photosynthesis could have generated that much biomass as anoxygenic photosynthesis would have been limited in electron donors. Similarly, in the 3.22 Gyr Moodies Group in South Africa, the presence of microbial mats and associated sedimentary structures in siliciclastic tidal and alluvial deposits [13,14] suggests the presence of a phototrophic community, which has been interpreted to consist of early cyanobacteria based on the mat morphology and facies association. Furthermore, recent findings of terrestrial microbial mats draping fluvial conglomerates with N isotopes suggestive of denitrification [14] strengthens the argument that localised sources of oxygen were already present at that time. This is because the presence of significant amounts of nitrate cannot be explained by lightning-induced oxidation of N-compounds but requires the activity of aerobic ammonium-oxidizing microorganisms.

Based on the distribution of Cr isotopes and redox-sensitive metals in both a palaeoweathering horizon and shallow-water IF from the ca. 2.96 Gyr Mozaan Group in South Africa, Crowe et al. [15] argued that there was already extensive mobilization of redox-sensitive elements from land to the oceans via oxidative weathering. Those authors also calculated a minimum estimate for atmospheric oxygen being 3×10^{-4} percent atmospheric levels (PAL): to place this value in context, previous estimates for the so-called Great Oxidation Event (GOE) at 2.32 Gyr placed atmospheric O_2 levels at only 10^{-5} PAL (e.g., [16]). That study, however, has been called into question on the grounds that the Cr isotope values were instead the product of modern oxidative weathering rather than Mesoarchean oxidative weathering [17]. Planavsky et al. [18] also measured Mo isotopes from the same IF units in the Mozaan Group and reported large negative $\delta^{98}Mo$ fractionations that are consistent with the sorption of Mo onto manganese (Mn) (oxyhydr)oxides that precipitated in the shallow water column. This is of significance since Mn(IV) (oxyhydr)oxide formation requires biologically-driven Mn(II) oxidation using O_2 as the electron acceptor, hence the shallow marine environment already had significant dissolved oxygen accumulation (for an alternate mechanism invoking Mn-based phototrophy, see [19]).

By 2.7 Ga, a wide range of geochemical analyses support the premise for widespread ocean oxygenation. Stüeken et al. [20] suggested that an increase in the total sulfur and Mo supply to marginal marine sediments at that time was best explained by the biological oxidation of crustal sulphide minerals. In 2.7–2.6 Ga black shales, enrichment in Mo, rhenium (Re) and osmium (Os), as well as fractionation of Fe and Mo isotopes, all suggest that O_2-rich niches already existed at that time [21–25]. Also, continuously increasing $\delta^{98}Mo$ values in the black shales, carbonates, and IF of the Marra Mamba and Wittenoom formations (2.6–2.5 Ga) in the Hamersley Basin have been tied to the sorption of light Mo isotopes onto Mn(IV)-oxides [25]. Perhaps one of the strongest pieces of evidence for oxygen availability at that time comes from the presence of extremely isotopically depleted kerogen within 2.72 to 2.59 Ga carbonates and shales in the Hamersley Province of Western Australia, the Kaapvaal Craton in South Africa, and the Superior Craton in Canada. Organic carbon $\delta^{13}C$ values in these metasediments are as low as −60‰ [26,27]. The most ^{13}C-depleted values have been ascribed to the assimilation of methane by chemolithoautotrophic, methanotrophic bacteria that in the modern world utilise electron acceptors such as O_2, sulfate (SO_4^{2-}), nitrate (NO_3^-) or even Mn(IV) and Fe(III) [28–33]. The presence of these metabolisms is a strong indication for the presence of O_2 because oxygen is either used directly as the terminal electron acceptor (TEA), or is required in the formation of alternative electron acceptors such as sulfate, nitrate and Mn(IV). Oxygen is not necessary for methane oxidation coupled to Fe(III) reduction because the latter can be formed via anoxygenic photosynthesis. Nitrogen isotope compositions of kerogens in minimally altered shales from the Campbellrand-Malmani carbonate platform in South Africa and broadly correlative sedimentary succession in Western Australia (Hamersley Group) show a significant rise in $\delta^{15}N$ values between 2.67 and 2.50 Ga [34,35]. Exceptionally high $\delta^{15}N$ values are also reported for the 2.72 Ga Tumbiana Formation [36]. This positive shift has been interpreted as evidence for the onset of nitrification-denitrification reactions in the surface oceans (e.g., [37]). Stromatolitic assemblages in the 2.72 Ga Tumbiana Formation, Western Australia, were suggested to have been constructed by photoautotrophs that may have utilised oxygenic photosynthesis [38]. More recent work has put forward the idea of filamentous bacteria, capable of gliding motility and phototaxis which tangle up upon contact, resulting in the formation of tufted mats. To date only a few microorganisms have been identified to be capable of such behavior, with cyanobacteria probably being the most prominent among them. Therefore, similar sedimentary structures in the Tumbiana Formation are a strong indicator of early cyanobacteria producing oxygen by 2.72 Ga [39,40]. Potential fossil assemblages of filamentous and coccoidal cyanobacterial colonies have been identified in the ca. 2.6 Gyr Campbellrand Group, South Africa [41]. However, a poor degree of preservation and the relative simplicity of those microfossils have raised questions about whether an unambiguous identification of cyanobacteria can be made [42,43], making the 1.9 Ga microfossils of the Belcher Islands, Canada, the earliest generally agreed upon fossils of cyanobacteria in the rock record [44].

2.2. Genetic evidence for an Archean evolution for cyanobacteria

The early evolution of photosynthesis sometime in the Eoarchean (4.0–3.6 Ga) or Paleoarchean (3.6–3.2 Ga) likely occurred within bacterial lineages that are no longer extant. While this presents a challenge when studying the evolution of early phototrophs, biological evidence has already provided insights into both the evolution of the core proteins involved in oxygenic photosynthesis [45,46] and the appearance of cyanobacteria's common ancestor inferred from genomic data [47–51]. For instance, recent studies support an early Archean origin of the core reaction center proteins (photosystem I and photosystem II, PSI and PSII, respectively), which are exclusively found in cyanobacteria and photosynthetic eukaryotes [46]. Biochemical and functional analysis of the sequence and structure of the core subunits of reaction centers of PSII predict that phototrophs already developed the capacity for water oxidation in the Paleoarchean, probably before 3.22 Ga [46]. While it remains unclear how efficient such ancient processes would have been during the Archean, a recent study [46] suggests evidence for low levels of oxygen being produced as the result of biological activity at this time. Other lines of evidence, such as the evolution of FtsH proteases, proteins specifically dedicated to the repair of PSII (D1 and D2), show that these proteins diverged early on, possibly between 3.8-3.5 Ga [52]. This is significant because the oxygenic lineage of PSII-FtsH proteases diverged before FtsH proteases found in all the other groups of phototrophs [52]. These findings support the view that genes associated with the photosynthetic process have co-evolved with key photosynthetic proteins [53], thus providing additional evidence for the early divergence of oxygenic phototrophs.

When looking at the biological record, it is worth noting that there are different levels of complexity when studying the early emergence of oxygenic phototrophs. At the gene level, the timing of the duplication event leading to the emergence of core reaction center proteins D1 and D2 at ~3.2 Ga [46] implies that an *inefficient* water oxidation metabolism would have been present 0.8 Gyr before the GOE, and the origin of the crown cyanobacteria group [48,51,54]. At the organismic level, phylogenomic and molecular clock analyses point to a much later origin of photosynthesis with most studies showing that the crown group of cyanobacteria appeared during the late Archean [48,51,54] or Paleoproterozoic [55,56]. It is important to emphasise that while oxygenic phototrophy can be traced back to the early Archean, highly sophisticated forms of D1 proteins (G3 and G4 which are known to bind to the Mn_4CaO_5 cluster or the water-splitting catalyst) are estimated to have originated near the GOE itself [46].

2.3. Geological evidence for a paleoproterozoic evolution for cyanobacteria

As an alternative to an Archean evolution, it has been proposed that cyanobacteria evolved much closer to the GOE, in the Palaeoproterozoic. The GOE represents a transition from an atmosphere that was essentially devoid of free oxygen ($O_2 \ll 10^{-5}$ PAL, 2 ppmv) to one with O_2 concentrations $> 10^{-5}$ PAL. These estimates derive from the pioneering study of Farquhar et al. [57] who discovered that marine sediments older than 2.45 Ga contain mass-independent fractionations of sulfur (S-MIF), while younger rocks do not. Farquhar et al. [58] hypothesized that the major source of the S-MIF signal is the photodissociation of SO_2 into water-soluble (sulfate, SO_4^{2-}) and water-insoluble fractions (elemental sulfur, S_8) that are preserved when contrasting isotopic compositions of reduced and oxidized sulfur species are deposited from the atmosphere and incorporated into sedimentary rocks. The signature of S-MIF photochemistry is not only rapidly homogenized in an oxygenated environment, but ozone also inhibits SO_2 photolysis by UVC irradiation. Indeed, Pavlov and Kasting [59] computed that O_2 levels as low as 10^{-5} PAL would prevent MIF-S from reaching the sediments. The disappearance of S-MIF from various locations worldwide has now been constrained to between 2.45 and 2.32 Ga [16,60–65], although the potential for minerals hosting the MIF signature to be cycled through terrestrial reservoirs and during subduction and volcanic processes means that MIF-S signals could be expected to be preserved for 10–100 million years after the GOE [66]. Other lines of geological evidence for the GOE include the first occurrences of "red beds" [67,68], copper deposits [69], iron rich paleosols [70], and the presence of extensive manganese deposits (see below) and phosphorites following the GOE [71,72]. Furthermore, well-rounded detrital pyrite, uraninite, and siderite grains are only found in clastic deposits before the GOE because these grains are unstable under oxic conditions [73–76], suggesting that atmospheric oxygen levels would have been lower than 3.2×10^{-5} PAL (~40 nM; [77]).

This rise of free atmospheric oxygen facilitated the onset of oxidative continental weathering reactions and increased the flux of dissolved sulfate and redox-sensitive trace elements to the oceans. Sulfate had two major sinks: (1) iron sulfide precipitation as a consequence of bacterial sulfate reduction in the water column, or (2) evaporitic precipitation of gypsum. In the first instance, Canfield [78] proposed that increased levels of sulfide in the oceans effectively titrated out any remaining Fe(II) in seawater, leading to the end of IF deposition. Evidence in support of higher sulfide production comes from increasing fractionation between sulfur isotopes; values for $^{34}S/^{32}S$ ($\delta^{34}S$) are centered on mantle values (0‰) prior to around 2.45 Ga but then increase to around 25‰ after 2.45 Ga [79]. In the second instance, primary sulfate evaporites are rarely reported before 2.45 Ga [80], confirming insufficient dissolved sulfate availability before that time.

Temporal trends in trace metal composition in Archean and Paleoproterozoic marine sediments also support the timing of the GOE. For instance, a compilation of the Cr contents in IF showed a significant enrichment beginning at 2.45 Ga in the Weeli Wolli Formation [81]. Given the poor solubility of Cr minerals, its mobilization and incorporation into IF indicates enhanced chemical weathering at that time, most likely associated with the evolution of aerobic continental pyrite oxidation. Similarly, a recent compilation of Cu isotopes in Precambrian marine sediments demonstrated a clear trend in the stable isotopes values whereby Cu isotopes in black shales after the GOE become progressively heavier. This trend has been attributed to world-wide changes in seawater composition, due to the combined effect of waning IF deposition, which prior to the GOE would have preferentially removed ^{65}Cu with Fe(III) (oxyhydr)oxides, and increased oxidative supply of ^{65}Cu derived from continental weathering due to preferential leaching of the heavier Cu isotope. This ^{65}Cu, in turn, would have become incorporated into planktonic biomass that scavenged Cu from seawater [82].

The Mn(IV) deposits of the 2.22 Gyr Hotazel Formation in South Africa (since been re-dated to between 2.42 and 2.39 Ga; [65]) have traditionally been considered some of the best proof for the presence of oxygen (e.g., [83]) because the oxidation of dissolved Mn(II) to solid-phase Mn(IV) (oxyhydr)oxides is thought to require O_2, and the latter's concentration exerts direct control on the rate of Mn(II) oxidation [84]. Moreover, the Mn deposits contain a prominent negative cerium (Ce) anomaly that has generally been thought to indicate seawater that was partially oxygenated. A similar sequence of Mn-enrichments with positive Ce anomalies have also been recently reported from the uppermost Hamersley Group and overlying Turee Creek Group [85,]. Where the story of Mn(II) oxidation really gets interesting is with the 2.45 Gyr Koegas Subgroup in South Africa, a mixture of chemical and clastic sediments where the BIF layers contain up to 17 wt% Mn. Johnson et al. [19] suggested that the initial Mn(IV) (oxyhydr)oxide precursor phases were likely formed via Mn(II)-based phototrophy, a metabolism that thus far has not been documented to exist in natural settings. Those authors argued against O_2 being the Mn(II) oxidant because of the presence of detrital pyrite grains and S-MIF in associated rocks, and importantly, that these sediments must have formed prior to the rise of atmospheric O_2 even though the timing of these sediments falls within the GOE window.

The Johnson et al. [19] study was not the first to suggest that there was minimal oxygen available on Earth prior to the GOE. Kopp et al. [2]

pointed out that the geological features of oxygen, such as red beds and paleosols, occurred immediately after the three glaciations recorded in the Huronian Supergroup of Canada (ending ~2.3 Ga) but before the 2.3–2.2 Ga Makganyene glaciations in South Africa (recall the Makganyene diamictites are now constrained to ca. 2.46 Ga as per Gumsley et al. [65]). Kopp et al. [2] also argued that global O_2 production after 2.3 Ga triggered the collapse of a methane greenhouse and initiated the Snowball Earth event associated with the Makganyene diamictites. In their model, the timing of these events means that cyanobacteria likely evolved in the interval between the Huronian glaciations and the Makganyene glaciation (i.e., within a few million years); note with the new age constraints this could be up to 150 Myr. A subsequent modelling exercise by Ward et al. [87] suggested that it might have taken as little as 100 Kyr following the emergence of cyanobacteria to initiate the GOE.

2.4. Genetic evidence for a paleoproterozoic evolution for cyanobacteria

To determine when oxygenic photosynthesis evolved we can also examine when the photosystems essential for oxygenic photosynthesis evolved. However, there is still some debate as to how the common ancestor of extant cyanobacteria acquired the ability to photosynthesize considering that their closest relatives, melainabacteria, lack photosynthetic machinery [88,89]. In the previous section we outlined the argument from those who advocate for an early origin for oxygenic photosynthesis where an early ancestral phototroph existed that contained both type I and type II reaction centres (RCs) and which subsequently saw selective loss of oxygenic photosynthesis [90–93]. However, another school of thought maintains that the common ancestor of extant cyanobacteria was a non-phototroph that acquired the ability to photosynthesize (both PSI and PSII) after the divergence of the cyanobacteria from melainabacteria [94]. This would suggest a rather late origin for oxygenic photosynthesis in the late Archean or early Paleoproterozoic between 2.6 to 2.5 Ga.

In short, the above studies argue that oxygenic photosynthesis evolved in the Paleoproterozoic. Ultimately, only the combination of in-depth geochemical analysis of the rock record together with molecular clock analyses can answer the question of when oxygenic photosynthesis developed. We would suggest, given careful evaluation of the previously discussed geochemical and molecular data, that oxygenic photosynthesis probably became of significance in the early Archean, perhaps as early as 0.8 Gyr before the GOE. However, the evidence presented does not explain why there was such a significant delay in the widespread oxygenation of the Earth's atmosphere and oceans. Moreover, it remains to be resolved where oxygenic photosynthesis developed. In the following section, we provide evidence which suggests that an offset between the evolution of oxygenic photosynthesis and the widespread oxygenation of the atmosphere can be explained by a terrestrial origin for early cyanobacteria.

2.5. A terrestrial origin for cyanobacteria

There is a significant body of evidence which suggests that the evolution of cyanobacteria occurred in terrestrial habitats. Firstly, large-scale phylogenomic analyses have consistently shown that living relatives of early divergent cyanobacteria can be found in low salinity and terrestrial environments [54,56,95,96]. Furthermore, phylogenomic evidence suggests that cyanobacteria colonized marine environments independently at different times in Earth's history. In fact, marine cyanobacteria lineages do not form a natural group; they are instead nested within freshwater species, providing further evidence for independent colonization events into marine environments at different times in history [48,50]. Evolutionary and molecular clock studies have found no evidence of marine planktonic cyanobacteria having any ancestors as early at the Paleoproterozoic [48]. Moreover, modern planktonic groups (e.g., *Prochlorococcus* and *Synechococcus*, *Crocosphaera* clade, and *Trichodesmium*) only appeared during the Neoproterozoic [50].

These genomic observations of a terrestrial origin for cyanobacteria are at odds with the long-held belief that colonization of the landmasses would be impossible prior to the accumulation of substantial amounts of oxygen in the atmosphere because, in the absence of an ozone shield, harmful UV radiation would bombard the Earth's surface [97]. However, it now appears likely that early terrestrial microbial habitats could have been protected from UV bombardment by inhabiting endolithic environments [98], growing under iron-enriched siliceous sediment [99], or by precipitating their own mineralized crusts (e.g., [100–102]). Indeed, Phoenix et al. [103] demonstrated that an iron-silica biomineral layer of only 150 μm thickness was sufficient to attenuate all incoming UV-C radiation while still allowing for the transmittance of 400–700 nm wavelength light required to facilitate photosynthesis. In other words, terrestrial colonization should not have been inhibited by irradiation with high levels of ultraviolet light.

Trait evolution analyses show that the earliest cyanobacteria were unicellular and had small cell diameters (*Gloeobacter*, *Synechococcus*-like) but filamentous forms evolved relatively early on and likely resembled modern relatives of *Pseudanabaena* [48]. These filamentous forms would have represented a morphological innovation that facilitated the formation of microbial mats. Such mats are dense, highly productive ecosystems which would have enabled an increase in cyanobacteria's ecological dominance during the Proterozoic [54,104]. Molecular clock analyses have also suggested that filamentous cyanobacteria appeared around the GOE [32,88,89], while most of the taxonomic and ecological diversity of extant cyanobacteria can be traced back to the late Paleoproterozoic and Mesoproterozoic [48,105].

Cyanobacterial lineages inhabited benthic, terrestrial and/or shelf environments for most of the Proterozoic with mat-dominated environments being even more common in the Precambrian than they are today as they are limited in extent by the activity of plants (which compete with mat formation) and animals (which graze on mats). The ubiquity of such environments is also reflected in the geological record which contains abundant examples of microbialites, including stromatolites, formed during the Archaean and Proterozoic [106–109], although whether or not these examples always represent cyanobacterial mats or whether they were produced by anoxygenic phototrophs is still an active area of debate [110].

The early establishment of mat-forming filamentous cyanobacteria and subsequent dominance of benthic microbial communities likely restricted primary productivity to terrestrial habitats and ocean margins [48,50]. However, it is unclear to which extent early terrestrial ecosystems contributed to global biogeochemical cycles [111]. The formation of cyanobacteria-dominated biological soil crusts has been proposed as one scenario which could explain the observation of transient periods of mild oxygenation and oxidative weathering before the GOE [20,111–113]. Nonetheless, numerous analog studies have suggested that potential O_2 production from ancient microbial mats may have been limited by H_2S, which can serve as an electron donor for anoxygenic photosynthesis and chemosynthesis, and thus enhance competition with cyanobacteria ([114] and references therein). In general, it is believed that the global impact of oxygenic photosynthesis was likely negligible until cyanobacteria started colonizing marine habitats [50]. The emergence of planktonic groups during the late Meso- to early Neoproterozoic (ca. 0.92 to 0.67 Ga) would subsequently have had a major impact on global biogeochemical cycles as they contribute to at least 25% of marine productivity in today's oceans [115].

Marine planktonic cyanobacteria evolved comparatively late and early representatives were restricted to shelf environments for much of the Proterozoic [48]. The spatial restrictions of those environments would have limited the extent of primary production and the extent of its biogeochemical influence. Consequently, it would be expected that terrestrial or near-shore iron cycling would be impacted by rising oxygen before there were any discernible changes in the marine iron

cycle. Only with the evolution of planktonic cyanobacteria and their spread into the ocean would there have been a more profound influence on the marine geochemical iron cycle. Evidence for this offset between the response of the terrestrial biosphere and the oxidation of the atmosphere in general can be found in the apparent discrepancy between the timing of widespread atmospheric oxygenation (as identified by the widespread disappearance of S-MIF), and earlier evidence for oxidative weathering on land (as discussed in the first sections of this review). Lalonde and Konhauser [113] attribute this discrepancy to the production of oxygen by cyanobacteria in benthic habitats, attached to sediments, rocks, soils or other natural solid substrates where oxidative weathering of the solid could proceed whilst in strong disequilibrium with the reducing atmosphere.

3. Consequences of oxygenic photosynthesis for the marine iron cycle

The evolution of oxygenic photosynthesis and the subsequent oxidation of Earth's atmosphere had dramatic effects on the entire web of reactions which characterize global biogeochemical cycling. No other element has been as central to the historical discussion of the atmospheric evolution of the Earth as iron. Certainly, the existence of extensive IFs deposited between 3.8 to 1.85 Ga can be used to trace the evolution of the marine redox state and marine geochemical cycling of iron. In the following sections, we discuss how the marine iron cycle evolved following the evolution and expansion of oxygenic photosynthesis and hypothesize how this evolution may have impacted the potential for different microbial iron-based metabolisms.

3.1. Marine iron cycling before the evolution and expansion of cyanobacteria

As outlined above, it is generally believed that the bulk early ocean waters were largely anoxic, with O_2 concentrations ranging from < 1 to 10 μM [116]. They were primarily ferruginous, with dissolved Fe(II) concentrations likely between 0.04 and 0.12 mM [117]; compared to modern day dissolved Fe concentrations of < 0.3 nM–2 nM [118].

Traditionally the deposition of IFs has been attributed to the reaction of free molecular oxygen with Fe(II) [119,120]. However, although evidence from the rock record and some molecular work points towards the antiquity of oxygenic photosynthesis (section 2.1/ 2.2), recent experimental evidence suggests that elevated Fe(II) concentrations [121] and higher UV fluxes on early Earth [102] might have impeded the distribution of early cyanobacteria beyond locally confined “oxygen oases” [116,122]. Therefore, the following discussion on early iron-cycling will be based on the assumption that prior to ~2.5 Ga the oceans had low dissolved oxygen [116,123].

As an alternative to the chemical oxidation of Fe(II) by free oxygen, photoferrotrophy – the photosynthetic process where anoxygenic phototrophs use Fe(II) as the electron acceptor for carbon fixation - was proposed (e.g., [124,125]). The metabolic by-product of this metabolism was likely a poorly soluble Fe(III) (oxyhydr)oxide [126] or, since the Precambrian ocean contained elevated concentrations of silica (up to 2.2 mM, [127]), a silica-ferrihydrite composite [128–130] or Fe(III)-silica gel [131,132]. Alternate hypotheses propose that primary IF minerals were mostly ferrous iron-bearing minerals such as greenalite (e.g., [133,134]), but hydrogeological constraints do not support this [135]. Previous studies have also demonstrated that the trace element inventory of the ancient ocean would have been sufficient to support a microbial community large enough to deposit all Fe(III) in IFs [136,137], and importantly, they would even have been able to do so under limiting light conditions [138]. Furthermore, a recent study suggested that even under nutrient limiting conditions, photoferrotrophs would have been able to outcompete early cyanobacteria and essentially oxidize all hydrothermally derived Fe(II) before it would have reached oxygenated surface waters [139].

There is also some evidence from the rock record suggesting the activity of photoferrotrophs during the deposition of IFs. This evidence reaches as far back as to the ca. 3.77 Ga Isua Supracrustal Belt [140]. Based on a modelling approach combined with independent S isotope data, Czaja et al. (2013) interpreted the positive and comparatively homogeneous δ^{56}Fe values to be indicative of anoxygenic, iron-based photosynthesis. Similarly, positive δ^{56}Fe values of between approx. 0.4 to 0.7‰ from the Nuvvuagittuq chemical sediments have been interpreted as being the result of partial Fe(II) oxidation by anoxygenic photosynthesis [141].

Photoferrotrophy is not the only microbial process leading to Fe(II) oxidation. Microbial Fe(II) oxidation coupled to nitrate reduction or oxygen reduction at low μM oxygen concentrations is also known [142]. Microaerophilic Fe(II) oxidation is obviously excluded in a predominantly anoxic setting, but nitrate-dependent Fe(II) oxidation is an anaerobic process [143]. Nitrate-dependent Fe(II) oxidation can either be enzymatically driven by microorganisms [143,144,145] or catalysed by the production of reactive N species formed as a by-product of denitrification [146]. However, the presence of oxidized N species such as nitrate is itself indicative of a more oxygenated ocean and thus is tightly linked to cyanobacterial evolution and expansion. The Mesoarchean N isotope record appears to consistently suggest an anaerobic nitrogen cycle dominated by nitrogen fixation [147], for which the enzyme is proposed to have evolved before 3.2 Ga [11]. Therefore, nitrate-dependent Fe(II) oxidation was probably unlikely to constitute a significant proportion of Fe(II) oxidation.

The oxidized iron formed by photoferrotrophs would have been precipitated in the form of mineral-cell aggregates [148], ultimately settling on the seafloor as precursor sediments to IFs [149]. Experimental studies showed that these Fe(III) mineral-cell aggregates would have a stoichiometric excess of iron compared to the co-precipitated carbon [150]. In other words, instead of the 4:1 Fe:C ratio predicted for photoferrotrophy, the aggregates could have had Fe:C ratios as high as 6:1. Such sediments would have been an ideal environment for dissimilatory Fe(III)-reducing (DIR) bacteria, which would have coupled the reduction of Fe(III) to the oxidation of the co-precipitated biomass, although some reduction of Fe(III) already during sedimentation could also be feasible. The significance of microbial Fe(III) mineral reduction for IF genesis was suggested many years ago [151], and molecular clock studies have suggested the antiquity of this metabolic process [152]. Indeed, there is ample evidence from the rock record, e.g., from the Eoarchean Isua Supracrustal Belt (Greenland), the Mesoarchean Mozaan Group (Pongola Supergroup, South Africa) or the Neoarchean to Paleoproterozoic IFs of the Hamersley Basin (Australia) and Transvaal Craton (South Africa), in the form of C- and Fe isotopic studies [153–158] demonstrating the significance of DIR for early microbial iron cycling in IF sediments. Although it should be noted that an alternative, abiotic origin of magnetite in the Hamersley IF via thermal decomposition of siderite has been proposed [159].

Konhauser et al. [149] suggested that under ideal circumstances as much as 70% of the initially precipitated Fe(III) minerals could have been reduced and cycled back into the water column as Fe(II). Their model suggested that fermenting bacteria and methanogens might have degraded biomass which was co-precipitated together with primary Fe (III) minerals and, therefore, provided additional substrates for Fe(III)-reducers. There is significant evidence for the existence of methane-based metabolisms in the Archean, a process which requires access to fermentation products (e.g., H_2, acetate, lactate). Thus, by extension, the presence of methanogens necessitates the presence of fermenters.

Methane was abundant prior to the GOE and molecular clock analyses suggest development of methanogenesis during the Eoarchean [88]. Additionally, highly negative δ^{13}C values in organic carbon have been interpreted as a sign of the activity of methane-oxidizing bacteria (methanotrophs) [26,27], which are thought to have evolved 3.1 Ga or later [88]. Such a microbial methane cycle could clearly influence carbon cycling in these ancient oceans and potentially provide organic

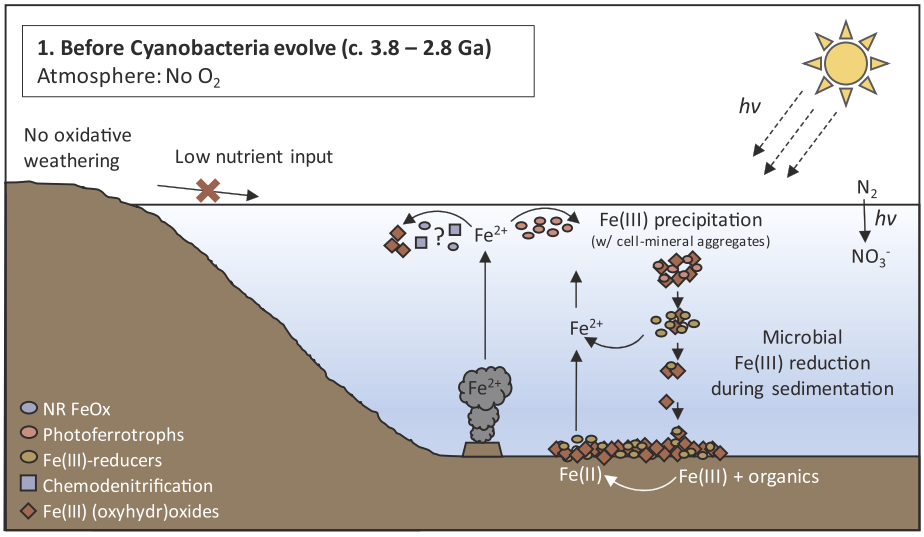

Fig. 1. Schematic of iron cycling in ancient oceans prior to the evolution of oxygenic photosynthesis. Anoxygenic phototrophy is the main mechanism of Fe(II) oxidation. Fe(II) is re-supplied by dissimilatory iron reduction occurring both in the sediment and the water column. There is a minor input of nitrate from atmospheric processes which could allow some nitrate dependent Fe(II) oxidation, but this process is likely a very minor contributor to iron cycling.

substrates for DIR. Furthermore, a recent *in-situ* study showed that methane oxidation can be coupled directly to Fe(III) reduction [160], which raises the possibly that methanotrophs could have contributed directly to an ancient iron cycle before the GOE (e.g., [149]). Alternatively, the mineralization of dead microbial biomass could have released ammonium, which could theoretically have provided a substrate for anaerobic ammonium oxidizing bacteria which can couple this reaction to Fe(III) reduction [161,162].

Given this literature, we propose that, if the origin of cyanobacteria was terrestrial and the expansion of cyanobacteria as planktonic forms was delayed as we suggest in section 2, iron cycling would have been controlled primarily by phototrophic Fe(II) oxidation and microbial Fe (III) reduction until the late Neoarchean (Fig. 1). In this scenario, photoferrotrophs provided a means of primary production and Fe(II) oxidation, with replenishment of Fe(II) from DIR closing the ancient iron cycle.

One factor which could have severely limited microbial iron cycling was the presence of H_2S in the water column. H_2S effectively titrates Fe (II) from solution and thus widespread euxinia (anoxic and sulfidic conditions) would have limited Fe(II) availability to iron-metabolizing microbes. Therefore, Fe(II):H_2S ratios > 1 would have been required for deposition of IFs and a widespread microbially-driven iron cycle [163]. One key player in sulfate-turnover in the oceans are sulfate-reducing bacteria. The antiquity of this metabolic pathway is recorded in the S isotope record of sedimentary barites of the 3.6–3.2 Ga Barberton Greenstone Belt (South Africa; [164]); sedimentary barites, pyrite and sulfides from the ~3.5 Ga Dresser Formation (Western Australia; [165]) and sedimentary barites of the 3.47 Ga North Pole area (Western Australia; [166]). While some sulfate might have been introduced to the Archean ocean by the photolysis of volcanic gases such as SO_2 [58,164], there was likely no additional inputs of sulfate to the early oceans before the evolution of oxygenic photosynthesis and the onset of widespread oxidative weathering [81]. Consequently, the sulfate concentrations in the Archean ocean could have been as low as 10 μM [167], and maybe even below 2.5 μM [168]. If true, this means microbial sulfate reduction, while old, was an insignificant or at least severely spatially limited process during that time. Concomitant low H_2S concentrations would have resulted in minimal crossover between early Fe- and S-cycles until ca. 1.8 Ga [78,169].

3.2. Effect of cyanobacteria expansion on marine iron cycle

It was suggested over a decade ago that a “whiff of oxygen” [170] could have already existed prior to the GOE possibly leading to “pervasive oxygenation” along Archean coastlines by 2.6 Ga [122], which is approximately 100–200 Ga before the GOE (arguably between ~2.45 and 2.32 Ga; [16,57,81]). Evidence from the marine [18] and terrestrial [15] rock record suggests that locally confined oxygenated areas could already have existed as far back as 3.0 Ga, forming local “oxygen oases”, with O_2 concentrations between 1 to 10 μM [116]. In a recent study on the 2.98 to 2.85 Gyr Mozaan Group (White Mfolozi Inlier, Pongola Supergroup), Ossa Ossa et al. [158] employed correlation analysis on Fe/Mn ratios and δ^{56}Fe values as well as δ^{98}Mo values. Based on their results they concluded that oxygen concentrations could even have exceeded the earlier maximum of 10 μM in the Archean. This suggests that early cyanobacteria (and oxygen) slowly spread from terrestrial habitats, where they first developed (as discussed in section 2 of this review), via rivers and lacustrine environments to the oceans, where their expansion probably came to a (temporary) hold. With time, cyanobacteria spread from the marine littoral zone and became more abundant in the ancient ocean, resulting in an oxygenated surface ocean layer in the late Archean [171]. A recent study has even demonstrated experimentally that the presence of ferric iron-silica colloids in the photic zone could have sheltered the plankton from incoming UV-C irradiation, thus allowing cyanobacteria to spread throughout more of the marine realm [102].

Despite their early presence, cyanobacteria probably had no critical direct effect on marine iron cycling initially. Although the emergence and spread of early cyanobacteria would have pushed photoferrotrophs deeper into the water column (Fig. 2), this would not have influenced the means by which the initial Fe(III) mineral phases in IFs would have been deposited. The photoferrotrophs would have been more proximal to the hydrothermally derived Fe(II) and could have, due to their adaptation to low light conditions [138] and competitive advantage over cyanobacteria under nutrient limiting conditions [139], oxidized all Fe(II) before it would have reached oxygenated surface waters. Supporting evidence from the rock record is provided by a study from Haugaard et al. [172] who suggested, based on iron isotope studies and paleo-environmental reconstructions, that photoferrotrophs could have deposited the primary Fe(III) mineral assemblages in the ~2.45 Gyr Joffre IF. Ultimately, the predominance of one oxidative process over the other is governed by the question of whether the redoxcline is above or below the photic depth. As long as the redoxcline remained above the photic depth, photoferrotrophy would have dominated Fe(II) oxidation and thus the deposition of IFs (Fig. 2). However, if the redoxcline moved below the photic depth (Fig. 3), abiotic oxidation of Fe(II) by O_2 produced via cyanobacteria and related dark Fe(II)-oxidizing mechanisms should have dominated Fe(II)-oxidation. Indeed, a recent study showed, that microaerophilic Fe(II)-oxidizing bacteria can compete with abiotic (chemical) Fe(II) oxidation in an O_2 concentration range

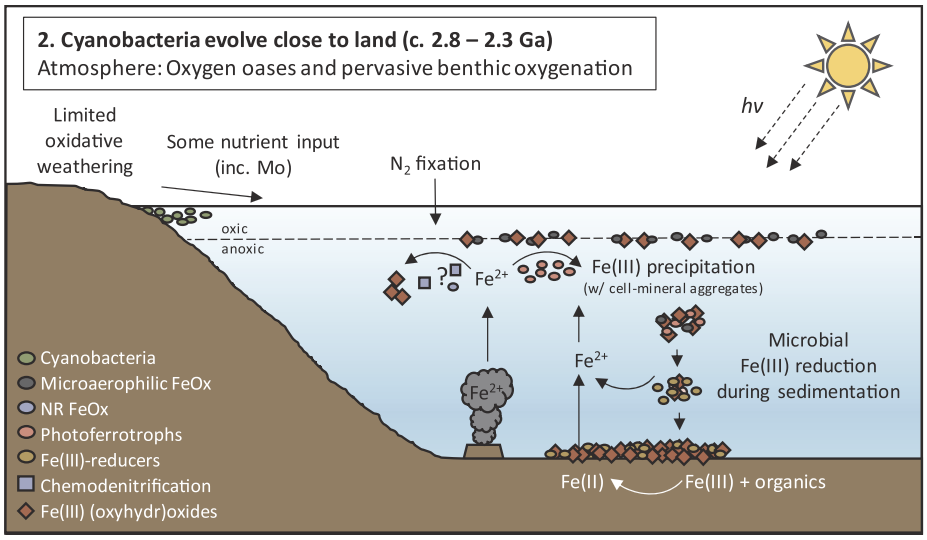

Fig. 2. Schematic of iron cycling in ancient oceans when oxygenic photosynthesis was limited to terrestrial or near-shore environments. Some redox stratification of the oceans could be possible enabling microaerophilic Fe(II)-oxidizers to become involved in the marine iron cycle. When the redoxcline remains above the photic zone, anoxygenic phototrophs remain the major driver of Fe(II) oxidation. Nitrogen fixation and an increase in atmospheric oxygen could enhance the contribution from nitrate-reducing Fe(II)-oxidizers.

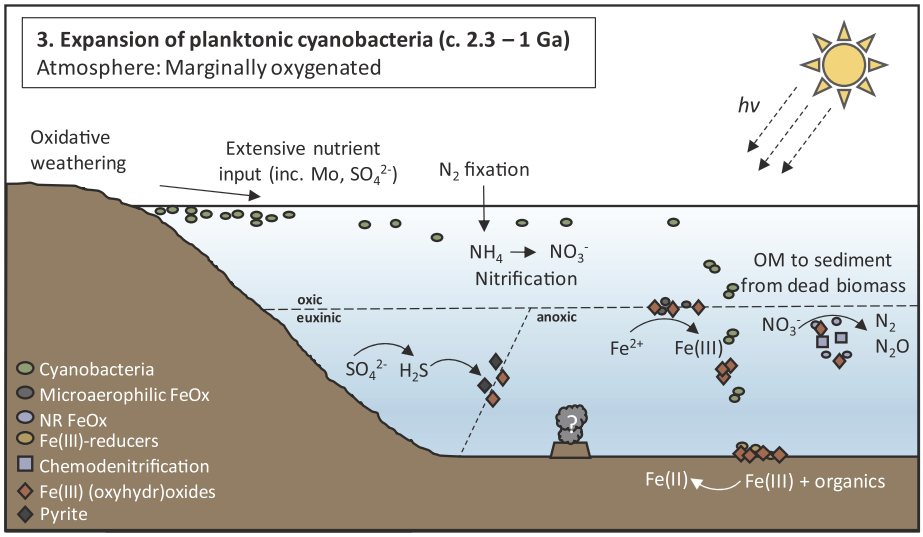

Fig. 3. Schematic of iron cycling in ancient oceans following the expansion of cyanobacteria in the marine realm. Atmospheric oxygenation is marginal with the deep oceans remaining anoxic. When the redoxcline is below the photic zone the contribution of anoxygenic phototrophs to iron cycling becomes negligible. Nitrate input increases, primarily from nitrification, as well as oxygen availability, which benefits microaerophilic and nitrate dependent Fe(II)-oxidizers. Hydrothermal input of iron may also have decreased around this time. Sulfate input from oxidative weathering led to sulfidic conditions in some near-shore areas which would lead to pyrite formation. IF deposition continues whilst the redoxcline remains above the depth of the shelf.

from 5 μM to approx. 50 μM [173–175]. Lower O_2 concentrations limited enzymatic Fe(II) oxidation while higher concentrations resulted in chemical Fe(II) oxidation being dominant. Therefore, microaerophilic Fe(II)-oxidizing bacteria would have found ideal conditions under low O_2 conditions leading up to the GOE.

The rise of oxygen and expansion of oxygen oases would also have potentially led to an increase in the diversity of iron-respiring microorganisms. Those microbes which use O_2 as their TEA are in competition with the abiotic oxidation of Fe(II) by oxygen, and are therefore "microaerophiles" existing at oxic-anoxic interfaces where the biotic reaction can compete with the abiotic reaction [173,174]. The significance of this metabolic pathway for IF deposition was first suggested by Holm [176] and their potential contribution to the formation of IFs is discussed extensively by Chan et al. [177] (Figs. 2 and 3). Modern nitrate-reducing Fe(II)-oxidizers contribute to Fe(II) oxidation either directly, by enzymatic oxidation of Fe(II) [143], or indirectly by production of reactive nitrogen species which react abiotically with Fe(II) in a process known as "chemodenitrification" [146,178]. In fact, it has recently been suggested that chemodenitrification may have led to significant fluxes of the greenhouse gas N_2O in the Proterozoic [179]. Both microaerophilic and nitrate-reducing Fe(II)-oxidizing metabolisms require oxygen to be produced first, thus they would be limited in extent before the evolution of cyanobacteria. However, with the spread of oxygen, both microaerophilic and nitrate-reducing Fe(II)-oxidizers would have become more significant for the marine microbial iron cycle (Figs. 2 and 3).

The Neoarchean (2.8–2.5 Ga) has also been suggested to have been a time of major microbial Fe(III) respiration as a result of the combined deposition of Fe(III) (oxyhydr)oxides and organic carbon [153]. Thus, microbial Fe(III) mineral reduction remained a significant diagenetic process in the IFs deposited immediately prior to or during the GOE. Furthermore, additional studies add to the increasing pool of isotopic data (C, O and Fe) that highlight the importance of DIR for the ancient Fe cycle [182–184]. Based on the previous discussion, photoferrotrophs could still provide the primary means of Fe(II) oxidation, where replenishment of Fe(II) by DIR could act to close the ancient iron cycle (Fig. 2).

Other alternative iron-metabolizing pathways were potentially also affected by increasing concentrations of oxygen. For example, it has been suggested that a significant decrease in oceanic Ni concentrations prior to the GOE would have resulted in a decline in methanogens [185,186], which would have resulted in a decreased significance of methane-based Fe(III) reduction [160]. Conversely, a decline in global methanogenesis and resulting higher availability of fermentation products (e.g., H_2, acetate), otherwise used by methanogens [187,188], could have resulted in a more pronounced DIR. Consequently, a decrease in methane-dependent Fe(III) reduction would not necessarily have resulted in a decreased turnover of Fe(III) (oxyhydr)oxides.

However, recent findings by Neubeck et al. [189] showed that methane production in some species of methanogens was unaffected by Ni concentration, thereby suggesting that the influence of declining oceanic Ni concentrations on the global rates of methane production in the Precambrian is not straightforward. At the same time, the increase in biological N-fixation could have increased the significance of NH_4^+-dependent Fe(III) reduction [161,162]. Therefore, other microbial processes (e.g. DIR and NH_4^+-dependent Fe(III) reduction) would become more important as a result of a shift in substrate availability.

The development of oxygenic photosynthesis and locally confined oxygen oasis would not only have influenced the iron cycle significantly, but as a result of oxidative weathering, would also have resulted in increased pyrite dissolution [81], resulting in an increased sulfate (and nutrient) flux to the ocean (Fig. 2). Increased biomass production by early cyanobacteria within the oxygen oases together with an increased sulfate flux could have stimulated locally confined activity of sulfate-reducing bacteria along the paleo-shoreline and shelf regions, resulting in the development of locally confined sulfidic pools [58]. Within those regions marine geochemical conditions would have been governed by the competition between Fe(II), O_2, organic matter input and H_2S accumulation [190]. This period of marine evolution is interpreted to be recorded e.g. in the ~2.66 Gyr Jeerinah Formation (Hamersley Province, Western Australia; [191]) and the ~2.5 Gyr Mount McRae Shale [190]. In these paleo-environments, locally confined euxinic conditions would have inhibited the upwelling Fe(II) from reaching the near-shore, resulting in the precipitation of FeS (Fig. 2). Consequently, Fe(II) would be inaccessible for microbial iron cycling. By contrast, the 2.5 Ga Mount McRae Shale shows N isotope signatures consistent with denitrification [192], leading those authors to speculate about the existence of nitrate dependent iron oxidation.

In summary, when cyanobacteria expanded into the oceans, ferruginous conditions would likely still have existed in most areas of the Archean ocean. At some point in time, however, locally confined oxygen oases and increased sulfate input to the oceans resulting from early oxidative weathering would have turned parts of the continental margins and shelf regions euxinic, thereby supressing microbial iron cycling. Additionally, oxygen oases would have enabled proliferation of Fe(II) oxidizers reliant on oxygen or nitrate, which we speculate could compete with photoferrotrophs in regions where the redox cline was still in the photic zone but would not be likely to dominate on a large scale.

3.3. Marine iron cycle following GOE

Following the evolution of planktonic cyanobacteria and their widespread expansion into the surface oceans, the production of O_2 would have pushed the redoxcline below the photic zone such that upwelling Fe(II) was oxidized abiotically before it could be available to photoferrotrophs (Fig. 3). Indeed, isotope evidence from the 2.3 to 2.2 Gyr Yuanjiacun IF suggests that by this time the oceans contained sufficient oxygen such that Fe(II) oxidation was not directly tied to the presence of cyanobacteria, yet the deep oceans remained ferruginous [193–195]. Following the GOE, the waters overlying the continental shelf (around 150 m deep) - where IFs were deposited [196] - may have become sufficiently oxygenated that deposition of Superior-type IFs ceased as the upwelling hydrothermal Fe(II) was oxidized before reaching the shelf (Fig. 3). Although this could have led to IF deposition in deeper waters, the preservation potential of those sediments would be less than of IFs deposited on the stable shelf. The implications then are that IFs might be absent from the rock record, an observation borne out by the limited extent of major IFs deposited between ca. 2.4 and 1.9 Ga [197,198].

Although the cessation of IF deposition during the above time interval was traditionally attributed to oxygenation of deep seawater (e.g., [199]), in the wake of the GOE, widespread oxidative weathering of pyrite on land would have resulted in an increased input of sulfate (and nutrients) to the oceans. Microbial turnover of sulfate and organic matter by sulfate-reducing bacteria in organic matter rich environments would have resulted in the formation of large quantities of H_2S along the ocean margins [78,169,200,201], resulting in quantitative titration of upwelling Fe(II) from the water column and the end of IF deposition on the shelf.

Evidence from the 1.89 Gyr Gunflint and Biwabik IFs suggests that even in the Palaeoproterozoic, when the surface ocean was fully oxygenated, sporadically high fluxes of reductants (Fe(II)) from hydrothermal sources could still overwhelm the abiotic oxidation of Fe(II), resulting in Fe(II) accumulation and subsequent IF deposition on continental shelves [202]. Under these conditions, oxygen produced by cyanobacteria clearly became the dominant oxidant for Fe(II) oxidation in the oceans. In turn, this would have resulted in a complete inhibition of Fe(II) oxidation by phototrophs in the surface ocean and restricted photoferrotrophs to a few specific sunlit, anoxic niches, such as coastal sediments and stratified lakes, much as they are today [203]. The competition between photoferrotrophs and cyanobacteria would also be confounded by the increase in nutrient input to the oceans from oxidative weathering, which would remove the competitive advantage photoferrotrophs had enjoyed in the oligotrophic conditions widespread prior to the GOE ([139,204] for an extensive review on the ocean trace element budget). With a fully oxygenated photic zone, anoxygenic phototrophs would be unable to proliferate [138] and “dark” Fe(II)-oxidizing metabolisms would become an increasingly important driver of microbially catalysed Fe(II) oxidation. In this scenario, microaerophilic Fe(II)-oxidizers may have dominated the Fe(II)-oxidizing community members along the deep redox-cline [177]. As oxidative weathering on land increased, even more Mo would be introduced into the oceans, enhancing N-fixation, and potentially encouraging nitrate-reducing Fe(II)-oxidizers.

The significance of DIR for the marine iron cycle is recorded in several IFs deposited either directly in the wake of the GOE (e.g., the 2.3 to 2.2 Gyr Yuanjiacun IF; [193,194]) or during the approx. 1.8 Ga resurgence of IFs (e.g. the Sokoman IF or the Lake Superior IFs [202,205,206]). Alternatively, higher Mo concentrations [207] would probably have furthered an increase in microbial Fe(III) reduction coupled to NH_4^+ oxidation (Fe-ammox) below the deep redox-cline and in the sediments. This would additionally be stimulated by higher sedimentary ammonium fluxes from ammonification during burial due to increased microbial N-fixation in surface waters [11,208,209] and subsequent microbial degradation of organic carbon.

When the deep oceans became oxygenated (Fig. 4), hydrothermally derived Fe(II) would be precipitated directly around submarine vents much as it does today (e.g., Loihii, Hawaii; [210]). Marine iron cycling would be confined almost exclusively to sedimentary environments, with extremely low Fe(II) concentrations (and thus almost no microbial iron cycling) in the water column.

4. Influence of oxygenic photosynthesis on terrestrial iron cycling

While in section 2.5 we discussed the hypothesis of a potential terrestrial evolution of cyanobacteria, we now investigate how their oxygen production would have influenced an early terrestrial microbial iron cycle. Most of the knowledge on Archean and Proterozoic iron cycling comes from marine deposits, yet it is very likely that the evolution of oxygenic photosynthesis would have also had major consequences for terrestrial iron cycling. In this case we use the term terrestrial to refer to any exposed continental crust, regardless of whether it is aquatic or not. We therefore include rivers, lakes, streams and ponds under this definition as well as soils, sediments and exposed rock surfaces. Unfortunately, due to lower aerial extent of continental land masses in the Archean (compared to today) and resulting lower likelihood of preservation than the abundant marine deposits, the geological record of life on land during Earth's ancient history is significantly more patchy than that found in marine systems [211–214]. Loss due to

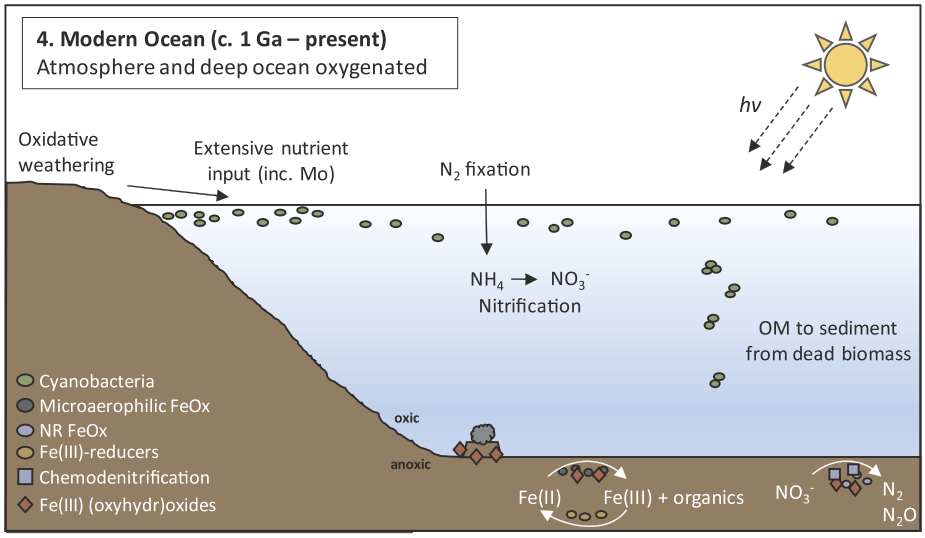

Fig. 4. Schematic of the marine iron cycle when oxygen penetration exceeds the depth of the shelf. Iron cycling proceeds similarly to today. Almost no Fe(II) can remain dissolved in the water column and most active iron cycling occurs in the sediments, or directly around hydrothermal vents.

erosion is also high for terrestrial deposits, meaning that those environments most likely to have had cyanobacterial communities were lost from the rock record.

What little understanding of terrestrial iron cycling we have comes from palaeosols - ancient soil horizons. Weathering of ancient soils under an anoxic atmosphere led to the mobilization and leaching of Fe (II). When oxygen is present, Fe(II) is oxidized and thus stabilized, preventing iron loss. It has been shown that before 2.4 Ga, palaeosols suffered significant iron loss whereas younger palaeosols generally show negligible loss of iron during weathering [70,215]. Although mobilization of iron from palaeosols can be explained by chemical processes (i.e., abiotic weathering of silicate minerals), the high abundance of aqueous Fe(II) implied by the observed iron mobilization in pre-GOE palaeosols allows us to speculate about the potential for iron-based metabolisms in these systems.

In modern terrestrial environments, Fe(II) is oxidized by the same three microbial processes as discussed in part 3 of this review: microaerophilic, anoxygenic phototrophic and nitrate dependent Fe(II) oxidation. In the modern environment, however, these processes are limited by the ubiquity of atmospheric oxygen which either competes with their metabolism (as in the case of microaerophilic Fe(II) oxidation) or even inhibits their activity completely because they are anaerobic (phototrophic and nitrate-reducing Fe(II) oxidation). In addition to benefitting from the dissolved Fe(II) produced and released from silicate weathering, these microorganisms are known to also directly oxidize crystalline Fe (II)-bearing minerals, including magnetite [216], biotite [217], and clay minerals [218]. On the other end of the iron cycle, given the relative paucity of TEAs such as O_2, NO_3^- and SO_4^{2-} in the Precambrian, Fe(III) may have been one of the few electron acceptors available for ancient chemolithotrophs. In fact, it has been shown that close relatives of the last common ancestor of modern life had the ability to conduct DIR [152]. From the marine record it is clear that DIR played a significant role in marine iron cycling pre GOE (cross-reference to section 3), and there is no clear reason why this would not have been a plausible microbial metabolism on the early landmasses as well. It can, therefore, be proposed that pre-GOE palaeosols with low O_2 and abundant Fe(II) would have represented an even more favourable environment for terrestrial microbial iron cycling than today, although the impact of such activity on global biogeochemistry may have been minor.

The palaeosol record also contains significant insights into ancient terrestrial biogeochemistry more generally. In the oldest palaeosol record, the 3.2 Gyr Moodies Group, Nabhan et al. [219] observed contemporaneous formation of pedogenic sulfate nodules and secondary pyrite rims with $\delta^{34}S_{VCDT}$ values between −20‰ and −24.5‰, which they interpreted as evidence for microbial processing of sulfur during soil formation at that time. Of particular interest are paleosols found at several localities near Schagen (Mpumalanga Province, Eastern Transvaal Supergroup, South Africa) which were formed prior to 2.6 Ga. Their high organic C content (up to 1.4 wt%) in 20 µm to 1 mm thick seams with $\delta^{13}C_{org}$ values between −14.4 and −17.4‰ PDB not only indicates that microbial mats existed on the soil surface [220], but the retention of iron and the increased ratio of Fe(III)/Fe(II) with depth suggests that the mats were composed of cyanobacteria and that oxygen concentrations, at least locally, were > 0.1% PAL [221]. Additional constraints on potential early terrestrial metabolisms is provided by a study on the 2.76 Gyr Mount Roe palaeosol, Western Australia [222]. The authors describe isotopic evidence indicative of methanotrophy which they suggest occurred around ephemeral ponds. The presence of methanotrophs necessitates the presence of methane-producing microorganisms. Methane could have provided an additional substrate for microbial Fe(III) reduction where the oxidation of methane would have been coupled to microbial reduction of Fe(III) [160].

The terrestrial rock record also includes some evidence of aquatic terrestrial habitats on the early landmasses. For example, Homann et al. [14] show direct fossil evidence for terrestrial microbial mats from a 3.22 Gyr fluvial deposit in the Moodies Group, South Africa. Buick [38] and Stüeken et al. [223] also provide textural and Mo isotopic evidence of oxygenic photosynthesis in 2.78 to 2.72 Gyr stromatolites of the Fortescue Group, Western Australia that were interpreted as having been formed in an ancient evaporitic lake. However, this interpretation is not unequivocal, as parts of the Tumbiana Formation were interpreted to represent coastal or shallow marine environments by previous work [224]. Although these existing records do not directly imply a role for iron-metabolizing bacteria specifically, they do suggest an active microbial community which could consist of oxygenic or anoxygenic phototrophs, as well as active microbial nitrogen, sulfur and methane cycling. Crucially, all of these processes can potentially be linked to microbial iron cycling.

5. Conclusions

The exact timing of the evolution of oxygenic photosynthesis remains the subject of much debate, but the impact this biological innovation has ultimately had on the Earth's biogeochemistry is undeniably huge. A significant body of evidence suggests that this innovation first developed in terrestrial environments where

cyanobacteria were responsible for “whiffs” of oxygen prior to the GOE. This would have had limited impact on the microbial iron cycle in the marine environment as the oceans would have remained primarily anoxic, and the microbial iron cycle would have been dominated by Fe (II) oxidation by anoxygenic phototrophs and Fe(III) reduction by DIR, much as it had been prior to the evolution of oxygenic photosynthesis. The subsequent evolution of planktonic cyanobacteria enabled expansion into the marine realm and led to progressive oxygenation of the atmosphere and oceans. Anoxygenic phototrophic Fe(II) oxidation likely remained the dominant mechanism of IF deposition until the redoxcline descended below the photic zone as anoxygenic phototrophs, which grow at lower light intensities, could oxidize upwelling Fe(II) before it reached cyanobacteria. Ultimately IF deposition would cease when the redoxcline descended below the depth of the shelf, and oxygen from oxidative photosynthesis would dominate Fe(II) removal from the water column. Increased availability of oxygen could have enabled expansion of new Fe(II)-oxidizing metabolisms such as microaerophilic and nitrate-reducing Fe(II)-oxidizers, but these are unlikely to have played a major role in precipitation of IFs. Under increasingly oxic conditions, however, these “dark” Fe(II)-oxidizing metabolisms would have found abundant niches in both marine and terrestrial systems where they could potentially influence the local biogeochemistry much as they continue to do today.

Acknowledgements

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