Evolution of cellular metabolism and the rise of a globally productive biosphere

Rogier Braakman[1,2]

[1] Department of Civil and Environmental Engineering,

[2] Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology,
Cambridge, MA, USA

Corresponding Author:

Rogier Braakman

Email address: rogierbraakman@gmail.com

PeerJ Preprints | https://doi.org/10.7287/peerj.preprints.27269v2 | CC BY 4.0 Open Access | rec: 18 Apr 2019, publ: 18 Apr 2019

Evolution of cellular metabolism and the rise of a globally productive biosphere

Rogier Braakman[1,2,*]
Departments of [1]Civil & Environmental Engineering and [2]Earth, Atmospheric & Planetary Science, Massachusetts Institute of Technology. [*]E-mail: rogierbraakman@gmail.com

Abstract

The metabolic processes of cells and chemical processes in the environment are fundamentally intertwined and have evolved in concert over billions of years. Here I argue that intrinsic properties of cellular metabolism imposed central constraints on the historical trajectories of biopsheric productivity and atmospheric oxygenation. Photosynthesis depends on iron, but iron is highly insoluble under the aerobic conditions produced by oxygenic photosynthesis. These counteracting constraints led to two major stages of Earth oxygenation. Cyanobacterial photosynthesis drove a major biospheric expansion near the Archean-Proterozoic boundary but subsequently remained largely restricted to continental boundaries and shallow aquatic environments, where weathering inputs made iron more accessible. The anoxic deep open ocean was rich in free iron during the Proterozoic, but this iron remained effectively inaccessible since a photosynthetic expansion would have quenched its own supply. Near the Proterozoic-Phanerozoic boundary, bioenergetic innovations allowed eukaryotic photosynthesis to expand into the deep open oceans and onto the continents, where nutrients are inherently harder to come by. Key insights into the ecological rise of eukaryotic photosynthesis emerge from analyses of marine *Synechococcus* and *Prochlorococcus*, abundant marine picocyanobacteria whose ancestors colonized the oceans in the Neoproterozoic. The reconstructed evolution of P*rochlorococcus* reveals a sequence of innovations that ultimately produced a form of photosynthesis more like that of green plant cells than other cyanobacteria. Innovations increased the energy flux of cells, thereby enhancing their ability to acquire sparse nutrients, and as by-product also increased the production of organic carbon waste. Some of these organic waste products in turn had the ability to chelate iron and make it bioavailable, thereby indirectly pushing the oceans through a transition from an anoxic state rich in free iron to an oxygenated state with organic carbon-bound iron. The periods of Earth history around cyanobacteria- and eukaryote-driven biospheric expansions share several other parallels. Both epochs have also been linked to major carbon cycle perturbations and global glaciations, as well as changes in the nature of mantle convection and plate tectonics. This suggests the dynamics of life and Earth are intimately intertwined across many levels and that general principles governed Neoarchean and Neoproterozoic transitions in these coupled dynamics.

Introduction

The oxygenation of Earth's crust and atmosphere is the result of a complex interplay of geological and biological forces, the untangling of which is a major challenge. Oxygen is produced by oxygenic photosynthesis and consumed by aerobic respiration as part of the biological carbon cycle (Fig. 1), but if these processes were perfectly oxygen could not accumulate. It is thus thought that the long-term sequestration of a small fraction (~0.1%) of photosynthetically-produced organic carbon, or pyrite produced through oxidation of organic carbon, within Earth's subsurface is responsible for the rise of atmospheric oxygen [1-7] (Fig. 1). Buried organic carbon and associated reducing power eventually return to the atmosphere when organic- or sulfide-bearing

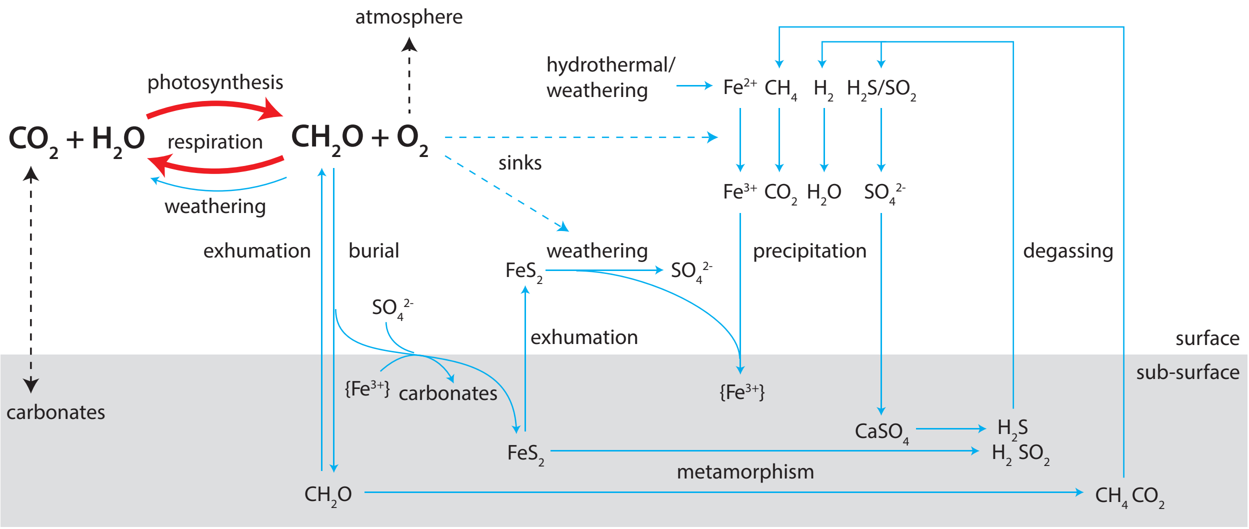

Figure 1. Schematic view of the coupled biological (red) and geological cycles of organic carbon and sulfur (blue). For simplification, chemical processes are shown without accurate stoichiometry and only key chemical species are highlighted. Organic carbon is represented in its general stoichiometry of CH_2O and iron oxide minerals are represented as $\{Fe^{3+}\}$. Long-term sequestration of organic carbon and pyrite in Earth's crust and mantle allows oxygen to accumulate in the atmosphere and oxidized minerals to accumulate in the crust. The organic carbon cycle is ultimately tied to the inorganic carbon cycle (shown as bidirectional arrows between CO_2 and carbonates), further linking the evolution of the biosphere and the solid Earth.

rocks are exhumed and oxidatively weathered, or when metamorphism during subduction leads to outgassing of CO_2 and reduced carbon/sulfur species, the latter of which can react with O_2 (Fig. 1) [1-3,8,9]. A key process that is less constrained is the subduction of organic carbon into the mantle, from where its recycling to the surface is slower than crustal recycling [4,10-15]. In this view of the carbon cycle (Fig. 1), an increase in the *steady state* atmospheric oxygen levels is thus linked to increase in the *steady state* organic carbon content of Earth's crust and/or mantle. Changes in O_2 sinks other than those derived from crustal recycling of organic carbon-derived reducing power, for example due to geologically-driven changes in the redox state of the mantle, crust and/or volcanic gasses, have also been argued to contribute to atmospheric oxygenation [16-21].

Earth oxygenation is generally thought to have proceeded in two major stages. The first stage, also known as the 'Great Oxidation Event' [17], began near the boundary between the Archean (4000-2500 Mya) and Proterozoic (2500-541 Mya) and produced atmospheric oxygen levels at around 0.1-1% of modern [2,22-28]. After a prolonged period of relative global stasis [29-31], atmospheric oxygen restarted its climb toward modern levels near the boundary between the Proterozoic and Phanerozoic (541 Mya – current), eventually increasing an additional 2-3 orders of magnitude and paving the way for the rise of large multi-cellular animals [32-40]. In this review I will focus on this second stage, also known as the 'Neoproterozoic Oxidation Event' [40], and in particular on metabolic innovations occurring in the oceanic biosphere at that time.

The basic relationship between the global carbon cycle and atmospheric oxygen (Fig. 1) suggests that understanding the balance between primary production and aerobic respiration, and the resulting impact on carbon burial, is key to understanding the history of Earth oxygenation. It has previously been argued that Neoproterozoic (1000-541 Mya) oxygenation was driven by effective decreases in the efficiency of respiration due to faster sinking of larger organisms and/or their fecal pellets [41-44] or because of changes in the composition sediments that more efficiently trapped organic matter [45,46]. While such factors likely played a role, I will argue here that the ultimate driver of Neoproterozoic oxygenation was a major increase in biospheric productivity. While all oxygenic photosynthesis is performed by cyanobacteria or photosynthetic eukaryotes (whose chloroplasts are derived from cyanobacteria), each of these broad groups contain a great diversity of lineages that have different physiologies, occupy different ecological niches and which arose at different times in Earth history [47-50]. Identifying the constraints and driving forces that underpin the evolutionary diversification of oxygenic photosynthesizers is important for understanding the evolution of the carbon cycle (Fig. 1).

Broadly speaking, the Neoproterozoic is when photosynthetic eukaryotes began to take over from cyanobacteria as Earth's dominant primary producers, eventually driving a major increase in global primary production [51-58]. Important exceptions that ultimately help explain this "rule" are the marine picocyanobacteria *Synechococcus* and *Prochlorococcus* [59-62], whose ancestors also arose in the Neoproterozoic [63,64] and which are estimated to account for around 25% of biological CO_2-fixation in the modern oceans [65]. We recently reconstructed the metabolic evolution of this group [66], which revealed key driving forces and feedbacks that help us understand both the long-term oxygenation of the oceans as well as the general ecological dominance of photosynthetic eukaryotes. To place observed metabolic innovations in context, I will first review the evolution of ocean chemistry between the Neoproterozoic and early Phanerozoic.

Biogeochemical dynamics of the Neoproterozoic and early Phanerozoic

Marine picocyanobacteria expanded into the oceans during a time of major upheaval in the whole Earth system. Geologic records from the period bridging the Neoproterozoic and early Phanerozoic indicate the breakup of the super-continent Rodinia [67-70], possible changes in the nature of plate tectonics linked to cooling of the mantle and crust [71-77], an expansion of shallow seas [69,78-80], major carbon cycle perturbations [41,81,82] and several "snowball Earth" episodes of global glaciation [83-86]. At the same time, ocean chemistry was undergoing a fundamental shift (Fig. 2). It has in recent decades become increasingly clear that, even as shallow waters became oxidized [87], the deep open ocean remained largely anoxic well into the Proterozoic, long after oxygen first began accumulating in the atmosphere [88]. It was first thought that Proterozoic oceans were mostly euxinic (rich in H_2S) [88], but more recent evidence suggests the oceans were instead largely ferruginous (rich in Fe^{2+}) [89,90], with euxinia restricted to regions of enhanced productivity near continental boundaries [29,91]. In contrast, the modern oceans are largely oxygenated. The exact time course of ocean oxygenation is actively being debated – recent evidence suggests the oceans may not have become permanently oxygenated until the early Ordovician (ca. 400 Mya) [92] or even the Triassic (ca. 200 Mya) [93] – but evidence for the initiation of this process reaches back to the Neoproterozoic [38,92-96].

Several biogeochemical feedbacks have been proposed to explain why the deep open ocean remained anoxic during the Proterozoic. Some authors have argued that oceanic primary production was nitrogen-limited, either due to the scavenging of Molybdenum and other trace metals that mediate nitrogen assimilation by sulfide ions in euxinic waters [53,29], or due to an

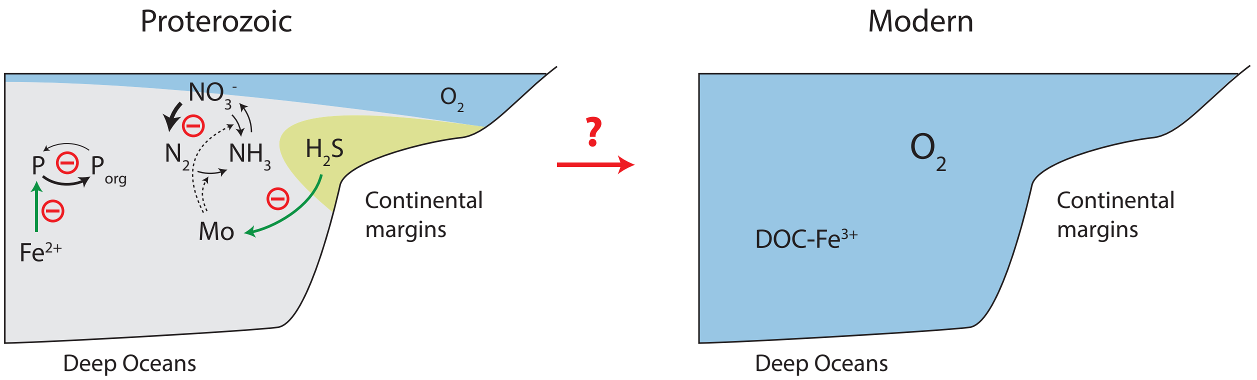

Figure 2. Neoproterozoic revolution in ocean chemistry. Negative feedbacks that have been argued to constrain ocean oxygenation are indicated with red minus signs. Processes that scavenge phosphorus [98-101] and/or molybdenum (Mo) [53,29] are indicated by green arrows. The role of molybdenum as a cofactor in nitrogen cycle reactions is indicated by dashed arrows. Differences in the relative rates of phosphorus [102] and nitrogen [97] cycling reactions are indicated by differences in the weight of arrows. DOC = dissolved organic carbon.

excess in the rate of denitrification relative to nitrification under low oxygen concentrations [97] (Fig. 2). Others have argued primary production was instead phosphorus-limited, either due to the scavenging of phosphate from riverine inputs and/or directly from the water column by abundant Fe^{2+} ions [98-101], or due to organic phosphate remineralization being limited by electron acceptors in the absence of O_2 [102]. Both sets of proposals are consistent with observations that post-Neoproterozoic oceans saw significant increases in the levels of both phosphate [101,103] and molybdenum [94,104], as well as isotopic shifts of sedimentary nitrogen that suggest the onset of a stable oceanic nitrate pool [105-111]. Such negative feedbacks (Fig. 2) have further been argued to lead to bi-stability on the path to full ocean oxygenation [112]. That is, a fully oxygenation ocean represents a biogeochemically stable state since it removes those factors that limit primary production, but while they are present those factors prevent oxygenation. It was therefore argued that transient large-scale perturbations in the redox state of the ocean due to global snowball Earth glaciations [85] were ultimately needed to trigger the transition to a fully oxygenated state [112].

The framework outlined above can be expanded upon by taking an ecophysiological view of the genomic record across the Neoproterozoic-Phanerozoic boundary. Based off an analysis of the metabolic innovations seen in *Synechococcus* and *Prochlorococcus*, we recently argued that an additional negative feedback preventing ocean oxygenation was built into the machinery of photosynthesis itself [66] (Fig. 3). That is, oxygenic photosynthesis depends on substantial amounts of iron [113], but iron is highly insoluble under aerobic conditions, especially at the pH of ambient seawater [114,115]. Thus, as ocean oxygenation proceeded, iron would become increasingly scarce [90,116], presenting a challenge not just to oxygenic photosynthesis (Fig. 3) but also to nitrogen fixation [117] and biological electron transfer more generally [118,119].

This hypothesized feedback (Fig. 3) is fundamentally different than those involving phosphorus and nitrogen (Fig. 2), as it is strengthened rather than weakened as oxygenation proceeds. As a result, transient perturbations to the ocean redox state alone are ultimately insufficient to explain persistent oxygenation. An important clue to understanding how the biosphere nevertheless overcame this evolutionary bottleneck lies in observations that in the extant oceans iron is not

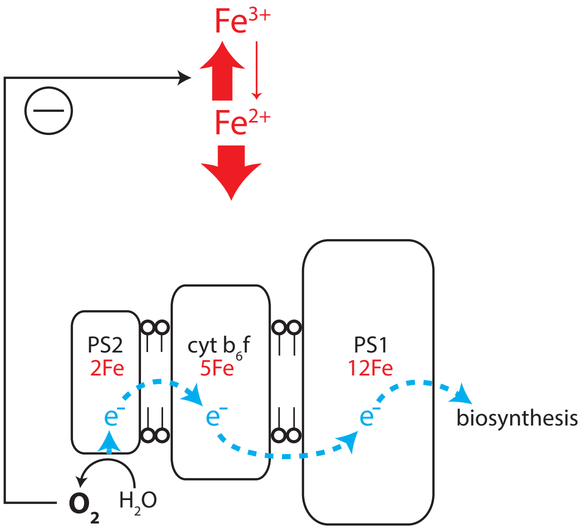

Fig. 3 Graphical representation of the hypothesis that ancestral cyanobacterial photosynthesis had a built-in negative feedback (black arrow highlighted by '-' sign) that prevented its expansion into the deep open ocean. Relative sizes of electron transfer components reflect their cellular stoichiometry in cyanobacteria. Red lettering indicates the number of iron atoms that components require. Red arrow directed from Fe^{2+} to photosynthetic machinery reflects assimilation flux needed to build photosynthetic machinery, which is counteracted by oxygen-driven flux to Fe^{3+}. Insolubility of Fe^{3+} in the presence of O_2 is highlighted by small flux back to Fe^{2+}. Blue dashes arrows reflect the flow of electrons arising from water splitting. Abbreviations: PS2 = photosystem II, cyt b_6f = cytochrome b_6f, PS1 = photosystem I.

dissolved as free ions but instead is bound to a vast pool of dissolved organic carbon (Fig. 2) [120,121]. While some iron is bound to special iron-scavenging siderophores, a large fraction is bound to more weakly-chelating compounds that are common metabolic intermediates or precursors of cellular building blocks, such as polysaccharides and simple carboxylic acids and/or alcohols [120-123]. This suggests that perhaps the evolution of cellular metabolism itself helped ancestral oxygenic photosynthesis overcome its inherently self-damping nature. To explore this possibility and the mechanisms involved, I will next review metabolic innovations of marine picocyanobacteria, which occurred between the Neoproterozoic and early Phanerozoic as the ocean became oxygenated and iron levels dropped.

Metabolic evolution of marine picocyanobacteria

Marine picocyanobacteria provide an ideal model system for understanding the evolution of the biogeochemical cycles as the ocean became oxygenated. Early evolution of this group took place across the Neoproterozoic-Phanerozoic boundary [63,64], and its physiological, ecological and genomic diversity has been characterized in detail [61,62,124]. We recently reconstructed the evolution of marine picocyanobacteria and showed that as they colonized the oceans their metabolic core underwent a global remodeling [66] (Fig. 4A). Remodeling is most extensive in *Prochlorococcus* and involves modifications to the pigments and stoichiometry of the photosynthetic machinery [60,62,124-129] as well as to core carbohydrate metabolism, wherein pathways were added for excreting organic carbon from the cell [66] (Fig. 4A). The latter is inferred from a range of observations, including: 1) the truncation of metabolic pathways that leave dead ends in the network (Fig. 4A), 2) genomic rearrangements that place export transporters next

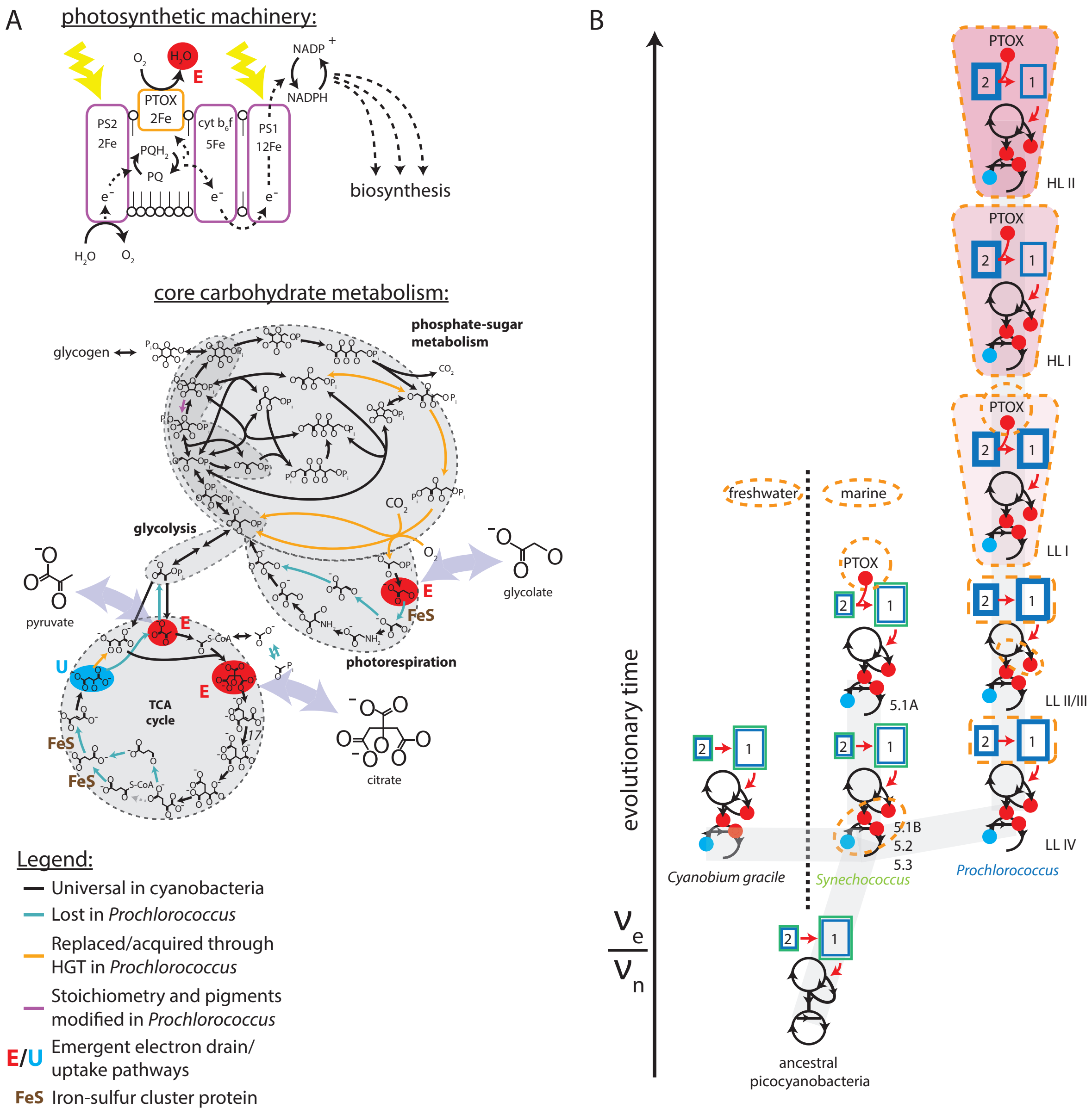

Fig. 4 Metabolic evolution of *Prochlorococcus*. **A)** Evolutionary changes in the metabolic core of *Prochlorococcus* relative to ancestral cyanobacteria, as indicated by colors in the legend [66]. Compounds identified as excretion pathways are highlighted with red dots and bi-directional grey arrows, while a compound identified as an uptake pathway is highlighted with a blue dot. **B)** Metabolic variants from panel A are drawn in simplified form along a gradient of an increasing electron-to-nutrient ratio, ν_e/ν_n. Red arrows indicate the flow of electrons and black arrows indicate the flow of carbon. The size of photosystem boxes reflects their cellular stoichiometry, their colors indicate major wavelengths of absorption and line thickness indicates absorption cross-section. Innovations are highlighted by dashed orange circles and those related to light damage protection/repair [148,149] are indicated by a darkening pink shade. Figure adapted from Figs. S1 & 4 from [66]. In the original tree in Ref [66] the phenotype of *Cyanobium gracile* was drawn as branching between ancestral picocyanobacteria and marine *Synechococcus*, but recent analyses suggest there were multiple incursions across the fresh water-marine boundary near the evolutionary roots of this group [150]. Abbreviations: LL = low-light adapted, HL = high-light adapted.

to core metabolic enzymes, including those that catalyze the final steps of truncated pathways [66], 3) synchronized gene expression of transporter-metabolic enzyme pairs that follow the daily rhythms of solar energy input [130,66] and 4) experimental studies showing excretion of glycolate

[131], one of the identified dead end metabolites [Fig. 4A). In addition to the low molecular weight carboxylic acids identified in these analyses (Fig. 4A), experiments suggest that *Synechococcus* and *Prochlorococcus* also excrete significant amounts of polysaccharides and other high molecular weight compounds [132-134].

Understanding what drove *Prochlorococcus*' metabolic innovations (Fig. 4A) requires a multi-level view of the system, as natural selection acts differently on metabolic benefits at different levels of organization. For example, since iron is insoluble under aerobic conditions [114,115] and some compounds *Prochlorococcus* excretes (carboxylic acids, polysaccharides) are known iron-chelators [66,122,123], it is tempting to conclude that increasing access to iron was a direct driver of its evolution. Similarly, many oceanic microbes require complex nutrient additions to grow [134,135], raising the possibility that interactions with sympatric heterotrophs drove *Prochlorococcus*' innovations. However, both of these scenarios involve extracellular sharing of resources among community members and it is thought such mutualisms can only evolve when physical colocation of cells ensures transmission of resource benefits from parents to offspring [137-139]. In contrast, *Prochlorococcus* populations are considered genetically well-mixed, consisting of individual planktonic cells that through fluid mixing are separated by tens of meters within an hour of division [140]. Theory suggests that in such conditions selection suppresses resource sharing, promoting population takeover by faster-growing freeloader mutants that receive the benefits of shared resources but do not incur the costs of producing them (a scenario also known as the "tragedy of the commons") [137-139]. That we nevertheless observed *Prochlorococcus* evolution progressing steadily in the direction of adding pathways for excreting organic carbon (Fig. 4) with no evidence of suppression suggests it must directly benefit individual cells, with any community-level effects emerging as an indirect by-product.

Studies of aerobic heterotrophs that can facultatively switch between respiration and fermentation have identified direct benefits of excreting organic carbon that could be relevant to *Prochlorococcus*. Fermentation pathways that involve excretion of incompletely oxidized carbon are more thermodynamically downhill and can sustain higher rates of ATP production than respiration pathways that fully oxidize carbon to CO_2 [141-143]. This allows cells with plentiful supplies of organic carbon to increase their growth rates by switching to fermentation and redirecting protein biomass from ATP production to biosynthesis [144-146]. However, *Prochlorococcus* has a lower intrinsic growth rate compared to other cyanobacteria [60,147] and since excreting organic carbon occurs downstream of photosynthesis it would not appear to affect the protein biomass requirement of ATP production. Perhaps more relevant to *Prochlorococcus*, some aerobic heterotrophs also switch on fermentation pathways under nutrient-limited growth conditions, where it is thought to help maintain redox balance by providing an outlet for excess reducing power [151-154]. Indeed, a recent study showed that *Prochloroccus* excretes a substantially larger fraction of the carbon it fixes under nutrient-limited relative to nutrient-replete conditions [155] However, many photosynthesizers can prevent redox imbalance by using 'photoacclimation' to decrease their harvesting of solar energy [156,157], and *Prochlorococcus* appears to have only a modest ability for photoacclimation [158,159]. That selection favored an ability to excrete organic carbon over an ability for photoacclimiation suggests that organic carbon excretion has other benefits than only responding to redox stress.

A more complete view emerges when examining changes in *Prochlorococcus*' metabolism in the context of its physiological, ecological and genomic diversity [61,62,124]. For example, in warm stable water columns *Prochlorococcus* differentiates by depth into a layered population structure, with recently diverging "high-light adapted" clades experiencing higher light levels near the surface and deeply branching "low-light adapted" clades experiencing lower light levels at the bottom of the eupotic zone [160-164]. Abovementioned changes to the photosystems [60,62,125-129] (Fig. 4A), which increase the absorption cross-section of cells [147,165], thus appear to reflect an evolutionary trend that increases the photosynthetic electron flux [66], defined as:

$$\nu_e = I\sigma_{PSII}\theta_{PSII}, \tag{1}$$

where I is light intensity, σ_{PSII} is the total cellular absorption cross-section of photosystem II (where water-splitting leads to the generation of an electron flux) and θ_{PSII} is the quantum efficiency of absorption.

An evolutionary increase the in the photosynthetic electron flux of *Prochlorococcus* cells further coincides with a general process of evolutionary 'streamlining' [166-168] that decreases their dependency on phosphorus, nitrogen and iron, key limiting nutrients in the oceans [169]. For example, *Prochlorococcus* genomes have undergone reduction in size and guanosine-cytosine content (AT base pairs require one fewer nitrogen atom than GC base pairs) [170], its proteins contain few nitrogen-rich amino acids [171], its membranes consist of glyco- and sulfolipids rather than phospholipids [172,173] and its modified metabolism (Fig. 4A) requires less iron [128,66]. Finally, *Prochlorococcus* has a lower growth rate than *Synechococcus*, which in turn has a lower growth rate than other cyanobacteria [60,147]. This suggests a decrease not just in the nutrient content of cells but in the uptake flux of nutrients [66], defined as:

$$\nu_n = \mu Q_n, \tag{2}$$

where μ is the specific growth rate and Q_n are the cellular nutrient quota. Combined evidence thus suggests that the addition of pathways for excreting organic carbon – an extracellular sink for electrons – reflects a general increase in the total throughput of electrons, as defined by the electron-to-nutrient flux ratio of cells, ν_e/ν_n (Fig. 4B). Since the photosynthetic electron flux carries solar energy into metabolism, an increase in ν_e/ν_n suggests an increase in the metabolic rate (energy time^{-1} mass^{-1}) of cells.

An important clue for why selection favored an increase in cellular metabolic rate comes from the extant population structure of *Prochlorococcus*. The most recently diverging, highest metabolic rate phenotypes (Fig. 4B) are the "high-light adapted" clades that live near the surface, where solar energy is abundant and nutrient concentrations are at their lowest [160-164]. This suggests there is a link between metabolic rate and nutrient acquisition [174,66], which can be elucidated by considering the free energy cost of the nutrient uptake reaction:

$$\Delta G_r = RT \ln\left(\frac{[n]_I}{[n]_E}\right) + ZF\Delta\psi, \tag{3}$$

where Z is the unit charge of nutrient ions, F is the Faraday constant, $\Delta\psi$ is the membrane potential and subscripts I and E refer to internal and external nutrients, respectively. Eq. 1 shows that as environmental nutrient concentrations ($[n]_E$) decrease, stronger energetic driving is needed to facilitate nutrient uptake. For active transport (i.e. $n_E + ATP \rightleftharpoons n_I + ADP + P_i$), increasing the energetic driving is achieved by increasing the $[ATP]/[ADP \times P_i]$ ratio, which is observed under nutrient-limited growth conditions in bacterial, plant and algal cells alike [175-178].

A parsimonious interpretation of the evidence is thus that selection for an increased metabolic rate in *Prochlorococcus* has lowered the nutrient concentration at which cells can grow [66]. Still somewhat unclear are the molecular details of how an increased metabolic rate leads to an increased ATP/ADP ratio and why this requires organic carbon excretion. Since cellular metabolism continually consumes ATP, cells can only increase ATP/ADP if they can create a temporary imbalance between the rates of ATP production and consumption until a new steady state at higher potential is created. In fast-growing heterotrophic cells an increase in the ATP/ADP ratio is linked to an increase in the consumption of organic carbon and use of fermentative pathways leading to excretion of partially oxidized carbon [151-153,179,180]. Nutrient-limited growth conditions – which requires an increase in the ATP/ADP ratio (Eq. 1) – similarly lead to an increased throughput and excretion of organic carbon in both phytoplankton [181-185], including *Prochlorococcus* [155] and heterotrophs [151-154]. These observations suggest that cells use increased carbon and ATP supplies to drive pathways into saturation, keeping a larger fraction of enzymes occupied by all but the limiting nutrient(s), thereby causing ATP production to outpace consumption and the ATP/ADP ratio to increase [66]. An increasing ATP/ADP ratio would in turn cause forward rates of ATP-consuming reactions to increase until ATP production and consumption are once again in balance. While in principle it would appear possible to drive pathways into saturation by decreasing their maximal rates (e.g. by lowering enzyme levels), possibly circumventing the need for excreting (excess) carbon, the pathways for assimilating carbon and limiting nutrients into biomass are intimately intertwined, making this a potentially counterproductive strategy.

Thus, while further study is needed, combined evidence led us to conclude that evolutionary increases in cellular metabolic rate and organic carbon excretion (Fig. 4) reflect the same driving force and allow *Prochlorococcus* cells to grow at lower nutrient concentrations [66]. This hypothesis can be developed into a mathematical model in two steps, the first of which is to relate the nutrient uptake flux to the electron and carbon fluxes [66]:

$$v_n = \frac{Q_n}{Q_C} v_e (\#C/\#e)(1-\beta), \qquad (4)$$

where Q_n/Q_C is the cellular stoichiometry of nutrient n and carbon, $\#C/\#e$ is the efficiency of carbon-fixation (i.e. the number of carbon that are fixed per electron obtained from water splitting), and β is the fraction ($0<\beta<1$) of the carbon flux that is excreted. The nutrient uptake flux can in turn be related to the free energy of the nutrient uptake reaction using reversible Michaelis-Menten kinetics [66]:

$$v_n = \frac{[n][E]k^+}{K_{M,n}} \left(1 - e^{\Delta_r G/RT}\right), \qquad (5)$$

where $[E]$ is the concentration of the uptake transporter enzyme, $K_{M,n}$ is its Michaelis constant, k^+ is the rate constant of the uptake reaction and the forward and backward reactions are related through $\Delta_r G = -RTln\left([n]_E K_{M,n_E} K_{eq}/[n]_I K_{M,n_I}\right)$ [186]. Finally, equations 4 and 5 can be combined to relate relevant features of cells to the nutrient concentrations at which they can grow [66]:

$$[n] = \frac{K_{M,n} v_n}{[E]k^+(1 - e^{\Delta_r G/RT})} = \frac{K_{M,n}}{[E]k^+} \frac{Q_n}{Q_C} \frac{v_e(\#C/\#e)(1-\beta)}{(1 - e^{\Delta_r G/RT})}, \qquad (6)$$

Equation 6 immediately shows that selection for growth at lower nutrient concentrations favors a decrease in the nutrient uptake flux (v_n). However, as outlined above, resulting decreases in the minimal subsistence nutrient concentration $[n]$ are self-limiting because it increases the free energy cost of uptake $\Delta_r G$ (Eq. 3). As argued above, cells are able to compensate for this increased cost by driving metabolic pathways into saturation, thereby driving up the ATP/ADP ratio, and excreting the resulting excess carbon. By this logic Eq. 6 thus suggests that selection for growth at lower nutrient concentrations favors increasing v_e/v_n as well as the excretion of organic carbon, as observed in the evolution of *Prochlorococcus* (Fig. 4B).

Evolutionary dynamics of *Prochlorococcus*

The reconstructed metabolic evolution (Fig. 4) and model of Eq. 6 provides a new perspective on the macroevolutionary diversification of *Prochlorococcus* and how it shaped the ocean ecosystem. It suggests the layered structure of extant *Prochlorococcus* populations [160-164] arose through a sequence of niche constructing adaptive radiations (Fig. 5). Each innovation that increased the harvesting of solar energy drew down nutrient levels at the surface, thereby restricting ancestral populations adapted to higher nutrient levels to greater depths, while driving up levels of dissolved organic carbon [66]. This in turn implies *Prochlorococcus* has an important role in shaping extant ocean chemistry, which is consistent with observations that its populations are densest in the tropical and sub-tropical surface oceans where nutrients are near-vanishing [162,164] and dissolved organic carbon levels are twice as high as in the rest of the oceans [187].

The proposed dynamic (Fig. 5) is consistent with a recent study on the evolution of nitrate assimilation in *Prochlorococcus* [188]. It was shown this trait is absent in basal *Prochlorococcus* clades, even though its evolution is governed by vertical inheritance going back to before the split between *Prochlorococcus* and *Synechococcus* [188]. Studies of seasonal ecological dynamics in *Prochlorococcus* had previously shown that cells with the ability to assimilate nitrate are selected for in summer months when light is intense and concentrations of all forms of nitrogen are low [189]. This led to the conclusion that basal clades originally occupied more of the water column before niche partitioning restricted them to the bottom of the water column (Fig. 5) where retention of nitrate assimilation genes became unfavorable [188].

Evolution of biospheric productivity in the oceans

The reconstructed evolutionary dynamic of *Prochlorococcus* (Fig. 4B & 5, Eq. 6) provides general insights into the evolution of the oceanic biosphere as a whole. Innovations increasing v_e/v_n reach back to the last common ancestor of all marine picocyanobacteria (Fig. 4B), and since such

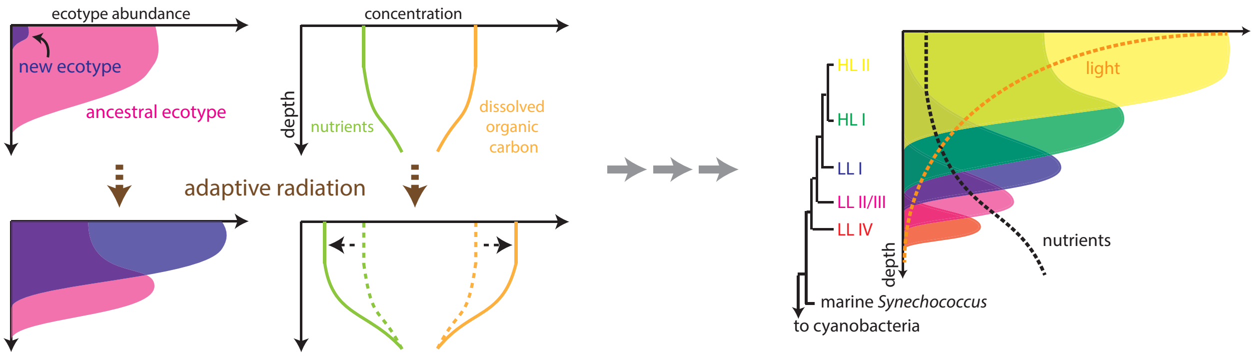

Fig. 5 Macroevolutionary dynamics leading to niche partitioning in *Prochlorococcus*. Panel on left shows the principles of niche constructing adaptive radiations. Innovations that increase cellular metabolic rate (Fig. 4) lead to the emergence of new populations (purple) that drive down nutrient levels (green curve) and increase dissolved organic carbon levels (orange curve). Ancestral populations (pink) are restricted to greater depth where nutrients remain elevated. A sequence of adaptive radiations leads to the extant population structure shown in panel on right. Populations are colored according to the labels on the consensus phylogeny shown next to the ecological panel. Adapted from Figs 1 & 4 from Ref [66].

innovations allow cells to grow at lower nutrient concentrations (Eq. 6), it helps explain how this group was able to colonize the open ocean in the face of nitrogen and/or phosphorus limitation (Fig. 2). Similarly, changes in the photosynthetic machinery and core metabolic pathways (Fig. 4A) decrease the iron requirements of cells [66,128], helping explain how photosynthesis was able to begin extending its reach in the face of declining iron levels as the ocean became oxygenated (Fig. 3). In addition, the classes of organic carbon compounds excreted by marine picocyanobacteria (carboxylic acids, polysaccharides) are known to chelate iron and enhance its bioavailability [66,122,123]. Thus, the evolution of marine picocyanobacteria added a positive feedback (Fig. 6) that counteracted the negative feedbacks built-in to ancestral cyanobacterial photosynthesis (Fig. 3) and paved the way for ocean oxygenation.

The identified positive feedback (Fig. 6) is linked to metabolic rate (Fig. 4), and so is strengthened with each innovation that enhances the harvesting of solar energy. The evolutionary process that produced such innovations in marine picocyanobacteria (Fig. 4) stretches out across the Neoproterozoic and Phanerozoic [63,64], which is relevant to discussion that ocean oxygenation played out over hundreds of millions of years [38,93-96]. Further, the innovations seen in marine picocyanobacteria (Fig. 4) are by no means unique to this group. Oceanic eukaryotic phytoplankton also have modified photosynthetic machineries that require less iron [190-192], modified membranes that require less phosphorus [172] and excrete large amounts of organic carbon under nutrient limitation [181-185]. This suggests that the reconstructed evolution of marine picocyanobacteria (Fig. 4) reflects general driving forces that allowed the oceanic biosphere as a whole to overcome the self-damping nature of ancestral cyanobacterial photosynthesis (Fig. 6).

Several additional positive biogeochemical feedbacks emerge from the positive feedback involving iron (Fig. 6). For example, the same classes of organic compounds (carboxylic acids, polysaccharides) released by marine picocyanobacteria are produced in terrestrial ecosystems and are known to enhance the weathering of rock minerals, releasing the iron and phosphorus they contain [193,194]. In the open ocean, rock minerals in wind-blown desert dust are the major source of iron [195], as well as a source of phosphorus [196,197]. Thus, the evolution of marine

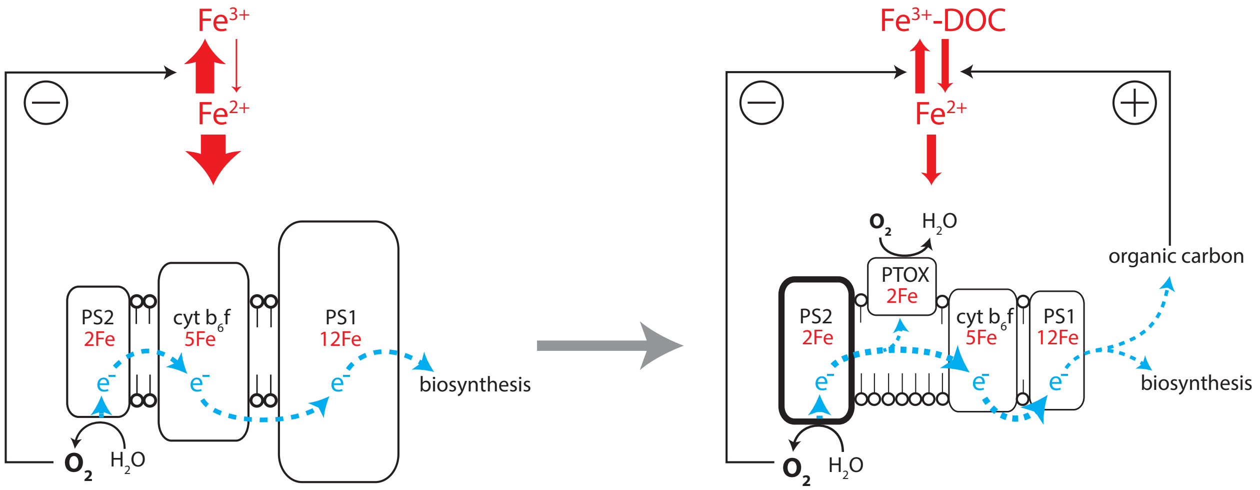

Fig. 6 Evolution of feedbacks involving iron in the machinery of photosynthesis. Left panel reflects photosynthetic machinery of ancestral cyanobacteria, right panel reflects photosynthetic machinery of *Prochlorococcus*. Relative size of electron transfer components reflects their cellular stoichiometry, line thickness reflects absorption cross-section. Relative thickness of red arrows directed from Fe^{2+} to photosynthetic machinery reflects qualitative differences in the cellular iron fluxes (v_{Fe}) needed to build photosynthetic machinery. A positive feedback ('+' sign) emerging in the metabolic evolution of marine picocyanobacteria (Fig. 4) counteracts the negative feedback ('-' sign) built into the machinery of photosynthesis (Fig. 3). Chelation by organic carbon increases solubility of Fe^{3+} in the presence of oxygen, as indicated by enhanced flux from Fe^{3+} to Fe^{2+} relative to the left panel. Dashed blue arrow reflects flow of electrons. Abbrevations: PTOX = plastoquinol terminal oxidase, others as in Fig. 3.

picocyanobacteria not only enhanced the bioavailability of iron as the ocean became oxygenated, but potentially also increased the supply of available iron and phosphorus into the oceans [66]. Such a link between the cycles of iron and phosphorus is consistent with observations that some oceanic heterotrophs release iron-chelating compounds when they are phosphorus-limited, presumably to dissolve minerals containing both iron and phosphorus [198]. In addition, while photosynthetically-produced organic carbon enhanced the bioavailability of iron in oxygenated environments (Fig. 6), overall iron levels still decreased significantly relative to those in the previously anoxic oceans [116]. This led to a decrease in the scavenging of phosphorus (Fig. 2) and a concomitant increase in its bioavailability [98-101]. Ocean oxygenation would have also lessened phosphorus limitation by increasing the supply of electron acceptors for the remineralization of organic phosphorus [98] (Fig. 2).

Further, the drawdown of nitrogen near the surface (Fig. 5) and an enhancement in the bioavailability of iron (Fig. 6) leads to conditions that generally promote nitrogen-fixation [199-201]. Indeed, recent analyses suggest global rates of nitrogen-fixation in the extant oceans are highest in the regions where *Prochlorococcus* dominates [202]. Ocean oxygenation would have moreover lifted any molybdenum-limitation by suppressing euxinia (Fig. 2), creating generally prime conditions for the expansion of oceanic nitrogen-fixation [53,29] and lessened nitrogen-limitation by decreasing the rate of denitrification relative to nitrification [97] (Fig. 2). These scenarios are consistent with molecular clocks that estimate Neoproterozoic origins of both planktonic marine nitrogen-fixers [63] and ammonia-oxidizing marine Thaumarcheota [203,204], both of which indicate an increasing influx and cycling of fixed nitrogen in the oceans. The geologic record leads to a similar conclusion, as sedimentary nitrogen isotopes display shifts toward modern ocean values in the Neoproterozoic, indicating the onset of a stable oceanic nitrate pool [105-111].

Convergent biogeochemical evolution in the oceans and on the continents

There are a wide range of parallels between the rise of marine picocyanobacteria and the rise of land plants. Key observations at the level of cellular metabolism come from analyses of the highly abundant oceanic alphaproteobacteria SAR11 [167,205], which like marine picocyanobacteria is estimated to have emerged during the Neoproterozoic [206]. Reconstructions suggest the metabolic core of SAR11 underwent a global remodeling that was complementary to that of *Prochlorococcus* (Fig. 4A), resulting in compatible pathways for the exchange of organic carbon between the two groups (Fig. 7, top panel) [63]. This is consistent with previous experiments that showed that SAR11 requires several of the compounds identified as excretion pathways in *Prochlorococcus* (Fig. 4A) [207,136]. The pathways involved in these exchanges are highly similar to those mediating metabolic interactions between chloroplasts and mitochondria in green plant cells. Intermediates of lower glycolysis and photorespiration mediate the flow of electrons and carbon from the photosynthetic to the heterotrophic components in both plant cells and in oceanic microbial ecosystems, while intermediates of the citric acid cycle mediate the flow of electrons and carbon in the opposite direction (Fig. 4A) [66].

Convergence in the metabolic evolution of the two systems extends from core pathways to their energy metabolism (Fig. 7, top panel). *Prochlorococcus* uses chlorophyll a and b instead of phycobilisomes [60] and has a PSII/PSI ratio that is significantly higher than other cyanobacteria [127,208,209], making its photosynthetic machinery rather more like that of green chloroplasts than other cyanobacteria [66]. The electron transport chains of the two systems further contain similar bypasses. The electron transport chains of *Prochlorococcus* and chloroplasts both contain plastoquinol terminal oxidase (PTOX), which creates a water-water cycle by redirecting electron flux immediately following photosystem II [128,210]. The electron transport chains of SAR11 and mitochondria in turn both contain alternative oxidase, which again creates a short cut in the reduction of oxygen to water by redirecting electrons immediately following complex I [210,211]. Finally, *Prochlorococcus* and some clades of SAR11 have lost catalase and the ability to detoxify peroxide (HOOH), a by-product of photosynthesis, and depend on other sympatric microbes for this function [212,213], just as chloroplasts and mitochondria depend on the peroxisome for this function [211].

Similarities between oceanic microbial ecosystems and land plants also include the timing and biogeochemical impact of their emergence on the Earth system (Fig. 7, bottom panel). The expansion of plants onto the continents dates to the early Phanerozoic [48], while their evolutionary roots lie in the Neoproterozoic [55,214-217], similar to the timeframes over which ancestral marine picocyanobacteria diversified into *Synechococcus* and *Prochlorococcus* [63,64]. In addition, under nutrient limitation plants excrete organic carbon from their roots, dissolving rocks minerals and making the iron and phosphorus within them available [218,219]. The resulting conditions promote nitrogen-fixation [199-201], and various plants have evolved symbioses with nitrogen-fixing bacteria in their rhizosphere [200,220], increasing the supply of fixed nitrogen into the terrestrial biosphere [221]. It has been suggested that the key contribution of plants to enhancing terrestrial nitrogen-fixation was to physically separate the oxygen-sensitive nitrogenase enzyme in soils and above-ground oxygen production in leaves [222]. However, planktonic

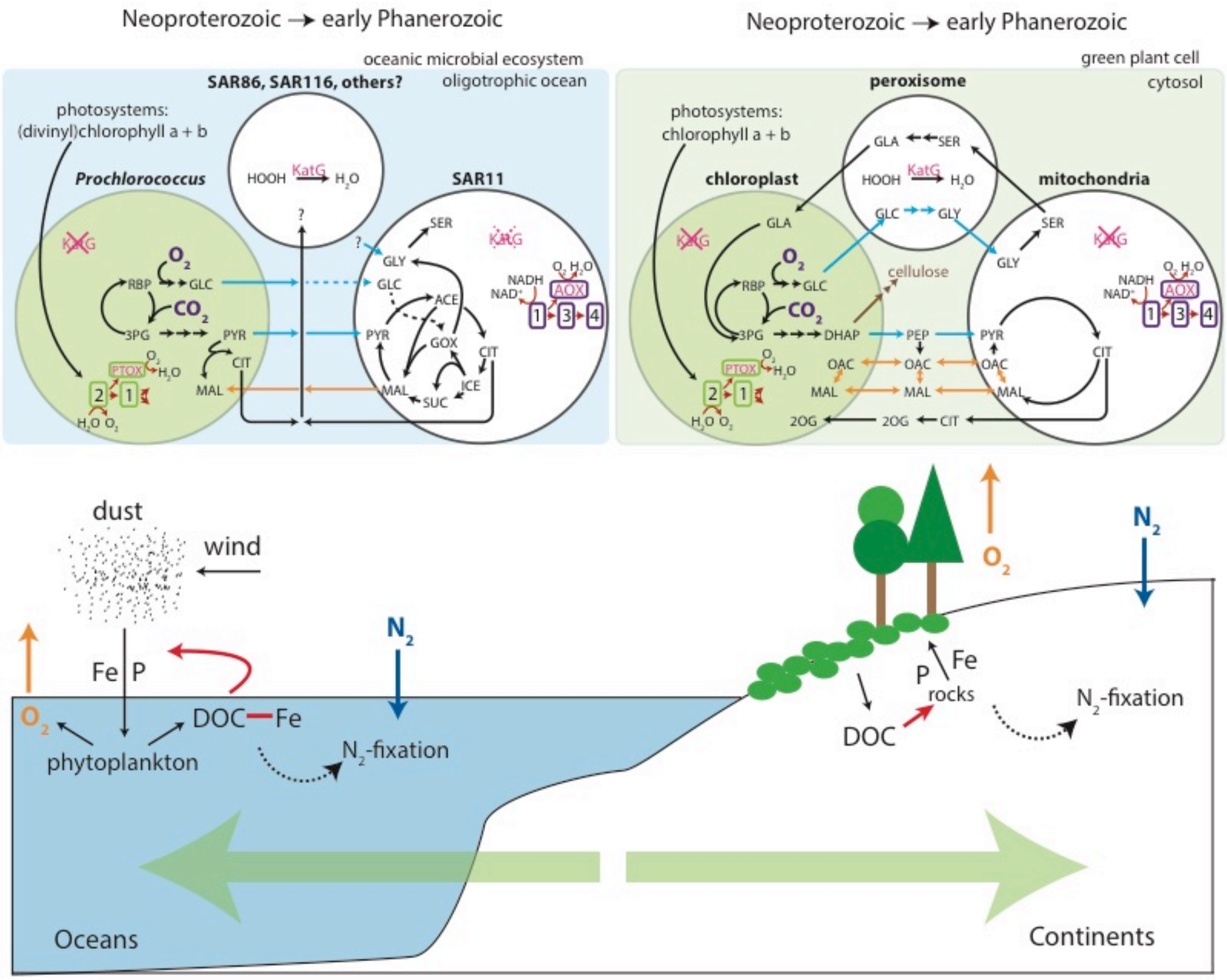

Fig. 7 Convergent biogeochemical evolution of green eukaryotic photosynthesis in the oceans and on the continents. Top panel: Similarities between the photosystems, electron transport chains and core carbohydrate metabolic pathways of oceanic microbial ecosystems and green plant cells. Metabolic reactions are shown in simplified form not accounting for stoichiometry. Blue arrows indicate flow of electrons and carbon from autotrophic to heterotrophic components, while orange arrows indicate flow of electrons and carbon in opposite direction. Bottom panel: Geochemical feedbacks driven by the evolution of eukaryotic photosynthesis on land and in the sea. Big green arrows indicate ecological expansion of green eukaryotic photosynthesis (panel A) away from continental boundaries. Red arrows reflect positive weathering feedbacks of photosynthetically produced organic carbon. Dashed arrows reflect the stimulation of nitrogen-fixation and dark blue arrows reflect increasing influx of nitrogen from the atmosphere into the oceanic/terrestrial biogeochemical cycles and. Orange arrows represent the increasing oxygen flux into the atmosphere due to increasing biospheric productivity. Top panel adapted from Fig. 5 of Ref [66] Abbreviations: RBP = ribose bisphosphate, GLC = glycolate, PYR = pyruvate, CIT = citrate, MAL = malate, GLY = glycine, SER = serine, ACE = acetyl-CoA, GOX = glyoxylate, SUC = succinate, ICE = isocitrate, GLA = glycerate, OAC = oxaloacetate, 2OG = 2-oxoglutarate, AOX = alternative oxidase, PTOX = plastoquinol terminal oxidase, KatG = catalase

nitrogen-fixers expanded into the oceans around the same time [63] without this help from plants, and in general nitrogen-fixing microbes expend most of their energy budget on managing intracellular oxygen as external levels increase [223]. This suggest the increase in metabolic power of eukaryotic photosynthesis and associated production of organic carbon was the more general facilitating factor stimulating nitrogen-fixation across environments (Fig. 7), working in concert with physical separation in terrestrial environments [222]. Either way, an increased influx of nitrogen into the terrestrial biosphere is consistent with molecular clocks estimating a Neoproterozoic rise of ammonia-oxidizing Thaumarcheota in terrestrial soils [203,204], paralleling their aforementioned Neoproterozoic rise in the oceans [203,204]. These observations have led to the arguments that the rise of land plants enhanced continental weathering [224-227] and organic carbon burial as the productivity of the terrestrial biosphere increased, driving an increase in atmospheric oxygen [228,229] (Fig. 7, bottom panel). The proposal outlined above (Fig. 6 and surrounding discussion) extends those arguments to the water column and highlights the convergent biogeochemical evolution of eukaryotic photosynthesis on land and in the sea (Fig. 7) [66].

Outlook: biospheric self-amplification, plate tectonics and Earth oxygenation

Cellular metabolism provides a unique lens into Earth history [230]. Looking through this lens in marine picocyanobacteria leads to a general framework in which ecosystems follow self-amplifying evolutionary trajectories (Fig. 8) [66]. This holds for particular groups, for example in the niche partitioning of *Prochlorococcus* (Fig. 5), as well as for the biosphere as a whole. As cells acquire innovations that allow them to obtain ever-sparser nutrients (Fig. 4, Eq. 6), more nutrients are driven from the environment into the living state, increasing total ecosystem biomass (Fig. 5 & 8). This in turn promotes the mobilization of nutrients at larger scales, for example through enhanced weathering of rocks in the case of iron and phosphorus, or by creating opportunities for nitrogen-fixers in the case of nitrogen (Fig. 7).

At the largest scale, the two major stages of biospheric expansion and Earth oxygenation are linked to the bioenergetic innovations of cyanobacterial and eukaryotic photosynthesis [66]. For most of the Proterozoic, a combination of feedbacks (Figs. 2 & 3) largely restricted cyanobacterial photosynthesis to shallow aquatic environments near continental boundaries, where weathering inputs made nutrients relatively more easily accessible than in the open ocean or on the continents. Near the end of the Proterozoic, the increasing cellular energy flux and associated production of organic carbon of eukaryotic photosynthesis, which from a metabolic perspective includes marine picocyanobacteria (Fig. 7), helped the biosphere push through these negative feedbacks and expand into the open ocean and onto the continents, where nutrients were inherently harder to come by as oxygenation proceeded (Figs. 6 & 7). This scenario is consistent with phylogenomic analyses suggesting freshwater origins for both cyanobacteria and photosynthetic eukaryotes [231,232] and molecular biomarker studies indicating a major expansion of eukaryotic green algae in the marine realm in the late Neoproterozoic [55]. The faster sinking of larger organisms and/or their fecal pellets [41-44] likely still acted as a positive feedback promoting ocean oxygenation in the Neoproterozoic and Phanerozoic (Fig. 1), but this feedback was driven from the bottom up as more food became available to higher trophic levels (Fig. 5 & 8) [55].

In addition to being linked to major biospheric expansions, the periods of Earth history around the Great and Neoproterozoic Oxidation Events share a number of other general similarities. Sediment records indicate that both periods had a turbulent climate with major carbon cycle perturbations [36,41,81,82,233,234] and global glaciations [83-86,235-239]. A range of geological and geochemical evidence further suggests major changes in the nature of plate tectonics and increases

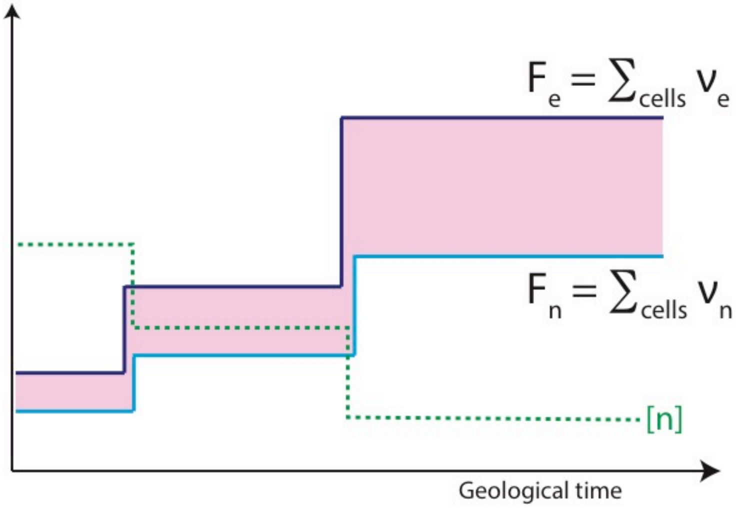

Fig. 8. Evolution of ecosystem-level fluxes of electron and nutrients ($F_{e,n}$) and environmental nutrient concentrations over geologic time. Innovations that increase metabolic rate (through increases in the electron-to-nutrient flux ratio, ν_e/ν_n) increase total ecosystem biomass by making more nutrients bioavailable and driving them into the living state (Fig. 5). At larger scales this promotes the influx of nutrients into the ecosystem from surrounding environments, through enhanced nitrogen-fixation and/or weathering feedbacks (Fig. 7). Ecosystem-level electron and nutrient fluxes $F_{e,n}$ are the sum (Σ_{cells}) of cellular nutrient and electron fluxes that make up the ecosystem.

in sub-aerial continental exposure in both the Neoarchean [18,19,75,240-247] and Neoproterozoic [69,71-74,76-80,248,249] leading up to atmospheric oxygenation. Finally, statistical analyses of the sediment record indicate increases in either the preservation of sediments or in the rates of sediment production during both epochs [78,250,251], the latter of which might be expected if more exposed continents were more prone to weathering. It should be noted that interpreting the large-scale structure of Earth history from the rock record requires caution, because samples become sparser in deep time and the signals they contain are prone to overprinting [82,87,2502]. See e.g. Refs. [75,253-255] for arguments that differences in the chemical composition of Earth's crust and in the creation and preservation of sedimentary signals rather than changes in plate tectonics and sedimentation rates best explain Neoproterozoic discontinuities. Still, the broad parallels of biogeochemical change across the Archean-Proterozoic and Proterozoic-Phanerozoic boundaries suggests that apparent discontinuities in the geologic and genomic records of both periods should be evaluated in the context of each other and that unifying mechanisms should be sought.

One key process that has likely always had a major role in mediating interconnections of biological and geological change is continental weathering and sedimentation. The weathering of rocks supplies life with essential nutrients, while biological activity enhances the weathering of rocks [218,219,224-227] (Fig. 7), creating a positive feedback loop. A positive bidirectional link between biospheric productivity and weathering and sedimentation is consistent with the large-scale record of sedimentary carbon. Isotopic patterns in this record indicate that the fraction of total carbon buried in sediments derived from organic carbon and inorganic carbonates is stable at a ratio of around ~20:80 throughout most of Earth history, although large transient divergences from this ratio are seen around both the Great and Neoproterozoic Oxidation Events [6,7]. The sediment record itself thus indicates that any major increases in the steady state burial of organic carbon must have been coupled to similar increases in the steady state burial of carbonates, the production of which is generally linked to weathering reactions [256,257]. Transient fluctuations in the relative burial of organic and inorganic carbon (and associated climatic instability) around the Great and Neoproterozoic Oxidation Events can then be interpreted as resulting from bifurcations in the carbon cycle as it transitioned between stable states [6,81].

A fundamental link between biospheric productivity and weathering/sedimentation rates also helps answer a conundrum regarding the relationship between the mechanisms of organic carbon burial and atmospheric oxygenation. The fraction of organic carbon that is ultimately buried after deposition is inversely proportional to the "oxygen exposure time", which is obtained by dividing the depth to which oxygen penetrates into sediments by the overall sedimentation rate [258]. The oxygen penetration depth of sediments in turn depends on their composition and on the oxygen concentration of bottom waters. As a consequence, Earth oxygenation effectively acts to stymy itself by decreasing the fractional burial of sedimentary organic carbon, *unless* increases in oxygen levels are coupled to increases in sedimentation rates and/or changes in the composition of sediment that make them less penetrable to oxygen [6]. Evidence for the latter around the Proterozoic-Phanerozoic boundary comes from analyses that suggest biologically-driven increases in the production of fine-grained clays and muds by the early Phanerozoic [45,46,259-261]. Sedimentary clay minerals have recently been shown to trap organic carbon and prevent breakdown even in the presence of oxygen through a combination of physical and chemical effects, significantly contributing to the global sequestration of organic carbon [262]. It thus appears that increases in overall weathering/sedimentation rates and in the production of less-penetrable sediments worked in tandem to counteract the negative effect of oxygenation on organic carbon burial, allowing oxygen to rise.

The existence of a positive feedback between biospheric productivity and continental weathering leads to two possible endmembers for interpreting the drivers of global change around the Great and Neoproterotezoic Oxidation Events. One possibility is that the solid Earth is the ultimate pacemaker of change – biospheric expansions occur when the cooling of the mantle and crust passes through tipping points that trigger changes in the nature of plate tectonics and/or continental exposure, thereby increasing the supply of rock-derived nutrients. In this scenario, the biosphere still plays a key role in unlocking the nutrient supply that fuels it, but this feedback is driven from the bottom up by changes in the solid Earth.

The other possibility is that life plays a more active role in driving change. Indeed, it has been argued that, by coupling solar energy into Earth's geochemical cycles, the evolution of photosynthesis accelerated the formation of lighter granites from heavier basalts, thereby increasing crustal buoyancy, promoting the rise of stable continents and directly influencing the mode of plate tectonics [263-265]. These arguments were subsequently extended to say that by modulating the production of sediments available to subduction, life directly influences the flow of water and other volatiles into the mantle and promoting greater continental exposure [266,267]. If such ideas are correct, then the evidence for a two-step expansion in biospheric productivity at the start and end of the Proterozoic (Fig. 7) and the broader biogeochemical parallels between the Archean-Proterozoic and Proterozoic-Phanerozoic boundaries suggest that similar mechanisms may have operated in both periods.

Framing the co-evolution of the biosphere and solid Earth as playing out between these two endmembers provides relevant context to discussions on the temporal relationship between the evolution of oxygenic photosynthesis and atmospheric oxygenation. Molecular clock estimates of when cyanobacterial and/or eukaryotic photosynthesis first arose vary significantly, largely due to differences in external date constraints (e.g. from fossils, biomarkers or other geochemical proxies) imposed on the calculations [215-217,268-273]. A range of genomic and geochemical evidence nevertheless suggests that the roots of cyanobacteria and the initiation of atmospheric oxygenation pre-date the Great Oxidation Event by several hundred million years [268,271,273-281]. Similarly, paleontological evidence and molecular clock estimates generally agree the roots of eukaryotic photosynthesis pre-date the Neoproterozoic Oxidation Event by at least several hundred million years [215-217,269,272]. This has led to major debates, because if oxygenic photosynthesizers are ultimately responsible for both stages of oxygenation, what explains the long delays between their evolutionary roots and major increases in atmospheric oxygen?

Considering the role of weathering provides insights to this question. If biospheric expansions require long-term increases in the weathering supply of nutrient-bound rock, then changes in the mode of plate tectonics and increases in continental weathering place central constraints on when major expansions can happen, even if the classes of metabolism ultimately driving those expansion already previously existed. Alternatively, if evolutionary increases in the coupling of solar energy into Earth's geochemical cycles played a central role in driving changes in solid Earth dynamics, then the long delays between photosynthetic innovations and their ecological expansions that trigger increases in atmospheric oxygen may simply reflect the inertia of changes in solid Earth dynamics in response to driving by the biosphere [263].

Considering the nature of metabolic evolution provides further clarification on why oxygenation was delayed relative to the roots of major photosynthetic groups. What we today recognize as cyanobacterial photosynthesis involved a multitude of innovations – encompassing core pathways, cofactors, photosynthetic and electron-transfer machinery and the (thylakoid) membranes that house them, damage protection mechanisms needed to adapt to an oxidizing environment [5,282-287] – and these were likely acquired over time rather than all at once. Similarly, the reconstructed evolution of marine picocyanobacteria (Fig. 4) highlights how the diversification and ecological expansion of eukaryotic photosynthesis (Fig. 7) involved the sequential acquisition of a complex set of innovations [66] over the course of hundreds of millions of years [63,64]. Finally, in the case of cyanobacteria, the first accumulation of oxygen also led to the eventual emergence of an ozone layer [25], which filtered out damaging UV radiation and allowed cyanobacteria to continue their expansion [288]. Thus, the size of habitats available to cyanobacteria and photosynthetic eukaryotes and their ability to fill those habitats in general thus likely increased in tandem during the rise of continents.

It has become increasingly clear that the biosphere is intimately intertwined with the rest of the Earth system and that evolution of the energy flows it mediates have far-reaching consequences for the planet. Reconstructing the evolutionary history of the biosphere is critical as we look toward a future in which humans are dramatically altering Earth's energetic landscape, but also poses major challenges. The two main repositories of Earth history are the planetary inventory of rocks and the DNA inside living cells, each of which have their own unique advantages and difficulties. The geologic record in principle provides direct information of the environmental conditions under which rocks were formed but gets increasingly difficult to interpret in deep time because the record becomes sparser and rocks have had a longer time to undergo post-depositional changes. The genomic record in turn is vast and reaches back to the first cells, in principle providing information about environmental processes and conditions shaping evolution throughout Earth history, but this information is indirect and decoding it is difficult, partly because direct temporal constraints are often lacking. Despite these challenges, the geologic and genomic records are highly complementary and metabolism provides a key lens for helping us align them and achieve a more integrated view of how Earth and the biosphere have changed together over time.

Acknowledgements

I thank Penny Chisholm and Mick Follows for generous support, encouragement and collaboration during the development of the ideas outlined here. I further thank John Raven, Ron Milo, Daniel Rothman, Kristin Bergmann, Patricia Sanchez-Barracaldo, Eric Smith, Forrest Horton, Paul Berube, Paul Falkowski, Yuichiro Ueno and Peter Cawood for useful feedback, discussions and suggestions of key references. This work was supported by a Simons Foundation Fellowship of the Life Sciences Research Foundation (to R.B), by the Simons Collaboration on Ocean Processes and Ecology, Award 329108 (to S.W. Chisholm and M.J. Follows) and by Simons Foundation Life Sciences Project Awards 337262 and 509034SCFY17 (to S.W. Chisholm).

References

[1] Garrels, R.M. and Lerman, A., 1981. Phanerozoic cycles of sedimentary carbon and sulfur. *Proceedings of the National Academy of Sciences*, *78*(8), pp.4652-4656.

[2] Holland, H.D., 1984. *The chemical evolution of the atmosphere and oceans*. Princeton University Press.

[3] Berner, R.A., Beerling, D.J., Dudley, R., Robinson, J.M. and Wildman Jr, R.A., 2003. Phanerozoic atmospheric oxygen. *Annual Review of Earth and Planetary Sciences*, *31*(1), pp.105-134.

[4] Hayes, J.M. and Waldbauer, J.R., 2006. The carbon cycle and associated redox processes through time. *Philosophical Transactions of the Royal Society of London B: Biological Sciences*, *361*(1470), pp.931-950.

[5] Falkowski, P.G. and Raven, J.A., 2007. *Aquatic photosynthesis*, 2nd ED. Princeton University Press.

[6] Rothman, D., 2015. Earth's carbon cycle: a mathematical perspective. *Bulletin of the American Mathematical Society*, *52*(1), pp.47-64.

[7] Krissansen-Totton, J., Buick, R. and Catling, D.C., 2015. A statistical analysis of the carbon isotope record from the Archean to Phanerozoic and implications for the rise of oxygen. *American Journal of Science*, *315*(4), pp.275-316.

[8] Ganino, C. and Arndt, N.T., 2009. Climate changes caused by degassing of sediments during the emplacement of large igneous provinces. *Geology*, *37*(4), pp.323-326.

[9] Edmonds, M. and Mather, T.A., 2017. Volcanic sulfides and outgassing. *Elements*, *13*(2), pp.105-110.

[10] Stachel, T., Brey, G.P. and Harris, J.W., 2005. Inclusions in sublithospheric diamonds: glimpses of deep Earth. *Elements*, *1*(2), pp.73-78.

[11] Walter, M.J., Kohn, S.C., Araujo, D., Bulanova, G.P., Smith, C.B., Gaillou, E., Wang, J., Steele, A. and Shirey, S.B., 2011. Deep mantle cycling of oceanic crust: evidence from diamonds and their mineral inclusions. *Science*, p.1209300.

[12] Sverjensky, D.A., Stagno, V. and Huang, F., 2014. Important role for organic carbon in subduction-zone fluids in the deep carbon cycle. *Nature Geoscience*, *7*(12), p.909.

[13] Buseck, P.R. and Beyssac, O., 2014. From organic matter to graphite: Graphitization. *Elements*, *10*(6), pp.421-426.

[14] Galvez, M.E., Connolly, J.A. and Manning, C.E., 2016. Implications for metal and volatile cycles from the pH of subduction zone fluids. *Nature*, *539*(7629), p.420.

[15] Duncan, M.S. and Dasgupta, R., 2017. Rise of Earth's atmospheric oxygen controlled by efficient subduction of organic carbon. *Nature Geoscience*, *10*(5), p.387.

[16] Kasting, J.F., Eggler, D.H. and Raeburn, S.P., 1993. Mantle redox evolution and the oxidation state of the Archean atmosphere. *The Journal of geology*, *101*(2), pp.245-257.

[17] Holland, H.D., 2002. Volcanic gases, black smokers, and the Great Oxidation Event. *Geochimica et Cosmochimica Acta*, *66*(21), pp.3811-3826.

[18] Kump, L.R. and Barley, M.E., 2007. Increased subaerial volcanism and the rise of atmospheric oxygen 2.5 billion years ago. *Nature*, *448*(7157), p.1033.

[19] Gaillard, F., Scaillet, B. and Arndt, N.T., 2011. Atmospheric oxygenation caused by a change in volcanic degassing pressure. *Nature*, *478*(7368), p.229.

[20] Lee, C.T.A., Yeung, L.Y., McKenzie, N.R., Yokoyama, Y., Ozaki, K. and Lenardic, A., 2016. Two-step rise of atmospheric oxygen linked to the growth of continents. *Nature Geoscience*, *9*(6), p.417.

[21] Smit, M.A. and Mezger, K., 2017. Earth's early O 2 cycle suppressed by primitive continents. *Nature geoscience*, *10*(10), p.788.

[22] Cloud, P.E., 1968. Atmospheric and hydrospheric evolution on the primitive Earth. *Science*, *160*(3829), pp.729-736.

[23] Walker, J.C., 1977. Evolution of the Atmosphere. *New York: Macmillan, and London: Collier Macmillan, 1977*.

[24] Kasting, J.F., 1987. Theoretical constraints on oxygen and carbon dioxide concentrations in the Precambrian atmosphere. *Precambrian research*, *34*(3-4), pp.205-229.

[25] Farquhar, J., Bao, H. and Thiemens, M., 2000. Atmospheric influence of Earth's earliest sulfur cycle. *Science*, *289*(5480), pp.756-758.

[26] Bekker, A., Holland, H.D., Wang, P.L., Rumble Iii, D., Stein, H.J., Hannah, J.L., Coetzee, L.L. and Beukes, N.J., 2004. Dating the rise of atmospheric oxygen. *Nature*, *427*(6970), p.117.

[27] Luo, G., Ono, S., Beukes, N.J., Wang, D.T., Xie, S. and Summons, R.E., 2016. Rapid oxygenation of Earth's atmosphere 2.33 billion years ago. *Science Advances*, *2*(5), p.e1600134.

[28] Blättler, C.L., Claire, M.W., Prave, A.R., Kirsimäe, K., Higgins, J.A., Medvedev, P.V., Romashkin, A.E., Rychanchik, D.V., Zerkle, A.L., Paiste, K. and Kreitsmann, T., 2018. Two-billion-year-old evaporites capture Earth's great oxidation. *Science*, *360*(6386), pp.320-323.

[29] Reinhard, C.T., Planavsky, N.J., Robbins, L.J., Partin, C.A., Gill, B.C., Lalonde, S.V., Bekker, A., Konhauser, K.O. and Lyons, T.W., 2013. Proterozoic ocean redox and biogeochemical stasis. *Proceedings of the National Academy of Sciences*, p.201208622.

[30] Cawood, P.A. and Hawkesworth, C.J., 2014. Earth's middle age. *Geology*, *42*(6), pp.503-506.

[31] Planavsky, N.J., Cole, D.B., Isson, T.T., Reinhard, C.T., Crockford, P.W., Sheldon, N.D. and Lyons, T.W., 2018. A case for low atmospheric oxygen levels during Earth's middle history. *Emerging Topics in Life Sciences*, p.ETLS20170161.

[32] Cloud Jr, P.E., 1948. Some problems and patterns of evolution exemplified by fossil invertebrates. *Evolution*, *2*(4), pp.322-350.

[33] Berkner, L.V. and Marshall, L.C., 1965. History of major atmospheric components. *Proceedings of the National Academy of Sciences*, 53 (6) 1215-1226

[34] Runnegar, B., 1991. Precambrian oxygen levels estimated from the biochemistry and physiology of early eukaryotes. *Palaeogeography, Palaeoclimatology, Palaeoecology*, *97*(1-2), pp.97-111.

[35] Derry, L.A., Kaufman, A.J. and Jacobsen, S.B., 1992. Sedimentary cycling and environmental change in the Late Proterozoic: evidence from stable and radiogenic isotopes. *Geochimica et Cosmochimica Acta*, *56*(3), pp.1317-1329.

[36] Des Marais, D.J., Strauss, H., Summons, R.E. and Hayes, J.M., 1992. Carbon isotope evidence for the stepwise oxidation of the Proterozoic environment. *Nature*, *359*(6396), p.605.

[37] Canfield, D.E. and Teske, A., 1996. Late Proterozoic rise in atmospheric oxygen concentration inferred from phylogenetic and sulphur-isotope studies. *Nature*, *382*(6587), p.127.

[38] Fike, D.A., Grotzinger, J.P., Pratt, L.M. and Summons, R.E., 2006. Oxidation of the Ediacaran ocean. *nature*, *444*(7120), p.744.

[39] Erwin, D.H., Laflamme, M., Tweedt, S.M., Sperling, E.A., Pisani, D. and Peterson, K.J., 2011. The Cambrian conundrum: early divergence and later ecological success in the early history of animals. *science*, *334*(6059), pp.1091-1097.

[40] Och, L.M. and Shields-Zhou, G.A., 2012. The Neoproterozoic oxygenation event: Environmental perturbations and biogeochemical cycling. *Earth-Science Reviews*, *110*(1-4), pp.26-57.

[41] Knoll, A.H., Hayes, J.M., Kaufman, A.J., Swett, K. and Lambert, I.B., 1986. Secular variation in carbon isotope ratios from Upper Proterozoic successions of Svalbard and East Greenland. *Nature*, *321*(6073), p.832.

[42] Logan, G.A., Hayes, J.M., Hieshima, G.B. and Summons, R.E., 1995. Terminal Proterozoic reorganization of biogeochemical cycles. *Nature*, *376*(6535), p.53.

[43] Butterfield, N.J., 2009. Oxygen, animals and oceanic ventilation: an alternative view. *Geobiology*, *7*(1), pp.1-7.

[44] Lenton, T.M., Boyle, R.A., Poulton, S.W., Shields-Zhou, G.A. and Butterfield, N.J., 2014. Co-evolution of eukaryotes and ocean oxygenation in the Neoproterozoic era. *Nature Geoscience*, *7*(4), p.257.

[45] Kennedy, M., Droser, M., Mayer, L.M., Pevear, D. and Mrofka, D., 2006. Late Precambrian oxygenation; inception of the clay mineral factory. *Science*, *311*(5766), pp.1446-1449.

[46] Knauth, L.P. and Kennedy, M.J., 2009. The late Precambrian greening of the Earth. *Nature*, *460*(7256), p.728.

[47] Falkowski, P.G., Katz, M.E., Knoll, A.H., Quigg, A., Raven, J.A., Schofield, O. and Taylor, F.J.R., 2004. The evolution of modern eukaryotic phytoplankton. *science*, *305*(5682), pp.354-360.

[48] Steemans, P., Le Hérissé, A., Melvin, J., Miller, M.A., Paris, F., Verniers, J. and Wellman, C.H., 2009. Origin and radiation of the earliest vascular land plants. *Science*, *324*(5925), pp.353-353.

[49] Falkowski, P. and Knoll, A.H. eds., 2011. *Evolution of primary producers in the sea*. Academic Press.

[50] Shih, P.M., Wu, D., Latifi, A., Axen, S.D., Fewer, D.P., Talla, E., Calteau, A., Cai, F., De Marsac, N.T., Rippka, R. and Herdman, M., 2013. Improving the coverage of the cyanobacterial phylum using diversity-driven genome sequencing. *Proceedings of the National Academy of Sciences*, *110*(3), pp.1053-1058.

[51] Butterfield, N.J., 1997. Plankton ecology and the Proterozoic-Phanerozoic transition. *Paleobiology*, *23*(2), pp.247-262.

[52] Vidal, G. and Moczydłowska-Vidal, M., 1997. Biodiversity, speciation, and extinction trends of Proterozoic and Cambrian phytoplankton. *Paleobiology*, *23*(2), pp.230-246.

[53] Anbar, A.D. and Knoll, A.H., 2002. Proterozoic ocean chemistry and evolution: a bioinorganic bridge? *Science*, *297*(5584), pp.1137-1142.

[54] Knoll, A.H., Javaux, E.J., Hewitt, D. and Cohen, P., 2006. Eukaryotic organisms in Proterozoic oceans. *Philosophical Transactions of the Royal Society of London B: Biological Sciences*, *361*(1470), pp.1023-1038.

[55] Brocks, J.J., Jarrett, A.J., Sirantoine, E., Hallmann, C., Hoshino, Y. and Liyanage, T., 2017. The rise of algae in Cryogenian oceans and the emergence of animals. *Nature*, *548*(7669), p.578.

[56] Isson, T.T., Love, G.D., Dupont, C.L., Reinhard, C.T., Zumberge, A.J., Asael, D., Gueguen, B., McCrow, J., Gill, B.C., Owens, J. and Rainbird, R.H., 2018. Tracking the rise of eukaryotes to ecological dominance with zinc isotopes. *Geobiology*.

[57] Gueneli, N., McKenna, A.M., Ohkouchi, N., Boreham, C.J., Beghin, J., Javaux, E.J. and Brocks, J.J., 2018. 1.1-billion-year-old porphyrins establish a marine ecosystem dominated by bacterial primary producers. *Proceedings of the National Academy of Sciences*, p.201803866.

[58] Crockford, P.W., Hayles, J.A., Bao, H., Planavsky, N.J., Bekker, A., Fralick, P.W., Halverson, G.P., Bui, T.H., Peng, Y. and Wing, B.A., 2018. Triple oxygen isotope evidence for limited mid-Proterozoic primary productivity. *Nature*, 559, pages613–616

[59] Waterbury, J.B., Watson, S.W., Guillard, R.R. and Brand, L.E., 1979. Widespread occurrence of a unicellular, marine, planktonic, cyanobacterium. *Nature*, *277*(5694), p.293.

[60] Chisholm, S.W., Olson, R.J., Zettler, E.R., Goericke, R., Waterbury, J.B. and Welschmeyer, N.A., 1988. A novel free-living prochlorophyte abundant in the oceanic euphotic zone. *Nature*, *334*(6180), p.340.

[61] Partensky, F., Hess, W.R. and Vaulot, D., 1999. Prochlorococcus, a marine photosynthetic prokaryote of global significance. *Microbiology and molecular biology reviews*, *63*(1), pp.106-127.

[62] Scanlan, D.J., Ostrowski, M., Mazard, S., Dufresne, A., Garczarek, L., Hess, W.R., Post, A.F., Hagemann, M., Paulsen, I. and Partensky, F., 2009. Ecological genomics of marine picocyanobacteria. *Microbiology and Molecular Biology Reviews*, *73*(2), pp.249-299.

[63] Sánchez-Baracaldo, P., Ridgwell, A. and Raven, J.A., 2014. A neoproterozoic transition in the marine nitrogen cycle. *Current Biology*, *24*(6), pp.652-657.

[64] Sánchez-Baracaldo, P., 2015. Origin of marine planktonic cyanobacteria. *Scientific reports*, *5*, p.17418.

[65] Flombaum, P., Gallegos, J.L., Gordillo, R.A., Rincón, J., Zabala, L.L., Jiao, N., Karl, D.M., Li, W.K., Lomas, M.W., Veneziano, D. and Vera, C.S., 2013. Present and future global distributions of the marine Cyanobacteria Prochlorococcus and Synechococcus. *Proceedings of the National Academy of Sciences*, *110*(24), pp.9824-9829.

[66] Braakman, R., Follows, M.J. and Chisholm, S.W., 2017. Metabolic evolution and the self-organization of ecosystems. *Proceedings of the National Academy of Sciences*, 114(14), E3091-E3100

[67] Valentine, J.W. and Moores, E.M., 1970. Plate-tectonic regulation of faunal diversity and sea level: a model. *Nature*, *228*(5272), p.657.

[68] Li, Z.X., Bogdanova, S.V., Collins, A.S., Davidson, A., De Waele, B., Ernst, R.E., Fitzsimons, I.C.W., Fuck, R.A., Gladkochub, D.P., Jacobs, J. and Karlstrom, K.E., 2008. Assembly, configuration, and break-up history of Rodinia: a synthesis. *Precambrian research*, *160*(1-2), pp.179-210.

[69] Bradley, D.C., 2011. Secular trends in the geologic record and the supercontinent cycle. *Earth-Science Reviews*, *108*(1-2), pp.16-33.

[70] Liu, C., Knoll, A.H. and Hazen, R.M., 2017. Geochemical and mineralogical evidence that Rodinian assembly was unique. *Nature communications*, *8*(1), p.1950.

[71] De Roever, W.P., 1956. Some differences between post-Paleozoic and older regional metamorphism. *Geologie en Mijnbouw*, *18*, pp.123-127.

[72] Ernst, W.G., 1972. Occurrence and mineralogic evolution of blueschist belts with time. *American Journal of Science*, *272*(7), pp.657-668.

[73] Maruyama, S., Liou, J.G. and Terabayashi, M., 1996. Blueschists and eclogites of the world and their exhumation. *International geology review*, *38*(6), pp.485-594.

[74] Brown, M., 2007. Metamorphic conditions in orogenic belts: a record of secular change. *International Geology Review*, *49*(3), pp.193-234.

[75] Korenaga, J., 2013. Initiation and evolution of plate tectonics on Earth: theories and observations. *Annual Review of Earth and Planetary Sciences*, *41*, pp.117-151.

[76] Stern, R.J., Leybourne, M.I. and Tsujimori, T., 2016. Kimberlites and the start of plate tectonics. *Geology*, *44*(10), pp.799-802.

[77] Brown, M. and Johnson, T., 2018. Secular change in metamorphism and the onset of global plate tectonics. *American Mineralogist*, *103*(2), pp.181-196.

[78] Ronov, A.B., Khain, V.E., Balukhovsky, A.N. and Seslavinsky, K.B., 1980. Quantitative analysis of Phanerozoic sedimentation. *Sedimentary Geology*, *25*(4), pp.311-325.

[79] Hallam, A., 1992. *Phanerozoic sea-level changes*. Columbia University Press.

[80] Peters, S.E. and Gaines, R.R., 2012. Formation of the 'Great Unconformity' as a trigger for the Cambrian explosion. *Nature*, *484*(7394), p.363.

[81] Rothman, D.H., Hayes, J.M. and Summons, R.E., 2003. Dynamics of the Neoproterozoic carbon cycle. *Proceedings of the National Academy of Sciences*, *100*(14), pp.8124-8129.

[82] Grotzinger, J.P., Fike, D.A. and Fischer, W.W., 2011. Enigmatic origin of the largest-known carbon isotope excursion in Earth's history. *Nature Geoscience*, *4*(5), p.285.

[83] Kirschvink, J.L., 1992. Late Proterozoic low-latitude global glaciation: the snowball Earth. The Proterozoic Biosphere: A Multidisciplinary Study, eds Schopf JW, Klein C, Des Marais D (Cambridge Univ Press, Cambridge, UK), pp 51–52.

[84] Hoffman, P.F., Kaufman, A.J., Halverson, G.P. and Schrag, D.P., 1998. A Neoproterozoic snowball earth. *science*, *281*(5381), pp.1342-1346.

[85] Pierrehumbert, R.T., Abbot, D.S., Voigt, A. and Koll, D., 2011. Climate of the Neoproterozoic. *Annual Review of Earth and Planetary Sciences*, *39*, pp.417-460.

[86] Hoffman, P.F., Abbot, D.S., Ashkenazy, Y., Benn, D.I., Brocks, J.J., Cohen, P.A., Cox, G.M., Creveling, J.R., Donnadieu, Y., Erwin, D.H. and Fairchild, I.J., 2017. Snowball Earth climate dynamics and Cryogenian geology-geobiology. *Science Advances*, *3*(11), p.e1600983.

[87] Slotznick, S.P., Webb, S.M., Kirschvink, J.L. and Fischer, W.W., 2019. Mid-Proterozoic ferruginous conditions reflect post-depositional processes. *Geophysical Research Letters*, 46. https://doi.org/10.1029/2018GL081496

[88] Canfield, D.E., 1998. A new model for Proterozoic ocean chemistry. *Nature*, *396*(6710), p.450.

[89] Canfield, D.E., Poulton, S.W., Knoll, A.H., Narbonne, G.M., Ross, G., Goldberg, T. and Strauss, H., 2008. Ferruginous conditions dominated later Neoproterozoic deep-water chemistry. *Science*, *321*(5891), pp.949-952.

[90] Planavsky, N.J., McGoldrick, P., Scott, C.T., Li, C., Reinhard, C.T., Kelly, A.E., Chu, X., Bekker, A., Love, G.D. and Lyons, T.W., 2011. Widespread iron-rich conditions in the mid-Proterozoic ocean. *Nature*, *477*(7365), p.448.

[91] Li, C., Love, G.D., Lyons, T.W., Fike, D.A., Sessions, A.L. and Chu, X., 2010. A stratified redox model for the Ediacaran ocean. *Science*, *328*(5974), pp.80-83.

[92] Sperling, E.A., Wolock, C.J., Morgan, A.S., Gill, B.C., Kunzmann, M., Halverson, G.P., Macdonald, F.A., Knoll, A.H. and Johnston, D.T., 2015. Statistical analysis of iron geochemical data suggests limited late Proterozoic oxygenation. *Nature*, *523*(7561), p.451.

[93] Lu, W., Ridgwell, A., Thomas, E., Hardisty, D.S., Luo, G., Algeo, T.J., Saltzman, M.R., Gill, B.C., Shen, Y., Ling, H.F. and Edwards, C.T., 2018. Late inception of a resiliently oxygenated upper ocean. *Science*, p.eaar5372.

[94] Scott, C., Lyons, T.W., Bekker, A., Shen, Y.A., Poulton, S.W., Chu, X.L. and Anbar, A.D., 2008. Tracing the stepwise oxygenation of the Proterozoic ocean. *Nature*, *452*(7186), p.456.

[95] Chen, X., Ling, H.F., Vance, D., Shields-Zhou, G.A., Zhu, M., Poulton, S.W., Och, L.M., Jiang, S.Y., Li, D., Cremonese, L. and Archer, C., 2015. Rise to modern levels of ocean oxygenation coincided with the Cambrian radiation of animals. *Nature communications*, *6*, p.7142.

[96] Kunzmann, M., Bui, T.H., Crockford, P.W., Halverson, G.P., Scott, C., Lyons, T.W. and Wing, B.A., 2017. Bacterial sulfur disproportionation constrains timing of Neoproterozoic oxygenation. *Geology*, *45*(3), pp.207-210.

[97] Fennel, K., Follows, M. and Falkowski, P.G., 2005. The co-evolution of the nitrogen, carbon and oxygen cycles in the Proterozoic ocean. *American Journal of Science*, *305*(6-8), pp.526-545.

[98] Zegeye, A., Bonneville, S., Benning, L.G., Sturm, A., Fowle, D.A., Jones, C., Canfield, D.E., Ruby, C., MacLean, L.C., Nomosatryo, S. and Crowe, S.A., 2012. Green rust formation controls nutrient availability in a ferruginous water column. *Geology*, *40*(7), pp.599-602.

[99] Laakso, T.A. and Schrag, D.P., 2014. Regulation of atmospheric oxygen during the Proterozoic. *Earth and Planetary Science Letters*, *388*, pp.81-91.

[100] Derry, L.A., 2015. Causes and consequences of mid-Proterozoic anoxia. *Geophysical Research Letters*, *42*(20), pp.8538-8546.

[101] Reinhard, C.T., Planavsky, N.J., Gill, B.C., Ozaki, K., Robbins, L.J., Lyons, T.W., Fischer, W.W., Wang, C., Cole, D.B. and Konhauser, K.O., 2017. Evolution of the global phosphorus cycle. *Nature*, *541*(7637), p.386.

[102] Kipp, M.A. and Stüeken, E.E., 2017. Biomass recycling and Earth's early phosphorus cycle. *Science advances*, *3*(11), p.eaao4795.

[103] Jones, C., Nomosatryo, S., Crowe, S.A., Bjerrum, C.J. and Canfield, D.E., 2015. Iron oxides, divalent cations, silica, and the early earth phosphorus crisis. *Geology*, *43*(2), pp.135-138.

[104] Large, R.R., Halpin, J.A., Danyushevsky, L.V., Maslennikov, V.V., Bull, S.W., Long, J.A., Gregory, D.D., Lounejeva, E., Lyons, T.W., Sack, P.J. and McGoldrick, P.J., 2014. Trace element content of sedimentary pyrite as a new proxy for deep-time ocean–atmosphere evolution. *Earth and Planetary Science Letters*, *389*, pp.209-220.

[105] Stüeken, E.E., 2013. A test of the nitrogen-limitation hypothesis for retarded eukaryote radiation: nitrogen isotopes across a Mesoproterozoic basinal profile. *Geochimica et Cosmochimica Acta*, *120*, pp.121-139.

[106] Kikumoto, R., Tahata, M., Nishizawa, M., Sawaki, Y., Maruyama, S., Shu, D., Han, J., Komiya, T., Takai, K. and Ueno, Y., 2014. Nitrogen isotope chemostratigraphy of the Ediacaran and Early Cambrian platform sequence at Three Gorges, South China. *Gondwana Research*, *25*(3), pp.1057-1069.

[107] Ader, M., Sansjofre, P., Halverson, G.P., Busigny, V., Trindade, R.I., Kunzmann, M. and Nogueira, A.C., 2014. Ocean redox structure across the Late Neoproterozoic Oxygenation Event: A nitrogen isotope perspective. *Earth and Planetary Science Letters*, *396*, pp.1-13.

[108] Wang, W., Guan, C., Zhou, C., Peng, Y., Pratt, L.M., Chen, X., Chen, L., Chen, Z., Yuan, X. and Xiao, S., 2017. Integrated carbon, sulfur, and nitrogen isotope chemostratigraphy of the Ediacaran Lantian Formation in South China: Spatial gradient, ocean redox oscillation, and fossil distribution. *Geobiology*, *15*(4), pp.552-571.

[109] Koehler, M.C., Stüeken, E.E., Kipp, M.A., Buick, R. and Knoll, A.H., 2017. Spatial and temporal trends in Precambrian nitrogen cycling: A Mesoproterozoic offshore nitrate minimum. *Geochimica et Cosmochimica Acta*, *198*, pp.315-337.

[110] Johnson, B.W., Poulton, S.W. and Goldblatt, C., 2017. Marine oxygen production and open water supported an active nitrogen cycle during the Marinoan Snowball Earth. *Nature Communications*, *8*(1), p.1316.

[111] Wang, X., Jiang, G., Shi, X., Peng, Y. and Morales, D., 2018. Nitrogen isotope constraints on the early Ediacaran ocean redox structure. *Geochimica et Cosmochimica Acta.*

[112] Laakso, T.A. and Schrag, D.P., 2017. A theory of atmospheric oxygen. *Geobiology*, *15*(3), pp.366-384.

[113] Raven, J.A., Evans, M.C. and Korb, R.E., 1999. The role of trace metals in photosynthetic electron transport in O2-evolving organisms. *Photosynthesis research*, *60*(2-3), pp.111-150.

[114] Kuma, K., Nishioka, J. and Matsunaga, K., 1996. Controls on iron (III) hydroxide solubility in seawater: the influence of pH and natural organic chelators. *Limnology and Oceanography*, *41*(3), pp.396-407.

[115] Jolivet, J.P., Chanéac, C. and Tronc, E., 2004. Iron oxide chemistry. From molecular clusters to extended solid networks. *Chemical Communications*, (5), pp.481-483.

[116] Saito, M.A., Sigman, D.M. and Morel, F.M., 2003. The bioinorganic chemistry of the ancient ocean: the co-evolution of cyanobacterial metal requirements and biogeochemical cycles at the Archean–Proterozoic boundary?. *Inorganica Chimica Acta*, *356*, pp.308-318.

[117] Falkowski, P.G., 1997. Evolution of the nitrogen cycle and its influence on the biological sequestration of CO2 in the ocean. *Nature*, *387*(6630), p.272.

[118] Dupont, C.L., Butcher, A., Valas, R.E., Bourne, P.E. and Caetano-Anollés, G., 2010. History of biological metal utilization inferred through phylogenomic analysis of protein structures. *Proceedings of the National Academy of Sciences*, *107*(23), pp.10567-10572.

[119] Jelen, B.I., Giovannelli, D. and Falkowski, P.G., 2016. The role of microbial electron transfer in the coevolution of the biosphere and geosphere. *Annual review of microbiology*, *70*.

[120] Rue, E.L. and Bruland, K.W., 1995. Complexation of iron (III) by natural organic ligands in the Central North Pacific as determined by a new competitive ligand equilibration/adsorptive cathodic stripping voltammetric method. *Marine chemistry*, *50*(1-4), pp.117-138.

[121] Gledhill, M. and Buck, K.N., 2012. The organic complexation of iron in the marine environment: a review. *Frontiers in microbiology*, *3*, p.69.

[122] Hassler, C.S., Schoemann, V., Nichols, C.M., Butler, E.C. and Boyd, P.W., 2011. Saccharides enhance iron bioavailability to Southern Ocean phytoplankton. *Proceedings of the National Academy of Sciences*, *108*(3), pp.1076-1081.

[123] Roe, K.L. and Barbeau, K.A., 2014. Uptake mechanisms for inorganic iron and ferric citrate in Trichodesmium erythraeum IMS101. *Metallomics*, *6*(11), pp.2042-2051.

[124] Biller, S.J., Berube, P.M., Lindell, D. and Chisholm, S.W., 2015. Prochlorococcus: the structure and function of collective diversity. *Nature Reviews Microbiology*, *13*(1), p.13.

[125] Ralf, G. and Repeta, D.J., 1992. The pigments of Prochlorococcus marinus: The presence of divinylchlorophyll a and b in a marine procaryote. *Limnology and Oceanography*, *37*(2), pp.425-433.

[126] Bibby, T.S., Nield, J., Partensky, F. and Barber, J., 2001. Oxyphotobacteria: Antenna ring around photosystem I. *Nature*, *413*(6856), p.590.

[127] Bibby, T.S., Mary, I., Nield, J., Partensky, F. and Barber, J., 2003. Low-light-adapted Prochlorococcus species possess specific antennae for each photosystem. *Nature*, *424*(6952), p.1051.

[128] Bailey, S., Melis, A., Mackey, K.R., Cardol, P., Finazzi, G., van Dijken, G., Berg, G.M., Arrigo, K., Shrager, J. and Grossman, A., 2008. Alternative photosynthetic electron flow to oxygen in marine Synechococcus. *Biochimica et Biophysica Acta (BBA)-Bioenergetics*, *1777*(3), pp.269-276.

[129] Zorz, J.K., Allanach, J.R., Murphy, C.D., Roodvoets, M.S., Campbell, D.A. and Cockshutt, A.M., 2015. The RUBISCO to photosystem II ratio limits the maximum photosynthetic rate in picocyanobacteria. *Life*, *5*(1), pp.403-417.

[130] Zinser, E.R., Lindell, D., Johnson, Z.I., Futschik, M.E., Steglich, C., Coleman, M.L., Wright, M.A., Rector, T., Steen, R., McNulty, N. and Thompson, L.R., 2009. Choreography of the transcriptome, photophysiology, and cell cycle of a minimal photoautotroph, Prochlorococcus. *PloS one*, *4*(4), p.e5135.

[131] Bertlisson, S., Berglund, O., Pullin, M.J. and Chisholm, S.W., 2005. Release of dissolved organic matter by Prochlorococcus. *Vie et Milieu*, *55*(3-4), pp.225-232.

[132] Biddanda, B. and Benner, R., 1997. Carbon, nitrogen, and carbohydrate fluxes during the production of particulate and dissolved organic matter by marine phytoplankton. *Limnology and Oceanography*, *42*(3), pp.506-518.

[133] Deng, W., Cruz, B.N. and Neuer, S., 2016. Effects of nutrient limitation on cell growth, TEP production and aggregate formation of marine Synechococcus. *Aquatic Microbial Ecology*, *78*(1), pp.39-49.

[134 Iuculano, F., Mazuecos, I.P., Reche, I. and Agustí, S., 2017. Prochlorococcus as a possible source for transparent exopolymer particles (TEP). *Frontiers in microbiology*, *8*, p.709.

[135] Tripp, H.J., Kitner, J.B., Schwalbach, M.S., Dacey, J.W., Wilhelm, L.J. and Giovannoni, S.J., 2008. SAR11 marine bacteria require exogenous reduced sulphur for growth. *Nature*, *452*(7188), p.741.

[136] Carini, P., Steindler, L., Beszteri, S. and Giovannoni, S.J., 2013. Nutrient requirements for growth of the extreme oligotroph ‘Candidatus Pelagibacter ubique’HTCC1062 on a defined medium. *The ISME journal*, *7*(3), p.592.

[137] Frank, S.A., 1998. *Foundations of social evolution*. Princeton University Press.

[138] West, S.A., Griffin, A.S., Gardner, A. and Diggle, S.P., 2006. Social evolution theory for microorganisms. *Nature Reviews Microbiology*, *4*(8), p.597.

[139] Rankin, D.J., Bargum, K. and Kokko, H., 2007. The tragedy of the commons in evolutionary biology. *Trends in ecology & evolution*, *22*(12), pp.643-651.

[140] Kashtan, N., Roggensack, S.E., Rodrigue, S., Thompson, J.W., Biller, S.J., Coe, A., Ding, H., Marttinen, P., Malmstrom, R.R., Stocker, R. and Follows, M.J., 2014. Single-cell genomics reveals hundreds of coexisting subpopulations in wild Prochlorococcus. *Science*, *344*(6182), pp.416-420.

[141] Angulo-Brown, F., Santillán, M. and Calleja-Quevedo, E., 1995. Thermodynamic optimality in some biochemical reactions. *Il Nuovo Cimento D*, *17*(1), pp.87-90.

[142] Waddell, T.G., Repovic, P., Meléndez-Hevia, E., Heinrich, R. and Montero, F., 1999. Optimization of glycolysis: new discussions. *Biochemical education*, *27*(1), pp.12-13.

[143] Pfeiffer, T., Schuster, S. and Bonhoeffer, S., 2001. Cooperation and competition in the evolution of ATP-producing pathways. *Science*, *292*(5516), pp.504-507.

[144] Molenaar, D., Van Berlo, R., De Ridder, D. and Teusink, B., 2009. Shifts in growth strategies reflect tradeoffs in cellular economics. *Molecular systems biology*, *5*(1), p.323.

[145] Flamholz, A., Noor, E., Bar-Even, A., Liebermeister, W. and Milo, R., 2013. Glycolytic strategy as a tradeoff between energy yield and protein cost. *Proceedings of the National Academy of Sciences*, p.201215283.

[146] Basan, M., Hui, S., Okano, H., Zhang, Z., Shen, Y., Williamson, J.R. and Hwa, T., 2015. Overflow metabolism in Escherichia coli results from efficient proteome allocation. *Nature*, *528*(7580), p.99.

[147] Moore, L.R., Goericke, R. and Chisholm, S.W., 1995. Comparative physiology of Synechococcus and Prochlorococcus: influence of light and temperature on growth, pigments, fluorescence and absorptive properties. *Marine Ecology Progress Series*, pp.259-275.

[148] Kettler, G.C., Martiny, A.C., Huang, K., Zucker, J., Coleman, M.L., Rodrigue, S., Chen, F., Lapidus, A., Ferriera, S., Johnson, J. and Steglich, C., 2007. Patterns and implications of gene gain and loss in the evolution of Prochlorococcus. *PLoS genetics*, *3*(12), p.e231.

[149] Partensky, F. and Garczarek, L., 2009. Prochlorococcus: advantages and limits of minimalism. *Annual Review of Marine Science*, *2*, pp.305-331

[150] Di Cesare, A., Cabello-Yeves, P.J., Chrismas, N.A., Sánchez-Baracaldo, P., Salcher, M.M. and Callieri, C., 2018. Genome analysis of the freshwater planktonic Vulcanococcus limneticus sp. nov. reveals horizontal transfer of nitrogenase operon and alternative pathways of nitrogen utilization. *BMC genomics*, *19*(1), p.259.

[151] Neijssel, O.M. and Tempest, D.W., 1975. The regulation of carbohydrate metabolism in Klebsiella aerogenes NCTC 418 organisms, growing in chemostat culture. *Archives of Microbiology*, *106*(3), pp.251-258.

[152] Russell, J.B. and Cook, G.M., 1995. Energetics of bacterial growth: balance of anabolic and catabolic reactions. *Microbiological reviews*, *59*(1), pp.48-62.

[153] Dauner, M., Storni, T. and Sauer, U., 2001. Bacillus subtilis metabolism and energetics in carbon-limited and excess-carbon chemostat culture. *Journal of bacteriology*, *183*(24), pp.7308-7317.

[154] Vemuri, G.N., Eiteman, M.A., McEwen, J.E., Olsson, L. and Nielsen, J., 2007. Increasing NADH oxidation reduces overflow metabolism in Saccharomyces cerevisiae. *Proceedings of the National Academy of Sciences*, *104*(7), pp.2402-2407.

[155] Szul, M.J., Dearth, S.P., Campagna, S.R. and Zinser, E.R., 2019. Carbon Fate and Flux in Prochlorococcus under Nitrogen Limitation. *mSystems*, *4*(1), pp.e00254-18.

[156] Falkowski, P.G. and LaRoche, J., 1991. Acclimation to spectral irradiance in algae. *Journal of Phycology*, *27*(1), pp.8-14.

[157] Walters, R.G., 2005. Towards an understanding of photosynthetic acclimation. *Journal of experimental botany*, *56*(411), pp.435-447.

[158] Bailey, S., Mann, N.H., Robinson, C. and Scanlan, D.J., 2005. The occurrence of rapidly reversible non-photochemical quenching of chlorophyll a fluorescence in cyanobacteria. *FEBS letters*, *579*(1), pp.275-280.

[159] Kulk, G., van de Poll, W.H., Visser, R.J. and Buma, A.G., 2011. Distinct differences in photoacclimation potential between prokaryotic and eukaryotic oceanic phytoplankton. *Journal of Experimental Marine Biology and Ecology*, *398*(1-2), pp.63-72.

[160] Moore, L.R., Rocap, G. and Chisholm, S.W., 1998. Physiology and molecular phylogeny of coexisting Prochlorococcus ecotypes. *Nature*, *393*(6684), p.464.

[161] West, N.J. and Scanlan, D.J., 1999. Niche-partitioning of Prochlorococcuspopulations in a stratified water column in the eastern North Atlantic Ocean. *Applied and environmental microbiology*, *65*(6), pp.2585-2591.

[162] Johnson, Z.I., Zinser, E.R., Coe, A., McNulty, N.P., Woodward, E.M.S. and Chisholm, S.W., 2006. Niche partitioning among Prochlorococcus ecotypes along ocean-scale environmental gradients. *Science*, *311*(5768), pp.1737-1740.

[163] Bouman, H.A., Ulloa, O., Scanlan, D.J., Zwirglmaier, K., Li, W.K., Platt, T., Stuart, V., Barlow, R., Leth, O., Clementson, L. and Lutz, V., 2006. Oceanographic basis of the global surface distribution of Prochlorococcus ecotypes. *Science*, *312*(5775), pp.918-921.

[164] Malmstrom, R.R., Coe, A., Kettler, G.C., Martiny, A.C., Frias-Lopez, J., Zinser, E.R. and Chisholm, S.W., 2010. Temporal dynamics of Prochlorococcus ecotypes in the Atlantic and Pacific oceans. *The ISME journal*, *4*(10), p.1252.

[165] Morel, A., Ahn, Y.H., Partensky, F., Vaulot, D. and Claustre, H., 1993. Prochlorococcus and Synechococcus: a comparative study of their optical properties in relation to their size and pigmentation. *Journal of Marine Research*, *51*(3), pp.617-649.

[166] Lynch, M. and Conery, J.S., 2003. The origins of genome complexity. *science*, *302*(5649), pp.1401-1404.

[167] Giovannoni, S.J., Tripp, H.J., Givan, S., Podar, M., Vergin, K.L., Baptista, D., Bibbs, L., Eads, J., Richardson, T.H., Noordewier, M. and Rappé, M.S., 2005. Genome streamlining in a cosmopolitan oceanic bacterium. *science*, *309*(5738), pp.1242-1245.

[168] Giovannoni, S.J., Thrash, J.C. and Temperton, B., 2014. Implications of streamlining theory for microbial ecology. *The ISME journal*, *8*(8), p.1553.

[169] Moore, C.M., Mills, M.M., Arrigo, K.R., Berman-Frank, I., Bopp, L., Boyd, P.W., Galbraith, E.D., Geider, R.J., Guieu, C., Jaccard, S.L. and Jickells, T.D., 2013. Processes and patterns of oceanic nutrient limitation. *Nature Geoscience*, *6*(9), p.701.

[170] Dufresne, A., Garczarek, L. and Partensky, F., 2005. Accelerated evolution associated with genome reduction in a free-living prokaryote. *Genome biology*, *6*(2), p.R14.

[171] Grzymski, J.J. and Dussaq, A.M., 2012. The significance of nitrogen cost minimization in proteomes of marine microorganisms. *The ISME journal*, *6*(1), p.71.

[172] Van Mooy, B.A., Rocap, G., Fredricks, H.F., Evans, C.T. and Devol, A.H., 2006. Sulfolipids dramatically decrease phosphorus demand by picocyanobacteria in oligotrophic marine environments. *Proceedings of the National Academy of Sciences*, *103*(23), pp.8607-8612.

[173] Van Mooy, B.A., Fredricks, H.F., Pedler, B.E., Dyhrman, S.T., Karl, D.M., Koblížek, M., Lomas, M.W., Mincer, T.J., Moore, L.R., Moutin, T. and Rappé, M.S., 2009. Phytoplankton in the ocean use non-phosphorus lipids in response to phosphorus scarcity. *Nature*, *458*(7234), p.69.

[174] Button, D.K., 1991. Biochemical basis for whole-cell uptake kinetics: specific affinity, oligotrophic capacity, and the meaning of the Michaelis constant. *Applied and Environmental Microbiology*, *57*(7), pp.2033-2038.

[175] Duff, S.M., Moorhead, G.B., Lefebvre, D.D. and Plaxton, W.C., 1989. Phosphate starvation inducible bypasses' of adenylate and phosphate dependent glycolytic enzymes in Brassica nigra suspension cells. *Plant Physiology*, *90*(4), pp.1275-1278.

[176] Theodorou, M.E., Elrifi, I.R., Turpin, D.H. and Plaxton, W.C., 1991. Effects of phosphorus limitation on respiratory metabolism in the green alga Selenastrum minutum. *Plant Physiology*, *95*(4), pp.1089-1095.

[177] Bulthuis, B.A., Koningstein, G.M., Stouthamer, A.H. and van Verseveld, H.W., 1993. The relation of proton motive force, adenylate energy charge and phosphorylation potential to the specific growth rate and efficiency of energy transduction in Bacillus licheniformis under aerobic growth conditions. *Antonie Van Leeuwenhoek*, *63*(1), pp.1-16.

[178] Gauthier, D.A. and Turpin, D.H., 1994. Inorganic phosphate (Pi) enhancement of dark respiration in the Pi-limited green alga Selenastrum minutum (interactions between H+/Pi cotransport, the plasmalemma H+-ATPase, and dark respiratory carbon flow). *Plant physiology*, *104*(2), pp.629-637.

[179] Neijssel, O.M. and Tempest, D.W., 1976. The role of energy-spilling reactions in the growth of Klebsiella aerogenes NCTC 418 in aerobic chemostat culture. *Archives of microbiology*, *110*(2-3), pp.305-311.

[180] Vander Heiden, M.G., Cantley, L.C. and Thompson, C.B., 2009. Understanding the Warburg effect: the metabolic requirements of cell proliferation. *science*, *324*(5930), pp.1029-1033.

[181] Fogg, G.E., 1983. The ecological significance of extracellular products of phytoplankton photosynthesis. *Botanica marina*, *26*(1), pp.3-14.

[182] Myklestad, S.M., 1995. Release of extracellular products by phytoplankton with special emphasis on polysaccharides. *Science of the total Environment*, *165*(1-3), pp.155-164.

[183] Alcoverro, T., Conte, E. and Mazzella, L., 2000. Production of mucilage by the Adriatic epipelic diatom Cylindrotheca closterium (Bacillariophyceae) under nutrient limitation. *Journal of Phycology*, *36*(6), pp.1087-1095.

[184] Staats, N., Stal, L.J. and Mur, L.R., 2000. Exopolysaccharide production by the epipelic diatom Cylindrotheca closterium: effects of nutrient conditions. *Journal of Experimental Marine Biology and Ecology*, *249*(1), pp.13-27.

[185] Wetz, M.S. and Wheeler, P.A., 2007. Release of dissolved organic matter by coastal diatoms. *Limnology and Oceanography*, *52*(2), pp.798-807.

[186] Beard, D.A. and Qian, H., 2007. Relationship between thermodynamic driving force and one-way fluxes in reversible processes. *PloS one*, *2*(1), p.e144.

[187] Hansell, D.A., Carlson, C.A., Repeta, D.J. and Schlitzer, R., 2009. Dissolved organic matter in the ocean: A controversy stimulates new insights. *Oceanography*, *22*(4), pp.202-211.

[188] Berube, P.M., Rasmussen, A., Braakman, R., Stepanauskas, R. and Chisholm, S.W., 2018. Emergence of trait variability through the lens of nitrogen assimilation in Prochlorococcus. *bioRxiv*, p.383927.

[189] Berube, P.M., Coe, A., Roggensack, S.E. and Chisholm, S.W., 2016. Temporal dynamics of Prochlorococcus cells with the potential for nitrate assimilation in the subtropical Atlantic and Pacific oceans. *Limnology and Oceanography*, *61*(2), pp.482-495.

[190] Sunda, W.G. and Huntsman, S.A., 1997. Interrelated influence of iron, light and cell size on marine phytoplankton growth. *Nature*, *390*(6658), p.389.

[191] Strzepek, R.F. and Harrison, P.J., 2004. Photosynthetic architecture differs in coastal and oceanic diatoms. *Nature*, *431*(7009), p.689.

[192] Cardol, P., Bailleul, B., Rappaport, F., Derelle, E., Béal, D., Breyton, C., Bailey, S., Wollman, F.A., Grossman, A., Moreau, H. and Finazzi, G., 2008. An original adaptation of photosynthesis in the marine green alga Ostreococcus. *Proceedings of the National Academy of Sciences*, *105*(22), pp.7881-7886.

[193] Banfield, J.F., Barker, W.W., Welch, S.A. and Taunton, A., 1999. Biological impact on mineral dissolution: application of the lichen model to understanding mineral weathering in the rhizosphere. *Proceedings of the National Academy of Sciences*, *96*(7), pp.3404-3411.

[194] Uroz, S., Calvaruso, C., Turpault, M.P. and Frey-Klett, P., 2009. Mineral weathering by bacteria: ecology, actors and mechanisms. *Trends in microbiology*, *17*(8), pp.378-387.

[195] Jickells, T.D., An, Z.S., Andersen, K.K., Baker, A.R., Bergametti, G., Brooks, N., Cao, J.J., Boyd, P.W., Duce, R.A., Hunter, K.A. and Kawahata, H., 2005. Global iron connections between desert dust, ocean biogeochemistry, and climate. *science*, *308*(5718), pp.67-71.

[196] Benitez-Nelson, C.R., 2000. The biogeochemical cycling of phosphorus in marine systems. *Earth-Science Reviews*, *51*(1-4), pp.109-135.

[197] Ridame, C. and Guieu, C., 2002. Saharan input of phosphate to the oligotrophic water of the open western Mediterranean Sea. *Limnology and Oceanography*, *47*(3), pp.856-869.

[198] Romano, S., Bondarev, V., Kölling, M., Dittmar, T. and Schulz-Vogt, H.N., 2017. Phosphate limitation triggers the dissolution of precipitated iron by the marine bacterium Pseudovibrio sp. FO-BEG1. *Frontiers in microbiology*, *8*, p.364.

[199] Tyrrell, T., 1999. The relative influences of nitrogen and phosphorus on oceanic primary production. *Nature*, *400*(6744), p.525.

[200] Vitousek, P.M., Cassman, K.E.N., Cleveland, C., Crews, T., Field, C.B., Grimm, N.B., Howarth, R.W., Marino, R., Martinelli, L., Rastetter, E.B. and Sprent, J.I., 2002. Towards an ecological understanding of biological nitrogen fixation. In *The Nitrogen Cycle at Regional to Global Scales* (pp. 1-45). Springer, Dordrecht.

[201] Mills, M.M., Ridame, C., Davey, M., La Roche, J. and Geider, R.J., 2004. Iron and phosphorus co-limit nitrogen fixation in the eastern tropical North Atlantic. *Nature*, *429*(6989), p.292.

[202] Wang, W.L., Moore, J.K., Martiny, A.C. and Primeau, F.W., 2019. Convergent estimates of marine nitrogen fixation. *Nature*, *566*(7743), p.205.

[203] Petitjean, C., Moreira, D., López-García, P. and Brochier-Armanet, C., 2012. Horizontal gene transfer of a chloroplast DnaJ-Fer protein to Thaumarchaeota and the evolutionary history of the DnaK chaperone system in Archaea. *BMC evolutionary biology*, *12*(1), p.226.

[204] Gubry-Rangin, C., Kratsch, C., Williams, T.A., McHardy, A.C., Embley, T.M., Prosser, J.I. and Macqueen, D.J., 2015. Coupling of diversification and pH adaptation during the evolution of terrestrial Thaumarchaeota. *Proceedings of the National Academy of Sciences*, *112*(30), pp.9370-9375.

[205] Morris, R.M., Rappé, M.S., Connon, S.A., Vergin, K.L., Siebold, W.A., Carlson, C.A. and Giovannoni, S.J., 2002. SAR11 clade dominates ocean surface bacterioplankton communities. *Nature*, *420*(6917), p.806.

[206] Luo, H., Csűros, M., Hughes, A.L. and Moran, M.A., 2013. Evolution of divergent life history strategies in marine alphaproteobacteria. *MBio*, *4*(4), pp.e00373-13.

[207] Schwalbach, M.S., Tripp, H.J., Steindler, L., Smith, D.P. and Giovannoni, S.J., 2010. The presence of the glycolysis operon in SAR11 genomes is positively correlated with ocean productivity. *Environmental microbiology*, *12*(2), pp.490-500.

[208] Partensky, F., La Roche, J., Wyman, K. and Falkowski, P.G., 1997. The divinyl-chlorophyll a/b-protein complexes of two strains of the oxyphototrophic marine prokaryote Prochlorococcus–characterization and response to changes in growth irradiance. *Photosynthesis research*, *51*(3), pp.209-222.

[209] Melis, A. and Brown, J.S., 1980. Stoichiometry of system I and system II reaction centers and of plastoquinone in different photosynthetic membranes. *Proceedings of the National Academy of Sciences*, *77*(8), pp.4712-4716.

[210] McDonald, A.E. and Vanlerberghe, G.C., 2005. Alternative oxidase and plastoquinol terminal oxidase in marine prokaryotes of the Sargasso Sea. *Gene*, *349*, pp.15-24.

[211] Noctor, G., De Paepe, R. and Foyer, C.H., 2007. Mitochondrial redox biology and homeostasis in plants. *Trends in plant science*, *12*(3), pp.125-134.

[212] Morris, J.J., Kirkegaard, R., Szul, M.J., Johnson, Z.I. and Zinser, E.R., 2008. Facilitation of robust growth of Prochlorococcus colonies and dilute liquid cultures by "helper" heterotrophic bacteria. *Applied and environmental microbiology*, *74*(14), pp.4530-4534.

[213] Morris, J.J., Johnson, Z.I., Szul, M.J., Keller, M. and Zinser, E.R., 2011. Dependence of the cyanobacterium Prochlorococcus on hydrogen peroxide scavenging microbes for growth at the ocean's surface. *PloS one*, *6*(2), p.e16805.

[214] Butterfield, N.J., Knoll, A.H. and Swett, K., 1988. Exceptional preservation of fossils in an Upper Proterozoic shale. *Nature*, *334*(6181), p.424.

[215] Douzery, E.J., Snell, E.A., Bapteste, E., Delsuc, F. and Philippe, H., 2004. The timing of eukaryotic evolution: does a relaxed molecular clock reconcile proteins and fossils?. *Proceedings of the National Academy of Sciences*, *101*(43), pp.15386-15391.

[216] Yoon, H.S., Hackett, J.D., Ciniglia, C., Pinto, G. and Bhattacharya, D., 2004. A molecular timeline for the origin of photosynthetic eukaryotes. *Molecular biology and evolution*, *21*(5), pp.809-818.

[217] Parfrey, L.W., Lahr, D.J., Knoll, A.H. and Katz, L.A., 2011. Estimating the timing of early eukaryotic diversification with multigene molecular clocks. *Proceedings of the National Academy of Sciences*, *108*(33), pp.13624-13629.

[218] Ryan, P.R., Delhaize, E. and Jones, D.L., 2001. Function and mechanism of organic anion exudation from plant roots. *Annual review of plant biology*, *52*(1), pp.527-560.

[219] Dakora, F.D. and Phillips, D.A., 2002. Root exudates as mediators of mineral acquisition in low-nutrient environments. In *Food Security in Nutrient-Stressed Environments: Exploiting Plants' Genetic Capabilities* (pp. 201-213). Springer, Dordrecht.

[220] Soltis, D.E., Soltis, P.S., Morgan, D.R., Swensen, S.M., Mullin, B.C., Dowd, J.M. and Martin, P.G., 1995. Chloroplast gene sequence data suggest a single origin of the predisposition for symbiotic nitrogen fixation in angiosperms. *Proceedings of the National Academy of Sciences*, *92*(7), pp.2647-2651.

[221] Gruber, N. and Galloway, J.N., 2008. An Earth-system perspective of the global nitrogen cycle. *Nature*, *451*(7176), p.293.

[222] Allen, J.F., Thake, B. and Martin, W.F., 2018. Nitrogenase inhibition limited oxygenation of the Proterozoic atmosphere. *bioRxiv*, p.475236.

[223] Inomura, K., Bragg, J. and Follows, M.J., 2017. A quantitative analysis of the direct and indirect costs of nitrogen fixation: a model based on Azotobacter vinelandii. *The ISME journal*, *11*(1), p.166.

[228] Berner, R.A. and Canfield, D.E., 1989. A new model for atmospheric oxygen over Phanerozoic time. *American Journal of Science*, *289*(4), pp.333-361.

[229] Berner, R.A., 2006. GEOCARBSULF: a combined model for Phanerozoic atmospheric O2 and CO2. *Geochimica et Cosmochimica Acta*, *70*(23), pp.5653-5664.

[230] Braakman, R. and Smith, E., 2012. The compositional and evolutionary logic of metabolism. *Physical biology*, *10*(1), p.011001.

[231] Sanchez-Baracaldo, P., Hayes, P.K. and BLANK, C.E., 2005. Morphological and habitat evolution in the Cyanobacteria using a compartmentalization approach. *Geobiology*, *3*(3), pp.145-165.

[232] Sánchez-Baracaldo, P., Raven, J.A., Pisani, D. and Knoll, A.H., 2017. Early photosynthetic eukaryotes inhabited low-salinity habitats. *Proceedings of the National Academy of Sciences*, *114*(37), pp.E7737-E7745.

[233] Schidlowski, M., Eichmann, R. and Junge, C.E., 1976. Carbon isotope geochemistry of the Precambrian Lomagundi carbonate province, Rhodesia. *Geochimica et Cosmochimica Acta*, *40*(4), pp.449-455.

[234] Karhu, J.A. and Holland, H.D., 1996. Carbon isotopes and the rise of atmospheric oxygen. *Geology*, *24*(10), pp.867-870.

[235] Evans, D.A., Beukes, N.J. and Kirschvink, J.L., 1997. Low-latitude glaciation in the Palaeoproterozoic era. *Nature*, *386*(6622), p.262.

[236] Williams, G.E. and Schmidt, P.W., 1997. Paleomagnetism of the Paleoproterozoic Gowganda and Lorrain formations, Ontario: low paleolatitude for Huronian glaciation. *Earth and Planetary Science Letters*, *153*(3-4), pp.157-169.

[237] Kirschvink, J.L., Gaidos, E.J., Bertani, L.E., Beukes, N.J., Gutzmer, J., Maepa, L.N. and Steinberger, R.E., 2000. Paleoproterozoic snowball Earth: Extreme climatic and geochemical global change and its biological consequences. *Proceedings of the National Academy of Sciences*, *97*(4), pp.1400-1405.

[238] Kopp, R.E., Kirschvink, J.L., Hilburn, I.A. and Nash, C.Z., 2005. The Paleoproterozoic snowball Earth: a climate disaster triggered by the evolution of oxygenic photosynthesis. *Proceedings of the National Academy of Sciences*, *102*(32), pp.11131-11136.

[239] Gumsley, A.P., Chamberlain, K.R., Bleeker, W., Söderlund, U., de Kock, M.O., Larsson, E.R. and Bekker, A., 2017. Timing and tempo of the Great Oxidation Event. *Proceedings of the National Academy of Sciences*, *114*(8), pp.1811-1816.

[240] Brown, M., 2006. Duality of thermal regimes is the distinctive characteristic of plate tectonics since the Neoarchean. *Geology*, *34*(11), pp.961-964.

[241] Cawood, P.A., Kroner, A. and Pisarevsky, S., 2006. Precambrian plate tectonics: criteria and evidence. *GSA today*, *16*(7), p.4.

[242] Condie, K.C. and Kröner, A., 2008. When did plate tectonics begin? Evidence from the geologic record. In *When did plate tectonics begin on planet Earth* (Vol. 440, pp. 281-294). Geological Society of America Special Papers.

[243] Keller, C.B. and Schoene, B., 2012. Statistical geochemistry reveals disruption in secular lithospheric evolution about 2.5 Gyr ago. *Nature*, *485*(7399), p.490.

[244] Cawood, P.A., Hawkesworth, C.J., Pisarevsky, S.A., Dhuime, B., Capitanio, F.A., Nebel, O., 2018. Geological archive of the onset of plate tectonics, *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences, 376*(2132), 20170405

[245] Arndt, N., 1999. Why was flood volcanism on submerged continental platforms so common in the Precambrian?. *Precambrian Research*, *97*(3-4), pp.155-164.

[246] Flament, N., Coltice, N. and Rey, P.F., 2008. A case for late-Archaean continental emergence from thermal evolution models and hypsometry. *Earth and Planetary Science Letters*, *275*(3-4), pp.326-336.

[247] Korenaga, J., Planavsky, N.J. and Evans, D.A., 2017. Global water cycle and the coevolution of the Earth's interior and surface environment. *Phil. Trans. R. Soc. A*, *375*(2094), p.20150393.

[248] Maruyama, S. and Liou, J.G., 2005. From snowball to Phaneorozic Earth. *International Geology Review*, *47*(8), pp.775-791.

[249] Lee, C.T.A., Caves, J., Jiang, H., Cao, W., Lenardic, A., McKenzie, N.R., Shorttle, O., Yin, Q.Z. and Dyer, B., 2018. Deep mantle roots and continental emergence: implications for whole-Earth elemental cycling, long-term climate, and the Cambrian explosion. *International Geology Review*, *60*(4), pp.431-448.

[250] Husson, J.M. and Peters, S.E., 2017. Atmospheric oxygenation driven by unsteady growth of the continental sedimentary reservoir. *Earth and Planetary Science Letters*, *460*, pp.68-75.

[251] Peters, S.E. and Husson, J.M., 2017. Sediment cycling on continental and oceanic crust. *Geology*, *45*(4), pp.323-326.

[252] Ahm, A.S.C., Bjerrum, C.J., Blättler, C.L., Swart, P.K. and Higgins, J.A., 2018. Quantifying early marine diagenesis in shallow-water carbonate sediments. *Geochimica et Cosmochimica Acta*, *236*, pp.140-159.

[253] Palin, R.M. and White, R.W., 2016. Emergence of blueschists on Earth linked to secular changes in oceanic crust composition. *Nature Geoscience*, *9*(1), p.60.

[254] Keller, B. and Schoene, B., 2018. Plate tectonics and continental basaltic geochemistry throughout Earth history. *Earth and Planetary Science Letters*, *481*, pp.290-304.

[255] Keller, C.B., Husson, J.M., Mitchell, R.N., Bottke, W.F., Gernon, T.M., Boehnke, P., Bell, E.A., Swanson-Hysell, N.L. and Peters, S.E., 2019. Neoproterozoic glacial origin of the Great Unconformity. *Proceedings of the National Academy of Sciences*, *116*(4), pp.1136-1145.

[256] Berner R.A., Lasaga, A.C., Garrels, R.M., 1983. The carbonate-silicate geochemical cycle and its effect on atmospheric carbon dioxide over the past 100 million years. *Am J Sci*, *283*, pp.641-683.

[257] Kump, L.R., Brantley, S.L. and Arthur, M.A., 2000. Chemical weathering, atmospheric CO2, and climate. *Annual Review of Earth and Planetary Sciences*, *28*(1), pp.611-667.

[258] Hartnett, H.E., Keil, R.G., Hedges, J.I. and Devol, A.H., 1998. Influence of oxygen exposure time on organic carbon preservation in continental margin sediments. *Nature*, *391*(6667), p.572.

[259] Tosca, N.J., Johnston, D.T., Mushegian, A., Rothman, D.H., Summons, R.E. and Knoll, A.H., 2010. Clay mineralogy, organic carbon burial, and redox evolution in Proterozoic oceans. *Geochimica et Cosmochimica Acta*, *74*(5), pp.1579-1592.

[260] Hazen, R.M., Sverjensky, D.A., Azzolini, D., Bish, D.L., Elmore, S.C., Hinnov, L. and Milliken, R.E., 2013. Clay mineral evolution. *American Mineralogist*, *98*(11-12), pp.2007-2029.

[261] McMahon, W.J. and Davies, N.S., 2018. Evolution of alluvial mudrock forced by early land plants. *Science*, *359*(6379), pp.1022-1024.

[262] Estes, E.R., Pockalny, R., D'Hondt, S., Inagaki, F., Morono, Y., Murray, R.W., Nordlund, D., Spivack, A.J., Wankel, S.D., Xiao, N. and Hansel, C.M., 2019. Persistent organic matter in oxic subseafloor sediment. *Nature Geoscience*, p.1.

[263] Rosing, M.T., Bird, D.K., Sleep, N.H., Glassley, W. and Albarede, F., 2006. The rise of continents—an essay on the geologic consequences of photosynthesis. *Palaeogeography, Palaeoclimatology, Palaeoecology*, *232*(2-4), pp.99-113.

[264] Lee, C.T.A., Morton, D.M., Little, M.G., Kistler, R., Horodyskyj, U.N., Leeman, W.P. and Agranier, A., 2008. Regulating continent growth and composition by chemical weathering. *Proceedings of the National Academy of Sciences*, *105*(13), pp.4981-4986.

[265] Sleep, N.H., Bird, D.K. and Pope, E., 2012. Paleontology of Earth's mantle. *Annual Review of Earth and Planetary Sciences*, *40*, pp.277-300.

[266] Höning, D., Hansen-Goos, H., Airo, A. and Spohn, T., 2014. Biotic vs. abiotic Earth: A model for mantle hydration and continental coverage. *Planetary and Space Science*, *98*, pp.5-13.

[267] Höning, D. and Spohn, T., 2016. Continental growth and mantle hydration as intertwined feedback cycles in the thermal evolution of Earth. *Physics of the Earth and Planetary Interiors*, *255*, pp.27-49.

[268] Blank, C.E. and Sanchez-Baracaldo, P., 2010. Timing of morphological and ecological innovations in the cyanobacteria–a key to understanding the rise in atmospheric oxygen. *Geobiology*, *8*(1), pp.1-23.

[269] Shih, P.M. and Matzke, N.J., 2013. Primary endosymbiosis events date to the later Proterozoic with cross-calibrated phylogenetic dating of duplicated ATPase proteins. *Proceedings of the National Academy of Sciences*, *110*(30), pp.12355-12360.

[270] Schirrmeister, B.E., Gugger, M. and Donoghue, P.C., 2015. Cyanobacteria and the Great Oxidation Event: evidence from genes and fossils. *Palaeontology*, *58*(5), pp.769-785.

[271] Shih, P.M., Hemp, J., Ward, L.M., Matzke, N.J. and Fischer, W.W., 2017. Crown group Oxyphotobacteria postdate the rise of oxygen. *Geobiology*, *15*(1), pp.19-29.

[272] Gibson, T.M., Shih, P.M., Cumming, V.M., Fischer, W.W., Crockford, P.W., Hodgskiss, M.S., Wörndle, S., Creaser, R.A., Rainbird, R.H., Skulski, T.M. and Halverson, G.P., 2017. Precise age of Bangiomorpha pubescens dates the origin of eukaryotic photosynthesis. *Geology*, *46*(2), pp.135-138.

[273] Magnabosco, C., Moore, K.R., Wolfe, J.M. and Fournier, G.P., 2018. Dating phototrophic microbial lineages with reticulate gene histories. *Geobiology*, *16*(2), pp.179-189.

[274] Anbar, A.D., Duan, Y., Lyons, T.W., Arnold, G.L., Kendall, B., Creaser, R.A., Kaufman, A.J., Gordon, G.W., Scott, C., Garvin, J. and Buick, R., 2007. A whiff of oxygen before the great oxidation event?. *Science*, *317*(5846), pp.1903-1906.

[274] Bosak, T., Liang, B., Sim, M.S. and Petroff, A.P., 2009. Morphological record of oxygenic photosynthesis in conical stromatolites. *Proceedings of the National Academy of Sciences*, *106*(27), pp.10939-10943.

[276] Farquhar, J., Zerkle, A.L. and Bekker, A., 2011. Geological constraints on the origin of oxygenic photosynthesis. *Photosynthesis research*, *107*(1), pp.11-36.

[277] Schirrmeister, B.E., de Vos, J.M., Antonelli, A. and Bagheri, H.C., 2013. Evolution of multicellularity coincided with increased diversification of cyanobacteria and the Great Oxidation Event. *Proceedings of the National Academy of Sciences*, *110*(5), pp.1791-1796.

[278] Crowe, S.A., Døssing, L.N., Beukes, N.J., Bau, M., Kruger, S.J., Frei, R. and Canfield, D.E., 2013. Atmospheric oxygenation three billion years ago. *Nature*, *501*(7468), p.535.

[279] Planavsky, N.J., Asael, D., Hofmann, A., Reinhard, C.T., Lalonde, S.V., Knudsen, A., Wang, X., Ossa, F.O., Pecoits, E., Smith, A.J. and Beukes, N.J., 2014. Evidence for oxygenic photosynthesis half a billion years before the Great Oxidation Event. *Nature Geoscience*, *7*(4), p.283.

[280] Wang, X., Planavsky, N.J., Hofmann, A., Saupe, E.E., De Corte, B.P., Philippot, P., LaLonde, S.V., Jemison, N.E., Zou, H., Ossa, F.O. and Rybacki, K., 2018. A Mesoarchean shift in uranium isotope systematics. *Geochimica et Cosmochimica Acta*, *238*, pp.438-452.

[281] Cardona, T., Sanchez-Baracaldo, P., Rutherford, A.W., Larkum, A.W.D, 2018. Early Archean origin of Photosystem II. *BioRxiv,* 109447

[282] Raymond, J. and Segrè, D., 2006. The effect of oxygen on biochemical networks and the evolution of complex life. *Science*, *311*(5768), pp.1764-1767.

[283] Hohmann-Marriott, M.F. and Blankenship, R.E., 2011. Evolution of photosynthesis. *Annual review of plant biology*, *62*, pp.515-548.

[284] Cardona, T., Murray, J.W. and Rutherford, A.W., 2015. Origin and evolution of water oxidation before the last common ancestor of the cyanobacteria. *Molecular biology and evolution*, *32*(5), pp.1310-1328.

[285] Fischer, W.W., Hemp, J. and Valentine, J.S., 2016. How did life survive Earth's great oxygenation? *Current opinion in chemical biology*, *31*, pp.166-178.

[286] Soo, R.M., Hemp, J., Parks, D.H., Fischer, W.W. and Hugenholtz, P., 2017. On the origins of oxygenic photosynthesis and aerobic respiration in Cyanobacteria. *Science*, *355*(6332), pp.1436-1440.

[287] Kacar, B., Hanson-Smith, V., Adam, Z.R. and Boekelheide, N., 2017. Constraining the timing of the Great Oxidation Event within the Rubisco phylogenetic tree. *Geobiology*, *15*(5), pp.628-640.

[288] Mloszewska, A.M., Cole, D.B., Planavsky, N.J., Kappler, A., Whitford, D.S., Owttrim, G.W. and Konhauser, K.O., 2018. UV radiation limited the expansion of cyanobacteria in early marine photic environments. *Nature communications*, *9*(1), p.3088.