The emergence of a globally productive biosphere

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The emergence of a globally productive biosphere

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Abstract

A productive biosphere and oxygenated atmosphere are defining features of Earth and are fundamentally linked. Here I argue that cellular metabolism imposes 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 biospheric expansion and Earth oxygenation. Near the Archean-Proterozoic boundary, cyanobacterial photosynthesis expanded in shallow aquatic environments and along the edges of continents, where weathering inputs made iron more easily accessible. The anoxic deep open ocean was rich in free iron, but this iron remained effectively inaccessible since a photosynthetic expansion would have quenched its own supply. Near the Proterozoic-Phanerozoic boundary, major bioenergetic innovations allowed eukaryotic photosynthesis to begin expanding out into the deep open ocean and onto the continents, eventually creating a globally productive biosphere. These arguments emerge from a recent reconstruction of metabolic evolution in marine *Synechococcus* and *Prochlorococcus*, abundant marine picocyanobacteria whose ancestors colonized the oceans in the Neoproterozoic. This reconstruction revealed a sequence of innovations that ultimately produced a form of photosynthesis in *Prochlorococcus* that is 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 a by-product increased production of iron-chelating organic carbon. This pushed the oceans through a transition from an anoxic state rich in free iron to an oxygenated state with organic carbon-bound iron. In addition to major increases in biospheric productivity, both the Neoarchean and Neoproterozoic have also been linked to global glaciations, major carbon cycle perturbations and changes in the nature of mantle convection and plate tectonics. This suggests the dynamics of life and Earth are intimately intertwined across levels and that similar general principles governed Neoarchean and Neoproterozoic transitions in these coupled dynamics.

Introduction

The oxygenation of Earth's atmosphere is the result of a complex interplay of geological and biological forces, and untangling these forces is a major scientific challenge. The ultimate source of oxygen is oxygenic photosynthesis, which is coupled to aerobic respiration as part of the biological carbon cycle (Fig. 1). However, if photosynthesis and respiration were perfectly coupled oxygen could not accumulate, and it is generally thought that the long-term sequestration of a small fraction (~0.1%) of the organic carbon produced by photosynthesis within Earth's subsurface is responsible for the rise of atmospheric oxygen [1-5]. Buried organic carbon eventually returns to the atmosphere as CO_2 when organic-bearing rocks are exhumed and oxidatively weathered, or when metamorphism during subduction leads to outgassing of CO_2 or reduced gasses, the latter of which can react with O_2 (Fig. 1) [2,6]. A potentially critical process that is less constrained is the subduction of organic carbon into the mantle, from where its recycling to the surface is slower than

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crustal recycling [2,7-12]. 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 abiotic sinks for O_2 other than outgassing of reducing power derived directly from buried organic carbon, for example due to redox changes in the mantle, crust and/or volcanic gasses, have also been argued to be important contributing processes [13-18].

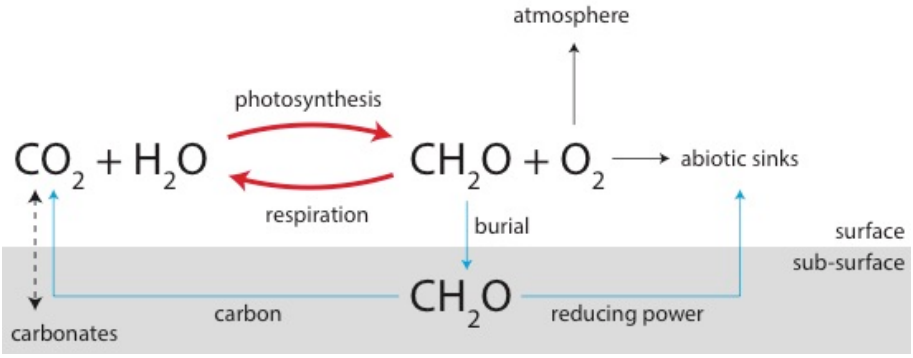

Figure 1. Simplified view of the coupled biological (red) and geological (blue) cycles of organic carbon and associated reducing power and their relationship to atmospheric oxygen. Oxygenic photosynthesis produces organic carbon (represented in its general stoichiometry of CH_2O) and oxygen from CO_2 and water, while aerobic respiration performs the reverse process. A small fraction (~0.1%) of organic carbon escapes oxidation through sequestration in sediments, allowing oxygen to accumulate in the atmosphere over geologic time. Geologic processes in the crust and mantle eventually recycle the carbon and reducing power within buried organic carbon back to the surface. 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.

There are generally considered to be two major stages of Earth oxygenation. The first stage, also known as the 'Great Oxidation Event' [14], occurred near the boundary between the Archean (4000-2500 Mya) and Proterozoic (2500-541 Mya) and is when the atmosphere first became permanently oxygenated at around 0.1-1% of modern levels [1,19-25]. After a prolonged period of relative global stasis [26-28], 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 [29-37]. In this review I will focus on this second stage, also known as the 'Neoproterozoic Oxidation Event' [37], 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 may have been driven by effective decreases in the efficiency of respiration due to faster sinking of larger organisms and/or their fecal pellets [38-41] or because of changes in the composition sediments that more efficiently trapped organic matter [42,43]. I will focus on possible sources of variation in global rates of photosynthesis, which is ultimately the source flux of both oxygen and the carbon whose burial allows accumulation of oxygen. While all oxygenic photosynthesis is performed by cyanobacteria or photosynthetic eukaryotes (whose chloroplasts are derived from cyanobacteria),

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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 [44-47]. Identifying the 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 the dominant primary producers, eventually driving a major increase in global primary production [48-55]. Important exceptions that ultimately help explain this "rule" are the marine picocyanobacteria *Synechococcus* and *Prochlorococcus* [56-59], whose ancestors also arose in the Neoproterozoic [60,61] and which are estimated to account for around 25% of biological CO_2-fixation in the modern oceans [62]. We recently reconstructed the metabolic evolution of this group [63], which revealed key evolutionary driving forces and biogeochemical 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 [64-67], possible changes in the nature of plate tectonics linked to cooling of the mantle and crust [68-74], an expansion of shallow seas [66,75-77], major carbon cycle perturbations [38,78,79] and several "snowball Earth" episodes of global glaciation [80-83]. At the same time, ocean chemistry was undergoing a fundamental shift (Fig. 2). It has in recent decades become increasingly clear that the deep open ocean remained largely anoxic well into the Proterozoic, long after oxygen first began accumulating in the atmosphere [84]. It was first thought that Proterozoic oceans were mostly euxinic (rich in H_2S) [84], but more recent evidence suggests the oceans were instead largely ferruginous (rich in Fe^{2+}) [85,86], with euxinia restricted to regions of enhanced productivity near continental boundaries [26,87]. 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) [88] or even the Triassic (ca. 200 Mya) [89] – but evidence for the initiation of this process reaches back to the Neoproterozoic [35,88-92].

Several biogeochemical feedbacks have been proposed to explain why the deep open ocean remained anoxic during the Proterozoic. Some proposals invoke nitrogen-limitation of oceanic primary production, either through the scavenging of Molybdenum and other trace metals that mediate nitrogen assimilation by sulfide ions in euxinic waters [50,26], or due to an excess in the rate of denitrification relative to nitrification under low oxygen concentrations [93] (Fig. 2). Other proposals invoke phosphorus-limitation of primary production, due to the scavenging of phosphate from riverine inputs and/or directly from the water column by abundant Fe^{2+} ions [94-97], or due to organic phosphate remineralization being limited by electron acceptors in the absence of O_2 [98]. Both sets of proposals are consistent with observations that post-Neoproterozoic oceans saw significant increases in the levels of both phosphate [97,99] and molybdenum [90,100], as well as isotopic shifts of sedimentary nitrogen that suggest the onset of a stable oceanic nitrate pool [101-

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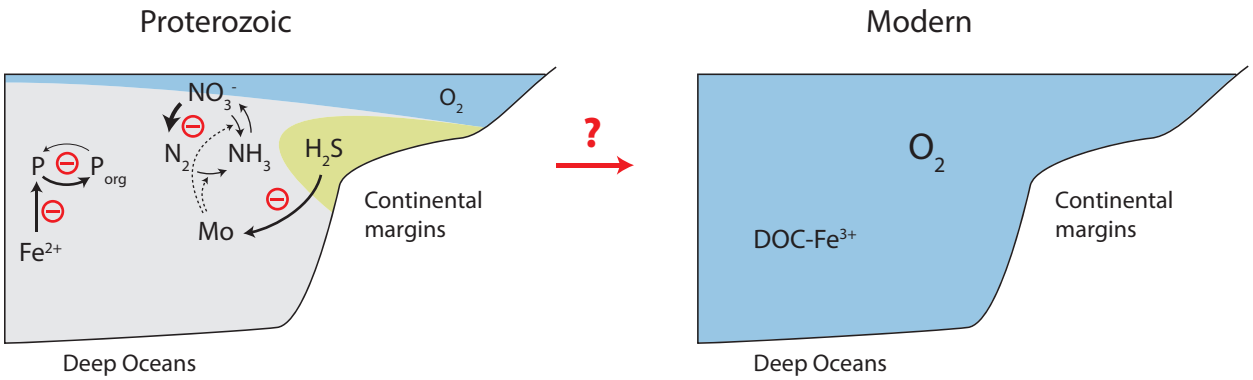

Figure 2. Neoproterozoic revolution in ocean chemistry. Negative feedbacks that have been argued to constrain ocean oxygenation are indicated with red minus signs. Processes that scavenge phosphorus [94-97] and/or molybdenum (Mo) [50,26] are indicated by green arrows. The role of molybdenum as a cofactor in nitrogen cycle reactions is indicated by dashed arrows. Differences in the relative rates of phosphorus [98] and nitrogen [93] cycling reactions are indicated by differences in the weight of arrows. DOC = dissolved organic carbon.

107]. Such negative feedbacks (Fig. 2) have been argued to lead to bi-stability on the path to full ocean oxygenation [108]. That is, full 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 [82] were ultimately needed to trigger the transition to a fully oxygenated state [108].

The framework outlined above can be expanded upon by taking an ecophysiogical 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 [63] (Fig. 3). Oxygenic photosynthesis depends on substantial amounts of iron [109], but iron is highly insoluble under aerobic conditions, especially at the pH of ambient seawater [110,111]. Thus, as ocean oxygenation proceeded, iron would become increasingly scarce [86, 112], presenting a challenge not just to oxygenic photosynthesis (Fig. 3) but also to nitrogen fixation [113] and biological electron transfer more generally [114,115].

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 the fact that in the extant oceans iron is not dissolved as free ions but instead is bound to a vast pool of dissolved organic carbon (Fig. 2) [116,117]. 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 [116,117,118,119]. This suggests that perhaps the evolution of cellular metabolism itself helped ancestral oxygenic photosynthesis overcome its inherently self-damping nature.

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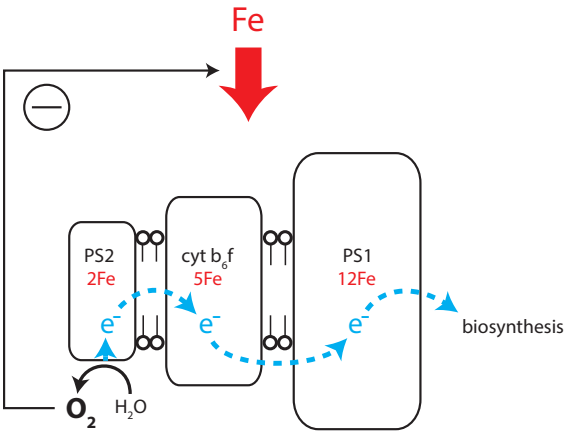

Fig. 3 Graphical representation of the hypothesis that ancestral cyanobacterial photosynthesis had a built-in negative feedback (black arrow highlighted by '-' sign) that prevented its expansion into the deep open ocean. Relative sizes of electron transfer components reflect their cellular stoichiometry in cyanobacteria. Red lettering indicates the number of iron atoms that components require and red arrow reflects influx of iron that cells need to build photosynthetic machinery. 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.

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 [60,61], and its physiological, ecological and genomic diversity has been characterized in detail [58,59,120]. We recently showed that as marine picocyanobacteria colonized the oceans their metabolic core underwent a global remodeling [63] (Fig. 4A). Remodeling is most extensive in *Prochlorococcus* and involves modifications to the pigments and stoichiometry of the photosynthetic machinery [57,59,121-125] as well as to core carbohydrate metabolism, wherein pathways were created for excreting organic carbon from the cell [63] (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 to core metabolic enzymes, including those that catalyze the final steps of truncated pathways [63], 3) synchronized gene expression of transporter-metabolic enzyme pairs that follow the daily rhythms of solar energy input [126,63] and 4) experimental studies showing excretion of glycolate [127], 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 [127-130].

Identifying the driving forces that underpin *Prochlorococcus*' metabolic innovations (Fig. 4A) requires looking at the system at multiple levels. Based on the insolubility of iron under aerobic conditions [110,111] it is tempting to conclude that cells evolved to excrete organic carbon to enhance its bioavailability (Fig. 3). Similarly, the difficulty of culturing many oceanic microbes without complex nutrient additions [131,132] suggests that interactions with sympatric heterotrophs is part of what drove *Prochlorococcus*' metabolic evolution. However, both scenarios involve extracellular sharing of resources between members of the community, and it is generally

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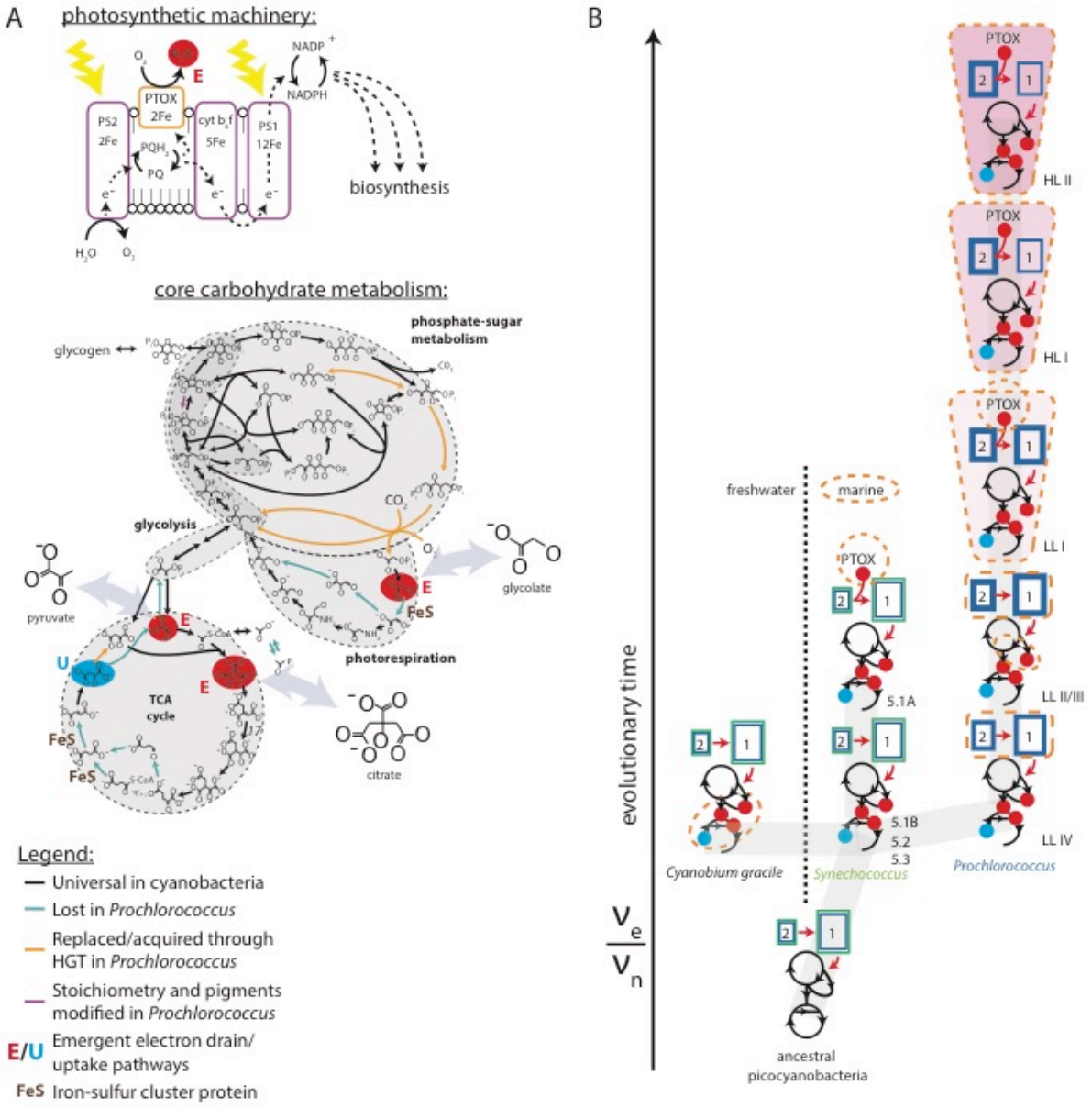

Fig. 4 Metabolic evolution of *Prochlorococcus*. **A)** Evolutionary changes in the metabolic core of *Prochlorococcus* relative to ancestral cyanobacteria, as indicated by colors in the inset [63]. Compounds identified as excretion pathways are highlighted with red dots and bi-directional grey arrows, 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, v_e/v_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 [137,138] are indicated by a darkening pink shade. Figure adapted from Figs. S1 & 4 from [63]. In the original tree in Ref [63] 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 [139]. Abbreviations: LL = low-light adapted, HL = high-light adapted.

178 thought such social interactions can only evolve when physical colocation of cells across
179 generation ensures that resource benefits are transmitted directly from parents to offspring

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[133,134]. In contrast, *Prochlorococcus* populations are made up of individual planktonic cells, and fluid dynamic calculations suggest that recently divided cells are separated by tens of meters within an hour and kilometers within a week [135], indicating they essentially never interact. Such well-mixed conditions are thought to lead to the "tragedy of the commons" [136], in which freeloading mutants that receive the benefits of shared resources but do not incur the costs of producing them take over the population and suppress sharing [133,134,136]. That selection nevertheless consistently favored the addition of pathways for excreting organic carbon in *Prochlorococcus* (Fig. 4A) suggests it must directly benefit individual cells, with any community-level benefits emerging as a by-product.

Studies of aerobic heterotrophs that can facultatively switch between respiration and fermentation have identified 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 [140-142]. 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 [143-145]. However, *Prochlorococcus* has a lower intrinsic growth rate compared to other cyanobacteria [57,146] 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 [147-150]. However, many photosynthesizers can prevent redox imbalance by using 'photoacclimation' to decrease their harvesting of solar energy [153,154], and *Prochlorococcus* appears to have only a modest ability for photoacclimation [151,152]. This suggests there are other benefits to increasing the throughput and excretion of organic carbon 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 [58,59,120]. 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 [155-159]. Abovementioned changes to the photosystems [57,59,121-125] (Fig. 4A), which increase the absorption cross-section of cells [160,146], thus appear to reflect an evolutionary trend that increases the photosynthetic electron flux [63], defined as:

$$\nu_e = I\sigma_{PSII}\theta_{PSII}, \quad (1)$$

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 further coincides with a general process of evolutionary 'streamlining' [161-163] that decreases the dependency of cells on phosphorus, nitrogen and iron, key limiting nutrients in the oceans [164]. For example, *Prochlorococcus* genomes have undergone reduction in size and guanosine-cytosine content (AT

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base pairs require one fewer nitrogen atom than GC base pairs) [165], its proteins contain few nitrogen-rich amino acids [166], its membranes consist of glyco- and sulfolipids rather than phospholipids [167,168] and its modified metabolism (Fig. 4A) requires less iron [124,63]. Finally, *Prochlorococcus* has a lower growth rate than *Synechococcus*, which in turn has a lower growth rate than other cyanobacteria [57,146]. This suggests a decrease not just in the nutrient content of cells but in the uptake flux of nutrients [63], defined as:

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

where μ is the specific growth rate and Q_n is 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 favor 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 [155-159]. This suggests there is a link between metabolic rate and nutrient acquisition [169,63], which can be elucidated by considering the free energy cost of the nutrient uptake reaction:

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

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 [170-173].

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 [63]. 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 [147-149,174,175]. 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 [175-179] and heterotrophs [147-150]. 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 by

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the limiting nutrient(s), thereby causing ATP production to outpace consumption and the ATP/ADP ratio to increase [63]. 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 [63]. 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 [63]:

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

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 [63]:

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

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 $\Delta_r G = -RTln\left([n]_E K_{M,n_E} K_{eq}/[n]_I K_{M,n_I}\right)$ [180]. Finally, equations 4 and 5 can be combined to relate relevant features of cells to the nutrient concentrations at which they can grow [63]:

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

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).

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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 [155-159] 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 [63]. 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 [157,159] and dissolved organic carbon levels are twice as high as in the rest of the oceans [182].

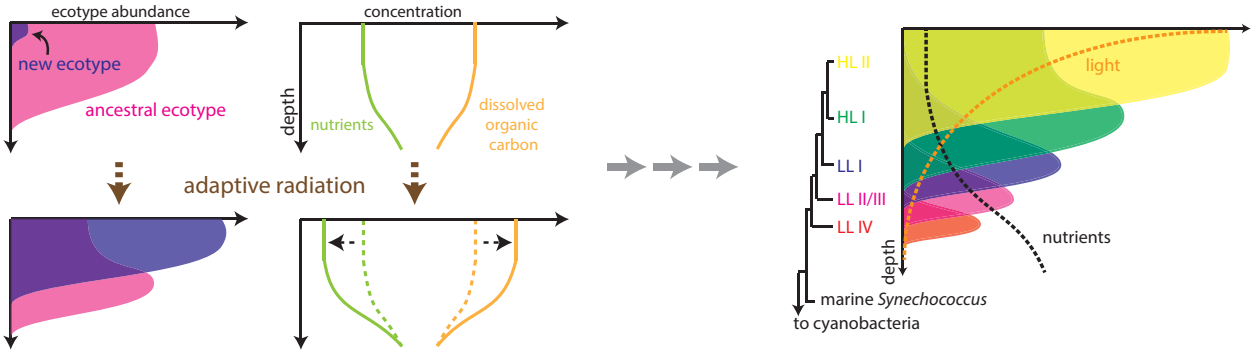

Fig. 5 Macroevolutionary dynamics leading to niche partitioning in *Prochlorococcus*. Panel on left shows the principles of niche constructing adaptive radiations. Innovations that increase cellular metabolic rate (Fig. 4) lead to the emergence of new populations (purple) that drive down nutrient levels (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 [63].

The proposed dynamic (Fig. 5) is consistent with a recent study on the evolution of nitrate assimilation in *Prochlorococcus* [183]. 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* [183]. 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 [184]. 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 [183].

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 innovations allow cells to grow at lower nutrient concentrations (Eq. 6), it helps explain how this

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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 [63,124], 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 [63,118,119]. 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.

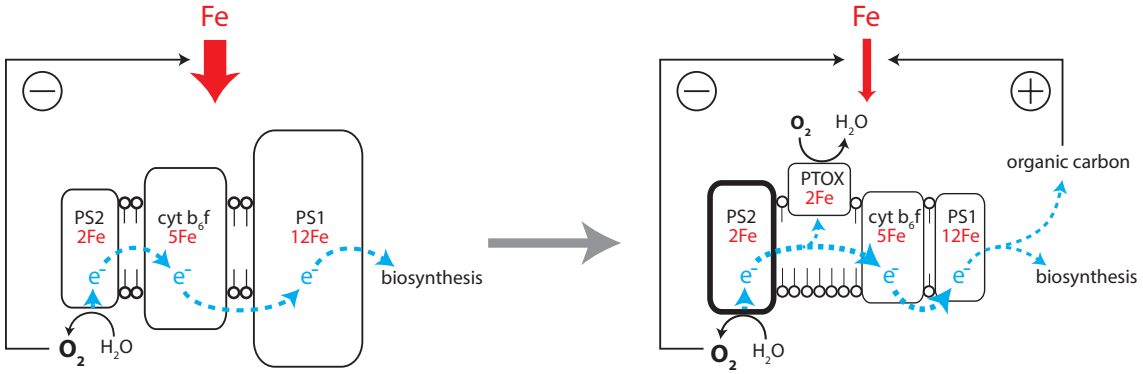

Fig. 6 Evolution of feedbacks involving iron in the machinery of photosynthesis. Left panel reflects photosynthetic machinery of ancestral cyanobacteria, right panel reflects photosynthetic machinery of *Prochlorococcus*. Relative size of electron transfer components reflects their cellular stoichiometry, line thickness reflects absorption cross-section. Relative thickness of red arrows reflects 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). Dashed blue arrow reflects flow of electrons. Abbrevations: PTOX = plastoquinol terminal oxidase, others as in Fig. 3.

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 [60,61], which is relevant to discussion that ocean oxygenation played out over hundreds of millions of years [35,89-92]. 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 [185-187], modified membranes that require less phosphorus [167] and excrete large amounts of organic carbon under nutrient limitation [176-180]. 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).

In principle, 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 [188,189]. In the open ocean, rock minerals in wind-blown desert dust

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are the major source of iron [190], as well as a source of phosphorus [191,192]. Thus, the evolution of marine 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 [63]. 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-limitated, presumably to dissolve minerals containing both iron and phosphorus [193]. 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 [112]. This led to a decrease in the scavenging of phosphorus (Fig. 2) and a concomitant increase in its bioavailability [94-97]. 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 promotes nitrogen-fixation [194-196]. 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 [50,26] and lessened nitrogen-limitation by decreasing the rate of denitrification relative to nitrification [93] (Fig. 2). These scenarios are consistent with molecular clocks that estimate Neoproterozoic origins of both planktonic marine nitrogen-fixers [60] and ammonia-oxidizing marine Thaumarcheota [197,198], 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 [101-107].

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 [162,199], which like marine picocyanobacteria is estimated to have emerged during the Neoproterozoic [200]. 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) [201,132]. 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) [63].

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 [57] and has a PSII/PSI ratio that is significantly higher than other cyanobacteria [123,202,203], making its photosynthetic machinery rather more like that of green chloroplasts

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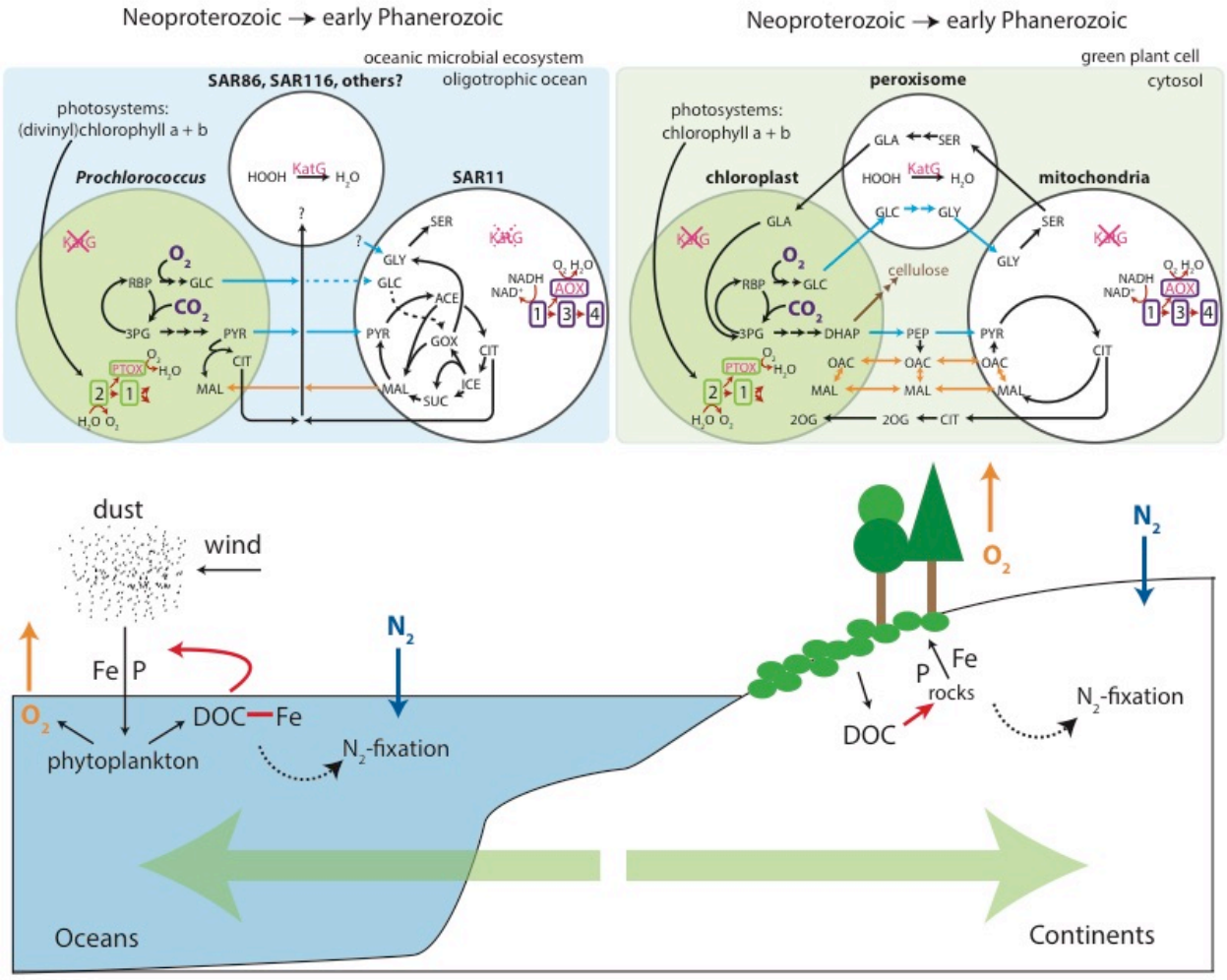

Fig. 7 Convergent biogeochemical evolution of green eukaryotic photosynthesis in the oceans and on the continents. Top panel: Similarities between the photosystems, electron transport chains and core carbohydrate metabolic pathways of oceanic microbial ecosystems and green plant cells. Metabolic reactions 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 [63] 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 = plastoquino terminal oxidase, KatG = catalase

than other cyanobacteria [63]. 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 [124,204]. 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 [204,205].

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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 [206,207], just as chloroplasts and mitochondria depend on the peroxisome for this function [205].

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 [45], while their evolutionary roots lie in the Neoproterozoic [52,208-211], similar to the timeframes over which ancestral marine picocyanobacteria diversified into *Synechococcus* and *Prochlorococcus* [60,61]. In addition, under nutrient limitation plants excrete organic carbon from their roots, dissolving rocks minerals and making the iron and phosphorus within them available [212,213]. The resulting conditions promote nitrogen-fixation [194-196], and various plants have evolved symbioses with nitrogen-fixing bacteria in their rhizosphere [195,214], increasing the supply of fixed nitrogen into the terrestrial biosphere [214]. This is consistent with molecular clocks estimating a Neoproterozoic rise of ammonia-oxidizing Thaumarcheota in terrestrial soils [197,198], paralleling their aforementioned Neoproterozoic rise in the oceans [197,198]. These observations have led to the arguments that the rise of land plants enhanced continental weathering and organic carbon burial as the productivity of the terrestrial biosphere increased, driving an increase in atmospheric oxygen [216,217] (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) [63].

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

Cellular metabolism provides a unique lens into Earth history [218]. Looking through this lens in marine picocyanobacteria leads to a general framework in which ecosystems follow self-amplifying evolutionary trajectories (Fig. 8) [63]. 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 [63]. A combination of feedbacks (Figs. 2 & 3) prevented cyanobacterial photosynthesis from expanding away from shallow aquatic environments near continental boundaries where weathering inputs made nutrients relatively more easily accessible than in the open ocean or on the continents. 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 [219,220] and molecular biomarker

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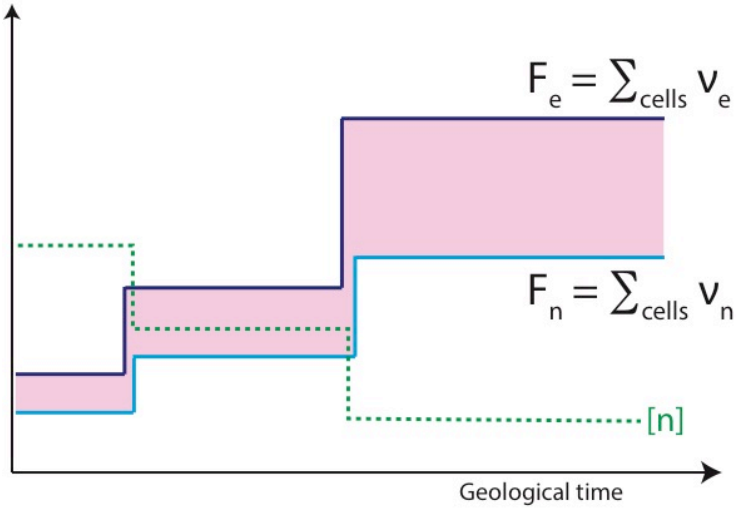

Fig. 8. Evolution of ecosystem-level fluxes of electron and nutrients ($F_{e,n}$) and environmental nutrient concentrations over geologic time. Innovations that increase metabolic rate (through increases in the electron-to-nutrient flux ratio, ν_e/ν_n) increase total ecosystem biomass by making more 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.

studies indicating a major expansion of eukaryotic green algae in the marine realm in the late Neoproterozoic [52]. The faster sinking of larger organisms and/or their fecal pellets [38-41] 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) [52].

In addition to being linked to major increases in biospheric productivity, the periods of Earth history around the Great and Neoproterozoic Oxidation Events share a number of other similarities. As with the Neoproterozoic-Phanerozoic boundary, sediments near the Archean-Proterozoic boundary indicate a turbulent climate, with major carbon cycle perturbations [33,221,222] and global glaciation events [223-227]. And, while the evolution of plate tectonics is vigorously debated, a range of geological and geochemical evidence suggests its initiation in the Neoarchean [15,16,72,228-232] and a shift toward deeper subduction of colder and thicker crust in the Neoproterozoic [66,68-71,73,74,77]. Both epochs thus appear to mark major transitions in the dynamics of the whole Earth system.

Major questions remain regarding the relative timing of the major bioenergetic innovations of photosynthesis and increases in atmospheric oxygen, as well as the time courses of the latter. Molecular clock estimates of when cyanobacteria or photosynthetic eukaryotes arose often disagree significantly with one another, to a large degree because of differences in the external date constraints (e.g. from fossils, biomarkers or other geochemical proxies) that are imposed on the calculations [209-211,233-238]. Nevertheless, a range of evidence suggests that the roots of cyanobacteria and the initiation of atmospheric oxygenation pre-date the Great Oxidation Event by several hundred million years [233,236,238-246]. 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 [209-211,234,237]. If

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photosynthetic innovations are ultimately responsible for both stages of oxygenation, what led to these long delays?

Perhaps changes in the nature of plate tectonics are part of the explanation. A significant Neoarchaean increase in the exposed continental surface area has been linked to both the initiation of plate tectonics [15,16,72,228-232] and to an associated increased influx of water into the mantle [16,247-249]. Thus, if early cyanobacterial photosynthesis were restricted to freshwater habitats [219] and continental boundaries (Fig. 7) [63], then growth of the size of exposed continents and continental boundaries would drive an ecological expansion of cyanobacteria over hundreds of millions of years. Moreover, the emergence of what we today recognize as cyanobacterial photosynthesis involved an elaborate set of innovations, encompassing core pathways, cofactors, photosystems, as well as damage protection mechanisms needed to adapt to a changing environment [3,250-255] and these were likely acquired over time rather than all at once. Oxygen accumulation further led to the eventual emergence of an ozone layer [22], which filtered out damaging UV radiation and allowed cyanobacteria to continue their expansion [256]. Thus, the size of habitats available to cyanobacteria and their ability to fill those habitats likely increased in tandem during the rise of continents. Indeed, it has been argued that the evolution of photosynthesis directly influenced the initiation of plate tectonics by increasing the chemical weathering of continents, thereby changing their composition and increasing the influx of water and other volatiles into the mantle [257-262].

A generally similar scenario may have played out in the Neoproterozoic. It has been argued the Neoproterozoic marked another increase in continental exposure as cold deep subduction was initiated [68-71,73,74], the influx of water into the mantle increased [70,262], and crustal buoyancy increased [263]. This is consistent with observations of a great ‘unconformity’ in Neoproterozoic sediments that indicates a significant drop in seawater levels and enhanced weathering of more exposed continents [66,75-77,262]. On the biological side, the reconstructed evolution of marine picocyanobacteria (Fig. 4) highlights how the diversification and ecological expansion of eukaryotic photosynthesis involved the sequential acquisition of a range of innovations [63] over the course of hundreds of millions of years [60,61]. Finally, as mentioned above, plants are known to chemically weather rocks [212,213], which led to the argument that the rise of land plants played a central role in the enhanced large-scale weathering of continents from the early Phanerozoic onward [264-267]. Evidence thus again points to a pattern of intimate co-evolution of photosynthesis and dynamics of Earth’s crust and mantle over hundreds of millions of years during the Neoproterozoic and early Phanerozoic.

The apparent similarities of Neoarchean and Neoproterozoic transitions in whole-Earth dynamics raises the possibility of similar positive feedbacks operating in both epochs. As the weatherability of continents increased in stages corresponding to their emergence, the actualized weathering rates increased in stages corresponding to biospheric self-amplification, with these mechanisms reinforcing each other. The weathering of rocks supplied the biosphere with key nutrients that fueled its expansion [Fig. 7 & 8), while subduction of volatile-bearing sediments produced through weathering helped fuel the rise of continents. The operation of such feedbacks is consistent with statistical analyses of the large-scale sediment record, which identified significant long-term increases in weathering and sedimentation rates in both the Neoarchean and Neoproterozoic

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[75,268,269]. If transitions in biogeochemical cycling at the surface and in the crust and mantle are fundamentally intertwined through weathering and subduction [257-262], then the long delays between photosynthetic innovations and rises in atmospheric oxygen may simply reflect the significantly greater inertia and longer timescales of change in solid Earth dynamics relative to changes in the dynamics of the biosphere, oceans and atmosphere.

A fundamental link between biospheric productivity and weathering and sedimentation rates is also 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 [4,5]. 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.

If increases in biospheric productivity increased weathering and sedimentation rates it was also help 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 in sediments is inversely proportional to the "oxygen exposure time", a measure that is the product of the overall sedimentation rate and how deeply oxygen penetrates into sediments, which in turn depends on the oxygen concentration of bottom waters [270]. As a consequence, Earth oxygenation effectively stymies itself by decreasing the fractional burial of sedimentary carbon, unless increases in oxygen levels are coupled to increases in sedimentation rates and/or changes in the composition of sediments that make them harder for oxygen to penetrate [4]. Evidence for the latter in the late Neoproterozoic and early Phanerozoic comes from analyses that suggest biologically-driven increases in the production of fine-grained clays and muds [42,43,271-273]. Thus, increases in the overall production sedimentation rates and in the production of less-penetrable sediments worked together to counteract the negative effect of oxygenation on carbon burial, allowing oxygen to rise.

The general framework outlined here leaves many questions unanswered. Why do major transitions in Earth's biogeochemical dynamics during the Neoarchean and Neoproterozoic happen when they do? Is it simply that the gradual cooling of the crust and mantle eventually passes through tipping points that cause changes in plate tectonics that trigger biospheric changes and the emergence of self-reinforcing feedbacks? Or do biological innovations play a more significant role, effectively speeding up the cooling of the solid Earth and pushing it toward tipping points? At finer temporal scales, what is the ordering and causal relationship of geological and biological changes that make up large-scale transitions? Do biological innovations ultimately drive climate perturbations through carbon cycle perturbations, or do geologically-driven climate changes trigger biological innovations, or is it both? Regardless of the exact details, the evidence of broad parallels between the transitions in the physical, chemical and biological dynamics of Earth during the Neoarchean and Neoproterozoic calls for general frameworks that treat these periods together.

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