Primary Productivity was Limited by Electron Donors Prior to the Advent of Oxygenic Photosynthesis

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Key Points:

- Before the evolution of oxygenic photosynthesis, electron donor limitation led to rates of biological productivity approximately 1000-fold lower than today.
- Abiotic fixed nitrogen fluxes exceeded the demands of the early biosphere, delaying the need for biological nitrogen fixation.
- The small size and weak biogeochemical cycling of the early biosphere may temper expectations for life on worlds without photosynthesis.

Abstract:

To evaluate productivity on the early Earth before the advent of oxygenic photosynthesis, we integrated estimates of net primary production by early anaerobic metabolisms as limited by geological fluxes of key electron donor compounds, phosphate, and fixed nitrogen. These calculations show that productivity was limited by fluxes of electron donor compounds to rates that were orders of magnitude lower than today. Results suggest that ferrous iron provided a minor fuel for net primary productivity compared to molecular hydrogen. Fluxes of fixed nitrogen and phosphate were in excess of demands by the electron donor limited biosphere, even without biological nitrogen fixation. This suggests that until life learned to use water as an electron donor for photosynthesis, the size and productivity of the biosphere were constrained by the geological supply of electron donors, and there may not have been much ecological pressure to evolve biological nitrogen fixation. Moreover, extremely low productivity in the absence of oxygenic photosynthesis has implications for the potential scale of biospheres on icy worlds such as Enceladus and Europa, where photosynthesis is not possible and life would be unable to escape electron donor limitation.

Plain Language Summary

Life on Earth today is fueled by oxygenic photosynthesis—the process performed by plants, algae, and Cyanobacteria that takes water, light, and carbon dioxide and produces sugar and oxygen. The raw materials for this process are abundant, so productivity is limited by nutrients such as phosphorous and fixed nitrogen. Oxygenic photosynthesis evolved midway through Earth history, and it has long been unclear how productive the biosphere was earlier in time. Here, we considered the compounds necessary for early metabolisms that may have fueled life on the early Earth—including iron and hydrogen compounds that fuel earlier "anoxygenic" photosynthesis. We determined that it was these "electron donor" compounds such as ferrous

iron and molecular hydrogen that were most limiting on the early Earth, and that the slow geological supply of these compounds resulted in a biosphere that was 1000-fold less productive than it is today. The innovation of using water as an electron donor allowed oxygenic photosynthesis to dominate primary production and made the Earth as productive as it is today. This impacts how productive we can expect life on other planets to be, and assumptions about when certain biochemical processes like those involving the cycling of nitrogen evolved.

Keywords: Methanogenesis, Anoxygenic Photosynthesis, Great Oxygenation Event, Archean Eon, Hydrogenotrophy, Photoferrotrophy

1 Introduction:

The rise of oxygen, or Great Oxygenation Event (GOE), marked the irreversible accumulation of dioxygen (O_2) in Earth's atmosphere ~2.3 billion years ago (Ga), and was ultimately driven by the evolution of oxygenic photosynthesis within the Cyanobacteria (Fischer et al. 2016). While the antiquity of oxygenic photosynthesis by Cyanobacteria remains a matter of significant debate (Rosing and Frei 2004, Johnson et al. 2013a, Johnson et al. 2013b, Crowe et al. 2013, Planavsky et al. 2014, Lyons et al. 2014, Fischer et al. 2016, Ward et al. 2016, Shih et al. 2017a), dioxygen is constrained to extremely low concentrations earlier in Earth history (Farquhar et al. 2000, Johnson et al. 2013a, Johnson et al. 2014), but rapidly accumulated to significant concentrations at the GOE (Goldblatt et al. 2006, Bekker and Holland 2012, Ward et al. 2016, Luo et al. 2016).

While the biosphere underwent a substantial transition to take advantage of the energetic and biosynthetic opportunities afforded by this new photosynthetic source of dioxygen (e.g. Raymond and Segrè 2006), another significant impact of oxygenic

photosynthesis was the ability for autotrophic organisms to make use of an essentially unlimited electron donor. The fixation of inorganic carbon into biomass fundamentally involves the reduction of CO_2 into organic forms via the transfer of electrons from an electron donor. The electron donor for oxygenic photosynthesis—water—is available in effectively unlimited supply, and so rates of primary productivity across Earth surface environments today are constrained by factors such as the availability of nutrients like fixed nitrogen and phosphorous (Tyrrel 1999). Before the evolution of oxygenic photosynthesis—whenever this metabolism evolved, whether it was near the GOE or much deeper in Archean time—biology would have been restricted to more limited electron donor compounds, including molecular hydrogen, ferrous iron, and reduced sulfur compounds (e.g. Kharecha et al. 2005, Canfield et al. 2006). These electron donors are ultimately sourced by geological processes such as volcanic outgassing and water/rock interactions at hydrothermal vents, and are created at far lower rates and present in environments at much lower abundances than water. This raises the possibility that electron donors—rather than nutrients like phosphate and fixed nitrogen—could have limited or co-limited rates of primary productivity on the early Earth, before the evolution of oxygenic photosynthesis.

Here, we considered the absolute contributions that electron donor compounds may have made to fuel primary productivity prior to oxygenic photosynthesis and compared these rates to those available from fluxes of nitrogen and phosphorous in order to determine the limiting factors and resulting productivity at this time.

2 What limited productivity of the early biosphere?

To determine the ultimate limiting factor for pre-oxygen productivity, one can compare the fluxes of nutrients to the Archean oceans, and the idealized rates of productivity they could have supported. We assumed that average cellular biomass follows Redfield Ratios of 106 C:

16 N: 1 P; while individual organisms can and do deviate substantially from these ratios, this appears to be a reasonable description of average elemental composition of ecosystem biomass (Weber and Deutsch 2010, Deutsch and Weber 2011). Furthermore, when cells deviate substantially from the Redfield Ratio (e.g. by members of the Cyanobacteria in the Sargasso Sea replacing membrane phospholipids with sulfolipids, raising their C: P value), this appears to be a derived trait (Van Mooy et al. 2006) that will only lower their overall nutrient demand, making the Redfield Ratio a conservative estimate of the amount of primary production given a certain amount of available nutrient. One can equate a supply of electron donors to fixation of organic carbon by assuming an average redox state of organic carbon similar to that of modern marine organisms of around -1 (Anderson 1995), therefore requiring 5 moles of electrons to fix one mole of CO_2 to one mole of biomass C. One can therefore make the relative availability of nutrients and electron donors directly comparable by equating both to potential production of organic carbon.

Below, we assembled the best available estimates for the fluxes of essential nutrients to the pre-oxygen biosphere, focusing on phosphate, fixed nitrogen, and the electron donor compounds molecular hydrogen and ferrous iron (Table 1). Estimates of the availability and fluxes of these compounds during Archean time are in many cases not well constrained and depend on poorly understood characteristics of the early Earth system such as atmospheric composition. Available constraints facilitate only order of magnitude estimates, and so this should be considered the level of accuracy for the results that follow.

Traditional measures of productivity (i.e. Gross Primary Productivity and Net Primary Productivity, GPP and NPP) are defined in terms of amount of organic carbon fixed by autotrophs per year (e.g. Field et al. 1998); these measures inherently incorporate productivity driven by recycled nutrients derived from the remineralization of organic matter. Nutrients can be preferentially remineralized from organic carbon (i.e. the C:P and C:N values of organic

matter increase as it is degraded, e.g. Clark et al. 1998, Berner 2006), allowing the recycling of these nutrients to fuel additional productivity (Thomas et al. 1999). The same is not true of electron donors—the respiration of organic matter yields stoichiometric amounts of electron donor compounds, and so remineralization and recycling can increase the apparent NPP of a system but not the total biomass carrying capacity (i.e. size of standing pool of organic carbon in the biosphere at a given time). As a result, it is useful to approach early Earth productivity in terms of a related but distinct value, NPPe, electron-equivalent Net Primary Productivity, defined here as a measure of the number of electrons entering the biosphere from inorganic sources per year. This is equivalent to gross primary production (the total number of moles of organic carbon fixed per year) minus the amount of organic carbon fixed using recycled electron donors. Because the recycling of electron donor compounds is stoichiometrically coupled to the remineralization of organic carbon, the total number of electrons available to the biosphere does not increase and this process is incapable of increasing the total biomass carrying capacity of the biosphere. This is in contrast to recycling of nutrients such as nitrogen and phosphorous, which are often preferentially remineralized without stochiometric remineralization of associated organic carbon, allowing recycled nutrients to contribute to net primary production (e.g. Thomas et al. 1999, Chen 2003). NPPe is therefore proportional to the carrying capacity of the biosphere in terms of amount of organic carbon that can accumulate at a given time.

Unlike some definitions of NPP, NPPe ignores internal recycling of electron donor compounds (e.g. re-release of ferrous iron from photosynthetically derived ferric-iron phases by dissimilatory iron reducing heterotrophic microbes). In modern environments, where >99% of carbon fixation is driven by oxygenic photosynthesis (Raven 2008) and electron donors are therefore unlimited, NPPe is readily equated to NPP (by multiplying carbon fluxes by the average oxidation state of organic carbon). As water isn't limiting to autotrophy,

remineralization of organic carbon and release of metabolic water does not increase rates of primary productivity (though preferential remineralization of organic matter can release nutrients to stimulate additional productivity). Before the evolution of oxygenic photosynthesis, it is valuable to consider that NPPe would have been significantly lower than NPP, as remineralization of organic matter and recycling can at best only result in stoichiometric recycling of electrons back to organic matter (though under anoxic conditions a large fraction of electrons are lost from the biosphere during remineralization via release of biogenic methane to the atmosphere, e.g. Crowe et al. 2011, Ward et al. 2016). NPPe therefore provides a helpful measure for tracking the biomass carrying capacity of the biosphere, as it is not inflated by stoichiometrically coupled remineralization and recycling.

2.1 Major electron donors

It is thought that the early, pre-oxygen biosphere was fueled by anaerobic autotrophic metabolisms such as methanogenesis and anoxygenic photosynthesis. As these metabolisms cannot utilize water as an electron donor, they rely on other electron donor compounds as sources of reducing power for carbon fixation such as molecular hydrogen (for hydrogenotrophic methanogenesis or anoxygenic photosynthesis) or reduced iron or sulfur species (for anoxygenic photosynthesis). A potential limit to the productivity of the early biosphere is therefore based on the availability of these electron donor compounds. In order to estimate the rates of primary production that these metabolisms could support, previous studies have employed steady state estimates of the concentrations of these electron donors (e.g. dissolved iron content of Archean seawater, and atmospheric hydrogen concentrations with models of upwelling or diffusive flux into the photic zone) (e.g. Kharecha et al. 2005, Canfield et al. 2006). These models assumed steady state concentrations balanced by biological oxidation, recycling, and geological supply. These steady states are stable only so long as the

geological supply of electron donors is sufficient to balance their biological consumption, but break down as biological productivity outpaces geological rates of supply, lowering potential rates of productivity no matter the steady state concentration or internal recycling of electron donor compounds. These previous estimates serve as upper-bound estimates of NPP or GPP, rather than NPPe, incorporating recycling fluxes that increase the apparent amount of carbon that has been fixed over a time period without actually shifting the carrying capacity of the Earth as a whole, as this recycling-driven productivity flux is stoichiometrically balanced by remineralization. Here, we focused on the number of electrons delivered from the solid Earth to the biosphere, and the resulting net amount of biomass (here considered as moles of organic carbon) that can be produced per year. We therefore used the flux of electron donors like ferrous iron and molecular hydrogen to the oceans/atmosphere, as estimated by geological processes like hydrothermal alteration of crust and volcanic outgassing, without assumption of particular steady state concentrations.

As discussed above, our estimates of NPPe ignore recycling of electron donors by design. The remineralization of organic carbon coupled to anaerobic respiration or fermentation processes, followed by fixation of organic carbon and consumption of recycled electron donors, stoichiometrically cancel. As a result, recycling in anoxic ecosystems can impact the growth rate of primary producers and gross primary production, but not shift the total biomass that the ecosystem can support at a particular time, as electron balance must be maintained. This is in contrast to oxygenic photosynthesis, in which preferential remineralization of nutrient-rich biomass can fertilize additional primary production without complete remineralization of preexisting biomass. Nutrient-rich components of organic matter are preferentially remineralized (resulting in degraded and buried organic matter with progressively higher C:N and C:P ratios than for fresh biomass, Clark et al. 1998, Berner 2006), resulting in recycling of

nutrients that can fuel further productivity. As a result, nutrients can be recycled to boost NPPe while electron donors cannot.

Ferrous iron (Fe^{2+}) is ultimately supplied from weathering and alteration of rocks, and so its supply to the biosphere is tied to the production and weathering of new crust. Fluxes of reduced iron from production and weathering of oceanic crust were derived from Lécuyer and Ricard (1999). It is assumed that the Fe^{2+}/Fe^{3+} ratio of new crustal material has been constant since accretion, following mantle redox (Canil 1997, Williams et al. 2012). Hydrothermal fluxes were derived from Elderfield and Schultz (1996). It is possible that hydrothermal fluxes may have been different than today, but even the sign of this difference remains uncertain: it has been argued that Archean hydrothermal fluxes may have been up to ten times higher than modern based on Des Marais (2000), but it is also possible that Archean hydrothermal fluxes were lower than today associated with sluggish tectonic rates (e.g., Korenaga 2006). Consequently we used modern hydrothermal fluxes to approximate those on the Archean Earth.

Molecular hydrogen is supplied to the fluid Earth by a variety of sources, including volcanism and water-rock interactions in the oceans and continental subsurface. Fluxes of volcanic gases including H_2 have been estimated by Holland (2002) and the contribution of various pathways of continental and oceanic water/rock interactions to H_2 fluxes have been collected by Sherwood Lollar et al. (2014) and were summarized in Table 1. Additional fluxes of H_2 may have been provided by other geological processes, such as magnetite authigenesis as has recently proposed for Mars (Tosca et al. 2018); however, the magnitude of these potential fluxes are not constrained for the early Earth, and so they are not included in our estimates here.

The fluxes of ferrous iron and molecular hydrogen to the Archean biosphere were estimated here to be of the same order ($\sim$1.5-6x10^{12} moles/year). If fluxes of both of these compounds are stoichiometrically oxidized to drive organic carbon fixation via anoxygenic photosynthesis, the contribution of hydrogen to productivity will be double that of iron as the

oxidation of H_2 to H^+ provides two electrons to the one from Fe^{2+} to Fe^{3+}. Therefore even in the most productive scenario presented here (Scenario 1, Table 2) hydrogen will fuel several times more productivity than iron.

2.2 Phosphate

Phosphate is a necessary component of all cells, and its availability is dependent on geological supply rather than biological fixation, and is therefore commonly taken to be the primary limiting nutrient for marine primary productivity over long timescales (Van Cappellen and Ingall 1996, Tyrrel 1999, Planavsky et al. 2010, Laakso and Schrag 2014, Reinhard et al. 2017). The availability of phosphate in seawater over time has been challenging to constrain; proxy records are complicated (e.g. Planavsky et al. 2010, Reinhard et al. 2017) and the concentrations of marine phosphate reflect the interplay of a wide range of geological, hydrological, biological, and other factors. We therefore examined a variety of influences on phosphate supply, recycling, and burial in order to make conservative estimates of the net availability of phosphate to the pre-oxygen biosphere.

The ultimate source of bio-available phosphate is chemical weathering of phosphate-bearing minerals in rocks. The extent of chemical weathering that occurred on the Archean Earth—and therefore the delivery of phosphate to the oceans—is evident through the extensive development of carbonate platforms at a similar cadence to modern carbonate-bearing basins (Grotzinger and James 2000); this requires similar fluxes of dissolved inorganic carbon and alkalinity, and thus chemical weathering products to the oceans (Higgins et al. 2009). It has even been suggested that weathering of phosphate during Archean time was more efficient due to the increased solubility of apatite in rain and river water made more acidic by elevated atmospheric pCO_2 (Hao et al. 2017).

While chemical weathering of continental crust is the primary mechanism for oceanic phosphate delivery today, weathering and alteration of seafloor basalts—such as at hydrothermal vents—may have been significant on the early Earth. Basalt typically contains much higher phosphorous concentrations than average continental crust (up to ~8000 ppm versus 700 ppm, Taylor et al. 1995, Horton 2015), and so has the potential to be a major phosphate source to the oceans. Hydrothermal vents in modern ocean basins are thought to be a net sink of phosphate (e.g. Elderfield and Schultz 1996) as a result of the sorption of phosphate to metal oxides that precipitate as metal-rich hydrothermal fluids interact with oxygenated seawater (Wheat et al. 1996). Before the oxygenation of the oceans led to extensive water column metal oxidation, hydrothermal systems may have instead served as a major source of phosphate to the oceans.

Since even the sign of difference in phosphate weathering between the Archean and modern Earth is unclear, a reasonable estimate is to use weathering-based phosphate delivery to the oceans from modern riverine input, around 7×10^{10} moles P/year (Tyrrel 1999) (Table 1). This estimate is approximate over a range of a few-fold, due to uncertainties in the lithology of the early crust and weathering rates, but is a reasonable starting estimate, particularly given that in the modern oceans most productivity is supported not by new delivery of phosphate, but by recycling. Biology has developed multiple strategies for maximizing uptake and recycling of this vital nutrient, and as a result the relationship between phosphate input and primary productivity in the modern ocean suggests that phosphorous is recycled on the order of 500 times between input to the ocean and burial (Tyrrel 1999). Whether this extent of efficient recycling occurred on the early Earth remains an open question, but it is reasonable to suspect that some recycling did occur. We therefore added an additional estimate for phosphate delivery to the photic zone to yield an estimate for comparison, via upwelling of nutrient-rich bottom waters in a manner analogous to the modern ocean using estimates of deep-water

phosphate concentrations (from phosphate concentrations in marine sedimentary rocks like banded iron formations) and typical rates of vertical mixing (eddy diffusivity) in marine basins. Assuming deep-water phosphate concentrations were about 10% of modern values due to sorption of phosphate onto iron oxides (Bjerrum and Canfield 2002), along with a typical linear vertical mixing rate of ~3 m/year (Broecker and Peng 1982), delivery of recycled bottom water phosphate to the surface ocean would be on the order of 4×10^{10} moles P/year (Table 1). This is a conservative estimate, as high silica concentrations in the Archean oceans may have hindered binding of phosphate to iron oxides (Konhauser et al. 2007). It is also possible that Archean iron formations were primarily deposited as ferrous-rich silicate phases (Rasmussen et al. 2015, Rasmussen et al. 2016), lowering the predicted abundance of iron oxides in the environment, and thus their potential for limiting phosphate availability (Supplemental Information); it was also hypothesized that modulation of deep water phosphate concentrations by the solubility of ferrous phosphate compounds such as vivianite may have occurred (Derry 2015).

2.3 Fixed nitrogen

Nitrogen is a critical element for all known life, where it is used in essential biomolecules such as amino and nucleic acids. However, most nitrogen on Earth is found as relatively unreactive N_2 in the atmosphere, and must be fixed to more bioavailable forms before it can be incorporated into biomass. In modern environments, fixed nitrogen is supplied primarily by diazotrophs using the nitrogenase enzyme complex (e.g. Canfield et al. 2010). The antiquity of nitrogenase—and biological nitrogen fixation more broadly—is contested, with estimates ranging from its presence in the last universal common ancestor of all organisms, to a much later evolution closer in time to the GOE (e.g. Weiss et al. 2016, Boyd et al. 2011). Despite some efforts to develop a Precambrian nitrogen isotope record, little consensus has been reached about the nature of the Archean nitrogen cycle (e.g. Garvin et al. 2009, Zerkle et

al. 2017), and even the N_2 content of the Archean atmosphere is poorly constrained (e.g. Som et al. 2016, Zerkle and Mikhail 2017). It is therefore challenging to assign with certainty the nature of the early nitrogen cycle, though some process or processes must have been responsible for supplying fixed nitrogen to the early biosphere. With the above caveats regarding knowledge of the early biological nitrogen cycle, a conservative bound for the nitrogen supply to the early biosphere is via estimates of abiotic mechanisms that are thought to have occurred at this time. Abiotic nitrogen fixation occurs through a variety of processes, including the fixation of N_2 into reduced forms via high temperature and reducing conditions at hydrothermal vents ($\sim 10^{10}$ moles N per year, Brandes et al. 1998), fixation of N_2 to NO (which would reach the oceans as NO_3^-, Mancinelli and McKay 1988, Wong et al. 2017) or to HCN (which would reach the oceans as NH_3, Navarro-Gonzalez et al. 2001) by lightning ($\sim 10^{12}$ moles N per year, Navarro-Gonzalez et al. 1998, Navarro-Gonzalez et al. 2001, Wong et al. 2017), and the photochemical production of HCN ($\sim 2 \times 10^{12}$ moles N per year, Tian et al. 2011). Very early in Earth history, abiotic nitrogen fixation rates may have been even higher due to additional production of N_2O and HCN via atmospheric chemistry driven by frequent coronal mass ejections, though this process may have become less significant by Archean time as the frequency of superflares declined (Airapetian et al. 2016).

The primary mechanism of abiotic N fixation, and the N species produced, is expected to vary with the CH_4: CO_2 ratio of the early atmosphere. Under a high CO_2 atmosphere, lightning-based N fixation would produce large fluxes of NO, which would reach the oceans as NO_3^- on the order of 10^{12} moles N/year (Mancinelli and McKay 1988, Navarro-Gonzalez et al 1998, Navarro Gonzalez et al 2001). However, under the relatively high methane concentrations that are hypothesized to have been present in the Archean atmosphere (e.g. Pavlov et al. 2000, Kasting et al. 2001, Pavlov et al. 2001), lightning-based N fixation would have primarily produced HCN (Navarro Gonzalez et al. 2001), and photochemical HCN

production may have been quite high (Tian et al. 2011), potentially totaling ~3×10^{12} moles N/yr. Under either scenario, fluxes of fixed nitrogen would have been on the order of 10^{12} moles N per year. This is a minimum value, disregarding any recycling of organic nitrogen, which may have been a significant process before O_2 was available to fuel nitrification and a complete nitrogen cycle (Zerkle and Mikhail 2017). Additional sources of bioavailable nitrogen to the early biosphere may have been through rock weathering, both of nitrogen in primary igneous rocks as well as recycling of fossil organic nitrogen in sediments (e.g. Houlton et al. 2018).

2.4 Other nutrients and electron donors

While sulfur isotope analysis of early Archean stromatolite and microbialite samples indicates that microbial sulfur cycling was active at this time (e.g. Shen et al. 2001, Bontognali et al. 2012), it is expected that sulfur-based autotrophy played only a minor role in the Archean oceans due to the rapid titration of sulfide to form iron-sulfide precursors and pyrite in an iron-rich water column (Walker and Brimblecombe 1985, Canfield 2004). As a result, sulfate concentrations were very low in Archean seawater (Habicht et al. 2002, Crowe et al. 2014, Paris et al. 2014), and so the contribution of sulfate reduction to remineralization was likely minor, and recycling of sulfur was minimal (Fischer et al. 2014). In sum it is therefore likely that sulfur metabolisms contributed only very small amounts of productivity to the Archean biosphere, 1-4 orders of magnitude less than molecular hydrogen (Kharecha et al. 2005, Canfield et al. 2006). Incorporation of a sulfur-based productivity model would shift the expected rates of productivity presented here slightly, but because the availability of sulfur is much less than iron (Walker and Brimblecombe 1985), this shift would be even smaller than the difference between an anoxygenic phototrophic biosphere with and without iron oxidation (Scenario 1 and Scenario 2 in Table 2). Assuming a volcanic SO_2 outgassing flux of ~10^{11}

moles/year (Ono et al. 2003), sulfur could fuel at most only about 4×10^{10} moles carbon fixed/year, less than 2% of the estimate for H_2-fueled productivity.

While it has been proposed previously that the supply of trace metal cofactors may have been a limitation to the productivity of early primary producers (e.g. Anbar and Knoll 2002, Saito et al. 2003), this has not been demonstrated for the anoxygenic organisms expected to drive much of primary productivity before the evolution of oxygenic photosynthesis. Consideration of individual trace metals shows that metals important to organisms performing methanogenesis and anoxygenic phototrophy (e.g. Fe, Ni) were relatively abundant early in Earth history compared to metals that are less essential for these organisms (e.g. Cu, Mo, Zn) (Williams and Rickaby 2012, Robbins et al. 2016). Methanogens and anoxygenic phototrophs may even have inherited their suite of metal cofactor demands as a result of their evolution and diversification in the early ferruginous oceans in a manner analogous to that which has been proposed for Cyanobacteria in euxinic Paleoproterozoic environments (Saito et al. 2003).

While a source of inorganic carbon is necessary to support autotrophic carbon fixation, this is not expected to have been limiting for the early biosphere. The composition of the Archean atmosphere is poorly constrained, but it is generally thought that pCO_2 and dissolved inorganic carbon was significantly higher than today (Hotinski et al. 2004, Fischer et al. 2009, Blättler et al. 2016), partially due to geological constraints such as the mineralogy of Archean paleosols (Rye et al. 1995) and partially as a satisfactory solution for maintaining a clement climate under the faint young sun (e.g. Kasting 1987). CO_2, as dissolved inorganic carbon, should therefore have been well in excess of the demands of the early biosphere, both as a source of carbon for fixation of biomass as well as the terminal electron acceptor for cellular redox balance in metabolisms like methanogenesis and anoxygenic photosynthesis. Because CO_2 is predicted to have been available as an abundant electron acceptor, primary production on the early Earth need not be considered electron acceptor limited, though the efficiency of

heterotrophic remineralization was likely limited in a manner similar to low-energy anaerobic ecosystems today in which the availability of electron acceptors limits the amount of energy conserved by, and resulting growth rate and yield of, respiratory heterotrophic microbes.

3 The electron donor-limited early biosphere

The results of these calculations show that H_2 was likely the most significant electron donor for the biosphere prior to water oxidation, with relatively minor contributions from ferrous iron and reduced sulfur species. Moreover, the results suggest that fluxes of nutrients like fixed nitrogen and phosphorus were in great excess to those of electron donors. This is important because it suggests that the geological supply of electron donors may have been a fundamental limit on primary productivity before the evolution of oxygenic photosynthesis (Figure 1, Table 2). While iron oxidation has been considered a significant source of energy to the early biosphere (e.g. Fischer and Knoll 2009), its relative contribution to rates of primary productivity is contested (e.g. Kharecha et al. 2005, Canfield et al. 2006), and depending on interpretations of the original mineralogy and genesis of iron formation sediment it is possible that biological iron oxidation in the Archean oceans was minimal (Rasmussen et al. 2013, Rasmussen et al. 2015, Rasmussen et al. 2016; Rasmussen et al. 2017, Johnson et al. 2018, Supplemental Information). Regardless of the topology of the early iron cycle, our estimates here for the maximum rates of iron-fueled productivity (Table 2) suggest that iron was at best a minor fuel for the early biosphere compared to molecular hydrogen. Though re-reduction of iron oxides could provide recycled ferrous iron to fuel additional productivity, this would be stoichiometrically balanced by organic carbon remineralization, and so would not contribute to increasing NPPe. Tallied altogether, we estimated that global NPPe was likely no higher than $\sim 1.375 \times 10^{13}$ moles e$^-$/yr (yielding $\sim 2.75 \times 10^{12}$ moles organic C/yr), and perhaps somewhat less if iron did not serve as an electron donor for photosynthesis. This value is more than 1000x

lower than modern productivity (Figure 2), and lower than previous estimates of Archean productivity (e.g. Kharecha et al. 2005, Canfield et al. 2006). This value is moreover an upper bound on productivity assuming perfect efficiency of converting electrons from H_2 into biomass; actual values of NPPe may have been lower due to relatively inefficient consumption of H_2 by methanogens (as discussed below) in H_2-replete but aphotic environments such as the subsurface or deep marine hydrothermal vents. While it is always possible that productivity was limited by other nutrients in localized environments, aspects of ecology, or other environmental challenges (e.g. temperature or UV stress), the results presented here suggest that it was the geological flux of electron donors that fundamentally limited primary production of the biosphere as a whole. This makes sense, as organisms have evolved to become more efficient with their use and recycling of nutrients (e.g. reducing phosphorous demand via alternative membrane lipids, Van Mooy et al. 2006, or diel reallocation of trace metals between photosynthesis and nitrogen fixation, Saito et al. 2011), but electron donors are stoichiometrically consumed during the fixation of organic carbon and other than reduction in cell size there is no apparent means for reducing cellular organic carbon demand.

Molecular hydrogen is an incredibly versatile and favorable electron donor for diverse metabolisms (hydrogenotrophy), including methanogenesis, acetogenesis, anoxygenic photosynthesis, and both aerobic and anaerobic lithotrophy. Of these, lithotrophy is not expected to have been significant before the rise of oxygen, as it relies on respiratory electron acceptors such as dioxygen or sulfate that were scarce prior to the evolution of oxygenic photosynthesis. Though the absolute ages of metabolic pathways are largely unknown, methanogenesis and acetogenesis are thought to be relatively ancient and among the earliest metabolisms to appear on Earth (Battistuzzi et al. 2004, Martin and Russell 2007), and so may have been responsible for primary productivity in the earliest stages of biosphere.

While the timing of evolution of anoxygenic photosynthesis is not well constrained, it may have been late relative to other anaerobic metabolisms due to the complexity of the electron transport chains associated with high potential metabolic pathways such as respiration and phototrophy (Fischer et al. 2016). The evolution of anoxygenic photosynthesis may have led to a significant boost in primary productivity, as this metabolism provides an efficient biochemical logic for carbon fixation per flux of electron donor compounds as compared to lithotrophic metabolisms (e.g. Ward et al. 2017). Methanogenic productivity is limited by the necessity of consuming electron donor compounds to supply cellular energy as well as to fix carbon—a limitation absent in anoxygenic phototrophs that can either directly generate NADPH via type I reaction centers and/or can run cyclic electron flow to generate ATP and complete reverse electron transport (Madigan et al. 2012). Methanogens, as a result, must channel electrons into methane to conserve energy, and only fix on the order of 1 mole of organic carbon for every 10 moles of methane generated, dropping their expected productivity by an order of magnitude (e.g. Thauer et al. 2008). This leads to a drop in yield from $\sim 2.4 \times 10^{14}$ cells/mol H_2 for anoxygenic phototrophs to $\sim 1.7 \times 10^{13}$ cells/mol H_2 for methanogens (assuming average oxidation state of organic carbon of -1, ~ 10 femtograms of carbon per cell, and maximum yields for methanogens without cytochromes of 3 g per mole of CH_4 (Whitman et al. 1998, Thauer et al. 2008). As a result of this relative inefficiency of methanogenesis, primary productivity could have increased by about a factor of ten following the evolution and expansion of anoxygenic photosynthesis (from Scenario 2 to Scenario 3 in Table 2 and Figure 1).

Determining the age of anoxygenic photosynthesis will therefore be important for understanding transitions in the scale of primary productivity through time. While there is some evidence for anoxygenic photosynthesis as early as ~ 3.4 Ga in the form of depth-dependent accumulation of organic carbon in microbial mat laminae (Tice and Lowe 2004), these

observations are unfortunately not diagnostic for any crown-group anoxygenic photosynthetic bacteria, and may record now extinct stem-group phototrophic lineages, as many extant anoxygenic phototrophic lineages appear to have radiated after the GOE following horizontal gene transfer of phototrophy genes from older, unknown donor lineages (e.g. Fischer et al. 2016, Shih et al. 2017b, Ward et al. 2018, Brinkmann et al. 2018). Less ambiguous evidence for the antiquity of anoxygenic photosynthesis comes from the biological record, which demonstrates by the relationships between oxygenic photosystems and anoxygenic reaction centers that some form of anoxygenic photosynthesis must have arisen much earlier than the evolution of oxygenic photosynthesis (Fischer et al. 2016). This evidence, however, only provides a sense of the relative timing of anoxygenic photosynthesis, with confirmation of absolute ages requiring additional insight from the rock record.

It is valuable to note that even for a molecular hydrogen-fueled early biosphere, iron serves as the ultimate source of most electrons from the solid Earth—water/rock interactions in hydrothermal vents, continental crust, and other environments result in the transfer of electrons from iron in rocks to molecular hydrogen, which is then released to the biosphere (Mayhew et al. 2013, Sherwood Lollar et al. 2014). Iron is the single largest reservoir of electrons in the Earth's crust (Walker and Brimblecombe 1985), yet is comparatively inaccessible to biology, and so the extent to which life can be rock-powered is dependent on the extent of hydrothermal alteration and delivery to the oceans. Thus at a planetary scale, water is the crucial intermediary in the transfer of electrons from rocks to life, particularly in the absence of photosynthesis.

3.1 Trends in primary production over Earth history

Based on the calculations presented above, it appears that geologically sourced electron donors, principally molecular hydrogen, set the fundamental limit for rates of net primary production before the evolution of oxygenic photosynthesis. These estimates are

approximate—given limited understanding of several aspects of the Archean Earth such as volcanic outgassing and weathering rates and atmospheric compositions, and the results carry the uncertainties associated with a few-fold error in any given input term.

These estimates, combined with known changes in productivity that occurred later in Earth history, after the rise of oxygenic photosynthesis, allow one to assemble an approximate trajectory of primary productivity through time (Figure 2). After the origin of life, the biosphere is expected to be supported by anoxic, nonphototrophic metabolisms such as methanogenesis and acetogenesis; productivity at this time would have been low, particularly given the inefficiency of these metabolisms in terms of carbon fixed per unit of electron donor consumed, and so NPPe was likely less than ~1.25×10^{12} moles e$^-$/year (i.e. ~0. 25×10^{12} moles organic carbon/yr). Following the evolution of anoxygenic photosynthesis somewhat later in Earth history (potentially by ~3.4 Ga, Tice and Lowe 2004), maximum NPPe would have risen by an order of magnitude to ~1.25×10^{13} moles e$^-$/year (i.e. ~0. 25×10^{13} moles organic carbon/yr), due to the increased energetic efficiency of photosynthetic metabolisms. Following the evolution of oxygenic photosynthesis by Cyanobacteria (perhaps as late as the GOE, ~2.3 Ga, Fischer et al. 2016, Shih et al. 2017a), and the introduction of water as a (virtually) unlimited electron donor, the productivity of the biosphere increased by the largest amount at any transition in Earth history. After the evolution of oxygenic photosynthesis, primary production was limited by the availability of nutrients such as phosphate (e.g. Reinhard et al. 2017), fixed nitrogen (e.g. Stüeken 2013), and perhaps trace metals (e.g. Anbar and Knoll 2002) and other trace molecules like vitamins (Monteverde et al. 2017). Productivity during this period is not well constrained, but geochemical evidence for anoxia in marine basins suggests that atmospheric oxygen concentrations and/or net productivity remained intermediate throughout the Proterozoic Eon (e.g. Reinhard et al. 2013, Crockford et al. 2018), perhaps maintained at a low-oxygen steady state by feedbacks related to modulation of phosphate availability due to interaction with

dissolved iron (Laakso and Schrag 2014, Derry 2015, Laakso and Schrag 2018). By the beginning of the Phanerozoic Eon, following the evolution and later diversification of eukaryotic algae in Proterozoic time (Brocks et al. 2017), marine productivity may have increased to near modern levels, while the evolution and expansion of land plants likely led to a near doubling of the total productivity of the biosphere as terrestrial productivity first became significant. A final boost to productivity may have been associated with the expansion of angiosperms in the Cenozoic (Boyce and Zwieniecki 2012, Boyce and Lee 2017), finally reaching the levels of productivity seen today—likely the highest in Earth history.

The pre-oxygen biosphere therefore appears to have been much lower in productivity than later in Earth history, and to have been more fundamentally constrained by geological, rather than biological, processes. In other words, before the GOE, the Earth set the tempo for the biosphere, and maintained it at low levels of productivity. As a result, while life may have had some limited impacts on the Earth system such as drawing down atmospheric concentrations of H_2 (limiting its efficacy as a greenhouse gas, e.g. Wordsworth and Pierrehumbert 2013) and converting H_2 into CH_4 (increasing greenhouse effect, e.g. Kasting 1987, or contributing to organic haze, Arney et al. 2017, though the magnitude of this flux depends on the relative H_2 consumption of methanogens versus phototrophs), the early biosphere may have been inefficient at driving many geochemical cycles and may have been less capable of serving as a self-regulating feedback to the Earth system. Gaia—in the sense of life as a self-regulating feedback capable of regulating climate and habitability of the planet (e.g. Lovelock and Margulis 1974)—may not have been born until relatively late in Earth history, after the evolution of oxygenic photosynthesis, when life finally became sufficiently productive to play a dominant role in controlling geochemical cycles and climate feedbacks on the surface of the Earth.

3.2 Implications of electron limitation on the biosphere before oxygenic photosynthesis

If nitrogen were not limiting to productivity before the rise of oxygen, there may not have been strong evolutionary pressure to evolve biological nitrogen fixation at this time. Nitrogen fixation is an energetically costly process, especially for the energy- and electron-limited organisms characteristic of the pre-oxygen biosphere, and so there would be a clear advantage to making use of abiotically fixed nitrogen rather than investing in biological nitrogen fixation via nitrogenase. While there may have still been locally nitrogen-limited environments conducive to the early evolution of nitrogenase, it is conceivable that the evolution of this enzyme complex (or at least emergence of the crown group forms that are found today), was relatively late, postdating the last universal common ancestor, after the evolution of anoxygenic photosynthesis, or potentially even as late as the GOE. This is consistent with some phylogenetic and molecular clock analyses of the evolution of the nitrogenase family (e.g. Boyd et al. 2011) but will require further evidence to confidently assess.

Alternatively, nitrogenase may have evolved much earlier but for a different function and was only later coopted for fixation of N_2. Under high-methane conditions, the product of atmospheric (lightning and photochemical) nitrogen fixation would primarily be HCN (Navarro-Gonzalez et al. 2001, Tian et al. 2011, Airapetian et al. 2016). Following rainout to the ocean, HCN could hydrolyze to form NH_4OH (Zahnle 1986), but can also be taken up directly by biology via nitrogenase (Dekas et al. 2009). One hypothesis holds that large fluxes of HCN to the oceans may therefore have triggered the evolution of nitrogenase first as a way to detoxify and take up HCN, and was only later coopted to N_2 fixation (e.g. Silver and Postgate 1973, Raymond 2005). These scenarios are consistent with a methanogen origin for nitrogenase as previously proposed (Boyd et al. 2011), an idea that gains strength given the shared ancestry and similar biochemistry between nitrogenase subunits and those involved in

the synthesis of coenzyme F430—a nickel-containing tetrapyrole used by methyl-coenzyme M reductase (e.g. Zheng et al. 2016). That in mind, the largely unexplained occurrence of N_2 and HCN fixation by methanogenic and ANME archaea in ammonia-rich sediments (e.g. Dekas et al. 2009) suggests that nitrogenase may play additional physiological roles in anaerobic and fixed-nitrogen replete environments that remain poorly understood (e.g. as an electron sink to maintain cellular redox balance).

The limitation of net primary productivity of anoxygenic biospheres by the availability of electron donors has significant implications not only for our understanding of the size of the biosphere on the early Earth, but potentially on other worlds as well. This is particularly relevant for ice-covered worlds like Europa and Enceladus, where the photosynthetic use of water as an electron donor is impossible due to the lack of light penetration to the ocean. As a result, the size and productivity of any biosphere on these worlds would be limited by the flux of electron donor compounds from water/rock interactions at the base of their subsurface oceans. Since anoxygenic photosynthesis would also be impossible in these environments, the efficiency and yield from consumption of these electron donors may be low. This would be true whether dioxygen is supplied to the ocean from radiolysis of ice on the surface or not; aerobic lithotrophic metabolisms typically have low efficiency per electron donor (Ward et al. 2017), of a similar order to methanogenesis (e.g. 40 Fe^{2+} oxidized to Fe^{3+} per 1 C fixed when using O_2, compared to 4-6 Fe^{2+} oxidized to Fe^{3+} per 1 C fixed when using light, Ehrenreich and Widdel 1994, Neubauer et al. 2002). This has valuable implications for the potential abundance, productivity, and detectability of life on icy moons, and can be leveraged to make expectations that bear on life detection missions. Of particular interest is the detection of H_2 in Enceladus' plume by Cassini (Waite et al. 2017), because an electron-limited biosphere would be expected to have consumed this H_2—unless another nutrient such as phosphorous can be shown to be even more limiting to a potential biosphere on Enceladus, the detection of H_2 at Enceladus

could be regarded as an 'antibiosignature' (Catling et al. 2018) indicating that this moon is

uninhabited even if it is habitable.

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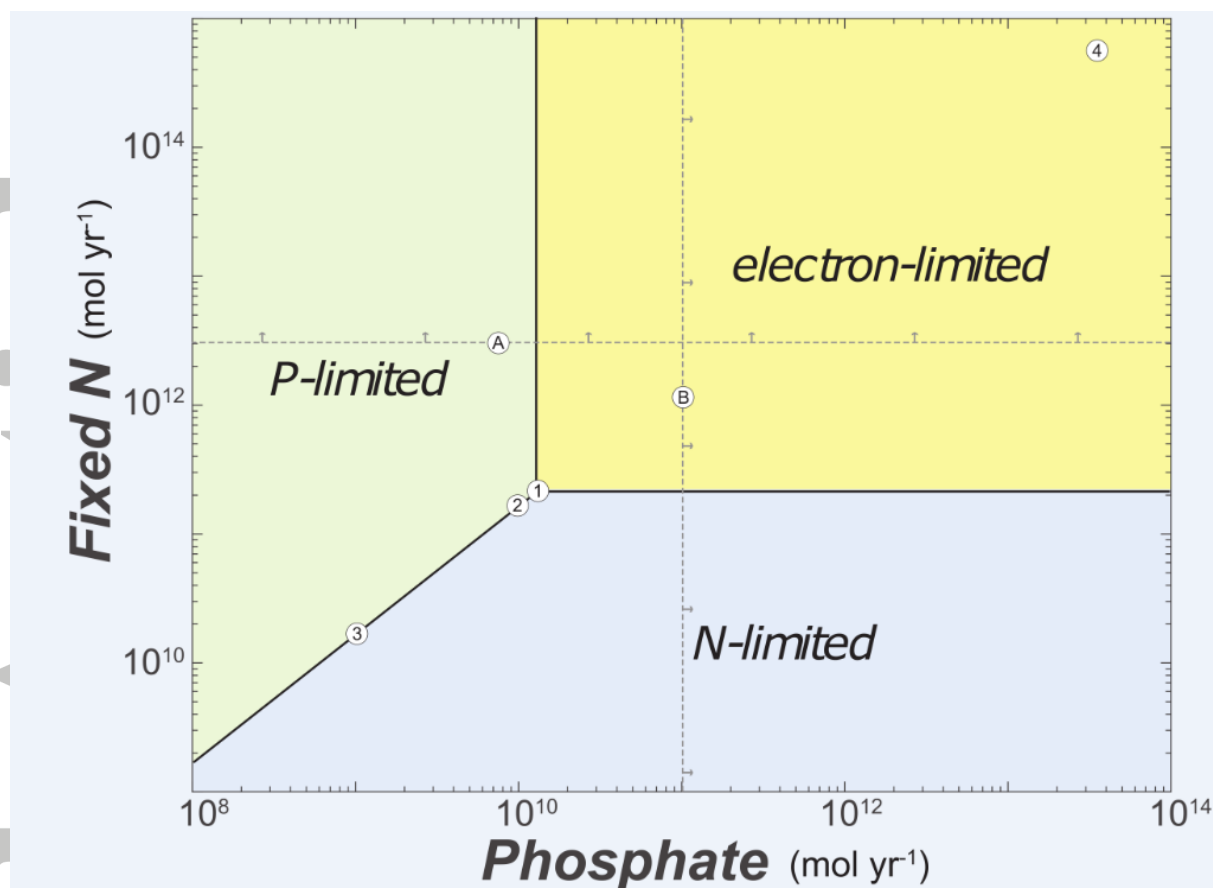
Table 1: Phosphate, fixed nitrogen, and electron donor fluxes to the pre-oxygen biosphere.

| Flux	Nutrient flux (10^{12} moles/yr)	Citation	Notes
Phosphate (rivers)	0.0722	Tyrrel 1999	New nutrient
Phosphate (upwelling)	0.04	10% average modern marine deep water P concentrations per Bjerrum and Canfield 2002, typical vertical mixing from Broecker and Peng 1982	Recycling flux from remineralization at depth and upwelling from deep water
Fixed N (photochemistry)	2	Tian et al. 2011	Production of HCN in relatively high CH_4 atmosphere
Fixed N (hydrothermal)	0.01	Brandes et al. 1998	
Fixed N (lightning)	0.714	Navarro-Gonzalez et al. 1998, Navarro-Gonzalex et al. 2001, Wong et al. 2017	NO from high CO_2 atmosphere, or HCN from high CH_4
H_2 (volcanic outgassing)	4.7	Holland 2002	
H_2 (water-rock interactions)	1.36	Sherwood Lollar et al. 2014	Sum of continental and oceanic fluxes
Fe^{2+} (hydrothermal)	0.19	Elderfield and Schultz 1996	
Fe^{2+} (production of new crust)	1.4	Lecuyer and Ricard 1999	

Table 2: Productivity scenarios referenced in Figure 1.

Scenario	Description	NPPe (10^{12} moles e$^-$/yr)	Required P flux (10^{12} moles/yr)	Required N flux (10^{12} moles/yr)
1	Electron donor limited anoxygenic photosynthesis (H_2 and Fe^{2+})	13.75	0.0259	0.415
2	Electron donor limited anoxygenic photosynthesis without photoferrotrophy (H_2)	12.15	0.0229	0.367
3	Electron donor limited methanogenesis (H_2)	1.215	0.00229	0.0367
4	Modern marine productivity (oxygenic photosynthesis)	20000	37.7	604

Figure 1: Phosphate and fixed nitrogen fluxes to the biosphere, and resulting phase space for limitation on productivity. Electron donor, N, and P limitation fields assuming productivity in Scenario 1 (anoxygenic photosynthesis limited by iron and hydrogen as electron donors). Scenarios 2 (anoxygenic photosynthesis without iron as an electron donor) and 3 (methanogenesis only) shift the electron limited field down and to the left. Predicted nitrogen (A) and phosphate fluxes (B) are well in excess of the demand of the electron limited rates of productivity predicted here, suggesting that the pre-oxygen biosphere was fundamentally limited by the supply of electron donor compounds.
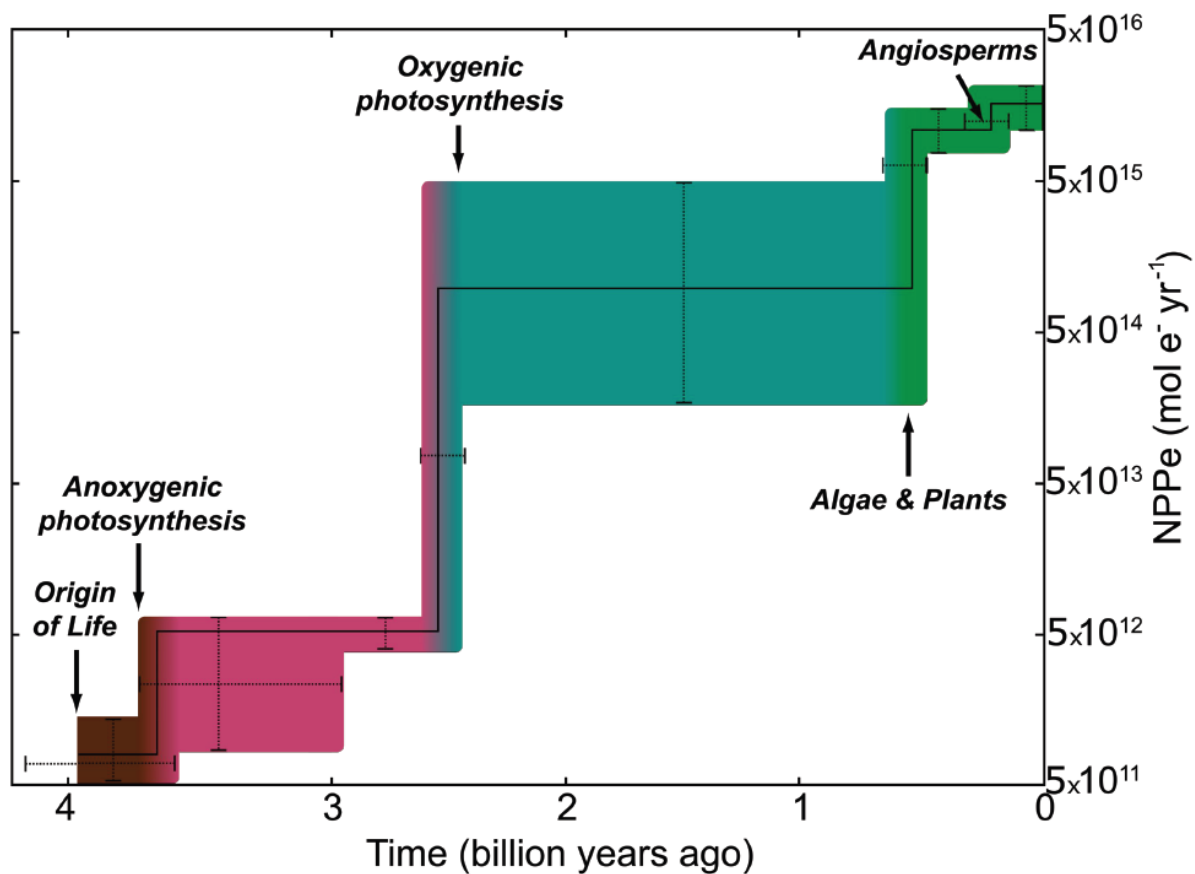
Figure 2: Estimates for the productivity of the biosphere (moles of electrons used to fix organic carbon per year, on a log scale) Earth history. To first order, the productivity of life on Earth has increased through time, beginning near 0 at the origin of life to the high rates observed today. The earliest biosphere was supported by nonphototrophic metabolisms like methanogenesis and acetogenesis (brown), limited by supply of electron donors and the efficiency of these metabolisms. Following the evolution of anoxygenic photosynthesis, productivity increased ~10-fold due to the inherent energetic efficiency of these metabolisms per supply of electron donor (pink). The evolution of oxygenic photosynthesis by Cyanobacteria (cyan), productivity increased drastically due to the use of water as an unlimited electron donor. Productivity throughout Proterozoic time is poorly constrained. The evolution and expansion of eukaryotic algae, land plants, and angiosperms led to subsequent increases in productivity to modern levels (green). Error bars capture uncertainty in timing of evolution of major autotrophic metabolisms (horizontal) as well as uncertainty in net primary productivity at a particular period in time (vertical) as discussed in section **3.1** of the text.