Anoxygenic photosynthesis modulated Proterozoic oxygen and sustained Earth’s middle age

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Contributed by A. H. Knoll, August 14, 2009 (sent for review January 6, 2009)

Molecular oxygen (O2) began to accumulate in the atmosphere and surface ocean ca. 2,400 million years ago (Ma), but the persistent oxygenation of water masses throughout the oceans developed much later, perhaps beginning as recently as 580–550 Ma. For much of the intervening interval, moderately oxic surface waters lay above an oxygen minimum zone (OMZ) that tended toward euxinia (anoxic and sulfidic). Here we illustrate how contributions to primary production by anoxygenic photoautotrophs (including physiologically versatile cyanobacteria) influenced biogeochemical cycling during Earth’s middle age, helping to perpetuate our planet’s intermediate redox state by tempering O2 production. Specifically, the ability to generate organic matter (OM) using sulfide as an electron donor enabled a positive biogeochemical feedback that sustained euxinia in the OMZ. On a geologic time scale, pyrite precipitation and burial governed a second feedback that moderated sulfide availability and water column oxygenation. Thus, we argue that the proportional contribution of anoxygenic photosynthesis to overall primary production would have influenced oceanic redox and the Proterozoic O2 budget. Later Neo-proterozoic collapse of widespread euxinia and a concomitant return to ferruginous (anoxic and Fe2+ rich) subsurface waters set in motion Earth’s transition from its prokaryote-dominated middle age, removing a physiological barrier to eukaryotic diversification (sulfide) and establishing, for the first time in Earth’s history, complete dominance of oxygenic photosynthesis in the oceans. This paved the way for the further oxygenation of the oceans and atmosphere and, ultimately, the evolution of complex multicellular organisms.

Oxidation of molecular oxygen (O2) and other electron acceptors provides Earth’s only major source of molecular and reduced forms of nitrogen and sulfur. Oxygenic photosynthesis introduces 3.4 x 1022 atoms of O2 annually into the atmosphere, with little net production of N2O. At the same time, anaerobic respiration of organic matter in aquatic ecosystems and anaerobic respiration by soil bacteria are the key processes sustaining the atmospheric O2 abundance and balance the O2 inventory in the atmosphere. Proterozoic surface waters underlain by a euxinic OMZ (OMZs) fixed N using anoxygenic photoautotrophs, which oxidize sulfide (S0) with a redox potential of −250 mV to sulfate (SO42−) with a potential of 650 mV. The gas exchange between atmospheric O2 and aquatic OMZs is driven by the redox state of the OMZ, which is characterized by a deep anoxic chemocline that separates oxygenated surface waters from the anoxic OMZ. Proterozoic OMZs were distinctive from modern OMZs, which are typically shallow, thermodynamic heterogeneities that are driven by nutrient cycling and produce methanogenesis.

In Proterozoic surface waters underlain by an anoxic OMZ, fixed N may have exerted fundamental control on total primary productivity (17, 29). Thus, when considering the aggregate of oxygenic and anoxygenic photosynthesis, the Proterozoic nitrogen (N) cycle must be taken into account simultaneously. In the modern oligotrophic ocean, upwelling of remineralized inorganic N provides most of the nutrient N (30) for photoautotrophs. In OMZs, however, N:P often falls well below the Redfield ratio of 16:1, suggesting net N loss via biological denitrification and anammox (31). In mid-Proterozoic oceans, lower PO2 and warmer temperatures (reducing O2 solubility) would have made sulfide much more available for anoxygenic photosynthesis, enhancing their potential contribution to overall primary production. Increasing the relative proportion of anoxygenic photosynthesis would have decreased the direct link between OM burial and O2 generation (Fig. 1). With this in mind, we explore the biogeochemical consequences of mixed oxygenic and anoxygenic photosynthesis in the oceans of Earth’s middle age. In Proterozoic surface waters underlain by an anoxic OMZ, fixed N may have exerted fundamental control on total primary productivity (17, 29). Thus, when considering the aggregate of oxygenic and anoxygenic photosynthesis, the Proterozoic nitrogen (N) cycle must be taken into account simultaneously. In the modern oligotrophic ocean, upwelling of remineralized inorganic N provides most of the nutrient N (30) for photoautotrophs. In OMZs, however, N:P often falls well below the Redfield ratio of 16:1, suggesting net N loss via biological denitrification and anammox (31). In mid-Proterozoic oceans, lower PO2 and warmer temperatures (reducing O2 solubility) would have made sulfide much more available for anoxygenic photosynthesis, enhancing their potential contribution to overall primary production. Increasing the relative proportion of anoxygenic photosynthesis would have decreased the direct link between OM burial and O2 generation (Fig. 1). With this in mind, we explore the biogeochemical consequences of mixed oxygenic and anoxygenic photosynthesis in the oceans of Earth’s middle age. In Proterozoic surface waters underlain by an anoxic OMZ, fixed N may have exerted fundamental control on total primary productivity (17, 29). Thus, when considering the aggregate of oxygenic and anoxygenic photosynthesis, the Proterozoic nitrogen (N) cycle must be taken into account simultaneously. In the modern oligotrophic ocean, upwelling of remineralized inorganic N provides most of the nutrient N (30) for photoautotrophs. In OMZs, however, N:P often falls well below the Redfield ratio of 16:1, suggesting net N loss via biological denitrification and anammox (31). In mid-Proterozoic oceans, lower PO2 and warmer temperatures (reducing O2 solubility) would have made sulfide much more available for anoxygenic photosynthesis, enhancing their potential contribution to overall primary production. Increasing the relative proportion of anoxygenic photosynthesis would have decreased the direct link between OM burial and O2 generation (Fig. 1). With this in mind, we explore the biogeochemical consequences of mixed oxygenic and anoxygenic photosynthesis in the oceans of Earth’s middle age.
Thus, a persistent fixed-N deficiency throughout the OMZ and photic zone (17, 31) becomes likely and would have conferred ecological advantage on photoautotrophs able to fix N2. In the Proterozoic ocean, then, both impinging sulfide and a scarcity of fixed-N would have favored diazotrophic (N2-fixing) photoautotrophic bacteria over eukaryotic algae. Molecular fossils of pigments derived from anoxygenic phototrophs provide direct evidence for photic zone euxinia in Proterozoic oceans (15); such data, however, remain limited.

Widespread OMZ euxinia thus would have exerted a strong influence on the nature of primary producers in mid-Proterozoic oceans. Trace metal scarcity in Proterozoic oceans might further have limited the amount of primary production, via its effects on certain key enzymes (17, 34). The effect of trace metal limitation on primary production in Proterozoic seas remains an area of active debate and experimentation (35–37), but regardless of its resolution, the predominant influence on marine redox conditions in mid-Proterozoic oceans was the proportional contribution of anoxygenic photosynthesis to overall primary production.

Regardless of the source of OM, for energetic reasons, oxidant would still be the favored oxidant for OM remineralization; and as is true today, the propensity toward water column anoxia would scale with the amount of exported OM. Importantly, however, it is the fraction of OM escaping aerobic respiration that would set limits on anoxic photosynthesis (38). In Proterozoic oceans, with low overall NO3− and Fe3+ availability, SO4^2− reduction would have been the principal reductive metabolism after aerobic respiration, generating sulfide within oxygen-depleted OMZs. An increase in photosynthetic electron donation from this sulfide source (rather than from H2O) would depress surface O2 concentrations further, simultaneously enhancing the potential for N2-fixation. This would increase both primary and, presumably, export production—an overall positive feedback on OMZ euxinia (39) (Fig. 2A) that would limit rather than foster PO2 accumulation. That is, when primary production includes a nontrivial contribution from anoxygenic photautotrophy, the generation of organic matter, in principle, exceeds the generation of oxygen available to complete the carbon cycle. This would increase the probability that the OMZ will become euxinic and, in consequence, that sulfidic conditions will encourage the potential for N2-fixation. This photic zone sulfide is available for further anoxygenic photosynthesis—establishing the feedback loop.

Over geologic time scales, OM burial permits O2 accumulation (40), but only to the extent that primary production is driven by oxygenic photoautotrophs. OM burial in anoxic sediments is usually accompanied by significant pyritization, a net oxidative process relative to sulfide, as it effectively combines H2S with S0. Here, the S0 produced by anoxygenic photosynthesis (26, 41–43) would pair with H2S and Fe^{2+}, satisfying the electron balance required for pyrite formation (Fig. 2B). Export of OM-associated S0 to sediments, at potentially significant sinking velocities (26), could have served as ballast before fecal pellets came to play this role. Alternatively, iron sulfides may have been produced in the water column, as sinking S0 would react with dissolved sulfide to produce polysulfides, an important precursor to pyrite production (44). Either mechanism would facilitate loss of sulfur to sedimentary burial at a rate no greater than twice Fe delivery, ameliorating the potential for runaway sulfide production (Fig. 2). Finally, as OM burial and pyritization are both electron sinks, they would increase the overall oxidation state of ambient seawater (45). This is not, however, equivalent to increasing the O2 concentration of the ocean-atmosphere system, especially if a fraction of buried carbon derives from anoxygenic species.

In mid-Proterozoic oceans, then, the cycle of primary production and remineralization would have established a system in which two conjoined feedback loops worked to perpetuate OMZ euxinia and maintain moderate, but not high, levels of O2 (Fig. 2). These biologically mediated feedbacks link PO2 and OMZ euxinia, whereas the burial of reducing potential (over geologic time scales) allows the accumulation of enough oxidizing capacity to avoid return to a largely anoxic fluid Earth like that of the Archean.

The relative contribution of anoxygenic photautotrophy to mid-Proterozoic PO2 need not have been large for their presence to be felt. Primary production in the modern ocean is \( \approx 1.5 \times 10^{15} \) mol C/year, with an organic carbon burial rate of \( 5.33 \times 10^{12} \) mol C/year (46, 47). When primary production is 100% oxygenic, the maximum rate at which O2 can accumulate is equivalent to the rate of carbon burial (\( \approx 5 \times 10^{12} \) mol O2/year). Because the theoretical maximum
in which $S_0$ is an oxidant byproduct of primary producers and provides sedimentary conditions for calculation details).

The loss of sulfide through pyrite burial dampens the potential for the burial of anoxygenically produced carbon is not strictly coupled to residual oxygen budgets, which would then produce less overall $O_2$, encourage $N_2$ fixation, increase primary production and carbon export, and increase the degree of euxinia (a positive feedback). For example, if we begin in A with an increase in OMZ sulfide, $P_{O_2}$ correspondingly decreases (thus a red arrow preceding the $P_{O_2}$ ellipse), propagating responses through the remainder of the system. The presence of sulfide increases the likelihood of anoxygenic (by cyanobacteria, purple $S$ bacteria, and/or green $S$ bacteria) contributions to primary productivity, which would then produce less overall $O_2$, encourage $N_2$ fixation, increase primary production and carbon export, and increase the degree of euxinia (a positive feedback). (B) A sulfide-rich ocean in which $S^2$ is an oxidant byproduct of primary producers and provides sedimentary conditions conducive to burial of both pyrite and carbon, although the burial of anoxygenically produced carbon is not strictly coupled to residual $O_2$ (no $O_2$ left behind). The loss of sulfate through pyrite burial dampens the extent of ocean euxinia (a negative feedback). The result is a system that maintains both oxygenic and anoxygenic photosynthesis.

can estimate a rate of diminished $O_2$ production of 0.4% $P_{O_2}$ per 10 million years, even with the relative contribution of anoxygenic photosynthesis at only $\approx 1\%$ of the total production. When considering that Proterozoic $O_2$ was likely much lower today, perhaps 1–10% of modern $O_2$ (or $P_{O_2}$ $\approx 0.2–2\%$), it is clear that even these humble contributions from anoxygenic photosynthesis, integrated across geologic time scales, would have impacted Earth’s surface oxygen budget. Although our arguments are framed in terms of water column budgets, they also apply to microbial mat systems, which were widespread on Proterozoic seafloors (51).

In contrast to the Proterozoic Eon, when euxinia was persistent, more recent episodes of euxinia in the Phanerozoic oceans have been transient, presumably because euxinia cannot not be sustained over multimillion year time scales in the face of the greater $P_{O_2}$ and, thus, the buffering capacity of the Phanerozoic atmosphere (SI Text).

If Earth’s middle age was self-sustaining, what drove its demise? Canfield and colleagues (4) recently reported that anoxic subsurface waters of later Neoproterozoic oceans returned to an iron-rich state more characteristic of Archean seas. This reversal resulted from the long-term removal of sulfur by the subduction of pyrite-rich Proterozoic marine sediments (52) (Fig. 2) and an increase in the proportional input of Fe to S into the ocean (53, 54). The loss of photic zone euxinia terminated quantitatively important contributions from sulfide-driven anoxygenic photosynthesis, thus ending control of the “sulfur world” on the oxidation state of the ocean-atmosphere system (Fig. 3). This switch removed two direct inhibitors of eukaryotic evolution: Sulfide, which is toxic to most eukaryotes, and low available $N$, as eukaryotic photoautotrophs cannot fix $N_2$ (55–57). More work is required to determine whether $N$ cycling (assimilatory and dissimilatory) and availability (balance of sources and sinks) would increase in a ferruginous ocean, relaxing $N$ stress and favoring algal diversification, or whether continued anoxia, despite the loss of euxinia, would keep available $N$ low.

Overall, these observations are consistent with the geologic record, as the oldest well-characterized eukaryotic microfossils occur in near-shore environments (58), where OMZ sulfide incursion was least likely. Similarly, the oldest eukaryotic fossils attributable to an extant phylum, phanerophyta red algae in ca. 1200 Ma rocks from Canada, lived on a tidal flat (59). Both incidents coincident with the late Neoproterozoic geochemical transition, microfossils associated with $N_2$-fixing cyanobacteria (Nostocales) decline strongly (60), diverse protists appear (56, 61, 62), and organic-rich sediments begin to record increases in sterase abundances (63) that herald the rise of green algae to ecological prominence.

We do not discount the possibility that tectonic circumstances also contributed to the perpetuation of Earth’s middle age, and we note that factors such as the low bioavailability of trace metals (14, 17, 34, 64, 65) may have further dampened the responsiveness of the Proterozoic biosphere to biogeochemical forcings. Our model, however, strongly implicates the sulfide-driven contribution of anoxygenic photoautotrophy to overall primary production in sustaining Earth’s “boring billion” years (20). The eventual exhaustion of this sulfide reservoir in the Neoproterozoic (4) allowed the strict biogeochemical coupling of $O_2$ accumulation to OM burial: The “carbon world.” Alone, this might not have driven an immediate increase in $P_{O_2}$, but it would have established a framework within which high rates of sedimentation and, hence, OM burial in late Neoproterozoic basins would have a significant and direct effect on global $O_2$ (55, 66).

Our model can be tested in a number of ways. Consistent with Canfield and colleagues (4), we predict that the loss of widespread OMZ euxinia will be resolved as an event separate from and earlier than the widespread oxygeneration of these water masses. If our model is correct, then as organic geochemical research proceeds, biomarkers for anoxygenic photoautotrophs will prove to be prominent in Proterozoic basins.
marked by OMZ euxinia (such as in reference 15), but rare thereafter. And, consistent with this, our model predicts that the timing of Neoproterozoic eukaryotic diversification, as recorded in both paleontological and biomarker records, will be linked stratigraphically to the demise of euxinic OMZs. These geological predictions should be addressed in light of experimental research aimed at constraining contributions from Fe^{2+} using anoxygenic photoautotrophs (67) and, possibly, cyanobacteria (68) to Neoproterozoic primary production, an avenue yet to be explored.

Together, these perspectives issue a challenge: How do we quantify the interplay between rates of mixed primary production, summing oxygenic and anoxygenic photosynthesis, and remineralization efficiencies (presuming differing availabilities of O_2, Fe^{3+}, and SO_4^{2-} through time) in a world where OM burial is not strictly linked to P_{O_2}, the ultimate source of electron acceptors? In the end, we may find that the three long lasting states of Earth’s biosphere — broadly, the anoxic Archean, intermediate Proterozoic, and fully oxygenated Phanerozoic— will find relatively straightforward explanation in primary production that was largely anoxic in the Archean, oxygenic in the Phanerozoic, and mixed in between.

ACKNOWLEDGMENTS. We thank P. Cohen, N. Tosca, P. Girguis, A. Anbar, P. Fromme, J. Golbeck, L. Jahnke, L. Miller, and R. Oremland for conversations and comments on early drafts; T. Lyons, D. Canfield, and M. Follows for insightful reviews; and W. Vernaas for stimulating early conversations on the flexibility of cyanobacterial metabolism. This work was supported by the Microbial Sciences Initiative at Harvard (to D.T.J.), National Aeronautics and Space Administration (NASA) Exobiology grant NNX07AV51G (to D.T.J. and A.H.K.), National Science Foundation Minority Postdoctoral Fellowship DBI-0511972 (to F.W.S.) and the NASA Astrobiology Institute (to A.H.K. and F.W.S.), and the David and Lucille Packard Foundation (to A.P.).


