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

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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 Neoproterozoic 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.

ocean chemistry | primary production | Proterozoic biosphere

Over the past decade, paleoenvironmental insights from iron speciation (1–7), sulfur isotopes (3, 8–12), Mo systematics (13, 14), and organic geochemistry (15) have converged on a view of Proterozoic oceans (16, 17). With the global cessation of iron formations \approx 1,840 million years ago (Ma) (5), euxinic water masses expanded beneath an oxygenated surface mixed layer. We do not know whether the oxygen minimum zone (OMZ) was always and everywhere euxinic (14, 18), but existing data suggest that euxinia was both widespread and persistent for an interval at least 1,000 Ma in duration (14). Deep ocean chemistry is less certain; mid-Proterozoic bottom waters have been modeled variously as sulfidic, anoxic but not sulfidic, and dysoxic (10, 13, 16, 19)—possibly all three existed in varying proportions. What mattered most for Proterozoic life (and, in fact, for the partial pressure of atmospheric oxygen; P_{O₂}), however, was the general state of waters within the photic zone and immediately beneath the oxygenated surface ocean. How the world persisted in this seemingly static state, distinct from both Archean and Phanerozoic biospheres, for a billion years (20) remains largely unknown.

Oxygenic photosynthesis provides Earth's only major source of molecular oxygen (O₂). In oxygenic cyanobacteria, photosystem I (PSI) strips electrons from chlorophyll to generate energy and reductants (ATP and NADPH), while a second photosystem (PSII), assisted by a Mn-based catalytic complex, replenishes the electron pool by oxidizing H₂O to O₂ (21). In contrast, green and

purple sulfur bacteria (anoxygenic photoautotrophs) commonly use sulfide to drive primary production with PSI- and PSII-like machinery, respectively (22, 23). In this case, the production of oxidized sulfur compounds (S⁰ or SO₄), rather than O₂, balances the formation of OM. Similarly, in the presence of sulfide, many cyanobacteria down-regulate PSII and obtain proportionally fewer (or no) electrons from water, instead oxidizing S²⁻ to S⁰, much like green S bacteria (24). Such versatile cyanobacteria are often observed where sulfide intrudes in the photic zone (25), not surprising insofar as the oxidizing potential required to extract electrons from sulfide is significantly lower than that for water (21, 26). Unlike most anoxygenic photoautotrophs, however, cyanobacteria can quickly reinstate PSII and O₂ generation when returned to an oxic environment (27).

In some present day stratified lakes, which often contain shallow chemoclines, anoxygenic photoautotrophs can dominate primary production (up to 83%) (26). Anoxic marine basins commonly have much deeper chemoclines; nonetheless, anoxygenic photosynthesis can still contribute to overall primary production (28). In mid-Proterozoic oceans, lower P_{O₂} and warmer temperatures (reducing O₂ solubility) would have made sulfide much more available for anoxygenic photoautotrophy, 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 NO₃⁻ 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 with a strong redoxcline, a microbial nutrient gauntlet would have developed as nutrient N (NO₃⁻ and/or NH₄⁺) ascended from deep waters toward the photic zone (29). Collectively, denitrification and anammox reactions would have removed upwardly advecting bioavailable N (31–33), and when the OMZ fell within the photic zone, anoxygenic photoautotrophs would have consumed much or all of remaining fixed N before it reached obligately oxygenic photoautotrophs in surface waters.

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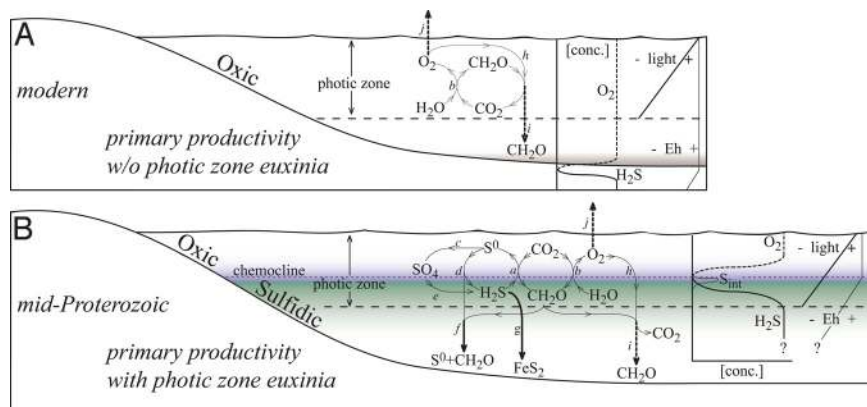


Fig. 1. A schematic representation of marine primary productivity during the modern (A) and postulated Proterozoic (B). Geochemical cycles not directly related to primary productivity are neglected for simplicity. Dark heavy arrows reflect exit channels. Letters associated with fluxes are as follows: a, anoxygenic photosynthesis; b, oxygenic photosynthesis; c, sulfur oxidation by disproportionation or (non)phototrophic S-oxidizers; d, S^0 respiration; e, sulfate reduction; f, S^0 -OM export/ballasting; g, pyrite formation; h, aerobic respiration; i, OM export; and j, O_2 export. (A) Primary productivity performed by oxygenic photosynthesis and where O_2 and CH_2O (OM) are produced in stoichiometric proportions. Light penetrates to a given depth, and due to available O_2 , Eh remains high throughout the water column. Only within the sediments is O_2 exhausted and sulfide allowed to accumulate, both encapsulated by a decrease in Eh. (B) A mixed community of primary producers, with surface oxygenic photosynthesis dominated by cyanobacteria (rather than algae) and subchemocline anoxygenic photosynthesis driven by sulfide. Here, OM production reflects the sum of all primary production pathways, which is balanced by the production of O_2 in surface waters and S^0 (or other oxidative intermediates: All represented as S_{int}) below the chemocline. As O_2 is depleted and sulfide concentrations increase, appreciable pools of S_{int} could accumulate. Light again decreases with depth, and as O_2 decreases across the chemocline, Eh would drop sharply. The specific chemistry of deep water will contribute to burial efficiencies, but is not central to our argument.

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 N_2 . In the Proterozoic ocean, then, both impinging sulfide and a scarcity of fixed-N would have favored diazotrophic (N_2 -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, oxygen 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 anoxygenic photosynthesis (38). In Proterozoic oceans, with low overall NO_3^- and Fe^{3+} availability, SO_4^{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 H_2O) would depress surface O_2 concentrations further, simultaneously enhancing the potential for N_2 -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 P_{O_2} accumulation. That is, when primary production includes a nontrivial contribution from anoxygenic photoautotrophy, 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 en-

croach on the photic zone. This photic zone sulfide is available for further anoxygenic photosynthesis—establishing the feedback loop.

Over geologic time scales, OM burial permits O_2 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 H_2S with S^0 . Here, the S^0 produced by anoxygenic photoautotrophy (26, 41–43) would pair with H_2S and Fe^{2+} , satisfying the electron balance required for pyrite formation (Fig. 2B). Export of OM-associated S^0 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 S^0 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 O_2 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 O_2 (Fig. 2). These biologically mediated feedbacks link P_{O_2} and OMZ euxinia, whereas the burial of reducing potential (over geological 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 photoautotrophy to mid-Proterozoic P_{O_2} 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 5.33×10^{12} mol C/year (46, 47). When primary production is 100% oxygenic, the maximum rate at which O_2 can accumulate is equivalent to the rate of carbon burial ($\approx 5 \times 10^{12}$ mol O_2 /year). Because the theoretical maximum

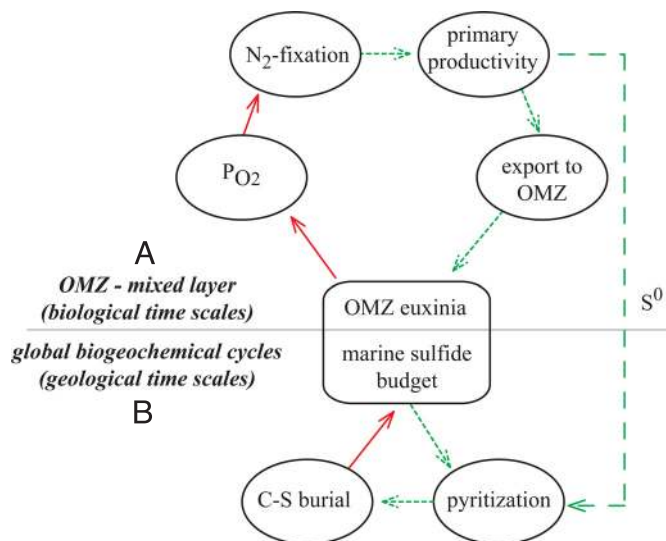


Fig. 2. A schematic view of feedbacks that acted to sustain Proterozoic environments on both short and long geologic time scales (A and B, respectively). The point of entrance into this cycle is the establishment of sulfidic conditions at $\approx 1,840$ Ma (5) and possibly earlier. Dashed green and solid red arrows note the direction of the feedback. If an increase in one quantity is followed by a decrease in the next, the connecting arrow is red (a negative feedback). If an increase in one quantity leads to an increase in the next, then the connecting arrow is green (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^0 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 sulfide through pyrite burial dampens the extent of ocean euxinia (a negative feedback). The result is a system that maintains both oxygenic and anoxygenic photosynthesis.

contribution from sulfide-using anoxygenic photoautotrophs is equal to integrated rates of sulfate reduction (38), the modern rate of net sulfide generation (2.62×10^{12} mol S/year) (48) sets an upper limit on the hypothetical contribution from anoxygenic photosynthesis to total modern primary production at $\approx 0.17\%$ (see *SI Text* for calculation details).

In this formulation, O_2 production is sensitive to: (i) The magnitude of overall primary production and burial fluxes and (ii) their respective ratios to overall sulfate reduction rates modified by the efficiency with which sulfide becomes available to autotrophs. Much of the sulfide produced in today's ocean will not be available for photoautotrophic oxidation, because the sulfide is produced deep within the marine realm, most commonly within sediments. However, in mid-Proterozoic oceans, although the magnitude of primary production may have been smaller (17), sulfate reduction rates would have been similar or higher, as a greater fraction of primary organic matter was not aerobically respired (49). When combined with increased sulfide availability near or within the photic zone (15, 50), these conditions enhanced the likelihood that photosynthetic sulfide oxidizers would moderate oxygen levels due to positive feedbacks (Fig. 2). Simply, as the ratio of export production to sulfate reduction approaches unity, the potential for anoxygenic photoautotrophy to buffer P_{O_2} increases. Thus, using approximations for Proterozoic sulfate reduction (reference 49 and *SI Text*) and keeping a modern burial efficiency (which likely underestimates Proterozoic burial due to low deep-water O_2), we

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 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 reversion 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, bangiophyte red algae in ca. 1200 Ma rocks from Canada, lived on a tidal flat (59). Broadly 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 sterane 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 further have 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 oxygenation 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

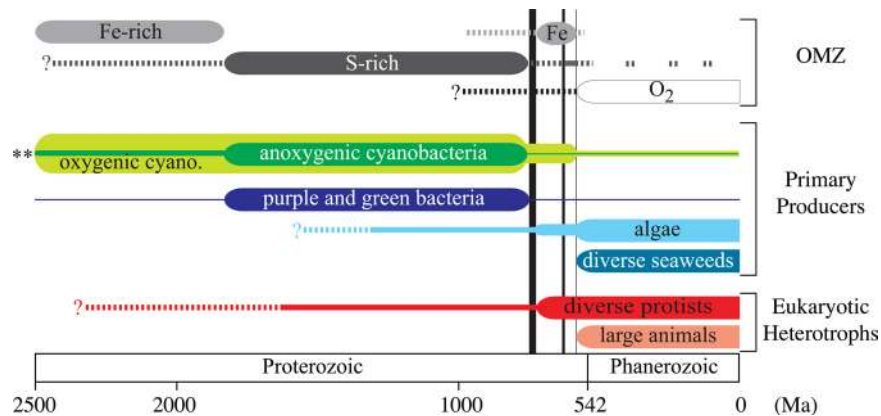


Fig. 3. A timeline showing OMZ chemistry (1–4, 7–10, 13, 14, 17), the relative contributions from different primary producers (17, 55, 69), and the evolution of eukaryotic heterotrophs (55–59, 70, 71). Band thicknesses approximate the importance of each feature through time. Dashed lines represent postulated or uncertain histories. The specific evolutionary sequence of oxygenic and anoxygenic photoautotrophs (including both cyanobacteria and purple/green S bacteria), marked here by **, rests in the Archean rock record (>2,500 Ma). As both processes had evolved by 1,800 Ma (23) (when our story begins), we make, nor require, any distinct sequence. The two thicker vertical lines represent the major Neoproterozoic glaciations (72), and the thinner line to the right marks the Ediacaran Gaskiers glaciation. The precise timing of Neoproterozoic climatic and biogeochemical events is the subject of ongoing research. We highlight the mixed contributions to primary productivity through the Proterozoic, a transition in OMZ chemistry at 800–700 Ma, and the coincident change in cyanobacteria, algal, protist, and animal abundances, based on body and molecular fossils.

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 anoxygenic in the Archean, oxygenic in the Phanerozoic, and mixed in between.

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