Anoxygenic Photosynthesis Modulated Proterozoic Oxygen and Sustained Earth’s Middle Age

The Harvard community has made this article openly available. Please share how this access benefits you. Your story matters.

Citation

Published Version
doi:10.1073/pnas.0909248106

Citable link
http://nrs.harvard.edu/urn-3:HUL.InstRepos:3934550

Terms of Use
This article was downloaded from Harvard University’s DASH repository, and is made available under the terms and conditions applicable to Other Posted Material, as set forth at http://nrs.harvard.edu/urn-3:HUL.InstRepos:dash.current.terms-of-use#LAA
Anoxygenic photosynthesis modulated Proterozoic oxygen and sustained Earth’s middle age

D. T. Johnstona,b,1,2, F. Wolfe-Simoona,1,2, A. Pearsona,2, and A. H. Knollb,2

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 prakoryote-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.

Over the past decade, palaeoenvironmental 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 ~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 of at least 1,000 Ma in duration (14). Deep ocean chemistry is less certain; mid-Proterozoic bottom waters have been modeled at least 1,000 Ma in duration (14). Deep ocean chemistry is less certain; mid-Proterozoic bottom waters have been modeled at least 1,000 Ma in duration (14). Deep ocean chemistry is less certain; mid-Proterozoic bottom waters have been modeled at least 1,000 Ma in duration (14). Deep ocean chemistry is less certain; mid-Proterozoic bottom waters have been modeled at least 1,000 Ma in duration (14). Deep ocean chemistry is less certain; mid-Proterozoic bottom waters have been modeled at least 1,000 Ma in duration (14).
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 photoautotrophy 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, oxidized OMZ euxinia 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 NO3\(^-\) 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\(_2\)O) 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\(_{O2}\) 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 oxidative photoautotrophs. OM burial in anoxic sediments is usually accompanied by significant pyritization, a net oxidative process relative to sulfide, as it effectively combines H\(_2\)S with S\(_0\). Here, the S\(_0\) produced by anoxygenic photoautotrophy (26, 41–43) would pair with H\(_2\)S and Fe\(^{3+}\), 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\(_{O2}\) 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 photoautotrophy to mid-Proterozoic P\(_{O2}\) 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 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
in which $S_0$ is an oxidant byproduct of primary producers and provides sedi-
O2 (no O2 left behind). The loss of sulfide through pyrite burial dampens the
the burial of anoxygenically produced carbon is not strictly coupled to residual
genic (by cyanobacteria, purple S bacteria, and/or green S bacteria) contribu-
in
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 remain-
der of the system. The presence of sulfide increases the likelihood of anoxy-
genic (by cyanobacteria, purple S bacteria, and/or green S bacteria) contribu-
tions 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 sedi-
mentary conditions conducive to burial of both pyrite and carbon, although
the burial of anoxogenically 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.

Fig. 2. A schematic view of feedbacks that acted to sustain Proterozoic
environments on both short and long geologic time scales (A and B, respec-
tively). The point of entrance into this cycle is the establishment of sulfidic
conditions at $\approx 1,840$ Ma ($S_0$) 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 remain-
der of the system. The presence of sulfide increases the likelihood of anoxy-
genic (by cyanobacteria, purple S bacteria, and/or green S bacteria) contribu-
tions 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 sedi-
mentary conditions conducive to burial of both pyrite and carbon, although
the burial of anoxogenically 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.

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 con-
sidering 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 persist-
tent, 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 subsur-
face 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 contri-
butions from sulfide-driven anoxygenic photosynthesis, thus ending
control of the “sulfur world” on the oxidation state of the ocean-
climate research proceeds, biomarkers for anoxygenic pho-
toautotrophs will prove to be prominent in Proterozoic basins

Our model can be tested in a number of ways. Consistent
with Canfield and colleagues (4), we predict that the loss of
wide 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 geo-
chemical research proceeds, biomarkers for anoxygenic pho-

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 con-
sidering 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 persist-
tent, 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 subsur-
face 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 contri-
butions from sulfide-driven anoxygenic photosynthesis, thus ending
control of the “sulfur world” on the oxidation state of the ocean-
climate research proceeds, biomarkers for anoxygenic pho-
toautotrophs will prove to be prominent in Proterozoic basins

Our model can be tested in a number of ways. Consistent
with Canfield and colleagues (4), we predict that the loss of
wide 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 geo-
chemical research proceeds, biomarkers for anoxygenic pho-

contribution from sulfide-using anoxygenic photoautotrophs is
equal to integrated rates of sulfate reduction (38), the modern rate
of net sulfide generation (2.62 $\times 10^{12}$ mol S/year) (48) sets an upper
limit on the hypothetical contribution from anoxygenic photosyn-
thesis 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 mag-
nitude 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

Our model can be tested in a number of ways. Consistent
with Canfield and colleagues (4), we predict that the loss of
wide 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 geo-
chemical research proceeds, biomarkers for anoxygenic pho-

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\(^{3+}\) using anoxicogenic 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\(_{O2}\), 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.

ACKNOWLEDGMENTS. We thank P. Cohen, N. Tosca, P. Girguis, A. Anbar, P. Fromme, J. Golbeck, L. Jahneke, L. Miller, and R. Oremland for conversations and comments on early drafts; T. Lyons, D. Canfield, and M. Follows for thoughtful 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.).


