

# An early productive ocean unfit for aerobics

Timothy W. Lyons<sup>1</sup> and Christopher T. Reinhard

Department of Earth Sciences, University of California, Riverside, CA 92521

Grasping the big picture of the early ocean used to be easy: no oxygen, and then oxygen. The crux of that popular model hinged on the almost universally accepted Great Oxidation Event, or GOE, during which appreciable free oxygen ( $O_2$ ) first accumulated in the atmosphere about 2.4 billion years ago. At the same time, as the old argument goes, the  $O_2$ -free, iron-rich earlier ocean gave way to one with oxygen at all depths. About a decade ago, Canfield (1) offered a very different possibility—that ventilation of the deep ocean lagged behind the GOE by more than a billion years, resulting in a vast, deep reservoir of hydrogen sulfide, but long-held presumptions about photosynthetic life in the surface waters remained untouched. In the first comprehensive biogeochemical model of this “Canfield Ocean,” Johnston et al. (2) in a recent issue of PNAS present a stunningly different take on those early photosynthesizers—one in which the upper, light-containing layers indeed drove biological production but without the expected concomitant release of oxygen. And it is this feedback that may explain a troubling uncertainty about the Canfield Ocean and this time interval in general—exactly how oxygen in the biosphere remained at only a fraction of modern levels for so long after the GOE.

Populations of photosynthesizing phytoplankton abound in the sunlit portions of the modern surface ocean, often to depths of 100 m or more. Using energy from the sun, they represent the dominant pathway by which carbon dioxide is fixed in the ocean and are the foundation (the primary producers) of the food chain. And  $O_2$  is their famous waste product. Much of the biomass formed in the surface ocean is degraded by aerobic bacteria on the spot, consuming the oxygen at a rate almost as fast as the gas is produced. The rest settles to the deep ocean, where the  $O_2$ -consuming respiration continues. This shallow-to-deep flow of material is known as the biological pump.

Canfield (1) speculated on how an analogous biological pump and associated oxygen loss in the deep ocean might have operated in the early world, after the GOE but well before the rise of animals about 700 million years ago—during a time interval known as the Proterozoic. There are two key pieces in this puzzle. First, because  $O_2$  levels in the atmosphere, in general,



**Fig. 1.** A modern analog for the ancient sulfidic ocean? (Upper) Mahoney Lake, British Columbia, Canada—perhaps like the Proterozoic ocean (2)—contains abundant  $H_2S$  in the photic zone. In the case of Mahoney Lake, the  $O_2$ - $H_2S$  interface is only 7 m deep—ideal conditions for anoxygenic photosynthesis. (Lower) A “plate” of profuse purple, S-oxidizing, anaerobic bacteria at this interface generates more than half of the primary production in the lake. (Lower photo by J. Glass, Arizona State University, Tempe, AZ.)

were still only a fraction of today’s, Canfield could confidently infer similarly lower concentrations in the ocean, given the exchange between the two. Add in the  $O_2$  consumption facilitated by a biological pump assumed to be robust, and anoxic conditions may have been pervasive throughout the deep global ocean.

Although  $O_2$  remained low or absent in the deep ocean, post-GOE levels in the atmosphere were sufficiently high (it doesn’t take much) to oxidize the mineral pyrite ( $FeS_2$ ) during weathering on the continents, leading to sulfate ( $SO_4^{2-}$ ) delivery to the ocean by rivers. This new flux of sulfate is key to the story because as it accumulated in the still anoxic deep ocean, sulfate-loving,  $O_2$ -loathing bacteria rereduced the sulfur to hydrogen sulfide ( $H_2S$ ), driving the solubility of dissolved iron in seawater to near null levels through pyrite formation rather than iron oxidation. This loss of iron dealt a deathblow to the vast

banded iron formations (BIFs)—the smoking gun for the earlier ferruginous ocean. In other words, Canfield (1) argued that  $H_2S$  began to build up throughout much, if not all, of the deep ocean beginning  $\approx 1.8$  billion years ago and persisted ubiquitously for a billion or more years.

The Canfield Ocean is nothing short of paradigm-busting, and evidence for euxinic (anoxic and sulfidic) conditions in the Proterozoic ocean has emerged over the past decade (refs. 3–7, reviewed in ref. 8). In fact, confidence in this model has inspired a new generation of research exploring the potential biological implications of global euxinia, such as decreased availability of bioessential trace metals (9). Molybdenum and copper, for example, are less soluble in the presence of  $H_2S$  and play key enzymatic roles in the nitrogen cycle, including  $N_2$  fixation by cyanobacteria (7, 9, 10).

Enter Johnston et al. (2). Astutely, the authors recognized that a challenge to the Canfield model is maintaining oxygen deficiency over such a long period. The problem: a tiny but critically important percentage of sinking biomass escapes decay in the deep ocean and underlying sediments and is buried, typically yielding a net increase in atmospheric and seawater  $O_2$ . And a strong negative feedback is in place because the anoxia induced by organic degradation actually increases the fraction of organic matter that escapes decay.

As is often the case, old rocks make more sense when viewed through a lens focused on the modern ocean. After having such a look, Johnston et al. (2) asked a key question: what if the primary production in the surface ocean that settles and decays to facilitate  $O_2$  loss in the deep ocean was triggered by a photosynthetic pathway that does not produce oxygen? Today, we only have to look to the Black Sea and many stratified lakes to see that such anoxygenic photosynthesis does occur and can even dominate primary production, at least in lakes.

There are two key ingredients to such systems. First, the subsurface waters in

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<sup>1</sup>To whom correspondence should be addressed. E-mail: timothy.lyons@ucr.edu.

the lake or ocean need to be anoxic and rich in dissolved  $H_2S$ —so far so good for the Canfield Ocean. Second, those euxinic waters need to extend upward into the photic zone, within the penetrative reach of sunlight. Certainty of shallow euxinia is a tougher box to check for the Proterozoic. More on this below, but for now, let's have look through that modern lens.

The Black Sea is  $\approx 2,000$  m deep, and, as the largest euxinic basin on the modern Earth, all but its upper 100 m are anoxic and loaded with  $H_2S$ . Despite being at the lower limits of adequate light penetration, this interface supports some primary production of organic matter by green sulfur bacteria. These phototrophic anaerobes are sustained by the juxtaposition of  $H_2S$ , which they oxidize for energy, and light, which catalyzes that oxidation. Euxinia, and shallow euxinia in particular, is not a common condition in the modern ocean; the other best examples come from lakes, where purple S-oxidizing anaerobic bacteria also thrive, presumably when  $H_2S$  is especially shallow (Fig. 1). Adding to the mix, Johnston et al. (2) point out that cyanobacteria, well-known perpetrators of oxygenic photosynthesis and the organism credited with the first oxygenation of the atmosphere, can switch to anoxygenic photosynthesis under euxinic conditions and subsist on  $H_2S$ .

As in any whodunit, Johnston et al. (2) introduce a lot of characters and subplots along the way. Amidst the details, however, a simple, elegant story line binds the pieces: a Proterozoic sea rich with  $H_2S$  in the photic zone could have sustained vast primary production without concomitant generation of oxygen. The ocean gains a sink for  $O_2$  via the decay of this biomass without the offsetting source.

Because the biological pump shuttles organic matter to the deep ocean, the surface waters show the wear of their losses through deficiencies in nitrogen and phosphorus, among other key nutrients. It is primarily through the upwelling of deep waters and the nutrients they contain from organic decay that primary production can persist. This relationship is the underpinning of the

authors' nutrient "gauntlet." Specifically, they argue, upward returning N is consumed in the deep part of the photic zone by the anoxygenic phototrophs and by processes that convert bioavailable ("fixed") nitrogen (e.g.,  $NH_4^+$ ) to less available  $N_2$  under oxygen-deficient conditions. Possible outcomes are ecological dominance by organisms that can provide their own bioavailable N (diazotrophs, such as cyanobacteria) at the expense of eukaryotic algae and, importantly, a decline in the relative amount of oxygenic photosynthesis.

Whether right in every detail or not, Johnston et al. (2) have designed a far-reaching thought experiment loaded with roadmaps for future research. Among the remaining questions: how strong is the physical evidence for a Canfield Ocean—the root of the Johnston et al. model? There is certainly evidence that euxinia was widespread during the Proterozoic, likely much more so than today, but few if any of the data actually demand a global Black Sea.

Johnston et al. (2) suggest that euxinia may have been confined to mid-depths in the water column, much like the oxygen minimum zones seen widely in the modern ocean. In such a case, the deep ocean may have been  $O_2$ -containing, or ferruginous, or sulfidic; it is hard to know—that record has largely been lost through subduction of deep ocean crust. Very limited data suggest that at least weakly oxygenated deep conditions were possible (7, 11). Also, most of the available records, with the key exception of molybdenum isotopes, are of proxies that speak mostly to local conditions, and restricted basins analogous to the modern Black Sea, not easily subducted, may be skewing our interpretations of the ancient global ocean. The extent of euxinic bottom waters as constrained by the molybdenum isotopes need not have been anything close to global. An even greater challenge is convincing the community that Proterozoic euxinia was widespread and shallow. There is precious little evidence for  $H_2S$  within the early photic zone; what does exist may reflect local condi-

tions (6). And there are challenges to maintaining  $H_2S$  in near-surface waters in a wind-stirred open ocean beneath an  $O_2$ -containing atmosphere.

Another important issue is whether global rates of biological nitrogen fixation would have been able to fuel the export flux of organic matter out of the photic zone necessary to maintain euxinia on long timescales. Loss of fixed N under anoxic conditions, combined with global limitation of  $N_2$  fixation owing to trace metal deficiencies (7, 9), could have acted as a negative feedback against euxinia, thereby decreasing the level of anoxygenic production. Happily, this novel view of ecology in the ocean comes with predictions, testable, for example, through analysis of diagnostic organic biomarkers (molecular fingerprints) and their isotopic properties. To date, direct evidence for voluminous production by cyanobacteria and/or anaerobic S-oxidizing bacteria has not been found.

At a minimum, Johnston et al. (2) have produced the first comprehensive conceptual model for chemical cycling and life in the ocean during the Proterozoic, with talking points galore awaiting dissection in graduate seminars. If that is not enough for fans of the early Earth, the authors even extrapolate their arguments to speculate on the causes behind Earth's animal-favoring, second great step in atmospheric oxygenation late in the Proterozoic. A return to iron-dominated conditions in the deep ocean, after a billion years of efficient pyrite burial under euxinia (12), may have seeded the demise of their anoxygenic factory, thriving up to that point on  $H_2S$ . There are more than a few layers of conjecture stacked at this point in the story, and the possibility that analogous, iron-based pathways of anoxygenic photosynthesis may have taken over remains fodder for conjecture. But if Johnston et al. are right, the torch of the dominant primary producers may have been passed, for the first time, to  $O_2$ -yielding photosynthesis, and the atmosphere and ocean would never again look so persistently and pervasively oxygen lean.

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