

Ancient Sulfur Cycling and Oxygenation of the Early Biosphere

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Deposition of banded iron formations marks periods of low sulfur concentration in the early ocean.
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The amount of sulfate in the early ocean was tied directly to oxygen levels in the atmosphere and the deep ocean. These concentrations and other environmentally diagnostic biogeochemical pathways of the sulfur cycle can be expressed through isotope fractionation between sulfate and pyrite. The balance between rising oxygen and sulfate concentrations and varying hydrothermal iron inputs led to a pattern of iron, oxygen, and sulfide domination that varied in time and space in the early deep ocean and was more complex than previously recognized. Through all this change, no element played a bigger role than sulfur as a recorder of early oxygenation of the biosphere and the coevolution of life.

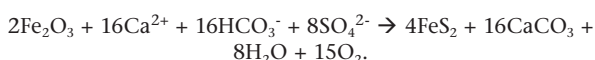
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BACKGROUND

Coupled C–S Cycling and Implications for Atmospheric Oxygen

The formation of sedimentary pyrite (FeS_2), the principal sink for reduced sulfur in marine systems, begins with the activity of prokaryotic microorganisms (Bacteria and Archaea) that reduce sulfate (SO_4^{2-}) while oxidizing organic substrates and, less commonly, hydrogen. Sulfate reduction requires biological mediation, except at temperatures much higher than those typical of most surficial marine settings (thermochemical reduction prevails at temperatures above 100°C). This anaerobic pathway of organic degradation dominates in modern oxygen-free marine sediments and water columns, as in the deep Black Sea. Because sulfate is so abundant in modern seawater—its 28 mM concentration ranks second only to chloride's among the anions—sulfate reduction takes a back seat only to aerobic respiration in terms of the quantity of organic matter remineralized (recycled) in the modern ocean.

The hydrogen sulfide (H_2S) formed as a waste product during sulfate reduction is highly reactive with iron oxides delivered to the ocean by rivers principally as coatings on detrital sedimentary grains. Reaction of H_2S with these oxides and other iron phases yields pyrite (FIG. 1) by way of metastable iron “monosulfide” precursors with stoichiometries closer to FeS . Because the organic matter oxidized during sulfate reduction comes mostly from oxygen-producing photosynthesis, the net result of pyrite formation and its subsequent burial is an increase in atmospheric oxygen. These multiple steps of sedimentary pyrite formation and the consequent impact on O_2 levels can be simplified in a net reaction:



Similarly, burial of organic matter equates to net photosynthesis, with a corresponding gain in atmospheric O_2 . This burial and, to a lesser degree, that of pyrite account for essentially all the oxygen released to the atmosphere. Together with O_2 -consuming oxidation of pyrite and organic matter, these processes modulate concentrations of atmospheric O_2 on geologic timescales. [Pathways of anoxygenic primary production

during the Precambrian via iron and H_2S oxidation in the photic zone may have tempered these effects (Johnston et al. 2009).]

Isotopic Fingerprints

Given that the O_2 content of the atmosphere reflects the net burial versus oxidation of pyrite and organic matter on geologic timescales, the question becomes how to deduce this balance over millions to billions of years of Earth history through proxies captured and preserved in the rock record. It is our good fortune that sulfate-reducing prokaryotes and O_2 -producing photosynthesis by diverse CO_2 -fixing (photoautotrophic) organisms favor the light isotopes of sulfur (^{32}S) and carbon (^{12}C), respectively, relative to their heavier cousins (^{34}S and ^{13}C). The simple explanation is that the S–O and C–O bonds of $^{32}\text{SO}_4^{2-}$ and $^{12}\text{CO}_2$ are more easily broken during heterotrophic sulfate reduction and autotrophic oxygenic photosynthesis.

The extent of isotopic discrimination, or fractionation, is large during these processes, which is true for light stable isotope systems in general (e.g. hydrogen in the extreme case), since the relative mass differences among the isotopes are far greater than those of heavier elements (e.g. iron and molybdenum). Typical isotopic signatures of photosynthesis are seen in product organic matter. These light-isotope enrichments are expressed as $^{13}\text{C}/^{12}\text{C}$ ratios that are on average 25 parts per thousand (‰) depleted in the heavy isotope relative to the parent CO_2 . Similarly, experiments yield H_2S during sulfate reduction that can be up to 45‰ depleted in ^{34}S relative to the sulfate. Sulfur fractionations seen in nature are often much larger, commonly ranging up to 1.5 times the maximum known from experiments. The roughly 60‰ offset seen between H_2S and SO_4^{2-} in the water column of the Black Sea is a good example.

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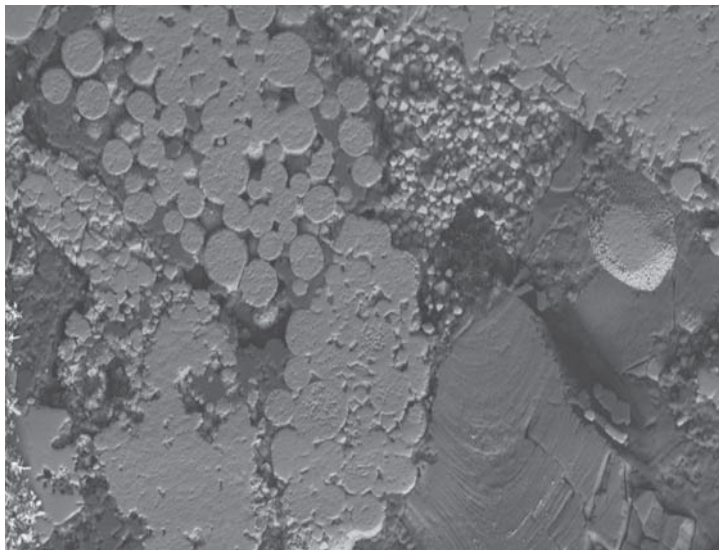


FIGURE 1 Scanning electron micrograph of framboidal pyrite in unmetamorphosed Devonian black shale from western New York. Framboids are roughly spherical, microcrystalline aggregates resembling raspberries, hence their name (from the French *framboise*). They are a common primary texture resulting from low-temperature, microbially mediated pyrite formation within anoxic sediments and water columns throughout geologic history. The framboids here are up to a few tens of micrometers across. PHOTO PROVIDED BY M. FORMOLO

The apparent discrepancy between natural and experimental systems is a subject of vigorous debate and ongoing research; for example, it is possible that the extent of fractionation in the laboratory, under the right experimental conditions, could be greater than that now observed. Other models have suggested that single-step sulfate reduction alone is not enough to explain the large fractionations seen in nature. Such models require additional S cycling by disproportionating prokaryotes that convert intermediate sulfur species, such as elemental sulfur and thiosulfate, into H_2S and SO_4^{2-} (Johnston 2010 this issue). With this recycling comes added isotope discrimination, further depleting the H_2S in ^{34}S and more than adequately explaining the apparent disparity between laboratory results and nature (Canfield and Thamdrup 1994). Another school of thought asserts instead that single-step fractionations in nature by sulfate-reducing prokaryotic microbes can exceed those now known from the lab. Regardless, disproportionation pathways are unquestionably an important part of the sulfur cycle. They have also factored prominently in interpretations of the Precambrian isotope record and will resurface in discussions below.

Most relevant to our focus here, and independent of these mechanistic details, is that microbial cycling of S results in H_2S and subsequently pyrite that are typically ^{34}S depleted, and the burial of this pyrite leaves the ocean enriched in ^{34}S (by ~21 parts per thousand in modern seawater, although this enrichment has varied through geologic time). From these relationships, we can surmise that secular trends in the C and S isotope compositions of CO_2 and SO_4^{2-} in seawater track the balance between the burial of pyrite and organic matter beneath the ocean and their oxidative recycling on land. When marine sediments are exposed on the continents, the isotope effects of burial can be offset by the return of dissolved CO_2 and SO_4^{2-} produced, with little isotopic fractionation, during weathering of organic matter and pyrite. These isotopic

systematics must be coupled, for reasons outlined above, to the varying O_2 content of the atmosphere. If we can extract the changing isotopic compositions of carbon and sulfur dissolved in the ocean, we should be able to estimate varying atmospheric O_2 levels using straightforward numerical models tied to the burial/weathering mass balances of pyrite and organic matter. Such models are well established and now buttress our understanding of the evolving O_2 content of the atmosphere, particularly in the Phanerozoic where isotope data are comparatively continuous across the last 500+ million years (Berner 2006). Past studies have most often relied on data extracted from sulfate-containing evaporites (gypsum and anhydrite) and, for carbon, well-preserved calcitic fossils (brachiopods in particular) or bulk fine-grained lithologies, when fossils are sparse or absent.

THE EARLY HISTORY OF SULFUR CYCLING

Before the Great Oxidation Event

Connections linking the amount of sulfate in ancient seawater, its S isotope ratio, and the amount of O_2 in the atmosphere did not escape the vigilant eyes of Precambrian workers decades ago (Schidlowski 1979). Sulfate in the ocean is supplied mostly by the weathering of pyrite and other sulfide minerals on the continents beneath an O_2 -containing atmosphere. Given this connection between sulfate and O_2 , we might expect the diagnostic sulfur isotope fingerprints of sulfate reduction and their relationship to sulfate concentration to be expressed in the geologic record at the transition from an O_2 -poor to an O_2 -containing atmosphere. Not surprisingly, the first clear, persistent record of large sulfur isotope fractionation is seen in pyrite deposited 2.3 to 2.4 billion years ago, roughly coincident with independent signals marking the first great transition in biospheric oxygenation (the so-called “Great Oxidation Event,” or GOE) (FIG. 2).

Among the independent fingerprints of atmospheric oxygenation are the disappearance of the reduced detrital minerals (pyrite, siderite, and uraninite) from ancient fluvial sediments and the first evidence for oxidation in ancient soil horizons (as reviewed in Canfield 2005 and Sverjensky and Lee 2010). But the true “smoking gun” for this fundamental shift from dominantly reducing to oxidizing Earth-surface conditions is another sulfur story, now well known: the disappearance of mass-independent fractionation (MIF) of sulfur isotopes in sulfate- and sulfide-bearing minerals about 2.4 billion years ago. The loss of these MIF signals points convincingly to the first accumulation of free O_2 in the atmosphere beyond the minute, trace levels of the earlier atmosphere (Farquhar and Wing 2003). Oxygen contents never again dropped low enough to yield MIF in the rock record, although dramatic post-GOE dips in atmospheric oxygen have been proposed (Canfield 2005; Frei et al. 2009). Theoretical constraints on the magnitude of oxygenation required for the loss of MIF demand only a small increase in O_2 , to values still much less than 1% of present atmospheric levels. The rise was likely higher. Yet despite what may have still been a relatively small O_2 increase, many proxies point similarly to a fundamental shift in Earth-surface oxidation at the GOE.

One explanation for an assumed lack of mass-dependent sulfur isotope fractionation in rocks deposited before the GOE (FIG. 2) is that bacterial sulfate reduction had not yet evolved because of the near-absence of sulfate in early seawater. Another idea, now more widely held, is that sulfate reduction is much older, dating back to the earliest well-preserved sedimentary rocks in Western Australia. The

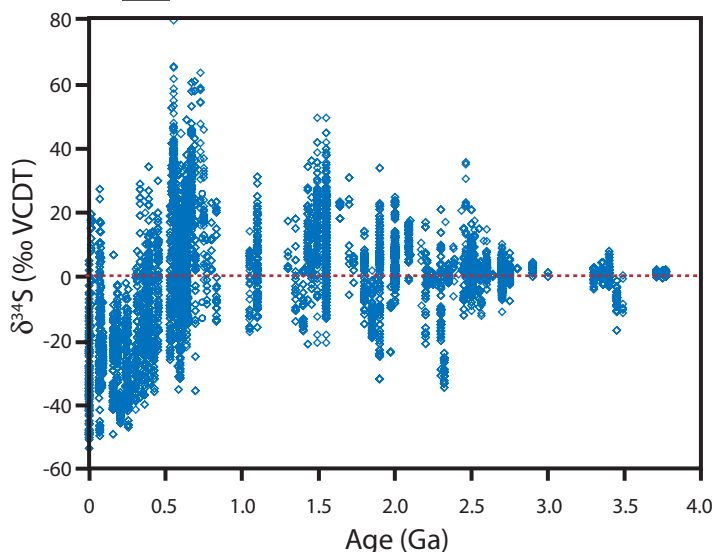


FIGURE 2 Summary of sedimentary pyrite S isotope data through time (Ga = billion years). The $\delta^{34}\text{S}$ notation is an expression of the $^{34}\text{S}/^{32}\text{S}$ ratio relative to the same ratio in standard material. By convention, a value of zero per mil (‰) has the same isotopic composition as undifferentiated bulk Earth—our starting point in sulfur isotope biogeochemistry. Positive and negative values respectively imply enrichment and depletion in ^{34}S relative to this standard, with large offsets from 0‰ reflecting the influence of biogeochemical cycling. VCDT refers to the Vienna Canyon Diablo Troilite standard, assumed to represent the undifferentiated bulk Earth. Data from many references (available on request). MODIFIED FROM CANFIELD (2005)

latter hypothesis is based on appreciable isotope offsets between co-occurring, 3.5-billion-year-old pyrite and barite (BaSO_4 ; Shen et al. 2001). If sulfate reduction was indeed such an ancient pathway, we are forced to explain why the isotopic fingerprint of a metabolism that evolved so long ago is otherwise expressed infrequently in rocks that predate the GOE. One possibility is that the arguments for active sulfate reduction 3.5 billion years ago are wrong. To some, for example, the data from 3.5-billion-year-old rocks reflect abiotic thermochemical processes.

If, however, you accept the arguments for the early onset of bacterial sulfate reduction, you are left with a fairly straightforward view of the pre-GOE (Archean) ocean: the predominance of small sulfur isotope fractionations in sedimentary pyrite must reflect very low levels of sulfate in an ocean beneath an oxygen-lean atmosphere. For this claim to stand, there must be a tight relationship between the magnitude of fractionation and the amount of sulfate in the ocean. In fact, experimental calibrations show this to be the case at very low sulfate concentrations and place the threshold at less than 1% of today's level, below which fractionations are negligible (Habicht et al. 2002). Whether this value from a few laboratory cultures provides the precise limits for the early ocean is hard to know, but the basic story of very low Archean sulfate concentrations is certain to remain intact apart from any future refinements. Consistent with low concentrations of sulfate, abundant banded iron formations (BIFs) suggest an anoxic ocean dominated by iron rather than sulfur (Fig. 3), although emerging evidence is indicating very early episodes of euxinia as well (e.g. 2.5 billion years ago; Reinhard et al. 2009). Euxinic waters are O_2 -free (anoxic) and, by definition, contain H_2S . The euxinic Black Sea is our largest modern example of a condition that was widespread, perhaps global, at times in the past, including substantial intervals of the Precambrian.

A quick look at the data reveals a broadening of the pyrite S isotope data by at least 2.3–2.4 billion years ago, presumably reflecting greater fractionation under higher levels of seawater sulfate (Figs. 2 AND 4). Some might suggest even earlier signals capturing pre-GOE sulfate increases. This possibility should come as no surprise, since some estimates place the onset of oxygenic photosynthesis at least 2.7 to 2.5 billion years ago (Brocks et al. 1999; Reinhard et al. 2009), with the possibility of a concurrent “whiff” and perhaps pulses of oxygen in the atmosphere (Anbar et al. 2007; Frei et al. 2009; Reinhard et al. 2009). With this oxygen production came increased oxidation of pyrite on the continents and sulfate delivery to the ocean beneath higher, but still low, atmospheric O_2 concentrations (Reinhard et al. 2009), supporting at least local euxinia. In this light, the purported large fractionations 3.5 billion years ago (e.g. Shen et al. 2001) must reflect locally concentrated levels of sulfate in evaporative settings. The same photochemical atmospheric reactions that yielded the signature MIF of the Archean would have produced small amounts of early sulfate that might have become abundant locally. Nevertheless, the GOE signaled a fundamental and persistent reorganization of sulfur cycling on a global scale.

Ocean Chemistry and Life during the Proterozoic (2.4 to 0.54 Billion Years Ago)

With the GOE came a world of change in the ocean and the atmosphere. Atmospheric oxygen was undoubtedly higher, as was sulfate in the ocean. That said, the state of the deep ocean between 2.4 and 2.0 billion years ago is one of the singular mysteries of the Precambrian world (Fig. 3). Proposed conditions are far ranging: (1) O_2 -free (anoxic) but iron-poor (Holland 2006), (2) oxic, or (3) anoxic and H_2S -containing (euxinic) (Canfield 2005; Scott et al. 2008). The BIF gap in this interval argues against persistently ferruginous (Fe^{2+} -containing) anoxic waters, and, truth be told, the limited available data point to the presence of euxinia (Scott et al. 2008) long before the emergence of the “Canfield Ocean” (Canfield 1998) later in the Proterozoic. This earlier euxinia could reflect an increased flux of sulfate to an ocean still lacking oxygen in the deep waters, given higher but still relatively low O_2 in the atmosphere. The interval between ~2.2 and 2.0 billion years ago contains the largest positive carbon isotope excursion in Earth history (the so-called Lomagundi event). Any relationship between the implied high levels of organic-carbon burial and increased O_2 in the atmosphere might have favored either oxic deep waters or greater sulfate delivery to still O_2 -lean conditions at depth (Fig. 4), yielding euxinia. BIFs reappear in a big way between ~2.0 and 1.8 billion years ago, recording, perhaps, reinvigorated hydrothermal inputs of iron to the ocean from submarine volcanism. Another possibility, assuming the deep ocean and atmosphere were previously oxygenated, is a return to very low oxygen levels (Canfield 2005), with decreased sulfate delivery to the ocean (Frei et al. 2009).

By ~1.8 billion years ago, the BIF-favoring conditions were gone, with iron solubility waning in the ocean through enhanced deep-water oxygenation (Holland 2006), decreasing iron inputs, or increasingly prevalent deep euxinia as a result of greater sulfate delivery (Canfield 1998; Poulton et al. 2004; Frei et al. 2009; reviewed in Lyons et al. 2009a, b). Both oxic and euxinic conditions promote low iron solubility. The atmosphere had long since stopped favoring the mass-independent S isotope behavior of the Archean, but O_2 remained a very long way from the ~20% levels present today. The possibility of euxinia for more than a billion years of Proterozoic history (Canfield 1998)

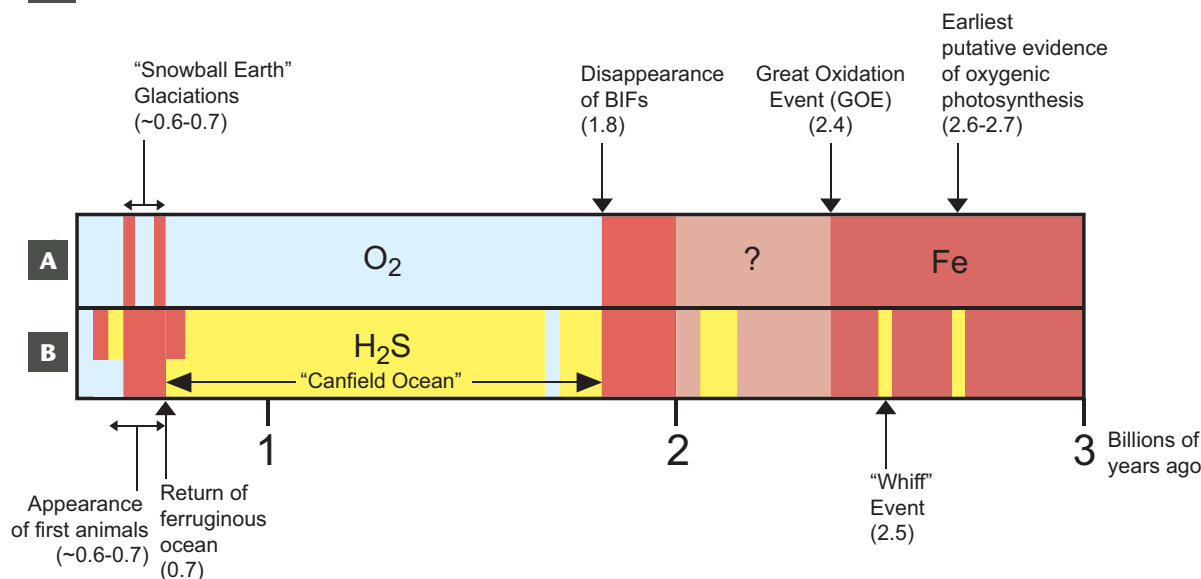


FIGURE 3 Timeline showing our best estimates for conditions in the deep ocean over Precambrian time. Dark red = ferruginous conditions, yellow = euxinia, and blue = oxic to suboxic conditions. **(A)** is dominated by the transition from early ferruginous to later oxic conditions (Holland et al. 2006). **(B)** incorporates diverse recent arguments for more variable conditions in the early deep ocean, including frequent euxinia (Canfield 1998). The more complex but still generalized temporal fabric shown in B may be better viewed in terms of coeval water-column structure. For example, euxinic waters during the late Archean and late Proterozoic might have overlain even deeper ferruginous waters in a redox stratification roughly analogous to a modern oxygen-minimum zone (Reinhard et al. 2009; Li et al. 2010). In others words, conditions were complexly variable in time and space, including important local controls that resulted in redox states limited to individual basins. Surface waters after 2.4 billion years ago are assumed to have contained appreciable, but largely unconstrained, amounts of O_2 . See text for additional details. MODIFIED FROM CANFIELD (2005) AND LYONS ET AL. (2009a, b)

and the predicted biological implications (e.g. Anbar and Knoll 2002) are hot topics in current Precambrian research (Fig. 3) (as reviewed by Lyons et al. 2009a, b).

One thing is clear: although sulfate delivery to the ocean increased across the GOE, the evidence points to still low concentrations in seawater throughout most of the Proterozoic (Fig. 4). We can imagine that comparatively low levels of oxygen in the atmosphere might have limited oxidative weathering. However, it is unlikely that the breakdown of pyrite was particularly sensitive to atmospheric O_2 concentrations greater than the threshold levels already exceeded at the GOE. (Another frontier in research is the scaling between oxidation of pyrite and other metal sulfides and atmospheric O_2 , which is not well known on global and geologic scales.)

Instead, we can argue that the abundance of pyrite formed within sulfidic sediments and water columns and subsequently buried beneath the Proterozoic ocean acted as a buffer against appreciable sulfate rise. Voluminous pyrite burial in the deep ocean may have exacerbated this buffering through subsequent seafloor subduction, which prevented later sulfur recycling and its return to the ocean via uplift and weathering (Canfield 2004). When the deep ocean is oxygenated, as has been the case over much of the last 500 million years, the formation of pyrite is restricted to organic-rich sediments along the ocean margin and is unlikely to be subducted. This shift allows for recycling and maintenance of steady-state sulfate concentrations at mostly higher levels.

The evidence that sulfate was low in the mid-Proterozoic comes in diverse forms. For example, despite a few notable exceptions, there is a general lack of bedded gypsum and anhydrite. Some of this scarcity must reflect the poor preservation of soluble calcium sulfate evaporites, but the difficulty of achieving gypsum saturation in a low-sulfate ocean was certainly a factor. The mid-Proterozoic is also known for abundant ^{34}S -enriched pyrite (Fig. 2), in contrast to the ^{34}S depletions that typify bacterial sulfate reduction. Although exceptions abound, the abundance of ^{34}S -enriched pyrite is consistent with a limited sulfate pool. Such a sulfate reservoir would yield isotopic discrimination that was correspondingly muted on the cellular level during sulfate reduction and/or during the complete or near-complete consumption of the sulfate pool on a larger scale as a consequence of pyrite burial (Lyons et al. 2009a). As a note of caution, deficiencies in seawater sulfate were likely exacerbated in restricted marginal marine basins that had limited exchange with the open ocean. Preferential preservation of these settings, as controlled by large-scale tectonics, may skew our data toward ^{34}S -enriched pyrite and bias our interpretations, in general, away from conditions in the open ocean. The deeper open ocean, which is not well preserved in the geologic record due to subduction, may have been the burial locus of much of the ^{34}S -depleted pyrite and the primary cause of the ^{34}S enrichments seen in sulfate of the same age.

Perhaps most notably, the mid-Proterozoic is also known for large isotopic variability in seawater sulfate on time-scales that were much shorter than those observed for similar amplitudes of variability over the last 500 million years (Kah et al. 2004; Gill et al. 2007). Under these lower concentrations, the residence time of sulfate in the ocean would have been short (compared to roughly 25 million years in the modern ocean), and the isotopic sensitivity of the reservoir to the quantity and isotopic composition of the fluxes would have been correspondingly high. These sulfur fluxes were dominated by inputs resulting from weathering and hydrothermal processes and by outputs through pyrite burial; the latter was likely enhanced by widespread euxinia during this time period, thus keeping sulfate concentrations low.

Earlier, we described the expanded range of sulfur isotope fractionations across the GOE as evidence for increasing sulfate content of the ocean. It is important to keep in mind, however, that these greater values need only reflect an increase in sulfate concentration to values greater than

1% of the modern seawater value, just as the loss of MIF need only signify an increase in atmospheric O₂ to concentrations that were still only a small fraction of today's. In other words, this was a defining, yet still small, step in biospheric oxygenation that nonetheless crossed critical thresholds in global redox chemistry. The precise sizes of the steps in atmospheric oxygenation are poorly known within the resolution of our proxies—yet the unambiguous sulfur signpost across the GOE, confirming that oxygenic photosynthesis had taken hold, heralds one of the great steps in the history of life on Earth.

By the late Proterozoic, the oxygenation state of Earth's surface took a second fundamental step—one that welcomed the first animals and presumably set the stage for a Phanerozoic world much more like today's. But what do we really know about conditions in the ocean during this interval? There is little doubt that the so-called "Snowball Earth" glaciations of the late Proterozoic pulled down sulfate levels to extreme lows, yielding an anoxic ocean that once again favored ferruginous intervals (Hurtgen et al. 2002). But the possibility also exists that an iron-dominated anoxic deep ocean prevailed over much of the late Proterozoic (Fig. 3; Canfield et al. 2008; Johnston et al. 2010; Li et al. 2010) after a billion years of efficient pyrite burial and subduction beneath an H₂S-rich mid-Proterozoic ocean (Canfield 2004). Other data argue for increasing oxygenation of the deep ocean during the Ediacaran—at the tail end of the Proterozoic (Fike et al. 2006; Canfield et al. 2007; Scott et al. 2008), and estimates for sulfate concentrations during the latest Proterozoic range from vanishingly small to those approaching modern levels (Lyons et al. 2009b). During the same time period, euxinic conditions have also been recorded (Li et al. 2010; Johnston et al. 2010).

At first glance the story may seem untidy, with seemingly conflicting observations suggesting very different ocean redox conditions over the same general time interval. But a parsimonious resolution is at hand: that is, an ocean that was complexly structured in space and over narrow slices of time, including the likelihood of persistent and perhaps pervasive redox layering in the ocean and strong local controls within individual marine basins (Reinhard et al. 2009; Johnston et al. 2009, 2010; Li et al. 2010). The big message in all this detail is that end-member ocean models for vast swaths of Archean and Proterozoic time have matured into images of more-textured biogeochemical evolution, reversibility, and lateral and vertical heterogeneity in the ocean (Fig. 3).

What do the pyrite data tell us? Just as the S isotopes show larger ranges and inferred fractionations across the GOE, the late Proterozoic is noted for a second major broadening of isotope values and inferred fractionations (Fig. 2), yielding for the first time the persistently and particularly large offsets between sulfate and pyrite that typify the last ~540 million years. This relationship could simply reflect large and rapid isotopic variability for the sulfate from which the pyrite was produced and/or greater concentrations of sulfate in seawater (although some indicators point to very low sulfate during this interval, as mentioned above). Canfield and Teske (1996) provided another model, which attributes the greater fractionation to disproportionation pathways responding to increasing oxidation of the surface ocean and concomitant production of the required intermediate sulfur species through partial oxidation of H₂S. They tied enhanced production of the intermediates to evolutionary radiation of nonphotosynthetic, marine sulfide-oxidizing bacteria in the late Proterozoic. Recent work pushes the existence of disproportionating prokaryotes to at least the mid-Proterozoic (Johnston et al. 2005),

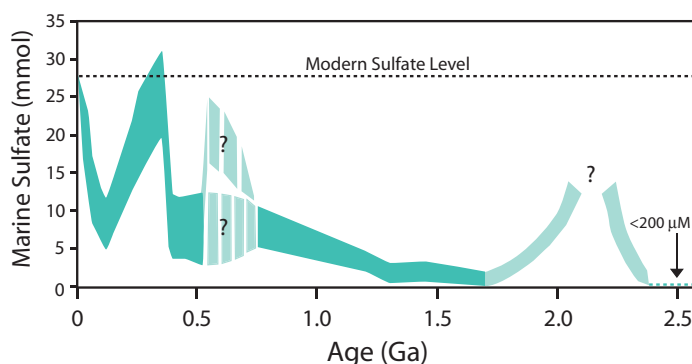


FIGURE 4 Schematic summary of seawater sulfate concentrations for the Precambrian and Phanerozoic. See text for additional details. BASED ON HABICHT ET AL. (2002), KAH ET AL. (2004), GILL ET AL. (2007), N. PLANAVSKY (PERSONAL COMMUNICATION), AND REFERENCES THEREIN

but it is reasonable to imagine that disproportionating microbes and their isotope effects became more prevalent under the increasingly oxidizing conditions of the late Proterozoic (Canfield and Teske 1996; Fike et al. 2006).

The story of sulfur in the Proterozoic ocean is also a tale of eukaryotic life. The age of the first eukaryotes is not easily agreed upon, with some work pushing the oldest records to at least 2.7 to 2.6 billion years ago (Brocks et al. 1999; compare Rasmussen et al. 2008). Independent of first appearances, the Proterozoic was undoubtedly a key time of eukaryotic diversification. As a backdrop, widespread H₂S in the sediments and water column may have reduced the availability of trace metals (e.g. molybdenum) that are key for diverse prokaryotic and eukaryotic enzymatic pathways. Such deficiencies in micronutrients would have impacted the evolutionary and ecological patterns of the early eukaryotes (Anbar and Knoll 2002; Scott et al. 2008) and the predominant prokaryotic metabolisms (reviewed in Lyons et al. 2009a, b). Then, further oxygenation in the late Proterozoic, as suggested by the sulfur isotope and trace metal data (Fike et al. 2006; Canfield et al. 2007; Scott et al. 2008; Li et al. 2010), seems to have ushered in the first animals.

In contrast to the negative impact from reduced trace metal availability, widespread sulfidic conditions in the water column may have factored positively in primary production in the Proterozoic ocean by promoting the anoxygenic photosynthetic activity of certain H₂S-oxidizing bacteria (Johnston et al. 2009). Canfield (1998) envisioned widespread and persistent euxinia for much of the mid-Proterozoic ocean. Although embraced as an overarching model, the full extent of this state remains poorly constrained, and ocean-wide euxinia at all depths below a surface oxic layer is not necessarily indicated (Scott et al. 2008; Johnston et al. 2009; Lyons et al. 2009a, b). Another hot topic is the transition from the Proterozoic to the early Phanerozoic. Suggestions that sulfate and oxygen remained low or returned to low levels during the Cambrian (Canfield 2004; Gill et al. 2007) have important implications for the explosion of animal diversity during the early Paleozoic.

OLD PROBLEMS SEEN THROUGH NEW WINDOWS

We have seen the value of tracking the sulfur isotope composition of seawater sulfate over time and the rewards that come with estimates of the isotope fractionation between sulfate and pyrite as a result of microbial cycling. Unfortunately, gypsum and anhydrite records of seawater sulfate composition are sparse in the Precambrian. Both

minerals have high solubilities and thus poor preservation potential, and gypsum saturation was less easily reached in the sulfate-poor early ocean. One approach growing in popularity is to extract the sulfate captured and preserved in the lattice of carbonate minerals (carbonate-associated sulfate, or CAS). In a perfect world, the sulfate is captured at the time of deposition and remains unaltered. Early workers showed that CAS can be abundant in carbonate rocks. But more importantly, Burdett et al. (1989) demonstrated in a pioneering paper that CAS can acquire and preserve the isotopic composition of seawater.

One of the primary attractions of the CAS method is the ubiquity of shallow-water carbonates over much of geologic time. Furthermore, these rocks can yield sulfur isotope data for pyrite and sulfate from the same sample, thus giving us—but not guaranteeing—the possibility of extracting the isotopic offset between SO_4^{2-} and H_2S during bacterial sulfate reduction (plus or minus any effects of disproportionation) within a single porewater or water-column reservoir.

WHAT LIES AHEAD?

No matter what side you take in the various debates, it is clear that sulfur has played a major, if not leading, role in our new views of the very old ocean and atmosphere. But with this success comes added responsibility. We are still a long way from understanding the limits that diagenesis may impose on the CAS proxy, for example. Our experiences have been encouraging (e.g. Kah et al. 2004; Gill et al. 2007, 2008), but we remain keenly aware of the problems that have surfaced in other CAS studies, where local, regional, and global variability (spatial and stratigraphic) is not easily explained by primary paleoceanographic conditions. As for all proxies, those hosted by carbonates in particular, caution is the operative term.

We do not yet understand the full range of controls on isotope fractionations tied to the sulfur biogeochemical cycle, including the role of sulfur disproportionation and the extent to which inferred fractionations unambiguously track paleoenvironmental conditions, such as seawater-sulfate concentrations. In studies of modern sediments, we can generate porewater data for co-occurring dissolved H_2S and SO_4^{2-} , but determinations of fractionations from these integrated records still require oversimplifying assumptions of closed-system behavior or sophisticated reactive-transport models.

The challenge is even greater for ancient rocks, in part because continuous, robust sulfate isotope records are sparse. Given this gap, pyrite and sulfate data that only loosely represent the same age and region are often compared. Previous work has shown that rapid isotopic variability in the ocean can make such comparison risky (Kah et al. 2004). Part of the solution lies with the novel approach of generating pyrite and sulfate isotope data from single samples, using CAS for the latter (Fike et al. 2006). But even then, the offset is only an approximation of the instantaneous fractionation during microbial sulfate reduction—plus or minus any additional biological processing. Different signals can be recorded at different times in the early history of the same sediment, just as porewater data are not easily tied to instantaneous, simultaneous processes. But we have taken big steps in the right direction, and first-order relationships have emerged and are holding up well under the scrutiny of additional work.

The degree to which specific metabolic processes, such as sulfate reduction and disproportionation of sulfur intermediates, can be recognized in the ancient record from

isotopic offsets between parent and product sulfur species is enhanced by recent studies emphasizing multiple S isotopes (^{32}S , ^{33}S , ^{34}S , and ^{36}S) (Johnston et al. 2005). These challenging but rewarding measurements and interpretations, supported by rigorous experimental work, are yielding unique fingerprints of specific sulfur metabolisms. Each new step will bring us closer to a better understanding of the early ocean and the complexity of its structure in time and space over billions of years of history.

CONCLUDING REMARKS

Among the elements, sulfur has played the greatest role in our understanding of early biospheric oxygenation. For example, studies have shown that the loss of mass-independent sulfur isotope fractionation is a consequence of the initial rise of atmospheric oxygen and that isotopic offsets between sulfate and sulfide constrain the amount of ancient seawater sulfate. Seawater sulfate derives primarily from oxidative weathering on the continents, so its delivery to the ocean is tied intimately to the amount of oxygen in the early atmosphere. Oxygen in the atmosphere and sulfate in the ocean were both low before the Great Oxidation Event about 2.4 billion years ago. That said, before the GOE, subtle and varying oxygen and sulfate contributions, along with variability in hydrothermal iron inputs, favored at least local euxinia and even weakly oxic surface waters in an ocean traditionally assumed to have been unyieldingly anoxic and ferruginous. Following the GOE, sulfate delivery increased, although atmospheric oxygen remained sufficiently low to permit widespread accumulation of sulfide in the sediments and deep water column. The spatiotemporal extent of these conditions, including the enigmatic state of the ocean between 2.4 and 2.0 billion years ago, remains an area of particularly active research. However, well beyond any uncertainty over where all the H_2S resided, its overall Proterozoic abundance and its impact on trace metal (micronutrient) solubility are certain to have influenced the patterns and rates of prokaryotic and eukaryotic evolution. These controls are an exciting area of active research.

The mix of arguments for the state of the deep ocean in the late Proterozoic seem to point in different directions, including (1) iron-dominated conditions, like those of the Archean; (2) increased oxygenation, in phase with the greater O_2 content of the atmosphere that spawned the advent and initial proliferation of animal life; and (3) even euxinia on at least local scales. But there is little reason for concern. The latest models are welcoming the possibility of temporal and spatial heterogeneity, particularly in an ocean operating at low, near-threshold levels of oxygen and sulfate. The likelihood of heterogeneity is not unique to the late Proterozoic, with mid-water-column euxinia and other variations of redox layering as well as localized conditions within restricted settings possible throughout the Precambrian. Sulfur has been a linchpin in our understanding of early oxygen in the atmosphere and ocean. The last two decades have seen a renaissance in studies of sulfur biogeochemistry, but the most exciting times lie ahead.

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REFERENCES

- Anbar AD, Knoll AH (2002) Proterozoic ocean chemistry and evolution: A bioinorganic bridge? *Science* 297: 1137-1142
- Anbar AD, Duan Y, Lyons TW, Arnold GL, Kendall B, Creaser RA, Kaufman AJ, Gordon GW, Scott C, Garvin J, Buick R (2007) A whiff of oxygen before the Great Oxidation Event? *Science* 317: 1903-1906
- Berner RA (2006) GEOCARBSULF: A combined model for Phanerozoic atmospheric O₂ and CO₂. *Geochimica et Cosmochimica Acta* 70: 5653-5664
- Brocks JJ, Logan GA, Buick R, Summons RE (1999) Archean molecular fossils and the early rise of eukaryotes. *Science* 285: 1033-1036
- Burdett JW, Arthur MA, Richardson M (1989) A Neogene seawater sulfur isotope age curve from calcareous pelagic microfossils. *Earth and Planetary Science Letters* 94: 189-198
- Canfield DE (1998) A new model for Proterozoic ocean chemistry. *Nature* 396: 450-453
- Canfield DE (2004) The evolution of the Earth surface sulfur reservoir. *American Journal of Science* 304: 839-861
- Canfield DE (2005) The early history of atmospheric oxygen: Homage to Robert M. Garrels. *Annual Review of Earth and Planetary Sciences* 33: 1-36
- Canfield DE, Teske A (1996) Late Proterozoic rise in atmospheric oxygen concentration inferred from phylogenetic and sulphur-isotope studies. *Nature* 382: 127-132
- Canfield DE, Thamdrup B (1994) The production of ³⁴S-depleted sulfide during bacterial disproportionation of elemental sulfur. *Science* 266: 1973-1975
- Canfield DE, Poulton SW, Narbonne GM (2007) Late-Neoproterozoic deep-ocean oxygenation and the rise of animal life. *Science* 315: 92-95
- Canfield DE, Poulton SW, Knoll AH, Narbonne GM, Ross G, Goldberg T, Strauss H (2008) Ferruginous conditions dominated later Neoproterozoic deep-water chemistry. *Science* 321: 949-952
- Farquhar J, Wing BA (2003) Multiple sulfur isotopes and the evolution of the atmosphere. *Earth and Planetary Science Letters* 213: 1-13
- Fike DA, Grotzinger JP, Pratt LM, Summons RE (2006) Oxidation of the Ediacaran ocean. *Nature* 444: 744-747
- Frei R, Gaucher C, Poulton SW, Canfield DE (2009) Fluctuations in Precambrian atmospheric oxygenation recorded by chromium isotopes. *Nature* 461: 250-253
- Gill BC, Lyons TW, Saltzman MR (2007) Parallel, high-resolution carbon and sulfur isotope records of the evolving Paleozoic marine sulfur reservoir. *Palaeogeography, Palaeoclimatology, Palaeoecology* 256: 156-173
- Gill BC, Lyons TW, Frank TD (2008) Behavior of carbonate-associated sulfate during meteoric diagenesis and implications for the sulfur isotope paleoproxy. *Geochimica et Cosmochimica Acta* 72: 4699-4711
- Habicht KS, Gade M, Thamdrup B, Berg P, Canfield DE (2002) Calibration of sulfate levels in the Archean ocean. *Science* 298: 2372-2374
- Holland H (2006) The oxygenation of the atmosphere and oceans. *Philosophical Transactions of the Royal Society B* 361: 903-915
- Hurtgen MT, Arthur MA, Suits NS, Kaufman AJ (2002) The sulfur isotopic composition of Neoproterozoic seawater sulfate: implications for snowball Earth? *Earth and Planetary Science Letters* 203: 413-429
- Johnston DT (2010) Touring the biogeochemical landscape of a sulfur-fueled world. *Elements* 6: 101-106
- Johnston DT, Wing BA, Farquhar J, Kaufman AJ, Strauss H, Lyons TW, Kah LC, Canfield DE (2005) Active microbial sulfur disproportionation in the Mesoproterozoic. *Science* 310: 1477-1479
- Johnston DT, Wolfe-Simon F, Pearson A, Knoll AH (2009) Anoxygenic photosynthesis modulated Proterozoic oxygen and sustained Earth's middle age. *Proceedings of the National Academy of Sciences* 106: 16925-16929
- Johnston DT, Poulton SW, Dehler C, Porter S, Husson J, Canfield DE, Knoll AH (2010) An emerging picture of Neoproterozoic ocean chemistry: Insights from the Chuar Group, Grand Canyon, USA. *Earth and Planetary Science Letters* 290: 64-73
- Kah LC, Lyons TW, Frank TD (2004) Low marine sulphate and protracted oxygenation of the Proterozoic biosphere. *Nature* 431: 834-838
- Li C, Love GD, Lyons TW, Fike DA, Sessions AL, Chu X (2010) A stratified redox model for the Ediacaran ocean. *Science* doi:10.1126/science.1182369
- Lyons TW, Anbar AD, Severmann S, Scott C, Gill BC (2009a) Tracking euxinia in the ancient ocean: A multiproxy perspective and Proterozoic case study. *Annual Review of Earth and Planetary Sciences* 37: 507-534
- Lyons TW, Reinhard CT, Scott C (2009b) Redox redux. *Geobiology* 7: 489-494
- Poulton SW, Fralick PW, Canfield DE (2004) The transition to a sulphidic ocean ~1.84 billion years ago. *Nature* 431: 173-177
- Rasmussen B, Fletcher IR, Brocks JJ, Kilburn MR (2008) Reassessing the first appearance of eukaryotes and cyanobacteria. *Nature* 455: 1101-1104
- Reinhard CT, Raiswell R, Scott C, Anbar AD, Lyons TW (2009) A late Archean sulfidic sea stimulated by early oxidative weathering of the continents. *Science* 326: 713-716
- Schidlowski M (1979) Antiquity and evolutionary status of bacterial sulfate reduction: Sulfur isotope evidence. *Origins of Life and Evolution of Biospheres* 9: 299-311
- Scott C, Lyons TW, Bekker A, Shen Y, Poulton SW, Chu X, Anbar AD (2008) Tracing the stepwise oxygenation of the Proterozoic ocean. *Nature* 452: 456-459
- Shen Y, Buick R, Canfield DE (2001) Isotopic evidence for microbial sulphate reduction in the early Archean era. *Nature* 410: 77-81
- Sverjensky DA, Lee N (2010) The Great Oxidation Event and mineral diversification. *Elements* 6: 31-36