SULFUR ISOTOPES AND THE STEPWISE OXYGENATION OF THE BIOSPHERE

Lee R. Kump[*]

Given a choice of elements to reconstruct the redox history of the planet, geochemists choose sulfur. Many biogeochemical processes fractionate the multiple stable isotopes of S in telltale ways, leaving their imprint in the sedimentary record. Detailing and interpreting that record has become the passion of the paleobiogeochemical community, especially researchers seeking to understand the redox evolution of the oceans and atmosphere through the Precambrian.

Until fairly recently, the main proxy of S biogeochemistry in Earth's past was the standardized isotope ratio of the two most abundant isotopes, ^{32}S and ^{34}S, expressed as $\delta^{34}S$, where

$$\delta^{34}S = \left(\frac{\left(^{34}S / {}^{32}S\right)_{sample} - \left(^{34}S / {}^{32}S\right)_{reference}}{\left(^{34}S / {}^{32}S\right)_{reference}} \right) \times 1000 \, .$$

Given the rarity of sedimentary sulfates, including gypsum and anhydrite, in the Precambrian, the chief repository of information about $\delta^{34}S$ during that time was sedimentary pyrite (FeS_2). Such pyrite typically formed during early diagenesis in anoxic sediments supporting bacterial sulfate reduction (BSR), assuming an adequate availability of reactive iron. The difference between the $\delta^{34}S$ of contemporaneous marine sulfate and sedimentary pyrite ($\Delta^{34}S_{sulfate-pyrite} = \delta^{34}S_{sulfate} - \delta^{34}S_{pyrite}$) depends on isotope discrimination during BSR, itself dependent on sulfate concentration below a threshold (~200 μM; Habicht et al. 2002); it also depends on the rate at which sulfate from the overlying seawater communicates with the diagenetic environment by diffusion: if the rate of sulfate reduction and mineralization into pyrite exceeds the exchange of sulfate between porewaters and the overlying seawater, the conversion from sulfate to sulfide is complete and $\Delta^{34}S_{sulfate-pyrite}$ tends towards zero. Thus, the range of pyrite $\delta^{34}S$ has been taken to be indicative of the overall magnitude of the isotopic difference between pyrite and seawater sulfate at any particular time in the Precambrian: the highest $\delta^{34}S$ values reflect complete sulfate utilization and thus the isotopic composition of the overlying seawater; the lowest values reflect fully expressed biological fractionation.

Low variability in pyrite $\delta^{34}S$ in the Archean has been interpreted to reflect sulfate-limiting conditions for BSR (FIG. 1). Increasing spread in the range of pyrite $\delta^{34}S$ values from the late Archean to the early Paleoproterozoic could represent a marked increase in the concentration of sulfate in seawater associated with the intensification of oxidative weathering during the Great Oxidation Event (GOE) at ca. 2.4 Ga (Kah et al. 2001; Canfield and Farquhar 2009; Shields-Zhou and Och 2011). Indeed, at the microscopic scale, ~2.4 Ga pyrites from glaciogenic sedimentary rocks from Western Australia (not shown in Figure 1) exhibit a huge (~90‰) range in $\delta^{34}S$ (Williford et al. 2011), the lowest values indicating nonsulfate-limited BSR. Moreover, roughly contemporaneous $\Delta^{34}S_{sulfate-pyrite}$ values from carbonate-associated sulfate and pyrite from South Africa document an increase in isotopic discrimination to values approaching 30‰ at the time of the Great Oxidation Event and associated glaciation (Guo et al. 2009).

Sulfur isotopes have also been used to argue for a second step in the oxygenation of the biosphere during the Neoproterozoic (1000–542 million years ago). Canfield and Teske (1996) proposed that the apparent Neoproterozoic expansion of the range of sulfur isotope fractionation in pyrite (FIG. 1) heralded the origin and global expression of an oxidative sulfur cycle and bacterial sulfur disproportionation (BSD), a redox reaction in which elemental sulfur is both reduced to sulfide and oxidized to sulfate. An increase in atmospheric oxygen content in the Neoproterozoic would have allowed for the oxygenation of the
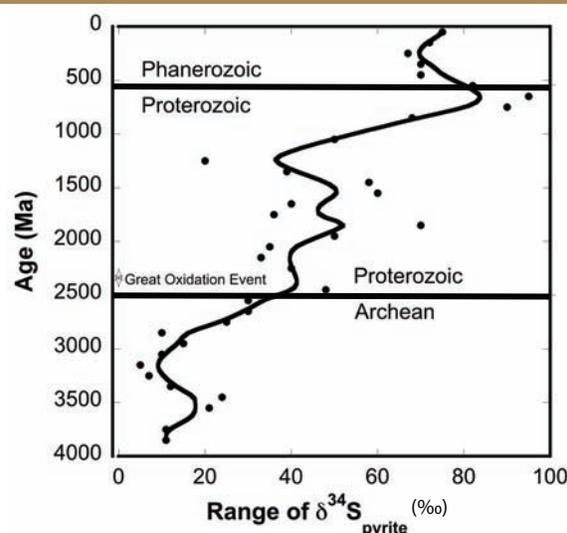
---
* Department of Geosciences, Pennsylvania State University
503 Deike Bldg, University Park, PA 16802, USA

FIGURE 1 Approximate range of $\delta^{34}S$ of pyrites binned into 100-million-year intervals, from the compilation by Williford et al. (2011) but excluding SIMS data; the smooth line is a geometrically weighted 100-point interpolation of the data.

deep ocean and for the rise to prominence of nonphotosynthetic pathways of sulfide oxidation to elemental sulfur, providing opportunities for sulfur disproportionation. The formation of sulfide from sulfide oxidation to elemental sulfur followed by BSD is a process that can impart additional isotope fractionation on the sulfide used to form pyrite (Canfield and Thamdrup 1994; Canfield and Teske 1996). Sulfur disproportionation leads to the production of ^{34}S-depleted H_2S and ^{34}S-enriched sulfate from sulfur intermediates produced during the aerobic microbial oxidation of H_2S (Canfield and Teske 1996). Indeed, BSD has been deemed necessary to explain some exceptionally low $\delta^{34}S$ values in pyrite forming in modern environments (Habicht and Canfield 2001). Canfield and Teske (1996) argued, therefore, that the evidence of BSD was consistent with other arguments for a second oxygenation event in the Neoproterozoic, one that provided a necessary, if not sufficient, condition for the origin and evolution of metazoans.

Subsequent work (Hurtgen et al. 2005; Fike et al. 2006) improved the temporal resolution of the $\delta^{34}S$ records of pyrite and sulfate in the Neoproterozoic. Hurtgen et al. (2005) found that the evidence for an increase in isotope discrimination was restricted to sedimentary rocks formed after 580 Ma, and Fike et al. (2006) refined this to be around 550 Ma. Furthermore, Hurtgen et al. (2005, 2009) suggested that the expansion of the $\delta^{34}S$ difference between sulfate and pyrite was the result not of the onset of BSD but rather of an increase in seawater sulfate concentrations (inferred from isotope variability as well as other geologic indicators; Halverson and Hurtgen 2007), which relaxed sulfate limitation on pyrite deposition rates and allowed for the expression of larger isotope fractionations (Hurtgen et al. 2009). A return to smaller $\Delta^{34}S_{sulfate-pyrite}$ in the Cambrian was noted by these authors, and Ries et al. (2009) argued that low seawater sulfate concentrations were reestablished by late Neoproterozoic times. These results challenged the tacit assumption of monotonic increases in oceanic sulfate concentrations through Earth history, driven by progressive oxidation of the oceans and atmosphere.

However, many of these studies were carried out in individual basins, raising the possibility that the $\Delta^{34}S_{sulfate-pyrite}$ values they exhibit may reflect basinal rather than global sulfur cycling. In the modern ocean, the $\delta^{34}S$ of sulfate is geographically uniform because of the long residence time (due to high concentration) of sulfate in the ocean. Ries et al. (2009) and Loyd et al. (2012) presented evidence for significant spatial variability in $\delta^{34}S$ of Neoproterozoic and Cambrian seawater sulfate. If so, then apparent expansions and contractions in $\Delta^{34}S_{sulfate-pyrite}$ during

the Neoproterozoic may reflect local variations in sulfate concentrations or other factors rather than global increases or decreases in either the importance of BSD or seawater sulfate concentrations.

Recent improvements in the accuracy of the analysis of the rarer stable isotopes of S (^{33}S and ^{36}S) have revolutionized the use of S isotopes in the reconstruction of S cycling in the Precambrian and for understanding the oxygenation of the atmosphere and ocean. Most notable of the resulting discoveries was the large extent of mass-independent fractionation (MIF) of the S isotopes exclusively in pyrite of Archean age (Farquhar et al. 2000), expressed as the deviation from the expected mass-dependent relationship between δ^{33}S and δ^{34}S:

$$\Delta^{33}S = \delta^{33}S - [(\delta^{34}S/1000 + 1)^{0.515} - 1)] \times 1000.$$

The explanation proposed by Farquhar et al. (2000), still widely (but not universally; Ohmoto et al. 2006; Watanabe et al. 2009) accepted today, is that the expression and preservation of MIF in sedimentary pyrite was possible only under an essentially anoxic atmosphere. Thus, the sulfur MIF record became the smoking gun for the GOE.

Of broader applicability to the paleobiogeochemistry community, though, are the more subtle variations in the relationships between the mass-dependent isotopic fractionations of the multiple sulfur isotopes that result from nonequilibrium fractionation during (primarily) biological processes. Included among these are BSR and BSD. Johnston et al. (2005) established the limits of possible variation in isotope space (Δ^{33}S versus δ^{34}S) of seawater sulfate influenced by BSR only, based on observed fractionations, and then showed that seawater sulfate proxies younger than 1300 Ma fell outside that range. These results pushed back the isotopic evidence for the origin of BSD of Canfield and Teske (1996) by several hundred million years.

Two new observations further complicate the interpretation of sulfur isotopes in terms of specific metabolic pathways. The first was by Canfield et al. (2010), who reported the first direct determination of isotope fractionations by natural populations of sulfate-reducing bacteria that significantly exceed the previously assumed upper limit of 48‰ for BSR: up to 70‰ for bacteria living in Lake Cadagno, Switzerland. The authors ruled out the possibility of BSD contributing to these large isotopic differences based on the pattern of δ^{34}S and Δ^{33}S variability and consistency with results from controlled incubation experiments where only BSR was occurring (Canfield et al. 2010); this left BSR as the only process fractionating sulfur at Lake Cadagno.

The second complication comes from the recent work of Shuhei Ono and colleagues (Sim et al. 2011), who found similarly high fractionations due to BSR alone in pure cultures. From these results and the field observations of Canfield et al. (2010), it appears that BSR can produce isotope effects that cover the range of Δ^{33}S–δ^{34}S values observed in Proterozoic and Phanerozoic seawater sulfate proxies that were formerly thought to be diagnostic of BSD.

These studies have their limitations. The sulfate-reducing bacteria of both Lake Cadagno and the strains used in the Sim et al. study are capable of BSD. In both cases, the authors make compelling, but not incontrovertible, claims that BSD is unimportant in the settings studied: the possibility remains that processes other than BSR were affecting sulfur isotope compositions. On the other hand, it is likely that once an oxidative sulfur cycle was established in the ocean, sulfur disproportionation became an important part of the process. The isotope data simply cannot be conclusively interpreted as diagnostic of that pathway.

When geochemists pull sulfur isotope analysis out of their toolbox, they do so knowing that, although its potential is great, its application and interpretation is complicated. As the tool has been refined, so too has our knowledge of the coupled evolution of life and environment during the critical but enigmatic period between the GOE and the metazoan revolution. A complete understanding of the events of this nearly 2-billion-year interval of Earth history, though, awaits further application of all the tools we have on the best-preserved sedimentary rocks, and, perhaps, the development of new tools that will finally crack the problem of the evolution of the sulfur cycle and the oxygenation of the biosphere. ◾

REFERENCES

Canfield DE, Farquhar J (2009) Animal evolution, bioturbation, and the sulfate concentration of the oceans. Proceedings of the National Academy of Sciences 106: 8123-8127

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, Farquhar J, Zerkle AL (2010) High isotope fractionations during sulfate reduction in a low-sulfate euxinic ocean analog. Geology 38: 415-418

Farquhar J, Bao H, Thiemens M (2000) Atmospheric influence of Earth's earliest sulfur cycle. Science 289: 756-758

Fike DA, Grotzinger JP, Pratt LM, Summons RE (2006) Oxidation of the Ediacaran ocean. Nature 444: 744-747

Guo QJ, Strauss H, Kaufman AJ, Schröder S, Gutzmer J, Wing B, Baker MA, Bekker A, Jin QS, Kim S-T, Farquhar J (2009) Reconstructing Earth's surface oxidation across the Archean–Proterozoic transition. Geology 37: 399-402

Habicht KS, Canfield DE (2001) Isotope fractionation by sulfate-reducing natural populations and the isotopic composition of sulfide in marine sediments. Geology 29: 555-558

Habicht KS, Gade M, Thamdrup B, Berg P, Canfield DE (2002) Calibration of sulfate levels in the Archean Ocean. Science 298: 2372-2374

Halverson GP, Hurtgen MT (2007) Ediacaran growth of the marine sulfate reservoir. Earth and Planetary Science Letters 263: 32-44

Hurtgen MT, Arthur MA, Halverson GP (2005) Neoproterozoic sulfur isotopes, the evolution of microbial sulfur species, and the burial efficiency of sulfide as sedimentary pyrite. Geology 33: 41-44

Hurtgen MT, Pruss SB, Knoll AH (2009) Evaluating the relationship between the carbon and sulfur cycles in the later Cambrian ocean: An example from the Port au Port Group, western Newfoundland, Canada. Earth and Planetary Science Letters 281: 288-297

Johnston DT, Farquhar, J, Wing BA, Kaufman AJ, Canfield DE, Habicht KS (2005) Multiple sulfur isotope fractionations in biological systems: A case study with sulfate reducers and sulfur disproportionators. American Journal of Science 305: 645-660

Kah LC, Lyons TW, Chesley J (2001) Geochemistry of a 1.2 Ga carbonate evaporite succession, northern Baffin and Bylot islands: Implications for Mesoproterozoic marine evolution. Precambrian Research 111: 203-234

Loyd SJ, Marenco PJ, Hagadorn JW, Lyons TW, Kaufman AJ, Sour-Tovar F, Corsetti FA (2012) Sustained low marine sulfate concentrations from the Neoproterozoic to the Cambrian: Insights from carbonates of northwestern Mexico and eastern California. Earth and Planetary Science Letters 339-340: 79-94

Ohmoto H, Watanabe Y, Ikemi H, Poulson SR, Taylor BE (2006) Sulphur isotope evidence for an oxic Archaean atmosphere. Nature 442: 908-911

Ries JB, Fike DA, Pratt LM, Lyons TW, Grotzinger JP (2009) Superheavy pyrite ($\delta^{34}S_{pyr} > \delta^{34}S_{CAS}$) in the terminal Proterozoic Nama Group, southern Namibia: A consequence of low seawater sulfate at the dawn of animal life. Geology 37: 743-746

Shields-Zhou G, Och L (2011) The case for a Neoproterozoic oxygenation event: Geochemical evidence and biological consequences. GSA Today 21: 4-11

Sim MS, Bosak T, Ono S (2011) Large sulfur isotope fractionation does not require disproportionation. Science 333: 74-77

Watanabe Y, Farquhar J, Ohmoto H (2009) Anomalous fractionations of sulfur isotopes during thermochemical sulfate reduction. Science 324: 370-373

Williford KH, Van Kranendonk MJV, Ushikubo T, Kozdon R, Valley JW (2011) Constraining atmospheric oxygen and seawater sulfate concentrations during Paleoproterozoic glaciation: In situ sulfur three-isotope microanalysis of pyrite from the Turee Creek Group, Western Australia. Geochimica et Cosmochimica Acta 75: 5686-5705 ◾

Lee R. Kump received his AB degree in geophysical sciences from the University of Chicago in 1981 and his PhD in marine sciences from the University of South Florida in 1986. He has been on the faculty of the Department of Geosciences at Penn State since 1986. Kump is a fellow of the Geological Society of America, the Geological Society of London, and the Geochemical Society/European Association of Geochemistry. His research interests include the evolution of ocean and atmosphere composition on geologic timescale, biogeochemical cycling in aquatic environments, human impact on coastal environments, and environmental change during extreme events in Earth history.