

## THE GENERATION OF MASS INDEPENDENT ISOTOPIC FRACTIONATIONS

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It is known that mass independent isotopic fractionations occur in a large variety of molecules in nature. Every oxygen bearing molecule in the earth's atmosphere is mass independent not co linear with mantle rocks and the oceans. (Thiemens, 2013). The cause of each but clearly these processes are pervasive in nature and further understanding problems in climate, atmospheric chemistry, fundamental reaction dynamics, aerosol transport, Martian atmospheric chemistry, solar system formation and evolution and apportionment of greenhouse gases.

Sulfur isotopes are used as a direct measure of oxygen levels and evolution. The basis for this is that photolysis of sulfur dioxide produces a MIF observed in Archean rocks. Variations in the anomalies magnitude over time and their ultimate removal are features that permit deeper insight into the early life's origin and evolution.  $\text{SO}_2$  occurs in the UV spectra region and in the present day atmosphere does not undergo photolysis because of filtration of UV light by stratospheric ozone. As the original paper of Farquhar, Bao and Thiemens (2001) demonstrated, for a low oxygen atmosphere, penetration of UV light to the earth's surface photo dissociates the short lived  $\text{SO}_2$  molecule exists, produces the sulfur MIF and reflects the oxygen levels of the atmosphere. This only occurs today during massive volcanoes such as Pinatubo and El Chichon where copious amount of  $\text{SO}_2$  are injected into the stratosphere where its UV photolysis occurs and is recorded in the ice record (review by Thiemens, 2013).

Shaheen et al (2011,2014) have shown in a high temporal resolution snow pit dug at the South Pole, most sulfate transported to the polar region is mass independent (sulfur and oxygen) and lies within the 4 isotope sulfur regime defined by the Archean record. The largest atmospheric anomaly recorded in recent times was in 1998 when there were *no* volcanoes present, or evidence for a direct  $\text{SO}_2$  route to the stratosphere. Various new routes for the production of the anomaly are discussed and what the consequences. It was also shown that globally collected atmospheric sulfate aerosols are also predominantly MIF and these signals do not derive from the stratosphere or  $\text{SO}_2$  photolysis.

In recent work by Chakraborty et al (2014) the isotopic fractionation of  $\text{N}_2$  was reported across wavelengths associated with different electronic surfaces. The nitrogen molecule is the only one where all surfaces and states and isotopic are all measured, consequently the process of the photodissociation may be precisely described. The results reveal the largest isotope effect ever measured and, show that present photochemical theories are inadequate for describing isotopic photodissociative processes.

References: Chakraborty et al (2014) Proc Nat. Acad. Science. Early on line. Shaheen et al (2014), Proc.Nat Acad Sci 111, 11979-11983; Shaheen et al (2013),Proc. Nat Acad Sci 110, 17662-17667; Thiemens (2013) Proc Nat Acad Sci. 110, 17631-17637.

## Reconstructing Earth's Early Sulfur Cycle

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The sulfur cycle has evolved dramatically over roughly 4 billion years of Earth history — from a prebiotic planetary titration of hydrothermal/magmatic sulfur and iron, through the emergence and ecological expansion of myriad sulfur-utilizing microbial metabolisms on a largely reducing Earth surface, to the pervasively oxidizing sulfur cycle familiar to us today — which serves as a fulcrum linking many of the Earth's most important global biogeochemical cycles. A number of secular “bottlenecks” in the progressive evolution of the sulfur cycle may have appeared, either permanently or transiently, during the earliest portion of Earth's rock record – the Archean. This talk will explore a small corner of this landscape, with a focus on some of the major fluxes and reservoirs of the sulfur cycle during Earth's earliest history and with an eye toward exciting opportunities that exist in the realm of interrogating empirical records in the context of quantitative models. The talk will first explore oxidative weathering as a key component of the Earth surface sulfur cycle — its importance in linking the global sulfur cycle with those of oxygen and carbon, its role in eliminating and/or propagating surface sulfur isotope signals, and the gaps that exist in our understanding of when this process began and ultimately rose to prominence. This will be followed by a discussion of the importance of marine sulfate reservoir size, an important indicator of redox poise in the global sulfur cycle. The focus here will be on a case study exploring the potential role of anaerobic oxidation of methane (AOM) as a metabolic link between the Earth surface sulfur cycle, atmospheric chemistry, and planetary climate prior to the secular accumulation of large quantities of oxygen in Earth's atmosphere.

### **Additional reading:**

Walker, J.C.G., and Brimblecombe, P. (1985) Iron and sulfur in the pre-biologic ocean. *Precambrian Research*, **28** 205-222.

Canfield, D.E., Habicht, K.S., Thamdrup, B. (2000) The Archean sulfur cycle and the early history of atmospheric oxygen. *Science*, **288**, 658-661.

Farquhar, J., Wu, N., Canfield, D.E., and Oduro, H. (2010) Connections between sulfur cycle evolution, sulfur isotopes, sediments, and base metal sulfide deposits. *Economic Geology*, **105**, 509-533.

## New approaches for understanding the Archean sulfur isotope record

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All rocks of early Precambrian age have complications introduced from post-depositional processes, but we do not have a strong understanding of how these processes might have impacted sulfur biogeochemical data. Most sulfur isotope measurements employed to date operate on ‘bulk’ samples, typically gram-sized or larger pieces. As such, they lack the ability to relate geochemistry to petrography (which allows one to tell time from cross-cutting relationships) at the scale of mineral grains. We have been working to bring to bear analytical techniques that allow mapping of properties of S-bearing phases at micrometer scales, in essence “imaging” the proxy data. We use light and electron microscopy for petrography, electron microprobe and synchrotron XRF for elemental composition, synchrotron X-ray spectroscopy for redox state and electronic structure, SQUID microscopy for remnant magnetism and the timing of iron mineralization, and secondary ion mass spectrometry (SIMS) to make isotope ratio measurements and inform bulk rock isotope data. The combination of these tools, and the ability to move back and forth between them working on the same samples is essential for untangling the complex histories associated with ancient sedimentary rocks and recovering accurate paleoenvironmental signals.

In this talk we will present data from the Late Archean-age Transvaal and Mt. Bruce Supergroups in South Africa and Western Australia, respectively. Both of these successions are exceptionally well preserved *for their age*. However each has multiple unique episodes of fluid flow and sulfur mineralization. In South Africa two key events impacted these strata—the 2.0 Ga Bushveld complex and crustal thickening in the western fold belt at 1.1 Ga. Strata in Western Australia have been impacted by many more metasomatic events (six that we can identify), but also oxidative weathering to substantial depths below the current Earth surface. Our observations show that these events have significantly impacted the sulfur isotope signals held by these rocks, but also provide some windows into early sedimentary products and primary sulfur cycle processes. These results provide support for hypotheses that microbial respiration of high valent sulfur compounds was important in environments rich in organic carbon. They also highlight that sulfur pools were much more dynamic compared to the characteristic timescales of sedimentary record.

### Further Reading:

Fischer WW, Fike DA, Johnson JE, Raub TD, Guan Y, Kirschvink JL, Eiler JM (2014) SQUID-SIMS is a useful approach to uncover primary signals in the Archean sulfur cycle, *Proceedings of the National Academy of Sciences*, 111, 5468-5473, doi: 10.1073/pnas.1322577111.

Johnson JE, Webb SM, Thomas K, Ono S, Kirschvink JL, Fischer WW (2013) Manganese-oxidizing photosynthesis before the rise of cyanobacteria, *Proceedings of the National Academy of Sciences*, 108, 11238-11243.

Paris G, Adkins JF, Sessions AL, Fischer WW (2014) Neoproterozoic carbonate-associated sulfate records positive D33S anomalies, *Science*, in press.

## Lacustrine constraints on Archean seawater sulfate

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The sulfur cycle has evolved through time and was characterized by much lower marine sulfate concentrations on the early Earth, but just how low remains uncertain. The low sulfate levels have been inferred mainly through interpretations of sulfur isotope patterns as preserved in ancient sedimentary rocks. Experimental calibrations of microbial sulfur isotope fractionation on both intact natural populations and pure laboratory cultures of sulfate reducers showed that large sulfur isotope fractionations occur when sulfate concentrations exceed about 200  $\mu\text{M}$ , whereas below this concentration, fractionation appeared to be suppressed. This calibration led to the original conclusion that the Archean ocean contained less than about 200  $\mu\text{M}$  sulfate. The distribution of mass independent sulfur isotopes in Archean sediments and box models of global sulfur cycling imply even lower Archean seawater sulfate of <60-80  $\mu\text{M}$ . Paradoxically, micro-scale sulfur isotope data from Archean pyrites reveal large sulfur isotope fractionations of up to 40 ‰ in the Archean—fractionations only seen at hundreds to thousands of  $\mu\text{M}$  sulfate in modern environments. Electron donor availability and sulfate reduction rates, however, also exert influence, with larger fractionation typically imparted when electron donors limit sulfate reduction rates, and this suggests the unexplored possibility for large fractionations in low sulfate (<100  $\mu\text{M}$ ) environments. To resolve the apparent paradox of high sulfur isotope fractionations in Archean oceans with low seawater sulfate, we explored sulfur cycling and isotope fractionation in Lake Matano, Indonesia, an extremely low-sulfate Archean ocean analogue. We report these results and use models informed by the sulfur cycle at Lake Matano to reconstruct Archean sulfate concentrations.

1. D. E. Canfield, *Geochimica Et Cosmochimica Acta* **65**, 1117 (Apr, 2001).
2. D. E. Canfield, J. Farquhar, A. L. Zerkle, *Geology* **38**, 415 (May, 2010).

## The MIF-S signature of Archean and Paleoproterozoic oceanic sulfate – implications for oxygen

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**Abstract:** Mass independent sulfur isotope signatures (MIF-S) are observed in a wide variety of rock types and are considered to be a continuous tracer of oxygen levels, possibly even providing a way to capture changes in atmospheric chemistry, including the rise of oxygen. Interpretation of this MIF-S record is, however, complicated because the record itself reflects not only MIF-S production mechanisms but also processing of a number of possible intermediate sulfur pools. One of the key intermediate pools is oceanic sulfate which could acquire its isotopic composition from a variety of possible sources.

Inferences about atmospheric exit channels for sulfate are inferred to carry negative  $\Delta^{33}\text{S}$ , and this is supported by Paleoarchean barites, biogenic pyrite, and VMS sulfides have negative  $\Delta^{33}\text{S}$ . This context has led to the assertion that oceanic sulfate started with negative  $\Delta^{33}\text{S}$  and may have carried this signature throughout the Archean. It has also been argued that oxidation reactions may transfer sulfur having MIF-S signatures with positive  $\Delta^{33}\text{S}$ . Such processes could have driven oceanic sulfate to positive  $\Delta^{33}\text{S}$  as a result of oxidation ‘events’ associated with low level oxygenation, and even have the potential to generate false signatures for low oxygen even after oxygen levels rose. Thirdly, there also appears to be a developing movement that questions whether the evidence for sulfate with negative  $\Delta^{33}\text{S}$  is compelling, and these arguments may be evolving to arguing that oceanic sulfate had positive  $\Delta^{33}\text{S}$  throughout much of the Archean. The record of  $\Delta^{33}\text{S}$  and other sulfur isotope ratios is complicated, and subject to a variety of possible interpretations. In some cases there may be evidence for sulfate with positive  $\Delta^{33}\text{S}$ . Given the potential importance of such an observation it is important to get the interpretation right. In my presentation, I will examine evidence that bears on the  $\Delta^{33}\text{S}$  of oceanic sulfate and explore how this fits into the current understanding of MIF generation and transfer to the rock record. I will also explore how this is linked to our understanding of how diagenetic processes, oxygen/oxidation, and the ecology of sulfur cycle may have evolved during the Archean.

### Further reading:

- Farquhar J., Cliff J., Zerkle, A.L., Kamysny A., Poulton S.W., Claire M., Adams D., and Harms B. (2013). Pathways for Neoarchean pyrite formation constrained by mass-independent sulfur isotopes. *Proc. Natl Acad Sci USA* 110(44), 17638.
- Halevey I. (2013). Production, preservation, and biological processing of mass-independent sulfur isotope fractionation in the Archean surface environment. *Proc. Natl Acad Sci USA* 110(44), 17644.
- Reinhard C. T., Planavsky N. J., and Lyons T. W. (2013) Long-term sedimentary recycling of rare sulphur isotope anomalies. *Nature* 497(7447), 100.