

## **The Impacts of Depositional Environment on $\delta^{34}\text{S}$ Records: Rethinking Stratigraphic Trends and Biogeochemical Interpretations**

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Sulfur isotope ratio data ( $\delta^{34}\text{S}$ ) have been used to provide significant insights into global biogeochemical cycling over Earth history, providing a framework for reconstructing both global redox budgets and microbial metabolic activity. However, as the record of ancient oceanic conditions becomes better resolved, reports of coeval but divergent isotopic proxies are becoming increasingly common. These sulfur isotope records are characterized not just by divergent  $\delta^{34}\text{S}$  values, but also by differences in the spatial signature and magnitude of isotopic variability. Such discordant data suggest that we do not fully understand how isotopic signatures are incorporated and eventually preserved in the rock record. Here we examine the spatial signature and magnitude of isotopic variability in modern marine systems as a function of depositional environment and differential microbial metabolic activity. Varying depositional conditions, particularly sedimentary reworking, are seen to play a major role in generating and modifying the isotopic signatures of sulfur phases in modern environments. These observations can be extrapolated to investigate records of sulfur cycling in ancient strata. The results suggest that many apparent secular  $\delta^{34}\text{S}$  trends may be related to changing depositional environment rather than changes in the global sulfur cycle. Further, this environmental dependence can also help explain coeval but discordant  $\delta^{34}\text{S}$  data from within and between sedimentary basins. Together, these observations provide new insights that enable us to reflect on and refine our interpretations of chemostratigraphic  $\delta^{34}\text{S}$  data that have the potential to constrain the behavior of the sulfur cycle over geological timescales.

### **Further reading:**

Jones, D.S., Fike, D.A., 2013. Dynamic sulfur and carbon cycling through the end-Ordovician extinction revealed by paired sulfate-pyrite  $\delta^{34}\text{S}$ . *Earth and Planetary Science Letters*, **363**: 144 - 155.

Aller, R.C., Madrid, V., Chistoserdov, A., Aller, J.Y., Heilbrun, C., 2010. Unsteady diagenetic processes and sulfur biogeochemistry in tropical deltaic muds: Implications for oceanic isotope cycles and the sedimentary record. *Geochimica et Cosmochimica Acta*, **74**: 4671 - 4692.

## The organic S record

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The molecular and isotopic composition of organic sulfur has been intensively studied in relation to the diagenesis of modern sediments (Aizenshtat and Amrani, 2004), but has remained largely untapped as a geologic archive of stratigraphic and Earth historical information. This is in marked contrast to the record of inorganic sulfur, which has provided invaluable clues to many aspects of Earth's biogeochemistry. This situation is poised to change, as new analytical techniques provide increasingly sensitive and specific means to interrogate the geologic organic S record. In this talk I will review what is known (in the modern) about controls on the molecular and isotopic composition of organic sulfur, and how it might change with thermal maturation over geologic timescales. I propose that the deep-time record of organic S isotopes is potentially well preserved, is likely to be highly complimentary to that of inorganic S, and may provide new insights into early Earth environmental conditions and biologic metabolism.

Recent biologic matter can comprise up to several percent S by weight, largely in the form of amino acids. Much (or possibly all) of this sulfur is lost during early degradation, and is replaced by abiotic reactions with reduced sulfur species, primarily sulfide and polysulfide. The isotopic composition of this sulfide appears highly variable, and may record environmental differences in the diagenetic environment. Increasing thermal stress does lead to some homogenization of this signal and concomitant enrichment of  $^{34}\text{S}$ , but even ancient organic matter preserves isotopic differences that probably reflect original environmental variability. For example, kerogen blebs within the 3.45 Ga Strelley Pool formation measured by ion probe methods record a nearly 60‰ range of  $\delta^{34}\text{S}$  values on the scale of hand samples (Bontognali et al., 2012). We interpret such variability as recording heterogeneous environmental conditions related to microbial sulfur cycling in mats and shallow sediments. However, isotopic variability of organic S at these length scales has not yet been investigated through most of Earth history, and we remain ignorant about whether it is a diagnostic feature of Precambrian or Archean rocks.

### References:

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- Bontognali T. R. et al. (2012) Sulfur isotopes of organic matter preserved in 3.45-billion-year-old stromatolites reveal microbial metabolism. *PNAS* **109**, 15146–15151.

## The S-cycle on early Mars

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Over the last decade our understanding of water on early Mars has grown exponentially, but the nature of the S-cycle has remained enigmatic. In 2004, the Mars Exploration Rover (MER) mission identified evaporites enriched in sulfate minerals derived from acidic and oxidising waters [e.g.,1]. At the same time, orbiting spectrometers identified hundreds of ancient sulfate-rich outcrops across the planet, supporting the view that acidic SO<sub>4</sub>-rich waters were widespread before aqueous activity largely ceased after ~3.5-3.0 Ga [2, 3]. However, clay minerals also dominate the earliest martian crust in apparent contrast with more acidic SO<sub>4</sub>-dominated chemistry [4]. In reconciling these observations, Bibring et al. [3] suggested that because most SO<sub>4</sub>-rich strata seem to post-date those that are clay-rich, sulfur was delivered to the martian surface relatively late (~3.5-3.0 Ga) in oxidised form through sustained volcanic activity, triggering a widespread shift from alkaline to acidic chemistry.

Recent analyses of fluviolacustrine mudstones by the Mars Science Laboratory (MSL), however, tell a different story. Geochemical and mineralogical data indicates deposition in dilute waters at alkaline pH [5-7], and recent experimental work from our laboratory indicates that strictly anoxic conditions and low DIC (and probably pCO<sub>2</sub>) were necessary to satisfy bulk geochemical and mineralogical constraints [8]. How can the MER, MSL and orbital observations be reconciled, and how might this change our view of S-cycling on early Mars?

Sedimentary rocks at the MER and MSL landing sites likely represent end-members of a common geochemical system, with redox acting as the master variable. MER sediment geochemistry is most consistent with the emergence and rapid oxidation of initially alkaline, anoxic and ferruginous S-bearing groundwater, eliminating the need for exogenous sulfate delivery [e.g., 9]. Oxidation of a low-CO<sub>2</sub> and weakly buffered system would have allowed Fe<sup>3+</sup> hydrolysis to lower pH, fixing SO<sub>4</sub> in mineral products. On the other hand, persistence of anoxic waters at the MSL site would have allowed authigenic Fe<sup>2+</sup> minerals to accumulate with sulfur mobility largely dependent on its redox state.

The geochemical evolution of the martian surface, then, is most consistent with spatially and/or temporally evolving redox rather than variable sulfate delivery. This view allows us to consider the origin and fate of S-species at the ancient martian surface in a different light. For example, S delivery to the martian surface may have been very early, supplied to crustal fluids as H<sub>2</sub>S from the anoxic weathering of volcanic sulfides. At the same time, volcanically-sourced S may have been delivered to a largely anoxic atmosphere, requiring that oxidation to SO<sub>4</sub> was completed in the hydrosphere [e.g.,10]. More problematic, however, is the absence of an obvious sedimentary electron sink, indicating either: (1) S-cycling on early Mars was dominated by oxidation with minimal reduction, producing a large and extensively recycled pool of SO<sub>4</sub>, or (2) only one half of the S-cycle on early Mars has so far been sampled. Many of these hypotheses are testable as the MSL rover moves upward through Mount Sharp stratigraphy, but early observations have profoundly impacted our view of the early martian surface and how sulfur may have been cycled.

### References:

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