

Rapid changes in the marine sulfur cycle during the Phanerozoic and their relation to marine redox and the evolution of animal life

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The Phanerozoic contains many perturbations to the sulfur cycle recorded in the sulfur isotope composition of marine sulfate. Commonly, these changes in the sulfur cycle are coupled to changes in other geochemical cycles and, importantly, to evolutionary changes within the biosphere (mass extinction and diversification events). Thus, understanding the marine sulfate record is paramount to understanding past environmental changes, the redox history of the oceans and atmosphere, and the history of life on our planet.

Close inspection of the Phanerozoic marine sulfate sulfur isotope record reveals higher-frequency variations superimposed on the first-order trend. An appreciation of these higher-order variations (10^6 yrs or less) in the sulfur cycle has followed the development of carbonate-associated sulfate or CAS as a proxy for the sulfate-S isotope composition of ancient seawater. While uncertainty concerning the universal preservation of primary marine isotope signals within CAS does remain, when applied appropriately, it has afforded us unparalleled insight to the sulfur cycle during portions of Earth history. This presentation will explore on the insight gleaned from the CAS record coupled with other proxy records from several intervals of the Phanerozoic.

Short-term positive sulfur isotope excursions occur during the Later Cambrian SPICE event (~499 Ma) and two of the Ocean Anoxic Events (OAEs) of the Mesozoic¹. Here, positive sulfur isotope excursions occur parallel to positive carbon isotope excursions. In the case of SPICE, these isotope excursions initiate at a mass extinction horizon. The relationship between these two isotope systems suggests that a transient increase in the burial of organic carbon and pyrite sulfur in marine sediments resulted in the isotope excursion. Further, box-modeling exercises suggest that this burial occurred primarily in sediments deposited under large-scale anoxic and sulfidic (euxinic) conditions, which is supported by other geochemical proxy records from these events.

In contrast to records from the SPICE and OAEs, sulfate-S isotopes during the Hirnantian Stage of the Ordovician (445 to 443 Ma) shows little variation² across both a large positive carbon isotope excursion and the Late Ordovician mass extinction events. The lack of a positive sulfate-S isotope excursion parallel to the carbon isotope excursion suggests a driver other than organic carbon burial and excludes the expansion of euxinic waters as a driver for the extinction events. However, a large, negative sulfate-S isotope shift of 15‰ does occur just before the Hirnantian. Numerical modeling of this drop suggests a decrease in the global rate of pyrite burial, ΔS , or combination of both as potential drivers. Either of these changes would have likely been induced by ocean oxygenation — an expected product of global cooling during the Late Ordovician, which increased dissolved oxygen solubility and enhanced deep ocean circulation.

¹Gill, B. C., Lyons, T. W., Young, S. A., Kump, L. R., Knoll, A. H., & Saltzman, M. R. (2011). Geochemical evidence for widespread euxinia in the Later Cambrian ocean. *Nature*, 469(7328), 80–83.

²Jones, D. S., & Fike, D. A. (2013). Dynamic sulfur and carbon cycling through the end-Ordovician extinction revealed by paired sulfate–pyrite $\delta^{34}S$. *Earth and Planetary Science Letters*, 363, 144–155.

A new high-resolution sulfur isotope record of Triassic seawater sulfate

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Changes in the sulfur isotope composition of dissolved marine sulfate through time reflect changes in the global sulfur cycle and are also intimately related to changes in the carbon and oxygen cycles. A large shift in the sulfur isotope composition of sulfate at the Permian/Triassic boundary has been recognized a long time ago (Claypool et al. 1980) and subsequently a number of studies were carried out to understand the causes and significance of this shift. Except for the study of Song et al. (2014) however, existing data for the Triassic are relatively sparse. In addition, the stratigraphic evolution of the sulfur isotope composition of seawater is poorly constrained due to the small number of samples analyzed and/or due to the limited stratigraphic intervals studied. In addition, in the last few years the Triassic timescale has been significantly changed due to new radiometric data on ash layers in China and northern Italy. Because of the inconsistencies in the timescales used, the correlation between different studies, and thus the construction of a generalized curve for the entire Triassic are very difficult. To obtain a more precise evolution of the sulfur cycle in the Triassic we have analyzed Middle to Upper Triassic evaporites in Northern Switzerland and combine these data with published studies on evaporites to obtain a sulfur isotope reconstruction of the entire Triassic period. The revised correlation between the well-dated marine Tethian sections in northern Italy and the evaporites from the northern Switzerland and from the Germanic basin reported in this study, allows for a precise dating of the evaporites. We will compare the evaporite-based reconstruction with the ones based on carbonate associated sulfate (CAS) and discuss the advantages and disadvantages of evaporites and CAS to reconstruct the history of the sulfur cycle in the Triassic. Finally we explore the causes of the observed variations and model the changes in sulfate concentration throughout the Triassic.

Claypool G. E., Holser W. T., Kaplan I. R., Sakai H. and Sak I. (1980) The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation. *Chem. Geol.* 28, 199–260.

Song, H., Tong, J., Algeo, T.J., Song, H., Qiu, H., Zhu, Y., Tian, L., Bates, S., Lyons, T.W., Luo, G., Kump, L.R. (2014). Early Triassic seawater sulfate drawdown. *Geochimica et Cosmochimica Acta*, 128, pp. 95-113

Phanerozoic Sulfur Cycling: Recycling and Burial

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Sulfate evaporite and pyrite burial, the main sinks of seawater sulfate, balance the combined riverine and volcanic source on long timescales to control the concentration and isotopic composition of seawater sulfate. Among other things, the relative proportions of sulfate and pyrite burial affect the coupling of the C and S cycles, and the oxidation state of Earth's surface environment. In principle, the geologic record of S isotope ratios in sedimentary pyrite and sulfate evaporites holds information about the partitioning of sulfate between these sinks, but the system is underconstrained. New stratigraphic constraints on the geologic abundance of sulfate evaporite deposits suggest that *i)* sulfate burial is highly episodic, *ii)* it depends on the existence of conditions suitable for preservation of sulfate evaporites rather than on the concentration of seawater sulfate, and *iii)* sulfur fluxes can be deconvolved into a short-term, rapidly cycled evaporite component, and a long-term net flux to/from the sedimentary rock reservoir.

The rapidly cycled evaporites form regularly in salt marshes, tidal flats, soils and encrustations, as well as episodically as massive sulfate deposits precipitated from restricted basins in regions of net evaporation. Their weathering contributes to the riverine sulfate flux, affecting both the concentration and isotopic composition of sulfate measured in present-day rivers. Their relatively young age makes them similar in isotopic composition to seawater sulfate and consequently, their precipitation from and return to the oceans has little effect on the isotopic composition of marine sulfate, other than by coming at the expense of the strongly fractionating sink of pyrite burial. Understanding the nature of sulfate mineral removal from and return to the oceans sheds light on the apparent residence time of seawater sulfate, as inferred from the geologic record of S isotopes, and on reorganizations of the S cycle in response to changes in sea level, tectonic events, and seawater chemistry.

For further reading:

1. Halevy I, Peters SE, Fischer WW (2012) Sulfate Burial Constraints on the Phanerozoic Sulfur Cycle. *Science* **337**:331-334.
2. Wu N, Farquhar J, Strauss H (2014) $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ records of Paleozoic seawater sulfate based on the analysis of carbonate associated sulfate. *Earth Planet. Sci. Lett.* **399**:44-51.

Extracting environmental information from Phanerozoic isotope records

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Using the sulfur isotope record to reconstruct paleo-environments relies on precise and well-calibrated insight into the processes and controls on both isotopic fractionation and overall S-cycling (elemental mass-balance). In thinking about the first-order open questions for Phanerozoic-scale sulfur cycling, topics of interest often include understanding pyrite burial (1, 2) and further unraveling the variability in the isotopic offset between sedimentary sulfate and sulfide minerals (termed epsilon: (3)). Put differently, this later point addresses the question of what type of environmental information is locked within S-isotope records. Much of our classic interpretive framework is adopted from carbon cycle-esque models (4) and often falls back on the size of the seawater sulfate reservoir as a primary control. However, many of these assumptions may not best represent the sulfur cycle. For instance, an alternative approach is provided via calibrating the relationship between isotopic fractionation and sulfate reduction rates (5). This rate relationship serves as a potential bridge between an observable isotope record and the biogeochemistry of a local depositional environment (or environmental condition surrounding a microorganism). As an example application of this relationship, I will discuss the possible connections between macrostrat-based predictions for the distribution of seafloor environments through time (6) and predicted sulfate reduction rates. Insight gained through this example serves as a guide for whether future targets should focus on the collection of new geological records or move to (re)visit fundamental processes that remain under-constrained (be they biological or physical).

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3. N. P. Wu, J. Farquhar, H. Strauss, S. T. Kim, D. E. Canfield, Evaluating the S-isotope fractionation associated with Phanerozoic pyrite burial. *Geochimica Et Cosmochimica Acta* **74**, 2053-2071 (2010); published online EpubApr (10.1016/j.gca.2009.12.012).
4. R. M. Garrels, A. Lerman, Phanerozoic cycles of sedimentary carbon and sulfur. *Proceedings of the National Academy of Sciences of the United States of America-Physical Sciences* **78**, 4652-4656 (1981).
5. W. D. Leavitt, A. S. Bradley, I. Halevy, D. T. Johnston, Influence of sulfate reduction rates on the Phanerozoic sulfur isotope record *Proceedings of the National Academy of Science*, (2013).
6. B. Hannisdal, S. E. Peters, On the Relationship between Macrostratigraphy and Geological Processes: Quantitative Information Capture and Sampling Robustness. *Journal of Geology* **118**, 111-130 (2010); published online EpubMar (10.1086/650180).