Sulfur multiple isotope constraints on the Cenozoic-Cretaceous sulfur cycle

BOSWELL A. WING[1], DAVID T. JOHNSTON[1],
SHUHEI ONO[2], JAMES FARQUHAR[1] AND ADINA PAYTAN[3]

[1]ESSIC and Department of Geology, University of Maryland, College Park, MD 20742, USA (wing@essic.umd.edu, dtj@geol.umd.edu, jfarquha@essic.umd.edu)
[2]Geophysical Laboratory, Carnegie Institution of Washington, Washington DC 20015, USA (s.ono@gl.ciw.edu)
[3]Department of Geological and Environmental Sciences, Stanford University, Stanford CA 94305, USA (apaytan@pangea.stanford.edu)

Marine barite provides a robust record of the isotopic evolution of seawater sulfate (Paytan et al., 1998, 2004). We are extending the existing data set of δ^{34}S values with high-precision sulfur multiple isotope measurements of marine barite from the last ~120 Ma. Measurements of ^{33}S and ^{36}S abundances provide information that is complementary to ^{34}S abundances for two reasons, both of which require high-precision measurements to be meaningfully applied. First, individual processes can fractionate sulfur multiple isotopes along trajectories other than the reference mass-dependent fractionation lines that are defined by

$$\Delta'^{33}S = ln(\delta^{33}S/1000+1) - 0.515 \times ln(\delta^{34}S/1000+1) = 0,$$

and

$$\Delta'^{36}S = ln(\delta^{36}S/1000+1) - 1.9 \times ln(\delta^{34}S/1000+1) = 0.$$

Second, the trace abundance approximation is valid for the sulfur multiple isotope system, which results in linear isotope mass-balance equations. Isotope fractionation follows an exponential relationship, however, and the co-operation of fractionation and mass balance can produce nonzero Δ'^{33}S and Δ'^{36}S. Recent calibrations of sulfur multiple isotope effects due to different bacterial metabolisms (e.g., Johnston et al., 2005) allow for a rigorous interpretation of the sulfur multiple isotope evolution of seawater sulfate. We use these calibrations in simple isotope mass-balance models to constrain relative mass fluxes through different sulfur conversion pathways. External reproducibility in sulfur multiple isotope measurements are <0.01‰ for Δ'^{33}S and <0.1‰ for Δ'^{36}S. At their present range of variability (e.g., $\Delta'^{33}S_{max}$-$\Delta'^{33}S_{min}$ ~ 0.08; $\Delta'^{36}S_{max}$-$\Delta'^{36}S_{min}$ ~ 1.0), our measurements are producing an information-rich record (Δ'^{33}S signal/noise > 8, Δ'^{36}S signal/noise > 10) of the Cenozoic-Cretaceous sulfur cycle.

References

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Using the multiple isotopes of sulfur to constrain microbial processes in the Proterozoic ocean

D.T. JOHNSTON [1], J. FARQUHAR [1], B.A. WING[1],
T. LYONS[2], L. KAH[3], H. STRAUSS[4]
AND D.E. CANFIELD[5]

[1]Dept. of Geology and ESSIC, Univ. of Maryland (dtj@geol.umd.edu)
[2]Dept. of Earth Sciences, Univ. of California, Riverside
[3]Dept. of Earth and Planetary Sciences, Univ. of Tennessee
[4]Geologisch-Paläontologisches Inst, Univ. Münster
[5]Inst of Biology, Univ. of Southern Denmark

It has been argued that widespread sulfidic deep ocean conditions during the Proterozoic resulted from a predominance of sulfate reducing bacteria (SRB) and their effects on the biogeochemical sulphur cycle [1]. It has further been suggested that sulfur disproportionation (SDB) metabolisms did not begin to play a significant role in the cycling of sulfur until early in the Neoproterozoic [1]. Differences in the metabolic style of SRB and SDB cause measurable differences in the $\Delta'^{33}S_{sulfate}$ that can be used to evaluate these hypotheses [2, 3].

Here we present measurements of the four stable isotopes of sulfur (^{32}S, ^{33}S, ^{34}S, ^{36}S) for proxies of seawater sulfate (CAS, evaporite sulfate, and barite) that we use to evaluate these hypotheses and to test our earlier proposals. Reproducibility of these measurements are 0.01 ‰ or better, clearly demonstrating a small negative excursion of $\Delta'^{33}S_{sulfate}$ from samples older than ~1 Ga and a small positive excursion for $\Delta'^{33}S_{sulfate}$ from samples younger than ~1 Ga (Fig 1.).

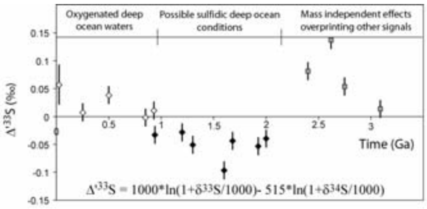

Figure 1: Δ'^{33}S of oceanic sulfate proxies versus time.

We interpret negative $\Delta'^{33}S_{sulfate}$ to imply a SRB dominated biogeochemical sulfur cycle while small positive $\Delta'^{33}S_{sulfate}$ may reflect the added influence of SDB, both have implications for the oxidation state of the Proterozoic ocean.

References

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