

Causes of sulfur isotope fractionation during thermochemical sulfate reduction by organic matter

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Interpretation of the evolution of the earth's early atmosphere has largely been based on the presence of mass independently fractionated sulfur (MIF-S) in Archean rocks. Through theoretical, experimental, and field-related investigations, we have been investigating the possibility that MIF-S signatures in sedimentary rocks were created during the thermochemical reduction of sulfate by organic matter.

Our experimental investigations using a variety of organic matter have shown the distinct importance of simple organic molecules (alanine and glycine) reacted with dissolved sulfur in the creation of large MIF-S signatures with variable $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ fractionations. Larger organic reductants (dried cyanobacteria, natural kerogen, charcoal) did not produce MIF-S signatures during reactions with sulfate or with $\text{SO}_{2(g)}$. These results suggest the availability of extremely small-sized simple, colloidal organic matter, such as those formed in hydrothermal systems (Graham et al., 2017 Goldschmidt Abstr) may have played a key role in MIF-S generation and constrain the settings where MIF-S is created. The dissolved sulfur species (Na_2SO_3 vs Na_2SO_4 vs sulfuric acid) and temperatures also show distinct effects on $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, and $\Delta^{36}\text{S}$ fractionation during TSR.

Measurable isotope shifts in residual sulfate as well as temperature dependence on the fractionation between organically bound and unbound sulfide species has allowed us to develop a schematic of the isotope effects that fractionate at different steps during TSR. The MIF-S generation during TSR may have occurred through surface chemisorption isotope effects (CSIF: Lasaga et al., 2008) and the magnetic isotope effect (MIR: Henry et al., 2011). The fractionation from both of these appears to increase with elevated temperatures. CSIF and classical kinetic isotope effect (KIE) are probably responsible for $\delta^{34}\text{S}$ fractionation between sulfate and reaction products (H_2S). Therefore, various combinations of these mechanisms was probably responsible for the $\Delta^{33}\text{S}$, $\Delta^{36}\text{S}$ and $\Delta^{34}\text{S}$ relationships observed in the experimental samples and may explain the trends observed in the Archean.