

Multiple sulfur isotope fractionation of microbial sulfate reduction

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Sulfur isotopic compositions have been demonstrated as excellent biomarkers of microbial life and unique proxies of ancient atmospheric and oceanic chemistry. As a biomarker, sulfur isotopes offer a distinctive and durable record of microbial activities and enhance the sensitivity of life detection. Model calculations and preliminary experiment with multiple sulfur isotopic compositions suggest that microbial sulfur metabolisms can produce diagnostic values of λ . Indeed, only one Archaea strain, *Archaeoglobus fulgidus*, has been studied so far. The result may not be able to represent a general population in ambient environments, since the strain was isolated from submarine hot spring.

The investigated microorganisms were obtained from the American Type Culture Collection. Three sulfate reducing bacteria, *Desulfovibrio gigas*, *Thermodesulfovibrio yellowstonii*, and *Desulfobacter hydrogenophilus*, were chosen in order to covering a wider range of substrate usage and optimum growth temperature. Batch culture experiments were performed to explore the variation in multiple sulfur isotope fractionation during dissimilatory sulfate reduction by pure cultures. Experimental conditions were designed to achieve optimum growth conditions with respect to electron donors, salinity and temperature. The isotopic composition was measured by isotope-ratio mass spectrometry and the isotope fractionation was calculated according to a Rayleigh fractionation model.

An excellent agreement of fractionation factor with previous study for *Thermodesulfovibrio yellowstonii* suggests no systematic variation among different laboratories. The fractionation factor ranges from 7.6 to 21.7 per mil and the λ value varies between 0.5092 and 0.5122 in this study. The range of λ value covers previous result and agrees with the prediction of model calculation. No convincing systematics can be correlated with the variation of organic substrate and temperature for different strains.

References

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Reconciling isotope effects of SO₂ photolysis with the Archean record of sulfur multiple isotopes

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A defining feature of the Archean sulfur multiple isotope record is the compact correlation between anomalous ³⁶S and ³³S abundances. Sulfur multiple isotope anomalies are quantified by

$$\Delta^{33}\text{S} = \ln(\delta^{33}\text{S}/1000+1) - 0.515 \times \ln(\delta^{34}\text{S}/1000+1), \text{ and}$$
$$\Delta^{36}\text{S} = \ln(\delta^{33}\text{S}/1000+1) - 1.9 \times \ln(\delta^{34}\text{S}/1000+1).$$

Their correlation results in $\Delta^{36}\text{S}/\Delta^{33}\text{S} \sim -1$. This common $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ likely reflects characteristic chemical and physical processes in the source region of the anomalous isotope effects. We report sulfur multiple isotope measurements of whole-rock samples from two Archean iron formations (Kuruman Iron Formation, RSA; Temagami Iron Formation, CAN). The iron formations represent distinct depositional settings that were influenced to different degrees by submarine volcanism. We take these differences as a crude indication of the 'geologic processing' undergone by the sulfur within each iron formation. Measurements from both sample suites exhibit the canonical $\Delta^{36}\text{S}/\Delta^{33}\text{S} \sim -1$ relationship, and illustrate that it is robust in the face of the geological homogenization.

Although the anomalous fractionation present in Archean sulfides and sulfates is broadly attributed to isotope effects during SO₂ photolysis, the measured $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ of ~ -1 stands in marked contrast to recent experimental results on broadband (180-360 nm) photolysis of SO₂. In these experiments, product elemental sulfur exhibits a net isotope fractionation of $\Delta^{36}\text{S}/\Delta^{33}\text{S} \sim -2$. We explore the implications of this dichotomy with ultrasimple isotope mass-balance models that incorporate atmospheric transport and reaction. The ultimate goal of this exercise is: (1) to identify combinations of transport and reaction parameters that might allow a single anomalous fractionation mechanism of $\Delta^{36}\text{S}/\Delta^{33}\text{S} \sim -2$ to produce the observed correlation; and (2) to characterize the isotope effects of any other fractionation mechanisms that may be required to produce the $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ correlation.