

6.5.15

Experimental constraints on anomalous S isotopic fractionation during UV irradiation of SO₂

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An emerging suite of sulfur isotopic measurements confirms and expands the record of mass-independent fractionation in Archean and Paleoproterozoic sulfides and sulfates. First-order interpretation of this record depends on the identification of chemical reactions that can produce the anomalous signature. Experiments demonstrate that mass-independent fractionation occurs during irradiation of a variety of gas phase sulfur-bearing molecules (SO₂, H₂S, CS₂, S₂F₁₀) under a range of experimental conditions (184.9 nm, 193 nm, 248 nm, and a continuous spectrum > 220 nm) [1,2]. Irradiation of SO₂ at 193 nm produces a large mass-independent fractionation in the photochemical products, which exhibit relationships among $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, and $\Delta^{36}\text{S}$ similar to those observed in sulfides and sulfates older than ~ 2.5 Ga [2].

We have previously taken the 193 nm experiments as a working model for the mass-independent fractionation of sulfur isotopes in the Archean atmosphere [3] but these experiments were conducted under specialized conditions (~ 1 nm wide window, excimer laser UV light source) that complicate their direct application to the atmospheric environment. We are conducting a set of experiments in which pure SO₂ is irradiated under broadband conditions (180–400 nm) as well as over select 20 nm windows. Experiments so far have produced elemental sulfur with large positive $\Delta^{33}\text{S}$, and have resulted in $\delta^{33}\text{S} - \delta^{34}\text{S}$ fractionation arrays with an exponential factor > 0.515. Both of these results are in line with recent, stratigraphically controlled isotopic measurements of Archean sulfides [4]. Experimental $\delta^{36}\text{S} - \delta^{34}\text{S}$ fractionation arrays are described by an exponential factor < 1.9, illustrating the importance of combined $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ measurements in extracting the photochemical evolution of Earth's early atmosphere from the Archean and Paleoproterozoic rock record.

References

- [1] Farquhar J., Bao. H. and Thiemens M.H. (2000) *Science* **289**, 756-758
- [2] Farquhar J., Savarino J., Airieau S. and Thiemens MH. (2001) *JGR* **106**, 32829-32839.
- [3] Farquhar J. and Wing B.A. (2003) *EPSL* **213**, 1-13
- [4] Ono S., Eigenbrode J.L., Pavlov A.A., Kharecha P., Rumble III D., Kasting J.F. and Freeman K.H. (2003) *EPSL* **213**, 15-30

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Combined ³⁴S/³³S/³²S, Pb-isotope and trace element data for a pyritic banded-iron formation from the 3.71 Ga Isua Greenstone Belt

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Interpretation of S-isotopes from ancient rocks requires knowledge of the origin of the host rock, the nature of the sulphides and the absolute ages of sulphide and host rock. These parameters are difficult to obtain from the oldest known terrestrial sulphides (SW Greenland) because the host rocks are deformed and metamorphosed, and many outcrops are metasomatised. Here we present new combined S-isotope, Pb-isotope and trace element data for a 3.71 Ga pyritic banded quartz-magnetite rock from the Isua Greenstone Belt (IGB). Many banded quartz-magnetite rocks from the IGB have been proposed to represent banded-iron formations (BIF). Because they are hydrogenous sediments they have trace element features unique to seawater. The IGB BIF selected for the present study (sample 248474) exhibits the required features (positive shale-normalised La, Eu, Gd and Y/Ho anomalies) and is thus regarded as a hydrogenous sediment with intact chemistry. The studied pyrite contains unradiogenic Pb ($^{206}\text{Pb}/^{204}\text{Pb} = 12.453 \pm 12$; $^{207}\text{Pb}/^{204}\text{Pb} = 13.911 \pm 15$; $^{208}\text{Pb}/^{204}\text{Pb} = 32.437 \pm 39$) generally compatible with an early Archaean age. It plots within error of the 3.71 Ga Pb-Pb regression line of whole rock IGB BIF samples [1]. The high $^{207}\text{Pb}/^{206}\text{Pb}$ ratio further indicates that the Pb derived from a high U/Pb source, which has been modelled as eroded Hadean crust [2] compatible with a primary sedimentary origin of Pb (and by implication S). Replicate S-isotope analysis ($^{34}\text{S}/^{33}\text{S}/^{32}\text{S}$) obtained with a newly developed technique by Continuous Flow-Isotope Ratio Mass Spectrometry indicates a positive $\Delta^{33}\text{S}$ of some 2 per mil. While our S-isotope data for the BIF sample are similar to those obtained earlier [3] we regard it as essential to back interpretation with combined data from the sulphides (S- and Pb-isotopes) and sedimentary host (trace elements).

References

- [1] Moorbath et al. (1973), *Nature* **245**, 138-139.
- [2] Kamber et al. (2003) *CMP* **145**, 25-46.
- [3] Mojzsis et al. (2003) *GCA* **67**, 1635-1658.