The origin of sulfur isotope mass-independent fractionation in Archean rocks

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Introduction

The discovery of unusual sulfur isotope fractionation in Archean and Paleoproterozoic rocks has promised to yield insights into the rise of O_2 and the nature of the sulfur cycle on ancient Earth [1], but interpretation has been hampered by the lack of a clear mechanism for the sulfur isotope signature. Proposed mechanisms include SO_2 photolysis [1-4], mass-independent fractionation (MIF) during atmospheric S_3 (thiozone) formation, and thermal sulfate reduction in sediments [5]. Studies focusing only on SO_2 photolysis, including measurements of isotopic cross sections [6], have yielded results differing greatly from theory [4], and have resulted in improbable interpretations [7].

Results

Here we report high-resolution ultraviolet cross section measurements of the sulfur isotopologues of SO_2 made with the UV FTS at Imperial College. This instrument has a dual-beam configuraton, allowing the D_2 lamp intensity to be monitored simultaneously with the gas absorption, effectively removing the lamp as a noise source. We measured cross sections at 1 cm^{-1} spectral resolution for $^{32}SO_2$, $^{33}SO_2$ and $^{34}SO_2$. Incorporating these cross sections into a simple atmospheric photochemical model, with a solar UV flux, yields sulfur MIF signatures for optically thin abundances of SO_2 due to small differences in the integrated cross sections. The $\Delta^{33}S$ values for SO and S produced by photolysis of SO_2 and SO, respectively, are positive in the 190-220 range, in contrast to the results of lower resolution cross section measurements of [6]. We therefore do not need to invoke an additional absorber to modify the sign of the MIF signature, as was done using OCS in [7]. We find that additional MIF by self-shielding by $^{32}SO_2$ places an upper limit on SO_2 of about 1 ppb. Our results imply that SO_2 photolysis alone is responsible for most of the Archean sulfur MIF record, and that sulfur MIF is a good proxy for the rise of O_2 in the earliest Paleoproterozoic. Work on $^{36}SO_2$ is in progress.

[1] Farquhar (2000) *Science* **289**, 756-758. [2] Farquhar (2001) *JGR* **106**, 32829-32840. [3] Pavlov & Kasting (2002) *Astrobiology* **2**, 27-41. [4] Lyons (2007) *GRL* **34**, L22811. [5] Watanabe et al. *Science* **324**, 370-372. [6] Danielache et al. (2008) *JGR* **113**, D17314. [7] Ueno et al. (2009) *PNAS* **106**, 14784-17789.