The mechanisms of mass-independent fractionation of sulfur isotopes

J. Lyons (1,2)

(1) Institute of Geophysics and Planetary Physics, University of California, Los Angeles, USA,
(2) Department of Earth and Space Sciences, University of California, Los Angeles
(jrl@ess.ucla.edu / Fax +1 310 206-3051)

The discovery of mass-independent fractionation (MIF) of sulfur isotopes in Archean and Paleoproterozoic sedimentary rocks (Farquhar et al. 2000a) has profoundly influenced our understanding of the sulfur cycle and the rise of O_2 on early Earth. Sulfur MIF is expected to arise from gas-phase atmospheric reactions involving SO_2 and H_2S. However, a quantitative understanding of the mechanisms remains elusive. Here I will discuss the most likely MIF mechanisms for sulfur isotopes, and use existing laboratory data (from the Thiemens and Farquhar laboratories) to place constraints on mechanism.

First, I give a brief description of the most relevant laboratory data: 1) Photolysis of H_2S yields elemental sulfur (S_{el}) with small $\Delta^{33}S$, and is primarily mass-dependently fractionated (Farquhar et al. 2000b); 2) Spark discharge of SO_2 yields S_{el} with small $\Delta^{33}S$, and is primarily mass-dependent (Wing et al. 2004); 3) SO_2 photolysis from 190-210 nm yields S_{el} with $\Delta^{33}S \sim +20\ \%$, along a $\delta^{33}S/\delta^{34}S$ slope ~ 0.6, which is a large MIF signature (Wing et al. 2004); 4) SO_2 photolysis at wavelengths > 220 nm yields SO_4^{2-} with $\Delta^{33}S \sim 3\ \%$, along a $\delta^{33}S/\delta^{34}S$ slope ~ 0.6 (Farquhar et al. 2001), also a significant MIF signature.

I will interpret this data within the context of two MIF mechanisms: a) non-RRKM effects, as suggested for O_3 (Gao and Marcus 2001), and b) isotope-selective photodissociation accompanying predissociation. Two additional mechanisms are hyperfine effects and near-resonant spin-orbit coupling (Bhattacharya et al. 2000), but here I will focus on a) and b). Non-RRKM effects result from a lack of intramolecular equilibrium within a vibrationally excited complex. In the case of O_3, Gao and Mar-

cus (2001) proposed that non-RRKM effects are strongest in symmetric isotopomers of O_3^*. The isoelectronic sulfur reaction, $S + S_2 \rightarrow S_3$, may also exhibit non-RRKM effects. However, the higher bond energy of S_3 (2.7 eV) versus O_3 (1.1 eV) may favor stabilization of S_3^*, and therefore diminish the magnitude of the MIF signature. Additionally, if the rate of the competing reaction, $S_2 + S_2 \rightarrow S_4$, is fast compared to $S + S_2 \rightarrow S_3$ during formation of S_{el}, then any MIF during S_3 formation may be of negligible importance. Also, if S_{el} forms primarily in surface reactions (e.g., walls) in the experiments, we can expect rapid stabilization of S_3^* and a diminished MIF effect. Thus, sulfur MIF during S_3 formation is not assured.

Mass-independent isotope-selective photodissociation is likely in SO ($\sim$ 200 nm) and SH (>250 nm), possible in SO_2, and unlikely in H_2S. The lack of a MIF signature for S_{el} produced by long-exposure H_2S photolysis results, in part, from the mass-dependence of $H_2S + h\nu \rightarrow SH + H$.

I will present kinetics calculations of the above H_2S and SO_2 photolysis experiments, and show how it is possible to use the results of these experiments to constrain the mechanism of MIF for atmospheric sulfur species.