Is SO_2 photolysis the source for Archean mass-independent sulfur isotope signatures?

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Sulfur isotope mass-independent fractionation (S-MIF) is observed in Archean rocks and is currently considered the best evidence for a low-oxygen early atmosphere [1]. Results from photochemical models suggest that the production and preservation of S-MIF places strict constraints on atmospheric oxygen levels during the Archean [2]. Much of our interpretation of S-MIF, however, is based on the hypothesis that SO_2 photolysis by ~200 nm radiation is the source of these anomalous isotope signatures.

We studied the sulfur isotope systematics of the photolysis of SO_2 under a range of experimental conditions, studying the effects of temperature (-60 to 25°C), total pressure (250 mbar to 1 bar), SO_2 pressure (down to 0.1 mbar) and the addition of other gases (CH_4, O_2). The systematics of the isotope effects observed during experiments support a major contribution from isotopologue self-shielding to S-MIF production during SO_2 photolysis [3].

If SO_2 photolysis were the dominant source of the Archean S-MIF signatures, experimental results suggest:

(1) SO_2 photolysis is occuring under high column densities of SO_2 (i.e. self-shielding regime), and thus S-MIF is predominantly produced in localized, transient volcanic plumes rather than in the background atmosphere.
(2) SO_2 photolysis is occuring at low total (i.e. N_2) pressures. Either atmospheric pressure during the Archean was lower than 1 bar, or photolysis must have been occuring at altitudes above 10 km (assuming a 1 bar atmosphere)
(3) Large mass-dependent fractionations are required prior to eventual preservation in the rock record to reduce the large $\delta^{34}S$ values produced during photolysis.
(4) High SO_2:H_2S ratios of volcanic gases are required for elemental sulfur to contain suffiently high S-MIF signatures (i.e. contribution from SO_2 relative to H_2S)

We conclude that the isotope systematics of SO_2 photolysis [3] are hard to reconcile with the geological data by itself. CS_2, SO and S_2 also undergo photolysis by predissociation and could be alternative source reactions for the Archean S-MIF signatures.

[1] Farquhar *et al* (2000) *Science* **289**, 756 [2] Pavlov and Kasting (2002) *Astrobiology* **2**(1), 27 [3] Ono *et al* (2013) *J. Geophys. Res. Atmos.* **118**, 2444