



# Atmospherically-derived mass-independent sulfur isotope signatures, and incorporation into sediments

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## ABSTRACT

The discovery of sulfur mass-independent fractionation (S-MIF) in Archean sediments has motivated new work on atmospheric sulfur chemistry. Laboratory experiments showed that SO<sub>2</sub> photolysis produces S-MIF at wavelengths both shortward of and longward of the SO<sub>2</sub> photodissociation wavelength of 220 nm. It has been argued that the underlying S-MIF mechanism at wavelengths <220 nm is SO<sub>2</sub> self-shielding. Additional S-MIF signatures associated with SO<sub>2</sub> photolysis are possible due to isotopologue-dependent variations in absorption intensity and dissociation probability, which must be evaluated through new spectral measurements. Here, I claim that SO<sub>2</sub> photoexcitation, near-UV CS<sub>2</sub> photolysis, OCS photolysis, non-statistical sulfur allotrope reactions, and surface reactions during thermochemical sulfate reduction are all unlikely sources of the largest Archean S-MIF, signatures with arguments presented for each proposed source. A potential problem with the theory proposed here is that large mass-dependent fractionation (MDF) accompanies S-MIF during SO<sub>2</sub> photolysis. The range of δ<sup>34</sup>S values is ~100‰ in photochemically produced elemental sulfur, which exceeds the δ<sup>34</sup>S range observed in Archean rocks by a factor of ~3–5, and represents a weakness of the photochemical theory for the origin of Archean S-MIF. A combination of chemical and biogenic MDF processes may have acted to reduce the δ<sup>34</sup>S range of SO<sub>2</sub> photolysis products. MDF during reactions that form elemental sulfur in the atmosphere and during aqueous phase reaction of HS<sup>-</sup> with Fe<sup>2+</sup> and FeS to form FeS<sub>2</sub> may have reduced δ<sup>34</sup>S values by ~40% relative to atmospheric SO. A simple mixing model suggests that a mixture of FeS<sub>2</sub> in sediments from both elemental sulfur (yielding pyrite with δ<sup>34</sup>S > 0 and Δ<sup>33</sup>S > 0) and from bacterial sulfate reduction (BSR) of BaSO<sub>4</sub> (yielding pyrite with δ<sup>34</sup>S < 0 and Δ<sup>33</sup>S < 0) may contribute to reducing δ<sup>34</sup>S from photochemical values to the observed range in Archean pyrites.

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## 1. Introduction

The discovery of MIF of sulfur isotopes in Archean and Paleoproterozoic sedimentary sulfides and sulfates (Farquhar et al., 2000a) promises to yield both qualitative and quantitative insights into the composition of the paleoatmosphere. Photolysis experiments on SO<sub>2</sub> and H<sub>2</sub>S, the two most abundant sulfur gases emitted during volcanism, have shown that SO<sub>2</sub> photolysis at a variety of wavelengths produces MIF in elemental sulfur (Farquhar et al., 2001; Wing et al., 2004; Pen and Clayton, 2008). By modeling the atmospheric chemistry of sulfur compounds in the early Earth atmosphere, it has been shown that preservation of an MIF signature in reduced and oxidized sulfur (elemental sulfur and sulfate, respectively) can occur only if the partial pressure of O<sub>2</sub> is <10<sup>-5</sup> times the present atmospheric level (PAL) (Pavlov and Kasting, 2002). A recent reanalysis of the atmospheric chemistry (Zahnle et al., 2006) suggests

that an excess of CH<sub>4</sub> and/or H<sub>2</sub> over O<sub>2</sub> is also necessary to maintain a sufficiently anoxic troposphere for elemental sulfur to form. In this work elemental sulfur aerosols are observed to form where the O<sub>2</sub> mixing ratio <10<sup>-12</sup>, suggesting that S-MIF may provide an even stronger constraint on pO<sub>2</sub> than inferred by Pavlov and Kasting (2002).

For relatively small isotopic fractionations, the magnitudes of sulfur MIF for the four stable isotopes of sulfur are given by the linear expressions

$$\Delta^{33}\text{S} = \delta^{33}\text{S} - 0.515\delta^{34}\text{S} \quad (1a)$$

$$\Delta^{36}\text{S} = \delta^{36}\text{S} - 1.90\delta^{34}\text{S} \quad (1b)$$

where  $\delta^x\text{S} = 10^3((^x\text{S}/^{32}\text{S})_{\text{sample}}/(^x\text{S}/^{32}\text{S})_{\text{ref}} - 1)$  for  $x = 33, 34$  or  $36$  and for a Vienna Canyon Diabolo Troilite (VCDT) reference. The values 0.515 and 1.90 are the high-temperature limit to the ratios of equilibrium partition functions for isotope exchange reactions, and ultimately arise from shifts in zero-point energy (ZPE) upon isotope

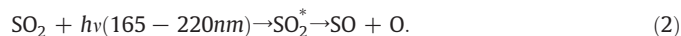
E-mail address: [jimlyons@ucla.edu](mailto:jimlyons@ucla.edu).

substitution. Because absorption cross sections are also modified by the changes in ZPE associated with isotope substitution (e.g., Liang et al., 2004), it is appropriate to utilize the equilibrium isotope exchange relations (1a) and (1b) to quantify mass-dependent fractionation even for photodissociation reactions, which are inherently disequilibrium processes.

Laboratory experiments have shown that sulfur MIF is present in elemental sulfur produced by photolysis of SO<sub>2</sub> (Farquhar et al., 2001; Wing et al., 2004; Pen and Clayton, 2008), but only very slight S-MIF is seen in the products of H<sub>2</sub>S photolysis (Farquhar et al., 2000b). Lyons (2007, 2008a) has demonstrated that self-shielding during SO<sub>2</sub> photolysis yields S-MIF signatures in elemental sulfur of ~10‰ for photolysis from 190–220 nm. Although the S-MIF signatures derived from SO<sub>2</sub> photolysis are of a magnitude comparable to ancient sedimentary pyrites (e.g., Farquhar et al., 2000a; Kamber and Whitehouse, 2007), the associated mass-dependent shifts are much larger than the range of δ<sup>34</sup>S observed in the rock record. I discuss this potential weakness of the SO<sub>2</sub> photolysis origin for S-MIF further below. I also consider other possible gas sources for atmospherically-derived S-MIF, and critique the recent suggestion from Lasaga et al. (2007) that S-MIF in Archean rocks is derived from surface S–C bonds of sulfate with organic matter in anoxic sediments during thermochemical sulfate reduction. Finally, I present a schematic illustration of how S-MIF-containing elemental sulfur aerosol is incorporated into sulfides and sulfates in marine sediments, and demonstrate how a mixture of pyrite derived from photochemically produced elemental sulfur and BSR-derived pyrite can have a reduced range of δ<sup>34</sup>S compared to that of SO<sub>2</sub> self-shielding.

## 2. Production of S-MIF signatures by photolysis of atmospheric SO<sub>2</sub>

Lyons (2007, 2008a) has presented theoretical spectra for the sulfur isotopologues of SO<sub>2</sub>, and showed how shifts in the spectra lead to S-MIF by SO<sub>2</sub> self-shielding. In a low-O<sub>2</sub> atmosphere with negligible O<sub>3</sub> absorption SO<sub>2</sub> photodissociation occurs by

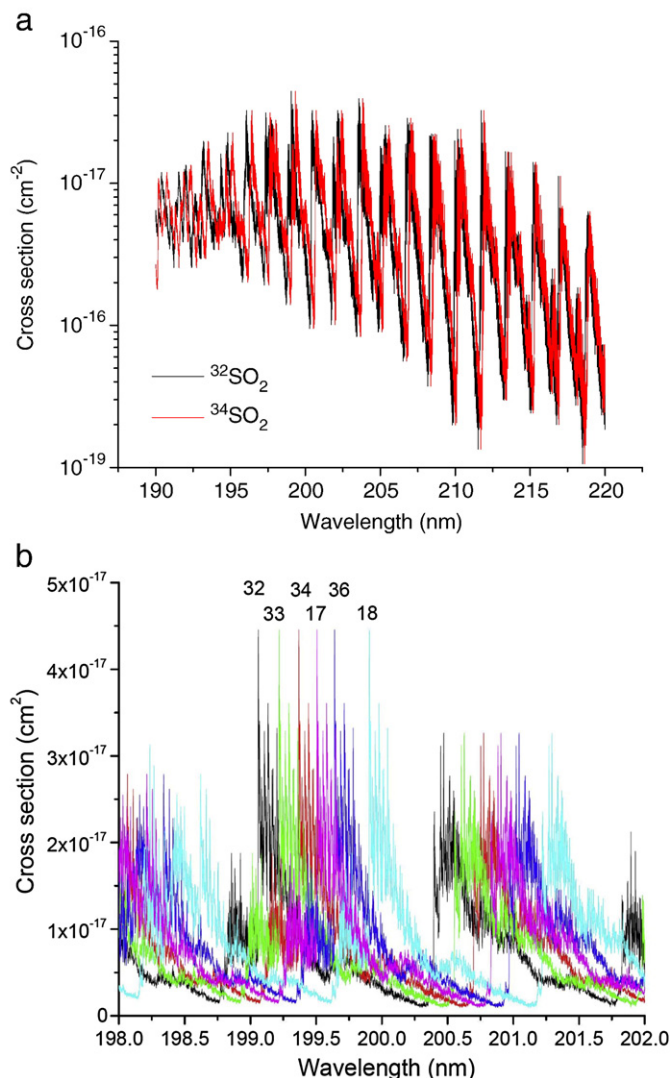


Absorption by CO<sub>2</sub> and H<sub>2</sub>O in the atmosphere limits the short wavelength photons to wavelengths greater than about 190 nm. Fig. 1a shows a high-resolution absorption spectrum for <sup>32</sup>SO<sub>2</sub> in the region 190–220 nm at 213 K (Freeman et al., 1984), and an estimated spectrum for <sup>34</sup>SO<sub>2</sub> (red curve). The structure in the spectrum is primarily due to bending mode progressions (Okazaki et al., 1997), for which each vibrational band peak corresponds to a particular bending mode quantum number. The rotational line structure (Fig. 1b) is resolved but very congested (i.e., many overlapping lines) due to perturbation from other states. Approximate spectra for the rare sulfur isotopologues of SO<sub>2</sub> were made by utilizing shifts in the vibronic band locations computed in ab initio cross section calculations of Ran et al. (2007), as described in detail in Lyons (2008a).

Radiative transfer calculations were performed in the context of modeling the photochemistry of sulfur in the early Earth atmosphere, with an emphasis on the photodissociation rates of the SO<sub>2</sub> isotopologues (Lyons 2007, 2008a). I will not present the details of those calculations here, but I will give the governing equations. Photolysis rate coefficients for each isotopologue, which give the photolysis rate in molecules per second at a particular location, are computed as

$$J_x(z) = \int \sigma_x(\lambda) \phi_x(\lambda) F_0(\lambda) e^{-\tau(\lambda,z)} d\lambda. \quad (3)$$

In this expression σ<sub>x</sub> is the absorption cross section of sulfur isotopologue x, φ<sub>x</sub> is the dissociation yield (fraction of molecules that actually dissociate), F<sub>0</sub> is the incident radiation intensity (photons cm<sup>-2</sup> s<sup>-1</sup> nm<sup>-1</sup>), and λ is wavelength. For photodissociation of SO<sub>2</sub>



**Fig. 1.** Estimated absorption spectra of SO<sub>2</sub> isotopologues. a) Spectra for <sup>32</sup>SO<sub>2</sub> (black) and <sup>34</sup>SO<sub>2</sub> (red) in the most important wavelength region for atmospheric photodissociation. The <sup>32</sup>SO<sub>2</sub> data are from Freeman et al. (1984). Vibrational band shifts for <sup>34</sup>SO<sub>2</sub> are from Ran et al. (2007) as described in Lyons (2007, 2008a). b) High resolution spectra showing rotational structure and shifted spectra showing all singly-substituted sulfur and oxygen SO<sub>2</sub> isotopologues. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

in an atmosphere with high CO<sub>2</sub> abundance (mixing ratio >10<sup>-3</sup>), the integration is from ~180–190 nm to the dissociation limit at 220 nm. Also in Eq. (3) is the optical depth τ defined as

$$\tau(\lambda, z) = \sum_i N_i(z) \sigma_i(\lambda) \quad (4)$$

where N<sub>i</sub> is the column density of absorber or scatterer i, z is the vertical coordinate (assuming normally incident radiation), and the sum is over all absorbers and scatterers, including all SO<sub>2</sub> isotopologues and CO<sub>2</sub>. Maximum self-shielding S-MIF signatures occur for a <sup>32</sup>SO<sub>2</sub> column density that corresponds to an optical depth ~unity. Maximum cross sections are ~4 × 10<sup>-17</sup> cm<sup>2</sup> (Fig. 1a), so that τ<sub>32</sub> = N<sub>32</sub>σ<sub>32</sub> ~ 1 implies a column density N<sub>32</sub> ~ 2.5 × 10<sup>16</sup> cm<sup>-2</sup>. For an optical depth of unity in the middle troposphere, and assuming a 1 bar N<sub>2</sub> atmosphere, this corresponds to an SO<sub>2</sub> mixing ratio ~3 ppb, or about 30 times the modern global background SO<sub>2</sub> abundance.

Atmospheric model results are shown in Fig. 2a for the column densities of residual SO<sub>2</sub> and product SO for pSO<sub>2</sub> = 10 ppb and

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