**Contribution of isotopologue self-shielding to sulfur mass-independent fractionation during sulfur dioxide photolysis**

The MIT Faculty has made this article openly available. Please share how this access benefits you. Your story matters.

<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>As Published</td>
<td><a href="http://dx.doi.org/10.1002/jgrd.50183">http://dx.doi.org/10.1002/jgrd.50183</a></td>
</tr>
<tr>
<td>Publisher</td>
<td></td>
</tr>
<tr>
<td>Version</td>
<td>Final published version</td>
</tr>
<tr>
<td>Accessed</td>
<td>Thu Mar 07 21:47:38 EST 2019</td>
</tr>
<tr>
<td>Citable Link</td>
<td><a href="http://hdl.handle.net/1721.1/85603">http://hdl.handle.net/1721.1/85603</a></td>
</tr>
<tr>
<td>Terms of Use</td>
<td>Article is made available in accordance with the publisher’s policy and may be subject to US copyright law. Please refer to the publisher’s site for terms of use.</td>
</tr>
<tr>
<td>Detailed Terms</td>
<td></td>
</tr>
</tbody>
</table>
Contribution of isotopologue self-shielding to sulfur mass-independent fractionation during sulfur dioxide photolysis

S. Ono,1 A. R. Whitehill,1 and J. R. Lyons2

Received 12 October 2012; revised 28 December 2012; accepted 9 January 2013; published 12 March 2013.

[1] Signatures of sulfur mass-independent fractionation (S-MIF) are observed for sulfur minerals in Archean rocks, and for modern stratospheric sulfate aerosols (SSA) deposited in polar ice. Ultraviolet light photolysis of SO2 is thought to be the most likely source for these S-MIF signatures, although several hypotheses have been proposed for the underlying mechanism(s) of S-MIF production. Laboratory SO2 photolysis experiments are carried out with a flow-through photochemical reactor with a broadband (Xe arc lamp) light source at 0.1 to 5 mbar SO2 in 0.25 to 1 bar N2 bath gas, in order to test the effect of SO2 pressure on the production of S-MIF. Elemental sulfur products yield high δ34S values up to 140 ‰, with $\delta^{32}S/\delta^{34}S$ of $0.59 \pm 0.04$ and $\Delta^{36}S/\Delta^{33}S$ ratios of $-4.6 \pm 1.3$ with respect to initial SO2. The magnitude of the isotope effect strongly depends on SO2 partial pressure, with larger fractionations at higher SO2 pressures, but saturates at an SO2 column density of $10^{18}$ molecules cm$^{-2}$. The observed pressure dependence and $\delta^{33}S/\delta^{34}S$ and $\Delta^{36}S/\Delta^{33}S$ ratios are consistent with model calculations based on synthesized SO2 isotopologue cross sections, suggesting a significant contribution of isotopologue self-shielding to S-MIF for high SO2 pressure (>0.1 mbar) experiments. Results of dual-cell experiments further support this conclusion. The measured isotopic patterns, in particular the $\Delta^{36}S/\Delta^{33}S$ relationships, closely match those measured for modern SSA from explosive volcanic eruptions. These isotope systematics could be used to trace the chemistry of SSA after large Plinian volcanic eruptions.


1. Introduction

[2] Sulfate and sulfide minerals in sedimentary rocks older than 2.4 Giga years ago (Ga) commonly show signatures of sulfur isotope mass-independent fractionation (S-MIF), anomalous isotope compositions that deviate from the mass-dependent scaling law of isotope fractionation [e.g., Farquhar et al., 2000a; Pavlov and Kasting, 2002; Ono et al., 2003]. Equilibrium, kinetic, and biological processes nominally fractionate four stable isotopes of sulfur ($^{32}S$, $^{33}S$, $^{34}S$, and $^{36}S$) in proportion to their difference in mass as predicted by the quantum mechanical theory of isotope fractionation [e.g., Urey, 1947]. Therefore, the preservation of SIF signatures indicate that a fundamental change in the sulfur cycle occurred at about 2.4 Ga. Assuming that the MIF signature is sourced from ultraviolet (UV) photolysis of SO2, production and preservation of S-MIF signatures are thought to only be possible under an anoxic early atmosphere that is UV transparent and allows rich sulfur atmospheric chemistry [Farquhar et al., 2000a, 2001; Pavlov and Kasting, 2002]. In addition, several works suggest potential secular structures in the Archean S-MIF record, such as changes in the magnitude of $^{33}S$ anomaly or in the relationship between the $^{32}S$ and $^{36}S$ anomalies [Ono et al., 2006a; Ohmoto et al., 2006; Farquhar et al., 2007; Zerkle et al., 2012]. A better understanding of the mechanisms responsible for the production of S-MIF during SO2 photolysis would provide additional constraints on the early evolution of the atmosphere beyond atmospheric oxygen levels.

[3] S-MIF signatures are also measured in stratospheric sulfate aerosols (SSA) deposited in polar ice [Savarino et al., 2003, Baroni et al., 2007, 2008]. These S-MIF signatures are only associated with large stratospheric eruptions (e.g., Pinatubo, 1991, Agung, 1963, Tambora, 1815) but not with predominantly tropospheric eruptions (e.g., Cerro Hudson, 1991), suggesting S-MIF can be used as a proxy for stratospheric volcanic events in the past [Savarino et al., 2003; Baroni et al., 2007, 2008]. The source reaction for S-MIF in the modern stratosphere, however, has been debated, because the MIF source mechanism is still not well constrained, and because of the difficulty in preserving S-MIF signatures in a present-day atmosphere [Savarino et al., 2003; Pavlov et al., 2005].
[4] Laboratory photochemical studies have shown that photolysis of SO$_2$ and photopolymerization of CS$_2$ both produce S-MIF [Farquhar et al., 2001; Masterson et al., 2011; Whitehill and Ono, 2012; Zmolek et al., 1999], but photolysis of H$_2$S and OCS does not [Farquhar et al., 2000b; Lin et al., 2011]. Both CS$_2$ and SO$_2$ exhibit fine structures in their UV absorption spectrum, suggesting that S-MIF is associated with the process of predissociation [Farquhar et al., 2001; Zmolek et al., 1999; Danielache et al., 2008; Lyons, 2007, 2008]. Two absorption bands of SO$_2$, from 190 to 220 nm and 240 to 340 nm, are thought to be important for S-MIF production [Farquhar et al., 2001; Danielache et al., 2008]. Laboratory experiments by Farquhar et al. [2001] showed that the pattern of S-MIF depends on the wavelength of excitation. This was used to link the 190 to 220 nm band to Archean S-MIF [Farquhar et al., 2001; Ueno et al., 2008; Lyons, 2007], and the 240 to 340 nm band to the S-MIF in SSA [Savarino et al., 2003; Baroni et al., 2007, 2008]. However, recent work using broadband radiation sources shows that S-MIF associated with the 240 to 340 nm is characterized by a positive correlation between $\Delta^{34}$S and $\Delta^{33}$S values, whereas negative correlations are observed in SSA [Whitehill and Ono, 2012]. Thus, in this study, we focus on the excitation of SO$_2$ under the 190 to 220 nm absorption region.

[5] Several hypotheses have been proposed for the mechanism underlying the production of S-MIF. A symmetry-dependent isotope effect, which has been suggested as the mechanism for oxygen isotope MIF during the ozone recombination reaction [Gao and Marcus, 2001], does not apply to SO$_2$, as sulfur isotope substitution does not change the molecular symmetry of SO$_2$. The SO$_2$ absorption band in the 190 to 220 nm region exhibits vibrational fine structure due to bending mode progressions of the $^1B_2 \rightarrow X^1A_1$ system (Figure 1-A) [Freeman et al., 1984]. Isotope substitutions shift the band positions and can produce isotope self-shielding due to differential optical column density (Figure 1) [Lyons, 2007, 2008]. In addition to the shift of band positions, sulfur isotope substitution can also affect the cross-section amplitude due to isotope differences in the Franck-Condon envelope and vibrational structures [Danielache et al., 2008; Tokue and Nanbu, 2010]. Molecular dynamics during predissociation, such as nonadiabatic resonances among various bound excited states of SO$_2$, may also contribute to S-MIF production [e.g., Masterson et al., 2011 and Zmolek et al., 1999 for CS$_2$].

[6] The goal of this study, therefore, is to test which of these three proposed mechanisms contributes predominantly to the observed S-MIF in Archean rocks, SSA, and laboratory photochemical experiments. Previous laboratory photochemical experiments employed static photochemical cells with SO$_2$ partial pressures (pSO$_2$) ranging from 6 mbar to over one bar [Farquhar et al., 2001; Masterson et al., 2011; Whitehill and Ono, 2012]. Isotopologue self-shielding is expected to take effect under these high SO$_2$ column densities (>3.3 x 10$^{19}$ molecules cm$^{-2}$) [Lyons, 2007, 2008]. We used a flow-through photochemical cell to measure S-MIF at pSO$_2$ as low as 0.1 mbar (corresponding column density at 3.8 x 10$^{16}$ molecules cm$^{-2}$), in order to test the contribution of isotopologue self-shielding. In addition, two photochemical cells are placed in series for some experiments to isolate the spectrum effects by only varying pSO$_2$ of the front cell, while holding pSO$_2$ of the rear cell constant. The experimental results are compared with isotope fractionation expected from synthetic isotopologue-dependent cross sections by Lyons [2007] that account only for the effect of band-position shifts. By experimentally studying the effect of SO$_2$ pressure, we also aimed to isolate the production of S-MIF by mechanisms other than self-shielding.

2. Method

2.1. Photochemical Experiments

[7] Photolysis experiments were carried out using a dual-cell flow-through photochemical reactor illustrated in Figure 2. Each cylindrical glass photochemical cell (15 cm length, 5 cm inside diameter) is equipped with two UV grade windows (Corning 7980 grade, > 90% UV transmittance above 190 nm) sealed by o-rings, and inlet and outlet ports (made of 3/8" o.d. glass tubes). For dual-cell experiments, two identical flow-through cells were placed in series. Premixed SO$_2$–N$_2$ gas (100 ppm or 5% SO$_2$) was diluted with pure N$_2$ (UHP grade) using digital mass flow controllers and flowed continuously through the photochemical cell. Pressure inside the cell was monitored with capacitance manometers (MKS, 1000 torr full scale). The reaction cell was pumped continuously with a diaphragm pump through a needle valve and a vacuum regulator for experiments under pN$_2$ less than 1 bar. Errors in pSO$_2$ are estimated to be...
2.2. Isotope Ratio Analysis

[11] A detailed description of the isotope ratio analysis method can be found in Ono et al. [2006b]. Approximately 2 mg of Ag$_2$S was reacted with elemental fluorine gas in externally heated nickel tubes (at 300 °C) to form SF$_6$. The product SF$_6$ is purified by gas chromatography, introduced to a gas source isotope ratio mass spectrometer (MAT 253, Thermo-Fisher), and measured for four ion beams of SF$_5^+$ (S$^{12}$F$_5^+$, S$^{33}$F$_5^+$, S$^{34}$F$_5^+$, and S$^{36}$F$_5^+$). A microvolume and sulfate was precipitated as barium sulfate. The first trap did not yield quantifiable (less than 1 mg) BaSO$_4$, suggesting that the majority of the SO$_3$ was trapped at the glass wool trap or on the walls of the photochemical cell. The barium sulfate was reduced to H$_2$S and precipitated as Ag$_2$S by the method described in Forrest and Newman [1977].

Between 5 and 10%, based upon the precision and accuracy of the mass flow controllers and the manometer. A 150 W Xenon arc lamp (Model 6254, Newport) in a lamp housing (Model 67005, Newport) was used as a light source for all experiments. The irradiance spectrum between 190 and 400 nm was monitored with a UV spectrometer (SPM-002BT, Photon Control, Burnaby, Canada), which was calibrated against Hg lamp lines for wavelength. The Xe arc lamp emits continuum radiation down to at least 190 nm (and possibly lower).

While the excitation of SO$_2$ by radiation in the 240 to 340 nm region ($^1A_2$, $^1B_1 \rightarrow ^1X'$) occurs in our experiments, the resulting low-energy excited states are rapidly quenched (within 4 to 300 ns for the singlet and triplet states, respectively) by collisions with N$_2$ before participating in any chemical reactions such as self-reaction with SO$_2$ [Sidebottom et al., 1972; Calvert et al., 1978; Whitehill and Ono, 2012].

UV irradiation of the SO$_3$ produces elemental sulfur (S$^0$), sulfur trioxide (SO$_3$), and residual SO$_2$ with the overall reaction stoichiometry [Ustinov et al., 1988]:

\[ 3\text{SO}_2 + h\nu \rightarrow 2\text{SO}_3 + S^0 \]

Upon photolysis, S$^0$ and SO$_3$ condensed inside the photochemical cell and on a glass wool filter placed at the outlet port, and were collected by rinsing with dichloromethane and deionized water, respectively. The S$^0$ was crystallized from dichloromethane by evaporation and reduced to H$_2$S by Cr reduction and precipitated as Ag$_2$S by a procedure modified from Gröger et al. [2009]. SO$_3$ rapidly hydrolyzes to sulfate in water and was precipitated as barium sulfate by the addition of a barium chloride solution. For two experiments (S-1020 and S-1021), residual SO$_2$ was collected by bubbling effluent in a series of two bubblers, the first containing 60 mL of 80% isopropyl alcohol, and the second 60 mL of 3% hydrogen peroxide, to capture SO$_3$ and residual SO$_2$, respectively. After photolysis, these trapping solutions were acidified to pH < 4 with 6 N HCl, and sulfate was precipitated as barium sulfate. The first trap did not yield quantifiable (less than 1 mg) BaSO$_4$, suggesting that the majority of the SO$_3$ was trapped at the glass wool trap or on the walls of the photochemical cell. The barium sulfate was reduced to H$_2$S and precipitated as Ag$_2$S by the method described in Forrest and Newman [1977].

**Figure 2.** Schematics of the dual-cell flow-through reactor used in this study. MFC: mass flow controller, CM: capacitance manometer, SP: spectrometer, F: glass wool filter, N: needle valve. The outlet of the front photochemical cell (right) is vented, pumped by a diaphragm pump (DP), or sampled for residual SO$_2$ using a set of bubblers. See text for details.

**Figure 3.** SO$_2$ isotope shift parameters used in this study [filled square, Lyons, 2007; 2008] compared to those derived experimentally [open circle, Danielache et al., 2008] and by ab-initio theoretical modeling [cross, Ran et al., 2007; open square, Tokue and Nanbu, 2010]. The energy shifts for isotopologues (in wavenumber cm$^{-1}$) are plotted against the frequency of $^{32}$SO$_2$. A, B, and C show the energy shift between $^{32}$SO$_2$ and $^{33}$SO$_2$, $^{35}$SO$_2$ and $^{34}$SO$_2$, and $^{32}$SO$_2$ and $^{36}$SO$_2$, respectively.
(0.4 mL) procedure was used for small samples (<1 mg Ag2S). Replicate analyses (N = 28) of the reference Ag2S IAEA-S-1 yielded 2σ standard deviations of 0.26%, 0.014%, and 0.19% for δ32S, Δ33S, and Δ34S, respectively [Ono et al., 2012]. Typical reproducibility for microvolume analyses of IAEA-S-1 is 0.9%, 0.08%, and 0.8% for δ32S, Δ33S, and Δ34S, respectively (2σ for 14 replicate analyses).

[12] Sulfur isotope compositions are reported in conventional δ notation, defined as:

\[ \delta^i S = \frac{R_\text{sa}}{R_i} - 1 \]  

where \( R \) is the ratio \( x^3S/x^32S \) (x = 32, 33, or 36) of sample \( R_\text{sa} \) and initial SO2 \( (R_i) \), respectively. The common multiplication factor of 1000 is omitted because it technically belongs to % symbol [Coplen, 2011]. The magnitude of S-MIF is reported using capital delta notations calculated according to:

\[ \Delta^{33} S = \frac{\langle 33 R_{sa}/33 R_i \rangle}{\langle 34 R_{sa}/34 R_i \rangle}^{0.515} - 1, \]  
\[ \Delta^{36} S = \frac{\langle 33 R_{sa}/33 R_i \rangle}{\langle 34 R_{sa}/34 R_i \rangle}^{1.90} - 1. \]  

[13] We use the definitions above among various definitions because they are mathematically consistent with the δ notation (i.e., deviation of the ratio from the expected ratio) [see Kaiser et al., 2004].

2.3. Modeling the Effect of Isotopologue Spectrum Overlap

[14] The isotope fractionation due to spectrum overlap was modeled using the SO2 cross section reported by Lyons [2007, 2008] (Figure 1). These cross sections are based on the high-resolution (0.002 nm) 32SO2 cross-section measurements of Freeman et al. [1984]. Cross sections for minor isotopologues are estimated by shifting band positions of the 32SO2 cross sections. Lyons [2007, 2008] used the

| Table 1. Results of Flow-through SO2 Photolysis Experiments. All Isotope Ratios Are Normalized Against That of Starting SO2. |
|---|---|---|---|---|---|---|---|
| S\(^i\), Front Cell | pSO2 (mbar) | pN\(_2\) (bar) | Flow Rate (scm) | \( \delta^{33} S \) (‰) | \( \delta^{34} S \) (‰) | \( \delta^{36} S \) (‰) | \( \Delta^{33} S \) (‰) | \( \Delta^{36} S \) (‰) |
| S-0705* | 0.10 | 1.0 | 478 | 23.21 | 40.37 | 65.8 | 2.56 | -11.4 |
| S-0707* | 0.11 | 1.0 | 233 | 21.72 | 37.85 | 58.1 | 2.36 | -14.0 |
| S-0630 | 0.29 | 1.0 | 86 | 39.63 | 69.26 | 108.5 | 4.39 | -24.0 |
| S-0711 | 0.29 | 1.0 | 86 | 35.49 | 61.31 | 93.5 | 4.29 | -23.4 |
| S-1006* | 0.29 | 1.0 | 86 | 36.91 | 63.36 | 98.5 | 4.62 | -22.6 |
| S-1011 | 0.59 | 1.0 | 85 | 48.49 | 82.91 | 128.0 | 6.35 | -30.5 |
| S-1020 | 0.59 | 1.0 | 254 | 48.45 | 83.92 | 132.1 | 5.83 | -28.6 |
| S-1021 | 0.60 | 1.0 | 503 | 48.38 | 82.90 | 128.9 | 6.24 | -29.6 |
| S-1007 | 1.09 | 1.0 | 183 | 71.31 | 125.41 | 209.3 | 8.07 | -33.8 |
| S-0708 | 1.17 | 1.0 | 85 | 63.63 | 110.96 | 181.4 | 7.53 | -32.7 |
| S-0713 | 1.17 | 1.0 | 85 | 63.48 | 111.07 | 180.8 | 7.33 | -33.4 |
| S-0706 | 2.92 | 1.0 | 85 | 71.90 | 128.03 | 219.0 | 7.41 | -30.4 |
| S-0714 | 2.92 | 1.0 | 85 | 76.23 | 137.15 | 237.8 | 7.30 | -30.4 |
| S-1013 | 0.25 | 0.25 | 25 | 33.34 | 52.64 | 74.2 | 6.40 | -25.6 |
| S-0905 | 0.44 | 0.22 | 25 | 52.29 | 84.76 | 128.2 | 9.11 | -33.4 |
| S-1012 | 0.51 | 0.25 | 25 | 50.03 | 81.00 | 122.0 | 8.74 | -32.3 |
| S-0907 | 0.89 | 0.22 | 25 | 71.94 | 118.67 | 188.4 | 11.79 | -39.7 |
| S-0906 | 0.97 | 0.24 | 25 | 75.14 | 126.95 | 207.3 | 10.96 | -37.9 |
| S-0830 | 0.49 | 0.49 | 50 | 50.78 | 85.37 | 131.9 | 7.37 | -31.2 |
| S-0902 | 1.01 | 0.50 | 50 | 69.07 | 111.07 | 180.8 | 7.30 | -30.4 |
| S-0921a | 2.50 | 0.50 | 50 | 78.43 | 135.71 | 230.1 | 10.02 | -34.1 |
| S-0921b | 5.00 | 0.50 | 50 | 79.12 | 138.59 | 240.4 | 9.34 | -30.7 |
| S\(^i\), Rear Cell | | | | | | | | |
| S-0707R* | 0.05 | 1.0 | 100 | 33.22 | 58.31 | 96.1 | 3.50 | -15.8 |
| S-0701R* | 0.11 | 1.0 | 100 | 46.90 | 82.89 | 133.9 | 4.84 | -25.3 |
| S-0630R* | 0.29 | 1.0 | 100 | 70.00 | 126.41 | 216.0 | 6.38 | -30.1 |

Residual SO2

| S-1020 | 0.59 | 1.0 | 254 | -1.13 | -2.16 | -3.9 | -0.01 | 0.2 |
| S-1021 | 0.60 | 1.0 | 503 | -0.63 | -1.17 | -2.0 | -0.02 | 0.2 |

SO2 Front Cell

| S-0705 | 0.10 | 1.0 | 478 | 6.88 | 12.75 | 21.6 | 0.33 | -2.7 |
| S-1025 | 0.58 | 1.0 | 86 | 9.40 | 17.92 | 32.7 | 0.21 | -1.6 |
| S-1020 | 0.59 | 1.0 | 254 | 11.27 | 21.41 | 38.2 | 0.30 | -2.8 |
| S-1021 | 0.60 | 1.0 | 503 | 10.25 | 19.34 | 34.1 | 0.33 | -2.9 |
| S-0708 | 1.17 | 1.0 | 85 | 12.21 | 23.03 | 41.1 | 0.41 | -3.0 |
| S-0706* | 2.92 | 1.0 | 85 | 10.02 | 18.72 | 34.5 | 0.42 | -1.3 |

SO2 Rear Cell

| S-0705R | 0.10 | 1.0 | 100 | 5.31 | 9.88 | 17.1 | 0.23 | -1.7 |
| S-0701R* | 0.11 | 1.0 | 100 | 2.27 | 4.32 | 7.7 | 0.05 | -0.5 |

*; microvolume analysis

These are pSO2 of the front cell. Rear cell pSO2 is held constant at 0.1 mbar
energy shift parameters adapted and extrapolated from ab-initio model study of Ran et al. [2007]. Figure 3 compares the isotopologue shift parameters from Lyons [2008] and Ran et al. [2007] as well as those from ab-initio wave-packet model calculation [Tokue and Nanbu, 2010], and experimental measurement [Danielache et al., 2008]. The isotope shift parameters used in this and previous studies agree well with the latest theoretical model by Tokue and Nanbu [2010], but experimental data by Danielache et al. [2008] show smaller magnitude energy shifts compared to theoretical values. A smaller isotope shift would produce a smaller effect of isotopologue self-shielding due to a higher degree of overlap in the fine vibrational structures.

Following previous studies [e.g., Lyons, 2008; Ueno et al., 2009], photolysis quantum yields for $^{34}$SO$_2$ are assumed to be wavelength (but not isotopologue) dependent above 205 nm and assumed to be unity below 205 nm [Okazaki et al. 1997]. The lamp output power ($F_{Xe}$) was approximated from the manufacturer’s data sheet as a function of wavelength ($\lambda$, in nm):

$$F_{Xe} = 0.11 \cdot 1.6 \cdot [14 - 9 \cdot \exp(-0.013/(\lambda - 200))]$$ (mW/nm).

[16] The first and second factors are to correct the efficiency of the condenser (F/1) and rear reflector, respectively. Transmission of quartz windows ($\tau_w$) are measured and fitted as:

$$\tau_w = 0.93 - 6.79 \cdot \exp(-0.027 \cdot \lambda).$$ (5)

[17] Total photolysis rates for each isotopologue are derived by integrating over wavelength between 190 and 220 nm and over the pathlength (15 cm) of the flow-through reactor. The major sources of error are the spectrum shape of the Xe lamp, and absorption by the optics and Schumann–Runge band of O$_2$ in the optical path (which is applicable for wavelengths shorter than 195 nm) [Whitehill and Ono, 2012]. The estimated fractionation factor, however, is only a weak function of spectrum shape of the incident light [Lyons, 2007]. The overall magnitude of the photon flux affects photolysis yield

**Figure 4.** Results of the SO$_2$ photolysis experiments in this study as a function of pSO$_2$ and pN$_2$ (closed symbols). Also shown are model results (solid lines) and results from static cell experiments by Masterson et al. [2011] (open symbols) from which data for pSO$_2$ of >750 mbar are excluded. (A) $\delta^{34}$S of the product S$^0$ as a function of pSO$_2$ and model calculations of self-shielding using the red-shifted isotopologue cross sections of Lyons [2007]. Red and blue solid lines represent model results for the front cell and rear cell (pSO$_2$ of the rear cell was at 0.1 mbar); dashed lines are the same model results for which the magnitude of the $\delta^{34}$S values were reduced by a factor of 1.9. (B) $\delta^{34}$S versus $\Delta^{33}$S and (C) $\delta^{34}$S versus $\Delta^{36}$S of the product S$^0$. The dashed and solid line in Figures 4-B and 4-C represent slopes expected for an ideal self-shielding ($\delta^{33}$S = $\delta^{34}$S = $\delta^{36}$S) and wholly mass-dependent fractionation ($\delta^{33}$S/0.515 $\approx$ $\delta^{34}$S $\approx$ $\delta^{36}$S/1.9), respectively.
but not isotope fractionation. We did not use the cross section from Danielache et al. [2008]. As discussed in Whitehill and Ono [2012], the cross section from Danielache et al. [2008] predicts negative $\Delta^{34}S$ values under the light spectrum of Xe lamp, which is not reproduced by laboratory Xe lamp SO$_2$ photolysis experiments.

[18] Self-shielding of $^{32}$SO$_2$, in an ideal case, is expected to fractionate all the minor isotopes at the same magnitude. The isotope composition of the resulting product would follow $\delta^{34}S \approx \delta^{32}S \approx \delta^{36}S$. This is only true, however, when there is no spectrum overlap between major and minor isotope absorption lines, and when the underlying continuum is very weak, as for the $^{12}$C$^{16}$O absorption band at 105.2 nm. In the case of SO$_2$ in the 190 to 220 nm range, the magnitude of isotope shift is relatively small compared to the peak width of individual vibrational bands (Figure 1-A and 1-B), and a substantial continuum is present at laboratory and atmospheric temperatures. These significant spectrum overlaps among different SO$_2$ isotopologue lines cause mutual shielding (e.g., $^{33}$SO$_2$, $^{34}$SO$_2$), which contributes mass-dependent fractionation. Due to a combination of self- and mutual-shielding effects, spectrum overlaps produce an isotope fractionation pattern that falls between ideal self-shielding ($\delta^{33}S/\delta^{34}S \approx 2.5$) and mass-dependent fractionation (i.e., $\delta^{33}S/\delta^{34}S \approx 0.515 \approx \delta^{34}S/\delta^{36}S$) (Lyons 2009).

4. Discussion

4.1. Source of S-MIF During Laboratory SO$_2$ Photolysis in the 190 to 220 nm Region

[22] The following reactions represent the photolysis of SO$_2$ under our experimental conditions:

\[
\begin{align*}
SO_2 + hv (190 \text{ to } 220 \text{ nm}) & \rightarrow SO + O \quad (R1) \\
SO_2 + O + M & \rightarrow SO_3 + M \quad (R2) \\
SO_3 + SO & \rightarrow 2SO_2 \quad (R3) \\
SO + SO + S & \rightarrow SO_2 + SO \quad (R4) \\
SO + O + M & \rightarrow SO_2 + M \quad (R5) \\
SO + hv & \rightarrow S + O \quad (R6)
\end{align*}
\]

where M is the third body molecule (N$_2$ in our experiments) [Farquhar et al., 2001; Okabe, 1978]. Reactions (R2), (R3), and (R4) are favored under high pSO$_2$ (> ca. 1 mbar), while (R5) and (R6) become important in low pSO$_2$ experiments. Atomic sulfur from reactions (R4) or (R6) polymerizes and forms S$_8$ aerosols. The above reactions do not include the excitation of SO$_2$ by radiation in the 240 to 340 nm region ($\lambda_{33}$, $\lambda_{34}$, $\lambda_{35}$), since the resulting low-energy excited states are rapidly quenched by N$_2$ [Sidebottom et al., 1972; Calvert et al., 1978; Lyons, 2009; Whitehill and Ono, 2012]. Previous static cell experiments used a 200±35 nm band-pass filter to isolate the photochemistry of SO$_2$ excited in the 190 to 220 nm versus the 240 to 340 nm absorption region [Whitehill and Ono, 2012]. We did not use the band-pass filter in this study because it would significantly limit the number of available photons (maximum transmission of the band-pass filter is 30%). The isotope pattern observed in this study (large $\delta^{35}S$ values and small $\delta^{33}S/\delta^{34}S$, negative $\Delta^{35}S/\Delta^{33}S$ values) is consistent with the 190 to 220 nm excitation band origin of the S-MIF. Isotope signatures for the 240–340 nm band ($^{33}S/^{34}S$ > 1 and $\Delta^{35}S/\Delta^{33}S = 0.64$) [Whitehill and Ono, 2012] are distinctly different from the isotope pattern observed in this study, suggesting only a minor (if not entirely absent) contribution from the excitation in the 240 to 340 nm regions.

[23] The qualitative agreement between measured S-MIF in the elemental S products and estimated S-MIF from spectrum overlap suggests a critical and significant contribution
of isotopologue self-shielding for the observed S-MIF during SO$_2$ photolysis under 190 to 220 nm excitation. Similarity between cross-section calculations and experimental results include (1) small S-MIF (and small $\delta^{34}$S values) at low pSO$_2$, increasing with increasing pSO$_2$ and reaching saturation at an SO$_2$ column density of $10^8$ molecules cm$^{-2}$, (2) $\delta^{33}$S/$\delta^{34}$S and $\delta^{33}$S/$\delta^{34}$S relationships, and (3) dual-cell experiments showing the change of S-MIF in the rear cell by changing only the pSO$_2$ of the front cell. The model calculation, however, overestimates the $\delta^{34}$S value by a factor of 1.9. This could be, in part, due to different temperatures for the cross-section measurement [213 K, Freeman et al., 1984] compared to our photochemical experiment (ca. 300 K), as well as a possible effect of chemistry following photolysis (i.e., R2 to R6) as discussed below. Higher temperature may affect the population of rotational energy levels and affect both the width and the amplitude of the absorption bands.

[24] Our experimental results indicate that $\Delta^{35}$S/$\delta^{34}$S and $\Delta^{36}$S/$\delta^{34}$S relationships also depend on pN$_2$ (low pN$_2$ favors larger $\Delta^{35}$S and $\Delta^{36}$S anomalies), consistent with the results of static cell experiments for pSO$_2$ with added helium [Masterson et al., 2011]. If observed S-MIF is indeed predominantly caused by self-shielding, the effect of bath gas pressure can be explained by pressure broadening of the absorption features at the low-energy side of the spectrum (>210 nm), where the fluorescence lifetime of the excited state SO$_2$ is comparable to the collision frequency [Katagiri et al., 1997]. Measurements of the pressure-broadening factor may provide key insights into the effect of bath gas on the S-MIF pattern. Masterson et al. [2011] observed decreasing magnitude of MIF at high pSO$_2$ (>30 mbar) by static cell experiments. While this may appear contradictory to our results showing smaller magnitude MIF at lower pSO$_2$ (<1 mbar), it is likely that the excess SO$_2$ at very high pSO$_2$ (30 mbar) would act as a bath gas, resulting in the observed lower S-MIF anomaly.

[25] The observed pSO$_2$ dependence provides critical insights into the potential contribution to MIF from mechanisms other than self-shielding. The S-MIF may originate—independent of a self-shielding mechanism—from quantum efficiencies for photolysis that are isotopologue dependent, such as nonadiabatic surface crossings [Zmolek et al., 1999; Muskatel et al., 2011] or from isotopologue-dependent absorption line strengths [Danielache et al., 2008]. Our experimental results suggest that these two effects make only a minor contribution to S-MIF ($\Delta^{35}$S < 2.5 $\%$) under our experimental conditions, because both mechanisms should be effective even at the lowest optical density. This does not, however, exclude the possibility of S-MIF in nature at much lower pSO$_2$. One also needs to be cautious in applying experimental results to natural conditions because sulfur isotope exchange reactions, such as,

$$^{32}\text{SO}_2 + ^{16}\text{O} \rightarrow ^{32}\text{SO}_2 + ^{32}\text{O},$$

(R7)

may be important and effectively minimize the S-MIF signatures in SO (x = 33, 34, or 36). Isotope exchange kinetics, however, are expected to be first order with respect to pSO$_2$. The saturation of $^{34}$S fractionation at 10 mbar pSO$_2$ (Figure 4-A) suggests that the isotope exchange reaction (R7) is relatively slow: if R7 were fast, one would expect to see decreasing $\delta^{34}$S with increasing pSO$_2$ above 10 mbar.

[26] Other than SO$_2$ photolysis itself (R1), any one of the reactions above (R2 to R6) could contribute to mass-dependent or mass-independent fractionation. Our experimental results can be used to eliminate some reactions from all the potential S-MIF source reactions. Small isotope effects at low pSO$_2$ suggest that (R5) and (R6) are not the main source of MIF, as these two reactions are favored under low pSO$_2$. The SO$_2$ oxidation reaction (R2) is mass dependent because the product SO$_3$ is fractionated only mass dependently (Table 1). The reactions SO + SO$_3$ (R3) or SO + SO (R4) are potential sources for S-MIF. Results of our experiments cannot fully exclude the possibility of S-MIF during (R3) and (R4). It is difficult to test the possibility, however, without knowing the mechanism and predicted isotope pattern (e.g., $\Delta^{35}$S/$\delta^{34}$S or $\Delta^{36}$S/$\delta^{34}$S ratios). The SO + SO reaction (R4) may produce SO-dimer intermediates, of which some of the low electronic states are symmetric, which could potentially produce symmetry-dependent MIF [Lyons, 2008]. Symmetry-dependent MIF, in an ideal case, would produce nearly equal enrichment in all minor isotopes (i.e., $\delta^{33}$S $\approx$ 1.04 $\delta^{34}$S $\approx$ $\delta^{35}$S, where the factor 1.04 accounts for the symmetric species with two $^{34}$S) and result in the $\Delta^{36}$S/$\Delta^{35}$S ratios of $\approx -1.6$ [Ono et al., 2009]. This is much higher than what we have measured.

4.2. Implication for the MIF in SSA

[27] Significant SO$_2$ isotope self-shielding is expected when the SO$_2$ column density exceeds ca. $10^{17}$ molecules cm$^{-2}$ (Figure 4-A). During large explosive volcanic events, such as the Mt. Pinatubo (1991) eruption, the SO$_2$ column density can reach and exceed these levels. The SO$_2$ column density following the Pinatubo (1991) eruption initially reached as high as $10^{19}$ molecules cm$^{-2}$. Within two weeks, the SO$_2$ cloud covered an area in excess of $10^{12}$ km$^2$ with an SO$_2$ column density above $10^{17}$ molecules cm$^{-2}$ [e.g., Guo et al., 2004]. Therefore, isotopologue self-shielding is expected to occur during direct photolysis of SO$_2$ following stratospheric volcanic events. In support of this hypothesis, S-MIF signatures (i.e., $\Delta^{35}$S/$\delta^{34}$S and $\Delta^{36}$S/$\delta^{34}$S ratios) produced by our experiments agree well with those for SSA trapped in polar ice [Savarino et al., 2003; Baroni et al., 2007, 2008] (Figures 5-C and 5-F).

[28] The isotope effect in the 190 to 220 nm region is exclusive to the stratosphere, since radiation in the 190 to 220 nm range is only available above 20 km due to absorption by O$_2$ and O$_3$ in this wavelength region [e.g., Farquhar et al., 2001]. This is consistent with the observation of S-MIF signatures for SSA exclusively from large stratospheric eruptions. Preservation of the S-MIF signature, however, remains problematic, since reaction with O$_2$ rapidly oxidizes SO back to SO$_2$.

$$\text{SO} + \text{O}_2 \rightarrow \text{SO}_2 + \text{O}$$

(R8)

Instead of SO$_2$ photolysis (R1), Savarino et al. [2003] suggest that the S-MIF in SSA sourced from photooxidation of SO$_2$:

$$^\ast\text{SO}_2 + \text{O}_2 \rightarrow \text{SO}_3 + \text{O}$$

(R9)

where $^\ast$SO$_2$ is excited state SO$_2$ produced by excitation under 240 to 330 nm absorption bands [Calvert et al., 1978; Chung et al., 1975; Savarino et al., 2003]. Transfer
of sulfur isotope signatures from *SO₂ to SO₃ would allow preservation of the S-MIF signature in *SO₂. A recent photochemical study, however, showed that the sulfur in SO₃ in reaction (R9) is largely (if not exclusively) derived from ground state SO₂ [Whitehill and Ono, 2012]. The study also showed that the 240 to 330 nm excitation band produces positive Δ³⁴S/Δ³³S values (~0.63) rather than the negative values observed in SSA, suggesting photo-oxidation (R9) is not a likely candidate for S-MIF in modern SSA.

The extent that reaction (R10) may contribute to sulfate formation can be estimated by comparing the kinetics of SO₂ oxidation by OH:

\[
\text{SO}_2 + \text{OH} + M \rightarrow \text{HSO}_3 + M \quad (R11)
\]

\[
\text{HSO}_3 + \text{O}_2 \rightarrow \text{SO}_3 + \text{HO}_2 \quad (R12)
\]

\[
\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 \quad (R13)
\]

At steady state with respect to SO, the fraction of SO₃ produced from SO (fₘ) is

\[
f_{\text{SO}} = \frac{J_1k_{10}}{k_{11}[\text{OH}][k_8 + k_{10}[M]] + J_1k_{10}}
\]

where \(k_8, k_{10},\) and \(k_{11}\) are the rate constants for R8, R10, and R11, respectively, and \(J_1\) is the photolysis rate of SO₂. As an example of SO₂ photolysis in a stratospheric volcanic
plume, we consider a total SO$_2$ column depth of 10 DU (2.7 $\times$ 10$^{17}$ cm$^{-2}$), which is distributed at height 27 $\pm$ 7 (FWHM) km [e.g., Aquila et al., 2012]. The model result shows that a rate constant of $k_{10}$ of 10$^{-36}$ cm$^6$/s (which is the maximum rate suggested by Black et al. [1982]) can allow R10 to contribute up to 10% of SO$_3$ formation at above 30 km (Figure 6). A smaller value of $k_{10}$ will decrease this contribution as shown in Figure 6. The maximum $\Delta^{33}$S value observed for sulfate aerosol in polar ice [1.4%, Baroni et al., 2007] is only 12% of the maximum $\Delta^{33}$S value observed in this study (11.8%), suggesting that the contribution of SO$_2$ photolysis at 12% or less can explain the polar ice S-MIF signatures (i.e., SO$_2$ + OH reaction is still a dominant source of SO$_2$ oxidation).

The presence of ash, ice particles, and other molecular constituents in the volcanic plume (e.g., HCl, H$_2$S) could modify sulfur chemistry in several ways. First, the fraction of O$_2$ in the plume will be somewhat lower than in clean stratospheric air. Second, O$_3$ and OH will be lower, possibly substantially lower, than in the background stratosphere due to surface reactions on plume particles. Lower OH will decrease the sulfite formation rate by reaction (R11) and increase the fraction of sulfite produced from SO (i.e., the second term in equation (6) increases). Faster conversion of SO to sulfate (R10) versus SO$_2$ to sulfate (R11) during initial plume chemistry, would be consistent with the observation by Baroni et al. [2007] that SSA with $\Delta^{33}$S > 0 was deposited first in Antarctic snow, followed by SSA with $\Delta^{33}$S < 0. Finally, reaction (R10) is likely to have a large activation energy and could be entirely negligible at stratospheric temperatures. Heterogeneous addition of SO and O$_2$ on ash or ice particles, could be rapid compared to gas-phase oxidation of SO$_2$.

Detailed modeling of stratospheric sulfur chemistry is beyond the scope of this study. Understanding the production and preservation of S-MIF signatures will provide a unique constraint on the origin and fate of stratospheric sulfur aerosols, which have a significant impact on global climate by compensating the greenhouse warming effects [Turco et al., 1982; Robock et al., 2008].

4.3. Implication to Archean S-MIF

Some well-preserved Archean rocks show characteristic $\Delta^{33}$S/$\Delta^{34}$S and $\Delta^{33}$S/$\Delta^{34}$S ratios of 0.9 and −0.9, respectively [e.g., Ono et al., 2003; Kaufman et al., 2007; Zerkle et al., 2012]. The ranges of $\Delta^{33}$S/$\Delta^{34}$S and $\Delta^{33}$S/$\Delta^{34}$S ratios produced by our experiments (0.086 ± 0.035 and −4.6 ± 1.3, respectively) do not match these main Archean arrays, suggesting that the main source reaction for Archean S-MIF may not be linked to our experimental results (Figures 4-A and 4-D). It is, however, conceivable that the isotopologue self-shielding could have made a secondary contribution to the structure of $\Delta^{33}$S/$\Delta^{34}$S record when high SO$_2$ column density was achieved after large volcanic eruptions. Studies of rocks from Neoarchean age (2.5 to 2.65 Ga) have shown several stratigraphic intervals with lower $\Delta^{33}$S/$\Delta^{34}$S ratios of −1.5 compared to a more common value of −0.9 [Kaufman et al., 2007; Zerkle et al., 2012]. In addition, data for rocks between 3.2 and 2.8 Ga are characterized by relatively small $\Delta^{33}$S values and with more negative $\Delta^{34}$S values (Figure 4-E). The cause of these secular changes in the structure of Archean S-MIF has been attributed to a variety of changes in atmospheric chemistry [Farquhar et al., 2007], including ephemeridal oxidation [Ono et al., 2006a; Ohmoto et al., 2006; Kaufman et al., 2007], the development of organic haze [Domagal-Goldman et al., 2008; Zerkle et al., 2012], or changes in volcanic gas SO$_2$/H$_2$S ratios [Halevy et al., 2010]. The results of this study suggest that the observed $\Delta^{36}$S/$\Delta^{33}$S trend can be explained by a combination of the main Archean S-MIF reaction (with $\Delta^{36}$S/$\Delta^{33}$S $\approx$ −0.9) and the isotope self-shielding due to increased volcanic SO$_2$ loading (with $\Delta^{36}$S/$\Delta^{33}$S $\approx$ −4.6). In particular, the Mesoarchean increase of SO$_2$ loading is consistent with abundant detrital and diagenetic pyrite in the Witwatersrand Supergroup, despite presumably low sulfate levels of the Archean oceans [Habicht et al., 2002]. Increased SO$_2$ loading would have had significant consequences on the early Earth’s climate, because a temporal increase of sulfate in surface environments would suppress microbial methanogenesis by competing for H$_2$ with sulfate reducers [Lovley and Klug, 1983]. The collapse of methanogens would have triggered the oldest known glaciations in the Witwatersrand-Pongola basins at ca. 2.9 Ga [Young et al., 1998; Ono et al., 2006a].

5. Conclusion

Sulfur isotope effects during the UV photolysis of SO$_2$ under a broadband light source were investigated with a flow-through photochemical reactor. The S-MIF signature and the $\delta^{34}$S values of S$^0$ products increase with increasing SO$_2$ pressure, but saturate at a column density of 10$^{18}$ molecules cm$^{-2}$. The SO$_2$ column density dependence, large $\delta^{34}$S

SO + O$_2$ $\rightarrow^{\text{photolysis}}$ SO$_3$ (R14)
values, and $\Delta^{33}S$/34S and $\Delta^{32}S$/34S relationships suggest an important contribution of isotopologue self-shielding to the observed mass-independent isotope effect. Results from dual-cell experiments further support this conclusion. The measured isotope pattern, in particular the $\Delta^{33}S$/34S ratios, show good agreement with data for SSA, suggesting that photolysis of SO$_2$ in the 190 to 220 nm region following large volcanic events could be the dominant source of the modern S-MIF in SSA. This implies there is a currently unknown mechanism for preserving the isotope signature of SO formed from SO$_2$ photolysis in the stratosphere. Although the results do not agree with the main Archean S-MIF array, SO$_2$ self-shielding could have contributed to the $\Delta^{33}S$/34S variations during parts of the Archean.

[34] Acknowledgments. Authors thank William J. Olzewski and Kat Thomas for assistance in sulfur isotope analysis, and Eliza Harris for proofreading. This work was supported by the NASA Exobiology Program, Grant No. NNX10AR85G to ONO and NNX10AR80G to Lyons. The authors also thank Sebastian Daniélache and two anonymous reviewers for constructive comments to the earlier version of the manuscript.

References


