Earth and Planetary Science Letters 306 (2011) 253–260

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

journal homepage: www.elsevier.com/locate/epsl

Sulfur mass-independent fractionation patterns in the broadband UV photolysis of sulfur dioxide: Pressure and third body effects

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ARTICLE INFO

Article history:
Received 4 January 2011
Received in revised form 31 March 2011
Accepted 6 April 2011
Available online 4 May 2011

Editor: R.W. Carlson

Keywords:
S-MIF
SO_2 isotopologues
UV photochemistry
minor sulfur isotopes

ABSTRACT

The production of mass-independent fractionation (MIF) in the products of the middle/far UV photolysis of SO_2 isotopologues has been linked to large S-MIF signatures observed in the pre-2.45 Ga rock record, and provides a valuable proxy for the evolution of atmospheric O_2. The origin of such large MIF signatures in photolytic products has recently been ascribed to the optical self-shielding of SO_2 isotopologues in photon-limited regions of the lower atmosphere. To better characterize the origin of such a signal we have performed pressure-variant broadband UV photolysis experiments of SO_2 and SO_2–He mixtures. Low pressure (~20 Torr) photolysis of SO_2 produces extractable sulfur with large $\delta^{34}S \approx 120–180‰$, $\Delta^{33}S \sim 20‰$, and $\Delta^{36}S/\Delta^{33}S \approx -2.5$, while near atmospheric pressures produce sulfur with $\Delta^{33}S \sim 2‰$, and $\Delta^{36}S/\Delta^{33}S \approx -12$. Similar experiments conducted with variable pressures of helium bath gas produce a similar diminution in $\Delta^{33}S$, and in both cases a $\Delta^{36}S/\Delta^{33}S$ ratio that is a linear function of pressure over several orders of magnitude. We postulate a photochemical and kinetic origin for the large S-MIF observed in these static cell experiments, produced from the excited state predissociative dynamics of SO_2, but cannot expressly rule out self-shielding as a contributor to fractionations observed here.

1. Introduction

Minor sulfur isotope fractionations in the Archean and earliest Proterozoic sedimentary rock record are characterized by a mass-independent isotopic signal (e.g. Farquhar et al., 2000). The origin of this isotopic signal is uncertain, but a number of arguments have been made to suggest that the production and transfer of this signal to the rock record is related to chemistry that occurred in the Archean atmosphere (Domagal-Goldman et al., 2008; Lyons, 2009; Pavlov and Kasting, 2002). These arguments are based on: the observation of similar isotopic signals in the present-day atmosphere (e.g. Romero and Thiemens, 2003), the generation of large mass-independent isotopic signals in far UV (~180–220 nm) experimental photolyses (Farquhar et al., 2000, 2001), and atmospheric radiative transfer models of self shielding of S-isotopologues in a hypothetical Archean atmosphere (Danielache et al., 2008; Lyons, 2007, 2008, 2009). The evolution of this minor sulfur isotope signal, and especially the $\Delta^{36}S$ to $\Delta^{33}S$ ratio, has thus been linked to evolution of the atmosphere and specifically, to the roles of oxygen, ozone, carbon dioxide, and organic aerosols in controlling atmospheric oxidation, chemistry, and radiative budget.

Sulfur dioxide photochemistry is presently the leading candidate for the source of this mass-independent signal because it is thought to be relevant in atmospheric sulfur chemistry and because SO_2 photolysis has yielded characteristically large mass-independent fractionations. The origin of the isotopic effects associated with the photodissociation of sulfur dioxide may be split it into several components: that related to the spectrum of light available for photolysis (self and mutual shielding), that related to the isotopologue specific probability of photoexcitation prior to dissociation, and that stemming from kinetic isotope effects (KIE) associated with state-to-state transformations for isotopologues from a bound state ultimately to dissociated products. While prior studies have included these different components in their examinations of sulfur dioxide photochemistry, it is not entirely clear which are needed to explain the effects that have been observed in experiments and in the rock record. For instance, some of the early studies (e.g., Farquhar et al., 2001; Farquhar and Wing, 2003) attributed the signal to primary photochemical isotope effects and did not consider the potential role of self shielding and photoabsorption. More recent studies by Danielache et al. (2008) and Lyons (2009) have discussed self shielding and photoabsorption effects. Self shielding can be broadly defined as a photophysical process producing isotopologue fractionation in photon limited gas-phase systems with structured absorption spectra. In the case of SO_2, the vibronic bands of $^{32}SO_2$ become optically thick before those containing the less abundant isotopologues. More radiation is

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doi:10.1016/j.epsl.2011.04.004

available for their respective photolyses, and thus the abundances of their photoproducts are selectively enhanced, with respect to the starting composition. With the possible exception of the observation of differences in the isotopologue peak profiles (peak shape, and absolute peak height) in the absorption cross sections measured by Danielache et al. (2008), little concrete evidence exists to support the possibility of processes other than self shielding (e.g., absorption-related effects or KIE in state-to-state transitions in establishing this mass-independent signal). It has also been noted (Lyons, 2009) that the spectral data are insufficient to demonstrate that shielding can completely explain the observations. In the study presented here, we seek to explore relative roles of self shielding and primary photochemical processes. We explore the pressure dependence of the mass-independent isotope fractionations produced during photolysis of sulfur dioxide and document a strong pressure dependence of S-MIF. We report on experiments with helium, an inert, non-shielding third body, to explore the possible kinetic and photochemical influence in the minor sulfur isotope patterns of the product elemental sulfur.

2. Methods

We use a high pressure Oriel D_2 lamp (Model 66079) source with an emission spectrum peaking at ~200 nm. The D_2 lamp provides a broadband continuum in the far UV, accessing a significant portion of $\tilde{C}(^1B_2)SO_2$, well below the onset of predissociation at 219 nm, and accesses comparatively little of the lower energy singlet states of SO_2.

SO_2 photolysis experiments were conducted using two cylindrical borosilicate photocells of respective volumes 165 cm^3 and 156 cm^3, and path lengths of 46 cm and 44 cm. The photocells were fitted with epoxy-sealed fused silica windows 2.5 cm in diameter and 3 mm thickness, and mounted on an optical bench. The photocells were pre-evacuated to 5 mTorr for more than 3 h, and filled to a desired pressure of cryogenically purified SO_2 (Matheson 99.999%), measured with a MKS Baratron 1000 Torr pressure gage (stated accuracy $\pm 0.5\%$). Operating pressures ranged from 25 to 920 Torr for pure SO_2 experiments, and operating pressures of helium were 100–670 Torr with a starting pressure of ~25 Torr SO_2. A small volume of initial SO_2 was aliquoted to a cold finger for starting composition analysis. SO_2 was condensed into the photocell coldfinger for 10 min, and for He–SO_2 experiments, a prefilled UHP (99.999%) helium lecture bottle was used to load He into each cell with frozen SO_2. The photolysis cells were sealed from the remaining portion of the vacuum line, and the entire cell wrapped in Al foil to prevent the scattering of UV radiation during the course of photolysis. Cells were fitted to the window of an electronic shutter of the D_2 lamp.

Photolyses of SO_2 and He–SO_2 were run with lamp current of 2.00 A for a period of 120 or 180 min to produce elemental sulfur S_{el} films and sulfur trioxide SO_3. Following the photolyses, condensable sulfur oxides were refrozen in the cell cold finger for 10 min and residual non-condensibles were pumped away. Elemental sulfur films usually formed within 3 cm of the reaction window. Helium was pumped away through a secondary LN_2 frozen U-trap to capture any unfrozen sulfur oxides. Non-condensible blanks were generally less than 30 mTorr for pure SO_2 experiments. The sulfur oxide mixture was then thawed and quantified, and either aliquoted or transferred entirely to a 15 mL glass cold-finger. Initial SO_2 and residual SO_x were converted to H_2SO_4 by direct injection of 30% H_2O_2 allowed to sit overnight. The elemental sulfur film was extracted with two rinses of CCl_4 followed by one rinse with MeOH with sonication, and allowed to dry in a double necked boiling flask with a septum port. Sulfate from initial SO_2 was converted to $BaSO_4$ by reaction with a 10% solution of $BaCl_2$, subsequently rinsed with MilliQ water, and dried overnight in a 90 °C oven prior to reduction.

Sulfate and elemental sulfur were converted to Ag_2S for isotopic analysis using published techniques. (Canfield et al., 1986; Forrest and Newman, 1977; Thode et al., 1961) Barium sulfate was converted to H_2S in a simple distillation apparatus with a gently boiled solution of 16% hypophosphorous acid, 32% hydriodic acid, and 52% hydrochloric acid for 3 h. Nitrogen gas was bubbled through the solution at a flow rate of ~15 mL/min and product H_2S was carried through a distilled water acid trap and into a trapping solution of 0.2 M Zn acetate, reacting to form a white precipitate of ZnS. ZnS was converted to silver sulfide by cation exchange with a 0.3 M solution of $AgNO_3$ allowed to sit overnight wrapped in Al foil. Elemental sulfur was converted to H_2S with a similar setup, following Canfield et al. (1986). A solution of Cr (II) was prepared by overnight reaction of a stirred and N_2 purged solution of chromium (III) chloride hexahydrate, 300 mesh Zn metal, and 0.5 M HCl. Double necked boiling flasks were sealed with a silicone septum and placed in the aforementioned distillation apparatus. Approximately 30 mL of 5 M HCl was syringe injected into the N_2 purged apparatus, followed by 30 mL of the azure blue Cr(II) solution. The solution was gently boiled for 3 h, and H_2S was also captured as precipitate ZnS. Converted Ag_2S was rinsed with ~100 mL milliQ water followed by 15 mL NH_4OH solution, and an additional 100 mL of milliQ water. Silver sulfide was dried overnight in a 90 °C prior to fluorination extraction for isotope analysis.

For initial SO_2 silver sulfide, approximately 2 mg of Ag_2S was wrapped in an Al foil boat, drop loaded into a Ni-tube, and fluorinated for 8 h at 250 °C with 10× stoichiometric excess of cryogenically purified F_2. Residual F_2 was removed from LN_2 frozen SF_6 via reaction with hot KBr. Product SF_6 was distilled to the injection loop of a gas chromatograph with a −110 °C EtOH slush for 10 min. SF_6 was eluted through a 1/8" composite column consisting of a 6-ft molecular sieve 5A and 6 ft Haysep Q (polyvinylbenzene) sulfur column. Eluted SF_6 was detected with a thermal conductivity detector (TCD) and captured in two liquid nitrogen cooled glass coils as it exited the column. Clean SF_6 was transferred to the inlet of a ThermoFinnigan MAT 253 in dual inlet (DI) mode for isotope analysis. The quadruple isotopic composition of the SF_6 was determined via IRMS of the $m/z = 127$, 128, 129, and 131 SF_5^+ ion beams for a minimum of three 8-step acquisitions against the working standard SF_6 at the University of Maryland stable isotope facility. We describe these measurements throughout the remainder of the document as previous studies have:

$$\delta^{3x}S = 1000 \times \left[\frac{\left({}^{3x}S / {}^{32}S \right)_{sample}}{\left({}^{3x}S / {}^{32}S \right)_{std}} - 1 \right]$$

Where $x = 3$, 4, and 6 refer to the minor isotopes of sulfur, referenced to the major isotope ^{32}S. For each experiment, the composition of the elemental sulfur produced is referenced to the starting composition of the initial SO_2.

For describing large mass-independent fractionations, we use the non-linear definitions of $\Delta^{3x}S$ (where $x = 3$ and 6). These definitions are calculated as below:

$$\Delta^{33}S = \delta^{33}S - 1000 \times \left[\left(1 + \frac{\delta^{34}S}{1000} \right)^{0.515} - 1 \right]$$

$$\Delta^{36}S = \delta^{33}S - 1000 \times \left[\left(1 + \frac{\delta^{34}S}{1000} \right)^{1.90} - 1 \right]$$

Fluorination extraction of silver sulfide derived from elemental sulfur were conducted in a similar manner, but sample sizes were significantly smaller, with all samples having less than 4 μmol S, and some with less than 0.8 μmol. Small samples were frozen into an intracapillary cold finger to minimize bellows dead volume while running in Dual Inlet mode. Measurement errors are estimated to be 0.3‰, 0.02‰, and 0.3‰ (1σ) for $\delta^{34}S$, $\Delta^{33}S$, and $\Delta^{36}S$, based on repeated measurements of the isotope standards IAEA-S1, IAEA-S2,