Mass-independent sulfur isotope fractionation during photochemistry of sulfur dioxide

by

Andrew Richard Whitehill

Submitted to the Department of Earth, Atmospheric, and Planetary Sciences
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Abstract

Mass-independent sulfur isotope signatures are observed in Archean and early Paleoproterozoic sedimentary sulfate and sulfide minerals, and provide the most robust constraints on early atmospheric oxygen levels. Smaller mass-independent sulfur isotope anomalies are observed in ice cores and interpreted as a tracer of stratospheric volcanic loading. Photochemistry of sulfur dioxide (SO\textsubscript{2}) has been implicated as a possible source of the mass-independent sulfur isotope signatures in both the modern stratosphere and on the early earth. However, the mechanisms responsible for the production of mass-independent sulfur isotope fractionation remain poorly constrained. This thesis investigates the multiple sulfur isotope systematics during photochemical reactions of sulfur dioxide as a function of a variety of experimental conditions. Two absorption regions of SO\textsubscript{2} are tested - photolysis in the 190 to 220 nm region and photoexcitation in the 250 to 350 nm region. Experimental conditions modified include temperature, SO\textsubscript{2} pressure, bath gas pressure, and addition of reactive gases (C\textsubscript{2}H\textsubscript{2}, O\textsubscript{2} and CH\textsubscript{4}). Results of photochemical experiments are compared with isotope systematics predicted from isotopologue-specific absorption cross-sections to identify potential mechanisms for the production of mass-independent fractionation during photochemical reactions. Strong similarity between the isotope systematics of SO\textsubscript{2} photolysis and ice core data suggest that SO\textsubscript{2} photolysis is responsible for the production of mass-independent sulfur isotope effects in the modern stratosphere. In contrast, significant discrepancies between the isotope signatures from SO\textsubscript{2} photochemistry and those in the Archean record suggest that, although SO\textsubscript{2} photolysis was likely an important process in the Archean atmosphere, an additional reaction likely contributes to the mass-independent sulfur isotope signatures preserved in the Archean rock record.

Thesis Supervisor: Shuhei Ono
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Chapter 1

Introduction

Molecular oxygen (O\textsubscript{2}) makes up almost 21% of the Earth's present atmosphere and is essential for aerobic life as we know it. However, the atmosphere had almost no free oxygen (O\textsubscript{2}) for the first 2 billion years of Earth's existence (Holland, 1999; Farquhar et al., 2000a; Pavlov and Kasting, 2002). The appearance of atmospheric oxygen at around 2.45 Ga ago, often called the Great Oxidation Event (Holland, 1999), marks one of the most profound and dramatic changes in the Earth's surface environment. Understanding the history and evolution of oxygen on the Earth's surface is essential for understanding the history and evolution of life on Earth, as well as for the search for life on other planets.

The strongest evidence for the Great Oxidation Event comes from the mass-independent sulfur isotope record through Earth's history (Figure 1-1). This record shows large mass-independent sulfur isotope anomalies (i.e. $\Delta^{33}\text{S} \neq 0$) in sedimentary (and metasedimentary) rocks older than circa 2.45 Ga, and the absence of significant anomalies (i.e. $-0.2\% < \Delta^{33}\text{S} < 0.4\%$) in more recent rocks. The presence of these mass-independent sulfur isotope anomalies are interpreted to be due to photochemical reactions in a low-oxygen early atmosphere (Farquhar et al., 2000a). This record provides the most sensitive constraints on atmospheric oxygen levels during the Archean (Farquhar et al., 2001; Pavlov and Kasting, 2002; Ono et al., 2003; Zahnle et al., 2006) and on the timing of the Great Oxidation Event (Bekker et al., 2004; Guo et al., 2009).
Figure 1-1: $\Delta^{33}\text{S}$ values of sulfate and sulfide samples as a function of age before present. Samples older than 2.4 Ga show large mass-independent sulfur isotope anomalies, whereas younger samples are close to mass-dependent. Data from Farquhar et al. (2000a, 2007); Hu et al. (2003); Mojzsis et al. (2003); Ono et al. (2003, 2006b,a, 2007, 2009a,b); Bekker et al. (2004); Johnston et al. (2005, 2006); Papineau et al. (2005); Whitehouse et al. (2005); Cates and Mojzsis (2006); Ohmoto et al. (2006); Bao et al. (2007); Hou et al. (2007); Kamber and Whitehouse (2007); Kaufman et al. (2007); Domagal-Goldman et al. (2008); Zerkle et al. (2012)
In addition to the presence of sulfur isotope mass-independent fractionation (S-MIF) in the geologic record, there are also significant patterns in the pre-2.45 Ga S-MIF record. In particular, there are both correlations and variability in the relationships between the isotopes (Figure 1-2). There is a general positive correlation between $\delta^{34}S$ and $\Delta^{33}S$ values (Ono et al., 2003) and a general negative correlation between $\Delta^{36}S$ and $\Delta^{38}S$ values (Farquhar et al., 2000a), which are believed to be characteristic of the photochemical source reaction. Understanding the mechanisms responsible for S-MIF production during photochemical reactions will allow us to better constrain environmental conditions during the Archean and better interpret the Archean S-MIF record. In particular, variability in the relationship between isotopes (i.e. $\Delta^{36}S/\Delta^{33}S$ ratios) during different periods of the Archean (Ono et al., 2006a; Farquhar et al., 2007) or within individual sections (Ono et al., 2009a; Zerkle et al., 2012) have been interpreted to be due to changes in environmental and atmospheric conditions. However, qualitative and quantitative interpretations of what the signatures mean require better understanding of the mechanisms responsible for S-MIF production.

In addition to S-MIF signatures in the Archean ($\Delta^{33}S < -2 \%$ to $\Delta^{33}S > 10 \%$, Figure 1-2), smaller S-MIF signatures ($-1.4 \% < \Delta^{33}S < 1.6 \%$) are observed in ice core records (Savarino et al., 2003) and some tropospheric sulfate aerosols (Romero and Thiemens, 2003; Guo et al., 2010). The ice core signatures are correlated to sulfate peaks in ice cores, which are associated with large volcanic eruptions with significant stratospheric influence (Savarino et al., 2003; Baroni et al., 2007, 2008). These signatures are thought to have been generated by ultraviolet photochemistry of sulfur species in the stratosphere (Savarino et al., 2003; Pavlov et al., 2005; Hattori et al., 2013). Again, however, the mechanisms responsible for the production of these signatures are poorly constrained, which has generated controversy and hindered interpretation of these signatures (Lanciki et al., 2012; Schmidt et al., 2012).

This thesis aims to provide experimental constraints on the isotopic systematics from photochemistry of sulfur dioxide ($SO_2$). Photochemistry of $SO_2$ has been suggested to be the source of the S-MIF anomalies in both the Archean (Farquhar et al.,
Figure 1-2: $\Delta^{33}\text{S}$ versus $\delta^{34}\text{S}$ (left) and $\Delta^{36}\text{S}$ versus $\Delta^{33}\text{S}$ (right) for samples older than 2.4 Ga. Data from Farquhar et al. (2000a, 2007); Hu et al. (2003); Mojzsis et al. (2003); Ono et al. (2003, 2006b,a, 2007, 2009a,b); Bekker et al. (2004); Johnston et al. (2005, 2006); Papineau et al. (2005); Whitehouse et al. (2005); Cates and Mojzsis (2006); Ohmoto et al. (2006); Bao et al. (2007); Hou et al. (2007); Kamber and Whitehouse (2007); Kaufman et al. (2007); Domagal-Goldman et al. (2008); Zerkle et al. (2012)
and the modern atmosphere (Savarino et al., 2003). Although suggestions have been made about mechanisms responsible for S-MIF production during SO₂ photochemistry (Farquhar et al., 2001; Lyons, 2007, 2008, 2009; Danielache et al., 2008, 2012; Ueno et al., 2009; Masterson et al., 2011; Hattori et al., 2013), the lack of experimental data supporting these mechanisms has limited their usefulness. Although some experimental work has been done previously (Farquhar et al., 2001; Masterson et al., 2011), there is a lack of experimental data on isotope fractionation during photochemical reactions of sulfur dioxide. Early studies have used narrow-band light sources (Farquhar et al., 2001) and high SO₂ pressures (Farquhar et al., 2001; Masterson et al., 2011), which are not atmospherically relevant. This thesis begins to address this gap by providing systematic experimental constraints on the isotope fractionations during the ultraviolet photolysis (190 nm to 220 nm) and photoexcitation (250 nm to 350 nm) of SO₂. The results from these experiments will update our interpretation of which reactions and mechanisms are responsible for the production of S-MIF in both the modern atmosphere and on the Archean earth.

1.1 Background

Sulfur has four stable isotopes – $^{32}$S, $^{33}$S, $^{34}$S, and $^{36}$S. Almost all known physical, chemical, and biological processes fractionate these isotopes in a mass-dependent manner, such that the fractionation in $^{33}$S relative to $^{32}$S is approximately half the fractionation in $^{34}$S relative to $^{32}$S (and the fractionation in $^{36}$S relative to $^{32}$S is approximately double the fractionation in $^{34}$S relative to $^{32}$S). The precise relationships predicted by thermodynamic theory are (Urey, 1947; Bigeleisen and Mayer, 1947; Hulston and Thode, 1965):

$$\delta^{33}S = 0.515 \times \delta^{34}S$$  \hspace{1cm} (1.1)

and

$$\delta^{36}S = 1.90 \times \delta^{34}S$$  \hspace{1cm} (1.2)
where isotopic δ values are defined as:

$$\delta^{3X}S = \frac{3XR_{sa}}{3XR_{std}} - 1$$  \hspace{1cm} (1.3)

$3XR$ is the molar ratio of $^{3XS}$ to $^{32S}$ ($3XR = ^{3XS}/^{32S}$, where $X = 3, 4,$ or $6$) of sample ($R_{sa}$) and a standard ($R_{std}$), respectively. Deviations from these mass-dependent scaling laws are referred to as mass-independent fractionation (MIF), and presented as $\Delta$ values, defined as:

$$\Delta^{33}S = (\delta^{33}S + 1)/(\delta^{34}S + 1)^{0.515} - 1$$  \hspace{1cm} (1.4)

$$\Delta^{36}S = (\delta^{36}S + 1)/(\delta^{34}S + 1)^{1.90} - 1$$  \hspace{1cm} (1.5)

Since very few processes are capable of producing S-MIF, the S-MIF records provide a unique and powerful tracer of processes occurring in the past. Interpreting this tracer, however, requires an understanding of the possible reactions and mechanisms responsible for the production of S-MIF. Currently, S-MIF has been observed during gas-phase photochemical reactions of CS$_2$ (Zmolek et al., 1999) and photolysis and other photochemical reactions of SO$_2$ (Farquhar et al., 2000b, 2001; Masterson et al., 2011; Whitehill and Ono, 2012; Ono et al., 2013; Whitehill et al., 2013). Significant S-MIF is not observed during photolysis of H$_2$S (Farquhar et al., 2000b) or OCS (Lin et al., 2011). With the exception of some condensed-phase magnetic isotope effects (Kopf and Ono, 2012; Oduro et al., 2011a), S-MIF has not been observed in non-photochemical processes.

SO$_2$ has four absorption bands in the ultraviolet (Figure 1-3). The absorption band in the 130 nm to 165 nm region is unlikely to be significant for terrestrial photochemistry in the lower or middle atmosphere, due to strong absorption by atmospheric gases (i.e. N$_2$ and CO$_2$) below around 180 nm to 190 nm. The SO$_2$ absorption band in the 350 nm to 400 nm range is several orders of magnitude weaker than the other absorption bands and is also unlikely to be significant to the chemistry of the atmosphere. Therefore, the middle two absorption bands (165 nm to 235 nm and 235 nm
to 350 nm will be the focus of this thesis.

The SO$_2$ absorption band in the 165 nm to 235 nm region corresponds to the $C(^1B_2) \leftrightarrow X(^1A_1)$ electronic transition. The dissociation threshold of SO$_2$ lies in the middle of this absorption band, at around 220 nm, and thus excitation of SO$_2$ into the $C(^1B_2)$ state results in the photolysis of SO$_2$ into SO and O. The photolysis quantum yield rises exponentially above the dissociation threshold (Katagiri et al., 1997). Farquhar et al. (2001) demonstrated S-MIF production during SO$_2$ photolysis using an ArF laser and Xe arc lamp. Later studies (Lyons, 2007; Danielache et al., 2008; Ueno et al., 2009) showed that the narrow-band (laser) light source might be the cause of anomalous isotope fractionation, since the laser light is resonant with intense transitions for $^{32}$SO$_2$ and $^{33}$SO$_2$, slightly off-resonant for $^{34}$SO$_2$, and completely off-resonant for $^{36}$SO$_2$. A broadband light source such as solar radiation would not necessarily produce the same anomalous isotope effects observed with a ArF laser.

Photolysis of SO$_2$ using broadband light sources (Masterson et al., 2011; Whitehill and Ono, 2012) have since been demonstrated to also produce S-MIF signatures, although not of the same magnitude as the ArF laser. Ono et al. (2013) argues that SO$_2$ photolysis produces anomalous isotope effects predominantly due to isotopo-
logue self-shielding, and shows that the magnitude of the anomalous isotope effects decreases with SO$_2$ column density (as the absorption band is no longer saturated). It is still unclear whether photolysis of SO$_2$ at low column densities will also produce S-MIF, although the signatures are likely to be small. Photolysis of SO$_2$ appears to be characterized by large enrichments in all the heavy sulfur isotopes (i.e. $^{33}$S, $^{34}$S, and $^{36}$S), although only moderate (on the order of 1% to 2% for $^{33}$S) S-MIF signatures. It is not clear that the large mass-dependent fractionations associated with photolysis of SO$_2$ are consistent with the relatively small range of $\delta^{34}$S values observed in the Archean rock record. In addition, the systematics of the isotope effects observed during experimental studies of SO$_2$ photolysis are not entirely consistent with the geologic values. Despite this, SO$_2$ photolysis remains the favored explanation for the Archean S-MIF signatures and requires further study.

The SO$_2$ absorption band in the 235 nm to 350 nm region is associated with the coupled $\tilde{\Lambda}^{(1}A_2), \tilde{B}^{(1}B_1) \leftarrow \tilde{X}^{(1}A_1)$ transition. Although excitation in this region does not contain enough energy to promote dissociation, SO$_2$ in the singlet excited state can be quenched to the lower-lying $\tilde{\alpha}^{(3}B_1)$ state, which is reactive. SO$_2$ in the $\tilde{\alpha}^{(3}B_1)$ state can react with SO$_2$, CO, CH$_4$, and other organics to produce a variety of products, some of which preserve the sulfur isotope signature of the excited-state SO$_2$. Although photochemistry in this region is not currently thought to be the dominant source of the Archean S-MIF signatures, it has been suggested as a source of the modern S-MIF signatures (Savarino et al., 2003; Hattori et al., 2013) and as possibly contributing to the Archean signatures (Zerkle et al., 2012; Whitehill and Ono, 2012). Recently-published absorption cross section data in this absorption region (Danielache et al., 2012) predict systematics different from recent experiments (Whitehill et al., 2013), suggesting a potentially interesting chemical source of S-MIF from excitation in this absorption region. It remains uncertain how important photochemistry in the 235 nm to 350 nm range is to the production of S-MIF in either the Archean or the modern atmosphere.
1.2 Goals

This thesis explores the physiochemical origin of the mass-independent sulfur isotope effects during photochemical reactions of sulfur dioxide and begins to address the lack of systematic experimental constraints on the isotope fractionation during SO$_2$ photochemistry. In particular, it addresses the effect of temperature, pressure, and SO$_2$ pressure on the isotope effects during the photoexcitation of SO$_2$ (250 nm to 350 nm) and the effects of temperature and added oxygen (O$_2$) and methane (CH$_4$) on the photolysis of SO$_2$ (190 nm to 220 nm). The comparison of cross-section data with experimental results is used to infer possible mechanisms for S-MIF production during SO$_2$ photolysis and SO$_2$ photoexcitation. The goal is to experimentally evaluate SO$_2$ photolysis and SO$_2$ photoexcitation as potential sources of the mass-independent sulfur isotope signatures in the modern atmosphere and in the Archean rock record.

Previous studies have attributed the S-MIF signatures in the Archean record to SO$_2$ photolysis (Farquhar et al., 2001; Pavlov and Kasting, 2002; Ono et al., 2003) and the modern S-MIF signatures to SO$_2$ photoexcitation (Savarino et al., 2003; Hattori et al., 2013). In this thesis, I will argue that SO$_2$ photolysis cannot explain the entirety of the Archean record, and that an additional reaction mechanism is required. I will also demonstrate that SO$_2$ photoexcitation is inconsistent with the modern S-MIF record and that modern S-MIF signatures are better explained by SO$_2$ photolysis. In addition, I will provide experimental insights into the mechanisms responsible for mass-independent fractionation during photochemical reactions. SO$_2$ photolysis produces S-MIF signatures primarily because of optical effects, such as differences in absorption cross-sections (Danielache et al., 2008) and optical shielding effects (Lyons, 2007). Although optical effects are also important for S-MIF formation during the photoexcitation of SO$_2$ (Danielache et al., 2008, 2012), it cannot explain the entirety of the S-MIF signatures observed, and an additional mechanism, such as isotopologue-selective intersystem crossing between excited singlet and triplet states, is required.
1.3 Layout

This thesis is arranged as an introduction, four data chapters, and a conclusion. Chapters 2, 3, and 4 are in the form of manuscripts for publication and have either been published or are submitted. Minor edits have been made from the published version for the sake of consistency. An overview of the chapters is presented below and in Table 1.1.

Chapter 2 presents the results of a series of experiments aimed at characterizing the isotope signatures from SO$_2$ photochemistry in the 190 nm to 220 nm region compared to the 250 nm to 330 nm region. All experiments were performed in a closed system photochemical reaction cell with pure SO$_2$. A series of different broadband light sources (i.e. lamps and optical filters) is used to separately characterize the isotope fractionation from the photolysis (190 nm to 220 nm) and photoexcitation (250 nm to 350 nm) regions. Both reduced (i.e. elemental sulfur) and oxidized (i.e. sulfate) products are analyzed. I show that the two different absorption bands produce distinct sulfur isotopic signatures, and that those signatures are different from the original (Farquhar et al., 2001) laser data. I also provide a comparison between experimental isotope data and predictions from isotopologue-specific absorption cross sections.

Based on the results presented in this chapter, I argue that SO$_2$ photoexcitation (250 nm to 350 nm) is unlikely to be responsible for the S-MIF signatures observed in ice cores, as previously suggested by Savarino et al. (2003). Instead, the isotope signatures more closely resembled the results from SO$_2$ photolysis experiments, an argument which is advanced by Ono et al. (2013) and in Chapter 4. Although SO$_2$ photolysis produces results similar to the Archean data, I argue that the observed isotope systematics from SO$_2$ photolysis are inconsistent with the Archean geologic record, and suggest that mixing between the two absorption bands could have been responsible for the Archean anomalies.

Chapter 3 explores the photoexcitation band of SO$_2$ (250 nm to 350 nm) in more depth, looking at the effect of SO$_2$ pressure and bath gas pressure on the isotope fractionation following the photoexcitation of SO$_2$. Acetylene (C$_2$H$_2$) is used to se-
lectively trap triplet-state SO$_2$, formed from intersystem crossing from the initially excited singlet state. A flow-through photochemical reaction system is used to achieve lower SO$_2$ column densities, where self-shielding will not be as significant. In addition, a series of optical filters are used to isolate radiation in different subregions of the absorption band to explore the wavelength dependence of the isotope effect.

Photoexcitation of SO$_2$ in the 250 nm to 350 nm region (followed by intersystem crossing and reaction with C$_2$H$_2$) produces large mass-independent sulfur isotope signatures ($+11\%_o < \Delta^{33}S < +78\%_o$), which are almost an order of magnitude larger than continuous flow SO$_2$ photolysis experiments (Ono et al., 2013). These large $\Delta^{33}S$ signatures are associated with moderately small ($-8\%_o < \delta^{34}S < +21\%_o$) $^{34}S$ fractionations. I argue that these isotope effects are inconsistent with a purely optical origin (i.e. differences in absorption cross-sections and self-shielding effects), and suggest that part of the anomalous isotope signature is produced during the intersystem crossing between the singlet and triplet states. A similar mechanism has previously been invoked to explain anomalous isotope effects during CS$_2$ photopolymerization (Zmolek et al., 1999), CO$_2$ photolysis (Bhattacharya et al., 2000), and CO photolysis (Chakraborty et al., 2008). These experiments confirm that photoexcitation of SO$_2$ produces S-MIF anomalies with positive $\Delta^{36}S/\Delta^{33}S$ ratios, which is significantly different from the S-MIF anomalies in both ice cores and the geologic record.

Chapter 4 explores the temperature effect on the isotope fractionation during the photochemistry (photolysis and photoexcitation) of SO$_2$, as well as testing the photolysis and photoexcitation of SO$_2$ in the presence of O$_2$. A temperature-controlled reaction cell is used to test the isotope signatures from SO$_2$ photolysis and SO$_2$ photolysis (in the presence of C$_2$H$_2$) at temperatures down to $-60^\circ$C. In addition, SO$_2$ is excited in the presence of molecular oxygen (O$_2$) and the resulting product sulfate is analyzed for isotope ratios. The goal is to test multiple hypotheses for the formation of S-MIF in the modern atmosphere.

Results show that temperature affects the magnitude of the S-MIF signatures during SO$_2$ photolysis but that it does not significantly affect the isotope systematics. SO$_2$ photolysis in the presence of O$_2$ is shown to produce sulfate with large
mass-independent sulfur isotope signatures consistent with those observed in stratospheric sulfate aerosol samples. Based on this finding, an argument is made that SO$_2$ photolysis in the presence of O$_2$ is responsible for the S-MIF signatures in the modern atmosphere. SO$_2$ photoexcitation in the presence of O$_2$ also produced sulfate with S-MIF, but with signatures significantly different from those observed in natural samples.

Chapter 5 explores the hypothesis that SO$_2$ photolysis in the presence of methane might change the isotope effects versus SO$_2$ photolysis in the absence of methane. It is shown that the presence of methane does not significantly affect the isotope ratios observed during SO$_2$ photolysis. The evidence that SO$_2$ photolysis is not responsible for the Archean S-MIF signatures is reviewed and the suggestion that SO photolysis might contribute to the Archean S-MIF signatures is explored.
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* Not discussed in this dissertation
Chapter 2

Excitation band dependence of sulfur isotope mass-independent fractionation during photochemistry of sulfur dioxide using broadband light sources

Foreward

This chapter has been published previously as Whitehill and Ono (2012).

2.1 Abstract

Ultraviolet photolysis of sulfur dioxide (SO\textsubscript{2}) is hypothesized to be the source of the sulfur isotope mass-independent fractionation (S-MIF) observed in Archean sulfate and sulfide minerals and modern stratospheric sulfate aerosols. A series of photochemical experiments were performed to examine the excitation band dependence of S-MIF during the photochemistry of SO\textsubscript{2} under broadband light sources (a xenon
arc lamp and a deuterium arc lamp). Optical filters (200 nm ± 35 nm bandpass and 250 nm longpass filters) were used to separately access two different excitation bands of SO\textsubscript{2} in the 190 nm to 220 nm and the 250 nm to 330 nm absorption regions, respectively.

UV irradiation of SO\textsubscript{2} in the 190 nm to 220 nm and 250 nm to 330 nm regions both produced elemental sulfur (S\textsuperscript{0}) and sulfur trioxide (SO\textsubscript{3}) as end products but yielded very different sulfur isotope signatures. The elemental sulfur products from direct photolysis in the 190 nm to 220 nm region were characterized by high $\delta^{34}$S values (154.7‰ to 212.0‰), modest $\Delta^{33}$S anomalies of 21‰ ± 3‰, and relatively constant $^{33}\lambda = \ln(\delta^{33}S + 1)/\ln(\delta^{34}S + 1)$ values of 0.64 ± 0.3, all with respect to the initial SO\textsubscript{2}. Photoexcitation in the 250 nm to 330 nm region produced elemental sulfur with $\delta^{34}$S values of 7.7‰ to 29.1‰ and $\Delta^{33}$S values of 15.0‰ ± 1.6‰. In both excitation regions, the SO\textsubscript{3} products were mass dependently fractionated relative to the SO\textsubscript{2} reservoir. The two different absorption regions produced contrasting $\Delta^{36}$S/$\Delta^{33}$S signatures in the elemental sulfur products, with $\Delta^{36}$S/$\Delta^{33}$S = -1.9 ± 0.3 and 0.64 ± 0.3 for the 190 nm to 220 nm and 250 nm to 330 nm bands, respectively.

Our results provide several critical constraints on the origin of the S-MIF signatures observed in modern stratospheric aerosols and in the Archean geological record. A lack of S-MIF in the sulfate product and positive $\Delta^{36}$S/$\Delta^{33}$S ratios for the elemental sulfur from SO\textsubscript{2} photo-oxidation demonstrate that photoexcitation in the 250 nm to 350 nm region is not a likely source for the S-MIF observed in modern stratospheric aerosols. Large $\delta^{34}$S fractionation, $^{33}\lambda$ values, and $\Delta^{36}$S/$\Delta^{33}$S ratios observed for the 190 nm to 220 nm band are qualitatively consistent with predictions from synthetic isotopologue-specific cross sections. These isotope patterns, however, are not compatible with the Archean rock record. We explore the possibility that S-MIF from both the 190 nm to 220 nm and the 250 nm to 330 nm absorption bands could have contributed to the Archean S-MIF signatures.
2.2 Introduction

Equilibrium and kinetic isotope fractionation theories predict that chemical reactions should fractionate the four stable sulfur isotopes ($^{32}$S, $^{33}$S, $^{34}$S, and $^{35}$S) such that $\delta^{33}$S = 0.515 $\times$ $\delta^{34}$S and $\delta^{36}$S = 1.90 $\times$ $\delta^{34}$S (see Section 2.3.4 for the definition of $\delta$ values) (Hulston and Thode, 1965). Deviations from these mass-dependent scaling laws are called mass-independent fractionation (MIF). Sulfur isotopes in terrestrial sulfate and sulfide minerals younger than ca. 2.4 Ga obey these mass-dependent scaling laws, whereas many samples older than ca. 2.4 Ga show significant deviations (e.g., Farquhar et al., 2000a; Ono et al., 2003; Kaufman et al., 2007). Contemporary stratospheric sulfate aerosols associated with some Plinian and Ultra-Plinian volcanic eruptions also show sulfur MIF (S-MIF), although with a smaller magnitude than the Archean samples (Savarino et al., 2003; Béroni et al., 2007). Since the majority of physical, chemical, and biological processes fractionate sulfur isotopes in a mass-dependent manner, these mass-independent signatures offer a unique tracer of processes occurring in the past.

The photolysis of sulfur dioxide (SO$_2$) in a low-oxygen early atmosphere is the most probable source of the S-MIF signature for the Archean and early Paleoproterozoic (Farquhar et al., 2000a). This is supported by the observation of S-MIF during the photolysis of SO$_2$ in laboratory experiments (Farquhar et al., 2000b, 2001; Masterson et al., 2011). In a low-oxygen atmosphere, both reduced (i.e., elemental sulfur, S$_8$) and oxidized (i.e., H$_2$SO$_4$) sulfur are stable and can carry distinct mass-independent isotope signatures into the sediment (e.g., Farquhar et al., 2001; Pavlov and Kasting, 2002; Ono et al., 2003). Atmospheric photochemical models predict that the preservation of this mass-independent signal is only possible when the atmospheric oxygen level is below $10^{-5}$ of present atmospheric levels (Pavlov and Kasting, 2002) and abundant reducing gases (e.g., CH$_4$ and H$_2$) are present in the troposphere (Zahnle et al., 2006). The presence of S-MIF in the geological record is accepted as the most compelling evidence for a reducing, anoxic early atmosphere, and its subsequent disappearance around ca. 2.4 Ga is attributed to the rise of oxygen during the
Great Oxidation Event (Farquhar et al., 2000a; Pavlov and Kasting, 2002).

The structure of the Archean sulfur isotope record could eventually provide quantitative insight into paleoatmospheric conditions during the Archean. Many Archean samples show a strong correlation between $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values, with $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios of approximately $-0.9$ (Farquhar et al., 2000a), although the exact relationship varies throughout the Archean (Farquhar et al., 2007; Kaufman et al., 2007; Ono et al., 2009a). There are also changes in the range of $\Delta^{33}\text{S}$ values during different periods in the Archean, with an attenuated MIF signal during the Mesoarchean bracketed by a larger range of $\Delta^{33}\text{S}$ values in the Paleoarchean and the Neoarchean (Ohmoto et al., 2006; Ono et al., 2006a; Farquhar et al., 2007; Halevy et al., 2010). With an improved understanding of the atmospheric source of the sulfur MIF signature, the relationship between $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ and the changes in $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios at different locations or times can be directly related to atmospheric conditions (Ono et al., 2006a, 2009a; Farquhar et al., 2007; Kaufman et al., 2007).

The physical chemistry responsible for the production of S-MIF during photochemical reactions, however, is still poorly understood. Production of S-MIF has been demonstrated experimentally for the photopolymerization of $\text{CS}_2$ (Zmolek et al., 1999) and photolysis of $\text{SO}_2$ (Farquhar et al., 2000b, 2001; Masterson et al., 2011). However, photolysis of $\text{H}_2\text{S}$ and $\text{OCS}$ produce little or no S-MIF (Farquhar et al., 2000b; Lin et al., 2011). The electronic spectra of $\text{CS}_2$ and $\text{SO}_2$ both exhibit strong vibrational and rotational structure that is absent in the electronic spectra of OCS and $\text{H}_2\text{S}$, suggesting a connection between absorption structure and MIF production during photolysis (Farquhar et al., 2001; Lyons, 2007, 2009). Isotopologue-specific absorption cross sections of $\text{SO}_2$ demonstrate that S-MIF can be caused by isotopologue self-shielding (Lyons, 2007, 2008) and differences in the widths and intensities of absorption bands between different isotopologues (Danielache et al., 2008). The S-MIF may also be due to the dissociation dynamics of $\text{SO}_2$ or an isotopologue-dependence of the photolysis quantum yield (Lyons, 2008; Masterson et al., 2011), as proposed to explain isotope effects during the photolysis of $\text{CO}_2$ (Bhattacharya et al., 2000), CO (Chakraborty et al., 2008), $\text{N}_2$ (Muskatel et al., 2011), and $\text{CS}_2$ (Zmolek et al., 1999).
SO$_2$ has two dominant absorption bands in the ultraviolet region, one at 190 nm to 220 nm and the other at 250 nm to 330 nm (Figure 2-1-C). Excitation by 190 nm to 220 nm radiation leads to direct photolysis (SO$_2$ $\rightarrow$ SO + O), whereas that by 250 nm to 330 nm radiation leads to indirect photooxidation through self-reaction in pure SO$_2$ experiments ($^*$SO$_2$ + SO$_2$ $\rightarrow$ SO$_3$ + SO, where $^*$SO$_2$ is electronically excited SO$_2$). Farquhar et al. (2000b, 2001) report results of laboratory experiments demonstrating that the photochemistry of SO$_2$ excited in these two regions produce different patterns in their sulfur MIF signatures (i.e., different $\delta^{33}$S/$\delta^{34}$S and $\Delta^{36}$S/$\Delta^{33}$S ratios). These results are used to attribute Archean S-MIF to the 190 nm to 220 nm band (Farquhar et al., 2001; Lyons, 2009; Ueno et al., 2009; Halevy et al., 2010), and modern S-MIF to the 250 nm to 330 nm band (Savarino et al., 2003; Bâroni et al., 2007). Later theoretical and spectroscopic studies, however, questioned the relevance of the narrow-band UV sources used as part of these early experiments (e.g., excimer lasers and Hg lamps) to photochemistry in a broadband regime (Danielache et al., 2008; Lyons, 2009; Ueno et al., 2009).

This study aims to (1) reevaluate the wavelength dependence of S-MIF observed in experiments by Farquhar et al. (2001) using broadband light sources, and to (2) test the strong sensitivity of the isotope fractionation to the spectral properties of the light source suggested by Ueno et al. (2009). We approach these goals by using two different light sources (xenon and deuterium arc lamps), as well as using two different optical filters to isolate particular parts of the UV spectrum. In addition, we compare the observed S-MIF patterns against those expected from theoretical and experimental SO$_2$ cross sections, in order to evaluate the cross sections and the possible influence of cross-sectional differences versus other factors in the S-MIF production during SO$_2$ photolysis.
Figure 2-1: (A) The spectral intensity of the Xe and D₂ light sources compared to the present day solar spectra, (B) the transmission of all windows and filters used in this study, and (C) the UV spectrum of SO₂ as a function of wavelength between 190 nm to 340 nm. Lamp intensities in (A) are based on data from the manufacturer (Newport Corporation) and the solar spectrum is from Rottman et al. (2006). The transmission of the cell windows and filters was measured using a spectrometer and a D₂ light source. The absorption spectrum of SO₂ is from the compilation of Manatt and Lane (1993). The absorption cross section is increased by a factor of 10 between 240 nm to 340 nm.
2.3 Methods

2.3.1 Photochemical experiments

Photolysis experiments were performed on pure SO$_2$ (99.9% plus, Sigma Aldrich) in a cylindrical glass reaction cell (length = 25.5 cm, inner diameter = 4.0 cm). A 150 W, UV-enhanced xenon (Xe) arc lamp (Newport Model 6254) was used as a light source for most of the experiments. Several full spectrum photolysis experiments were performed using a 30 W, high-irradiance deuterium (D$_2$) lamp (Newport 63163) to test the sensitivity of the isotope effects to the spectral differences between the D$_2$ lamp and the Xe lamp (Figure 2-1-A). The reaction cell was equipped with two removable UV-grade SiO$_2$ windows (Corning 7980) with transmittance above 90% between 190 nm and 400 nm (Figure 2-1-B). Along with the full spectrum experiments, additional experiments were performed that separately isolated two absorption bands of SO$_2$. A 200 nm ± 35 nm (full width at half maximum, FWHM) bandpass filter (Model 200-B, Acton Research, Acton, MA) was used to isolate the 190 nm to 220 nm absorption band and a 250 nm longpass filter (ZUL0250, Asahi Spectra, Torrance, CA) was used to isolate the 250 nm to 330 nm absorption band (Figure 2-1-B). Due to its higher total irradiance, the Xe lamp was used as the light source for all experiments done with filters. All experiments were performed in the presence of laboratory air, with a distance of around 20 cm between the lamp bulb and the front window of the reaction cell. Spectral interference from the Schumann-Runge bands of O$_2$ (175 nm to 200 nm) is significant below 195 nm, but becomes negligible at higher wavelengths (Section 2.8.1, Figure 2-9). Spectral interference from the Hartley band of ozone (approximately 200 nm to 300 nm) is expected to be negligible (Section 2.8.1, Figure 2-10).

Experiments were performed at SO$_2$ pressures ranging from 4.8 torr to 25.7 torr and durations ranging from 4 h to 24 h. UV irradiation of SO$_2$ produces elemental sulfur (S$^0$) and sulfur trioxide (SO$_3$) with an overall stoichiometry of (Ustinov et al., 1988):

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

(R.2.1)
Elemental sulfur and SO₃ condensed on the windows and inner walls of the reaction cell during the photochemical experiments and were collected by rinsing the reaction cell first with dichloromethane (DCM) and then with deionized water. The elemental sulfur products were dissolved in the DCM and SO₃ was hydrated (to H₂SO₄) and dissolved in the aqueous phase. 10 mL of 0.5 M BaCl₂ solution was added to the aqueous phase to precipitate sulfate as barium sulfate. In addition, initial and residual SO₂ from each experiment were condensed in a glass vial at −196°C (77 K) and precipitated as barium sulfate with the addition of 0.25 M BaCl₂ solution in 15% H₂O₂. In several of the experiments the reaction cell was rinsed with only DCM and only the elemental sulfur product was collected.

Care was taken to minimize cross contamination and potential blanks. After each experiment, both windows were removed from the cell, and the cell and windows were rinsed well with DCM, ethanol, and water, and then washed. They were rinsed with deionized water and dried in an 80°C (353.15 K) oven overnight. Prior to each experiment, the cell was evacuated overnight and tested for leaks. Dark reaction tests (with SO₂ in the cell but no light) produced no extractable elemental sulfur or sulfate products.

2.3.2 Isotope analysis of photochemical products

Barium sulfate from initial and residual SO₂ and product SO₃ was extracted using the method of Forrest and Newman (1977). In brief, dried barium sulfate was refluxed with 50 mL of a 105:64:31 (v:v:v) solution of concentrated HCl (37%), HI (48%), and H₃PO₂ (50%) for approximately 2 h. Elemental sulfur was recrystallized from the DCM and reduced using the modified chromium chloride method of Canfield et al. (1986) and Hsieh and Shieh (1997). A 1 M solution of chromium (III) chloride (acidified with 40 mL of concentrated HCl per liter of solution) was reduced for at least 2 h over zinc metal (1 g of zinc per 10 mL of chromium solution). The elemental sulfur product was refluxed for 3 h with 40 mL of the reduced chromium solution, 20 mL of 6 N HCl, and 10 mL of ethanol. In both cases, nitrogen was bubbled through the solutions for the duration of the experiments as a carrier gas. The H₂S evolved was
trapped initially by a 0.18 M zinc acetate solution (buffered with 30 mL of acetic acid per liter of solution) and subsequently precipitated as Ag₂S with addition of 5 mL of a 0.1 M AgNO₃ solution.

Isotope ratio analyses were performed at the Stable Isotope Geobiology Laboratory at MIT, using a procedure similar to that described by Ono et al. (2006b). Approximately 2 mg of Ag₂S was reacted under ca. 55 torr of fluorine gas (F₂) for at least 8 h at 300 °C. The resultant SF₆ was then purified cryogenically and by gas chromatography. The isotope ratios of pure SF₆ were measured by a Thermo Scientific MAT 253 Stable Isotope Ratio Mass Spectrometer. Ions for $^{32}$SF²⁺, $^{33}$SF²⁺, $^{34}$SF²⁺, and $^{36}$SF²⁺ ($m/z = 127, 128, 129, and 131$, respectively) were monitored using dual-inlet mode. Replicate analyses ($N = 28$) of the reference material IAEA-S-1 yielded 2σ standard deviations of 0.26 ‰, 0.014 ‰, and 0.19 ‰ for $\delta^{34}$S, $\Delta^{33}$S, and $\Delta^{36}$S, respectively. For several smaller samples (< 0.2 mg Ag₂S), a microvolume (0.4 mL volume) cryotrap was used. Typical reproducibility for micro volume analyses of IAEA-S-1 is 0.9 ‰, 0.08 ‰, and 0.8 ‰ for $\delta^{34}$S, $\Delta^{33}$S, and $\Delta^{36}$S, respectively (2σ for 14 replicate analyses).

2.3.3 Modeling fractionation from isotopologue-specific cross sections

Experimental results were compared with the isotope signatures predicted from isotopologue-specific cross sections. Two different sets of cross sections were used in the calculations, one by Lyons (2007, 2008) and one by Danielache et al. (2008). The Lyons (2007, 2008) cross sections are based on the high-resolution (0.002 nm) $^{32}$SO₂ cross section measurements of Freeman et al. (1984). Cross sections for minor isotopologues were estimated by shifting the $^{32}$SO₂ cross sections by an amount based on calculations by Ran et al. (2007), as described by Lyons (2008). The Danielache et al. (2008) cross sections are lower resolution (25 cm⁻¹), and contain only $^{32}$SO₂, $^{33}$SO₂, and $^{34}$SO₂, but are based on experimental measurements of isotopically enriched SO₂. Therefore, they take into account not only shifts in the absorption peaks.
but also differences in peak shape and intensity due to isotope substitution. Isotope effects due to differences in the photolysis rates of individual isotopologues were estimated as described in Lyons (2007) and integrated over the 190 nm to 220 nm spectral region and the optical path length of the reaction cell.

The major uncertainty in the calculation is the photon flux of the Xe and D₂ lamps, which are approximated using spectra supplied by the manufacturer (Newport Corporation, Irving, CA). These values are corrected for the transmittance of the optical filter and reaction cell windows, which were measured using a CCD spectrometer (0.7 nm resolution, Model SPM-002-BT, Photon Control, Burnaby, Canada) (Figures 2-1-A and 2-1-B). The interference of oxygen (O₂) and ozone (O₃) is relatively minor compared to the uncertainty in the light source spectrum and was not considered in these calculations. Calculations including the spectral interference of oxygen show only a minor effect for calculated isotope fractionation factors.

### 2.3.4 Notations

Isotopic results are presented in delta notation relative to the isotopic signature of the initial SO₂:

\[
\delta^{3X}S = \frac{^{3X}R_{sa}}{^{3X}R_i} - 1
\]  

(2.1)

where \(^{3X}R\) is the molar ratio of \(^{3X}S\) to \(^{32}S\) (\(^{3X}R = ^{3X}S/^{32}S\), where \(X = 3, 4, \text{ or } 6\)) of sample \((R_{sa})\) and initial \(SO_2\) \((R_i)\), respectively. Note that we omit the common multiplication factor of 1000, since it technically belongs to the %osymbol (Coplen, 2011).

We present the deviation from mass-dependence using the capital delta notation recommended by Miller (2002) and Kaiser et al. (2004):

\[
\Delta^{33}S = \left(\frac{^{33}R_{sa}}{^{33}R_i}\right)/\left(\frac{^{34}R_{sa}}{^{34}R_i}\right)^{0.515} - 1
\]  

(2.2)

\[
\Delta^{36}S = \left(\frac{^{36}R_{sa}}{^{36}R_i}\right)/\left(\frac{^{34}R_{sa}}{^{34}R_i}\right)^{1.90} - 1
\]  

(2.3)
In delta notation these are expressed as:

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

\[
\Delta^{36}S = \left( \delta^{36}S + 1 \right) / \left( \delta^{34}S + 1 \right)^{1.90} - 1
\]

We also look at the relationships between fractionations of $^{33}S$ ($^{36}S$) and $^{34}S$, and use the following notation:

\[
^{33}\lambda = \ln(\delta^{33}S + 1) / \ln(\delta^{34}S + 1)
\]

\[
^{36}\lambda = \ln(\delta^{36}S + 1) / \ln(\delta^{34}S + 1)
\]

### 2.4 Results

The isotopic results from all experiments are presented in Tables 2.1 and 2.2 and Figures 2-2 and 2-3.

#### 2.4.1 Results from Xe, D$_2$, and 200 nm bandpass experiments

The full spectrum Xe and D$_2$ lamp experiments and the 200 nm bandpass experiments all produced elemental sulfur that was highly enriched in $^{34}S$ ($\delta^{34}S = +154.7\%$ to $+212.0\%$), with positive $\Delta^{33}S$ values ($+19.4\%$ to $+24.3\%$) and negative $\Delta^{36}S$ values ($-42.5\%$ to $-35.2\%$). This resulted in $\Delta^{36}S/\Delta^{33}S$ ratios of $-1.79$ to $-1.65$ for the D$_2$ lamp experiments and $-2.19$ to $-1.90$ for the Xe and 200 nm bandpass experiments. The $^{33}\lambda$ values of these experiments were $0.62$ to $0.67$, with the larger values generally associated with experiments at lower pressure and vice versa. These generally match the pattern observed previously by Masterson et al. (2011) (Figure 2-4).

The residual SO$_2$ for the Xe, D$_2$, and 200 nm bandpass experiments was consistently depleted in $^{34}S$ ($\delta^{34}S = -54.4\%$ to $-16.4\%$) and had negative $\Delta^{33}S$ values ($-6.1\%$ to $-1.1\%$) and positive $\Delta^{36}S$ values ($+1.3\%$ to $+8.5\%$). This is expected from isotope mass-balance considerations.
Table 2.1: Conditions, yields, and elemental sulfur ($S^0$) results from static photochemical experiments.

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<th>Time</th>
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* Denotes a sample where the elemental sulfur was analyzed using the microvolume procedure.
Table 2.2: Residual sulfur dioxide (SO₂) and product sulfur trioxide (SO₃) results from static photochemical experiments.

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<td>0.76</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DFS-2</td>
<td>-16.61</td>
<td>-27.61</td>
<td>-50.45</td>
<td>-2.33</td>
<td>1.43</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DFS-3</td>
<td>3.01</td>
<td>7.21</td>
<td>14.51</td>
<td>-0.69</td>
<td>0.70</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Names correspond to experiments in Table 2.1.
Figure 2-2: $\Delta^{33}S$ versus $\delta^{34}S$ for the (A) full spectrum Xe experiments, (B) full spectrum D$_2$ experiments, (C) 200 nm bandpass filter experiments, and (D) 250 nm longpass filter experiments.

Figure 2-3: $\Delta^{36}S$ versus $\Delta^{33}S$ for the elemental sulfur products for different photolysis experiments compared to the Archean slope ($-0.9$).
Figure 2-4: Pressure dependence of $^{33}\lambda$ and $^{36}\lambda$ values compared to the data of Masterson et al. (2011). Masterson et al. (2011) data for pure SO$_2$ with pressure below 160 torr was fit with an exponential curve and plotted alongside the values reported in this work. $^{33}\lambda$ values observed here are consistent with the Masterson et al. (2011) values. $^{36}\lambda$ values for the D$_2$ lamp experiments are consistent with the Masterson et al. (2011) values, which were also measured using a D$_2$ arc lamp, but Xe lamp and 200 nm bandpass data are lower than predicted from the Masterson et al. (2011) data.
The $\text{SO}_3$ products displayed a range of $\delta^{34}\text{S}$ values ($-15.0\%$ to $+10.7\%$), but were consistently enriched in $^{34}\text{S}$ relative to the residual $\text{SO}_2$ for the same experiments. The $\Delta^{33}\text{S}$ values ($-3.5\%$ to $-0.3\%$) and the $\Delta^{36}\text{S}$ values ($+0.7\%$ to $+8.6\%$) are of the same sign but a smaller magnitude than the residual $\text{SO}_2$ from the same experiments, suggesting that the isotope signatures of the $\text{SO}_3$ are derived from the residual $\text{SO}_2$ with a mass-dependent isotope effect.

### Results from 250 nm longpass experiments

The Xe lamp with the 250 nm longpass filter also produced elemental sulfur enriched in $^{34}\text{S}$, but with $\delta^{34}\text{S}$ values ($+7.7\%$ to $+29.1\%$) almost an order of magnitude smaller than the Xe, $D_2$, and 200 nm bandpass experiments. $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values were all positive ($+13.4\%$ to $+16.5\%$ and $+8.7\%$ to $+11.1\%$, respectively), producing positive $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ values of 0.61 to 0.67. $\Delta^{33}\text{S}$ values are relatively constant in experiments run at different conditions and do not show significant pressure dependence, whereas $\delta^{34}\text{S}$ values (and $\delta^{33}\text{S}$ and $\delta^{36}\text{S}$ values) vary as a function of the initial $\text{SO}_2$ pressure, with lower pressures producing higher $\delta^{34}\text{S}$ values and vice versa.

The residual $\text{SO}_2$ from these experiments yielded a small range of $\delta^{34}\text{S}$ values ($-2.3\%$ to $+1.1\%$) and had negative $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values ($-3.91\%$ to $-0.53\%$ and $-3.1\%$ to $-0.3\%$, respectively). Product $\text{SO}_3$ had negative $\delta^{34}\text{S}$ values ($-17.4\%$ to $-4.7\%$), negative $\Delta^{33}\text{S}$ values ($-1.20\%$ to $0.00\%$), and negative or near zero $\Delta^{36}\text{S}$ values ($-0.8\%$ to $+0.1\%$).

### Results from cross section modeling

Results ($\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, $^{33}\lambda$) from calculations using both the Lyons (2007, 2008) and the Danielache et al. (2008) cross sections are compared with our experimental results in Figure 2-6. Both the Lyons (2007, 2008) and the Danielache et al. (2008) cross sections predict that the isotope effects are not a strong function of pressure except at very low column densities (less than approximately $9 \times 10^{17}$ molecules cm$^{-2}$, or less than 1 torr total pressure in our experiments). This is because $\text{SO}_2$ is optically
thick in our experimental conditions, such that the 190 nm to 220 nm absorption lines are nearly completely saturated (Figure 2-5). Both sets of cross sections predict high $^{34}\text{S}/^{32}\text{S}$ fractionations; $\delta^{34}\text{S}$ values of $+125\%$ to $+165\%$ for the Danielache et al. (2008) and $+300\%$ to $+310\%$ for the Lyons (2007, 2008) cross sections, respectively. These high $^{34}\text{S}/^{32}\text{S}$ fractionations are consistent with our experimental results (Figure 2-6), although the Lyons (2007, 2008) cross sections over predict the $\delta^{34}\text{S}$ values. The experimental $\Delta^{33}\text{S}$ values agree qualitatively with the Lyons (2007, 2008) cross section calculations and the $\text{D}_2$ lamp calculations for the Danielache et al. (2008) cross sections, predicting positive $\Delta^{33}\text{S}$ values on the order of $+9\%$ to $+15\%$. The Danielache et al. (2008) cross sections predict negative $\Delta^{33}\text{S}$ values for the full spectrum Xe and the 200 nm bandpass experiments.

The Lyons (2007, 2008) cross sections predict $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ values of approximately $-27\%$ for the $\text{D}_2$ experiments and $-14\%$ to $-16\%$ for the Xe and 200 nm bandpass experiments (Figure 2-7). Calculated $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ values are $-1.9$ for the $\text{D}_2$ lamp, $-1.5$ to $-1.6$ for the 200 nm bandpass experiments, and $-1.4$ to $-1.45$ for the Xe lamp experiments. These values, particularly the $\text{D}_2$ lamp predictions, are similar to the $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios ($-1.65$ to $-2.19$) observed in our experiments (Figure 2-7).

2.5 Discussion

2.5.1 Photochemistry of SO$_2$

The photochemistry of SO$_2$ has been studied extensively and is reviewed elsewhere (e.g., Okabe, 1971; Calvert et al., 1978; Heicklen et al., 1980). Here, we focus on the two strong ultraviolet absorption regions of SO$_2$, a strong absorption from 165 nm to 240 nm and a weaker absorption from 250 nm to 330 nm (Figure 2-1-C). SO$_2$ has additional UV absorption bands at 130 nm to 165 nm and 350 nm to 400 nm, but they are not likely to be significant to atmospheric chemistry on Earth and are not studied here.

Photoexcitation in the 165 nm to 240 nm absorption region corresponds to a
Figure 2-5: Simulations of photon flux as a function of wavelength for four depths within the reaction cell, at pressure of 5 torr SO₂ (left) and 20 torr SO₂ (right), for all four filter / lamp conditions tested. The four lines in each plot represent the photon flux at the front of the reaction cell (top line, black), 1 cm into the cell (top middle line, green), 5 cm into the cell (bottom middle line, blue) and at the rest of the reaction cell (bottom line, orange). The 190 nm to 220 nm region is mostly saturated by about 5 cm into the cell, and completely saturated at the rear of the cell. The 250 nm to 330 nm region saturates more slowly (due to the lower absorption of SO₂ in this region) but is still mostly saturated by the rear of the photocell, except at the low and high ends of the absorption band. Simulated based on the cross-section compilation of Manatt and Lane (1993).
Figure 2-6: Comparison of the Lyons (2007, 2008) (A,C,E) and the Danielache et al. (2008) (B,D,F) cross section calculations and the experimental data.
\[ \text{Figure 2-7: Calculated } \Delta^{36}\text{S values (A) and } \Delta^{36}\text{S}/\Delta^{33}\text{S ratios from the Lyons (2007, 2008) cross sections compared with our experimental data.} \]

\[ 1\text{B}_2 \leftarrow 1\text{A}_1 \text{ transition. Below 218.7 nm (Becker et al., 1995), } \text{SO}_2(1\text{B}_2) \text{ dissociates into } \text{SO}(3\Sigma^-) + \text{O}(3\text{P}_2). \text{ The photolysis quantum yield increases with decreasing wavelength between 219 nm to 210 nm, below which the quantum yield is near unity (Okazaki et al., 1995).} \]

\[
\text{SO}_2(1\text{A}_1) + hv(165 \text{ nm to } 240 \text{ nm}) \rightarrow \text{SO}_2(1\text{B}_2) \quad \text{(R 2.2)}
\]

\[
\text{SO}_2(1\text{B}_2) \rightarrow \text{SO}(3\Sigma^-) + \text{O}(3\text{P}_2) \quad \text{(R 2.3)}
\]

The photolysis of \( \text{SO}_2 \) in this wavelength region (i.e., R 2.2 and R 2.3) is thought to produce anomalous isotope fractionation due to isotopologue self-shielding (Lyons, 2007) or isotopologue differences in cross section amplitudes (Danielache et al., 2008; Ueno et al., 2009). The exact dissociation pathway is complicated by state crossing among multiple low-lying excited states (see Katagiri et al., 1997). The quantum efficiency of the state crossing also has the potential to cause mass-independent isotope effects by a mechanism similar to that suggested for \( \text{CS}_2 \) (Zmolek et al., 1999) and
other molecules (Bhattacharya et al., 2000; Chakraborty et al., 2008; Muskatel et al., 2011).

In our reaction cell, atomic oxygen produced from the photolysis of SO₂ (R.2.3) will react with a ground-state SO₂ molecules to form SO₃:

\[ \text{SO}_2 + O + M \rightarrow \text{SO}_3 + M \]  \hspace{1cm} (R.2.4)

Because the fused silica windows and the small amount of oxygen (approximately 20 cm column of laboratory air, see Section 2.8.1) between the lamp and the reaction cell both absorb a significant fraction of the photons shorter than ca. 190 nm, we will discuss our results in terms of photolysis in the 190 nm to 220 nm region. This is also the region most relevant to the atmosphere, because absorption by CO₂ and H₂O will attenuate most of the light below 190 nm (Lyons, 2007; Ueno et al., 2009).

Photoexcitation in the 250 nm to 330 nm absorption region corresponds to the excitation of SO₂ into two singlet excited states (e.g., Heicklen et al., 1980):

\[ \text{SO}_2^{(1A_1)} + h\nu(250\text{ nm to 330 nm}) \rightarrow \text{SO}_2^{(1A_2, 1B_1)} \]  \hspace{1cm} (R.2.5)

and is followed by:

\[ ^1\text{SO}_2 \rightarrow \text{SO}_2(+h\nu) \]  \hspace{1cm} (R.2.6)

\[ ^1\text{SO}_2 \rightarrow ^3\text{SO}_2 \]  \hspace{1cm} (R.2.7)

\[ ^1\text{SO}_2 + M \rightarrow \text{SO}_2 + M \]  \hspace{1cm} (R.2.8)

\[ ^1\text{SO}_2 + M \rightarrow ^3\text{SO}_2 + M \]  \hspace{1cm} (R.2.9)

\[ ^3\text{SO}_2 \rightarrow \text{SO}_2(+h\nu) \]  \hspace{1cm} (R.2.10)

\[ ^3\text{SO}_2 + M \rightarrow \text{SO}_2 + M \]  \hspace{1cm} (R.2.11)

where \(^1\text{SO}_2\) and \(^3\text{SO}_2\) are the excited singlet and triplet electronic states of SO₂, respectively. The \(^1\text{SO}_2\) is quenched by collisions to the ground state (R.2.8) or a lower energy excited triplet (likely \(^3\text{B}_1\)) state (R.2.9), whereas deactivation by non-
collision processes (R 2.6 and R 2.7) are expected to be slow under our experimental conditions (Rao et al., 1969; Heicklen et al., 1980). Rate constants and lifetimes for these reactions are given in Table 2.3.

Unlike the 190 nm to 220 nm region, photoexcitation in the 250 nm to 330 nm region does not lead to direct photolysis. Instead, $^1$SO$_2$ and $^3$SO$_2$ react with ground state SO$_2$ to produce SO and SO$_3$ via the following photo-oxidation reactions (Chung et al., 1975):

$^1$SO$_2$ + SO$_2$ → SO$_3$ + SO  \hspace{1cm} (R 2.12)

$^3$SO$_2$ + SO$_2$ → SO$_3$ + SO  \hspace{1cm} (R 2.13)

In systems with other species, such as organics or CO, other reactions are also possible (Calvert et al., 1978; Heicklen et al., 1980). The potential importance of these reactions in an Archean atmosphere is discussed in Section 2.5.6.

Once SO is produced, it can be photolyzed (R 2.14), react with other SO molecules (R 2.15), or react with SO$_3$ (R 2.16):

SO + hv(<230 nm) → S + O  \hspace{1cm} (R 2.14)

SO + SO → S + SO$_2$  \hspace{1cm} (R 2.15)

SO + SO$_3$ → 2SO$_2$  \hspace{1cm} (R 2.16)

In our static photochemical experiments, most of the SO will react back to SO$_2$ via R 2.16, and a small amount will react via R 2.14 or R 2.15 to form elemental sulfur (Chung et al., 1975).

Once S is created, it can polymerize to form polysulfur species ($S_2$, $S_3$, $S_4$, ..., $S_8$; Kasting et al., 1989; Pavlov and Kasting, 2002). From the chemistry outlined above, it is possible to produce SO$_3$ (or sulfate) and elemental sulfur from photochemistry in both the 190 nm to 220 nm absorption band and the 250 nm to 330 nm absorption band. Estimated rates for the photolysis in the 190 nm to 220 nm region, photoexcitation in the 250 nm to 330 nm region, and SO production from photochemistry in the 250 nm to 330 nm region (via the photo-oxidation mechanism, R 2.12 and R 2.13)
Table 2.3: Rates and lifetimes of excited state SO\(_2\) species in 1 atm of N\(_2\) and in 10 torr of pure SO\(_2\)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate constant(^a)</th>
<th>Lifetime(^b)(s)</th>
<th>Lifetime (s) 1 atm N(_2)</th>
<th>Lifetime (s) 10 torr SO(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photolysis / Photoexcitation Reactions</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(R 2.2+R 2.3) SO(_2) + hv(180 nm to 220 nm) → SO + O</td>
<td>2.4 × 10(^{-4})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(R 2.5) SO(_2) + hv(250 nm to 330 nm) → ^3SO(_2)</td>
<td>1.8 × 10(^{-3})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Singlet Excited State Quenching Reactions</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(R 2.6) ^1SO(_2) → SO(_2) + hv</td>
<td>2.2 × 10(^4)</td>
<td>4.5 × 10(^{-5})</td>
<td>4.5 × 10(^{-5})</td>
<td></td>
</tr>
<tr>
<td>(R 2.7) ^1SO(_2) → ^3SO(_2)</td>
<td>1.5 × 10(^3)</td>
<td>6.7 × 10(^{-4})</td>
<td>6.7 × 10(^{-4})</td>
<td></td>
</tr>
<tr>
<td>(R 2.8) ^1SO(_2) + M → SO(_2) + M</td>
<td>^c1 × 10(^{-11})</td>
<td>4.1 × 10(^{-9})</td>
<td>^d1.1 × 10(^{-7})</td>
<td></td>
</tr>
<tr>
<td>(R 2.9) ^1SO(_2) + M → ^3SO(_2) + M</td>
<td>^d1 × 10(^{-12})</td>
<td>4.1 × 10(^{-8})</td>
<td>1.0 × 10(^{-6})</td>
<td></td>
</tr>
<tr>
<td>(R 2.12) ^1SO(_2) + SO(_2) → SO(_3) + SO</td>
<td>4 × 10(^{-12})</td>
<td></td>
<td>7.7 × 10(^{-7})</td>
<td></td>
</tr>
<tr>
<td>Triplet Excited State Quenching Reactions</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(R 2.10) ^3SO(_2) → SO(_2) + hv</td>
<td>1.1 × 10(^3)</td>
<td>9.1 × 10(^{-4})</td>
<td>9.1 × 10(^{-4})</td>
<td></td>
</tr>
<tr>
<td>(R 2.11) ^3SO(_2) + M → SO(_2) + M</td>
<td>^e1.1 × 10(^{-13})</td>
<td>1.0 × 10(^{-6})</td>
<td>^f5.3 × 10(^{-6})</td>
<td></td>
</tr>
<tr>
<td>(R 2.13) ^3SO(_2) + SO(_2) → SO(_3) + SO</td>
<td>7 × 10(^{-14})</td>
<td></td>
<td>4.4 × 10(^{-5})</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)First order rate constants are in s\(^{-1}\) and second order rate constants are in cm\(^3\) molecule\(^{-1}\) s\(^{-1}\).

Unless otherwise noted, rates are from Table 4 of Turco et al. (1982) and references therein, and assume M = N\(_2\). Photolysis and photoexcitation rates assume a solar spectrum (Rottman et al., 2006) with no absorbing species other than SO\(_2\).

\(^b\)Lifetimes calculated assuming 1 atm total pressure at 25 °C (number density of 2.46 × 10\(^{19}\)). Lifetimes calculated based on low-pressure rate constants, unless otherwise noted.

\(^c\)Approximate rate. For M = SO\(_2\), the rate is 2.9 × 10\(^{-11}\) (from Rao et al. 1969, after subtracting the rate of R 2.12).

\(^d\)Approximate rate. For M = SO\(_2\), the rate is 3.0 × 10\(^{-12}\) (from Rao et al. 1969).

\(^e\)This rate is from Su et al. (1977). For M = SO\(_2\), the rate is 5.8 × 10\(^{-13}\) (from Sidebottom et al. 1971, after subtracting the rate of R 2.13).

\(^f\)Lifetime was calculated as suggested by Su et al. (1977), taking into account the pressure saturation effect for physical quenching of ^3SO\(_2\). This is roughly an order of magnitude longer than predicted by the low-pressure rate constant.

\(^g\)Calculated using the rates for M = SO\(_2\).
are given in Table 2.4 to estimate the relative contribution of the two photoexcitation bands under different light sources.

Table 2.4: Estimated photolysis (190 nm to 220 nm), photoexcitation (250 nm to 330 nm), and photo-oxidation rates for 10 torr of SO₂ with different light source / filter conditions.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Photolysis Rate&lt;sup&gt;a&lt;/sup&gt; 190 nm to 220 nm</th>
<th>Photolysis Rate&lt;sup&gt;a&lt;/sup&gt; 250 nm to 330 nm</th>
<th>Photo-oxidation Rate&lt;sup&gt;b&lt;/sup&gt; 250 nm to 330 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xe Lamp</td>
<td>$6.7 \times 10^{13}$</td>
<td>$5.0 \times 10^{14}$</td>
<td>$5.9 \times 10^{13}$</td>
</tr>
<tr>
<td>D₂ Lamp</td>
<td>$1.4 \times 10^{13}$</td>
<td>$1.1 \times 10^{13}$</td>
<td>$1.3 \times 10^{12}$</td>
</tr>
<tr>
<td>Xe + 200 nm BP</td>
<td>$2.0 \times 10^{13}$</td>
<td>$5.3 \times 10^{12}$</td>
<td>$6.4 \times 10^{11}$</td>
</tr>
<tr>
<td>Xe + 250 nm LP</td>
<td>$3.9 \times 10^{11}$</td>
<td>$4.6 \times 10^{14}$</td>
<td>$5.6 \times 10^{13}$</td>
</tr>
</tbody>
</table>

<sup>a</sup> Rates are given in molecules cm⁻³ s⁻¹ and calculated assuming a 25.5 cm path length, 10 torr of pure SO₂, the photon fluxes given by Rottman et al. (2006), the window and filter transmissions given in Figure 2-1B, and the SO₂ absorption cross sections of Manatt and Lane (1993). Photolysis rates between 5 torr and 25 torr are within 0.5% of the values here. Photoexcitation rates vary by ±20% of the values reported here between 5 torr and 25 torr, with higher values at higher SO₂ pressures.

<sup>b</sup> Rates are given in molecules cm⁻³ s⁻¹. Photo-oxidation rate is the rate of SO or SO₃ production via R 2.12 and R 2.13. These are calculated assuming steady state number densities for $^{34}$SO₂ and $^{33}$SO₂. Photo-oxidation rates vary by ±20% between 5 torr and 25 torr, with higher values at higher SO₂ pressure and vice versa.

### 2.5.2 Sulfur isotope effects in 190 nm to 220 nm versus 250 nm to 330 nm regions

Until recently (i.e., Masterson et al., 2011), there had been only two published studies presenting the mass-independent sulfur isotope signatures during laboratory SO₂ photochemistry under different conditions (Farquhar et al., 2000b, 2001). These early studies have been pivotal in our understanding of the sources of S-MIF and have guided the interpretation of mass-independent isotope signatures in both the modern atmosphere and in the Archean rock record. New experimental results allow us to revise and update our understanding of the isotope effects during SO₂ photochem-
istry, particularly with regard to the isotope effects due to direct photolysis (R 2.2 and R 2.3) in the 190 nm to 220 nm wavelength region versus indirect photo-oxidation (R 2.5 to R 2.13) in the 250 nm to 330 nm wavelength region.

Farquhar et al. (2001) reported the isotope data of the products produced from photochemical experiments using a Xe arc lamp, which they attributed to photochemical processes occurring above 220 nm. This was based on the spectral properties of Xe arc lamp sources (strong continuum irradiance above 220 nm, weaker irradiance below 220 nm, Figure 2-1-A). This led to the assumption that the Farquhar et al. (2001) 193 nm ArF photolysis results represent the isotope fractionation associated with photolysis in the 190 nm to 220 nm region and that the Xe arc lamp results were representative of photochemistry in the 250 nm to 330 nm region. Although narrow band photolysis experiments provide useful information, later studies questioned their applicability to understanding isotope effects from broad-band radiation sources like the sun (Lyons, 2007; Danielache et al., 2008; Ueno et al., 2009).

The isotopic similarity between our 200 nm bandpass experiments and the full spectrum Xe lamp experiments suggest that the isotopic results from photolysis with a full spectrum Xe arc lamp (including that from Farquhar et al., 2001) are due primarily to direct photolysis in the 190 nm to 220 nm region, and that photolysis in the 250 nm to 330 nm region produces S0 with distinct isotopic (and mass-independent) signatures different from those suggested earlier (i.e., Farquhar et al., 2001). Full spectrum Xe lamp photolysis (Figures 2-2-A and 2-3) produces elemental sulfur highly enriched in 34S relative to 32S (δ34S = 154.6‰ to +168.7‰) with consistent 33λ values (0.64 to 0.67) and negative Δ36S/Δ33S values (-1.96 to -1.90). This is similar to the elemental sulfur results using the 200 nm bandpass filter (Figures 2-2-B and 2-3; δ34S = 171.7‰ to +200.7‰, 33λ = 0.62 to 0.66, Δ36S/Δ33S = -2.19 to -1.92), but considerably different from the elemental sulfur formed using the 250 nm longpass filter (Figures 2-2-D and 2-3), which had smaller 34S/32S fractionations (δ34S = +7.7‰ to +29.1‰), larger and more variable 33λ values (0.98 to 2.65), and positive Δ36S/Δ33S ratios (0.61 to 0.67). Results in the residual SO2 and SO3 products also show similarity between the full spectrum Xe lamp and
the 200 nm bandpass filter experiments, with considerable differences between these and the 250 nm longpass filter results (Figure 2-2). Photolysis experiments using a D$_2$ arc lamp, both reported here and in Masterson et al. (2011), also produce products with a similar isotopic distribution to the 200 nm bandpass experiments (e.g., $\delta^{34}$S values of +191.0‰ to +212.0‰, $^{33}$λ values of 0.63 to 0.64, and $\Delta^{36}$S/$\Delta^{33}$S ratios of -1.79 to -1.65 for the experiments reported here), suggesting that they are also due to photochemistry in the 190 nm to 220 nm photolysis band as well. This is supported by the relative rates of direct photolysis in the 190 nm to 220 nm region and photo-oxidation by the 250 nm to 330 nm radiation, as given in Table 2.4.

Although the full spectrum Xe arc lamp results reported here and those reported by Farquhar et al. (2001) produce similar isotope effects in the residual SO$_2$ (depleted in $^{34}$S, $^{33}$λ ratios of 0.60 to 0.61 for our experiments and 0.56 for the Farquhar et al. 2001 experiments), our results for SO$_3$ show negative $\Delta^{33}$S values, whereas the Farquhar et al. (2001) results show positive $\Delta^{33}$S values in the sulfate products. The dominant source of sulfate in the photochemical system is the oxidation of the residual SO$_2$ by O (R 2.4), followed by hydrolysis with water vapor present in the reaction cell or introduced when the cell is exposed to air. Thus, unless R 2.4 is a source of mass-independent fractionation, it seems unlikely that the residual SO$_2$ and SO$_3$ should have $\Delta^{33}$S values with the opposite sign, as reported by Farquhar et al. (2001). We measured negative $\Delta^{33}$S values for both the residual SO$_2$ and the SO$_3$ (Table 2.2). The negative $\Delta^{33}$S signatures in the SO$_3$ and the residual SO$_2$ appear to be generated from isotope mass-balance constraints, due to the removal of elemental sulfur with positive $\Delta^{33}$S values. The $\Delta^{33}$S value of the SO$_3$ is inherited from the residual SO$_2$ via the mass-dependent reaction R 2.4.

2.5.3 S-MIF in modern stratospheric aerosols - photo-oxidation and unlikely mechanism

Mass-independent sulfur isotope signatures have been measured in tropospheric sulfate aerosols (Romero and Thiemens, 2003; Guo et al., 2010), as well as in sulfate
aerosols preserved in Antarctic snow and ice associated with large volcanic events (Savarino et al., 2003; Báróni et al., 2007). It is generally agreed that the aerosols containing S-MIF are likely stratospheric in origin, although the exact mechanism responsible for producing the anomalous isotope signature remains uncertain. Photolysis reactions of sulfur gases are the most likely source of the modern S-MIF. Although OCS photolysis can be a major contributor to stratospheric sulfate (e.g., Crutzen, 1976; Turco et al., 1980), cross-section measurements (Hattori et al., 2011) and experimental photolysis results (Lin et al., 2011) show that OCS photolysis does not produce S-MIF. Pavlov et al. (2005) suggested SO₃ photolysis as the source of S-MIF, but SO₃ cross sections (Burkholder and McKeen, 1997) have only weak vibronic structure and are not a promising candidate for sulfur MIF production (Lyons, 2009). This leaves photochemical reactions of SO₂ (photolysis or photoexcitation) as the most likely source of the stratospheric S-MIF signature, although it is possible that it could be produced by some other unknown mechanism(s).

Although direct photolysis of SO₂ (R 2.2 and R 2.3) produces SO with S-MIF and is the most likely source of the Archean S-MIF signature, SO in the modern atmosphere is rapidly reoxidized to SO₂, predominantly by O₂ (Black et al., 1982a,b; Savarino et al., 2003), preventing the preservation of the isotope signature in SO. Model calculations (Pavlov et al., 2005) predict that the isotope signature from the direct photolysis of SO₂ cannot be preserved below an altitude of 50 km, making it an unlikely source for the stratospheric S-MIF. Savarino et al. (2003) suggest that SO₃ formed from excited SO₂ produced in the 250 nm to 330 nm region could produce S-MIF in modern stratospheric aerosols. As discussed in Section 2.5.1, irradiation of SO₂ in the 250 nm to 330 nm wavelength region produces excited states of SO₂ that can react with ground-state SO₂ molecules (R 2.12 and R 2.13) to produce SO and SO₃. Savarino et al. (2003) suggest that SO₃ (and subsequently sulfate) formed from these reactions could represent a significant fraction of sulfate produced in the days following a major stratospheric SO₂ input due to a volcanic eruption such as Pinatubo (1991 eruption). Give the reaction stoichiometry of the *SO₂ + SO₂ → SO + SO₃ reactions (R 2.12 and R 2.13), it is reasonable to assume that at least part of the S-
MIF signature in the excited \(^{35}\text{SO}_2\) is transferred to the \(\text{SO}_3\) product. An anomalous isotope signature transferred to the \(\text{SO}_3\) product can be aerosolized and separated from the parent \(\text{SO}_2\) pool, allowing for the preservation of S-MIF even in an oxygen-rich atmosphere (Savarino et al., 2003).

Our photochemical results using the 250 nm longpass filter show large mass-independent isotope effects in the elemental sulfur products formed from \(\text{SO}_2\) in R 2.12 and R 2.13, but almost no mass-independent sulfur isotope anomalies in the \(\text{SO}_3\) product (Figure 2-2-D, Table 2.2). When there is a mass-independent isotope signature in the \(\text{SO}_3\) product, it appears to be inherited from the residual \(\text{SO}_2\) rather than the \(^{35}\text{SO}_2\) species. This suggests that the \(^{35}\text{SO}_2 + \text{SO}_2 \rightarrow \text{SO} + \text{SO}_3\) reactions occur via an O atom transfer from the excited state molecule, which contains S-MIF, to the mass-dependent ground state molecule. As a result, any mass-independent isotope signature in the \(^{35}\text{SO}_2\) is transferred to the \(\text{SO}\) product and not the \(\text{SO}_3\) product.

If \(\text{SO}\) is rapidly deoxidized to \(\text{SO}_2\), the residual \(\text{SO}_2\) will not develop a mass-independent isotope signature, and thus the \(\text{SO}_3\) formed from R 2.12 and R 2.13 will also be mass dependent. The formation of aerosols containing sulfur MIF from photooxidation in the 250 nm to 330 nm region would require some mechanism of trapping or removing \(\text{SO}_2\) from the surrounding \(\text{SO}_2\) before it is re-oxidized, allowing the parent \(\text{SO}_2\) gas to develop a substantial mass-independent signature. If such a trapping mechanism did exist, direct photolysis of \(\text{SO}_2\) (in the 190 nm to 220 nm region) would be the dominant source of MIF, since it occurs via direct dissociation rather than requiring bimolecular \(^{35}\text{SO}_2 + \text{SO}_2\) reactions. In addition, the S-MIF signatures observed in the modern atmosphere contain negative \(\Delta^{36}\text{S}/\Delta^{33}\text{S}\) ratios (approximately \(-4.7\), Savarino et al. 2003), which is more consistent with the negative \(\Delta^{36}\text{S}/\Delta^{33}\text{S}\) values observed from photochemistry in the 190 nm to 220 nm region than the positive \(\Delta^{36}\text{S}/\Delta^{33}\text{S}\) values observed from photochemistry in the 250 nm to 330 nm region. Therefore, it is unlikely that photoexcitation of \(\text{SO}_2\) in the 250 nm to 350 nm region could make a significant contribution to the sulfur mass-independent isotope anomalies observed in stratospheric-derived sulfate aerosols. The mechanistic source of the modern stratospheric S-MIF remains enigmatic.
2.5.4 Comparison of absorption cross sections with experimental data

The ability to predict the isotope fractionations during SO$_2$ photolysis based on isotopologue-specific cross sections would allow us to better constrain the atmospheric conditions necessary to produce the S-MIF signature observed in the geological record (e.g., Ueno et al., 2009; Halevy et al., 2010). However, such cross sections must be validated by comparison with experimental data before they can be applied with confidence to atmospheric models of the Archean. For this reason, we compared our experimental results with predictions based on two published isotopologue-specific cross sections of SO$_2$, one by Lyons (2007, 2008) and one by Danielache et al. (2008).

The cross sections are used to predict the instantaneous isotopic signature of the SO produced by SO$_2$ photolysis. We do not consider the quantum efficiency of photolysis, where non-adiabatic effects could contribute to the production of MIF (Bhattacharya et al., 2000; Chakraborty et al., 2008; Muskatel et al., 2011). In addition, our reported isotope signatures are measured for the accumulated elemental sulfur product over the course of an experiment. There are a series of reactions occurring between the production of SO and the production of elemental sulfur, including reactions with SO$_3$ (R 2.16), photolysis of SO (R 2.14), disproportionation of SO (R 2.15), and various reactions between elemental sulfur species (S$_2$, S$_3$, ..., S$_8$), all of which might have mass-dependent (and potentially mass-independent) isotope effects associated with them. However, we assume that these additional isotope effects are relatively minor compared to the large fractionations associated with the initial photolysis reaction.

The Lyons (2007, 2008) cross sections predict $\delta^{34}S$ values about 100% higher than our measured values (predicted $\delta^{34}S = +300\%$ to $+320\%$, experimental $\delta^{34}S = +155\%$ to $+212\%$) and $\Delta^{33}S$ values lower than our experimental values (predicted $\Delta^{33}S = +9.5\%$, $+10.5\%$, and $+14.0\%$ for the 200 nm bandpass, Xe, and D$_2$, respectively; experimental $\Delta^{33}S = +18\%$ to $+24\%$). The magnitude of the predicted $\Delta^{36}S$ values are also smaller than our measured values (Figure 2-7). The Lyons
cross sections are based on cross sections measured by Freeman et al. (1984) at 213 K, whereas our experiments were run at room temperature (295 K). Temperature will affect the vibration and rotational state distribution of the ground state SO\(_2\), as well as the Doppler widths of the absorption bands, resulting in larger peak cross sections and sharper bands at lower temperature (Wu et al., 2000; Rufus et al., 2009). As a result, the \(^{34}\text{S}/^{32}\text{S}\) fractionation is expected to be smaller at higher temperatures, which could potentially account for some of the differences between the predicted isotope effects and those measured in our experiments. The Lyons (2007, 2008) cross sections take into account peak shifts due to isotope substitution but do not account for changes in absorption intensities or peak shapes. As shown by Danielache et al. (2008), differences in the shape of the absorption cross sections could produce additional mass-independent effects beyond just the peak shifts. Although there are some quantitative differences, the Lyons (2007, 2008) cross sections show good qualitative agreement with our experimental results, since both yield large positive \(\delta^{34}\text{S}\) values, positive \(\Delta^{33}\text{S}\) values, and negative \(\Delta^{36}\text{S}\) values, and similar behavior between the Xe, D\(_2\), and 200 nm bandpass experiments. In addition, there is relatively good quantitative agreement between the predicted and measured \(\Delta^{36}\text{S}/\Delta^{33}\text{S}\) ratios (Figure 2-7), especially for the D\(_2\) lamp.

The Danielache et al. (2008) cross sections give very good quantitative agreement with our experimental data for photolysis using a D\(_2\) arc lamp (\(\delta^{34}\text{S} = 165\%, \Delta^{33}\text{S} = 13\%, \Delta^{36}\text{S} = 0.60\)). However, the Danielache et al. (2008) cross sections predict negative \(\Delta^{33}\text{S}\) values (\(-6\%\) to \(-4\%) for photolysis using the Xe lamp and the 200 nm bandpass filter, whereas we measured positive \(\Delta^{33}\text{S}\) values in these experiments. These predicted negative \(\Delta^{33}\text{S}\) values under certain light regimes is significant, since it serves as a basis for the Ueno et al. (2009) model for a high OCS Archean atmosphere. The Danielache et al. (2008) cross sections predict that, in general, broadband photolysis below 202 nm should produce positive \(\Delta^{33}\text{S}\) signature in elemental sulfur, while photolysis above 202 nm should produce negative \(\Delta^{33}\text{S}\) signatures (Ueno et al., 2009). Therefore, we should expect to see a sign difference in the \(\Delta^{33}\text{S}\) between the Xe lamp, which has a considerably higher photon flux above 200 nm.
than below, and the D\textsubscript{2} lamp, which has a higher intensity below 200 nm. Instead, we see very little difference between the light sources, suggesting that the sensitivity of the isotope effects to the detailed shape of the light spectrum is not as strong as suggested by Danielache et al. (2008) and Ueno et al. (2009). The xenon arc lamp used in these experiments has similar spectral characteristics to the solar spectrum (Figure 2-1-A), and thus the lack of agreement between our results and calculations based on the Danielache et al. (2008) cross sections suggest that caution should be used when using the cross sections to quantitatively model isotope fractionation in the early atmosphere.

It is possible that the discrepancies between the experimental results and the Danielache et al. (2008) cross sections are due in part to the high column densities (\textsuperscript{32}SO\textsubscript{2} is over 99% saturated in the 190 nm to 220 nm region, Figure 2-5) at which the experiments reported here were run, and the low resolution (ca. 25 cm\textsuperscript{-1}) of the Danielache et al. (2008) cross sections. For high column density experiments such as those reported here, self-shielding of SO\textsubscript{2} isotopologues (e.g., Lyons, 2007) will be very significant. It is likely that, for SO\textsubscript{2}, these effects will dependent not only on the broad vibrational structure of the absorption bands but also on the finer rotational features. To achieve a better correspondence between cross-section measurements and photolysis experiments, it is necessary to either measure higher-resolution cross sections or to perform experiments at considerably lower column densities. However, the strong similarity between the predictions for the D\textsubscript{2} lamp and the experimental results are very promising, and suggest that, with higher resolution data, it might be possible to achieve agreement between laboratory photolysis experiments and cross-section predictions.

2.5.5 Source of S-MIF in the 250 nm to 330 nm photo-oxidation channel

As discussed above (Section 2.5.4), the S-MIF produced during direct photolysis in the 190 nm to 220 nm band can be explained relatively well by the spectroscopic data and
isotopologue self-shielding. The S-MIF pattern produced by indirect photo-oxidation in the 250 nm to 330 nm region, however, suggests that S-MIF might be produced by a different mechanism. Isotopologue self-shielding is expected to produce $^{36}\lambda$ values between 1.0 and 1.9, which would produce a negative $\Delta^{36}\text{S}$ anomaly, whereas our results show a positive anomaly in both $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$.

The structured vibrational band of the 250 nm to 330 nm region has been assigned to the forbidden $^1A_2 \leftrightarrow ^1A_1$ transition, which is made allowed by vibronic (Herzberg-Teller) coupling through the antisymmetric stretch vibrational mode (Hamada and Merer, 1974, 1975). This transition gains intensity through Born-Oppenheimer coupling between the $^1A_2$ and $^1B_1$ states (Hamada and Merer, 1975). A weaker $^1B_1 \leftrightarrow ^1A_1$ transition underlies the $^1A_2 \leftrightarrow ^1A_1$ transition, and the $^1B_1$ state is strongly coupled to the $^1A_1$ state via Renner coupling (Brand et al., 1976). There are also likely spin-orbit interactions between the singlet states and one or more triplet states (Brand et al., 1976).

It is possible that the isotopologue-specific differences in the strength of the couplings between the multiple excited states or in the collisionally-induced intersystem crossing rates could contribute to the anomalous fractionation in the 250 nm to 330 nm region. A similar mechanism was suggested to explain the anomalous isotope fractionation during CS$_2$ photopolymerization (Zmolek et al., 1999). CS$_2$ shares many characteristics with SO$_2$, including strong couplings between multiple overlapping electronic states that cause significant spectral perturbations (Hamada and Merer 1975 and Brand et al. 1976 for SO$_2$; Jungen et al. 1973 for CS$_2$), and anomalously long fluorescence lifetimes (Douglas, 1966) exhibiting biexponential decay processes (Brus and McDonald 1973 and Brus and McDonald 1974 for SO$_2$; Brus 1971 for CS$_2$).

2.5.6 Possible contribution of 250 nm to 330 nm band SO$_2$ to the Archean S-MIF signature

It is generally assumed that direct photolysis of SO$_2$ is responsible for the observed Archean S-MIF signatures in the rock record (Farquhar et al., 2001; Lyons, 2007; Ueno
There are a number of key differences between our experimental results and the Archean isotope data that still need to be resolved. Elemental sulfur formed in our experiments has large enrichments in $^{34}\text{S}$ ($\delta^{34}\text{S} > +150\%_\circ$), modest $\Delta^{33}\text{S}$ values (+21\%$_\circ \pm 3\%_\circ$), and $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ values of $-1.9 \pm 0.3$ (Table 2.1). In contrast, Archean pyrite data, particularly from late Archean basins, yield a range of $\delta^{34}\text{S}$ values from $-10\%_\circ$ to $+25\%_\circ$, $\Delta^{33}\text{S}$ values from $-2.5\%_\circ$ to $+9.5\%_\circ$, and $\Delta^{36}\text{S}/\Delta^{33}\text{S} \approx -0.9$ (e.g., Farquhar et al., 2000a; Kamber and Whitehouse, 2007; Kaufman et al., 2007; Ono et al., 2009a,b). In addition, some sets of samples are characterized by a linear relationship with $\delta^{33}\text{S} = 1.4 \times \delta^{34}\text{S}$ (Ono et al., 2003, 2009a,b; Kaufman et al., 2007), which is much higher than the $\Delta^{33}\lambda$ values of 0.64 measured in our experiments. This requires a $^{34}\text{S}$ fractionation of approximately 100\% between the production of SO (or elemental sulfur) and its deposition in the sediments. No (non-photolysis) sulfur gas phase reactions are currently known to produce such large mass-dependent isotope effects (e.g., Tanaka et al., 1994; Harris et al., 2012). Microbial sulfate reduction can produce $\delta^{34}\text{S}$ effects as large as 70\% (Canfield et al., 2010; Sim et al., 2011), but the magnitude of the fractionation is variable and rarely achieves the highest values. Mixing with crustal (mass-dependent) sulfur can lower the $\delta^{34}\text{S}$ values, but it will also dilute the $\Delta^{33}\text{S}$ signal. These issues have been discussed previously by Lyons (2009).

These discrepancies (the large $\delta^{34}\text{S}$ values and the incorrect $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios) could be due in part to the differences in the behavior within our experimental system versus that in an Archean atmosphere. Such differences include the presence of a bath gas ($\text{N}_2$), the $\text{SO}_2$ number density, the spectral properties of the light photolyzing the $\text{SO}_2$, or the temperature of the photolysis. The presence of a bath gas has been shown to reduce the degree of MIF ($\Delta^{33}\lambda$ values become smaller with added helium) and does not reproduce Archean $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ values (Masterson et al., 2011). The $\text{SO}_2$ partial pressure and temperature would likely affect the isotope fractionation pattern and will be tested in future studies.

Here, we test the potential that photochemistry in the 250 nm to 330 nm region could have contributed to the Archean S-MIF signatures. Our data in the 250 nm to 330 nm photo excitation region show relatively large $\Delta^{33}\text{S}$ values ($+15\%_\circ \pm 2\%_\circ$)
with small $\delta^{34}\text{S}$ values ($<30\%$), similar to the Archean signatures. One issue with photoexcitation in the 250 nm to 330 nm region is that it produces elemental sulfur with a positive $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratio of $0.64 \pm 0.03$, which has the opposite sign as the Archean trend of $-0.9$. However, mixing the signatures of the 190 nm to 220 nm band and the 250 nm to 330 nm band in the right proportions would be able to produce the Archean $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratio of $-0.9$. This would also reduce the $\delta^{34}\text{S}$ value of the sulfur product (compared to pure 190 nm to 220 nm photolysis), and the variability in the contribution of the two channels could offer a possible explanation for some of the variability in $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ values during different parts of the Archean (Ono et al., 2006a; Farquhar et al., 2007; Kaufman et al., 2007; Ono et al., 2009a).

Although the $\text{SO}_2$ cross sections are an order of magnitude smaller in the 250 nm to 330 nm region than in the 190 nm to 220 nm region (Figure 2-1-C), the solar actinic flux is approximately two order of magnitude higher in this region (Figure 2-1-A), resulting in a higher rate of excitation into the lower energy states ($^{1}\text{A}_2$ or $^{1}\text{B}_1$) than to the higher energy $^{1}\text{B}_2$ state in the absence of other absorbing gases (Table 2.3, Figure 2-8). However, preservation of the isotope signatures created from excitation into one of these lower energy singlet states (hereafter $^{1}\text{SO}_2$) would have been hindered by quenching with other atmospheric gases such as $\text{N}_2$ ($R_{2.8}$). In a nitrogen atmosphere, it is estimated that only 3.3% of the $^{1}\text{SO}_2$ molecules will undergo intersystem crossing to produce $^{3}\text{SO}_2$ ($R_{2.9}$; Horowitz and Calvert 1972), although that value may be higher and wavelength dependent (Calvert et al., 1978). The lifetime of $^{3}\text{SO}_2$ upon collision ($R_{2.11}$) is estimated to be about 1 $\mu$s in 1 atm of $\text{N}_2$ (Table 2.5). If there are reactions fast enough to compete with reaction $R_{2.11}$, such a reaction could allow for the preservation of the S-MIF signature from the 250 nm to 330 nm excitation band.

Possible species that could react with $^{3}\text{SO}_2$ include CO, alkanes, and $\text{C}_2\text{H}_2$. Table 2.5 summarizes a simple analysis for the lifetime of $^{3}\text{SO}_2$ against several chemical reactions for possible mixing ratios of the reactants. Figure 2-8 shows the relative amount of $\text{SO}_2$ excited in the 250 nm to 330 nm absorption region versus the 190 nm to 220 nm absorption region, and the portion that might be preserved via reactions with CO, $\text{SO}_2$, alkanes, or $\text{C}_2\text{H}_2$, using the hypothetical concentrations of species given in
Table 2.5: Lifetime of $^{3}\text{SO}_2$ against chemical reactions in a hypothetical Archean atmosphere. The lifetimes are estimated from rate constants and possible mixing ratios suggested by previous studies. Lifetime is calculated assuming a total pressure of 1 atm.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate constant$^a$</th>
<th>Possible mixing ratio$^b$</th>
<th>$^{3}\text{SO}_2$ Lifetime$^c$(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical quenching reaction</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{3}\text{SO}_2 + N_2 \rightarrow \text{SO}_2 + N_2$</td>
<td>$1.1 \times 10^{-13}$</td>
<td>1</td>
<td>$1.0 \times 10^{-6}$</td>
</tr>
<tr>
<td>Chemical reactions</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{3}\text{SO}_2 + \text{SO}_2 \rightarrow \text{SO} + \text{SO}_3$</td>
<td>$8.0 \times 10^{-14}$</td>
<td>10 ppm</td>
<td>$5.0 \times 10^{-3}$</td>
</tr>
<tr>
<td>$^{3}\text{SO}_2 + \text{CO} \rightarrow \text{SO} + \text{CO}_2$</td>
<td>$4.3 \times 10^{-15}$</td>
<td>1%</td>
<td>$9.4 \times 10^{-4}$</td>
</tr>
<tr>
<td>$^{3}\text{SO}_2 + \text{CH}_4 \rightarrow \text{HSO}_2 + \text{CH}_3$</td>
<td>$5.6 \times 10^{-15}$</td>
<td>1000 ppm</td>
<td>$7.1 \times 10^{-3}$</td>
</tr>
<tr>
<td>$^{3}\text{SO}_2 + \text{C}_2\text{H}_6 \rightarrow \text{HSO}_2 + \text{C}_2\text{H}_5$</td>
<td>$5.1 \times 10^{-14}$</td>
<td>4 ppm</td>
<td>$2.0 \times 10^{-1}$</td>
</tr>
<tr>
<td>$^{3}\text{SO}_2 + \text{C}_3\text{H}_8 \rightarrow \text{HSO}_2 + \text{C}_3\text{H}_7$</td>
<td>$3.9 \times 10^{-13}$</td>
<td>1 ppb</td>
<td>$1.0 \times 10^2$</td>
</tr>
<tr>
<td>$^{3}\text{SO}_2 + \text{C}_2\text{H}_2 \rightarrow \text{CO} + \text{aerosol}$</td>
<td>$2.6 \times 10^{-12}$</td>
<td>0.032 ppt</td>
<td>$4.9 \times 10^5$</td>
</tr>
</tbody>
</table>

$^a$ Second order rate constants are in cm$^3$ molecule$^{-1}$ s$^{-1}$ from Su et al. (1977) and Wampler et al. (1978).

$^b$ Mixing ratio for CO is taken from Ueno et al. (2009); mixing ratios for CH$_4$, C$_2$H$_6$, C$_3$H$_8$, and C$_2$H$_2$ are taken from Haqq-Misra et al. (2008) for a model atmosphere containing 1000 ppm each of CO$_2$ and CH$_4$.

$^c$ The lifetime for the $^{3}\text{SO}_2 + N_2$ reaction was calculated as suggested by Su et al. (1977), taking into account the pressure saturation effect for physical quenching of $^{3}\text{SO}_2$. 
Figure 2-8: The relative rates of different photochemical processes to direct photolysis in a theoretical Archean atmosphere (Table 2.5). We assumed the modern solar spectrum of Rottman et al. (2006) and the SO$_2$ cross sections of (Manatt and Lane, 1993) in calculating the relative rates of direct photolysis versus photoexcitation. In addition, we assume a 3.3% intersystem crossing ratio for collisions with N$_2$ (Horowitz and Calvert, 1972).

Table 2.5 and the solar spectral irradiance in Figure 2-1-A. As shown in Figure 2-8, photoexcitation occurs faster than direct photolysis, but preservation of the isotope signature would be difficult unless abundant organic compounds were present in the atmosphere. Dense organic haze layers (Sagan and Chyba, 1997; Haqq-Misra et al., 2008; Wolf and Toon, 2010) might not only have assisted with the preservation of the 250 nm to 330 nm signatures but could also have selectively shielded the 190 nm to 220 nm region, reducing the rate of direct photolysis. High concentrations of CO in a reducing atmosphere would also have helped preserve the isotope signatures. More kinetic data for reactions between $^3$SO$_2$ and organic compounds and for reactions involving HSO$_2$ may help to determine the fate of $^3$SO$_2$ (and SO) in the Archean atmosphere and help us to better evaluate the potential for preservation of S-MIF created in the 250 nm to 330 nm absorption region.

### 2.6 Conclusions

We report the results of laboratory experiments demonstrating the excitation band dependence of the sulfur isotope mass-independent fractionation during photochemical reactions of SO$_2$. Elemental sulfur produced from broadband excitation into the
190 nm to 220 nm absorption band is characterized by high $\delta^{34}S$ values (> +150%), $^{33}\lambda$ values of 0.62 to 0.67, and negative $\Delta^{36}S/\Delta^{33}S$ ratios of -2.19 to -1.65, all with respect to the initial SO$_2$. Elemental sulfur from photoexcitation into the 250 nm to 330 nm region shows a very different S-MIF signature, characterized by positive $\Delta^{33}S$ values (+13.4% to +16.5%) and positive $\Delta^{36}S/\Delta^{33}S$ ratios (0.61 to 0.67), with moderate $^{34}S$ fractionation ($\delta^{34} < +30\%$). These results contrast with previous observations by Farquhar et al. (2001) based on narrow-band light sources, and allow assignment of the excitation band dependence of sulfur MIF under broadband light regimes. The similarity of the isotope signatures for the Xe and D$_2$ light sources is not entirely consistent from the Danielache et al. (2008) cross sections, and suggests that the isotope effects during SO$_2$ photolysis may not be as sensitive to the exact spectral properties of the light source as previously suggested. Despite this, predictions with the Danielache et al. (2008) cross sections for the D$_2$ lamp experiments are consistent with our observed values, presenting hope that future isotopologue-specific cross sections can be used to accurately predict isotope effects during SO$_2$ photolysis in the 190 nm to 220 nm region.

The observed isotope patterns suggest that S-MIF in modern stratospheric aerosols may carry signatures of direct photolysis from the 190 nm to 220 nm region, although a mechanism for preserving the signature (which is produced in SO) remains enigmatic. The lack of S-MIF in the sulfate products from photo-oxidation of SO$_2$ in the 250 nm to 330 nm region, as well as the positive $\Delta^{36}S/\Delta^{33}S$ ratios in the elemental sulfur products compared to negative values in stratospheric sulfate aerosols, suggest that photo-oxidation of SO$_2$ in the 250 nm to 330 nm region is not a likely mechanism for the production of S-MIF in the modern atmosphere. The S-MIF signatures observed in our experiments for the 190 nm to 220 nm band do not match the Archean signatures, as they produce very high $\delta^{34}S$ values and $\Delta^{36}S/\Delta^{33}S$ values lower than observed in Archean samples. These discrepancies could be explained by the contribution of S-MIF from the 250 nm to 330 nm photoexcitation band, although our simple model shows that preservation of this signature is difficult and only possible under certain atmospheric conditions, such as an organic rich atmosphere.
2.7 Acknowledgements

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2.8 Supplementary information

2.8.1 Spectral interference form O$_2$ and O$_3$

Simulations were performed to test the effects of oxygen absorption on the spectral structure of the light reaching the front of the photocell. Absorption cross sections for the Schumann-Runge bands of oxygen (Yoshino et al., 1992) were used to calculate the total transmission of a 20 cm column of laboratory air (20% oxygen at 1 atmosphere total pressure). The results are shown in Figure 2-9. They suggest that the Schumann-Runge bands of oxygen would have absorbed a considerable portion of the photons below 190 nm, but only had a minor (less than 10%) effect for wavelengths greater than 195.5 nm, and an effect of less than 0.1% above around 200 nm. Absorption in the Herzberg continuum region of O$_2$ (200 nm to 260 nm) is weak and does not affect the photon fluxes under our experimental conditions.

There is also potential spectral interference from ozone produced from the photolysis of O$_2$. The reaction cell and light were set up inside a chamber that was vented to limit the buildup of ozone during the experiments. Ozone concentrations were measured at several locations during one full-spectrum Xenon lamp experiment using a calibrated Ozone Monitor (Model 205 Ozone Monitor, 2B Technologies, InDevR, Inc.). After the Xenon lamp had been running for an hour, ozone concentrations at the exhaust fan of the lamp were 2100 ppb ± 200 ppb (1σ) and concentrations right in front of the lamp housing were 2100 ppb ± 600 ppb (1σ). Concentrations in front of the photocell were considerably lower, 300 ppb ± 200 ppb. At no point were
Figure 2-9: Transmission of a 20cm column of 0.2 atm of oxygen, simulating the potential interference of O₂ on the spectral properties of our experiments. The Schumann-Runge bands of O₂ absorb a considerable fraction of photons below around 190 nm, but are mostly transparent to light above about 200 nm. Transmission above 200 nm is greater than 0.999 and is not shown. Calculated using cross-sections for the Schumann-Runge bands of O₂ from Yoshino et al. (1992).

concentrations above 4000 ppb measured.

The transmission of a 20 cm column of ozone at two different concentrations (10000 ppb and 1000 ppb) is shown in Figure 2-10. Note that even at concentrations of 10,000 ppb, which is a factor of 2.5 higher than the maximum concentrations we measured (less than 4000 ppb), ozone will only have a minimal (less than 5%) effect on the rate of photoexcitation in the 250 nm to 330 nm absorption band, and even less of an effect on the 190 nm to 220 nm band. Ozone concentrations for our other experimental conditions (D₂ lamp, 200 nm bandpass, and 250 nm longpass experiments) should be comparable or lower than those measured for the full-spectrum Xe lamp. Therefore, ozone absorption is not likely to cause significant spectral interference in our experiments.
Figure 2-10: Transmission of a 20 cm column of ozone with mixing ratios of 10,000 ppb and 1,000 ppb, assuming 1 atmosphere total pressure. Transmission for ozone mixing ratios of 100 ppb and lower are greater than 0.999 in the 180 nm to 360 nm region. Note that measured ozone concentrations during a full spectrum Xe lamp experiment were all lower than 4000 ppb. Calculated using ozone cross sections from (Molina and Molina, 1986).
Chapter 3

Vibronic origin of sulfur mass-independent isotope effect in photoexcitation of SO$_2$ and the implication to the early earth's atmosphere

Foreward

This chapter has been published previously as Whitehill et al. (2013). Theoretical work, including all ab initio calculations and wave packet calculations, were performed by Daiqian Xie (Nanjing University, Nanjing, China) and Hua Guo (University of New Mexico, Albuquerque, NM, USA).

3.1 Abstract

Signatures of mass-independent isotope fractionation (MIF) are found in the oxygen ($^{16}$O, $^{17}$O, $^{18}$O) and sulfur ($^{32}$S, $^{33}$S, $^{34}$S, $^{36}$S) isotope systems and serve as important
tracers of past and present atmospheric processes. These unique isotope signatures signify the breakdown of the traditional theory of stable isotope fractionation, but the physical chemistry of these isotope effects remains poorly understood. We report the production of large sulfur isotope MIF, with $\Delta^{33}\text{S}$ up to 78 $\%$ and $\Delta^{36}\text{S}$ up to 110 $\%$, from the broadband excitation of SO$_2$ in the 250 nm to 350 nm absorption region. Acetylene is used to selectively trap the triplet-state SO$_2$ ($\tilde{a}^3\text{B}_1$), which results from intersystem crossing from the excited singlet ($\tilde{A}^1\text{A}_2/\tilde{B}^1\text{B}_1$) states. The observed MIF signature differs considerably from that predicted by isotopologue-specific absorption cross-sections of SO$_2$ and is insensitive to the wavelength region of excitation (above or below 300 nm), suggesting that the MIF originates not from the initial excitation of SO$_2$ to the singlet state but from an isotope selective spin-orbit interaction between the singlet ($\tilde{A}^1\text{A}_2/\tilde{B}^1\text{B}_1$) and triplet ($\tilde{a}^3\text{B}_1$) manifolds. Calculations based on high-level potential energy surfaces of the multiple excited states show a considerable lifetime anomaly for $^{33}\text{SO}_2$ and $^{36}\text{SO}_2$ for the low vibrational levels of the $\tilde{A}^1\text{A}_2$ state. These results demonstrate that the isotope selectivity of accidental near-resonance interactions between states is of critical importance in understanding the origin of MIF in photochemical systems.

3.2 Introduction

Stable isotope fractionation theory predicts that the magnitude of stable isotope fractionation scales with the differences in isotopic mass (Urey, 1947; Bigeleisen and Mayer, 1947). Almost all physical, chemical, and biological processes in nature follow this mass-dependent scaling law, resulting in nearly all terrestrial materials with oxygen having $\delta^{17}\text{O} = 0.52 \times \delta^{18}\text{O}$, whereas those with sulfur have $\delta^{33}\text{S} = 0.515 \times \delta^{34}\text{S}$ and $\delta^{36}\text{S} = 1.90 \times \delta^{34}\text{S}$. Significant deviations from these mass-dependent scaling laws are referred to as mass-independent fractionation (MIF), and serve as important tracers in the earth and planetary sciences (see Thiemens, 1999, 2006; Thiemens et al., 2012).

Early studies suggested that MIF could result only from nucleosynthetic processes
(Hulston and Thode, 1965), and the earliest measurements of oxygen MIF in calcium-aluminum inclusions of meteorites were originally interpreted to be nucleosynthetic in origin (Clayton et al., 1973). It eventually was suggested (Arrhenius et al., 1979) that chemical processes, such as tunneling or processes associated with predissociation, also might produce MIF. The first experimental evidence for a chemical origin of MIF came from ozone generated by an electric discharge or UV radiation (Thiemens and Heidenreich, 1983; Thiemens and Jackson, 1987). The discovery of oxygen MIF in stratospheric ozone (Mauersberger, 1987) soon triggered intense research into the physiochemical origin of MIF in the ozone system (see Mauersberger et al., 2005; Schinke et al., 2006; Ivanov and Babikov, 2013).

For the sulfur isotope system ($^{32}$S, $^{33}$S, $^{34}$S, $^{36}$S), Farquhar et al. (2000a) made the remarkable discovery that mass-independent sulfur isotope fractionation (S-MIF) is prevalent in sedimentary rocks older than ca. 2.4 Ga but absent in rocks from subsequent periods. The disappearance of S-MIF at about 2.4 Ga (Bekker et al., 2004; Guo et al., 2009) signifies a fundamental change in the Earth’s surface sulfur cycles, and generally is linked to the suppression of both SO$_2$ photolysis and the formation of elemental sulfur aerosols by the rise of atmospheric oxygen levels (Farquhar et al., 2000a, 2001; Pavlov and Kasting, 2002). The Archean S-MIF is considered the most compelling evidence for an anoxic early atmosphere and constrains Archean oxygen levels to be less than $10^{-5}$ of present levels (Pavlov and Kasting, 2002). This model of oxygen evolution, however, depends critically on the assumption that UV photolysis of SO$_2$ by $\sim$ 200 nm radiation is the ultimate source of the anomalous sulfur isotope signature (Farquhar et al., 2001). Constraining the source of the S-MIF requires a thorough understanding of the physiochemical origins of S-MIF during the photochemistry of SO$_2$.

SO$_2$ exhibits two strong absorption band systems in the UV region: one between 185 nm and 235 nm ($^{3}B_2 \leftarrow X^1A_1$) and the other from 240 nm to 350 nm ($^{1}A_2, ^{1}B_1 \leftarrow X^1A_1$) (Heicklen et al., 1980, and references therein); we will refer to them as the photolysis and photoexcitation bands, respectively. Excitation into the photolysis band leads to the predissociation of SO$_2$ into SO and O below 220 nm.
Laboratory experiments by Farquhar et al. (2001) showed production of large ($\Delta^{33}\text{S}$ up to 70%) S-MIF by SO$_2$ photolysis using an ArF (193nm) excimer laser source. This was used to link the high-energy photolysis band system to Archean S-MIF, and fueled subsequent detailed investigations (e.g., Ran et al., 2007; Lyons, 2007; Danielache et al., 2008; Masterson et al., 2011; Whitehill and Ono, 2012; Ono et al., 2013) into the S-MIF production from photochemistry in this region. However, recent experiments (Masterson et al., 2011; Whitehill and Ono, 2012; Ono et al., 2013) using broadband (as opposed to laser) light sources show S-MIF patterns different from the 193nm experiments by Farquhar et al. (2001). Large magnitude ($\Delta^{33}\text{S} > 2.5\%\text{o}$) MIF is produced only by experiments with high SO$_2$ column densities, suggesting a strong contribution from spectroscopic self- and mutual-shielding, although additional mechanisms also may play a role (Ono et al., 2013). The elemental sulfur products produced by these experiments are characterized by large $\delta^{34}\text{S}$ fractionations and $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios that differ from those observed in the Archean rock record (Masterson et al., 2011; Whitehill and Ono, 2012; Ono et al., 2013). Discrepancies between experimental results and the geological record require a reanalysis of the origin of Archean S-MIF signatures.

SO$_2$ photochemistry in the photoexcitation (240 nm to 350 nm) band also has been shown to produce S-MIF (Farquhar et al., 2001; Whitehill and Ono, 2012; Danielache et al., 2012; Hattori et al., 2013) and has been implicated as the source of S-MIF in stratospheric sulfate aerosols trapped in polar ice (Savarino et al., 2003; Bàroni et al., 2007, 2008; Hattori et al., 2013). It also has been suggested that SO$_2$ photochemistry in the photoexcitation band might have made secondary contributions to S-MIF signatures during some periods of the Archean (Whitehill and Ono, 2012; Zerkle et al., 2012). This band system is associated with the excitation of SO$_2$ into a mixed $\tilde{A}^1\text{A}_2/\tilde{B}^1\text{B}_1$ state, which also interacts with lower-lying triplet ($\tilde{a}^3\text{B}_1$, also possibly $\tilde{b}^3\text{A}_2$; Figure 3-1; Heicklen et al., 1980). Recently published absorption cross-sections of isotopically enriched SO$_2$ (Danielache et al., 2012) in this region allow the accurate prediction of the MIF produced during the initial excitation step (Hattori et al., 2013). In this study, we focus on the production of S-MIF by SO$_2$ excited into the pho-
to excitation band, and compare the results with the measured isotopologue specific cross-sections, to test the importance of chemistry after photoexcitation. Our results show a strong dependence of the S-MIF on the SO₂ and bath gas pressures but not on the detailed spectrum regions of excitation, suggesting that isotopologue selective vibronic coupling produces significant S-MIF independent of absorption cross-section differences. A theoretical model is also presented to test this hypothesis.

3.3 Methods

A series of SO₂ photochemical experiments were carried out using a flow-through photochemical system to investigate S-MIF as a function of SO₂ (0.1 mbar to 10 mbar) and nitrogen bath gas (260 mbar to 1010 mbar) pressures (Table 3.1). A broadband radiation source (150 W Xe arc lamp) was used to excite SO₂ to the mixed $\tilde{A}^1A_2/\tilde{B}^1B_1$ manifold. A 250 nm long pass filter was used to avoid photochemistry from the higher energy photolysis band ($\tilde{C}^1B_2 \rightarrow \tilde{X}^1A_1$) of SO₂. Photochemistry of SO₂ in the photoexcitation band was studied previously and showed rapid quenching of singlet SO₂ by bath gas (e.g., N₂, CO₂) and reaction of the resulting triplet SO₂ with SO, SO₂, and organic molecules (see Heicklen et al., 1980) (Figure 3-1). Experiments were carried out in the presence of acetylene (10 mbar), which efficiently reacts with triplet-state SO₂ (Kelly et al., 1976) and produces organosulfur aerosols, previously characterized as (C₃H₄S₂O₃)₃ (Luria et al., 1974). These were captured and analyzed for quadruple sulfur isotope ratios using techniques described in Oduro et al. (2011b) and Ono et al. (2013).

3.4 Results of photochemical experiments

All experiments produced organosulfur compounds that had minor fractionations in $^{34}\text{S} (-7.0\% < \delta^{34}\text{S} < +20.8\%)$, but were highly enriched in both $^{33}\text{S}$ and $^{36}\text{S} (+9.1\% < \delta^{33}\text{S} < +87.3\%$ and $+13.8\% < \delta^{36}\text{S} < +135.7\%)$ (Table 3.1 and Figure 3-2). This resulted in positive $\Delta^{33}\text{S} (+11.9\%$ to $+77.8\%)$ and $\Delta^{36}\text{S} (+24.3\%$ to $+A_3$.
Figure 3-1: Photochemistry of SO$_2$ in the 240 nm to 400 nm region. (A) UV absorption cross-section for SO$_2$ between 240 nm and 400 nm (from Vandaele et al., 2009; Hermans et al., 2009). (B) Vertical lines showing the spectral ranges for the different optical filters tested. (C) Schematic of the photochemistry of the experiments. SO$_2$ initially is excited into the coupled $\tilde{B}^1B_1/\tilde{A}^1A_2$ states. It vibrationally relaxes (VR) via collisions with the bath gas. At low vibrational levels of the $\tilde{A}^1A_2$ state, intersystem crossing may lead to irreversible crossing to the $\tilde{a}^3B_1$ state as the result of vibrational relaxation of the $\tilde{a}^3B_1$ state below the origin of the $\tilde{A}^1A_2$ band. Isotope effects due to near-resonant spin-orbit coupling between the singlet and triplet states in this region may lead to mass-independent isotope anomalies in the resulting triplet-state SO$_2$. The triplet-state SO$_2$ finally reacts with acetylene (C$_2$H$_2$) to form the organosulfur products analyzed in this study. (D) Potential energy surfaces for the singlet and triplet states of SO$_2$ as a function of the O-SO Jacobi distance with the S-O distance and the Jacobi angle optimized.
Table 3.1: Conditions and results from photochemical experiments

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</table>

* LP = longpass, SP = shortpass, numbers in units of nm
+109.8 \%e) values, and positive $\Delta^{36}S/\Delta^{33}S$ ratios of 1.12 to 2.25. With the exception of our lowest pSO$_2$ experiment (0.1 mbar), experiments at lower SO$_2$ pressure produced higher $\Delta^{33}S$ and $\Delta^{36}S$ values than experiments at higher SO$_2$ pressures under the range of conditions studied, suggesting isotopologue self-shielding is not the dominant source of the observed S-MIF anomaly. The sensitivity to pSO$_2$ might reflect energy transfer between mass-independently fractionated singlet or triplet-state SO$_2$ and mass-dependently fractionated ground-state SO$_2$. Such energy transfer might dilute the MIF signal by exciting non-MIF SO$_2$ into the reactive triplet state. In addition to pSO$_2$ dependence, $\Delta^{33}S$ values increased as total pressure decreased for experiments run at the same SO$_2$ pressure. $\Delta^{36}S/\Delta^{33}S$ ratios were sensitive to the total pressure of the system, with higher values (1.98 to 2.25) at the highest pressure tested (1013 mbar) and lower values (1.12 to 1.27) at the lowest pressure (253 mbar) (Figure 3-2A). These results, particularly the positive $\Delta^{36}S$ and $\Delta^{33}S$ values and small $\delta^{34}S$ values, are consistent with the previous experiments (Whitehill and Ono, 2012) performed with pure SO$_2$ without N$_2$ or C$_2$H$_2$, suggesting that the observed isotope signature is characteristic of this absorption band system and not a result of the N$_2$ or C$_2$H$_2$ used in the experiment.

To test the sensitivity of the isotope effects to the detailed spectral regions of the excitation, experiments were performed with a series of longpass (250 nm, 295 nm, and 305 nm) and shortpass (300 nm and 350 nm) filters (Figure 3-3). The use of optical filters allows testing for S-MIF signals from the high- or low-energy side of the band system (Figure 3-1). Experiments performed at the same SO$_2$ pressure (10 mbar) and total pressure (507 mbar) conditions but with different filters to isolate the 250 nm to 300 nm, >295 nm, or >305 nm regions produced remarkably similar isotopic results, with $\Delta^{33}S$ between +30 \%e and +36 \%e and $\Delta^{36}S$ between +49 \%e and +66 \%e (Figure 3-2B). This result suggests that the anomalous enrichment in $^{33}S$ and $^{36}S$ is not a strong function of excitation wavelength within this absorption band, at least within a broadband regime. Several experiments were performed with 320 nm longpass and 350 nm shortpass filters. This wavelength region corresponds to excitation into the $\tilde{A}^1A_2$ only; it is below the origin of the $\tilde{B}^1B_1$ state (Shaw et al., 1980) and above
Figure 3-2: Isotopic results from experiments and calculations. (A) Results ($\Delta^{36}S$ vs. $\Delta^{33}S$) from experiments using the 250 nm long pass filter for a variety of SO$_2$ pressures (italics, in mbar) and total pressures (bold, in mbar). (B) Results ($\Delta^{36}S$ vs. $\Delta^{33}S$) from experiments using various combinations of shortpass (SP) and long-pass (LP) filters. The 320 LP experiments also used a 350 SP filter, and the 300 SP experiments also used a 250 LP filter. Also in the figure ($\times$ symbols) are the results from calculations based on the Danielache et al. (2012) cross-sections for the conditions tested here. (C) Results ($\Delta^{33}S$ vs. $\delta^{34}S$) from all experiments, showing the large $\Delta^{33}S$ values associated with small $\delta^{34}S$ values. Symbols are the same as in A and B.
Figure 3-3: Transmission for all optical filters used in experiments. Transmission includes the effects of the reaction cell window, water filter, and optical filters. Transmissions were measured using a 30 W deuterium arc lamp with a spectrometer (SPM-002-BT; Photon Control) that has a grating blazed at 250 nm. The apparent increase in transmission below 240 nm is the result of spectrometer noise, as shown by measured dark noise (black line).

the spin-forbidden $\tilde{a}^3B_1 \rightarrow \tilde{X}^1A_1$ transition of SO$_2$, which lies between 350 nm and 390 nm (see references in Heicklen et al., 1980). The experiments were carried out at higher SO$_2$ (50.7 mbar) and acetylene (101 mbar) pressures, but the same total pressure (507 mbar). These produced lower $\Delta^{33}\text{S}$ (+11.9% to +13.5%) and $\Delta^{36}\text{S}$ (+24.3% to +28.0%) values, consistent with the higher SO$_2$ pressure, but with $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ values (2.05 to 2.08) similar to the rest of the filter experiments (1.61 to 1.95) (Figure 3-2). The presence of S-MIF signatures from excitation exclusively into the $\tilde{A}^1A_2$ state suggests that vibronic interactions between the two singlet states ($\tilde{B}^1B_1$ and $\tilde{A}^1A_2$) make a negligible contribution to the observed S-MIF signatures.

3.5 Source of MIF signatures

Danielache et al. (2012) reported UV cross-sections for isotopically enriched SO$_2$ (i.e., $^{32}$SO$_2$, $^{33}$SO$_2$, $^{34}$SO$_2$, and $^{36}$SO$_2$) in the 250 nm to 320 nm region. These cross-sections are measured at 8 cm$^{-1}$ resolution, at room temperature, and at 1 mbar to 7 mbar SO$_2$, and characterize the magnitude of the isotopic shifts in band positions
and intensities. The measured cross-sections (Danielache et al., 2012) were used to predict S-MIF signatures under the experimental conditions (spectral irradiance and SO$_2$ column densities) tested here and are compared with experimental results in Figure 3-2-B. The results show that differences in the absorption cross-sections can account for only a small fraction ( < 25%) of the large (up to +78%) $\Delta^{33}$S values observed in the 250 nm longpass experiments and cannot account for the large positive $\Delta^{36}$S values (up to +110%) observed. In particular, the cross-sections predict large negative $\Delta^{36}$S values for a variety of broadband light sources (Figure 3-2-B and Figure 7 in Danielache et al., 2012), in contrast to the large positive values observed. Even accounting for the systematic errors (2.5%) and the standard error of the mean (SEM, 5% to 10%) for the measured cross-sections (see results and discussion in Danielache et al., 2012), the cross-sections still cannot explain the $\Delta^{36}$S values observed (Figure 3-2-B).

The above cross-section model also includes the effect of self- and mutual-shielding of absorption lines under experimental conditions. Self-shielding occurs when the major isotopologue line (i.e., $^{32}$SO$_2$) saturates under optically thick conditions. In this study, large S-MIF signatures are observed even under optically thin conditions. The experiments with the lowest pSO$_2$ (column density of $4 \times 10^{16}$ molecule cm$^{-2}$) had over 95% optical transmission, where self-shielding is not expected to play a major role. The magnitude of S-MIF increases with decreasing SO$_2$ pressure, which is opposite from what is expected from self-shielding. We therefore exclude absorption-based effects, such as self-shielding or absorption cross-section differences as the main source of the observed S-MIF signatures.

Other proposed mechanisms of MIF production include nuclear field shift isotope effects, magnetic isotope effects, and symmetry-based isotope effects. The magnitude of nuclear field shift effects has been estimated to be insignificant for the sulfur isotope system because of the small nuclear size difference among isotopologues (Schauble, 2007). Magnetic isotope effects would produce anomalies only in $^{33}$S and cannot explain the large $\Delta^{36}$S values observed in the experiments. A symmetry-based isotope effect is also unlikely because of the lack of any intermediates or transition states with
symmetrically equivalent sulfur atoms. In addition, a symmetry-based isotope effect would predict positive $\Delta^{33}\text{S}$ values and negative $\Delta^{36}\text{S}$ values (Ono et al., 2009a), whereas positive $\Delta^{33}\text{S}$ and positive $\Delta^{36}\text{S}$ values are observed in the present experiments.

3.6 Intersystem crossing as a potential origin of S-MIF

Although isotope substitution shifts the vibrational and rotational energy level spacing in a mass-dependent manner, the magnitude of the shifts will be different for different excited electronic states. In systems in which the vibration-rotation levels of multiple low-lying electronic states overlap, the interactions between states may exhibit strong and level-specific isotope selectivity. In particular, pairs of levels capable of interacting with each other and that are near-degenerate for one isotopologue may be nondegenerate for other isotopologues. These effects were cited previously as a source of S-MIF during the photopolymerization of CS$_2$ (Colman et al., 1996; Zmolek et al., 1999) and oxygen MIF during the photodissociation of CO$_2$ (Bhattacharya et al., 2000) and CO (Chakraborty et al., 2008). In these three cases, the anomalous isotope effects have been attributed to differences in intersystem crossing (ISC) rates from an initially excited singlet state to a reactive (or dissociative) triplet state. Similar spin-orbit effects have been shown to cause anomalous LIF intensities in $^{37}\text{ClO}_2$ vs. $^{35}\text{ClO}_2$ for particular vibrational bands (Lim et al., 1999). A recent study by Muskatel et al. (2011) demonstrates a theoretical basis for similar isotope effects during the photolysis of N$_2$. In particular, they note that the accidental overlap between different electronic states of N$_2$ may cause large isotope effects in certain regions of the spectrum. The importance of accidental degeneracies between interacting states in producing environmentally relevant MIF signatures remains controversial, as it has been suggested that self-shielding might have contributed to the isotope signatures observed during the CS$_2$ (Lyons, 2009) and CO (Lyons et al., 2009; Federman and

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Young, 2009; Yin et al., 2009) (see also Chakraborty et al., 2009) experiments. In addition, isotope effects from local interactions are likely to be isolated to narrow spectral regions where the interactions occur.

Several previous spectroscopic studies of SO\(_2\) showed isotopologue-specific perturbations in the 250 nm to 350 nm absorption region. Analysis of several absorption bands of S\(^{18}\)O\(_2\) corresponding to the Cemets "B" and "E" bands (310.9 nm and 304.4 nm, respectively) revealed that these bands of S\(^{18}\)O\(_2\) were significantly less perturbed than corresponding bands of S\(^{16}\)O\(_2\) (Hamada and Merer, 1975), suggesting different coupling strengths for different isotopologues. Baskin et al. (1995) reported a strong \(^3\)\(^2\)SO\(_2\) vibrational peak at 30995 cm\(^{-1}\) (322.6 nm) that had no corresponding \(^3\)\(^4\)SO\(_2\) peak at the expected location. This was attributed to perturbations caused by accidentally near-degenerate vibronic interactions in one isotopic species but not the other.

If anomalous isotope effects were purely the result of isolated interactions at particular vibrational levels, a strong wavelength selectivity to the anomalous isotope effects would be expected, with certain regions (i.e., around the localized near-degeneracies) producing considerably larger MIF than other regions. One of the features of the present experiments is that the MIF signature shows remarkable similarity in both the higher (250 nm to 300 nm) and lower (295 nm to 350 nm and 305 nm to 350 nm) energy regions of the absorption band (Figures 3-1 and 3-2-B). Experiments isolating only the 320 nm to 350 nm absorption region, which lies below the origin of the \(\tilde{B}\)\(^1\)B\(_1\) state and corresponds to excitation into only the \(\tilde{A}\)\(^1\)A\(_2\) state, also produces S-MIF consistent with the other experiments, although with a smaller magnitude, because of the different experimental conditions (i.e., higher SO\(_2\) pressure).

All our experiments were performed at relatively high total pressures (253 mbar to 1013 mbar) in the presence of a bath gas (N\(_2\)). Under these conditions, the collision lifetime (on the order of nanoseconds) is considerably shorter than the fluorescence lifetime (on the order of microseconds), allowing rapid collision-induced rotational and vibrational relaxation of the excited state (Heicklen et al., 1980; Su et al., 1978). Time-resolved fluorescence experiments performed at 1.33 mbar of pure SO\(_2\) showed
strong resonance fluorescence from the excited level accompanied by significant fluorescence from vibrationally relaxed molecules (Bae et al., 1998). At higher SO$_2$ pressures of 26.6 mbar, fluorescence from highly excited states (266 nm) contained no resonance fluorescence, with the dominant fluorescence occurring around 325.5 nm and 370 nm, near the origin of the $\tilde{B}^1$B$_1$ and $\tilde{A}^1$A$_2$ states, respectively, suggesting rapid and nearly complete collisional vibrational thermalization (Zhang et al., 2010). Although the collision-induced ISC might occur from any state, the rate of collision-induced vibrational relaxation is faster than the rate of collision-induced ISC (Bae et al., 1998), at least for some states. Thus, at high bath gas pressure, the ISC reaction is more likely to occur from lower vibrational levels of the singlet state. This also increases the likelihood of vibrational relaxation of the $\tilde{\alpha}^3$B$_1$ state below the origin of the $\tilde{A}^1$A$_2$ state, preventing crossing back to the singlet manifold. As a result, localized near-degenerate interactions at low vibrational levels of the singlet state will be selectively expressed regardless of the state and vibrational levels initially excited into. This allows a mechanism for the expression of S-MIF from localized near-degenerate spin-orbit interactions, and also may explain the pressure dependence on the relationship between $\Delta^{36}$S and $\Delta^{33}$S values.

3.7 Theoretical basis for proposed mechanism

To better understand the isotope effects during the ISC reaction of SO$_2$, high-level ab initio calculations of the global potential energy surfaces (PESs) for the low-lying singlet and triplet states of SO$_2$ were carried out (Section 3.11.3). In the Clements bands (Clements, 1935), about 3.5 eV above the ground electronic (X'A$_1$) state, there are two nonadiabatically coupled singlet ($\tilde{A}^1$A$_2$ and $\tilde{B}^1$B$_1$) and three triplet ($\tilde{\alpha}^3$B$_1$, $\tilde{\beta}^3$A$_2$, and $\tilde{\gamma}^3$B$_2$) electronic states (Müller and Köppel, 1994; Katagiri et al., 1997; Lévêque et al., 2013) (Figure 3-1-D). The $\tilde{\gamma}^3$B$_2$ state was not included in the present analysis, as it has no interaction with other states because of its symmetry. For each of the remaining states, 19000 symmetric unique points were determined at the internally contracted multi reference configuration interaction (MRCI) level.
Figure 3-4: Comparison between the calculated total absorption cross-section and experiment (Vandaele et al., 2009) as a function of the photon energy.

(Werner and Knowles, 1988) with the augmented correlation-consistent polarized valence triple-zeta (aug-cc-pVTZ) basis set (Dunning, 1989) for both the sulfur and oxygen atoms. The Davidson correction (Q) (Langhoff and Davidson, 1974) was applied to account for the effect of higher excitations and to reduce size-consistency errors. Nonadiabatic couplings between the two singlet states have been determined in a quasi-diabatic representation (Simah et al., 1999). In addition, the spin-orbit (SO) interactions between the singlet and triplet states has been computed using the unperturbed MRCI wave functions and Breit-Pauli Hamiltonian. As shown in Figure 3-4, the calculated absorption cross-section for the Clement bands is in good agreement with experiment. Importantly, the potential energy minimum of the $\tilde{a}^3B_1$ state is about 0.2 eV lower than that of the lowest singlet state, facilitating ISC.
Table 3.2: Vibrational energy levels on the singlet manifold for four sulfur isotopomers

<table>
<thead>
<tr>
<th>(v₁, v₂, v₃)</th>
<th>^{32}\text{S}, \text{cm}^{-1}</th>
<th>^{33}\text{S}, \text{cm}^{-1}</th>
<th>^{34}\text{S}, \text{cm}^{-1}</th>
<th>^{36}\text{S}, \text{cm}^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two singlet $B_1$ and $A_2$ states in quasi-diabatic representation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0, 0, 0)</td>
<td>27242.19</td>
<td>27237.84</td>
<td>27233.73</td>
<td>27226.11</td>
</tr>
<tr>
<td>(0, 1, 0)</td>
<td>27617.21</td>
<td>27612.14</td>
<td>27607.34</td>
<td>27598.39</td>
</tr>
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<td>27660.79</td>
<td>27654.50</td>
<td>27642.83</td>
</tr>
<tr>
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<td>27958.93</td>
<td>27953.00</td>
<td>27947.36</td>
<td>27936.80</td>
</tr>
<tr>
<td>(0, 1, 1)</td>
<td>27986.16</td>
<td>27976.05</td>
<td>27969.33</td>
<td>27956.84</td>
</tr>
<tr>
<td>(0, 0, 2)</td>
<td>28090.72</td>
<td>28081.63</td>
<td>28073.06</td>
<td>28057.20</td>
</tr>
<tr>
<td>(1, 0, 0)</td>
<td>28255.69</td>
<td>28247.69</td>
<td>28240.23</td>
<td>28225.57</td>
</tr>
<tr>
<td>Triplet $B_1$ state in adiabatic representation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0, 0, 0)</td>
<td>25730.64</td>
<td>25725.66</td>
<td>25720.96</td>
<td>25712.23</td>
</tr>
<tr>
<td>(0, 1, 0)</td>
<td>26133.61</td>
<td>26126.76</td>
<td>26120.27</td>
<td>26108.16</td>
</tr>
<tr>
<td>(0, 2, 0)</td>
<td>26517.05</td>
<td>26508.28</td>
<td>26499.94</td>
<td>26484.37</td>
</tr>
<tr>
<td>(0, 0, 1)</td>
<td>26531.64</td>
<td>26521.71</td>
<td>26512.32</td>
<td>26494.88</td>
</tr>
<tr>
<td>(1, 0, 0)</td>
<td>26684.24</td>
<td>26577.27</td>
<td>26570.71</td>
<td>26558.56</td>
</tr>
<tr>
<td>(0, 3, 0)</td>
<td>26889.62</td>
<td>26878.98</td>
<td>26868.87</td>
<td>26849.97</td>
</tr>
<tr>
<td>(0, 1, 1)</td>
<td>26951.35</td>
<td>26939.22</td>
<td>26927.74</td>
<td>26906.36</td>
</tr>
<tr>
<td>(1, 1, 0)</td>
<td>26982.48</td>
<td>26973.86</td>
<td>26965.70</td>
<td>26950.52</td>
</tr>
<tr>
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<td>27237.47</td>
<td>27225.66</td>
<td>27203.56</td>
</tr>
<tr>
<td>(0, 0, 2)</td>
<td>27310.74</td>
<td>27299.19</td>
<td>27288.21</td>
<td>27267.63</td>
</tr>
</tbody>
</table>

Franck-Condon transitions with a 250 nm to 350 nm photon bring SO₂ from the ground $X^1A_1$ state to the excited $A^1A_2/B^1B_1$ manifold. As discussed above, we assume that the excited SO₂ is relaxed quickly to low vibrational levels (Table 3.2) of the lowest singlet $A^1A_2$ state because of fast nonadiabatic mixing between the two singlet states and efficient collisions with the bath gas. The ISC to the lowest triplet $\tilde{a}^3B_1$ state follows (Table 3.2), which was modeled using a wave packet method. In particular, the time-dependent Schrödinger equation was solved numerically (Kosloff, 1988) with the nonadiabatically coupled full-dimensional Hamiltonian for the $B^1B_1/\tilde{A}^1A_2/\tilde{a}^3B_1$ manifold ($J = 0$), as described in Section 3.11.3. Four (000, 100, 010, and 001) vibrational eigenfunctions on the $\tilde{A}^1A_2$ state were used as the initial wave packed, and the $\tilde{a}^3B_1$ triplet-state population is artificially absorbed to account for the irreversibility of the ISC as a result of collisional relaxation. The parameters used in our calculations are listed in Table 3.3.

The lifetime of the $\tilde{A}^1A_2$ state is extracted from the population decay curve (Table 3.4) and used to estimate the isotope effects for ISC from each vibrational level. As shown in Figures 3-5 and 3-6, the results clearly show the decay rates are different.
Table 3.3: Parameters used in dynamics calculations. Atomic units are used unless stated otherwise.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values</th>
</tr>
</thead>
</table>
| Grid/basis range and size | \( R \in [2.2, 8.0], N_R = 224 \)  
| | \( r \in [2.2, 7.0], N_r = 224 \)  
| | \( f_{\text{max}} = 89, N_f = 90 \) over \([0, 180^\circ] \)  
| Damping | \( \exp \left[ -0.06 \left( \frac{R-6.4}{R_{\text{end}}-6.4} \right)^2 \right] \), for \( 8.0 > R > 6.4 \) with \( R_{\text{end}} = 8.0 \)  
| | \( \exp \left[ -0.075 \left( \frac{r-5.4}{r_{\text{end}}-5.4} \right)^2 \right] \), for \( 7.0 > R > 5.4 \) with \( R_{\text{end}} = 7.0 \)  
| | \( = 1, \) otherwise  
| Damping constant on the triplet state | \( \exp(-\alpha) = 0.9999 \)  

Table 3.4: ISC induced lifetime of low-lying singlet vibrational states

<table>
<thead>
<tr>
<th>((v_1, v_2, v_3))</th>
<th>(^{32}\text{S}, ) ps</th>
<th>(^{33}\text{S}, ) ps</th>
<th>(^{34}\text{S}, ) ps</th>
<th>(^{36}\text{S}, ) ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0, 0, 0)</td>
<td>6072.7</td>
<td>5068.1</td>
<td>3378.9</td>
<td>1026.7</td>
</tr>
<tr>
<td>(1, 0, 0)</td>
<td>32.6</td>
<td>22.5</td>
<td>13.3</td>
<td>3.7</td>
</tr>
<tr>
<td>(0, 1, 0)</td>
<td>18.3</td>
<td>24.4</td>
<td>62.8</td>
<td>220.3</td>
</tr>
<tr>
<td>(0, 0, 1)</td>
<td>1677.4</td>
<td>1688.4</td>
<td>1628.6</td>
<td>1257.8</td>
</tr>
</tbody>
</table>

among the sulfur isotopologues and are not mass dependent. In particular, the \((000)\), \((100)\), and \((001)\) vibrational levels show large anomalies in the decay rate of \(^{36}\text{SO}_2\), suggesting a strong mass-independent effect in \(^{36}\text{S}\). Similarly, decay from the \((010)\) level shows large MIF in \(^{33}\text{S}\). Therefore, combined contributions from MIF at the \((100)\) and \((010)\) levels would explain the experimental results of positive \(\Delta^{33}\text{S}\) and \(\Delta^{36}\text{S}\) values. It is clear that this simple model cannot fully account for the experimental results; a significant number of approximations were involved. For example, the relative energies of various electronic states might not be determined accurately by the ab initio method. In addition, it is likely that the singlet excited-state \(\text{SO}_2\) decays from a range of vibrational and rotational levels. Nevertheless, these results clearly demonstrate that there is a very strong, isotope-specific dependence on the excited-state lifetimes from individual vibrational levels.
Figure 3-5: Results for lifetime calculations for  \( \tilde{A}^1A_2 \) states. (A and B) Decay of singer populations for several sulfur isotopologues from the (010) and (100) states (3.4). (C and D) Isotope fractionation factor estimated from the lifetime of \( \tilde{A}^1A_2 \) state calculated for the four low-lying vibrational levels: 

\[
33E = \frac{33k}{32k} / \left( \frac{34k}{32k} \right)^{0.515} - 1
\]

and 

\[
36E = \frac{36k}{32k} / \left( \frac{34k}{32k} \right)^{1.9} - 1,
\]

where \( k \) are rate constants for \( ^X \text{SO}_2 \).
Figure 3-6: Decay of singlet populations for several sulfur isotopologues from the (000) vibrational state.
3.8 Implications for S-MIF signatures observed in nature

The photolysis of SO₂ in the 185 nm to 220 nm absorption region currently is considered the most likely source reaction for Archean S-MIF (Farquhar et al., 2001; Pavlov and Kasting, 2002; Lyons, 2007; Danielache et al., 2008; Masterson et al., 2011). However, there are several issues with SO₂ photolysis as a source of the Archean S-MIF signatures. Broadband photolysis of SO₂ under a range of experimental conditions (e.g., SO₂ pressures, bath gas pressures, light sources) produces large δ⁳⁴S values (up to +212 %₀) associated with relatively small Δ³³S values (maximum +25 %₀), resulting in low δ³³S/δ³⁴S ratios of 0.55 to 0.66 (Masterson et al., 2011; Whitehill and Ono, 2012; Ono et al., 2013). In contrast, the Archean record contains large Δ³³S values (from −4 %₀ to +12 %₀) associated with high δ³³S/δ³⁴S ratios of up to 1.4 (e.g., Ono et al., 2003; Kaufman et al., 2007). In addition, S-MIF signatures produced during SO₂ photolysis become very small (Δ³³S < +2.5 %₀) at low SO₂ column densities (Ono et al., 2013), indicating that the production of large (Δ³³S > +2.5 %₀) S-MIF anomalies would require the maintenance of high SO₂ column densities in the atmosphere. Sediment diagenesis and biological processes in the oceans likely mix sulfides with different Δ³³S values and dilute the S-MIF signal (Halevy et al., 2010) such that the source reaction likely would have produced Δ³³S values much larger than +12 %₀. Significant questions remain as to whether 185 nm to 220 nm photolysis of SO₂ was the source of Archean S-MIF.

The S-MIF signatures produced in this study contain large (Δ³³S up to +78 %₀) MIF associated with small (< +25 %₀) δ³⁴S values. In contrast to the photolysis band, the S-MIF signatures from the excitation band do not require a high SO₂ column density to produce large S-MIF. The major issues with the excitation band as a source of the Archean S-MIF signature are the difficulty in preserving the isotope signatures from excited-state SO₂ (relative to SO produced from SO₂ photolysis) and the positive Δ³⁶S/Δ³³S ratios (Archean rocks have Δ³⁶S/Δ³³S ≈ −1.5 to −0.9; see Farquhar et al., 2000a; Zerkle et al., 2012; Kaufman et al., 2007). Several authors (Whitehill...
and Ono, 2012; Zerkle et al., 2012) have suggested that SO₂ photochemistry from
the photoexcitation region might have contributed to the Archean S-MIF signatures,
and studies have shown that the UV irradiation of SO₂ in the presence of methane
produces organosulfur aerosols (presumably derived from ³SO₂) that might have con-
tributed to the preservation of the Archean S-MIF signature (DeWitt et al., 2010).
The discrepancy in the Δ³⁶S/Δ³³S values requires additional study, but our calcula-
tions suggest that MIF in ³³S and ³⁶S are produced from ISC at different vibrational
levels, and our experiments demonstrated that the Δ³⁶S/Δ³³S ratio is a function of
pN₂ and could potentially produce the Archean ratio under certain conditions. It
should be noted that the Δ³⁶S/Δ³³S values produced from experimental photolysis
of SO₂ using broadband radiation sources is too low (−1.6 under pure SO₂, but as low
as −6.0 with N₂) to explain the Δ³⁶S/Δ³³S ratios observed in the Archean record. As
suggested in Whitehill and Ono (2012), contributions from both absorption regions
might explain the Archean S-MIF signal.

Several authors (Savarino et al., 2003; Båróni et al., 2007, 2008; Hattori et al.,
2013) have suggested that excited-state photochemistry in the photoexcitation band
might be responsible for the S-MIF signatures observed in modern stratospheric
sulfate aerosols. Reaction of excited-state SO₂, particularly triplet ³SO₂, with ei-
ther ground state SO₂ (i.e., ³SO₂ + SO₂ → SO + SO₃; Savarino et al., 2003) or O₂
(i.e., ³SO₂ + O₂ → SO₃ + O; Hattori et al., 2013) theoretically could preserve mass-
dependently fractionated SO₃, and SO₃ might be hydrolyzed to form stable sulfuric
acid aerosols. Whitehill and Ono (2012), however, presented isotopic evidence that
the ³SO₂ + SO₂ reaction primarily occurs via O-atom transfer from the excited-state
species to the ground-state species, thus producing MIF signatures in SO, but mass-
dependently fractionated SO₃. Hattori et al. (2013) modeled the modern stratosphere
following a large volcanic eruption and suggested that the ³SO₂ formed from the pho-
toexcitation band might react with O₂ to form mass-independently fractionated SO₃.
Their isotopic agreement, however, critically depends on the assumption that the
cross-sections of Danielache et al. (2012) accurately predict the isotope ratios of the
reactive (i.e., triplet) SO₂ species. As we demonstrate here, significant differences
between the isotope signatures predicted by the cross-sections and those observed experimentally are the result of vibronic effects after the initial excitation step, which are not taken into account in Hattori et al. (2013). Ono et al. (2013) showed that the isotopic signatures from SO$_2$ photolysis in a self-shielding regime match those from stratospheric sulfate aerosols, although a mechanism for the preservation of SO in the modern atmosphere requires additional research.

3.9 Conclusions

We report the production of very large S-MIF signatures, with $\Delta^{33}$S up to +78%$\varepsilon$ and $\Delta^{36}$S up to +110%$\varepsilon$, from SO$_2$ photochemistry in the 250 nm to 350 nm region. The origin of the S-MIF is attributed to ISC at excitation wavelengths below 320 nm. Isotope effects due primarily to absorption, as predicted by isotopologue-specific cross-sections, do not contribute significantly to the large S-MIF observed, particularly in $^{36}$S. Rapid vibrational relaxation allows expression of S-MIF signatures from localized accidental degeneracies regardless of the initially excited vibronic level. The same mechanism, however, may not be applied to the 180 nm to 220 nm band systems of SO$_2$ because the quantum efficiency of photolysis is near unity below 205 nm (Katagiri et al., 1997), and the lifetime is sufficiently short that little vibrational relaxation occurs. Although the S-MIF signatures observed in this study, particularly the $\Delta^{36}$S/$\Delta^{33}$S ratios, do not match those from the Archean, the photochemistry in the photoexcitation band can produce large mass-independent signatures (i.e., $\Delta^{33}$S values) with relatively small mass-dependent fractionations (i.e., $\delta^{34}$S values), which is necessary to explain the preservation of large Archean S-MIF signatures. Photochemistry from the 250 nm to 350 nm absorption region should be explored further as a possible source for the geological S-MIF signatures.
3.10 Acknowledgements

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3.11 Supplementary Information

3.11.1 Photochemical Experiments

Photochemical experiments were performed in a cylindrical glass photochemical reaction (15.3 cm path length, 5.2 cm inner diameter) with 3/8 inch o.d. inlet and outlet ports 2 cm from the front and rear. Two UV-grade fused silica (Corning 7980) windows (transmission > 90% down to 200 nm) were used on either side of the reactor and sealed with O-rings. Flow rates of acetylene (atomic absorption grade), nitrogen (ultra high purity grade), and 5% SO$_2$ (premixed with N$_2$) into the photochemical reactor were controlled with a series of mass-flow controllers. Several low-pSO$_2$ experiments (0.3 mbar and 0.1 mbar) used 1000 ppm SO$_2$ (premixed with N$_2$), and two experiments with the 320 nm longpass filter used pure SO$_2$ (99.9%+). The gas pressure was measured at the inlet side immediately before the reactor using a capacitance manometer (MKS Baratron Type 722A, 1000 torr full scale). After leaving the reactor, the gas was passed through two 8 cm to 9 cm long glass tubes packed with glass wool (to trap the organosulfur products), then passed through an electronically controlled proportionating valve before being pumped by a diaphragm pump. The proportionating valve was controlled using proportional-integral-derivative (PID) control by LabView software (National Instruments Corporation) and could maintain the total pressure within the photochemical reactor to ±0.3 mbar of a set point pressure.
for the duration of the experiment.

Experiments were run at a constant acetylene partial pressure of 10.1 mbar and varying SO\textsubscript{2} and total (SO\textsubscript{2} + N\textsubscript{2} + acetylene) pressures (Table 3.1). Total flow rates were controlled to maintain a 40 s residence time within the reactor (i.e., total flow rates of 500 mL min\textsuperscript{-1}, 250 mL min\textsuperscript{-1}, and 125 mL min\textsuperscript{-1} for 1013 mbar, 507 mbar, and 253 mbar experiments, respectively). Additional experiments were performed at 0.3 mbar and 0.1 mbar SO\textsubscript{2} and using various optical filters (Table 3.1). Because of the varying rates of product formation under different conditions, reaction times were varied between 1 h to 45 h.

During experiments, the photochemical reactor was irradiated with a 150 W UV-enhanced Xenon arc lamp (Model 6254; Newport). The lamp was housed in a lamp housing (Model 67005; Newport), which focused and collimated the light to a 1.5 inch diameter column. The collimated light was passed through a liquid filter (Model 51945; Newport) filled with deionized (18.2 MΩ) water to absorb infrared radiation emitted by the lamp. Before entering the photochemical reactor, the light was passed through a 250 nm longpass filter (ZUL0250; Asahi Spectra) to eliminate radiation from the strong 180 nm to 220 nm absorption band of SO\textsubscript{2}. Several experiments were performed with combinations of optical filters to test the wavelength dependence of the isotope effect in the 250 nm to 350 nm region (Table 3.1 and Figure 3-3). These filters included a series of longpass (295 nm, 305 nm, and 320 nm, 20CGA series; Newport) and shortpass (300 nm and 350 nm, ZUS0300 and ZUS0350, respectively; Asahi Spectra) filters. Conditions for each experiment are given in Table 3.1.

Immediately following each experiment, ethanol and water were used to rinse the reactor and to collect aerosol products. The water / ethanol and the glass wool used to trap the aerosols were stored at −20 °C until the Raney nickel hydrodesulfurization extraction. Organosulfur compounds were reduced to H\textsubscript{2}S and then precipitated as Ag\textsubscript{2}S using the Raney nickel hydrodesulfurization extraction procedure of Oduro et al. (2011b). In brief, Raney nickel was activated with 1 M NaOH and rinsed with deionized water. Approximately 1 mL of activated Raney nickel in water was pipetted into the bottom of a a round-bottomed flask. One milliliter of 1 M NaOH was added,
as was several milliliters of ethanol. The water and ethanol used to rinse the reaction cell, along with the glass wool used to collect the aerosols, then were added to the flask, and the flask was placed on an extraction line with a condenser. The solution was refluxed gently for 30 min and then allowed to cool. A syringe was used to slowly add 20 mL of a solution of aluminum foil in concentrated HCl (0.5 g aluminum foil per 100 mL concentrated HCl), after which the solution was refluxed for 2 h. A nitrogen carrier gas was used to carry the evolved H$_2$S through a condenser and a solution of silver nitrate (0.08 M) in 0.31 M nitric acid. The silver nitrate trapped the H$_2$S as silver sulfide.

The silver sulfide was rinsed several times, dried, and weighed. It was then fluorinated and analyzed for quadruple sulfur isotope ratios following a procedure described in Ono et al. (2006b). In brief, Ag$_2$S was reacted with excess elemental fluorine gas in externally heated nickel tubes (at 300 °C) to form SF$_6$. The product SF$_6$ was 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$_6^+$ ($^{32}$SF$_6^+$, $^{33}$SF$_6^+$, $^{34}$SF$_6^+$, and $^{36}$SF$_6^+$). A microvolume (0.4 mL) procedure was used for small samples (<0.3 mg Ag$_2$S). Replicate analyses ($n = 28$) of the reference Ag$_2$S IAEA-S-1 yielded 2σ standard deviations of 0.26‰, 0.014‰, and 0.19‰ for $\delta^{34}$S, $\Delta^{33}$S, and $\Delta^{36}$S, respectively. Typical reproducibility for microvolume analyses of IAEA-S-1 is 0.9‰, 0.08‰, and 0.8‰ for $\delta^{34}$S, $\Delta^{33}$S, and $\Delta^{36}$S, respectively (2σ for 14 replicate analyses).

### 3.11.2 Modeling the isotope fractionation from cross-section data

The isotope fractionation from the initial excitation step ($\tilde{A}^1A_2,\tilde{B}^1B_1 \rightarrow \tilde{X}^1A_1$) was modeled using the UV absorption cross-sections for sulfur isotope-enriched SO$_2$ ($^{32}$SO$_2$, $^{33}$SO$_2$, $^{34}$SO$_2$, and $^{36}$SO$_2$) reported by Danielache et al. (2012). These cross-sections are measured between 250 nm and 320 nm, at room temperature, and at a resolution of 8 cm$^{-1}$. Photoexcitation rates are estimated as a function of wavelength.
(λ) and optical depth within the reaction cell (z) as:

\[
\tau_k(z) = \int_{\lambda_{250\text{nm}}}^{\lambda_{320\text{nm}}} \sigma(\lambda) \times F_0(\lambda) \times \exp(-\tau(\lambda, z)) d\lambda
\]  \hspace{1cm} (3.1)

where \( x = 32, 33, 34, 36 \) and corresponds to the respective isotope \(^x\text{SO}_2\); \( \tau_k(z) \) is the first order rate constant of excitation of \(^x\text{SO}_2\) into the singlet (\( \tilde{\text{A}}^1\text{A}_2/\tilde{\text{B}}^1\text{B}_1 \)) state, as a function of depth within the reaction cell (z); \( \sigma(\lambda) \) is the cross section of \(^x\text{SO}_2\) at a wavelength of \( \lambda \), as measured in Danielache et al. (2012); \( F_0(\lambda) \) is the photon flux from the light source at a wavelength of \( \lambda \), accounting for the lamp spectrum and all optics (filters, windows, etc.); and \( \tau(\lambda, z) \) is the opacity term that accounts for absorption within the cell and is given by:

\[
\tau(\lambda, z) = z \cdot \left( 32\sigma(\lambda)^{32}N + 33\sigma(\lambda)^{33}N + 34\sigma(\lambda)^{34}N + 36\sigma(\lambda)^{36}N \right)
\]  \hspace{1cm} (3.2)

where \( \tau N \) is the number density of \(^x\text{SO}_2\) within the reaction cell.

The average excitation rate in the cell is obtained by averaging \( \tau_k(z) \) over the length of the photochemical reactor (z = 0 cm to 15.3 cm).

3.11.3 Theoretical calculations

In our ab initio calculations, the \( \text{SO}_2 \) molecule was treated in \( C_s \) symmetry. The molecular orbitals (MOs) were determined by state-averaged complete active space self-consistent field (CASSCF) calculations, with a full valence active space involving 18 electrons in 12 active orbitals. After determining the MOs, internally contracted multireference configuration interaction (icMRCI; Knowles and Werner, 1988; Werner and Knowles, 1988) calculations were carried out to capture the dynamical correlation of the electrons, and the Davidson correction (Q; Langhoff and Davidson, 1974) was applied to account for higher excitations and to reduce size-consistency errors. The augmented correlation-consistent polarized valence triple-zeta (aug-cc-pVTZ) basis set was used for both the sulfur and oxygen atoms (Dunning, 1989; Woon and Dunning, 1993). The ab initio calculations of the four excited states were carried out with
the MOLPRO 2010 package of ab initio programs.

The singlet $\tilde{1}B_2$ and $\tilde{A}^1A_1$ states are nonadiabatically coupled with a conical intersection (Müller and Köppel, 1994; Léveque et al., 2013). As a result, a quasi-diabatic representation was used. This representation is related to the adiabatic representation with an orthogonal transformation, which is determined by a mixing angle (Werner et al., 1988). On the other hand, only the lowest $\tilde{\sigma}^3B_1$ state was studied. From our calculations, the spin-orbit (SO) coupling elements between the singlet and triplet states were found to be very small; the absolute numerical values calculated are around 40 cm$^{-1}$ in the Franck-Condon region. The coordinate dependence was found to be weak, and the value of SO couplings was fixed at a constant (40 cm$^{-1}$) in our dynamics calculations.

The three potential energy surfaces (PESs; two for singlets and one for triplet) were expressed in internal coordinates with a cubic spline fit. Approximately 19000 points were chosen in a grid in which the bond distances $R_1$ and $R_2$ were varied from 1.15 Å to 6.0 Å and the O-S-O angle was covered from 0° to 180° at every 10°. The PESs are shown in Figure 3-1-D, and the calculated absorption cross-section is compared in Figure 3-4 with the low-resolution experimental spectrum for the $B$ band (Vandaele et al., 2009). The excellent agreement validates the PESs. The details of the ab initio calculations and diabatization is given in Xie et al. (2013).

The time-dependent quantum mechanical method (Kosloff, 1988) was used to characterize the intersystem crossing (ISC) dynamics. The total Hamiltonian ($J = 0$) in the O’ + SO Jacobi coordinates $(R, r, \gamma)$ may be written as ($\hbar = 1$):

$$
\hat{H} = \hat{T}_R + \hat{T}_r + \hat{T}_j + V(R, r, \gamma)
$$

$$
= -\frac{1}{2\mu_R} \frac{\partial^2}{\partial R^2} - \frac{1}{2\mu_r} \frac{\partial^2}{\partial r^2} + \left( \frac{1}{2\mu_r r^2} + \frac{1}{2\mu_R R^2} \right) \hat{j}^2 + V(R, r, \gamma) \tag{3.3}
$$

where $R$ denotes the distance between O’ and the center of mass of SO, $r$ is the SO bond distance, and $\gamma$ is the angle between the vectors $\mathbf{R}$ and $\mathbf{r}$, $\mu_R$ and $\mu_r$ are the corresponding reduced masses, $\hat{j}$ is the diatomic rotational angular momentum operator, and the electronic orbital and spin angular momenta are ignored. $V(R, r, \gamma)$
is the electronic potential energy matrix in the diabatic representation

\[
V = \begin{pmatrix}
V_{11} & V_{12} & V_{13} \\
V_{21} & V_{22} & V_{23} \\
V_{31} & V_{32} & V_{33}
\end{pmatrix}
\]  

(3.4)

where \(V_{11}\) and \(V_{22}\) are two singlet \(B_1\) and \(A_1\) states, respectively; \(V_{33}\) is the triplet \(B_1\) state; \(V_{12}\) is the coupling between two singlet states; and \(V_{13}\) and \(V_{23}\) are the spin-orbit couplings chosen as a constant 40 cm\(^{-1}\) in the calculations. The Hamiltonian was discretized using a mixed representation consisting of a discrete value representation (DVR) of the radial degrees of freedom and a finite basis representation (FBR) of the angular degree of freedom (Light and Carrington, 2000).

A few lowest vibrational energy levels of the singlet states and the lowest triplet state have been determined and are listed in Table 3.2 for the four sulfur isotopomers. The initial wave packets for the ISC calculations were chosen as one of the vibrational states in the singlet manifold. The second-order split operator method (Feit et al., 1982) was used to propagate the wave packet,

\[
\begin{pmatrix}
\varphi_1(t + \Delta t) \\
\varphi_2(t + \Delta t) \\
\varphi_3(t + \Delta t)
\end{pmatrix} = e^{-i\hat{H}\Delta t/\hbar} \begin{pmatrix}
\varphi_1(t) \\
\varphi_2(t) \\
\varphi_3(t)
\end{pmatrix}
\]

\[
= e^{-i\hat{V}\Delta t/2\hbar}e^{-i\hat{T}_j\Delta t/2\hbar}e^{-i(\hat{T}_R + \hat{T}_j)\Delta t\hbar}e^{-i\hat{T}_R\Delta t/2\hbar}e^{-i\hat{V}\Delta t/2\hbar} \begin{pmatrix}
\varphi_1(t) \\
\varphi_2(t) \\
\varphi_3(t)
\end{pmatrix}
\]

(3.5)

and the time step \(\Delta t\) was 10 a.u. During the propagation, the fast sine Fourier transform was used to evaluate the action of the radial kinetic energy operators \(\hat{T}_R\) and \(\hat{T}_j\) onto the wave packet. The angular kinetic energy operator \(\hat{T}_j\) can act on the wave packet directly in FBR. The action of the potential energy operator on the wave packet was evaluated in DVR. Because the potential energy matrix in diabetic representation is nondiagonal, the transformation between diabetic and adiabatic representations is
needed during the propagation. The numerical parameters used in our calculations are listed in Table 3.3. To simulate the irreversibility of the intersystem crossing, and artificial absorption potential was added on the triplet state, which was chosen as a constant (Table 3.2). The decay of the singlet state population was computed and is shown in Figure 3-6 for the (000) vibrational level of four sulfur isotopomers. The lifetimes extracted from the decay curves are collected in Table 3.4.
Chapter 4

SO$_2$ photolysis as a source for sulfur mass-independent isotope signatures in stratospheric aerosols

Foreward

This chapter has been published previously as Whitehill et al. (2014).

4.1 Abstract

Signatures of sulfur isotope mass-independent fractionation (S-MIF) have been observed in stratospheric sulfate aerosols deposited in polar ice. The S-MIF signatures are thought to be associated with stratospheric photochemistry following stratospheric volcanic eruptions, but the exact mechanism responsible for the production and preservation of these signatures is debated. In order to identify the origin and the mechanism of preservation for these signatures, a series of laboratory photochemical experiments were carried out to investigate the effect of temperature and added O$_2$ on S-MIF produced by the two absorption band systems of SO$_2$: photolysis in the 190 nm to 220 nm region and photoexcitation in the 250 nm to 350 nm region. The SO$_2$ photolysis (SO$_2$ + $h\nu$ $\rightarrow$ SO + O) experiments showed S-MIF signals with
large $^{34}\text{S}/^{32}\text{S}$ fractionation, which increases with decreasing temperature. The overall S-MIF pattern observed for photolysis experiments, including high $^{34}\text{S}/^{32}\text{S}$ fractionations, positive mass-independent anomalies in $^{33}\text{S}$, and negative anomalies in $^{36}\text{S}$, is consistent with a major contribution from optical isotopologue screening effects and data for stratospheric sulfate aerosols. In contrast, $\text{SO}_2$ photoexcitation produced products with positive MIF anomalies in both $^{33}\text{S}$ and $^{36}\text{S}$ that is different from stratospheric aerosols, but could contribute to the observed signatures. $\text{SO}_2$ photolysis in the presence of $\text{O}_2$ produced $\text{SO}_3$ with S-MIF signals, suggesting the transfer of the MIF signals of $\text{SO}$ to $\text{SO}_3$ by the $\text{SO} + \text{O}_2 + \text{M} \rightarrow \text{SO}_3 + \text{M}$ reaction. Based on our experimental results, we estimate a termolecular rate constant on the order of $10^{-37} \text{cm}^6\text{molecule}^{-2}\text{s}^{-1}$. This rate can explain the preservation of mass independent isotope signatures in stratospheric sulfate aerosols and provides a minor, but important, oxidation pathway for stratospheric $\text{SO}_2$. The production and preservation of S-MIF signals in the stratosphere requires a high $\text{SO}_2$ column density to allow for optical isotopologue screening effects to occur and to generate a large enough signature that it can be preserved. In addition, the $\text{SO}_2$ plume must reach an altitude of around 20 km to 25 km, where $\text{SO}_2$ photolysis becomes a dominant process. These experiments are the first step towards understanding the origin of the sulfur isotope anomalies in stratospheric sulfate aerosols.

4.2 Introduction

Explosive volcanic eruptions that inject sulfur dioxide ($\text{SO}_2$) into the stratosphere can cause perturbations to the stratospheric sulfur cycle for years following eruptions. The increase in stratospheric sulfate aerosols associated with injections of $\text{SO}_2$ result in stratospheric warming and tropospheric cooling, and can also trigger changes in atmospheric circulation and increases in ozone depletion (Robock, 2000). Perturbations to the stratospheric sulfur cycle following large volcanic eruptions are recorded as changes in sulfur isotope ratios, as measured in stratospheric sulfate aerosol samples (Castleman et al., 1974), as well as in ice core records (Savarino et al., 2003; Bároni
The reaction with OH is the dominant oxidation pathway for SO₂ in the stratosphere:

\[ \text{SO}_2 + \text{OH} + \text{M} \rightarrow \text{HOSO}_2 + \text{M} \]  \hspace{1cm} (R.4.1)

This reaction is followed by:

\[ \text{HOSO}_2 + \text{O}_2 \rightarrow \text{SO}_3 + \text{HO}_2 \]  \hspace{1cm} (R.4.2)

In the presence of H₂O, SO₃ readily forms sulfuric acid (H₂SO₄) via:

\[ \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 \]  \hspace{1cm} (R.4.3)

Ab-initio transition state theory calculations of the isotope effect for OH oxidation (R.4.1) predict that ³⁴SO₂ is oxidized 0.9% slower than ³²SO₂ (Tanaka et al., 1994), although calculations with RRKM theory predicts an inverse isotope effect, in which ³⁴SO₂ reacts 12% to 15% faster than ³²SO₂ (Leung et al., 2001). Experimental studies of OH oxidation (R.4.1) showed an inverse isotope effect, but with a smaller magnitude, with ³⁴SO₂ reaction about 1% faster than ³²SO₂ (Harris et al., 2012). Although the experimentally measured isotope effect might be sufficient to explain the roughly 2% enrichment in H₂³⁴SO₄ relative to H₂³²SO₄ following the major Mt. Agung (1963) eruption (Castleman et al., 1974), the large observed isotope effect suggests the possibility of an additional oxidation reaction with larger ³⁴S fractionations.

An additional unexplained observation is the isotope anomalies in ³³S/³²S and ³⁶S/³²S ratios relative to ³⁴S/³³S ratios. These signatures of mass-independent fractionation (MIF) have been observed in ice cores associated with large volcanic eruptions (Savarino et al., 2003; Bároni et al., 2007, 2008; Lanciki, 2010; Lanciki et al., 2012). Ice core sulfate peaks are commonly used to reconstruct the impact of past volcanic activity, which is critical to forcing climate models (Robock, 2000). For several years following large injections of SO₂ into the stratosphere, stratosphere-derived sulfate can dominate sulfate deposition in ice cores and, when corrected for back-
ground levels, can preserve the sulfur isotopic composition of stratospheric sulfate aerosols. Experimental studies demonstrate that OH oxidation of SO$_2$ (R4.1) does not produce mass-independent sulfur isotope anomalies (Harris et al., 2012, 2013), so an additional oxidation mechanism is required to produce the mass-independent sulfur isotope signatures. Three reactions have been proposed to explain these isotope anomalies: excited-state photochemistry of SO$_2$ in the 250 nm to 350 nm absorption region (Savarino et al., 2003; Hattori et al., 2013), SO$_2$ photolysis in the 190 nm to 220 nm absorption region (Ono et al., 2013), and SO$_3$ photolysis (Pavlov et al., 2005).

We present results of laboratory photochemical experiments that support SO$_2$ photolysis as the main source for the MIF signatures observed in stratospheric sulfate aerosols following some large (stratospheric) volcanic eruptions. In particular, SO$_2$ photolysis produces large MIF anomalies, as well as large mass-dependent isotope fractionations (Masterson et al., 2011; Whitehill and Ono, 2012; Ono et al., 2013) that are consistent with the isotopic signatures observed in stratospheric sulfate aerosols in ice cores (Ono et al., 2013).

Photolysis of SO$_2$ occurs above around 20 km to 25 km in the wavelength region of 190 nm to 220 nm, which lies in the spectral window between the Schumann–Runge absorption edge of oxygen (O$_2$) and the Hartley bands of ozone (O$_2$). SO$_2$ photolysis produces sulfur monoxide (SO) and O($^3$P) via the following reaction:

$$\text{SO}_2 + h\nu \rightarrow \text{SO} + \text{O}(^3\text{P})$$  \hspace{1cm} (R 4.4)

It is generally accepted that this reaction is followed by rapid oxidation of SO to SO$_2$ via (Black et al., 1982a; Savarino et al., 2003; Pavlov et al., 2005):

$$\text{SO} + \text{O}_2 \rightarrow \text{SO}_2 + \text{O}(^3\text{P})$$  \hspace{1cm} (R 4.5)

Reactions (R 4.4) and (R 4.5) combine to form a null cycle for sulfur, but catalyze the formation of odd oxygen (Bekki, 1995). If SO is completely oxidized to SO$_2$, no isotopic signature from SO$_2$ photolysis can be preserved (Pavlov et al., 2005).

We propose an additional channel where SO is oxidized directly to SO$_3$ via the
termolecular reaction:

\[ \text{SO + O}_2 + \text{M} \rightarrow \text{SO}_3 + \text{M} \]  \hspace{1cm} (R 4.6)

A previous study by Black et al. (1982a) showed that the maximum termolecular rate constant for Reaction (R4.6) is \(1.0 \times 10^{-36} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}\). This rate is considered too slow to play an important role for stratospheric chemistry (Black et al., 1982a). However, given the large isotope effects produced during \(\text{SO}_2\) photolysis, even a minor contribution from Reaction (R4.6) will produce a significant signal on the sulfur isotopic composition of stratospheric sulfate aerosols.

We present results from laboratory photochemical experiments that investigate the effect of temperature and molecular oxygen on the isotope effects produced during \(\text{SO}_2\) photolysis (190 nm to 220 nm) and \(\text{SO}_2\) photoexcitation (250 nm to 350 nm). Using the results of the experiments in the presence of molecular oxygen, we calculate a lower bound estimate on the rate of Reaction (R4.6). Finally, we present a simple steady state photochemical model to show that the rate constraints on Reaction (R4.6) are sufficient for it to make a significant contribution to the isotopic composition of stratospheric sulfate aerosols during volcanically perturbed periods.

4.3 Methods

4.3.1 Photochemical reaction set-up

Conditions for all photochemical experiments are listed in Table 4.1. All experiments were performed in a cylindrical glass photochemical reaction cell with a path length of 15.3 cm and an inner diameter of 5.2 cm (Ono et al., 2013). Temperature-controlled experiments were performed in a jacketed cell of the same dimensions. The front window of the cell was made of UV-grade \(\text{SiO}_2\) (Corning 7980) with greater than 90\% transmittance at wavelengths longer than 190 nm. The window was sealed to the cell with an o-ring and held in place securely with a plastic clamp. Temperature-controlled experiments also utilized a second pre-cell (5.3 cm path length) attached to the front of the window of the reaction cell and held under vacuum. The purpose
of the pre-cell was to thermally insulate the front window and prevent condensation from occurring on the front window during low temperature experiments.

A series of mass-flow controllers controlled the flow rate of gases into the cell. Gas entered the cell through an inlet at the rear of the cell (for temperature cell experiments) or the front of the cell (for other experiments) and exited the cell through an outlet at the opposite end of the cell. An 8 cm to 10 cm length of glass tubing packed with glass wool was placed immediately after the cell exit to trap aerosols formed within the cell. Following the aerosol trap, the gas was flowed through a proportionating valve to a vacuum pump. A capacitance manometer placed before the entrance to the cell monitored the pressure within the cell. The proportionating valve was used to control the pressure within the cell to within 30 Pa of a set point pressure, which was usually 101.3 kPa.

Prior to each temperature-controlled experiment, the reaction cell was flushed with nitrogen (N\textsubscript{2}) for several hours and the chiller was allowed to reach its set point temperature and equilibrate for at least an hour. The temperature of the reaction cell was calibrated relative to the chiller setpoint temperature on two occasions using a series of K-type thermocouples suspended within the cell. During calibrations, N\textsubscript{2} (without SO\textsubscript{2}) was flowed through the cell at a rate of 3.33 cm\textsuperscript{3} s\textsuperscript{-1} (200 sccm, standard cubic centimeters per minute). Thermocouples placed at the front and rear of the cell gave consistent measurements to within 5 K, with a higher gradient at lower temperature. No significant differences were observed between the two calibrations. Results for the temperature calibrations are shown in Figure 4-1.

4.3.2 Temperature effect on SO\textsubscript{2} photolysis (190 nm to 220 nm) and photoexcitation (250 nm to 350 nm)

The temperature effect on SO\textsubscript{2} photolysis (190 nm to 220 nm) was tested using the temperature-controlled reaction cell described in Section 4.3.1. Experiments were performed in a nitrogen-flushed glove box to prevent the spectral interference from the Schumann–Runge bands of oxygen (O\textsubscript{2}). A 200 W deuterium (D\textsubscript{2}) arc lamp (D
Figure 4-1: Results of the temperature calibration for the temperature controlled photochemical reactor described in Section 4.3.1. The linear regression shown was used to calibrate the temperature within the cell based on the setpoint temperature of the chiller. The regression line is $(T_{\text{Cell/}^\circ\text{C}}) = 0.8160 \times (T_{\text{Chiller/}^\circ\text{C}}) + 2.3514$.

200 F, Heraeus Noblelight) was used as the light source without optical filters. The output from the lamp was collimated using a fused silica plano-convex lens. 1000 ppm SO$_2$ (in N$_2$) was flowed through the cell at a rate of 3.33 cm$^3$s$^{-1}$ (200 scfm) for all experiments, and pressure within the cell was held constant at 101.3 kPa, giving an SO$_2$ partial pressure of 0.10 kPa within the cell.

Following photolysis experiments, the cell was removed from the glove box and rinsed well with dichloromethane to dissolve any elemental sulfur that was formed. The glass wool in the aerosol trap was also collected and rinsed with dichloromethane. Elemental sulfur was recrystallized from the dichloromethane and converted to silver sulfide using the reduced chromium chloride method (Whitehill and Ono, 2012; Canfield et al., 1986). Multiple sulfur isotope ratios were measured as described in Section 4.3.4.

Photoexcitation experiments were performed in a room air atmosphere using a 150 W UV-enhanced xenon (Xe) arc lamp (Newport Model 6254) housed in a lamp housing (Newport Model 67005), which focused and collimated the light to a 3.3 cm diameter beam. The light was passed through a liquid filter (Newport Model 51945).
filled with deionized (18.2 MΩ) water and a 250 nm longpass filter (Asahi Spectra, ZUL0250).

Following Whitehill et al. (2013), acetylene (C₂H₂) was used to trap triplet excited-state \( \text{SO}_2 \) (\( ^3\text{SO}_2 \)). During experiments, 5 % \( \text{SO}_2 \) (in \( \text{N}_2 \)), pure \( \text{C}_2\text{H}_2 \) (Atomic Absorption Grade), and pure \( \text{N}_2 \) (Ultra High Purity Grade) were flowed through the cell continuously at a rate of 0.67 \( \text{cm}^3 \text{s}^{-1} \) (40 sccm), 0.03 \( \text{cm}^3 \text{s}^{-1} \) (2 sccm), and 2.63 \( \text{cm}^3 \text{s}^{-1} \) (158 sccm), respectively. Pressure in the cell was held constant at 101.3 kPa, giving a total flow rate of 3.33 \( \text{cm}^3 \text{s}^{-1} \), an \( \text{SO}_2 \) partial pressure of 1.01 kPa, and a \( \text{C}_2\text{H}_2 \) partial pressure of 1.01 kPa within the cell during the experiments.

Following the experiments, the interior walls of the cell and the window were rinsed with ethanol and water to dissolve any organosulfur products formed. The glass wool in the aerosol trap was also collected. The organosulfur aerosol products were converted to silver sulfide using the Raney nickel hydrodesulfurization method of Oduro et al. (2011b). Multiple sulfur isotope ratios were measured as described in Section 4.3.4.

4.3.3 \( \text{SO}_2 \) photochemistry in the presence of \( \text{O}_2 \)

The photochemistry of \( \text{SO}_2+\text{O}_2 \) with ultraviolet radiation was studied using a reaction cell at room temperature. The 150 W Xe arc lamp (described in Section 4.3.2) was used as the light source without the liquid filter. Several experiments were performed with a 200 ± 35 nm bandpass filter (Model 200-B, Acton Research, Acton, MA), a 250 nm longpass filter (Asahi Spectra, ZUL0250), or a 280 nm (285 nm cut-on) longpass filter (Newport Model FSR-WG280) to isolate particular absorption bands of \( \text{SO}_2 \), but most experiments were performed with the Xe lamp and no filters.

Following experiments, the cell was rinsed well first with dichloromethane and then with water. Although sulfate was the dominant product, the cell was rinsed well with dichloromethane first to ensure the removal of elemental sulfur. For two experiments performed with no oxygen, elemental sulfur was recovered. After running the cell with water, 5.0 cm\(^3\) of a 1.0 mol dm\(^{-3}\) solution of barium chloride (\( \text{BaCl}_2 \)) was added to the water used to rinse the cell to precipitate sulfate as barium sulfate.
Barium sulfate was rinsed several times with deionized water and dried. The glass wool inside the aerosol trap was combined with the barium sulfate and all sulfate was converted to silver sulfide using the method of Forrest and Newman (1977). Multiple sulfur isotope ratios were measured as described in Section 4.3.4.

4.3.4 Isotope analysis of photochemical products

Photochemical products were converted to silver sulfide ($\text{Ag}_2\text{S}$). $\text{Ag}_2\text{S}$ was rinsed well three to four times with deionized water and then dried completely at 353 K. Dried $\text{Ag}_2\text{S}$ was weighed for total yield and about 8 $\mu$mol of $\text{Ag}_2\text{S}$ was weighed into an aluminum foil capsule for isotope analysis. Capsules were loaded into nickel reaction chambers and reacted under approximately 7.2 kPa of fluorine gas ($\text{F}_2$) for at least 8 h at 573 K. The resultant $\text{SF}_6$ was purified cryogenically and by gas chromatography. Isotope ratios of pure $\text{SF}_6$ were measured as $\text{SF}_6^+$ ions using a Thermo Scientific MAT 253 Isotope Ratio Mass Spectrometer. For samples where less than 1.6 $\mu$mol of $\text{Ag}_2\text{S}$ was recovered, a microvolume (0.4 cm$^3$ volume) cold finger was used to concentrate the samples for analysis.

Replicate analyses ($N = 28$) of the reference material IAEA-S-1 gave 2$\sigma$ standard deviations of 0.26‰ for $\delta^{34}\text{S}$, 0.014‰ for $\Delta^{33}\text{S}$, and 0.19‰ for $\Delta^{36}\text{S}$ for standard isotope ratio mass spectrometry analysis. Microvolume analyses for smaller samples gave 2$\sigma$ standard deviations for replicate analyses of IAEA-S-1 ($N = 14$) of 0.9‰ for $\delta^{34}\text{S}$, 0.08‰ for $\Delta^{33}\text{S}$, and 0.8‰ for $\Delta^{36}\text{S}$. Replicate experiments performed under identical conditions had differences larger than the analytical uncertainty, suggesting experimental variability was the dominant source of uncertainty in our measurements.

4.3.5 Definitions

Isotopic results will be presented with conventional $\delta$ notation, as relative deviations of isotope ratios with respect to reference sulfur.
\[ \delta^xS = \frac{x R_{\text{product}}}{x R_{\text{reference}}} - 1 \]  \hspace{1cm} (4.1)

where \( x = 33, 34, \) or \( 36 \) and \( x R \) is the ratio of \( ^xS \) to \( ^{32}S \) in the substance. For experimental results all isotope ratios will be normalized to the isotope ratios of the initial SO\(_2\). For natural samples (i.e. stratospheric sulfate aerosol samples), the reference is Vienna Canyon Diablo Troilite (V-CDT).

Mass-independent isotope fractionations in \( ^{33}S/^{32}S \) and \( ^{36}S/^{32}S \) ratios (relative to \( ^{34}S/^{32}S \) ratios) will be presented as \( \Delta^{33}S \) and \( \Delta^{36}S \) values, respectively. These are defined as:

\[ \Delta^{33}S = \frac{\left(\delta^{33}S + 1\right)}{\left(\delta^{34}S + 1\right)^{0.515}} - 1 \]  \hspace{1cm} (4.2)

and

\[ \Delta^{36}S = \frac{\left(\delta^{36}S + 1\right)}{\left(\delta^{34}S + 1\right)^{1.90}} - 1 \]  \hspace{1cm} (4.3)

Almost all physical, chemical, and biological processes fractionate isotopes mass-dependently (i.e. \( \Delta^{33}S \) and \( \Delta^{36}S \) are approximately equal to 0). SO\(_2\) photochemistry, as well as the photochemistry of other sulfur gases such as CS\(_2\), are some of the few exceptions that have been shown to produce mass-independent fractionation. Therefore, non-zero \( \Delta^{33}S \) and \( \Delta^{36}S \) values can be unique tracers of photochemical processes.

### 4.4 Results

All experiments performed are summarized in Table 4.1. Results from temperature experiments on SO\(_2\) photolysis and SO\(_2\) photoexcitation are given in Tables 4.2 and 4.3, whereas results from SO\(_2\) + O\(_2\) experiments are presented in Tables 4.4 and 4.5.
4.4.1 Temperature Experiments

Results from the temperature experiments (Section 4.3.2) are shown in Figure 4-2. The SO₂ photolysis (190 nm to 220 nm) experiments (Table 4.2) revealed that the magnitude of the isotope effects increase with decreasing temperature, from +129 % to +191 %, +5.5 % to +9.1 % and −24.1 % to −35.8 % for δ⁳⁴S, Δ⁳⁴S, and Δ³⁶S, respectively. The relationship between isotopes (i.e. Δ³³S vs. δ³⁴S and Δ³⁶S vs. Δ³³S) did not change significantly as temperature was decreased (0.04 to 0.05 for Δ³³S/δ³⁴S and −3.9 to −4.6 for Δ³⁶S/Δ³³S). Variability between duplicate experiments also increased at lower temperatures, highlighting the difficulty of the low temperature experiments and indicating a strong sensitivity to experimental conditions.

SO₂ photoexcitation (250 nm to 350 nm) show decreasing magnitude Δ³³S and Δ³⁶S values at lower temperature (+22.8 % to +19.0 % and +52.5 % to +46.0 % for Δ³³S and Δ³⁶S, respectively; Table 4.3). Even at lower temperatures, the product from SO₂ photoexcitation experiments show positive Δ³³S and Δ³⁶S values, as shown previously in room temperature experiments (Whitehill and Ono, 2012; Whitehill et al., 2013). As discussed previously (Whitehill et al., 2013), these signatures do not match predictions from isotopologue-specific absorption cross-sections (Danielache et al., 2012), suggesting an additional isotope effect beyond differences in the initial excitation for different isotopologues.

4.4.2 Oxygen experiments

SO₂ photolysis and photoexcitation in the presence of molecular oxygen (O₂) produced mass-independent sulfur isotope signatures in sulfate products (Tables 4.4 and 111
Table 4.2: Isotope ratios of elemental sulfur products from the \( \text{SO}_2 \) photolysis temperature experiments (Section 4.3.2)

<table>
<thead>
<tr>
<th>( T / \text{K} )</th>
<th>( \delta^{33}\text{S}/%_\text{o} )</th>
<th>( \delta^{34}\text{S}/%_\text{o} )</th>
<th>( \delta^{36}\text{S}/%_\text{o} )</th>
<th>( \Delta^{33}\text{S}/%_\text{o} )</th>
<th>( \Delta^{36}\text{S}/%_\text{o} )</th>
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<td>349.12</td>
<td>8.02</td>
<td>-32.4</td>
</tr>
<tr>
<td>225</td>
<td>97.85</td>
<td>177.76</td>
<td>315.71</td>
<td>9.13</td>
<td>-35.8</td>
</tr>
<tr>
<td>250</td>
<td>87.19</td>
<td>161.31</td>
<td>288.97</td>
<td>6.61</td>
<td>-29.8</td>
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<td>250</td>
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<td>146.58</td>
<td>259.31</td>
<td>7.18</td>
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<td>275</td>
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<td>236.37</td>
<td>5.57</td>
<td>-24.1</td>
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<td>70.35</td>
<td>129.04</td>
<td>227.26</td>
<td>5.50</td>
<td>-25.5</td>
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</tbody>
</table>

Table 4.3: Isotope ratios of organosulfur sulfur products from the \( \text{SO}_2 \) photoexcitation temperature experiments (Section 4.3.2)

<table>
<thead>
<tr>
<th>( T / \text{K} )</th>
<th>( \delta^{33}\text{S}/%_\text{o} )</th>
<th>( \delta^{34}\text{S}/%_\text{o} )</th>
<th>( \delta^{36}\text{S}/%_\text{o} )</th>
<th>( \Delta^{33}\text{S}/%_\text{o} )</th>
<th>( \Delta^{36}\text{S}/%_\text{o} )</th>
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<td>65.72</td>
<td>19.01</td>
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<td>67.09</td>
<td>19.73</td>
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</tr>
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<td>250</td>
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<td>64.39</td>
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<td>49.7</td>
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<tr>
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<td>6.37</td>
<td>62.38</td>
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</tr>
<tr>
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</tr>
<tr>
<td>275</td>
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<td>4.84</td>
<td>61.27</td>
<td>22.84</td>
<td>51.6</td>
</tr>
</tbody>
</table>

Figure 4-2: Results of the temperature experiments for \( \text{SO}_2 \) photolysis and \( \text{SO}_2 \) photoexcitation (Section 4.3.2). Results from \( \text{SO}_2 \) photolysis experiments (phot) are shown in filled symbols and \( \text{SO}_2 \) photoexcitation experiments (excit) are in empty symbols.
Table 4.4: Results from experiments of SO\textsubscript{2} photolysis in the presence of varying amounts of O\textsubscript{2} (Section 4.3.3) used to estimate $k_{R4.6}$ (Sections 4.5.3 and 4.5.4) 

<table>
<thead>
<tr>
<th>Product</th>
<th>pO\textsubscript{2} kPa</th>
<th>Time/ks</th>
<th>Yield/pmol S</th>
<th>$\delta^{33}$S/$%$</th>
<th>$\delta^{34}$S/$%$</th>
<th>$\delta^{35}$S/$%$</th>
<th>$\delta^{36}$S/$%$</th>
<th>$\Delta^{33}$S/$%$</th>
<th>$\Delta^{36}$S/$%$</th>
<th>calculated $k_{R4.6}$/$\text{cm}^6\text{molecule}^{-2}\text{s}^{-1}$</th>
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<tbody>
<tr>
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<td>21.6</td>
<td>74.00</td>
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<td>-31.9</td>
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<td>137.52</td>
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<td></td>
<td></td>
</tr>
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<td>S\textsuperscript{0} avg</td>
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</tr>
<tr>
<td>*S\textsuperscript{03}\textsubscript{-1}</td>
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<tr>
<td>*S\textsuperscript{03}\textsubscript{-2}</td>
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<td></td>
</tr>
<tr>
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<td></td>
</tr>
<tr>
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<td>89.24</td>
<td>150.93</td>
<td>5.59</td>
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<td>1.1 x 10\textsuperscript{-37}</td>
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<tr>
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<td>SO\textsubscript{3}</td>
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<td>8.1 x 10\textsuperscript{-38}</td>
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</table>

* S\textsuperscript{0}\textsuperscript{-1} and SO\textsubscript{3}\textsuperscript{-1} are elemental sulfur and SO\textsubscript{3} from the same experiment. Similarly, S\textsuperscript{0}\textsuperscript{-2} and SO\textsubscript{3}\textsuperscript{-2} are elemental sulfur and SO\textsubscript{3} from the same experiment.

4.5). Isotope ratios of this product sulfate are shown in Figure 4-3 and compared with stratospheric sulfate aerosol data from ice cores (Savarino et al., 2003; Bárioni et al., 2007, 2008; Lanciki, 2010; Lanciki et al., 2012). Strong agreement between the Xe lamp data, 200 nm bandpass (200 BP) data, and previous SO\textsubscript{2} photolysis data (Ono et al., 2013) suggest an SO\textsubscript{2} photolysis source for the isotope effects during broadband SO\textsubscript{2} irradiation with the Xe lamp light source.

Experiments focusing on the photoexcitation band of SO\textsubscript{2} using the 250 nm long-pass filter (250 LP) and the 280 nm longpass filter (280 LP) display a different isotope signature, characterized by positive $\Delta^{33}$S and $\Delta^{36}$S values, whereas sulfate from SO\textsubscript{2} photolysis has positive $\Delta^{33}$S and negative $\Delta^{36}$S values. This is consistent with previous findings (Whitehill and Ono, 2012; Whitehill et al., 2013) and demonstrates the MIF in this band region is not produced by chemistry related to acetylene or oxygen.

However, the magnitude of the sulfur MIF signatures (i.e. $\Delta^{33}$S and $\Delta^{36}$S values) are considerably smaller than previous experiments using C\textsubscript{2}H\textsubscript{2} (Table 4.3, Whitehill et al., 2013). This suggests that a considerable amount of sulfate in the system is being produced by a mass-dependent process, such as $^{16}$SO\textsubscript{2} + SO\textsubscript{2} $\rightarrow$ SO + SO\textsubscript{3} (Whitehill and Ono, 2012). This would dilute the MIF signature. In addition, there
Table 4.5: Results from additional experiments of \( \text{SO}_2 \) photolysis in the presence of \( \text{O}_2 \) (Section 4.3.3). All results are from sulfate (\( \text{SO}_3 \)) product. Experiments were performed at a constant total pressure of 101.3 kPa unless marked otherwise. Filter types are: 200 BP = 200 nm bandpass filter, 250 LP = 250 nm longpass filter, 280 LP = 280 nm longpass filter.

<table>
<thead>
<tr>
<th>Filter</th>
<th>( p\text{SO}_2 )</th>
<th>( p\text{O}_2 )</th>
<th>Flow/Time/Yield</th>
<th>( \delta^{33}\text{S} / % )</th>
<th>( \delta^{34}\text{S} / % )</th>
<th>( \Delta^{33}\text{S} / % )</th>
<th>( \Delta^{38}\text{S} / % )</th>
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<td>19.00</td>
<td>16.67 1.8 62.3</td>
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<td>117.84</td>
<td>4.22</td>
</tr>
<tr>
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<td>18.99</td>
<td>6.67 12.8 105.7</td>
<td>34.71</td>
<td>60.89</td>
<td>104.88</td>
<td>3.69</td>
</tr>
<tr>
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<td>3.22</td>
<td>4.25</td>
<td>9.34</td>
<td>1.03</td>
</tr>
</tbody>
</table>

* Experiment performed at 7.7 kPa total pressure to test low pressure limit.

Figure 4-3: Isotopic results of the \( \text{SO}_2 + \text{O}_2 \) experiments described in Section 4.3.3, compared with stratospheric sulfate aerosol samples (SSA Data) from Savarino et al. (2003); Bároni et al. (2007, 2008); Lanciki (2010); Lanciki et al. (2012).
is considerable variability (i.e. a factor of approximately 2) observed between the two 250 nm longpass filter experiments, despite identical experimental conditions. The cause of this variability is uncertain but could relate to the amount of water vapor in the system.

4.5 Discussion

4.5.1 Origin of mass-independent fractionation during SO₂ photochemistry

The differences in the photophysics and photochemistry between the photolysis region (190 nm to 220 nm) and the photoexcitation region (250 nm to 350 nm) suggest different mechanisms for MIF formation, as discussed previously (Whitehill and Ono, 2012; Ono et al., 2013; Whitehill et al., 2013).

In the 165 nm to 235 nm wavelength region, SO₂ photolysis occurs through predissociation from the bound C₁B₂ state. Near the dissociation threshold of 218.7 nm (Becker et al., 1995), the quantum yield of photolysis is less than unity, although it increases to greater than 0.99 at wavelengths shorter than 215 nm (Katagiri et al., 1997). In the region where the quantum yield is close to unity (i.e. less than 215 nm), the isotope effects due to SO₂ photolysis should be determined entirely by the differences in absorption cross-sections between the different isotopologues of SO₂ (e.g., by isotopologue specific Franck-Condon coupling; Danielache et al. 2008) and optical screening effects under high SO₂ column densities (Lyons, 2007, 2008; Ono et al., 2013). In the narrow spectral region from 215 nm to 218.7 nm, where the quantum yield of photodissociation varies, it is possible that quantum yield differences between isotopologues could potentially produce additional isotope effects beyond those predicted from absorption cross-sections. However, in this region, photodissociation occurs primarily via vibronic mixing of the C₁B₂ state levels with the dissociative continuum of the electronic ground X₁A₁ state (Katagiri et al., 1997). Due to the high density of vibronic levels for the X₁A₁ state, it is unlikely that there will be sig-
nificant isotope effects in the coupling strength between the $\tilde{C}^1B_2$ and $\tilde{X}^1A_1$ states. Dissociation occurring through mixing with repulsive singlet and triplet states is expected to be small, as is the nonadiabatic coupling of the $\tilde{C}^1B_2$ and $\tilde{D}^1A_1$ states (Tokue and Nanbu, 2010).

For laboratory experiments, the observed isotope effects for $\text{SO}_2$ photolysis is a function not only of differences in the absorption cross-sections (Danielache et al., 2008) but also a function of the $\text{SO}_2$ column density. This is because the $\text{SO}_2$ absorption cross-section has significant fine structure, which causing optical screening effects to occur (Lyons, 2007). This optical screening effect produces larger isotope effects at higher $\text{SO}_2$ column densities (Ono et al., 2013). In addition to the above effects, there appears to be a total (or bath gas) pressure effect on $\Delta^{33}\text{S}$ values. This manifests as reduced $\Delta^{33}\text{S}$ values at higher total (i.e. bath gas) pressures, which is observed with He, $\text{SO}_2$, and $\text{N}_2$ bath gases (Masterson et al., 2011; Whitehill and Ono, 2012; Ono et al., 2013). The mechanism responsible for these pressure effects is still uncertain, but it could suggest that $^{33}\text{SO}_2$ has a longer excited-state lifetime prior to dissociation than the other isotopologues.

$\text{SO}_2$ photoexcitation in the 250 nm to 350 nm absorption region also produces absorption-based isotope effects due to differences in cross-sections and self-shielding. In addition, it produces isotope effects by a completely different mechanism. $\text{SO}_2$ photoexcitation in the 250 nm to 350 nm region occurs by initial excitation into a coupled $\tilde{A}^1A_2/\tilde{B}^1B_1$ singlet excited state that undergoes intersystem crossing to the photochemically active triplet $\tilde{a}^3B_1$ state. Unlike $\text{SO}_2$ photolysis, where the quantum yield of reaction (i.e. photolysis) is near unity, the quantum yield for intersystem crossing between the singlet and triplet states is highly variable and state-dependent. Due to the relatively low density of states in the crossing region ($\tilde{A}^1A_2 \rightarrow \tilde{a}^3B_1$), the branching between quenching to the ground state and intersystem crossing to the triplet state will be a strong function of isotope substitution. Whitehill et al. (2013) argue that this isotope selective intersystem crossing is the origin of part of the isotope effects in photochemical products following $\text{SO}_2$ photoexcitation in the 250 nm to 350 nm absorption region.
Photoexcitation of SO$_2$ in the presence of O$_2$ produces sulfate with both positive $\Delta^{33}$S and positive $\Delta^{36}$S values, similar to the organic sulfur observed in Whitehill et al. (2013) and the elemental sulfur in Whitehill and Ono (2012). This suggests that the anomalous isotope signatures observed from photoexcitation in previous studies are a result of the photophysics and photochemistry of excited-state SO$_2$ rather than the chemistry of the subsequent reactions (i.e., the chemistry with acetylene). Our experimental results show a significant discrepancy with isotope effects predicted by isotopologue-specific absorption cross-sections (Danielache et al., 2012; Hattori et al., 2013) for the 250 nm to 320 nm region (Whitehill et al., 2013). This is expected if isotope selective intersystem crossing is contributing to the isotope signals in addition to cross section differences and shielding effects.

4.5.2 Temperature effects on SO$_2$ photolysis

Lyons (2007, 2008) presented isotopologue-specific absorption cross-sections for SO$_2$ in the 190 nm to 220 nm absorption region by shifting the measured $^{32}$SO$_2$ absorption cross-sections of Freeman et al. (1984) by an amount based on the calculated isotope shifts of Ran et al. (2007). It has been unclear whether these absorption cross-sections can correctly predict the isotope effects due to SO$_2$ photolysis (Danielache et al., 2008), as they include only the isotope shifts and not other potential differences among isotopologues. Previous comparisons with experimental data showed significant discrepancies (i.e. a factor of $\sim$ 2 in $\delta^{34}$S values) between experimental data and that predicted by the Lyons (2007, 2008) cross-sections (Whitehill and Ono, 2012; Ono et al., 2013). Such discrepancies were attributed to the difference in temperature between the Lyons (2007, 2008) cross-sections, which are based on cross-sections measured at 213 K (Freeman et al., 1984) and the temperature of the experiments (298 K). Given the new temperature data in the present study, it is possible to compare calculations based on the Lyons (2007, 2008) cross-sections with temperature-dependent experimental isotope data. Calculations were performed as described in previous papers (Whitehill and Ono, 2012; Ono et al., 2013) and are compared to experimental data in Figure 4-4.
Figure 4-4: Comparison of $\text{SO}_2$ photolysis temperature experiment results with predictions from isotopologue-specific absorption cross-sections (CS).
Excellent agreement with the Lyons (2007, 2008) cross-sections can be seen when the observed temperature dependence on $\delta^{34}\text{S}$ are extrapolated back to 213 K. A similar strong agreement is also seen in the $\Delta^{36}\text{S}$ values. This new data fills in the major gap between predictions based on the Lyons (2007, 2008) cross-sections and the room temperature experimental data, and provides further support to an optical origin of mass-independent fractionation during $\text{SO}_2$ photolysis under laboratory conditions (Ono et al., 2013).

Despite the strong agreement for $\delta^{34}\text{S}$ and $\Delta^{36}\text{S}$ values the Lyons (2007, 2008) cross-sections over-predict the magnitude of the mass-independent isotope anomaly in $^{33}\text{S}$ (i.e. $\Delta^{33}\text{S}$ values) when compared with experimental data. There are several possible explanations for this. One reason is that there are significant differences between the actual cross-sections and those predicted by shifting the $^{32}\text{SO}_2$ cross-sections for $^{33}\text{SO}_2$. Measurements by Danielache et al. (2008) at room temperature suggest that there are some differences between the isotopologue-specific absorption cross-sections aside from just the spectral shifts accounted for by Lyons (2007, 2008). A second possibility is that the high total pressure (101.3 kPa, including the $\text{N}_2$ bath gas) of the experiments caused a decrease in the $\Delta^{33}\text{S}$ value relative to the values observed at lower pressures. It has been previously observed (Masterson et al., 2011; Whitehill and Ono, 2012; Ono et al., 2013) that $\Delta^{33}\text{S}$ values decrease in the presence of high bath gas pressures. This pressure quenching effect is most noticeable for $\Delta^{33}\text{S}$ and does not affect $\delta^{34}\text{S}$ or $\Delta^{36}\text{S}$ values as strongly.

The Lyons (2007, 2008) cross sections are semi-empirical; they take the measured $^{32}\text{SO}_2$ cross-sections of Freeman et al. (1984) and shift them using the theoretical isotope shifts predicted by Ran et al. (2007). Although the Lyons (2007, 2008) cross-sections are not necessarily accurate, the Lyons (2007, 2008) cross-sections seem to accurately predict the isotope effects during $\text{SO}_2$ photolysis under low temperature (ca. 213 K) conditions, such as those in the stratosphere.
4.5.3 Constraining the rate of the SO + O\(_2\) + M reaction using product formation

Our results demonstrate that the photolysis of SO\(_2\) in the presence of molecular oxygen (O\(_2\)) produces large amounts of sulfate with considerable mass-independent sulfur isotope anomalies. In our experimental system, there are three dominant pathways for SO\(_3\) formation: OH oxidation of SO\(_2\) (Reactions R4.1 and R4.2, if water is present), O\(_2\) oxidation of SO from SO\(_2\) photolysis (Reactions R4.4 and R4.6), and O oxidation of SO\(_2\) via

\[ \text{SO}_2 + \text{O} + \text{M} \rightarrow \text{SO}_3 + \text{M} \]  

(R4.7)

OH and O oxidation of SO\(_2\) (Reactions R4.1 and R4.7) are mass dependent (Harris et al., 2012; Whitehill and Ono, 2012; Ono et al., 2013). However, oxidation of SO via Reaction R4.6 will trap the isotopic composition of SO as SO\(_3\) and carry the mass-independent sulfur isotope signature from SO\(_2\) photolysis (Reaction R4.4).

We performed a series of experiments at a total pressure of 101.3 kPa, a flow rate of 6.67 cm\(^3\) s\(^{-1}\) (400 sccm) and an SO\(_2\) partial pressure of 0.127 kPa (Table 4.4, Figure 4-5). The partial pressure of molecular oxygen was varied from 0 kPa to 19.8 kPa (0% to 19.5% O\(_2\)). In all experiments, SO\(_2\) was photolyzed via Reaction R4.4. In the experiments with no oxygen, both elemental sulfur (S\(^0\)) and SO\(_3\) aerosols were formed, with the elemental sulfur (S and related species) formed from SO via

\[ \text{SO} + \text{SO} \rightarrow \text{SO}_2 + \text{S} \]  

(R4.8)

SO photolysis is expected to be a minor source of S compared to Reaction R4.8. In the absence of oxygen, SO\(_3\) is formed primarily via O oxidation of SO\(_2\) (Reaction R4.7), which is mass dependent (Ono et al., 2013).

At 5.1 kPa O\(_2\) and above, elemental sulfur formation was shut off and SO\(_3\) was the major product. Under these conditions, oxidation of SO (to SO\(_2\) or SO\(_3\) via Reactions R4.5 and R4.6) competes with SO disproportionation (Reaction R4.8).

By comparing the \(\Delta^{33}\text{S}\) value of elemental sulfur in the absence of O\(_2\) (0 kPa
Figure 4-5: $\Delta^{33}S$ values of sulfate from photolysis of SO$_2$ in the presence of O$_2$ compared with elemental sulfur and sulfate from SO$_2$ photolysis in the absence of O$_2$. Conditions are described in Section 4.5.3 and Table 4.4.

O$_2$) with the $\Delta^{33}S$ value of sulfate in the presence of O$_2$ (5.1 kPa to 19.8 kPa O$_2$), it is possible to estimate the fraction of sulfate formed through Reaction R.4.6. In particular,

$$f_{R.4.6} = \frac{\Delta^{33}S_{\text{sulfate with } O_2}}{\Delta^{33}S_{\text{S}, \text{ no } O_2}}$$

(4.4)

where $f_{R.4.6}$ is the fraction of total SO$_3$ formed that comes from Reaction R.4.6. Given the product yields (Table 4.4), the time each experiment was run, and the volume of the reaction cell (approximately 325 cm$^3$), the sulfate formation rate per unit volume per unit time can be calculated. In experiments with 5.1 kPa to 19.8 kPa O$_2$, the sulfate formation rates were between $5.3 \times 10^{12}$ molecule cm$^{-3}$ s$^{-1}$ and $1.2 \times 10^{13}$ molecule cm$^{-3}$ s$^{-1}$. Combining this with the $f_{R.4.6}$ values calculated from Equation 4.4, we can estimate the rate of sulfate formation from Reaction R.4.6 under our experimental conditions. This gave a rate for Reaction R.4.6 of $3.6 \times 10^{12}$ molecule cm$^{-3}$ s$^{-1}$ to $6.6 \times 10^{12}$ molecule cm$^{-3}$ s$^{-1}$. Assuming Reaction
R 4.6 is a termolecular reaction, the rate for Reaction R 4.6 can be written as:

\[ \text{rate R 4.6} = k_{R4.6} [\text{SO}][O_2][M] \]  

(4.5)

where \( k_{R4.6} \) is the termolecular rate constant for Reaction R 4.6 and [SO], [O_2], and [M] are the concentrations of SO, O_2, and total third body gases (M = N_2, O_2) in the reaction cell. In Equation 4.5, the [O_2] and [M] terms are known from the experimental conditions. The [SO] term is estimated by assuming a photochemical steady state for SO in the cell. SO production via Reaction R 4.4 is balanced by SO destruction via Reactions R 4.5 and R 4.6. This gives us a steady state SO concentration of:

\[ [\text{SO}] = \frac{J_{\text{SO}_2}[\text{SO}_2]}{k_{R4.5}[O_2] + k_{R4.6}[O_2][M]} \]  

(4.6)

where \( J_{\text{SO}_2} \) is the photolysis rate constant for Reaction R 4.4. This photolysis rate constant was calculated assuming a spectral irradiance for our 150 W Xe arc lamp of:

\[ F_0/\text{mW nm}^{-1} = 0.11 \cdot 1.6 \cdot (14 - 9 \cdot \exp(-0.013 \cdot (\lambda/\text{nm} - 200))) \]  

(4.7)

where \( F_0 \) is the spectral irradiance of the xenon lamp at wavelength \( \lambda \) (Ono et al., 2013). This flux might be modified slightly as a function of the distance between the cell and the lamp, due to interferences from the absorption of oxygen. However, sensitivity studies performed here and previously (Whitehill and Ono, 2012) suggest that the effect of the oxygen absorption on the total \( \text{SO}_2 \) photolysis rate is minor compared to the uncertainty in the lamp photon flux. The lamp photon flux data was determined from the manufacturer’s data and uncertainty estimates were not available. Despite this, the function used by Ono et al. (2013) (Equation 4.7) was used to obtain an estimate for the total \( \text{SO}_2 \) photolysis rate.

The spectral irradiance of the lamp was used to calculate the photon flux entering the cell, accounting for absorption of the cell windows from measured transmission data. The \( \text{SO}_2 \) absorption cross-sections of Manatt and Lane (1993) were used to calculate the photolysis rate in the cell, accounting for optical screening effects from
SO₂ and O₂ within the cell. With an SO₂ partial pressure of 0.127 kPa, this provided a photolysis rate constant of $J_{SO_2} = 5.2 \times 10^{-3} \text{s}^{-1}$. The rate constant for reaction R 4.5 is $k_{R4.5} = 8.0 \times 10^{-17} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ (Sander et al., 2011) at room temperature (298 K). Using these values and Equations 4.6 and 4.7, the rate constant for Reaction R 4.6 was calculated iteratively. Calculated rate constants ranged from $k_{R4.6} = 7.3 \times 10^{-38} \text{cm}^6\text{molecule}^{-2}\text{s}^{-1}$ to $k_{R4.6} = 1.4 \times 10^{-37} \text{cm}^6\text{molecule}^{-2}\text{s}^{-1}$, with an average value of $k_{R4.6} = 1.1 \times 10^{-37} \text{cm}^6\text{molecule}^{-2}\text{s}^{-1}$ (Table 4.4). This rate estimate is consistent with the upper bound on $k_{R4.6} \leq 1 \times 10^{-36} \text{cm}^6\text{molecule}^{-2}\text{s}^{-1}$ by Black et al. (1982a).

The calculated rate constant ($k_{R4.6}$) appears to decrease at 19.8 kPa O₂ compared with the calculated rate for lower $pO_2$ values. It is unclear why this behavior is observed. The relatively strong agreement for the other conditions strengthens our confidence that the model is robust.

The derived rate constant carries uncertainty due to a number of sources of error in the rate calculation. One source of error in the calculation is in the spectral irradiance of the xenon lamp, which was fit from the manufacturer’s literature and not directly measured. Because the spectral irradiance is likely to change during the lamp’s lifetime, the actual spectral irradiance at the time the experiments were performed might be different than the values calculated here. As the spectral irradiance in the high-energy side of the ultraviolet (190 nm to 220 nm) is likely to decrease over the course of the lamp’s lifetime, this makes the calculated SO₂ photolysis rate (and resulting SO number density) an upper bound. Reducing the SO₂ photolysis rate increases the effective rate constant. A second source of error is the assumption that we trapped 100% of the SO₃ formed as sulfate. It is possible that some fraction of the SO₃ remained in the gas phase and did not condense as aerosol particles. A third source of error is the assumption that Reaction R 4.6 behaves as a termolecular reaction despite the high total pressure (101.3 kPa) of the system. It is possible that the reaction is saturated at (or near) this pressure and is thus behaving as an effective bimolecular reaction. In any of these three cases, the estimate of the rate constant for Reaction R 4.6 would be a lower bound on the actual termolecular rate constant.
It is also important to consider the impact of water vapor within the system. Although attempts were made to minimize the amount of water vapor in the system, there was almost certainly some water vapor in the system during our experiments. This is evidenced by the visible formation of sulfate aerosols from SO$_3$ during the experiments. Unfortunately, we did not have the analytical capability to quantitatively constrain the amount of water vapor in the system during the experiments. The Zero Air and Nitrogen used as a source of gas to the cell has a maximum of 3 ppm H$_2$O (by volume), but there could be additional water absorbed onto the surfaces of the system while the cell is disassembled. We assume 100% of the SO$_3$ was trapped as sulfate, giving a lower bound estimate on the rate of Reaction R4.6.

### 4.5.4 Constraining the rate of the SO + O$_2$ + M reaction using a kinetic model

To further constrain the rate of Reaction R 4.6 (the SO+O$_2$+M $\rightarrow$ SO$_3$+M reaction) we constructed a kinetic model of the chemistry occurring within the cell. We used the same data and conditions as in Section 4.5.3, but explicitly modeled the chemistry occurring within the system. SO$_2$ photolysis rates were calculated as discussed in Section 4.5.3, using the cross sections of Manatt and Lane (1993). Oxygen and ozone photolysis rates were calculated using the cross-sections of Yoshino et al. (1988, 1992) for O$_2$ and Molina and Molina (1986) for O$_3$. Quantum yields for O($^1$D) versus O($^3$P) formation from O$_3$ photolysis were parameterized based on the recommendations of DeMore et al. (1997). Photolysis rates for HO$_2$ and H$_2$O$_2$ were calculated using the recommended cross-sections of Sander et al. (2011). HO$_2$ photolysis was assumed to produce O($^1$D) and OH as products, and H$_2$O$_2$ photolysis was assumed to produce 2 $\times$ OH).

Reactions considered, rate constants for this reactions, and the sources for the rate constants are given in Tables 4.6, 4.7, and 4.8. Effective second-order rate constants (calculated assuming $T = 298$ K and $[M] = 2.5 \times 10^{19}$ molecule cm$^{-3}$) were used for termolecular reactions. Initial guesses were made for the concentration of species
within the system. The system was assumed to be in photochemical steady state and solved iteratively until convergence. Comparisons were made between the data and the calculations for \( f_{R,4.6} \) values (Equation 4.4). Simulations were performed with values of \( k_{R,4.6} \) of \( 1.0 \times 10^{-37} \text{cm}^6 \text{molecule}^{-2} \text{s}^{-1} \), \( 1.0 \times 10^{-36} \text{cm}^6 \text{molecule}^{-2} \text{s}^{-1} \), and \( 1.0 \times 10^{-35} \text{cm}^6 \text{molecule}^{-2} \text{s}^{-1} \). Since the amount of water vapor in the system was not constrained experimentally, three simulations were performed, with \( \text{H}_2\text{O} \) concentrations of 0 ppm (by volume), 10 ppm (by volume), and 100 ppm (by volume), which spans a range of reasonable estimates for water vapor concentration in the system. Although water vapor in the bath gas (\( \text{N}_2 \) and \( \text{N}_2/\text{O}_2 \)) are less than 3 ppm (by volume), additional water could be absorbed onto the inner surfaces of the cell and released during the experiment. Results for 0 ppm \( \text{H}_2\text{O} \) and 10 ppm \( \text{H}_2\text{O} \) predict rates for Reaction R 4.6 on the order of \( 1.0 \times 10^{-36} \text{cm}^6 \text{molecule}^{-2} \text{s}^{-1} \), with predictions for 100 ppm \( \text{H}_2\text{O} \) being slightly higher.

There is a discrepancy between model prediction and the observed experimental behavior. In particular, lower \( \text{O}_2 \) fractions produce higher estimated rates and vice versa. In addition, the model predicts rates mostly higher than the previous upper bound on the rate calculated by Black et al. (1982a) of \( 1.0 \times 10^{-36} \text{cm}^6 \text{molecule}^{-2} \text{s}^{-1} \). Helium was used as a bath gas for the Black et al. (1982a) experiments, as compared with nitrogen or nitrogen / oxygen used as the bath gas here. Nitrogen (\( \text{N}_2 \)) and oxygen (\( \text{O}_2 \)) are a more efficient third body quenchers than helium. Thus, the rate of the termolecular reaction with nitrogen (or nitrogen/oxygen) as a bath gas could be higher than the maximum constraint suggested by Black et al. (1982a). There is also an order of magnitude discrepancy between the predictions here and those in Section 4.5.3, with those in Section 4.5.3 being an order of magnitude smaller than those in Section 4.5.4. This could be based on the assumption that 100% of the \( \text{SO}_3 \) was trapped as sulfate in Section 4.5.3, whereas the actual amount might be less than that (implying a higher rate than predicted in Section 4.5.3). However, the model predicts rate constants within an order of magnitude of previous constraints from the literature (Black et al., 1982a) and Section 4.5.3. Based on this work, we estimate the rate of this reaction to be on the order of \( 1.0 \times 10^{-37} \text{cm}^6 \text{molecule}^{-2} \text{s}^{-1} \).
to $1.0 \times 10^{-36}$ cm$^6$ molecule$^{-2}$ s$^{-1}$. Future work is necessary to better constrain the rate of this reaction.

4.5.5 Contribution of the SO + O$_2$ + M reaction to sulfate formation in the stratosphere

To determine the significance of Reaction R 4.6 to sulfate formation in the stratosphere, we compared the rate of sulfate formation via Reaction R 4.6 to that formed via OH oxidation of SO$_2$ (Reaction R 4.1) and O oxidation of SO$_2$ (Reaction R 4.7) under a select set of atmospheric conditions. We assumed an atmospheric temperature and pressure profile of the US Standard Atmosphere 1976 (COESA (Committee on Extension to the Standard Atmosphere), 1976) and noon-time O, OH, and O$_3$ concentrations given by DeMore et al. (1997). Spectral photon flux in the 180 nm to 220 nm region was calculated as a function of altitude for a solar zenith angle of 40° by assuming the spectral photon irradiance of Rottman et al. (2006) at the top of the atmosphere and O$_2$, O$_3$, and CO$_2$ being dominant absorbers. Absorption cross-sections of O$_2$ (Yoshino et al., 1988, 1992), O$_3$ (Molina and Molina, 1986), and CO$_2$ (Shemansky, 1972) were used with the concentrations and column density data for the species to calculate the transmission of the atmosphere to radiation in the 180 nm to 220 nm absorption region at different altitudes. SO$_2$ photolysis rate constants ($J_{SO_2}$) were calculated as a function of altitudes using the calculated spectral photon fluxes and the SO$_2$ absorption cross-sections of Manatt and Lane (1993).

The lifetime of SO with respect to oxidation by O$_2$ (i.e. R 4.5 and R 4.6) is relatively short (on the order of seconds), so SO and SO$_2$ were assumed to be in photochemical steady state, i.e.

$$\frac{[SO]}{[SO_2]} = \frac{J_{SO_2}}{k_{R4.5}[O_2] + k_{R4.6}[O_2][M]}$$ (4.8)

The rate constant $k_{R4.5}$ was calculated as a function of altitude (i.e. temperature) based on the recommendations of Sander et al. (2011). $k_{R4.6}$ was varied between $1.0 \times 10^{-37}$ cm$^6$ molecule$^{-2}$ s$^{-1}$ and $1.0 \times 10^{-36}$ cm$^6$ molecule$^{-2}$ s$^{-1}$ to encompass the
Table 4.6: Reactions and rate constants included in the kinetic model of the chemistry occurring within reaction cell. I. Photochemical Reactions and Oₓ, O(¹D) Chemistry. Rate constants have units of s⁻¹ for first order reactions, cm³ molecule⁻¹ s⁻¹ for second order reactions (and effective second order reactions), and cm⁶ molecule⁻² s⁻¹ for third order reactions.

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<th>Reaction Number</th>
<th>Reaction</th>
<th>Rate constant</th>
<th>Reaction Order</th>
<th>Source</th>
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<td></td>
</tr>
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<td>1</td>
<td>O₂ + hν → O + O</td>
<td>1.01 × 10⁻⁵</td>
<td>1</td>
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<td>5.71 × 10⁻³</td>
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<td>Molina and Molina (1986)</td>
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<td>3</td>
<td>O₃ + hν → O(¹D) + O₂</td>
<td>1.04 × 10⁻¹</td>
<td>1</td>
<td>Molina and Molina (1986)</td>
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<td>4</td>
<td>H₂O₂ + hν → OH + OH</td>
<td>1.74 × 10⁻³</td>
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<td>Sander et al. (2011)</td>
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<td>HO₂ + hν → O(¹D) + OH</td>
<td>1.51 × 10⁻²</td>
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<td>Sander et al. (2011)</td>
</tr>
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<td>6</td>
<td>SO₂ + hν → SO + O</td>
<td>5.20 × 10⁻³</td>
<td>1</td>
<td>Manatt and Lane (1993)</td>
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<td>7</td>
<td>SO + hν → S + O</td>
<td>9.70 × 10⁻³</td>
<td>1</td>
<td>Phillips (1981)</td>
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<td>Oₓ Chemistry</td>
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<tr>
<td>8</td>
<td>O + O + M → O₂ + M</td>
<td>2.50 × 10⁻¹⁴</td>
<td>*2</td>
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<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>13</td>
<td>O(¹D) + O₂ → O + O₂</td>
<td>1.20 × 10⁻¹⁰</td>
<td>2</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>14</td>
<td>O(¹D) + H₂ → OH + H</td>
<td>1.20 × 10⁻¹⁰</td>
<td>2</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>15</td>
<td>O(¹D) + H₂O → OH + OH</td>
<td>2.00 × 10⁻¹⁰</td>
<td>2</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>16</td>
<td>O(¹D) + N₂ → O + N₂</td>
<td>3.10 × 10⁻¹¹</td>
<td>2</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>17</td>
<td>O(¹D) + SO₂ → product</td>
<td>2.20 × 10⁻¹⁰</td>
<td>2</td>
<td>Sander et al. (2011)</td>
</tr>
</tbody>
</table>

* Effective second order reactions based on falloff curves for [M] = 2.5 × 10¹⁹ and M = N₂, O₂. See sources for additional information.
Table 4.7: Reactions and rate constants included in the kinetic model of the chemistry occurring within reaction cell. II. HOx Chemistry. Rate constants have units of $s^{-1}$ for first order reactions, $cm^3/molecule^{-1}s^{-1}$ for second order reactions (and effective second order reactions), and $cm^6/molecule^{-2}s^{-1}$ for third order reactions.

<table>
<thead>
<tr>
<th>Reaction Number</th>
<th>Reaction</th>
<th>Rate constant</th>
<th>Reaction Order</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>H0x Chemistry</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>$O + OH \rightarrow O_2 + H$</td>
<td>$3.30 \times 10^{-11}$</td>
<td>2</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>19</td>
<td>$O + HO_2 \rightarrow OH + O_2$</td>
<td>$5.90 \times 10^{-11}$</td>
<td>2</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>20</td>
<td>$O + H_2O_2 \rightarrow OH + HO_2$</td>
<td>$1.80 \times 10^{-15}$</td>
<td>2</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>21</td>
<td>$H + O_2 + M \rightarrow HO_2 + M$</td>
<td>$9.74 \times 10^{-13}$</td>
<td>2</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>22</td>
<td>$H + O_3 \rightarrow OH + O_2$</td>
<td>$2.90 \times 10^{-11}$</td>
<td>2</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>23</td>
<td>$H + HO_2 \rightarrow OH + OH$</td>
<td>$7.20 \times 10^{-11}$</td>
<td>2</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>24</td>
<td>$H + HO_2 \rightarrow O + H_2O$</td>
<td>$1.60 \times 10^{-12}$</td>
<td>2</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>25</td>
<td>$H + HO_2 \rightarrow H_2 + O_2$</td>
<td>$6.90 \times 10^{-12}$</td>
<td>2</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>26</td>
<td>$OH + O_3 \rightarrow HO_2 + O_2$</td>
<td>$7.30 \times 10^{-14}$</td>
<td>2</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>27</td>
<td>$OH + H_2 \rightarrow H_2O + H$</td>
<td>$6.70 \times 10^{-15}$</td>
<td>2</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>28</td>
<td>$OH + OH \rightarrow H_2O + O$</td>
<td>$1.80 \times 10^{-12}$</td>
<td>2</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>29</td>
<td>$OH + OH + M \rightarrow H_2O_2 + M$</td>
<td>$6.35 \times 10^{-12}$</td>
<td>2</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>30</td>
<td>$OH + HO_2 \rightarrow H_2O + O_2$</td>
<td>$1.10 \times 10^{-10}$</td>
<td>2</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>31</td>
<td>$OH + H_2O_2 \rightarrow H_2O + HO_2$</td>
<td>$1.80 \times 10^{-12}$</td>
<td>2</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>32</td>
<td>$HO_2 + O_3 \rightarrow OH + O_2 + O_2$</td>
<td>$1.90 \times 10^{-15}$</td>
<td>2</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>33</td>
<td>$HO_2 + HO_2(M) \rightarrow H_2O_2 + O_2(M)$</td>
<td>$2.55 \times 10^{-12}$</td>
<td>2</td>
<td>Sander et al. (2011)</td>
</tr>
</tbody>
</table>

* Effective second order reactions based on falloff curves for $[M] = 2.5 \times 10^{19}$ and $M = N_2$, $O_2$. See sources for additional information.
Table 4.8: Reactions and rate constants included in the kinetic model of the chemistry occurring within reaction cell. III. SOx chemistry and others. Rate constants have units of s\(^{-1}\) for first order reactions, cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) for second order reactions (and effective second order reactions), and cm\(^6\) molecule\(^{-2}\) s\(^{-1}\) for third order reactions.

<table>
<thead>
<tr>
<th>Reaction Number</th>
<th>Reaction</th>
<th>Rate constant</th>
<th>Reaction Order</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>34</td>
<td>O + SO(_2) + M → SO(_3) + M</td>
<td>1.29 × 10(^{-11})</td>
<td>2</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>35</td>
<td>O(_3) + SO(_2) → SO(_3) + O(_2)</td>
<td>2.00 × 10(^{-22})</td>
<td>2</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>36</td>
<td>OH + S → H + SO</td>
<td>6.60 × 10(^{-11})</td>
<td>2</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>37</td>
<td>OH + SO → H + SO(_2)</td>
<td>8.30 × 10(^{-11})</td>
<td>2</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>38</td>
<td>OH + SO(_2) + M → HOSO(_2) + M</td>
<td>9.64 × 10(^{-13})</td>
<td>2</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>39</td>
<td>HO(_2) + SO(_2) → OH + SO(_3)</td>
<td>1.00 × 10(^{-18})</td>
<td>2</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>40</td>
<td>S + O(_2) → SO + O</td>
<td>2.30 × 10(^{-12})</td>
<td>2</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>41</td>
<td>S + O(_3) → SO + O(_2)</td>
<td>1.20 × 10(^{-11})</td>
<td>2</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>42</td>
<td>SO + O(_2) → SO(_2) + O</td>
<td>8.00 × 10(^{-17})</td>
<td>2</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>43</td>
<td>SO + O(_2) + M → SO(_3) + M</td>
<td>Varies</td>
<td>3</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>44</td>
<td>SO + O(_3) → SO(_2) + O(_2)</td>
<td>8.40 × 10(^{-14})</td>
<td>2</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>45</td>
<td>HOSO(_2) + O(_2) → HO(_2) + SO(_3)</td>
<td>4.30 × 10(^{-13})</td>
<td>2</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>46</td>
<td>SO + HO(_2) → SO(_2) + OH</td>
<td>2.80 × 10(^{-11})</td>
<td>2</td>
<td>DeMore et al. (1997)</td>
</tr>
<tr>
<td>47</td>
<td>SO + SO → SO(_2) + S</td>
<td>8.30 × 10(^{-16})</td>
<td>2</td>
<td>Chung et al. (1975)</td>
</tr>
<tr>
<td>48</td>
<td>SO + O + M → SO(_2) + M</td>
<td>1.30 × 10(^{-11})</td>
<td>2</td>
<td>Cobos et al. (1985)</td>
</tr>
<tr>
<td>49</td>
<td>SO + SO(_2) → SO(_2) + SO(_2)</td>
<td>1.99 × 10(^{-15})</td>
<td>2</td>
<td>Chung et al. (1975)</td>
</tr>
<tr>
<td>50</td>
<td>S + S + M → S(_2) + M</td>
<td>7.49 × 10(^{-14})</td>
<td>2</td>
<td>Pavlov and Kasting (2002)</td>
</tr>
<tr>
<td>51</td>
<td>SO(_3) + H(_2)O + H(_2)O → aerosol</td>
<td>2.89 × 10(^{-31})</td>
<td>3 (special)</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>Other</td>
<td>Exit rate from cell</td>
<td>2.10 × 10(^{-2})</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

* Effective second order reactions based on falloff curves for [M] = 2.5 × 10\(^{19}\) and M = N\(_2\), O\(_2\). See sources for additional information.
Figure 4-6: Results of kinetic model (Section 4.5.4, Table 4.6) compared to experimental data (circles) for $f_{R4.6}$ (Equation 4.4) versus fraction of SO$_3$ formed from Reaction R 4.6 in the model. Contours on the plot are labeled with the value of rate constant $k_{R4.6}$ input into the model for a given run.
Figure 4-7: Fraction of sulfate derived from reaction channel R 4.6 \( (f_{SO}) \) as a function of altitude for different values of \( k_{R4.6} \).

Order of magnitude rate estimates from Sections 4.5.3 and 4.5.4. SO oxidation by other oxidants (O\(_3\), NO\(_3\), etc.) was assumed to be minor compared to oxidation by O\(_2\) given the minor concentration of most of these species compared with that of O\(_2\). Using \([SO] / [SO_2]\) ratio, the rates of Reactions R4.1, R4.6 and R4.7 can be compared. Assuming these three reactions are the dominant source of SO\(_3\) (and subsequently sulfate) in the stratosphere, the fraction of sulfate from Reaction R4.6 \( (f_{SO}) \) can be calculated as:

\[
f_{SO} = \frac{[SO]}{[SO_2]} \cdot \frac{k_{R4.6}[O_2][M]}{k_{SO_2^+OH}[OH] + k_{SO_2^+O}[O] + \frac{[SO]}{[SO_2]} \cdot k_{R4.6}[O_2][M]}
\]

The rate constants \( k_{SO_2^+OH} \) and \( k_{SO_2^+O} \) are the effective bimolecular rate constants for Reactions R4.1 and R4.7, as recommended by Sander et al. (2011). \( f_{SO} \) values were calculated for a 40° solar zenith angle (local noon at 40°N latitude and a 0° solar declination angle) and are shown in Figure 4-7. Given that SO, OH, and O\(^{3}\)P are all formed as a result of photochemistry, they should have similar daily cycles. As a result, the \( f_{SO} \) values calculated for local noon should be similar to the daily average \( f_{SO} \) values.
As seen in Figure 4-7, the lower estimate for $k_{R4.6}$ ($1.0 \times 10^{-37} \text{ cm}^6 \text{ molecule}^{-2} \text{s}^{-1}$) gives 4% to 10% of sulfate from Reaction R4.6 between 25 km and 50 km altitude. A faster estimate for $k_{R4.6}$ of $2.0 \times 10^{-37} \text{ cm}^6 \text{ molecule}^{-2} \text{s}^{-1}$ gives 8% to 18% of sulfate from Reaction R4.6 between 25 km and 50 km altitude. The upper bound estimate for the rate ($k_{R4.6} = 1.0 \times 10^{-36} \text{ cm}^6 \text{ molecule}^{-2} \text{s}^{-1}$, from Black et al. 1982a) suggests that over 45% of sulfate could be coming from Reaction R4.6 between 31 km and 34 km altitude and is probably unrealistic. The contribution from reaction R4.6 depends upon the amount of photons available for SO$_2$ photolysis, which increases with altitude because of less absorption by the Schumann–Runge band of O$_2$ and the Hartley bands of O$_3$. The rate of Reaction R4.6 decreases at higher altitudes as total number density decreases. The maximum $f_{SO}$ values, thus, is between 30 km to 35 km altitude (Figure 4-7).

Some insight into the rate can be obtained from SO$_2$ lifetimes in the stratosphere. Following the Mt. Pinatubo (1991) eruption, the Total Ozone Mapping Spectrometer (TOMS) data (Bluth et al., 1992) and Microwave Limb Sounder (MLS) data (Read et al., 1993) were used to estimate an e-folding time of 33 days to 35 days for SO$_2$ in the stratosphere. A later reanalysis of the TOMS data and TIROS Optical Vertical Sounder (TOVS) data (Guo et al., 2004) reduced this value to 25 days. Bekki and Pyle (1994) modeled the SO$_2$ decay following the Mt. Pinatubo eruption, considering Reaction R4.1 (OH oxidation) as the only sink of SO$_2$ in the stratosphere. Their modeled decay times for SO$_2$ (40 days) are considerably longer than the measured value of 25 days. Bekki and Pyle (1994) attribute this to uncertainties in the OH number densities. The discrepancy, however, could be explained in part by SO$_2$ photolysis followed by Reaction R4.6. Including of the SO$_2$ photolysis sink would decrease the lifetimes for SO$_2$ above around 25 km. The presence of this reaction would also suggest that OH concentrations estimated by Read et al. (1993) based on SO$_2$ lifetimes might overestimate OH concentrations above around 25 km altitude.

SO$_2$ photolysis is self-limiting, as SO$_2$ photolysis near the top of the volcanic SO$_2$ plume absorbs ultraviolet radiation in the range that SO$_2$ photolysis occurs. As a result, SO$_2$ photolysis lower in the eruption cloud is reduced and depends on
the overlying \( \text{SO}_2 \) column density. This would potentially reduce the significance of Reaction R 4.6 under heavy \( \text{SO}_2 \) loading.

Optical shielding effects increase the magnitude of the isotope effect from \( \text{SO}_2 \) photolysis under high \( \text{SO}_2 \) column densities (Lyons, 2007; Ono et al., 2013). Thus, the isotope fractionation occurring in a volcanic cloud is a tradeoff between larger fractionations but lower photolysis rates at higher column densities versus smaller fractionations but higher photolysis rates at lower column densities. Although the instantaneous fractionation factors can be estimated using our results and cross sections by Lyons (2007, 2008), the temporal evolution of isotope signatures of sulfate aerosol will require a model that can accurately incorporate both chemistry and dynamics of the stratosphere.

Given the large signal produced by \( \text{SO}_2 \) photolysis, over 100 \( \% \) and 10 \( \% \) for \( \delta^{34} \text{S} \) and \( \Delta^{33} \text{S} \) values, respectively (Whitehill and Ono, 2012; Ono et al., 2013), even a 10 \( \% \) contribution from Reaction R 4.6 could make a substantial contribution to the isotope signature of sulfate formed above circa 25 km altitude. Given the strong similarity in the isotopic signature of stratospheric sulfate aerosols from volcanic eruptions and those produced during \( \text{SO}_2 \) photolysis (Figure 4-3), it is likely that \( \text{SO}_2 \) photolysis plays an important role in the sulfur isotope budget of stratospheric sulfate aerosols. The initial sulfate formed from \( \text{SO}_2 \) photolysis (followed by Reaction R 4.6) will contain positive \( \delta^{34} \text{S} \) and \( \Delta^{33} \text{S} \) values and negative \( \Delta^{36} \text{S} \) values. Over time, due to mass balance, the residual \( \text{SO}_2 \) will obtained negative \( \delta^{34} \text{S} \) and \( \Delta^{33} \text{S} \) values and positive \( \Delta^{36} \text{S} \) values. This explains the temporal evolution of the isotopic signatures observed in aerosol samples (for \( \delta^{34} \text{S} \), Castleman et al. 1974) and ice cores (Bároni et al., 2007), which goes from positive \( \delta^{34} \text{S} \) and \( \Delta^{33} \text{S} \) values shortly after an eruption to negative values as time progresses.
4.5.6 Insignificance of excited-state photochemistry of SO$_2$ in the stratosphere

It has been suggested previously (Savarino et al., 2003; Hattori et al., 2013) that excited-state photochemistry of SO$_2$ in the 250 nm to 350 nm absorption region (i.e. the $\tilde{A}^1A_2/\tilde{B}^1B_1$ states) might be the dominant source of the sulfur isotope ratios in stratospheric sulfate aerosols. Previous results (Whitehill and Ono, 2012; Whitehill et al., 2013) have demonstrated that SO$_2$ photoexcitation in this region produces mass-independent sulfur isotope signatures with positive $\Delta^{36}$S/$\Delta^{33}$S ratios, as opposed to the negative $\Delta^{36}$S/$\Delta^{33}$S ratios measured for stratospheric sulfate aerosols.

This study further demonstrates that SO$_2$ photoexcitation in the 250 nm to 350 nm absorption region produces positive $\Delta^{36}$S/$\Delta^{33}$S ratios, even at temperatures approaching stratospheric temperatures. Our previous experiments (Whitehill and Ono, 2012; Whitehill et al., 2013) have been questioned as being inapplicable to the modern atmosphere (Hattori et al., 2013) due to the experimental conditions (i.e. the addition of C$_2$H$_2$ to trap triplet-state SO$_2$). In the present study, we tested SO$_2$ photoexcitation with two different longpass filters (250 nm longpass filter and 280 nm longpass filter) in a N$_2$/O$_2$ bath gas. In all cases, we produced sulfate products with positive $\Delta^{36}$S/$\Delta^{33}$S ratios. Therefore, our experiments do not provide support for SO$_2$ photoexcitation as the dominant source of the isotope anomalies in modern atmospheric samples.

However, contribution from both absorption bands to the isotope effects observed in stratospheric sulfate aerosols is possible and should be considered further. Despite the strong correspondence between $\Delta^{36}$S/$\Delta^{33}$S ratios in our photolysis experiments and stratospheric sulfate aerosol samples (Figure 4-3), the stratospheric sulfate aerosol samples produces a slightly shallower (less negative) $\Delta^{36}$S/$\Delta^{33}$S slope than the majority of our experimental samples. This could be due in part to the effect of pressure on $\Delta^{36}$S/$\Delta^{33}$S ratios (Masterson et al., 2011), as the one experiment performed at 7.7 kPa total pressure (Table 4.5) produced a $\Delta^{36}$S/$\Delta^{33}$S more similar to the stratospheric sulfate aerosol samples than the experiments performed at 101.3 kPa total...
pressure. It could also be due, however, to mixing between the negative $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ signatures from SO$_2$ photolysis and the positive $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ signatures from SO$_2$ photoexcitation. It is critical that future experiments further explore the isotope effects within these two absorption regions. However, it is also clear that SO$_2$ photoexcitation alone is not likely to be responsible for the isotope signatures and that SO$_2$ photolysis is necessary as well.

4.5.7 Caveats for Experimental Studies

There are a number of difficulties with directly applying photochemical results from laboratory studies to processes occurring in the natural environment. One issue is the difference between the spectral photon flux of the Xe and D$_2$ arc lamps as compared with the solar spectrum. Comparisons of data from different light sources (Xe versus D$_2$ lamps) were made previously in static photochemical experiments (Whitehill and Ono, 2012) and showed minor differences depending upon the light source. However, despite the large differences in the spectral photon flux between the Xe and D$_2$ light sources, the patterns in the isotope fractionation (i.e. $\delta^{34}\text{S}$ versus $\Delta^{33}\text{S}$ versus $\Delta^{36}\text{S}$) are similar. Both the Xe and D$_2$ light sources are broadband, unstructured light sources in the 180 nm to 220 nm absorption region, where SO$_2$ photolysis occurs. The solar spectrum, although also broadband, has considerably more fine structure in the spectrum, due to absorption by other gases such as O$_2$. As demonstrated in early SO$_2$ photolysis experiments (Farquhar et al., 2001), highly structured light sources (such as laser light sources) can cause anomalous isotope effects different from those observed in a broadband regime (Whitehill and Ono, 2012).

Unfortunately, the currently available measured absorption cross-sections (Danielache et al., 2008) are inconsistent observed isotope effects from photochemical experiments (Whitehill and Ono, 2012). As shown by Ueno et al. (2009), they predict negative $\Delta^{33}\text{S}$ values from SO$_2$ photolysis under reasonable atmospheric conditions. Experimental studies show positive $\Delta^{33}\text{S}$ values near zero (except in the self-shielding regime; Ono et al., 2013) under similar conditions. It is also important to note that the considerable uncertainties in the cross-section measurements (on the
permil to percent level) are too large to be considered quantitative for the degrees of mass-independent fractionation observed in these reactions. Future, higher-precision and higher resolution cross-section measurements should resolve some of these discrepancies and allow for stratospheric fractionations under solar spectral conditions to be modeled. In the absence of this data, however, experiments using solar-like spectra (i.e. Xe arc lamp) can provide a first order constraint on the types of isotope fractionations expected under a solar regime.

Another major issue with the experiments that was discussed above is the poor control in the experiments over the amount of water in the system. Due to the fact that experiments were performed at room temperature rather than at vacuum, it is difficult to put definitive constraints on the amount of water present in the system. Although attempts were made to flush the systems with nitrogen (< 3 ppb H₂O) prior to each experiment, water could be adsorbed onto the surfaces of the system. The presence of water will cause HОx chemistry to occur and open up an additional (mass-dependent, Harris et al., 2012) channel for sulfate formation. The amount of water in the system also affects the amount of SO₃ that ends up as sulfate aerosols. This is particularly an issue when attempting to estimate the rate of reactions in the system (Section 4.5.3 and 4.5.4). Varying amounts of water within the system during different experiments could explain some of the isotopic variability between replicate experiments (Tables 4.4 and 4.5). Photoexcitation (250 nm to 350 nm) experiments performed in an identical photochemical system but with the addition of acetylene (C₂H₂) are not strongly affected by the presence of trace amounts of water in the system, and showed considerably better isotopic reproducibility (Whitehill et al., 2013; Table 4.3) then SO₂ photolysis experiments (Ono et al., 2013; Tables 4.2, 4.4, and 4.5). This suggests that variability in trace amounts of water present in the system could have a significant affect on the isotopic signatures during SO₂ photolysis, and that water vapor should be carefully controlled in future experiments.
4.5.8 Production and preservation of mass-independent sulfur isotope signatures in ice cores

The results presented in this paper can explain the production and preservation of mass-independent sulfur isotope signatures in the modern atmosphere. Large volcanic eruptions, such as Pinatubo (1991) and Agung (1963) inject large amounts of SO$_2$ into the stratosphere. Both direct injection into higher altitudes (i.e. above 20 km to 25 km) or stratospheric transport of the SO$_2$ plume can bring SO$_2$ to a sufficient altitude for SO$_2$ photolysis to occur. The process of SO$_2$ photolysis produces large mass-independent sulfur isotope signatures in SO products, particularly when there is high SO$_2$ loading (and thus optical screening effects). Reaction of SO with O$_2$ to produce SO$_3$ (via Reaction R4.6) provides a pathway for the isotopic signature of SO to be preserved as SO$_3$, which can subsequently form sulfate aerosols. Some portion of the sulfate aerosols containing the mass-independent sulfur isotope signatures are transported to polar regions, where they can be deposited in polar precipitation and preserved in ice core records. A schematic illustration of the process is shown in Figure 4-8.

Some eruptions, despite their stratospheric influence, produce sulfate peaks in ice core records but do not contain mass-independent sulfur isotope signatures. Such eruptions include Cerro Hudson (1991, Savarino et al. 2003) and Laki (1783, Lanciki et al. 2012). Schmidt et al. (2012) discussed this issue previously and concluded that the Laki aerosols deposited in the Greenland ice cores were predominantly upper tropospheric or lower stratospheric in origin. Estimates for the height of the Laki (1783) eruption plume are only 15 km (Thordarson and Self, 2003), which penetrates the stratosphere but is not sufficiently high for SO$_2$ photolysis to be a dominant process (Schmidt et al., 2012). Due to the higher latitude of the eruption, transport processes are unlikely to bring the eruption plume to a sufficient altitude (25 km) for SO$_2$ photolysis to occur. Thus, despite the stratospheric influence of the Laki eruption, mass-independent sulfur isotope signatures in the preserved aerosols would not be expected. The situation is similar for the Cerro Hudson (1991) eruption, which
UV radiation (190 nm to 220 nm)

SO$_2$ + hv $\rightarrow$ SO + O (MIF production)

SO + O$_2$ + M $\rightarrow$ SO$_3$ + M (MIF preservation)

SO$_2$ + OH $\rightarrow$ HOSO$_2$ (no MIF)

Sulfate Aerosols

Deposition (in snow / ice)

Figure 4-8: Schematic illustration of the production and preservation of mass-independent fractionation (MIF) in sulfur isotopes following explosive volcanic eruptions. Low latitude eruptions such as Pinatubo (1991) inject large amounts of SO$_2$ into the stratosphere. Through stratospheric transport, it is brought to altitudes where SO$_2$ photolysis can occur, producing large MIF signatures. The product of SO$_2$ photolysis, SO, is preserved via termolecular reaction with O$_2$. The resulting SO$_3$ forms sulfate aerosols, which are deposited at high latitudes in polar snow and ice core records. SO$_2$ oxidation below 25 km is dominantly by OH, which is a mass-dependent process.
had an injection height of 11 km to 16 km (Schoeberl et al., 1993). Again, given the high latitude of the eruption, transport processes are likely insufficient to bring the plume to a sufficient altitude for SO$_2$ photolysis to become a dominant process.

In contrast with this are major low-latitude eruptions such as Pinatubo (1991). Although the initial injection of the Pinatubo eruption was probably localized below 25 km, the evolution of the plume resulted in the plume reaching altitudes of 30 km or higher (Gobbi et al., 1992), sufficient altitudes for SO$_2$ photolysis to play a role in the oxidation to sulfate. The largest mass-independent sulfur isotopes signatures (with $\Delta^{33}$S > 1‰) observed to date are from the Samalas (1257, Lavigne et al. 2013) eruption (Lanciki et al., 2012). Evidence suggests the eruption plume from this eruption reached a minimum of 34 km altitude, with a likely estimate being 43 km altitude (Lavigne et al., 2013). At this altitude, SO$_2$ photolysis would become a dominant process and could explain why the signature from this eruption is significantly larger than the other eruptions. Thus, SO$_2$ photolysis, followed by SO oxidation to SO$_3$ (via Reaction R 4.6), presents a consistent mechanism through which mass-independent sulfur isotope signatures can be produced and preserved in the modern, oxygenated atmosphere.

4.5.9 Conclusions

Laboratory photochemical experiments were carried out to investigate the production of mass-independent sulfur isotope effects under stratospheric conditions. For SO$_2$ photolysis in the 190 nm to 220 nm region, the magnitude of the mass-independent isotope signature increases with decreasing temperature. The isotope systematics, in particular the $\delta^{34}$S and $\Delta^{33}$S values, show excellent agreement with an optical self-screening model based on synthetic absorption cross sections (Lyons, 2007). SO$_2$ photoexcitation experiments show similar signatures to previous experimental studies (Whitehill and Ono, 2012; Whitehill et al., 2013), with positive $\Delta^{33}$S and positive $\Delta^{36}$S values, but that differ significantly from expectations based on absorption cross sections (Danielache et al., 2012).

The SO$_3$ (recovered as sulfate) products from SO$_2$ photolysis in the presence
of molecular oxygen carry mass-independent sulfur isotope signatures, suggesting a pathway for the direct oxidation of SO to SO₃. We hypothesize that the SO + O₂ + M → SO₃ + M reaction (Reaction R.4.6) and estimate the termolecular rate constant of the reaction to be on the order of 10⁻³⁷ cm⁶ molecule⁻² s⁻¹ or faster. This is consistent with previous constraints on the maximum rate of this reaction (Black et al., 1982a).

Depending on the rate of Reaction R.4.6, we predict that on the order of 10% of sulfate above 25 km altitude could be derived from the SO+O₂+M channel. Given the large isotope fractionations produced during SO₂ photolysis, our model can explain the source and preservation mechanism of mass-independent sulfur isotope signatures measured in stratospheric sulfate aerosols in polar ice samples. Our model explains the temporal evolution of δ³⁴S and Δ³³S values following major volcanic eruptions, and constrains the maximum altitude of the plume to above 20 km to 25 km when non-zero Δ³³S values are observed.

4.5.10 Acknowledgements

The authors would like to thank William J. Olszewski for his assistance in sulfur isotope analysis, and support from NASA Exobiology (NNX10AR85G to S.O., and 11-EXO11-0107 to H.G.) and NSF FESD (Award 1338810 to S.O.). The authors would like to thank editor Thomas Rockmann and reviewers Matthew Johnson and Joel Savarino for their comments.
Chapter 5

SO$_2$ photolysis in the presence of methane: Discrepancies between SO$_2$ photolysis data and the Archean record

5.1 Introduction

The presence of mass-independent sulfur isotope signatures in the geologic record prior to 2.4 Ga provides the best constraints on atmospheric oxygen levels during the Archean (Farquhar et al., 2000a; Pavlov and Kasting, 2002), and the disappearance of sulfur isotope mass-independent fractionation (S-MIF) at 2.4 Ga provides our best constraints on the timing of the Great Oxidation Event (Bekker et al., 2004; Guo et al., 2009). Interpretation of the mass-independent sulfur isotope record beyond its connection with atmospheric oxygen has been limited by the lack of constraints on the source mechanisms responsible for S-MIF production. Early studies showed considerable correlation between mass-independent fractionation in $^{33}$S (i.e. $\Delta^{33}$S values) and mass-independent fractionation in $^{36}$S ($\Delta^{36}$S values), with $\Delta^{36}$S/$\Delta^{33}$S ratios of around −1 (Farquhar et al., 2000a), which was believed to be indicative of
the S-MIF source reaction (Farquhar et al., 2001). Later studies found variability in $\Delta^{36}S/\Delta^{33}S$ ratios during different periods of the Archean and suggested possible changes in ultraviolet transparency of the atmosphere, source reaction, or some other environmental or atmospheric parameter (Farquhar et al., 2007; Zerkle et al., 2012). Once the S-MIF source reactions are identified and their isotopic signatures are well constrained experimentally, it should be possible to directly link the patterns in the isotopic record to changes in environmental conditions during the Archean.

Early experimental studies suggested that SO$_2$ photolysis ($\text{SO}_2 + h\nu \rightarrow \text{SO} + \text{O}$) was a likely source reaction for the Archean S-MIF signatures (Farquhar et al., 2001). This was based in part on the fact that SO$_2$ photolysis was shown to produce large S-MIF signatures, but also based on the results of ArF (193.3 nm) laser photolysis experiments that seemed to reproduce the isotope systematics of the Archean. Based on these experiments, Farquhar et al. (2001) suggested that SO$_2$ photolysis at high energies was a possible mechanism for explaining the Archean S-MIF signatures. Modeling studies followed which demonstrated the feasibility of SO$_2$ photolysis as a source of S-MIF during the Archean, particularly in a low-oxygen atmosphere (Pavlov and Kasting, 2002; Ono et al., 2003). Although 193.3 nm photolysis of SO$_2$ (using an ArF laser) makes signatures with large $\Delta^{33}S$ values and $\Delta^{36}S/\Delta^{33}S$ ratios similar to the Archean, the presence of negative $\delta^{34}S$ values associated with the positive $\Delta^{33}S$ values is different from the largely positive correlations between $\delta^{34}S$ and $\Delta^{33}S$ values observed in many Archean sections (Ono et al., 2003; Bao et al., 2007; Kamber and Whitehouse, 2007). In addition, the applicability of the 193.3 nm experiments to natural systems (with broadband solar radiation) has been questioned (Lyons, 2007), and broadband photolysis studies (Masterson et al., 2011; Whitehill and Ono, 2012; Ono et al., 2013) have been shown to produce different results. In addition, isotopologue-specific absorption cross-sections (Danielache et al., 2008) suggest different results from both the original Farquhar et al. (2001) experiments and later broadband experiments, suggesting that SO$_2$ photolysis should produce SO with negative $\Delta^{33}S$ values, rather than the positive values observed in experiments (Masterson et al., 2011; Whitehill and Ono, 2012; Ono et al., 2013). Part of this discrepancy may be
due to the large uncertainties in the cross-section measurements (Danielache et al., 2008) or the high column densities at which the experiments are run (Lyons, 2007).

Although broadband photolysis studies using Xe and D$_2$ arc lamps have been able to produce "Archean-like" S-MIF signatures, with positive $\Delta^{33}\text{S}/\delta^{34}\text{S}$ ratios and negative $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios (Masterson et al., 2011; Whitehill and Ono, 2012; Ono et al., 2013), there remain considerable discrepancies between the isotope signatures during experimental studies and those observed in the geologic record (Whitehill and Ono, 2012; Whitehill et al., 2013; Ono et al., 2013). Attempts to resolve these discrepancies have repeatedly failed. In this paper, we will discuss an attempt to resolve this issue through the photolysis of SO$_2$ in a reducing atmosphere with methane (CH$_4$). We show that the isotopic results of SO$_2$ photolysis in the presence of CH$_4$ are identical to SO$_2$ photolysis in an inert bath gas, suggesting that the presence or absence of CH$_4$ may affect elemental sulfur formation rate (Zahnle et al., 2006; DeWitt et al., 2010), but does not considerably alter the isotope ratio of the elemental sulfur formed from SO$_2$ photolysis.

With the exception of the initial Farquhar et al. (2001) experiments, some of which were performed in the presence of CO$_2$ or H$_2$O, the majority of SO$_2$ photolysis experiments that look at isotopes have been performed either as pure SO$_2$ (Masterson et al., 2011; Whitehill and Ono, 2012) or SO$_2$ in the presence of an inert bath gas such as He (Masterson et al., 2011) or N$_2$ (Ono et al., 2013). Recently, Whitehill et al. (2013) used C$_2$H$_2$ to selectively trap excited-state SO$_2$ species from the photoexcitation region (250 nm to 350 nm) as organosulfur aerosols. Additionally, Whitehill et al. (2014) showed that SO$_2$ photolysis in an oxidizing atmosphere (i.e. in the presence of O$_2$) produces SO$_3$ with large S-MIF anomalies. Although these experiments, particularly the O$_2$ experiments, are relevant to attempting to explain S-MIF signatures in the modern atmosphere, they are probably not applicable to the Archean.

Results from aerosol mass spectrometry experiments suggest that photolysis of SO$_2$ in the presence of CH$_4$ increases the yield of elemental sulfur and, under some conditions, produces organic sulfur aerosols such as methanesulfonic acid (DeWitt et al., 2010). Modeling studies also suggest that methane was essential to the preser-
vation of elemental sulfur in the Archean atmosphere, and that the collapse of methane could have resulted in the loss of S-MIF signatures (Zahnle et al., 2006). In addition, Whitehill and Ono (2012) hypothesized that methane in the Archean atmosphere could have aided in the preservation of isotope signatures from SO\textsubscript{2} in the photoexcitation band (250 nm to 350 nm). The presence of methane, and in particular the CH\textsubscript{4}:CO ratio, would also affect the presence of organic hazes, which could modify the ultraviolet transparency of the atmosphere and affect the systematics of S-MIF signature (Zerkle et al., 2012). Since methane potentially affects atmospheric exit channels, it could also affect the reaction pathway and could have an effect on the isotope ratios of elemental sulfur products from SO\textsubscript{2} photolysis.

To test the effect of methane on the isotope signature during SO\textsubscript{2} photolysis, we performed a series of SO\textsubscript{2} photolysis experiments in the presence of methane. The goal was to determine whether added methane significantly affected the isotope signatures during SO\textsubscript{2} photolysis by altering the reaction pathways, and to determine whether S-MIF signatures could provide additional insight into atmospheric CH\textsubscript{4} during the Archean. We show that broadband SO\textsubscript{2} photolysis (with a Xe arc lamp) in the presence of CH\textsubscript{4} (up to 1.01 kPa) does not produce isotopic signatures distinct from SO\textsubscript{2} photolysis in a pure N\textsubscript{2} bath gas. In particular, photolysis of SO\textsubscript{2} in the presence versus absence of methane produces similar isotopic signatures.

The issue of the discrepancies between SO\textsubscript{2} photolysis experiments and the Archean geologic record remains unresolved. We discuss these continuing discrepancies and suggest that SO\textsubscript{2} photolysis might not be responsible for the entirety of the S-MIF signature in the Archean record. We suggest that a second reaction capable of producing S-MIF, such as SO photolysis, might be overprinting the SO\textsubscript{2} photolysis signature in the geologic record and must be further studied.

5.2 Methods

SO\textsubscript{2} photolysis experiments were performed in a 15.3 cm path length, cylindrical glass photochemical reaction cell used in previous studies (Ono et al., 2013; Whitehill et al.,
Gas was flowed continuously through the reaction cell for the duration of the experiments. Gas flow rates were controlled by a series of mass-flow controllers located upstream of the reaction cell and gases were mixed prior to entering the cell. A manometer placed immediately before the reaction cell was used to monitor pressure within the cell. A UV-grade SiO₂ window was secured on either end of the reaction cell. Immediately following the cell, gas was flowed through an 8 cm to 10 cm long glass tube packed with glass wool, which was used to trap any aerosols generated within the cell. Downstream of the aerosol trap was a proportionating valve followed by a vacuum pump. The proportionating valve was opened and closed incrementally to maintain pressure within the reaction cell to ±30 Pa of 101.3 kPa.

During experiments, the cell was irradiated with a 150 W Xe arc lamp. Following experiments, the cell and the aerosol filter were rinsed well with dichloromethane. Elemental sulfur (i.e. S₈) was recrystallized from the dichloromethane and converted to silver sulfide following the method of Canfield et al. (1986). Silver sulfide was fluorinated under approximately 7.2 kPa of fluorine gas (F₂) for at least 8 h at 573 K. Resultant SF₆ was purified cryogenically and by gas chromatography and analyzed for quadruple sulfur isotope ratios on a Thermo Scientific MAT 253 Isotope Ratio Mass Spectrometer. Replicate analyses (N = 28) of the reference material IAEA-S-1 gave 2σ standard deviations of 0.26 ‰ for δ³⁴S, 0.014 ‰ for Δ³³S, and 0.19 ‰ for Δ³⁶S for standard isotope ratio mass spectrometry analysis.

### 5.2.1 Definitions

Isotopic results will be presented with conventional δ notation, as relative deviations of isotope ratios with respect to reference sulfur.

\[
\delta^xS = \frac{^xR_{product}}{^xR_{reference}} - 1 
\]  

(5.1)

where \( x = 33, 34, \) or 36 and \(^xR\) is the ratio of \(^xS\) to \(^{32}S\) in the substance. For experimental results all isotope ratios will be normalized to the isotope ratios of the
initial \( \text{SO}_2 \). For natural samples (i.e. Archean samples), the reference is Vienna Canyon Diablo Troilite (V-CDT).

Mass-independent isotope fractionations in \( ^{33}\text{S}/^{32}\text{S} \) and \( ^{36}\text{S}/^{32}\text{S} \) ratios (relative to \( ^{34}\text{S}/^{32}\text{S} \) ratios) will be presented as \( \Delta^{33}\text{S} \) and \( \Delta^{36}\text{S} \) values, respectively. These are defined as:

\[
\Delta^{33}\text{S} = \frac{\delta^{33}\text{S} + 1}{(\delta^{34}\text{S} + 1)^{0.515}} - 1 \quad (5.2)
\]

and

\[
\Delta^{36}\text{S} = \frac{\delta^{36}\text{S} + 1}{(\delta^{34}\text{S} + 1)^{1.90}} - 1 \quad (5.3)
\]

### 5.3 Results

Elemental sulfur isotope results from all new experiments are presented in Table 5.1. Results of the photolysis of \( \text{SO}_2 \) in the presence of \( \text{CH}_4 \) were similar to previously reported results of \( \text{SO}_2 \) photolysis in the absence of \( \text{CH}_4 \) (Ono et al., 2013). In particular, the relationship between \( \delta^{34}\text{S} \), \( \Delta^{33}\text{S} \), and \( \Delta^{36}\text{S} \) values are similar to previous flow-through \( \text{SO}_2 \) photolysis experiments, but considerable different from the Archean data and static photocell experiments (Figure 5-1). In addition, the magnitude of the isotope fractionation shows an identical relationship to \( \text{SO}_2 \) column density as the previously reported \( \text{SO}_2 \) photolysis experiments (Figure 5-2) performed under similar conditions (101.3 kPa total pressure). No significant difference was observed in the isotope signatures between the photolysis of \( \text{SO}_2 \) in the presence versus absence of \( \text{CH}_4 \).
Table 5.1: Results from experiments testing photolysis of SO₂ in the presence of methane.

<table>
<thead>
<tr>
<th>pSO₂/ kPa</th>
<th>pCH₄/ kPa</th>
<th>Flow Rate/ sccm</th>
<th>Time/ h</th>
<th>Yield/ μmol S</th>
<th>δ³³S/ %</th>
<th>δ³⁴S/ %</th>
<th>δ³⁶S/ %</th>
<th>Δ³³S/ %</th>
<th>Δ³⁶S/ %</th>
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<td>45.1*</td>
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<td>24.53</td>
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<td>2.29</td>
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<td>30.55</td>
<td>46.32</td>
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<td>104.23</td>
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<td>7.16</td>
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<td>10.19</td>
<td>-32.13</td>
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</table>

* Silver sulfide was discolored (grayish) and anomalously yields were anomalously high (> 40 μmol).
Figure 5-1: Isotopic systematics of SO$_2$ photolysis experiments compared with Archean data. Archean data includes pre-2.4 Ga data from Farquhar et al. (2000a, 2007); Hu et al. (2003); Mojzsis et al. (2003); Ono et al. (2003, 2006a, 2009a,b); Papineau et al. (2005); Whitehouse et al. (2005); Cates and Mojzsis (2006); Ohmoto et al. (2006); Bao et al. (2007); Hou et al. (2007); Kamber and Whitehouse (2007); Kaufman et al. (2007); Domagal-Goldman et al. (2008); Zerkle et al. (2012); ?. Flow (N$_2$) data includes photolysis experiments from Ono et al. (2013), oxygen-free photolysis experiments from Whitehill et al. (2014), and the present study. Flow (CH$_4$) data includes data from present study. Static data includes data from Masterson et al. (2011) and Whitehill and Ono (2012).
5.4 Discussion

5.4.1 SO₂ photolysis and the Archean S-MIF record

Results from SO₂ photolysis experiments reveal several significant issues with SO₂ photolysis as the primary source of the Archean S-MIF signatures. Although the elemental sulfur products have the correct sign of isotope anomalies (i.e. positive δ³⁴S, positive Δ³³S, and negative Δ³⁶S values), the relationship between isotope ratios in experimental data is different from that observed in the Archean record. There are three fundamental issues with the experimental data that make it difficult to reconcile with the Archean record. The first issue is that the magnitude of the Δ³³S and Δ³⁶S values decrease significantly as the SO₂ column density is decreased. This was first shown by Ono et al. (2013), and is consistent with the new results presented here (Figure 5-2). This requires high SO₂ column densities (> 10¹⁷ molecules cm⁻²) to produce the magnitude of Δ³³S values (up to 10 % or higher) in the Archean record. Although high SO₂ column densities could occur in the immediate aftermath...
of volcanic activity, the SO₂ plume is likely to dissipate relatively rapidly. It is possible that the majority of the S-MIF signature observed in the rock record is due to elemental sulfur formation in the immediate aftermath of volcanic eruptions, and thus is preserving the high column density SO₂ signatures. Photochemical models of the Archean atmosphere tend to focus on steady-state behavior and assume a steady flux of SO₂ into the atmosphere (Pavlov and Kasting, 2002; Zahnle et al., 2006; Ueno et al., 2008; Halevy et al., 2010). If it is the case that S-MIF formation is dominantly a periodic event following large volcanic influxes of SO₂ into the atmosphere, steady-state photochemical models are unlikely to accurately reflect the process of S-MIF formation. The conditions necessary to produce and preserve S-MIF in a volcanic plume with high SO₂ column densities will depend highly on the chemistry within the plume rather than background, steady-state conditions.

The column density effect is not the only issue with SO₂ photolysis as an explanation for the Archean S-MIF signatures. There are also significant discrepancies between the isotope systematics from SO₂ photolysis and those observed in the Archean record. This is most striking in the relationship between δ³⁴S and Δ³³S values (Figure 5-1). In particular, although SO₂ photolysis experiments are capable of producing the full range of Δ³³S values observed in the geologic record, large Δ³³S values are generally associated with large δ³⁴S values. The range of δ³⁴S values in Archean rocks is relatively narrow (−40%o < δ³⁴S < +30%o; Johnston 2011), and there is no evidence for large δ³⁴S values (δ³⁴S > +100%o) in the geologic record. It is possible that SO₂ photolysis did produce large δ³⁴S values during the Archean, and that a subsequent mass-dependent fractionation process (such as microbial sulfate reduction or some uncharacterized photochemical process) reduced the δ³⁴S value to the range we observe in rocks (< +30%o). However, such a process would, by mass balance considerations, necessitate a pool of highly ³⁴S enriched sulfur during the Archean. It is possible that such a pool existed and was not preserved; however, the lack of any evidence for such a pool makes this scenario seem unlikely. It is possible that future studies will reveal large positive δ³⁴S values in Archean rocks, but mass-balance considerations on present data suggest that SO₂ photolysis is unlikely to be
able to reproduce the Archean record.

The third issue with SO2 photolysis is with regard to the relationship in mass-independent isotope fractionation in $^{33}\text{S}$ and $^{36}\text{S}$ - in particular, $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios. Although mass-dependent fractionation processes, dilution, and mixing processes can change $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values, the effect on the relationship between $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ is relatively minor, particularly for samples with large $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ signatures (i.e. $\Delta^{33}\text{S} > 5\%e$). Therefore, the relatively consistent relationship between $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values ($\Delta^{36}\text{S}/\Delta^{33}\text{S} \approx -1$) observed for most Archean samples is believed to be indicative of the S-MIF source reaction. In addition, variability in this relationship has been linked to changing atmospheric or environmental conditions during different periods of the Archean (Farquhar et al., 2007; Zerkle et al., 2012). Although early SO2 photolysis experiments were able to produce Archean-like $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios using laser (ArF) and broadband (Xe) light sources (Farquhar et al., 2000b, 2001), all more recent studies fail to reproduce the Archean trend (Masterson et al., 2011; Whitehill and Ono, 2012; Ono et al., 2013; Whitehill et al., 2014). Because the new data presented here is indistinguishable from that in Ono et al. (2013), it also fails resolve the discrepancy between experimental data and the Archean record.

Variability is observed in $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios under different experimental conditions. In particular, higher total pressure tends to produce smaller (more negative) $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios. This is due predominantly to the pressure effect described by Masterson et al. (2011), which disproportionately affects $\Delta^{33}\text{S}$ values relative to $\delta^{34}\text{S}$ and $\Delta^{36}\text{S}$ values. However, both pure SO2 experiments (down to 0.67 kPa) and SO2 in the presence of a bath gas (up to 101.3 kPa N2 or 86.4 kPa He) fail to reproduce the Archean $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ trend. It is possible that differences in experimental conditions, such as spectral photon flux of the light source or the presence of other absorbing gases, could alter the $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratio to match that of the Archean. However, given the other issues with SO2 photolysis, we find it a more likely scenario that an alternative reaction (or reactions) could be contributing to the S-MIF signatures observed in the Archean record.

One major question regarding our experiments is whether we can simulate atmo-
spheric isotope effects in our photochemical reactor. Ono et al. (2013) and Whitehill et al. (2014) demonstrated that the isotope systematics (i.e. the relationship between $\delta^{34}\text{S}$, $\Delta^{32}\text{S}$, and $\Delta^{36}\text{S}$) from SO$_2$ photolysis experiments closely match the signatures produced from SO$_2$ photolysis in the modern stratosphere, as preserved in ice core records (Savarino et al., 2003; Bároni et al., 2007, 2008; Lanciki, 2010; Lanciki et al., 2012). This provides evidence that our photochemical system is capable of reproducing atmospheric signatures, at least in the modern atmosphere. However, the modern atmosphere is well constrained, whereas we have very few constraints on the Archean atmosphere. It is possible that systematic differences between the Archean atmosphere and our photochemical system (and the modern atmosphere) could account for the differences between experiments and geologic samples.

Another possibility that must be considered is that an additional source reaction, possibly SO photolysis, also contributed to the production of mass-independent sulfur isotope signatures during the Archean. Recent theoretical cross-sections of SO suggest that SO photolysis might be capable of producing S-MIF due to optical (i.e. absorption) isotope effects (Danielache et al., 2014). In addition, SO could potentially produce anomalous isotope signatures due to quantum yield effects, similar to those observed for SO$_2$ photoexcitation (Whitehill et al., 2013). SO photolysis (at wavelengths below 230 nm) occurs through excitation into an initially bound $B(^3\Sigma^-)$ state, which is associated with the $S(^1D) + O(^3P)$ asymptote. In order for dissociation to occur, it must cross with one of a number of other quasi-bound or repulsive states associated with the lower $S(^3P) + O(^3P)$ asymptote. The rate of crossing between states could be a strong function of isotope substitution, as suggested for the intersystem crossing reaction of SO$_2$ in the 250 nm to 350 nm region (Whitehill et al., 2013), and for other molecules (Zmolek et al., 1999; Bhattacharya et al., 2000; Chakraborty et al., 2008; Muskatel et al., 2011).

5.5 Conclusions

SO$_2$ photolysis in the presence of methane (CH$_4$) is shown to produce identical isotope
signatures to SO$_2$ photolysis in the absence of methane. This suggests that methane does not considerably affect the chemistry of the reactions following SO$_2$ photolysis, or that the effect on the isotopes is small relative to the large isotope effect due to SO$_2$ photolysis. Experimental data from all the broadband SO$_2$ photolysis experiments is synthesized and used to argue that SO$_2$ photolysis is not consistent with the Archean S-MIF signatures. Instead, a suggestion is made that SO photolysis should be explored as possibly contributing to S-MIF production in the Archean atmosphere.
Chapter 6

Conclusions

6.1 SO₂ photolysis versus SO₂ photoexcitation

The isotope effects from two different absorption bands of SO₂ – SO₂ photolysis in the 190 nm to 220 nm region and SO₂ photoexcitation in the 250 nm to 350 nm region – are examined using two broadband light sources, Xe and D₂ arc lamps, and a variety of optical filters. The effect of various factors on isotope fractionation, including SO₂ pressure (pSO₂), nitrogen bath gas pressure (pN₂), and temperature (T) are explored for both absorption bands of SO₂. The two different absorption regions are shown to produce distinct patterns of mass-independent sulfur isotope fractionation (i.e. $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios), with SO₂ photolysis producing negative $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios and SO₂ photoexcitation producing positive $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios. The detailed isotope systematics ($\delta^{33}\text{S}/\Delta^{34}\text{S}$ and $\Delta^{33}\text{S}/\Delta^{36}\text{S}$) are shown to be dependent upon experimental conditions, including temperature, total pressure, and SO₂ pressure. These patterns in mass-independent sulfur isotope fractionations can be used to draw inferences about the sources of sulfur mass-independent fractionation (S-MIF) in natural samples.

Experimental results are compared with predictions from synthetic (Lyons, 2007) and experimental (Danielache et al., 2008) isotopologue-specific absorption cross-sections. These comparisons are used to provide insight into possible mechanisms for S-MIF formation during photochemical reactions of SO₂. Strong similarities be-
ween the cross-section predictions and the observed isotope effects are used to argue that the S-MIF formed during SO$_2$ photolysis (190 nm to 220 nm) is predominantly optical in origin and can be predicted well once sufficiently precise, accurate, and well-resolved isotopologue specific absorption cross-sections are measured. SO$_2$ photolysis at low column densities does not produce significant S-MIF signatures, and the majority of the signature observed in experimental systems is due to self shielding.

In contrast, there are significant discrepancies between the S-MIF signatures observed during the photoexcitation of SO$_2$ (250 nm to 350 nm) and those predicted from cross-sections. This suggests that optical effects (due entirely to predictions based on absorption cross-sections and the incident photon spectral flux) are not the only source of S-MIF during SO$_2$ photoexcitation, but that an additional mechanism, such as an isotopologue-selective intersystem crossing reaction, must be contributing to the S-MIF signatures. This mechanism has been previously suggested in other systems (Zmolek et al., 1999; Bhattacharya et al., 2000; Chakraborty et al., 2008) but has never been proven to produce anomalous isotope signatures. Although definitive proof is still lacking, an argument is made that the fractionations during SO$_2$ photoexcitation are not consistent with other hypothetical S-MIF production mechanisms, and a theoretical basis for the effect is provided.

The insights into S-MIF production mechanisms provided by this work can be used to predict other systems which might produce mass-independent fractionation. For example, both CS$_2$ and SO have strongly structured absorption spectra, suggesting that optical effects (like self-shielding or cross-section differences) could be important in these systems as well. Similarities between photopolymerization of CS$_2$ and photoexcitation of SO$_2$ support the intersystem crossing mechanism suggested by Zmolek et al. (1999). In addition, SO photolysis might be a candidate for producing anomalous isotope effects due to expected isotopologue-selective coupling of excited states, similar to SO$_2$ photoexcitation. Future work should be done on these systems to better constrain the mechanisms responsible for S-MIF formation.
6.2 Sulfur dioxide photochemistry and the Archean rock record

Mass-independent sulfur isotope signatures are ubiquitous in sedimentary sulfate and sulfide minerals older than circa 2.45 billion years (Ga). These enigmatic signatures are assumed to be atmospheric in origin, due largely to the fact that photochemical reactions are one of the few known sources of mass-independent isotope effects. Although early studies showed strong similarities between the isotope fractionation during SO$_2$ photolysis and that observed in the geologic record (Farquhar et al., 2001), more recent experiments show considerable discrepancies. An argument is made based on multiple lines of isotopic evidence that SO$_2$ photolysis is not the primary source of the Archean S-MIF signatures. In particular, the low $\Delta^{33}$S values at small SO$_2$ column densities (Ono et al., 2013) is difficult to reconcile with the model constraints on SO$_2$ levels during the Archean (Halevy et al., 2010). In addition, the large $\delta^{34}$S fractionations observed during SO$_2$ photolysis experiments are not consistent with the limited range of $\delta^{34}$S values in geologic samples that contain S-MIF. Together with inconsistencies in the relationship between $\Delta^{33}$S and $\Delta^{36}$S (i.e. $\Delta^{36}$S/$\Delta^{33}$S ratios), an argument is made that SO$_2$ photolysis is not the major or dominant source of S-MIF during the Archean. The isotopic systematics of the Archean S-MIF record requires a second S-MIF producing reaction in addition to SO$_2$ photolysis. The suggestion is made that SO photolysis might be this second reaction in the Archean. Future research should focus on SO photolysis and other potential reactions capable of producing S-MIF to resolve the discrepancies between S-MIF produced during photochemical experiments and that observed in the rock record.
6.3 Sulfur dioxide photolysis and the modern atmosphere

In addition to the S-MIF signatures in the Archean rock record, there are also minor mass-independent sulfur isotope anomalies observed in ice core samples associated with large volcanic eruptions. These signatures are likely produced in the stratosphere, although the mechanism responsible for the production and preservation of these signatures has previously been debated (Savarino et al., 2003; Pavlov et al., 2005; Hattori et al., 2013; Ono et al., 2013). Multiple possible theories for S-MIF production in the modern atmosphere were tested, including excited-state SO\textsubscript{2} reactions and SO\textsubscript{2} photolysis. Ono et al. (2013) showed that SO\textsubscript{2} photolysis produces signatures with similar isotopic systematics (i.e. \(\delta^{34}\text{S} \) versus \(\Delta^{33}\text{S} \) versus \(\Delta^{36}\text{S} \)) to the signatures observed in ice cores. In this thesis, I show that SO\textsubscript{2} photoexcitation (in the 250 nm to 350 nm region) produces isotope signatures significantly different from that observed in ice cores. In particular, SO\textsubscript{2} photoexcitation produces positive \(\Delta^{36}\text{S}/\Delta^{33}\text{S} \) ratios under a range of experimental conditions (temperature, pressure, \(p\text{SO}_2 \)) and reaction pathways (\(^s\text{SO}_2 + \text{SO}_2, ^s\text{SO}_2 + \text{C}_2\text{H}_2, ^s\text{SO}_2 + \text{O}_2 \)). This is contrasted to largely negative \(\Delta^{36}\text{S}/\Delta^{33}\text{S} \) ratios observed during SO\textsubscript{2} photolysis and in ice core samples.

Although both SO\textsubscript{2} photolysis and SO\textsubscript{2} photoexcitation are known to produce mass-independent sulfur isotope fractionation (Farquhar et al., 2001; Whitehill and Ono, 2012), the preservation of the signatures in the modern atmosphere has been the subject of debate (Savarino et al., 2003; Pavlov et al., 2005; Schmidt et al., 2012; Hattori et al., 2013; Ono et al., 2013). It was previously argued that the isotope signatures from SO\textsubscript{2} photolysis could not be preserved in a high-oxygen atmosphere (Savarino et al., 2003; Pavlov et al., 2005). In this thesis, it is shown that SO\textsubscript{2} photolysis in the presence of oxygen produces sulfate with large S-MIF signatures that match those in ice cores. It is suggested that this sulfate is produced via the \(\text{SO} + \text{O}_2 + \text{M} \rightarrow \text{SO}_3 + \text{M} \) reaction hypothesized by Ono et al. (2013). If that is the case, then simple kinetic constraints on the rate of this reaction suggest it
could be a minor contributor to sulfate formation in the stratosphere above certain altitudes (about 20 km to 25 km dependent upon atmospheric conditions). I provide a mechanism for S-MIF production and preservation in the modern atmosphere that is consistent with both experimental data and measurements of natural samples. This is the first step in understanding and interpreting S-MIF data from ice cores. Future work should focus on using multi-dimensional chemical transport modeling to constrain the range of conditions under which the proposed reaction could contribute significantly to the formation of stratospheric sulfate aerosols.
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