

No Evidence for S Isotope Fractionation During SO₂ Oxidation at a Continental Location

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Sulfur isotope fractionation during SO₂ oxidation has been shown to occur in laboratory experiments¹ but this has not been observed in whole air samples². Here we replicate the laboratory experiments in a systematic manner using ambient air. Particulate matter and SO₂ in ambient air were collected at Calgary in the Fall of 2012 using high volume samplers and impingers. Atmospheric SO₂ and SO₄ concentrations and isotope characteristics were determined. Variations in the concentration of SO₂ and SO₄ in the atmosphere did not reflect changes in $\delta^{34}\text{S}$ values, suggesting the independence of $\delta^{34}\text{S}$ from concentration. Average $\delta^{34}\text{S}_{\text{SO}_2}$ (\pm std. dev.) from the high volume samplers was $+13.2\text{‰} \pm 0.2\text{‰}$. SO₂ from the impinger method over the same sampling period yielded a $\delta^{34}\text{S}_{\text{SO}_2}$ value of $+14.0\text{‰} \pm 0.2\text{‰}$. Standard deviation for the impinger samples could not be calculated and hence this $\pm 0.2\text{‰}$ is the precision due to the spectrometer. $\delta^{34}\text{S}_{\text{SO}_4}$ values (\pm std. dev.) ranged from $+9.9\text{‰} \pm 0.5\text{‰}$ to $+15.3\text{‰} \pm 0.2\text{‰}$. $\delta^{34}\text{S}_{\text{SO}_2}$ values from the high volume and impinger samples were similar ($+13.2\text{‰}$ versus $+14.0\text{‰}$, respectively) which shows these collection methods are equivalent. Differences between the impinger and high volume sampler $\delta^{34}\text{S}$ values for SO₂ and

submicron aerosol SO₄ were used to gauge sulfur isotope fractionation. Standard deviations for differences were greater than averages ($\Delta\delta^{34}\text{S}_{\text{SO}_2}$ avg. = -0.80‰ , $s=1.76\text{‰}$; fine $\Delta\delta^{34}\text{S}_{\text{SO}_4}$ avg. = $+0.28\text{‰}$, $s=5.15\text{‰}$), indicating little to no fractionation. Additionally, $\delta^{34}\text{S}_{\text{SO}_2}$ and $\delta^{34}\text{S}_{\text{SO}_4}$ values were compared to the maximum percent SO₂ that may have reacted to form SO₄. No pattern was evident so the conclusion is that sulfur isotope fractionation in ambient air is negligible under the conditions sampled.

Literature: 1. Harris, E., Sinha, B., Hoppe, P., Foley, S., Borrmann, S. (2012). Fractionation of sulfur isotopes during heterogeneous oxidation of SO₂ on sea salt aerosol: a new tool to investigate non-sea salt sulfate production in the marine boundary layer. *Atmos. Chem. Phys.* 12. 2. Norman, A.L., Krouse, H.R., MacLeod, J. (2004). *Air Pollution Modeling and Its Application XVI*.

Keywords: Isotopes – atoms of an element with the same number of protons but a different number of neutrons in the nucleus, Fractionation – a change in the ratio of heavy to light isotopes due to some biological, chemical, or physical process, Sulfur, Sulfate, Sulfur dioxide, Oxidation, Atmosphere.

$$\delta^{34}\text{S}(\text{‰}) = \left(\frac{\left\{ \frac{^{34}\text{S}}{^{32}\text{S}} \right\}_{\text{sample}}}{\left\{ \frac{^{34}\text{S}}{^{32}\text{S}} \right\}_{\text{standard}}} - 1 \right) \times 1000$$

Figure 1:

Chemical equations for the oxidation of SO_2 to SO_4 with photochemistry. M refers to light energy.

H_2SO_4 is a diprotic acid and is ionized to H^+ and SO_4^{2-}

Introduction

Variations of natural sulfur isotope abundances in atmospheric sulfur compounds have been used to track the contributions of isotopically distinct sources of SO_2 (sulfur dioxide), and their oxidation to SO_4 (sulfate) in marine and continental airsheds¹. For example, SO_2 isotope analysis of well-mixed air on Saturna Island, Canada, indicated SO_2 contributions to the atmosphere originating from a U.S. oil refinery and tidal flats². A key assumption in these apportionment studies is that isotope fractionation during SO_2 oxidation is small so that they accurately reflect their source. This assumption can be tested by studying if fractionation either occurs or not during oxidation, which is detectable by comparing isotope values of SO_2 and SO_4 . Isotope fractionation is the separation of isotopes of an element as a result of the difference in mass between their nuclei. Processes resulting in large sulfur isotope fractionation include bacterial conversion of sulfur compounds, such as in bacterial sulfate reduction wherein the heavy sulfur isotope (^{34}S) is favored in the product, H_2S (hydrogen sulfide), which is consequently lost from the reactant pool. However, very little isotope fractionation has been observed in association with many other sulfur conversion processes, such as mineral salt formation, condensation of sulfate precipitates, or dissolution of sulfides³.

Atmospheric sulfur can be both naturally occurring and anthropogenic. Sources of naturally occurring sulfur include volcanic exhalations, sea spray, and hydrogen sulfide from anoxic ocean waters and sea marshes. Anthropogenic sources include aeolian transport of pulverized sulfide ores or sulfur emissions from ore smelting activities, vehicular emissions, as well as the combustion of coal,

and petroleum products. Especially in Alberta, emissions from processing and extracting sour gas (any gas containing large amounts of hydrogen sulfide) could be contributing significantly to local levels of atmospheric sulfur⁴. Of the naturally occurring isotopes of sulfur, the four most stable are ^{32}S , ^{33}S , ^{34}S and ^{36}S ³.

SO_2 in the atmosphere is oxidized in gas phase, in aqueous phase in raindrops, and on the surfaces of particles⁵. The rates of oxidation processes within the atmosphere are influenced by temperature and reactions with light (photochemistry). A common pathway for the oxidation of SO_2 to SO_4 (sulfate) with the effects of photochemistry is given in Figure 2^{5,6}. Finlayson-Pitts and Pitts⁵ also found that SO_2 oxidation is greater during the day and in the summer months than at night and in the winter months. This may have changed the findings of the study if it was performed during summer instead of the winter (though collection occurred during both day and night). It is during the above process and similar processes that sulfur isotope fractionation may occur.

In a study performed by Harris et al. (2012), isotopic fractionation of sulfur was demonstrated during heterogeneous oxidation of SO_2 on sea salt aerosol⁷. It was also found that as pH increased isotopic fractionation was larger. Harris et al. also studied isotope fractionation for SO_2 oxidation reactions with O_3 (ozone) and salts. The fractionation factor ($\alpha_{34} = R_{\text{product}}/R_{\text{reactant}}$ where $R = ^{34}\text{S}/^{32}\text{S}$) Harris et al. measured showed that fractionation by ozone in water droplets and sea salt aerosol favoured the heavier sulfur isotope, ^{34}S , in the product sulfate ($\alpha_{\text{seasalt}} = 1.0124 \pm 0.0017$). Conversely, oxidation in NaOCl (sodium hypochlorite) droplets favoured ^{32}S , in sulfate ($\alpha_{\text{OCl}} = 0.9882 \pm 0.0036$). As such, the products were enriched in ^{34}S and ^{32}S respectively. Samples for Harris et al.'s⁷ study were collected using an impinger (liquid filled vial into which air or a gas is bubbled), which is one method used in this study to find $\delta^{34}\text{S}$ values of SO_2 .

Whether or not sulfur isotope fractionation occurs during SO_2 oxidation in ambient samples in the atmosphere has been the focus of a number of studies. For example, Norman et al. (2004 and 2009) showed no evidence for sulfur isotope fractionation during SO_2 oxidation in the city of Calgary, Alberta and on

the west coast of Canada^{2,8}. High volume samplers, rather than impingers were used to collect particulate matter on a series of filters, followed by a filter treated with a K_2CO_3 (potassium carbonate) or triethanolamine and glycerol mixture, to trap SO_2 . The discrepancy between the findings of Harris et al. and Norman could in fact be due to the different collection methods (impinger vs high volume). In the current study the high volume method from Norman⁹ was used to obtain $\delta^{34}S$ values for both SO_2 and submicron aerosol SO_4 , which was then compared directly to the impinger SO_2 values to resolve the discrepancy in methods.

The experiment described here replicates the methods of Harris et al.'s⁷ study to determine whether sulfur fractionation is indeed occurring during SO_2 oxidation in the atmosphere. If the null hypothesis is rejected then sulfur isotope fractionation does occur during SO_2 oxidation in ambient air in a non-marine environment. This will be evidenced by little to no difference between the $\delta^{34}S_{SO_2}$ and $\delta^{34}S_{SO_4}$ values. Marine and non-marine environments may differ in regards to fractionation as sea salt aerosols could influence the process⁷. If the high volume and impinger samplers yield the same isotope values then the question of collection method interfering with fractionation will also be resolved.

Methods

2.1 Nomenclature and Notation: The isotopic composition of a sample is expressed with the δ (delta) notation, which is defined as the ratio of a heavy isotope to the most abundant isotope in the sample compared to a standard (Fig. 1). The most abundant isotope in this case is ^{32}S . Since isotope effects are commonly quite small, it is useful to refer to the differences in parts per thousand (‰). The accepted standard that is used is $^{32}S/^{34}S = 22.22$ from troilite in the Canyon Diablo meteorite³.

2.2 Impingers: The impinger method was used to obtain only SO_4 samples. Air was bubbled into a series of impingers in a manner similar to the setup used in the study performed by Harris⁷. Two of the three impingers were filled with a solution of 5% H_2O_2 (30% H_2O_2 and de-ionized water in a 1:5 ratio). Each impinger was filled with ~ 70 mL of this solution and an additional amount was sometimes added to samples during collection if the solution was running

low. An empty third impinger was used for overflow; in the event some solution entered the tubes it would be deposited here instead of in the diaphragm pump (Fig. 3A). The impingers were placed inside a rooftop laboratory at the University of Calgary. Tubing with a 0.45 micron glass filter to remove dust was brought through a window and was connected to the impinger. A diaphragm pump was attached to the downstream side of the impinger and drew in air at a rate of 1.0 L/min \pm 0.1 L/min (\pm precision). Six samples were collected for an average of three days each from Oct. 18, 2012 through to Dec. 6, 2012.

Sample solutions from the impingers were poured into a graduated cylinder and rinsed with de-ionized water to quantitatively transfer all the SO_4 . The total volume was recorded and two 10mL vials were filled for ion chromatography from which a concentration was obtained. $BaCl_2$ (5ml) was added to the remaining sample to precipitate $BaSO_4$ and sufficient HCl (hydrochloric acid) was added to ensure no $BaCO_3$ was present (pH <3). The solutions were then evaporated on a hot plate and reduced to less than 50 mL. The samples were then filtered using a 0.4 μ m nucleopore filter paper, similar to the process in Seguin et al.¹⁰. The precipitate mass, normalized for the volume of air sampled, was used to obtain sulfate concentrations gravimetrically. Samples were run through the mass spectrometer in the Applied Isotope Geochemistry lab in the University of Calgary. The analytic precision for the isotopic analyses was $\pm 0.2\%$ and the values were also corrected for blank sulfur.

2.3 High Volume Samplers: The high volume sampler method yielded both SO_2 and SO_4 samples. Air was drawn through a series of slotted filter papers using high volume samplers so that particulate matter in the air was filtered out. Two high volume samplers were run in unison in this study, one to obtain $\delta^{34}S_{SO_2}$ values and the other to obtain $\delta^{34}S_{SO_4}$ values. On one sampler a total particulate filter overlaying an SO_2 filter was deployed so that any particulates such as dust particles would be filtered out and only the SO_2 would be collected. The second sampler was fitted with five slotted size-segregated filters, housed in a cascade impactor, so only fine aerosols (<0.49 microns in diameter) were collected on the underlying particulate fibre filter (Fig. 3B). Flow rates were 800 L/min \pm 1 L/min and 1000 L/min \pm 1 L/min for the two samplers respectively. A malfunction occurred

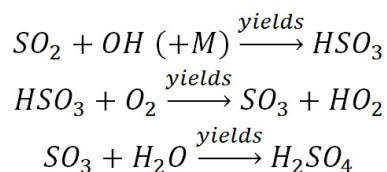


Figure 2:

Formula for delta notation. Delta notation is the standard way to represent the isotopic composition of a sample.

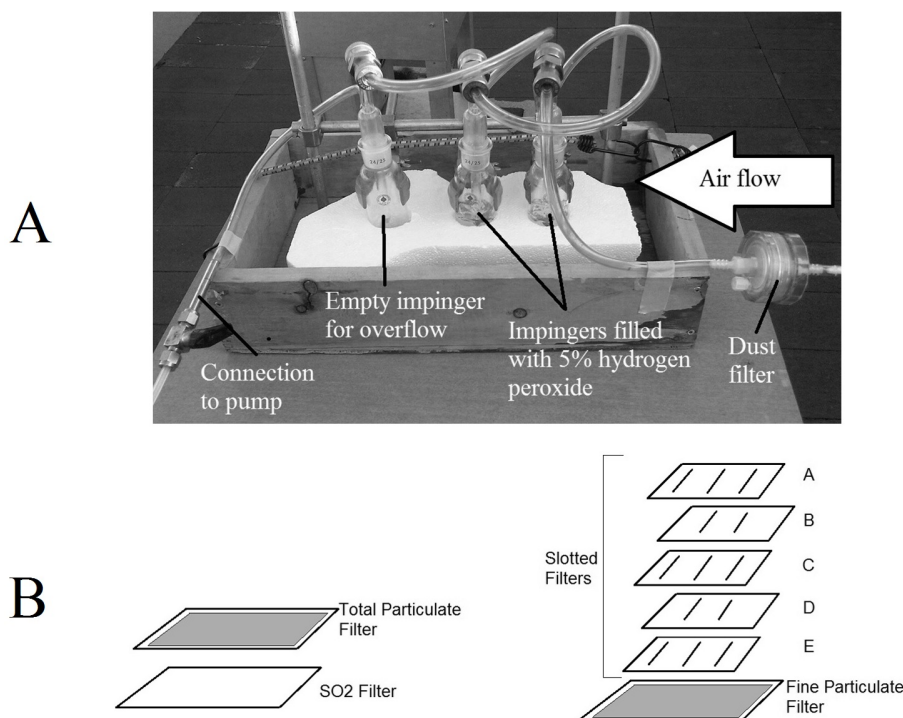


Figure 3:

Set-up of the impinger (A) and high volume (B) apparatus that were used to collect the samples from which δS values were then obtained. The high volume setup on the left collected for SO_2 while the setup on the right collected fine particulates for SO_4 .

during the collection period of sample 2 resulting in unreliable concentrations for the fine particulate matter sample. A new high volume sampler (1020 L/min \pm 1 L/min) was then installed and for samples 3 through 6, the new sampler operated with the cascade impactor while the total particulate filter and SO_2 filter were on the second sampler (740 L/min \pm 1 L/min). Six samples were collected outdoors on the roof of Science B (approx. 100m above ground) at the University of Calgary from Oct. 18, 2012 through to Dec. 6, 2012: each sampling period was approximately three days and corresponded to impinger sampling times. The flow rates and total

times that each sample was collected for were then used to calculate the total volume of air that passed through the filters and hence the concentrations of SO_4 and SO_2 could then be calculated. Precipitation conditions were noted as particulates could adhere to snow or rain, and hence would not be collected by the high volume samplers (Table 1).

Filter papers collected at the end of each sampling period were prepared according to the methods detailed in Seguin et al. ¹⁰.

2.4 Measurement Uncertainties: A variety of equipment was used during sample collection, each with its associated uncertainties. Sampling time

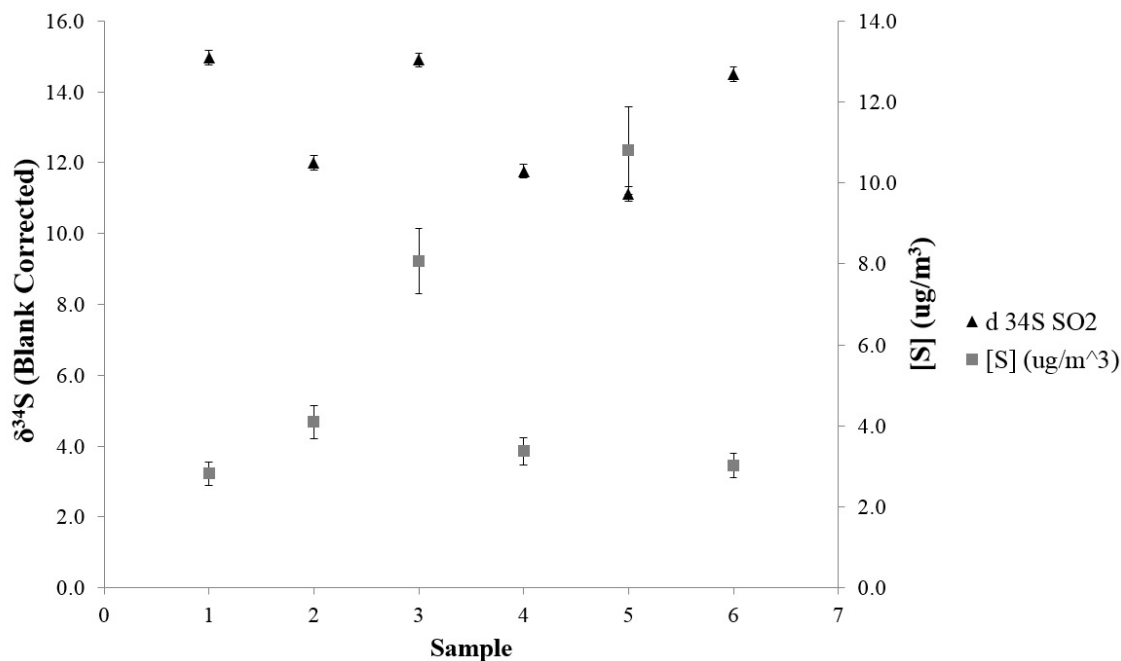


Figure 4:

$\delta^{34}\text{S}_{\text{SO}_2}$ values and concentrations of SO_2 in the atmosphere from six different samples collected using SO_2 filters in a high volume sampler. Bars represent the total uncertainty introduced in analysis and in the measurements made. No apparent correlation between $\delta^{34}\text{S}_{\text{SO}_2}$ and SO_2 concentration can be noted.

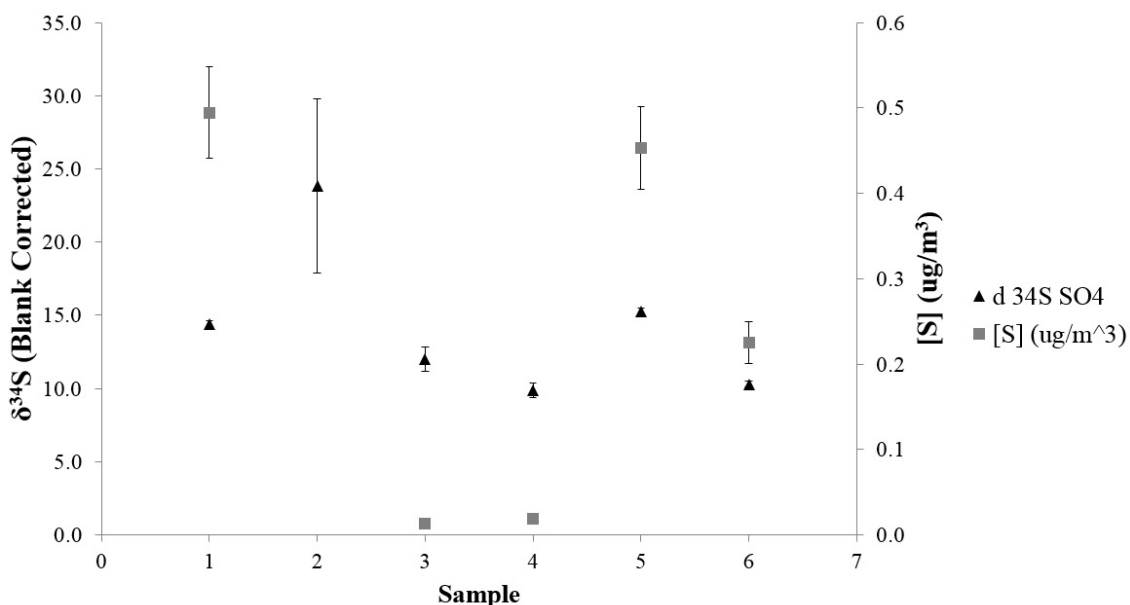


Figure 5:

$\delta^{34}\text{S}_{\text{SO}_4}$ values and concentrations of SO_4 in the atmosphere from six different samples collected using fine particulate filters in a high volume sampler. Bars represent the total uncertainty introduced in analysis and in the measurements made. For sample 2 the high volume sampler malfunctioned and an accurate time period was not known, so [S] was not calculated. No apparent correlation between $\delta^{34}\text{S}_{\text{SO}_4}$ and SO_4 concentration can be noted.

was monitored on an iPhone® clock to the nearest minute. A graduated cylinder to measure volume had an uncertainty of 1 mL. A Kurz Instruments Inc. High-Volume Sampler Calibrator was used to measure the air flow rate into the samplers with an uncertainty of 14.2 L/min. The impinger flow rate, measured with a rotameter, had an uncertainty of 0.20 L/min.

Quantities which were then calculated based on these measurements used the standard error propagation formula proposed by NIST (National Institute of Standards and Technology) to find the associated uncertainties¹¹.

Results

3.1 Impingers: Impinger sample 2 froze during collection and was disregarded. Samples 1, 3, 4, and 5 had minimal precipitate and were combined into one sample to obtain a $\delta^{34}\text{S}_{\text{SO}_2}$ value of $+14.0\% \pm 0.2\%$. As such, standard deviation could not be calculated and hence the $\pm 0.2\%$ is precision due to the spectrometer. A weighted average (the sum of each samples SO_2 concentration multiplied by its collection time, divided by collection time of all samples) of these four samples was calculated and this was used to obtain an SO_2 concentration in the air of $6.4 \mu\text{g}/\text{m}^3 \pm 1.3 \mu\text{g}/\text{m}^3$ (\pm std. dev.). Impinger sample 6 was not detected by the mass spectrometer.

3.2 High Volume Samplers: The $\delta^{34}\text{S}_{\text{SO}_2}$ values obtained from the SO_2 from the high volume samplers was, on average (\pm std. dev.) $+13.2\% \pm 0.2\%$ (Fig. 4). $\delta^{34}\text{S}_{\text{SO}_2}$ values ranged from $+11.1\% \pm 0.2\%$ to $+15.0\% \pm 0.2\%$, similar to what has been observed for Calgary in previous occasions by Norman et al.². No pattern in $\delta^{34}\text{S}$ values for SO_2 was observed over time or with concentrations (Fig. 4).

$\delta^{34}\text{S}_{\text{SO}_4}$ values for submicron aerosols were similar for samples 1, 3, 4, 5, and 6 while sample 2 had the most positive $\delta^{34}\text{S}$ value measured in this study ($+23.8\% \pm 5.9\%$) (Fig. 5, Table 1). Note that the sampling period for sample 2 was shorter than for the other samples. $\delta^{34}\text{S}_{\text{SO}_4}$ values for submicron aerosols ranged from $+9.9\% \pm 0.5\%$ to $+15.3\% \pm 0.2\%$. Concentrations for SO_4 in the six samples were significantly smaller ($t=3.80$, $df=5.06$, $p < 0.05$) than the corresponding SO_2 concentrations by an order of magnitude and varied from $0.0 \mu\text{g}/\text{m}^3$ to $0.5 \mu\text{g}/\text{m}^3 \pm 0.1 \mu\text{g}/\text{m}^3$. Samples 3 and 4 had much smaller

concentrations than samples 1, 5, and 6; essentially at $0 \mu\text{g}/\text{m}^3$. Such small concentrations are indicative of very clean air, which is common after precipitation events, and which likely affected sample 4 but not 3 (Table 1). However, this did not appear to have an effect on their $\delta^{34}\text{S}_{\text{SO}_4}$ values: the sulfur isotope composition of samples 3 and 4 were similar to the other samples collected.

$\delta^{34}\text{S}$ values and concentrations from the SO_2 and fine particulate filters did not follow patterns as would be expected if a particular oxidation pathway and isotope fractionation process were favoured⁷. Snow events were logged during the collection of samples 1, 2, 4, and 5 (Table 1) but this appears to have had no effect on the data obtained as the SO_2 and SO_4 $\delta^{34}\text{S}$ values remained within a narrow range and, in some cases, were similar to the samples collected when no snow events occurred.

Discussion

This study is the first to directly compare two methods of assessing fractionation of sulfur. The two methods compared were those of impingers and high volume samplers. A mean $\delta^{34}\text{S}_{\text{SO}_2}$ value of $+13.2\% \pm 0.2\%$ was found for SO_2 from the high volume sampler and variations in SO_2 concentrations ranged from $2.8 \pm 0.3 \mu\text{g}/\text{m}^3$ to $10.8 \pm 1.1 \mu\text{g}/\text{m}^3$. $\delta^{34}\text{S}_{\text{SO}_2}$ values were independent of SO_2 concentration. Similarly, $\delta^{34}\text{S}_{\text{SO}_4}$ values for fine particulate matter ranged between $+9.9\% \pm 0.5\%$ to $+15.3\% \pm 0.2\%$ while the SO_4 concentrations were highly variable. Again this suggests that the $\delta^{34}\text{S}_{\text{SO}_4}$ values were not dependent upon the SO_4 concentration in the air. Samples 3 and 4 had minimal SO_4 concentrations, indicating the air on the days these samples were collected was exceptionally clean. These two samples should be particularly representative of whether or not fractionation occurred as the smallest fraction of SO_2 reaction can be reasonably assumed. This low SO_4 concentration is particularly common after precipitation events and a snow event was recorded during the collection of sample 4.

The $\delta^{34}\text{S}_{\text{SO}_2}$ values from the SO_2 filters were plotted against the $\delta^{34}\text{S}_{\text{SO}_4}$ values from the fine particulate filters in Fig. 6 to determine whether isotope fractionation could be detected. If fractionation were to occur, a consistent difference in the $\delta^{34}\text{S}_{\text{SO}_2}$ and $\delta^{34}\text{S}_{\text{SO}_4}$ values should be observed.

High Volume Filter Results								
Sample	Dates of Collection (mm/dd)	Total Time Collected (minutes)	Snow Event (Yes/No)	$\delta^{34}\text{S}_{\text{SO}_2}$ (‰)	$[\text{SO}_2]$ ($\mu\text{g}/\text{m}^3$)	$\delta^{34}\text{S}_{\text{SO}_4}$ (‰)	$[\text{SO}_4]$ ($\mu\text{g}/\text{m}^3$)	Max S Reacted (%)
1	18/10 to 23/10	2954 ± 0.5	Y	15.0 ± 0.2	2.8 ± 0.3	14.4 ± 0.2	0.5 ± 0.1	17.5
2	6/11 to 9/11	4135 ± 0.5	Y	12.0 ± 0.2	4.1 ± 0.4	23.8 ± 5.9	-	-
3	21/11 to 27/11	4277 ± 0.5	N	14.9 ± 0.2	8.1 ± 0.8	12.0 ± 0.8	0.0 ± 0.0	0.2
4	27/11 to 30/11	3952 ± 0.5	Y	11.8 ± 0.2	3.4 ± 0.3	9.9 ± 0.5	0.0 ± 0.0	0.6
5	30/11 to 3/12	4077 ± 0.5	Y	11.1 ± 0.2	10.8 ± 1.1	15.3 ± 0.2	0.5 ± 0.0	4.2
6	3/12 to 6/12	4091 ± 0.5	N	14.5 ± 0.2	3.0 ± 0.3	10.3 ± 0.2	0.2 ± 0.0	7.5
Impinger Results								
1-5	18/10 to 3/12	15289 ± 0.5	-	+14.0 ± 0.2	6.4 ± 1.3			
6	3/12 to 6/12	4100 ± 0.5	-	-	-			

Table 1:

Dates and times the six samples were collected for, precipitation events, and results. No concentration for high volume sample 2 was calculated as the time of collection was unknown. Impinger samples 1-5 were combined to get a single reading (except for sample 2 which froze). Impinger sample 6 was below the detection limit of the mass spectrometer.

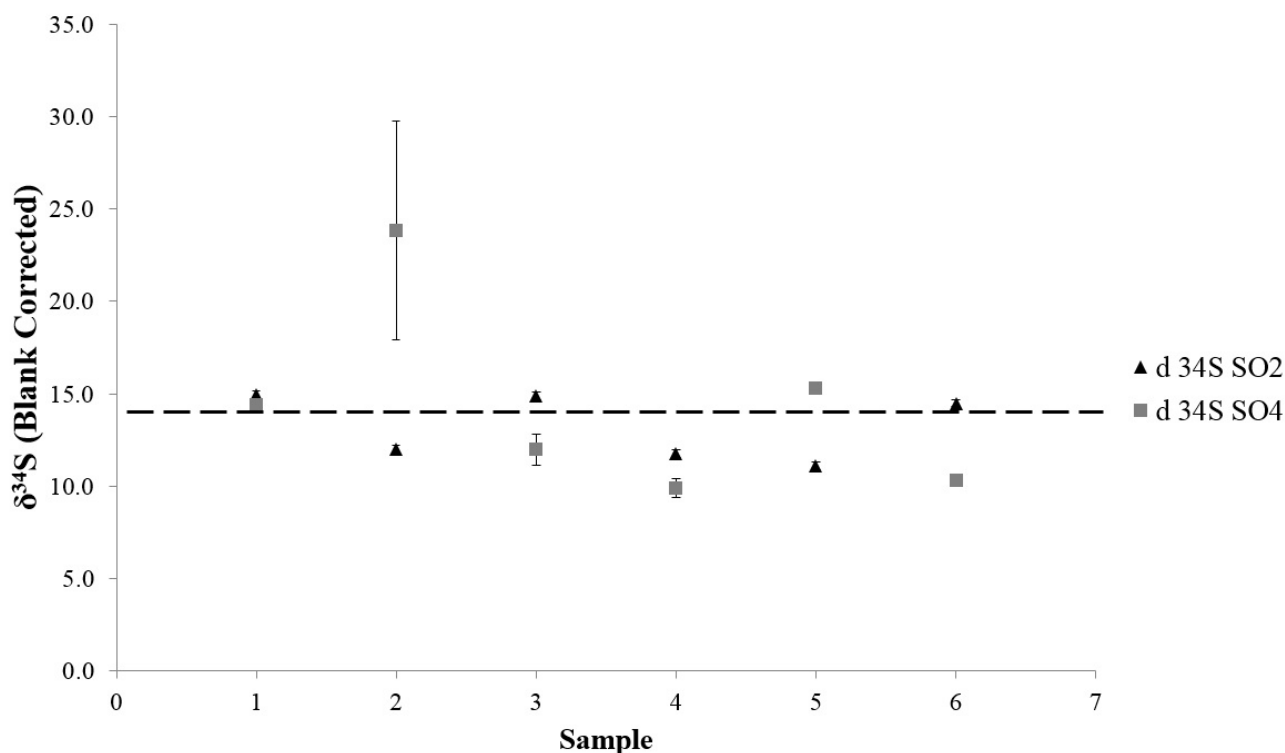


Figure 6:

Comparison of $\delta^{34}\text{S}_{\text{SO}_2}$ and $\delta^{34}\text{S}_{\text{SO}_4}$. Bars represent the total uncertainty introduced in analysis and in the measurements made. The line at 14.01‰ represents the $\delta^{34}\text{S}_{\text{SO}_2}$ value obtained by impinger samples 1 through 5. Note that sample number is not a variable of interest but rather was included to help organize the data. The similarity between the $\delta^{34}\text{S}_{\text{SO}_2}$ and $\delta^{34}\text{S}_{\text{SO}_4}$ values but lack of a consistent difference indicates no sulfur isotope fractionation occurred. The similarity between the $\delta^{34}\text{S}_{\text{SO}_2}$ values and the impinger value (dotted line) indicates that the high volume and impinger method yield similar isotopic results.

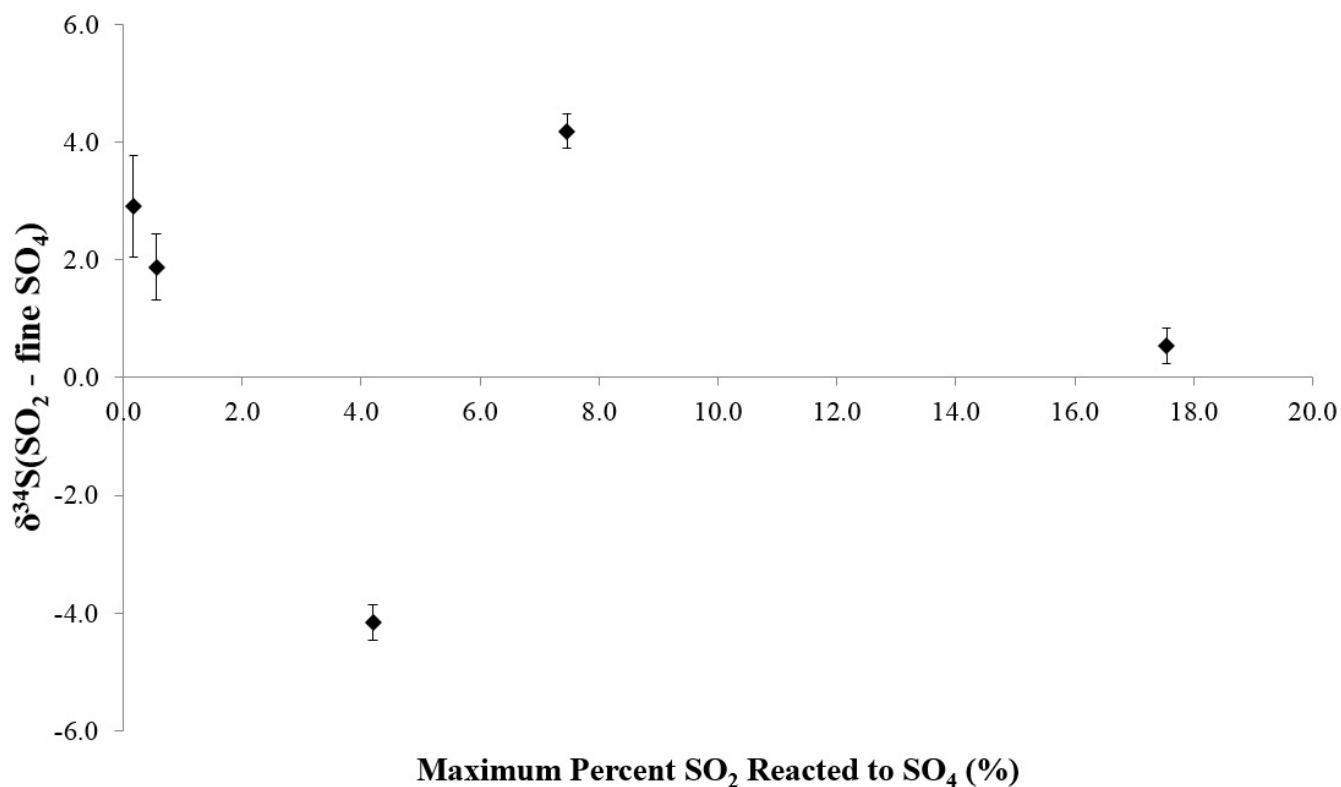


Figure 7:

Comparison of the $\Delta\delta^{34}\text{S}_{\text{SO}_2-\text{SO}_4(\text{fine})}$ to the maximum percent of SO_2 that reacted to form SO_4 . No trend between fraction of reaction (percent SO_2 reacted) and difference in delta values was noticeable and so no sulfur isotope fractionation was occurring.

Sample	$\Delta\delta^{34}\text{S}(\text{SO}_2\text{-impinger})$	$\Delta\delta^{34}\text{S}(\text{fine SO}_4\text{-impinger})$
1	0.96	0.42
2	-2.01	9.83
3	0.89	-2.02
4	-2.25	-4.12
5	-2.89	1.27
6	0.48	-3.70
Average	-0.80	0.28
Standard Deviation	1.76	5.15

Table 2:

Quantification of Figure 6. Differences between the impinger values and the $\delta^{34}\text{S}_{\text{SO}_2}$ and $\delta^{34}\text{S}_{\text{SO}_4}$ with the associated averages and standard deviations. The standard deviations were larger than the averages, indicating a lack of consistent differences and hence no sulfur isotope fractionation.

Aside from sample 2 (which is associated with a high volume sampler malfunction), the $\delta^{34}\text{S}_{\text{SO}_2}$ and $\delta^{34}\text{S}_{\text{SO}_4}$ values of the remaining samples were very close to one another and, on average, were near +14‰, the value obtained for SO_2 by the impingers. The similarity in the $\delta^{34}\text{S}_{\text{SO}_2}$ and $\delta^{34}\text{S}_{\text{SO}_4}$ values (but lack of a consistent difference) in the samples indicates that no sulfur isotope fractionation occurred. Figure 6 is also quantified in Table 2, where the averages and standard deviations of the differences between $\delta^{34}\text{S}_{\text{SO}_2}$ and $\delta^{34}\text{S}_{\text{SO}_4}$ from the high volume samplers compared to the $\delta^{34}\text{S}_{\text{SO}_2}$ from the impinger were calculated. It was found that the standard deviations were larger than the averages, indicating lack of a consistent difference (Table 2). Further verification that no fractionation occurred is seen in Figure 7. The $\delta^{34}\text{S}_{\text{SO}_2}$ and $\delta^{34}\text{S}_{\text{SO}_4}$ values were compared by subtracting the $\delta^{34}\text{S}_{\text{SO}_4}$ from the $\delta^{34}\text{S}_{\text{SO}_2}$ then calculating the maximum percent of SO_2 that reacted to form SO_4 . The difference in δ values was plotted versus the maximum percent of SO_2 that reacted (Fig. 7), and if isotope fractionation were occurring then a trend (such as an increase in the difference between $\delta^{34}\text{S}_{\text{SO}_2}$ and $\delta^{34}\text{S}_{\text{SO}_4}$ with an increase in maximum percent SO_2 reacted) in the data as the fraction of reaction proceeded³ should be evident. The lack of a trend with fraction of reaction demonstrates that no fractionation occurred.

Though this study was replicated over time, there was not a spatial component. Based on sampling location, the occurrence and amount of fractionation could vary due to large differences in atmospheric SO_2 concentrations, environmental conditions, or other such factors (such as sea salt aerosols in a marine setting). Confidence is added to this study though given that no relation was found between sulfur concentration and $\delta^{34}\text{S}$ value (Fig. 4 and Fig. 5). Furthermore, a range of high volume samplers could also be implemented to account for possible bias from a specific sampler. This may have been adjusted for when one of the high volume samplers malfunctioned and a new one was implemented, but this possibility could also be incorporated into future studies (along with a spatial component).

As a result of the findings, the study failed to reject the null hypothesis but is in contrast to what Harris⁷ found by sampling sea salt aerosols with impingers. It does however correspond to the findings of Norman⁸ who also showed no evidence

of fractionation occurring. As such, apportionment studies of sulfur isotopes can assume that isotope fractionation during SO_2 oxidation is small and hence accurately reflect their source. It is important to note that the $\delta^{34}\text{S}_{\text{SO}_2}$ value of $+14.0\text{‰} \pm 0.2\text{‰}$ obtained by the impingers was nearly identical to the $\delta^{34}\text{S}_{\text{SO}_2}$ values obtained by the SO_2 filter papers $+13.2\text{‰} \pm 0.2\text{‰}$ (Fig. 6). The impingers and the SO_2 filters also yielded close results for the same concentration of SO_2 in the atmosphere for the same sampling period. The similarity in the results of both methods means that neither is detecting a unique artifact that is not being picked up by the other method, hence either method could be used with confidence that similar results would be obtained.

Conclusion

Impingers and high volume samplers with total particulate, fine particulate, and SO_2 filters were used to collect samples from which $\delta^{34}\text{S}_{\text{SO}_2}$, $\delta^{34}\text{S}_{\text{SO}_4}$, $[\text{SO}_4]$, and $[\text{SO}_2]$ values were calculated. It was found that the impinger method and the SO_2 filters yielded similar $\delta^{34}\text{S}_{\text{SO}_2}$ values of around +14.0‰. The important finding of this study is that no fractionation was found to occur during SO_2 oxidation in ambient air in a non-marine environment.

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