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Sulfur isotope fractionation during oxidation of sulfur dioxide: gas-phase oxidation by OH radicals and aqueous oxidation by H$_2$O$_2$, O$_3$ and iron catalysis

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Abstract. The oxidation of SO$_2$ to sulfate is a key reaction in determining the role of sulfate in the environment through its effect on aerosol size distribution and composition. Sulfur isotope analysis has been used to investigate sources and chemical processes of sulfur dioxide and sulfate in the atmosphere, however interpretation of measured sulfur isotope ratios is challenging due to a lack of reliable information on the isotopic fractionation involved in major transformation pathways. This paper presents laboratory measurements of the fractionation factors for the major atmospheric oxidation reactions for SO$_2$: gas-phase oxidation by OH radicals, and aqueous oxidation by H$_2$O$_2$, O$_3$ and a radical chain reaction initiated by iron. The measured fractionation factors for $^{34}$S/$^{32}$S during the gas-phase reaction is $\alpha_{\text{OH}} = (1.0089\pm0.0007) - ((4.5\pm5)\times10^{-5})T(\degree\text{C})$. The measured fractionation factor for $^{34}$S/$^{32}$S during aqueous oxidation by H$_2$O$_2$ or O$_3$ is $\alpha_{\text{aq}} = (1.0167\pm0.0019) - ((8.7\pm3.5)\times10^{-5})T(\degree\text{C})$. The observed fractionation during oxidation by H$_2$O$_2$ and O$_3$ appeared to be controlled primarily by protonation and acid-base equilibria of S(IV) in solution, which is the reason that there is no significant difference between the fractionation produced by the two oxidants within the experimental error. The isotopic fractionation factor from a radical chain reaction in solution catalysed by iron is $\alpha_{\text{Fe}} = (0.9894\pm0.0043)$ at 19$\degree$C for $^{34}$S/$^{32}$S. Fractionation was mass-dependent with regards to $^{33}$S/$^{32}$S for all the reactions investigated. The radical chain reaction mechanism was the only measured reaction that had a faster rate for the light isotopes. The results presented in this study will be particularly useful to determine the importance of the transition metal-catalysed oxidation pathway compared to other oxidation pathways, but other main oxidation pathways cannot be distinguished based on stable sulfur isotope measurements alone.

1 Introduction

Sulfate and sulfur dioxide play an important role in environmental chemistry and climate through their effect on aerosols. The majority of anthropogenic sulfur is released directly as SO$_2$, and a significant fraction of biogenic and natural sulfur (e.g. OCS, DMS) is also either directly released as SO$_2$ or oxidised to SO$_2$ in the atmosphere (Berresheim et al., 2002; Seinfeld and Pandis, 1998). Around 50% of global atmospheric sulfur dioxide is then oxidised to sulfate, while the rest is lost through dry and wet deposition (Chin et al., 1996). The oxidation pathway – heterogeneous or homogeneous – is an important factor because it determines the effect that sulfate will have on the environment.

Homogeneous oxidation in the gas phase by OH radicals follows several steps (Tanaka et al., 1994):

\begin{align*}
\text{SO}_2 + \text{OH} + \text{M} & \rightarrow \text{HOSO}_2 + \text{M} \quad (1) \\
\text{HOSO}_2 + \text{O}_2 & \rightarrow \text{SO}_3 + \text{HO}_2 \quad (2) \\
\text{SO}_3 + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{SO}_4 \quad (3)
\end{align*}
The product is sulfuric acid, which can stick to the surface of existing particles or nucleate to form new particles in the atmosphere (Benson et al., 2008; Kulmala et al., 2004). These new particles have a direct radiative effect and may also grow to act as cloud condensation nuclei (CCN).

Heterogeneous oxidation acts upon S(IV) in solution or on particle surfaces. The major oxidants are H2O2, O3 and O2, the latter being catalysed by Fe3+ and other transition metal ions in a radical chain reaction pathway (Herrmann et al., 2000). The dissolution of SO2 before oxidation follows several steps (Eriksen, 1972a):

\[
\text{SO}_2(g) \leftrightarrow \text{SO}_2(aq) \tag{4}
\]
\[
\text{SO}_2(aq) + \text{H}_2\text{O} \leftrightarrow \text{HSO}_3^- + \text{H}^+ \tag{5}
\]
\[
\text{HSO}_3^- + \text{H}^+ \leftrightarrow \text{H}_2\text{SO}_3 \tag{6}
\]
\[
\text{HSO}_3^- \leftrightarrow \text{SO}_3^{2-} + \text{H}^+ \tag{7}
\]
\[
2\text{HSO}_3^- \rightarrow \text{H}_2\text{O} + \text{S}_2\text{O}_5^{2-} \tag{8}
\]

Equation (6) has a pK_a of 1.77 and Eq. (7) has a pK_a of 7.19 (Moore et al., 2005). Oxidation by H2O2 is not significantly dependent on pH within normal atmospheric pH ranges (pH = 2–7), while oxidation by transition metal catalysis and O3 becomes faster as pH increases (Seinfeld and Pandis, 1998). Heterogeneous oxidation produces sulfate on the surface of particles or in droplets, changing their CCN activity and lifetime through growth and increased hygroscopicity (Bower and Choularton, 1993; Mertes et al., 2005). Thus, a comprehensive knowledge of the oxidation and removal of SO2 and sulfate is key to understanding and modelling aerosol and cloud formation and processes and their effects on past and future climate.

Aerosol direct and indirect effects continue to contribute the largest uncertainty to estimates of anthropogenic global mean radiative forcing (IPCC, 2007). Global emissions of anthropogenic sulfur in Europe and North America have decreased significantly in the past few decades, however as Asian sulfur emissions are increasing due to energy demand and coal use, and are not expected to decrease until at least 2020 (IPCC, 2007), anthropogenic emissions are likely to remain the major global source of non-sea salt sulfate (Chin et al., 1996; Seinfeld and Pandis, 1998). Understanding the sulfur cycle is therefore necessary to reduce the uncertainty in aerosol forcing estimates.

This study presents measurements of stable sulfur isotope fractionation during gas-phase oxidation by the OH radical and oxidation in the aqueous phase by H2O2 or O3 will only be possible if stable sulphur isotope analysis is combined with studying the mass independent oxygen isotopic fractionation.

2 Sulfur isotopes in the environment

The isotopic composition of sulfur in the environment reflects its sources, transport and chemistry, so measurements of stable sulfur isotopes can be effectively used to constrain the sulfur cycle. Sulfur has four naturally-occurring stable isotopes: 32S, 33S, 34S and 36S. The isotopic composition of a sulfur sample is represented by its delta value, which is the permil deviation of the ratio of a heavy isotope to the most abundant isotope (32S) in the sample compared to a standard ratio:

\[
\delta^{34}S (\text{%o}) = \left( \frac{n(34S)_{\text{sample}}}{n(32S)_{\text{sample}}} - 1 \right) \times 1000 \tag{9}
\]

where \(n\) is the number of atoms, \(^{34}\)S is one of the heavy isotopes, \(^{33}\)S, \(^{34}\)S or \(^{36}\)S, and V-CDT is the international sulfur isotope standard, Vienna Canyon Diablo Troilite, which has isotopic ratios of \(^{34}\)S/\(^{32}\)S = 0.044163 and \(^{33}\)S/\(^{32}\)S = 0.007877 (Ding et al., 2001).

Chemical reactions, for example the oxidation of SO2 to sulfate, cause fractionation of isotope ratios between reactants and products as long as the reaction does not go to completion. The fractionation may be due to equilibrium or kinetic discrimination, and is represented by the fractionation factor \(\alpha\). For an irreversible reaction, fractionation is kinetic and \(\alpha\) is the ratio of the rate constants: \(\alpha = k_3/k_{32}\). When the reactant is present as an infinite reservoir and not affected by the reaction, \(\alpha_{34}\) can be calculated from the isotopic compositions of products and reactants:

\[
\alpha_{34} = \frac{R_{\text{products}}}{R_{\text{reactants}}} \tag{10}
\]

where \(R = \frac{34S}{32S}\). Thus, \(\alpha > 1\) indicates that the heavy isotopes react faster than the light isotopes. The permil differences between reactants and products with regards to \(\alpha\) and reaction extent in a closed system are described by the Rayleigh laws (Mariotti et al., 1981; Krouse and Grinenko, 1991), which are discussed in Sects. 3.2.3 and 4.1.1. Thus, isotopic fractionation can not only distinguish between reactions: For known irreversible reactions in a closed system, the isotopic fractionation can provide quantitative information about how far the reaction has gone to completion.

The isotopic composition of many major sources of atmospheric sulfur have been measured (e.g., Rees et al., 1978; Krouse et al., 1991; Nielsen et al., 1991; Sanusi et al., 2006). The isotopic composition of anthropogenic sources is highly variable on a global scale, though individual sources are often well constrained. The isotopic composition of industrial emissions is also affected by process technology such
as the flue gas desulfurization unit of an industrial plant (Derda et al., 2007). However, for field studies measuring the isotopic composition of both ambient SO$_2$ and sulfate, the major limitation to interpreting atmospheric isotope measurements is the lack of laboratory studies of the isotopic fractionation factors involved in the most common atmospheric reactions of sulfur (Tanaka et al., 1994; Novak et al., 2001; Tichomirowa et al., 2007). For heterogeneous oxidation, equilibrium fractionation of $^{34}$S/$^{32}$S during the uptake of SO$_2$ into solution and the subsequent acid-base equilibria has been measured in several studies. The results range between $\alpha_{\text{het}} = 1.010$ and 1.017 at 25°C (Egiazarov et al., 1971; Eriksen, 1972a). So far, the isotopic effect of the terminating oxidation of S(IV) to S(VI) has not been investigated.

The kinetic fractionation during homogeneous gas-phase oxidation of SO$_2$ by OH radicals has been estimated to be $\alpha_{\text{hom}} = 0.991$ by ab initio calculations (Tanaka et al., 1994) or to be $\alpha_{\text{hom}} = 1.14$ by RRKM theory (Leung et al., 2001). The discrepancy between these two estimates is larger than the measured variation in atmospheric sulfur samples (Norman et al., 2006). Several atmospheric studies have also tried to infer the fractionation during this reaction. Seasonality in data, with lower $\delta^{34}$S values measured for sulfate in summer, could show that the gas-phase fractionation factor is less than the heterogeneous fractionation factor and probably less than 1 (Saltzman et al., 1983; Sinha et al., 2008a). However, seasonality may also be explained by changing sources or the temperature-dependence of fractionation factors (Caron et al., 1986; Novak et al., 2001; Ohizumi et al., 1997). The study of $\Delta^{17}$O of sulfate trapped in ice cores showed that the ratio of gas-phase to aqueous-phase oxidation was higher and the $\delta^{34}$S was lower during the last glacial maximum than the preceding and subsequent interglacials (Alexander et al., 2002, 2003). The authors suggest isotopic fractionation progressively affects the SO$_2$ reservoir during transport as the sulfate is removed quickly, thus the data would show that $\alpha_{\text{hom}} > \alpha_{\text{het}}$. However, this progressive depletion in the reservoir signature has not been explicitly modelled and compared with measurements, so the isotopic composition in the ice-core could be directly representative of the oxidation and show that $\alpha_{\text{hom}} < \alpha_{\text{het}}$. Therefore, the goal of this study is to determine sulfur isotope fractionation factors for the main oxidation pathways of SO$_2$ to facilitate the use of sulfur isotopes in understanding the atmospheric sulfur cycle.

3 Experimental

3.1 Apparatus

The reaction system used to investigate the oxidation of SO$_2$ is shown in Fig. 1. The reactors were made of glass and their internal surfaces were coated with FEP 121a (Dupont) to minimise wall loss of H$_2$SO$_4$. PFA tubing and connectors were used for gas transfer between experimental components. Pressure was monitored with a capacitance manometer. The reactor had a thermostatted jacket connected to a circulating cooler (Julabo Labortechnik GmbH, Model F81-HL) to regulate temperature. The actual gas-phase reaction temperature was calibrated to the set temperature of the Julabo instrument with a PT-100Ω resistance.
sensor fitted into the glass reactor. The flows of all gases to the reactor were controlled using mass flow controllers referenced to standard conditions of temperature and pressure for \( N_2 \) \( (T_s = 273.15 \text{ K}, P_s = 1013.25 \text{ mBar}) \) (MKS Instruments Deutschland GmbH, uncertainty = 0.5 % of reading plus 0.2 % of full scale), and flows and leaks were checked regularly with a Gilibrator (Sensidyne, uncertainty < 1 % of reading). \( \text{SO}_2 \) gas (Westfalen AG, Linde AG, both 102 ppm ± 2 % in synthetic air) was diluted with synthetic air (Westfalen AG, 20.5 % \( \text{O}_2 \) in \( \text{N}_2 \)) to the desired concentration before it entered the reactor. The outflow from the reactor passed through the \( \text{H}_2\text{SO}_4 \) glass and \( \text{SO}_2 \) bubbler collectors, described in detail in Sect. 3.4. The length of tubing from the reactor to the \( \text{H}_2\text{SO}_4 \) collectors was < 7 cm, which would lead to a maximum of ∼22 % loss of \( \text{H}_2\text{SO}_4 \) according to the wall loss calculations from Zasyakin et al. (1997) (Eq. 15). This will be higher than the actual wall loss as the estimate is for glass and not PFA. The sulfuric acid will at this stage be nucleated (see Section 3.4.1), thus the isotopic effect will be negligible as the relative mass difference due to an isotopic substitution in a particle will be \( \ll 1 \) %. Most experiments were run for 7–8 h to generate sufficient product for isotopic analysis. The exact conditions of each experiment are detailed in the relevant section.

Following each experiment, the collection systems were emptied immediately. The solution from the \( \text{SO}_2 \) bubblers, containing hydrogen peroxide and sulfate, was poured into a clean beaker and the bubblers were rinsed with MilliQ water several times into the beaker. The \( \text{H}_2\text{SO}_4 \) trap was rinsed at least five times with MilliQ water to remove all the adsorbed \( \text{H}_2\text{SO}_4 \), and the solution was collected in a beaker. An excess of \( \text{BaCl}_2 \) was added to each solution to precipitate \( \text{S(VI)} \) as \( \text{BaSO}_4 \), as well as sufficient \( \text{HCl} \) to lower the pH to approximately 3 for optimal precipitation (Rees and Holt, 1991). After at least 12 h to ensure complete precipitation, the solutions were filtered through Nucleapore track-etch polycarbonate membrane filters (Whatman Ltd.) with 0.2 µm pores, which had been coated with a 10 nm thick gold layer using a sputter coater (Bal-tec GmbH, Model SC-050) prior to sample collection. Several rinses with MilliQ water removed any remaining \( \text{BaCl}_2 \) from the \( \text{BaSO}_4 \) precipitate and the filters were dried at room temperature. Samples with a large amount of material, where sulfate grains were clumped in groups, were gold-coated to prevent charging during SEM and NanoSIMS analysis.

### 3.2 Aqueous oxidation

#### 3.2.1 Aqueous oxidation by the radical chain reaction mechanism

Aqueous oxidation by a radical chain reaction initiated by \( \text{Fe}^{3+} \) (Herrmann et al., 2000) was measured by bubbling \( \text{SO}_2 \) through a solution containing 0.1 M \( \text{Fe(Cl)}_2 \) and 0.1 M \( \text{Fe(Cl)}_3 \). The product sulfate was collected from two bubblers in series. The quantity and isotopic composition of the sulfate in the second bubbler was equal to that in the first bubbler, showing the \( \text{SO}_2 \) was not significantly depleted.

#### 3.2.2 Aqueous oxidation by \( \text{H}_2\text{O}_2 \) in bulk aqueous phase

\( \text{SO}_2 \) gas was collected by bubbling through a solution of 6 % \( \text{H}_2\text{O}_2 \) in an ice bath, thus the fractionation during collection of \( \text{SO}_2 \) is a direct measure of the fractionation during oxidation of \( \text{SO}_2 \) by \( \text{H}_2\text{O}_2 \) in solution at 0 °C under non-equilibrium conditions. This reaction was run eight times under a variety of conditions to fully characterise collection of \( \text{SO}_2 \) as described later in Section 3.4.2, and these experiments gave a robust value for the fractionation of sulfur isotopes during oxidation of \( \text{SO}_2 \) by \( \text{H}_2\text{O}_2 \).

#### 3.2.3 Aqueous oxidation by \( \text{H}_2\text{O}_2 \) and \( \text{O}_3 \) in droplets

Oxidation by \( \text{H}_2\text{O}_2 \) and \( \text{O}_3 \) in the atmosphere occurs primarily in droplets and not in the bulk phase, thus it is necessary to investigate whether droplet-specific effects such as surface tension, the difference in saturation vapour pressure over a curved surface compared to a bulk solution, and changes in droplet pH as the reaction proceeds, affect the isotopic fractionation.

Reactor 2 (Fig. 1) did not produce detectable OH (see Sect. 3.3.1 for details of OH quantification) at the reaction point where the humid, UV-irradiated air was mixed with the \( \text{SO}_2 \) flow. A small amount of \( \text{OH} \) was generated at the lamp tip in this reactor, however the residence time of humidified air at the lamp was short and all \( \text{OH} \) generated was lost before reaching the reaction point. \( \text{H}_2\text{O}_2 \) was produced following \( \text{H}_2\text{O} \) photolysis to \( \text{OH} \), and as the lifetime of \( \text{H}_2\text{O}_2 \) is longer than that of the OH radical, ∼5 ppbv (mol mol⁻¹ gas at atmospheric pressure; ppbv will only be used to discuss gas phase concentrations in this paper) of \( \text{H}_2\text{O}_2 \) is present at the reaction point. \( \text{O}_3 \) resulted from \( \text{O}_2 \) photolysis and was present at concentrations of > 10 ppmv at the reaction point.

The reaction was therefore run in Reactor 2 at close to 100 % relative humidity to investigate aqueous oxidation by \( \text{H}_2\text{O}_2 \) and \( \text{O}_3 \) in droplets rather than a bulk solution in the absence of OH. The experiments were run at room temperature. Humid air was generated by bubbling synthetic air through water and was added both through the photolysis tube and through a second entry into the reactor normally used to monitor pressure. Neither flow passed through a trap to break up or remove large droplets and the humidity was negligibly reduced by the addition of 10 sccm dry \( \text{SO}_2 \) gas to make a total flow of 600 sccm, so the reactor was operated at 98 % relative humidity in the presence of droplets. Although oxidation by ozone would initially dominate, the pH in the system would very quickly decrease as sulfate was generated so the bulk of the reaction would be due to \( \text{H}_2\text{O}_2 \) (Seinfeld and Pandis, 1998). A very large amount of product
(>1 mg) was generated, which significantly altered the isotopic composition of the SO$_2$ gas. The fractionation factor $\alpha$ must therefore be found from the Rayleigh equations for residual reactants and products (Mariotti et al., 1981; Nriagu et al., 1991):

$$\alpha = \frac{\ln \left( \frac{R_P}{R_0} \right)}{\ln(f)} + 1$$  \hspace{1cm} (11)

and

$$\alpha = \frac{\ln \left[ 1 - (1 - f) \frac{R_P}{R_0} \right]}{\ln(f)}$$ \hspace{1cm} (12)

where $f$ is the fraction of reactant (SO$_2$) remaining after the reaction time (residence time = 26 seconds) and $R_0$, $R_K$ and $R_P$ are the isotope ratios $^{34}$S/$^{32}$S for the initial gas, the residual reactant and the product respectively. The reaction extent can be found from the isotopic mass balance:

$$\delta^{34}S_i = f \delta^{34}S_{SO_2} + (1 - f) \delta^{34}S_{H_2SO_4}$$  \hspace{1cm} (13)

where $\delta^{34}S_i$ is the initial composition of SO$_2$ and $\delta^{34}S_{SO_2}$ and $\delta^{34}S_{H_2SO_4}$ are the isotopic compositions of residual SO$_2$ and product H$_2$SO$_4$ when a fraction $f$ of the initial SO$_2$ remains. Around 65 % of SO$_2$ was oxidised under high humidity conditions.

To isolate the effect of O$_3$ on the product isotopic composition, the reaction was run with a glass attachment that passed dry synthetic air over the Hg lamp to generate 1000 ppm ozone. As the photolysed air was dry the H$_2$O$_2$ concentration will be negligible. Humidified air at 40 % relative humidity was added to the reactor and was not exposed to UV light. The product sulfate and the residual SO$_2$ were collected and there was no significant change in the SO$_2$ isotopic composition.

### 3.3 Gas-phase oxidation

OH radicals were generated from the photolysis of water vapour, and allowed to react with SO$_2$ in the reactor shown in Fig. 1. The SO$_2$ concentration was much higher than the OH concentration so the isotopic composition of SO$_2$ was not significantly affected by the reaction. The sulfuric acid gas product was collected, as described previously in Sect. 3.1, to determine the value of the fractionation factor for the reaction of SO$_2$ and OH.

#### 3.3.1 OH generation

OH was generated from the photolysis of water vapour at around 30 % relative humidity. 100 sccm of humidified nitrogen was passed over a low-pressure mercury vapour lamp (Jelight Company Inc., USA), which produces light at 184.9 nm resulting in the generation of OH radicals (Cantrell et al., 1997):

$$\text{H}_2\text{O} + h\nu \rightarrow \text{OH} + \text{H}$$  \hspace{1cm} (14)

The OH concentration was determined by chemical titration with pyrrole (Sinha et al., 2008b, 2009), which entered the reactor through the SO$_2$ inlet and thus saw the same OH flux as SO$_2$. Two similar reactors were used to measure the OH + SO$_2$ reaction and the influence of potential interfering reactions (Fig. 1). Reactor 1 produced 11 ppbv of OH. Reactor 2 did not produce detectable OH at the reaction point and was used to measure interferences. A small amount of OH would have been generated at the lamp tip, however the residence time of humidified water at the lamp was short and all OH generated was lost before entering the reactor.

The OH concentration is dependent on the water vapour concentration (Young et al., 2008). In these experiments the relative humidity is kept constant by passing the humid air stream through glass wool held at the reaction temperature, in order to remove excess humidity and large droplets so that aqueous oxidation is minimised, thus the water vapour concentration will change exponentially with temperature according to the vapour pressure of water. The quantity of sulfate produced at the four different reaction temperatures was measured as described in Sect. 3.5.2 and found to follow the expected exponential relationship as shown in Fig. 2b.

### 3.4 Collection of SO$_2$ and H$_2$SO$_4$ products

#### 3.4.1 H$_2$SO$_4$ collection

Sulfate is removed from the gas stream by passing through two 40-cm long glass vessels with a rough inside wall, which will increase turbulence and internal surface area (Fig. 1).
Two forms of sulfate product need to be collected in the experiments:

1. **Aqueous droplet oxidation** will result in water droplets containing sulfate. These will be lost to the glass walls by gravitational settling and by electrostatic attraction, which leads to collisions with the walls (Lai, 2006). This is a bulk process and is assumed not to introduce a significant isotopic effect, and will be very efficient given the length and roughness of the collectors.

2. **Sulfuric acid gas** will initially be produced in the gas-phase oxidation experiments but will nucleate to form particles of 1.5–2 nm diameter as the concentration of H$_2$SO$_4$ is >0.01–0.1 of the saturation vapour pressure (33 ppbv for 99% H$_2$SO$_4$) (Kulmala et al., 2004, 2007). The loss of H$_2$SO$_4$ to the walls of glass vessels is described by:

$$[\text{H}_2\text{SO}_4]_0 - [\text{H}_2\text{SO}_4]_t = e^{-kt}$$

where $[\text{H}_2\text{SO}_4]_0$ and $[\text{H}_2\text{SO}_4]_t$ are the gas phase concentrations of H$_2$SO$_4$ at time = 0 and time = $t$, $k$ is the diffusion-limited first order reaction coefficient: $k = 3.65 \frac{D}{r^2}$, $D$ is the diffusion coefficient and $r$ is the radius of the reactor (Zasyptakin et al., 1997; Young et al., 2008). $D = 0.095 \text{cm}^2 \text{s}^{-1}$ in dry air at atmospheric pressure and decreases to 0.075 $\text{cm}^2 \text{s}^{-1}$ at high humidity (Hanson and Eisele, 2000). These equations apply only to well-established laminar flow conditions in a cylindrical reactor and can provide a lower limit to wall loss in this system. Nanoparticles in the size range of 2 nm will follow Brownian motion, like the sulfuric acid gas molecules, thus the wall loss calculation can be extended to estimate the loss of these ultrafine particles. The diffusion coefficient for 2 nm particles is $\sim$0.035 cm$^2$ s$^{-1}$ (extrapolated from Rudjak et al. (2009)), so the predicted wall loss will be $\sim$97% in the two condensers. The actual wall loss will be considerably higher than predicted as turbulence and electrostatic attraction in the system will increase the frequency of collisions with the walls. At this efficiency, there should be no significant difference between the initial and the product isotopic composition.

No isotopic standard of gaseous H$_2$SO$_4$ was available, so the fractionation during collection was measured by analysing the product from two collectors arranged in series. A flow of N$_2$ 6.0 (Westfalen AG) was passed through a 1 M solution of H$_2$SO$_4$ and the resulting mixture flowed through the two 40 cm-long glass collection vessels. This experiment will involve collection primarily of sulfuric acid droplets and not gas, however the results are relevant to the collection in the experiments since the gas-phase experiments will primarily result in freshly-nucleated particles while the aqueous droplet phase experiments will result in sulfate in droplets.

Following the experiment, the collectors were rinsed and sulfate was precipitated by adding BaCl$_2$ and analysed as described in Sect. 3.5. The average measured differences between the $\delta^{34}$S and $\delta^{33}$S of the two collectors are $-1.1 \pm 2.6 \%e$ and $-0.3 \pm 1.5 \%e$ respectively, showing that there is no systematic fractionation introduced beyond the precision of the measurement (Table 1). A small or insignificant difference between the two collectors can only be achieved with a low collection efficiency or a fractionation factor close to 1, otherwise the $\delta^{34}$S and $\delta^{33}$S of the H$_2$SO$_4$ entering the second collector would be altered by the first collector. A high efficiency was theoretically predicted, and supported by the fact that very little product was seen on the second filter during analysis. Therefore, the fractionation introduced by this collection method is insignificant and the $\delta^{33}$S and $\delta^{34}$S of H$_2$SO$_4$ in later experiments does not need to be corrected for an isotopic change during collection.

It is important to consider possible breakthrough of H$_2$SO$_4$ gas to the SO$_2$ gas collection system. Although H$_2$SO$_4$ is efficiently removed, when the H$_2$SO$_4$ concentration was more than three times as high as the SO$_2$ concentration, breakthrough of H$_2$SO$_4$ could be detected in the isotopic composition of SO$_2$. The sensitivity of the isotopic composition of the SO$_2$ to breakthrough also depends on the difference in $\delta^{34}$S between SO$_2$ and H$_2$SO$_4$. To completely avoid effects from breakthrough of H$_2$SO$_4$ the reaction yield was kept below two thirds of the total SO$_2$.

### 3.4.2 SO$_2$ collection

Sulfur dioxide is traditionally collected on filters impregnated with alkaline solutions such as Na$_2$CO$_3$ (Novak et al., 2001; Huygen, 1963). A variety of solutions were tested with varying amounts of Na$_2$CO$_3$, BaCl$_2$, triethanolamine, glycerol and H$_2$O$_2$, and the average fractionation factor was measured as $\alpha_{34} = 1.007 \pm 0.003$ for all methods tested. The recovery of SO$_2$ was found to vary from less than 5% to more than 40% depending on the length of time that SO$_2$ was collected and the amount taken up relative to the alkalinity capacity of the filter, rather than on the solution composition. The fractionation in the final product could then vary from at least 4.5 to 10.6 ‰, with even larger variations introduced for longer experiments or very high filter loads. This method of collection is not suitable for our laboratory experiments due to the low relative humidity and high concentrations of SO$_2$ in our samples combined with the need for a constant, correctable isotopic fractionation.

Alternatively, SO$_2$ can be collected by passing the gas stream through bubblers containing hydrogen peroxide, which oxidises the S(IV) in the solution to sulfate (US-EPA, 2010). This method was tested by passing SO$_2$ of known isotopic composition ($\delta^{34}$S = 1.25±0.3 ‰) through two bubblers in series containing a solution of 6% hydrogen peroxide, held at 0 °C in an ice bath to increase SO$_2$ solubility (Fig. 1). Following the experiment a BaSO$_4$ precipitate was
prepared by adding BaCl₂, and the precipitate was collected on a gold-coated Nuclepore filter. This experiment was repeated eight times, seven of which were analysed with the NanoSIMS as described in Sect. 3.5.3. One sample was analysed by traditional dual-inlet isotope ratio mass spectrometry at the Massachusetts Institute of Technology according to the methods described in Ono et al. (2006). The reaction conditions are shown in Table 2.

### 3.5 SEM and NanoSIMS analysis

#### 3.5.1 Scanning electron microscopy

A LEO 1530 field emission scanning electron microscope (SEM) with an Oxford Instruments ultra-thin-window energy-dispersive x-ray detector (EDX) was used to locate and characterise particles before NanoSIMS analysis. The samples were directly analysed in the SEM after collection on gold-coated filters without any further treatment. The SEM was operated with an accelerating voltage of between 10 and 20 keV, a 60 µm aperture and a working distance of 9.6 mm. “High current mode” was used to increase the EDX signal and improve elemental sensitivity. All samples were viewed with the SEM to investigate the coverage, size and shape of sulfate grains. A transfer of the coordinate system between the NanoSIMS and the SEM is possible using several well-defined origin points, which allows the same grain or area to be found and analysed in both instruments. An example of a barium sulfate grain with its EDX spectrum is shown in Fig. 3.

#### 3.5.2 Quantification with the SEM

The EDX spectrum can be used to roughly quantify compounds and particles on the filters, and thus estimate the extent of reactions. An automatic analysis of the filter is taken, with EDX analysis points distributed at regular intervals in each image. As long as the diameter of the largest particle is smaller than the distance between EDX points, the probability of the point falling on a particular particle is proportional to the area covered by that type of particle (Winterholter, 2007). Moreover, if an element is just in one form, for example sulfur is only present as BaSO₄, the number of points with a sulfur signal will be proportional to the area covered by BaSO₄. The volume and hence mass of BaSO₄ can be found by considering the average height of the BaSO₄ grains, as long as it is evenly distributed and not clumped in large heaps. The sample height was estimated to be 0.2 µm based on the movement in the Z-direction of the microscope needed to focus on the filter and on the top of a representative number of BaSO₄ grains. The largest source of uncertainty for quantification of the collected BaSO₄ is that grains can flake off the filter during handling of the samples.

The presence of a “signal” for an element in this quantification method requires differentiating between background noise and actual signal. Quantifying sulfur compounds on gold filters is challenging, because the gold peak overlaps strongly with the sulfur peak, as shown in Fig. 3. The contribution of the gold peak to the sulfur peak approximately follows a Gaussian distribution, as gold is present in all sampled EDX points. An example is shown in Fig. 4. The sulfur signal is superimposed on the Gaussian distribution of the gold signal, as the X-ray emission depth and spot size means the gold signal will always be present even when the sampling point falls on a barium sulfate grain (Goldstein et al., 1981). Thus, the presence of a significant sulfur signal was defined as falling above the 99.9 % confidence limit for the gold Gaussian distribution ($x > \mu + 3.09\sigma$). The contribution of S in BaSO₄ to the signal in the sulfur channel shows a peak, however the number of sulfur points is too low to calculate the Gaussian distribution for these samples. To account for the tail of the Gaussian curve of Au that is above the 3.09σ limit, which could be a large part of the signal at low sulfate concentrations, the integrated background (bcg)

---

**Table 1.** Fractionation of $^{34}\text{S}/^{32}\text{S}$ and $^{33}\text{S}/^{32}\text{S}$ between two collectors in series during collection of H₂SO₄.

<table>
<thead>
<tr>
<th>Run #</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Date</td>
<td>2 Nov 2009</td>
<td>3 Nov 2009</td>
<td>23 Feb 2010</td>
<td></td>
</tr>
<tr>
<td>N₂ flow rate (sccm)</td>
<td>1500</td>
<td>1500</td>
<td>1720</td>
<td></td>
</tr>
<tr>
<td>Length (h)</td>
<td>6.3</td>
<td>8.3</td>
<td>6.1</td>
<td></td>
</tr>
<tr>
<td>$\delta^{34}\text{S}_1 - \delta^{34}\text{S}_2$</td>
<td>$-3.3 \pm 2.1$</td>
<td>$2.4 \pm 2.5$</td>
<td>$-4.2 \pm 7.9$</td>
<td>$-1.1 \pm 2.6$</td>
</tr>
<tr>
<td>$\delta^{33}\text{S}_1 - \delta^{33}\text{S}_2$</td>
<td>$0.7 \pm 2.2$</td>
<td>$-0.4 \pm 2.3$</td>
<td>$0.9 \pm 3.6$</td>
<td>$0.3 \pm 1.5$</td>
</tr>
</tbody>
</table>

---

**Fig. 3.** EDX spectrum and SEM image of a typical BaSO₄ grain.
Table 2. Fractionation of $^{34}\text{S}/^{32}\text{S}$ during collection of SO$_2$ in a solution of 6 % H$_2$O$_2$.

<table>
<thead>
<tr>
<th>Run #</th>
<th>Date</th>
<th>Length (h)</th>
<th>H$_2$O$_2$ volume (mL)</th>
<th>[H$_2$O$_2$] (%)</th>
<th>[SO$_2$] (ppm)</th>
<th>SO$_2$ flow rate (sccm)</th>
<th>Gas Temperature</th>
<th>$f$</th>
<th>$\delta^{34}\text{S}$, 1st bubbler</th>
<th>$\delta^{34}\text{S}$, 2nd bubbler</th>
<th>$\delta^{34}\text{S}$, product</th>
<th>$\alpha_{34}$</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>30.10.09</td>
<td>6.0</td>
<td>180</td>
<td>5</td>
<td>7.6</td>
<td>1022</td>
<td>Room T</td>
<td>0.57</td>
<td>14.3±2.1</td>
<td>3.2±1.8</td>
<td>10.1±2.8</td>
<td>1.017</td>
</tr>
<tr>
<td>2</td>
<td>05.11.09</td>
<td>6.6</td>
<td>180</td>
<td>5</td>
<td>7.6</td>
<td>1022</td>
<td>Room T</td>
<td>0.83</td>
<td>9.6±3.5</td>
<td>8.9±3.5</td>
<td>9.3±4.9</td>
<td>1.016</td>
</tr>
<tr>
<td>3</td>
<td>10.11.09</td>
<td>5.6</td>
<td>180</td>
<td>5</td>
<td>7.6</td>
<td>1022</td>
<td>Room T</td>
<td>0.58</td>
<td>8.7±7.8</td>
<td>8.6±7.7</td>
<td>6.6±7.9</td>
<td>1.011</td>
</tr>
<tr>
<td>4</td>
<td>19.02.10</td>
<td>3.0</td>
<td>300</td>
<td>5</td>
<td>0.35</td>
<td>1700</td>
<td>Room T</td>
<td>1.25</td>
<td>12.5±1.5</td>
<td>3.2±0.9</td>
<td>9.1±1.7</td>
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<tr>
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<td>2.9</td>
<td>300</td>
<td>5</td>
<td>0.35</td>
<td>1700</td>
<td>Room T</td>
<td>1.14</td>
<td>11.4±2.4</td>
<td>4.3±5.5</td>
<td>8.7±6.0</td>
<td>1.015</td>
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<tr>
<td>6</td>
<td>31.03.10</td>
<td>4.1</td>
<td>300</td>
<td>5</td>
<td>0.35</td>
<td>1700</td>
<td>40 °C</td>
<td>1.15</td>
<td>11.5±1.3</td>
<td>5.4±2.2</td>
<td>9.2±2.5</td>
<td>1.015</td>
</tr>
<tr>
<td>7</td>
<td>21.04.10</td>
<td>5.6</td>
<td>300</td>
<td>5</td>
<td>0.13</td>
<td>1700</td>
<td>Room T</td>
<td>1.11</td>
<td>11.5±1.3</td>
<td>5.4±2.2</td>
<td>9.2±2.5</td>
<td>1.019</td>
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<td>8</td>
<td>19.07.10</td>
<td>6.6</td>
<td>300</td>
<td>5</td>
<td>0.39</td>
<td>600</td>
<td>Room T</td>
<td>0.66</td>
<td>11.1±0.8</td>
<td>3.7±0.7</td>
<td>9.2±0.7</td>
<td>1.016</td>
</tr>
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<td>Average</td>
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<td></td>
<td>0.61</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1 Measured by traditional dual-inlet isotope ratio mass spectrometry (Ono et al., 2006). 2 All values are corrected for the initial isotopic composition of +1.25 %. 3 Found from $\delta^{34}\text{S}_\text{tot} = (\delta^{34}\text{S}_1 + f \delta^{34}\text{S}_2) / (1 + f)$ for samples where the bubblers were measured separately.

Fig. 4. Frequency of signal height in the sulfur channel of an automatic EDX analysis of BaSO$_4$ on a gold-coated filter. The measured signal for the sulfur channel is shown in blue and the Gaussian fit to the contribution from the gold peak is shown in red.

above the $3.09\sigma$ limit was subtracted, and the number of points with a significant sulfur signal was defined as:

$$n(x > \text{bcg}) = n(x > \mu + 3.09\sigma) - 0.001[n(\text{total})]$$  \hspace{1cm} (16)

The Gaussian curve does not always fit cleanly to the data. For samples where the area coverage is significantly less than 25 %, a second estimate of the $3\sigma$ limit can be approximated by $\sqrt{Q_0 + 1.726(Q_u - Q_b)}$, where $Q_u$ and $Q_b$ are the upper and lower quartiles of the raw signal for the element of interest. This has previously been used to define the background of an SEM-EDX signal for a similar quantification method (Winterholler, 2007; Stoyan, 1998). EDX points with the signal for both barium and sulfur above the background are then used to quantify BaSO$_4$. The quantity of sulfate measured for a sample with the two methods has an average uncertainty of 40 % and shows no systematic offset. The sulfate production in each experiment is an average of at least two duplicate samples both measured with the two methods. The limit of detection for quantification is the amount of sulfate when only one point shows a significant signal, and thus it depends on the total number of points taken. For most samples 10 000 EDX points were measured, giving a detection limit of 0.2 mmol of sulfate, or 0.18 ppbv at the typical flow rate of 600 sccm.

3.5.3 NanoSIMS

The sulfur isotopic composition was determined with the Cameca NanoSIMS 50 ion probe at the Max Planck Institute for Chemistry in Mainz (Hoppe, 2006; Groener and Hoppe, 2006). The NanoSIMS 50 has a high lateral resolution (<100 nm) and high sensitivity and can simultaneously measure up to five different masses through a multicollection system, allowing high precision analysis of the small sample quantities (<<1 mg) required for this study. The use of this...
instrument to analyse sulfur isotope ratios is described in detail elsewhere (Winterholler et al., 2006, 2008), and only a brief description will be given here.

BaSO$_4$ is analysed directly without further processing after it is collected on gold-coated filters as described in Sect. 3.1. A $\sim$1 pA Cs$^+$ beam is focused onto a $\sim$100 nm sized spot and rastered in a 2 $\mu$m $\times$ 2 $\mu$m grid over the grain of interest. The ejected secondary ions are carried into the mass spectrometer and multicollection system. Each measurement consists of 200–400 cycles of 4.096 s duration preceded by varying lengths of presputtering until the gold coating is removed and the count rate is stable. Presputtering is carried out on an area of at least 10 $\mu$m $\times$ 10 $\mu$m to avoid crater effects in the analysed area. Secondary ions of $^{16}$O$^-$, $^{32}$S$^-$, $^{33}$S$^-$, $^{34}$S$^-$ and $^{36}$S$^-$ were simultaneously detected in five electron multipliers at high mass resolution (M/ΔM > 3900 for $^{35}$S). The detector dead time is 44 ns and the count rates were corrected accordingly. The energy slit was set at a bandpass of 20 eV and the transmission was set at 15–20 % with the fifth entrance slit (10×100 µm) and the fourth aperture slit (80×80 µm) in order to reduce the effect of quasi-simultaneous arrival (QSA; Slodzian et al. (2001)).

Mass-dependent and mass-independent instrumental mass fractionation (IMF) can occur at several stages of the SIMS analysis, so the IMF correction factor in each measurement session is determined with the commercially available BaSO$_4$ isotope standards IAEA-SO5 and IAEA-SO6. Correction for the quasi-simultaneous arrival (QSA) effect was carried out as described by Slodzian et al. (2004), however a factor of 0.75 rather than 0.69 was used as this minimised the dependence on count rate best for these samples.

The number of counts is assumed to follow a Poisson distribution, so the counting statistical error is $\sqrt{n}$, i.e. the relative error is $1/\sqrt{n}$ (Bevington and Robinson, 1992). Some spot-to-spot variation is also seen between individual measurements on a filter, most likely due to topographic effects or nanoscale inhomogeneity. Thus, at least five grains on each sample filter were measured, and a weighted average was calculated using $1/\sigma^2$ for the weighting function, where $\sigma$ is the counting statistical error of individual measurements. To calculate the overall measurement uncertainty the error of the weighted mean is multiplied by $\sqrt{\chi^2}$ for $\chi^2 > 1$ in order to account for the larger uncertainty introduced by the spot-to-spot variability. The counting statistical error was typically 1–2 % for and the overall error for each sample 2–5 %.

4 Results and discussion

4.1 Aqueous oxidation

The fractionation factors during aqueous oxidation by H$_2$O$_2$, O$_3$ and radical chain reaction initiated by Fe are shown in Fig. 5 and Table 3. All oxidants other than O$_3$ produce mass-dependent fractionation, and the deviation from the mass-dependent fractionation line seen for O$_3$ is almost certainly a measurement artefact as only two samples were measured. $^{33}$S measurements with the NanoSIMS are more uncertain than $^{34}$S measurements. They can be systematically inaccurate on a individual filter due to factors such as a change in the interference from $^{32}$SH between the sample and the standard; thus they are only reliable if a larger number of samples are measured. The radical chain reaction, which has a fractionation factor of $\alpha_{34} = 0.9894 \pm 0.0043$ at 19°C, is the only measured aqueous reaction to favour the light isotope. This agrees relatively well with measurements by Saltzman et al. (1983), where a fractionation factor of 0.996 for oxidation of HSO$_4^-$ by dissolved O$_2$ was indicated by laboratory experiments.

4.1.1 Isotopic fractionation during SO$_2$ collection

SO$_2$ was collected by bubbling through a solution of H$_2$O$_2$, which oxidises the S(IV) to sulfate. The collection is not complete, and as > 1 % of SO$_2$ is oxidised it can no longer be considered an unchanged reservoir. Thus the isotopic composition of the product depends on the value of the kinetic fractionation factor $\alpha (= k_{34}/k_{32})$ and the fraction of reactant remaining, as described by the Rayleigh fractionation laws (Mariotti et al., 1981; Nriagu et al., 1991). Equation (12) from Sect. 3.2.3 can be used directly for the first bubbler, and adapted to represent the second bubblers in series:

$$\alpha_2 = \frac{\ln \left[ 1 - (1 - f) \frac{R_{P_2}}{R_0} \right]}{\ln(f)}$$

(17)

where $\alpha_2$ is the value of $\alpha_{34}$ calculated from the second bubbler, $f$ is the fraction of reactant (SO$_2$) remaining and $R_0$, [Further text continues with equations and descriptions related to the scientific content.]
and $R_P$ are the isotope ratios $^{34}$S/$^{32}$S for the initial gas and the product of the second bubbler respectively. $R_0^*$ is the initial isotopic composition entering the second bubbler, that is, the residual SO$_2$ remaining after the first bubbler: $R_0^* = R_0 f_1^α_1 - 1$.

The collection efficiency $(1 - f)$ must be known to find $α$ from these equations. Grains can flake off the filter during handling when a large amount of product is present (i.e. a layer rather than individual grains), leading to greater losses from the filter from the first bubbler as it has more product. Thus quantification by SEM-EDX as described in Sect. 3.5.2 does not give an accurate value for $f$. Gravimetric determination of $f$ is not possible due to the interference from co-precipitated BaCl$_2$ and the very small quantities of sulfate on the second filter. The fraction of SO$_2$ remaining was therefore determined as the value that would give an equal $α$ for the first and second collectors, found for each experiment by iteration with Eqs. (12) and (17). The weighted average of the individual values shows that 39 % of SO$_2$ is collected per bubbler. The total collection efficiency of two bafflers in series is $63\pm11\%$. A higher concentration of H$_2$O$_2$ may be expected to improve collection efficiency, however this was not possible as it resulted in destruction of the gold-coating on the filters during filtering to collect BaSO$_4$.

Equations (12) and (17) were then used to find $α$ for each bubbler measurement. The reaction conditions and results are shown in Table 2 and Fig. 6. The weighted average $α_{34}$ is $1.0160\pm0.0013$ at 0°C, which results in a product $δ^{34}$S change of $+9.2\pm0.7\%$ following the two bafflers. This is consistent with expectations for aqueous oxidation by H$_2$O$_2$ (Eriksen, 1972a; Egiazarov et al., 1971) and is robust over a large range of flows and SO$_2$ concentrations. The gas temperature does not affect the measured fractionation since the filter is held at 0°C and the quantity of gas passed through the sampling system is not sufficient to change the temperature within the collection system.

Measurements of $δ^{33}$S by NanoSIMS are more uncertain than $δ^{34}$S due to counting statistics. The measured $α_{33}$ is $1.007\pm0.002$, which is not significantly different from the value expected for mass-dependent fractionation (MDF; $α_{33}/α_{34} = 0.515$, t-test, $P = 0.05$). The mass-dependent nature of the fractionation is confirmed by the high precision fluorination measurement of Sample 8, which showed $Δ^{33}$S = $0.05\%$. The change in $δ^{34}$SO$_3$ and $δ^{33}$SO$_4$ due to reactions of interest in all other experiments can be isolated by considering the measured fractionation due to collection and the initial isotopic composition.

### 4.1.2 Temperature-dependence of fractionation during oxidation by H$_2$O$_2$ and O$_3$

Several previous studies have considered the fractionation during aqueous SO$_2$ oxidation and the combined results are presented in Fig. 7. The weighted linear fit to all points shown in Fig. 7 (except those for SO$_2$(g) $\leftrightarrow$ SO$_2$(aq)) shows that:

$$α_{aq} = (1.0167\pm0.0019) - ((8.7\pm3.5) \times 10^{-5}) T$$ (18)

where $T$ is the temperature in degrees celsius. There is no significant difference between the $α_{34}$ at 19°C measured for H$_2$O$_2$/O$_3$ ($α_{34} = 1.0118\pm0.0040$) and O$_3$ ($α_{34} = 1.0174\pm0.0028$) in droplets and the bulk H$_2$O$_2$ measurements ($α_{34} = 1.0151\pm0.0013$). This shows that droplet-specific effects do not affect isotopic fractionation, and thus the results of bulk phase experiments are relevant to atmospheric reactions, which will primarily occur in droplets. The droplet measurements have a larger uncertainty, which is due to small variations in reaction conditions, particularly relative humidity.

The previous studies do not consider oxidation to S(VI) (see Eqs. (4)–(8)), and comparison of the measured fractionation can show which stages of the reaction are most important for isotopic fractionation. Chmielewski et al. (2002) and Eriksen (1972b) consider only the equilibrium SO$_2$(g)$\leftrightarrow$SO$_2$(aq) and measure a much lower fractionation factor ($α = 1.00256$ at 10°C). This shows that physical phase transfer is responsible for only a small part of isotopic fractionation, and protonation and acid-base equilibria in solution cause the majority of fractionation for the SO$_2$(g)$\leftrightarrow$S(IV) (aq) system.

The results of Egiazarov et al. (1971) and Eriksen (1972a,b,c,d) compare well with the results of the present study, although these earlier studies both consider only the equilibrium to S(IV) in solution while this study includes oxidation to S(VI). This shows that the terminating oxidation reaction has a negligible effect on isotopic fractionation,
explaining why H$_2$O$_2$ and O$_3$ produce the same fractionation factors despite very different mechanisms (Savarino et al., 2000). Eriksen (1972a) considers the equilibrium between 1 M NaHSO$_3$ at low pH as acid is constantly added to the system, thus the concentration of SO$_2^{−}$ will be negligible. The experiments of Egiazarov et al. (1971) consider the equilibration of 3 M NaHSO$_3$ at pH≈4, so unlike Eriksen (1972a) these results will include some equilibration to SO$_3^{2−}$ as well as significant production of S$_2$O$_3^{2−}$. The fractionation factor measured by Egiazarov et al. (1971) (α = 1.0173±0.0003 at 25 °C) is slightly higher than the fractionation factor measured by Eriksen (1972a) (α = 1.01033±0.00041 at 25 °C), suggesting that equilibration towards higher-pH forms of S(IV) introduces a further enrichment of $^{34}$S. The rate of S(IV) oxidation by O$_3$ increases by several orders of magnitude as the pH increases above 5.5 (Botha et al., 1994), and the fractionation factor measured for O$_3$ in this study (α = 1.0174±0.0028) is slightly higher than that measured for H$_2$O$_2$ oxidation (α = 1.0151±0.0013), supporting the hypothesis that equilibration to higher pH increases fractionation, while the terminating oxidation to O$_3$ may have little effect on isotopic fractionation. Results investigating the isotope effect of flue gas desulfurization provide another value of the fractionation factor at high pH for comparison: Derda et al. (2007) measured α$_{34}$ of 1.0026 for aqueous oxidation in a wet lime solution producing gypsum (the fractionation factor has been adjusted to have the same definition as the present study). This would provide a first estimate for the isotope fractionation during oxidation in an alkaline solution, but meaningful comparison with the results obtained in the present study is difficult, since an industrial scale process is not comparable to the carefully controlled environment of a laboratory reactor, and the process temperature has not been reported by Derda et al. (2007). The difference between measured fractionation during oxidation by O$_3$ and H$_2$O$_2$ in this study is not significant considering the experimental error and a more detailed study of the pH-dependence of this system would be needed to fully resolve isotopic effects for each step in the pathway from SO$_2$(g) → sulfate.

4.2 Gas-phase oxidation of SO$_2$ by OH radicals

4.2.1 Quantification of interferences

Before calculating fractionation factors for SO$_2$ oxidation by OH radicals, a consideration of interferences from background sulfate is necessary. Possible interferences are sulfate impurities in reagents, direct photolysis of SO$_2$, and reaction in the gaseous or aqueous phase with oxidants such as H$_2$O$_2$, HO$_2$ and O$_3$, which are also generated during the photolysis of water (Atkinson et al., 2004). SO$_2$ photolysis can follow a number of pathways under UV light (Farquhar et al., 2001). The wavelength-dependent quantum yield of the different pathways is not well known and the fractionation occurring is not well-constrained (Farquhar et al., 2001; Lyons, 2009). The gas phase reactions of SO$_2$ with photochemical products other than OH are very slow (Atkinson et al., 2004), however oxidation on glass surfaces with adsorbed water could lead to sulfate production.

The trace sulfate content present in the MilliQ water used to rinse the product sulfate from the collectors was tested by adding BaCl$_2$ to 500 mL of MilliQ water. The BaSO$_4$ was then collected and quantified in the SEM. The effect of this blank (1.6±1 µg L$^{-1}$) on the measured sulfate concentration was then converted to mol of blank per mole of sulfur produced during the experiment based on the volume of MilliQ used to wash the collectors and the quantity of sulfate produced in the individual experiment. The interference from sulfate impurities in MilliQ water contributed 6 % by mass of the total sulfate at −25 °C and less than 2.5 % of sulfate for all other temperatures. The equivalent in ppbv based on the average volume of MilliQ used to wash the collectors and the quantity of sulfate produced for an 8-h experiment considering flow rate, concentration temperature and pressure is shown in Fig. 2.

Oxidation by photochemical products other than OH, such as H$_2$O$_2$, HO$_2$ and O$_3$, was tested with Reactor 2, which passed water vapour through UV light but did not produce detectable OH at the reaction point. A numerical simulation (Facsimile model, MCPA Software, Ltd.) of the chemical processes involved was run to investigate the species that would be present in the reactor following the photolysis of water, and may oxidise SO$_2$. The species produced by Reactor 1 for the photolysis of water in synthetic air to generate 11 ppbv OH followed by immediate mixing with 1 ppm SO$_2$ are shown in Fig. 8.

Direct photolysis of SO$_2$ was measured by adding humidity 10 cm after the lamp, to ensure the water was not photolysed while allowing the reaction SO$_2$ + H$_2$O → H$_2$SO$_4$ to occur. This was done with both Reactors 1 and 2 so that direct photolysis of SO$_2$ and reaction with other lamp products, discussed in the previous paragraph, could be separated.
The rate of pyrrole photolysis was measured to be the same for both reactors, so it can be assumed that the photolysis of SO$_2$ is also comparable between the two reactors. Direct photolysis was measured with both the standard Hg lamp, which produces 185 and 254 nm lines, and with an O$_3$-free Hg lamp, which emits only the 254 nm line. The whole reaction system was also run with no lamps switched on to measure the quantity of sulfate oxidised by trace compounds in the water or glass walls. The quantification of these interferences is shown in Fig. 2. No sulfate was measured when SO$_2$ was run through the reaction system in the absence of humidity.

The quantity of sulfate produced under UV light does not significantly differ between Reactors 1 and 2, O$_3$-free or normal Hg lamps, and whether humidity is passed over the lamp or not. Thus, all experiments with UV light were combined to find a background of 0.60±0.40 ppbv sulfate in the absence of OH radicals at room temperature. The quantity of sulfate produced in the absence of UV light was 1.04±0.10 ppbv, i.e., compatible with the former value within errors, and the $\delta^{34}$S values of the products in experiments with irradiation are not significantly different from the $\delta^{34}$S of the products in the absence of UV light (Fig. 9), thus the background sulfate is not due to irradiation. The quantity of sulfate collected in the absence of OH radicals was found to have an exponential relationship to temperature and thus was proportional to water vapour pressure. The measured temperature dependencies of sulfate quantity for no OH and OH experiments were adequately described by exponential curves and the fits were used to quantify the percentage contribution of the background to the total sulfate at each experimental temperature. The reaction of interest, SO$_2$ + OH, contributes between 77 and 85 % of the total collected sulfate, depending on the reaction temperature. As the average isotopic composition of the background (δ$^{34}$S = 13.0±1.5 ‰) is consistent with that expected from aqueous oxidation (δ$^{34}$S = 15.1±1.3 ‰), and the quantity of background sulfate varies with the vapour pressure of water, it can be assumed the background sulfate reaction is aqueous oxidation due to an impurity in the water or an oxidation reaction in an H$_2$O surface layer on the glass walls of the collector. As the fractionation for aqueous oxidation has a much lower uncertainty due to the large number of measurements and its temperature dependence is known, it can be used to correct for the background in the SO$_2$ + OH reaction.

### 4.2.2 Isotopic fractionation during the gas-phase oxidation of SO$_2$ by OH radicals

The oxidation of SO$_2$ by OH radicals in the gas phase was measured at four different temperatures in twelve individual experiments. The results are presented in Table 4 and Fig. 10. The correction for aqueous background oxidation as described in Sect. 4.2.1 has only a small effect on the results as it accounts for less than 25 % of sulfate production. The weighted fit to all points gives a temperature-dependent fractionation factor for $^{34}$S of:

$$\alpha_{OH} = (1.0089±0.0007) - ((4±5) \times 10^{-5}) T$$  \hspace{1cm} (19)

The measured fractionation factor for $^{33}$S is

$$\alpha_{OH} = (1.0043±0.0010) + ((1±4) \times 10^{-5}) T$$  \hspace{1cm} (20)

### Table 4. Temperature dependent fractionation factors during the gas-phase oxidation of SO$_2$ by OH radicals.

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$n$</th>
<th>$\alpha_{34}$</th>
<th>$\sigma$</th>
<th>$\alpha_{33}$</th>
<th>$\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-20</td>
<td>2</td>
<td>1.0095</td>
<td>0.0013</td>
<td>1.0034</td>
<td>0.0014</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>1.0088</td>
<td>0.0030</td>
<td>1.0053</td>
<td>0.0012</td>
</tr>
<tr>
<td>19</td>
<td>4</td>
<td>1.0113</td>
<td>0.0024</td>
<td>1.0053</td>
<td>0.0049</td>
</tr>
<tr>
<td>38</td>
<td>3</td>
<td>1.0052</td>
<td>0.0028</td>
<td>1.0034</td>
<td>0.0009</td>
</tr>
</tbody>
</table>

Fig. 8. Facsimile model of potential oxidants and H$_2$SO$_4$ produced as 11 ppbv OH is generated from the photolysis of water in 20 % oxygen and mixed with 1 ppm SO$_2$ at atmospheric pressure.

Fig. 9. Isotopic composition of interferences in the reaction of SO$_2$ and OH. See Fig. 2 for explanation of legend numbers. Aq. ox. shows the isotopic composition of the products of aqueous oxidation by H$_2$O$_2$ or O$_3$. Error bars are the 1σ standard deviation.
This is not significantly different from the fractionation of $^{33}\text{S}$ predicted from a mass-dependent relationship to $^{34}\text{S}$.

Ab initio calculations using transition state theory for the reaction $\text{SO}_2 + \text{OH} \rightarrow \text{HOSO}_2$ by Tanaka et al. (1994) estimated a fractionation factor for $^{34}\text{S}/^{32}\text{S}$ of 0.991, similar in magnitude but opposite in direction to the fractionation factor measured in this study. Leung et al. (2001) calculated the fractionation factor to be 1.14 based on RRKM theory. They found that although the positive difference in critical energies of the transition states would lead to a fractionation factor of <1, this is overcome by the denser vibrational manifolds of the $^{34}\text{S}$ transition state. However, the authors state that even considering the uncertainties in all parameters used they predict a fractionation factor $>1.07$, almost 10 times larger in magnitude than the factor measured in this study. Even a fractionation factor of 1.07 rather than 1.14 is significantly larger than the variation observed in atmospheric samples (e.g. Norman et al. (2006); Novak et al. (2001)), so it is likely that RRKM theory can accurately predict the direction and not the magnitude of this isotope effect. This is in agreement with recent results from Lin et al. (2011) and Hattori et al. (2011), which found a similar overprediction of the sulfur isotopic fractionation during the photolysis of OCS by RRKM theory (Leung et al., 2002).

### 4.3 Comparison to previous studies

A number of studies have used field measurements to estimate the value of the fractionation factors for $\text{SO}_2$ oxidation. Atmospheric measurements of $\delta^{34}\text{SO}_2$, and $\langle \delta^{34}\text{SO}_2 - \delta^{34}\text{SO}_3 \rangle$ are often lower in summer than in winter (Mukai et al., 2001; Mayer et al., 1995; Saltzman et al., 1983). Oxidation by OH is expected to be highest in summer and this may therefore show that the fractionation factor for gas-

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*Fig. 10*. Temperature dependent fractionation factors during the gas-phase oxidation of $\text{SO}_2$ by OH radicals. Pale points represent individual experiments while dark points with error bars are the average and 1σ error of the mean at each temperature.
measured in this study, the overall preindustrial change in $\delta^{34}S$ between SO$_2$ and product sulfate would be +5.5‰. Alexander et al. (2003) saw a decrease in $\delta^{34}S_{\text{mss}}$ of $\sim$3‰ during glacial periods, which would mean a change in $\delta^{34}S$ between SO$_2$ and product sulfate of +2.5‰ if sources were unchanged. Oxidation by transitional metal catalysis would need to increase from 8% to 35% of the total sulfate production to account for this change if the proportions of sulfate produced from the other oxidation pathways and the overall sulfur budget remained the same. A 10% increase in transition-metal catalysed sulfate production was modelled for the pre-industrial to industrial periods by Sofen et al. (2011), thus a 27% increase due to much higher dust loads in glacial times is not unreasonable.

5 Conclusions

This study measured the fractionation factors for the most common pathways of SO$_2$ oxidation: gas phase oxidation by OH radicals, and aqueous phase oxidation by H$_2$O$_2$, O$_3$, and a radical chain reaction initiated by Fe. The fractionation factors for these oxidation pathways are now well constrained compared to the previous estimates. A summary diagram of the main processes in the continental sulfur cycle and the fractionation factors involved is shown in Fig. 11. Isotopic measurements can now be used to constrain the dominant oxidation pathway in environmental samples by excluding pathways that do not agree with observed fractionation. A Cameca NanoSIMS 50 was used to measure the isotopic composition of the sulfate produced from the different reactions, which allowed these previously unknown fractionation factors to be measured despite the difficulties of obtaining enough product for traditional isotope measurement instruments. However, factors such as sample topography and charging mean that NanoSIMS results have a far greater uncertainty than traditional measurement techniques, and NanoSIMS measurement error contributes the major uncertainty in the results. NanoSIMS analysis allowed the reactor and collection system to be developed and the reaction to be thoroughly investigated for interfering reactions; the next step in laboratory studies of these fractionation factors would be to increase the sulfate production capacity of the system to allow traditional measurements with high precision, such as isotope ratio mass spectrometry (Ono et al., 2006).

The fractionation factors presented in this paper will allow stable sulfur isotopes to be used to understand the partitioning between these pathways in atmospheric samples, particularly if $\Delta^{17}O$ of sulfate is also measured allowing differentiation between oxidation by H$_2$O$_2$, O$_3$ and all other oxidants. The combined effect of uncertainty and variation in the isotopic composition of sources and fractionation during oxidation means field studies need to simultaneously measure both SO$_2$ and sulfate isotopic composition to gain insight into the sulfur cycle. Combining modelling with field studies of sulfur isotopes in the atmosphere can then use these fractionation factors to gain an increased understanding of the sulfur cycle and its effect on radiative forcing, aerosols and cloud condensation nuclei. Based on the unique fractionation factor of the reaction, sulfur isotope ratios will be particularly useful to constrain the importance of transition-metal-catalysed sulfur dioxide oxidation in the atmosphere, which was the only reaction found to favour the light isotope in the current study.

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