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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Sulfur isotope fractionation during oxidation of sulfur dioxide: gas-phase oxidation by OH radicals and aqueous oxidation by H_2O_2, O_3 and iron catalysis" *by* E. Harris et al.

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We thank Becky Alexander and the two anonymous reviewers for their helpful comments on the paper. We will discuss below the changes that have been made in response to the reviewer's comments. We will begin with the major structural changes made in response to Reviewer #2 and follow with the minor changes.

Major Changes in Structure

The structure of the paper now reads (sections that were moved are in italics):
Abstract
1 Introduction
2 Sulfur isotopes in the environment
3 Experimental
3.1 Apparatus
3.2 Aqueous oxidation
3.2.1 Aqueous oxidation by the radical chain reaction mechanism
3.2.2 Aqueous oxidation by H_2O_2 in bulk aqueous phase
3.2.3 Aqueous oxidation by H_2O_2 and O_3 in aqueous droplets
3.3 Gas phase oxidation
3.3.1 OH generation
3.4 Collection of SO_2 and H_2SO_4 products
3.4.1 H_2SO_4 collection
3.4.2 SO_2 collection
3.5 SEM and NanoSIMS analysis
3.5.1 Scanning electron microscopy
3.5.2 Quantification with the SEM
3.5.3 NanoSIMS
4 Results and discussion
4.1 Aqueous oxidation
4.1.1 Isotopic fractionation during SO_2 collection
4.1.2 Oxidation by H_2O_2 and O_3
4.2 Gas-phase oxidation of SO_2 by OH radicals
4.2.1 Quantification of interferences
4.2.2 Isotopic fractionation during the gas-phase oxidation of SO_2 by OH radicals
4.3 Comparison to previous studies

5 Conclusions

Figures were reordered accordingly.

The changes required in the text of the manuscript due to the re-ordering of paragraphs are discussed in more detail below:

- The first paragraph of the section ‘Experimental - Aqueous oxidation by H_2O_2 and O_3 in bulk aqueous phase’ (P23974 L9-11) was expanded to:

  “SO_2 gas was collected by bubbling through a solution of 6% H_2O_2 in an ice bath, thus the fractionation during collection of SO_2 is a direct measure of the fractionation during oxidation of SO_2 by H_2O_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 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 SO_2 by H_2O_2.”

- The following sentence was added at the beginning of the ‘Experimental - Aqueous oxidation by H_2O_2 and O_3 in aqueous droplets’ in order to emphasise the importance of studying oxidation but in droplets and in the bulk phase:

  “Oxidation by H_2O_2 and 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.”

- A brief introduction was added to the section ‘Experimental - 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 Figure 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.”

- The section ‘Experimental - Collection of SO_2 and H_2SO_4 products’ was moved to follow the section ‘Gas Phase Oxidation’. The portion of this section from P23972 L17 - P23973 L29 was moved to ‘Results and discussion’ and given the new title ‘Fractionation during SO_2 collection’. Some sentences were added to the start of this section: “SO_2 was collected by bubbling through a solution of H_2O_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...”

  The subsection ‘$\mathbf{H_2}$SO$_\mathbf{4}$ collection’ was reorganised to emphasise nucleation of sulfuric acid after gas-phase production:

  “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 results 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_2SO_4 is $>$0.01-0.1 of the saturation vapour pressure (33

ppbv for 99% H_2SO_4) [...] there should be no significant difference between the initial and the product isotopic composition.

No isotopic standard of gaseous H_2SO_4 was available, so the fractionation during collection was measured by analysing the product from two collectors arranged in series."

- The discussion of Rayleigh equations now first appears in Section 'Experimental - Aqueous oxidation by H_2O_2 and O_3 in droplets' thus the full equations were moved from the Section 'Results - Aqueous oxidation - Isotopic fractionation during SO_2 collection', and just the equation for the second bubbler was left in this section.
- The section 3.5.2 'Interferences' was moved to 'Results - Gas-phase oxidation of SO_2 by OH radicals' and the title changed to 'Quantification of interferences'. The sentence "Before calculating fractionation factors for SO_2 oxidation by OH radicals, a consideration of interferences from background sulfate is necessary" was added to the start of the section. The previous results section for gas phase oxidation was given a new sub-heading, 'Isotopic fractionation during the gas-phase oxidation of SO_2 by OH radicals.'

Minor Changes

The minor changes will be presented in the order they appear in the revised manuscript, following the structural changes described under 'Major Changes'.

- P23963 L11 has been changed to: "where *n* is the number of atoms, ^{x}S is one of the heavy isotopes, ^{33}S, ^{34}S or ^{36}S"

- P23963 L13: 'reactions' has been changed to 'reactants'
- P23963 L16: The Derda et al. (2007) paper mentioned by Reviewer #3 had a different definition for α than we used, thus we realised the importance of unambiguously defining α and added to P23963 L16:

  "When the reactant is present as an infinite reservoir and not affected by the reaction, α_{34} can be calculated from the isotopic compositions of products and reactants:

  $$\alpha_{34} = \frac{R_{products}}{R_{reactants}} \tag{1}$$

  where R = $\frac{^{34}S}{^{32}S}$. Thus, α>1 indicates..."
- P23963 L24-P23964 L4: In response to comments from the reviewers we have expanded our statement concerning the isotopic composition of the major atmospheric sulfur sources and changed the listed references:

  "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)."
- P23965 L18: More detail was added with regards to the reaction set-up:

  "The length of tubing from the reactor to the H_2SO_4 collectors was <7 cm, which would lead to a maximum of ~22% loss of H_2SO_4 according to the wall loss calculations from Zasypkin et al. (1997) and Young et al. (2008) (Equation 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 $<<1\%$. Most experiments were run for 7–8 hours to generate sufficient product for isotopic analysis."

- P23965 L27 - P23966 L1 has been rephrased to give more detail regarding the filters used:

  "After at least 12 hours to ensure complete precipitation, the solutions were filtered through Nuclepore 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 SCD-050) prior to sample collection."

- P23974 L12-22 was altered and expanded to clarify the use of the second reactor to investigate aqueous oxidation in droplets:

  "Reactor 2 (Fig. 1) did not produce detectable OH (see Section 3.3.1 for details of OH quantification) at the reaction point where the humid, UV-irradiated air was mixed with the SO_2 flow. A small amount of OH was generated at the lamp tip in this reactor, however the residence time of humidifed air at the lamp was short and all OH generated was lost before reaching the reaction point. H_2O_2 was produced following H_2O photolysis to OH, and as the lifetime of H_2O_2 is longer than that of the OH radical, $\sim$5 ppbv (mol mol^{-1} gas at atmospheric pressure; ppbv will only be used to discuss gas phase concentrations in this paper) of H_2O_2 is present at the reaction point. O_3 resulted from 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 H_2O_2 and 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 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..."

- P23970 L11: 'just' has been removed

- P23970 L25: Clarification of the relevance of the measurements of fractionation during collection of H_2SO_4 was added on P23970 at the end of L25:

  "...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."

- P23971 L15-19 was changed to:

  "The sensitivity of the isotopic composition of the SO_2 to breakthrough also depends on the difference in δ^{34}S between SO_2 and H_2SO_4. To completely avoid effects from breakthrough of H_2SO_4 the reaction yield was kept below two thirds of the total SO_2."

- P23978 L4: The MIF for O_3 oxidation presented in this paper in Figure 8 is very unlikely to be 'real', and this is now specified in the text:

  "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."

- P23978 L8: The values under discussion have been added to the text to facilitate reading:

  "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."

- P23973 L12: Reviewer #2 wondered why we cannot use a higher concentration of H_2O_2 to achieve better SO_2 collection efficiency, so we have added the following to the text:

  "A higher concentration of H_2O_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 $BaSO_4$."

- P23978 L16-20: The following sentences were added to justify using the droplet experiments in the calculation of the fractionation factor, despite the higher uncertainty:

  "There is no significant difference between the α_{34} at 19°C measured for H_2O_2/O_3 ($\alpha_{34} = 1.0118 \pm 0.0040$) and O_3 ($\alpha_{34} = 1.0174 \pm 0.0028$) in droplets and the bulk H_2O_2 measurements ($\alpha_{34} = 1.0151 \pm 0.0013$). 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."

- P23979 L5 was added to emphasise why we believe the terminating oxidant has little effect on isotopic fractionation during aqueous oxidation by H_2O_2 and O_3:

  "...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_2O_2 and O_3 produce the same fractionation factors despite very different mechanisms (Savarino et al. 2000)..."

- P23979 L16: The values under discussion have been added to the text to facilitate reading:

  "...the fractionation factor measured for O_3 in this study (α = 1.0174±0.0028) is slightly higher than that measured for H_2O_2 oxidation (α = 1.0151±0.0013), supporting..."

- P23979 L18: The following sentences were added to compare our measured fractionation factors with those measured during flue gas desulfurization:

  "...the terminating oxidation to O_3 may have little effect on isotopic fractionation. Results investigating the isotopic effect of flue gas desulfurization provide another value 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..."

- P23976 L15-19: The units of the sulfate background in MilliQ water compared to the sulfate from the reaction of interest was clarified:

“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 % of the total sulfate at $-25\,^{\circ}$C and less than 2.5 % of sulfate for all other temperatures. The equivalent in ppb based on the average volume of MilliQ used to wash the collectors and the quantity of sulfate produced for an 8 hour experiment considering flow rate, concentration temperature and pressure is shown in Figure 2.”

- P23976 L20 - P23977 L7 was expanded to emphasise the reason for using two reaction systems to investigate the background for the OH reaction, and to clarify the purpose of a Facsimile model and the associated diagram:

  "Oxidation by lamp products other than OH, such as H_2O_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 $SO_3 + H_2O \rightarrow H_2SO_4$ to occur..."

- P23977 L18-19 was expanded to, “Thus, all experiments with UV light were com-

bined to find a background of 0.60 ± 0.40 ppbv sulfate in the absence of OH radicals at room temperature.” to clarify the identity of the background.

- P23980 L20: In light of recent results the following sentence was added to the end of the paragraph:

  “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).”

- P23981 L11-18: The discussion on OH oxidation during stratospheric volcanic eruptions was expanded:

  The δ^{34}S of stratospheric sulfate aerosol has been observed to first increase and then strongly decrease in the months following the eruption of Mt. Agung (Castleman et al. 1974), consistent with stratospheric oxidation favouring ^{34}S and progressively depleting the SO_2 reservoir. This was suggested to show that oxidation by OH favours the heavy isotope, as OH is normally the dominant stratospheric oxidant for SO_2 (Leung et al. 2001). However, strong Δ^{33}S signals found in ice core records of volcanic sulfate of the same event suggest photochemical oxidation is the dominant process producing these aerosols: The huge amount of SO_2 released during the eruption depletes the stratosphere of OH which means oxidation pathways, such as photolysis, which are normally not important in stratospheric SO_2 oxidation can begin to have a significant effect (Savarino et al. 2003a,b,c, Baroni et al. 2007, 2008). The contribution of OH and other oxidation pathways to oxidation of SO_2 following a stratospheric volcanic eruption is not well constrained, thus measurements from these eruptions are not reliable indicators of the magnitude and direction of α_{OH}.

- P23981 L19: We have extended the discussion paragraph beginning on P23981 L19 with the following:

“Considering the pre-industrial partitioning between the sulfate production pathways from Sofen et al. (2011) and the fractionation factors measured in this study, the overall preindustrial change in δ^{34}S between SO$_2$ and product sulfate would be +5.5‰. Alexander et al. (2003) saw a decrease in δ^{34}S$_{nss}$ of $\sim$3‰ during glacial periods, which would mean a change in δ^{34}S between SO$_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.”

- P23982 L6: We have expanded the conclusion was expanded to address the question of uncertainty:

  “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, and a summary diagram of the main processes in the continental sulfur cycle and the fractionation factors involved is shown in Figure 11. 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 smaller uncertainty.

  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 Δ^{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...”

- Throughout the paper, ppb has been changed to ppbv and the definition of the unit was clarified when it was first used: ‘mol mol^{-1} gas; ppbv will only be used to discuss gas phase concentrations in this paper’

- Table 2: “by Shuhei Ono (2010)” has been removed from the caption of Table 2

- Summary diagram: A summary diagram was added to the conclusion of the paper, to sum up the results and emphasise their importance in the sulfur cycle.

Additional Minor Changes

- We noted that some numbers in our manuscript were not always rounded of to the last significant digit. All fractionation factors through the text and in Tables 3 and 4 now have the correct number of significant figures.

- The labels on Figure 7 (Temperature dependence of fractionation during aqueous oxidation...) were confusing and have been clarified.

- Some figures were missing a description of what the error bars referred to. All error bars are the 1σ standard deviation, and this has now been added to all figure captions.

References

Alexander, B., Thiemens, M. H., Farquhar, J., Kaufman, A. J., Savarino, J., and Delmas, R. J.: East Antarctic ice core sulfur isotope measurements over a complete glacial-interglacial cycle, J. Geophys. Res.-Atmos., 108, 4786,doi:10.1029/2003JD003513, 2003.

Alexander, B.: Interactive comment on “Sulfur isotope analysis of individual aerosol particles – a new tool for studying heterogeneous oxidation processes in the marine environment” by B. Sinha et al., Atmos. Chem. Phys. Discuss., 9, S296—S298, 2009.

Baroni, M., Thiemens, M. H., Delmas, R. J. and Savarino, J.: Mass-independent sulfur isotopic compositions in stratospheric volcanic eruptions. Science, 315, 84-87, 2007.

Baroni, M., Savarino, J., Cole-Dai, J. H., Rai, V. K. and Thiemens, M. H.: Anomalous sulfur isotope compositions of volcanic sulfate over the last millennium in Antarctic ice cores. Journal of Geophysical Research-atmospheres, 113, D20112, 2008.

Castleman, A. W., Munkelwitz, H. R. and Manowitz, B.: Isotopic Studies of Sulfur Component of Stratospheric Aerosol Layer. Tellus, 26, 222-234, 1974.

Derda, M., Chmielewski, A. G., and Licki, J.: Sulphur isotope compositions of components of coal and S-isotope fractionation during its combustion and flue gas desulphurization, Isotopes in Environmental and Health Studies, 43, 57-63, 2007.

Eriksen, T. E.: Sulfur Isotope Effects 1. Isotopic Exchange Coefficient for Sulfur Isotopes 34S-32S in System SO2(g)-HSO3(aq) at 25, 35, and 45 Degrees C, Acta Chemica Scandinavica, 26, 573, 1972.

Hattori, S., Danielache, S., Johnson, M., Schmidt, J., Kjaergaard, H., Toyoda, S., Ueno, Y., and Yoshida, N.: Ultraviolet absorption cross sections of carbonyl sulfide isotopologues OC32S, OC33S, OC34S and O13CS: isotopic fractionation in photolysis and atmospheric implications, Atmos. Chem. Phys., 11, 10293-10303, 2011.

Krouse, H., Grinenko, L., Grinenko, V., Newman, L., Forrest, J., Nakai, N., Tsuji, Y., Yatsumimi, T., Takeuchi, V., Robinson, B., Stewart, M., Gunatilaka, A., Plumb, L., Smith, J., Buzek, F., Cerny, J., Sramek, J., Menon, A., Iyer, G., Venkatasubramanian, V., Egboka, B., Irogbenachi, M. and Eligwe, C.: Krouse, H. and Grinenko, V. (Eds.) Stable Isotopes: Natural and Anthropogenic Sulphur in the Environment, Chapter 8. Case Studies and Potential Applications. John Wiley and Sons, 307-416, 1991.

Lai, A. C.: Investigation of Electrostatic Forces on Particle Deposition in a Test Chamber, Indoor Built Environ., 15, 179–186, 2006.

Leung, F. Y., Colussi, A. J., and Hoffmann, M. R.: Sulfur isotopic fractionation in the gas-phase oxidation of sulfur dioxide initiated by hydroxyl radicals, Journal of Physical Chemistry A, 105, 8073-8076, 2001.

Leung, F. Y., Colussi, A. J., Hoffmann, M. R., and Toon, G. C.: Isotopic fractionation of carbonyl sulfide in the atmosphere: Implications for the source of background stratospheric sulfate aerosol, Geophys. Res. Lett., 29, 1474, doi:10.1029/2001g1013955, 2002.

Lin, Y., Sim, M. S., and Ono, S.: Multiple-sulfur isotope effects during photolysis of carbonyl sulfide, Atmos. Chem. Phys., 11, 10283-10292, 2011.

Nielsen, H., Pilot, J., Grinenko, L., Grinenko, V., Lein, A., Smith, J. and Pankina, R.: Krouse, H. and Grinenko, V. (Eds.) Stable Isotopes: Natural and Anthropogenic Sulphur in the Environment, Chapter 4. Lithospheric Sources of Sulfur. John Wiley and Sons, 65-132, 1991.

Novak, M., Jackova, I., and Prechova, E.: Temporal Trends in the Isotope Signature of Air-Borne Sulfur in Central Europe, Environ. Sci. Technol., 35, 255–260, 2001.

Rees, C. E., Jenkins, W. J. and Monster, J.: Sulfur Isotopic Composition of Ocean Water Sulfate. Geochimica et Cosmochimica Acta, 42, 377-381, 1978.

Sanusi, A. A., Norman, A.-L., Burridge, C., Wadleigh, M. and Tang, W.W.: Determination of the S isotope composition of methanesulfonic acid. Analytical Chemistry, 78, 4964-4968, 2006.

Savarino, J., Lee, C. C. W. and Thiemens, M. H.: Laboratory oxygen isotopic study of sulfur (IV) oxidation: Origin of the mass-independent oxygen isotopic anomaly in atmospheric sulfates and sulfate mineral deposits on Earth. Journal of Geophysical Research-Atmospheres, 105, 29079-29088, 2000.

Savarino, J., Bekki, S., Cole-Dai, J. H. and Thiemens, M. H.: Evidence from sulfate mass independent oxygen isotopic compositions of dramatic changes in atmospheric oxidation following massive volcanic eruptions Journal of Geophysical Research-Atmospheres, 108, 2003a.

Savarino, J., Romero, A., Cole-Dai, J., Bekki, S. and Thiemens, M. H.: UV induced mass-independent sulfur isotope fractionation in stratospheric volcanic sulfate Geophysical Research Letters, 30, 2003b.

Savarino, J., Romero, A., Cole-Dai, J. and Thiemens, M. H.: UV induced mass-independent sulfur composition in stratospheric volcanic eruptions. Geochimica et Cosmochimica Acta, 67, A417-A417, 2003c.

Sinha, B. E., Hoppe, P., Huth, J., Foley, S., and Andreae, M. O.: Sulfur isotope analysis of individual aerosol particles – a new tool for studying heterogeneous oxidation processes in the marine environment, Atmos. Chem. Phys. Discuss., 9, 3307-3365, 2009.

Sofen, E. D., Alexander, B., and Kunasek, S. A.: The impact of anthropogenic emissions on atmospheric sulfate production pathways, oxidants, and ice core Δ^{17}O(SO$_4^2$), Atmos. Chem. Phys., 11, 3565-3578,doi:10.5194/acp-11-3565-2011, 2011.

Tanaka, N., Rye, D. M., Xiao, Y., and Lasaga, A. C.: Use of Stable Sulfur Isotope Systematics for Evaluating Oxidation Reaction Pathways and in-Cloud Scavenging of Sulfur-Dioxide in the Atmosphere, Geophys. Res. Lett., 21, 1519–1522, 1994.

Tichomirowa, M., Haubrich, F., Klein, M., and Matschullat, J. Regional and temporal (1992-2004) evolution of air-borne sulphur isotope composition in Saxony, southeastern Germany, central Europe. Isotopes in Environmental and Health Studies, 43, 295-305, 2007.

Young, L. H., Benson, D. R., Kameel, F. R., Pierce, J. R., Junninen, H., Kulmala, M., and Lee, S.-H.: Laboratory studies of H_2SO_4/H_2O binary homogeneous nucleation from the SO_2+OH reaction: evaluation of the experimental setup and preliminary results, Atmospheric Chemistry and Physics, 8, 4997-5016, doi:10.5194/acp-8-4997-2008, 2008.

Zasypkin, A., Grigor'eva, V., Korchak, V., and Gerschenson, Y.: A formula for summing of kinetic resistances for mobile and stationary media: I. Cylindrical reactor, Kinetics and Catalysis, 38, 842–851, 1997.