Atmos. Chem. Phys. Discuss., 11, C10437–C10456, 2011
www.atmos-chem-phys-discuss.net/11/C10437/2011/
© Author(s) 2011. This work is distributed under
the Creative Commons Attribute 3.0 License.

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.

E. Harris

eliza.harris@mpic.de

Received and published: 16 October 2011

We thank the anonymous reviewer for agreeing to review the manuscript. The comments were thorough and helpful and have improved the structure of the manuscript. Comments leading to major changes in the manuscript are addressed first. Minor comments and small changes are addressed pointwise after.

Major changes

- "The structure of the paper is confusing [...] Why not presenting the paper in the same way an experiment is done: 1/ apparatus 2/ oxidation processes 3/ extractions 4/ analysis 5/discussion?"

We have carried out major restructuring of the paper in response to the reviewer's comments. Overall, the structure now reads (only subsections that were changed are shown):
Section 3 - Experimental
3.1 Apparatus
3.2 Aqueous Oxidation
3.3 Gas Phase Oxidation
3.4 Collection of SO_2 and H_2SO_4 products
3.5 SEM and NanoSIMS analysis
Section 4 - Results
4.1 Aqueous Oxidation
4.1.1 Isotopic fractionation during SO_2 collection
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

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 sections 3.4 'Aqueous oxidation' and 3.5 'Gas Phase oxidation' were moved to directly follow the section 3.1 'Apparatus'.

The first paragraph of the section ‘Aqueous oxidation by H_2O_2 and O_3’ (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 section 3.3 ‘Collection of SO_2 and H_2SO_4 products’ was moved to follow the section ‘Gas Phase Oxidation’, however the portion of this section from P23972 L17 - P23973 L29 was moved to Results and given the new title ‘Fractionation during SO_2 collection’.

Some sentences were added to the start of this section: ‘SO_2 was 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 discussion of Rayleigh equations now first appears in Section 3.2.3 ‘Aqueous oxidation by H2O2 and O3 in droplets’ thus the full equations were moved from the Section ‘Fractionation during SO_2 collection’, and just the equation for the second bubbler was left in the Section ‘Fractionation during SO_2 collection’.

The section 3.5.2 ‘Interferences’ was moved to Results 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

Two comments pertain to why a second reactor was used to quantify possible interferences competing with the reaction of SO_2 with OH and for studying aqueous oxidation in droplets rather than the bulk phase.

- Page C9817 L6: "I don’t understand the reasons of using two gas flow systems? If you don’t want OH radical in the flow just switch off the UV" and
- Page C9819 L10 "How H2O2 can be produced in the flow system without OH? What high humidity means? Why O3 is produced in the H2O2 experiment? How the water is introduced? By a nebulizer? How do they know that droplets are generated in the flow system? What are their sizes?" adress the same question and pertain to how the aqeous oxidation in droplet was studied.

In the revised structure of the manuscript Reactor 2 is discussed first, and in detail, in Section 3.2 ‘Aqueous Oxidation’.

The paragraph on P23974 L12-22 was altered and expanded to clarify these points:
"Reactor 2 (Fig. 1), did not produce detectable OH (see Section 3.3.1) 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 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 run in Reactor 2 at $\sim$100% relative humidity to investigate aqueous oxidation by H_2O_2 and O_3 in droplets rather than a bulk solution. 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..."

The results obtained using the experiments conducted in Reactor 2 are discussed again while quantifying possible interferences competing with the reaction of SO_2 with OH in Reactor 1. Taking into consideration the reviewer's point we have altered the structure of the paragraph on P23976 L20 - P23977 L7 and have emphasised why two seperate systems are required:

"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 Facsimile model (MCPA Software, Ltd.), which is designed to solve chemical kinetic equations, 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 ppb OH followed by immediate mixing with 1 ppm SO_2 are shown in Fig. 5."

Twice the reviewer questions why we study the aqueous phase reactions both in the bulk phase and in individual droplets.

- Page C9817 L8: "It is mentioned that bulk aqueous phase reactions and droplet generated phase reactions give similar results but with the latter less accurate . So why it is these data that are presented in figure 9 and use to calculate the fractionation factor? Why not doing the experiment in liquid phase then instead of a flow system if the former is more accurate and easier to implement?"

- Page C9819 L8: "I'm confused by the aqueous phase oxidation as it is described in page 23974. Why again using a flow system if a “becker” reaction chamber works better?”

In our paper we have used two approaches to investigate aqueous oxidation and replicated both experiments multiple times. The purpose of doing droplet phase experiments in addition to the bulk phase experiments was to test whether there is a significant effect on fractionation from surface tension, the difference in saturation vapour pressure, and other factors such changes in droplet pH while the reaction proceeds, which may differ between droplets and a bulk liquid phase. We considered this relevant as the reaction will be occurring in droplets and not in the bulk phase in the atmosphere.

Following the structural changes discussed earlier ‘Aqueous oxidation by H_2O_2 and O_3’ (section 3.2.2) has been split to section 3.2.2 ‘Aqueous oxidation by H_2O_2 in bulk aqueous phase’ and section 3.2.3 ‘Aqueous oxidation by H_2O_2 and O_3 in droplets’.

The following sentence was added at the beginning of the new section 3.2.3 in order to emphasise the importance of the two methods: ‘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.’

We have included the data obtained from droplet experiments in the calculation of the overall fractionation factor as there is no valid reason to reject it; as the fit is weighted by the error of the individual points this particular point will have very little effect on the result. We have clarified this by changing P23978 L16-20 to, “There is no significant difference between the α_{34} measured for H_2O_2/O_3 ($\alpha_{34} = 1.0118 \pm 0.004$) and O_3 ($\alpha_{34} = 1.0174 \pm 0.003$) in droplets and the bulk H_2O_2 measurements ($\alpha_{34} = 1.0151 \pm 0.001$).

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."

- Page C9817 L13: "Specific comments In the abstract it is mentioned “radical chain reaction” for the Fe oxidation, OH oxidation in gas phase is also a radical chain reaction as shown by reaction 1 to 3. Please re word accordingly"

The OH reaction is not a radical chain reaction. A radical chain reaction has an ‘initiation step’ (for example, $S(IV) + Fe^{3+} \rightarrow \cdot SO_3^{2-} + Fe^{2+}$) which produces a radical that can then continuously react in the ‘propagation step’, always producing another radical (for example, $\cdot SO_5^- + \cdot SO_5^- \rightarrow \cdot SO_4^- + \cdot SO_4^- + O_2$) to continue the chain until the ‘termination step’ is reached (for example, $\cdot SO_4^- + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-}$), in which a radical is quenched and the chain does not continue (see Herrmann et al. (2000, 2010)).

- Page C9817 L16: "To better understand the issues, a figure summing up the main processes and associated fractionations, starting from S source emissions (range of isotope values) to S dissolution (known fractionations) followed by oxidation processes and indicating clearly where they are improving the knowledge will definitely help the readers."

A summary diagram will be added to the conclusion of the paper. The diagram is shown at the end of this comment.

- Page C9817 L20: "Patris et al. 2000 citation in the introduction is incorrect as these authors assumed no fractionation during oxidation transport and deposition to ice caps thus it cannot be claimed that they have measured major sources of atmospheric sulphur "

The referee is right in questioning Patris et al. (2000) with respect to their assumption that no fractionation occurs during oxidation, transport and deposition of sulfur in the environment, however this issue is not specific to Patris et al. (2000). Most studies on ambient aerosol particles or ice cores published in the peer-reviewed literature used sulfur isotopes to quantify source contributions to sulfate aerosol and are based on similar assumptions. We have changed the citations to include only such studies that measured primary sources directly at the source: Rees et al. (1978), Krouse et al. (1991), Nielsen et al. (1991) and Sanusi et al. (2006).

- Page C9817 L23: "No detail is given about the set up of the entire system..."

The reviewer is correct in pointing out the importance of wall loss for sulfuric acid gas. We have clarified this point by adding the following at the end of L18 P23965:

The length of tubing from the reactor to the H_2SO_4 collectors was $<$7 cm, which would lead to a maximum of $\sim$50% loss of H_2SO_4 according to the wall loss calculations from Hanson and Eisele (2000) and Young et al. (2008) (Equation 11). The actual wall loss will be negligible as the H_2SO_4 gas will not stick to the PFA tubing and the partial pressure of H_2SO_4 is at all times significantly less than the vapour pressure (33 ppbv for 99% H_2SO_4).

- Page C9818 L1: "Is there any reference for the gold-coated nucleopore filters?"

The text on P23965 L27 - P23966 L1 has been rephrased: “After at least 12 h 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.”

- Page C9818 L2: "It is very annoying that the authors give little numbers in their text..."

It is unclear what numbers should be in the text on P23966 L17 and P23972 L7. On P23979 L16 the values under discussion have been added:

...the fractionation factor measured for O_3 in this study ($\alpha = 1.017 \pm 0.0028$) is slightly higher than that measured for H_2O_2 oxidation ($\alpha = 1.015 \pm 0.0013$), supporting...

On several occasions the reviewer stresses that he thinks we should have determined the sulfate concentrations in all samples using ion chromatography. We thank the reviewer for pointing out to us the potential to use ion chromatography for sulfate quantification. While we agree that for some of our samples this would have been a feasible approach, it can not be used for all samples, and we do not believe that using it on those samples where sufficient sulfate was generated would have significantly improved our results.

- Page C9818 L5: "It is very disturbing to read how the authors quantify the sulfate concentration..."
- Page C9819 L3: "Page 23973 line 7 f could have been easily quantified using ion chromatography. Also from their table 2 I have calculated that ca. 120 umol of S flow through the system at 7 ppm of SO2 for 6 h at 1 l/min. This is far from a very small quantities (even at 63% yield of recovery) and will have posed no problem if concentrations were. measured by IC and should still be accessible to gravimetric determination as BaSO4"
- Page C9818 L24: " Again a IC would have been an advantage."

Quantifying the fraction reacted for the bulk aqueous phase experiments (P23973 L3-12) by using the value of f giving an equal α for the two bubblers assumes only that

flow conditions are equivalent between the two bubblers, which is a valid assumption as temperature, flow rate and all other parameters are equal. As this experiment was repeated eight times and the results agree well, this method of estimating the fraction reacted does not introduce much extra uncertainty into estimates of α. Thus, although ion chromatography would have saved time and effort and will be potentially useful in future experiments on bulk solutions, it will not significantly alter or improve the values determined in the paper. In fact, our results agree well with two previous studies that studied the fractionation of aqueous oxidation while keeping the system in a infinite reservoir for SO_2, indicating that both approaches lead to valid results. Difficulties related to the gravimetric approach were discussed P23973 L7.

As far as the the fractionation during H_2O_2 oxidation in aqueous droplets is concerned (discussed on P23974 L12 - P23975 L1), the measured δ^{34}S of this experiment was quite uncertain which translates into a large uncertainty in calculated α. A less uncertain estimate of the fraction reacted would only improve the results if the measurement uncertainty is also improved upon.

For sulfate production from OH and the associated blanks and interferences (P23977 L16-29), the concentrations of the various interferences are very low - for example, 7 $\times 10^{-9}$ M for the sulfate background of MilliQ water - thus ion chromatographic analysis would not have been possible (Harris 2003). While SEM quantification has a fairly low precision and is not a commonly used method, it permits analysis of these extremely low sulfate concentrations. For these experiments, quantification was used only for the background correction and not for fractionation factor calculation with Rayleigh equations; the system was set up as an infinite reservoir for SO_2, as $<$1% of SO_2 was oxidised to sulfate.

- Page C9818 L17: "I'm confused by the way they use the terms sulfuric acid gas..."

The sulfuric acid is unlikely to be gas at most stages of the experiments. Due to its extremely low vapour pressure it may well nucleate with the water even when it is generated as gas, while the H_2SO_4 generated from the bubbler will indeed be droplets and not gas. This has been addressed throughout the paper:

P23969 L25 was extended to: ‘Sulfuric acid gas (in gas-phase oxidation experiments - this is expected not to be a pure gas but will probably primarily contain freshly nucleated particles from the sulfuric acid gas and water vapour) and sulfate in aqueous droplets (for aqueous oxidation experiments) are first removed from the product gas stream by irreversible “wall loss” in a glass vessel with high surface area.’

Clarification of the relevance 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 it is relevant to the collection in the experiments to measure fractionation factors: the gas-phase experiments will primarily result in freshly-nucleated particles while the aqueous droplet phase experiments will result in sulfate in droplets. The fractionation of the gas phase portion of H_2SO_4 is not tested by the experiments, however it is expected to be negligible due to the very high efficiency of wall loss and it will also represent only a small proportion of sulfate.small proportion of sulfate. Following the experiment, the collectors were rinsed sulfate was precipitated by adding $BaCl_2$ and analysed as described in Sect. 3.5.’

- Page C9818 L26: "Collection of SO2 by filter seems no less noisy than by bubbling...."

We collected SO_2 in bubblers because it was more reproducible than on filters as the reviewer rightly noted. This was primarily because the fraction collected was very variable and hard to constrain on filters, whereas 63% was reproducibly collected by the bubblers. The concentration of H_2O_2 could not be increased to improve collection as the more concentrated H_2O_2 solutions destroyed the gold-coating on the filters during

filtering to collect $BaSO_4$. To clarify in the paper we have added the following sentence to the end of the paragraph on P23973 L3-12:

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 $BaSO_4$.

- Page C9819 L14: "It is very surprising that O3 oxidation and H2O2 will give the same fractionation factor as these reactions are very differents (see Savarino, et al. (2000), Journal of Geophysical Research, 15(D23), 29,079-029,089 and reference therein). This is not discussed at all in the paper. Same can be concluded about comparison of OH gas phase fractionation and aqueous phase?"

This point is discussed in section 4.1.1, P23978 L21 - P23979 L22. The two oxidants do not result in different fractionation factors, despite different mechanisms, because the terminating oxidant has a negligible effect on isotopic fractionation. The following sentence was added at the end of L5 P23979 to make the point more clear:

...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)...

The same can clearly not be concluded for the OH reaction which does not involve dissolution and dissociation in an aqueous phase and moreover does not have a fractionation factor that agrees with that for H_2O_2 and O_3 (1.0113 ± 0.0024 for OH compared to 1.015 ± 0.0013 for H_2O_2 at room temperature).

- Page C9819 L19: "When using ppb unit..."

We have used the ppbv unit, which is routinely used in the field of atmospheric chemistry, as it is independent of temperature and pressure. Using this unit simplifies comparisons in the different sections of the paper for the reader, because it is in a useful order of magnitude for the concentrations in this study (mol cm^{-3} would always be in the range $\times 10^{14}$ which is more difficult to remember and comprehend). To remove any ambiguity all instances of ‘ppb’ have been changed to ‘ppbv’ and the following clarification was added at the first instance of ppbv: ‘mol mol^{-1} gas; ppbv will only be used to discuss gas phase concentrations in this paper’

- Page C2819 L21: "The 6% blanks of total sulfate is it in mass or volume? It is difficult for me to calculatethe concentration of sulfate in these 500 ml of blank solution. Furthermore for isotope analysis the important parameter is the mass of sample vs mass of blank not the comparison of concentrations as volume of sample/blank can vary. Again a IC would have been an advantage"

The units and concentrations have been made clearer regarding the MilliQ blank (P23976 L15-19):

The trace sulfate content present in the MilliQ water used to rinse the 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 6.

- Page C9819 L26 - Page C9820 L10: "The apparent MIF of O_3 oxidation needs to

be solved..."

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 (P23978 L4): ‘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.’

- Page C9820 L2 “However, the difference between measured fractionation during oxidation by O3 and H2O2 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 SO2(g) ! sulfate. Âÿz The sentence actually recognizes that their experiments is limited by their uncertainty May be with a “becker” type experiment this could have been solved too? Uncertainties are in the range of the observed fractionations, where are the majors uncertainties? How can someone else improve the experiment? This needs to be mentioned in the text/conclusion"

The major uncertainties have been discussed in Page 23979. Previous results from “becker” type experiments suggest that the pH may possibly affect the isotope fractionation, however neither of the two experiments discussed has been repeated independently by a different researcher. Moreover, in atmospheric aerosol particles and droplets the pH is not a constant - it changes as the reaction proceeds - which is why we investigated the reaction in droplets and not only in bulk solution.

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_2O_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 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. Modelling and field....

- P9820 L11: "OH is still the major oxidation pathway..."

We do not argue that OH is not the major stratospheric oxidation pathway for SO_2, but only that OH cannot be reliably considered to be the dominant oxidant following stratospheric volcanic eruptions which alter the stratospheric chemistry by depleting the stratospheric OH. Therefore, the fractionation in sulfate produced from SO_2 in these eruptions is not a good indicator of the fractionation factor for SO_2 + OH. We have added to the paragraph on P23981 L11-18 to emphasise this:

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}.

- Page C9820 L15: "I do not agree with the authors when they claim that fractionation factors for these oxidation pathways are now well constrained. This is not what their results show. This not even what they wrote a paragraph before. OH/O3/H2O2 fractionation factor overlap due to their uncertainty and at present it will still be impossible to deduce from atmospheric observations the mechanism of sulfate formation except with Fe+O2. It may actually never the case if their narrow ranges are confirmed but as presented I'm not convinced that this is the case but this is how science works"

We have addressed this along with the comment from Page C9819 L26 - Page C9820 L10 by further discussing the uncertainties in the conclusion and by clarifying, 'The fractionation factors for gas phase oxidation by OH radicals and radical chain reaction initiated by Fe are now well constrained *compared to the previous estimates*'.

The results in this paper are a big improvement on the previous estimates which were discussed in section 2 ‘Sulfur isotopes in the environment’.

The fact that $OH/O_3/H_2O_2$ fractionation factors overlap due to their uncertainty is a disappointment for researchers intending to differentiate between gas phase and aqueous phase oxidation using isotopic techniques. On the other hand the same results explain why source apportionment of sulfur using stable sulfur isotopes can and has been successful even though most sources emit SO_2 while the isotopic signatures are typically measured on sulfate. Whenever sulfur IV to VI conversion under ambient conditions is dominated by these three oxidants and SO_2 from sources is sampled using bubblers with H_2O_2 or filters with a buffer the measured isotopic composition on aerosol sulfate and collected SO_2 were close enough to conclude that no isotopic fractionation is introduced during oxidation (for example, Saltzman et al. (1983), Mayer et al. (1995)). Only recently direct sampling of SO_2 (g) for stable isotope analysis from ambient air canisters has become the norm.

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.

Hanson, D. R. and Eisele, F.: Diffusion of H_2SO_4 in humidified nitrogen: Hydrated H_2SO_4. Journal of Physical Chemistry A, 104, 1715-1719, 2000.

Harris, D.: Quantitative Chemical Analysis, Sixth Edition. W.H. Freeman and Company, 2003.

Herrmann, H., Ervens, B., Jacobi, H. W., Wolke, R., Nowacki, P. and Zellner, R.: CAPRAM2.3: A chemical aqueous phase radical mechanism for tropospheric chemistry. Journal of Atmospheric Chemistry, 36, 231-284, 2000.

Herrmann, H., Hoffmann, D., Schaefer, T., Brauer, P. and Tilgner, A.: Tropospheric Aqueous-Phase Free-Radical Chemistry: Radical Sources, Spectra, Reaction Kinetics and Prediction Tools. Chemphyschem, 11, 3796-3822, 2010.

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.

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.

Mayer, B., Feger, K. H., Giesemann, A. and Jäger, H.-J.: Interpretation of sulfur cycling in two catchments in the Black Forest (Germany) using stable sulfur and oxygen isotope data. Biogeochemistry, 30, 31-58, 1995.

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.

Norman, A. L., Anlauf, K., Hayden, K., Thompson, B., Brook, J. R., Li, S. M. and Bottenheim, J.: Aerosol sulphate and its oxidation on the Pacific NW coast: S and O isotopes in PM2.5. Atmospheric Environment, 40, 2676-2689, 2006.

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

Saltzman, E. S., Brass, G. and Price, D.: The mechanism of sulfate aerosol formation: Chemical and sulfur isotopic evidence. Geophysical Research Letters, 10, 513-516, 1983.

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. W., Hoppe, P., Huth, J., Foley, S. and Andreae, M. O.: Sulfur isotope analyses of individual aerosol particles in the urban aerosol at a central European site (Mainz, Germany). Atmospheric Chemistry and Physics, 8, 7217-7238, 2008.

Sinha, B. W., 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. Atmospheric Chemistry and Physics Discussions, 9, 3307-3365, 2009.

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, 2008.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 23959, 2011.

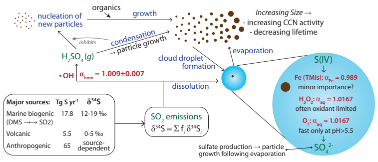

Fig. 11. A summary of sulfur isotopes and the continental sulfur cycle. Emission quantities for the different sources are taken from Sofen et al. (2011) and δ^{34}S values from sources are from Calhoun et al. (1991), Patris et al. (2002) and Norman et al. (2006).

47

Fig. 1. Summary diagram, in response to the reviewer's comment on Page C9817 L16