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Interactive comment on “Sulfur isotope fractionation during oxidation of sulfur dioxide: gas-phase oxidation by OH radicals and aqueous oxidation by H₂O₂, O₃ and iron catalysis” by E. Harris et al.

Anonymous Referee #2

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General comments This MS describes a methodology used to infer the sulfur isotope fractionations during atmospheric relevant conversions of SO₂ to sulfate . These experiments attempt to fill a important gap in the atmospheric sulfur isotope observations namely measuring the fractionation factors at the process level. These are a long-awaited experiments, but in its present form the manuscript needs revisions before being published. I give below the reason why.

The structure of the paper is confusing, especially the experimental section , the core of the paper. The authors start with a description of the apparatus and then jump to

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analysis techniques and end this section with collection products . Next sections treat the oxidation processes and interferences before ending with the discussion section

I found very painful to follow the paper and while reviewing realized that the structure was not logic. Why not presenting the paper in the same way an experiment is done: 1/ apparatus 2/ oxidation processes 3/ extractions 4/ analysis 5/discussion?

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.

It is mentioned (page 23978 line 17) 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?

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

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.

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 sulfur

No detail is given about the set up of the entire system. How long are the Teflon tubing that connect the different sections of the apparatus? This is fundamental as H₂SO₄ will condense quickly on wall taking into account the very low partial pressure of sulphuric acid at room temperature (33 ppbv for 99% H₂SO₄)

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Is there any reference for the gold-coated nucleopore filters? I guess this is not common. It is very annoying that the authors give little numbers in their text and always refer to tables or figures, eg. Pages 23966 line 17, page 23972 line 7 page 23979 line 16 → give numbers in text

It is very disturbing to read how authors quantify the sulfate concentration (blank yield, etc). They use a SEM image which is very unusual. Today ion chromatography is the norm to quantify sulfate in water. It is cheap, easy to use, accurate and sensitive. Why not having use this technique? If they had no access in their lab it would have been easy to find a lab with this capacity. This is a major weakness of their method. With IC there is no risk of loss, only a tiny aliquot is necessary, almost real time progression of reaction can be followed, etc. I'm wondering how IC would have improved there experimental work to a point where I'm questioning if it is not actually necessary to redo the whole experiment as concentration is fundamental to establish fractionation factors accurately. One other option could have been to keep the system in a infinite reservoir for SO₂ thus producing fractionation factors directly without mass consideration, assuming a quantitative recovery of the product.

I'm confused also by the way they use the terms sulphuric acid gas as some times it seems to refer to H₂SO₄ gas and other times H₂SO₄ droplets. For instance in page 23970 when bubbling N₂ through 1M H₂SO₄ solution, is it gas or droplets they are talking about? Gas H₂SO₄ is impossible considering the solubility of H₂SO₄ in dilute solution (actually it is so great that there is no accepted value; meaning that the vapor pressure of H₂SO₄ gas above a dilute H₂SO₄ water solution is much lower than 10 pptv!) <http://webbook.nist.gov/cgi/cbook.cgi?ID=C7664939&Mask=10#Solubility> Thus this experiment to mimic their collection during the oxidation of SO₂ is by no mean equivalent.

Collection of SO₂ by filter seems no less noisy than by bubbling. Looking at their figure 4, range of variability is better for SO₂ trapped in H₂O₂ solution than on alkaline filters

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The efficiency of this trapping is only 63% with two traps, why did they not try to increase H₂O₂ concentration up to 30%?

Page 23973 line 7 f could have been easily quantified using ion chromatography. Also from their table 2 I have calculated that ca. 120 μmol 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

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?

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?

It is very surprising that O₃ oxidation and H₂O₂ will give the same fractionation factor as these reactions are very different (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?

When using ppb unit (which it is not a SI unit) is it by volume of gas or mass of water? Use mol.mol⁻¹ for volume or g.g⁻¹ for mass

The 6% blanks of total sulfate is it in mass or volume? It is difficult for me to calculate the 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 apparent MIF of O₃ oxidation needs to be solved, it is fundamental for the sulfur

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isotope chemistry and could have a enormous impact if confirmed. I'm confused by this sentence "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. 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

OH is still the major oxidation pathway in the stratosphere. The fact that MIF S is present in stratospheric sulfate does not mean OH reaction is excluded. Photolysis of SO₂ in stratosphere is a minor route which has huge consequence for isotope but not for the production rate of sulfuric acid.

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.

In conclusion I'm not opposing to its publication but the final paper needs to integrate my major comments.

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

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