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Atmospheric Chemistry and Physics Discussions
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Interactive comment on “Effect of NO_X, O_3 and NH_3 on sulfur isotope composition during heterogeneous oxidation of SO_2: a laboratory investigation” *by* Zhaobing Guo et al.

Anonymous Referee #1

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Major comments

I think this study adds information on the sulfur isotopic fractionation ratio (δS34) from several heterogeneous SO2 oxidation pathways involving hematite with NOx, ozone, and NH3. However, I do not think that the results presented here allow the authors to draw conclusions about the relative importance of different pathways in real field observations. This is my largest concern. The authors only include the three heterogeneous pathways they measured in this study's laboratory experiments when interpreting observed δS34 using the Rayleigh distillation model. However, there are also other aqueous-phase and gas-phase reactions with different fractionation factors (e.g.

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Harris et al., 2012a, b; who also show it is not possible to distinguish between some pathways based on S34 alone). For example, Shao et al. (2019) found heterogeneous oxidation of SO2 on all aerosols was only 20% in wintertime in China, with alkaline dust (for which hematite is possibly an analog) contributing a total of only 9%. Even without considering additional reactions which would create a very underconstrained problem with no solution, the authors are solving for three unknowns (the relative importance of their three studied reactions) using only two equations (equation 3 and line 199). How is this possible? I am a bit confused that the authors do not show or use the concentrations of potential oxidants measured at the field site to address the relative importance of different pathways, although they are vaguely referred to in lines 202-203.

I think the authors should also explain in more detail why hematite is chosen. Is it a true analog of mineral dust? How do the reactions involving hematite in this paper relate to the aqueous-phase transition metal ion catalyzed SO2 oxidation discussed at length in the literature? Is there aerosol water present at RH=40% and thus the possibility of aqueous-phase oxidation reactions in hematite leachate? How does this study of fractionation in reactions with only iron-containing hematite relate to/inform interpretation of previous results for actual desert dust (e.g., Harris et al., 2012b)? I think these questions should be addressed explicitly in the paper.

General comments

Overall, I find the explication of the laboratory experimental results confusing as it is difficult to determine what has been found in previous studies vs. what is being interpreted from the results of this study, in light of the literature. For each of the previous studies cited during the explanation of your laboratory results, I would like more information so I know how similar their experimental set-up was and am able to better interpret how your work compares. I will give examples in the line-by-line comments.

I think the focus of the paper should be made more clear - if the purpose is specifically to address sulfate formation during pollution / haze events, specific seasons and/or in specific regions, or if these results would be applicable generally. Some line-by-line comments below also address this.

Yields of sulfate are currently given in absolute grams – it would be helpful for comparison purposes to also give in terms of a relative fraction of product vs. (SO2) reactant loss.

Line-by-line comments

- Line 37: “the formation mechanism of sulfate is still unclear”: is this globally, during pollution/extreme haze events, or in China specifically? Given that there is no discussion of, e.g., DMS oxidation, or oxidations by HOCl/HOBr (Q. Chen et al. (2017), GRL), I think the focus in the introduction should be narrowed appropriately and it would make more clear why which studies are cited in this introduction.

- Line 39: Li et al. (2018): there are two citations that are Li et al. (2018), please specify which one

- Line 42: please add a citation to this sentence (“the synergistic effect. . . promotes the conversion of SO2 to sulfate”) or make more clear if it is related to previous citations in this paragraph.

- Line 45-46: “measured sulfur isotopic fractionation” – could you please specify which isotopic ratio this paper is studying (e.g., is it δS34 or something else)?

- Line 51: there are two Chen et al. (2017) papers in the references, please specify which one

- Line 59-60: please add a citation to this sentence (e.g., Harris et al., 2012b)

- Line 70: I would reword “the causes of subsequent sulfates” to something like “the subsequent formation of sulfate”

- Line 83-84: could you state the average temperature and RH at the sample site? I don’t know what “similarly” means in this context.

- Section 2.1: add a sentence or two to very clearly distinguish between the field sampling vs. the laboratory experiments, e.g., a beginning sentence for each of the first two paragraphs of this section. In fact, I would move the sentence in lines 95-96 in Section 3 to the first paragraph, and the sentence in line 100-102 to the 2nd paragraph.

Figures:

- All figures: it would be very helpful if Figure 2a,3a,4a and 2b,3b,4b had the same y-axis range. It makes it harder to compare across oxidants otherwise. Is each point based on a single measurement, or are multiple samples taken? If the latter, the standard deviation/error should be shown. If not, I think it would be helpful to add either perpendicular lines on the points or shading to indicate the accuracy of the measurements, as ±0.2 per mil is as large as some of the changes in δ34S caused by changing the volume ratios of oxidants. I believe the y-axis label should be changed from to δ34S.

- Figures 2 and 3: what kind of curve-fitting is being done here? Splines? A polynomial function? I think the nonlinear curves mislead the reader to think that there is a change in the isotopic fractionation between measured values that we cannot know for sure from the experiments performed here alone (e.g., the “both O2+light” blue line in figure 2b between 1:1 and 1:4 ratio makes it seem like it is decreasing, but that is a product of the nonlinear curve-fitting being done with only 3 points. maybe it’s actually flat or slightly increasing if it was a linear trend instead). I would either remove the lines entirely and only show points, or simply draw lines between each set of points as this is the simplest type of fitting to do and there is such limited data to justify a polynomial fit.

- Figure 3 caption: “(The dotted line represents the trend as it should be).” What does this mean? This is not explained in the text. I think the dotted line should be removed unless it can be explained why this would be known from theory.

- Figure 4: I would make this a line graph instead of a bar chart, I am not sure why it is different from Figures 2 and 3. Also, I would remove the arrows from Figure 4a, I do know what this adds. Explain why you did not do a 1:1 ratio experiment (e.g., it requires ammonia in excess).

NOx results description:

- Lines 103 – 104 (First sentence of this paragraph): To me, the way this is currently worded makes it unclear whether this is something known before or based specifically on the results of this study and what is shown in Figures 2 to 4. What do you mean by taking ion strength into account? How is that accounted for in the presentation of Figures 2-4?

- Lines 109-110: "In addition, the increase in the amount of NOx was another key factor that led to the acceleration of sulfate formation (Cheng et al., 2016)." It is not clear whether this refers to results from your study, Cheng et al. (2016), or both. Please revise to clarify.

- Lines 123-124: "Therefore, under dark conditions, the sulfur isotope value was mainly affected by oxygen and the catalytic action of Fe(III), resulting in the enrichment of lighter sulfur isotopes (Han et al., 2016a)." Similar to the above comments. Please clarify if this is the case for both your experiments and previous work; if not, please state that explicitly.

- Line 149-151: I think Harris et al. (2012a) should be cited here, which is about OH in the gas-phase. I am not sure though how OH in the gas phase would relate to heterogeneous oxidation here. If I am mistaken, more explanation is needed of how Harris et al. (2012b) relates to your study and OH.

- Line 154: specify which Harris et al. 2012 paper

Ozone results description:

- Reactions R4 & R5: the sentence before says, "which was described as". Please give the citation where these reactions were described.

- Line 136-137: what mineral did Nicoals et al. (2019) use? Would it behave the same as the hematite used in your study?

- Lines 138-139: “Under dark conditions, photolysis of O3 were negligible, thus surface reactions will be solely responsible for sulfate production (Harris et al., 2013a).” I find this sentence confusing. I think I understand what you mean, but please restate so it is clear that during your study and in general, there is no photolysis of ozone in the dark, so any sulfate production during the dark does not involve the ozone photolysis pathway. I think it would make more sense to introduce the ozone photolysis pathway (lines 140-147) first and then interpret your experimental results in the light and dark.

- Line 153-154: “In addition, uptake and decomposition of ozone under irradiation increased the basicity of the surface, which was conducive to enrich heavy sulfur isotopes (Hanisch et al., 2003).” Again, reword to clarify what you are assuming to apply to your study vs. what you actually can determine from your results. As an example, something like this would help clarify for me as a reader: “It is possible that the uptake and decomposition of ozone under irradiation in our study would increase the basicity of the surface, which Hanisch et al. (2003) found to increase enrichment of heavy sulfur isotopes and is consistent with the increased enrichment in our irradiated ozone experiments.”

NH3 results description (lines 156 – 175)

- Line 158-160: “The extent of aerosol neutralization was determined principally by the ambient concentration of NH3 and the oxidation rate of SO2 (Kong et al., 2019).” I don’t know if this sentence is needed. In your study, you are not determining the aerosol neutralization, correct? To me, it sounds like it is referencing the methods of the previous study (Donaldson et al., 2010), which described the neuralization of the ammonium salts. I am not sure if this is what you meant.

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- Line 163-164: “Moreover, the oxygen vacancies in α-Fe2O3 may lead to the formation of sulfate on α-Fe2O3 (Wang et al., 2019).” Is this only for the ammonia experiments specifically, or would this statement actually apply to all of your laboratory experiments? Please explain.

- line 166-167 “ Under only-light, NH3, which increased the alkalinity by producing OH- from hydrolysis, dominated in the reaction, leading to an increase of δ34S values (Jiang et al., 2017).” : Please separate out which part of this sentence is based on the results found here vs. the part that is coming from Jiang et al. (2017). My guess would be that the δ34S part is the results from this study, and the alkalinity by producing OH from hydrolysis is from Jiang et al. (2017), but it is not obvious to me as a reader.

- Line 167-168: “O2 with Fe3+ as catalyst dominant in the presence of only-oxygen favored light sulfur isotopes, which was consistent with above results.” Are the “above results” from Jiang et al. (2017), or the δ34S results found in your laboratory experiment? Can you please explain more clearly why δ34S decreases during only-O2 experiments when ammonia is increased but not when ozone or NOx are increased? How does ammonia affect the transition-metal-ion catalyzed pathway?

- Line 168-169: “The δ34S values of sulfate increased with the increases of sulfate concentrations under the combined oxygen with light (Doi et al., 2004).” Is this the results of Doi et al. (2004) for ammonia experiments? This seems to conflict with your results, which show in Fig. 4b that δ34S stays the same under the combined oxygen with light for higher ammonia (which caused higher sulfate production in figure 4a).

- Line 169-170: “Therefore, we inferred that O2 and light had a synergistic effect on the sulfur isotope compositions in the presence of NH3.” I am not sure how this relates to the previous sentence citing Doi et al. (2004). To me it seems that the effects cancel each other out: under increasing ammonia, the “only O2” experiment has decreased δ34S while the “only light” experiment has increased δ34S and the “both O2 + light” experiment has nearly constant δ34S. Perhaps a different word besides “synergistic” would be more specific.

- Line 171-173: “The δ34S values from main biogenic source of NH3 were on the low side, indicating that the effects of NH3 on sulfur isotopic compositions were relatively mild (Han et al., 2016a; Grewling et al., 2019).” Again, I do not know what part of this sentence is based on the results of your laboratory experiments here vs. these previous studies that are cited. What does the biogenic nature of NH3 have to do with your experiments?

Rayleigh distillation and enrichment, lines 176-205

- Line 181 (equation 1): It is not clear to me if this equation is needed as it seems it is not used and instead equation 2 (line 289) is. If it is used, can it be made more clear how and why the two equations are presented?

- Line 193 and Figure 5: what does “simulations” mean exactly? What data is specifically being plotted here? What do the shaded regions around each line mean? Please add that to the figure caption. A standard deviation is given for the emissions, but not the other lines.

- Equation 3, Lines 199-202: Please explain how three unknowns are solved with only two equations.

Citations referenced here that are not in the original paper:

Shao et al. 2019: https://www.atmos-chem-phys.net/19/6107/2019/acp-19-6107-2019.pdf

Q. Chen et al. 2017: https://agupubs.onlinelibrary.wiley.com/doi/pdf/10.1002/2017GL073812

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