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Atmospheric Chemistry and Physics Discussions

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 #2

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I have read this manuscript, and I found that I mostly agree with previous comments from referee #1. This study provides sulfur isotopic fractionation for sulfate formation from SO2 in the presence of NOx, O3, and NH3. Although these experimental results show some interesting phenomena, I do not think that these results lead to the conclusions drawn by the authors. Note that SO2 has two oxygen atoms and SO42- has four oxygen atoms, thus we have to think the origins of oxygen atoms in sulfate formation. The effect of NH3 for sulfate formation is interesting, because the presence of NH3 may change pH in liquid and promote the pH-dependent process such as O3, TMI, NO2. Unfortunately, I found a lack of this viewpoint throughout this manuscript.

The most important concern related to this experiment is what oxidation processes were included in each experimental system. Previous experimental results by Harris et al. showed the S isotope fractionations for gas-phase oxidation (i.e. SO2+OH) and aqueous oxidations by O3, H2O2, and O2 catalyzed by TMI. They also reported fractionation in SO2 oxidation on the dust surface. Compared to these results, this manuscript provides S isotopic fractionation for sulfate formation with different conditions, but I do not understand which oxidation processes were occurred in each system. Simply speaking, I do not understand which oxidants worked in each condition. Probably, there were mixed effects of different oxidation processes, which is so confusing. Thus, I do not agree that this experiment can directly be applied for the interpretation of observational data sets.

The 2nd important concern is the conclusions of this study that NOx played a major in the different heterogeneous oxidation process of SO2, which cannot be lead by these experimental results and interpretation. Particularly, in eq (3), authors hypothesized that sulfate is only formed via three pathways of SO2 + NOx, O3, and NH3, but this is not true (as mentioned above). Thus, the conclusion lead by this calculation is not appropriate. These comments are almost the same as referee #1 of "how is this possible?".

Overall, I think this manuscript should be reconsidered. Detailed comments from referee #1 were very helpful and I do not have additional comments.

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