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Atmospheric Chemistry and Physics Discussions

Interactive comment on "An isotope view on ionising radiation as a source of sulphuric acid" *by* M. B. Enghoff et al.

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Response to Referee 2

Dear Anonymous Referee 2. Thank you very much for your constructive criticism and comments, which we attempt to answer point-by-point below. Please note that all references to page numbers refer to the Discussion paper.

Authors claim experiments with gamma radiation produced distinct isotope pattern, suggesting the gamma radiation could be important part of SO_2 *oxidation. d34S values, however, do not appear to be very distinct for the experiments with gamma radiation. Thus, it appears very hard to support the authors' main conclusion.*

We agree that the values are not totally distinct, but nevertheless they are more than 2 standard deviations apart (figure 2). Furthermore, based on the yields between the O_3-1 and the O_3-gamma-1 samples, we conclude that the oxidation is not taking place in the bottle but inside the reaction chamber and thus it is a proper gaseous/atmospheric phenomenon. To make the difference between the gaseous and aqueous oxidation clear we make the following change:

p. 5047 l. 10. The sentence is rephrased to "...while the liquid phase ozone oxidation process takes place in all experiments, the amount of sulphate produced via this process should be small in the first bottle, compared to the amount produced in experiments that had other formation processes present. The effect of the aqueous oxidation process on δ^{34}S in the first bottle will thus be small since the amount produced by the gas phase processes are larger (see Tab. 1 for a comparison of the sample masses recovered)."

Aqueous O_3 oxidation is always present, and it is not clear how one can evaluate this blank level.

We have measured this by running the experiments where the O_3 oxidation was the only oxidation pathway – the yields are listed in Table 1. See also our explanation further down.

It might help if authors can comment followings. 1) What is the distinct isotope pattern that characterizes ionizing radiation? As authors state, in the abstract, "the pattern of isotope enrichment produced by gamma rays is similar, but not equal, to that produced by aqueous oxidation of SO_2 by ozone." From Fig. 2, the signal is not very clear if gamma radiation makes much difference in isotope fractionation. I would suggest authors to clearly state what is the distinct signatures that is produced by gamma radiation. The gamma radiation data actually plot between liquid phase O_3 oxidation and oxidation by OH.

Any distinct signature from gamma radiation is not known apart from the speculation on p. 5042 l. 3 and the measurement present in our paper. As explained in p5051 l.16

the information on yield and fractionation lead to the conclusion of gamma-ray induced production being similar to liquid oxidation via ozone.

2) Blank level of liquid phase O_3 oxidation Authors state (in page 5047 line 13), "While the liquid phase ozone oxidation process takes place in all experiments, the amount of sulphate produced via this process should be small in the first bottle, compared to the amount produced in experiments that had other formation processes present - any effect this would have on the d34S values is less than one standard deviation" Authors may need to present some supports for this assessment. In addition, it is not clear what one standard deviation refers to (1s of analytical error?). In particular, in page 5051, it is said that expected yield from gamma radiation is very very small (23 ng of $BaSO_4$ as opposed to 5 mg $BaSO_4$ in the sample?). Any signals from gamma radiation could be swamped by liquid oxidation by ozone (depending upon the blank levels but it is not clear what they are). Replying this may require some additional experiments to assess the blank (liquid phase- O_3 oxidation) level in each bottle (1, 2 and 3).

Regarding our first statement (p. 5047 l. 13) it refers to the observation that we for the experiment with only liquid phase oxidation (O_3-1) collect 2.8 mg of sample from the first bottle, compared to 19.4 for the gamma experiment (O_3-γ-1). Thus, unless there is a huge difference in fractionation, the effect from the liquid phase oxidation should not be large. This is supported by the fact that our results for O_3-UV-1 agree quite well with those of Harris et al (ACP 12, 2012). We recognize that the mention of the effect being less than 1 standard deviation can be confusing and the sentence will be rephrased as mentioned above. This should also make it clearer that we have measured the production from the O_3-oxidation process.

With regards to our second statement (p. 5051) that the expected yield form gamma radiation is very small, this only refers to the amount formed due to OH produced directly by the gamma rays. Since the isotopic signature of O_3-γ-1 is different from O_3-1 and the amount of sample recovered is much higher than in O_3-1 we conclude that the majority of sample O_3-γ-1 is due to the gamma radiation and since the OH

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process cannot account for this amount of sample (or the isotopic signature) it must be from another process initiated by the gamma rays.

3) Reactions are quite involved 5049, line 15, "0.2 of each O(1D) from R7 becomes OH". Is 0.8 of O(1D) remains, would it oxidize SO_2*?*

The remaining O(1D) is quenched back to the ground state O(3P) – this will be added to the paper on p. 5049 l. 16.

O(3P) can also react with SO_2 but this reaction is much slower than the OH pathway and thus insignificant.

The section 3.3 seems a bit detractive since the production of mass-independent signature by UV radiation is not the primary focus of the study. However, narrow band excitation clearly adds potential complication to the experimental result. It might be the best if you can avoid it but it might be important. Either case, the reaction is quit involved and this makes very difficult to isolate the effect of gamma ray radiation.

We think that section 3.3 is important since it assesses the contribution from the SO_2 excitation pathway. Since this effect, based on our estimate, seems to be small we can compare our result to the Harris et al result. Any deviation from the Harris et al result could then be supposed to be due to the liquid oxidation effect and since our result agrees well with Harris et al we can say with some confidence that our result for O_3-UV-1 is not affected by liquid phase oxidation to any big degree and thus the O_3-γ-1 probably isn't either.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 5039, 2012.

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