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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.

Anonymous Referee #2

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Enghoff et al. present results of a series of experiments to test the importance of ionizing radiation (gamma radiation) in oxidation of sulfur dioxide and following aerosol formation. They present sulphur isotope data from four experiment

1) aqueous oxidation by O3 (two data points) 2) oxidation by OH (produced by O3 photolysis) 3) ozone + gamma radiation 4) O3+UV+gamma radiation.

Authors claim experiments with gamma radiation produced distinct isotope pattern, suggesting the gamma radiation could be important part of SO2 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. Aqueous O3 oxidation is always present, and it is not clear how one can evaluate

this blank level.

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 SO2 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 O3 oxidation and oxidation by OH.

2) Blank level of liquid phase O3 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 BaSO4 as opposed to 5 mg BaSO4 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-O3 oxidation) level in each bottle (1, 2 and 3).

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 SO2?

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.

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