

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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Dear Anonymous Referee 1.

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.

My concern arises mainly from the limited statistics, only 1 experiment from each system is presented (understandably, since one experiment runs for a week). On the other hand, the experiments with and without gamma-radiation differ significantly in amount of recovered mass – probably that is really indicating the significant contribution from ionizing radiation. Still, I would recommend authors slightly amend the presentation of

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the used method, and explanations concerning e.g. expected and observed $\Delta^{33}\text{S}$. As a non-expert reader I had significant problems in understanding the data.

The introduction has been simplified by shortening the paragraph (p. 5042 l.20) "It is known that the photolytic fractionation of sulphur compounds is wavelength dependent (Farquhar et al., 2000b) and a study by Farquhar et al. (2001) showed that NMD signals can be produced by photolysing SO_2 at low wavelengths (<220 nm) and that the type of UV lamp had significant impact on the isotopic composition. Another possible source for NMD is the oxidation channel of excited SO_2 , a process very likely to happen in the atmosphere." to "It is known that the photolytic fractionation of sulphur compounds is wavelength dependent (Farquhar et al., 2000b) and another possible source for NMD is the oxidation channel of excited SO_2 , a process very likely to happen in the atmosphere."

Regarding expected $\Delta^{33}\text{S}$ we discuss this on p. 5043 l. 3.

We have modified the caption of Fig. 2 to emphasize the errors in both δ and Δ .

I undertood that $\Delta^{33}\text{S}=0$ is assumed except of the reaction proceeding via SO_2 exitation. What is causing then negative NMD? Because O_3 -gamma-1 is closer to MDF line than O_3 -1 wouldn't it mean that the gamma-radiation related process have positive NMD to balance the negative from O_3 -1.

Yes, but the yield of O_3 -gamma-1 is 10 fold larger than O_3 -1 so the measured isotope signature is largely dominated by the gamma process. The $\Delta^{33}\text{S}$ for the O_3 -gamma-1 experiment is very close to 0 and we are not able to explain the small deviation (this is mentioned on p. 5050 l. 21).

Furthermore I did not understand the "Isotopic mixing line", is that just a line to guide an eye?

The point of the line is indeed to guide the eye. It shows the basic fractionation that is present, to some degree, in all samples: The ozone fractionation (O_3 -1) and then

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goes towards the fractionation for the other processes. It also shows that O_3 -UV- γ -1 appears to be a linear combination of O_3 -UV-1 and O_3 - γ -1. We will add the following to p. 5048 l. 17: "The isotopic mixing line in Fig. 2 shows the basic fractionation present in all samples from the ozone process towards the fractionation for the other processes. Following the mixing line we note that the values of both. . .". The line is also explained in the caption of Fig. 2.

I did not understand why recovered mass in O_3 -3 sample is 100-fold to O_3 -1? How much mass was in O_3 -gamma-3 and O_3 -UV-gamma-3?

Yes, it is puzzling why there is more in the last bottle. Due to the bubbling process where the liquid and air in the bottles are mixed with magnetic stirrers some liquid is transported from bottles 1 and 2 to bottle 3. It may be that the liquid being transported is processed along the way, resulting in an accumulation of sulphate in the final bottle. The line starting on p 5047 l. 7 will be changed to: "Note that the yields in the experiment without UV and gamma radiation increased for each bottle counting from the chamber and that the isotopic signature of this material is consistent with oxidation of SO_2 by O_3 . In the experiment with UV and the experiment with gamma there was more sample in the third bottle than in the second but also more in the first than in the second, indicating that two processes were taking place"

Fig. 2. Legend. Please write out MDF (mass dependent fractionation?)

We will do this.

Authors state that in atmospheric $[SO_2]$ the efficiency of gamma-radiation related mechanism drops drastically. The atmospheric significance should be possible to assess based on the data because the ionization rate and $[SO_2]$ are known. Is it negligible? Can it explain any of the observed "missing" sulphuric acid in atmosphere. In current form the connection of paper's conclusions to "atmospheric chemistry and physics" is still weak.

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We have added a paragraph discussing the potential atmospheric impact in more detail.

p. 5052 l. 7-11 replaced with " These experiments clearly suggest that ions may catalyze SO_2 oxidation. However, any ion catalysed mechanism will terminate with collision with OH since the OH^- ion is highly stable with a very large electron affinity. In other words, the electron becomes chemically immobilized. The contribution is thus dependent on the ratio of SO_2 to OH and the ion production rate and we note that in these experiments, the relative concentration of SO_2 to OH was much larger than in the atmosphere. The ion induced contribution should be compared to the oxidation of SO_2 by OH. The third-order rate constant for this reaction is about $4.5 \cdot 10^{-31} \text{ cm}^6 \text{ s}^{-1}$ (Seinfeld and Pandis, Appendix B). The gamma-induced pathway scales with $P_{ion} \cdot [SO_2] / [OH]$, where P_{ion} is the ion production rate. The UV pathway scales with $[SO_2] \cdot [OH] \cdot M \cdot k$, where k is the rate constant. Since both pathways scale with $[SO_2]$ the relative contribution of the ion mechanism to the UV mechanism does not depend on $[SO_2]$. On the other hand it depends on $[OH]^2$ and on the ion production rate. Thus the relative contribution can vary greatly and will be larger at night when there is little or no OH available. For a daytime $[OH]$ of e.g. $2 \cdot 10^6 \text{ cm}^{-3}$ and an ion production rate of $4 \text{ cm}^{-3} \text{ s}^{-1}$ the relative contribution will be 9%. This is of course a very rough estimate and a definitive answer will require more work on determining the exact mechanism, such as has been started by Bork et al (ACP 12, 3639–3652, 2012)".

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

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