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Atmospheric Chemistry and Physics Discussions

Interactive comment on “Sulfur isotope fractionation during oxidation of sulfur dioxide: gas-phase oxidation by OH radicals and aqueous oxidation by H_2O_2, O_3 and iron catalysis” *by* E. Harris et al.

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We thank the reviewer, Becky Alexander, for agreeing to review the manuscript and will incorporate all the suggestions for improvement. In fact, her very helpful suggestions as reviewer of the manuscript Sinha et al. (2009) have prompted us to undertake this research and perform laboratory experiments prior to any further measurements on ambient particle (Alexander 2009). We will address each comment pointwise below.

- "Equation 9: Define “n”"

  P23963 L11 has been changed to: "where *n* is the number of atoms, ^{x}S is one of the heavy isotopes, ^{33}S, ^{34}S or ^{36}S"

- P23963 L13: "Change “reactions” to “reactants”" and P23970 L11: "Remove “just”"

  P23963 L13: ‘reactions’ has been changed to ‘reactants’, P23970 L11: ‘just’ has been removed

- "Figure 6 and associated discussion in text: I don’t know what a facsimile model is and don’t understand what this figure is trying to demonstrate."

  We expanded the text on P23977 L2-3 "A facsimile model run of the species produced by Reactor 1 is shown in Fig. 6 for the photolysis of water in synthetic air to generate 11 ppb OH followed by immediate mixing with 1 ppm SO_2." to: "A Facsimile model (MCPA Software, Ltd.), which is designed to solve chemical kinetic equations, was run to investigate the species that would be present in the reactor following the photolysis of water and may oxidise SO_2. The species produced by Reactor 1 for the photolysis of water in synthetic air to generate 11 ppb OH followed by immediate mixing with 1 ppm SO_2 are shown in Fig. 6."

- "P23977 L18-19: 0.6 ppb background of what species?"

  The background referred to on P23977 L18-19 was sulfate produced from SO_2 in the absence of OH radicals. This is now specified in the text.

- "Paragraph beginning on P23981 L19: Interpretation of the ice core data in Alexander et al. (2003) is speculative. Combined observations and modeling of Δ^{17}O suggests that metal catalyzed oxidation by O_2 is negligible in the southern hemisphere during the Holocene (Sofen et al. 2011). Although it is likely more important in the glacial period due to the increased dust source, it may still represent a very small fraction of total sulfate formation. Based on your measured fractionation factors, can you estimate how much of an increase in the metal catalyzed oxidation pathway is needed to explain the observations reported in Alexander et al. (2003) based on this explanation alone? Is this reasonable?"

We have extended the discussion paragraph beginning on P23981 L19 with the following: "Considering the pre-industrial partitioning between the sulfate production pathways from Sofen et al. (2011) and the fractionation factors measured in this study, the overall preindustrial change in δ^{34}S between SO$_2$ and product sulfate would be +5.5‰. Alexander et al. (2003) saw a decrease in δ^{34}S$_{nss}$ of $\sim$3‰during glacial periods, which would mean a change in δ^{34}S between SO$_2$ and product sulfate of +2.5‰if sources were unchanged. Oxidation by transitional metal catalysis would need to increase from 8% to 35% of the total sulfate production to account for this change if the proportions of sulfate produced from the other oxidation pathways and the overall sulfur budget remained the same. A 10% increase in transition-metal catalysed sulfate production was modelled for the pre-industrial to industrial periods by Sofen et al. (2011), thus a 27% increase due to much higher dust loads in glacial times is not unreasonable.’

- "Table 2: Don’t need to write “by Shuhei Ono (2010)” since he is an author."

  We have removed “by Shuhei Ono (2010)” from the caption of Table 2

Alexander, B., Thiemens, M. H., Farquhar, J., Kaufman, A. J., Savarino, J., and Delmas, R. J.: East Antarctic ice core sulfur isotope measurements over a complete glacial-interglacial cycle, J. Geophys. Res.-Atmos., 108, 4786, doi:10.1029/2003JD003513, 2003.

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Sinha, B. E., Hoppe, P., Huth, J., Foley, S., and Andreae, M. O.: Sulfur isotope analysis of individual aerosol particles – a new tool for studying heterogeneous oxidation processes in the marine environment, Atmos. Chem. Phys. Discuss., 9, 3307-3365, 2009.

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atmospheric sulfate production pathways, oxidants, and ice core Δ^{17}O(SO$_4^2$), Atmos. Chem. Phys., 11, 3565-3578, doi:10.5194/acp-11-3565-2011, 2011.