

## ***Interactive comment on “The sensitivity of the oxygen isotopes of ice core sulfate to changing oxidant concentrations since the preindustrial” by E. D. Sofen et al.***

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We thank the referee for taking the time to review and provide feedback on this paper. Our responses to the referee's questions are provided below:

*Line 24-28, p20609: Due to the widely varying model approaches and the nonlinearity of oxidant chemistry, a proxy is needed for model validation of PI oxidant concentrations. In this study, we consider the oxygen isotopes of atmospheric sulfate extracted from ice cores as a potential constraint for oxidant concentrations in a global model. The rationale for the study of mass-independent isotopes is supposed to be provided by these 2 sentences? Please, can the authors give us some background information*

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*on isotopes and the constraints they provide and why can they be used as proxies of atmospheric oxidant levels? Could the authors also tell us briefly about what people have done on this topic? No need to get into details but at least give some brief explanations in general terms with references (see Brenninkmeijer et al, Chemical Review (2003) for a general review on isotopic chemistry, Thiemens et al. (Science, 1999) for MIF isotopes and Morin et al, Science (2008) on combining different types of MIF isotopes). The authors should not elaborate on the specifics of their isotopic study without presenting first the topic in general term in an extended introduction.*

Further introductory material on sulfate formation (section 2) and past work on the oxygen isotopes of sulfate have been added (end of section 1). While the  $\Delta^{17}\text{O}$  of nitrate can serve a similar purpose to that of sulfate as a tracer of atmospheric oxidation, the more complex chemical cycling and postdepositional processing of nitrate are issues that are not considered in this paper.

*The authors also do not even tell us what they will be doing in this paper. I think it would be useful and rather standard to give a short plan of the paper.*

Thank you for this suggestion. A summary has been added to the end of Section 1.

*Line 14-15, p 20613: Here is the concluding sentence of the Results and discussion section: “ These results suggest that a low bias in the late-1800s O<sub>3</sub> reconstructions may be responsible for the discrepancy with PI O<sub>3</sub> modeling results”. Reading it, I could not help thinking about a quote from D. Jacob (Harvard): “Nobody believes a modeling paper except the author, everybody believes an observational paper –except the author”. I don't think they can conclude this on the basis of their modelling results only.*

Yes, the “blame” for the disagreement between late-1800s O<sub>3</sub> and the model was overstated here. This section has been revised to acknowledge that either the model or the measurements may be responsible for the mismatch. Please see the last paragraph of section 5 for details

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*The authors would be in a stronger position to make such a claim if they discuss first the limitations of the modelling approach and how they may impact the conclusions. - For example, the authors use the winds and temperature for 1989-1991. Can they show what would happen if they were forcing the model with completely different years? Does it have any significant impact? Do they think a present-day forcing derived from 3 years only is valid for the preindustrial period*

This study is focused on the change in oxidants due to changes in anthropogenic emissions (as is now better described in the introduction), and studies of this nature regularly treat an average over three years as adequate for capturing natural variability in meteorological fields (see, for example, Wu et al., 2008 (3-year runs), Lamarque et al., 2005 (2-year runs); Wong et al., 2004 (1.5-3.5 year runs), Shindell et al., 2003 (5-year runs)). Also, by averaging over three years, we make sure our results are not based on an anomalous year (e.g. El Nino). We now give the  $1\sigma$  standard deviation of the mean of the 3 year runs when reporting oxidant concentrations and  $\Delta^{17}\text{O}_{\text{SO}_4}$ .

*I am also wondering how sensitive the results are to heterogeneous chemistry and halogen chemistry because it is clear that the support for heterogeneous chemistry (aerosols and so on) or the sources of halogen have certainly changed between preindustrial time and present-day.*

Section 2 now discusses how halogens may play a significant role in sulfate formation in the marine boundary layer. However, the isotopic composition of HOCl/HOBr, the anomaly that they pass to sulfate during formation, and the importance of this sulfate formation pathway remain unmeasured and is highly uncertain. Therefore, they are not included in the model (addressed in the model description section). Although it has been suggested that S(IV) oxidation by HOBr is important in the MBL (e.g. Vogt et al., 1996), there has so far been no observational evidence. If this reaction (or another reaction) is shown to be important for sulfate formation, our conclusions will need to be revisited. This is now discussed at the end of section 5.

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*The model also assumes photochemical equilibrium when deriving the MIF anomaly. Is it valid at night? This is an issue for the D17O of nitrate, not sulfate, as there is no photochemical cycling involved in sulfate formation, as there is in the NOx cycling prior to nitrate formation. I am sure that the authors know very well the model and its deficiencies, so they can try to consider the important sources of errors and how some of the important factors (other than emissions) may have changed since preindustrial time.*

This paper represents the first global modeling study of preindustrial oxidants that includes the D17O proxy, and so we start by focusing on just the change due to emissions, as has been done in many prior oxidant modeling papers. In the future, we plan to do a more comprehensive study of the role of climate on paleo-oxidants. The introduction has been modified to convey this. The variability in D17O and oxidant concentrations due to interannual variations in meteorological fields is now included in Section 5.

*Last sentence: Line 1-2, 20617 : “. . .help to further constrain paleo-oxidants, as all non- oxidant factors that impact sulfate or nitrate formation are mutually exclusive.”. What is this last sentence mean? What are the non-oxidant factors? Why are they mutually exclusive? The authors should not finish the paper with this obscure statement.*

This statement has been removed from the paper since we do not consider  $\Delta^{17}\text{O}_{\text{NO}_3}$  here.

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