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## ***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.**

### **Anonymous Referee #1**

Received and published: 25 October 2010

The paper by Sofen and coauthors entitled “The sensitivity of the oxygen isotopes of ice core sulfate to changing oxidant concentrations since the preindustrial” is a modelling study of the change in mass-independent (MIF) isotopic anomaly of sulfate driven by changes in tropospheric oxidant levels. The results show that the MIF anomaly can be indicators of tropospheric oxidant levels. It is not a new finding but it confirms the conclusions of previous studies. The scientific quality and content are good enough for ACP. The paper is reasonably well written. However, some parts require more work in terms of writing up and analysis. This paper does not have an introduction as such (does not have what is commonly expected in an introduction). There is no discussion of the limitations of the modelling approach and how they impact some

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of the conclusions. Without such a discussion, some of the claims look hollow (see below). They do not discuss the works that have been done on this topic. I can only recommend publication once these comments are addressed.

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 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. 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.

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. 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

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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? - 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. The model also assumes photochemical equilibrium when deriving the MIF anomaly. Is it valid at night? 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.

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.

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Interactive comment on Atmos. Chem. Phys. Discuss., 10, 20607, 2010.

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