

Interactive comment on “WAIS Divide ice core suggests sustained changes in the atmospheric formation pathways of sulfate and nitrate since the 19th century in the extratropical Southern Hemisphere” by E. D. Sofen et al.

Anonymous Referee #1

Received and published: 18 November 2013

This paper presents the sulfate and nitrate record from the WAIS divide ice core (~2400 yr) and uses a Monte Carlo box model to interpret these measurements. This paper should be accepted to ACP upon addressing the following major and minor comments. The majority of the major comments refer to the modeling section of the manuscript, which should be modified for clarity.

Major comments:

1. Given that postdepositional processing of nitrate (vs snow accumulation rate) is

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deemed to be important for the nitrate record. A clearer picture of what is known of nitrate loss from the snowpack should be presented in the introduction. Section 2.3 lines 20–25 present a picture that these processes are known and well characterized, but this is not necessarily the case. This section should be updated to reflect a more realistic picture of the current state of this knowledge.

2. The description of the Monte Carlo box model is currently unclear. An appendix or online supplement that describes the steps used for the Monte Carlo calculations is needed. For nitrate, it states that first steady state NO₂ production is calculated, followed by oxidation of NO₂ to nitrate. However, it's not clear exactly how this is done by varying the oxidant concentrations (described in 3.4.3) to test the sensitivity isotopic of composition to the level of atmospheric oxidants. Is this run similar to a constrained photochemical box model using GEOS-Chem and the varying oxidant concentrations as the constraints?

3. There are two other major limitations of this box modeling approach, first it is limited by assuming that photochemistry has not been significantly modified due to meteorological conditions (cloud cover, etc) over the past 2400 yr. Second, it assumes the same aerosol load for the present and past sulfate record. Can the authors comment on these two limitations? Tests based on varying the aerosol load (maybe by a factor of two) can at least provide some idea of how the sulfate record would be modified by changes in atmospheric aerosols.

4. The phrase "global aerosol simulation" (Section 3.4.1) may lead the reader to understand that the authors used the average global aerosol load for the sulfate calculations. Please specify the region used for the box model here to avoid confusion.

5. Some runs testing the sensitivity of the results to the assumption that BrO = 1 pmol/mol should be considered. BrO concentrations across Antarctica may be in the range from 0–5 pmol/mol or even more. Are the conclusions of the paper the same if there is more BrO present than 1 pmol/mol?

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6. By varying the oxidants independently in the box model, the authors note that interactions between the oxidants cannot be tested. However, we know that in the atmosphere oxidant concentrations are not independent. For example, OH and RO₂ cannot be independently varied. Is it possible to test how varying these together would change the conclusions? Or, can the authors comment if the conclusions are robust despite this assumption?

Minor comments:

1. When discussing the box model, is it more appropriate to describe GEOS-Chem as a constraint or an initial condition than a boundary condition?
2. The LaTeX formatting of the % symbol is incorrect in the manuscript, please update this to be `\perthousand`.
3. The first line of the introduction has an error in the molecular formula for sulfate.
4. P23094 L4, change "lack of change" to "lack of changes"
5. P23096 L25, after Antarctica. A reference or references are needed here.
6. P23097, should be noted that these studies (ground based and model) studies are limited to knowledge of present day processes.
7. P23098 L24, some more references for knowledge of nitrate processing are needed. For example: Honrath, et al., GRL, 1999.
8. P23102 L7, a more general reference to GEOS-Chem seems warranted here. Perhaps move the references from P23121 L5 here.
9. P23107 L13, Specify what other measurements are shown for clarity.
10. P23107 L14, the order of the reference to Figs 3 and 4 should be changed in the text.
11. May be worth noting in the text or the appendix if the recent developments from Mao

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et al., 2013 in GEOS-Chem are included in the simulations (HO₂ uptake on aerosols) for clarity. This could be clarified by stating if the simulations are the same runs presented in Alexander et al., 2009 and/or 2012.

12. Fig. 2 caption, please make clear what the words "thick lines" are referring to.
13. Fig. 5, it would be helpful to add present day observations to the figure as a reference.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 23089, 2013.

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