Response to reviewers.

Sofen, E. D., Alexander, B., Steig, E. J., Thiemens, M. H., Kunasek, S. A., Amos, H. M., Schauer, A. J., Hastings, M. G., Bautista, J., Jackson, T. L., Vogel, L. E., McConnell, J. R., Pasteris, D. R., and Saltzman, E. S.: 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, Atmos. Chem. Phys. Discuss., 13, 23089-23138, doi:10.5194/acpd-13-23089-2013, 2013.

We thank Dr. Tsunogia and the two anonymous reviewers for their detailed comments on our manuscript. We address the responses to all three reviewers in order here. Reviewer comments are in *italics* and our response is in Roman characters.

Reviewer 1 comments:

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 ?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.

We thank the reviewer for suggesting improvements to this section. We have elaborated on snowpack nitrate chemistry in section 2.2 and 2.3. Ultimately, I disagree with this characterization of postdepositional processing being poorly understood, as we have a good conceptual understanding but poor quantitation of postdepositional processing, particularly with respect to the amount of nitrate in ice cores that is preserved versus impacted by postdepositional processing. As described in Section 2.3, we have a good conceptual model for how postdepositional processing occurs (UV photolysis dependent on solar flux, snow properties, and absorbing impurities in snow, release of NOx from snow by wind pumping, and transport and re-oxidation to nitrate in the polar boundary layer). We lack a quantitative understanding of the rate of snowpack nitrate photolysis (due to uncertainties in e.g. the quantum yield and the amount of snow nitrate available for photolysis), relative importance of transport to oxidation, and isotopic fractionation during photolysis/emission of NOx. The wording in Section 2.3 has been altered to clarify what is/is not known. Ultimately, we argue that postdepositional processing is not important for the WAIS Divide nitrate record due to the relatively high snow accumulation rate and low d15N values.

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?

Section 3.4.1 has been revised to provide a clearer description of the box models. They are not full photochemical box models, but, as the reviewer points out, use archived oxidants from GEOS-Chem as boundary conditions.

In Section 3.4.3, perhaps the key factor that was not clear is that the Monte Carlo model is run to simulate a full year of sulfate or nitrate formation using a fixed seasonal cycle for the boundary conditions, before the oxidant boundary conditions are perturbed and another iteration of a year-long simulation is conducted. Section 3.4.3 has been revised to clarify this.

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 meteo- rological 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.

Sea salt and dust concentrations are varied over an annual cycle in the model by a factor of X. Concentration measurements of sulfate and nitrate at WAIS Divide and other Antarctic ice core sites suggest no significant change in the deposition of sulfate and nitrate aerosols over the time period of interest (See Figures 3 and 4), which suggests that the sulfate and nitrate aerosol load has not changed dramatically. These observations allow us to rule out changes in sulfur and nitrogen sources as causes of the observed variability in their isotopic composition. Meteorological changes during the recent part of the Holocene (e.g. between the ``preindustrial'', approx. 1800 CE, and present-day) are small and likely have a minor impact on oxidant photochemistry, particularly compared to the changes due to anthropogenic emissions changes [Murray et al., ACPD, 2013]. We certainly do not expect there to have been an abrupt change in meteorological conditions around the time of the step increase in sulfate D17O. Any changes in meteorological conditions that impact nitrate formation (and thus nitrate D17O) will do so by way of its impact on oxidant abundances, which is what we very in the box model.

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.

The sentence has been revised to read ``The sulfate model goes a step further to calculate concentrations based on the production rates from the box model using Southern Ocean boundary conditions and the global mean lifetime for each form of sulfate (gas-phase, aqueous, or heterogeneous) based on a global sulfate aerosol simulation [Alexander et al., 2009].''

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?

As described in Section 6.1 and 6.4, adding BrO increases the sensitivity of nitrate $\Delta^{17}O$ to changes in the other oxidants, particularly OH. Increasing [BrO] further increases the sensitivity of $\Delta^{17}O$ to RO_2 or OH. Given the conceptual understanding of the relationship between BrO and sensitivity of nitrate $\Delta^{17}O$ to changes in other oxidants, it does not seem necessary to conduct additional sensitivity studies.

?6. By varying the oxidants independently in the box model, the authors note that inter- actions 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?

Thank you for raising this issue. We realize that the interactions between oxidants are important in terms of the complete picture of atmospheric chemistry, but are challenging to capture in a box model framework that is intended to capture large spatial and temporal scales. We considered parameterizations of relationships between oxidants akin to Prather [GRL, 1994] in which OH is related to CO and CH_4, but no similar approach exists to interrelate all the oxidants involved in sulfate or nitrate formation. Our global model sensitivity studies included in the appendix do explore how oxidants co-vary when the model is forced by emissions changes comparable to those associated with anthropogenic activity and ultimately lead to the conclusion that it is difficult to reconcile the changes in oxidants suggested by sulfate $\Delta^{17}O$ with reasonable constraints from the global model and our understanding of the changes between the preindustrial period and present-day.

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?

Thank you for the suggestion, but I believe that the GEOS-Chem oxidant model output are best described as boundary conditions to the box model as within one iteration of the monte carlo simulation the model does not modify the oxidant concentrations. The description of the box model has been revised to generally improve clarity.

2. The LaTeX formating of the \permil symbol is incorrect in the manuscript, please update this to be \perthousand.

The Copernicus manual specifies using \permil, which is used throughout the manuscript. I assume if \perthousand is now preferred, this will be addressed with the editorial staff during typesetting. I have not been able to find where the symbol appears incorrectly. Perhaps this is a PDF reader/system font problem?

3. The first line of the introduction has an error in the molecular formula for sulfate.

Fixed

4. P23094 L4, change "lack of change" to "lack of changes"

Fixed

5. P23096 L25, after Antarctica. A reference or references are needed here.

Added references to Blunier et al., 2005, Frey, et al. 2009, and Erbland, et al., 2013.

6. P23097, should be noted that these studies (ground based and model) studies are limited to knowledge of present day processes.

Added clarification that transport analyses of Parish and Bromwich [2007] and Masclin [2013] are specific to present-day meteorology.

7. P23098 L24, some more references for knowledge of nitrate processing are needed. For example: Honrath, et al., GRL, 1999.

Added Honrath reference and additional discussion of snowpack nitrate to this section.

8. P23102 L7, a more general reference to GEOS-Chem seems warranted here. Perhaps move the references from P23121 L5 here.

The Alexander reference is specific to the current version of the sulfate model. I have added general references for GEOS-Chem (Bey et al., 2001) and the GEOS-Chem offline aerosol model (Park et al., 2004).

9. P23107 L13, Specify what other measurements are shown for clarity.

It seems repetitive to specify the whole list of other measurements (and leads to a run-on sentence), as I then list them below as they pertain to sulfate and nitrate. The sentence has been modified to specify that the other chemical observations are listed below.

10. P23107 L14, the order of the reference to Figs 3 and 4 should be changed in the text.

Order reversed.

11. May be worth noting in the text or the appendix if the recent developments from Mao 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.
I have clarified that these simulations do not include HO_2 uptake onto aerosols.

12. Fig. 2 caption, please make clear what the words "thick lines" are referring to.
Reworded for clarity.

13. Fig. 5, it would be helpful to add present day observations to the figure as a reference.

Added modeled preindustrial-to-present-day change in oxidants from Sofen et al. [2011] as a guide on the scale of the oxidant changes that are of interest.

Reviewer 2 comments (Dr. Tsunogai):

As you requested, I have read this manuscript. This is an important paper that reports very rare data on sulfate and nitrate Delta17O in Antarctic ice core spanning the last 2400years.The sampling and analytical procedures are well and the data are consistent. Possible temporal variation in the values of Delta17O-O3, however, was not properly discussed in this paper. To our best knowledge on past variability of atmospheric ozone, tropospheric ozone during preindustrial ages was around 1/2 to 2/3 of the present and the relative mixing ratio of stratospheric-derived ozone within total tropo- spheric ozone was much higher than the present. If this was the case, the Delta17O- O3 could be highly different from the present and thus sulfate and nitrate Delta17O. The authors, however, seem to apply the same Delta17-O3 with that obtained for the present to preindustrial. If so, the authors should add discussions to justify this. If not, they should clarify the Delta17O-O3 values of preindustrial tropospheric ozone used in their calculation, together with the theoretical backgrounds. Besides, the graphics (Figs.3-4, especially) is not fine enough and should be improved.

The reviewer raises an interesting point that $\Delta^{17}O(O_3)$ may have varied with time due to changes in the relative importance of stratospheric O_3 to the tropospheric O_3 budget as local O_3 production changes. Presumably, this suggestion implies that in the preindustrial Holocene, $\Delta^{17}O(O_3)$ was higher as the flux of high $\Delta^{17}O$ O_3 from the stratosphere would represent a larger fraction of tropospheric ozone. In the manuscript, we have explored how the sensitivity of our conclusions depends on $\Delta^{17}O$ (O_3) due to the uncertainty in its present-day value. As shown in Lyons [2001] (Fig. 1), the observations of tropospheric and stratospheric $\Delta^{17}O(O_3)$ show significant overlap. To estimate the impact of changes in stratosphere-troposphere exchange on $\Delta^{17}O$, we consider the upper end of stratospheric $\Delta^{17}O(O_3)$ observations (e.g. 43 per mil) to remain consistent with our tropospheric assumption, while assuming a change in the contribution of stratospheric ozone to high-latitude Southern Hemisphere ozone formation from 60% to 40% [Lelieveld and Dentener, 2000]. This represents a 2.7 per mil decrease in $\Delta^{17}O(O_3)$. Considering the highest-$\Delta^{17}O$ sulfate sample (e.g., that for which O3 plays the largest role in sulfate formation), a complete shift from stratospheric $\Delta^{17}O(O_3)$ to tropospheric $\Delta^{17}O(O_3)$ could result in a decrease in sulfate $\Delta^{17}O$ of up to 0.3 per mil. However, this is contrary to the increase in $\Delta^{17}O$ that we observe over the past 200 years. Changes in $\Delta^{17}O(O_3)$ will have a larger effect on nitrate $\Delta^{17}O$ because of the greater importance of ozone in nitrate formation than sulfate formation, contributing up to a 2.7 per mil decrease in nitrate $\Delta^{17}O$. This could contribute to the observed decrease in ice core nitrate $\Delta^{17}O$, however we would expect it to also appear in sulfate $\Delta^{17}O$, but it does not. Furthermore, in the scenario described above, both [O3] and $\Delta^{17}O(O_3)$ will change in tandem, with increasing [O3] reducing the $\Delta^{17}O(O_3)$, which may weaken the impact of the changing isotopic composition of ozone on sulfate and nitrate, as the O3 will play an increasing role in producing that sulfate or nitrate. Discussion of this has been added to the background information. However, lacking more detailed information on the preindustrial and present-day ozone budgets (e.g. from tagged tracer simulations, ideally including isotopic modeling), we make the typical paleoclimate assumption that $\Delta^{17}O(O_3)$ has not varied with time.

Reviewer #3 comments:

I have only minor comments to the paper, which are listed in the following.
Specific comments
P. 23092, L. 11: "Oxygen isotope measurements from ice cores can provide... and how they change over time". Add references [Hastings et al., 2005 Global Biochemical Cycles, 19(4); Hastings et al., 2009 Science, 324, 1288]
References for both sulfate and nitrate have been added.

P. 94, L. 16: which is the standard deviation on the mean Δ17O(O3)? Include if possible.
Added standard deviation of $\Delta^{17}O(O_3)$ (+/-5 per mil for the combined data of Krankowsky, Johnston, and Vicars.)

P. 97, L. 4 – 7: include reference after the sentence. Include the altitude level at which the back-trajectories were calculated
Moved Masclin et al., 2013 reference up a sentence. Added back trajectory elevation details.

P.97, L. hydrocarbons (HC)
Added abbreviation HC

P. 97, L. 18: Include the daylight NO3- photolysis pathway in figure 1.b
The daylight NO3- photolysis pathway has been added to figure 1.b

P. 98, L. 24: Indicates the snow accumulation range at East Antarctica, mention if it significantly differed or not during the last two millennia.

Added the accumulation rate at Dome C where the 340 per mil enrichments have been measured. Long-term trends in East Antarctica over the past two thousand years are small and inconsistent (some positive, some negative).

P. 99, L. 6. P. 99, L. 6. Which is the standard deviation on the accumulation rate? To which period this accumulation rate corresponds? Which method was used to estimate this accumulation?. Include them on the methods part.

The accumulation rate is calculated based on the annual layer thickness corrected for thinning and densification. A reference (Fegyveresi et al., 2011) has been added for the accumulation rate methodology. The standard deviation is (± 0.04 m a^{-1}) and has been added to the text.

P.23100, L. 4. Which method was employed? Was freeze-drying or plain evaporation? Could you include the magnitude of δ15N (NO3-) fractionation by using the evaporation technique? (perhaps as supplementary information).

We did not measure d15N in the evaporated samples. In the samples that were evaporated, we first took an aliquot for d15N prior to evaporation. We then measured the d15N on those samples using P.chlororaphis, because this method can handle lower concentrations than P. aureofaciens (so preconcentration was necessary for P. chlororaphis). For the samples that were concentrated using the resin, we could measure al the isotopes in one shot with P. aureofaciens. I have revised the nitrate isotope section (3.3.1) of the methods to lay this out more clearly.

P. 100, L. 16: which bacteria strain was employed in the analyses?

P.~aureofaciens for all but the $d^{15}N$ measurements conducted on the WDC05A core, which used P.~chlororaphis. This has been added to the manuscript.

P. 105, L. 18: you are suggesting a change in the chemistry of DMS to explain the variations of the MSA/nssSO42- ratio, could you infer that those changes were induced by temperature variations that will change the ratio?

Changes in the MSA/nssSO42- ratio could be driven by either temperature (influencing reaction rates), oxidant abundances (OH) or the abundance of reactive halogens (BrO) which plays a significant role in the oxidation of DMS and has a different MSA/nssSO4 branching ratio than does OH.

Figure 3. You have not mentioned how the MSA, Na+, Sulfur, pH have been measured; please include the methodology or references in the methods section.

These measurements were made on Joe McConnell's CFA system at the Desert Research Institute as described in McConnell et al., [2002]. The reference has been added to the manuscript.

Technical corrections

Thanks to the reviewer for the detailed reading. All corrections have been made, except for the sentence at P.105, L. 15 which is a complete sentence.