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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

E. D. Sofen et al.

General comments

The manuscript presents valuable $\Delta^{17}O(SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ data from ice cores from WAIS Divide, which are used as proxies of sulphate and nitrate formation pathways. The results by Sofen et al., show that the downward trend in $\Delta^{17}O(NO_3^-)$ observed in the ice core data since 1860 implies a decrease in the O_3 to RO_2 ratio in extratropical Southern Hemisphere, which is consistent with global modelling studies. Moreover, the increase in ice core $\Delta^{17}O(SO_4^{2-})$ observed in the early 19th century suggests an increase in aqueous- phase sulphate formation by O3; however a lack of understanding about sulfate formation in the remote MBL avoids further conclusions involving other oxidant agents such as HOCl and HOBr.

The manuscript presents an interesting work which has implications to ice core interpretation and atmospheric modelling, giving new and valuable insights into nitrate and sulfate formation and relative abundances of atmospheric oxidants during the last 200 years. 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]

P. 94, L. 16: which is the standard deviation on the mean Δ17O(O3)? Include if possible.

P. 97, L. 4 – 7: include reference after the sentence. Include the altitude level at which the back-trajectories were calculated.

P.97, L. hydrocarbons (HC)

P. 97, L. 18: Include the daylight NO_3^- photolysis pathway in 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.

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.

P.23100, L. 4. Which method was employed? Was freeze-drying or plain evaporation? Could you include the magnitude of $\delta^{15}N$ (NO_3^-) fractionation by using the evaporation technique? (perhaps as supplementary information).

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

P. 105, L. 18: you are suggesting a change in the chemistry of DMS to explain the variations of the MSA/nssSO_4^{2-} ratio, could you infer that those changes were induced by temperature variations that will change the ratio?

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.

Technical corrections

P.93, L.8: the highest

P. 94, L. 16: The mean observed $\Delta^{17}O(O_3)$ is 25 ‰ (Krankowsky et al., 1995; Johnston and Thiemens,1997), but measurements using cryogenic trapping of O_3 are complicated by low O_3 abundances and potential for contamination by atmospheric O_2 which can bias $^{17}O(O_3)$ towards lower values (Brenninkmeijer et al., 2003).

P.96, L. 6: by transition

P.23100, L. 1: $\delta^{15}N$ was measured

P.100, L. 12: the ice samples

P. 100, L. 16: Nitrate was converted

P.102, L. 1: isotopic composition of sulfate and nitrate

P.103, L. 21 aldehydes

P.105, L. 15: “influenced by the 1810 and Tambora volcanic eruptions”, the sentence is incomplete.

P. 107, L. 14: (Figs. 3 and 4)

Figures

1.b: write hν.