Atmospheric Chemistry and Physics Discussions

Atmos. Chem. Phys. Discuss., referee comment RC2
https://doi.org/10.5194/acp-2022-417-RC2, 2022

Comment on acp-2022-417

Anonymous Referee #2

Referee comment on "On the potential fingerprint of the Antarctic ozone hole in ice-core nitrate isotopes: a case study based on a South Pole ice core" by Yanzhi Cao et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-417-RC2, 2022

Cao et al. measure nitrate isotopes and concentrations in a 60-year firn core from South Pole and perform air-snow nitrate transfer simulations using the TRANSITS model to investigate whether nitrate isotopes at the site reflect changes in stratospheric ozone. The results are similar to previous Antarctic studies of ice core with similar snow accumulation rates that indicate d15N(NO3-) is insensitive to total column ozone. Decreases in the D17O(NO3-) record during the ozone hole are qualitatively attributed to atmospheric oxidization changes in the extratropical Southern Hemisphere nitrate source regions. The new dataset is a valuable contribution however, the manuscript could be improved by furthering our understanding of ice core nitrate isotopes in Antarctica which have a unique and not fully understood fingerprint. As such, I believe the authors have an opportunity to use the ice core dataset and the TRANSITS model to advance our understanding of ice core D17O(NO3-) to make a new and valuable contribution to the literature. I look forward to seeing the published.

Suggestions for improvement

A paper on nitrate isotopes in a snow pit (1960-2000) from the low-accumulation Dome A site was just published in June (Shi et al., 2022) and the authors conclude that nitrate isotopes (d18O, D17O, and d15N) record stratospheric ozone depletion and ultra-violet radiation at the Dome A site. The authors have discussed the modelled response of d15N(NO3-) to total column ozone at South Pole versus Dome A sites. Please update the manuscript in light of the newly published paper.

Shi, G., Hu, Y., Ma, H., Jiang, S., Chen, Z., Hu, Z., et al. (2022). Snow nitrate isotopes in

central Antarctica record the prolonged period of stratospheric ozone depletion from □1960 to 2000. Geophysical Research Letters, 49, e2022GL098986. https://doi.org/10.1029/2022GL098986.

Now that there are a number of d15N(NO3-) measurements across Antarctica, a discussion on the sensitivity of d15N(NO3-) and D17O(NO3-) to total column ozone at various ice cores sites, including the new Dome A record, would be valuable addition for the community to make progress on the use of d15N(NO3-) and D17O(NO3-) as a UV or total column ozone proxy.

Another recently published study (July 2022) on nitrate isotopes in relatively high accumulation rate sites (Summit Greenland) also highlights the importance of understanding post-depositional effects of ice core nitrate and it would be worth citing this paper.

Jiang, Z., Savarino, J., Alexander, B., Erbland, J., Jaffrezo, J.-L., and Geng, L.: Impacts of post-depositional processing on nitrate isotopes in the snow and the overlying atmosphere at Summit, Greenland, The Cryosphere, 16, 2709–2724, https://doi.org/10.5194/tc-16-2709-2022, 2022.

There are extremely scare measurements of e-folding depth in Antarctica. A much shallower e-folding depth of 2-5 cm was observed at DML. This was also shallower than estimated by Zatko et al. (2013). What is the uncertainty on your estimated e-folding depth of 20 cm? How appropriate is that estimate in the context of measurements and modelled estimates? Given that recent studies have shown the importance of e-folding depth on nitrate recycling, a discussion and sensitivity analysis of a range of possible e-folding depths for South Pole site is highly encouraged.

Please add a section of assessing the validity of the TRANSITS model especially in regards to D17O(NO3-). The model doesn't simulate the observed decreasing D17O(NO3-) trend from ~1976 to 2000. Why is this? How much can you take away from the simulated D17O(NO3-) results? How can you improve the model? How does the model help you understand D17O(NO3-) at South Pole. TRANSITS simulations of D17O(NO3-) would be an area where the authors can contribute new understanding to the literature.

Introducing the South Pole site in terms of the snow accumulation and also atmospheric nitrate isotopes (Walters et al., 2019) in the introduction would be helpful to put the site into context of other records given that the nitrate isotopes are sensitive to accumulation rate.

It is not always clear in the discussion if the authors are talking about the results from TRANSITS or observations.

Specific comments

L1 The title is misleading as nitrate isotopes at South Pole do not reflect changes stratospheric ozone changes.

L26 HCl and ClONO2

L65-67 The photic zone at DML is 15 cm which is less than Dome C (Winton et al., 2020).

L71-73 This sentence focusses on fractionation constants on the EAP. Relevant to this study are fractionation constants in the "transition zone" characterized by snow accumulation rates typical of sites located between the EAP and coast (5–20 cm yr−1 w.e.; Erbland et al. 2015).

L86-102 Recent studies have shown the importance of e-folding depth on nitrate recycling. This is important to mention here.

L108-111 See the recently published paper by Shi et al. (2022)

L131 Did you decontaminate the samples?

L134 Suggest moving reference to Geng et al. further up in the methods section.

L119-136 Please add protocols for minimising contamination. Please state the sample resolution in terms of depth and age here.

L133 UW

L138-140 This sentence seems out of place.

L164 How did you calculate the e-folding depth?

L223-226 Seems out of place.

L234 Add the dates of the pit

L282 Can you use the approach of Weller et al. (2004) to calculate nitrate loss? And then compare to the TRANSITS estimate of nitrate loss?

L295 Heading should reflect that this section is about TRANSITS modelling

L334 This assumption ignores other factors that influence e-folding depth. While we don't know how e-folding depth changes over time, based on changes in grain size, snow density and impurity content it is fair to assume e-folding depth at any site is not constant through time. Sensitivity studies show that nitrate isotopes are sensitive to changes in e-folding depth.

L346-357 Update in light of the published work by Shi et al. (2022).

L359 The ice core data in the figures suggest interannual variability.

L391 A concluding sentence about oxidation for this paragraph would be helpful here.

L424 The EAST ANTARCTIC PLATEAU snow sourced

Figures: It would be very helpful for the reader to visualise the TCO and nitrate isotope trends on the same figure.

Fig. 5: please add in the nitrate isotope observations.