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Comment on Cao et al.

Anonymous Referee #1

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-RC1, 2022

Stable isotopes of nitrate preserved in ice cores hold the potential to reveal past variability of stratospheric ozone over Antarctica. However, there are many factors affecting ice core nitrate concentration as well as its stable isotopic composition. Efforts to understand those processes and their influence are therefore much needed.

In this manuscript, Cao et al. presents such an effort using two shallow ice cores from the South Pole dating from 1944 to 2005. Because the time span of the cores nicely encompasses the period of the Antarctic ozone hole since 1976, the nitrate isotope records within serve as a nice archive to investigate the relative contribution of different factors on the nitrate isotopes. Observationally, the authors find that the d15N of nitrate has large variability and the D17O of nitrate displays a long-term decline (on top of the variability). Aided by a snow photochemical model, they conclude that:

(1) Ozone hole—which enhances UV flux arrived at the ice sheet surface—alone cannot account for the large variability of d15N, so accumulation rates must be the dominant factor here.

(2) Nonetheless, if snow accumulation rates are somewhat stable, the variability could potentially reflect post-depositional processes driven by UV—and by extension by ozone variability.

(3) Finally, the trend in D17O seems to be compatible with a change of atmospheric oxidant ratios in the extratropical southern hemisphere.

Overall, this paper is timely and interesting, and falls within the scope of Atmospheric Chemistry and Physics. It is well-written and easy to follow. I enjoy reading it and believe

it could be published on ACP after making some minor revisions and adding some clarifying statements. I should say, however, that the photochemical modeling is out of my area of expertise, so I am may not be qualified to assess the robustness of the model. I hope other reviewers could comment on the modeling aspect more authoritatively.

General comments:

First, in the Introduction (from Line 51 and onward) there seems to be no mention of other attempts to reconstruct ozone and the authors proceed to discuss the principles of stable isotopes of nitrate preserved in ice cores as a potential ozone proxy. Non-ozone specialists may wonder if there are other ways to know ozone in the past. A quick review of the existing methods with their strengths and limitations discussed could be helpful here. The readers will also be able to understand the value of the isotope records in ice-core nitrate.

Second, in the Discussion 4.3, the lines of reasoning could benefit from a simple re-structure: why not putting the 4.3.2 and 4.3.3 first? This way you could discuss the reject the alternative hypotheses, leaving the most plausible explanation (changes in the O3/HOx ratio) on the table.

Third, one key point of the paper is that Dome A might be a good place to study nitrate isotopes because of its low snow accumulation rates. This might foreshadow a follow-up study from that very site, which is great. For the present study, however, can you also calculate the expected d15N variability induced by stratospheric ozone in other East Antarctic sites such as Vostok, Dome C, and Dome F where deep ice cores have been drilled? This could be summarized with a new figure. Though it does not necessarily mean that you have those samples, I think this exercise could benefit the ice core communities in general.

Specific comments:

Line 21: "but" and "nevertheless" are repetitive. "Nevertheless, this enrichment is small and masked by …" sounds better.

Line 21: the second half of this line could be simplified by saying "… masked by the effects of snow accumulation rates at the South Pole ..." In essence the snow accumulation rates have two parts: internal variability superimposed on a long-term trend. They could be discussed in greater detail in the main text without complicating the message here in the abstract.

Line 32: consider changing “protecting life on land” into “and protects life on land”. No need for using the nonfinite verb here.

Line 44: missing an “of” after “shifting”.

Line 57: “ozone which determines surface UV radiation.” This seems to suggest that there are lots of “ozone” and the one being talked about is the one that determines surface UV radiation. Yet, in fact you are just describing stratospheric ozone, so no need for the defining relative clause here, and there should be a comma “,” before “which”.

Line 61: missing an “as” after “deposited”.

Line 78: this sentence is not very clear. By saying “it is a mass-independent fractionation signal” it is implied that photolysis is a mass-dependent process. If this is the case, please explicit state so.

Line 129: can you specify which years were binned to the adjacent samples? This could be provided as a supplementary table.

Line 190: “were from data extrapolation” could be better phrased as “were extrapolated”.

Line 216: missing a blank between “years” and “1944”.

Line 218, 231, 237, 245, and 251: please specify the meaning of the number after the ± sign. Is it one standard deviation?

Line 263: there are two “similar to the observation”. Please consider rephrasing.

Line 278: change “pronounced” to “reproduced”?

Line 283: I would appreciate you putting the numbers into a greater perspective here. At face values, about 75% of the primary nitrate was lost, leaving 25% nitrate behind. On the other hand, you mentioned that re-deposited nitrate contributed to the preserved nitrate. Does this mean that the loss of *primary* nitrate exceeds 75%? Similarly, please

specify what the ~40% nitrate loss calculated by the photochemical model refers to, perhaps with the help of Figure 2: is the nitrate in the combined surface and photic layer?

Line 305: the shading area in Figure 4 does not correspond to the periods with an ozone hole.

Line 307: is this from the sensitivity test? If so Figure 5 should be mentioned. Alternatively, you could just discuss d15N of nitrate exclusively in section 4.2 (which now needs a new title of course), and leave the discussion of D17O entirely to the next section.

Line 364: "discern" might not be the proper word choice here. "Investigate" or "Examine" sounds more logical.

Line 455: "Had snow accumulation rate at Dome A stayed …" Technically this sentence shouldn't be in subjunctive mood, because by doing so you are implying that accumulation rates at Dome A were, in fact, not stable. Yet, the accumulation rate history is not known, so you could just use "If" instead of "Had" to indicate a possibility.

Figure 2: should be "Archived" instead of "Achieved" layer?

Figure 3: per the text, the "ozone hole period" begins right after 1976, but in the figure here, the ozone hole starts around 1979 C.E.? Please make them consistent with each other.

Figure 4: please add some visual guidance to mark the ozone hole period.

Figure 5: same as Figure 4, a little visual cue of the ozone hold period (or simply the beginning of it) would be nice.