Anonymous Referee #1

We are very grateful to the reviewer for reviewing this manuscript. We have carefully considered the suggestions and make changes accordingly. Below we list detailed responses to the suggestions and comments. The suggestions and comments are in italics, followed by our responses in normal font with changes highlighted in blue.

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.

Response: We agree with the reviewer that it would be great if there are other proxies can be used to reconstruct past column ozone density. But to our best knowledge, UV-sensitive chemical species preserved in snow are the known potential candidates, and nitrate is one of them and is the mostly studied. To make this point more cleared, in the revised manuscript we have added a statement at the beginning of this paragraph as follows:

"However, to reconstruct past changes in stratospheric ozone is difficult due to the lack of reliable proxies. UV-light sensitive chemicals in snow including nitrate (Frey et al., 2009) and bromine (Abbatt et al., 2012) have been sought to investigate changes in surface UV conditions and the potential links to stratospheric ozone. The occurrence of an ozone hole⋯"

Second, in the Discussion 4.3, the lines of reasoning could benefit from a simple restructure: 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.

Response: Thanks for this suggestion. We have changed the orders of the subsections in 4.3 to make the most plausible explanation in the last subsection.

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.

Response: Thanks for this suggestion. Using TRANSITS model, we calculated the enrichments in $\delta^{15}N(NO_3^-)$ and $\Delta^{17}O(NO_3^-)$ caused by ozone hole alone (keeping other factors the same) in other East Antarctic sites including Dome A, Dome C, Vostok, Dome Fuji, and a west Antarctic site WAIS Divide in addition to the South Pole. In the revised manuscript, we added a new subsection (new subsection 4.3) to present this table with relevant discussion.

"4.3 Estimated effects of the ozone hole on snow nitrate isotopes in other Antarctic sites

In order to search for signals of the ozone hole, we used the TRANSITS model to further explore the maximum possible responses of ice-core preserved $\delta^{15}N(NO_3^-)$ and $\Delta^{17}O(NO_3^-)$ to the ozone hole at other Antarctic sites, including Dome A, Dome C, Vostok, Dome Fuji, and the West Antarctic Ice Sheet (WAIS) Divide in addition to the South Pole. The responses are defined as the differences between the isotopes before the ozone hole period and those in years with the most depletion. The results are listed in Table 1. As shown in the table, except WAIS Divide, other sites all display bigger responses to the ozone hole, especially the three East Antarctic Plateau sites. These patterns are mainly determined by the differences in snow accumulations rates at these sites (Frezzotti et al., 2013; Erbland et al., 2015; Shi et al., 2022), i.e., lower snow accumulation rates correspond to longer durations of nitrate in the photic zone, leading to larger effects of the ozone hole. In particular, at Vostok, Dome C and Dome A, the ozone hole alone can result in enrichments in $\delta^{15}N(NO_3^-)$ by 31.2 ‰, 30.7 ‰ and 26.5 ‰, respectively. These values are higher than that (~6.9 ‰) at the South Pole, and since the effects of the ozone hole were gradually increased given the enhanced level of depletion from ~ 1976 to the mid-1990s, gradual increase in $\delta^{15}N(NO_3^-)$ might be possibly detected as long as snow accumulation rate at these sites stayed relatively constant before and in the period of the ozone hole. However, at east Antarctic Plateau sites (i.e., Vostok, Dome C and Dome A) where snow accumulation rates are extremely low, $\delta^{15}N(NO_3^-)$ of preserved nitrate is above 300 ‰. It would be difficult to determine changes of ~ 30 ‰ out of more than 300 ‰, especially considering the increasing pattern of snow accumulation rate in the East Antarctic Plateau since the ~1970s (Thomas et al., 2017) and the fact that ice-core $\delta^{15}N(NO_3^-)$ is very sensitive to snow accumulation rate (Akers et al., 2022). Nevertheless, a recent study by Shi et al. (2022) reported firn core nitrate concentration and isotopes at Dome A, where nitrate concentrations in the 1990s and after decreased by close to one third compared to that in the 1970s (i.e., ~18 ng g^{-1} to ~ 12 ng g^{-1}), with 20 to 30 ‰ increases in $\delta^{15}N(NO_3^-)$ and > 5 ‰ decreases in

$\Delta^{17}O(NO_3^-)$. These appear to be qualitatively consistent with the effects of the ozone hole. However quick analyses indicate that changes in nitrate mass do not agree with the degrees of isotope changes resulted from the photo-driven post-depositional processing. For example, our preliminary calculations using the TRANSITs model suggest that at Dome A the ozone hole can only induce maximum 2.8 ng g^{-1} decreases in nitrate concentration, and as little as 0.9 ‰ decreases in $\Delta^{17}O(NO_3^-)$. These results imply there are probably other factors regulating the observed nitrate concentration and isotopes at Dome A. Note Shi et al. (2022) also did TRANSITs modeling study, but the model parameters are not clear, e.g., snow e-folding depth, quantum yield of snow nitrate photolysis, and the modeled results can't be reproduced given local Dome A conditions we complied. A comprehensive modeling effort in combination with more thoughtful analyses on the observed data are necessary to investigate whether the signals can be detected at Dome A."

Table 1. Model calculated maximum isotope changes resulted from the Antarctic ozone hole (i.e., the differences between isotopes in the pre-ozone hole period and that in years with the most depletion) at different Antarctic sites.

Site name	**Latitude (◦)**	**Longitude (◦)**	**Snow accumulation rate ($kg\ m^{-2}\ yr^{-1}$)**	**$\Delta(\delta^{15}N(NO_3^-))$ ‰**	**$\Delta(\Delta^{17}O(NO_3^-))$ ‰**
South Pole	-90	0	75	6.9	-0.8
Dome A	-80.5	77.12	24.4	26.5	-0.9
Dome C	-75.1	123.33	28	30.7	-1.1
Vostok	-78.47	106.84	21.5	31.2	-1.2
Dome Fuji	-77.32	39.7	28.8	16.3	-1.2
WAIS Divide	-79.48	-112.09	200	1.0	-0.3

Specific comments:

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

Response: Thanks for this suggestion. We have made this correction in the revised manuscript.

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.

Response: Thanks for this suggestion. We have made this correction in the revised manuscript.

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

Response: Thanks for this suggestion. We have made this correction in the revised manuscript.

Line 44: missing an "of" after "shifting".

Response: Thanks for this suggestion. We have made this correction in the revised manuscript.

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".*

Response: Thanks for this suggestion. We have deleted the words after ozone in this sentence in the revised manuscript

Line 61: missing an "as" after "deposited".

Response: Thanks for this suggestion. We have made this correction in the revised manuscript.

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.

Response: Yes, the photolysis is a mass-dependent process. We add the following statement in our revised text:

"…and further fractionations/alteration during nitrate recycling. Snow nitrate photolysis doesn't directly influence $\Delta 17O$ because it is a mass-independent fractionation signal while photolysis only induces mass-dependent fractionation (McCabe et al., 2005)."

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

Response: Thanks for this suggestion. The samples that were combined with the adjacent ones and the corresponding years were summarized in the table below and the table has been added as SI table in the revised manuscript:

Sample ID	Corresponding years (C.E.)
S1	2004-2005
S21	1983-1984
S23	1980-1981
S29	1973-1974
S32	1969-1970
S33	1967-1968
S35	1964-1965
S40	1958-1959
S41	1956-1957
S42	1954-1955
S43	1952-1953
S45	1949-1950
S47	1946-1947

S48	1944-1945

Line 190: "were from data extrapolation" could be better phrased as "were extrapolated".
Response: Thanks for this suggestion. We have made this correction in the revised manuscript.

Line 216: missing a blank between "years" and "1944".
Response: Corrected as suggested.

Line 218, 231, 237, 245, and 251: please specify the meaning of the number after the sign. Is it one standard deviation?
Response: Yes, it is one standard deviation. We have added (1σ) after these values to indicate the meaning of the number after the sign.

Line 263: there are two "similar to the observation". Please consider rephrasing.
Response: Thank you for raising this issue. We have rewritten the sentence as follows:
"…Over the studied period, the modeled average ω(NO3-) and $\delta^{15}N(NO_3^-)$ are (91.4 ± 38.1) ng g-1 (1σ) and (59.1 ± 12.8) ‰ (1σ), respectively, similar to the observations. The modeled long-term trend in $\delta^{15}N(NO_3^-)$ is also similar to the observation and displays no expected response…".

Line 278: change "pronounced" to "reproduced"?
Response: Corrected as suggested.

*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?*
Response: We guess the face-value of 75 % was estimated by comparison of the **summer surface** concentration ($\omega(NO_3^-)$ = ~ 400 ng g^{-1}) and that of the firn core average ~ 100 ng g^{-1}. First of all, this is not correct, as one have to use at least the annual mean of the surface snow concentration as the starting point to estimate the lost, and in winter surface snow concentration is much lower than in summer as observed by Walters et al. 2019 at the South Pole (this is also true for other polar sites).

Regarding the reported ~ 40 % loss from our calculation, this is the net loss, i.e., the difference between the finally preserved nitrate and primary nitrate. In the revised manuscript, we have added Equation.2 to indicate how this is calculated: (f_{loss}):

$$f_{\text{loss}} = 1 - \frac{F_A}{F_{pri}} \tag{2}$$

where F_A represents the archival flux of nitrate (Fig. 2).

Line 305: the shading area in Figure 4 does not correspond to the periods with an ozone hole.
Response: In the revised manuscript, we merged Figure 3 and Figure 4 and plotted a new Figure 3. Grey shading area corresponds to the ozone hole period.

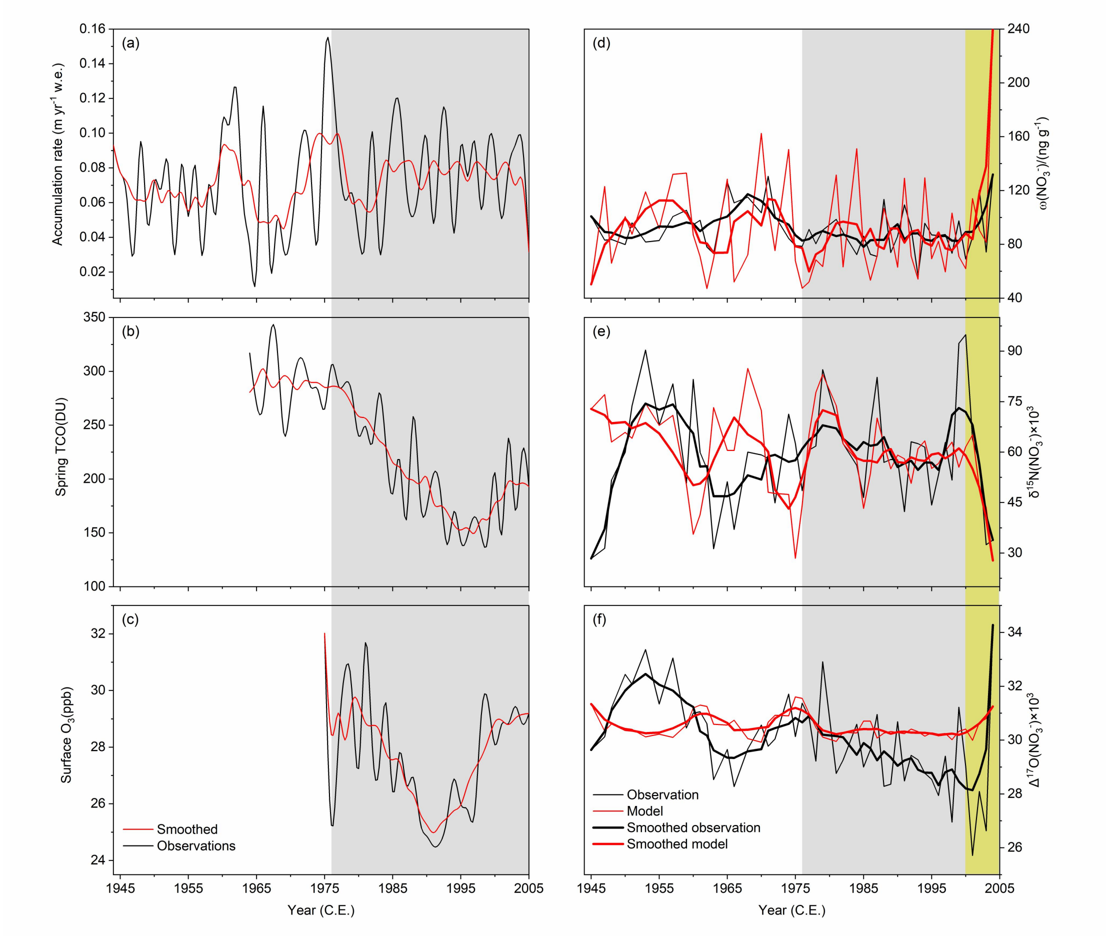

Figure 3. Left panels: time series of annual snow accumulation rate (a), spring (average from September 22 to October 13) TCO (total column ozone) (b), and summer half year surface O_3 concentrations (c) at the South Pole over the period of the ice core record. Red curves are the 5-year moving averages. Right panels: ice core nitrate concentration and isotopic compositions at the South Pole in 1944-2005 (black: observations; red: modeled). The thin lines represent the observed and modeled annual (d) $\omega(NO_3^-)$, (e) $\delta^{15}N(NO_3^-)$ and (f) $\Delta^{17}O(NO_3^-)$ from 1944-2005. The thick lines represent the 5-year moving averages. Yellow shaded area represents the period with changes in nitrate concentrations and isotopes from surface snow to below the photic zone. Grey shading area represents the ozone hole period.

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.

Response: No, this is from the TRANSITs modeled result shown in Fig.3f above. We have made more detailed illustrations as follows:

"…In comparison, the observed $\Delta^{17}O(NO_3^-)$ record indicates a decreasing trend starting approximately with the onset of the ozone hole (Fig.3f, black lines). This appears to be qualitatively consistent with the expected effects of the ozone hole, but the model with consideration of the ozone hole did not reproduce any apparent decreases in $\Delta^{17}O(NO_3^-)$ in the period of the ozone hole (Fig.3f, red lines).".

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

Response: We agree and have revised it accordingly.

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.

Response: We agree and have revised it accordingly.

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

Response: Yes, I have revised it in manuscript.

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.

Response: Thanks for this suggestion. We have made this consistent (~ 1976) in the revised manuscript.

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

Response: We have added grey shading area in the Figure 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.

Response: Thanks for this suggestion. We have done this in the revised manuscript.

Reference

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