

Dear Dr. Muller

We are grateful for the efforts of editor and reviewers to review this manuscript, and for their comments and suggestions that improve this manuscript significantly. In the response below we have addressed the remaining minor comments.

Editor

Comments to the author:

Dear Authors,

congratulations!

I also would ask you to address the remaining minor comments (see reviews).

One little issue from my side:

l. 18 change "was of" -> "showed"

Response: Thank you, this has been corrected in the revised manuscript.

Greetings Rolf Müller

Anonymous Referee #1

The authors made a good effort to extensively consider reviewer comments. Although the prediction about Dome A's capabilities of preserving the ozone hole signals in its $\delta^{15}\text{N}$ is somewhat challenged by the actual observation reported by Shi et al (2022), the manuscript in my opinion is still very interesting and informative. As a result, I happily recommend publication after a few points are resolved.

Line 57: The relative word "which" is still needed, but a comma must be inserted before "which".

Response: Thank you, we have revised it accordingly.

Line 139: Please define "UW".

Response: UW refers to University of Washington. In the revised manuscript, we have spelled out this abbreviation.

Line 231: There appears to be a missing "±" sign between 0.073 and 0.029.

Response: Thank you, we have added the "±" sign in the revised manuscript.

Line 374 and onward: It is argued that "However, at east Antarctic Plateau sites (i.e., Vostok, Dome C and Dome A) where snow accumulation rates are extremely low, $\delta^{15}\text{N}(\text{NO}_3^-)$ of preserved nitrate is above 300 ‰. It would be difficult to determine changes of ~ 30 ‰ out of more than 300 ‰, ..." This might not necessarily be the case, because what matters is the variability of $\delta^{15}\text{N}(\text{NO}_3^-)$. Suppose in an extreme case where the $\delta^{15}\text{N}(\text{NO}_3^-)$ is simply a flat line, then the exact δ values do not matter. You could instead calculate the standard deviation (1σ) of the observed, detrended $\delta^{15}\text{N}(\text{NO}_3^-)$ in

those sites if those data are available. At least the Dome A dataset is publicly available at <https://doi.org/10.11888/Cryos.tpd.272669>, kudos to the authors of Shi et al (2022). Then you could compare the 2.8σ (the minimal difference in order to be statistically significant at $p = 0.05$) with the model prediction of $\Delta(\delta^{15}\text{N}(\text{NO}_3^-))$. This comparison could potentially represent a more rigorous and robust statistical analysis and actually answers if a signal could be retrieved.

Response: We agree that in case the variability of $\delta^{15}\text{N}(\text{NO}_3^-)$ is very small than the response of isotope to the ozone hole can be detected. In the revised manuscript of the last submission we have emphasized this situation in lines 370 to 371 as follows: "...gradual increase in $\delta^{15}\text{N}(\text{NO}_3^-)$ might still be possibly detected as long as snow accumulation rate at these sites stayed relatively constant before and in the period of the ozone hole...".

Regarding the observed variations in $\delta^{15}\text{N}(\text{NO}_3^-)$ at Dome A and Dome C, the 2 standard deviation is above 40 ‰, i.e., Dome A \sim 40 ‰ (Shi et al., 2022) and Dome C \sim 44 ‰ (Erbland et al., 2013), without considering the values in the photic zone. These values are all larger than the modeled response of $\Delta(\delta^{15}\text{N}(\text{NO}_3^-))$ to the ozone hole. This is due to the large variations in the annual snow accumulation at these sites, and since at these sites the snow accumulation rates are very low, small changes in snow accumulation rate would lead to large enough changes in $\delta^{15}\text{N}(\text{NO}_3^-)$ that is comparable to that caused by the ozone hole.

Line 394: "Non-local" processes?

Response: Thank you, we have replaced "No local processes" with "Non-local processes" in the revised manuscript.

Line 460 & 500-501: It has also been observed in Dome A (Shi et al, 2022). If this is a pan-Antarctic phenomenon, it might be used to strengthen your argument in Section 4.4.3.

Response: Thank you for this suggestion, in the revised manuscript we have included the data from Shi et al. (2022) and made changes as follows:

In Section 4.4.3: "Similar decreases in $\Delta^{17}\text{O}(\text{NO}_3^-)$ over the past few decades were also observed in other Antarctic ice cores. Sofen et al. (2014) found that in the WAIS Divide ice core, $\Delta^{17}\text{O}(\text{NO}_3^-)$ has a long-term downward trend in the past 150 years, and a step decrease occurred after the 1970s. Meanwhile, $\delta^{15}\text{N}(\text{NO}_3^-)$ in the WAIS Divide ice core over the same period of $\Delta^{17}\text{O}(\text{NO}_3^-)$ decrease didn't have any long-term trends. A recent study by Shi et al. (2022) also indicate a downward trend of $\Delta^{17}\text{O}(\text{NO}_3^-)$ after the 1970s which is unlikely be explained by the effects of the ozone hole. These coherent decreases in $\Delta^{17}\text{O}(\text{NO}_3^-)$ in West, East and Central Antarctica after the 1970s may imply changes in nitrate chemistry in the source region. Assisted by box-model sensitivity studies, Sofen et al. (2014) have attributed the WAIS Divide ice-core $\Delta^{17}\text{O}(\text{NO}_3^-)$ decrease in the past 150 years (including that after the 1970s) to decreases in the O_3 to RO_2 ratio in extratropical Southern Hemisphere NO_x source regions. Decreases in O_3 to RO_2 ratio means a reduced importance of O_3 oxidation in the conversion of NO to NO_2 , leading to lower $\Delta^{17}\text{O}(\text{NO}_3^-)$ and subsequently lower $\Delta^{17}\text{O}(\text{NO}_3^-)$. Long-range transport of nitrate from the NO_x source regions to Antarctica can then lead to lower $\Delta^{17}\text{O}(\text{NO}_3^-)$ in primary nitrate. This at least qualitatively explains the observed decreasing $\Delta^{17}\text{O}(\text{NO}_3^-)$ trend."

In addition, in the conclusion we have also added a statement to include the $\Delta^{17}\text{O}(\text{NO}_3^-)$ data from Shi et al. (2022):

“...Such decreases in the same period have also been observed in the WAIS Divide ice core (Sofen et al., 2014) and Dome A snow pit (Shi et al., 2022). This decrease can’t be explained by post-depositional processing even including the effects of the ozone hole...”

Anonymous Referee #2

The authors have done a good job responding to and addressing the reviewer comments. Thank you for this valuable contribution to the literature. I look forward to seeing the paper published.

Regarding the Shi et al. (2022) study at Dome A, I agree with the authors and am pleased to read their independent assessment of the study in terms of:

- *The timing of changes in the nitrate isotope snow pit record and ozone do not line up*
- *The modelling results cannot be reproduced given the parameters reported*

At present, the modelling and observations at Dome A do not appear to support the conclusions drawn in Shi et al. (2022). This is not to say that $\delta^{15}\text{N-NO}_3$ should be discarded if other processes are taken into account. My suggestion for the final manuscript is for the authors to emphasize the difference in the Dome A TRANSITS results between this study and those reported in Shi et al. (2022) to leave the scientific debate open about the sensitivity of the ozone proxy at the site.

Response: We agree. Actually, in the revised manuscript we submitted last time, we have briefly compared the model concentration and $\Delta^{17}\text{O}(\text{NO}_3^-)$ with the observations and modeled results from Shi et al. (2022). In the final form of this submission, we have emphasized more the differences of the two TRANSITS model outputs in Section 4.3 (blue is the added statements):
“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 compiled. For example, Shi et al. (2022) stated when modeling the Dome A situation, similar parameters to Dome C (Erbland et al., 2015) were used except snow accumulation rate and TCO. However, the quantum yield is 0.026 (Erbland et al., 2015), and using this same quantum yield at Dome A will give a predicted $\delta^{15}\text{N}(\text{NO}_3^-)$ value of 1150 ‰ in preserved snow, three times higher than the observations as well as the modeled results of Shi et al. (2022). In addition, Shi et al. (2022) didn’t present the modeled result of $\Delta^{17}\text{O}(\text{NO}_3^-)$ though the model is able to predict $\Delta^{17}\text{O}(\text{NO}_3^-)$.”

Note in this manuscript we don’t want to spend too much time on the results of Dome A presented by Shi et al. (2022), and our coauthors are going to have another study with measured Dome C data to explicitly deal with the Dome A case.

What do the results in Table 1 imply for the use of $\delta^{15}\text{N-NO}_3$ as an ozone proxy?

Response: The results in Table 1 indicates that the magnitude of the response of $\delta^{15}\text{N}(\text{NO}_3^-)$ to the ozone hole is larger at site with lower snow accumulation rate. Ideally, the response is more possible to be identified at sites with lower snow accumulation rate. However, whether the response can be detected also depends on many other factors (e.g., variations in snow accumulations rate, snow LAIs, etc.).

Specific comments:

L112 “firn core” should be “snow pit”.

Response: We agree and have revised it accordingly.

L111-116 Please proofread here and ALL additional text.

Response: Thanks for this suggestion. We have proofread this sentence and all other text with necessary corrections.

L380-381 Please add how much ozone changed over this period and include the dates. This would be useful information for Table 1 caption too. Otherwise, it is not clear what the nitrate isotope response corresponds to.

Response: Thanks for this suggestion. We have added a column that indicate the spring ozone depletion value from 1979 to 1998 in Table 1 and also added the dates in this sentence:

Site name	Latitude	Longitude	Snow accumulation Rate	Spring ozone Depletion ^a	$\Delta(\delta^{15}\text{N}(\text{NO}_3^-))$	$\Delta(\Delta^{17}\text{O}(\text{NO}_3^-))$
	(°)	(°)	(kg m ⁻² yr ⁻¹)	DU	‰	‰
South Pole	-90	0	75	158	6.9	-0.8
Dome A	-80.5	77.12	24.4	139	26.5	-0.9
Dome C	-75.1	123.33	28	171	30.7	-1.1
Vostok	-78.47	106.84	21.5	165	31.2	-1.2
Dome Fuji	-77.32	39.7	28.8	166	16.3	-1.2
WAIS Divide	-79.48	-112.09	200	143	1.8	-0.7

a. The depletion refers to the difference of the spring TCO before the ozone hole period (use that in 1979 as the representative) and that in the year of 1998 when the ozone hole was the largest.

L398 delete “quick” and replace with “our” or similar.

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