

We appreciate the reviewer for the time and efforts to review this manuscript. Below we list detailed responses to the suggestions and comments. The suggestions and comments are in italics, followed by the response in normal font with changes highlighted in blue.

### **Comments from Reviewer3**

*Review of Atmospheric and snow nitrate isotope systematics at Summit, Greenland: the reality of the post-depositional effect by Jiang et al.*

*As said in the title this paper sets out to document the reality and state of knowledge of the post-depositional effect which changes the isotope distributions in nitrate after deposition and before archiving. The paper presents some nice data, but unfortunately it is not always strong enough to make definite conclusions. The discussion is sometimes too speculative as detailed below.*

*Please define exactly what is meant by 'post-depositional'. I presume it means 'after deposition to the surface and before becoming part of the permanent archive'. How long is this period? Why does post-depositional processing end? What evidence is there that there are not also long-term changes in deep ice? What is the physical mechanism ending post depositional processing?*

**Response:** Thanks for these comments. As all three reviewers pointed out, we realized that some of our conclusions are too strong based on the compiled data presented here. We have weakened some of our original discussions especially those regarding the relationship between  $\Delta^{17}\text{O}(\text{NO}_3^-)/\delta^{18}\text{O}(\text{NO}_3^-)$ , as well as the title. Please see our detailed responses below.

Post-depositional processing involving snow nitrate includes evaporation of gaseous  $\text{HNO}_3$  and photo-decomposition at UV wavelengths (mainly 290-350 nm). Current studies have suggested that photolysis dominates snow nitrate loss (Erbland et al., 2013; Frey et al., 2009; Shi et al., 2019), so in this study “post-depositional” only considers the photolysis of snow nitrate. Since the actinic flux rapidly attenuates in the upper 30 to 60 cm snow layer (i.e., the photic zone), snow buried below the photic zone is considered to be archived. While the burial speed is determined by snow accumulation rate and the depth of the photic zone, which could be as short as about half a year (e.g., at Summit) or as long as up to ten years (Erbland et al., 2013; Shi et al., 2015) at Dome A/Dome C in East Antarctica. We have refined these relative explanations in the revised manuscript to make it clearer for readers who are not already familiar with these terms. We have added the following statement in our revised manuscript:

“...Thus, the final archival snow nitrate, defined as the nitrate buried below the photic zone, would largely be impacted by post-depositional processing and be important to consider in the interpretation of ice core nitrate records. The degree of the photo-driven post-depositional processing is influenced by three main factors including snow accumulation rate, surface actinic flux and light penetration depth in snow...”

*The abstract should do a better job of communicating the impact and implications of the study. What is known now that was unknown or uncertain before?*

**Response:** We thank the reviewer for this comment. In the revised manuscript, we have added one more sentence to state the implications of this study:

“Although with uncertainties, the data compiled in this study suggested post-depositional processing at Summit can result in changes in nitrate isotopes, especially  $\delta^{15}\text{N}(\text{NO}_3^-)$ , consistent with a previous modeling study. This reinforces the importance of understanding the effects of post-depositional processing before ice-core nitrate isotope interpretation, even for sites with relatively high snow accumulation rate”.

*It is clear that this research group is quite accomplished at the methods used. The main issue is in the value and implications of the results that are obtained. After decades of research on isotopic abundances in snowpack nitrate, I would ask the authors to make a clear statement in the discussion or conclusion about the state of the field, both what has been learned, and what the information could be used for if only post-depositional processing could be understood in detail. I get the impression that there will always be some uncertainty. For example the uncertainties in delta values in the abstract are around 50%, and similar large uncertainties are shown in Figure 2. How much would these uncertainties have to be reduced in order to be able to derive useful numbers from the nitrate record, and is it reasonable to believe that this can be achieved?*

**Response:** Thanks for the suggestions. In the conclusion, we have added a paragraph as asked by the reviewer:

“Nitrate isotopes in polar ice cores have been sought to reflect past changes in NO<sub>x</sub> emissions and atmospheric oxidation environments (Alexander et al., et al., 2015; Hastings et al., 2005, 2009; Geng et al., 2014, 2017, Wolff, 1995). Although some important progress has been made (e.g., Geng et al., 2017), most interpretations of ice core nitrate records remain qualitative because the effects of post-depositional processing on nitrate and its isotopes have not been quantified. The latter requires a comprehensive understanding of the degree of post-depositional processing, as well as its influences on ice-core nitrate isotope preservation at different time scales. This is also true for ice-core drilling sites with high snow accumulation rates, where to what degree nitrate isotopes are changed upon archival is a subject of debate (Fibiger et al., 2013; Geng et al., 2015; Hastings et al., 2005; Jiang et al., 2021).

To address this debate, in this study, we reported ...”

What is more, in the end of the second paragraph of the conclusion, we have added the following statements in the revised manuscript:

“...These conclusions reinforce the importance of quantitative assessment of the post-depositional processing on snow nitrate isotopes even at sites with relative high snow accumulation rate (Jiang et al., 2021). Further numerical modeling is needed to correct the post-depositional processing effects on  $\delta^{15}\text{N}(\text{NO}_3^-)$ , which is essential to the better use of snowpack/ice core  $\delta^{15}\text{N}(\text{NO}_3^-)$  to retrieve information regarding the historical variability in NO<sub>x</sub> sources (Hasting et al., 2004, 2009).”.

*Line 109, add a reference for the cage effect mechanism.*

**Response:** We have added McCabe et al. (2005) and Meusinger et al. (2014) as references therein.

*Line 380, are there physical mechanisms that could explain the spring-summer differences such as recrystallization?*

**Response:** We think recrystallization is irrelevant to the discussions here as we are seeking the explanation for why the atmospheric  $\delta^{15}\text{N}(\text{NO}_3^-)$  is most depleted in spring instead of in summer, as the photolytic NO<sub>x</sub> flux from snow maximizes in summer with very depleted  $\delta^{15}\text{N}$  values. Our hypothesis is that owing to the more unstable boundary layer in summer that favors the export of NO<sub>x</sub> instead of locally reforming nitrate, or an increase in  $\delta^{15}\text{N}$  of primary nitrate which also contributes to local atmospheric nitrate. So far no known physical mechanisms can explain this detail of the observed seasonality.

*Please discuss the origin of the time lag between the mean SZA and the PIE plot shown in Figure 3. Very nice data here, thank you.*

**Response:** Thanks for the comment. SZA is the smallest in summer when actinic flux is the maximum, but PIE is determined by the total amount of actinic flux received by nitrate in snow between deposition to the surface and burial below the photic ozone. Owing to polar winter when there is no sunlight, over a year nitrate deposited in spring received the most actinic flux (accumulated UV-B dose in Figure 2). As a result, PIE is the largest in spring instead of in summer when actinic flux is the strongest. We have explained this in the manuscript.

*At line 498, it is not clear what 'kinetic adsorption' is and how this is different from 'adsorption'. Do you mean to say that at Summit, given higher snowfall, scavenging of nitrate is complete, while it is incomplete at Dome-C? Please rewrite and clarify, to benefit those outside your immediate research field.*

*At times the discussion is speculative and I would encourage the authors to keep it tight and focused - give numbers and reasons and try to conserve ink.*

**Response:** The “kinetic adsorption” is not different from “adsorption”. To avoid confusions, we have deleted “kinetic” in the revised manuscript.

*Line 714, 'We analysed the relationships and found that the linearity of ..in snowpack is different from that of atmospheric and surface snow.' I am confused because isn't linearity always linearity? Maybe there is another word such as slope or curvature, that would be more appropriate.*

**Response:** Here we meant the slope of the regression between snowpack  $\Delta^{17}\text{O}/^{18}\text{O}(\text{NO}_3^-)$  are different with that of atmospheric and surface snow  $\Delta^{17}\text{O}/^{18}\text{O}(\text{NO}_3^-)$ . We have avoided the use of the word “linearity” in the revised manuscript. Thanks.

### **Technical**

*The writing is generally fine with only some minor issues that are easily addressed with*

*a good proofreading.*

*Line 130, I suggest change to read '...post-depositional processing, snow samples covering the entire photic zone must be considered.'*

**Response:** Thanks for this suggestion. We have changed the sentence accordingly.

*Line 132, check the sentence 'To thoughtfully evaluate', in simplified form it seems to say, 'Nitrate isotopes are necessary.' Please rewrite, just simply and clearly.*

**Response:** We have shortened this sentence as follows:

“*To thoughtfully evaluate the effects of post-depositional processing at Summit, nitrate isotopes in the atmosphere and in snow covering a full cycle of polar seasons with distinct actinic flux variations are necessary...*”.

### **Reference:**

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