

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

Comments from Meredith Hastings

This work utilizes newly reported atmospheric nitrate measurements from Summit, Greenland to compare with others sets of data (from different years) from the atmosphere, surface snow and snowpack. The purpose of the study is to conclude that post-depositional processing can explain nitrate isotope systematics in the snow and air at Summit, Greenland. The overall subject matter is of relevance to Cryosphere and its readership. The conclusions drawn, and the title of the paper, do not fit with the evidence presented and the authors should consider the points below and better justify their conclusions.

Response: First we would like to thank Dr. Hastings for her detailed comments on this manuscript. But as stated by Dr. Hastings in her comments and will be discussed here, clearly there is debate on the interpretation of the data and the embedded information in the data. Based on data of currently available and many of the reasons we have discussed in our previous papers (Jiang et al., 2021 TC), we can't agree with the interpretations provided by Dr. Hastings's group.

While there are clearly differences of interpretation in the already published literature between my group and the authors here, new data definitely raises the potential for new interpretations. But it is important that the hypotheses, data, discussion and conclusions be consistent with what is “prove-able” within the constraints of the new data. Using “reality” in the title is inappropriate – at best it an overemphasis that this new work is somehow more important or more “realistic” than the large body of previously published work; at worst it is a direct insult to the work that has come before (including work by the authors of this manuscript). In fact, this quote from the conclusion negates the use of “reality” in the title: “In the end, we note the limitation of the compiled data. These data were collected by different groups at different time, and with different sampling methods as well as different temporal resolutions.” (page 29, line 724)

Response: As both reviewers pointed out, we notice that the usage of word ‘reality’ may have overstated the conclusion bases on current data of available. So in the revised manuscript, we have changed the title to “Impacts of post-depositional processing on nitrate isotopes in the snow and the overlying atmosphere at Summit, Greenland”.

A serious matter to consider first and foremost is what this new data represents in terms of the budget of nitrate in the air, snow and snowpack at Summit, Greenland. The new data is isotope measurements of aerosols collected using a high-volume air sampler with glass fiber filters. Quoting from the manuscript “Glass fiber filters have been shown to collect both aerosol and gas-phase nitrate with high efficiency (Erbland et al., 2013; Frey et al., 2009).” This has, in fact, not been shown directly.

*And it is critical to consider since the data here is used as a comparison to other datasets and conclusions are drawn based upon the difference in isotope values amongst the different sample types, which were also collected with different methods. Therefore, the difference in the isotopes of different sample types has to be real and represent the environmental values and be sure not to represent any fractionation or changes associated with the collection technique. **Validation of the method for complete collection of HNO₃(g) is critical to the interpretation here.** The manuscript refers to Erbland et al (2013) for evidence that complete collection of both nitrate phases takes place. Erbland et al. (2013) reported that concurrently collected samples of atmospheric HNO₃ by denuder tubes coated in sodium bicarbonate matched well with the average values found by the hi-vol sampling and therefore were deemed representative of atmospheric HNO₃ + aerosol nitrate at Dome C. The climate conditions, phase partitioning of atmospheric nitrate, accumulation rate, etc can all be very different at Summit than Dome C and therefore it is appropriate to review and consider what evidence there is that HNO₃ and aerosol nitrate are quantitatively collected at Summit. Please note too that Frey et al. (2009) study at Dome C does not present any evidence for quantitative collection; Frey et al (2009) refers to Morin et al., 2007 which was an ocean-based cruise collection using the same methods but the conditions were such that the likelihood of complete HNO₃ collection on filtered alkaline (sea salt) aerosols was high. Due to the difficulty of capturing both gas and particle phase nitrate under different conditions there is a body of literature that include methods discussions (see for instance Huang et al., *Atm Research*, 2004; Chiwa et al., *Env Ass Monitoring*, 2008; Ames and Malm, *Atm Env*, 2001; Lavery et al., *Air & Waste Management Ass*, 2009; and EPA CASTNET methods papers). The ideal method depends on the time of deployment, how polluted or pristine the expected air masses are, temperature, flow rate, and location (marine atmosphere, coastal, or inland). According to EPA recommendations, a filter pack with a particle filter (Teflon, quartz, GF/F, etc.) and a cellulose backup filter impregnated with NaCl or Na₂CO₃ will quantitatively collect particulate nitrate and nitric acid in a large variety of sampling conditions. As the addition of NaCl improves the efficiency of collecting nitric acid it is frequently assumed that both nitrate and nitric acid are collected with high efficiency in the marine boundary layer where there are high sea salt concentrations as Morin et al., 2009 points out (underlining added for emphasis): “The exact nature of the nitrate species trapped on the filters during sampling has been an issue for decades, owing to evaporative loss of ammonium nitrate species and sampling of nitric acid together with particulate nitrate [Schaap et al., 2004]. Prospero and Savoie [1989] have advocated that filters loaded with sea salt should quantitatively collect nitric acid together with particulate nitrate, which should then be the case for these samples collected in the MBL... Therefore, the analyzed nitrate is referred to as atmospheric nitrate, assumed to be the sum of gas phase nitric acid and particulate nitrate.”*

Response: We thank the reviewer to bring this issue. Indeed, collection efficiency using filters is a long lasting issue. But as the reviewer pointed out, glass fiber filter

loaded with NaCl or used in MBL has been demonstrated to effectively collect HNO_3 and p-NO_3^- . In fact, the glass fiber filters used in this study were with high NaCl blank ($>5 \mu\text{mol}$ on rinsed glass fiber filters), which should be able to quantitatively collect both HNO_3 and p-NO_3^- , as evidenced by the various studies quoted by the reviewer. In particular, Erbland et al. (2013) study found good agreement in their measured atmospheric nitrate concentration by using HVAS+glass fiber filter with the annular denuder method and suggested **that this was caused by the high NaCl blank in the glass filter**. At Dome C, gaseous nitric acid dominates total atmospheric nitrate ($>90\%$), similar to the situation at Summit where gaseous nitric acid account for 94% of total atmospheric nitrate (Dibb et al., 1994). The high collection efficiency of glass fiber filter for gaseous HNO_3 as seen for Dome C comparison, should be applicable to Summit, unless there are other factors influencing the collection efficiency of HNO_3 and p-NO_3^- . But at least from the literature (already largely quoted by the reviewers), NaCl appears to be the most important factor.

In addition, we can compare our aerosol data with other studies to verify the collection efficiency. We have found another study at Summit that used the filter method to collect atmospheric nitrate and tested its collection efficiency (Silvente and Legrand, 1993). The Silvente and Legrand (1993) study simultaneously collected atmospheric nitrate with a denuder system and a Nylon filter system with flow rate of 30 L m^{-3} . Their results suggested that under conditions with atmosphere nitrate concentration less than 30 ng m^{-3} the filter method produced similar results compared with the denuder method. Although we note the different filter type used, our measured average nitrate concentration ($19.9 \pm 19.1 \text{ ng m}^{-3}$ from the filter is very close to Silvente and Legrand (1993) measured nitrate concentration at Summit (20 ng m^{-3}).

Our measured atmospheric $\delta^{15}\text{N}(\text{NO}_3^-)$ ($-19.1 \pm 7 \text{ ‰}$, $n=10$) is also comparable to the results from Fibiger et al. (2016) ($-16.0 \pm 6 \text{ ‰}$ for 2010 and $-17.7 \pm 13 \text{ ‰}$ respectively) covering the same months but in different years (2001-2002 vs 2010/2011) with different methods (HVAS vs mist chamber). But we note, the Jarvis et al. (2009) study, despite using the same collection method with Fibiger et al. (2016) study (i.e., mist chamber), gave very different results in both $\delta^{15}\text{N}(\text{NO}_3^-)$ and concentrations from our study and the Fibiger et al. (2016) study. As discussed in the original manuscript, we don't know the reason since information on the sampling details were not available.

We have also compared our measured atmospheric nitrate concentration with many other previous studies at Summit. The results in different years are summarized below. As can be seen, the measurement results are generally in the same range except for Jarvis et al. (2009) which suggested a much higher concentration than other studies.

Year	Month	type	Conc	Reference
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(ng m ⁻³)				
1991	7-8	denuder	38 ± 53	Silvente and Legrand, 1993
1993	6-7	Mist chamber	55 ± 37	Dibb et al., 1994
1993	5-7	Teflon Zefluor filter	26 ± 2.9	Bergin et al., 1995
1994	5-8	Mist chamber	32 ± 37	Dibb et al., 1994
1995	4-7	Mist chamber	27 ± 32	Dibb et al., 1998
2001-2002	annual	glass fiber filters	19.9 ± 19.1	This work
2006	5-7	Mist chamber	202	Jarvis et al., 2009
2010	5-6	Mist chamber	32 ± 30	Fibiger et al., 2016
2011	5-6	Mist chamber	42 ± 22	Fibiger et al., 2016

In summary, we think the filter we used in this study have effectively collected HNO₃ and p-NO₃⁻. In the revised manuscript, to validate the quantitatively collection of atmospheric nitrate, we have add the flowing statement in the main text:

“Glass fiber filters have been shown to be capable of collecting atmospheric nitrate with high efficiency even when gas phase nitrate dominates total atmospheric nitrate (Erbland et al., 2013). This is likely due to the high NaCl blank in the glass fiber filter, which is known to promote the collection efficiency of atmospheric nitrate (Morin et al., 2007; Erbland et al., 2013).”.

*The vast majority of nitrate at Summit is wet-deposited via scavenging of HNO₃(g). This is stated in the manuscript at the bottom of page 20 (though see specific comments below on references for this). This is important to validation of the method (above) since the air is filtered through a GF/F with no pre-treatment and must quantitatively collect all HNO₃(g). Additionally, when it snows, both in cloud and below cloud processes (rainout + washout) will contribute to the nitrate that is deposited. However, the arguments and interpretation in this work appear to require that the atmospheric samples represent all (or most) of the nitrate that is deposited to the snow. For the interpretation here to stand, the input from the atmosphere must be constant in d15N and any differences in the snowpack from that in the air are only due to post-depositional processing. **Yet, the input of primary nitrate could change remarkably due to HNO₃(g) scavenged from above the surface at Summit (i.e from cloud to ground) and the snow then would not represent only that which is near the surface (i.e. it could differ in d15N because it contains more than just what is at the surface). This needs to be addressed in the context of the interpretation here.***

Response: The quantitative collection of nitrate was addressed in a previous response. Regarding the representativeness of the filter sampling at the surface, we think the fast mixing in the boundary layer will homogenize the boundary layer during one sampling period. The average eddy diffusion time for Summit summer conditions is 3.4 h for 25 m boundary layer height according to Cohen et al. (2006). Choosing a mean boundary layer height of 200 m (Cohen et al., 2006), this means the boundary layer would be mixed in 1.1 day, which is less than the time resolution of our atmosphere samples (3 to 4 days per sample). So the filter sampled nitrate is similar to snow which scavenges nitrate in air when it falls.

In addition, we should always expect that the local boundary layer reflects a combined effect from primary nitrate and locally reformed nitrate. This is especially evident for the measured $\Delta^{17}\text{O}(\text{NO}_3^-)$ value. If our collected atmospheric nitrate only reflect impact from snow source nitrate, then according to the Kunasek et al. (2009) and Jiang et al. (2021)’s calculation, the $\Delta^{17}\text{O}(\text{NO}_3^-)$ in middle summer should be close to 20 ‰ (19.7 ± 0.3 ‰ in Jiang et al., 2021 and 18.9 ‰ in Kunasek et al., 2009) considering the measured HOx and ozone levels at Summit. This is however much lower than the observed $\Delta^{17}\text{O}(\text{NO}_3^-)$ (>24 ‰).

*The atmospheric data (from a single year and almost half the samples are not used b/c of blank issues) suggests that within the surface atmosphere at Summit there is no seasonal variation in the d15N signal. It is entirely possible that this pool of atmospheric nitrate is controlled by local processes. **This does NOT negate that the snow can still represent a vast majority of primary nitrate deposition and that the***

seasonal differences found in the snow represent much more than the local dynamics. The data we collected in Fibiger et al. 2013 and 2016 were concurrent collections of snow and atmospheric samples so that we could detail, at the same time, the dynamics in the snow and in the air. We went looking to detail that post-depositional release of NO_x and reformation of nitrate locally COULD explain the isotopic composition of nitrate in the snow, especially D17O – but this hypothesis was not supported by what we found. Our results suggest that the nitrate in surface snow does not change isotopically in concert with what is happening in the surface air. It is hypothesized in Fibiger et al. that this can be explained by the fact that the surface air represents a small fraction of the nitrate that is deposited in the snow in real time. (Wet deposition at Summit is frequent, and in spring and summer, even when there is not fresh snow, fog deposition often occurs (see Bergin et al., 1993 already cited). This interpretation agreed with a snow-air model that was able to reproduce a suite of gas phase concentrations in the air at Summit, including NO_x, HNO₃(g) and halogens with as little as 6% of the nitrate being photolyzed (as discussed in Fibiger et al., 2016). **It must be proven in this new work that the atmospheric data near the surface at Summit is what is most important in terms of the input of total nitrate to the snow such that the snowpack does NOT represent much more than what is happening in the air AT Summit.**

Response: It is too speculative to assume the atmospheric data is only controlled by local processes. Long-range transport nitrate depositing to snow has to first pass through the boundary layer, while as discussed and responded to earlier, the filter effectively collects HNO₃ and p-NO₃⁻ in the air which is a combined signal of nitrate from long-range transport and local production. Again, the mixing of nitrate in the boundary layer is much faster than the sampling duration so what we sampled should represent atmospheric boundary layer nitrate instead of something only controlled by snow nitrate photo-recycling. This is especially clear given our atmospheric $\delta^{18}\text{O}/\Delta^{17}\text{O}(\text{NO}_3^-)$ relationships are almost identically to the surface snow relationships reported by Fibiger et al. (2013), despite that these samples were collected in different years. We also wanted to note that we don't attempt to refute that snowpack represents the majority of primary nitrate deposition, as our modeling work has already suggested that the reformed nitrate flux at most contributes 25% to local atmospheric nitrate burden at Summit.

Back to the Fibiger et al. (2016) study, they didn't observe an expected increase in surface snow $\Delta^{17}\text{O}(\text{NO}_3^-)$ when atmospheric BrO concentration was increased by a few ppt. This is perhaps their most important direct (from our reading) evidence to conclude or suggest that “*the nitrate in surface snow does not change isotopically in concert with what is happening in the surface air*”. What happens in the air related to nitrate can only be reflected by collecting nitrate, but not by something deduced from BrO observations. We have discussed the reasons in detail in our previous paper (Jiang et al., 2021 TC) as well as in our responses to Dr. Hastings (who posted general comments during the open discussion). Here we just repeat our main points: First of all, increased BrO concentration (by a few ppt) in the air won't necessarily result in higher atmospheric $\Delta^{17}\text{O}(\text{NO}_3^-)$, nor snow $\Delta^{17}\text{O}(\text{NO}_3^-)$. This is because the production of BrO

will consume O₃. This is a tradeoff regarding their effects on $\Delta^{17}\text{O}$ of NO₂ which determines $\Delta^{17}\text{O}(\text{NO}_3^-)$. In addition, observations at Summit suggested BrO concentration always co-varied with OH/ HO₂/RO₂ (Liao et al., 2011) because they are both controlled by local photochemistry. If OH and HO₂/RO₂ concentration also increased (the authors didn't assess these radicals) at the same time, they would decrease $\Delta^{17}\text{O}(\text{NO}_3^-)$, offsetting the effects of increased BrO on atmospheric $\Delta^{17}\text{O}(\text{NO}_3^-)$. Second, whether or not the reformed nitrate in the air during the short duration of increased BrO (only a few hours) was able to influence local nitrate budget is questionable. The Jiang et al. (2021) model results suggested that locally formed nitrate can account for at most 25% of the deposited nitrate in summer and the rest is from transport. Additional nitrate due to BrO oxidation is only a small part of this locally formed nitrate, and whether its effect on atmospheric $\Delta^{17}\text{O}(\text{NO}_3^-)$ is detectable or not is also questionable. Third, the $\Delta^{17}\text{O}(\text{NO}_3^-)$ of surface snow (1-3 cm) was used by Fibiger et al. (2016) to compare with the effect of atmospheric BrO concentration increase. But the dry deposition flux of atmospheric nitrate is too low to significantly impact this "surface" snow nitrate concentration in short time scales (e.g., the duration of observed BrO). In summary, the Fibiger et al. (2016) cannot provide any evidence that nitrate in the air (or even the surface air) is disconnected with surface snow nitrate. In fact, the Fibiger et al. (2016) stated in their paper "**BrO chemistry does not have a significant influence on the formation of local HNO₃ at Summit**" (because they cannot explain the observed lower **atmospheric** $\delta^{18}\text{O}(\text{HNO}_3)$ with higher BrO concentration). This is exactly what we think their observations can demonstrate. If BrO chemistry is not important for atmospheric nitrate at Summit, it's not surprise to expect no correlation between BrO concentration and **atmospheric** $\Delta^{17}\text{O}(\text{NO}_3^-)$, let along in **surface snow**.

In addition, we also would like to repeat that '6% of the nitrate being photolyzed' is wrong. According to Fibiger et al. (2013) this value should be 2%. Fibiger et al. (2013) estimated the loss fraction by multiplying 0.1 % (loss fraction in 3 days in the upper 10 cm snow, they cited from Thomas et al. (2011)) with a factor of 21 (resident time in photic zone at Summit). The '0.1 %' they used in this calculation is an underestimate. From the supplemental file of Thomas et al. (2011) (Figure 9), the '0.1 %' value actually should be around 1% to 2%.

*I commend the authors on the collection and measurement of this important dataset and compiling many other datasets for comparison. The authors do a very good job of compiling the data comparison in the fairest way possible (e.g. mass-weighting sub-monthly data into monthly averages to compare with other data that is only reported as monthly averages), but we need to acknowledge that there is still a fair amount of comparing apples to oranges here. **There are no statistical comparisons presented in the manuscript and this should be addressed** (see specific comments below). While I appreciate the purpose in reducing "the spatial and temporal heterogeneities" for the comparison here, this heterogeneity is real and the standard deviations/variability should be included in any statistical comparisons. The manuscript argues that there are "systematic changes" in $d_{15}\text{N}$ between the air, surface snow and snowpack (all*

from different years and different sample collection methods) that can be explained by post-depositional processing. **But the differences shown between 2 out of 3 months in the wintertime are as large as observed in the spring and summer.** Yes, the spring and summer months compiled data are consistently different, but the difference in December appears to about 16 per mil and the difference in February is 9 per mil (Figure 2b)! This needs to be explained within the framework presented here. This difference does not fit with the conclusion that post-depositional photolysis of nitrate can explain these types of differences nor does it fit with the idea that deposition of nitrate imparts a fractionation since this large difference does not exist in either October or January. **Also left unexplained is the divergence of $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ behavior in the winter months atmospheric data (Figure 1c).**

Response: First, we would appreciate the reviewer's point on the data collection and reduction. It is difficult to compare data covering different years, however if one looks at the seasonality of isotopes in snow, these studies in general show very similar patterns, especially for $\delta^{15}\text{N}(\text{NO}_3^-)$ and $\Delta^{17}\text{O}(\text{NO}_3^-)$. As the seasonal patterns should be the same under a same background climate, we would expect that compiled seasonal patterns in snowpack should also represent that in the year of the aerosol sample collected. Regarding statistical assessments, we could have conducted student-T test. However, most of the data we found in the literature is already averaged, and some of them are monthly averages while others are seasonal averages (but only sampled in one or two months of a particular season). This means the sample size is difficult to determine and without this (freedom) t-test can't be conducted. Nevertheless, as seen in Figure 2b, in the seasons with sunlight, the atmospheric and snowpack difference is real, as averages of the atmospheric data plus one standard deviation is still lower than the snowpack averages plus one standard deviation.

Regarding the atmospheric and snowpack $\delta^{15}\text{N}(\text{NO}_3^-)$ difference in December, we realized it is somewhat out of range. Typically, the winter $\delta^{15}\text{N}(\text{NO}_3^-)$ valley shall be around -10 ‰ in Summit snowpack (Hastings et al., 2004; Jarvis et al., 2009). But our compiled data indicated the winter mean is (-1.2 ± 1.6) ‰. This is likely due to the dating uncertainties of the Geng et al. (2014) snowpack: the assigned Dec. snow in **2005** possesses $\delta^{15}\text{N}(\text{NO}_3^-)$ of $\sim 2\text{-}3$ ‰ which is abnormally high. It is possible that in dating the 2006 spring snow were treated as 2005 winter snow, or even in the year winter snow was mixed with spring snow by wind. In any case, we noted there is an anomaly in Geng et al. (2014) snowpit that the $\delta^{15}\text{N}(\text{NO}_3^-)$ value in the winter valley of 2005 is higher than other two valleys (~ 0 vs. -10 ‰). The February $\delta^{15}\text{N}(\text{NO}_3^-)$ difference in atmosphere and surface snow is not unexpected as the average PIE in February is 8.4 ‰ that could fully account for observed enrichment in snowpack $\delta^{15}\text{N}(\text{NO}_3^-)$.

Regarding oxygen isotopic data, it appears in Figure 1c that the relationship between $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ in winter and summer is different. We thank the reviewer for this point, and think this could be an evidence that summer half-year atmospheric nitrate is influenced by local processes (local recycle) while the winter nitrate is not. We have included this evidence in the revised manuscript. We have added the following discussion about the $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ relationships in Sec 4.2.3:

“Our atmospheric $\Delta^{17}\text{O}(\text{NO}_3^-)$ and $\delta^{18}\text{O}(\text{NO}_3^-)$ data exhibited some interesting features. As seen in Fig 1c, atmospheric $\Delta^{17}\text{O}(\text{NO}_3^-)$ and $\delta^{18}\text{O}(\text{NO}_3^-)$ appears to diverge during winter while in summer they were closely linked. The different $\Delta^{17}\text{O}/\delta^{18}\text{O}(\text{NO}_3^-)$ relationships in different seasons likely suggest different nitrate sources into local atmosphere, more specifically, the perturbation from snow-sourced nitrate in summer. In winter, owing to the low temperature and lack of sunlight, local nitrate production is suppressed and atmospheric nitrate is dominated by primary nitrate via long-range transport. In summer, the reformed atmospheric nitrate from NO_x emitted by sunlit snow would possess oxygen isotope signals imprinted by local oxidation conditions that is different from primary nitrate. Although the $\Delta^{17}\text{O}/\delta^{18}\text{O}(\text{NO}_3^-)$ relationships for primary nitrate could also vary seasonally, the above explanation is further supported by the observed substantial NO_x flux from snow in summer (Honrath et al., 2002) as well as the very negative atmospheric $\delta^{15}\text{N}(\text{NO}_3^-)$.”

Finally, it is a stretch to use the word “systematic” when several months (out of 12) do not follow this systematic response and the aerosol data represent 1 year of data collection (with only 55% of the data included in this study) while much of the snow and snowpack representing repeated sampling of the the snow/multiple snowpits/multiple studies.

Response: Here we used the word “systematic” to represent the overall patterns of the seasonal atmospheric and snow $\delta^{15}\text{N}(\text{NO}_3^-)$, as they appear to follow the amounts of accumulated UV-B dose (but oppositely). And as shown in Figure 2b, only one month (i.e., the Dec. $\delta^{15}\text{N}(\text{NO}_3^-)$ values) but not several months appears to not follow the accumulated UV-B dose pattern. In particular, Feb. snow is expected to be influenced by sunlight because polar sun rises in March when nitrate deposited to snow in Feb. is still in the photic zone. Especially, if looking at the patterns of the snowpack $\delta^{15}\text{N}(\text{NO}_3^-)$ and the accumulated UV dose (Figure 2a and 2b), in general the higher the accumulated UV dose, the larger the snowpack $\delta^{15}\text{N}(\text{NO}_3^-)$. Note the highest $\delta^{15}\text{N}(\text{NO}_3^-)$ appears in spring when the accumulated UV dose is also the highest in a year.

The assumption that the isotopic composition in the air must stay constant underlies discussion of the $d18\text{O}$ data from the air and snow as well and does not agree with modeling or observational studies. Kunasek et al cannot explain higher than expected $D17\text{O}$ values in snowpack summertime snow based on local photochemistry. Global modeling studies by Alexander et al do an excellent job of predicting the seasonal cycle in $D17\text{O}$ throughout the year (based on long-range transport of nitrate and no post-depositional processing!) but shows a mismatch in spring (model overestimates) and summer (model underestimates). Fibiger et al. (2013, 2016) show interannual isotopic variability in the observations of surface snow and atmospheric samples ($\text{HNO}_3(\text{g})$ only). This manuscript reports interannual differences in $d18\text{O}$ of nitrate as “inconsistent.” Fibiger et al. (2016) show and explain interannual differences based on differences in long-range transport,

changing the source regions from which primary nitrate is transported to Summit (which also impacts chemistry).

Response: First we are confused by “*The assumption that the isotopic composition in the air must stay constant*”. We didn’t make this assumption in this manuscript so we didn’t completely catch the question.

Regarding the modeling work, in Alexander et al. (2020), their modeled atmospheric $\Delta^{17}\text{O}(\text{NO}_3^-)$ didn’t involve transport of nitrate among different atmosphere grids. Instead Alexander et al. (2020) modelled local HOx and ozone radical concentrations and calculated $\Delta^{17}\text{O}$ of nitrate produced **in situ**. The Alexander et al. (2020) study basically is not different from the method used in Jiang et al. (2021) and Kunasek et al. (2009) except for involving more elaborate chemistry schemes. All these three studies suggested local chemistry can not fully account for the observed atmospheric $\Delta^{17}\text{O}(\text{NO}_3^-)$ and this is why both Jiang et al. (2021) and Kunasek et al. (2009) invoked seasonal changes in $\Delta^{17}\text{O}$ of primary nitrate to explain the summer mismatch. Please also note, in TRANSITs model the wintertime atmospheric nitrate is completely controlled by primary nitrate as there is no locally reformed nitrate owing to the lack of sunlight, which is different with the other two models.

Regarding the $\delta^{18}\text{O}(\text{NO}_3^-)$ data inconsistencies, there are way more questions to be answered. Fibiger et al. (2016) attributed the different **surface snow** $\delta^{18}\text{O}(\text{NO}_3^-)$ in different years to changes in nitrate source region but did not explain why the air-snow $\delta^{18}\text{O}(\text{NO}_3^-)$ relationship as well as the observed **atmospheric** $\delta^{18}\text{O}(\text{NO}_3^-)$ were so different in two years. Also remains unexplained in Fibiger et al. (2016) was why the BrO concentration in 2010 was much higher than 2011 while the atmospheric $\delta^{18}\text{O}(\text{NO}_3^-)$ was much lower in 2011.

Specific comments on manuscript:

It would be helpful if the abstract and introduction better reviewed prior work and results in Greenland. Much of what we are able to quantify about the impacts of post-depositional loss and recycling come from the body of work by Savarino in colleagues at Dome C. It’s important to contextualize this and also contextualize the differences between the records in Greenland versus Antarctica. Currently in the introduction this all presented as “this is what happens to nitrate in snow period”. (In my mind, the question is why don’t we see more loss of nitrate in Greenland than we do?!? The exposure of the snow to sunlight, despite the accumulation rate, should still lead to more loss than is actually observed).

Response: We think we have made a thoughtful introduction with relevant studies regarding the post-depositional processing loss of snow nitrate at Greenland as much as possible. **In addition, we don’t agree that the observed snow nitrate loss is less than we expect.** Using the observed snow-flux of NO_x at Summit, we have estimated the rate of snow nitrate photolysis (i.e., quantum yield of snow nitrate photolysis in Jiang et al. 2021), and then according to the actinic flux at Summit, the snow photochemical model calculated a maximum loss of 21% which is within the range (<7 % to 25 %) estimated by comparing surface snow nitrate concentration and

snowpack nitrate concentration in two observational studies (Burkhart et al., 2004; Dibb et al., 2007). What is more, under this level of estimated snow nitrate loss, the caused $\delta^{15}\text{N}(\text{NO}_3^-)$ change is also consistent with the observations, i.e., spring summer snow has more nitrate loss (due to the more accumulated UV dose received upon archival), and with higher $\delta^{15}\text{N}(\text{NO}_3^-)$ than fall and winter snow.

If we use the approach in Fibiger et al. (2013), but correct the value used to estimate the loss fraction from 0.1 % to 1% (which is 1 % nitrate loss in three days in 10 cm depth, details in response above), this will produce a loss fraction of ~21 % that is consistent with our model estimation (Jiang et al., 2021). We have discussed this in our previous response to the general comments by Dr. Hastings in Jiang et al. (2021).

In summary, we believe that based on current observations and modelling results, the observed snow nitrate loss upon archival at Summit can be well explained by the effects of snow nitrate photolysis.

It would be useful in the introduction to clearly explain the differences between post-depositional loss versus recycling/processing of nitrate versus nitrate-snow sourced NO_x-back to nitrate that is now different than originally deposited.

Response: Thanks for this suggestion. We have added the following statement in the revised manuscript:

“...Photolysis of snow nitrate would emit NO_x to the overlying atmosphere, which would subsequently reform nitrate under local oxidation conditions and redeposit to the surface. This recycling of snow nitrate not only changes the initially deposited nitrate (isotope) signal, but also leads to a redistribution of snowpack nitrate...”.

It's also important to be abundantly clear about how the words archived versus preserved are used in the text and it is likely worthwhile to define these in the introduction.

Response: Thanks for this suggestion. We have added the following statement in our main text:

“...Thus, the final archived snow nitrate, defined as nitrate buried below the photic zone, would be largely impacted by post-depositional processing and this needs to be fully understood when interpreting ice core nitrate records ...”.

Line 21: “...hinders interpretation of ice-core nitrate concentrations and isotope records.” Given that Geng et al. alone have at least 3 different published papers where they interpret ice core records (let alone the many other papers that could also be named here), this sentence is not useful nor descriptive of the literature. This debate also hinders current understanding of atmospheric chemistry and deposition processes.

Response: We meant “quantitative interpretation”, so in the revised manuscript, we have added “quantitative” before “interpretation of ice-core”.

Line 24: this line says “atmospheric aerosol nitrate” which does not reflect that the atmospheric measurements are used as aerosol + gas phase nitrate

Response: Thanks for this suggestion. We have deleted the word “aerosol” and added definition of atmospheric nitrate in the main text.

Line 27: suggest rephrasing this line as with several negatives it currently reads as if the seasonality is the same between the snow and atmosphere; perhaps the following “...displayed no apparent seasonality, which is distinct from seasonal $\delta^{15}\text{N-NO}_3^-$ variations observed in snowpack.”

Response: Thanks for this suggestion. We have changed this sentence as follows: “...displayed minima in spring which is distinct from the observed spring $\delta^{15}\text{N}(\text{NO}_3^-)$ maxima in snowpack...”.

Please indicate what the standard deviations represent and how many samples (n) are included.

Response: We have added in the revised version accordingly:

“...The atmospheric $\delta^{15}\text{N}(\text{NO}_3^-)$ remained negative throughout the year, ranging from -3.1‰ to -47.9‰ with a mean of $(-14.8 \pm 7.3)\text{‰}$ ($n = 54$), and displayed minima in spring which is distinct from the observed spring $\delta^{15}\text{N}(\text{NO}_3^-)$ maxima in snowpack. The spring average atmosphere $\delta^{15}\text{N}(\text{NO}_3^-)$ was $(-17.9 \pm 8.3)\text{‰}$ ($n = 21$), significantly depleted compared to snowpack spring average of $(4.6 \pm 2.1)\text{‰}$, with surface snow $\delta^{15}\text{N}(\text{NO}_3^-)$ of $(-6.8 \pm 0.5)\text{‰}$ that is in between...”

Line 43: The degree of change in $\delta^{18}\text{O}$ being larger than that in $\Delta^{17}\text{O}$ is a weird comparison to make. Since $\Delta^{17}\text{O}$ represents the difference between $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ and both of those isotopes change with mass-dependent processes the $\Delta^{17}\text{O}$ remains the same. Since the manuscript is to be read by an audience that includes non-isotope specialists, it would be useful to be clear about this.

Response: We have changed the statements regarding the $\delta^{18}\text{O}/\Delta^{17}\text{O}(\text{NO}_3^-)$ relationship as following: “...This likely suggests the oxygen isotopes are also affected before preservation in the snow at Summit, but the degree of change for $\delta^{18}\text{O}(\text{NO}_3^-)$ should be larger than that of $\Delta^{17}\text{O}(\text{NO}_3^-)$ given that photolysis is a mass-dependent process that directly affects $\delta^{18}\text{O}(\text{NO}_3^-)$ in snow but not $\Delta^{17}\text{O}(\text{NO}_3^-)$.”.

Line 51: There is no citation for Alexander et al., 2019 in the manuscript. (And as an aside, the modeling work in Alexander 2009 and 2020 does not deal with the impacts of post-depositional processing).

Response: Thanks for this comment. The right citation is Alexander et al., 2020 and has been corrected in the revised manuscript.

Line 59: “...increases in $\delta^{15}\text{N}$ and decreases in $\delta^{18}\text{O}/\Delta^{17}\text{O}$...” is only consistently true in Antarctica. See general comment above on the need to better discuss results and interpretation from Antarctica versus Greenland. This difference is compelling and would set the paper up better for how and why it’s really important to try to resolve our understanding of post-depositional processing of nitrate and the interpretation of isotopes of nitrate.

Response: This sentence describes the general patterns of the impacts of post-depositional processing on observed in Antarctica. But it doesn't mean it can be detected anywhere regardless of the degree of post-depositional processing. In this case, the patterns can't be detected in Summit, Greenland. But in Western Greenland, Curtis et al. (2018) study provides an example on how post-depositional processing changes snow nitrate $\delta^{15}\text{N}(\text{NO}_3^-)$. Curtis et al. (2018) found a significant coastal to inland gradient in snow $\delta^{15}\text{N}(\text{NO}_3^-)$ which they attributed to different degree of post-depositional processing, similar to the coastal to inland gradient observed in Antarctica.

Line 69: "...has not been directly observed/evidenced in the field." Please see Shi et al., Isotope Fractionation of Nitrate During Volatilization in Snow: A Field Investigation in Antarctica, Geophysical Research Letters, 2019.

Response: We are well aware of this paper, but it was a laboratory experiment conducted by collecting Dome A snow and measuring its changes in a room at Zhongshan station (a coastal site). It is not a direct observation nor can be viewed as direct evidence, and in any case they concluded "the evaporation of nitrate is minimal under typical polar area temperature range".

Line 73: Geng et al. 2015 is not an appropriate reference here as it deals with deep ice core samples (the sentence refers to snowpack). It's important to include more context here – none of the other references are work done in Greenland.

Response: We have deleted this citation and added the Curtis et al. (2018) study.

Line 84: impurities in the snow also affect the chemistry and the form of nitrate in the snow – e.g. NaNO_3 or CaNO_3 and that can also impact post-depositional processing.

Response: Thanks for this suggestion. We have added the following statement: "...The higher dust concentration during glacial periods could also reduce the volatilization of snow nitrate (Röthlisberger et al., 2000). ...".

Lines 125-130: This is only true if the majority of the nitrate in snow comes from the surface atmosphere at Summit. See general comments above.

I think it could be better explained here that what is being referred to is the loss of nitrate from depth changes the isotopic composition in that snow layer. The snow sourced NO_x from at depth, IF it re-forms nitrate and is re-deposited would change the surface snow values. It's also important to explain that the at depth layer should then reflect loss only based on the fractionation values presented in this manuscript (ie increase in $d^{15}\text{N}$, increase in $d^{18}\text{O}$). The surface value would be a mix of reformed nitrate and the original nitrate deposited.

The last sentence in this paragraph is really important so I think it is worth re-visiting the explanation here.

Response: Thanks for the suggestion. Regarding the representativeness of atmospheric or surface atmosphere, again as we have discussed earlier, within the time scale of boundary layer mixing and sampling duration, the air sample collected at the surface

should well represent the boundary layer. When snow fall occurs it effectively scavenges atmospheric nitrate and brings it to the ground. To elucidate more on this point, we note that most of the snow precipitation at Summit is formed via low-level mixed-phase cloud, the height of which is typically several hundred meters above the surface (Guy et al., 2021; Pettersen et al., 2018). The precipitation as well as the low-level mixed-phase cloud could both increase turbulent mixing down into the surface mixed layer (Pettersen et al., 2018). Thus at Summit, a more realistic picture regarding the mixing state of the local atmospheric boundary layer should be that the local boundary layer nitrate represents a mixture of upper tropospheric nitrate as well as snow sourced nitrate in summer. And we agree that in summer, the summer snow nitrate is a mix of the re-formed nitrate and primary nitrate.

Lines 145-150: Were the GFFs pre-cleaned or pre-combusted before use in the field? If so, how? If not, why not?

Response: All glass fiber filters were pre-cleaned by an overnight soak and several rinses with ultra-pure water, then dried in a clean room and stored in clean plastic food storage bags till used. We have added the following statement:

“...All glass fiber filters were pre-cleaned by an overnight soak and several rinses with ultra-pure water, then dried in a clean room and stored in clean plastic food storage bags till used...”.

Line 156-167: Only 54 samples “out of 97 were determined to be valid”. Please report the concentrations of the blank and how they were determined. Do they represent lab blanks or field blanks? What concentration is deemed not valid? What times of year are the dropped sample from? Does this skew the data in favor of particular months? For instance Figure 2 has no atmospheric data at all in September reported? And why is there no surface snow for Aug, Sep, Nov or Dec?

Response: To make the description of the experiment procedure clearer, we have added the following statement:

“...Each sample covering 3-4 days were routinely collected over the year, with a total of 97 samples. We have also collected 9 blanks during the sampling period in different months, with the same sampling procedure but limited the sampling time to 1 minute. These samples were stored frozen until analysis.

Measurements of nitrate concentrations and isotopes were conducted in the laboratory at the Institute des Géosciences de l’Environnement, Grenoble, France in 2013. Nitrate collected on the glass fiber filters was first extracted by about 40 ml of 18 MΩ water via centrifugation using Millipore Centricon™ filter units. The samples were then measured for nitrate concentrations by colorimetry using the Saltzman method (Vicar et al., 2012). The average nitrate concentration in the filtrate for all atmospheric samples were $(1363 \pm 1603) \text{ ng g}^{-1}$, while that of the nine blank samples were $(183 \pm 44) \text{ ng g}^{-1}$. Among these samples, 54 out of 97 were determined to be valid by comparing the extracted nitrate concentration with blank, i.e., only samples with concentration exceeding 3 times the blank samples were judged as valid for further analyses. These samples were then individually concentrated on a 0.3 mL resin

bed with anionic exchange resin (Bio– Rad™ AG 1–X8, chloride form) and eluted with 5×2 mL of NaCl solution (1M). The isotopic compositions of each sample were determined by using the bacterial denitrifier method. Briefly, NO_3^- in each sample was converted to N_2O by denitrifying bacteria under anaerobic conditions. N_2O was then thermally decomposed into N_2 and O_2 on a gold tube heated at 800°C . The N_2 and O_2 were then separated by a gas chromatography column and injected into an isotope ratio mass spectrometer (Thermo Finnigan™ MAT 253) for isotope analyses of $^{15}\text{N}/^{14}\text{N}$, $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$. To correct for the potential isotope fractionation during laboratory isotope analysis, international reference materials (IAEA- NO_3 , USGS-32, 34 and 35) were used for data calibration. We treated the reference materials the same as the filtrations from filter samples, e.g., making the reference material solution using 1M NaCl solution. The measured nitrate isotope ratio of each atmosphere sample was further corrected by deducting the contribution of the filter blanks. The overall measurement uncertainties were estimated to be 0.6 ‰ for $\delta^{18}\text{O}$, and 0.3 ‰ for both $\Delta^{17}\text{O}$ and $\delta^{15}\text{N}(\text{NO}_3^-)$”, line 185-210

The lack of atmospheric isotope data mainly centered in September and October owing to the low nitrate concentrations in filters in these months (not exceed 3 times of filed blank). We don’t find monthly surface snow data in these months reported in the literature.

Were reference materials treated to the same procedures as the samples? i.e. were the reference materials put through the concentrating method as the samples were. Was a nitrate blank measured on the NaCl? or on the concentrating process on the whole? This is important to ensure no artificial isotopic change to the environmental sample. The denitrifier method induces fractionation of the d18O during the conversion to N_2O and is corrected for by the samples being compared to reference materials treated in the same way. Any other pre-treatment of samples should also apply to reference materials to be sure it can be corrected for unless it is made clear that the pre-treatment causes no isotopic effects.

Response: We have made careful calibration for the NaCl solution blank. Please see our response above.

What are the measurement uncertainties reported here based upon?

Response: The measurement uncertainty was based on the reduced standard deviations of the residuals from the linear regression between the measured reference materials and their expected values, as described in Erbland et al. (2013).

Line 207: please be careful to distinguish between aerosol (only) nitrate, aerosol + gas phase nitrate, and gas phase only.

Response: Thanks for this suggestion. We have changed the usage of “aerosol nitrate” into “atmospheric nitrate” throughout the text.

Table 1: It would be useful to include the type of method used (i.e. filter type) and whether the collections represent aerosol, aerosol + gas, or gas only to help in

summarizing the different types of collections. In general when making comparisons of different datasets in the text, the difference in the isotope values is presented and THEN it is discussed that the samples actually represent different things (ie aerosol + gas versus gas only).

Response: Thanks for this suggestion. We have added the corresponding items in the table 1.

Line 217-220: I agree that it is odd to have a higher summertime d18O. But the validity of the data should be questioned based on evidence that somehow the higher values are biased in some way. For instance, an outlier test could be used. Is it not at all possible that a higher d18O could represent something anomalous that summer at Summit? could there have not been any different chemistry that could contribute to higher values (for instance, stratospheric intrusions)?

Response: We agree that statistical methods would provide a more firm comparison here. Unfortunately, we didn't have the original surface snow data reported by Jarvis et al. (2009). Stratospheric intrusions are unlikely to be reasonable here as it's known that stratospheric transport is rather weak in Arctic region, such as suggested by Stohl. (2006).

The line that "different groups" data were not averaged is also a bit odd. The Jarvis, Kunasek, and several Geng studies all measured samples at the University of Washington IsoLab. I suggest providing a different wording of justification here.

Response: We deleted the usage of "different groups" in the sentence.

Figure 1: It would be useful to also plot the calculated accumulation rate over the year since this is used in several calculations within the paper.

Response: Thanks for this suggestion. We have added the monthly accumulation rate in Figure 2.

Line 323: This is another place where a statistical test should be used to justify "out of range" and therefore why the data is not included.

Response: We think that when the data is overlapped within each other's uncertainty range, using statistical method such as a T-test could help to discern whether the difference between two groups of data are statistically different. But when the range of data is not overlapped, it's unnecessary to rely on statistical method to judge whether it is out of range, as in the scenario described in the text.

Line 342: "This systematic enrichment refutes the previous hypothesis that seasonal variation in snowpack....was driven by shift in the relative importance of NOx source...". See my argument against "systematic enrichment" in the general comments above. This alone does not negate the interpretation of nitrate in snow majorly representing long-range transported primary nitrate rather than local only. Additionally, the Jiang et al (2021) model could just as well explain the seasonality in the d15N snowpit profile when varying the d15N of primary nitrate (ie the "source"

value). In fact, this is noted on line 393-395 that the Jiang et al (2021) model shows “that the primary nitrate flux dominates the nitrate budget at Summit, even in mid-summer”. This seems to directly contrast with statements in the paper where primary nitrate does not play an important role at Summit.

Response: We have responded to the “systematic” question earlier, and repeated here: Here we used the word “systematic” to represent the overall patterns of the seasonal atmospheric and snow $\delta^{15}\text{N}(\text{NO}_3^-)$, as they appear to follow the amounts of accumulated UV-B dose (but oppositely). As in fact only the Dec. value in snowpack appeared to be out of the system. Feb. snow is also expected to be influenced by sunlight as polar sun rises in March when Feb. snow is still in the photic zone. Especially, if looking at the patterns of the snowpack $\delta^{15}\text{N}(\text{NO}_3^-)$ and the accumulated UV dose (Figure 2a and 2b), in general the higher the accumulated UV dose, the larger the snowpack $\delta^{15}\text{N}(\text{NO}_3^-)$. Note the highest $\delta^{15}\text{N}(\text{NO}_3^-)$ appears in spring when the accumulated UV dose is also the highest in a year.

And again, throughout this manuscript, as well as the Jiang et al. 2021 study, we never attempt to refute that the majority of snow nitrate deposited at Summit originates from primary nitrate deposition, as our modeling work suggested that the reformed nitrate flux at most contributes 25% to local atmospheric nitrate burden even in summer. It is the $\delta^{15}\text{N}(\text{NO}_3^-)$ that we focused on and its seasonality is determined or at least largely influenced by post-depositional processing and thus cannot be ignored in its interpretation, especially for ice core where the relative weight of post-depositional effect can vary a lot. In the Jiang et al. (2021) model, if we varied the $\delta^{15}\text{N}(\text{NO}_3^-)$ signature of primary nitrate as much as observed in snowpack, we have to turn off snow photochemistry, otherwise the predicted magnitude of seasonal $\delta^{15}\text{N}(\text{NO}_3^-)$ difference would be almost 2 times what is observed. Primary nitrate dominates the Summit nitrate budget, but the seasonal loss of nitrate is driven by the seasonal shift of actinic flux which drives snow nitrate photochemistry. As a result, even though the annual net loss of nitrate is small, the seasonal difference, especially the $\delta^{15}\text{N}(\text{NO}_3^-)$ could be large. The large N-isotope fractionation associated with snow nitrate photolysis can result in large $\delta^{15}\text{N}(\text{NO}_3^-)$ changes despite small amount of nitrate loss.

Line 360: this is a bit confusing and connects to my comment about clarifying the different processes in the snow in the introduction. I think readers might be confused here that a depleted $\delta^{15}\text{N}$ source to the atmosphere requires that that NO_3^- be lost from the snow and the isotopic composition in the snow where the NO_3^- was lost will be changed (which has a different isotopic impact if that snow-sourced NO_x is re-deposited locally).

Response: Thank, to be clearer, we have added the following statement in the revised manuscript:

“... is qualitatively consistent with the effects of snow nitrate photolysis which enriches snow $\delta^{15}\text{N}(\text{NO}_3^-)$ while providing a snow-source of depleted $\delta^{15}\text{N}(\text{NO}_3^-)$ to the atmosphere. In fact, the negative isotope fractionation factor associated with nitrate photolysis would favor the release of NO_x with lighter ^{14}N , which would

rapidly reform nitrate in the overlying atmosphere with depleted $\delta^{15}\text{N}(\text{NO}_3^-)$, given the short lifetime of NO_x at Summit (typical several hours in summer)”

Line 367-370: this does not explain nor include mention of the fact that Dec and Feb look very different in the atmosphere versus the snow (this is related to my general comment above).

Response: We have explained this earlier.

Line 395-400: This does not address that differences in transport were connected to different isotopic compositions of nitrate at Summit in Fibiger et al (2016).

Response: We admit that there are many issues related to the atmospheric and snow nitrate chemistry as well as the isotopes, and that this data set cannot address them all. For example, the differences in transport were invoked to account for the **surface snow** $\delta^{18}\text{O}(\text{NO}_3^-)$ differences in two years. But at the time we noted that in Fibiger et al (2016) the $\delta^{15}\text{N}(\text{NO}_3^-)$ in atmosphere and surface snow is not different for two different years, in contrast to $\delta^{18}\text{O}(\text{NO}_3^-)$ which is very different. This is difficult to explain as to why difference in transport only induces changes in $\delta^{18}\text{O}$ but not impact $\delta^{15}\text{N}$, as it's $\delta^{15}\text{N}(\text{NO}_3^-)$ typically used to track the source region instead of $\delta^{18}\text{O}$. This is out of the scope of this manuscript, but can be explored once more data are available.

Line 407-415: there needs to be clarifying language in here to distinguish between observations being shown here, prior model calculations, prior observations and calculation being done here.

Response: Thanks for this suggestion. We have made the statements more specific when talking about different types of data (observation vs model):

“Compared to surface snow nitrate, snowpack nitrate was enriched by (12.8 ± 2.6) ‰ in spring in our compiled dataset, as seen in Fig 2b. This value should reflect the effect of post-depositional processing on snow nitrate throughout its preservation, i.e., time from being deposited at the surface to being archived below the photic zone. In Jiang et al. (2021), this effect was defined as PIE, i.e., the photo-induced isotope effect, and calculated as the difference between surface snow $\delta^{15}\text{N}(\text{NO}_3^-)$ and archived snow $\delta^{15}\text{N}(\text{NO}_3^-)$. The averaged PIE in spring calculated by the TRANSITS model is (14.3 ± 1.1) ‰, consistent with the observations.”

Line 408 says the difference between snowpack and the snow is 12.8 per mil in spring. Is this model or data calculated? the TRANSITS model predicts a difference value of 14.3 per mil, which is “consistent with the compiled data”. In Figure 2b, the surface snow (blue symbols) appears to be ~ -8 per mil and the snowpack is +3 per mil in April (so the difference is ~11 per mil); there is no surface snow data shown for March; May (or between May and June?) the difference is only ~3 per mil. So how and when is the Jiang et al calculation and TRANSITS model calculation consistent with the compiled data?

Response: The $(12.8 \pm 2.6) \text{‰}$ **seasonal difference** is based on the observed average surface snow $\delta^{15}\text{N}(\text{NO}_3^-)$ from Jarvis et al. (2009) $(-6.8 \pm 0.5) \text{‰}$, $n=84$) and snowpack seasonal average $\delta^{15}\text{N}(\text{NO}_3^-)$ from Geng et al. (2014) $(6 \pm 2.6 \text{‰})$. Note there are two years of data in Jarvis et al. (2009) but only the seasonal average value and standard error is reported.

Then on line 444 snow and atmosphere are compared and it is reported that the difference in spring should be 9.8 per mil – this is true for Apr, but in Mar and May-June the difference is larger and again (close to 20 per mil in Mar!). If I am misreading this then the text needs to be clarified and it would be helpful to refer directly to figures when speaking of the data here.

Response: Note here we compare atmospheric nitrate with surface snow nitrate. Owing to the seasonal resolution of the Jarvis et al. (2009) dataset, **we only compared the seasonal mean here instead of any specified month**. In addition, the surface snow $\delta^{15}\text{N}(\text{NO}_3^-)$ data is significantly higher in Fibiger et al. (2016) than in Jarvis et al. (2009) which call for more data to resolve this issue.

Line 446 says the difference between atmosphere and snow is negligible in winter, but this is only true of 1 of the 3 months in winter in Figure 2b.

Response: Here we compare atmospheric nitrate with surface snow nitrate. Similar to the response above, only **seasonal** average values were compared here. The winter average atmospheric $\delta^{15}\text{N}(\text{NO}_3^-)$ is $(-12.9 \pm 4.6) \text{‰}$, while that of surface snow is $(-11.7 \pm 2.3) \text{‰}$.

It would be useful to include the Jiang et al (2021) model output as part of the figures since values produced in that work are referred to at least 4 times in the manuscript.

Response: The modeled $\delta^{15}\text{N}(\text{NO}_3^-)$ change (PIE) from deposition to archival have been compared in Jiang et al. (2021) and we do not repeat here. Again, the strength of model is to predict changes in isotopes caused by post-depositional processing related to a starting point, and that was what we have been focused on when using the model.

Line 408-415: I think preservation of the value below the photic zone is important and should be clarified in the introduction as to this expectation. However, I'll also note that Erbland's study with the TRANSITS model predicted values below the photic zone, which agreed with a few individual samples from depths below the photic zone compared to results from within the photic zone in several areas of the East Antarctic Ice Sheet. In a follow up study, Shi et al. (ACP, 2015) presented complete profiles along the EAIS between the surface and below the photic zone and found that the case for an exponential increase in the isotopes was highly sensitive to the depth over which it is assumed the photic zone is relevant. This does need a response but it would be good for the authors to re-review that work to be sure to be consistent with the peer-reviewed literature.

Response: Thanks for this suggestion, we have already added the definition of archival nitrate in the introduction as mentioned above. However, as pointed out by

reviewer 1, Shi et al. (2015) may have misunderstood the extrapolation method in Erbland et al. (2013). That Erbland et al. (2013) assumed an exponential increase in $\delta^{15}\text{N}(\text{NO}_3^-)$ in the photic zone is only true when assuming local meteorological and chemical **conditions remain unchanged**. Below the photic zone, the archived nitrate $\delta^{15}\text{N}$ is a combination of photolysis-induced fractionation plus surface condition changes, so it's natural to see the asymptotic values vary with depth, **and this is not because the assumption of the photic zone depth**, but instead due to changes in other factors such as snow accumulation rate/impurities concentrations, TCO, and even primary nitrate inputs.

Line 430: Equation 3 – a simplified form of the PIE is really valuable. It's agreement with TRANSITS seems a bit circular since the equation is based upon the TRANSITS model. It should be better explained here what this simplified equation does NOT include relative to TRANSITS so that the simplified version is applied by other groups in the future under situations that are appropriate. For instance, does the $A(t)$ in Eq 3 considers an e-folding depth that is impacted by impurities in the snow?

Response: Eq(3) is the mathematical representation of the integral effect of photolysis on $\delta^{15}\text{N}(\text{NO}_3^-)$ in TRANSIST model. The difference is that the J value used here is in a simplified form, i.e., J decreases exponentially with depth. The other difference includes: 1) the changes in nitrogen isotope fractionation factor with depth is also not considered as both calculation and experiment suggested it's insensitive to the attenuation with depth (Berhanu et al., 2015); 2) the diffusion smoothing effect is not considered here either (it should not be important as the observed $\delta^{15}\text{N}(\text{NO}_3^-)$ profile in Dome A and Dome C doesn't show distinct smoothing in $\delta^{15}\text{N}(\text{NO}_3^-)$); 3) the cage effect is not considered. We have changed the word of "agree with" into "is consistent with". $A(t)$ in Eq 3 represents the accumulation rate at a given time t , only z_e depends on the impurities in snow. We have added the following statement as follow:

"...Here we don't consider the changes of ε with depth as both the TRANSITS model calculation and laboratory experimental results suggested ε is not sensitive to the attenuation of radiation in snow (Berhanu et al., 2015). The diffusion smoothing in $\delta^{15}\text{N}(\text{NO}_3^-)$ is also not considered, as the observed multi-year snowpack $\delta^{15}\text{N}(\text{NO}_3^-)$ profiles don't show any distinct smoothing (Frey et al., 2009; Shi et al., 2015). the cage effect is also neglected in Eq(3), which may not hold when the snow accumulation is relatively low. Essentially Eq(3) is the same as Eq(2), because they both describe the total actinic flux received by a specific snow layer before archival, but Eq(3) provides a direct way to evaluate the induced isotope effects on $\delta^{15}\text{N}$...", line 489-495

Line 450: Is this based on comparing means? Medians? The medians in Fig 3 of Fibiger et al show differences of only 9-12 per mil not 12-15 per mil. Please clarify.

Response: Here we used the average value (thanks for the origin data we downloaded it from the Arctic Data Center). We have added the phrase "on average" when describing it.

Also, why is the atmospheric nitrate oxygen isotopic data from Fibiger et al. NOT included in Fig 2?

Response: The Fibiger et al. (2016) $\delta^{15}\text{N}$ data has been plotted in Fig2b and $\delta^{18}\text{O}$ data was not included because of the rather large discrepancy between the two years and they are out of range of other studies including the values for snow. In the revised manuscript, we have added a statement in the Figure caption, stating the range of the Fibiger et al. (2016) $\delta^{18}\text{O}$ data and explaining it is out of the range of other data in the same figure as follows:

“The atmospheric $\delta^{18}\text{O}(\text{HNO}_3)$ data in Fibiger et al. (2016) is out of range ($(54.2 \pm 8.5) \text{‰}$ in 2010, $(90.5 \pm 12.5) \text{‰}$ in 2010) and thus is not shown here.”

Line 471-483: “Compared to surface snow, atmospheric nitrate is more influenced by snow-sourced nitrate...” Yes. This is because the snow represent more than the surface atmosphere at Summit. And while this is stated as “snow is a much larger reservoir of nitrate compared to the atmosphere” on Line 481, the context here is not clear (see general comments above on this).

Response: We think we have different meaning regarding this sentence. We meant to explain that owing to fact that atmospheric nitrate is such a small nitrate reservoir that it could be easily impacted by the snow sourced nitrate, while for the surface snow, once deposited, it would not be rapidly altered as the dry deposition of snow sourced nitrate was too low to significantly impact it.

It's not clear why the Erbland reference is relevant here since it does not apply to Greenland (and for instance in the discussion above while dry deposition at Summit is infrequent fresh snow and fog deposition are frequent). You should also include these references in discussing wet versus dry deposition and the budget of nitrate in the atmosphere at Summit:

Dibb, J. E., R.W. Talbot, and M. H. Bergin (1994) Soluble acidic species in air and snow at Summit, Greenland; GRL; 1627-1630.

Dibb, J. E., R. W. Talbot, J. W. Munger, D. J. Jacob, and S.-M. Fan (1998) Air-snow exchange of HNO_3 and NO_y at Summit, Greenland; JGR; 3475-3486.

Response: Thanks for this suggestion. We have deleted Erbland et al. (2013) and cited the more related references.

Lines 494-510: this discussion would be useful earlier in the manuscript to layout an expectation for how the results will be interpreted.

Response: Thanks for this suggestion. We add a brief description in the opening paragraph in this section:

“...Previous studies suggest there were several processes occurring at the air–snow interface related to nitrate deposition and preservation that could lead to nitrogen fractionation, including (i) fractionations during snow nitrate photolysis and physical release (Berhanu et al., 2014; Erbland et al., 2013; Frey et al., 2009; Jiang et al., 2021;

Shi et al., 2019), and (ii) the proposed fractionation during nitrate deposition [related to the different deposition mechanisms](#) (Erbland et al., 2013)...”, line 404-405

Line 512: Are there updated stake measurements at Summit that could be checked for this? The Burkhardt et al. study is a bit dated, and accumulation rate at Summit could be with climate change in the last decade? Also, how many years is the lowest weekly average accumulation rate observed since the Burkhardt et al. study is not at all representative of accumulation measured during the time periods of the compiled data or the atmospheric data presented here.

Response: The Burkhardt et al. (2004) stake-measured accumulation rate data covered from 1997 to 2002. This study used data from 2004 to 2010 to calculate the average weekly accumulation rate. We have compared our calculated monthly accumulation rate with Burkhardt et al. (2004) and Castellani et al. (2015) and found good agreement during three periods (1997 to 2002, 2004 to 2010, 2010 to 2013). The common feature is with a minimum accumulation rate in May-June and a maximum in August-September.

Line 513: “and presumably more nitrate dry deposition occurred...” Why is this presumed? And is this consistent with one page ago where the dry deposition flux was considered to always be “very low” ?

Response: Here we meant when wet precipitation is low, dry nitrate deposition would be relatively more important. It is a relative term, and the overall dry flux could be still low.

Line 553: This should read as “The cage effect incorporates water D17O (~0 per mil) in the formation of nitrate and therefore lowers the overall D17O of the nitrate compared to nitrate formed in the atmosphere.” (or something like that). The way this is written now is not actually correct and will definitely confuse readers.

Response: Thanks for this suggestion. We have changed the statement as follows: “...[The cage effect incorporates water with \$\Delta^{17}\text{O}\$ around 0 ‰ in the reformed nitrate and therefore lowers the overall \$\Delta^{17}\text{O}\$ of the nitrate compared to nitrate first deposited onto snow...](#)”.

Line 563: “the cage effect is negligible”. It needs to be said here that the Jiang et al (2021) model output does not match well AT ALL with the D17O snow profile. So I think it is unfair to bring conclusions from that study regarding D17O into here as if they are “proven” by a model that does not actually explain/match the observations.

Response: We just wanted to explain a bit more that the Jiang et al. (2021) model study is explicitly focused on to what degree the magnitude of the observed seasonality can be explained by post-depositional processing, and the TRANSITS model we used here was not constructed to predict the isotopes of snow nitrate ($\delta^{15}\text{N}$ and $\Delta^{17}\text{O}$), but to assess their **changes** due to post-depositional processing. Using the model, the cage effects on $\Delta^{17}\text{O}$ is negligible, and the overall effects from post-depositional processing on snowpack $\Delta^{17}\text{O}$ is also small. We don't see why the model

has to reproduce the observed $\Delta^{17}\text{O}$ to conclude anything on the effects of “cage effect” and post-depositional processing. That the model only considering post-depositional processing can't explain the observed $\Delta^{17}\text{O}$ is exactly demonstrating that the effects of post-depositional processing (including the cage effect which is a part of it) is small.

Line 569: “Locally reformed nitrate under sunlight in the summer half year would possess low D17O compared to primary nitrate deposited earlier in the season...” And yet, the Kunasek et al study based on local photochemistry at Summit cannot explain the HIGHER THAN EXPECTED summertime D17O values. And the global GEOS-Chem modeling studies (Alexander et al, 2009, 2020) fit the seasonality of D17O at Summit very well, but UNDERESTIMATE summertime values and OVERESTIMATE spring values.

Response: We don't see any issue here. “the Kunasek et al study based on local photochemistry at Summit cannot explain the HIGHER THAN EXPECTED summertime D17O values.” - This is actually the same we are saying here: the reformed nitrate is with relatively low $\Delta^{17}\text{O}(\text{NO}_3^-)$ and thus primary nitrate with relatively high $\Delta^{17}\text{O}(\text{NO}_3^-)$ is necessary to be involved to explain the observations.

Line 575-583: Data from different years should not necessarily be expected to be consistent. The wording should be changed here or the authors should justify why this should be expected. If photolysis alone can always explain the seasonality of nitrate isotopes then it SHOULD be the same every year. The observed (real) differences in the Fibiger et al dataset are explained in that work in terms of variability in transport and chemistry (ie source regions). There is no reason to dismiss some of the d18O data in Fibiger et al. I'll also point out (for my own gratification) that our lab is the only lab that independently reports d18O data from the N2O method and D17O from the N2/O2 method b/c the N2/O2 method is known to cause mass dependent inconsistencies in d18O and d17O (which do not affect the D17O result).

Response: We don't fully understand the question. Here we are just stating that the $\delta^{18}\text{O}(\text{NO}_3^-)$ data are different, or more variable compared to $\Delta^{17}\text{O}(\text{NO}_3^-)$ and/or $\delta^{15}\text{N}(\text{NO}_3^-)$. This is from observations, and in line 580 and 581 of the original manuscript, we clearly stated that “The larger variability in $\delta^{18}\text{O}(\text{NO}_3^-)$ is somewhat expected,....”. We are not saying they should be consistent. Regarding the Fibiger et al. (2016) study, again if transport could explain the large difference in $\delta^{18}\text{O}(\text{NO}_3^-)$ in the two field seasons, but then why is $\delta^{15}\text{N}(\text{NO}_3^-)$ the same for the two seasons? These are questions need to be explored but not in this manuscript.

Line 616: again, why should the data from different years be consistent if transport, accumulation, deposition all change between seasons and interannually?

Response: Here we wanted to describe that due to the lack of sufficient surface snow data, and the large difference of the $\delta^{18}\text{O}(\text{NO}_3^-)$ data reported by the two studies, we cannot deduce or explore whether or not oxygen isotope fractionation occurs during nitrate deposition.

Line 633: What happens to the $\delta^{15}\text{N}$ during the cage effect reformation of nitrate? It is only discussed for $\delta^{18}\text{O}$ (and D17O).

Response: The detailed secondary chemistry of nitrate photolysis is very complex and its induced isotope fractionation effect for $\delta^{15}\text{N}$, to best of our knowledge, still remains unexplored. However, current field and laboratory photolysis experiments results indicate that photolytic process should dominate the total fractionation effect (Berhanu et al., 2014; Meusinger et al., 2014). The calculated fractionation factor using the absorption cross section for $^{14}\text{NO}_3^-$ and $^{15}\text{NO}_3^-$ provided theoretical results under different spectrum of incident light consistent with the experiment results, suggesting that photolytic process shall be the primary factor inducing the $\delta^{15}\text{N}$ fractionation during nitrate photolysis.

Line 653: I would argue that the framing in Fibiger et al (2013) is that the relationship between $\delta^{18}\text{O}$ and D17O is not evidence alone that post-depositional processing does not occur – we attempt to explain how that relationship should change is an important amount of processing were to occur and that does not fit with the observations, therefore we conclude that it is not very important. This was then followed up with the concurrent snow-air sampling in Fibiger et al (2016).

Response: We agree that Fibiger et al (2013) indeed considered multiple factors impacting snow nitrate $\Delta^{17}\text{O}$ and $\delta^{18}\text{O}(\text{NO}_3^-)$ and they concluded that the found relationship between $\Delta^{17}\text{O}/\delta^{18}\text{O}(\text{NO}_3^-)$ can not explained by post-depositional processing. But this can only lead to the conclusion that the **surface snow** nitrate didn't undergo sufficient amount of photolysis, as only surface snow samples were involved. The same for the Fibiger et al (2016) study which was also only based on atmospheric and surface snow samples. Consider the high snow accumulation rate (~65 cm per year) as well as the depth of the photic zone (30-40 cm), the surface snow samples apparently cannot represent the whole snowpack. What is more, none of these two studies cover a complete year, and thus the effect of the seasonally different actinic flux cannot be assessed.

Figure 4 discussion: The fact that relationship between $\delta^{18}\text{O}$ and D17O is so similar in the atmosphere and snow and the snowpack is different could just as easily be explained by deposition of more nitrate than what is apparent at the surface at Summit. And if it cannot be explained by this, this hypothesis needs to be tested and dismissed.

Response: We don't agree with this hypothesis since it sounds like the snowpack nitrate was directly buried without first deposited to the surface. We note that the correlation between surface snow $\Delta^{17}\text{O}/\delta^{18}\text{O}(\text{NO}_3^-)$ was similar in two different years, even if they were derived from different source region and different chemistry as suggested by Fibiger et al. (2016).

Line 682: Earlier in the manuscript it states that the isotopes are preserved upon archival. Again, please take care to qualify the language in the introduction and then use it consistently in the manuscript.

Response: Thanks for this suggestion. We have added the definition of archived nitrate in the introduction section:

“...This recycle of snow nitrate not only changes the initially deposited nitrate (isotope) signal, but also leads to a redistribution of snowpack nitrate. Thus, the final archival snow nitrate, defined as the nitrate buried below the photic zone, would largely be impacted by post-depositional processing and disturb the interpretation of ice core nitrate records...”

Line 694: This also discussed in Shi et al, ACP, 2015.

Response: Shi et al. (2015) study concluded that “*Predicting the impact of post-depositional loss, and therefore changes in the isotopes with depth, is highly sensitive to the depth interval over which an exponential change is assumed.*”, which is distinctly different with the conclusion drawn here. As responded earlier, “*the depth interval over which an exponential change is assumed*” is a misunderstanding of the Erbland et al. 2013 study. One has to first determine the depth of the photic zone, but not to assume it.

Line 703: “...snowpack nitrate can only be explained by the effect of the photo-driven post-depositional processing...” This is the only hypothesis tested here and there are a number of flaws that need to be visited before this conclusion can be drawn.

Response: The detailed response to these “flaws” have been responded earlier and we don’t see any issue with this conclusion.

Line 710: Most of the previous work done does NOT say unequivocally that atmospheric nitrate is solely dependent on primary nitrate.

Response: We agree, and we just wanted to emphasize it.

In fact, Fibiger et al’s work shows that indeed there is an impact of snow sourced nitrate on the atmosphere at Summit! It’s just a small part of the pool contained in the snow such that what is ultimately preserved DOES reflect primary nitrate. This is not in fact disproved in this study.

Response: We don’t know how “*ultimately preserved DOES reflect primary nitrate*” can be concluded by the Fibiger et al 2013 and 2016 studies. **Their work only relied on atmospheric and surface snow samples in a few months (most in May and June) of a year, and these samples are far from “ultimately preserved”.** For the archive what is important is the continuity between atmosphere, surface snow and buried snow up to the photic zone. All reservoirs have to be considered.

Typographic errors:

Line 217: even inconsistence does not make sense grammatically

Line 253: was should be were

Line 313: Hasting should be Hastings
Figure 2 caption: does should be dose?
Line 376: remove be at the end of the line
Line 406: remove snow before snowpack
Line 451: closed should be close
Line 713: inconsistence is not a word
Line 720: the photo is a typo

Response: Thanks for these suggestions. We have corrected these typos accordingly.

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