

## Comments:

*I think it is critically important that the authors do more to compare with the larger body of isotopic measurements of nitrate in the snow and atmosphere at Summit, Greenland. The conclusions drawn here focus on the loss and recycling of nitrate when the model can just as well explain the observations based on a change in the primary nitrate isotopic signal rather than photolytic redistribution of nitrate in the snow. A number of works from my research group on surface snow and snowpack at Summit, Greenland have all concluded that photolytic loss OR recycling cannot explain the observations presented in those studies. If the model here is indeed correct, this is an opportunity then to re-interpret those conclusions. Or better constrain the model and present stronger evidence-based conclusions. Simply put – the model has multiple tuning options to improve agreement between predictions and observations, but can it actually explain what's observed at Summit?*

**Response:** We appreciate Dr. Hastings's efforts reading and raising concerns about this manuscript. Before we respond to Dr. Hastings's specific comments below, we would like to clarify a few things:

1) Dr. Hastings may have misunderstood the purpose of this manuscript. This manuscript 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** caused by post-depositional processing of nitrate after primary deposition. As shown by field observations and laboratory experiments, snow nitrate will be photolyzed as long as sunlight is available (Chu and Anastasio, 2003, Dibb et al., 1998; Honrath et al., 2002; Meusinger et al., 2014).

**Therefore, given the significant differences in actinic flux between the summer half year and winter half year in the polar regions, seasonality in photochemistry and the degree of post-depositional processing should be questioned.** Our model reproduced the observed snowpack NO<sub>x</sub> flux in summer conditions at Summit (modeled  $2.96 \times 10^{12}$  molecules  $\text{m}^{-2} \text{s}^{-1}$ , vs.  $2.52 \times 10^{12}$  molecules  $\text{m}^{-2} \text{s}^{-1}$  observed by Honrath et al., 2002), and it showed that the photo-driven post-depositional processing can explain the magnitude of the seasonality (difference between summer and winter) in  $\delta^{15}\text{N}$ , **no matter what  $\delta^{15}\text{N}$  values were assumed for primary nitrate.** At the same time, the model cannot explain the magnitude of the seasonality in  $\Delta^{17}\text{O}$ . This is consistent with previous work in Antarctica, and just as expected: photolysis induces large N isotope fractionations, but won't directly influence  $\Delta^{17}\text{O}$ . Note changes in  $\Delta^{17}\text{O}$  upon nitrate preservation observed in East Antarctic Plateau (where snow accumulation rate is very low) is mainly caused by cage effect, in addition to recycling of nitrate at the air-snow interface. At Summit, the cage effect is small (0.1 ‰) due to its high snow accumulation rate.

2) The disagreement between us and Dr. Hastings is that we don't think surface snow nitrate alone can be used to determine the degree of post-depositional processing, nor can O-isotopes be used to quantify post-depositional processing. These, however, were what Dr. Hastings's previous work relied upon to draw their

conclusions (Fibiger et al., 2013; Fibiger et al., 2016). The former is because post-depositional loss occurs not just at the surface but throughout the depth of the snow photic zone (35-45 cm at Summit), and becomes more apparent deeper in the snowpack where it is isolated from atmospheric deposition (i.e., where it experiences nitrate loss but not recycling). For the latter, O-isotopes cannot be used to quantify post-depositional processing because other factors dominate their seasonal variations. We discuss with more detail below on why O-isotopes should not be used in our point-by-point response to Dr. Hastings's specific comments.

3) Keeping in mind that this manuscript focuses on the effect of post-depositional processing on the seasonality of nitrate isotopes in snowpack, we did not ignore any relevant observations: previous publications with seasonal isotope data available were all well compared or used to constrain our model, including Hastings et al. (2004), Jarvis et al. (2009) and Geng et al. (2014). The model explains all of these observations (seasonal differences) well. What is more, the model also explained the differences in  $\delta^{15}\text{N}$  of nitrate in surface snow and snow at depth observed by Jarvis et al. (2009).

Finally, we would like to also point out that, there were numerous studies at Summit that observed/measured either direct emissions of  $\text{NO}_x$  and HONO from snowpack or loss of snow nitrate upon preservation (e.g., Dibb et al., 1998; Munger et al., 1999; Honrath et al., 2002; Burkhardt et al., 2004; Dibb et al., 2007). Our model results are qualitatively and quantitatively consistent with these studies in terms of both the observed snowpack  $\text{NO}_x$  flux and nitrate loss. In comparison, conclusions of Dr. Hastings's studies were not consistent with these observations (Hastings et al., 2004; Fibiger et al., 2013; Fibiger et al., 2016).

### ***Spatial heterogeneity***

*First and foremost, the issue of spatial heterogeneity in the isotopic composition of snowpits and surface snow mean that comparing with a single year of observations and suggesting that everything can be explained is not appropriate. I understand the purpose of the study here is to focus on the loss of nitrate from within the photolytic zone and the model then suggests that much of this snow-sourced  $\text{NO}_x$  is re-deposited as nitrate at the surface. Hence the interest in using the surface snow observations we published in Jarvis et al. (2009). However, there are additional observations that could be compared with to better understand if the need for photolysis in the model is actually correct. For starters, Fibiger et al. (2016) present observations of  $d15\text{N}$ ,  $d18\text{O}$  and  $D17\text{O}$  in surface snow and in atmospheric nitrate for two years (2010 and 2011) in the spring (May/June). Both the surface snow observations and the atmospheric observations should be compared with the model predictions. Jarvis et al (2009) also includes atmospheric observations that are neglected here.*

**Response:** There is no spatial heterogeneity of the seasonal patterns of nitrate concentrations nor isotopes at Summit. All snowpit data from Summit show a consistent

range in the **seasonality** of  $\delta^{15}\text{N}$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  (Geng et al., 2014; Hastings et al., 2004; Jarvis et al., 2009; Kunasek et al., 2008). In addition, we did not use “a single year of observations”, the snowpack data from Geng et al. (2014) covers 3 years, and the surface snow and snowpack data from Jarvis et al. (2009) also covers 2 years.

We didn't use the Fibiger et al. (2016) data because it does not provide any information on seasonality, which is the focus of this paper. Data from Fibiger et al. (2016) were only for May/June, and the Jarvis et al (2009) atmospheric data also only included two months (i.e., March 24 to April 21, and May 24 to July 6). Without knowing the data covering the rest of the year, or samples collected in the same season but at depth, those data are not useful for examining seasonality. Note the model meant to predict **the changes** that occur between primary deposition and preservation, it can't predict the actual values in the air **unless the values of primary nitrate are known**.

*Additionally, it is inappropriate to compare the range in surface values to the range found in snowpits and suggest that this represents real change in the isotopes (lines 65-85; ~line 240) – again there is significant spatial heterogeneity to contend with and the comparison with observations should be an envelope or a distribution and not a single line. Furthermore, it appears that one year of surface snow values is being compared to an averaged snowpit from a different year? Again, spatial AND temporal heterogeneity could easily explain a big portion of this difference (if not all). Also, the “higher” values in the snowpit than in surface snow neglect the fact that it is possible that there is also local contamination of the snow by the presence of the field camp/field work – this is well discussed and direct evidence for the isotopic values associated with this potential source are given in Fibiger et al. (2016).*

**Response:** We actually compared the annual and seasonal averages with standard deviations ( $\pm$ ), the data were averaged with two years of surface snow data from Jarvis et al. (2009), and we did not simply compare the ranges. Regarding the spatial and/or temporal heterogeneities, **our snowpit and that reported by Jarvis et al. (2009) with which we compared were all collected in 2007 and both covered from 2004 to 2007**. Especially, the snowpit samples from Jarvis et al. (2009) and Geng et al. (2014) displayed similar  $\delta^{15}\text{N}(\text{NO}_3^-)$  ranges and seasonality, and it is the Jarvis et al. snowpit data that show an enrichment in  $\delta^{15}\text{N}(\text{NO}_3^-)$  when compared with their surface snow sample (Figure 5b of Jarvis et al.): among seven of eight seasons the snowpack  $\delta^{15}\text{N}$  was significantly enriched compared to surface snow samples in Jarvis et al. (2009). **In the abstract of Jarvis et al. (2009), quote, “Photolytic recycling and loss will increase the  $\delta^{15}\text{N}$  of buried snow nitrate, the degree to which depends on the nitrogen isotope fractionation of nitrate photolysis”**. In this study, we quantified the “degree” using the model with experimentally determined fractionation factors associated with photolysis.

Fibiger et al (2016) discussed that “local contamination of the snow by camp power generator emissions” would lead to nitrate with high  $\delta^{15}\text{N}$ , and Dr. Hastings suggested here this could possibly explain the high snowpit  $\delta^{15}\text{N}$  values. However, contamination is unlikely to explain the seasonality given that several snowpits collected and measured by three different groups show similar seasonality and high  $\delta^{15}\text{N}$ . In addition, among

seven of eight seasons the snowpack  $\delta^{15}\text{N}$  was significantly enriched compared to surface snow samples in Jarvis et al. (2009). This is impossible to explain with contamination.

### ***Fpri assumptions***

*The assumptions of the values for Fpri (both concentration and isotopically) need to be better justified. The Fibiger et al. (2016) surface snow isotope data ALL fall within a 3-end member plot (see Figure 8 in that paper) that are suggested to represent the primary nitrate signatures (this includes D17O data from Fibiger et al. (GRL, 2013) as well). Why not use these end-members as an a priori assumption/test? Why assume surface snow values when authors of the current work have argued in other papers that even the top few cm misrepresents what is happening in the very surface layer of the snow? It is stated in this paper that the Fpri assumptions could be underestimates – which directly agrees with the values presented in Fibiger et al. So again, why not use these values compared to the constant 0 and 30 per mil assumptions for  $\delta^{15}\text{N}$  and D17O, respectively. In fact, if the highest endmember values for D17O found in Fibiger et al (2016) (39 per mil) were used for D17O primary it likely would much better fit the seasonal D17O observations than the model currently does! This offers much in the way of better constraining our understanding of nitrate in snow at Summit that weakens the current manuscripts as presented.*

**Response:** The Fibiger et al. (2016) reported measurement of nitrate isotopes ( $\delta^{15}\text{N}/\Delta^{17}\text{O}$ ) in atmosphere and surface snow at Summit over two months (May to June), making it impossible to use this dataset to inform the seasonal variations in isotopes of primary nitrate. Instead, the Jarvis et al (2009) gave seasonal isotope values from surface snow that we used as sensitivity tests, and we have stated clearly that the surface snow values do not represent that of primary nitrate, but represent the intermediate state between primary nitrate and the final preserved nitrate.

Regarding  $\Delta^{17}\text{O}(\text{NO}_3^-)$ , as we have stated in the manuscript and earlier in our response, the purpose of this manuscript was to investigate the effect of post-depositional processing on the seasonality of snowpack nitrate and its isotopes, and the TRANSITS model applied to this study was never aimed to predict the isotopes of snow nitrate, but to assess the **changes** caused by post-depositional processing upon the preservation of nitrate. What is more, it is well understood that photo-driven post-depositional processing can lead to large N isotope fractionation, while not directly affecting  $\Delta^{17}\text{O}$  that is a mass-independent fractionation signal (Berhanu et al., 2015). Therefore, we should expect a large isotope affect from post-depositional processing on  $\delta^{15}\text{N}$  but not on  $\Delta^{17}\text{O}$ , which is what exactly the model predicted.

### ***D17O mismatch***

*A critical point is that the model cannot match the D17O observations. The authors note that a primary signal therefore must be important in driving the seasonality. Yet, the global chemical modeling results of Alexander et al. (2020) do not match the D17O observations at Summit either, and GEOS-Chem does not include exchange with the snow/post-depositional processing of nitrate. Why not discuss these results compared*

to the understanding trying to be made locally here? With neither a chemical transport model nor a box model matching the results our understanding clearly has a long way to go and there is an important opportunity for the authors to make an advance here. For instance, the key point in the beginning is that post-depositional processing does not significantly affect  $\Delta^{17}\text{O}$ . What is significant? The GEOS-Chem model simulations predict the seasonality of  $\Delta^{17}\text{O}$  well but overestimates the values; would the 2.1 per mil decrease here because of recycling help to resolve much of this over-estimation? If it does, isn't that significant? The lack of significance seems to be related to the fact that 2.1 per mil is much different than the 9 per mil difference seen in the observations, but the co-authors of this work have used changes as small as 2 per mil to argue for significant changes in atmospheric oxidation pathways in other environments. In fact, in the spring surface snow alone the median  $\Delta^{17}\text{O}$  values between 2010 and 2011 change by  $\sim 3$  per mil (Fibiger et al., 2013) – which again can reflect spatial and temporal heterogeneity OR differences in chemistry between years (both of which are not considered in this study).

**Response:** Please see our response to the last comment. Again, it is not our objective to predict the snow  $\Delta^{17}\text{O}$ , but instead to predict **the changes induced by post depositional processing**. What Dr. Hastings asked would be best addressed through incorporation of the snow column model into a chemical transport model such as GEOS-Chem, which is out of the scope of this manuscript.

In addition, “significance” used here is to represent a relative term, and “significant or not” depends on what it is compared with. For averages over a period of hundreds of years, 2 permil difference is significant; while for a seasonal difference of  $> 9$  permil caused mainly by seasonal formation pathway differences, 2 permil difference caused by the post-depositional processing is less significant. Since significance is a statistical term and here we don't use it in statistical sense, we will replace “significant” with “important” in the revised manuscript such as “post-depositional processing is not **important** in determining the  $\Delta^{17}\text{O}$  seasonality”.

### **Other fractionation effects**

*The authors discuss re-formation of nitrate in the snow – does this induce an isotopic effect on  $d_{15}\text{N}$ ? It should be addressed that re-formation within the snow that impacts  $\Delta^{17}\text{O}$  should also impact  $d_{15}\text{N}$  (and  $d_{18}\text{O}$ ) as well.*

*The potential for loss via evaporation/volatilization of nitrate should also be considered (Shi et al., Isotope fractionation of nitrate during volatilization in snow: A field investigation in Antarctica. Geophys Res Lett. 46(6):3287-3297. 10.1029/2019GL081968, 2019)*

**Response:** There are essential differences in nitrogen and oxygen during reformation of snow nitrate. The recombination effect of snow nitrate would induce change in  $\Delta^{17}\text{O}$  because of the secondary chemistry during reformation of nitrate (McCabe et al., 2005; Meusinger et al., 2014), such as exchange with oxygen isotopes of ice. But from the Meusinger et al. experiment, there is no evidence that nitrogen isotopes are altered during reformation. If the reformation is quantitative, one would not expect an isotope effect.

We have added some discussions for physical loss of snow nitrate in our revised manuscript although this study focuses on photolysis impact on snow nitrate, which is thought to be the dominant post depositional process (Erbland et al., 2013; Frey et al., 2009; Berhanu et al., 2015). The Shi et al. (2019) experiment was flawed. They collected snow at the inland Dome A location and put it in an open-door room at Zhongshan Station (a coastal site). Dome A snow is of much higher nitrate concentrations than in snow at the coast (500 ppb at Dome A while 30 ppb at the coast, Shi et al., 2015); thus, a re-equilibrium between snow and the overlying air will be established which will artificially enhance the physical release (evaporation).

In addition, in both evaporation experiments of Shi et al. 2019 and earlier by Erbland et al. (2013), when mass loss is significant at higher temperature, the fractionation factor is very small. At Summit, even using a 25 % mass loss from evaporation (the maximum loss fraction given by Dibb et al. (2007)) and a fractionation constant of 3.6 ‰ (Erbland et al., 2013), only a 1 per mil difference in  $\delta^{15}\text{N}$  can be induced, which is negligible compared to the photolysis induced fractionation.

### ***The conclusion of 21% loss***

*The key conclusion of the manuscript is that “as much as 21% of nitrate is lost”. In the model the majority of this nitrate is not actually lost – it’s redistributed. And the model better explains the seasonality based on a primary signal change. On net, more like 2% of nitrate is actually lost and this agrees with what Fibiger et al (2016)’s observational study based on isotopes found and what Thomas et al. (2011)’s modeling study based on gas phase and snow concentrations of a variety of species found.*

**Response:** We stated clearly in abstract and conclusion that ‘up to 21 % of nitrate was **lost and/or redistributed** after deposition’, and this ratio of loss is referred to a specific (seasonal, monthly or finer resolution) layer below the photic ozone. This value is consistent, or at least within the range of nitrate loss estimated by Dibb et al. 2007 who compared surface snow nitrate concentrations with concentrations at depth. For **annual net loss** it is 4.1 %, assuming 35 % snow sourced nitrate was transported away (export). The fraction of export could be larger, as suggested by Honrath et al. (2002) who concluded that without wet deposition such as snowfall or fog deposition the  $\text{NO}_x$  or  $\text{HNO}_3$  emitted from sunlit snow should be largely exported from local boundary layer at Summit.

When focusing on the seasonality of the isotopes in our manuscript, it is important to distinguish net annual loss from loss of a specific layer. The **net** annual loss can be small since recycling occurs, but the nitrate at depth gets redistributed to the surface snow. Therefore, for specific snow layers below the surface, the loss is larger and so are the isotope effects. It is the loss of a specific layer that determines the **changes** in  $\delta^{15}\text{N}$  from nitrate deposition to its final preservation and influences  $\delta^{15}\text{N}$  seasonality. This is the entire point of this manuscript. Given the seasonally varying actinic flux and snow accumulation rate, we think our calculation is reliable and agrees well with previous studies.

In addition, we would like to point out that the conclusion of ‘**2% of nitrate is**

*actually lost*' from Fibiger et al. (2013) was likely flawed. 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 a severe underestimate. From the supplemental file of Thomas et al. (2011) (Figure 9), the '0.1 %' value actually should be around 1% to 2%.

*Quoting here from the discussion section of Fibiger et al (2016): "Previously, it was thought that local recycling of NO<sub>3</sub> might be important at Summit [Jarvis et al., 2009; Kunasek et al., 2008]. If this were true, however, there should be some connection between local gas phase concentrations and the isotopes of NO<sub>3</sub> in the snow. If HNO<sub>3</sub> were formed locally and deposited by cloud-to-ground scavenging of NO<sub>3</sub> in the snow (Figure 1, arrows d and g), then BrO concentrations above 1 pptv should be influencing NO<sub>3</sub> in the snow [Kunasek et al., 2008; Morin et al., 2007] via reactions (R6) through (R9). In particular, we expect that when BrO is high, the  $\Delta 17O$  and  $\delta 18O$  of nitrate would also be high, as BrO retains the anomalous isotopic signature of the O<sub>3</sub> from which it is derived. The local signal, if important, should be present in the snow as the lifetimes of NO and HNO<sub>3</sub> at Summit are only a few hours. This is evident in the atmospheric HNO<sub>3</sub> and NO concentrations at Summit, as both approach zero at low solar zenith angle. This is evidence that there is some loss or recycling of NO<sub>3</sub> from the snow in Greenland [Honrath et al., 1999], but as noted above, as little as 2% of NO<sub>3</sub> loss from the snow can account for observed NO<sub>x</sub> concentrations above the snow [Thomas et al., 2011]. This photolysis of NO<sub>3</sub> to NO<sub>x</sub> has a significant influence on local NO<sub>x</sub> concentrations and the  $\delta 15N$ -HNO<sub>3</sub> in the atmosphere at Summit, but appears small enough to not have a significant effect on the residual NO<sub>3</sub> in the snow. If photolysis of NO<sub>3</sub> to NO<sub>x</sub> followed by deposition of locally formed HNO<sub>3</sub> (Figure 1, arrows a, c, and d) was having a strong influence on the NO<sub>3</sub> in the snow, we would expect that snow NO<sub>3</sub> concentrations would reflect NO and HNO<sub>3</sub> atmospheric concentrations. There was, however, no connection found between the local concentrations of BrO, NO, or NO<sub>y</sub> and any of the isotopes of NO<sub>3</sub> or [NO<sub>3</sub>]. This lack of relationship was found using 3, 5, and 12 h back averages of the gas phase data, from each time point that a snow sample was taken, accounting for potential variations in the lifetime of NO<sub>x</sub> against deposition as NO<sub>3</sub>. This indicates that local chemistry, either through recycling of NO<sub>3</sub> or local conversion of NO<sub>x</sub> to NO<sub>3</sub>, is not influencing the NO<sub>3</sub> preserved in the snow. This lack of relationship is true both across each season and over shorter timescales within." In the end, our work has suggested that photolytic loss and recycling may be taking place but it represent a very small portion of the overall nitrate in the snow. The authors of present student should be obliged to provide clear evidence as to why this conclusion is not justified.*

**Response:** As responded earlier, the Fibiger et al (2013, 2016) studies were flawed by the fact that only atmospheric and surface snow samples were used and assessed, while it is the samples below the photic zone that should be used to fully quantify the effect of post-depositional processing. In addition, the arguments themselves used by

these studies were also with faults that we describe in details as follows:

Both Fibiger et al. (2013) and Fibiger et al. (2016) concluded that post-depositional processing was negligible at Summit, and the arguments were mainly based on O-isotopes. Fibiger et al. (2013) drew their conclusion because they observed a strong relationship between  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}(\text{NO}_3^-)$  in their **surface snow samples**. But we don't agree that this is evidence of small to no photolysis. First of all, in East Antarctica where severe post-depositional processing occurs, strong correlations between  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}(\text{NO}_3^-)$  in snow and/or aerosol were also observed (Erbland et al., 2013; Frey et al., 2009). **In particular, similar correlations between  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}(\text{NO}_3^-)$  were found in atmospheric and surface snow nitrate at Dome C (attached Figure 1.1, 1.2 and 1.3), where photolysis of snow nitrate has been unambiguously proved to be dominant** (Erbland et al., 2013). So correlations between  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}(\text{NO}_3^-)$  should be viewed as direct transfer of atmospheric signal to surface snow and cannot be viewed as evidence of little to no post-depositional processing.

Second, at Summit, the strong correlation between  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  of nitrate only presents in surface snow ( $R^2=0.9$ ) and becomes weaker ( $R^2=0.32$ ) at depth (Attached Figure 2), suggesting that post-depositional processing takes effect over the duration of the residence time of nitrate in the snow photic zone. This is consistent with the observations at Dome C where the correlations get worse from atmospheric nitrate to snowpit nitrate (Figure 1.1., 1.2 and 1.3). Overall, given the snow accumulation rate at Summit, nitrate stays at the surface (1~2 cm) by only ~one week on average, while it takes nitrate about half year to be buried beneath the photic zone and be ultimately preserved.

Regarding the Fibiger et al. (2016) study, they concluded there is little to no local recycling snow nitrate because that they did not observe increases in snow  $\Delta^{17}\text{O}(\text{NO}_3^-)$  when **atmospheric** BrO concentration increased by ~ a few ppt. However, such argument is biased for several reasons and their assessment was not quantitative. First, BrO originates from local photochemistry as it has a very short lifetime and can't be from long-range transport, and the production of BrO will consume  $\text{O}_3$ . This is a tradeoff regarding their effects on  $\Delta^{17}\text{O}$  of  $\text{NO}_2$  which determines  $\Delta^{17}\text{O}(\text{NO}_3^-)$ . Indeed, BrO could also form nitrate through hydrolysis of  $\text{BrONO}_2$ , which will increase  $\Delta^{17}\text{O}(\text{NO}_3^-)$ . But when BrO concentration increased, how did OH and  $\text{HO}_2/\text{RO}_2$  change as they all related to photochemistry? Observations at Summit suggested BrO concentration always co-varied with OH/  $\text{HO}_2/\text{RO}_2$  (Liao et al., 2011) because they were both controlled by local actinic flux conditions. If OH and  $\text{HO}_2/\text{RO}_2$  concentration also increased (the authors didn't assess these radicals) at the same time, they would decrease  $\Delta^{17}\text{O}(\text{NO}_3^-)$ . Under this circumstance, increases in snow  $\Delta^{17}\text{O}(\text{NO}_3^-)$  is unlikely to occur.

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 unknown. Our calculation suggested that the locally formed nitrate can account for at most 25% of the deposited nitrate in summer and the rest is from transport. Additional nitrate formed from the increased  $\text{BrONO}_2$  hydrolysis is only a part of this locally formed

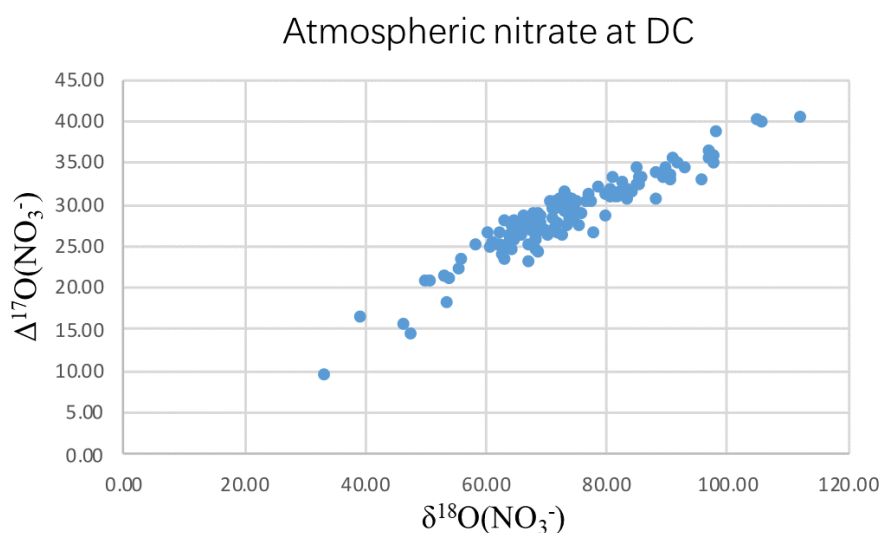


nitrate, and whether its effects on  $\Delta^{17}\text{O}$  is detectable or not has to be carefully assessed, which is beyond the scope of the paper.

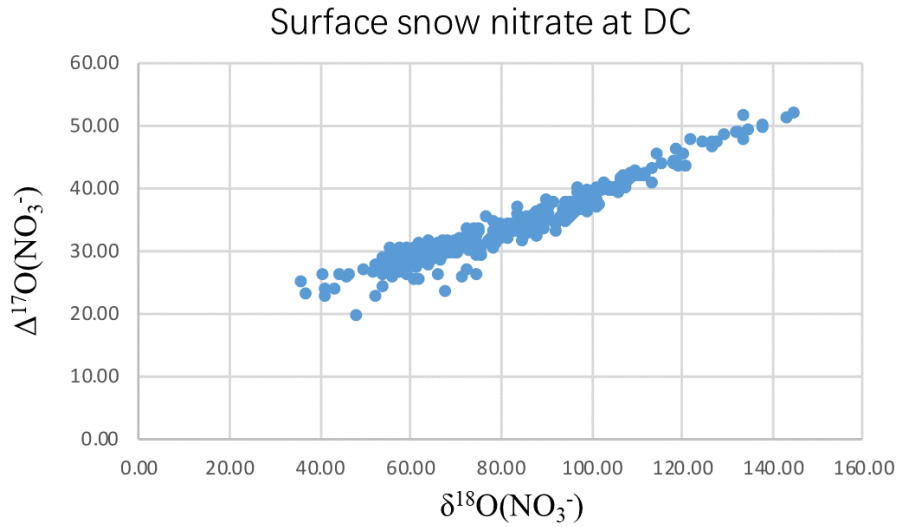
Third, the  $\Delta^{17}\text{O}(\text{NO}_3^-)$  of surface snow (1-3 cm) was used by Fibiger et al. (2016) to compare with the effect of atmospheric BrO concentration increase. Honrath et al. (2002) reported the daily dry depositional flux of atmospheric nitrate at Summit to be  $7.16 \times 10^{11}$  molecules  $\text{m}^{-2} \text{s}^{-1}$ . If **no wet deposition** occurs, the **newly deposited nitrate** during their sampling period (4 to 12 hours) only constitutes a minor fraction of surface snow nitrate: average surface snow (top 2 cm) nitrate concentration at Summit is 100 ppb, which takes about 94 days for dry deposition of atmospheric nitrate to accumulate to this amount. Therefore, even if atmospheric nitrate  $\Delta^{17}\text{O}$  indeed increased because of the BrO concentration increase over a duration of a few hours, it is unlikely to be detectable in snow sample.

Therefore, the conclusion of Fibiger et al. (2016) study was not reliable either. In addition, quoting here the Jarvis et al. 2009 paper that Dr. Hastings is the second author, in their abstract: “*Measurements of isotopically labeled nitrate in surface snow confirm that photolytic recycling of snowpack nitrate, in which photolyzed nitrate products recombine to form  $\text{HNO}_3$  that is subsequently redeposited to the snow surface, does occur at Summit*”. There is a much larger N-isotope effect associated with the post-depositional processing compared to O-isotopes, and it is also the nitrogen isotopes that should be used to reflect and/or assess the effect of post-depositional processing as has been done in Antarctica.

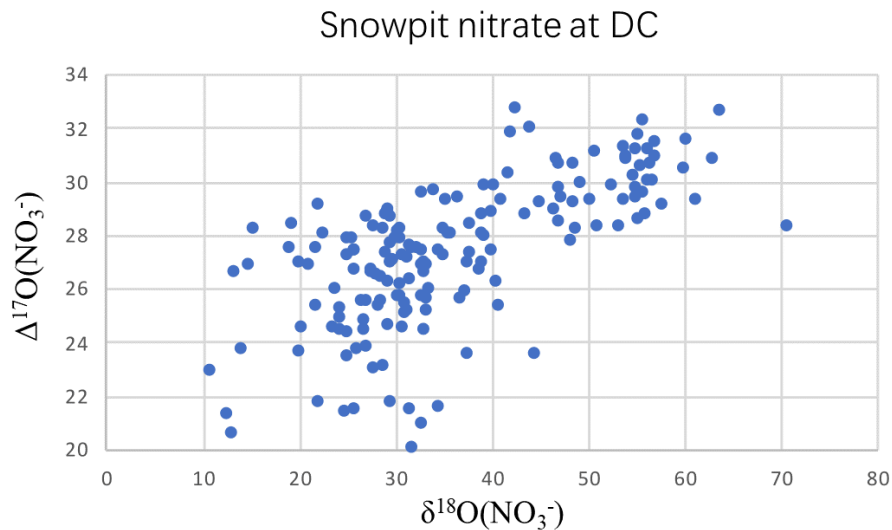
In summary, neither Fibiger et al. 2013 nor 2016 studies can really inform the actual degree of post-depositional processing at Summit for the reasons stated above.



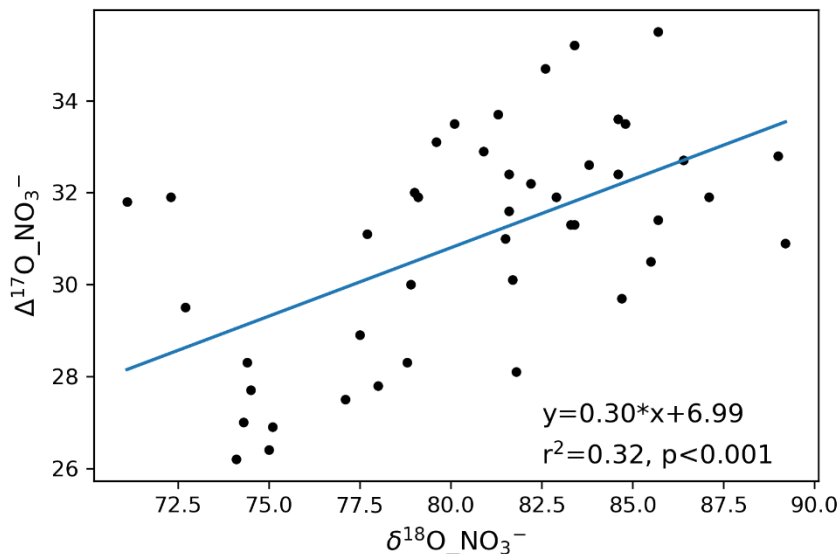
**Figure 1.1** Scatter plot of  $\delta^{18}\text{O}(\text{NO}_3^-)$  versus  $\Delta^{17}\text{O}(\text{NO}_3^-)$  in the atmosphere at Dome C, Antarctic (Erbland et al., 2013).



**Figure 1.2** Scatter plot of  $\delta^{18}\text{O}(\text{NO}_3^-)$  versus  $\Delta^{17}\text{O}(\text{NO}_3^-)$  in the surface snow at DC. Note the relatively low snow accumulation rate at DC ( $\sim 10$  cm per year) leads to significant post-depositional processing thereby. However, the strong correlation between  $\delta^{18}\text{O}(\text{NO}_3^-)$  and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  similar to Summit is also observed, suggesting the uppermost snow nitrate doesn't undergo much post-depositional processing but a direct representation of atmospheric nitrate signals.



**Figure 1.3** Scatter plot of  $\delta^{18}\text{O}(\text{NO}_3^-)$  versus  $\Delta^{17}\text{O}(\text{NO}_3^-)$  in the bulk snowpack at DC. The strong correlation weakens when referring to the whole snowpack as a result of post-depositional processing (Erbland et al., 2013).



**Figure 2.** Correlation between  $\delta^{18}\text{O}(\text{NO}_3^-)$  versus  $\Delta^{17}\text{O}(\text{NO}_3^-)$  in the bulk snowpack ( $\sim 2\text{m}$ ) at Summit (Geng et al., 2014). This correlation is much weaker than that in surface snow reported by Fibiger et al. 2013 ( $r^2=0.9$ ). The  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}(\text{NO}_3^-)$  correlation at depth becomes worse, and which reflects the effect of post-depositional processing.

*An approach that truly considers past work and challenges/reconsiders previous interpretations, based on a robust comparison between the model and observations, is needed and not provided in this manuscript. Rather, model results are presented that 1) show that the isotopic composition of preserved nitrate is quite sensitive to the assumed signature in nitrate when first deposited, and 2) suggest that photolysis of nitrate may significantly modify the seasonal profile in  $\delta^{15}\text{N}$  if enough of the nitrate in the snow is photolyzed. The authors assert that the seasonal variation in the isotopic composition of deposited nitrate is too poorly constrained to consider that it might be preserved largely unaltered (our conclusion from multiple prior studies), and conclude that the observed seasonal pattern is created by post-depositional photolysis (their assumption at the outset, neglecting prior peer-reviewed work).*

**Response:** We appreciate the large body of studies conducted by Dr. Hastings's group, but again the "conclusion from multiple prior studies" were mainly based on surface snow samples and O isotopes that are not suitable to determine the effect of post-depositional processing, and can't be simply compared with the TRANSITS model results. We have argued this in the introduction part of our manuscript.

The seasonality in  $\delta^{15}\text{N}$  on which the model focused is independent of the values of primary nitrate  $\delta^{15}\text{N}$ , so is the difference in  $\delta^{15}\text{N}$  between primary nitrate and the finally preserved nitrate (i.e., PIE, the photo-induced isotope effect in the model). The modeled photolysis of snow nitrate is well constrained by, and comparable with the observed snowpack NOx emissions, and the modeled seasonality and  $\delta^{15}\text{N}$  change upon preservation compare well with observed snowpack  $\delta^{15}\text{N}$  seasonality (Hastings et al., 2004, Jarvis 2009 and Geng et al. 2014), and the observed difference in  $\delta^{15}\text{N}$  between

surface snow nitrate and that at depth (Jarvis et al., 2009), respectively. Therefore, we think we present a robust comparison between the model and observations, and did not ignore any prior peer-reviewed work. The Fibiger et al (2013, 2016) studies we have briefly discussed in the introduction and stated why we don't agree with their conclusions. We did not compare the data in these two studies though, because they only reported data in a couple of months and no seasonal information can be informed, and thus are not suitable to include in the model comparison.

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