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# **Impacts of the photo-driven post-depositional processing on snow nitrate and its isotopes at Summit, Greenland: a model-based study**

**Zhuang Jiang<sup>1</sup>, Becky Alexander<sup>2</sup>, Joel Savarino<sup>3</sup>, Joseph Erbland<sup>3</sup>, Lei Geng<sup>1,4,5,6\*</sup>**

<sup>1</sup>Anhui Province Key Laboratory of Polar Environment and Global Change, School of Earth and Space Sciences, University of Science and Technology of China, Hefei, Anhui, China

<sup>2</sup>Department of Atmospheric Sciences, University of Washington, Seattle WA, USA

<sup>3</sup>Univ. Grenoble Alpes, CNRS, IRD, G-INP, Institut des Géosciences de l'Environnement, Grenoble, France

<sup>4</sup>Laboratory for Ocean Dynamics and Climate, Pilot Qingdao National Laboratory for Marine Science and Technology, Qingdao, Shandong, China

<sup>5</sup>CAS Center for Excellence in Comparative Planetology, University of Science and Technology of China, Hefei, Anhui, China

<sup>6</sup>Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei, Anhui, China

\*Corresponding to: Lei Geng (genglei@ustc.edu.cn)

## **Key Points:**

- Snow nitrate is redistributed in the photic zone by post-depositional processing
- As much as 21 % snow nitrate is lost after deposition
- The observed seasonality of snow  $\delta^{15}\text{N}(\text{NO}_3^-)$  is explained by the post-depositional processing

## **Abstract**

Atmospheric information embedded in ice-core nitrate is disturbed by post-depositional processing of snow nitrate. Such processes were thought to be minimal at Summit, Greenland due to the high snow accumulation rate, but the effects on nitrate preservations have not been thoroughly assessed. Here we used a layered snow photochemical column model to investigate the loss of snow nitrate through the post-depositional processing at Summit, and the induced effects on snow nitrate isotopes ( $\delta^{15}\text{N}$  and  $\Delta^{17}\text{O}$ ). We found significant redistribution of nitrate in the upper snowpack caused by the post-depositional processing, and up to 21 % of nitrate was lost after deposition. The model reproduced the observed  $\delta^{15}\text{N}$  seasonality considering only the effects of the post-depositional processing, with a relatively small seasonal  $\Delta^{17}\text{O}$  change ( $\sim 3\text{‰}$ ) compared to the observations ( $9\text{‰}$ ). The results highlight the importance of the post-depositional processing in snow nitrate preservation even at high snow accumulation sites.

## **Plain Language Summary**

Ice-core nitrate contains information regarding past atmospheric abundances of  $\text{NO}_x$  and oxidants which are important for ozone and secondary aerosol production, as well as for the removal of greenhouse gases. However, after deposition, snow nitrate will be recycled back to the air, and this process disturbs the link between ice core nitrate and the atmosphere. It has been thought that fast snowfall will bury nitrate quickly and limit the degree of change in nitrate and its isotopes after deposition, and

thus snowpack or ice-core nitrate in regions with high snow accumulation such as Summit Greenland would be representatives of atmospheric signals. Here we demonstrate that even at high snow accumulation site, the process after deposition is still very active and leads to severe changes in nitrate and its isotopes compared to the atmospheric origins, and such changes have to be considered and/or corrected when using ice-core nitrate concentration and isotope records to retrieve past atmospheric  $\text{NO}_x$  and oxidant information.

## 1. Introduction

Nitrate ( $\text{NO}_3^-$ ) is one of the most abundant inorganic ions preserved in ice cores. Nitrate is the final product of atmospheric  $\text{NO}_x$  ( $= \text{NO} + \text{NO}_2$ ), and ice-core nitrate has been sought to provide information on past atmospheric  $\text{NO}_x$  abundance (Wolff, 1995). One of the major subjects of ice-core nitrate studies involves the oxygen mass-independent isotope fractionation signal ( $\Delta^{17}\text{O} = \delta^{18}\text{O} - 0.52 \times \delta^{17}\text{O}$ ) of nitrate, which is a proxy to reconstruct past atmospheric oxidation capacity (Alexander & Mickley, 2015; Alexander et al., 2004; Geng et al., 2017). There are many factors, e.g., atmospheric chemistry and transport, deposition and post-depositional processing of nitrate, affecting ice core nitrate and its isotopes (Geng et al., 2014; Geng et al., 2015; Morin et al., 2008; Wolff et al., 2008).

Deposition of atmospheric nitrate to snow is not irreversible. After deposition, nitrate can undergo post-depositional processing which causes changes in its concentration and isotopes (Blunier et al., 2005; Erbland et al., 2013; Frey et al.,

2009). The post-depositional processing includes physical release of  $\text{HNO}_3$  (i.e., desorption and evaporation) from snow and ultraviolet photolysis of snow nitrate. Both processes result in loss of snow nitrate and isotope fractionations of nitrogen and oxygen. However, laboratory experiments and model calculations indicate a minor influence of the physical processes and it is photolysis that dominates the post-depositional processing (Erland et al., 2013; Frey et al., 2009; Shi et al., 2019).

Snow nitrate photolysis occurs when exposed to sunlight at wavelengths less than 345 nm (Chu & Anastasio, 2003). The dominant photolysis products are  $\text{NO}_2$ , which can be effectively transported to the overlying atmosphere via diffusion or wind pumping (Zatko et al., 2013) and impacts local atmosphere oxidation environment (Thomas et al., 2012). The released  $\text{NO}_2$  can reform  $\text{HNO}_3$  in the overlying atmosphere, which will be then redeposited or exported from the site of photolysis. The above-mentioned processes form a cycle of nitrate between the air–snow interface, resulting in redistribution of nitrate in snow layers.

The isotopic composition of nitrate changes significantly during photolysis. The isotope fractionation factors ( $\epsilon_p$ ) associated with snow nitrate photolysis is -47.9 ‰ for  $\delta^{15}\text{N}$  and -34 ‰ and  $\delta^{18}\text{O}$  under the conditions at Dome C, Antarctica (Berhanu et al., 2014; Frey et al., 2009). These large negative values indicate that snow nitrate photolysis would induce large isotope fractionation which leave the nitrate remaining in the snowpack enriched in heavier isotopes (i.e.,  $^{15}\text{N}$  and  $^{18}\text{O}$ ). In comparison,  $\Delta^{17}\text{O}(\text{NO}_3^-)$  in snow will not be disturbed by photolysis directly. However, part of the photolysis product can undergo recombination reactions to reform nitrate before

escaping from snow (i.e., the cage effect) (McCabe et al., 2005; Meusinger et al., 2014). This process results in exchanges of oxygen atom with snow water, leading to decreases in snow  $\Delta^{17}\text{O}(\text{NO}_3^-)$  and  $\delta^{18}\text{O}(\text{NO}_3^-)$ . These isotope effects in snow nitrate photolysis have been documented in multiple snowpack studies across east Antarctica, with increasing  $\delta^{15}\text{N}$  and decreasing  $\Delta^{17}\text{O}(\text{NO}_3^-)/\delta^{18}\text{O}(\text{NO}_3^-)$  with depth (Erbland et al., 2013; Frey et al., 2009).

The degree of the photo-driven post-depositional processing is influenced by several factors including actinic flux, snow light-absorbing impurities (e.g., black carbon, organic acid and mineral dust) and snow accumulation rate (Zatko et al., 2013). Snowpit observations from coastal to inland Antarctica reveal that the degree of the post-depositional processing and the induced isotope effects vary dramatically with snow accumulation rate (Erbland et al., 2013; Shi et al., 2015). Snow accumulation rate determines the residence time of nitrate in the snow photic zone where photolysis occurs and is defined as 3 times the e-folding depth of actinic flux in snow, and thus at sites with high snow accumulation rate the degree of post-depositional processing will be limited.

Distinct seasonality in the concentration and isotopes of snowpack nitrate were observed at Summit Greenland (Geng et al., 2014; Hastings et al., 2004). The seasonality of  $\delta^{15}\text{N}$  was attributed to the variations in  $\text{NO}_x$  sources (Hastings et al., 2004) and a later study by Fibiger et al. (2013) further suggested at this site nitrate is largely preserved and its isotopic composition is representative of atmospheric nitrate. The effect of post-depositional processing was thought to be minimum at Summit (Hastings

et al., 2004; Fibiger et al., 2013), largely due to the high snow accumulation rate (65 cm of accumulated snow per year) (Dibb & Fehsenfeld, 2004). Nevertheless, there is evidence that post-depositional processing is active at this site. For example, Burkhardt et al. (2004) and Dibb et al. (2007) have estimated < 7 % to 25 % loss of nitrate after deposition based on concentration measurements. Regardless of the various degrees of post-depositional processing of snow nitrate at Summit suggested by different studies, the large isotope fractionation factors associated with snow nitrate photolysis may induce significant isotope effects even for relatively small degree of post-depositional processing.

In this study, in order to investigate the impacts of snow nitrate photolysis on the preservation of nitrate and its isotopes at Summit, Greenland, we used a snow photochemical column model (TRANSITS, Transfer of Atmospheric Nitrate Stable Isotopes To the Snow, Erbland et al., 2015) to simulate the recycling of nitrate at the air-snow interface, and compared the modeled seasonal variations in snowpack nitrate concentrations and isotopes with observations. The results should add insights into the preservation of nitrate at high snow accumulation sites and shed light on the interpretation of ice-core nitrate and its isotopes.

## **2. Model description**

TRANSITS is a multi-layer, 1-D model that simulates the recycling of nitrate at the air-snow interface, as well as the preservation of nitrate and its isotopes. In brief, the model divides a year into 52-time steps (i.e., weekly temporal resolution) and at

each time step the snowpack is divided into 1 mm layers where photolysis of nitrate and the associated  $\text{NO}_2$  production are calculated according to the depth-dependent actinic flux and nitrate concentration.  $\text{NO}_2$  is then transported to the overlying atmosphere where it is re-oxidized to nitrate. At the next time step, a portion of the reformed nitrate together with primary nitrate originating from long-range transport deposit to snow surface. When snowfall occurs, the snowpack moves down a certain depth and the newly deposited snow on the top is immediately re-divided into 1 mm layers. A snow layer is archived once it is buried below the photic zone.

At each step, the model also calculates the isotope effects associated with the recycling of nitrate at the air-snow interface. In the model, nitrogen isotope fractionation mainly occurs during the photolysis of snow nitrate with a wavelength sensitive fractionation constant  $\epsilon_p$ , and another fractionation occurs during the deposition of nitrate with a fractionation constant  $\epsilon_d$ . The effect on oxygen isotopes is only calculated for  $\Delta^{17}\text{O}$ , which is caused by 1) exchange of oxygen atoms with water during snow nitrate photolysis (i.e., the cage effect), and 2) the local atmospheric  $\text{NO-NO}_2$  cycling and the subsequent conversion of  $\text{NO}_2$  to  $\text{HNO}_3$ .

To run the model, actinic flux and its e-folding depth in snowpack, snow accumulation rate, as well as other atmospheric properties including the boundary layer height, surface ozone and  $\text{HO}_x$  concentrations are needed. Additional model inputs are the flux of primary nitrate from long-range transport ( $F_{\text{pri}}$ , the ultimate source of nitrate to the ice sheet) and its isotopic composition (i.e.,  $\delta^{15}\text{N}$  and  $\Delta^{17}\text{O}$ ).



In this study, we run the model from the year 2004 to 2007 constrained by observations of local conditions at Summit. The modeled snow nitrate concentration and isotope profiles were then compared with the observations (Geng et al., 2014). Model parameterization and initiation are described in the following section.

## **2.1 Model inputs**

### **2.1.1. Atmospheric characterization**

The overlying atmosphere at Summit was assumed to be a well-mixed one-dimensional box with constant boundary layer height of 156 m (Cohen et al., 2007), where primary nitrate and snow-sourced nitrate are mixed. Weekly air temperature, surface pressure, surface ozone concentration and total column ozone (TCO) at Summit were obtained from the NOAA ozonesonde dataset (<https://www.esrl.noaa.gov/gmd/ozwv/ozsondes/sum.html>). Local OH, peroxy radicals ( $\text{RO}_2$ ,  $\text{HO}_2$ ) and BrO concentrations used to calculate the cycling of NO and  $\text{NO}_2$  and the subsequent reformation of  $\text{HNO}_3$  were parameterized as described in *SI*.

### **2.1.2 Radiative transfer and nitrate photolysis rate in snow**

The actinic flux in snow was obtained by using the Troposphere Ultraviolet and Visible (TUV) radiation model (Madronich et al., 1998) and the Two-stream Analytical Radiative TransfEr in Snow (TARTES) model (Libois et al., 2013). Downward actinic flux spectrum at snow surface from 280 to 350 nm in 1 nm increments was calculated using the TUV model constrained by the observed TCO. The radiative transfer inside the snowpack was then computed using the TARTES

model. Given Summit snow physical and chemical properties, we calculated an e-folding depth of 12.3 cm which is comparable to other studies (*SI*).

The photolysis rate constant of snow  $\text{NO}_3^-$  was calculated by:

$$J(z) = \int_{280 \text{ nm}}^{350 \text{ nm}} \Phi(\lambda) \times \sigma_{\text{NO}_3^-}(\lambda) \times I(z, \lambda) d\lambda \quad (1)$$

Where  $I$  is the actinic flux as a function of wavelength and depth in snowpack,  $\Phi$  and  $\sigma$  is the quantum yield and absorption cross section of nitrate photolysis, respectively. To calculate  $J(z)$ , we used the absorption cross sections of  $^{14}\text{NO}_3^-$  and  $^{15}\text{NO}_3^-$  calculated by the *ZPE* shift method from Berhanu et al. (2014) and the depth and wavelength dependent  $I$  calculated using the TARTES model. A quantum yield of 0.002 was estimated based on observed  $j_0(\text{NO}_3^-)$  in surface snow (*SI*).

### 2.1.3 Flux of primary nitrate ( $F_{\text{pri}}$ ) and the export fraction

Primary nitrate from long range transport was assumed to be the only external nitrate source for Summit. Given the mean snow accumulation rate ( $250 \text{ kg m}^{-2} \text{ a}^{-1}$ ), and the mean snowpack nitrate concentration ( $117 \text{ ng g}^{-1}$ ) at Summit, a minimum  $F_{\text{pri}}$  of  $6.6 \times 10^{-6} \text{ kgN m}^{-2} \text{ a}^{-1}$  was estimated and used in the model. This value is at the same order of magnitude as calculated by Zatzko et al. (2016) using the GEOS-Chem model ( $\sim 2 \times 10^{-6} \text{ kgN m}^{-2} \text{ a}^{-1}$ ). In order to investigate the effect of the photo-driven post-depositional processing on snowpack nitrate profiles, we assumed that  $F_{\text{pri}}$  was equally distributed in 52 weeks in a year, and with constant  $\delta^{15}\text{N}$  and  $\Delta^{17}\text{O}$  values of 0‰ and 30‰, respectively. The  $\delta^{15}\text{N}$  and  $\Delta^{17}\text{O}$  values are close to their observed annual average in Summit snow (Geng et al., 2014).

Another parameter influencing the preservation of nitrate is the export fraction,  $f_{\text{exp}}$ , which represents the fraction of the snow sourced  $\text{NO}_x$  and nitrate transported away from the site of photolysis via wind. According to Summit conditions, we estimated a  $f_{\text{exp}}$  of 0.15 (SI) following the method used by Erbland et al. (2015).

### 2.1.3 Calculation of the isotope effects

The nitrogen isotope fractionation constant ( $^{15}\epsilon_p$ ) during photolysis was calculated from the ratio of  $^{14}\text{NO}_3^-$  and  $^{15}\text{NO}_3^-$  photolysis rates ( $^{15}\epsilon_p = J^{15}/J^{14} - 1$ ), while for the fractionation constant associated with nitrate deposition, we adopted a  $\epsilon_d$  of 10 ‰ following Erbland et al. (2013). As the photolysis rate constant is wavelength sensitive, the calculated  $^{15}\epsilon_p$  varies seasonally (Figure 3a). For oxygen isotopes, the  $\Delta^{17}\text{O}$  of the reformed nitrate in the air was assumed to be 2/3 of  $\Delta^{17}\text{O}(\text{NO}_2)$ , and  $\Delta^{17}\text{O}(\text{NO}_2)$  was estimated according to the  $\text{O}_3$  and BrO oxidation of NO to  $\text{NO}_2$  versus  $\text{HO}_2$  and  $\text{RO}_2$  oxidation in the NO- $\text{NO}_2$  cycling. The  $\Delta^{17}\text{O}$  value of bulk  $\text{O}_3$  was  $(22.9 \pm 1.9)$  ‰ (Vicars et al. 2012), that of BrO was 34.3 ‰, and other oxidants were 0‰. We assumed a cage effect of 15 % following Erbland et al. (2015).

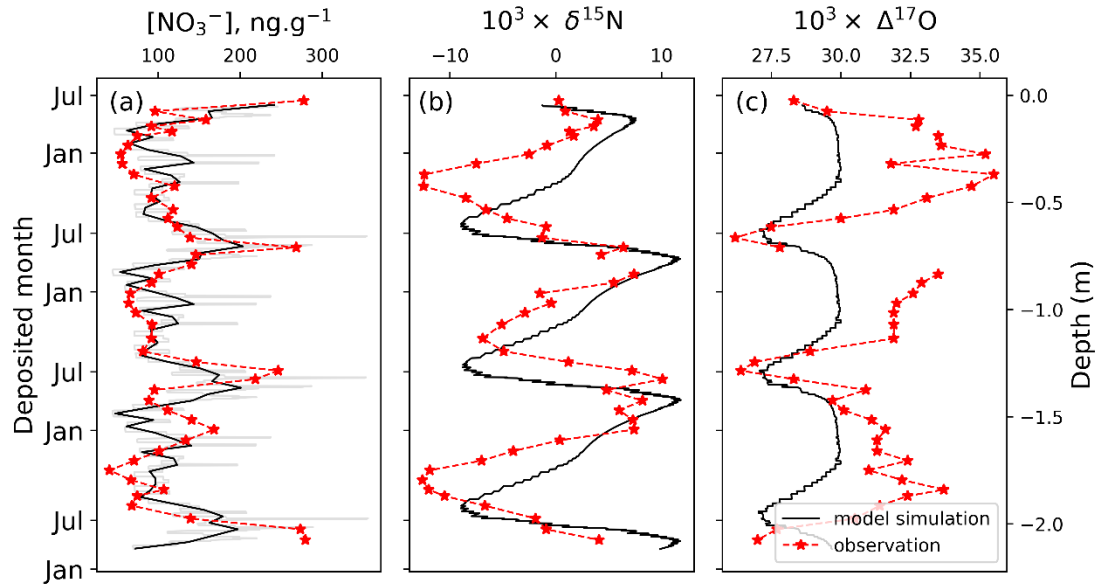
## 2.2. Model initiation

The model was initiated by deposition of primary nitrate mixed with snow-sourced nitrate formed through  $\text{NO}_2$  emitted from the snowpack. The flux and isotope composition of the primary nitrate were set as described in the previous section. A real snowpack with a depth of 2.1 m and known nitrate concentration and isotope profiles (Geng et al., 2014) was used for the snowpack at time  $(t) = 0$ . We run the model from July 2004 to July 2007. Snow accumulates weekly (i.e., 52-time steps

in year) on the top of the pre-existing snowpack. The weekly snow accumulation rate used in the model is shown in Figure S1, which were obtained by averaging the observed snow accumulation of the same week (week 1<sup>th</sup> to week 52<sup>th</sup>) of a year over the 5 years' of observations at Summit from 2003 to 2007 (data are available at [ftp://ftp.summitcamp.org/pub/data/GEOSummit/Bales\\_UCM/BambooForest/BambooForestAccumulationLog.xls](ftp://ftp.summitcamp.org/pub/data/GEOSummit/Bales_UCM/BambooForest/BambooForestAccumulationLog.xls)). This averaged weekly snow accumulation rate was repeated for 3 years in the model. Average instead of real accumulation data were used to avoid negative values in some weeks due to wind blowing which causes net loss instead of gain of snow. After three years' simulation, the snow nitrate concentration and isotope profiles above the pre-existing snowpack were taken to compare with observations at Summit previously reported by Geng et al. (2014).

### **3. Results and discussion**

#### **3.1 The simulated snowpack nitrate depth profiles at Summit, Greenland**



**Figure 1.** Comparison between the observed and modeled snowpack nitrate profiles. We used same snow accumulation rate for each year in the model. The measured minimum  $\Delta^{17}\text{O}(\text{NO}_3^-)$  is used as indicator of June-July when local photochemistry is most active.

Figure 1 shows the observed and modeled weekly snowpack nitrate concentration and its isotopes (i.e.,  $\delta^{15}\text{N}$  and  $\Delta^{17}\text{O}$ ) from July 2004 to 2007. The observations were from a snowpit collected in July 2007 so that the top of the observed profiles represents a summer, and we used the observed  $\Delta^{17}\text{O}$  minimum to identify other summers to match the modeled profiles with the observations.

As shown in Figure 1, nitrate concentrations and isotopes in the modeled snowpack display similar seasonal patterns as the observations, except for  $\Delta^{17}\text{O}$  whose magnitude of the seasonal change is much smaller than the observation. The modeled depth-average  $\text{NO}_3^-$  concentration was  $(115 \pm 55) \text{ ng g}^{-1}$ , similar to the observed value of  $(117 \pm 62) \text{ ng g}^{-1}$ . The modeled concentration profile displays high variability which is likely caused by variations in weekly snow accumulation. Nevertheless, clear summer peaks and winter valleys similar to the observations are seen in the modeled profile. Since the input of primary nitrate remained the same

throughout a year, the summer high nitrate concentration in the model was caused by the relative low snow accumulation rate in late spring and early summer (Figure S1) and then the redistribution of snow nitrate caused by the post-depositional processing. In particular, without photolysis, the concentration peak should appear in late spring/early summer when snow accumulation rate was low. But throughout summer, nitrate deposited earlier was recycled back to the surface continuously, shifting the peak to appear later in summer. The recycling relies on strong summer solar radiation which activates both snow chemistry and atmospheric chemistry. The result highlights the importance of local chemistry in the seasonal distribution of snow nitrate concentrations.

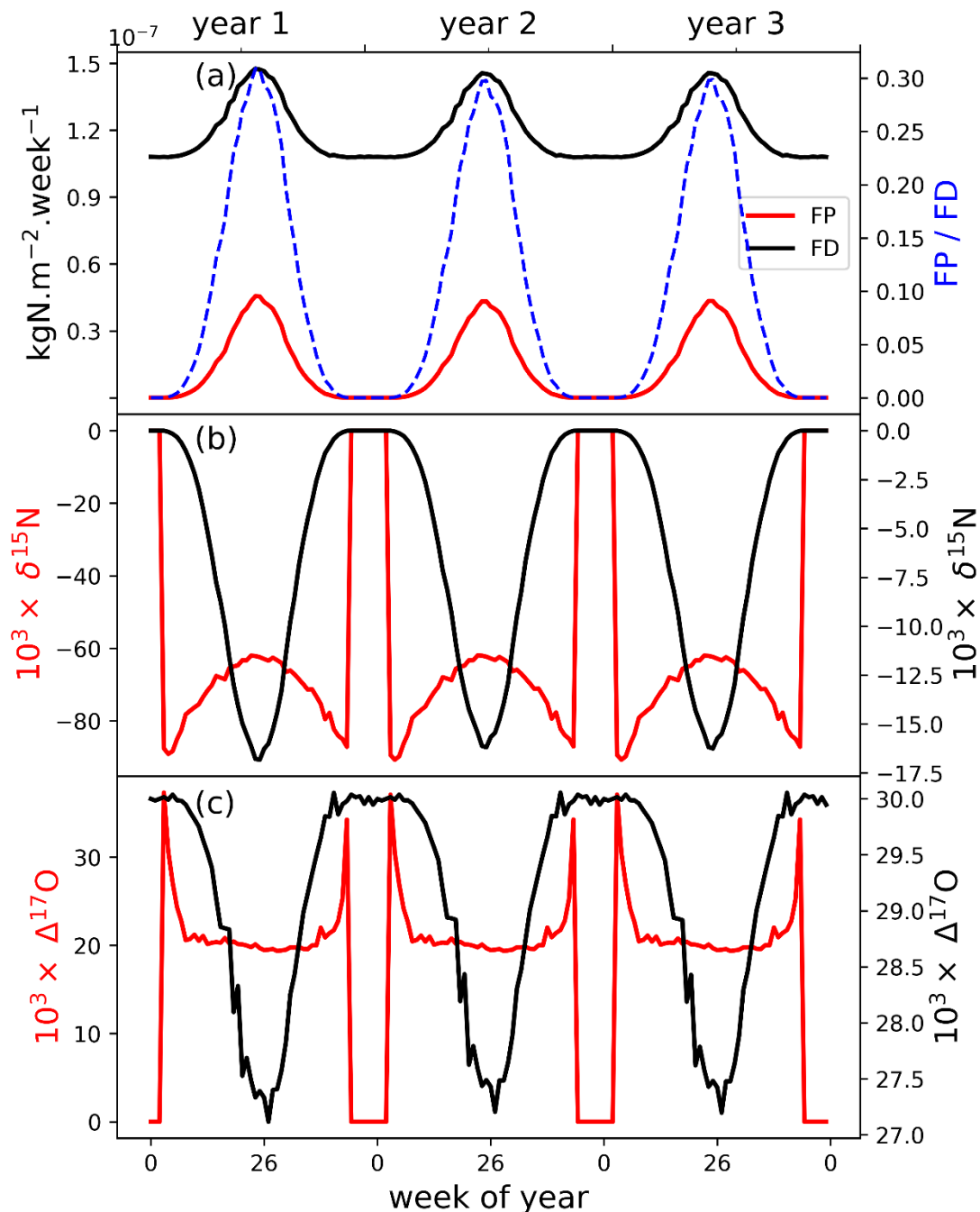
The strong photolysis in summer also explains why the modeled  $\Delta^{17}\text{O}(\text{NO}_3^-)$  deviated by about  $-3\text{‰}$  from primary nitrate ( $\Delta^{17}\text{O}(\text{NO}_3^-) = 30\text{‰}$ ). In summer, nitrate reformed in the overlying atmosphere is mainly through OH oxidation of  $\text{NO}_2$ . In the model, nitrate formed through this process possessed  $\Delta^{17}\text{O}$  of  $(19.7 \pm 0.3)\text{‰}$  on average. This value is close to the model results ( $18.9\text{‰}$ ) by Kunasek et al. (2008) who used a box model assuming local  $\text{NO}_x$  chemistry is the only nitrate source and produced summer  $\Delta^{17}\text{O}(\text{NO}_3^-)$  ( $2\text{--}7\text{‰}$ ) lower than the observations. In our model, the  $\Delta^{17}\text{O}(\text{NO}_3^-)$  of  $F_{\text{pri}}$  was  $30\text{‰}$ , and  $F_{\text{pri}}$  mixed with the reformed nitrate resulting in  $3\text{‰}$  lower  $\Delta^{17}\text{O}(\text{NO}_3^-)$  in summer than in other seasons (Figure 2c). In comparison, the observed seasonal  $\Delta^{17}\text{O}(\text{NO}_3^-)$  change is about  $9\text{‰}$ , suggesting that the observed seasonality of  $\Delta^{17}\text{O}(\text{NO}_3^-)$  at Summit is probably mainly caused by the seasonal differences in  $\Delta^{17}\text{O}(\text{NO}_3^-)$  of  $F_{\text{pri}}$  which was not taking into account in our model,

though the model didn't consider local winter chemistry either. In addition, cage effect during the photolysis would further reduce  $\Delta^{17}\text{O}(\text{NO}_3^-)$  in snow, but this effect is negligible as discussed in section 3.3.

For  $\delta^{15}\text{N}(\text{NO}_3^-)$ , although with some discrepancies, the modeled seasonal pattern reproduced the observations reasonably well. The discrepancies could be due to that the model didn't consider  $\delta^{15}\text{N}$  variations of  $F_{\text{pri}}$ , and the interannual variability in snow accumulation. In addition, the model didn't consider the seasonal differences in local  $\text{NO}_x$  chemistry and the associated isotope effect (Jarvis et al., 2008). The modeled  $\delta^{15}\text{N}(\text{NO}_3^-)$  ranged from -9.5 ‰ to 11.9 ‰ in a year with a spring peak. In comparison, the observed  $\delta^{15}\text{N}(\text{NO}_3^-)$  varies from -12.6 ‰ to 10.1 ‰ over a year, and also with a spring peak (Hastings et al. 2004; Geng et al. 2014). In our model, since  $\delta^{15}\text{N}(\text{NO}_3^-)$  of  $F_{\text{pri}}$  remained constant (0 ‰) throughout a year, the modeled seasonal changes in  $\delta^{15}\text{N}(\text{NO}_3^-)$  was entirely caused by the post-depositional processing. Post-depositional processing starts after polar sunrise and continues to operate until the beginning of polar winter. During this time, the effect of post-depositional processing accumulates, and the spring snow layer has experienced the largest degree of post-depositional processing and thus exhibits the most enriched  $\delta^{15}\text{N}$ . This is demonstrated by the lost fraction of snow nitrate after deposition. As shown in Figure 3a, throughout a year the lost fraction of nitrate is the highest in the 18<sup>th</sup> week (i.e., the first week of May). The accumulated snow thickness at Summit is  $\sim (65 \pm 10) \text{ cm a}^{-1}$  (Figure S1), which is twice the depth of the photic zone at Summit, therefore there should be no additional

post-depositional processing after a year and the spring high  $\delta^{15}\text{N}(\text{NO}_3^-)$  caused by the post-depositional processing is preserved as seen in the model and observations.

### 3.2 Seasonality of photolysis flux (FP) and deposition flux (FD)



**Figure 2.** Weekly distribution of photolysis flux (FP) and deposition flux (FD) and their nitrate isotopic compositions.



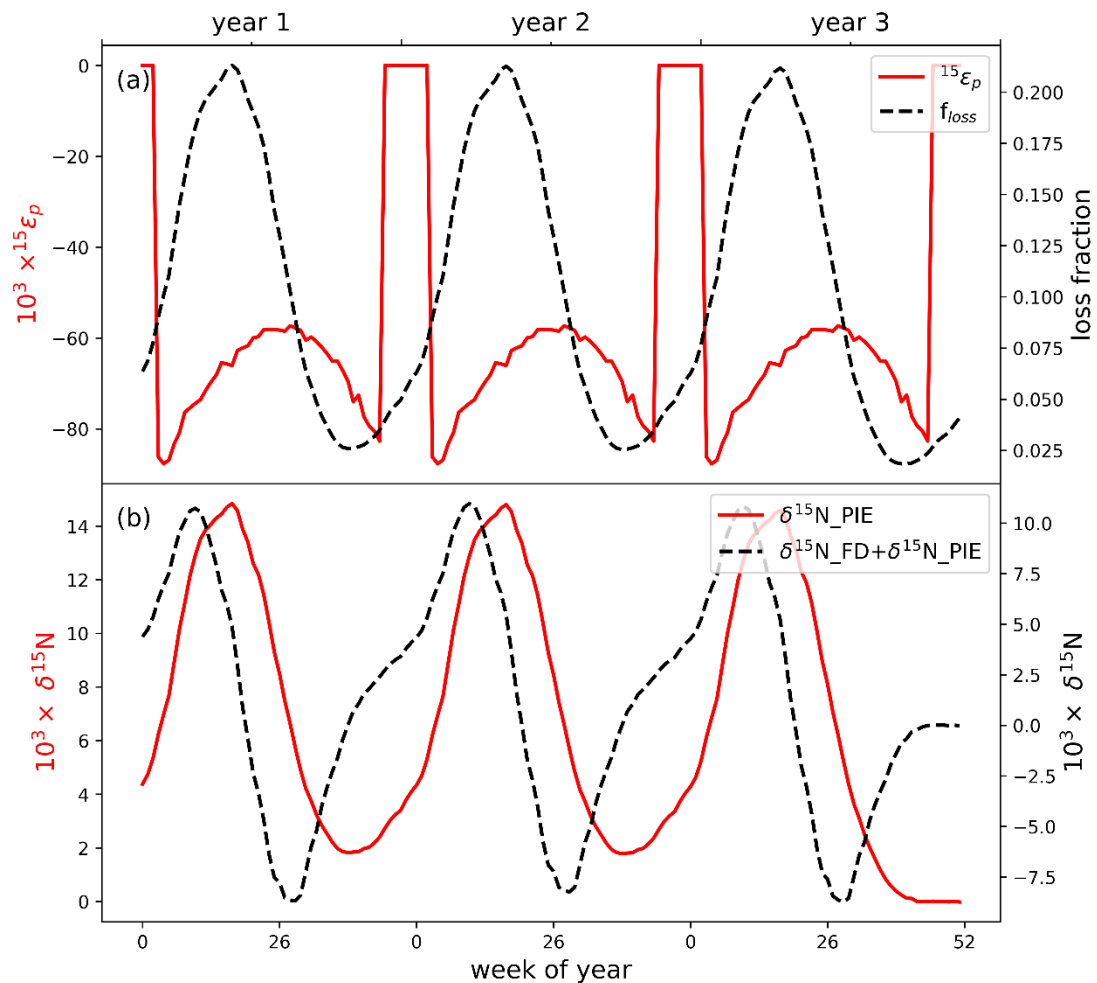
To discern the processes leading to the seasonal isotope patterns, we investigated the weekly nitrate deposition flux (FD) and its isotopes, as well as the weekly flux of snow-sourced nitrate (FP) and its isotopes in the model. Figure 2 displays the magnitude and isotope composition of nitrate in FP and FD. During mid-summer when actinic flux reached its maximum, FP also reached a maximum (and is zero in winter). FD was a mixture of  $F_{\text{pri}}$  and FP, so it also reached a maximum in summer due to the contribution of FP. This in part explains the modeled summer peak of nitrate concentration.

The  $\delta^{15}\text{N}$  of FP was severely depleted compared to  $F_{\text{pri}}$ .  $\delta^{15}\text{N}$  of FP gradually increased from the onset of photolysis, and reached the highest in mid-summer and decreased after that (Figure 2b). This is mainly caused by the wavelength-dependent  $\epsilon_p$  which varied from -57 ‰ to -87 ‰ at Summit (Figure 3a) and reached its highest value in mid-summer. The  $\delta^{15}\text{N}(\text{NO}_3^-)$  of FD again was a combined effect of FP and  $F_{\text{pri}}$ . Therefore  $\delta^{15}\text{N}(\text{NO}_3^-)$  of FD was the lowest in summer when the contribution of FP was the largest, and the highest in winter when there was no contribution from FP. This seasonal pattern in  $\delta^{15}\text{N}(\text{NO}_3^-)$  of FD represents the seasonal  $\delta^{15}\text{N}(\text{NO}_3^-)$  change in surface snow. In addition, the modeled seasonal pattern of  $\delta^{15}\text{N}(\text{NO}_3^-)$  in FD is consistent with that of atmospheric  $\delta^{15}\text{N}(\text{NO}_3^-)$  measured both in Greenland and Antarctica where summer low  $\delta^{15}\text{N}(\text{NO}_3^-)$  was observed (Erbland et al., 2013; Morin et al., 2008; Walters et al., 2019). This is due to the contribution of snow-sourced nitrate that is depleted in  $\delta^{15}\text{N}$  relative to atmospheric nitrate. The isotope effect in  $\delta^{15}\text{N}$  during the deposition of nitrate was also calculated but turned out to be negligible (SI).

After deposition, the post-depositional processing enriches  $\delta^{15}\text{N}(\text{NO}_3^-)$  in snow through photolysis until that snow layer is buried under the photic zone. Here we defined the enrichment in snow  $\delta^{15}\text{N}(\text{NO}_3^-)$  caused by the photolysis as PIE (the photolysis-induced isotope effect), which was the highest in the 18<sup>th</sup> week of the year, corresponding to the highest remaining fraction (Figure 3a). As  $\delta^{15}\text{N}(\text{NO}_3^-)$  of FD represents the  $\delta^{15}\text{N}$  value of nitrate in surface snow which peaked in winter, FD and PIE together determined the seasonal variations of snowpack  $\delta^{15}\text{N}(\text{NO}_3^-)$ , resulting in a  $\delta^{15}\text{N}(\text{NO}_3^-)$  maximum earlier than that of PIE (Figure 3b) as  $\delta^{15}\text{N}(\text{NO}_3^-)$  of FD peaked in winter.

The modeled  $\Delta^{17}\text{O}(\text{NO}_3^-)$  of FP is mainly determined by local atmospheric chemistry, e.g., the NO-NO<sub>2</sub> cycling and the subsequent formation of HNO<sub>3</sub>. Under the prescribed Summit atmospheric conditions, we calculated the  $\Delta^{17}\text{O}(\text{NO}_3^-)$  of FP with a mean of  $(19.7 \pm 0.3) \text{‰}$  over the period of photolysis. This  $\Delta^{17}\text{O}(\text{NO}_3^-)$  of FP combined with  $F_{\text{pri}}$  ( $\Delta^{17}\text{O} = 30 \text{‰}$ ), leading to a summer minimum  $\Delta^{17}\text{O}$  of FD that was 2.9 ‰ lower than that of  $F_{\text{pri}}$ . An additional  $\sim 0.1 \text{‰}$  difference was induced upon archival from the cage effect.

### **3.3 Loss of snow nitrate due to photolysis at Summit**



**Figure 3.** (a) The fraction of loss after deposition and the photolysis fractionation factor at different weeks. (b) PIE: the photolysis-induced isotope effect. PIE plus  $\delta^{15}N(NO_3^-)$  of FD presents the snow  $\delta^{15}N(NO_3^-)$  profile at the last step.

The lost fraction ( $f_{loss}$ ) of snow nitrate upon archival was plotted in Figure 3a, calculated as the difference in nitrate concentration of an archived layer to the concentration when it was at the surface. As shown in Figure 3a, throughout a year, the  $f_{loss}$  varied from 1.8 % to 21.3 %, similar to the < 7 % to 25 % loss estimated by Burkhardt et al. (2004) and Dibb et al. (2007). In particular, Dibb et al. (2007) calculated the average  $NO_3^-$  concentrations in fresh and buried snow layers, and found a mean of ~ 9 % loss which is in good agreement with our calculated mean  $f_{loss}$  of  $(10.6 \pm 6.7)$  %. Note  $f_{loss}$  calculated here was referred to a specific archived layer relative to when it was at the surface, and part of the loss was actually recycled to layers above that

specific layer. Therefore, the net loss integrated over a certain period should be less than the loss of a specific layer.

Here we calculated the annual net loss  $f_{loss}$  as follows:

$$\bar{f}_{loss\_annual} = 1 - \frac{F_a}{F_{pri}}$$

Where  $F_a$  represents the modeled archived flux of nitrate ( $6.52 \times 10^{-6} \text{ kgN m}^2 \text{ a}^{-1}$ ), and the  $\bar{f}_{loss\_annual}$  was calculated as 1.7 %. This is consistent with the annual mean  $\delta^{15}\text{N}(\text{NO}_3^-)$  which was just 0.97 ‰ enriched compared to  $\delta^{15}\text{N}$  of  $F_{pri}$ . This result suggests that although photochemistry was active and resulted in significant redistribution of snow nitrate in the photic zone at Summit, the annual net loss was very small. For  $\Delta^{17}\text{O}(\text{NO}_3^-)$  upon archival, the annual mean was 1.09 ‰ lower than  $\Delta^{17}\text{O}$  of  $F_{pri}$ . These values represent the integrated effects of the post-depositional processing on isotopes of the archived nitrate.

The annual net loss in the model was determined by  $f_{exp}$ . Although  $f_{exp}$  didn't influence the loss fraction of a specific snow layer, it determined how much of the reformed nitrate was recycled back to snow. Owing to the high summer OH concentration and low wind speed at Summit, the snow emitted  $\text{NO}_x$  can be oxidized to  $\text{HNO}_3$  rapidly. In our simulation,  $f_{exp}$  was mainly determined by the competition between the horizontal transport of nitrate and deposition to the surface. In calculation of  $f_{exp}$ , only dry deposition of gaseous  $\text{HNO}_3$  was considered as Zakto et al. (2016) suggested dry deposition of  $\text{HNO}_3$  dominates summer nitrate deposition flux at Summit. In Figure S2, we investigated the sensitivity of the annual net loss, as well as the annual mean snow  $\Delta^{17}\text{O}(\text{NO}_3^-)$  and  $\delta^{15}\text{N}(\text{NO}_3^-)$  upon archival to  $f_{exp}$ . As shown in Figure S2,

changes in snow  $\Delta^{17}\text{O}(\text{NO}_3^-)$  decreased with increasing  $f_{exp}$  while  $\delta^{15}\text{N}(\text{NO}_3^-)$  was the opposite, because a larger  $f_{exp}$  corresponded to less contribution of FP to FD. Under the extreme circumstance with a  $f_{exp}$  of 1, i.e., all snow-sourced nitrate was transported away,  $\delta^{15}\text{N}(\text{NO}_3^-)$  in snow was on average 6.65 ‰ enriched compared to primary  $F_{pri}$  under present day Summit conditions, while  $\Delta^{17}\text{O}(\text{NO}_3^-)$  was only 0.19 ‰ lower than  $\Delta^{17}\text{O}$  of  $F_{pri}$  which was caused by the cage effect.

#### **4. Conclusions**

In this study we applied the TRANSITS model to investigate the impact of the photo-driven post-depositional processing on the preservation of nitrate and its isotopes at Summit Greenland. The results suggest that the photo-driven post-depositional processing is very active at Summit, causing significant redistribution of snow nitrate accompanied by isotope effects in the photic zone. Despite the high snow accumulation rate at Summit, up to 21 % loss of nitrate occurred after deposition in spring snow layers, resulting in a spring  $\delta^{15}\text{N}(\text{NO}_3^-)$  peak consistent with the observations. The model, which only considers the effects of the photo-derived post-depositional processing, reproduced the observed seasonal patterns of snow nitrate concentration and  $\delta^{15}\text{N}(\text{NO}_3^-)$ . In comparison, the post-depositional processing led to a less than 3 ‰ seasonal change in  $\Delta^{17}\text{O}$ . Our results demonstrate the dominant role of local photochemistry in determining the seasonality of snow nitrate concentrations and  $\delta^{15}\text{N}(\text{NO}_3^-)$  at Summit. The latter was previously attributed to

seasonal variations in the relative contributions of different  $\text{NO}_x$  sources (Hastings et al., 2004).

Due to the fast cycling of nitrate at the air-snow interface, the annual net loss ( $\sim 2\%$ ) and the associated annual mean changes in  $\delta^{15}\text{N}(\text{NO}_3^-)$  ( $< 1\%$ ) and  $\Delta^{17}\text{O}(\text{NO}_3^-)$  ( $\sim 1\%$ ) caused by post-depositional processing were small under present day conditions at Summit, Greenland. However, the net loss and the associated isotope effects could be increased in periods with much reduced snow accumulation rate. For example, considering only the glacial-interglacial changes in snow accumulation rate and dust concentrations at Summit as recorded in the GISP2 ice core (Geng et al., 2015), the model calculated a 32% annual nitrate loss in the glacial period and a glacial-interglacial  $\delta^{15}\text{N}(\text{NO}_3^-)$  difference of about 10 ‰. In comparison, the observed glacial-interglacial  $\delta^{15}\text{N}(\text{NO}_3^-)$  difference is  $(16.7 \pm 4.8)\%$  and the inferred loss fraction in the glacial period is (45-53) % (Geng et al., 2015). This suggests that changes in the degree of post-depositional processing caused by the glacial-interglacial differences in snow accumulation rate and dust concentration alone can explain the majority (47-84 %) of the observed glacial-interglacial  $\delta^{15}\text{N}(\text{NO}_3^-)$  difference. Other factors, e.g., the glacial-interglacial difference in  $f_{\text{exp}}$  due to different local meteorological conditions, would also influence the loss fraction and thus the  $\delta^{15}\text{N}(\text{NO}_3^-)$  difference.

Overall, our results reinforce the effects of post-depositional processing on ice-core nitrate concentrations and isotopes even at high snow accumulation rate sites, and such effects have to be quantified and corrected in order to use ice-core nitrate

records to retrieve past information on NO<sub>x</sub> emissions and abundance and atmospheric oxidation capacity.

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