Atmospheric and snow nitrate isotope systematics at Summit, Greenland: the reality of the post-depositional effect

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20   **Abstract**

The effect of post–depositional processing on the preservation of snow nitrate
isotopes at Summit, Greenland remains a subject of debate which hinders the
interpretations of ice–core nitrate concentrations and isotope records. Here we present
the first year–round observations of atmospheric aerosol nitrate and its isotopic
25   compositions at Summit, and compare them with published surface snow and snowpack
observations. The atmospheric $\delta^{15}N(NO_3^-)$ remained negative throughout the year,
ranging from –3.1 ‰ to –47.9 ‰ with a mean of (–14.8 ± 7.3) ‰, and displayed no
apparent seasonality that is different from the distinct seasonal $\delta^{15}N(NO_3^-)$ variations
observed in snowpack. The spring average aerosol $\delta^{15}N(NO_3^-)$ was (–17.9 ± 8.3) ‰,
30   significantly depleted compared to snowpack spring average of (4.6 ± 2.1) ‰, with
surface snow $\delta^{15}N(NO_3^-)$ of (–6.8 ± 0.5) ‰ that is in between. The differences in
aerosol, surface snow and snowpack $\delta^{15}N(NO_3^-)$ are best explained by the photo-driven
post–depositional processing of snow nitrate, with potential contributions from

fractionation during nitrate deposition. In contrast to $\delta^{15}N(NO_3^-)$, the atmospheric

35    $\Delta^{17}O(NO_3^-)$ was of similar seasonal pattern and magnitude of change to that in

snowpack, suggesting little to no changes in $\Delta^{17}O(NO_3^-)$ from photolysis, consistent

with previous modeling results. The atmospheric $\delta^{18}O(NO_3^-)$ varied similarly as

atmospheric $\Delta^{17}O(NO_3^-)$, with summer low and winter high values. However, the

difference between atmospheric and snow $\delta^{18}O(NO_3^-)$ was larger than that of

40    $\Delta^{17}O(NO_3^-)$, and the linear relationships between $\delta^{18}O/\Delta^{17}O(NO_3^-)$ were different for

atmospheric and snowpack samples. This suggests the oxygen isotopes are also affected

before preservation in the snow at Summit, but the degree of change for $\delta^{18}O(NO_3^-)$ is

larger than that of $\Delta^{17}O(NO_3^-)$ given that photolysis is a mass-dependent process.

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1. Introduction

Ice-core nitrate and its isotopes are potential proxies to constrain atmospheric

variability of NO_x and oxidants concentrations in past atmospheres. However, this can

be compromised by the impacts of post-depositional processing on nitrate

50   concentrations and isotopes (i.e., $\delta^{15}N$, $\delta^{18}O$ and $\Delta^{17}O$, where $\Delta^{17}O = \delta^{17}O - 0.52 \times$

$\delta^{18}O$) (Alexander et al., 2019; Savarino et al., 2016; Wolff et al., 2008). Nitrate is

chemically reactive in snow upon exposure to sunlight and thus its deposition to snow

is not irreversible (Blunier et al., 2005; Erbland et al., 2013; Frey et al., 2009).

Numerous studies across Antarctica and Greenland have observed decreases in snow

55   nitrate concentrations with depth in the snowpack (Erbland et al., 2013; Frey et al., 2009;

Mulvaney et al., 1998; Röthlisberger et al., 2000) and/or emissions of NO_x and HONO

from snowpack (Dibb et al., 1998; Frey et al., 2015; Honrath et al., 2002; Jones et al.,

2001). Follow–up studies further indicate changes in the isotopic compositions of snow

nitrate at depth in the snowpack, i.e., increases in $\delta^{15}N$ and decreases in $\delta^{18}O/\Delta^{17}O$

60   (Blunier et al., 2005; Curtis et al., 2018; Erbland et al., 2013; Frey et al., 2009; Shi et

al., 2015). Processes leading to such changes were referred to as post–depositional

processing, and $\delta^{15}N$ of the archived nitrate was used to reflect the degree of post–

depositional processing due to its high sensitivity to these processes (Erbland et al.,

2013; Frey et al., 2009; Geng et al., 2015; Jiang et al., 2021; Shi et al., 2015; Winton et al., 2020).

Post–depositional processing of snow nitrate is mainly initiated by photolysis (Berhanu et al., 2014; Erbland et al., 2013; Frey et al., 2009; Zatko et al., 2016). The evaporation of nitrate from snow grains may also contribute but this process has not been directly observed/evidenced in the field. Observations and/or modelling of snowpack nitrate concentration and isotope profiles across many different sites (e.g., Summit in Greenland, Dronning Maud Land (DML) and Dome A/Dome C in Antarctica) in general agree that photolysis dominates post–depositional processing (Erbland et al., 2013; Frey et al., 2009; Geng et al., 2015; Jiang et al., 2021; Winton et al., 2020; Shi et al., 2015; Shi et al., 2019). The degree of the photo–driven post–depositional processing is influenced by three main factors including snow accumulation rate, surface actinic flux and light penetration depth in snow (i.e., the photic zone where actinic flux decreases exponentially) (Zatko et al., 2013). Snow and ice–core nitrate isotope records have shown variations in $\delta^{15}N(NO_3^-)$ in response to varying snow accumulation rate as well as light–absorbing impurities (e.g., BC, dust, etc.) that influences light penetration depth in snow. For example, Geng et al. (2014) found correlations between $\delta^{15}N(NO_3^-)$ and snow accumulation rate across the GISP2 ice core record, except in periods with very low snow accumulation rate (<0.08 m ice a^{-1}) and high dust concentrations when $\delta^{15}N(NO_3^-)$ was correlated with dust concentration. These correlations reflect the effect of snow accumulation rate and snow light absorbing impurities on the degree of post–depositional processing, respectively. At the West Antarctica ice sheet divide, where snow accumulation rate is high (0.24 m ice a^{-1}) at present, a decreasing trend in snow accumulation rate since 2400 yr BP led to an increasing trend in the degree of post–depositional processing as indicated by elevated $\delta^{15}N(NO_3^-)$ (Sofen et al., 2014).

Variations in surface actinic flux (especially the UVB radiation) would also induce changes in the degree of post–depositional processing and leave signals in the preserved nitrate in snow and ice cores. Previous studies (Erbland et al 2013; Frey et al., 2009; McCabe et al. 2007) proposed that $\delta^{15}N(NO_3^-)$ preserved in snow and ice cores may serve as a proxy of total column ozone (TCO) due to its influence on surface UVB

radiation, while a recent study suggested the preserved $\delta^{15}N(NO_3^-)$ is more sensitive to

95   snow accumulation rate and light penetration depth, but less to TCO (Winton et al., 2020). Nevertheless, in periods with relatively constant snow accumulation rate but distinct surface actinic flux, e.g., the switch of the polar night and polar day over a year, and the Antarctic ozone hole period, changes in the degree of post–depositional processing and thus the associated isotope effects are expected. Using a snow column

100   photochemical model (the TRANSITS model by Erbland et al., (2015)), Jiang et al. (2021) explicitly quantified the effects of post–depositional processing on snow nitrate and its isotopes on seasonal scale at Summit, Greenland. Owing to the seasonal differences in surface actinic flux, the model predicted a seasonal variation in $\delta^{15}N(NO_3^-)$ snowpack similar to the observations. On annual scale, the model predicted

105   a ≈ 4 % net nitrate mass loss, which is within the range estimated by previous studies (Burkhart et al., 2004; Dibb et al., 2007) but is subject to uncertainties in the fraction of the snow–sourced nitrate exported from the region. In contrast, the model predicted minimum changes in $\Delta^{17}O$ of snow nitrate on both seasonal and annual scale because the photo-driven post-depositional processing affects $\Delta^{17}O$ mainly from the cage effect

110   (i.e., the intermediate photo-products (NO_2^- and NO_2) exchange with water oxygen or react with radicals such as OH in snow grains to regenerate nitrate before being emitted to the atmosphere) which is however minimum at Summit given the high snow accumulation. The study by Jiang et al. (2021) further suggested that seasonal $\delta^{15}N(NO_3^-)$ variations in snowpack at Summit, Greenland is caused by photo–driven

115   post–depositional processing, an alternative to previous interpretations that attributed the seasonality to NO_x source variability (Hastings et al. 2004). Jarvis et al. (2009) also found enrichment in snowpack $\delta^{15}N(NO_3^-)$ compared to the surface snow samples at Summit, Greenland, providing observational evidence of post–depositional processing altering snow $\delta^{15}N(NO_3^-)$ at this high snow accumulation rate site. These results are in

120   conflict with the conclusion of Fibiger et al. (2013, 2016) who suggested that there is little to no isotope effect caused by post–depositonal processing relying on the oxygen isotopes of nitrate. However, as argued by Jiang et al. (2021), the nitrogen isotopes are more sensitive to post-depositional processing. In addition, Fibiger et al. (2013, 2016)

collected atmospheric and surface snow samples in May and June. The process of

125   photolysis of snow nitrate to NO_x, oxidation of snow-sourced NO_x to nitrate, followed by re-deposition of snow-sourced nitrate will render the isotopic composition of atmospheric and surface snow nitrate similar to each other. Nitrate at depth but still in the photic zone experiences photolysis, but is isolated from surface deposition, making post-depositional loss more apparent in the isotope observations. Therefore, in order to

130   reflect the full picture of post-depositional processing, considering snow samples covering the entire photic zone (~ 40 cm at Summit) is necessary (Jiang et al., 2021).

       To thoughtfully evaluate the effects of post-depositional processing at Summit, Greenland, and to verify the modeling results by Jiang et al. (2021), nitrate isotopes in the atmosphere and in snow covering a full cycle of polar night vs. polar day (i.e., a

135   cycle with distinct actinic flux variations) are necessary. Here, we present the first year–round observations of nitrate isotopes in the air at Summit, and compare them with similar observations in surface snow and in snow at depth (i.e., snowpack) to conduct a comprehensive evaluation on the seasonality in nitrate isotopes in both air and in snow, as has already been done in Antarctica (Erbland et al., 2013; Frey et al., 2009; Winton

140   et al., 2020). These observations provide information regarding the evolution of nitrate isotopes from atmospheric nitrate to its final preservation in snowpack, which is critical to assess the post-depositional changes of nitrate isotopes.

2. Methods

2.1 aerosol sampling and measurements

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       From July 2001 to July 2002, atmospheric samples were collected at Summit, Greenland by using a high–volume air sampler (HVAS) with glass fiber filters (20.3 × 25.4 cm). 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). Each sample

150   covering 3-4 days were routinely collected over the year, with a total of 97 samples. 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 18 MΩ water via centrifugation using Millipore

155   Centricon™ filter units. The samples were then measured for nitrate concentrations by

ion chromatography. Among these samples, 54 out of 97 were determined to be valid

by comparing the extracted nitrate concentration with blank. 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

160   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 ℃. 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

165   253) for isotope analyses of $^{15}N/^{14}N$, $^{17}O/^{16}O$ and $^{18}O/^{16}O$. International reference

materials (IAEA USGS-32, 34 and 35) were used for data calibration. The measurement

uncertainties were 0.6 ‰ for $\delta^{18}O$, and 0.3 ‰ for both $\Delta^{17}O$ and $\delta^{15}N(NO_3^-)$.

2.2 Atmosphere, surface snow and snowpack data compilation

From the literature, we collected nitrate isotope data ($\delta^{15}N$, $\delta^{18}O$ and $\Delta^{17}O$) of

170   atmospheric particulate or gas-phase nitrate, surface snow and snowpack nitrate

available at Summit, Greenland (Fibiger et al., 2013; Fibiger et al., 2015; Geng et al.,

2014; Hastings et al., 2004; Jarvis et al., 2009; Kunasek et al., 2008). Details about these

data (e.g., sample type, depth, age) and the corresponding references are listed in Table

1. Note that in some early publications only the seasonal averages instead of the original

175   data with finer resolution were available. These data were compiled to produce a dataset

including all seasons for nitrate in the air, surface snow and snowpack by averaging

samples covering multiple years and/or by different groups to reduce the spatial and

temporal heterogeneities. For samples with resolution finer than monthly, we compiled

them as their mass-weighted monthly averages (if the mass information for each sample

180   is known), and for samples with coarser than monthly resolution, seasonal averages

were used.

For aerosol and surface snow samples, age information was indicated as the time

of sampling. Snowpack samples require a conversion from depth to age. The snowpack

samples from Hastings et al. (2004) and Kunasek et al. (2008) were dated by seasonal

185 binning according to measured accumulation rate and water isotopes, and their age information was used as is. For samples from Geng et al. (2014), we recalculated the dating by bamboo stake measured snow accumulation data (Burkhart et al., 2004; Dibb et al., 2004; Kuhns et al, 1997) constrained by snow density and further justified by seasonal peaks of Na^+ and Cl^-/Na^+ ratio. This is similar to the dating method in Hastings

190 et al. (2004) and the only difference is which proxy was used as the seasonal marker. Briefly, we used the bamboo stake measurements of weekly snow accumulation at Summit and the snowpack density profile to estimate the deposition timing of each samples in the 2.1 m snowpack that was collected in July of 2007. We first converted the thickness of each sample (referred to as D_m) to a fresh snow thickness (referred to

195 as D_f) by the following equation:

$$D_f = D_m \times \frac{\rho_m}{\rho_f} \tag{1}$$

Where ρ_m is the real snow density at each depth from field measurement (Geng et al., 2014), and ρ_f is the fresh snow density (0.32 g.cm^{-3}; Dibb et al., 2004). These fresh snow thicknesses were then stacked to construct an idealized snow depth profile

200 without densification due to compaction and/or metamorphism. This idealized depth profile was then matched the stacked depth by the observed average weekly snow accumulation rate to determine the exact age for each sample. A previous study showed that using the stack measured accumulation rate is capable of reconstructing the vertical profile of snowpack nitrate (Burkhart et al., 2004). This dating method has uncertainties,

205 mostly owing to the large variability of measured accumulation rate among different stakes (Burkhart et al., 2004). To reduce the uncertainties in our dating results, we calculated their monthly average and compared with aerosol and/or surface snow data with a similar or coarser time resolution. The compiled $\delta^{15}N$ and $\Delta^{17}O$ data in monthly resolution display seasonal patterns similar to their original seasonal variations

210 observed in snowpack, and the Cl^-/Na^+ ratio of the compiled samples also displays summer high and winter low as has been previously observed snowpack or firn cores (Geng et al., 2014), corroborating the dating method in terms of capturing the

seasonality (Figure 2e). The monthly $\Delta^{17}O$ values compiled from Geng et al. (2014) data were further averaged with the monthly $\Delta^{17}O$ values reported by Kunasek et al. (2008) to generate the final snowpack monthly $\Delta^{17}O$ data. In comparison to $\Delta^{17}O$, the $\delta^{18}O$ data from different groups indicated a much larger range of variability, and even inconsistence as the data from Jarvis et al (2009) indicated a winter peak of $\delta^{18}O$ instead of summer which is different from other studies (e.g., Geng et al., 2014) and difficult to explain from current understanding of nitrate chemistry. Therefore, we didn't average the $\delta^{18}O$ data from different groups.

	Isotopes	Period	Resolution	Depth	Reference
Atmosphere	$\delta^{15}N/\Delta^{17}O/\delta^{18}O$	July 2001 to July 2002	3-5 day	–	This study
	$\delta^{15}N/\Delta^{17}O/\delta^{18}O$	June to July 2010/2011	0.5-1 day	–	Fibiger at al., 2016
	$\delta^{15}N/\delta^{18}O$	March 2006 to Jul 2006	>2 day	–	Jarvis et al., 2009
Surface snow	$\delta^{15}N/\delta^{18}O$	March 2006 to Jul 2006	–	–	Jarvis et al., 2009
	$\delta^{15}N/\Delta^{17}O/\delta^{18}O$	June to July 2010/2011	0.5-3 cm	0.5-3 cm	Fibiger at al., 2016
Snowpack	$\delta^{15}N/\Delta^{17}O/\delta^{18}O$	July 2004– July 2007	3-5 cm	0-2.1 m	Geng et al., 2014
	$\delta^{15}N/\delta^{18}O$	Spring 2000 to	3 cm	0-1 m	Hasting et al., 2004

	summer 2001			
$\delta^{15}N/\delta^{18}O$	Summer 2005 to summer 2007	5 cm	0-1 and 0-2 m	Jarvis et al., 2009
$\Delta^{17}O$	January 2001 to July 2007	5 cm	0-2 m	Kunasek et al., 2008

Table1. Nitrate isotope data information and references.

3. Results

225 **3.1 Year–round atmospheric nitrate concentrations and isotopes at Summit, Greenland**
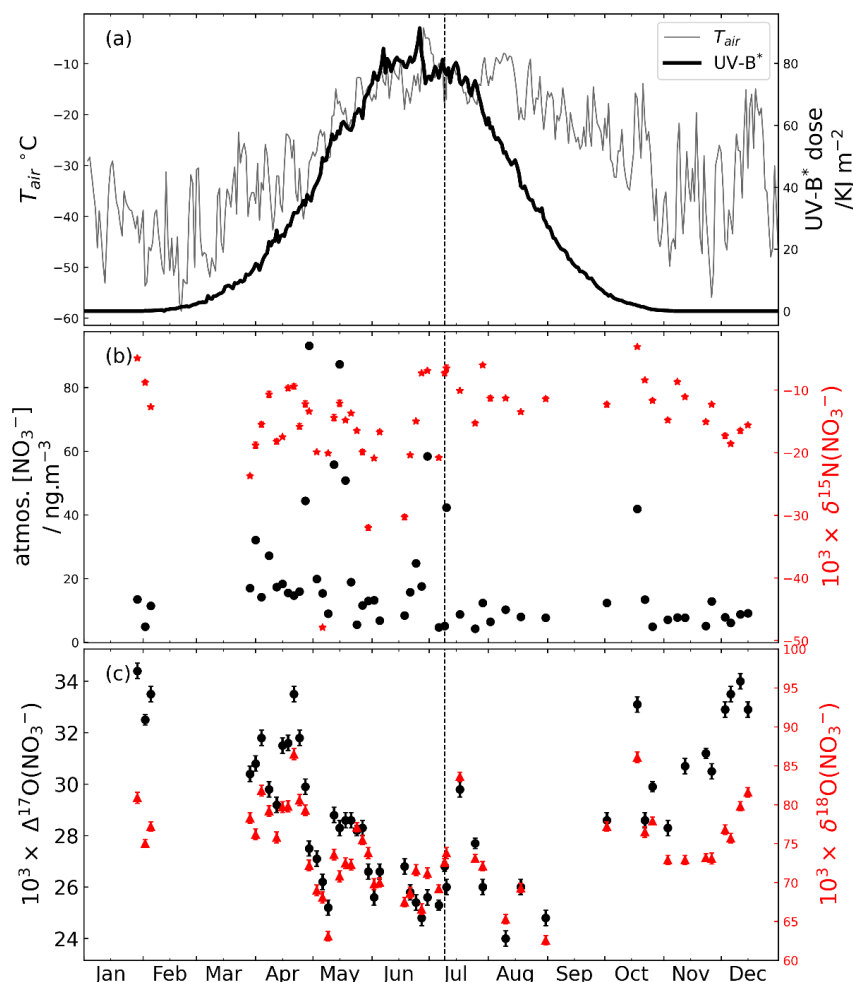
Figure1. Aerosol nitrate concentrations and isotopes at Summit over the sampling period (July 2001 to July 2002). (**a**) Daily air temperature and observed UV-B* (280-320 nm) dose at Summit, Greenland from July 2001 to July 2002 (data source: NSF Arctic Data Center, link: https://arcticdata.io/catalog/data), (**b**) NO_3^- concentration (black circle) and $\delta^{15}N(NO_3^-)$ (red star), (**c**) $\Delta^{17}O(NO_3^-)$ (black circle) and $\delta^{18}O(NO_3^-)$ (red triangle). The dashed line presents the starting date of the datasets.

The measured nitrate concentrations and its isotopic compositions ($\delta^{15}N$, $\Delta^{17}O$ and $\delta^{18}O$) in the filter samples are shown in Figure 1, together with surface air temperature and UV-B* level (wavelength ranges from 280 to 320 nm) measured at Summit station. As shown in the figure, the annual mean atmospheric NO_3^- concentration was (19.9 ± 19.1) ng m⁻³ and most of them ranged from ~ 1 to 95 ng m⁻³, consistent with the values

240   reported by Dibb et al. (1998) and Fibiger et al. (2016). There was no distinct seasonal pattern in atmospheric nitrate concentrations, but some spikes (samples with much higher nitrate concentrations than average) in spring/summer months were observed, typical to intrusion of Arctic haze events at the altitude of the Ice Sheet (Quinn et al., 2007; Jaffrezo et al., 1997).

245   The atmospheric $\delta^{15}N(NO_3^-)$ was negative throughout the year with an annual mean of (–14.8 ± 7.3) ‰. There was also no distinct seasonal pattern in $\delta^{15}N(NO_3^-)$ observed, though the average for the winter half year was (–12.0 ± 4.2) ‰ is slightly less negative than that (–16.0 ± 3.9‰) in the summer half year. The mean atmospheric $\delta^{15}N(NO_3^-)$ from May to June was (–19.3 ± 9.6) ‰, close to the value of (–16.8 ± 8.7) ‰

250   reported by Fibiger et al. (2016) covering the same months. In addition, some extremely negative $\delta^{15}N(NO_3^-)$ values (< –30 ‰) were observed in spring/summer months. Such very low $\delta^{15}N(NO_3^-)$ values was also observed by Fibiger et al. (2016).

       The atmospheric $\Delta^{17}O$ (NO_3^-) values ranged from 24.0 ‰ to 34.4 ‰ with a seasonal minimum near mid–summer, concurrent with the maximum UV-B* radiation

255   intensity (Figure 1a), and a peak in winter. The atmospheric $\delta^{18}O(NO_3^-)$ data ranged from 49.7 to 86.5 ‰ and displayed an almost identical seasonal pattern with $\Delta^{17}O(NO_3^-)$ as expected. The $\delta^{18}O(NO_3^-)$ values between March to June ranged from 63.1 to 86.5 ‰, much higher than the values (24 to 50‰) reported by Jarvis et al. (2009), and in the upper band of that (37.4 to 93.4 ‰) reported by Fibiger et al. (2016) over the same

260   months (but in different years). Note that the Jarvis et al. (2009) and Fibiger et al. (2016) studies reported values for atmospheric gas–phase HNO_3 instead of bulk nitrate. Overall, the absolute values and the seasonal patterns of $\Delta^{17}O(NO_3^-)$ were similar to those observed in snowpack samples at Summit (Kunasek et al., 2008; Geng et al. 2014), while those of $\delta^{18}O(NO_3^-)$ were similar to that reported for snowpack samples by

265   Hastings et al. (2004).

3.2 Compiled seasonal $\delta^{15}N$, $\delta^{18}O$ and $\Delta^{17}O$ in atmospheric, surface snow and snowpack nitrate

       The compiled nitrate isotopes (i.e., $\delta^{15}N/\delta^{18}O/\Delta^{17}O$) with monthly or seasonal

270 resolutions are plotted in Figure 2. These compiled data of atmospheric, surface snow and snowpack averages should represent the status of nitrate before deposition, after deposition, and archival, respectively. To validate our dating results on the snowpack data, we also plotted the resampled monthly snowpack Na^+ concentration and Cl^-/Na^+ ratio. As shown in Figure 2e, the Na^+ concentration and Cl^-/Na^+ ratio displayed clear

275 winter and summer peak, respectively, indicating a general reliability of our dating method. We also calculated the accumulated UV-B[*] daily dose for nitrate deposited in different weeks of a year using Eq (2):

$$UVB^*_{toal} = \sum UVB^*(t) * \exp\left(-\sum \frac{A(t)}{z_e}\right) \tag{2}$$

where A(t) and z_e represent the weekly snow accumulation rate and e-folding depth

280 (12.3 cm, Jiang et al. (2021) at Summit, respectively. The daily UV-B[*](t) dose was shown in Figure 2a. The accumulated UV-B[*] dose computed here represents the integrated UV-B[*] radiation that snow nitrate received from being deposited to surface snow until being buried below the photic zone ($\approx$ 40 cm according to Jiang et al. (2021)). This gives a first order estimation of the total radiation (i.e., the degree of post-

285 depositional processing) that the archived nitrate experienced at Summit.

The snowpack samples from Geng et al. (2014) cover ~ 3 years snow accumulation, and we averaged the monthly data of the three years for each month. As shown in Figure 2b, its seasonal $\delta^{15}N(NO_3^-)$ variation displays an overall good agreement with that reported by Hastings et al. (2004) and Jarvis et al. (2009) with a spring peak. In general,

290 the $\delta^{15}N(NO_3^-)$ data among different sample types indicated a systematic pattern for spring/summer samples, with the atmospheric samples the most depleted (-16.0 ± 7.9) ‰ and the snowpack samples the most enriched (2.7 $\pm$ 3.0) ‰, while the surface snow samples were in between (-5.8 ± 0.7) ‰. In addition, the snowpack $\delta^{15}N(NO_3^-)$ data indicated a clear spring/summer maximum coincident with the maximum accumulated

295 UV-B[*] dose (Figure 2a), while the surface snow $\delta^{15}N(NO_3^-)$ were only moderately enriched in spring/summer compared to other seasons. For atmospheric $\delta^{15}N(NO_3^-)$, although uncertainties of the monthly averages were large, they were moderately depleted in spring/summer compared to other seasons, opposite to the surface snow and

snowpack data. In addition, for fall and winter seasons, the $\delta^{15}N(NO_3^-)$ values of

300   different sample types converged, opposite to their behaviors in spring/summer when

they diverged. Note that the atmospheric samples from Jarvis et al (2009) collected in

April and May were for gas–phase HNO_3, and their $\delta^{15}N(NO_3^-)$ values were higher than

that in aerosol nitrate measured by this study, but within the range of those in surface

snow, and lower than those in snowpack.

305   The compiled monthly $\Delta^{17}O(NO_3^-)$ values are shown in Figure 2c. Atmospheric

$\Delta^{17}O(NO_3^-)$ values were consistent with the snowpack values throughout the year, and

both atmospheric and snowpack $\Delta^{17}O(NO_3^-)$ reached a seasonal minimum in summer.

Surface snow $\Delta^{17}O(NO_3^-)$ were only available in May and June as reported by Fibiger

et al. (2016), and although highly variable, their averages were consistent with the May

310   and June $\Delta^{17}O(NO_3^-)$ averages in the atmosphere and snowpack.

        The compiled $\delta^{18}O(NO_3^-)$ results are shown in Figure 2d. Although the summer

minimum for the snowpack data from Geng et al. (2014) was not as obvious as those

reported by Hasting et al. (2004) and the atmospheric data reported in this study, the

$\delta^{18}O(NO_3^-)$ data in general indicated a summer minimum. In comparison, the surface

315   snow and snowpack data from Jarvis et al. (2009) indicated a fall minimum, and the

original data of Jarvis et al. (2009) indicated a clear summer maximum in the year of

2005. These data are nevertheless difficult to interpret given current understanding of

nitrate formation mechanisms which should lead to a summer low and winter high for

$\delta^{18}O(NO_3^-)$. But we note that caution should be taken when interpreting the Jarvis et al.

320   (2009) data, as there was a large difference in $\delta^{18}O(NO_3^-)$ data from one winter (69.5 ±

5.0) ‰ ($n = 7$) to the next (101.1 ± 7.9) ‰ ($n = 4$). In addition, the $\delta^{18}O(NO_3^-)$ of

atmospheric nitrate in gas-phase samples collected by Jarvis et al. (2009) in March and

June, and by Fibiger et al. (2016) in May and June were almost all out of range (in the

lower band) of the snow samples and were not plotted in Figure 2d. Overall, the

325    $\delta^{18}O(NO_3^-)$ data were more variable than the $\Delta^{17}O(NO_3^-)$ data and there were

inconsistences among different observations.
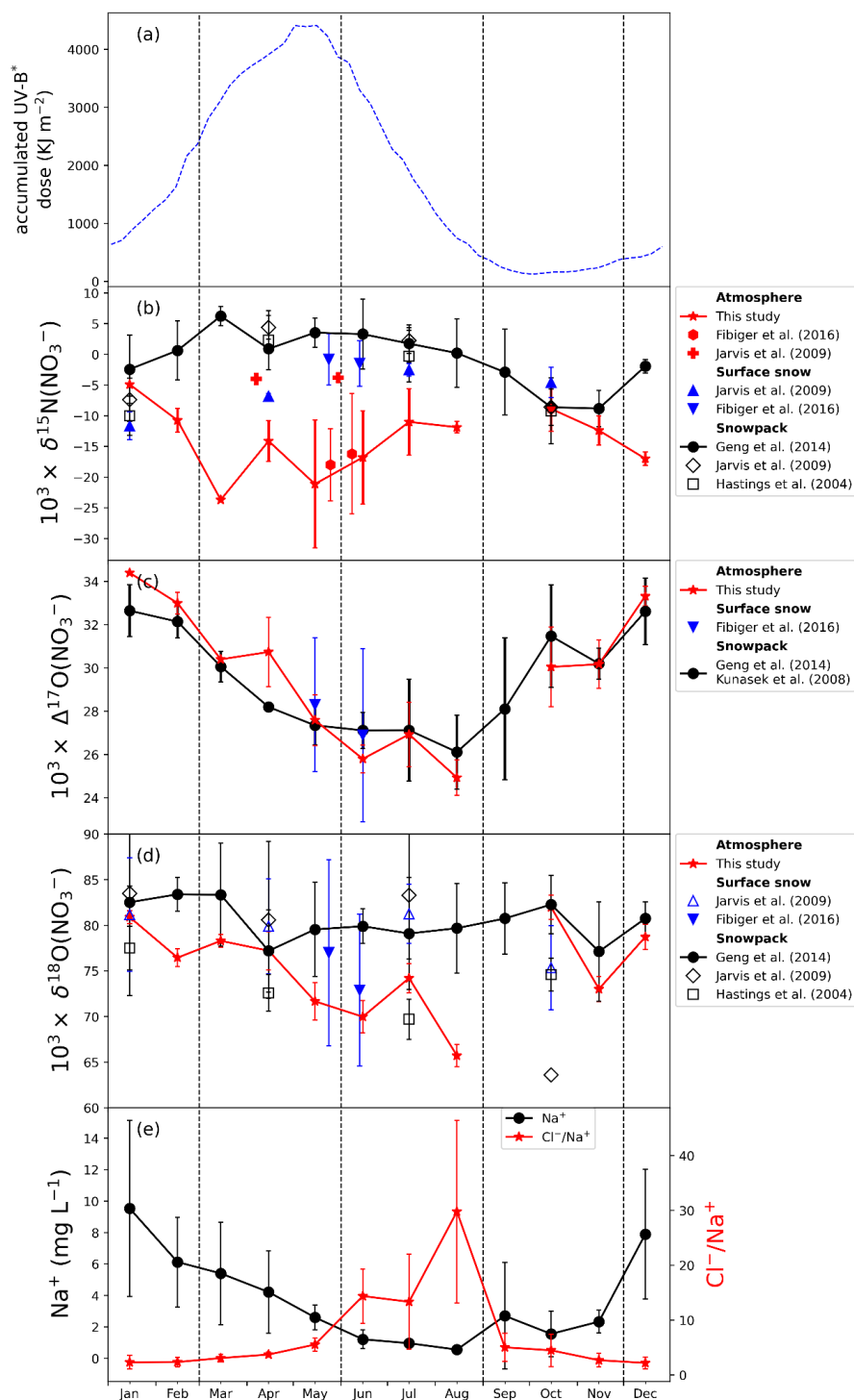
Figure 2. (**a**) Cumulative UV-B* does as function of the deposited time, calculated according to Eq (2); (**b-d**) Compiled monthly and/or seasonal atmospheric, surface snow and snowpack $\delta^{15}N/\Delta^{17}O/\delta^{18}O(NO_3^-)$ data at Summit, Greenland. (**e**) Compiled monthly snowpack Na^+ concentration and Cl^-/Na^+ ratio. The seasonal data (represented by the open markers) were plotted against the central month of each season. The vertical lines represent the interval of seasons. Data sources were summarized in Table 1.

4. Discussion

4.1 Seasonal $\delta^{15}N(NO_3^-)$ and its difference between atmospheric, surface snow and snowpack nitrate

The atmospheric, surface snow and snowpack samples represent different stages of nitrate in the deposition and preservation processes. The compiled results in Figure 2b indicated a systematic enrichment in $\delta^{15}N(NO_3^-)$ from deposition to preservation for spring/summer nitrate. This systematic enrichment refutes the previous hypothesis that seasonal variation in snowpack $\delta^{15}N(NO_3^-)$ at Summit was driven by shifts in the relative importance of NO_x sources (Hastings et al., 2004). Instead, local processes leading to fractionations in $\delta^{15}N(NO_3^-)$ are needed to reconcile the observed differences between atmospheric and snowpack $\delta^{15}N(NO_3^-)$. 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 (Erbland et al., 2013). Jiang et al. (2021) has discussed the effect of the physical release on nitrate isotopes and suggested that this effect is negligible at Summit. In the following sections, we discussed the other processes and compared with the modeling study results from Jiang et al. (2021), to discern the exact cause(s) of the observed systematic changes in $\delta^{15}N(NO_3^-)$ from the atmosphere to snowpack.

4.1.2 The effects of snow nitrate photolysis

The $\delta^{15}N(NO_3^-)$ pattern in the summer half year among different type of samples, i.e., atmospheric $\delta^{15}N(NO_3^-)$ < surface snow $\delta^{15}N(NO_3^-)$ < snowpack $\delta^{15}N(NO_3^-)$, is

qualitatively consistent with the effects of snow nitrate photolysis which enriches snow $\delta^{15}N(NO_3^-)$ while providing a snow-source of depleted $\delta^{15}N(NO_3^-)$ to the atmosphere. The snowpack $\delta^{15}N(NO_3^-)$ variations within a year showed a similar trend with the accumulated UV-B* dose (Figure 2a and 2b), i.e., the $\delta^{15}N(NO_3^-)$ peak and valley corresponded to the seasons with the highest (i.e., spring) and the lowest (i.e., fall) accumulated UV-B* dose, respectively. The accumulated UV-B* dose reflects the total amount of radiation leading to photolysis (wavelength of 280 to 320 nm) that snow nitrate received before archival for a given snow layer. In contrast, during the winter half year when there is an absence of sunlight, $\delta^{15}N(NO_3^-)$ among different types of samples are similar, suggesting that the physical transfer between atmosphere and snowpack (deposition, evaporation) leads to negligible ^{15}N isotopic fractionations.

The atmospheric $\delta^{15}N(NO_3^-)$ in the summer half year should represent the combined signal of primary nitrate from long-range transport and the snow-sourced nitrate from photolysis (Jiang et al., 2021), while in winter atmospheric $\delta^{15}N(NO_3^-)$ should be less influenced by snow-sourced nitrate and perhaps dominated by primary nitrate. Snow-sourced atmospheric nitrate is very depleted in $\delta^{15}N(NO_3^-)$ (< -70 ‰ at Summit, Jiang et al., 2021), and its flux to the overlying atmosphere should be maximize in summer when surface UV radiation is the strongest. All else being equal, one should expect the summer atmospheric $\delta^{15}N(NO_3^-)$ to be the lowest throughout the year. This appears to be in conflict with the observations which indicated the spring atmospheric $\delta^{15}N(NO_3^-)$ was the lowest. Possible explanations to this could be related to spring-summer differences in the export fraction of the snow-sourced nitrate or the $\delta^{15}N(NO_3^-)$ of primary nitrate. Cohen et al. (2006) conducted studies on the boundary layer dynamics at Summit and found that sustained stable surface layer conditions were frequently observed during spring at Summit, while in summer the boundary layer became more convective. The more stable boundary layer conditions in spring may lower the export fraction of the snow-sourced nitrate compared to summer, which tends to lower the spring atmospheric $\delta^{15}N(NO_3^-)$ as more snow-sourced nitrate with extremely low $\delta^{15}N$ will accumulate in the local boundary layer. Honrath et al. (2002) found that at Summit, in summer the snow-sourced nitrate (their measured form was

390 NO$_x$) was not balanced by downward HNO$_3$ flux and suggested that without wet deposition the emitted NO$_x$ and reformed HNO$_3$ should be largely exported from the local boundary layer. In addition, Jiang et al. (2021) suggested that the primary nitrate flux dominates the nitrate budget at Summit, and even in mid-summer the snow-sourced nitrate only accounts for about 25% of total atmospheric nitrate. If δ^{15}N of primary

395 nitrate in summer was higher than that of primary nitrate in spring, the local atmospheric δ^{15}N(NO$_3^-$) at Summit could be still higher in summer even when the contribution of snow-sourced nitrate was larger. Other possible explanations could be (i) the area of snow cover in the Arctic basin is larger in spring than summer, which acts to increase the snow-sourced nitrate with depleted δ^{15}N(NO$_3^-$) and may offset the

400 effects of higher summer actinic flux on snow nitrate photolysis; (ii) the planetary boundary layer in summer is probably higher than that in spring at Summit, so the effects of snow-sourced nitrate on atmospheric nitrate budget is greater in spring than in summer.

To better understand the effects of the photo-driven post-depositional processing,

405 we quantitatively compared and analyzed the δ^{15}N(NO$_3^-$) averages in spring when the isotopic differences between surface snow and snow snowpack are the most pronounced as indicated by the compiled data and the modeling results by Jiang et al. (2021). Compared to surface snow nitrate, snowpack nitrate was enriched by (12.8 ± 2.6) ‰ in spring. This value should reflect the effect of post-depositional processing on

410 snow nitrate throughout its preservation, i.e., from being deposited in 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 δ^{15}N(NO$_3^-$) and archived snow δ^{15}N(NO$_3^-$). The PIE in spring calculated by the TRANSITS model is averaged at (14.3 ± 1.1) ‰, consistent with the compiled

415 data. Here we propose a simplified formula of PIE for quick assessment of the photo-driven post-depositional processing effect on δ^{15}N(NO$_3^-$) at any sites of interest:

$$\text{PIE}(t_0) = \delta^{15}N(t_a) - \delta^{15}N(t_0) = -\int_{t_0}^{t_a} \varepsilon(t)J(t)\exp\left(-\frac{1}{z_e}\int_{t_0}^{t}A(t)dt\right)dt \quad (3)$$

Where t_0 represents the time of nitrate deposited on snow surface in a year (i.e., the

starting time of photolysis), and t_a is the time for snow nitrate to reach a depth below

420 the snow photic zone (i.e., the archival layer) (3 times the e-folding depth). t is the time

variable between t_0 and t_a. ε and J represent the N isotope fractionation factor and nitrate

photolysis rate constant for snow nitrate at surface conditions, respectively. Both ε and

J varies seasonally owing to the timely-varied actinic flux, while J also varies with

depth which is constrained by the exponential term. z_e and $A(t)$ represent the e-folding

425 depth and snow accumulation rate, respectively. 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 $\delta^{15}N$.

For illustrative purposes, we calculated PIE of snow nitrate deposited at different times

of the year under typical Summit conditions and compare with the model output from

430 Jiang et al. (2021). As shown in Figure 3, the calculated PIE according to Equation (3)

agrees well with the output from the TRANSITS model. Using Equation (3), one should

be able to quickly assess the effect of photolysis on the preserved snow $\delta^{15}N(NO_3^-)$ as

long as the J value and weekly or seasonal accumulation rate are known.
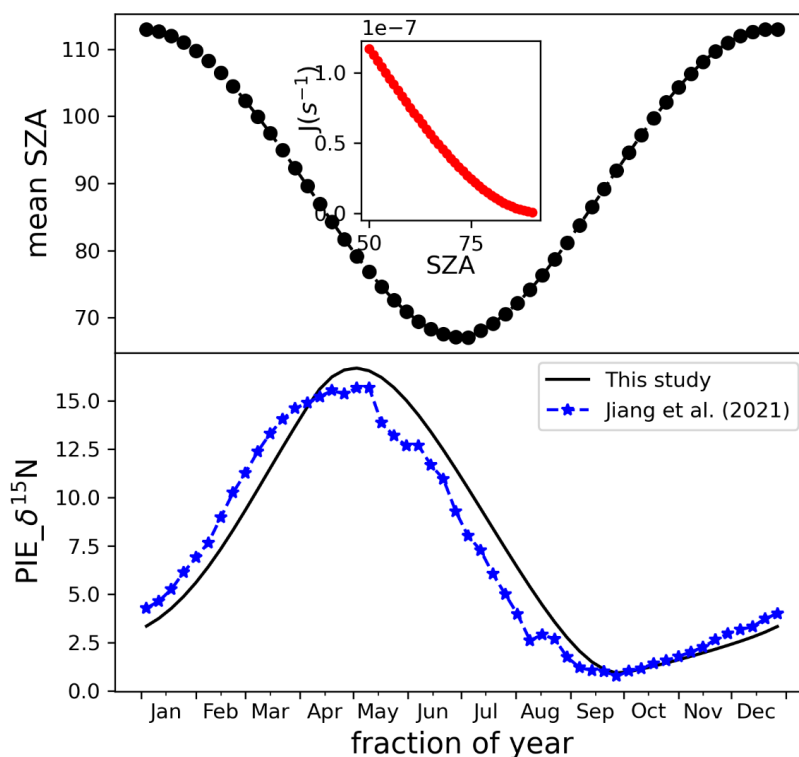
Figure 3. Upper panel: mean solar zenith angle (SZA) (shown in black circles) at Summit within a year and nitrate photolysis rate constant (J) as a function of SZA (shown in red circles in the inset). The summertime J value is from Galbavy et al. (2007) and we scaled it with SZA to obtain J values for other months for simplicity. Lower panel: calculated PIE using Equation (3) and that from the TRANSITs model in Jiang et al. (2021), weekly snow accumulation rates were from bamboo stick measurements by Dibb et al. (2004).

The $\delta^{15}N(NO_3^-)$ of atmospheric nitrate was depleted by (9.8 ± 5.1) ‰ relative to surface snow nitrate during spring. In summer, the enrichment was (9.1 ± 5.1) ‰, and decreased to (4.0 ± 4.3) ‰ in fall and became negligible in winter. Fibiger et al. (2015) and Jarvis et al. (2009) made short-term field observations at Summit in spring/early summer in different years, by simultaneously collecting atmospheric gas-phase HNO_3 and surface snow for isotope analyses. The Fibiger et al. (2015) results suggested that the surface snow nitrate was enriched in $\delta^{15}N(NO_3^-)$ by ~12-15 ‰ compared to atmospheric nitrate in May and June, closed to result (~ 10 ‰) of the compiled data. However, despite using similar sampling techniques (mist chamber) for collection of

gas-phase HNO_3 in March and May, Jarvis et al. (2009) found no significant $\delta^{15}N(NO_3^-)$ differences between gas-phase and surface snow nitrate. Note that the reported nitrate

455 concentration from Jarvis et al. (2009) was high (>3 nmol m^{-3}, which equals to 94.8 pptv assuming average temperature of 255 K and pressure of 670 mbar at Summit in spring) compared to other studies (ranges from 10 to 20 pptv) (Dibb et al., 2010; Fibiger et al., 2016; Dibb et al., 1998 and this study). This may imply potential contamination during sampling of the gas-phase HNO_3, which remains to be explored and confirmed.

460 Nevertheless, the enrichments of $\delta^{15}N(NO_3^-)$ in surface snow compared to atmospheric nitrate and its seasonal difference (larger in the summer half year) also imply the effect of the photo-driven post-depositional processing. Erbland et al. (2013) also observed enriched $\delta^{15}N(NO_3^-)$ in surface snow nitrate compared to atmospheric nitrate at Dome C, Antarctica. At Dome C, the seasonal pattern of the surface snow-

465 atmosphere enrichments was similar to that at Summit, being the largest in Austral spring (~ 30 ‰) and the smallest in Austral winter (~ 10 ‰). In addition, the enrichment at Dome C was observed throughout the year, and even in winter there was still a ~ 10 ‰ enrichment. The elevated enrichment of $\delta^{15}N(NO_3^-)$ in surface snow nitrate compared to atmospheric nitrate in spring/summer observed both at Summit and Dome C suggest

470 the role of photolysis as proposed by Erbland et al. (2013). Compared to surface snow, atmospheric nitrate is more influenced by snow-sourced nitrate which is severely depleted in $\delta^{15}N$ (–60 to –100 ‰, Jiang et al. (2021)). In addition, surface snow nitrate has experienced photolysis which tends to increase its $\delta^{15}N$ relative to the originally deposited nitrate. Winton et al. (2020) also suggested that at DML low snow

475 accumulation rate and ample solar radiation tends to alter the original deposited nitrate signal through photolysis even for the skin layers (defined as the upper most 0.5 cm snow). At Summit, although the snow accumulation rate is high compared to the East Antarctic plateau, unless frequent snowfall occurs to wash out atmospheric nitrate to refresh the surface snow $\delta^{15}N(NO_3^-)$, dry deposition of atmospheric nitrate is unable to

480 influence the budget of nitrate in surface snow (1-3 cm) and disturb its $\delta^{15}N(NO_3^-)$ even in a period of a few weeks (Jiang et al. 2021). This is because (i) snow is a much larger reservoir of nitrate compared to the atmosphere and (ii) the nitrate dry deposition flux

is very low (Bergin et al., 1995; Erbland et al., 2013; Jiang et al. 2021).

4.1.2 The potential role of nitrogen isotope fractionation during deposition

Different from Summit, around +10 ‰ enrichment in surface snow $\delta^{15}N(NO_3^-)$ compared to atmospheric nitrate exists at Dome C during winter in the absence of sunlight. Erbland et al. (2013) attributed this winter enrichment to nitrogen isotope fractionation during nitrate deposition which increases $\delta^{15}N(NO_3^-)$ in the deposited nitrate compared to the atmospheric pool, and suggested this also contributes to the observed surface snow to atmospheric enrichment in spring/summer. However, the Summit data indicated no such enrichment in the winter, and this appears to be in conflict with the suggested deposition fractionation by Erbland et al. (2013). Although detailed physical mechanism leading to the deposition fractionation remains unknown, we speculated that the fractionation might be related to the form of deposition. Given the large difference in snow accumulation rate at Summit (250 kg m^{-2} a^{-1}) and Dome C (25 kg m^{-2} a^{-1}), their main nitrate deposition mechanism might be quite different. At Dome C, nitrate concentration in the skin layer is mainly controlled by kinetic adsorption and co–condensation of atmospheric nitrate (Bock et al., 2016; Frey et al., 2009; Chan et al., 2018). While at Summit, the dominant mechanism for nitrate incorporation into snow grain is the surface uptake during wet scavenging of atmospheric nitrate (Röthlisberger et al., 2002). Since wet deposition can efficiently scavenge atmospheric nitrate, a more complete removal of atmospheric nitrate at Summit compared to Dome C may occur, which would induce little to no isotope fractionation in $\delta^{15}N$ due to mass balance. However, for surface snow that continues to incorporate atmospheric nitrate via co–condensation or dry deposition (adsorption/desorption) after snowfall events, isotope fractionation could occur and leads to detectable enrichments in surface snow nitrate. The surface snow to atmospheric nitrate enrichments of $\delta^{15}N(NO_3^-)$ at Summit also appears to support the speculated role of fractionation during nitrate deposition. As shown in Figure 2b, the maximum enrichments occurred in spring/summer, which was also the time with the lowest weekly average snow accumulation rate in a year (Burkhart et al., 2004; Jiang

et al, 2021) and presumably more nitrate dry deposition occurred which leads to large isotope fractionation effect.

515   In summary, the systematic differences in $\delta^{15}N(NO_3^-)$ between atmospheric, surface snow and snowpack samples are consistent with the expected effects of the photo-driven post-depositional processing, while the occurrence and mechanism(s) of nitrogen isotope fractionation during deposition and its contribution to the surface snow-atmospheric $\delta^{15}N(NO_3^-)$ enrichment need to be further explored and confirmed.

520

4.2 The oxygen isotope systematics

4.2.1 The similarity of $\Delta^{17}O(NO_3^-)$ in atmospheric and snowpack nitrate

The atmospheric and snowpack $\Delta^{17}O(NO_3^-)$ display similar seasonality and their absolute values were similar (Figure 2c). The seasonal variations in $\Delta^{17}O(NO_3^-)$ is well

525   understood as the seasonal shift of dominant HNO_3 formation pathways from summer (NO_2 + OH → HNO_3 with low $\Delta^{17}O$) to winter (N_2O_5 hydrolysis with high $\Delta^{17}O$) (Alexander et al., 2020), so we don't discuss the cause of the seasonality in further detail. In the following discussion, we focus on the processes occurring at the air-snow interface and in snow and their effects on $\Delta^{17}O(NO_3^-)$.

530   Frey et al. (2009) proposed that nitrate in the uppermost layer of snow should reach equilibrium with atmospheric nitrate to maintain consistent isotope ratios. However, the large difference between atmospheric and surface snow $\delta^{15}N(NO_3^-)$ at Dome C Antarctica and Summit Greenland suggests no equilibrium. Conversely, an equilibrium in $\Delta^{17}O(NO_3^-)$ appears to exist. Erbland et al. (2013) made year-round

535   observations of atmospheric nitrate and nitrate in the skin layer at Dome C, and found that $\Delta^{17}O(NO_3^-)$ in the skin layer was similar to atmospheric $\Delta^{17}O(NO_3^-)$ except in spring when $\Delta^{17}O(NO_3^-)$ was ~ 5 ‰ higher than the former. This was explained by a reservoir effect by Erbland et al. (2013), as the surface snow is always a much larger reservoir for nitrate relative to the atmosphere, and there might be a delay in skin layer

540   nitrate variations compared to the changes in atmospheric nitrate.

Although annual surface snow $\Delta^{17}O(NO_3^-)$ data are not available at Summit, the two short–term observations by Fibiger et al. (2016) show that the atmospheric and

surface snow $\Delta^{17}O(NO_3^-)$ are not significantly different. Note that the Fibiger et al (2016) surface snow data have much finer temporal resolution (4-12 hours) and show

545   larger variability, but the averages fell well within the ranges of the atmospheric and snowpack data at longer time resolution. As proposed by Frey et al. (2009), one should expect a similar trend in atmospheric and surface snow $\Delta^{17}O(NO_3^-)$ (i.e., an equilibrium). This is because $\Delta^{17}O(NO_3^-)$ is a mass-independent fractionation signal and won't be affected by deposition process nor directly affected by snow nitrate

550   photolysis, as these processes only induce mass-dependent fractionation. Once deposited, the only process that would influence snow $\Delta^{17}O(NO_3^-)$ is the cage effect (Frey et al., 2009; McCabe et al., 2005; Meusinger et al., 2014). The cage effect therefore incorporates water $\Delta^{17}O$ (~ 0 ‰) to snow nitrate and lowers its $\Delta^{17}O$. But, as observed and/or discussed by Erbland et al. (2013) and Jiang et al. (2021), the cage

555   effect is likely an accumulated effect over long time periods and it won't significantly affect $\Delta^{17}O(NO_3^-)$ in the skin layer nor surface snow. Therefore, the surface snow nitrate should possess similar or identical $\Delta^{17}O$ signal as atmospheric nitrate, as is observed.

From the surface snow to its final archival, $\Delta^{17}O(NO_3^-)$ would be further modified

560   by the cage effect. The cage effect on snow $\Delta^{17}O(NO_3^-)$ is most evident at sites with low snow accumulation rate such as Dome C (Erbland et al., 2013; Frey et al., 2009), where nitrate stays in the photic zone for 4 to 5 years. In comparison, at Summit, the cage effect is negligible (<0.3 ‰ upon archival, calculated by Jiang et al. (2021)) owing its fast archival (less than a half year) given the high snow accumulation rate, the

565   archived snow nitrate should carry similar $\Delta^{17}O$ signal to its deposited value at the surface, which is in turn determined by atmospheric nitrate. Therefore, snowpack $\Delta^{17}O(NO_3^-)$ should be very similar to that of atmospheric nitrate, as is observed (Figure 2c). However, this doesn't mean that snow nitrate $\Delta^{17}O(NO_3^-)$ can be directly linked to primary nitrate. Locally reformed nitrate under sunlight in the summer half year would

570   possess low $\Delta^{17}O$ compared to primary nitrate deposited earlier in the season (Kunasek et al., 2009; Jiang et al., 2021) and contributes to the local atmospheric nitrate budget (Jiang et al., 2021).

4.2.2 The atmospheric, surface snow and snowpack $\delta^{18}O(NO_3^-)$

575   Compared to $\delta^{15}N(NO_3^-)$ and $\Delta^{17}O(NO_3^-)$, $\delta^{18}O(NO_3^-)$ displays a much larger variability in terms of monthly averages as well as in the magnitude of the seasonal variations, and are sometimes inconsistent even for the same type of samples (i.e., atmospheric vs. snow) measured by the same group. For example, Fibiger et al. (2016) reported average atmospheric $\delta^{18}O(NO_3^-)$ in May and June in one year of ~ 54 ‰ while

580   in the other year it was ~ 91 ‰. The larger variability in $\delta^{18}O(NO_3^-)$ is somewhat expected, as it is influenced by $\delta^{18}O$ in precursor gases (NO, NO_2), radicals (O_3, OH, BrO, HO_2, RO_2, etc), and atmospheric water, as well as fractionations during formation (Michalski et al., 2012). Additionally, snow nitrate photolysis also directly influences $\delta^{18}O$ with a fractionation factor calculated to be –34 ‰ by Frey et al. (2009), but does

585   not affect $\Delta^{17}O$ owing to its mass-independent nature. Some of these processes act to enrich $\delta^{18}O$ (e.g., photolysis) while others act to deplete $\delta^{18}O$ (e.g., OH oxidation and/or exchange with water).

Conventionally, variations in $\delta^{18}O(NO_3^-)$ are also used to track nitrate oxidation formation mechanisms, similar to $\Delta^{17}O$ (Michalski et al., 2012; and references therein).

590   In general, under sunlight, nitrate formed from NO_2 + OH reaction possesses lower $\delta^{18}O$ than that formed from N_2O_5 hydrolysis under dark conditions. The latter involves more oxygen atoms transferred from O_3 which possesses very high $\delta^{18}O$ (90-120 ‰, Johnston et al., 1997; Krankowsky et al., 1995). As a result, higher winter $\delta^{18}O(NO_3^-)$ and lower summer $\delta^{18}O(NO_3^-)$ should be expected, as observed for the atmospheric

595   nitrate in this study and many others (Erbland et al., 2013; Savarino et al., 2007; Walters et al., 2019). This is also why we noted that the $\delta^{18}O(NO_3^-)$ data in Jarvis et al. (2009) should be treated with caution as it indicated a summer maximum, which is difficult to understand given current knowledge. In the following discussion, we do not attempt to describe this discrepancy in Jarvis et al. (2009) compared to other observations and our

600   understanding of processes controlling nitrate $\delta^{18}O$.

Theoretically, after deposition of nitrate to the snow surface, both snow nitrate photolysis and the cage effect will all affect $\delta^{18}O(NO_3^-)$ in opposite directions. Similar

to $\Delta^{17}O(NO_3^-)$, there was also an (quasi) equilibrium in $\delta^{18}O(NO_3^-)$ between atmospheric and skin layer snow nitrate observed at Dome C, Antarctica (Erbland et al., 2013). Atmospheric gas-phase and surface snow nitrate $\delta^{18}O(NO_3^-)$ at Summit has been reported by Jarvis et al. (2009) and Fibiger et al. (2015) for spring and summer months. While the Jarvis et al. (2009) study suggested that the surface snow nitrate $\delta^{18}O(NO_3^-)$ was on average 40 ‰ higher than atmospheric gas phase HNO_3, the Fibiger et al. (2016) study found that surface snow $\delta^{18}O(NO_3^-)$ was lower than atmospheric nitrate in one year but higher in another. The atmospheric gas-phase nitrate $\delta^{18}O(NO_3^-)$ reported by Jarvis et al. (2009) and Fibiger et al. (2016) were also lower than the atmospheric $\delta^{18}O(NO_3^-)$ data reported by this study. The seasonal atmospheric and surface snow $\delta^{18}O(NO_3^-)$ data at Summit also didn't indicate an equilibrium. Overall, the proposed equilibrium between atmospheric and surface snow nitrate $\delta^{18}O(NO_3^-)$ is not supported by current observations.

Because of the lack of sufficient surface snow samples, and the inconsistency among the limited observations by Jarvis et al. (2009) and Fibiger et al. (2015), we are unable to assess the potential oxygen isotope fractionation effects during nitrate deposition. But we note that this could also alter $\delta^{18}O(NO_3^-)$ in analogy with $\delta^{15}N(NO_3^-)$ and therefore this point needs to be further explored. After deposition, the post–depositional processing will impact the snow $\delta^{18}O(NO_3^-)$ in a similar matter as it impacts $\delta^{15}N$. The typical photolysis isotope fractionation factor ($^{18}\varepsilon_p$) for ^{18}O at Summit was calculated to be –32.8 ‰ using the ZPE shift method following Frey et al. (2009). Using the maximum loss fraction of 21% for spring snow from Jiang et al. (2021) and applying the Rayleigh equation, we calculated a maximum PIE of 7.7 ‰ for $\delta^{18}O(NO_3^-)$. This means upon archival, snow $\delta^{18}O(NO_3^-)$ would be enriched by up to 7.7 ‰ by considering only the photolysis fractionation. Conversely, the cage effect works to decrease snow $\delta^{18}O(NO_3^-)$ by exchanging oxygen atoms with water. A quantification of this effect (but an over-simplified one) is to consider the fraction of exchange of nitrate oxygen atom with water during the recombination chemistry, but one should keep in mind that the complex kinetic isotope fractionation during the recombination reactions could also affect $\delta^{18}O(NO_3^-)$ in snow. Here we used a simple

mass balance method to assess the magnitude of changes in $\delta^{18}O(NO_3^-)$ through the apparent "exchange" caused by the cage effect:

$$635 \quad \delta^{18}O(NO_3^-)_{finnal} = \frac{f_c * (1 - f_{rem}) * \delta^{18}O(H_2O) + f_{rem} * \delta^{18}O(NO_3^-)_{initial}}{f_c * (1 - f_{rem}) + f_{rem}} \quad (4)$$

where f_{rem} and f_c represent the remaining fraction of snow nitrate after photolysis and the fraction of exchange of nitrate oxygen atom with water via cage effect, respectively. Taking snow $\delta^{18}O(H_2O)$ to be –35 ‰ (Hastings et al., 2004) and snow nitrate $\delta^{18}O(NO_3^-)$ to be 80 ‰ (Geng et al., 2014) at Summit, and adapting the f_{rem} and f_c calculated by Jiang et al. (2021) to be 0.79 and 0.15, respectively, we calculated a maximum decrease in $\delta^{18}O(NO_3^-)$ of 4.4 ‰ upon archival caused by the cage effect. This is in contrast to $\Delta^{17}O$, as the very different $\delta^{18}O(H_2O)$ and $\delta^{18}O(NO_3^-)$ value makes the effect significant even for small amount of exchange. Note f_c used here was a purely empirical parameter adapting from Erbland et al. (2015), by best fitting the decreasing trend in $\Delta^{17}O(NO_3^-)$ observed in Dome C snowpack. If we doubled f_c (from 15 % to 30 %), an 8.4 ‰ decrease in $\delta^{18}O(NO_3^-)$ could be caused by the cage effect at Summit.

These simplified calculations suggest that there might be a difference in atmospheric $\delta^{18}O(NO_3^-)$ and snowpack $\delta^{18}O(NO_3^-)$ at Summit, but the magnitude and direction depend on the relative degrees of photolysis fractionation, the cage effect, and also other processes mentioned above (e.g., the kinetic isotope fractionation during secondary nitrate formation).

4.2.3 The relationship between $\Delta^{17}O(NO_3^-)$ and $\delta^{18}O(NO_3^-)$

Fibiger et al. (2013) found a strong linear relationship between their measured $\Delta^{17}O(NO_3^-)/\delta^{18}O(NO_3^-)$ in surface snow samples at Summit. Based on this relationship they proposed a direct transfer of atmospheric oxygen isotope signals to surface snow at Summit. However, as discussed in Jiang et al. (2021), this relationship should not be viewed as an evidence of little to no post-depositional processing. Instead, examining the $\Delta^{17}O(NO_3^-)/\delta^{18}O(NO_3^-)$ relationships among atmospheric, surface snow and snowpack samples may provide some clues on whether or not the photo-driven post-depositional processing impacts the $\Delta^{17}O(NO_3^-)/\delta^{18}O(NO_3^-)$ ratio, since post-

depositional processing influences $\Delta^{17}O(NO_3^-)$ and $\delta^{18}O(NO_3^-)$ differently. Here we plotted our atmospheric and snowpack $\Delta^{17}O(NO_3^-)/\delta^{18}O(NO_3^-)$ data together with the four months (in year 2010 and 2011) of surface snow data from Fibiger et al (2013) in

665   Figure 4.
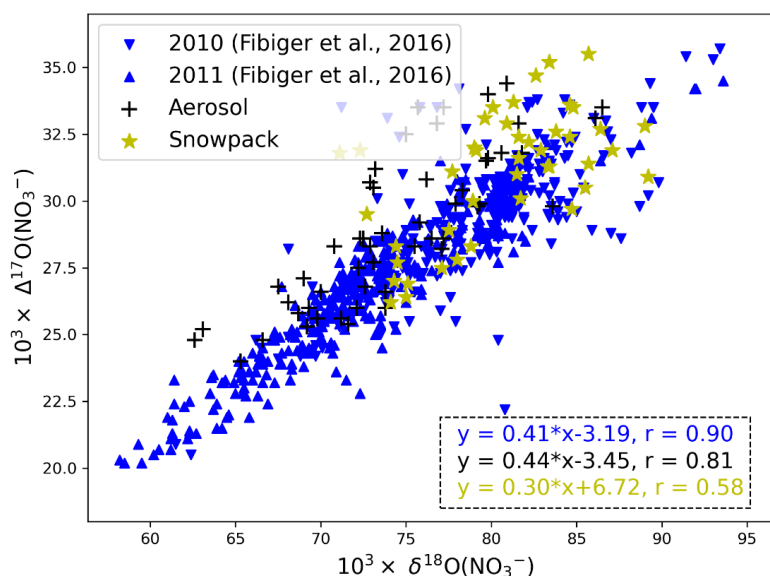
Figure 4. Relationship between $\Delta^{17}O(NO_3^-)/\delta^{18}O(NO_3^-)$ for all atmospheric (this study), surface snow (Fibiger et al., 2013) and snowpack data (Geng et al., 2014). Note the
670   Fibiger et al. (2013) data was only for four months (May to June in 2010 and 2011), and the abnormal $\Delta^{17}O(NO_3^-)$ value less than 20 ‰ was abandoned.

As shown in Figure 4, the linear relationship between atmospheric $\Delta^{17}O/\delta^{18}O(NO_3^-)$ ($\Delta^{17}O(NO_3^-)) = (0.44 \pm 0.04) \times \delta^{18}O(NO_3^-) - (3.45 \pm 3.28)$, r = 0.81) is very similar to
675   the reported surface snow relationship ($\Delta^{17}O(NO_3^-)) = (0.41 \pm 0.01) \times \delta^{18}O(NO_3^-) - (3.19 \pm 0.41)$, r = 0.90) despite their different time coverages. Such a relationship suggests that the linearity of $\Delta^{17}O/\delta^{18}O(NO_3^-)$ in surface snow may directly originate from atmospheric nitrate, consistent with the conclusion of Fibiger et al. (2013). However, in the snowpack data, the linearity between $\Delta^{17}O$ and $\delta^{18}O(NO_3^-)$ ($\Delta^{17}O(NO_3^-)$
680      $= (0.30 \pm 0.06) \times \delta^{18}O(NO_3^-) + (6.72 \pm 5.29)$, r = 0.58) was significantly different from that of aerosol or surface snow nitrate, suggesting that post–depositional processing

likely has changed the originally deposited oxygen isotope signals up on archival. Furthermore, if the $\Delta^{17}O(NO_3^-)$ was only negligibly altered after deposition as calculated by Jiang et al. (2021), the smaller slope for snowpack $\Delta^{17}O/\delta^{18}O(NO_3^-)$

685   compared to that for atmospheric and surface snow samples suggests an enrichment of $\delta^{18}O(NO_3^-)$ at depth, similar to $\delta^{15}N$. This suggests that the fractionation of $\delta^{18}O$ from photolysis exceeds that of the cage effect at Summit. This is consistent with the large impact on $\delta^{15}N$ from photolysis and the small impact on $\Delta^{17}O$ from the cage effect. We note that similar observations, i.e., better linearity of $\Delta^{17}O/\delta^{18}O(NO_3^-)$ in atmosphere

690   and surface snow nitrate than that in the whole snowpack, were observed at Dome C where the photolysis of snow nitrate has been unambiguously shown to be dominant (Erbland et al., 2013). This emphasizes again that, when evaluating the degree of post–depositional processing, one should consider samples covering the all depth of the photic zone, not only surface samples.

695

4. Conclusion

In this study, we reported the first year-round atmospheric nitrate isotopes measurements for Summit, Greenland. The atmospheric $\delta^{15}N(NO_3^-)$ displayed systematic differences from surface snow and snowpack $\delta^{15}N(NO_3^-)$ values at Summit

700   compiled from the literature. In general, atmospheric, surface snow, and snowpack $\delta^{15}N(NO_3^-)$ diverged when there was sunlight but converged in the absence of sunlight. The gradual enrichments in $\delta^{15}N(NO_3^-)$ from atmospheric nitrate to surface snow nitrate, and finally to snowpack nitrate can only be explained by the effect of the photo-driven post-depositional processing, and the enrichment after deposition can also be

705   quantitatively explained by the photo-induced effect (PIE). We proposed a simplified method for estimating PIE that can quickly assess the degree of $\delta^{15}N(NO_3^-)$ enrichment from the time of deposition to preservation in snow beneath the snow photic zone. Unlike $\delta^{15}N(NO_3^-)$, snowpack and atmospheric $\Delta^{17}O(NO_3^-)$ displayed very similar seasonal patterns and absolute values, suggesting that it is well preserved, consistent

710   with Jiang et al. (2021). We emphasize that atmospheric nitrate is not solely dependent on primary nitrate from long-range transport as it is also influenced by snow-sourced

nitrate in the summer half year. The $\delta^{18}O(NO_3^-)$ data were more variable and showed some inconsistence among different observations. We analyzed the relationships between $\Delta^{17}O$ and $\delta^{18}O(NO_3^-)$ among different types of samples, and found that the

715   linearity of $\Delta^{17}O/\delta^{18}O(NO_3^-)$ in snowpack is different from that of atmospheric and surface snow. This suggests that the degree of preservation for $\Delta^{17}O$ and $\delta^{18}O(NO_3^-)$ are likely different from each other at Summit, mainly due to the fact that photo-driven post-depositional processing drives mass-dependent fractionation of isotopes which directly affects $\delta^{18}O(NO_3^-)$ but not $\Delta^{17}O(NO_3^-)$. Overall, our analyses suggest that

720   thephoto-driven post–depositional processing impacts both $\delta^{15}N$ and $\delta^{18}O(NO_3^-)$ at Summit. As a result, the signals of primary nitrate $\delta^{15}N(NO_3^-)$ is unlikely preserved at this site, and $\Delta^{17}O$ and $\delta^{18}O(NO_3^-)$ of primary nitrate are also disturbed but to different degrees.

In the end, we note the limitations of the compiled data. These data were collected

725   by different groups at different time, and with different sampling methods as well as different temporal resolutions. Although theoretically, the seasonality of the isotopes should be similar in different years or for samples collected and measured by different groups, and the heterogeneity of the samples was reduced by taking weighted average, there were some aspects and inconsistencies in the data that are difficult to interpret.

730   Simultaneous collection of atmospheric, surface snow and snowpack samples with similar resolution for at least one complete year in the future should be conducted. This will provide a more consistent and solid dataset to improve or confirm the current understanding of nitrate preservation and isotope variations at Summit, Greenland. This is not only important for nitrate isotope record interpretation at this site, but also for

735   other sites with similar or higher snow accumulation rate such as the WAIS (West Antarctic Ice Sheet) Divide.

Data availability. The atmospheric aerosol nitrate isotope data and the compiled dataset will be provided upon direct request to the corresponding author.

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Author contributions.

L.G conceived this study. JL.J. and J.E. collected and analyzed the aerosol samples respectively. Z.J. compiled the dataset, analyzed the data, developed the formula used in calculation and wrote the manuscript with L.G. J. S. and B.A. provided suggestions for data interpretation. All authors gave feedback on the paper writing.

Competing interests. Some authors are members of the editorial board of *The Cryosphere*. The peer-review process was guided by an independent editor, and the authors have also no other competing interests to declare.

Acknowledgements: L.G. acknowledges financial support from the National Natural Science Foundation of China (Awards: 41822605, 41871051 and 41727901), the Fundamental Research Funds for Central Universities, the Strategic Priority Research Program of Chinese Academy of Sciences (XDB 41000000), and the National Key R&D Program of China (2019YFC1509100). This work was partially supported by the French national programme LEFE/INSU (IMAGO), the ANR grants ANR-15-IDEX-02 (project IDEX Université Grenoble Alpes) (J.S.). J.S. and JL.J. thank the French Polar institute (Institut Polaire Français IPEV, previously IFRTP) for field and funding support, and PNCA / CNRS-INSU for funding the SCIRA program (JL. J.). Gilles Aymoz is warmly acknowledged for setting up the experiments on site, together with winter over American people employed by PICO for sample maintenance during the sampling year. B. A. acknowledges support from NSF (award PLR 1542723).

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