



# A 60-year atmospheric nitrate isotope record from a Southeast Greenland ice core with minimal post-depositional alteration

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Abstract. Stable isotopes of atmospheric nitrate (NO<sub>3</sub><sup>-</sup>) are valuable tools for tracing nitrogen sources and processes; however, their signals in ice core records are often disrupted by post-depositional processes. The ice core from the southeastern Dome (SE-Dome) in Greenland is a potential record of variations in atmospheric chemistry that has experienced less post-depositional effects owing to a high accumulation rate (~1 m w e a<sup>-1</sup>). Herein, we report 60-year (1959–2014)  $\delta^{15}$ N(NO<sub>3</sub><sup>-</sup>) and  $\Delta^{17}$ O(NO<sub>3</sub><sup>-</sup>) records from the SE-Dome ice core.  $\delta^{15}$ N(NO<sub>3</sub><sup>-</sup>) decreased from 1960 to 1974 and exhibited clear seasonal changes (high in summer and low in winter).  $\Delta^{17}$ O(NO<sub>3</sub><sup>-</sup>) did not exhibit any significant long-term trends, but did contain seasonal patterns.

- 25 The mass-weighted annual average of  $\delta^{15}N(NO_3^-)$  values in the SE-Dome core were 4.2 ± 2.8 ‰ lower than those in the Greenland Summit ice core between 1959–2006. The Transfer of Atmospheric Nitrate Stable Isotopes To the Snow (TRANSITS) model under the SE-Dome condition estimated changes of only 0.9 ‰ in  $\delta^{15}N(NO_3^-)$  and -0.2 ‰ in  $\Delta^{17}O(NO_3^-)$  from the initial deposition. Although differences in the source of NO<sub>3</sub><sup>-</sup> cannot be discounted, the lower  $\delta^{15}N(NO_3^-)$  values observed at the SE-Dome compared to the Summit were likely due to reduced post-depositional alteration. Therefore, the SE-
- 30 Dome ice core NO<sub>3</sub><sup>-</sup> record offers a precise reconstruction of NO<sub>x</sub> emissions and atmospheric oxidation chemistry during transport, preserving records from both North America and Western Europe, thereby providing reliable insight into atmospheric nitrogen cycling.

#### **1** Introduction

35 Nitrate  $(NO_3^-)$  and its precursors  $(NO_x = NO + NO_2)$  play important roles in the atmosphere. Tropospheric  $NO_x$  cycling produces ozone  $(O_3)$ , a key component of the atmospheric oxidative capacity (Finlayson et al., 1999). The final oxidation



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product (HNO<sub>3</sub>) of NO<sub>x</sub> emitted from various sources is a component of acid rain (Shammas et al., 2020) and particulate matter (as NO<sub>3</sub><sup>-</sup>, Zhai et al., 2021), and is eventually deposited to the surface as a nutrient (Duce et al., 2008). Owing to increasing fossil fuel and chemical fertilizer use since the beginning of the Industrial Revolution, NO<sub>x</sub> levels in the atmosphere have increased, which is reflected in the elevated NO<sub>3</sub><sup>-</sup> concentrations in ice cores, including those collected from Greenland (Neftel et al., 1985; Mayewski et al., 1986).

In addition to NO<sub>3</sub><sup>-</sup> concentrations, its stable isotopic compositions provide valuable information. Nitrogen isotopes ( $\delta^{15}$ N) differ among NO<sub>x</sub> sources and can be used to identify the origin of the NO<sub>3</sub><sup>-</sup> (Hastings et al., 2010, 2013). Previous studies of Greenland ice cores have identified decreases in the  $\delta^{15}$ N values of NO<sub>3</sub><sup>-</sup> ( $\delta^{15}$ N(NO<sub>3</sub><sup>-</sup>)) as early as 1850 CE, which subsequently accelerated after 1950 CE (Hastings et al., 2009; Geng et al., 2014). These decreases in  $\delta^{15}$ N have been interpreted as a change

- 45 accelerated after 1950 CE (Hastings et al., 2009; Geng et al., 2014). These decreases in  $\delta^{15}$ N have been interpreted as a change in source: increased anthropogenic emissions of NO<sub>x</sub> from fossil fuel combustion (Hastings et al., 2009) and/or NO<sub>x</sub> derived from soil amended with fertilizer (Felix & Elliott, 2013). However, atmospheric NO<sub>3</sub><sup>-</sup> formation comprises two stages: photochemical cycling of NO and NO<sub>2</sub> and the oxidation of NO<sub>2</sub> into HNO<sub>3</sub> (Alexander et al., 2020). In addition, complex factors control  $\delta^{15}$ N(NO<sub>3</sub><sup>-</sup>). Previous studies have shown that isotopic fractionation can occur during gas–particle partitioning
- solution and washout (Freyer, 1991), kinetic NO<sub>2</sub> oxidation (Walters & Michalski, 2015a), and NO<sub>x</sub> cycle equilibrium in the atmosphere (Walters et al., 2015b; Walters and Michalski, 2016). Another interpretation of the decrease in  $\delta^{15}$ N in ice cores is related to changes in isotopic fractionation between gaseous HNO<sub>3</sub> and particulate NO<sub>3</sub><sup>-</sup> that resulted from acidity changes (Geng et al., 2014). The mass-independent oxygen isotope fractionation signals ( $\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O$ ) of NO<sub>x</sub> and NO<sub>3</sub><sup>-</sup> can reflect the oxygen source during oxidation (Michalski et al., 2003; Alexander et al., 2009). Positive  $\Delta^{17}O$  values of NO<sub>3</sub><sup>-</sup> ( $\Delta^{17}O(NO_3^-)$ )
- occur as a result of excess <sup>17</sup>O (i.e., deviation from mass-dependent fractionation) transferred from O<sub>3</sub> to NO<sub>3</sub><sup>-</sup> during photochemical cycling of NO and NO<sub>2</sub> and the oxidation of NO<sub>2</sub> into HNO<sub>3</sub>. Thus, mid to high latitudes have  $\Delta^{17}O(NO_3^-)$ values of 22–34 ‰ for atmospheric deposition (Michalski et al., 2003, 2012). Since NO<sub>3</sub><sup>-</sup> deposited to ice core are preserved in ice cores, past atmospheric chemistry has been discussed by measuring  $\Delta^{17}O(NO_3^-)$  in ice cores (Geng et al., 2017).
- However, post-depositional NO<sub>3</sub><sup>-</sup> loss in snow/ice can reduce NO<sub>3</sub><sup>-</sup> concentrations and change its isotopic compositions
  (Röthlisberger et al., 2000, 2002; Frey et al., 2009; Akers et al., 2022). NO<sub>3</sub><sup>-</sup> in snow can undergo photolysis by ultraviolet (UV) light (λ = 290–350 nm, Berhanu et al., 2014), which produces NO<sub>2</sub> that is released into the atmosphere via diffusion or wind pumping. Although NO<sub>2</sub> can partially re-oxidize into NO<sub>3</sub><sup>-</sup> in the atmosphere, post-depositional processes can lead to decreases in the NO<sub>3</sub><sup>-</sup> concentrations in ice cores (Meusinger et al., 2014; Erbland et al., 2015). In addition, post-depositional processes can also cause significant isotopic fractionation (from -47.9 ‰ to -55.8 ‰) and the remaining NO<sub>3</sub><sup>-</sup> becomes enriched in <sup>15</sup>N (Berhanu et al., 2015). In contrast, Δ<sup>17</sup>O(NO<sub>3</sub><sup>-</sup>) is not directly affected by photolysis but instead by the cage effect, in which the intermediate photoproducts (NO<sub>2</sub> and NO<sub>3</sub><sup>-</sup>) exchange with water oxygen or react with radicals (e.g., OH)
- in snow grains to regenerate NO<sub>3</sub><sup>-</sup> after being emitted to the atmosphere (McCabe et al., 2005; Jiang et al., 2021). The alteration of  $\Delta^{17}O(NO_3^-)$  can also occur through the re-oxidation of NO<sub>2</sub> sourced from snow, which leads to nitrate formation in the overlying atmosphere (Erbland et al., 2013). Because NO<sub>3</sub><sup>-</sup> photolysis in snow only occurs in the photic zone, the degree of
- 70 post-depositional alteration is mostly controlled by the snow accumulation rate, as demonstrated in Antarctica (Akers et al., 2022). Even at the Greenland Summit ice core site, the δ<sup>15</sup>N(NO<sub>3</sub><sup>-</sup>) values of the snowpack are higher than those of the surface snow and the overlying atmosphere (Jarvis et al., 2009; Geng et al., 2014; Fibiger et al., 2016). The Greenland Ice Sheet Project 2 (GISP2) ice core exhibits decreasing δ<sup>15</sup>N(NO<sub>3</sub><sup>-</sup>) values from glacial to interglacial periods (Hastings et al., 2005; Geng et al., 2015), which has been interpreted as the result of two potential causes: (1) changes in the NO<sub>x</sub> source or (2) post-depositional effects related to the snow accumulation rate and dust concentrations. Overall, given the impacts of post-
- $^{75}$  depositional effects related to the snow accumulation rate and dust concentrations. Overall, given the impact depositional processes, ice core records of NO<sub>3</sub><sup>-</sup> and its isotopes require careful consideration.

Compared with the Summit site, the southeastern Dome (SE-Dome) site in Greenland has distinct characteristics, including a snow accumulation rate of  $1.01 \pm 0.22$  m w e a<sup>-1</sup> (1960–2014) (Iizuka et al., 2017), which is approximately four times greater than that at the Summit site ( $0.22 \pm 0.05$  m w e a<sup>-1</sup>, Fig. 1b) (Geng et al., 2014). Based on the Mann–Kendall test for monotonic

trends (Kendall, 1975; Mann, 1945), no significant decadal trends in snow accumulation were observed at both the SE-Dome (Kawakami et al., 2023) and the Summit (p > 0.05). The Summit and SE-Dome sites cover similar source origins from North America and Western Europe, based on Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) 7-d backward trajectory modelling (Figs. 1a and 1b). In this study, we present the  $\delta^{15}N(NO_3^-)$  and  $\Delta^{17}O(NO_3^-)$  records obtained from a 90.45 m ice core drilled at the SE-Dome site. To investigate the effect of snow NO<sub>3</sub><sup>-</sup> photolysis on NO<sub>3</sub><sup>-</sup> preservation and its isotopic





85 composition, we applied the Transfer of Atmospheric Nitrate Stable Isotopes To the Snow (TRANSITS) model (Erbland et al., 2015; Jiang et al., 2021) and modified its conditions for the SE-Dome site. Based on the results, we argue that the SE-Dome ice core is suitable for reconstructing changes in human-induced atmospheric NO<sub>3</sub><sup>-</sup> over the Northern Hemisphere, particularly for eastern North America and western Europe.



Figure 1. Probability distributions for the air masses overlying the (a) SE-Dome and (b) Summit sites from 7-day three-dimensional back trajectory analysis based on HYSPLIT modeling (1960–2019). Detailed back trajectory analysis procedures were the same as lizuka et al. (2018). (c) Annual accumulation rate at the SE-Dome (Furukawa et al., 2017) and Summit (Geng et al., 2014).

#### 2 Materials and Methods

#### 2.1. Samples

- This study was based on a 90.45 m ice core drilled at the SE-Dome site in 2015 (67.18° N, 36.37° W, 3170 m a.s.l., Iizuka et al., 2016). The age-depth scale was determined using the oxygen isotope matching method, which matches the δ<sup>18</sup>O variations between ice core records and isotope-enabled climate model estimates, and indicated that this ice core covers the period 1959 to 2014 (Furukawa et al., 2017). The reliability of this dating method generally falls within the 95 % confidence interval (typically around an average of ±0.9 months). The greatest uncertainty was reported at 2 months in some years (Furukawa et al., 2017). We divided the ice core samples into four seasons: spring (March 21–June 20), summer (June 21–September 20),
- 100 autumn (September 21–December 20), and winter (December 21–March 20). For samples analyzed at a two-season resolution (1959–1980 and 1995–2014), spring and summer were combined into summer, whereas autumn and winter were combined into winter.

All SE-Dome ice core samples used in this study were stored in a refrigerated room (-50 °C) at the Institute of Low-Temperature Science (Hokkaido University, Sapporo, Japan). Each ice sample (3 × 4 cm cross-dimension) was cut using a band saw in a refrigerated room (-20 °C) and decontaminated by removing the outermost ~5 mm of ice with a ceramic knife

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in a class 10,000 clean booth, resulting in a loss of approximately 30 % of the original sample weight. The remaining 70 % of the cleaned samples were shipped frozen ( $\sim$ -20 °C) to the Tokyo Institute of Technology (Tokyo Tech, Yokohama, Japan). The samples were then stored in a freezer at -30 °C until analysis.

#### 2.2 Sample analysis

- 110 NO<sub>3</sub><sup>-</sup> in each sample (n = 136) was separated from other ions using ion chromatography (IC, Dionex Integrion, Thermo Fisher Scientific) according to the methods described by Noro et al. (2018). Changes in the isotopic compositions of NO<sub>3</sub><sup>-</sup> during ion chromatographic (IC) separation were <0.4 ‰ for  $\delta^{15}$ N values and within the analytical error range for  $\Delta^{17}$ O values (Noro et al., 2018). Changes in the isotopic compositions of NO<sub>3</sub><sup>-</sup> during ion separation were negligible, as determined previously (Noro et al., 2018). After ion separation, NO<sub>3</sub><sup>-</sup> in solution was converted and neutralized to the Na<sup>+</sup> form by passing
- 115 it through an ion exchange column. The isotopic compositions of  $NO_3^-$  were measured using a bacterial method coupled with N<sub>2</sub>O decomposition via microwave induced plasma (MIP), which was developed at Tokyo Tech (Hattori et al., 2016). Isotopic reference materials, as well as United States Geological Survey (USGS) standards 32, 34, 35, and their mixtures (prepared in 18.2 M $\Omega$  cm water), were also analyzed using the same analytical processes with the samples.

Stable isotopic compositions are reported as  $\delta X = R_{\text{sample}}/R_{\text{reference}} - 1$ , where X denotes <sup>15</sup>N, <sup>17</sup>O, or <sup>18</sup>O, and R denotes the isotope ratios such as <sup>15</sup>N/<sup>14</sup>N, <sup>17</sup>O/<sup>16</sup>O, and <sup>18</sup>O/<sup>16</sup>O, determined for both sample and standard materials. The  $\delta^{15}$ N,  $\delta^{18}$ O, and  $\Delta^{17}$ O values are reported in permil (‰) notation. The  $\delta^{15}$ N values are relative to atmospheric N<sub>2</sub> (air), while the  $\delta^{18}$ O and  $\Delta^{17}$ O values are relative to Vienna Standard Mean Ocean Water. By propagating the analytical uncertainties for the IC separation and replicating isotopic measurements of USGS standards 34, 35, and 32, the estimated combined uncertainties were ±0.4 ‰ for both  $\delta^{15}$ N(NO<sub>3</sub><sup>-</sup>) and  $\Delta^{17}$ O(NO<sub>3</sub><sup>-</sup>).

## 125 2.3 TRANSITS modeling

The TRANSITS model (Erbland et al., 2015), a multi-layer 1D isotopic model, was used to simulate NO<sub>3</sub><sup>-</sup> recycling across the air-snow interface (i.e., UV photolysis of NO<sub>3</sub><sup>-</sup>, NO<sub>x</sub> emission, local NO<sub>2</sub> oxidation, and NO<sub>3</sub><sup>-</sup> deposition) and its associated isotopic effects. The model is operated at a weekly resolution (52 time steps per year), and the default snow depth resolution is 1 mm. In each step,  $NO_3^-$  photolysis is calculated according to the depth-dependent photochemical flux and  $NO_3^-$ 130 concentration. All generated NO<sub>2</sub> enters the upper atmosphere and is re-oxidized to  $NO_3^-$ , which is deposited on the surface snow with the primary NO<sub>3</sub><sup>-</sup> from long-range transport in the next step. The original snow moves downward as snowfall continues, and newly deposited snow is divided into 1 mm layers. Once the NO<sub>3</sub><sup>-</sup> is buried beneath the light transmission band, the layer is regarded as an archive. We adapted the parameters of the TRANSITS model, originally developed for the Summit site by Jiang et al. (2021). This model reproduces the seasonal variation pattern of  $\delta^{15}N(NO_3^{-1})$  in the surface snow at the Summit reported by Jarvis et al. (2009), highlighting the importance of post-depositional processes at the Summit. In addition, 135 this model estimated the net loss of NO<sub>3</sub><sup>-</sup> (4.1 %) and associated changes in  $\delta^{15}N(NO_3^-)$  (+2.6 ‰) and  $\Delta^{17}O(NO_3^-)$  (-0.9 ‰) between primary deposition and NO<sub>3</sub><sup>-</sup> archived in the ace, under an estimate of the horizontal export fraction of locally reoxidized NO<sub>3</sub><sup>-</sup> ( $f_{exp}$ ) of 35% (Jiang et al., 2021). In this study, we applied the same model under the SE-Dome condition by adjusting the parameters to examine the effects of snow  $NO_3^-$  photolysis on  $NO_3^-$  concentration and its isotopes.

- 140 The snow accumulation rate was set at 1.01 m w e a<sup>-1</sup>, based on the 1960–2014 average from SE-Dome ice core data (Iizuka et al., 2017), with additional tests conducted at rates of 0.25, 0.6, and 1.4 m w e a<sup>-1</sup>. The mass balance of NO<sub>3</sub><sup>-</sup> between the snow and atmosphere depends on NO<sub>3</sub><sup>-</sup> influxes and outfluxes. We expressed the NO<sub>3</sub><sup>-</sup> flux as  $F_Y$ , which includes the primary NO<sub>3</sub><sup>-</sup> flux from long-range transport ( $F_{pri}$ ), NO<sub>3</sub><sup>-</sup> flux from NO<sub>3</sub><sup>-</sup> photolysis ( $F_P$ ), atmospheric NO<sub>3</sub><sup>-</sup> deposition flux ( $F_D$ ), and ice-core NO<sub>3</sub><sup>-</sup> flux buried beneath the light band ( $F_A$ ). These fluxes reflect changes in NO<sub>3</sub><sup>-</sup> and its isotopic compositions in
- 145 the snow and atmosphere. The TRANSITS model considers that two processes can change  $\delta^{15}N(NO_3^-)$  as a result of isotope fractionation from UV photolysis and NO<sub>3</sub><sup>-</sup> deposition (i.e., co-condensation and dry deposition). The nitrogen isotope fractionation constant during photolysis ( ${}^{15}\varepsilon_p$ ) was calculated using a ratio of  ${}^{14}NO_3^-$  and  ${}^{15}NO_3^-$  photolysis rates ( ${}^{15}\varepsilon_p = {}^{15}J/{}^{14}J$  1, where *J* represents the photolysis rate constant) in each snow layer (Erbland et al., 2013). The *J* at different depths (*z*) (*J*(*z*)) was calculated according to Equation (1):

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

. . .

(1)





(2)

where *I* is the actinic flux and  $\Phi$  and  $\sigma$  are the quantum yield and absorption cross-section of NO<sub>3</sub><sup>-</sup> photolysis, respectively. The quantum yield of NO<sub>3</sub><sup>-</sup> photolysis has significant uncertainties (Meusinger et al., 2014). However, it is unlikely that the quantum yield of NO<sub>3</sub><sup>-</sup> photolysis would differ substantially between the SE-Dome and Summit sites. Since this study compares the differences between these sites, which have notably different snow accumulation rates, the quantum yield of NO<sub>3</sub><sup>-</sup> photolysis at the SE-Dome site was set to the same value (0.002) as that estimated for the Greenland Summit site by Jiang et al. (2021). The absorption cross sections of <sup>14</sup>NO<sub>3</sub><sup>-</sup> (<sup>14</sup> $\sigma$ NO<sub>3</sub><sup>-</sup>) and <sup>15</sup>NO<sub>3</sub><sup>-</sup> (<sup>15</sup> $\sigma$ NO<sub>3</sub><sup>-</sup>) were derived from Berhanu et al. (2014). The nitrogen isotope fractionation constant during deposition (<sup>15</sup> $\varepsilon$ <sub>d</sub>) was set to +10 ‰ (Erbland et al., 2015). For the oxygen isotopes, only the mass-independent fractionation signal ( $\Delta$ <sup>17</sup>O) was modeled. The cage effect (i.e., decrease in  $\Delta$ <sup>17</sup>O of the snow NO<sub>3</sub><sup>-</sup> owing to secondary chemistry during NO<sub>3</sub><sup>-</sup> photolysis, McCabe et al., 2005) was set to 15 % according to Erbland et al. (2015), and the TRANSITS model calculated the exchange of oxygen atoms with water during UV photolysis and atmospheric NO–NO<sub>2</sub> cycling, both of which alter  $\Delta$ <sup>17</sup>O. The  $\Delta$ <sup>17</sup>O(NO<sub>3</sub><sup>-</sup>) fractionation mechanisms in the TRANSITS model during these processes are explained in detail in Jiang et al. (2021).

The atmospheric boundary layer at the SE-Dome site was assumed to be a zero-dimensional well-mixed box, and the snowpack was assumed to be a stack of snow layers deposited at different times. Weekly air temperatures (*T*), pressures (*P*), and average boundary layer heights (*h*) from 1950–2020 were obtained from the second-generation European Centre for Medium-Range Weather Forecast atmospheric analysis of global climate (ERA5) (Hersbach et al., 2020; Khalzan et al., 2022). O<sub>3</sub>, OH, peroxyl radical (RO<sub>2</sub> and HO<sub>2</sub>), and BrO concentrations were used to calculate the rates of NO–NO<sub>2</sub> cycling and NO<sub>2</sub> oxidation to HNO<sub>3</sub>. However, because these records were not available for the SE-Dome, they were extracted from the outputs of the v.12.9.3 (<u>https://zenodo.org/records/3959279</u>, last accessed: 7 Jan 2024) GEOS-Chem atmospheric chemical transport model (http://www.geos-chem.org, last accessed: 7 Jan 2024) using the Modern-Era Retrospective analysis for Research and Applications, Version 2 (MERRA-2) meteorological field, with 4° latitudinal and 5° longitudinal resolutions. The GEOS-Chem model was run for year 2017 after a one-year spin up run, and the monthly averages for the O<sub>3</sub>, OH, HO<sub>2</sub>, and BrO concentrations in the planetary boundary layer in the SE-Dome grid were used. We selected 2017 as the representative period,

- which should not vary significantly from other recent years and should ensure robust outcomes. Given that tropospheric O<sub>3</sub>
  concentrations were comparable between the SE-Dome and Summit grids in the GEOS-Chem model, the total O<sub>3</sub> column (TCO) was set to the same (266 to 408 DU) as that used in a previous study of the Summit site (Jiang et al., 2021). F<sub>pri</sub> was estimated to be 16.4, 23.6, 13.3, 11.5 mg-N m<sup>-2</sup> a<sup>-1</sup> for spring, summer, fall and winter respectively, based on the seasonal NO<sub>3</sub><sup>-</sup> fluxes at the SE-Dome site from 1960 to 2014 (Iizuka et al., 2018).
- An e-folding depth, which is the depth to which light enters the snow layer and attenuates to an initial intensity of 1/e (owing to absorption and scattering), for the SE-Dome site was calculated using the snow density ( $\rho_{snow}$ ), the calculated specific surface area (SSA), and fixed light-absorbing impurity concentrations (Jiang et al., 2021). The  $\rho_{snow}$  of 400 kg m<sup>-3</sup> for the SE-Dome site was obtained from an observation at the SE-Dome (Oyabu et al., 2016). The SSA for the SE-Dome site was determined to be 46.95 m<sup>2</sup> kg<sup>-1</sup> using the relationship between the SSA and  $\rho_{snow}$ , according to a previous study (Domine et al., 2007) as follows:
- 185 SSA =  $-174.13 \times \ln(\rho_{\text{snow}}) + 306.4$ ,

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where SSA is in units of cm<sup>2</sup> g<sup>-1</sup> and the units for  $\rho_{\text{snow}}$  was changed to g cm<sup>-3</sup>. For the light-absorbing impurity concentrations, we established constant concentrations of the three main light-absorbing impurities in snow: dust, soot (BC), and organic humic-like substances (HULIS). The dust concentration was set to 33.94 ng g<sup>-1</sup> according to an average concentration for the SE-Dome ice core from 1960–2014 (Amino et al., 2021). Owing to a lack of direct observations for BC and HULIS at the SE-Dome, we assumed these concentrations based on the Ca<sup>2+</sup> concentration ratio between the Summit and SE-Dome sites. Here, *[BC]*<sub>summit</sub> and *[HULIS]*<sub>summit</sub> were set to 1.4 and 31 ng g<sup>-1</sup>, respectively, according to Jiang et al. (2021). Furthermore, [Ca<sup>2+</sup>]

- at the Summit site was set to 6.5 ng  $g^{-1}$  according to an average of 2 m shallow snow pack observation (Geng et al., 2014); [Ca<sup>2+</sup>] at the SE-Dome site was set to 11.6 ng  $g^{-1}$  according to an average from the SE-Dome ice core from 1960–2014 (Iizuka et al., 2018). Thus, *[BC]*<sub>SE-Dome</sub> and *[HULIS]*<sub>SE-Dome</sub> were calculated as 2.2 and 47.6 ng  $g^{-1}$ , respectively, and used for the model calculation. An e-folding depth of 10 cm was obtained based on the above inputs. The calculated e-folding depth for the SE-
- Dome site was consistent with previous estimates from the GEOS-Chem model investigating the impact of post-depositional effect in snow (Zatko et al., 2016).





The horizontal export fraction of locally re-oxidized  $NO_3^-$  ( $f_{exp}$ ) under the SE-Dome condition was calculated with the same scheme described for the Antarctic Plateau (Erbland et al., 2015) and Greenland Summit (Jiang et al., 2021), as following 200 equations.

$$f_{\exp} = \frac{\frac{1}{\tau_1}}{\frac{1}{\tau_1} + \frac{1}{\tau_2}} \times \left( 1 + \frac{\frac{1}{\tau_2}}{\frac{1}{\tau_3} + \frac{1}{\tau_1}} \right)$$
(3)

$$\tau_1 = \frac{L}{V_{\rm h}} \tag{4}$$

$$\tau_2 = \frac{\tau_2}{k[\text{OH}] * \text{OH}}$$
(5)
$$\tau_3 = \frac{H}{V_A}$$
(6)

(6)

In these equations,  $\tau_1$ ,  $\tau_2$ , and  $\tau_3$  represent the lifetimes of horizontal transport, oxidation of NO<sub>2</sub> by OH radicals, and vertical deposition, respectively. L and H denote the summer boundary layer height and horizontal characteristic, while  $V_{\rm h}$  is the mean horizontal wind speed, k is the rate constant for the NO<sub>2</sub> + OH reaction, and  $V_d$  is the dry deposition velocity of HNO<sub>3</sub> (Jiang et al., 2021). The values used for the calculation is summarized in Table S2, and the same physicochemical values as those of Summit were used, while parameters such as temperature and boundary layer height were incorporated from ERA5 data. We

210 obtained  $f_{exp}$  to be 47% under the SE-Dome condition, but the calculated  $f_{exp}$  may oversimplify the processes governing NO<sub>3</sub><sup>-</sup> deposition and the chemical loss pathways of NOx as discussed previously (Jiang et al., 2021). Therefore, we considered the sensitivity of post-depositional alteration to variations in  $f_{exp}$  between initial deposition and ice core analysis.

At the initial time (t = 0) in the TRANSITS model, the NO<sub>3</sub><sup>-</sup> concentration was set to 71.12 ng g<sup>-1</sup> based on the average NO<sub>3</sub><sup>-</sup> concentration in the SE-Dome I ice core (Iizuka et al., 2018), while the  $\delta^{15}N(NO_3^-)$  and  $\Delta^{17}O(NO_3^-)$  values in the snowpack 215 were set to 0 ‰ and 30 ‰, respectively, according to previous TRANSITS settings (Erbland et al., 2015; Jiang et al., 2021). This initial isotopic parameter does not affect the model interpretation of changes in  $\delta^{15}N(NO_3^-)$  and  $\Delta^{17}O(NO_3^-)$  due to postdepositional processing. Three-year distributions of NO<sub>3</sub><sup>-</sup> and its isotopes were simulated with and without NO<sub>3</sub><sup>-</sup> photolysis scenarios under the SE-Dome condition, from which profiles of NO<sub>3</sub><sup>-</sup> concentrations,  $\delta^{15}N(NO_3^{-})$ , and  $\Delta^{17}O(NO_3^{-})$  were output. 220 The parameters used in the TRANSITS model are summarized in Table 1 and Supplement data file 1.

#### 2.4 Statistical analysis

XLSTAT 2023 (Addinsoft, Paris, France) was used for the Mann-Kendall trend analysis over 1959-2014. SPSS 25 (IBM SPSS, Armonk, NY, USA) was used to perform the *t*-tests of annual changes in  $\delta^{15}N(NO_3^-)$  and  $NO_3^-$  concentrations. Statistical significance was set at p < 0.05.

#### 225 **3 Results**

#### 3.1 Nitrate isotope records from the SE-Dome ice core

The NO<sub>3</sub><sup>-</sup> isotope data and fluxes obtained from the SE-Dome ice core are shown in Figs. 2 and S1. The seasonal variations were larger in the samples analyzed at a four-season resolution (1981–1994), which may have been caused by age errors (Furukawa et al., 2017). Accordingly, mass-weighted averages were calculated for the summer and winter fractions from the seasonal samples during 1981–1994. From 1959 to 2014, the  $\delta^{15}N(NO_3^-)$  values were generally higher in summer (-2.9 ±

230 2.6 ‰) than in winter (-6.9 ± 2.9 ‰) (Figs. 2a and S1a). To assess annual changes in  $\delta^{15}N(NO_3^{-1})$  over this period, we calculated the annual mass-weighted average  $\delta^{15}N(NO_3^{-})$  values and found that they decreased from 1959 to 1974 and exhibited no





significant (p > 0.05) trends after 1975 (mean value of  $-4.8 \pm 1.3$  ‰) (Fig. 2a). No clear relationship was observed between the annual variations in  $\delta^{15}$ N(NO<sub>3</sub><sup>-</sup>) and NO<sub>3</sub><sup>-</sup> concentrations (p = 0.37).

Using a similar method as for  $\delta^{15}N(NO_3^-)$ , we also calculated the mass-weighted average and annual mass-weighted average for  $\Delta^{17}O(NO_3^-)$ .  $\Delta^{17}O(NO_3^-)$  also exhibited a seasonal pattern, with lower values in the summer (27.8 ± 1.3 ‰) than those in the winter (31.3 ± 1.9 ‰), yielding a mass-weighted average of 29.3 ± 1.2 ‰ over the entire period (Figs. 2b and S1). The average annual  $\Delta^{17}O(NO_3^-)$  values were relatively high (~33 ‰) in 1988, and low values were observed in 2013 and 2014 (Fig. 2b). Excluding these particular years, no significant annual increases or decreases (p > 0.05) were observed in the 240  $\Delta^{17}O(NO_3^-)$  values.



Figure 2. NO<sub>3</sub><sup>-</sup> isotope data and fluxes from the SE-Dome ice core. (a)  $\delta^{15}N(NO_3^{-})$ , (b)  $\Delta^{17}O(NO_3^{-})$ , and (c) NO<sub>3</sub><sup>-</sup> flux (mmol m<sup>-2</sup> a<sup>-1</sup>).

#### **3.2 TRANSITS model results**

We aimed to know the changes in NO<sub>3</sub><sup>-</sup> from primary deposition to the ice core archive. However, these changes primarily depend on the  $f_{exp}$  value—the fraction of NO<sub>3</sub><sup>-</sup> exported from the site of photolysis. Therefore, we calculated the dependency of the  $\delta^{15}N(NO_3^-)$  and  $\Delta^{17}O(NO_3^-)$  values on  $f_{exp}$  at the SE-Dome using the same approach as Jiang et al. (2021) (Fig. 3). The





post-depositional alterations in  $\delta^{15}N(NO_3^{-})$  and  $\Delta^{17}O(NO_3^{-})$  between initial deposition and ice-core NO<sub>3</sub><sup>-</sup> concentration at the SE-Dome were dependent on  $f_{exp}$ . However, the degree to which the changes in  $\delta^{15}N(NO_3^-)$  and  $\Delta^{17}O(NO_3^-)$  were dependent on  $f_{exp}$  was less evident at the SE-Dome than at the Summit (Fig. 3). Notably, even when the snow accumulation rate for SE-Dome is adjusted from the minimum  $(0.6 \text{ m w e } a^{-1})$  to the maximum  $(1.4 \text{ m w.e. } a^{-1})$  values, as shown in Fig. 1c, the results 250 indicate that changes in  $\delta^{15}N(NO_3^-)$  and  $\Delta^{17}O(NO_3^-)$  are less sensitive to  $f_{exp}$  compared to Summit. Furthermore, when a snow accumulation rate of 0.25 m w.e.  $a^{-1}$ , equivalent to that used in the Summit study (Jiang et al., 2021), was applied, the variations were nearly identical to those observed at Summit (Fig. S2). This suggests that the differences in post-depositional alterations for  $\delta^{15}N(NO_3^-)$  and  $\Delta^{17}O(NO_3^-)$  are primarily caused by differences in accumulation rates.

Using the method of Erbland et al. (2015), fexp was calculated as 47 % at the SE-Dome, reflecting an estimated net loss of 1.4 % due to post-depositional alteration in NO<sub>3</sub><sup>-</sup> concentration at the SE-Dome, with corresponding changes in  $\delta^{15}N(NO_3^{-})$ 255 and  $\Delta^{17}O(NO_3^{-})$  of +0.9 ‰ and -0.2 ‰, respectively (Fig. 3). In contrast, the estimated under the Summit condition showed greater net loss in NO<sub>3</sub><sup>-</sup> (4.1 %) and associated changes in  $\delta^{15}$ N(NO<sub>3</sub><sup>-</sup>) (+2.6 ‰) and  $\Delta^{17}$ O(NO<sub>3</sub><sup>-</sup>) (-0.9 ‰) when  $f_{exp}$  value is 35 % estimated previously (Jiang et al., 2021). Thus, even when using the same evaluation criteria, the post-depositional alteration in NO<sub>3</sub> and its isotopic compositions at the SE-Dome were smaller than those at the Summit. We note that, at an 260 extreme condition of  $f_{exp} = 100\%$ , the estimated changes in  $\delta^{15}N(NO_3^{-})$  from initial deposition due to post-depositional processing under the SE-Dome condition were +1.8 ‰, which is significantly lower than that under the Summit condition of





Figure 3. Sensitivity of the changes in  $\delta^{15}N(NO_3^-)$  and  $\Delta^{17}O(NO_3^-)$  of the ice-core nitrate to  $f_{exp}$ . Positive/negative values indicate deviations from initial deposition. The shaded area in the SE-Dome calculations represents results obtained using 265 snow accumulation rates of 0.6 and 1.4 m w e a<sup>-1</sup>.

Figure 4 shows the results obtained from the TRANSITS model for NO<sub>3</sub><sup>-</sup> and its isotopic compositions for the SE-Dome site with considering  $f_{exp}$  value of 47%. The model considering photolysis showed a maximum 6 % decrease in the annual NO<sub>3</sub><sup>-</sup> concentrations during spring and early summer compared to the scenario without photolysis (Fig. 4a). The post-depositional effects (primarily due to photolytic isotopic fractionation) caused a fluctuation from -1 to +2 ‰ in  $\delta^{15}N(NO_3^{-})$ , with higher





values in summer  $(1.3 \pm 0.7 \%)$  and lower values in winter  $(0.2 \pm 0.2 \%)$  (Fig. 4b). The variation in the  $\Delta^{17}O(NO_3^-)$  value, which was initially set at 30 ‰, is attributed to a slight decrease in atmospheric NO<sub>3</sub><sup>-</sup> concentration owing to its re-oxidization during spring to summer. Thus, when photolysis is minimal in the autumn and winter, the  $\Delta^{17}O(NO_3^-)$  values remained close to the initial value (30 ‰) (Fig. 4c). Conversely, during spring and summer, when  $\delta^{15}N(NO_3^-)$  values increase, a decreasing  $\Delta^{17}O(NO_3^-)$  trend was observed (Fig. 4c). However, the extent of this change is minimal, with values reaching a minimum of ~29.6 ‰. The seasonality in NO<sub>3</sub><sup>-</sup> concentration and post-depositional alteration in its isotopic composition were less obvious at the SE-Dome than that at the Summit, where  $\delta^{15}N(NO_3^-)$  varied by >5 ‰ and  $\Delta^{17}O(NO_3^-)$  by ~2 ‰ (Jiang et al., 2021).



Figure 4. TRANSITS model results for the SE -Dome site. (a) NO<sub>3</sub><sup>-</sup> concentration, (b)  $\delta^{15}N(NO_3^{-})$ , and (c)  $\Delta^{17}O(NO_3^{-})$ . The black and red lines represent the variations calculated without and with NO<sub>3</sub><sup>-</sup> photolysis, respectively.





#### **4** Discussion

#### 4.1 $\delta^{15}N(NO_3^{-})$ values from the SE-Dome and Summit sites

Figure 5 shows the annual average  $\delta^{15}N(NO_3^{-})$  values obtained from the SE-Dome ice core and the previously published  $\delta^{15}N(NO_3^{-})$  values from the Summit site (Hastings et al., 2009; Geng et al., 2014). Decreasing trends in  $\delta^{15}N(NO_3^{-})$  were observed in both the Summit and SE-Dome ice cores until approximately 1974, after which no clear changes occurred (Fig. 5). Notably, based on the overlapping analysis period from 1959 to 2006 (n = 44), the annual  $\delta^{15}N(NO_3^{-})$  values in the SE-Dome ice core were found to be  $4.2 \pm 2.8$  % lower than those in the Summit ice core (Fig. 5). The observed differences in  $\delta^{15}N(NO_3^{-})$  values between the SE-Dome and Summit may be attributed to (1) variations in the  $\delta^{15}N$  values of NO<sub>3</sub><sup>-</sup> deposited at the two sites and/or (2) variations in the degree of post-depositional alterations between the two sites. These two points are discussed in detail below.



Figure 5. δ<sup>15</sup>N(NO<sub>3</sub><sup>-</sup>) values obtained from the SE-Dome (this study) and Summit (Hastings et al., 2009; Geng et al., 2014) ice cores.

First, regarding the differences in the  $\delta^{15}$ N values of NO<sub>3</sub><sup>-</sup> deposited at the two sites, there are two main sources for the NO<sub>3</sub><sup>-</sup> deposited in the Greenland ice core. One long-range source is derived primarily from anthropogenic sources outside of Greenland. The other source involves NO<sub>x</sub> released from NO<sub>3</sub><sup>-</sup> photolysis within the snowpack, which is then re-oxidized and redeposited. Although the air masses at the SE-Dome and Summit sites have similar source regions—North America and Western Europe (Figs. 1a and 1b)—the degree of influence from reactive nitrogen sources differed between sites (Fig. S3). At the SE-Dome, the contributions from outside Greenland were relatively high, with nearly equal influence from North America and EU countries (Fig. S3a). In contrast, the contributions from EU countries were relatively low at the Summit, while the

- 300 North American countries (mostly Eastern Canada) and inner Greenland had greater contributions (Fig. S3b). NO<sub>x</sub> sources from Western Europe and North America are not necessarily similar; for example, differences in the relative contributions of various NO<sub>x</sub> sources are reflected in their  $\delta^{15}$ N values, with NO<sub>x</sub> from coal and biomass tending to have higher  $\delta^{15}$ N values, while NO<sub>x</sub> from oil, natural gas, and soil tends to have lower  $\delta^{15}$ N values (e.g., Elliot et al., 2019). To date, there have been no studies comprehensively comparing the isotopic composition of atmospheric NO<sub>3</sub><sup>-</sup> between Europe and North America. The
- 305 limited available data shows that  $\delta^{15}$ N values in total atmospheric NO<sub>3</sub><sup>-</sup> (sum of gaseous HNO<sub>3</sub> and particulate NO<sub>3</sub><sup>-</sup>) at the northeast US range -10 to +5 ‰ (Bekker et al., 2023), while those in rainwater NO<sub>3</sub><sup>-</sup> (including both gaseous HNO<sub>3</sub> and particulate NO<sub>3</sub><sup>-</sup>) in Switzerland range -12 to +6 ‰ (Freyer, 1991), which cannot be distinguished from each other. A recent





study (Song et al., 2021) compiled the  $\delta^{15}N$  values of precipitated NO<sub>3</sub><sup>-</sup> between urban and non-urban areas in Europe (n = 8 and n = 15, respectively) and North America (n = 10 and n = 73, respectively), showing no clear distinction between the two regions, though Europe exhibited slightly higher values. Hence, there is no clear evidence that the long-term  $\delta^{15}N$  trends in European countries consistently remain lower than those in the USA or Canada, and thus, the ~4‰ lower  $\delta^{15}N(NO_3^-)$  values observed in the SE-Dome, which is relatively more influenced by air masses from Europe, cannot be explained solely by differences in air mass origin.

Considering the potential impact of snow-sourced NO<sub>x</sub> and re-oxidized NO<sub>3</sub><sup>-</sup>, it is important to note that the extent of recycled NO<sub>x</sub> from NO<sub>3</sub><sup>-</sup> photolysis in the Greenland ice sheet differed between these two sites. As modeled by Zatko et al. (2016), recycled NO<sub>x</sub> is typically more important at inland sites such as the Summit than coastal sites such as the SE-Dome. Additionally, the contribution of air masses from inside Greenland was higher at the Summit than at the SE-Dome (Fig. S3). Nevertheless, the  $\delta^{15}$ N values of NO<sub>x</sub> and re-oxidized NO<sub>3</sub><sup>-</sup> are typically low due to isotopic fractionation during NO<sub>3</sub><sup>-</sup> photolysis in the snow and ice, with  $\delta^{15}$ N(NO<sub>3</sub><sup>-</sup>) in high-latitude air masses attributed to photochemical NO<sub>x</sub> production in

320 snow, resulting in  $\delta^{15}N(NO_3^-)$  values of -10 to -43 ‰ in polar regions (e.g., Savarino et al., 2007; Morin et al., 2009; Shi et al., 2021). Thus, the contribution of locally recycled NO<sub>3</sub><sup>-</sup>, which was greater at the Summit, cannot explain why  $\delta^{15}N(NO_3^-)$  values were lower at the SE-Dome than at the Summit.

Finally, regarding the differences in post-depositional alterations between two sites, we applied parameters specific to the SE-Dome in the TRANSITS model (Figs. 3 and 4). The model results for the SE-Dome, accounting for post-depositional  $NO_3^-$  related to a set  $NO_2^-$  loss of 1.2 % and increase of 10.0 % in  $S^{15}N(NO_2^-)$  (see Section 2.2). In comparison, the

- 325 photolysis, showed a net NO<sub>3</sub><sup>-</sup> loss of 1.3 % and increase of +0.9 ‰ in  $\delta^{15}N(NO_3^-)$  (see Section 3.2). In comparison, the Summit condition resulted in a ~4 % net NO<sub>3</sub><sup>-</sup> loss and +2.6 ‰ increase in  $\delta^{15}N(NO_3^-)$  (Jiang et al., 2021). Although the lower  $\delta^{15}N(NO_3^-)$  values at the SE-Dome can be partially explained by the model, they cannot be fully accounted for quantitatively. However, the estimated +2.6 ‰ increase in  $\delta^{15}N(NO_3^-)$  at the Summit may be underestimated due to an underestimation in  $f_{exp}$  (Jiang et al., 2021). Indeed, an observational study (Honrath et al., 2002) indicates that most of the NO<sub>x</sub> and/or HNO<sub>3</sub>
- 330 emitted from the snow at Summit is largely exported from the local boundary layer if no wet deposition occurs, suggesting that the  $f_{exp}$  value can reach ~1 under Summit conditions. Therefore, the actual net NO<sub>3</sub><sup>-</sup> loss and  $\delta^{15}$ N(NO<sub>3</sub><sup>-</sup>) variation at the Summit may have been larger than the 4 % estimated by Jiang et al. (2021). Thus, when considering higher  $f_{exp}$  values, the difference due to post-depositional alterations could be higher than the modeled difference between the SE-Dome (+0.9 ‰, this study) and Summit (+2.6 ‰, Jiang et al., 2021). Indeed, when considering an extreme condition of  $f_{exp} = 100$  %, the difference between the SE-Dome tend SE Dome here  $\delta^{5}$  (Tig 2) Overall alterations for an extreme condition of  $f_{exp}$  = 100 %, the
- 335 difference between the Summit and SE-Dome becomes ~5 ‰ (Fig. 3). Overall, although there is some uncertainty in the model, it is likely that the SE-Dome experienced less post-depositional alteration, thus preserving the atmospheric  $\delta^{15}N(NO_3^-)$  values more effectively than at the Summit.

Although the contribution of different NO<sub>3</sub><sup>-</sup> sources cannot be entirely ruled out, our analysis shows that the observed  $\delta^{15}N(NO_3^-)$  value at SE-Dome, which is  $4.2 \pm 2.8\%$  lower than that at Summit, can largely be attributed to differences in post-depositional alterations.

#### 4.2 Seasonal variations in NO3<sup>-</sup> isotopes

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The post-depositional effect, as estimated from the TRANSITS model, yielded a summer-winter difference in  $\delta^{15}N(NO_3^{-})$  of  $1.1 \pm 0.7$  ‰ and a difference smaller than 0.5 ‰ in  $\Delta^{17}O(NO_3^{-})$ , as described in Section 3.2 (Figs. 4b and 4c). In contrast, except for the anomalous years (1959–1961, 1972, 1995, 2005, and 2013), the observed summer–winter differences for respective years in the SE-Dome ice core were  $5.3 \pm 2.4$  ‰ (0.4–9.8 ‰) for  $\delta^{15}N(NO_3^{-})$  and  $-4.2 \pm 1.5$  ‰ (from -8.2 to -0.4 ‰) for  $\Delta^{17}O(NO_3^{-})$ , respectively (Figs. 2a and 2b), which were larger than the differences estimated by the TRANSITS model. Thus, the observed differences between the summer and winter NO\_3^{-} isotopes were not solely explained by post-depositional alteration. Consequently, seasonal differences in  $\delta^{15}N(NO_3^{-})$  and  $\Delta^{17}O(NO_3^{-})$  likely reflect atmospheric changes.

The observed seasonal  $\delta^{15}N(NO_3^-)$  trend (high in summer and low in winter) at the SE-Dome site was consistent with observations made at two coastal Arctic sites (Morin et al., 2008, 2012) but inconsistent with typical seasonal  $\delta^{15}N(NO_3^-)$ values of aerosols in mid-latitude regions that are high in winter and low in summer (Freyer, 1991; Freyer et al., 1996; Lim et al., 2022). Although the specific process has yet been identified, the factors controlling high  $\delta^{15}N(NO_3^-)$  values in the summer have been comprehensively reviewed (Jiang et al., 2024 and references therein). One possibility is that physicochemical transformations of  $NO_3^-$  related to temperature influence  $\delta^{15}N(NO_3^-)$  values, as suggested by a strong correlation between high





355 δ<sup>15</sup>N(NO<sub>3</sub><sup>-</sup>) values and summer air temperatures (Morin et al., 2008). Another possibility is the incursion of anthropogenic sources, as proposed by Morin et al. (2009), which is supported by indicates that air parcels originating from regions with greater anthropogenic influence carry higher δ<sup>15</sup>N(NO<sub>3</sub><sup>-</sup>) values. This is supported by observational studies on atmospheric δ<sup>15</sup>N(NO<sub>3</sub><sup>-</sup>) (e.g., Vicars and Savarino, 2014) and the increased frequency of air masses originating from North America during summer compared to winter (Kahl et al., 1997). While definitive conclusions regarding these observations have not yet been
determined, it is hypothesized that the observations may be influenced by a combination of factors, including NO<sub>x</sub> sources, gas–particle partitioning variability influenced by temperature (Freyer, 1991) and acidity (Geng et al., 2014), oxidation pathways (Walters et al., 2016), and differences in transport efficiency and removal processes (Heaton, 1987; Beyn et al., 2014). Future studies should examine the differences in δ<sup>15</sup>N(NO<sub>3</sub><sup>-</sup>) variations between both the source and remote regions. Such comparative analyses could enhance the current understanding of the underlying processes that influence isotopic compositions in different geographical contexts.

The observed seasonal changes in  $\Delta^{17}O(NO_3^{-})$  (high in winter and low in summer, Fig. 2b) were consistent with typical seasonal variations in  $\Delta^{17}O(NO_3^{-})$  (e.g., Michalski et al., 2003). In summer, increased sunlight promotes the formation of HNO<sub>3</sub> via NO<sub>2</sub> + OH reactions, leading to lower  $\Delta^{17}O(NO_3^{-})$  values. Conversely, in winter, N<sub>2</sub>O<sub>5</sub> hydrolytic or NO<sub>3</sub> radical pathways forming HNO<sub>3</sub> in the presence of O<sub>3</sub> predominate and result in increased  $\Delta^{17}O(NO_3^{-})$  levels. Although this kind of seasonal variation in  $\Delta^{17}O(NO_3^{-})$  is well known, we confirmed the historic occurrence of similar seasonal variations in the atmosphere. Although the scope of the current study limits further discussion in this regard, future research should explore the differences in  $\Delta^{17}O(NO_3^{-})$  between summer and winter during the preindustrial period when anthropogenic contributions of NO<sub>3</sub><sup>-</sup> were significantly lower.

#### 4.3 Decadal variations in NO3<sup>-</sup> isotopes

- As discussed in Section 4.1, the SE-Dome ice core-recorded atmospheric NO<sub>3</sub><sup>-</sup> deposition with minimal post-depositional effects. The decadal δ<sup>15</sup>N(NO<sub>3</sub><sup>-</sup>) trend obtained from ice cores in Greenland has been interpreted to indicate changes in the NO<sub>x</sub> source (Hastings et al., 2009) and/or atmospheric acidity from the beginning of the Industrial Revolution to the present (Geng et al., 2014). However, if δ<sup>15</sup>N(NO<sub>3</sub><sup>-</sup>) is primarily controlled by atmospheric acidity, as proposed by Geng et al. (2014), then δ<sup>15</sup>N(NO<sub>3</sub><sup>-</sup>) should have increased after approximately 1975 when the atmospheric acidity decreased (owing to SO<sub>2</sub> emission controls, Hattori et al., 2021). The δ<sup>15</sup>N(NO<sub>3</sub><sup>-</sup>) trend. In response to emission controls since 1975, reasonable changes in dominant NO<sub>x</sub> emissions are expected, which can affect the δ<sup>15</sup>N(NO<sub>3</sub><sup>-</sup>) values. However, many factors control δ<sup>15</sup>N(NO<sub>3</sub><sup>-</sup>) in the atmosphere. As this study only covers a relatively limited period (60 years), future studies should address and compare
- longer ice core records from different regions. Such comparisons would be beneficial for understanding the factors behind
   isotopic variations, thereby enabling more accurate interpretations of isotopic records reconstructed from ice cores.

The unusually high NO<sub>3</sub><sup>-</sup> fluxes observed in the summer of 1987 (1.97 mmol m<sup>-2</sup> a<sup>-1</sup>) and the spring of 1992 (1.38 mmol m<sup>-2</sup> a<sup>-1</sup>) were also notable (Fig. 2c). The extent of forest fires in North America can be the primary driver of this phenomenon, based on coincident high NH<sub>4</sub><sup>+</sup> fluxes during these periods (Iizuka et al., 2018). In 1992, the Mt. Pinatubo eruption may have influenced the observations, considering the high SO<sub>4</sub><sup>2-</sup> concentration (13.7 µmol L<sup>-1</sup>, Iizuka et al., 2018). The δ<sup>15</sup>N(NO<sub>3</sub><sup>-</sup>) values during the summer of 1987 (1.3 ‰) and the spring of 1992 (4.8 ‰) were relatively high compared with other years during which δ<sup>15</sup>N(NO<sub>3</sub><sup>-</sup>) was less than 0 ‰. These higher δ<sup>15</sup>N(NO<sub>3</sub><sup>-</sup>) values may be related to biomass burning associated with forest fires (1.3 ± 4.3 ‰, Zong et al., 2022). Stratospheric NO<sub>3</sub><sup>-</sup> inputs may also have high δ<sup>15</sup>N values, as observed in Antarctic aerosols (Savarino et al., 2007). However, the Δ<sup>17</sup>O(NO<sub>3</sub><sup>-</sup>) values in the summer of 1987 (28.2 ‰) and the spring of 1992 (29.5 ‰) were not clearly different from other years, which is not consistent with high Δ<sup>17</sup>O(NO<sub>3</sub><sup>-</sup>) trend during pre-industrial biomass-burning (i.e., forest fires) reported in the previous study (Alexander et al., 2004). We also note that no biomass burning tracers were detected both in 1987 and 1992 (Parvin et al., 2019). Further research is therefore required to link nitrate isotopes with specific events such as biomass burning.

The  $\Delta^{17}O(NO_3^{-})$  record from the SE-Dome core did not exhibit clear trends during the past 60 years. During this period, changes in atmospheric oxidants have occurred, such as increases in tropospheric O<sub>3</sub> over Arctic regions (Law et al., 2023). It is reasonable to estimate that higher O<sub>3</sub> can induce increases in  $\Delta^{17}O(NO_3^{-})$  by: (1) promoting NO<sub>2</sub> formation from NO + O<sub>3</sub> reactions and (2) promoting NO<sub>2</sub> oxidation to NO<sub>3</sub> (and subsequently to HNO<sub>3</sub>) by O<sub>3</sub>. However, such changes were not





recorded in the  $\Delta^{17}O(NO_3^-)$  data from the SE-Dome ice core. During this period, atmospheric sulfate formation was changed by the promotion of in-cloud S(IV) + O<sub>3</sub> reactions, based on increases in  $\Delta^{17}O(SO_4^{2-})$  from the same SE-Dome ice core (Hattori et al., 2021). Thus, further research is required to determine the mechanism(s) behind the observed constant  $\Delta^{17}O(NO_3^-)$  values in ice cores after emission controls by comparing  $\Delta^{17}O(NO_3^-)$  values estimated using chemical transport models such as GEOS-Chem. Based on the  $\Delta^{17}O(NO_3^-)$  values recorded in the GISP2 ice core, the variations have been attributed to the intricate BrONO<sub>2</sub> hydrolysis mechanism, which extends beyond the small fluctuations in the O<sub>3</sub>/(HO<sub>2</sub>+RO<sub>2</sub>) ratio in the relatively colder

climate of a glacial period (Geng et al., 2017). Thus, reactive halogen chemistry may also be a factor that impacts changes in

the atmospheric oxidizing capacity, specifically in high-latitude regions in the Northern Hemisphere.

#### 410 **4.4 Comparisons with other ice core data**

The  $\delta^{15}N(NO_3^-)$  value of ice cores collected in Lomonosovfonna, Svalbard, was  $-6.9 \pm 1.9$  ‰ after 1950 (Vega et al., 2015), which is lower than that at the SE-Dome and Summit. Given that snow accumulation at Lomonosovfonna ( $0.55 \pm 0.1$  m w e  $a^{-1}$ , Vega et al., 2015) was higher than at the Summit, these low  $\delta^{15}N(NO_3^-)$  values may reflect less post-depositional alterations. Notably, the relatively low  $\delta^{15}N(NO_3^-)$  values at Lomonosovfonna and the SE-Dome were consistent with the low  $\delta^{15}N(NO_3^-)$ 

- 415 values in aerosols observed at two Arctic stations (Morin et al., 2008, 2012). Notably, the SE-Dome and Svalbard both had lower  $\delta^{15}N(NO_3^{-})$  values and higher accumulation rates than the Summit. Additionally, Svalbard is closer to Europe than Greenland, which may indicate a regional source difference. Ice-core  $\delta^{15}N(NO_3^{-})$  records reported from the Lomonosovfonna also exhibited decreasing trends until the 1970s, whereas an increase in  $\delta^{15}N(NO_3^{-})$  was only observed at Lomonosovfonna after the 1990s (Vega et al., 2015). Such differences may be attributed to differences in NO<sub>x</sub> sources and spatial chemistries in
- 420 the Arctic, although it is unclear whether this difference was caused by anthropogenic sources, natural sources, transport, or a combination of these factors.

 $\delta^{15}N(NO_3^-)$  records in ice cores from the Tibetan Plateau also exhibit decreasing trends from 1955 to 2011 (Li et al., 2020). The  $\delta^{15}N(NO_3^-)$  of this Tibetan Plateau ice core (4.2 ± 3.1 ‰ in 1951–2011) is also substantially higher than those of Arctic ice cores, indicating a different regional context. Comparing  $\delta^{15}N(NO_3^-)$  records from different locations would be beneficial

- 425 for determining the regional physical/chemical behaviors of  $NO_3^-$  from emission to deposition. This would allow us to better assess the impacts of human activity on nitrogen cycling and take corresponding measures to reduce the adverse effects of  $NO_3^-$  on climate and biogeochemical cycles. However, in Antarctica (Akers et al., 2022), the ice-core  $\delta^{15}N(NO_3^-)$  values varied significantly depending on the snow accumulation rate. It is therefore important to estimate post-depositional alteration for each ice core, refine models with recent information (Shi et al., 2023), and perform reverse calculations for atmospheric
- 430  $\delta^{15}N(NO_3^{-})$  (Jiang et al., 2024). Notably, a recent study emphasized the potential impact of microbial alterations to both NO<sub>3</sub><sup>-</sup> concentrations and its isotopic compositions in an Asian glacier (Hattori et al., 2023); thus, interpretations of NO<sub>3</sub><sup>-</sup> concentrations and  $\delta^{15}N(NO_3^{-})$  records in ice cores should proceed with caution. We recommend that interpretations of NO<sub>3</sub><sup>-</sup> concentrations and  $\delta^{15}N(NO_3^{-})$  records in ice cores should be accompanied by  $\Delta^{17}O(NO_3^{-})$  or  $\delta^{18}O(NO_3^{-})$  records whenever possible to verify atmospheric NO<sub>3</sub><sup>-</sup> preservation without post-depositional biological alteration.

#### 435 **5** Conclusions

In this study, we reported ~60-year (1959–2014) records of NO<sub>3</sub><sup>-</sup> isotopic compositions from the SE-Dome ice core in Greenland. The observed  $\delta^{15}N(NO_3^-)$  values in the SE-Dome ice core were consistently ~4 ‰ lower than those in the Summit ice core record. The high snow accumulation rate at the SE-Dome site reduces the sensitivity of NO<sub>3</sub><sup>-</sup> to post-depositional processes, which was supported by outputs from the TRANSITS model. Therefore, we concluded that the SE-Dome ice core,

- which exhibits superior NO<sub>3</sub><sup>-</sup> preservation, is a promising tool for reconstructing changes in atmospheric nitrogen cycling driven by anthropogenic activity. This study was based on results from the SE-Dome I ice core (~90 m), which covers the past 60 years. The SE-Dome II core (drilled in 2021) preserves records that extend back to 1800 CE (Iizuka et al., 2021; Kawakami et al., 2023). Thus, there is considerable potential for future research aimed at reconstructing NO<sub>3</sub><sup>-</sup> aerosol dynamics from the beginning of the Industrial Revolution to the present. Additionally, while regional comparisons of ice-core  $\delta^{15}N(NO_3^-)$  records
- 445 are beneficial for describing the regional physicochemical behaviours of NO<sub>3</sub><sup>-</sup>, it is necessary to account for regional differences in post-depositional alteration when analysing the spatiotemporal variations in atmospheric NO<sub>3</sub><sup>-</sup> isotopes.





## Data availability

The data used in this study named "Figure data file final" will be available in the Hokkaido University Collection of Scholarly and Academic Papers (https://eprints.lib.hokudai.ac.jp/dspace/) once the paper is accepted.

#### 450 Author contributions

SH conceptualized the study; ZW, SH, AT, SI, ZJ, SM, and YI curated the data; ZW, SH, AT, ZJ, SI, and YI performed the formal analysis; SH and YI acquired funding; SH, AT, NY, KF, SI, SM, and YI conducted the investigation; SH, ZJ, LG, and JS developed the methodology; SH managed the project; ZW and SH validated the results; ZW, KF, SH, and ZJ visualized the data; ZW and SH wrote the original draft; KF, SI, ZJ, LG, JS, RU, AL, and YI reviewed and edited the manuscript.

#### 455 **Competing interests**

The authors declare no conflicts of interest.

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Parameters	Description	Value	Unit	Data origin
d	Snow density	400	${ m kg}~{ m m}^{-3}$	Oyabu et al., (2016)
SSA	Snow-specific surface area	46.95	${ m m}^2{ m kg}^{-1}$	Domine et al., (2007)
$[BC]_{ m SE-Dome}$	BC concentration	2.2	${\rm ng~g^{-1}}$	See text
[Dust]	Dust concentration	33.94	${\rm ng}~{\rm g}^{-1}$	Amino et al., (2021)
[HULIS]SE-Dome	HULIS concentration	47.6	${\rm ng}~{\rm g}^{-1}$	See text
TCO	Total column ozone	See Supplement data file 1	DU	Jiang et al., (2021)
Ч	Boundary layer height		ш	
T	Temperature		°C	ERA5(Hersbach et al., (2020); Khalzan et al., (2022))
Ρ	Pressure	See Supplement data file 1	hPa	
$O_3$	O <sub>3</sub> concentration	$26.66 \sim 32.30$	dqq	GEOS-Chem v12.9.3
BrO	BrO concentration	$0.06 \sim 0.76$	ppt	(https://doi.org/10.5281/zenodo.3974569, last access:
$OH/HO_2$	OH/HO <sub>2</sub> concentration	See Supplement data file 1	ppt	30 August 2023)
${}^{V}$	Snow accumulation	101	${ m cm}~{ m a}^{-1}$	Iizuka et al., (2017)
$F_{ m pri}$	Primary Nitrate flux	16.28	$\rm kgNm^{-2}a^{-1}$	Iizuka et al., (2018)
$f_{ m exp}$	Export fraction	47%	I	See Table S2.
15 Gp	N isotope fractionation constant during photolysis	$^{15}\mathrm{Ep}=J^{15}/J^{14}-1$	%00	Frhland et al. (2013)
15 <sub>6d</sub>	N isotope fractionation constant during deposition	10	%00	
$f_{ m cage}$	Cage effect	15	%	Erbland et al., (2015)

Table 1. Parameters used in the Transfer of Atmospheric Nitrate Stable Isotopes To the Snow (TRANSITS) model for the SE-Dome ice core.





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# A 60-year atmospheric nitrate isotope record from a Southeast Greenland ice core with minimal postdepositional alteration

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Figure S1. The seasonal change of observed NO<sub>3</sub><sup>-</sup> isotopes and concentration SE-Dome ice core. (a)  $\delta^{15}N(NO_3^-)$  (1959-2014), (b)  $\delta^{15}N(NO_3^-)$  (1959-1974), (c)  $\delta^{15}N(NO_3^-)$  (1975-1980 & 1995-2014), (d)  $\delta^{15}N(NO_3^-)$  (1981-1993), (e)  $\Delta^{17}O(NO_3^-)$  (1959-2014), (f)  $\Delta^{17}O(NO_3^-)$  (1959-1980 & 1995-2014), (g)  $\Delta^{17}O(NO_3^-)$  (1981-1994) and (h) the NO<sub>3</sub><sup>-</sup> flux (mmol m<sup>-2</sup> yr<sup>-1</sup>).



**Figure S2.** The sensitivity of the changes in  $\delta^{15}N(NO_3^-)$  and  $\Delta^{17}O(NO_3^-)$  of the ice-core nitrate to  $f_{exp}$  with different snow accumulation rate (*A*). (a) A = 0.25 m w e a<sup>-1</sup> which equals to that in Summit; (b) A = 0.6 m w e a<sup>-1</sup>; (c) A = 1.01 m w e a<sup>-1</sup>: (d) A = 1.4 m w e a<sup>-1</sup>.



**Figure S3.** Time series of regional contributions of air mass origins for SE-Dome (b) and Summit 39 (c). The regions are shown at the top. Greenland in gray, North America in purple (Canada and the 40 U.S.), Europe (EU) in green, Russia in blue.

Table S1 The samples and corresponding years

		1	1	05					
Year	Seasonal	$\delta^{18}$ O	⊿ <sup>17</sup> O	$\delta^{15}$ N	Year	Seasonal	$\delta^{18}\mathrm{O}$	⊿ <sup>17</sup> O	$\delta^{15}$ N
1959	summer	79	27.4	0.5	1988	spring	88.5	32.8	-3.4
1959	winter	76.6	26.5	-1.2	1988	summer	86.7	33.4	-6.2
1960	summer	83.1	30	-4.3	1988	autumn	85.5	34	-7.9
1961	winter	76.5	27.2	-1.6	1988	winter	87.5	33.9	-6.1
1961	summer	80.1	27.7	-0.5	1989	spring	80.9	29	-2.4
1962	winter	78.1	27.5	-0.5	1989	summer	86.8	34.5	-8.6
1962	summer	77.7	28.4	1.4	1989	autumn	80.9	30.3	-1.3
1963	winter	87.1	33.9	-3.4	1989	winter	83.9	31.9	-5.3
1963	summer	76.6	27.8	2	1990	spring	74	26.2	-3.1
1964	winter	85.9	33.4	-2	1990	summer	77.8	30	-8.3
1964	summer	76.5	26.7	0.1	1990	autumn	86	32.6	-9.7
1965	winter	79.8	31.5	-4.4	1991	spring	74.7	28	-1.6
1965	summer	80.7	30.2	2.5	1991	summer	70.4	25.9	-0.5
1966	winter	77	30.7	-6	1991	autumn	84.3	32.5	-9.1
1966	summer	73	26.9	-0.3	1991	winter	83.7	32.8	-6.4
1967	winter	80.3	31.1	-7.4	1992	spring	79.3	29.5	4.8
1967	summer	73.7	26.6	-1.4	1992	summer	78.6	28.1	-6.3
1968	winter	79.8	30.4	-4.1	1992	autumn	82.8	32	-7.9
1968	summer	76	27.4	-1.8	1993	summer	87	34.2	-8.6
1969	winter	80.9	30.9	-5.7	1993	autumn	85.6	34.5	-9.8
1969	summer	73	26.4	-0.3	1993	winter	84.7	32.6	-10
1970	winter	83.9	32	-4.3	1994	spring	76	27.8	-0.9
1970	summer	75.8	27.2	-1.8	1994	summer	78.9	28.2	-4
1971	winter	82.3	32.1	-7	1994	winter	82.4	29.5	-4.4
1971	summer	75.8	27.4	0.8	1994	autumn	83.4	31.2	-9.1
1972	winter	82.3	32.7	-9	1995	summer	83.1	31.7	-7.6
1972	summer	74.3	26.6	-7.2	1996	winter	78.1	29.4	-5.7
1973	winter	78.9	30.4	-6.2	1996	summer	77.3	28.1	-1.9
1973	summer	75.7	27.6	-4.1	1997	winter	82.7	32.7	-9.2
1974	winter	79.2	30.4	-7.1	1997	summer	78	28.2	-0.5
1974	summer	75.6	27.7	-5.8	1998	winter	82.3	32.2	-9.7
1975	winter	79.7	31.8	-12.4	1998	summer	77.2	27.6	-1.6
1975	summer	80.6	28.9	-0.3	1999	winter	83.1	31.6	-4.8
1976	winter	80.9	30.4	-8.3	1999	summer	78.4	28.7	-1.2
1976	summer	75.4	26.9	-3	2000	winter	83	32.3	-8.6
1977	winter	81.5	31.4	-12.8	2000	summer	74.9	27.6	-3
1977	summer	77.8	28.2	-3.6	2001	winter	83.7	32.9	-8.4
1978	winter	87.2	32.5	-13.3	2001	summer	78.3	29.5	-3.8
1978	summer	76.1	27.9	-2	2002	winter	81.1	31.1	-9
1979	winter	85.5	33	-9.2	2002	summer	74.1	26.7	-4.2
1979	summer	76.6	27.8	-4.7	2003	winter	80.9	31.8	-9.7
1980	winter	84.1	32.9	-8.6	2003	summer	76.9	28.4	-3.2

Year	Seasonal	$\delta^{18}$ O	$\Delta^{17}O$	$\delta^{15}$ N	Year	Seasonal	$\delta^{18}\mathrm{O}$	$\Delta^{17}O$	$\delta^{15}$ N
1980	summer	74.6	26.7	-3.7	2004	winter	81.7	31.4	-6
1981	winter	80.7	31	-7.2	2004	summer	76.6	27.8	-2.2
1981	spring	77.5	28.8	-4.6	2005	winter	82.7	31.3	-5.4
1981	summer	75.1	27.3	-2.4	2005	summer	81.7	30.9	-5.2
1981	autumn	84.7	33.9	-12.6	2006	winter	80.2	30.1	-2.2
1981	winter	74.6	26.8	-2.1	2006	summer	76.9	27.9	-1.9
1982	Spring	76.1	28.2	-4.4	2007	winter	82.2	32.1	-6.8
1982	summer	81.3	31.9	-7.5	2007	summer	75.7	28.8	-3.5
1982	autumn	83.2	32.1	-9.5	2008	winter	82.6	33.5	-9.1
1982	winter	72.3	26.8	-4.6	2008	summer	77.1	28.8	-3.7
1983	Spring	72.1	26.8	-3.2	2009	winter	78.1	31.6	-9
1983	summer	80.1	28.9	-2.3	2009	summer	71.7	27.3	-3.6
1983	autumn	87	33.6	-6.1	2010	winter	80.9	32.8	-7.3
1983	winter	86.4	34.1	-10.3	2010	summer	74.7	28.1	-4
1984	Spring	76.3	27.8	-6.8	2011	winter	81.9	32.5	-5
1984	Summer	73.7	27.6	-3.9	2011	summer	70.2	26.2	-2.4
1984	autumn	83.1	31.5	-3.3	2012	winter	82.8	33.6	-7.7
1984	winter	82.7	32.3	-9.4	2012	summer	73.6	27.2	-1.4
1985	Spring	71.5	27.6	-5.5	2013	winter	75.1	29.8	-8.4
1985	summer	73.7	26.7	-2	2013	summer	73.7	26.8	-1.6
1985	autumn	82.8	31.8	-6.2	2014	winter	65.1	24.6	-6.3
1985	winter	86.2	34.4	-7.4	2014	summer	67	24.2	-3.9
1986	Spring	70	26.2	-5.3	2015	winter	82.1	32.4	-7.5
1986	summer	83.7	31.4	-4.2					
1986	autumn	89.6	35	-11.4					
1987	spring	81.4	32.7	-13.5					
1987	summer	77.4	28.2	1.3					
1987	autumn	83.4	32.9	-11.9					
1987	winter	90.4	35.1	-10.1					
1988	spring	88.5	32.8	-3.4					
1988	summer	86.7	33.4	-6.2					
1988	autumn	85.5	34	-7.9					
1988	winter	87.5	33.9	-6.1					

Parameters	Parameters	Description	Value	Unit	Data origin
	Г	Summer boundary layer height	3.50E+05	ш	Honrath et al., 2002
	рЛ	The dry deposition velocity of HNO <sub>3</sub>	0.0063	m s <sup>-1</sup>	Björkman et al., 2013
	<i>k</i> [OH]	The rate constant for the $NO_2 + OH$ reaction	1.09373E-11		Atkinson et al., 2004
	$V_{ m h}$	Mean horizontal wind speed	5	m s <sup>-1</sup>	Mcdowell et al., 2020
Summit	[HO]	Measured average OH radical concentration in summer	6.30E+06	mloec cm-3	Sjostedt et al., 2006
	Н	Horizontal characteristic	156	Ш	Characteristic length of summit of the Greenland ice cap; Honrath et al., 2002
	Г	Summer boundary layer height	Same as Summit	ш	
	Рd	The dry deposition velocity of HNO <sub>3</sub>	Same as Summit	m s <sup>-1</sup>	I
	[HO] <i>\</i>	The rate constant for the $NO_2 + OH$ reaction	1.13E-11		
SE-Dome	$V_{ m h}$	Mean horizontal wind speed	5.2	m s <sup>-1</sup>	ED A 5(Herebach et al. (2020).
	[HO]	Measured average OH radical concentration in summer	1.02E+06	mloec cm-3	Khalzan et al., (2022))
	Н	Horizontal characteristic	235.31	ш	

 Table S2 Parameters used for calculating fexp in Summit and SE-Dome ice core

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