An inverse model to correct for the effects of post-depositional processing on ice-core nitrate and its isotopes: model framework and applications in Summit, Greenland and Dome C, Antarctica

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Abstract

Comprehensive evaluation of the effects of post-depositional processing is a prerequisite for appropriately interpreting ice-core records of nitrate concentration and isotopes. In this study, we developed an inverse model that uses archived snow/ice-core nitrate signals to reconstruct primary nitrate flux and its isotopes. The model was then applied to two polar sites, Summit, Greenland and Dome C, Antarctica using measured snow nitrate concentration and isotope profiles[perhaps say the time period, was this one year, 10 years, 100 years?]. At Summit, the model successfully reproduced the observed atmospheric $\delta^{15}N(NO_3^-)$ and $\Delta^{17}O(NO_3^-)$ and their seasonality. The model was also able to reasonably reproduce the observed skin layer and atmospheric $\delta^{15}N(NO_3^-)$ and $\Delta^{17}O(NO_3^-)$ at Dome C at the annual scale. In addition, the model also calculated the depositional flux of nitrate prior to postdepositional processing, termed primary nitrate flux (F_{pri}). The calculated F_{pri} at Summit was 6.9×10^{-6} kgN m^2 a^{-1}. Calculated $\Delta^{17}O(NO_3^-)$ of F_{pri} is consistent with atmospheric? observations in the northern hemisphere; however, the calculated $\delta^{15}N(NO_3^-)$ of F_{pri} displays an opposite seasonal pattern to atmospheric? observations in the northern mid-latitudes. The calculated Fpri at Dome C, varies from 1.5 to 2.2 $\times 10^{-6}$ kgN m^{-2} a^{-1}. In contrast to Summit, calculated D17O and d15N at Dome C is consistent with atmospheric observations in two Arctic coastal sites. The calculated F_{pri} at Dome C is close to previous estimated stratospheric denitrification flux in Antarctica, and the high $\delta^{15}N(NO_3^-)$ and $\Delta^{17}O(NO_3^-)$ of F_{pri} at Dome C also point towards the dominate role of stratospheric origin of primary nitrate to Dome C.

1. Introduction

Nitrate ion (NO_3^-) is routinely measured in polar snow and ice cores. The precursor of atmospheric nitrate is nitrogen oxides NO_x (=NO+NO_2), which plays a fundamental role in the production of tropospheric ozone and interconversion of atmospheric HO_x (= OH+HO_2) radicals (Seinfeld et al., 1998; Sillman, 1999). Given the potential link between ice-core nitrate and atmospheric NO_x, some previous studies proposed that ice-core nitrate records could be used to derive information regarding past atmospheric NO_x abundance (Dibb et al., 1998; Röthlisberger et al., 2000). In addition, the oxygen isotope mass-independent fractionation signal ($\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O$) of nitrate is a promising proxy of atmospheric O_3/HO_x ratio and is directly related to atmospheric oxidizing environment (Alexander et al., 2004; Alexander et al., 2015; Geng et al., 2017; Sofen et al., 2014). These unique features render ice core nitrate a potentially useful proxy to retrieve information on atmospheric oxidation environment in the past (Alexander et al., 2015).

Interpretations of ice-core nitrate records are, however, not straightforward (Wolff et al., 2008). Unlike other less reactive species in ice cores such as sulfate, ice-core nitrate may not be able to directly track its atmospheric abundance (Iizuka et al., 2018). To link ice-core nitrate to atmospheric NO_x abundance, other information including the conversion rate of NO_x to nitrate, the mean lifetime of atmospheric nitrate, and the impact of post-depositional processing must be considered (Wolff, 1995; Wolff et al., 2008). Among these factors, the post-depositional processing of snow nitrate is the first gap in linking ice-core nitrate to atmospheric nitrate and/or NO_x.

Snow nitrate is reactive under exposure to sunlight and can be photolyzed to form NO_x and HONO (Honrath et al., 2002; Chu and Anastasio, 2003), which is rapidly transported to the overlying atmosphere via diffusion and wind pumping (Zatko et al., 2013). These photoproducts subsequently reform nitrate (i.e., snow-sourced nitrate) and deposit locally or be exported away, leading to a recycling of nitrate at the air-snow interface (Erbland et al., 2013; Frey et al., 2009). This post-depositional processing not only disturbs the link between nitrate in snow and its atmospheric precursors but also alters its isotopic signals (Erbland et al., 2013; Jiang et al., 2021; Jiang et al., 2022; Shi et al., 2015).

It is expected that the degree of postdepositional processing varies with changes in factors such as snow accumulation rate under different climates (Geng et al., 2015), causing corresponding shifts in the preserved nitrate signals. For example, the lower snow accumulation rate in glacial times would favor a higher degree of post-depositional processing with elevated $\delta^{15}N(NO_3^-)$ relative to the Holocene as reflected by the GISP2 ice-core records (Geng et al., 2015; Hastings et al., 2005). Moreover, both observational and modeling studies have suggested that at sites with relatively high snow accumulation rates such as Summit, Greenland, the post-depositional processing of snow nitrate under present day conditions also has a significant impact on seasonal $\delta^{15}N(NO_3^-)$ variations, although its integral effects at the annual scale are limited (Jiang et al., 2021; Jiang et al., 2022). In addition, the $\Delta^{17}O$ of snow nitrate would also be altered via secondary chemistry during photolysis on snow grain (i.e., the cage effect) and this effect is enhanced with lower snow accumulation rates (Erbland et al., 2013; Frey et al., 2009; Mccabe et al., 2005; Meusinger et al., 2014). Thus, it is critical to evaluate the impact of post-depositional processing on ice core nitrate records before interpretation, especially for records covering different climates with changes in snow accumulation rates.

Primary nitrate to the polar ice sheets mainly originates from midlatitudes via long-range transport and with extra contributions from stratospheric input (Lee et al., 2014; Legrand and Delmas, 1986; Fischer et al., 1998; Savarino et al., 2007). To build the link between ice-core and atmospheric nitrate, Geng et al. (2015) proposed a simple method of using $\delta^{15}N(NO_3^-)$ to estimate the fractional loss of snow nitrate caused by post-depositional processing. This method takes advantage of the high sensitivity of $\delta^{15}N(NO_3^-)$to the degree of photolytic loss (Erbland et al., 2013; Frey et al., 2009). If $\delta^{15}N$ of the initially deposited nitrate can be assumed, the residual fraction of snow nitrate can be calculated by applying a Rayleigh type isotope fractionation model. The photolysis fractionation constant ($^{15}\varepsilon_p$) can be estimated via the prescribed actinic flux spectrum and the absorption cross section for different nitrate isotopologues (Berhanu et al., 2014). Based on this method, Geng et al. (2015) estimated that as much as 45-

53% of snow nitrate was lost after deposition during the last glacial time in the GISP2 ice core record. However, it's difficult to justify the assumed δ^{15}N of deposited nitrate under different climates, and the method cannot correct for postdepositional modification of Δ^{17}O(NO_3^-).

Erbland et al. (2015) developed a 1-D snow photochemistry model (TRANISTS) that quantifies the effects of post-depositional processing on the preservations of nitrate and its isotopes in ice cores. The model comprises a series of physicochemical processes, including UV photolysis of snow nitrate, emission of NO_x to the overlying atmosphere, local oxidation and nitrate deposition. In addition, changes in the isotopic composition of nitrate (δ^{15}N and Δ^{17}O) at each subprocess are also explicitly incorporated. The model has been applied in various locations with different snow accumulation rates and well reproduced the observed snowpack nitrate and isotope profiles in Greenland and Antarctica? (Erbland et al., 2015; Jiang et al., 2021; Winton et al., 2020; Zatko et al., 2016). Based on model sensitivity tests, Erbland et al. (2015) proposed a framework to correct for the effects of post-depositional processing and to retrieve atmospheric information related to Fpri at Dome C. However, the framework is rather complicated, and it assumes δ^{15}N of the archived nitrate is exclusively determined by the degree of nitrate post-depositional processing. Therefore, the framework cannot be applied to sites with moderate or high snow accumulation rates such as WAIS Divide, Antarctica and Summit, Greenland, where factors other than post-depositional processing may also contribute to δ^{15}N variations across different periods and/or climates (Hastings et al., 2005; Jiang et al., 2021).

In ummarys, TRANSITS is a forward model, and it requires prior knowledge of the distribution (e.g., weekly or monthly) of primary nitrate flux and isotopes as model inputs, which is usually unavailable due to the lack of direct observationsIn this study, we developed an inverse modeling framework (i.e., the inverse of the TRANISTS model) that uses snowpack and/or ice-core preserved nitrate signals (concentrations and isotopes) as model inputs, and properties of primary nitrate including its flux and isotopes (δ^{15}N and Δ^{17}O) can be directly retrieved with constraints from snow accumulation rate and other known parameters (e.g., snow physicochemical properties).

We assessed the model with observations at Summit, Greenland and Dome C, Antarctica, two representative sites with approximately the high-end and low-end snow accumulation rates at present day conditions.

2. Model description

The inverse model is designed based on the framework of the TRANSITS model but in an opposite direction of operating flows. The principle of the inverse model is that the archived snow nitrate concentration and isotope profiles from measurements are treated as model input, and they evolve inversely over time through the snow photic zone (defined as 3 times of the snow e-folding depth where the radiation decreases to 1/*e* of its initial intensity at snow surface) to recover their initial states at the surface and then in the local atmosphere as well as in primary nitrate. A schematic view of the inverse model is shown in Fig. 1.

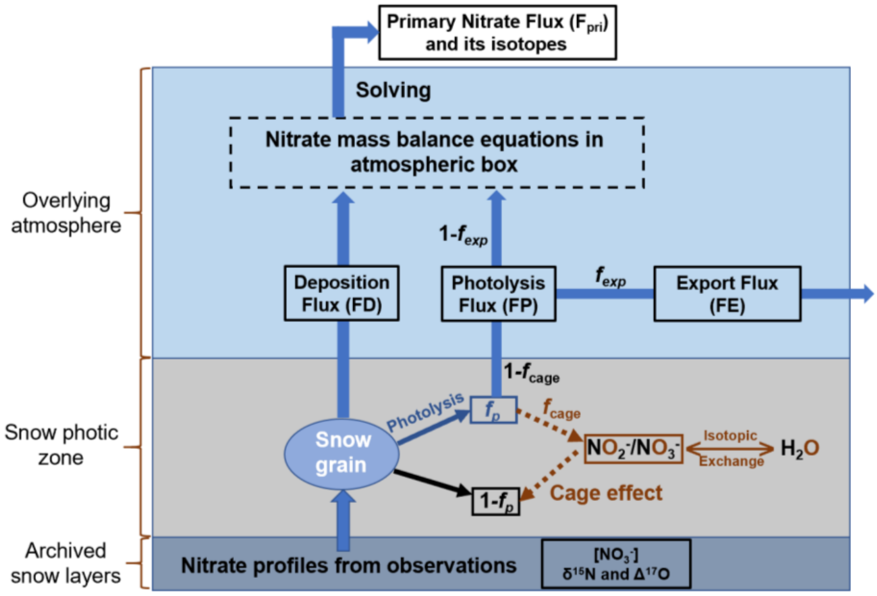

Figure 1. Schematic plot of the model domains of the inverse model including the atmospheric box, the snow photic zone and the archived snow layers, where f_{exp} represents the fraction of nitrate exported from the site of photolysis. The nitrate isotopic and mass balance relationships on snow grains during photolysis are also shown, where f_p represents the fraction of snow nitrate being photolyzed, and f_c represents the fraction of photolyzed nitrate experiencing the cage effect (i.e., exchange of oxygen isotopes with snow water).

The inverse model inherits most of the original processes and features in TRANSITS but with several modifications. In accordance with the TRANSITS model, the domains of the inverse model are represented by a 1-D atmosphere and snow column. As shown in Fig. 1, the model contains three vertical layers, including the overlying atmospheric boundary layer which is treated as a single well-mixed box, and the underlying snowpack which is further separated into a snow photic zone and the archived snow layers beneath the photic zone. The model time step is set to be one week by default. During each time step, the mass conservation equations in the atmospheric box are represented as follows:

$$\frac{\mathrm{d}m_a}{\mathrm{dt}} = F_{pri} + FP - FE - FD \tag{1}$$

$$\frac{\mathrm{d}(m_a \times \delta_a)}{\mathrm{dt}} = F_{pri} \times \delta F_{pri} + FP \times \delta FP - FE \times \delta FE - FD \times \delta FD \tag{2}$$

$$\frac{\mathrm{d}(m_a \times \Delta_a)}{\mathrm{dt}} = F_{pri} \times \Delta F_{pri} + FP \times \Delta FP - FE \times \Delta FE - FD \times \Delta FD \tag{3}$$

where the subscript “a” represents the atmospheric box, i.e., m_a refers to the mass of atmospheric nitrate, and δ_a and Δ_a refer to δ^{15}N and Δ^{17}O of atmospheric nitrate, respectively. Different nitrate fluxes transported in and out of the atmospheric box are denoted as FP, FE, and FD, where FP refers to the photolytic nitrate flux (the snow-sourced nitrate), FD refers to the atmospheric deposition nitrate flux, and FE refers to the exported nitrate flux that is horizontally transported out of the atmospheric box via air flow. Following Erbland et al. (2015), FE is assumed to be a constant portion (f_{exp}) of FP (i.e., FE = f_{exp} × FP) and maintains the isotopic signatures of FP.

In Eq. (1-3), the LHS (left-hand side) terms are two to three orders of magnitude smaller than nitrate fluxes in and out of the atmospheric box. Erbland et al. (2015) showed that the atmospheric nitrate mass was a factor of ~10^{-3} smaller than the surface snow nitrate reservoir at Dome C, and similar results were also found at Summit in Jiang et al. (2021). Thus, d(m_a)/dt is assumed to be zero in each time step, which leads to simplified formulas for calculating F_{pri} via Eq. (4-6) as follows:

$$F_{pri} \approx FD - FP\left(1 - f_{exp}\right) \tag{4}$$

$$\delta F_{pri} \approx \frac{FD \times \delta FD - FP \times \left(1 - f_{exp}\right) \times \delta FP}{FD - FP \times \left(1 - f_{exp}\right)} \tag{5}$$

$$\Delta F_{pri} \approx \frac{FD \times \Delta FD - FP \times (1 - f_{exp}) \times \Delta FP}{FD - FP \times (1 - f_{exp})} \tag{6}$$

Hence, if the magnitude and isotopic compositions of FP and FD in each time step are known, F_{pri} can be calculated. FP and FD are calculated from the inverse evolution of snowpack nitrate are described in the following sections.

2.1 The backward evolution of snowpack nitrate

Starting with an arbitrary snowpack nitrate depth profile at a given time step, changes in nitrate concentration and isotopic compositions (δ^{15}N and Δ^{17}O) in a certain snow layer in the photic zone induced by photolysis can be calculated as follows:

$$cN_n' = \frac{cN_n}{(1 - f_p) + f_c f_p} \tag{7}$$

$$\delta N_n' = \delta N_n - \frac{(1 - f_p)(1 - f_c)\bar{\varepsilon}_p ln(1 - f_p)}{(1 - f_p) + f_c f_p} \tag{8}$$

$$\Delta N_n' = \Delta N_n \frac{(1 - f_p) + f_c f_p}{(1 - f_p) + \frac{2}{3} f_c f_p} \tag{9}$$

where cN_n, δN_n and ΔN_n represent the concentration, δ^{15}N and Δ^{17}O of nitrate in the n^{th} snowpack layer, respectively, and the quotation mark in superscript refers to the initial state before being photolyzed at each time step. These equations are based on the nitrate mass and isotopic balances on snow grains during photolysis as shown in Fig. 1, and detailed derivations of these equations are in *SI*.

In Eq (7-9), f_p represents the fraction of snow nitrate that undergoes photolysis at each time step, and f_c represents the fraction of nitrate photolysis intermediate undergoing the cage effect (Meusinger et al., 2014) which leads to apparent oxygen isotope exchange with water and lowers Δ^{17}O by a factor of 2/3. The potential isotope effect on δ^{15}N during cage effect remains unknown and is not considered. The value of f_p is calculated by the first-order reaction of nitrate photolysis:

$$f_p = 1 - \exp\left(-\int_0^{dt} J(t, z)dt\right) \tag{10}$$

where *J* represents the rate constant of nitrate photolysis that varies with time and depth of the snow layer. *J* is calculated from actinic flux (*I*), the quantum yield (*Φ*), and the absorption cross section (σ) of nitrate photolysis as follows:

$$J(t,z) = \int_{280\,nm}^{350\,nm} \Phi(\lambda) \times \sigma_{NO_3^-}(\lambda) \times I(z,\lambda)\, d\lambda \qquad (11)$$

The rate constant of $^{15}NO_3^-$ photolysis (J^*) is also calculated from the absorption cross section of the heavy isotopologue from Berhanu et al. (2014), and the photolysis fractionation constant for nitrogen isotope ε_p is calculated via:

$$\varepsilon_p(t,z) = \frac{J^*(t,z)}{J(t,z)} - 1 \qquad (12)$$

The solar zenith angle changes with time during each time step, leading to changes in the spectrum of actinic flux and subsequently changes in ε_p. To simplify the calculation, in Eq. (8) the average nitrogen isotope fractionation constant $\overline{\varepsilon_p}$ is used. The radiative transfer in snowpack is calculated using the parameterization from Zatko et al. (2013) to achieve fast online calculations, and this parameterization has been shown to be capable of providing consistent results with a high-order snowpack radiative transfer model DISORT (Zatko et al., 2013). The upper boundary conditions for the parameterization, i.e., the direct and diffuse components of the irradiance at the snow surface, are calculated offline using the Troposphere Ultraviolet and Visible (TUV) radiation model (Madronich et al., 1998) at different total column ozone (TCO) and solar zenith angle conditions.

The relationships between cN_n, δN_n, ΔN_n and cN_n', $\delta N_n'$, $\Delta N_n'$ in the snowpack are illustrated in Fig. 2. cN_n, δN_n and ΔN_n in the nth layer at a certain time step are the initial values, while cN_n', $\delta N_n'$ and $\Delta N_n'$ are the values before photolysis at this time step (calculated by Eq (7-9)) and are also the values after photolysis in the prior time step when it was in the $(n\text{-}1)^{th}$ layer. By repeating this operation, the initially deposited values of nitrate concentration and isotopes for a given snow layer without influence from the photo-driven post-depositional processing (i.e., when this layer was at the surface) can be calculated, which is be further linked to FD.

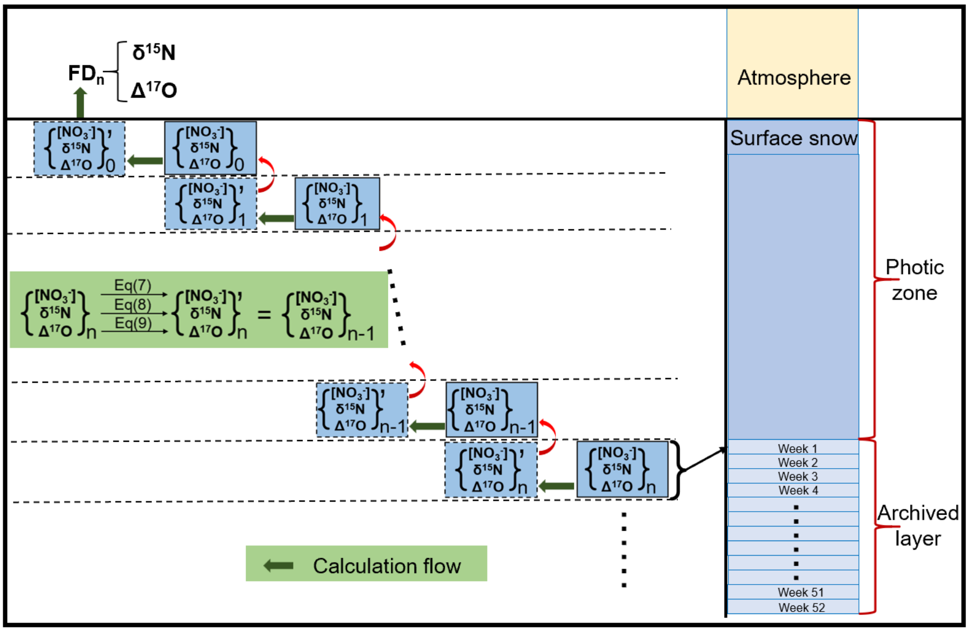

Figure 2. Schematic of the evolution of snowpack nitrate from the archived layer to its initial state at the snow surface. The quotation mark in the superscript of the bracket represents the status of snow nitrate before photolysis at each time step.

2.2 Determinations of FP and FD

FP and FD are determined during the inverse evolution of snowpack nitrate profiles. As shown in Fig. 1, FP and its δ^{15}N from the n^{th} snow layer can be calculated via the mass balance relationships:

$$FP_n = cN'_n f_p (1 - f_c) \rho_{snow} d_n / \Delta t \tag{13}$$

$$\delta FP_n = \delta N_n - \frac{\bar{\varepsilon}_p (1 - f_p) ln(1 - f_p)}{f_p} \tag{14}$$

In Eq (13), ρ_{snow} is the density of snow, d_{n} is the thickness of the n^{th} snow layer, which is equal to the accumulated snow thickness at one time step, and Δt is the default model time step (1 week). Eq (14) implicitly assumes that the reformed nitrate in the overlying atmosphere keeps the same δ^{15}N signals of the snow-emitted photoproduct of NO_2 because of isotope mass balance, i.e., essentially all NO_2 is oxidized into nitrate at one time step. FP emitted from the whole snowpack and its δ^{15}N can be calculated by:

$$FP = \sum FP_n \tag{15}$$

$$\delta FP = \frac{\sum FP_n * \delta FP_n}{\sum FP_n} \tag{16}$$

For $\Delta^{17}O$ of FP, extra knowledge of the oxidizing agent concentrations in the local atmosphere including HO_2, RO_2 and O_3 must be provided (*SI*). This is because the emitted NO_x would achieve photochemical steady state rapidly, thus erasing any original $\Delta^{17}O$ signal inherited from the snowpack nitrate. The subsequent conversion of NO_2 to nitrate would also determine 1/3 of the oxygen atom of the newly formed nitrate.

FD and its isotopic signals can be obtained from the uppermost snow layer before photolysis occurs as illustrated in Fig.2:

$$FD = cN_0'\rho_{snow}d_0/\Delta t \tag{17}$$

$$\delta FD = \delta N_0' \tag{18}$$

$$\Delta FD = \Delta N_0' \tag{19}$$

The calculated FP and FD in each time step are further used to calculate F_{pri} according to Eq (4-6).

2.3 The choice of model initial conditions

To run the model, an appropriate archival snow nitrate (isotopic) profile should be assigned as model initial conditions with seasonal or monthly resolution, though ideally weekly or finer resolution data are the best. The archived nitrate profile could be dated by using various types of seasonal markers, such as the $\delta^{18}O$ of H_2O, the ion concentrations or their ratios, and the snow accumulation rates (Hastings et al., 2004; Furukawa et al., 2017; Dibb et al., 2007).

3. Model evaluations

Because of the lack direct observations of primary nitrate apart from snow-sourced nitrate, we evaluated the model performance with other observations, including nitrate isotopes in surface snow and the overlying atmosphere. The deposited nitrate flux FD represents the state of nitrate that has just deposited onto the surface snow and is close to the definition of the skin layer of snowpack, i.e., the uppermost several millimeters of surface snow (Erbland et al., 2013; Winton et al., 2020). Thus, if there are sufficient high-resolution skin layer observations, a direct comparison with the model output can be performed (i.e., FD vs. skin layer measurements). Moreover, since FD originates from the local atmosphere, if the air-snow nitrate transfer function (i.e., the mass and isotope relationships between atmospheric nitrate and the deposited nitrate) is known, the calculated FD could be used to infer the state of local atmospheric nitrate. In this study, the isotope transfer function is applied instead of the mass transfer function because of its simplicity, especially for $\Delta^{17}O$, which is assumed to be conserved during deposition owing to its mass-independent nature. For $\delta^{15}N$, we assume that the deposition of atmospheric nitrate is associated with a fractionation constant (ε_d) of +10 ‰ following Erbland et al. (2013). In all, we can either directly compare the modeled isotopes of FD with the observed values in the skin layer or with local atmospheric signals by including the differences (only for $\delta^{15}N$) between FD and atmospheric nitrate.

In this study, we chose two typical polar sites, Summit, Greenland, and Dome C, Antarctica to conduct case studies in order to test the performance of the inverse model. These two sites were chosen for several reasons. First, these two sites represent typical polar sites with both relatively high (Summit) and extremely low (Dome C) snow accumulation rates. Second, there are sufficient atmospheric and/or snow observations at these two sites, which informs model input parameters and allows for comparison of the model results with observations. Third, these two sites are hot spots of ice core drilling, and future work using the inverse model on ice core nitrate records from these sites can be performed. In addition, there have already been studies simulating the post-depositional processing of snow nitrate at these two sites by using the forward TRANSITS model (Erbland et al., 2015; Jiang et al., 2021). Most of the model parameters in this study are kept the same as the original TRANISTS simulation unless otherwise mentioned. The major parameters used in this study are summarized in Table 1. Below, we specifically describe how we chose the initial model values/conditions for simulations at these two sites.

Table 1. Major parameters used in the model simulations at two different sites.

Site	Dome C, Antarctica	Summit, Greenland

Parameter	Value	Reference	Value	Reference
Accumulation rate (A)	28 kg m^{-2} a^{-1}	Erbland et al. (2015)	250 kg m^{-2} a^{-1}	Dibb et al., (2014)
Quantum yield (Φ)	0.015	Adjusted[a]	0.002	Jiang et al., (2021)
Cage effect fraction (f_c)	0.15	Erbland et al. (2015)	0.15	Erbland et al. (2015)
Nitrate export fraction (f_{exp})	0.2	Erbland et al. (2015)	0.35	Jiang et al., (2021)
Deposition fractionation factor (ε_d)	+10 ‰	Erbland et al. (2013)	+10 ‰	Erbland et al. (2013)
Δ^{17}O(NO$_3^-$) of FP	-	Erbland et al. (2013)	-	Jiang et al., (2021)

[a] Adjusted according to the best fit of snowpack nitrate δ^{15}N profile at Dome C (*SI*).

3.1 Summit, Greenland

Summit, Greenland is a typical site with high snow accumulation rate (250 kg m^{-2} a^{-1}, Dibb et al., 2004) at present, and weekly resolved snow accumulation data exists (Burkhart et al., 2004), allowing for the precise dating of the snowpack nitrate profile (Jiang et al., 2022). The weekly archival snowpack nitrate records at Summit compiled in Jiang et al. (2022) were adapted as initial model values.

3.2 Dome C, Antarctica

The present snow accumulation rate at Dome C, Antarctica is extremely low (28 kg m^{-2} a^{-1}, Erbland et al., 2013), and it is currently impossible to discern seasonal or sub-seasonal nitrate patterns owing to the limited resolution of snowpack measurements. Erbland et al. (2013) reported five snowpack nitrate depth profiles at Dome C that extended just below the photic zone. To predict the final archived nitrate concentration and isotopes, Erbland et al. (2013) fitted these depth profiles with an exponential function, and the obtained asymptotic values were regarded as the final preserved nitrate signal. The average asymptotic values for the five snowpacks were (21.2 ± 18.1) ng g^{-1}, (273.6 ± 64.0) ‰ and (26.0 ± 1.9) ‰ for nitrate concentration, δ^{15}N and Δ^{17}O, respectively. These values were used as the annual averages of the preserved nitrate at Dome C in this study.

We note the seasonality of the archived nitrate concentration is important because it determines the magnitude of FP and FD at each time step in the model. In simulations of Dome C, we designed three cases with different weekly concentration distributions in a year. In case 1, the weekly nitrate concentrations were assumed to be uniform throughout a year. In case 2, the weekly archival nitrate concentrations were assumed to be a Gaussian-type distribution to match the observed seasonality in skin layer nitrate concentrations at Dome C (Erbland et al., 2013):

$$c(n) = c_a \times \left(a + b \times \exp\left(-\frac{(n - n_0)^2}{\sigma^2}\right)\right) \tag{20}$$

In Eq (20), c_a represents the annual average snow nitrate concentration, n represents the week number (1 to 52) and the shape parameters (a, b, σ) were determined by the best fit of skin layer nitrate concentrations (*SI*). n_0 represents the week when nitrate concentration peaks in a year and was set to be 26 according to the observed maximum nitrate concentrations in the skin layer in local midsummer (Erbland et al., 2013). However, since nitrate deposited in different weeks of a year would have experienced different amounts of total actinic flux and nitrate deposited in autumn undergoes minimal degree of photolysis (Jiang et al., 2022), it is likely that the summer peak would shift toward autumn by final preservation. As such, we also prescribed a “shifted peak” distribution in case 3, and in this case n_0 was set equal to 35 in Eq. (20), while other parameters were the same as in case 2.

To determine the uncertainties in the model results caused by these artificially assumed nitrate profiles, we applied a Monte Carlo method, i.e., the exact initial value in snow at each week was set arbitrarily as follows:

$$c_r = c_a + \mathbf{U}(-\sigma, \sigma) \tag{21}$$

where c_a represents the prescribed initial value of annual-mean snow nitrate concentration in each case as described above, **U** represents a uniformly distributed random variable and σ represents the standard error of the observed ca The obtained time series with random error was normalized again as final model inputs. All three cases were repeated 1000 times, and the model results were used to evaluate the uncertainties.

For isotopic ratios (δ^{15}N and Δ^{17}O) of the archived nitrate, their seasonality was omitted in this study to simplify the model calculations, and for the results at Dome C we only compared the modeled results with observations at annual scale given the unknown seasonal inputs of these parameters. Note to reconstruct atmospheric signals of $\delta^{15}N$ and $\Delta^{17}O$ from ice core records usually it is that annual or coarser resolution data are used.

4. Results and discussion

4.1 Model results at Summit, Greenland

4.1.1 Comparison of local atmospheric variations

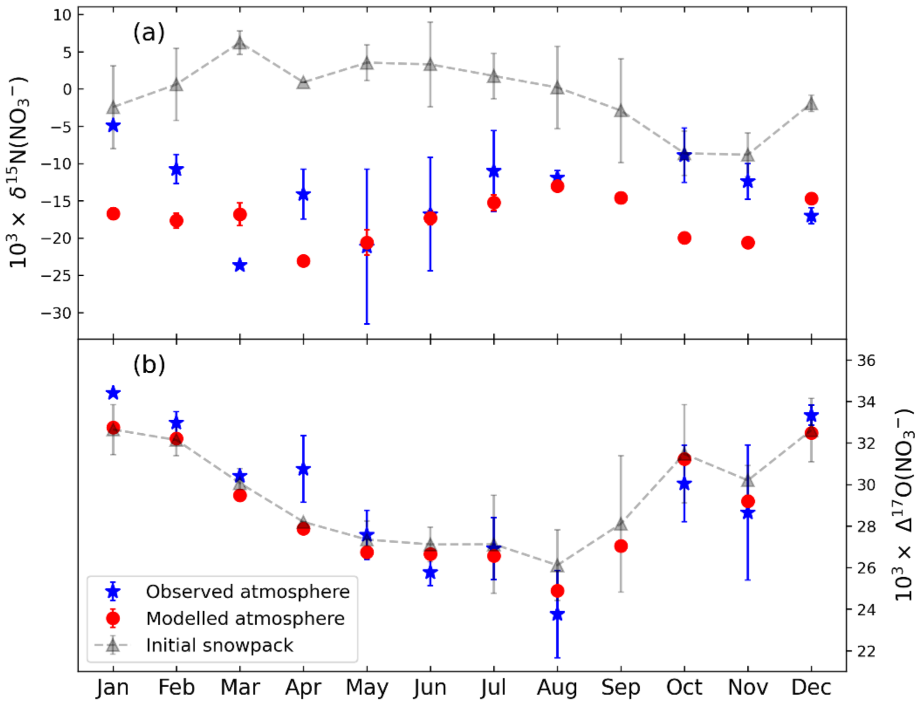

Figure 3. Comparison between the modeled (red dots) and observed (blue stars) seasonal variations in atmospheric nitrate (**a**) $\delta^{15}N$ and (**b**) $\Delta^{17}O$ at Summit Greenland. The dashed line with gray triangle represents the adapted snowpack results as model inputs (Jiang et al. 2022). The atmospheric observations were from Jiang et al. (2022).

Currently there are no skin layer observations at Summit and the atmospheric nitrate isotopes reported by Jiang et al. (2022) were used for model comparison. To reduce the uncertainty of model results owing to uncertainties associated with the weekly dating of snowpack, we only compared the modeled monthly averages with observations, and the uncertainties of the monthly model results were calculated as one standard error of the mean of results from different weeks. As shown in Fig. 3, the modeled seasonal variations in atmospheric $\delta^{15}N(NO_3^-)$ and $\Delta^{17}O(NO_3^-)$ agree well with the observed seasonality. In addition, the modeled and observed atmospheric $\Delta^{17}O(NO_3^-)$ are both close to snowpack $\Delta^{17}O(NO_3^-)$. This is just as expected at Summit since the deposition of atmospheric nitrate is assumed to be a mass-independent process. The only process that can alter $\Delta^{17}O(NO_3^-)$ in snow is the cage effect, which is negligible under present Summit conditions. The inverse model calculated a small cage effect of 0.15 ‰ on $\Delta^{17}O(NO_3^-)$ by comparing the annual weighted average of FA (FA = the archival nitrate flux below the photic zone) and FD, which is close to the value of 0.19 ‰ predicted by the forward TRANSITS model (Jiang et al., 2021).

For $\delta^{15}N(NO_3^-)$, the modeled atmospheric $\delta^{15}N(NO_3^-)$ seasonality is comparable to the observations, but the absolute values display some discrepancies in autumn and winter. In particular, the modeled and observed average $\delta^{15}N(NO_3^-)$ values in the summer half-year (from March to August) are -17.6 ± 3.5 ‰ and -16.0 ± 7.8 ‰, respectively, while in the winter half-year they are -16.0 ± 7.8 ‰ and -12.0 ± 4.1 ‰, respectively. The model-observation difference in the winter half year may be related to the model set-up of a constant ε_d of +10 ‰. As discussed by Jiang et al. (2022), the partition between nitrate deposition mechanisms (i.e., wet vs. dry deposition) may result in seasonally different air-snow transfer functions for $\delta^{15}N(NO_3^-)$. It has been observed that $\delta^{15}N(NO_3^-)$ of dry deposition is generally higher than wet deposition (Beyn et al., 2014; Heaton, 1987). This implies that dry deposition likely possesses a larger ε_d, perhaps because wet deposition can scavenge all or most of atmospheric nitrate leading to small to no isotope fractionation. Given the potential seasonal changes in the relative fraction of dry versus wet deposition at Summit, using a constant ε_d in the model would likely cause discrepancies in one season but not in the other. For example, if more wet deposition occurs in the winter half year at Summit, the model-observation discrepancies in the winter half year should be expected, as wet deposition may result in a smaller isotope effect.. However, some observations at Summit indicate that snowfall activities are more frequent and severe in summer months (June-September) instead of in winter (Castellani et al., 2015; Bennartz et al., 2019).

Alternatively, we note the ε_d itself may have a seasonality which could be caused by the temperature dependence of nitrate absorption onto ice grains (Abbatt, 1997) or be influence by other mechanisms such as the stability of the boundary layer. In fact, observations at Dome C indicated the averaged enrichment in skin layer $\delta^{15}N(NO_3^-)$ related to atmospheric $\delta^{15}N(NO_3^-)$ is +25 ‰ in summer, while in winter the value is +10 ‰ (Erbland et al., 2013). This may indicate a larger ε_d in summer than in winter, though the summer skin layer $\delta^{15}N(NO_3^-)$ is probably more or less influenced by photolysis which tends to increase $\delta^{15}N(NO_3^-)$. However, in the inverse model, ε_d was set as +10 ‰ throughout the year for Summit (note this value is consistent with the observed difference between surface snow and local atmospheric $\delta^{15}N(NO_3^-)$ at Summit in May and June (Fibiger et al., 2016)). If at Summit the ε_d in winter is lower than that in summer, the modeled average $\delta^{15}N(NO_3^-)$ in the winter half year would have been underestimated. This at least explains in part the model-observation discrepancies in winter half year $\delta^{15}N(NO_3^-)$. Future work on the degree of nitrogen isotope fractionation during atmospheric nitrate deposition and the causal factors are necessary to further investigate this issue.

4.1.2 Flux and isotopes of primary nitrate

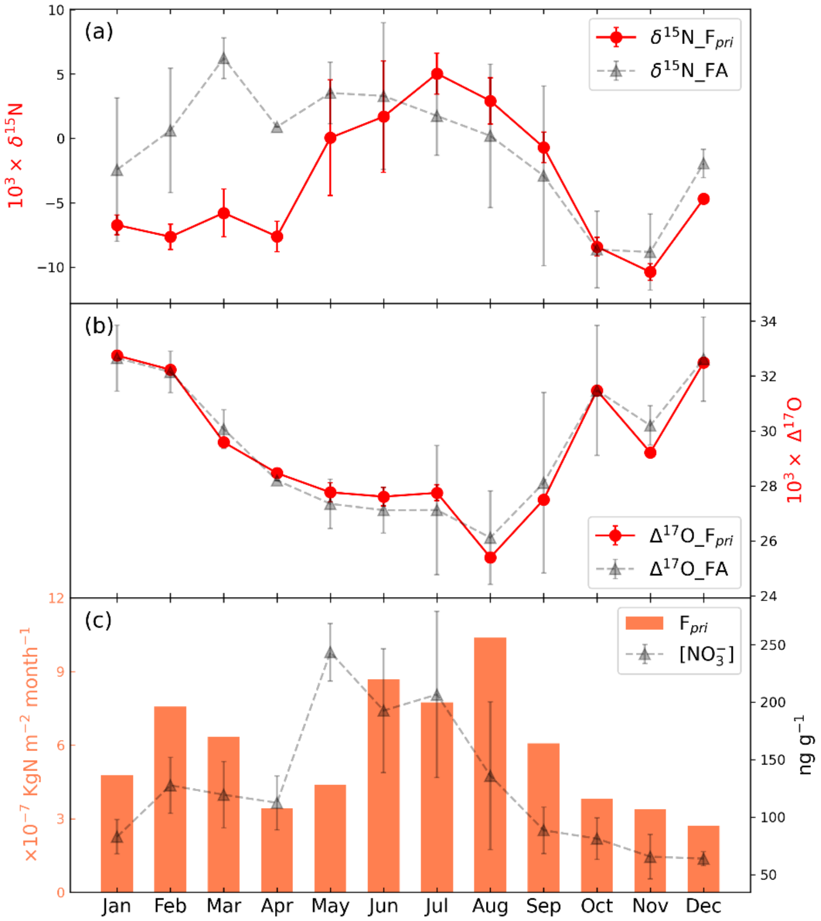

Figure 4. The modeled monthly (**a**) $\delta^{15}N$, (**b**) $\Delta^{17}O$ and (**c**) fluxes of primary nitrate (F_{pri}) to Summit Greenland. The concentration, $\delta^{15}N$ and $\Delta^{17}O$ values of the archived snow nitrate as model inputs are also shown for comparison (gray triangle with dashed line).

The major function of the inverse model is to reconstruct the primary nitrate flux and its isotopes by using ice core nitrate records. Primary nitrate flux is closely associated with atmospheric nitrate on the regional scale and could be further linked to the atmospheric abundance of its precursor NO_x. The isotopic composition of F_{pri} could provide extra information. For example, the $\delta^{15}N$ of F_{pri} may be used to infer the variations in NO_x source emissions if other factors influencing isotope fractionation during the atmospheric conversion of NO_x to nitrate can be constrained. The $\Delta^{17}O$ of F_{pri} depends on the relative concentration of major atmospheric oxidations such as O_3 and HO_2/RO_2 radicals and thus could be used to reflect regional atmospheric oxidation environment (Geng et al., 2017; Sofen et al., 2014).

The model-calculated seasonal variations in F_{pri} to Summit are shown in Fig. 4. The annual flux of primary nitrate was calculated to be 6.96 × 10^{-6} kgN m^2 a^{-1}, which is similar (≈ 2-3 × 10^{-6} kgN m^2 a^{-1}) to model results from Zatko et al. (2016) using the GEOS-Chem model. The seasonality of F_{pri} displays a bimodal mode with a major summer peak and a secondary peak in late winter/early spring, in contrast the preserved snowpack nitrate concentration which peaks in spring/summer. The maximum F_{pri} in summer could be caused by the enhanced temperature-dependent precursor NO_x emissions such as from soil microbes (Pilegaard et al., 2006) as well as the more active photochemistry in summer, both of which would promote more efficient atmospheric nitrate production. It is interesting that the secondary F_{pri} peak in early spring is coincident with the timing of the spring Arctic haze phenomenon (Quinn et al., 2007), as well as the occasional spring nitrate concentration peak in snowpack and ice cores at Summit (Geng et al., 2014), though the exact timing of the seasonal peaks needs further investigation.

The modeled $\Delta^{17}O$ of F_{pri} is close to the measurement in snowpack with minimum values in summer, suggesting the $\Delta^{17}O$ signal of primary nitrate is well preserved under current Summit conditions. The seasonal variations in $\Delta^{17}O$ of F_{pri} can be understood in terms of the different production mechanisms of atmospheric nitrate (Alexander et al., 2020). In summer, ample solar radiation enhances the photochemical production of HNO_3 from the NO_2+OH pathway, the $\Delta^{17}O$ of which is lowest compared with other nitrate formation pathways. While in winter, the dominant N_2O_5 hydrolysis pathway produces nitrate with high $\Delta^{17}O$. Such seasonal patterns have been widely observed globally as summarized in Alexander et al. (2020).

The modeled $\delta^{15}N$ of F_{pri} ranges from −10.3 ‰ to 5.0 ‰ which falls well within the reported atmospheric $\delta^{15}N(NO_3^-)$ values in continental and marine boundary layer in both hemispheres in regions without impact from snowpack emission (Li et al., 2022; Lim et al., 2022; Morin et al., 2009; Shi et al., 2021). However, the seasonal pattern of $\delta^{15}N$ of F_{pri} which displays a summer maximum is opposite to the typical seasonal pattern of atmospheric $\delta^{15}N(NO_3^-)$ found in mid-latitude continental areas, where higher $\delta^{15}N(NO_3^-)$ values in winter and lower $\delta^{15}N(NO_3^-)$ values in summer are widely observed (e.g., Beyn et al., 2014; Freyer, 1991; Fang et al., 2021; Lim et al., 2022; Esquivel Hernández et al., 2022). This summer high and winter low $\delta^{15}N(NO_3^-)$ in F_{pri} is instead consistent with the observations at two Arctic coastal sites (Morin et al., 2012; Morin et al., 2008), where the summer high atmospheric $\delta^{15}N(NO_3^-)$ is strongly correlated with air temperature. Morin et al. (2008) suggest the $\delta^{15}N(NO_3^-)$-temperature relationship observed at the Arctic coastal sites may be related to physicochemical transformations of nitrate in Arctic and during the transport of nitrate and reactive nitrogens from the mid-latitudes, though the specific mechsmimes is unkonwn.

Another possibility to explain the modeled summer higher $\delta^{15}N(NO_3^-)$ in F_{pri} is that there may be more anthropogenic nitrate transported from mid-latitudes to Greenland in summer than in winter. F_{pri} is comprised of nitrate originating from the mid-latitudes as well as nitrate formed in the Arctic region. Morin et al. (2009) suggested that air parcels originating from regions with more anthropogenic impacts carries nitrate with higher $\delta^{15}N$, which was confirmed by subsequent studies (Li et al., 2022; Vicars and Savarino, 2014; Shi et al., 2021). The increased frequency of air sources originating from the North America in summer compared to winter (Kahl et al., 1997) could thus lead to more anthropogenic nitrate to Greenland in summer, resulting in higher summer $\delta^{15}N$ of primary nitrate than winter.

The potential link between $\delta^{15}N$ of F_{pri} and its precursor NO_x emissions is not further discussed here, as recent studies have shown that the isotopic effect during NO_x photo-recycling is complex (Li et al., 2020) and may dominate $\delta^{15}N$ variations in atmospheric nitrate (Fang et al., 2021; Li et al., 2021). More comprehensive studies on the isotopic effects during atmospheric nitrate formation as well as the potential fractionation during transport are required to further link $\delta^{15}N$ of F_{pri} with its precursors and/or source regions.

4.2 Model results at Dome C, Antarctica

4.2.1 Snowpack nitrate profile in the photic zone

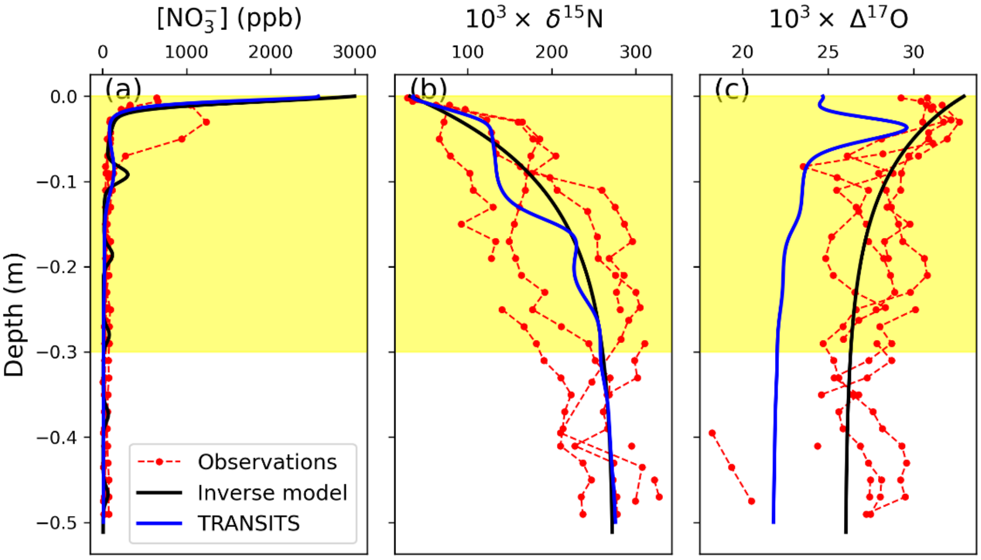

Figure 5. Comparison between the observed and modeled snowpack nitrate concentrations, δ^{15}N, and Δ^{17}O at Dome C. The red lines with circles represent four observed snowpack nitrate profiles at Dome C from Erbland et al. (2013) and Frey et al. (2009), while the blue and black lines are modeled results from the TRANSITS forward and the inverse models, respectively. The yellow background represents the depth of the photic zone.

Since Dome C snowpack exhibits very distinct trends in the concentration and isotopic ratio of nitrate in the photic zone, we first examine the modeled summer snowpack nitrate profile at Dome C in comparison with the previous observations (Erbland et al., 2013; Frey et al., 2009) in Fig. 5. The TRANSITS forward model results (Erbland et al., 2015) are also shown in Fig. 5 for comparison. Both models reproduce the observed decrease in nitrate concentration and the large enrichments in δ^{15}N(NO_3^-) well. We note that the predicted surface snow nitrate concentration is higher than the observations by both models. This is because the modeled concentration represents the state that atmospheric nitrate has just deposited onto the snow surface, while the observed skin layer snow may have already undergone snow metamorphism and/or post-depositional processing (Winton et al., 2020). This is also supported by recent observations at Dome C that newly deposited diamond dust could possess nitrate concentrations up to 2000 ppb (Winton et al., 2020), within the range of model predictions.

The decreasing trend in $\Delta^{17}O(NO_3^-)$ within the photic zone is also reproduced by these two models, caused mainly by the cage effect during nitrate photolysis. However, the TRANSITS forward model appears to underestimate snowpack $\Delta^{17}O(NO_3^-)$ while the inverse model performs better in snowpack $\Delta^{17}O(NO_3^-)$ simulation. This is because in the TRANSITS forward model, snow $\Delta^{17}O(NO_3^-)$ is controlled by a combination of $\Delta^{17}O(NO_3^-)$ of FD and the subsequent cage effect after deposition. At Dome C, $\Delta^{17}O(NO_3^-)$ of FD is dominated by locally formed atmospheric nitrate (i.e., FP) (Erbland et al., 2015), which is in turn determined by the prescribed $\Delta^{17}O$ transfer during NO-NO_2 cycling and the subsequent OH oxidation of NO_2 under sunlight conditions in the model. However, as demonstrated by Savarino et al. (2016), the above-mentioned method of $\Delta^{17}O(NO_3^-)$ calculation significantly underestimates atmospheric $\Delta^{17}O(NO_3^-)$ at Dome C, probably due to yet unknown chemistry and/or $\Delta^{17}O$ transfer mechanisms. In comparison, the inverse model calculates snow $\Delta^{17}O(NO_3^-)$ from the archived snow $\Delta^{17}O(NO_3^-)$ by deducting the cage effect. Therefore, although the inverse model uses the same method as the TRANSITS forward model to calculate $\Delta^{17}O(NO_3^-)$ of locally formed atmospheric nitrate and also underestimates atmospheric $\Delta^{17}O(NO_3^-)$, it doesn’t affect snowpack $\Delta^{17}O(NO_3^-)$.

Overall, the consistency of the modeled and observed snowpack nitrate profiles suggests that the effect of post-depositional processing is properly represented by the inverse model. This confirms that the inverse model can properly reproduce snow nitrate concentrations and isotopes in the photic zone, which are intermediate status between archived and atmospheric nitrate.

4.2.2 Skin layer and atmospheric nitrate

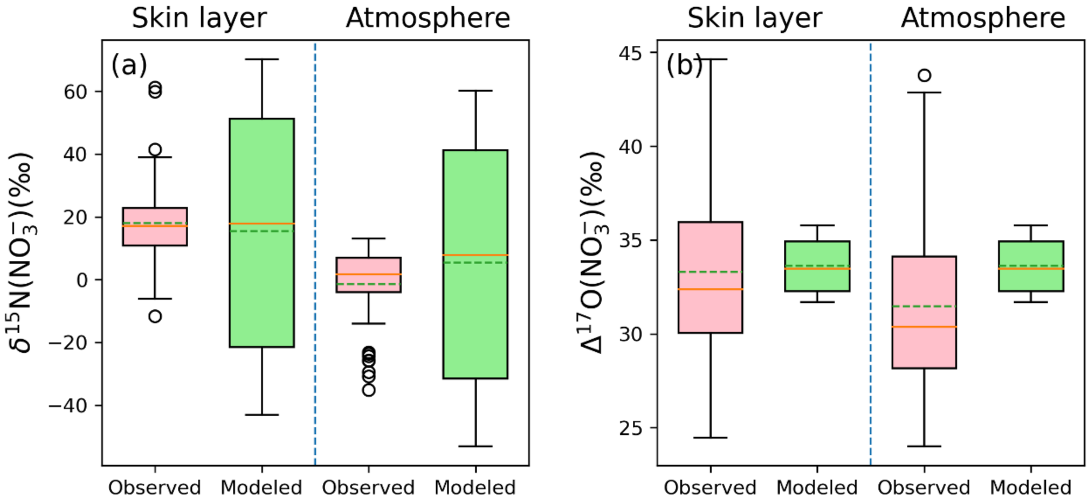

Figure 6. Comparison between the observed and modeled annual averages of $\delta^{15}N(NO_3^-)$ and $\Delta^{17}O(NO_3^-)$ in the atmosphere and snow skin layer at Dome C. The solid line in the box plot indicates the median value, while the dash line represents the average value.

For Dome C, since the seasonal information of the archived nitrate profiles is unknown, although the time step in the model was set to one week, we mainly focus on the annual average values. We note that the modeled isotopic compositions of snowpack and skin layer nitrate are irrelevant to the prescribed nitrate concentration seasonality. This is because the total nitrate loss fraction and the induced isotopic effect only depend on the total amount of actinic flux received during snow burial. In the following discussion we only report and discuss the modeled isotopes of local atmospheric and skin layer nitrate from case 1, i.e., the archived snow nitrate concentration was assumed to be constant throughout the year.

The observed annual average $\delta^{15}N(NO_3^-)$ and $\Delta^{17}O(NO_3^-)$ values in the skin layer at Dome C are 18.0 ± 11.7 ‰ and 33.6 ± 1.4 ‰, respectively (Erbland et al., 2013), while the modeled skin-layer values are 15.7 ± 38.6 ‰ and 33.3 ± 4.7 ‰, respectively, in good agreement with the observations. The observed annual average atmospheric $\delta^{15}N(NO_3^-)$ and $\Delta^{17}O(NO_3^-)$ values are -1.3 ± 11.6 ‰ and 31.4 ± 4.6 ‰, respectively, while the modeled values are 8.0 ± 11.7 ‰ and 33.6 ± 1.4 ‰, respectively. Note the average observed $\delta^{15}N$ values in this study were calculated as arithmetic mean instead of mass-weighted mean reported in Erbland et al. (2013) since the inverse model cannot directly calculate the nitrate concentration in the atmosphere. Nevertheless, the modeled averages are similar to the observed averages except for atmospheric $\delta^{15}N(NO_3^-)$. The difference between the modeled and observed atmospheric $\delta^{15}N(NO_3^-)$ could be again related to constant ε_d used in the model. As discussed earlier, in the model we followed Erbland et al. (2015) to set ε_d = 10 ‰ throughout the year, while observations at Dome C indicate that ε_d could be as large as 25 ‰ in summer instead of 10 ‰ [need a reference]. Hence the modeled atmospheric $\delta^{15}N(NO_3^-)$ could be overestimated. This reinforces that it is necessary to furher explore the isotope effects on $\delta^{15}N(NO_3^-)$ during atmospheric nitrate deposition.

4.2.3 Flux and isotopes of primary nitrate

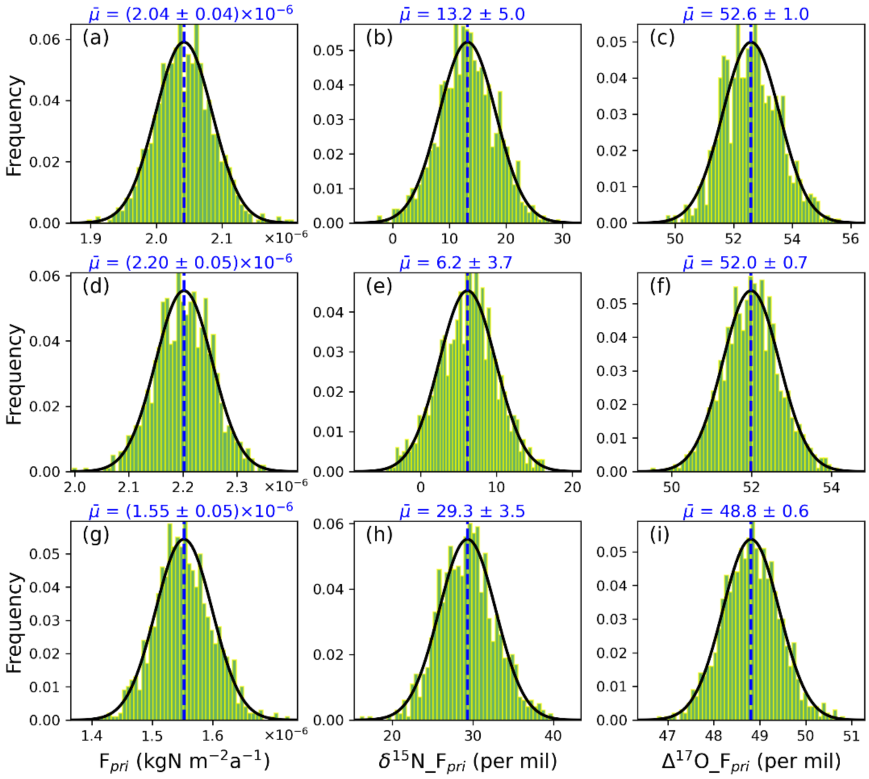

Figure 7. Frequency histogram of the calculated primary nitrate flux and its mean $\delta^{15}N/\Delta^{17}O$ values at Dome C under three different archival snow nitrate concentration distributions: (**a-c**) Case 1: uniform distribution, (**d-f**) Case 2: Gaussian-type function, (**g-i**) Case 3: shifted Gaussian-type function. The black solid lines represent the fitted Gaussian function of the frequency distribution. The blue dashed lines represent the mean values of F_{pri} and its $\delta^{15}N$ and $\Delta^{17}O$, which are labeled on the top of each subplot.

In Fig. 7, the flux of primary nitrate (F_{pri}) and its mean isotopes from the 3 difference cases (i.e., different nitrate concentration seasonality in archived snow) are displayed. Similar to the previous section, we only focus on their annual means. Note when calculating $\delta^{15}N(NO_3^-)$ and $\Delta^{17}O(NO_3^-)$ of F_{pri}, values of locally formed atmospheric nitrate are necessary. As discussed in 4.2.1, the inverse model follows the same method in the TRANSITS forward model to calculate $\Delta^{17}O(NO_3^-)$ of locally formed atmospheric nitrate (i.e., FP in the model), therefore it underestimates $\Delta^{17}O(NO_3^-)$ of FP. This is evident at Dome C where in summer the snow sourced nitrate (i.e., FP) dominates the atmospheric nitrate budget (Erbland et al., 2015), and the calculated $\Delta^{17}O(NO_3^-)$ of FP is about 6 ‰ lower than observed atmospheric $\Delta^{17}O(NO_3^-)$. Thus, in the inverse model, when calculating $\Delta^{17}O(NO_3^-)$ of F_{pri} at Dome C, $\Delta^{17}O(NO_3^-)$ of FP was not calculated using the model default method as in the TRANSITS forward model, but prescribed as the observed $\Delta^{17}O(NO_3^-)$. Otherwise, the modeled $\Delta^{17}O(NO_3^-)$ of F_{pri} would be higher than 70 ‰, which is highly unrealistic. Note, this is not an issue at Summit Greenland because FP doesn't dominate the atmospheric nitrate budget in summer there.

As shown in Fig. 7, although the prescribed archived nitrate concentration seasonality does not alter the modeled snowpack and atmospheric nitrate isotopes, it has a profound impact on the modeled primary nitrate flux and its isotopes. In particular, under the three cases of different seasonal distributions of the archived snow nitrate concentrations, the modeled F_{pri} and its annual mean $\delta^{15}N$ and $\Delta^{17}O$ range from 1.5 to 2.2 $\times 10^{-6}$ kgN m^{-2} a^{-1}, 6.2 to 29.3 ‰ and 48.8 to 52.6 ‰, respectively. The inverse model calculated F_{pri} is smaller than the value used in the original TRANSITS forward model (8.2×10^{-6} kgN m^{-2} a^{-1}) in Erbland et al. (2015), but this is easily resolved given the large uncertainty in the asymptotic nitrate concentration used as model input.

The modeled annual mean $\delta^{15}N$ of F_{pri} ranges from 6.2-29.3 ‰, in contrast with the observed atmospheric $\delta^{15}N(NO_3^-)$ in southern mid-latitude area or the Southern Ocean where $\delta^{15}N(NO_3^-)$ is in general negative or close to 0 (Morin et al., 2009; Shi et al., 2018; Shi et al., 2021). The modeled positive $\delta^{15}N$ of F_{pri} is however consistent with the wintertime atmospheric $\delta^{15}N(NO_3^-)$ observed in Antarctica when the effect of photolysis is null and local atmospheric nitrate likely reflects F_{pri}. The maximum atmospheric $\delta^{15}N(NO_3^-)$ in winter was found to be 10.8 ‰ at DDU (Savarino et al., 2007), 12.8 ‰ at Dome C (Erbland et al., 2013) and 13.9 ‰ at Zhongshan station (Shi et al., 2022). These positive $\delta^{15}N$ values have been link to stratospheric denitrification as nitrate produced in stratosphere is suggested to be 19 ± 3 ‰ by considering the fractionation induced by different of N_2O photolysis channels (Savarino et al., 2007). Therefore, the modeled magnitude and $\delta^{15}N$ of F_{pri} points towards the dominance of stratospheric denitrification in nitrate budget at Dome C.

The modeled $\Delta^{17}O$ of F_{pri} is also very high for all three cases (48.8-52.6 ‰). The measured bulk $\Delta^{17}O$ of surface ozone in Antarctica is about 26 ‰ (Ishino et al., 2017; Savarino et al., 2015) that fits well with the global tropospheric average of 25.4 ‰ (Vicars and Savarino, 2014). Given that the oxygen mass-independent fractionation signal of ozone is mainly occupied by the terminal oxygen atom and transferred to other molecular, atmospheric nitrate of tropospheric origin should possess a $\Delta^{17}O$ signal less than 39 ‰ (Mauersberger et al., 2003; Savarino et al., 2008), which cannot explain our calculated high $\Delta^{17}O$ of F_{pri}. However, the bulk $\Delta^{17}O$ of stratospheric ozone was measured to be 34.3 ± 3.6 ‰ (Lämmerzahl et al., 2002; Krankowsky et al., 2000), which indicated that nitrate produced in the stratosphere could gain a higher $\Delta^{17}O$ signature from ozone (Lyons, 2001). It has been observed in Antarctica that the atmospheric $\Delta^{17}O(NO_3^-)$ could exceed 40 ‰ in winter and early spring when stratospheric denitrification occurs (Ishino et al., 2017; Walters et al., 2019; Erbland et al., 2013; Savarino et al., 2007; Shi et al., 2022). A recent study also revealed that the surface snow $\Delta^{17}O(NO_3^-)$ at Dome C frequently exceeds 40 ‰ during winter/spring and could sometimes reach up to 50 ‰ (Akers et al., 2022). As we mentioned previously, these winter $\Delta^{17}O(NO_3^-)$ observations likely reflect the primary nitrate signal at that time since the photolysis of snow nitrate does not occur due to lack of sunlight. Thus, the high modeled $\Delta^{17}O$ of F_{pri} seems to again indicate a dominant role of stratosphere denitrification in external nitrate source to Dome C, similar to what can be reflected from the modeled $\delta^{15}N$ of primary nitrate. In addition, Erbland et al (2015) estimated that stratospheric denitrification nitrate flux is $(4.1 \pm 2.5)\times10^{-6}$ kgN m^{-2} a^{-1} in Antarctica, while our calculated F_{pri} of 1.5 - 2.2 $\times 10^{-6}$ kgN m^{-2} a^{-1} at Dome C is within the same range.

In sum, we acknowledge that there are many factors that would affect the model results, such as the initial snow nitrate concentration and isotopes, the export fraction (f_{exp}), and the cage effect fraction (f_c). These need to be further explored by observations to improve the model performance.

5. Model sensitivity tests: the impact of f_{exp} and f_c

In this section, we report the sensitivity test results to elucidate the impact of two model parameters that lack of direct observational constraints, the export fraction (f_{exp}) and the cage effect fraction (f_c). We mainly focus on the annual net loss and the differences in isotopes between F_{pri} and FA in accordance with the resolution of ice core measurements.

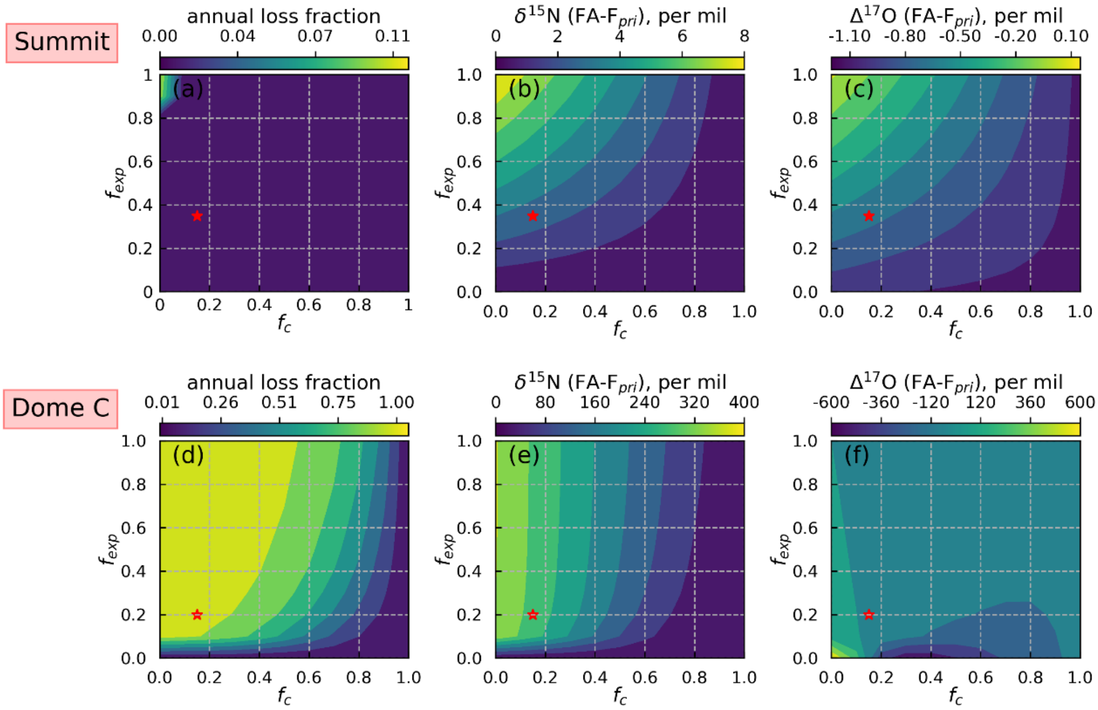

Figure 8. Model sensitivity test results of two parameters f_{exp} and f_c for Summit (**a-c**) and Dome C (**d-f**). The annual nitrate loss fraction is defined as 1-FA/F_{pri} following Jiang et al. (2021). Red stars represent the values of f_{exp} and f_c used in model simulations.

The sensitivity test results are shown in Fig 8. The annual loss fraction (defined as 1-FA/F_{pri}) represents the final preservation of primary nitrate after post-depositional processing (Jiang et al., 2021). The inverse model predicts an annual loss fraction of

3.5% under present Summit conditions, which is close to the TRANSITS forward model prediction of 4.1% (Jiang et al., 2021). This small discrepancy is likely caused by the use of simplified snow radiative transfer parameterization in the inverse model. In addition, the differences of δ^{15}N and Δ^{17}O between FA and F_{pri} are also in good agreement with the TRANSITS forward model. As expected, larger f_{exp} and smaller f_c would promote a more effective photo-recycling of snow nitrate and the associated isotope effects, resulting in a higher degree of net loss in F_{pri} and larger isotopic effects. However, under present-day conditions, the preserved snow nitrate concentrations and isotopes at the annual scale is only altered slightly and the degree of changes is insensitive to f_{exp} and f_c.

For Dome C, the model results are sensitive to f_{exp} when f_c is small, and becomes sensitive to f_c when f_{exp} is larger. In addition, the Δ^{17}O results display a nonlinear response to these two parameters, especially when f_{exp} approaches zero (Fig. 8f). A similar phenomenon was seen in the TRANSITS forward model simulations in Erbland et al. (2015), where they found that the model results could not converge when f_{exp} was set to zero. The high sensitivity of model parameters renders it is difficult to reconstruct the historical variations in primary nitrate based on ice core records at Dome C unless these parameters were precisely constrained. For present day conditions, f_{exp} and f_c could be constrained by atmospheric and snowpack observations (Erbland et al., 2015) but it is unknown if these values could be applied to different climates. In addition, the difficulties in choosing an appropriate archival nitrate concentration profile as model initial conditions would add extra uncertainties to the model results.

6. Conclusions and implications

In this study, we introduce an inverse model which is designed to correct for the effects of post-depositional processing on ice-core nitrate concentration and its isotopes. The model was tested against present-day Summit, Greenland and Dome C, Antarctica conditions to validate its performance under different snow accumulation rates. Model results compared to observations demonstrate that the inverse model is capable of adequately correcting the effect of post-depositional processing. The modeled atmospheric nitrate $\delta^{15}N/\Delta^{17}O$ at Summit are generally in good agreement with observations but with slight underestimate in winter $\delta^{15}N(NO_3^-)$, which is likely because the model doesn't treat the likely seasonal differences in nitrogen isotope fractionation during deposition (ε_d) . At Dome C, the model also well reproduced the observed snowpack nitrate profiles in the photic zone, the annual skin layer $\delta^{15}N/\Delta^{17}O(NO_3^-)$, and atmospheric $\Delta^{17}O(NO_3^-)$ at Dome C, but again overestimated the average atmospheric $\delta^{15}N(NO_3^-)$ probably also due a low bias in ε_d used in the model. This suggests a better quantification on the isotope fractionation of $\delta^{15}N(NO_3^-)$ during deposition is needed.

The inverse working flow of this new model also enables us to qualitatively retrieve information regarding primary nitrate deposition flux (Fpri) from the archived snow nitrate. The calculated seasonality in $\delta^{15}N$ of F_{pri} at Summit displays a maximum in mid-summer that is distinct from the observed spring $\delta^{15}N(NO_3^-)$ peak in snowpack. This seasonal pattern is in contrast with observed atmospheric $\delta^{15}N(NO_3^-)$ variations in mid-latitudes which is thought to be the major aerosol source region to Summit, but is consistent with the atmospheric $\delta^{15}N(NO_3^-)$ variations observed in the high-latitude Arctic region. The $\delta^{15}N$ of F_{pri} may reflect seasonally-varied main source regions to Greenland or a dominate role of high-latitude nitrate transport to Summit. At Dome C, both the magnitude of F_{pri} and its $\delta^{15}N/\Delta^{17}O$ indicate a dominant role of stratospheric denitrification on nitrate budget at Dome C.

The inverse model is designed to help interpret ice core nitrate records. Applying the inverse model to ice core nitrate records needs knowlege of initial conditions. In particular, archived snow nitrate concentration and its $\delta^{15}N/\Delta^{17}O$, the snow accumulation rate, temperature, and light absorption impurity concentrations must be known for a given ice core. In addition, chemistry-climate models such as the ICECAP or GCAP model (Murray et al., 2021; Murray et al., 2014) would be also necessary to provide extra constraints, such as the oxidizing agent concentrations, total column ozone (TCO), wind field and boundary layer heights for the past climates and are required to estimate $\Delta^{17}O$ of FP and f_{exp} (Alexander et al., 2020; Jiang et al., 2021). The calculated primary nitrate flux and its $\delta^{15}N$ and $\Delta^{17}O$ can be further combined with the chemistry-climate model results to interpret its climate implications such as the variations in tropospheric NO_x and oxidant abundance, which would improve our understanding of key factors controlling the variability in atmospheric oxidation capacity under different climates.

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