

We are grateful to the reviewer for the valuable suggestions and/or comments which improve the manuscript significantly. Below we list the detailed responses to the reviewer's suggestions and comments. The comments are listed in italics, followed by the response in normal font with changes highlighted in blue.

Response to Referee #2

The paper by Jiang et al. presents for the first time an inverse model (based on the forward model from Erbland et al.) to reconstruct atmospheric nitrate load and its nitrogen AND oxygen isotopic signatures based on snow pack data. In particular, it includes the postdepositional loss/recycling of nitrate by photolysis and nitrate reformation and compares the results from two ice core end members (Summit, Dome C) with atmospheric information. Overall, the results agree surprisingly well with atmospheric observations and for example support a clear stratospheric origin of the primary nitrate at Dome C. This all justifies the publication of this paper in ACP with minor revisions.

Response: We are grateful to the reviewer for the time involved in reviewing the manuscript and for the encouraging comments on the merits of this work.

Having said that, the paper is not always easy to follow and I am afraid that especially readers not familiar with the respective background of the mass balance and Rayleigh fractionation equations would need more guidance. I would therefore suggest to expand the Appendix A to give a more detailed derivation.

Response: Thanks for this suggestion. We have added more detailed explanations on Eq(A2-4) in the Appendix A. The following text was added in the revised manuscript.

“ The direct photolysis of snow nitrate can be described by the Rayleigh equation. We define the first-order photolysis rate constant of $^{14}\text{NO}_3^-$ and $^{15}\text{NO}_3^-$ as J and J^* and their concentration in snow as c and c^* respectively. The chemical kinetic equations of c and c^* can be represented as follows:

$$\frac{dc}{dt} = -Jc \quad (\text{A2})$$

$$\frac{dc^*}{dt} = -J^*c^* \quad (\text{A3})$$

Integrating Eq(A2) and Eq(A3) yields Eq(A4) and Eq(A5):

$$c(t) = c(0)e^{-\int_0^t J dt} \quad (\text{A4})$$

$$c^*(t) = c^*(0)e^{-\int_0^t J^* dt} \quad (\text{A5})$$

Here $c(0)$ represents the initial concentration before photolysis. The evolution of the isotopic ratio R which is defined as the ratio of c and c^* follows Eq(A6):

$$R(t) = \frac{c^*(t)}{c(t)} = \frac{c^*(0)}{c(0)} e^{-\int_0^t (J^* - J) dt} = R(0) e^{-\int_0^t (J^* - J) dt} \quad (\text{A6})$$

Since the delta value $\delta^{15}\text{N}$ equals to $R_{\text{spl}}/R_{\text{ref}} - 1$ where R_{spl} and R_{ref} refer to the isotope ratio of sample and standard respectively, Eq(A6) can be further expanded to:

$$\begin{aligned} \ln \frac{1 + \delta(t)}{1 + \delta(0)} &= \ln \frac{R(t)}{R(0)} = - \int_0^t (J^* - J) dt \\ &= - \int_0^t J \varepsilon_p dt = - \bar{\varepsilon}_p \int_0^t J dt = \bar{\varepsilon}_p \ln(1 - f_p) \end{aligned} \quad (\text{A7})$$

which is consistent with the form of the Rayleigh equation.

By applying the first-order Taylor expansion of $\ln(1 + \delta^{15}\text{N}(\text{NO}_3^-)) \approx \delta^{15}\text{N}(\text{NO}_3^-)$, we obtain the relationship between the $\delta^{15}\text{N}(\text{NO}_3^-)$ before and after photolysis:

$$\delta^{15}\text{N}(\text{SN}_r) \approx \delta^{15}\text{N}(\text{SN}') - \bar{\varepsilon}_p \ln(1 - f_p) \quad (\text{A8})$$

The $\delta^{15}\text{N}$ of the emitted NO_2 can be calculate via the mass balance equation:

$$\delta^{15}\text{N}(\text{SN}') = (1 - f_p) \delta^{15}\text{N}(\text{SN}_r) + f_p \delta^{15}\text{N}(\text{NO}_2) \quad (\text{A9})$$

Combining Eq(A8) and Eq(A9) would yield:

$$\delta^{15}\text{N}(\text{NO}_2) \approx \delta^{15}\text{N}(\text{SN}') + \frac{\bar{\varepsilon}_p (1 - f_p) \ln(1 - f_p)}{f_p} \quad (\text{A10})$$

Because part of the photoproduct would undergo cage effect to reform nitrate (Fig A1), the final state of snow $\delta^{15}\text{N}(\text{NO}_3^-)$ after photolysis can be calculated via isotopic mass balance equation:

$$\begin{aligned} \delta^{15}\text{N}(\text{SN}) &= \frac{(1 - f_p) \delta^{15}\text{N}(\text{SN}_r) + f_c f_p \delta^{15}\text{N}(\text{NO}_2)}{1 - f_p + f_c f_p} \\ &= \delta^{15}\text{N}(\text{SN}') - \frac{(1 - f_p)(1 - f_c) \bar{\varepsilon}_p \ln(1 - f_p)}{(1 - f_p) + f_c f_p} \end{aligned} \quad (\text{A11})$$

which is equal to Eq (8)...”

I also felt that the discussion of initial deposition and re-deposition of nitrate produced during photolysis needs somewhat more explanation in the beginning. In the end this process may easily explain, the observed deviations of the atmospheric $\delta^{15}\text{N}$ in observations and model results in certain months.

Response: Thanks for this suggestion. We have added the following text in the introduction part:

“...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). The reformed nitrate would inherit $\Delta^{17}\text{O}$ signals under local oxidation conditions that is different from primary nitrate, and the re-deposition of atmospheric nitrate could also result in nitrogen isotopic fractionation depending on the different deposition mechanisms (Erbland et al., 2013; Jiang et al., 2022). Thus, post-depositional processing not only disturbs the link between nitrate in snow and its atmospheric precursors but also alters its isotopic signals.... But since these processes are initiated by sunlight, the post-depositional processing is muted in polar winter when sunlight is absent.”

Finally, a comparison with the results by Shi et al. in GRL (10.1029/2023GL103778), who also include oxygen isotopes in a forward model approach, is still missing in the discussion.

Response: We noticed the publication of the Shi et al. paper after our manuscript was in discussion. Due to the similar topic, we have carefully examined the new work by Shi et al. (2023). From their paper and model source code (<https://cstr.cn/18406.11.Cryos.tpd.300476>), we think the modeling approach in Shi et al. (2023) is basically the same as the TRANSITS model, except that Shi et al. (2023) extends the same procedures to simulate $\delta^{18}\text{O}(\text{NO}_3^-)$. We also note that a couple of years ago Joel Savarino provided the TRANSITS model code to Guitao Shi, the leading author of the Shi et al. (2023) study.

Since Shi et al. (2023) adopted a constant upper boundary condition for snowpack (i.e., constant deposited nitrate flux and isotopes), their model mainly focus on the pure photolytic effect on snow nitrate isotopes, which has been fully incorporated by the TRANSITS model. The only difference in their work is that the photolysis effect on snow $\delta^{18}\text{O}(\text{NO}_3^-)$ is considered, but we notice that Shi et al. (2023) model had to scale the theoretical fractionation factor ($^{18}\epsilon_p$) to make the model results consistent with the observations. It remains unclear why the theoretical fractionation factor calculated using the ZPE shifted method (Frey et al., 2009) works well on $\delta^{15}\text{N}(\text{NO}_3^-)$ but not on $\delta^{18}\text{O}(\text{NO}_3^-)$. It appears to us that the uncertainty in the fractionation factors severely limits the extension of their method to other sites.

In summary, given the similarities in the modeling approach, logic, framework and others between Shi et al. (2023) and the TRANSITS model, it appears to us that it is not necessary to further compare our results with the Shi et al (2023) results, since we have already compared our model with the TRANSITS model.

In the revised manuscript, we have added the following citation of the Shi et al. (2023) with a brief discussion in the introduction after we introduced the TRANSITS model:

“...In addition, changes in the isotopic composition of nitrate ($\delta^{15}\text{N}$ and $\Delta^{17}\text{O}$) at each step of the post-depositional processing are also explicitly incorporated. Recently, Shi et al. (2023) extended or followed the TRANSITS model framework to include snowpack $\delta^{18}\text{O}(\text{NO}_3^-)$ simulation during the preservation of nitrate in snow. The latter was built upon the same chemical processes related to modeling $\Delta^{17}\text{O}(\text{NO}_3^-)$ changes during the post-depositional processing. However, the fractionation factor of $\delta^{18}\text{O}$ during snow nitrate photolysis ($^{18}\epsilon_p$) had to be scaled to reproduce the observations. In this case it remains unclear why the theoretical fractionation factor calculated using the ZPE shifted method (Frey et al., 2009) works well on $\delta^{15}\text{N}(\text{NO}_3^-)$ but not on $\delta^{18}\text{O}(\text{NO}_3^-)$. Nevertheless, the uncertainties associated with $\delta^{18}\text{O}$ fractionations during snow nitrate photolysis and other processes (e.g., the cage effect, reformation of nitrate from NO_2 , etc.) make this simulation less useful and reliable than for $\Delta^{17}\text{O}(\text{NO}_3^-)$, for which there are much less influencing factors and are easier to constrain...”

Apart from this I made several comments and language corrections in the annotated pdf file attached.

Response: Thanks for the detailed check. We have revised these typos accordingly in the main text. The response to each specified comment is listed below.

Line 49: is it the ratio of O₃/HO_x in the atmosphere or also of their individual reaction rates with NO_x. Please specify

Response: Thanks for this question. It is the relative differences in the individual reaction rates that eventually determines the isotopes. However, since most of the related reactions are gas-phase reactions, basically it is mainly the relative concentrations of O₃ versus HO_x that determines the rate differences (though the reaction rate constants are moderately dependent on temperature). In general, it can be approximated by the relative abundances of O₃ versus HO_x (i.e., the ratio of O₃/HO_x) that determines $\Delta^{17}\text{O}(\text{NO}_3^-)$, as frequently used in literature.

Line 223: weighted by what and averaged over what time scale?

Response: In the inverse model, the algorithm to calculate the average ε_p is described by the following equation:

$$\bar{\varepsilon}_p = \frac{\sum_0^{90} \varepsilon_p(\text{sza})\Delta t(\text{sza})}{\sum_0^{90} \Delta t(\text{sza})} \quad (1)$$

In Eq(1), the ε_p at different solar zenith angle (SZA) is first computed under the prescribed total column ozone. Then the average ε_p for each week is computed by the weighted average of ε_p over the duration of each SZA. Eq(1) can be regarded as the arithmetic mean of ε_p over the entire week when the value is set to 0 if SZA is larger than 90 degrees. We changed the sentence as follows:

“...To simplify the calculation, in Eq. (8) $\bar{\varepsilon}_p$ in a certain week is calculated by the weighted average of nitrogen isotope fractionation constant over the durations of different solar zenith angles (0-90 degree)...”

Lines 295-296: somewhere you need to specify what the deposition process of nitrate is. Is this gas phase adsorption or wet and dry deposition of particulate nitrate?

Response: At the beginning of section 3, we add the following statement:

“...The deposited nitrate flux FD represents the state of nitrate that has just deposited onto the surface snow via dry deposition of gaseous nitrate or wet scavange from the atmosphere and is close to the definition of the skin layer of snowpack...”

Lines 347-350:This is confusing. Local midsummer at Dome C should be around week 0

Response: In our model week 0 starts in winter (i.e, the first week of January in the northern hemisphere or the first week of July in the southern hemisphere). We emphasize this point at the beginning of this paragraph in the revised version:

“In Eq (20), c_a represents the annual average snow nitrate concentration, n represents the week number (1 to 52, here week 1 is defined as the first week in January for the

northern hemisphere sites or the first week in July for the southern hemisphere sites) and the shape parameters (a , b , σ) were determined by the best fit of skin layer nitrate concentrations (Appendix D)...

Line 366: is this assumption justified? How large is the measured seasonality in $d15N$ and $D17O$?

Response: Thank you for this question. Unfortunately, by far there is no report on the seasonality in $\delta^{15}N$ and $\Delta^{17}O$ of archived nitrate at Dome C due to the extremely low snow accumulation rate which prevent high-resolution sampling to reveal the snowpack seasonality, so technically we can't justify this assumption. However, we speculate that the magnitude of seasonality (~ 20 - 30%) in archived $\delta^{15}N(NO_3^-)$ should be much lower compared to the archived values (up to 334% , Erbland et al., 2013), and its impact should be small.

Line 518: what exactly do you mean by summer snowpack? The profiles in Figure 5 cover a few years of snow deposition not just summer, so I assume you refer mainly to the summer atmospheric NO_3 concentration? Please explain

Response: Sorry for the confusion, we meant to use "summer snowpack" to represent the snowpack collected in summer. To avoid confusion, we delete the usage of "summer snowpack" and just refer to as "snowpack"

Line 568: do you mean: "are not affected by" ??? the wording is confusing as anything is irrelevant for a prescribed parameter as it is prescribed :-)

Response: Thanks for pointing this out. It is a typo. We change the statement as follow:

"...We note that the modeled isotopic compositions of snowpack and skin layer nitrate are **not affected by** the prescribed nitrate concentration seasonality..."

Line 690: looking at Fig. 8 I would say that the isotopic signature is largely independent of f_{exp} if f_{exp} is larger than 0.1-0.2

Response: We add the following statement for the sensitivity of $\delta^{15}N$:

"...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 particular, the isotopic signature is largely independent of f_{exp} when f_{exp} is larger than 0.1-0.2.** In addition, the $\Delta^{17}O$ results display a non-monotonic response to these two parameters..."

Line 754: The language is incorrect here. f_p denotes the total photolyzed NO_3 while $f_p \times f_c$ denotes the fraction photolyzed and caged as correctly displayed in A1

Response: Thanks for pointing this out. We revised this sentence as follows:

"...As shown in Fig. A1, assuming a fraction (f_p) of initial snow nitrate was photolyzed and **a fraction (f_c) of these photolyzed nitrate** has undergone the cage effect, the mass balance equation for snow nitrate can be written as..."

Line 763: This is not self-explanatory. What you refer to is that you made the approximation $\ln(1+d^{15}N) \approx d^{15}N$. Spell it out

Response: We change the sentence as follow:

“Here we apply the first-order Taylor expansion of $\ln(1+\delta^{15}\text{N}(\text{NO}_3^-)) \approx \delta^{15}\text{N}(\text{NO}_3^-)$.”

Line 766: there is a sign error in this equation . Plugging A2 and A3 into the first line of equation A4 (mass balance) would give (fc-1) not (1-fc) in the second line. In equ 8 it is correct

Response: Thank you for this point. We have corrected this error in the revised version.