

The Cryosphere Discuss., referee comment RC1
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Comment on tc-2021-355

Meredith Hastings (Referee)

Referee comment on "Impacts of post-depositional processing on nitrate isotopes in the snow and the overlying atmosphere at Summit, Greenland" by Zhuang Jiang et al., The Cryosphere Discuss., <https://doi.org/10.5194/tc-2021-355-RC1>, 2022

This work utilizes newly reported atmospheric nitrate measurements from Summit, Greenland to compare with others sets of data (from different years) from the atmosphere, surface snow and snowpack. The purpose of the study is to conclude that post-depositional processing can explain nitrate isotope systematics in the snow and air at Summit, Greenland. The overall subject matter is of relevance to Cryosphere and its readership. The conclusions drawn, and the title of the paper, do not fit with the evidence presented and the authors should consider the points below and better justify their conclusions.

While there are clearly differences of interpretation in the already published literature between my group and the authors here, new data definitely raises the potential for new interpretations. But it is important that the hypotheses, data, discussion and conclusions be consistent with what is "prove-able" within the constraints of the new data. **Using "reality" in the title is inappropriate** – at best it an overemphasis that this new work is somehow more important or more "realistic" than the large body of previously published work; at worst it is a direct insult to the work that has come before (including work by the authors of this manuscript). In fact, this quote from the conclusion negates the use of "reality" in the title: "In the end, we note the limitation of the compiled data. These data were collected by different groups at different time, and with different sampling methods as well as different temporal resolutions." (page 29, line 724)

A serious matter to consider first and foremost is what this new data represents in terms of the budget of nitrate in the air, snow and snowpack at Summit, Greenland. The new data is isotope measurements of aerosols collected using a high-volume air sampler with glass fiber filters. Quoting from the manuscript "Glass fiber filters have been shown to collect both aerosol and gas-phase nitrate with high efficiency (Erbland et al., 2013; Frey et al., 2009)." This has, in fact, not been shown directly. And it is critical to consider since the data here is used as a comparison to other datasets and conclusions are drawn based upon the difference in isotope values amongst the different sample types, which were also collected with different methods. Therefore, the difference in the isotopes of different sample types has to be *real* and represent the environmental values and be sure not to

represent any fractionation or changes associated with the collection technique.

Validation of the method for complete collection of HNO₃(g) is critical to the interpretation here. The manuscript refers to Erbland et al (2013) for evidence that complete collection of both nitrate phases takes place. Erbland et al. (2013) reported that concurrently collected samples of atmospheric HNO₃ by denuder tubes coated in sodium bicarbonate matched well with the average values found by the hi-vol sampling and therefore were deemed representative of atmospheric HNO₃ + aerosol nitrate at Dome C. The climate conditions, phase partitioning of atmospheric nitrate, accumulation rate, etc can all be very different at Summit than Dome C and therefore it is appropriate to review and consider what evidence there is that HNO₃ and aerosol nitrate are *quantitatively* collected at Summit. Please note too that Frey et al. (2009) study at Dome C does not present any evidence for quantitative collection; Frey et al (2009) refers to Morin et al., 2007 which was an ocean-based cruise collection using the same methods but the conditions were such that the likelihood of complete HNO₃ collection on filtered alkaline (sea salt) aerosols was high. Due to the difficulty of capturing both gas and particle phase nitrate under different conditions there is a body of literature that include methods discussions (see for instance Huang et al., *Atm Research*, 2004; Chiwa et al., *Env Ass Monitoring*, 2008; Ames and Malm, *Atm Env*, 2001; Lavery et al., *Air & Waste Management Ass*, 2009; and EPA CASTNET methods papers). The ideal method depends on the time of deployment, how polluted or pristine the expected air masses are, temperature, flow rate, and location (marine atmosphere, coastal, or inland). According to EPA recommendations, a filter pack with a particle filter (Teflon, quartz, GF/F, etc.) and a cellulose backup filter impregnated with NaCl or Na₂CO₃ will quantitatively collect particulate nitrate and nitric acid in a large variety of sampling conditions. As the addition of NaCl improves the efficiency of collecting nitric acid it is frequently assumed that both nitrate and nitric acid are collected with high efficiency in the marine boundary layer where there are high sea salt concentrations as Morin et al., 2009 points out (underlining added for emphasis): "The exact nature of the nitrate species trapped on the filters during sampling has been an issue for decades, owing to evaporative loss of ammonium nitrate species and sampling of nitric acid together with particulate nitrate [Schaap et al., 2004]. Prospero and Savoie [1989] have advocated that filters loaded with sea salt should quantitatively collect nitric acid together with particulate nitrate, which should then be the case for these samples collected in the MBL... Therefore, the analyzed nitrate is referred to as atmospheric nitrate, assumed to be the sum of gas phase nitric acid and particulate nitrate."

The vast majority of nitrate at Summit is wet-deposited via scavenging of HNO₃(g). This is stated in the manuscript at the bottom of page 20 (though see specific comments below on references for this). This is important to validation of the method (above) since the air is filtered through a GF/F with no pre-treatment and must quantitatively collect all HNO₃(g). Additionally, when it snows, both in cloud and below cloud processes (rainout + washout) will contribute to the nitrate that is deposited. However, the arguments and interpretation in this work appear to require that the atmospheric samples represent all (or most) of the nitrate that is deposited to the snow. For the interpretation here to stand, the input from the atmosphere must be constant in d¹⁵N and any differences in the snowpack from that in the air are only due to post-depositional processing. **Yet, the input of primary nitrate could change remarkably due to HNO₃(g) scavenged from above the surface at Summit (i.e from cloud to ground) and the snow then would not represent only that which is near the surface (i.e. it could differ in d¹⁵N because it contains more than just what is at the surface).** This needs to be addressed in the context of the interpretation here.

The atmospheric data (from a single year and almost half the samples are not used b/c of blank issues) suggests that within the surface atmosphere at Summit there is no seasonal variation in the d15N signal. It is entirely possible that this pool of atmospheric nitrate is controlled by local processes. **This does NOT negate that the snow can still represent a vast majority of primary nitrate deposition and that the seasonal differences found in the snow represent much more than the local dynamics.** The data we collected in Fibiger et al. 2013 and 2016 were concurrent collections of snow and atmospheric samples so that we could detail, at the same time, the dynamics in the snow and in the air. We went looking to detail that post-depositional release of NO_x and reformation of nitrate locally COULD explain the isotopic composition of nitrate in the snow, especially D17O – but this hypothesis was not supported by what we found. Our results suggest that the nitrate in surface snow does not change isotopically in concert with what is happening in the surface air. It is hypothesized in Fibiger et al. that this can be explained by the fact that the surface air represents a small fraction of the nitrate that is deposited in the snow in real time. (Wet deposition at Summit is frequent, and in spring and summer, even when there is not fresh snow, fog deposition often occurs (see Bergin et al., 1993 already cited). This interpretation agreed with a snow-air model that was able to reproduce a suite of gas phase concentrations in the air at Summit, including NO_x, HNO₃(g) and halogens with as little as 6% of the nitrate being photolyzed (as discussed in Fibiger et al., 2016). **It must be proven in this new work that the atmospheric data near the surface at Summit is what is most important in terms of the input of total nitrate to the snow such that the snowpack does NOT represent much more than what is happening in the air AT Summit.**

I commend the authors on the collection and measurement of this important dataset and compiling many other datasets for comparison. The authors do a very good job of compiling the data comparison in the fairest way possible (e.g. mass-weighting sub-monthly data into monthly averages to compare with other data that is only reported as monthly averages), but we need to acknowledge that there is still a fair amount of comparing apples to oranges here. **There are no statistical comparisons presented in the manuscript and this should be addressed** (see specific comments below). While I appreciate the purpose in reducing “the spatial and temporal heterogeneities” for the comparison here, this heterogeneity is real and the standard deviations/variability should be included in any statistical comparisons. The manuscript argues that there are “systematic changes” in d15N between the air, surface snow and snowpack (all from different years and different sample collection methods) that can be explained by post-depositional processing. But **the differences shown between 2 out of 3 months in the wintertime are as large as observed in the spring and summer.** Yes, the spring and summer months compiled data are consistently different, but the difference in December appears to about 16 per mil and the difference in February is 9 per mil (Figure 2b)! This needs to be explained within the framework presented here. This difference does not fit with the conclusion that post-depositional photolysis of nitrate can explain these types of differences nor does it fit with the idea that deposition of nitrate imparts a fractionation since this large difference does not exist in either October or January. **Also left unexplained is the divergence of d18O and D17O behavior in the winter months atmospheric data** (Figure 1c). Finally, it is a stretch to use the word “systematic” when several months (out of 12) do not follow this systematic response and the aerosol data represent 1 year of data collection (with only 55% of the data included in this study) while much of the snow and snowpack representing repeated sampling of the the snow/multiple snowpits/multiple studies.

The assumption that the isotopic composition in the air must stay constant underlies

discussion of the d18O data from the air and snow as well and does not agree with modeling or observational studies. Kunasek et al cannot explain higher than expected D17O values in snowpack summertime snow based on local photochemistry. Global modeling studies by Alexander et al do an excellent job of predicting the seasonal cycle in D17O throughout the year (based on long-range transport of nitrate and no post-depositional processing!) but shows a mismatch in spring (model overestimates) and summer (model underestimates). Fibiger et al. (2013, 2016) show interannual isotopic variability in the observations of surface snow and atmospheric samples (HNO₃(g) only). This manuscript reports interannual differences in d18O of nitrate as "inconsistent." Fibiger et al. (2016) show and explain interannual differences based on differences in long-range transport, changing the source regions from which primary nitrate is transported to Summit (which also impacts chemistry).

Specific comments on manuscript:

It would be helpful if the abstract and introduction better reviewed prior work and results in Greenland. Much of what we are able to quantify about the impacts of post-depositional loss and recycling come from the body of work by Savarino in colleagues at Dome C. It's important to contextualize this and also contextualize the differences between the records in Greenland versus Antarctica. Currently in the introduction this all presented as "this is what happens to nitrate in snow period". (In my mind, the question is why don't we see more loss of nitrate in Greenland than we do?!? The exposure of the snow to sunlight, despite the accumulation rate, should still lead to more loss than is actually observed).

It would be useful in the introduction to clearly explain the differences between post-depositional loss versus recycling/processing of nitrate versus nitrate-snow sourced NO_x-back to nitrate that is now different than originally deposited.

It's also important to be abundantly clear about how the words archived versus preserved are used in the text and it is likely worthwhile to define these in the introduction.

Line 21: "...hinders interpretation of ice-core nitrate concentrations and isotope records." Given that Geng et al. alone have at least 3 different published papers where they interpret ice core records (let alone the many other papers that could also be named here), this sentence is not useful nor descriptive of the literature. This debate also hinders current understanding of atmospheric chemistry and deposition processes.

Line 24: this line says "atmospheric aerosol nitrate" which does not reflect that the atmospheric measurements are used as aerosol + gas phase nitrate

Line 27: suggest rephrasing this line as with several negatives it currently reads as if the seasonality is the same between the snow and atmosphere; perhaps the following

"...displayed no apparent seasonality, which is distinct from seasonal d15N-NO₃- variations observed in snowpack."

Please indicate what the standard deviations represent and how many samples (n) are included.

Line 43: The degree of change in d18O being larger than that in D17O is a weird comparison to make. Since D17O represents the difference between d17O and d18O and both of those isotopes change with mass-dependent processes the D17O remains the same. Since the manuscript is to be read by an audience that includes non-isotope specialists, it would be useful to be clear about this.

Line 51: There is no citation for Alexander et al., 2019 in the manuscript. (And as an aside, the modeling work in Alexander 2009 and 2020 does not deal with the impacts of post-depositional processing).

Line 59: "...increases in d15N and decreases in d18O/D17O..." is only consistently true in Antarctica. See general comment above on the need to better discuss results and interpretation from Antarctica versus Greenland. This difference is compelling and would set the paper up better for how and why it's really important to try to resolve our understanding of post-depositional processing of nitrate and the interpretation of isotopes of nitrate.

Line 69: "...has not been directly observed/evidenced in the field." Please see Shi et al., Isotope Fractionation of Nitrate During Volatilization in Snow: A Field Investigation in Antarctica, Geophysical Research Letters, 2019.

Line 73: Geng et al. 2015 is not an appropriate reference here as it deals with deep ice core samples (the sentence refers to snowpack). It's important to include more context here – none of the other references are work done in Greenland.

Line 84: impurities in the snow also affect the chemistry and the form of nitrate in the snow – e.g. NaNO₃ or CaNO₃ and that can also impact post-depositional processing.

Lines 125-130: This is only true if the majority of the nitrate in snow comes from the surface atmosphere at Summit. See general comments above.

I think it could be better explained here that what is being referred to is the loss of nitrate

from depth changes the isotopic composition in that snow layer. The snow sourced NO_x from at depth, IF it re-forms nitrate and is re-deposited would change the surface snow values. It's also important to explain that the at depth layer should then reflect loss only based on the fractionation values presented in this manuscript (ie increase in d15N, increase in d18O). The surface value would be a mix of reformed nitrate and the original nitrate deposited.

The last sentence in this paragraph is really important so I think it is worth re-visiting the explanation here.

Lines 145-150: Were the GFFs pre-cleaned or pre-combusted before use in the field? If so, how? If not, why not?

Line 156-167: Only 54 samples "out of 97 were determined to be valid". Please report the concentrations of the blank and how they were determined. Do they represent lab blanks or field blanks? What concentration is deemed not valid? What times of year are the dropped sample from? Does this skew the data in favor of particular months? For instance Figure 2 has no atmospheric data at all in September reported? And why is there no surface snow for Aug, Sep, Nov or Dec?

Were reference materials treated to the same procedures as the samples? i.e. were the reference materials put through the concentrating method as the samples were. Was a nitrate blank measured on the NaCl? or on the concentrating process on the whole? This is important to ensure no artificial isotopic change to the environmental sample. The denitrifier method induces fractionation of the d18O during the conversion to N₂O and is corrected for by the samples being compared to reference materials treated in the same way. Any other pre-treatment of samples should also apply to reference materials to be sure it can be corrected for unless it is made clear that the pre-treatment causes no isotopic effects.

What are the measurement uncertainties reported here based upon?

Line 207: please be careful to distinguish between aerosol (only) nitrate, aerosol + gas phase nitrate, and gas phase only.

Table 1: It would be useful to include the type of method used (i.e. filter type) and whether the collections represent aerosol, aerosol + gas, or gas only to help in summarizing the different types of collections. In general when making comparisons of different datasets in the text, the difference in the isotope values is presented and THEN it is discussed that the samples actually represent different things (ie aerosol + gas versus gas only).

Line 217-220: II agree that it is odd to have a higher summertime d18O. But the validity of the data should be questioned based on evidence that somehow the higher values are biased in some way. For instance, an outlier test could be used. Is it not at all possible that a higher d18O could represent something anomalous that summer at Summit? could there have not been any different chemistry that could contribute to higher values (for instance, stratospheric intrusions)?

The line that "different groups" data were not averaged is also a bit odd. The Jarvis, Kunasek, and several Geng studies all measured samples at the University of Washington IsoLab. I suggest providing a different wording of justification here.

Figure 1: It would be useful to also plot the calculated accumulation rate over the year since this is used in several calculations within the paper.

Line 323: This is another place where a statistical test should be used to justify "out of range" and therefore why the data is not included.

Line 342: "This systematic enrichment refutes the previous hypothesis that seasonal variation in snowpack...was driven by shift in the relative importance of NO_x source...". See my argument against "systematic enrichment" in the general comments above. This alone does not negate the interpretation of nitrate in snow majorly representing long-range transported primary nitrate rather than local only. Additionally, the Jiang et al (2021) model could just as well explain the seasonality in the d15N snowpit profile when varying the d15N of primary nitrate (ie the "source" value). In fact, this is noted on line 393-395 that the Jiang et al (2021) model shows "that the primary nitrate flux dominates the nitrate budget at Summit, even in mid-summer". This seems to directly contrast with statements in the paper where primary nitrate does not play an important role at Summit.

Line 360: this is a bit confusing and connects to my comment about clarifying the different processes in the snow in the introduction. I think readers might be confused here that a depleted d15N source to the atmosphere requires that that NO₃⁻ be lost from the snow and the isotopic composition in the snow where the NO₃⁻ was lost will be changed (which has a different isotopic impact if that snow-sourced NO_x is re-deposited locally).

Line 367-370: this does not explain nor include mention of the fact that Dec and Feb look very different in the atmosphere versus the snow (this is related to my general comment above).

Line 395-400: This does not address that differences in transport were connected to different isotopic compositions of nitrate at Summit in Fibiger et al (2016).

Line 407-415: there needs to be clarifying language in here to distinguish between observations being shown here, prior model calculations, prior observations and calculation being done here.

Line 408 says the difference between snowpack and the snow is 12.8 per mil in spring. Is this model or data calculated? the TRANSITS model predicts a difference value of 14.3 per mil, which is "consistent with the compiled data". In Figure 2b, the surface snow (blue symbols) appears to be ~ -8 per mil and the snowpack is $+3$ per mil in April (so the difference is ~ 11 per mil); there is no surface snow data shown for March; May (or between May and June?) the difference is only ~ 3 per mil. So how and when is the Jiang et al calculation and TRANSITS model calculation consistent with the compiled data?

Then on line 444 snow and atmosphere are compared and it is reported that the difference in spring should be 9.8 per mil – this is true for Apr, but in Mar and May-June the difference is larger and again (close to 20 per mil in Mar!). If I am mis-reading this then the text needs to be clarified and it would be helpful to refer directly to figures when speaking of the data here.

Line 446 says the difference between atmosphere and snow is negligible in winter, but this is only true of 1 of the 3 months in winter in Figure 2b.

It would be useful to include the Jiang et al (2021) model output as part of the figures since values produced in that work are referred to at least 4 times in the manuscript.

Line 408-415: I think preservation of the value below the photic zone is important and should be clarified in the introduction as to this expectation. However, I'll also note that Erbland's study with the TRANSITS model predicted values below the photic zone, which agreed with a few individual samples from depths below the photic zone compared to results from within the photic zone in several areas of the East Antarctic Ice Sheet. In a follow up study, Shi et al. (ACP, 2015) presented complete profiles along the EAIS between the surface and below the photic zone and found that the case for an exponential increase in the isotopes was highly sensitive to the depth over which it is assumed the photic zone is relevant. This does need a response but it would be good for the authors to re-review that work to be sure to be consistent with the peer-reviewed literature.

Line 430: Equation 3 – a simplified form of the PIE is really valuable. It's agreement with TRANSITS seems a bit circular since the equation is based upon the TRANSITS model. It should be better explained here what this simplified equation does NOT include relative to TRANSITS so that the simplified version is applied by other groups in the future under situations that are appropriate. For instance, does the $A(t)$ in Eq 3 considers an e-folding depth that is impacted by impurities in the snow?

Line 450: Is this based on comparing means? Medians? The medians in Fig 3 of Fibiger et al show differences of only 9-12 per mil not 12-15 per mil. Please clarify.

Also, why is the atmospheric nitrate oxygen isotopic data from Fibiger et al. NOT included in Fig 2?

Line 471-483: "Compared to surface snow, atmospheric nitrate is more influenced by snow-sourced nitrate..." Yes. This is because the snow represent more than the surface atmosphere at Summit. And while this is stated as "snow is a much larger reservoir of nitrate compared to the atmosphere" on Line 481, the context here is not clear (see general comments above on this).

It's not clear why the Erbland reference is relevant here since it does not apply to Greenland (and for instance in the discussion above while dry deposition at Summit is infrequent fresh snow and fog deposition are frequent). You should also include these references in discussing wet versus dry deposition and the budget of nitrate in the atmosphere at Summit:

Dibb, J. E., R.W. Talbot, and M. H. Bergin (1994) Soluble acidic species in air and snow at Summit, Greenland; GRL; 1627-1630.

Dibb, J. E., R. W. Talbot, J. W. Munger, D. J. Jacob, and S.-M. Fan (1998) Air-snow exchange of HNO₃ and NO_y at Summit, Greenland; JGR; 3475-3486.

Lines 494-510: this discussion would be useful earlier in the manuscript to layout an expectation for how the results will be interpreted.

Line 512: Are there updated stake measurements at Summit that could be checked for this? The Burkhardt et al. study is a bit dated, and accumulation rate at Summit could be with climate change in the last decade? Also, how many years is the lowest weekly average accumulation rate observed since the Burkhardt et al. study is not at all representative of accumulation measured during the time periods of the compiled data or the atmospheric data presented here.

Line 513: "and presumably more nitrate dry deposition occurred..." Why is this presumed? And is this consistent with one page ago where the dry deposition flux was considered to always be "very low" ?

Line 553: This should read as “The cage effect incorporates water D17O (~0 per mil) in the formation of nitrate and therefore lowers the overall D17O of the nitrate compared to nitrate formed in the atmosphere.” (or something like that). The way this is written now is not actually correct and will definitely confuse readers.

Line 563: “the cage effect is negligible”. It needs to be said here that the Jiang et al (2021) model output does not match well AT ALL with the D17O snow profile. So I think it is unfair to bring conclusions from that study regarding D17O into here as if they are “proven” by a model that does not actually explain/match the observations.

Line 569: “Locally reformed nitrate under sunlight in the summer half year would possess low D17O compared to primary nitrate deposited earlier in the season...” And yet, the Kunasek et al study based on local photochemistry at Summit cannot explain the HIGHER THAN EXPECTED summertime D17O values. And the global GEOS-Chem modeling studies (Alexander et al, 2009, 2020) fit the seasonality of D17O at Summit very well, but UNDERESTIMATE summertime values and OVERESTIMATE spring values.

Line 575-583: Data from different years should not necessarily be expected to be consistent. The wording should be changed here or the authors should justify why this should be expected. If photolysis alone can always explain the seasonality of nitrate isotopes then it SHOULD be the same every year. The observed (real) differences in the Fibiger et al dataset are explained in that work in terms of variability in transport and chemistry (ie source regions). There is no reason to dismiss some of the d18O data in Fibiger et al. I’ll also point out (for my own gratification) that our lab is the only lab that independently reports d18O data from the N2O method and D17O from the N2/O2 method b/c the N2/O2 method is known to cause mass dependent inconsistencies in d18O and d17O (which do not affect the D17O result).

Line 616: again, why should the data from different years be consistent if transport, accumulation, deposition all change between seasons and interannually?

Line 633: What happens to the d15N during the cage effect reformation of nitrate? It is only discussed for d18O (and D17O).

Line 653: I would argue that the framing in Fibiger et al (2013) is that the relationship between d18O and D17O is not evidence alone that post-depositional processing does not occur – we attempt to explain how that relationship should change is an important amount of processing were to occur and that does not fit with the observations, therefore we conclude that it is not very important. This was then followed up with the concurrent snow-air sampling in Fibiger et al (2016).

Figure 4 discussion: The fact that relationship between d18O and D17O is so similar in the

atmosphere and snow and the snowpack is different could just as easily be explained by deposition of more nitrate than what is apparent at the surface at Summit. And if it cannot be explained by this, this hypothesis needs to be tested and dismissed.

Line 682: Earlier in the manuscript it states that the isotopes are preserved upon archival. Again, please take care to qualify the language in the introduction and then use it consistently in the manuscript.

Line 694: This also discussed in Shi et al, ACP, 2015.

Line 703: "...snowpack nitrate can only be explained by the effect of the photo-driven post-depositional processing..." This is the only hypothesis tested here and there are a number of flaws that need to be visited before this conclusion can be drawn.

Line 710: Most of the previous work done does NOT say unequivocally that atmospheric nitrate is solely dependent on primary nitrate. In fact, Fibiger et al's work shows that indeed there is an impact of snow sourced nitrate on the atmosphere at Summit! It's just a small part of the pool contained in the snow such that what is ultimately preserved DOES reflect primary nitrate. This is not in fact disproved in this study.

Typographic errors:

Line 217: even inconsistence does not make sense grammatically

Line 253: was should be were

Line 313: Hasting should be Hastings

Figure 2 caption: does should be dose?

Line 376: remove be at the end of the line

Line 406: remove snow before snowpack

Line 451: closed should be close

Line 713: inconsistence is not a word

Line 720: thephoto is a typo

