EGUsphere, referee comment RC1
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Comment on egusphere-2022-812

Anonymous Referee #1

Referee comment on "Photolytic modification of seasonal nitrate isotope cycles in East Antarctica" by Pete D. Akers et al., EGUsphere, https://doi.org/10.5194/egusphere-2022-812-RC1, 2022

The purpose of this work was to investigate the isotopic composition of nitrate in snow in East Antarctica at site with intermediate accumulation rates. The emphasis on intermediate accumlation is important since a great deal of the community's understanding of post-depositional processing of nitrate in snow is based on work in very low accmulation sites closer to the interior of the continent. The dataset overall adds to data from remote regions that are difficult to sample and our undestanding is likely very skewed by the limited data availabe. The data presented discusses the potential archiving of seasonal cycles in the isotopes of nitrate, presents understanding based on all three of d15N, d18O and D17O, and quantifies connections between the preservation of isotopes with surface mass balance based on accumulation rates. the new data does not necessarily yield brand new understanding, but it importantly documents what is well known and can be applied in this context and what is not well understood. Overall the manscript is very well written (the introduction overall is a particularly nice summary esp. for readers who do not focus on this type of work). The methods are sound and well-justified. My comments overall are minor in extent.

It seems like a missed opportunity to not compare this work with expectations predicted with the modeling work of Zatko, Alexander, and others (https://acp.copernicus.org/articles/16/2819/2016/). It's important to give the field in general more tools for exploring larger scale implications/interpretation of these types of records. and the Zatko modeling work had so little data to compare with in modeling the entire Antarctic interior.

My only other general comment is that it would be worth some extra attention being paid to suggestions for an independent proxy of photolysis. As the literature stands now, several works in Antarctica have shown evidence that d15N of nitrate IS a proxy for column ozone/extent of photolysis. Given the other published work by these same authors putting forward d15N as a proxy for SMB it seems worthwhile to think through more carefully what the criteria is for another proxy that would make d15N even more useful

and under what SMB conditions is d15N already useful (ie we would not need this independent proxy).

In the results (~ line 275) it is reported that there is a lack of correlation between d15N and d18O, but there is a significant correlation with D17O. Yet, d18O and D17O are well correlated (r=0.51 "fairly strong positive correlation"). What impact does the larger analytical error for d18O measurements have on these relationships? I recognize the authors link this instead to an offset in the timing of the d18O cycle compared to d15N, but this may be something that should be a bit more highlighted in the discussion. For instance can the offset be quantified? Clearly the d18O can be directly impacted by the loss of nitrate while the D17O would remain the same, so what does the other 49% of varability in d18O and D17O teach us? Are the slopes amongst the different sites different in a way that can be explained physically? While I appreciate the reporting of these relationships, they are not necessarily instructive of any particular mechanistic understanding as the manuscript is written currently.

Section 5.1 - it would make sense to include some discussion of the coastal data and interpretation provided by Shi et al (The Cryosphere, 2018) -- www.the-cryosphere.net/12/1177/2018/ .

Line 366 -- this should be rephrased. The observed APPARENT fractionation factors are similar to those observed in other FIELD studies but this disagrees with the laboratory and theoretical predictions (especially of Frey et al 2009 cited here). This is all outlined in the introduction of the paper. The apparent fractionations do not necessarily reflect "NO3- photolytic fractionation" since this fractionation(s) are not currently predicted by theory to be positive. This should be rephrased to address that the apparent factors are representative of the impact of NO3- photolytic fractionation (ie there may be competing reaction or re-formation of nitrate in situ in the snow that leads to lowering D17O and d18O as reported in other works already cited within the manuscript). Moreover, the skin layer elevated values compared to the snow hint at an indication that maybe the theoretically predicted negative fractionation factors for d18O are being expresssed. This should be reflected on a bit more in the discussion here.

A schematic representation of the discussion in lines 425-435 would be useful/would make this article more appealiing to a larger readership.

Line 436 -- again, I take issue with linked a lowering of d18O and D18O specifically to photolysis. It is not the photolysis necessarily that leads to the lowering -- the only mechanisms reported in the literature involve re-oxidation of the photolytic products (ie this cannot be explained by photolysis alone and therefore could vary in different snow environments espeicllay given the large range of apparent factors observed in the field.

Line 470-480 -- the d18O and D17O being "notably higher in the skin layer than at 1 m depth" is not obvious in Figure 5. In fact, given the large uncertainty envelope for the

relaionships with SMB it's not a clearly true statement that these values are significantly different. It should be better addressed as to why the skin layers appear to stay relatively consistent across SMB versus at 1m depth. This combined with the higher d15N and higher d18O does seem to hint at direct loss (vs re-combination) happening in that skin layer?

Line 474 -- please phrase as "**apparent** isotopic fractionation factors"

Line 480 -- please phrase as "part of a annual isotopic cycle" or similar

Line 485 -- this is an important recommendation but also needs to be written within the context of also knowing SMB. Is the 50 cm range at 1-1.5 m depth specific to these intermediate SMBs? I think this call to the communtiy should be given more specifciity given different accumulation rates in regions where ice cores are drilled.

Line 496 -- change "supports" to "is consistent with photolysis". The evidence does not support theoretical predictions of the impact of photolysis on d18O.

Line 511 -- is initial NO3- the initially deposited nitrate at the snow surface or is it the "primary" nitrate signal as I have seen it called in other Savarino papers?