

Comments on Akers et al. “Photolytic modification of seasonal nitrate isotope cycles in East Antarctica”

Akers et al. reported new dataset of nitrate concentrations and isotopic composition in snow collected along traverse with generally intermediate snow accumulation rate ($100\text{-}200\text{ kg m}^{-2}\text{ a}^{-1}$) in East Antarctica. The authors collected three types of snow samples, the uppermost skin layer, the 100cm depth snow, and snow pits samples, and then they analyzed the concentrations, and $\delta^{15}\text{N}$, $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ of nitrate in these samples. With these data, the authors made an assessment of the degree of nitrate photolysis among different sites. They concluded that the primary deposition signals may be largely preserved, especially in the high snow accumulation rate sites, but the photolytic loss of nitrate occurs, with a higher degree of loss in drier sites. These findings are of significance to interpret the nitrate records in ice cores recovered from the East Antarctica where a large part of regions feature the intermediate snow accumulation rate. In general, this paper is well written/organized and fits the scope of Atmospheric Chemistry and Physics. Congratulations to the authors for that they collected so many snow samples in the very harsh Antarctic environments and provided the comprehensive nitrate isotope dataset. I recommend the publication of the work, and I only have several comments that may help improve/clarify the interpretation of the data.

First, the authors made an extensive interpretation of the 100cm depth data. The 100cm depth snow samples were collected by mixing a 5-10cm thick layer of snow from 100cm below the surface. Considering that snow accumulation rate ranges from ~ 100 to $200\text{ kg m}^{-2}\text{ a}^{-1}$ along the traverse in this study, this 5-10 cm snow layer likely only covers a single season. In this case, it is unknown what the 100cm depth snow can present (summertime or wintertime snow, or a mixing?). It seems unlikely to date the 100cm snow without a snow pit sampling, considering that the snow accumulation varies both spatially and temporally. Based on this, I donot think it is reasonably to calculate/interpret the apparent fractionation constant (ϵ_{app}) using the skin layer data versus the 100cm snow data (note that you only have two points for ϵ_{app} calculation) at one site. At a specific site, the 100cm snow from wintertime or summertime deposition may result in distinct ϵ_{app} values. From Table 3, the $^{15}\epsilon_{\text{app}}$ varies between about -20 and -70‰, and both positive and negative $^{18}\epsilon_{\text{app}}$ and $^{17}E_{\text{app}}$ are present along the traverse. It is suspected that the sampled 100cm snow at different sites may be from different season deposition. Then, comparison between the skin layer and 100cm snow data will be challenging, because the 100cm snow may from different seasons at different sites. In my opinion, the interpretation of the 100cm snow data would be uncertain before clarifying what the sample/data can present, though I noticed that the authors have clearly pointed out the uncertainty of the 100cm snow at the end of the discussion.

Second, the authors dated the snow pits based on the concentrations and isotopic composition of nitrate. Do they have other parameters such as water isotopes and other chemical ions that were usually used for snow/ice dating? In addition, the authors are encouraged to clarify how they separate the snow pit sample groups (warm season versus cold season). In my opinion, the snow pit data are rather valuable as these pits cover different snow accumulations, and thus the snow pit data may be explored further. For instance, is it possible to quantify the overall degree of snow nitrate photolysis degree at different sites and its relation to snow accumulation rate? From Figure 4, it seems that photolytic processing at P1 is rather minor? Or based on these comprehensive snow pit data, is it possible to suggest a threshold of snow accumulation (or an accumulation range), above which the photolytic processing of nitrate

would be minor? Because previous investigations based on nitrate concentration data have proposed that post-depositional loss become insignificant at sites with snow accumulation rate above $\sim 100 \text{ kg m}^{-2} \text{ a}^{-1}$. This would be of great significance to the precise interpretation of ice core nitrate (and its isotopes) records in the regions with intermediate snow accumulation rate.

Other minor/specific comments:

The Introduction section, in my opinion, is generally good.

L36-40, please also consider a recent work on both atmospheric and snowfall nitrate annual cycles at a coastal site, East Antarctica. (Shi, G., Li, C., Li, Y., Chen, Z., Ding, M., Ma, H., Jiang, S., An, C., Guo, J., Sun, B., Hastings, M.G., 2022. Isotopic constraints on sources, production, and phase partitioning for nitrate in the atmosphere and snowfall in coastal East Antarctica. *Earth and Planetary Science Letters* 578, 117300.)

L107, could you please be specific about the unknowns regarding atmospheric nitrate budget in Antarctica?

L119-121, Erbland et al. (2013) suggested an overall oxygen isotopic equilibrium at the Dome C air-snow interface?

Figure 1, the unit of mass fraction of nitrate in the atmosphere should be ng m^{-3} , not ng g^{-1} .

Section 2.3, maybe several factors such as stratospheric ozone (TCO) influencing snow nitrate photolysis can be included, in addition to snow accumulation rate.

L156, a space is needed between NO_3^- and cycles

L160-162, a good point here. In addition to the downward transport of NO_x may undergo oxidation to form nitrate, NO_x from snow nitrate photolysis in the interstitial air may also be re-oxidized before it is pumped by wind to the overlying atmosphere. Now, we know nothing about this process.

L189-193, both nitrate concentration measurements and snow sample pre-concentration were conducted at Dome C?

L201, what do you mean by “ $\pm 0.7-1.1$ ” and the other values?

L270-271, how did you remove the linear trends of the data?

L317-318, I don't think the apparent fractionation constants are generally consistent at different sites according to the following description: $^{15}\epsilon_{\text{app}}$ varies between -25 and -66 ‰, and both positive and negative values are for the $^{18}\epsilon_{\text{app}}$ and $^{17}E_{\text{app}}$. In my opinion, the negative $^{18}\epsilon_{\text{app}}$ and $^{17}E_{\text{app}}$ values may be associated with that the sampled 100cm depth snow is the wintertime deposition which features elevated oxygen isotopic ratios of nitrate. Even after 2-3 years of photolysis, these values may be still higher than the skin layer values (summertime deposition). Again, this point raises the question that what the depth snow sample can present.

L354, DDU and Zhongshan are the only available observations on the complete isotopes of atmospheric nitrate in coastal Antarctica.

L368-370, the apparent fractionation of oxygen isotopes is related to both the photolytic loss and re-oxidation of photoproducts in the snow grain condensed phase. These two processes dominate the $^{18}\epsilon_{\text{app}}$ and $^{17}E_{\text{app}}$. Up to date, the oxygen isotopic effects of a single photolytic loss process remain unknown.

L410-415, if the very clear negative trends in oxygen isotope values with depth in P2 and P3 suggest the cumulative effects of snow nitrate photolysis, the synchronously increase trends in $\delta^{15}\text{N}$ would be also expected assuming the relatively constant atmospheric inputs of nitrate. But the observations show no clear trends in $\delta^{15}\text{N}$. Can the authors explain this difference?

L447-454, is it possible that the “skin layer” nitrate has experienced some extent of photolytic processing, though the extent may be rather small. Considering that the sample skin layer thickness is comparable at different sites, and the varied snow accumulation rates would result in the different exposure time of the “skin layer” at the sampling sites. Then, the higher $\delta^{15}\text{N}$ and lower oxygen isotopic ratios would be expected at the low snow accumulation sites. Is this maybe an additional reason for the observed relationships?

L 473-475, from Figure 4, it seems that the cumulative effects of photolytic loss are more evident on oxygen isotopes than on the nitrogen isotope (the trends in oxygen isotopes are more significant)?

Supplementary information:

L50-55, caption of Figure S2, typos, please check.