

Interactive comment on “Air-snow transfer of nitrate on the East Antarctic Plateau – Part 1: Isotopic evidence for a photolytically driven dynamic equilibrium” by J. Erbland et al.

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We appreciate and commend the authors on the immense effort to produce such an amazing dataset. Below we detail a few comments on the interpretation of the data, most not addressed by the reviews already posted.

1. “Quantitative” collection of atmospheric nitrate

From manuscript (p 28,565): “Atmospheric samples were collected at DC during the same time period on glass fiber filters (20.3cm~25.4cm) using a high-volume air sampler (HVAS) which has been used during previous campaigns and has been shown to quantitatively trap both particulate nitrate and gaseous HNO₃ (Frey et al., 2009).”

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The methods employed here for atmospheric sampling have NOT been shown to quantitatively trap both particulate nitrate and gaseous HNO₃. Nor have they been directly shown to quantitatively capture the isotopes of atmospheric nitrate. This is very important in terms of interpretation of the data herein. In particular, it should be directly justified, with evidence, that fractionation upon collection of nitrate cannot explain the difference between the atmospheric samples and the snow “skin” layer.

The present manuscript references Frey et al., 2009 and Frey et al., 2009 reference Morin et al., 2007 for the observation that HNO₃ is trapped quantitatively (see the end of this comment for quoted material from these references). Morin et al., 2007 acknowledge the difficulty of collecting particulate and gaseous nitrate quantitatively and do not show any observations proving that both are in fact collected quantitatively. Furthermore, and of greater importance, the current manuscript and Frey et al., 2009 both use glass fiber filters as the substrate for collection, whereas the Morin et al., 2007 paper uses cellulose substrates for collection. Due to the importance of nitrate/nitric acid to air quality monitoring there is a litany of literature on method comparisons to capture both species (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 (as Morin et al., 2009 points out), 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.

From Frey et al. 2009: “The atmospheric NO₃- collected on glass fiber filters represents

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the sum of atmospheric particulate NO₃⁻ (p-NO₃⁻) and gaseous nitric acid (HNO₃). The bulk of HNO₃ present in the gas phase adsorbed most likely to aerosols on the filter. This is supported by the observation that second-stage filters (Whatman 41), known to trap HNO₃ quantitatively (Morin et al., 2007), showed either very low NO₃⁻ concentrations or none at all."

[Note here that "very low" NO₃⁻ concentration could still induce an isotopic fractionation even if the amount of NO₃⁻ "lost" is small.]

From Morin et al. 2007: "Existing literature on the collection of atmospheric inorganic nitrate by means of high volume sampling on a variety of media show that none is devoid of sampling artifact (e.g. Schaap et al., 2002). The use of cellulose acetate filters leads to the quantitative collection of both particulate nitrate (p-NO₃⁻), in the form of ammonium nitrate and other nitrate salts) and gaseous nitric acid (HNO₃), the sum of which being referred to as total inorganic nitrate (TIN, Bottenheim et al., 1993). However, it is worth keeping in mind that the measurements of $\Delta^{17}\text{O}(\text{NO}_3^-)$ based on filter collection are not suspected to be sensitive to the chemical form of nitrate (either gaseous HNO₃ or particulate NO₃⁻) because any fractionation occurring at the interface between the gas phase and the particulate phase obeys mass-dependent relationships, without affecting the $\Delta^{17}\text{O}$ value."

From Morin et al. 2009: "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."

2. "Skin layer" collection

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It seems very difficult to accurately and precisely collect 1 kilogram of snow from only the top 3-4 millimeters. Please detail how this done to know that indeed only 3-4 mm is collected.

3. Nitrate evaporation experiments.

Why not report $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ data for the evaporation experiments and similarly quantify fractionation as done for $\delta^{15}\text{N}$? The $\Delta^{17}\text{O}$ would be important since it should remain constant and provide confirmation that only mass-dependent processes are occurring. This data would also help support the supposition that there was no deposition of external HNO₃.

Why not compare with the fractionation factor for evaporative loss calculated by Frey et al. 2009 for $\delta^{18}\text{O}$?

The amount of loss (due to sublimation only) reported in the -10C experiment seems implausibly large especially given that conditions were controlled, in a closed and dark room. From what is reported (28,565-28,566) we calculate an average snow density of 0.1875 g/cm³. Assuming a 0.72 lowering of the surface (how sublimation is usually assessed but not sure if the sides of the snow on the plates were exposed or not), lowering = 2.88 cm. Given the density above this yields a sublimation rate of 5.4 mm water equivalent day⁻¹. This is roughly one order of magnitude greater than the rates measured at low-latitude, high elevation glaciers during the dry season (when sublimation is most significant and is promoted by strong radiation, clear skies, high wind speeds, low relative humidities and warm temperatures (Hastenrath, 1978; Ginot et al., 2001 and references therein; Wagnon et al., 2003; Favier et al., 2004). Some comparison or context for the rates of sublimation would be worth discussing.

4. Analytical reproducibility

The values of reference material corrected to should be reported. This is important for at least two reasons. First, in the future the accepted values may change (as has

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happened for IAEA-N3). Second, Bohlke et al., 2003, which is reference by Frey et al. 2009 for the isotopic reference values, does not use the linear definition for $\Delta^{17}\text{O}$ and therefore the values reported in that reference should not be used when calculating $\Delta^{17}\text{O}$ from the linear equation. If this has been taken into consideration then it should be said so, or at the very least report the isotopic reference values that are being corrected to so that other studies may directly compare.

5. Data reduction

It is unclear how the best-fits are determined for the “asymptotic” functions. Further, the fits reported (e.g., Table 1) would benefit from some calculation of the significance of the “fit” (i.e. along the lines of r^2).

6. Continued changes in isotopes below several e-folding depths

How do you explain continued enrichment in $\delta^{15}\text{N}$ below 30 cm, indeed to 70cm? Could the recycling of nitrate within the firn and re-deposition potentially explain this? How can this be ruled out?

7. Theoretical framework

On page 28,578 – why use the calculated fractionation factors in Frey et al. as opposed to the “observed” values found and reported in this work?

8. Isotopic offset between atmosphere and snow

Page 28,579 - why assume that deposition causes a fractionation? There are several other possible explanations that should be considered or ruled out: Can fractionation be caused by atmospheric sampling (see comment 1 above)? And can new deposition offset some the fractionation experienced by previously deposited HNO_3 ? Furthermore, how does a constant offset indicate equilibrium? If it is at equilibrium shouldn't the $\Delta^{17}\text{O}$ be equal between the atmospheric samples and the snow? If they are not does this not indicate mixing or exchange?

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9. Application to Greenland glacial/interglacial record

Page 28,585: “Those observations support our assertion that the $\delta^{15}\text{N}$ data presented by Hastings et al. (2005) for the Summit ice core must be interpreted in light of the possible variations in the post-depositional processing of nitrate.”

The Hastings et al., 2005 publication begins with the idea that post-depositional loss of nitrate might explain the change between the interglacial (IG) and glacial (G) period, but this cannot be reconciled with the understanding of the fractionations (or lack thereof) associated with post-depositional processes. Therefore, the Greenland record IS considered “in light of possible variations in the post-depositional processing of nitrate.” In the present manuscript, it is calculated that a 70 per mil change could have occurred due to the change in snow accumulation between the IG/G. How then can only an 18 per mil shift in $\delta^{15}\text{N}$ be explained? And how can you reconcile the increase in $\delta^{18}\text{O}$ with an increase in $\delta^{15}\text{N}$, which contrasts with almost ALL of the data shown here? Also note that nitrate concentration does NOT significantly change between the IG/G in the Greenland record.

The current manuscript equates interglacial and glacial conditions at Summit, Greenland to two sites in East Antarctica. There are several factors that make this comparison unjustified: 1) the dust content of Greenland ice, particularly in the glacial, which may lead to preservation of nitrate but at the very least suggests very different alkaline conditions of the snow in the glacial period; 2) the fact that the glacial record in Greenland shows an INCREASE in BOTH $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$, while the East Antarctic data show enrichment of $\delta^{15}\text{N}$ with a concurrent decrease in $\delta^{18}\text{O}$ at sites where it is “proven” that post-depositional processing is occurring; 3) while these sites might “mimic” temperature and accumulation rate, they do not mimic atmospheric conditions that directly influence the nature and form of atmospheric nitrate (see Beine paper in Svalbard for example) that would be deposited. Lastly, there is no mention or comparison of the East Antarctic snow records and the snow data at Summit, Greenland (Hastings et al., 2004; Jarvis et al., 2009; Kunasek et al., 2008), which all contrast with the data shown

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here. Without treatment or consideration of any of the above, we suggest that it is inappropriate to draw conclusions or implications about the glacial/interglacial record in Greenland based on the study here.

Submitted on behalf of the Hastings lab group including Aron Buffen, Katye Altieri, Dorothy Fibiger, and Rebecca Fahringer

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