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#### Recommended Citation

Fibiger, D. L., M. G. Hastings, J. E. Dibb, and L. G. Huey (2013), The preservation of atmospheric nitrate in snow at Summit, Greenland, *Geophys. Res. Lett.*, 40, 3484–3489, doi:10.1002/grl.50659.

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## The preservation of atmospheric nitrate in snow at Summit, Greenland

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Received 10 April 2013; revised 7 June 2013; accepted 12 June 2013; published 9 July 2013.

[1] There is great interest in using nitrate ( $\text{NO}_3^-$ ) isotopic composition in ice cores to track the history of precursor nitrogen oxides ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ) in the atmosphere.  $\text{NO}_3^-$ , however, can be lost from the snow by surface processes, such as photolysis back to  $\text{NO}_x$  upon exposure to sunlight, making it difficult to interpret records of  $\text{NO}_3^-$  as a tracer of atmospheric  $\text{NO}_x$  loading. In a campaign consisting of two field seasons (May–June) at Summit, Greenland, high temporal frequency surface snow samples were collected and analyzed for the oxygen isotopic composition of  $\text{NO}_3^-$ . The strong, linear relationship observed between the oxygen isotopes of  $\text{NO}_3^-$ , in both 2010 and 2011, is difficult to explain in the presence of significant postdepositional processing of  $\text{NO}_3^-$ , unless several unrelated variables change in concert. Therefore, the isotopic signature of  $\text{NO}_3^-$  in the snow at Summit is most feasibly explained as preserved atmospheric  $\text{NO}_3^-$  deposition. **Citation:** Fibiger, D. L., M. G. Hastings, J. E. Dibb, and L. G. Huey (2013), The preservation of atmospheric nitrate in snow at Summit, Greenland, *Geophys. Res. Lett.*, 40, 3484–3489, doi:10.1002/grl.50659.

### 1. Introduction

[2] Ideally, nitrate ( $\text{NO}_3^-$ ), a major ion present in ice cores, could be used to trace the history of its precursor nitrogen oxides ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ) sources and impact on the atmosphere. Natural (lightning, microbial process in soils, and stratospheric  $\text{N}_2\text{O}$  oxidation) and anthropogenic (fossil fuels combustion and biomass/biofuel burning) sources both make important contributions to the global atmospheric burden of  $\text{NO}_x$ ; these emissions have a direct impact on the oxidation capacity of the atmosphere through  $\text{NO}_x$  interactions with ozone ( $\text{O}_3$ ) and  $\text{HO}_x$  (hydroxyl and hydroperoxyl radicals). Understanding of  $\text{NO}_3^-$  concentration records has long been complicated by the fact that  $\text{NO}_3^-$  can be postdepositionally processed in surface snow [Honrath *et al.*, 1999]. Recent studies of the isotopic composition of  $\text{NO}_3^-$  in snow have aimed to trace the preservation of  $\text{NO}_x$  source and chemistry

signals and/or assess the postdepositional loss of  $\text{NO}_3^-$  [Blunier *et al.*, 2005; Frey *et al.*, 2009; Hastings *et al.*, 2009].

[3] At Summit, Greenland (72.6°N, 38.5°W), observations of  $\text{NO}_x$  fluxes from the snow have been ascribed to the photolysis of snow  $\text{NO}_3^-$  [Dibb *et al.*, 2002; Honrath *et al.*, 1999] with  $\text{NO}_x$  concentrations of up to 50 pptv measured in the boundary layer [Yang *et al.*, 2002]. In addition, it has been suggested, based on nitrate concentration ( $[\text{NO}_3^-]$ ), that 5–25% of  $\text{NO}_3^-$  is lost from the snow [Burkhart *et al.*, 2004; Dibb *et al.*, 2007]. This large amount of loss does not fit with current modeling simulations [Thomas *et al.*, 2011], which suggest that very little  $\text{NO}_3^-$  loss is required to explain the locally observed atmospheric concentrations of  $\text{NO}_x$  in the summertime boundary layer.

[4] The nitrogen and oxygen isotopic composition of  $\text{NO}_3^-$  has been used to document the postdepositional processing of snow  $\text{NO}_3^-$  in polar environments. In low snow accumulation environments, such as Dome C, Antarctica (10 cm of snow per year [Rothlisberger *et al.*, 2000]), the isotopes serve as a tracer of postdepositional loss [Blunier *et al.*, 2005; Frey *et al.*, 2009; Rothlisberger *et al.*, 2002]. In higher accumulation environments, such as Summit (65 cm of snow per year [Dibb and Fahnestock, 2004]), work thus far has indicated that the majority of  $\text{NO}_3^-$  and its isotopic composition is preserved in the snow [Hastings *et al.*, 2004, 2009; Jarvis *et al.*, 2009]. It is possible, however, that recycling of  $\text{NO}_3^-$  occurs locally, i.e., postdepositional loss of  $\text{NO}_3^-$  from the snow as  $\text{NO}_x$ , followed by local oxidation of  $\text{NO}_x$  to  $\text{NO}_3^-$  and redeposition. At Summit, accumulation occurs year-round [Dibb and Fahnestock, 2004], with riming and fog in addition to snow deposition possible during the spring and summer.

[5] Here we use the isotopic composition of  $\text{NO}_3^-$  to quantify the significance of postdepositional processing of  $\text{NO}_3^-$  in snow. This work presents the first complete oxygen isotopic measurements,  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$ , for  $\text{NO}_3^-$  in surface snow at Summit with both ( $\delta = (R_{\text{sample}}/R_{\text{VSMOW}} - 1) * 1000\%$ , where  $R = {}^{18}\text{O}/{}^{16}\text{O}$  for  $\delta^{18}\text{O}$  and  $R = {}^{17}\text{O}/{}^{16}\text{O}$  for  $\delta^{17}\text{O}$ ,  $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 * \delta^{18}\text{O}\%$ ) reported. The oxygen isotopic composition of atmospheric  $\text{NO}_3^-$  is representative of the oxidation pathways of  $\text{NO}_3^-$  formation.  $\Delta^{17}\text{O}$  is the measure of deviation from the typical “mass-dependent” relationship between  ${}^{18}\text{O}$  and  ${}^{17}\text{O}$ , and anomalously high  $\Delta^{17}\text{O}$  values are found in atmospheric  $\text{NO}_3^-$  as a result of the interaction of  $\text{NO}_x$  with  $\text{O}_3$ .

[6] Both modeling and observational studies suggest that photolysis is the primary driver of  $\text{NO}_3^-$  loss from the snowpack; while other postdepositional processes such as evaporation and volatilization may contribute some to  $\text{NO}_3^-$  loss, they are not believed to be as important in locations with low  $[\text{NO}_3^-]$  and temperatures [Frey *et al.*, 2009; Rothlisberger *et al.*, 2002]. The various photolysis pathways (Figure 1) should induce different effects on the oxygen isotopes of  $\text{NO}_3^-$  due to fractionation and exchange of oxygen atoms. Based on theoretical calculations [Frey *et al.*, 2009],

Additional supporting information may be found in the online version of this article.

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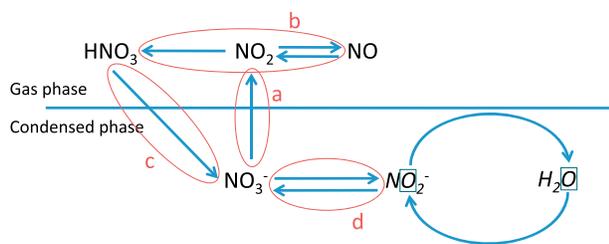
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**Figure 1.** A simplified schematic of reaction pathways for photolysis of  $\text{NO}_3^-$  in snow. Pathway a represents photolytic loss of  $\text{NO}_3^-$ , with pathway b showing  $\text{NO}_x$  cycling and pathway c showing redeposition. Pathway d shows an example mechanism for  $\text{NO}_3^-$  exchanging O atoms with  $\text{H}_2\text{O}$ . The  $\text{NO}_2^-$  here should be considered representative of any  $\text{NO}_3^-$  photolysis product trapped in the condensed phase that can be oxidized back to  $\text{NO}_3^-$ .  $\text{H}_2\text{O}$  represents any oxidant in the condensed phase that shares the isotopic composition of  $\text{H}_2\text{O}$ .

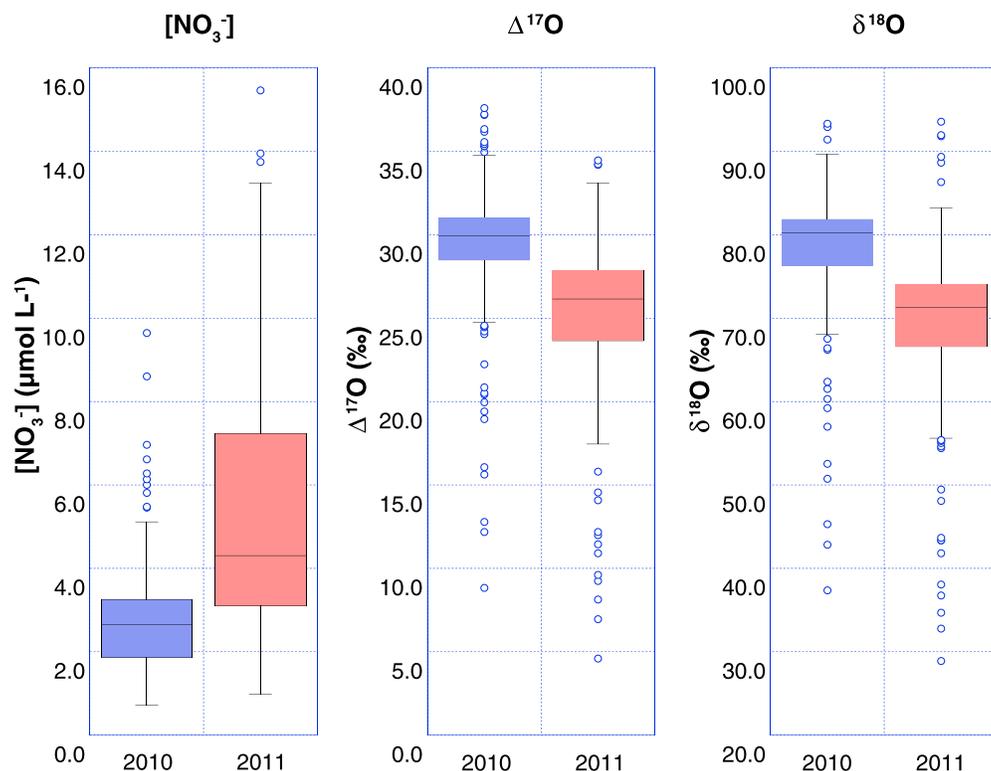
photolysis of  $\text{NO}_3^-$  to gas-phase  $\text{NO}_2$  (Figure 1, pathway a) should increase  $\delta^{18}\text{O}-\text{NO}_3^-$  in the surface snow, while  $\Delta^{17}\text{O}-\text{NO}_3^-$  should remain constant. The resulting  $\text{NO}_2$  may be cycled as  $\text{NO}_x$  in the atmosphere and, ultimately, converted back to  $\text{HNO}_3$  (Figure 1, pathway b). If  $\text{HNO}_3$  is formed and redeposited locally, this would imprint a local oxidant composition on the snow  $\text{NO}_3^-$  (Figure 1, pathway c). It is also possible that  $\text{NO}_3^-$  is photolyzed to a compound (e.g.,  $\text{NO}_2^-$ ) that remains in the condensed phase (Figure 1, pathway d) and is capable of exchanging oxygen atoms with an oxidant also in the condensed phase. In this case, the

resultant  $\text{NO}_3^-$  will have an isotopic composition that is similar to that of water (snow).

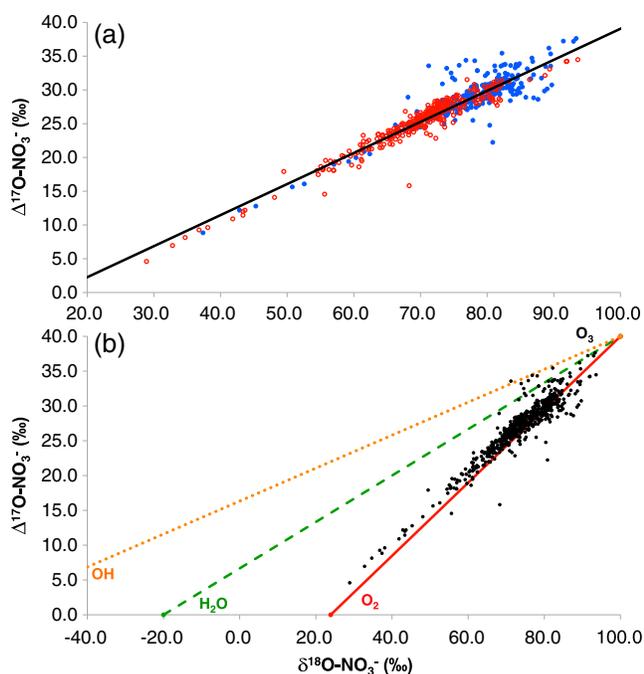
## 2. Methods

[7] Two field seasons were conducted: 17 May to 22 June 2010 and 24 May to 26 June 2011. Throughout both, surface snow samples, comprising the top 1–2 cm of snow from 100 to 400  $\text{cm}^2$  areas, were collected every 4–12 h and included all major snowfall events. At each sampling time, three replicate samples were collected adjacent to each other within a 10 m by 5 m section of the clean air sector using a Lexan scraper, and each snow sample was stored frozen in a high-density polyethylene bottle until analysis, with all materials precleaned in 18  $\text{M}\Omega$   $\text{cm}$  water. The samples were then analyzed for a suite of ion concentrations at the University of New Hampshire, including  $\text{NO}_3^-$ , on a Dionex ion chromatograph. (Dibb *et al.* [2007] provided details on the sampling and analytical protocols, as well as data screening criteria.)

[8] The complete isotopic composition of  $\text{NO}_3^-$  was measured at Brown University for each sample. The  $\delta^{18}\text{O}-\text{NO}_3^-$  and  $\Delta^{17}\text{O}-\text{NO}_3^-$  are quantified using the bacterial denitrifier method [Casciotti *et al.*, 2002; Kaiser *et al.*, 2007], where nitrous oxide ( $\text{N}_2\text{O}$ ) generated from  $\text{NO}_3^-$  by denitrifying bacteria is used to determine  $\delta^{18}\text{O}$ , and  $\Delta^{17}\text{O}$  is determined by quantitatively decomposing the  $\text{N}_2\text{O}$  into molecular oxygen ( $\text{O}_2$ ) and nitrogen ( $\text{N}_2$ ). The supporting information includes further discussion of measurement techniques and data correction. In contrast to other studies, the  $\delta^{18}\text{O}-\text{NO}_3^-$  and  $\Delta^{17}\text{O}-\text{NO}_3^-$  data should be considered independent since different aliquots of the samples are run separately for



**Figure 2.** (left)  $[\text{NO}_3^-]$ , (middle)  $\Delta^{17}\text{O}$ , and (right)  $\delta^{18}\text{O}-\text{NO}_3^-$  comparison for the 2010 ( $n=277$ ) and 2011 ( $n=345$ ) seasons, which show remarkably different average values and ranges. The black lines indicate median values, with the boxes encompassing the upper and lower quartiles. The individual points are more than 1.5 times the interquartile distance.



**Figure 3.** The 2010 and 2011 surface snow  $\Delta^{17}\text{O-NO}_3^-$  versus  $\delta^{18}\text{O-NO}_3^-$ . (a) All data points for 2010 (blue, solid circles) and 2011 (red, open circles) are shown. The best fit line for all data is  $\Delta^{17}\text{O} = 0.46 * \delta^{18}\text{O} - 6.9$  ( $R^2 = 0.9$ ). (b) All data (black solid circles) relative to possible oxidant mixing lines are shown (see section 4.2). Note the change in scale for  $\delta^{18}\text{O-NO}_3^-$  between the graphs.

$\delta^{18}\text{O-NO}_3^-$  (quantified from  $\text{N}_2\text{O}$ ) and  $\Delta^{17}\text{O-NO}_3^-$  (quantified from  $\text{O}_2$ ). The most realistic picture of precision is obtained from a pooled standard deviation of sample replicates, which is 0.7‰ ( $n = 271$ ) for  $\delta^{18}\text{O}$  and 0.9‰ ( $n = 271$ ) for  $\Delta^{17}\text{O}$ . (See Table S1 in the supporting information for additional error statistics.)

[9] In addition to the  $\text{NO}_3^-$  analysis, a selection of samples from each field season was analyzed for  $\delta^{18}\text{O-H}_2\text{O}$  and  $\delta\text{D-H}_2\text{O}$ . The isotopes of water were measured on a Picarro isotopic water liquid analyzer (L1102-i) with a precision better than 0.2‰.

### 3. Results

[10] The 2010 and 2011 field seasons show markedly different ranges and average values for  $\text{NO}_3^-$  concentration and oxygen isotopes (Figure 2). Comparable high temporal resolution measurements of surface snow are not available for  $\Delta^{17}\text{O-NO}_3^-$ , but measurements from 1 and 2 m snowpits at Summit ranged from  $\sim 23\%$  to 30‰ for summertime snow [Kunasek *et al.*, 2008], similar to the mean values observed in the May–June surface snow. An average  $\Delta^{17}\text{O-NO}_3^-$  of 26‰ calculated for atmospheric  $\text{NO}_3^-$  in June from a global 3-D atmospheric chemistry model simulation [Alexander *et al.*, 2009] also compares generally well with the surface snow mean values found in 2010 and 2011. Interestingly, there is a great deal of variability in  $\Delta^{17}\text{O-NO}_3^-$  measured in surface snow, even within a single day, which is not represented by previous snow pit data. Jarvis *et al.* [2009] reported  $\delta^{18}\text{O}$  of surface snow with a range shifted slightly higher

(45‰ to 108‰ versus 30‰ to 95‰) than what was observed in the 2010 and 2011 seasons.

[11] Despite the differences in range and average values (Figure 2), similar relationships between  $[\text{NO}_3^-]$ ,  $\delta^{18}\text{O-NO}_3^-$ , and  $\Delta^{17}\text{O-NO}_3^-$  were found in both seasons. In both the 2010 and 2011 field seasons, no correlation was found in the surface snow between  $[\text{NO}_3^-]$  and the oxygen isotopic composition of  $\text{NO}_3^-$  (Figure S1). On the other hand, in both seasons, a very strong linear relationship was found between  $\delta^{18}\text{O-NO}_3^-$  and  $\Delta^{17}\text{O-NO}_3^-$  (Figure 3a). As outlined below, this relationship is difficult to explain in the presence of significant postdepositional processing of  $\text{NO}_3^-$  given what is known about isotope effects of photolytic processes.

## 4. Discussion

[12] In interpreting the isotope results, the discussion below focuses on photolysis as a primary driver of the potential postdepositional processing of  $\text{NO}_3^-$  in snow at Summit. The possible impacts of photolytic loss of  $\text{NO}_3^-$ , exchange of oxygen atoms within the snow and photolytic driven exchange of oxygen atoms in the snow, are considered.

### 4.1. Isotopic Impacts of $\text{NO}_3^-$ Processing

[13] As discussed above (section 1), different photolysis pathways will induce different isotopic effects. For  $\text{NO}_3^-$  deposited to the snow that is then photolyzed, a theoretical fractionation factor,  $\epsilon_{18}$ , that assumes Rayleigh fractionation, can be used to quantify the change in  $\delta^{18}\text{O}$  with the degree of photolytic loss of  $\text{NO}_3^-$  as follows:

$$\ln(\delta^{18}\text{O}_{\text{final}} + 1000) = \epsilon_{18} * \ln\left(\frac{[\text{NO}_3^-]_{\text{final}}}{[\text{NO}_3^-]_{\text{initial}}}\right) + \ln(\delta^{18}\text{O}_{\text{initial}} + 1000) \quad (1)$$

[14] For conditions at Dome C, Frey *et al.* [2009] calculated  $\epsilon_{18}$  as  $-34\%$  serving to increase the residual  $\delta^{18}\text{O-NO}_3^-$  in the snow ( $\delta^{18}\text{O}_{\text{final}}$ ) and recalculated for average Summit radiation conditions,  $\epsilon_{18} = -32\%$ . As a mass dependent process, the loss of  $\text{NO}_3^-$  from the snow should have no impact on the  $\Delta^{17}\text{O-NO}_3^-$ . If we assume that some portion of the data presented in Figure 3a reflects direct deposition, photolysis would serve to move the snow composition away from the observed  $\Delta^{17}\text{O-NO}_3^-$  versus  $\delta^{18}\text{O-NO}_3^-$  relationship along lines of constant  $\Delta^{17}\text{O}$  by differing amounts depending on the amount of loss. There is, however, considerable uncertainty associated with the calculated oxygen enrichment factor for photolysis of  $\text{NO}_3^-$ : the calculations are for the gas phase only (i.e., there is no consideration of matrix effects), the quantum yield has no wavelength dependence, and it is assumed that photolyzed  $\text{NO}_3^-$  is lost directly to the gas phase only as  $\text{NO}_2$ .

[15] The enrichment in snow  $\delta^{18}\text{O-NO}_3^-$  due to photolytic loss fits neither with the data from Summit nor with other measurements of photolytic loss made in the laboratory or field [Frey *et al.*, 2009; McCabe *et al.*, 2005]. In laboratory photolysis experiments and in situ snow measurements, depletion in  $^{18}\text{O}$  has been observed and assumed to be the result of competing factors of enrichment due to photolysis and mixing of the residual  $\text{NO}_3^-$  with a source depleted in  $^{18}\text{O}$ . The most likely source of this low  $\delta^{18}\text{O}$ , due to its abundance, is water or an isotopically similar oxidant. Indeed, laboratory studies of photolysis of nitrate have shown, when

beginning with a single  $\text{NO}_3^-$  source, that photolysis of USGS35  $\text{NaNO}_3$  results in a single line for  $\delta^{17}\text{O}-\text{NO}_3^-$  versus  $\delta^{18}\text{O}-\text{NO}_3^-$  that has markedly different slopes when in waters of differing isotopic composition [McCabe *et al.*, 2005].

[16] If  $\text{NO}_3^-$  were to simply exchange oxygen atoms with water, with no loss at all, the expected result would be for the  $\delta^{18}\text{O}-\text{NO}_3^-$  and  $\Delta^{17}\text{O}-\text{NO}_3^-$  to be pulled toward that of water. (For our samples,  $\delta^{18}\text{O}-\text{H}_2\text{O} = -38\text{‰}$  to  $-20\text{‰}$  and  $\Delta^{17}\text{O}-\text{H}_2\text{O} = 0\text{‰}$ .) This would serve to decrease both  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  of the  $\text{NO}_3^-$  in the snow, though not in the ratio that fits with our observations. For example, starting at the mean values for 2011 ( $\delta^{18}\text{O}-\text{NO}_3^- = 70.1\text{‰}$  and  $\Delta^{17}\text{O}-\text{NO}_3^- = 25.3\text{‰}$ ), if 10% of the oxygen atoms were to exchange with water of  $\delta^{18}\text{O} = -38\text{‰}$ , the new isotopic composition would be  $\delta^{18}\text{O}-\text{NO}_3^- = 59.3\text{‰}$  and  $\Delta^{17}\text{O}-\text{NO}_3^- = 22.8\text{‰}$ , using equation (2).

$$\delta^{18}\text{O}-\text{NO}_3^-(\text{final}) = 0.9 \cdot \delta^{18}\text{O}-\text{NO}_3^-(\text{initial}) + 0.1 \cdot \delta^{18}\text{O}-\text{H}_2\text{O} \quad (2)$$

[17] If the water  $\delta^{18}\text{O} = -20\text{‰}$ ,  $\delta^{18}\text{O}-\text{NO}_3^- = 61.1\text{‰}$ , and  $\Delta^{17}\text{O}-\text{NO}_3^-$  would remain at 22.8‰. With increasing exchange, the data point would move toward the isotopic composition of water, i.e., a line set by the water composition end point (or range) and the starting composition of the  $\text{NO}_3^-$  (e.g., Figure 3b, green dashed line). The slope of increasing exchange would vary from 0.07 to 0.33 depending upon the initial  $\text{NO}_3^-$  composition and the composition of water but would never be equal to the observed value of 0.46.

[18] The competing processes of enrichment due to photolysis and mixing with a depleted oxygen source could result in apparent fractionation along the relationship we observe between  $\delta^{18}\text{O}-\text{NO}_3^-$  and  $\Delta^{17}\text{O}-\text{NO}_3^-$ , if they happen in a specific ratio. With a higher degree of loss, a larger amount of mixing with the depleted source would be required to maintain this relationship. This seems plausible, as the proposed mechanisms for mixing with water involve branching photolysis, with some fraction of the  $\text{NO}_3^-$  becoming  $\text{NO}_x$  and another portion of  $\text{NO}_3^-$  following a path that remains in the condensed phase. The condensed phase  $\text{NO}_2^-/\text{NO}_2$  can exchange oxygen atoms with the solvent water and then reform  $\text{NO}_3^-$  (Figure 1, pathway d). As more  $\text{NO}_3^-$  is photolyzed to gas-phase  $\text{NO}_x$ , more  $\text{NO}_3^-$  may also be photolyzed to the condensed-phase substance ( $\text{NO}_2^-$ ), thus increasing the oxygen exchange with water. As long as these reactions occur in the necessary ratios, the linear relationship between  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  of the residual nitrate can be maintained. For instance, using the range of  $\text{NO}_3^-$  loss from snow concentration studies [Burkhart *et al.*, 2004; Dibb *et al.*, 2007], if a 10% loss of  $\text{NO}_3^-$  were occurring, 7% of the remaining  $\text{NO}_3^-$  oxygen atoms must exchange with water in order to maintain the observed relationship between  $\delta^{18}\text{O}-\text{NO}_3^-$  and  $\Delta^{17}\text{O}-\text{NO}_3^-$ , (i.e., applying equation (1) and then equation (2)). At a 25% loss, a 16% exchange is needed, assuming that the water has a  $\delta^{18}\text{O}$  of  $-30\text{‰}$  and  $\Delta^{17}\text{O}$  of 0‰.

[19] If the water had a constant  $\delta^{18}\text{O}$ , competing photolytic enrichment and exchange with water would be a logical explanation for the relationship observed between  $\delta^{18}\text{O}-\text{NO}_3^-$  and  $\Delta^{17}\text{O}-\text{NO}_3^-$ . The water observed over the May–June 2010 and May–June 2011 seasons, however, varies in  $\delta^{18}\text{O}$  from  $-38\text{‰}$  to  $-20\text{‰}$ . With a 25% photolytic loss and water with  $\delta^{18}\text{O}$  of  $-20\text{‰}$ , a 22% exchange of remaining oxygen atoms is required to maintain the relationship between  $\delta^{18}\text{O}-\text{NO}_3^-$  and  $\Delta^{17}\text{O}-\text{NO}_3^-$ , while with water  $\delta^{18}\text{O}$  of  $-38\text{‰}$ ,

a 15% exchange is required to maintain the relationship. The differences in exchange required with varying water isotopic composition change with differing degrees of  $\text{NO}_3^-$  loss. If the isotopic composition of the water were to vary in concert with the photolysis of  $\text{NO}_3^-$ , we would expect to find a relationship between  $\delta^{18}\text{O}-\text{H}_2\text{O}$  and  $\delta^{18}\text{O}-\text{NO}_3^-$ , but there is none.

[20] If the degree of  $\text{NO}_3^-$  photolysis and the  $\delta^{18}\text{O}-\text{H}_2\text{O}$  were to vary synchronously, that would require them to both be controlled by the same factors. If the only control on sublimation of water, and therefore  $\delta^{18}\text{O}-\text{H}_2\text{O}$  increase, was actinic flux, then it would be possible to relate it to the degree of photolysis of  $\text{NO}_3^-$ . The  $\delta^{18}\text{O}-\text{H}_2\text{O}$  should, however, be primarily controlled by relative humidity, which should have no effect on  $\text{NO}_3^-$  photolysis. In addition, concurrent changes in  $\text{NO}_3^-$  photolysis and  $\delta^{18}\text{O}-\text{H}_2\text{O}$  would require  $\delta^{18}\text{O}-\text{H}_2\text{O}$  to reset to the same values each evening before  $\text{NO}_3^-$  photolysis restarts in the morning. This is improbable, as the water deposition can come from a variety of sources with different  $\delta^{18}\text{O}-\text{H}_2\text{O}$ , e.g., riming, fog deposition, or fresh snowfall. In addition, if sublimation were driving the change in  $\delta^{18}\text{O}-\text{H}_2\text{O}$ , there should be a change in deuterium excess in the snow [Stichler *et al.*, 2001], but all the samples fall along a line with a slope of 8 ( $\delta^{18}\text{O} = 8.0 \cdot \delta\text{D} + 6.0$ ,  $R^2 = 0.99$ ). This indicates that all isotopic changes in water are derived at equilibrium; therefore, sublimation cannot be the source of variation in  $\delta^{18}\text{O}-\text{H}_2\text{O}$ . The most likely source of  $\delta^{18}\text{O}-\text{H}_2\text{O}$  variation is deposition of new water.

[21] Additionally, stratospheric  $\text{O}_3$  concentration, and therefore UV penetration to the surface at Summit, is an important control on the photolysis of  $\text{NO}_3^-$ . It is notable that despite significant depletion in stratospheric  $\text{O}_3$  during spring 2011 compared to spring 2010 [Manney *et al.*, 2011], the observed relationship between  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  of  $\text{NO}_3^-$  is the same in both years (Figure 3a).

[22] In summary, the observed relationship between  $\delta^{18}\text{O}-\text{NO}_3^-$  and  $\Delta^{17}\text{O}-\text{NO}_3^-$  cannot be explained by postdepositional processing of  $\text{NO}_3^-$  in the snow, considering our current understanding of the isotopic imprints of the processes discussed above. The oxygen isotopic signals observed in  $\text{NO}_3^-$  at Summit are more plausibly explained as representing atmospheric  $\text{NO}_3^-$  deposition to Summit.

#### 4.2. Atmospheric Production of $\text{NO}_3^-$

[23] Most linear relationships of the type found between  $\delta^{18}\text{O}-\text{NO}_3^-$  and  $\Delta^{17}\text{O}-\text{NO}_3^-$  at Summit are interpreted as the result of mixing of different oxidants that react with  $\text{NO}_x$  to produce atmospheric  $\text{NO}_3^-$  [e.g., Michalski *et al.*, 2004]. The linear relationship between  $\delta^{18}\text{O}-\text{NO}_3^-$  and  $\Delta^{17}\text{O}-\text{NO}_3^-$  suggests isotopic mixing between a high end-member with  $\delta^{18}\text{O} = 100\text{‰}$  and  $\Delta^{17}\text{O} = 39\text{‰}$  and a low end-member with  $\delta^{18}\text{O} = 18\text{‰}$  and  $\Delta^{17}\text{O} = 0\text{‰}$  (Figure 3a). The high end-member likely results from stratospheric  $\text{O}_3$ . The lower end-member is more difficult to identify. The atmospheric oxidant with the closest isotopic composition is molecular oxygen ( $\text{O}_2$ ) ( $\delta^{18}\text{O}-\text{O}_2 = 23.9\text{‰}$ ,  $\Delta^{17}\text{O}-\text{O}_2 = 0\text{‰}$  versus Vienna standard mean ocean water [Barkan and Luz, 2005]). A mixing line between these two oxidants ( $\text{O}_2$  and stratospheric  $\text{O}_3$ ) (Figure 3b, red solid line) is the best fit to the surface snow data, compared with other oxidants of  $\Delta^{17}\text{O} = 0\text{‰}$ . For instance,  $\text{H}_2\text{O}$  vapor (or OH in isotopic equilibrium) would have  $\delta^{18}\text{O}$  between  $-30\text{‰}$  and  $-10\text{‰}$  (Figure 3b, green dashed line shows  $-20\text{‰}$ ), which does not fit the data. If

OH maintains some of its O<sub>3</sub> character from O(<sup>1</sup>D) [e.g., Kunasek *et al.*, 2008], the mixing line would remain the same, but the lower endpoint would be moved toward O<sub>3</sub>. Assuming an equilibrium fractionation of 44‰ between OH and H<sub>2</sub>O [Michalski *et al.*, 2012] results in an OH–O<sub>3</sub> mixing line that is an even worse fit for the data (Figure 3b, orange dotted line). Thus, it would appear that oxygen atoms from stratospheric O<sub>3</sub> and atmospheric O<sub>2</sub> are the main controls on the isotopic composition of NO<sub>3</sub><sup>−</sup> that is ultimately deposited to Summit. Furthermore, the influence of the stratosphere on NO<sub>3</sub><sup>−</sup> (e.g., NO<sub>3</sub><sup>−</sup> formed in the troposphere via reaction of NO<sub>x</sub> and stratospheric O<sub>3</sub>) may account for the higher than expected summertime Δ<sup>17</sup>O–NO<sub>3</sub><sup>−</sup> at Summit based on models [Alexander *et al.*, 2009; Kunasek *et al.*, 2008].

#### 4.3. NO<sub>x</sub> Production From Snow NO<sub>3</sub><sup>−</sup>

[24] The conclusion, based upon the isotopic data, that the NO<sub>3</sub><sup>−</sup> seen in Summit snow is a direct atmospheric signal that reflects little to no postdepositional loss contrasts with the estimates of NO<sub>3</sub><sup>−</sup> loss based upon snow concentration measurements made in the past [Burkhart *et al.*, 2004; Dibb *et al.*, 2007]. Gas-phase observations and recent modeling work, however, suggest that very small fractions of NO<sub>3</sub><sup>−</sup> are involved in the postdepositional processing at Summit [Honrath *et al.*, 1999; Thomas *et al.*, 2011].

[25] Honrath *et al.* [1999] calculated that only a tiny amount of the NO<sub>3</sub><sup>−</sup> must photolyze in order to give a 1000 pptv NO<sub>x</sub> concentration in the interstitial snow (firn) air (i.e., 6 × 10<sup>−11</sup>% of the NO<sub>3</sub><sup>−</sup> in a 5 μmol L<sup>−1</sup> snow sample must be converted to NO<sub>x</sub>). These numbers, however, were never translated into boundary layer concentrations.

[26] In a 1-D model that matches well with observed NO<sub>x</sub> concentrations, Thomas *et al.* [2011] showed that only 0.10% of the NO<sub>3</sub><sup>−</sup> in the top 10 cm of snow is required to be lost over a 3 day period in order to explain the NO<sub>x</sub> concentrations measured in the boundary layer at Summit. Assuming a summer accumulation rate of 5.1 cm mo<sup>−1</sup> [Dibb and Fahnestock, 2004], the top 10 cm of snow will be entirely replaced by fresh snow in less than 60 days. In that case, a loss of 2.1% of the NO<sub>3</sub><sup>−</sup> in the snow is required to account for the measured NO<sub>x</sub> concentrations, backing our interpretation that the postdepositional processing of NO<sub>3</sub><sup>−</sup> is small in magnitude and has little to no effect on the isotopes observed.

[27] The contrast between prior snow concentration measurements and the isotopic measurements, as well as the modeled NO<sub>3</sub><sup>−</sup> loss, is difficult to reconcile. We have demonstrated that large photolytic losses of NO<sub>3</sub><sup>−</sup> are not driving these measurements. Evaporative loss or volatilization of HNO<sub>3</sub> will also not account for the discrepancy, as HNO<sub>3</sub> concentrations in the atmosphere would have to be 4–10 times larger than the NO<sub>x</sub> concentrations, which is inconsistent with measurements at Summit [Dibb *et al.*, 1998; Honrath *et al.*, 2002]. The lower amount of NO<sub>3</sub><sup>−</sup> loss predicted from NO<sub>x</sub> concentrations in air fits with the isotope data, while loss predicted from snow concentration measurements does not. It is possible that the calculations based on snow concentrations are confounded by the spatial heterogeneity of NO<sub>3</sub><sup>−</sup> or by fluctuations in water content (e.g., evaporation). The isotopes of NO<sub>3</sub><sup>−</sup>, therefore, present a more sensitive record of NO<sub>3</sub><sup>−</sup> chemistry than concentration alone in the snow at Summit.

## 5. Conclusions and Implications

[28] The isotopic composition of NO<sub>3</sub><sup>−</sup> in the snow at Summit, Greenland, is largely preserved and is representative of atmospheric NO<sub>3</sub><sup>−</sup> deposition to Summit. NO<sub>3</sub><sup>−</sup> at Summit shows a mix of oxidation processes by stratospheric O<sub>3</sub> and an unknown oxidant of low Δ<sup>17</sup>O and δ<sup>18</sup>O that is isotopically similar to O<sub>2</sub>, which influence NO<sub>x</sub> cycling and the formation of NO<sub>3</sub><sup>−</sup>. It remains uncertain what accumulation rate is required to preserve the NO<sub>3</sub><sup>−</sup> signal, but at Summit, photolytically driven postdepositional processing is so small in magnitude that it does not have a significant effect on NO<sub>3</sub><sup>−</sup> concentration or isotopes in the snow. Simultaneous observations of gas-phase species and isotopes of NO<sub>3</sub><sup>−</sup> in air and snow may distinguish whether the signal represents regionally formed or long-range transported NO<sub>3</sub><sup>−</sup>. In high accumulation areas, such as Summit, isotopic records of ice-core NO<sub>3</sub><sup>−</sup> can be interpreted as a preserved atmospheric signal and used as a tracer of past NO<sub>x</sub> and atmospheric oxidation conditions.

[29] **Acknowledgments.** This work was supported by the National Science Foundation under grant 0909374 (Arctic Natural Sciences). We thank C. Corr and E. Scheuer for their help with field sampling and ion analysis and Polar Field Services for their support with logistics.

[30] The Editor thanks two anonymous reviewers for their assistance in evaluating this paper.

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