Seasonal variations in N and O isotopes of nitrate in snow at Summit, Greenland: Implications for the study of nitrate in snow and ice cores

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[1] Nitrogen and oxygen isotopes of NO\textsubscript{3} have been measured in snow and firn from Summit, Greenland. The $^{15}$N/$^{14}$N and $^{18}$O/$^{16}$O ratios of NO\textsubscript{3} in recently fallen snow are similar to those of surface snow. Diurnal variation is observed in $^{15}$N/$^{14}$N of NO\textsubscript{3}, and possibly $^{18}$O/$^{16}$O, suggesting fractionating loss of NO\textsubscript{3} from snow during the day, which is subsequently recovered at night. A larger seasonal variation is observed, with higher $^{15}$N/$^{14}$N and lower $^{18}$O/$^{16}$O of NO\textsubscript{3} in summer than winter, which cannot be explained by postdepositional fractionation. The generally high $^{18}$O/$^{16}$O of NO\textsubscript{3} in Greenland snow ($\delta^{18}$O versus VSMOW = 65.2 to 79.6‰) indicates that oxygen atoms from ozone have been incorporated into NO\textsubscript{3} that was subsequently deposited as HNO\textsubscript{3}. The lower mean $\delta^{18}$O of NO\textsubscript{3} in summer snow relative to winter (68.9‰ in summer 2000 and 70.5‰ in summer 2001 versus 77.5‰ in winter 2000–01) is a result of summertime HNO\textsubscript{3} production via NO\textsubscript{2} reaction with hydroxyl radical (OH), which dilutes the high $\delta^{18}$O imparted on NO\textsubscript{3} from ozone. The higher mean $^{15}$N/$^{14}$N of NO\textsubscript{3} observed in snow from spring ($\delta^{15}$N versus air N\textsubscript{2} = +5.9‰ in 2000 and −1.4‰ in 2001) and summer (+0.1‰ in 2000 and −0.8‰ in 2001) than fall (−9.2‰ in 2000) and winter (−10.0‰ in 2000–01) is more difficult to explain with seasonal photochemistry, given current knowledge. The seasonal $^{15}$N/$^{14}$N change may reflect NO\textsubscript{x} sources, with a greater fall and wintertime contribution from fossil fuel emissions relative to other inputs of NO\textsubscript{x} (i.e., biogenic soil emissions, biomass burning, and lightning). INDEX TERMS: 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 9315 Information Related to Geographic Region: Arctic region; 1863 Hydrology: Snow and ice (1827); 0322 Atmospheric Composition and Structure: Constituent sources and sinks; KEYWORDS: Greenland snow, isotopes, nitrate


1. Introduction

[2] Nitrate (NO\textsubscript{3}) is one of the major anions found in snow. NO\textsubscript{3} deposition results from reactions between nitrogen oxides (NO\textsubscript{x} = NO + NO\textsubscript{2}), ozone (O\textsubscript{3}) and hydroxyl radical (OH). Globally, the main sources of NO\textsubscript{x} are fossil fuel and biomass burning, biogenic soil emissions, and lightning, with minor contributions from aircraft emissions and the stratosphere. Although a recent increase in NO\textsubscript{3} concentration ([NO\textsubscript{3}]) in ice cores has been associated with increasing anthropogenic emissions of NO\textsubscript{x} [Mayewski et al., 1990; Neftel et al., 1985], the contribution from natural sources of NO\textsubscript{x} today and in pre-industrial ice remains unclear [e.g., Wolff, 1995]. The link between the atmospheric concentration of NO\textsubscript{x} and [NO\textsubscript{3}] in ice core records is particularly problematic because postdepositional processing can impact the [NO\textsubscript{3}] in snow.

[3] Postdepositional processes that may influence snow [NO\textsubscript{3}] include photolysis in surface snow layers and evaporative loss of HNO\textsubscript{3} [Cotter et al., 2003; Dibb et al., 2002; Honrath et al., 2002; Davis et al., 2001; Jones et al., 2000; Röthlisberger et al., 2000; Dibb et al., 1998; Fischer et al., 1998; Legrand and Kirchner, 1990]. Beyond its effect on snow composition, photolysis of NO\textsubscript{3} could release significant quantities of NO\textsubscript{x} and OH into the atmosphere above the snowpack [Wolff et al., 2002; Honrath et al., 2002; Yang et al., 2002; Dominé and Shepson, 2002]. This
may extend the impact of NO emissions beyond what would otherwise be expected from our current understanding based on atmospheric chemistry models.

[4] Since the lifetime of NO is on the order of days, low concentrations of NO are found in the remote troposphere, far from its major continental sources. Both modeling [e.g., Moxim et al., 1996; Wang et al., 1998; Fan et al., 1994] and observational studies [e.g., Bottenheim and Gallant, 1989; Bottenheim et al., 1984, 1993; Honrath and Jaffe, 1992] have shown that peroxyacetyl nitrate (PAN = CH3C(O)OONO2) is the dominant form of reactive nitrogen in the arctic troposphere in winter and spring. PAN is produced via oxidation of hydrocarbons in the presence of NO. At low temperatures, such as those found in the upper troposphere, PAN is stable and serves as a reservoir species of NO, providing a mechanism for the long-range transport of NO to remote regions [Crutzen, 1974; Singh and Hanst, 1981; Moxim et al., 1996]. Thermal and photolytic decomposition of PAN in the late spring and summer is expected to provide a source of NO to the arctic troposphere, which is then predominantly lost via reaction with OH to form HNO3 [Singh et al., 1992; Fan et al., 1994; Yang et al., 1995; Moxim et al., 1996; Wang et al., 1998]. Several studies have suggested that buildup of PAN during the arctic winter and subsequent decomposition in the spring and summer contributes to high [NO3] observed in snow during the warmer months [e.g., Munger et al., 1999; Yang et al., 1995]. During the arctic winter (polar night), the hydrolysis of NO2 (formed from NO2 + NO) is the predominant sink for NO3 [Den tenter and Crutzen, 1993; Stroud et al., 2003; Tie et al., 2003]. Based on a model constrained by observations from the Tropospheric Ozone Production about the Spring Equinox (TOPSE) campaign, Stroud et al. (2003) find that the importance of this reaction decreases into the spring, becoming negligible by May because of the photolytic sensitivity of NO3.

[5] The isotopic composition of NO3 offers a tool for the study of NO3 in snow and ice cores that complements concentration measurements. The oxygen (O) isotopic composition of atmospheric NO3 contains information about the oxidants that react with NO to produce NO3 [Hastings et al., 2003; Michalski et al., 2003]. The nitrogen (N) isotopic composition of atmospheric NO3 may preserve signatures of different NO sources [e.g., Hastings et al., 2003; Xiao and Liu, 2002; Russell et al., 1998; Heaton, 1986; Freyer, 1978] and/or it may be impacted by NO3 chemistry in the atmosphere [Freyer et al., 1993]. Here we report measurements of the N and O isotopic composition (δ15N and δ18O) of NO3 in snow from Summit, Greenland (72.5°N, 38.4°W, 3200 m altitude). The purpose of this study is (1) to understand the isotopic composition of NO3 in terms of present NO3 chemistry and (2) to investigate the impact of postdepositional processing on the isotopes of NO3 in surface snow. These results can then be applied to ice core studies of NO3 in the effort to reconstruct past emissions sources and atmospheric cycling of NO3.

2. Methods
2.1. Field Sampling
[6] Two 30 cm snowpits were sampled every 6 cm with a clean stainless steel sampler on 7 March 2001. Surface snow, fresh snow and two 1 m snowpits were sampled in early August (8/2–8/11) of 2001 at Summit, Greenland. All equipment used for sampling and storage was cleaned with dilute hydrochloric acid and deionized water. The outside layer of the snowpit wall was scraped with a clean knife to guard against any contamination from digging the snowpit. The March snowpits were located approximately 10 m from each other. In August, two 1 m snowpits, located approximately 100 m apart, were sampled in 3 cm increments. The August snowpits were located ~200 m from the site of the March snowpits. During collection, the samples were placed directly into clean 250 ml Nalgene amber HDPE. The bottles were thawed overnight, and approximately 20 ml was decanted into 60 ml HDPE bottles for analysis of δ18O of snow at the University of Washington. The 250 ml bottles were refrozen and shipped frozen to Princeton University for stable isotope analysis of NO3.

[7] On two days, 4 and 5 August, near-surface snow samples were collected at different times during the day next to one of the snowpits. In an effort to avoid any possible contamination of the surface snow, in particular from the close proximity to the excavated snow from the snowpit, a layer of surface snow ~2 cm thick was collected and discarded. Then, using a clean stainless steel sampler, a sample of snow was placed directly into an amber bottle on the morning of 4 August. Subsequent samples were collected next to the morning sample at 13:00 and 19:30 (local time (LT)), and this was repeated adjacent to the 4 August sample site on 5 August; it did not snow on either 4 or 5 August.

[8] Throughout the sampling period, surface snow samples (n = 14) were also collected with a clean stainless steel sampler in various locations. On 7 August a sample bottle was left out to collect fresh, falling snow (n = 1), and on 11 August fresh snow was collected from the snow surface just after a precipitation event (n = 2). We refer to these three samples as “fresh snow” in the following discussion of our results.

2.2. Laboratory Analysis
[9] High-resolution study of the isotopic ratios in NO3 from the Greenland snowpack depends on the use of a sensitive method, since NO3 concentrations are low (typically <2 µmol 1-1) and sample volume is limited. The isotopic ratios (15N/14N and 18O/16O) of NO3 were determined at Princeton using the denitrifier method, which has a sample size requirement of 10 nmol N (i.e., 10 ml of a 1 µmol 1-1 NO3 sample) [Sigman et al., 2001; Casciotti et al., 2002]. NO3 is quantitatively converted to nitrous oxide (N2O), utilizing denitrifying bacteria that lack N2O-reductase. The isotopic composition of the N2O is then measured on a DeltaPlus IRMS in continuous flow mode to determine the 15N/14N and 18O/16O ratios from the 45/44 and 46/44 ion current ratios, respectively. For this dataset, repeated measurements indicated a typical reproducibility of 0.2‰ and 0.3‰ (1 standard deviation (SD)) for 15N/14N and 18O/16O, respectively. Throughout the text, isotopic ratios are reported using delta (δ) notation in units of “per mil” (%): δ15Nsample = ([15N/14N]sample/[15N/14N]reference) - 1) × 1000 ‰ and δ18Osample = ([18O/16O]sample/[18O/16O]reference) - 1) × 1000 ‰, where the 15N/14N reference is N2 in air and the 18O/16O reference is Vienna Standard Mean Ocean Water (VSMOW). Each batch of samples is referenced to the inter-
nationally recognized standard IAEA-NO-3, which has an assigned value of 4.7‰ for $\delta^{15}N$ [Böhleke and Copley, 1995] and a reported range of 22.7 to 25.6‰ for $\delta^{18}O$ [Böhleke et al., 2003, and references therein]. For consistency with our previously published work we adopt a value of 22.7‰ for the $\delta^{18}O$ of IAEA-NO-3. Our data can be subsequently corrected once a $\delta^{18}O$ of IAEA-NO-3 has been firmly established. An additional reference sample, USGS53, is run with each batch of samples as a secondary check on our correction scheme.

[10] The $\delta^{15}N$ determined from isotopic measurements of N$_2$O must be corrected for the contribution of $^{15}N$N$^1$O to the peak at mass 45. This correction typically assumes a mass-dependent relationship between $\delta^{15}O$ and $\delta^{18}O$ ($\delta^{15}O \approx 0.52 \times \delta^{18}O$) of the N$_2$O analyte, which does not necessarily hold for N$_2$O produced from atmospheric NO$_3$ samples (see Hastings et al. [2003] for further discussion). The $\delta^{15}O$ and $\delta^{18}O$ of atmospheric NO$_3$ are considered “mass-independent,” such that the quantity $\Delta^{15}O = \delta^{15}O - 0.52 \times \delta^{18}O$ is non-zero [e.g., Michalski et al., 2002, 2003]. Two bacterial strains, Pseudomonas chlororaphis and Pseudomonas aureofaciens, are routinely used for the isotopic analysis of NO$_3$. During denitrification, exchange between oxygen atoms of water and nitrogen oxide intermediates occurs to a significant degree with P. chlororaphis, but at very low levels with P. aureofaciens [Ye et al., 1991; Casciotti et al., 2002]. As a result, the oxygen in N$_2$O produced by P. chlororaphis is typically derived primarily from (mass-dependent) water, while oxygen in N$_2$O produced by P. aureofaciens represents the sample NO$_3$ [Casciotti et al., 2002; Hastings et al., 2003]. The $\delta^{15}N$ of atmospheric NO$_3$ determined with P. aureofaciens and corrected for a mass-dependent contribution from $\delta^{15}O$ may overestimate the true $\delta^{15}N$ by $1-2\%$ [Sigman et al., 2001]. This overestimate is less for the $\delta^{15}N$ of atmospheric NO$_3$ determined with P. chlororaphis, but still depends upon the variation in the degree of exchange with water during denitrification by this strain. For ice from Greenland covering the time period 1760–1976 AD, the mean $\Delta^{15}O$ of NO$_3$ is 28.0 ± 0.9‰ [Alexander et al., 2004; B. Alexander, personal communication]. Assuming this $\Delta^{15}O$ and utilizing the $\delta^{18}O$ of NO$_3$ for our samples from P. aureofaciens, we estimate $\delta^{15}O$ and use this to correct our $\delta^{15}N$ data. This correction results in an overall mean change of −0.6‰ to the $\delta^{15}N$ of NO$_3$ determined with P. chlororaphis.

[11] Nitrate concentration ([NO$_3^-$]) for all samples was determined by ion chromatography on a Dionex DX500 instrument using a 25 μl injection loop and Dionex AS4A column. All samples had [NO$_3^-$] above the instrument’s reported detection limit of <0.003 μmol l$^{-1}$. Nitrite concentrations were negligible compared to nitrate concentrations (<0.3% of [NO$_3^-$]); therefore, nitrite is not considered separately in the isotope analysis. The snowpit samples from August 2001 were analyzed for $\delta^{18}O$ of H$_2$O (snow) at University of Washington using standard CO$_2$ equilibration [e.g., Craig, 1961].

### 3. Results

#### 3.1. [NO$_3^-$] in the Snowpack

[11] The range and seasonality in [NO$_3^-$] found in this study is similar to that found in several previous Greenland studies [Yang et al., 1995; Whitlow et al., 1992; Davidson et al., 1989; Steffensen, 1988]. [NO$_3^-$] in the August and March snowpit samples ranges from 0.8 to 5.9 μmol l$^{-1}$ (Figure 1a). Overall, average [NO$_3^-$] ± 1 SD for the two August snowpits is 1.9 ± 0.7 μmol l$^{-1}$ and 2.5 ± 1.3 μmol l$^{-1}$ for Pit 1 and Pit 2, respectively. Although there are similarities between the profiles of the two snowpits, they are significantly different overall (based on a two-tailed t-test, p < 0.02). The range and variability in the snowpit [NO$_3^-$] is very similar to [NO$_3^-$] data collected by Burkhardt et al. [2004] for 10 snowpits sampled in July of 1998. Based on the seasonal binning described above, [NO$_3^-$] tends to be higher in spring and summer than fall and winter, with a local maximum in summer (Figure 2a and Table 2). This is similar to the observations reported in the previous studies mentioned above, although Burkhardt et al. [2004] find no clear seasonality in [NO$_3^-$].

#### 3.2. The $\delta^{15}N$ and $\delta^{18}O$ of NO$_3^-$ in the Snowpack

[14] The $\delta^{15}N$ of NO$_3^-$ for all the snowpit samples collected in August and March ranges from −15.3‰ to +16.7‰ versus atmospheric N$_2$ (Figure 1b). There is some spatial heterogeneity in the $\delta^{15}N$ of NO$_3^-$, but the two pits collected in August and the two pits collected in March show similar patterns. Overall, and in contrast to the [NO$_3^-$], the $\delta^{15}N$ of NO$_3^-$ is not significantly different between the August snowpits. Considering the large range and spatial heterogeneity in $\delta^{15}N$, comparison of the March and August
samples shows that the $\delta^{15}$N of NO$_3^-$ does not change significantly between the time of initial deposition and subsequent burial by more snowfall (Figure 1b).

The overall average $\delta^{15}$N of NO$_3^-$ from surface snow samples collected in various locations near Summit camp is $-5.5 \pm 1.1\%$ (n = 14, Table 3). Fresh snow collected on 7 August has a $\delta^{15}$N of $-6.9\%$, which is very similar to surface snow ($-6.4\%$) collected the next day. This similarity is also seen for the $\delta^{18}$O of NO$_3^-$ and suggests, to first order, that the snow reflects the isotopic composition of atmospheric HNO$_3$. Based on the seasonal binning, the average $\delta^{15}$N of NO$_3^-$ is significantly (p < 0.01) higher in the summer ($0.1\%$ in 2000, $-0.9\%$ in 2001) than winter ($-10.0\%$) (Figure 2b and Table 2). The springtime NO$_3^-$ has the highest average $\delta^{15}$N ($+5.9\%$) in 2000, but in 2001 the spring $\delta^{15}$N of NO$_3^-$ is similar to that found in summer. The fall $\delta^{15}$N average is $-9.2\%$, similar to that of wintertime snow.

Overall, the $\delta^{18}$O of NO$_3^-$ in the upper meter of snow ranges from 65.2 to 79.6$\%$ versus VSMOW (Figure 1c). As with the $\delta^{15}$N of NO$_3^-$, the $\delta^{18}$O of NO$_3^-$ profiles show some spatial variability between the different snowpits, but their difference is not significant. The $\delta^{18}$O of NO$_3^-$ in the March shallow snowpit samples also appears to be preserved in the August depth profiles, within the limits of the observed spatial variability (Figure 1c). Surface snow samples collected between 2 and 11 August have an average $\delta^{18}$O of NO$_3^-$ of $66.9 \pm 2.2\%$ (n = 14, Table 3). The gradual changes found in the $\delta^{18}$O of NO$_3^-$ profile (Figure 1c) and the observation that fresh snow has a similar $\delta^{18}$O to snow found at the surface suggests that the exchange of O atoms between NO$_3^-$ and water in the snowpack is unlikely since we would expect the $\delta^{18}$O of NO$_3^-$ to be driven much lower than observed (see $\delta^{18}$O of snow in Figure 1d). In contrast to the $\delta^{15}$N of NO$_3^-$, the average $\delta^{18}$O of NO$_3^-$ in winter snow is significantly (p < 0.01%) higher (77.5$\%$) than in summer (70.5$\%$ in 2000, 68.9$\%$ in 2001) (Figure 2c and Table 2). The fall and spring seasons appear to represent transitions between the other two seasons, with the fall averaging 74.6$\%$ and the spring averaging 69.8$\%$ in 2000 and 75.4$\%$ in 2001 (Table 2). The snowpit samples collected in March represent the previous winter’s snow. Their average values are therefore shown for comparison with results from the wintertime samples in the August snowpits (Figure 2) and are included in the average winter values shown in Table 2.

### 3.3. Diurnal Variation in $\delta^{18}$O and $\delta^{15}$N of NO$_3^-$ in Surface Snow

In an effort to assess whether the isotopes of NO$_3^-$ change throughout the day, near-surface snow samples were collected in the morning (07:30 LT), at midday (13:00 LT), and at “night” (19:30 LT) on 4 and 5 August 2001. The Sun did not actually set during the sampling period, but did drop towards the horizon at night. To depict this, the solar zenith angle (as cos $\theta$) is shown along with the concentration and isotope results (Figure 3). The [NO$_3^-$] for these six samples ranges from 1.2 to 1.7 $\mu$mol l$^{-1}$, increasing by 0.5 $\mu$mol l$^{-1}$ between the morning and evening sample on August 4th but then remaining fairly constant through the night of August 5th (Figure 3a). In contrast to the [NO$_3^-$], the isotopes exhibit marked changes during the sampling period. The $\delta^{15}$N of NO$_3^-$ in these surface samples ranges from 6.4$\%$ to 9.2$\%$.
Figure 2. Seasonal averages of (a) [NO$_3^-$] (μmol l$^{-1}$), (b) $\delta^{15}$N of NO$_3^-$ (% versus atmospheric N$_2$), and (c) $\delta^{18}$O of NO$_3^-$ (% versus VSMOW) for the August snowpits. Seasonal bins are described in Table 1. Shown for comparison with the August snowpits are the March snowpit samples (gray squares), which represent the previous winter’s snow. The error bars indicate ±1 SD for the samples averaged over spring (MAM = March, April, May), summer (JJA = June, July, August), fall (SON = September, October, November), and winter (DJF = December, January, February).

from −3.2 to +2.0‰. In general, the $\delta^{15}$N of NO$_3^-$ in the snow at night appears to be much lower than during the day (Figure 3b). $\delta^{15}$N decreases from +2.0 to +1.6‰ between the morning and midday samples on August 4th, and then from +1.6 to −2.9‰ between midday and night. A large increase in $\delta^{18}$O is then observed between the night on August 4th and morning on August 5th (−2.9 to +0.19‰). A large decrease between the midday and night samples is found again on August 5th. The $\delta^{18}$O of NO$_3^-$ (Figure 3c) behaves like the $\delta^{15}$N for the first five sample times, but then increases by 0.5‰ between midday and night on August 5th, while $\delta^{15}$N decreases by 3.9‰. Overall, the amplitude of variation in $\delta^{18}$O is smaller than in $\delta^{15}$N of NO$_3^-$ from these few samples, it appears that both the $\delta^{15}$N and $\delta^{18}$O of NO$_3^-$ vary diurnally at Summit. However, the concentration changes over the same time period are minimal, suggesting that the mechanism responsible for the isotopic variations involves a large isotope effect.

It should be noted that a similar diurnal change in the isotopes of NO$_3^-$ is found in surface snow samples collected on August 4th at a different location (Table 3). These samples are surface snow (as opposed to the near-surface snow samples) and are therefore not included in Figure 3.

4. Interpretation

4.1. Impact of Photolysis and Evaporative Loss

Several studies have measured a flux of NO$_3^-$ out of the snowpack at Summit and recognized photolysis of NO$_3^-$ as its likely source [e.g., Dibb et al., 2002; Honrath et al., 2002], although evaporative loss of HNO$_3$ from snow has also been suggested [e.g., Dibb et al., 1998; Röhlisberger et al., 2002, and references therein]. Whether such postdepositional processing significantly alters the isotopes of NO$_3^-$ depends both on (1) the fraction of NO$_3^-$ that is lost from the snowpack, and (2) the isotope effects associated with the photolysis and/or evaporation. Overall, we would expect the loss of NO$_3^-$ via these processes to cause enrichment in both $^{15}$N and $^{18}$O of the NO$_3^-$ left behind in the snowpack. The increase in $\delta^{15}$N and $\delta^{18}$O of NO$_3^-$ in surface snow from night into day fits this qualitative expectation (Figure 3b). However, the subsequent decrease in $\delta^{15}$N and $\delta^{18}$O on the night of August 4th suggests that the NO$_3^-$ (as HNO$_3$) was re-deposited, either by direct contact with the snow surface or by deposition via fog. Heavy fog was noted on the evening of the 4th, and fog deposition of NO$_3^-$ has been observed previously at Summit [Bergin et al., 1995]. The night of August 5th was also very humid, and riming or direct uptake of HNO$_3$ could have occurred. The dissimilar behavior of $\delta^{15}$N and $\delta^{18}$O on the night of the 5th is somewhat surprising. However, the $\delta^{18}$O of NO$_3^-$ is dependent upon the oxidation pathway that produces HNO$_3$ from NO$_x$ [Hastings et al., 2003; Michalski et al., 2003]. Thus, it is possible that the NO$_x$ “re-deposited” to the snow on the night of the 5th encountered an oxidant that had a different $\delta^{18}$O signature than that on the night of the 4th. Overall, these first data might imply that significant net loss of NO$_3^-$ does not occur since much of the NO$_3^-$ is recycled back to the snow as NO$_3^-$ On the timescale of two days this is not surprising, since Honrath et al. [2002] observed days when the average rate of NO$_3^-$ emission was matched by HNO$_3$ deposition.

Although we observe diurnal changes in the isotopic composition of NO$_3^-$, the processing of NO$_3^-$ in surface snow does not appear to dominate the signals observed in the snowpack. Little change in the isotopes is observed for surface snow samples collected in March and the “same snow” re-sampled at ~33 cm depth in the August snowpits.
(Figures 2b and 2c). This implies that postdepositional processing of NO$_3^-$ on this timescale is minimal or that, overall, a significant net loss of NO$_3^-$ from the snowpack due to processing does not occur. Based on the interpretation of [NO$_3^-$] measurements in snow from Summit, Burkart et al. [2004] suggest that a maximum of 7% loss of NO$_3^-$ occurs on an annual timescale. More isotopic measurements are needed in order to identify the mechanisms contributing to the observed diurnal variation, as well as to determine whether there are changes to the isotopic composition of NO$_3^-$ on longer timescales. Additionally, further measurements will help to verify our initial hypothesis that a large isotope effect must be associated with the loss of NO$_3^-$ since there are large changes in the isotopic composition of NO$_3^-$ despite the lack of a detectable change in [NO$_3^-$].

4.2. Controls on the $\delta^{18}$O of NO$_3^-$

[21] Since surface processing of NO$_3^-$ does not appear to dominate the observed seasonal isotopic signals, we will now consider the $\delta^{18}$O of NO$_3^-$ in terms of the larger scale tropospheric chemistry that produces HNO$_3$ from NO$_3^-$ prior to deposition at Summit. The range in $\delta^{18}$O of NO$_3^-$ in the upper meter of snow at Summit, Greenland, is similar to that found in measurements of precipitation and aerosol nitrate in various environments [e.g., Michalski et al., 2003; Hastings et al., 2003; Williard et al., 2001, and references therein]. Studies in Bermuda and La Jolla, California have concluded that the oxygen isotopic composition of HNO$_3$ is dependent upon the oxidation pathway that produces HNO$_3$ from NO$_3^-$ in the atmosphere [Hastings et al., 2003; Michalski et al., 2003]. The high $\delta^{18}$O of atmospheric NO$_3^-$ results from NO$_3^-$ interactions with O$_3$, the $\delta^{18}$O of which is in the range of ~90 to 122‰ (versus VSMOW) [Johnston and Thiemens, 1997; Krankowsky et al., 1995]. The $\delta^{18}$O of hydroxyl radical (OH), on the other hand, is expected to reflect the oxygen isotopic composition of water vapor in the troposphere [Dubey et al., 1997], which is typically less than zero.

[22] In spring and summer, thermal decomposition of PAN provides NO$_2$ to the arctic troposphere. To first order, we can think of summertime HNO$_3$ as the result of reaction of NO$_2$ and OH in the following (simplified) reactions:

$$\text{NO}_2 + h\nu \rightarrow \text{NO} + O$$

$$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$$

$$\text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M}$$

In the resulting HNO$_3$, OH dilutes the high $\delta^{18}$O signal imparted on NO$_2$ by O$_3$. In the winter, we expect HNO$_3$ to be primarily produced via hydrolysis of N$_2$O$_5$ [Stroud et al., 2003; Tie et al., 2003; Yang et al., 1995]:

$$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$$

$$\text{NO}_2 + \text{NO}_3 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M}$$

$$\text{N}_2\text{O}_5 + \text{H}_2\text{O}_{\text{surface/aerosol}} \rightarrow 2\text{HNO}_3$$

This pathway of HNO$_3$ production is only important in winter and early spring (polar night) because NO$_2$ and N$_2$O$_5$ are rapidly destroyed by photolysis. We expect HNO$_3$ produced from N$_2$O$_5$ hydrolysis to result in a higher $\delta^{18}$O of NO$_3^-$ than the “OH pathway,” since there is more interaction with O$_3$ and a lack of dilution by reaction with OH. Simply put, we can think of HNO$_3$ produced via the

### Table 2. Overall Seasonal Averages (±1 Standard Deviation) for NO$_3^-$ Concentration, $\delta^{18}$O and $\delta^{15}$N of NO$_3^-$, and $\delta^{18}$O of Snow

<table>
<thead>
<tr>
<th>Season$^a$</th>
<th>[NO$_3^-$], µmol l$^{-1}$</th>
<th>$\delta^{18}$O of NO$_3^-$, % vs VSMOW</th>
<th>$\delta^{15}$N of NO$_3^-$, % vs air N$_2$</th>
<th>$\delta^{18}$O of Snow$^b$, % vs SMOW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spring 2000</td>
<td>2.7 ± 1.1</td>
<td>69.8 ± 2.1</td>
<td>5.9 ± 6.2</td>
<td>−36.7 ± 2.6</td>
</tr>
<tr>
<td>Summer 2000</td>
<td>2.5 ± 1.2</td>
<td>70.5 ± 2.4</td>
<td>0.1 ± 2.8</td>
<td>−30.2 ± 1.8</td>
</tr>
<tr>
<td>Fall 2000</td>
<td>1.6 ± 0.7</td>
<td>74.6 ± 1.8</td>
<td>−9.2 ± 5.4</td>
<td>−32.8 ± 3.1</td>
</tr>
<tr>
<td>Winter$^c$ 2000–01</td>
<td>2.0 ± 0.7</td>
<td>77.5 ± 2.4</td>
<td>−10.0 ± 3.2</td>
<td>−40.1 ± 1.0</td>
</tr>
<tr>
<td>Spring 2001</td>
<td>1.7 ± 0.4</td>
<td>75.4 ± 1.9</td>
<td>−1.4 ± 3.0</td>
<td>−36.1 ± 1.5</td>
</tr>
<tr>
<td>Summer 2001</td>
<td>2.8 ± 1.5</td>
<td>68.9 ± 2.1</td>
<td>−0.8 ± 5.3</td>
<td>−30.4 ± 1.3</td>
</tr>
</tbody>
</table>

$^a$Seasons are as described in Table 1.

$^b$The $\delta^{18}$O of snow is a proxy for temperature with the lowest values corresponding to the coldest temperatures [e.g., Grootes and Stuiver, 1997].

$^c$Winter includes the wintertime snow from both August and March snowpits.

### Table 3. NO$_3^-$ Concentration, $\delta^{18}$O and $\delta^{15}$N of NO$_3^-$ in Surface Snow Samples Collected in August 2001

<table>
<thead>
<tr>
<th>Sampling Date and Time$^a$</th>
<th>[NO$_3^-$], µmol l$^{-1}$</th>
<th>$\delta^{18}$O of NO$_3^-$, % vs VSMOW</th>
<th>$\delta^{15}$N of NO$_3^-$, % vs air N$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Snow</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8/2 17:00</td>
<td>4.5</td>
<td>69.5</td>
<td>−4.4</td>
</tr>
<tr>
<td>8/3 09:00</td>
<td>3.7</td>
<td>68.4</td>
<td>−4.7</td>
</tr>
<tr>
<td>8/4 07:30</td>
<td>3.4</td>
<td>69.3</td>
<td>−4.5</td>
</tr>
<tr>
<td>20:00</td>
<td>3.5</td>
<td>68.5</td>
<td>−5.2</td>
</tr>
<tr>
<td>8/6 15:00</td>
<td>5.8</td>
<td>65.9</td>
<td>−5.4</td>
</tr>
<tr>
<td>8/15 15:00</td>
<td>5.9</td>
<td>64.9</td>
<td>−6.4</td>
</tr>
<tr>
<td>Average ± 1 SD</td>
<td>4.4 ± 1.0</td>
<td>66.9 ± 2.2</td>
<td>−5.5 ± 1.1</td>
</tr>
</tbody>
</table>

| Fresh Snow$^b$ | | | |
|----------------|----------------|----------------|
| 8/7 01:00 | 4.9 | 64.9 | −6.9 |
| 8/11 08:00 | 3.7 | 63.7 | −6.9 |
| 3.6 | 63.9 | −7.0 |
| Average ± 1 SD | 4.1 ± 0.7 | 64.2 ± 0.6 | −6.9 ± 0.1 |

$^a$Replicate samples were collected at the same time in separate bottles.

$^b$This refers to snow collected just after (8/7) and during (8/11) a snowfall event (see section 2.1).
entire amplitude of the observed seasonal

difficulty in the winter but similar to or higher than in the
summer at Summit (Table 2). The lower than in the winter but similar to or higher than in the
seasonal pattern in $\delta^{18}$O of NO$_3^-$ in snow at Summit to that observed in
Bermuda rain. At Bermuda, Hastings et al. [2003] find a
range in $\delta^{18}$O of 60.3 to 86.5%, with a significantly higher
average $\delta^{18}$O observed in cool season NO$_3^-$ deposition
(76.9 ± 6.3%) in comparison to that found in the warm
season (68.6 ± 3.6%). The difference between the average
winter (77.5 ± 2.4%) and summer (69.8 ± 2.4%) for 2000
and 2001 $\delta^{18}$O in Summit snow is similar to that found
in Bermuda rain, although a smaller range (65.2 to 79.6%)
and less variability in $\delta^{18}$O of NO$_3^-$ is found in Summit snow.
From the Bermuda study, it appears that the $\delta^{18}$O of NO$_3^-$
may be sensitive to [OH]. The similarity between summer-
time $\delta^{18}$O of NO$_3^-$ at Bermuda and Greenland could indicate
that OH concentrations that influence summer production of
HNO$_3$ in the northern high latitudes is similar to that in the
extratropical North Atlantic Basin. The global tropospheric
distribution of OH reported by Spivakovsky et al. [2000]
shows 10–20 $\times 10^5$ molecules cm$^{-3}$ for the northern high
latitudes and 20 $\times 10^5$ molecules cm$^{-3}$ for the extratropical
North Atlantic at 700 hPa in July. Further measurements
and modeling are needed to quantify the sensitivity of the
oxygen isotopic composition of NO$_3^-$ to atmospheric mixing
eratios of OH and O$_3$.

[25] For the winter, we might have expected to find
higher $\delta^{18}$O of NO$_3^-$ in Greenland than Bermuda since both
the OH and N$_2$O$_5$ pathways of HNO$_3$ production influence
NO$_3^-$ in the extratropics, while the lack of photochemistry in
the winter in Greenland minimizes the influence of OH.
One possible explanation is that the $\delta^{18}$O of O$_3$ is different
for these two environments. Only a few datasets of the
isotopic composition of tropospheric O$_3$ exist because the
measurement is challenging at ambient O$_3$ concentrations
[Krunkowsky et al., 1995; Johnston and Thiemens, 1997].
Based on the $\delta^{18}$O of NO$_3^-$ measurements, we might infer
that the $\delta^{18}$O of O$_3$ influencing NO$_3^-$ chemistry in Greenland
is lower than that influencing atmospheric chemistry over the
North Atlantic. Indeed, laboratory studies have shown
that formation of O$_3$ under colder temperatures can lead to
lower $\delta^{18}$O of O$_3$ (see Brenninkmeijer et al. [2003] for a
review).

4.3. Controls on the $\delta^{15}$N of NO$_3^-$

[26] The $\delta^{15}$N of NO$_3^-$ in Summit snow falls in the large
range reported for precipitation NO$_3^-$ in previous studies
[see Kendall, 1998; Russell et al., 1998, and references
therein]. Although the ~30‰ range in $\delta^{15}$N found at
Summit is large in comparison to other study sites [e.g.,
Russell et al., 1998; Garten, 1992; Freyer, 1978; Moore,
1977], the sampling resolution here is much higher than
previous studies. The only previous $\delta^{15}$N of NO$_3^-$ data from
Summit exhibit a range from ~5 to +3‰ in 8 snowpack
samples, with a slight preference for positive $\delta^{15}$N during
summer [Freyer et al., 1996], in agreement with our data.

[27] There is some evidence that interactions between
reactive nitrogen species can impact the N isotopes of NO$_3^-$.
For example, Freyer et al. [1993] find that the cyclic
interconversions of NO and N$_2$O$_5$ affect the $\delta^{15}$N of NO$_2$
(and therefore of HNO$_3$). The Freyer et al. study was of an

Figure 3. Results of (a) [NO$_3^-$] (µmol l$^{-1}$), (b) $\delta^{15}$N of
NO$_3^-$ (% versus atmospheric N$_2$), and (c) $\delta^{18}$O of NO$_3^-$
(‰ versus VSMOW) for six near-surface snow samples
collected in the morning (07:30 LT), midday (13:00 LT),
and night (19:30 LT) on 4 and 5 August 2001. Gray bars
highlight “nighttime,” or time when the Sun drops toward
the horizon, corresponding to times when the cosine of the
solar zenith angle (cos 0) is small (d). The closed circles in
(d) indicate sampling times. “OH pathway” as having two out of three oxygen atoms
from O$_3$, while the 2HNO$_3$ produced via N$_2$O$_5$ hydrolysis

can have as many as five out of six oxygen atoms from O$_3$.
(Note that oxygen isotopic exchange during hydrolysis is
not expected [e.g., Michalski et al., 2003].) The difference
in the $\delta^{18}$O of NO$_3^-$ corresponding to these two
end-member mechanisms of HNO$_3$ production can explain the
entire amplitude of the observed seasonal $\delta^{18}$O change
[Hastings et al., 2003]. The $\delta^{18}$O of NO$_3^-$ in the spring
is lower than in the winter but similar to or higher than in the
summer at Summit (Table 2). The $\delta^{18}$O of NO$_3^-$ in spring
2001 implies that production of HNO$_3$ in this season is a
mix of N$_2$O$_5$ hydrolysis and the reaction of NO$_2$ with OH,
and confirms that hydrolysis of N$_2$O$_5$ is likely still
contributing to HNO$_3$ deposition in the arctic spring, as
found in the model study by Stroud et al. [2003]. The
relatively large variation in springtime $\delta^{18}$O of NO$_3^-$ and the
difference found between the two spring seasons captured
in the snowpits suggest that the contribution of N$_2$O$_5$
hydrolysis to HNO$_3$ production in the spring is variable
(Table 2 and Figure 2c). This is most likely related to
annual variations in the timing of increasing air temperatures
and changes in cloud cover, since photoysis and high
temperatures can act to destroy PAN, NO$_3^-$ and N$_2$O$_5$. The
urban, polluted site in Jülich, Germany where the concentration of NOx often exceeds that of O3. Their explanation for higher wintertime $\delta^{15}N$ of NO2 is based largely on the observation of a large equilibrium isotope effect ($\alpha = 1.028$ at 25°C) between NO and NO2 [Begun and Melton, 1956], which works to increase the $\delta^{15}N$ of NO2 and decrease that of NO. Freyer et al. argue that because NO and NO2 are of comparable concentrations during the winter at Jülich, the $\delta^{15}N$ of NO2 can deviate significantly from the mean $\delta^{15}N$ of NOx, such that the $\delta^{15}N$ of NO2 would be $\sim 14\%$ higher than that of NO, if the NOx/NO2 ratio is 0.5. Higher O3 levels in the summer lead to nearly complete conversion of NO to NO2, such that the $\delta^{15}N$ of NO2 must be, by mass balance, equivalent to the mean $\delta^{15}N$ of NO3, explaining the lower summertime $\delta^{15}N$ of NO2.

[29] Although direct measurements are limited, the ratios of NOx to O3 and NO to NO2 are expected to be very different at Summit than at the urban site in the Freyer et al. [1993] study. Indeed, the seasonal cycle in $\delta^{15}N$ of NOx at Summit is opposite of that at Jülich, with higher $\delta^{15}N$ in the summer. Nevertheless, given the large nitrogen isotope effect considered by Freyer et al., it is possible that the higher $\delta^{15}N$ of NOx during summer results from a lower NOx/NO2 ratio at that time, as the $\delta^{15}N$ of NO2 could be significantly higher than that of NO, under these conditions. A few summertime studies have shown boundary layer average [NOx] and [O3] on the order of 0.050 ppbv and 45 ppbv, respectively [e.g., Yang et al., 2002; Dibb et al., 2002; Honrath et al., 1999] (O3 data for Summit also provided by NOAA/CMDL, available at www.cmdl.noaa.gov). There is little to no information on [NOx] during winter at Summit. However, with a lack of photolysis and typical surface O3 concentrations of >40 ppbv, we expect NOx to exist primarily as NO2, so that the $\delta^{15}N$ of NOx should equal that of NO2 (O3 data for Summit provided by NOAA/CMDL, available at www.cmdl.noaa.gov). Assuming no change in the $\delta^{15}N$ of NOx, one would thus predict a lower $\delta^{15}N$ of NO2 in the winter, which agrees at least qualitatively with the observation of lower $\delta^{15}N$ of NO2 in wintertime snow.

[29] The above scenario focuses on local processing of NOx as a possible influence on the $\delta^{15}N$ of NO2, which is subsequently converted to HNO3. However, this explanation for the seasonal $\delta^{15}N$ signal assumes a constant $\delta^{15}N$ for NOx being supplied to the atmosphere over Summit. This would require that previous atmospheric processing, such as we discuss above, is not occurring upwind of Summit; that is, we are assuming that Summit always sits at the beginning of the NOx loss process. While the short lifetime of NOx makes this assumption credible, this then implies that most of the NOx being supplied to Summit is deposited there. In this case, partitioning between NO and NO2 would have little impact on the $\delta^{15}N$ of HNO3 being deposited at Summit. In addition, Bermuda shows a similar seasonal variation in the $\delta^{15}N$ of NO3, where the NOx/NO2 ratio is high and seasonally invariant (based on chemical transport model results from MOZART-2 [Horowitz et al., 2003] and GEOS-CHEM [Bey et al., 2001]). This makes us skeptical of an NO/NO2 partitioning explanation for the $\delta^{15}N$ of NO3 in Summit snow. Finally, if NO/NO2 partitioning were the sole driver of the seasonal $\delta^{15}N$ change, the same global models would predict the highest $\delta^{15}N$ during the summer (the season with the lowest NOx/NO2 ratio), whereas the Summit 2000 data show a maximum in the spring (Figure 2 and Table 2).

[30] Long-range transport of NOx to Greenland primarily occurs via PAN formation. It is not known whether there are isotope effects associated with production and destruction of PAN that could significantly alter the isotopic signature of the source NOx. More generally, there is an obvious need to determine the isotopic relationships among important reactive nitrogen oxides (e.g., NO, NO3, PAN, NOx, N2O5). Once these relationships are better constrained, they can be incorporated into atmospheric chemistry models to quantify the impact of isotopic effects associated with chemical processing relative to the contribution of NOx sources in determining the $\delta^{15}N$ of atmospheric NO3. In any case, given current knowledge, photochemical processing of NOx cannot be ruled out as a contributor to the $\delta^{15}N$ of atmospheric NO3, but an unambiguous processing-based mechanism to explain the observed seasonal isotopic changes in Summit snow does not emerge.

[31] Given our current understanding, we believe that variation in the sources of NOx is the most straightforward explanation for the seasonal changes in $\delta^{15}N$ of NOx at Summit. Several studies have inferred that the $\delta^{15}N$ of NOx contains NOx source signatures [Freyer, 1978, 1991; Garten, 1996; Russell et al., 1998; Xiao and Liu, 2002; Hastings et al., 2003]. The $\delta^{15}N$ of NOx from a few emission sources has been determined. Heaton [1990] reports measurements of the $\delta^{15}N$ of NOx from vehicle emissions (−13 to −2%, varying with vehicle load) and coal combustion (+6 to +9%) in South Africa. Hoering [1957] finds that the $\delta^{15}N$ of NOx from electrical discharges (analogous to lightning) is between −0.5 and +1.4‰. No direct measurements exist for $\delta^{15}N$ of NOx from biomass burning, biogenic soil emissions, or stratospheric injection. However, measurements of $\delta^{15}N$ of NO3 in pre-industrial ice suggest that natural sources of NO3 have positive $\delta^{15}N$ source signatures: Freyer et al. [1996] find that the $\delta^{15}N$ of NO3 in pre-1950 ice at Summit is much higher (+12 to +18‰) in comparison to post-1950 (−5 to +5‰), and measurements of the $\delta^{15}N$ of NO3 in the GISP2 ice core show positive values throughout the pre-industrial Holocene [Galanter et al., 2001; Hastings, 2004]. Thus, the higher $\delta^{15}N$ of NO3 found in spring and summer snow at Summit could be due to a seasonal increase in the contribution from sources of NOx such as biomass burning, lightning, and biogenic soil emissions. Three-dimensional back trajectories have shown that summertime transport of air from North America to Summit tends to occur from the lowest 1500 m of the atmosphere, where surface emissions of NOx from biomass burning and soils are important [Miller et al., 2002]. In fact, biomass burning is the dominant contributor to summertime total surface NOx emissions in the northern high latitudes of North America and Eurasia [Galanter et al., 2000], and the contribution from biogenic soil emissions is significant in spring and summer in the northern mid-latitudes [Yienger and Levy, 1995]. The difference in average $\delta^{15}N$ between spring 2000 and 2001 might then be explained by a difference in the contribution of these NOx sources, particularly since major transport pathways to Summit in this season can be more variable than in summer [see Kahl et al., 1997]. The lower fall and winter $\delta^{15}N$
 coincide with rapid transport to Summit from highly industrialized regions of the Northern Hemisphere [Kahl et al., 1997], NO$_3^-$ in Bermuda rain points to anthropogenic (fossil fuel) sources as a contributor of low $\delta^{15}$N NO$_3^-$ [Hastings et al., 2003]. The range of Summit wintertime $\delta^{15}$N also falls in the range of previous measurements of NO$_3^-$ from vehicle emissions, although this range is admittedly large [Heaton, 1990].

5. Conclusions

[32] We observe diurnal variation in the $\delta^{15}$N and $\delta^{18}$O of NO$_3^-$ in surface snow at Summit. Our preliminary conclusion from these data is that NO$_3^-$ lost from the snow during the day is primarily recycled back to the snow at night. In addition, the $\delta^{15}$N and $\delta^{18}$O of NO$_3^-$ were not altered significantly in snow located at the surface in March and subsequently re-sampled at depth in early August. Both of these findings imply that postdepositional processing of NO$_3^-$ does not determine the seasonal variations observed in the isotopic composition of NO$_3^-$.

[33] Using snow pits to reconstruct the seasonal cycle, we find higher $\delta^{15}$N and lower $\delta^{18}$O of NO$_3^-$ in summer than in winter snow. The lower $\delta^{18}$O of NO$_3^-$ in summer is the result of reaction between NO$_2$ and OH to produce HNO$_3$, which dilutes the high $\delta^{18}$O signature of O$_3$ in NO$_2$. In winter, hydrolysis of N$_2$O$_3$ is expected to dominate HNO$_3$ formation, leading to higher $\delta^{18}$O of NO$_3^-$ because of a larger contribution from O$_3$. In addition, the high $\delta^{18}$O of NO$_3^-$ observed throughout the upper meter of snow indicates that exchange of NO$_3^-$ oxygen atoms with water is not significant, since this would drive the $\delta^{18}$O of NO$_3^-$ much lower.

[34] Although we cannot rule out isotopic effects associated with the chemical processing of precursor reactive nitrogen species, our interpretation of the seasonal cycle in $\delta^{15}$N of NO$_3^-$ is based on seasonal variation in the relative contributions of different NO$_3^-$ sources. The higher $\delta^{15}$N found in spring and summer snow might be explained by an increased contribution of NO$_3^-$ from sources such as biomass burning, biogenic soil emissions, and lightning. The lower fall and winter $\delta^{15}$N agree with the range observed for $\delta^{15}$N of NO$_3^-$ from fossil fuel combustion. Additional in situ measurements of both concentrations and isotopic ratios in odd nitrogen species at Summit are needed to better determine the impact that isotope fractionations may have on the seasonal $\delta^{15}$N of NO$_3^-$.

[35] The isotopic composition of NO$_3^-$ offers a new tool for the investigation of NO$_3^-$ chemistry and sources that contribute to NO$_3^-$ deposition. This has clear implications for study of the processing of NO$_3^-$ in surface snow, as well as interpretation of ice core records of NO$_3^-$.

This marked difference between Summit and Dome C may be associated with their differences in accumulation rate, through its effect on postdepositional processing. Additionally, the alkalinity contributed by the high dust content at Summit may play a role in reducing postdepositional loss of HNO$_3$ in Greenland relative to that observed in Antarctica [e.g., Fuhrer and Legrand, 1997; Röthlisberger et al., 2000, and references therein].

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References


Crutzen, P. J. (1974), Photochemical reaction initiated by influencing ozone Chemistry and sources that contribute to NO$_3^-$ deposition. This has clear implications for study of the processing of NO$_3^-$ in surface snow, as well as interpretation of ice core records of NO$_3^-$.

This isotopic composition of NO$_3^-$ offers a new tool for the investigation of NO$_3^-$ chemistry and sources that contribute to NO$_3^-$ deposition. This has clear implications for study of the processing of NO$_3^-$ in surface snow, as well as interpretation of ice core records of NO$_3^-$. The isotopic composition of NO$_3^-$ in ice cores holds promise to elucidate the impact that isotope fractionations may have on the seasonal $\delta^{15}$N of NO$_3^-$. The higher $\delta^{15}$N found in spring and summer snow might be explained by an increased contribution of NO$_3^-$ from sources such as biomass burning, biogenic soil emissions, and lightning. The lower fall and winter $\delta^{15}$N agree with the range observed for $\delta^{15}$N of NO$_3^-$ from fossil fuel combustion. Additional in situ measurements of both concentrations and isotopic ratios in odd nitrogen species at Summit are needed to better determine the impact that isotope fractionations may have on the seasonal $\delta^{15}$N of NO$_3^-$. The isotopic composition of NO$_3^-$ offers a new tool for the investigation of NO$_3^-$ chemistry and sources that contribute to NO$_3^-$. This has clear implications for study of the processing of NO$_3^-$ in surface snow, as well as interpretation of ice core records of NO$_3^-$. The isotopic composition of NO$_3^-$ in ice cores holds promise to elucidate changes in atmospheric chemistry, oxidizing capacity of the atmosphere and fluctuations in the sources of NO$_3^-$ with climate change. It is interesting to note that both the concentration and $\delta^{15}$N of NO$_3^-$ in Antarctic snow (Dome C) suggest significant fractionating loss of NO$_3^-$ due to photolysis and/or evaporation [Floc'h and Blumner, 2004].


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