

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_3^- have been measured in snow and firn from Summit, Greenland. The $^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$ ratios of NO_3^- in recently fallen snow are similar to those of surface snow. Diurnal variation is observed in $^{15}\text{N}/^{14}\text{N}$ of NO_3^- , and possibly $^{18}\text{O}/^{16}\text{O}$, suggesting fractionating loss of NO_3^- from snow during the day, which is subsequently recovered at night. A larger seasonal variation is observed, with higher $^{15}\text{N}/^{14}\text{N}$ and lower $^{18}\text{O}/^{16}\text{O}$ of NO_3^- in summer than winter, which cannot be explained by postdepositional fractionation. The generally high $^{18}\text{O}/^{16}\text{O}$ of NO_3^- in Greenland snow ($\delta^{18}\text{O}$ versus VSMOW = 65.2 to 79.6‰) indicates that oxygen atoms from ozone have been incorporated into NO_x that was subsequently deposited as HNO_3 . The lower mean $\delta^{18}\text{O}$ of NO_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_3 production via NO_2 reaction with hydroxyl radical (OH), which dilutes the high $\delta^{18}\text{O}$ imparted on NO_2 from ozone. The higher mean $^{15}\text{N}/^{14}\text{N}$ of NO_3^- observed in snow from spring ($\delta^{15}\text{N}$ versus air N_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 $^{15}\text{N}/^{14}\text{N}$ change may reflect NO_x sources, with a greater fall and wintertime contribution from fossil fuel emissions relative to other inputs of NO_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

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1. Introduction

[2] Nitrate (NO_3^-) is one of the major anions found in snow. NO_3^- deposition results from reactions between nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$), ozone (O_3) and hydroxyl radical (OH). Globally, the main sources of NO_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_3^- concentration ($[\text{NO}_3^-]$) in ice cores has been associated with increasing anthropogenic emissions of NO_x [Mayewski *et al.*, 1990; Neftel *et al.*, 1985], the contribution from

natural sources of NO_x today and in pre-industrial ice remains unclear [e.g., Wolff, 1995]. The link between the atmospheric concentration of NO_x and $[\text{NO}_3^-]$ in ice core records is particularly problematic because postdepositional processing can impact the $[\text{NO}_3^-]$ in snow.

[3] Postdepositional processes that may influence snow $[\text{NO}_3^-]$ include photolysis in surface snow layers and evaporative loss of HNO_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_3^- could release significant quantities of NO_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_x emissions beyond what would otherwise be expected from our current understanding based on atmospheric chemistry models.

[4] Since the lifetime of NO_x is on the order of days, low concentrations of NO_x 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.*, 1986, 1993; Honrath and Jaffe, 1992] have shown that peroxyacetyl nitrate ($\text{PAN} = \text{CH}_3\text{C}(\text{O})\text{OONO}_2$) 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_2 . At low temperatures, such as those found in the upper troposphere, PAN is stable and serves as a reservoir species of NO_x , providing a mechanism for the long-range transport of NO_x 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_2 to the arctic troposphere, which is then predominantly lost via reaction with OH to form HNO_3 [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 $[\text{NO}_3^-]$ 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 N_2O_5 (formed from $\text{NO}_2 + \text{NO}_3$) is the predominant sink for NO_x [Dentener 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 NO_3 .

[5] The isotopic composition of NO_3^- offers a tool for the study of NO_3^- in snow and ice cores that complements concentration measurements. The oxygen (O) isotopic composition of atmospheric NO_3^- contains information about the oxidants that react with NO_x to produce NO_3^- [Hastings *et al.*, 2003; Michalski *et al.*, 2003]. The nitrogen (N) isotopic composition of atmospheric NO_3^- may preserve signatures of different NO_x 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 NO_x chemistry in the atmosphere [Freyer *et al.*, 1993]. Here we report measurements of the N and O isotopic composition ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$) of NO_3^- 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 NO_3^- in terms of present NO_x chemistry and (2) to investigate the impact of postdepositional processing on the isotopes of NO_3^- in surface snow. These results can then be applied to ice core studies of NO_3^- in the effort to reconstruct past emissions sources and atmospheric cycling of NO_x .

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 $\delta^{18}\text{O}$ of snow at the University of Washington. The 250 ml bottles were refrozen and shipped frozen to Princeton University for stable isotope analysis of NO_3^- .

[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 isotope ratios in NO_3^- from the Greenland snowpack depends on the use of a sensitive method, since NO_3^- concentrations are low (typically $< 2 \mu\text{mol l}^{-1}$) and sample volume is limited. The isotope ratios ($^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$) of NO_3^- were determined at Princeton using the denitrifier method, which has a sample size requirement of 10 nmol N (i.e., 10 ml of a $1 \mu\text{mol l}^{-1}$ NO_3^- sample) [Sigman *et al.*, 2001; Casciotti *et al.*, 2002]. NO_3^- is quantitatively converted to nitrous oxide (N_2O), utilizing denitrifying bacteria that lack N_2O -reductase. The isotopic composition of the N_2O is then measured on a DeltaPlus IRMS in continuous flow mode to determine the $^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$ 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 $^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$, respectively. Throughout the text, isotope ratios are reported using delta (δ) notation in units of “per mil” (‰): $\delta^{15}\text{N}_{\text{sample}} = ((^{15}\text{N}/^{14}\text{N})_{\text{sample}} / (^{15}\text{N}/^{14}\text{N})_{\text{reference}} - 1) \times 1000 \text{ ‰}$ and $\delta^{18}\text{O}_{\text{sample}} = ((^{18}\text{O}/^{16}\text{O})_{\text{sample}} / (^{18}\text{O}/^{16}\text{O})_{\text{reference}} - 1) \times 1000 \text{ ‰}$, where the $^{15}\text{N}/^{14}\text{N}$ reference is N_2 in air and the $^{18}\text{O}/^{16}\text{O}$ reference is Vienna Standard Mean Ocean Water (VSMOW). Each batch of samples is referenced to the inter-

Table 1. Seasonal Bins for 1 m Snowpits Sampled at 3 cm Resolution in August 2001

Depth in Snowpit, m	Season Represented ^a
0.0–0.15	summer 2001 ^b
0.15–0.33	spring 2001
0.33–0.48	winter 2000–01
0.48–0.63	fall 2000
0.63–0.84	summer 2000
0.84–0.99	spring 2000

^aSummer: June, July, August; spring: March, April, May; winter: December, January, February; fall: September, October, November.

^bSummer 2001 represents June, July, and the first week of August.

nationally recognized standard IAEA-NO-3, which has an assigned value of 4.7‰ for $\delta^{15}\text{N}$ [Böhlke and Coplen, 1995] and a reported range of 22.7 to 25.6‰ for $\delta^{18}\text{O}$ [Böhlke et al., 2003, and references therein]. For consistency with our previously published work we adopt a value of 22.7‰ for the $\delta^{18}\text{O}$ of IAEA-NO-3. Our data can be subsequently corrected once a $\delta^{18}\text{O}$ of IAEA-NO-3 has been firmly established. An additional reference sample, USGS35, is run with each batch of samples as a secondary check on our correction scheme.

[10] The $\delta^{15}\text{N}$ determined from isotopic measurements of N_2O must be corrected for the contribution of $^{14}\text{N}^{14}\text{N}^{17}\text{O}$ to the peak at mass 45. This correction typically assumes a mass-dependent relationship between $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ ($\delta^{17}\text{O} \approx 0.52 \times \delta^{18}\text{O}$) of the N_2O analyte, which does not necessarily hold for N_2O produced from atmospheric NO_3^- samples (see Hastings et al. [2003] for further discussion). The $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ of atmospheric NO_3^- are considered “mass-independent,” such that the quantity $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$ 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_2O produced by *P. chlororaphis* is typically derived primarily from (mass-dependent) water, while oxygen in N_2O produced by *P. aureofaciens* represents the sample NO_3^- [Casciotti et al., 2002; Hastings et al., 2003]. The $\delta^{15}\text{N}$ of atmospheric NO_3^- determined with *P. aureofaciens* and corrected for a mass-dependent contribution from $\delta^{17}\text{O}$ may overestimate the true $\delta^{15}\text{N}$ by 1–2‰ [Sigman et al., 2001]. This overestimate is less for the $\delta^{15}\text{N}$ 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 $\Delta^{17}\text{O}$ of NO_3^- is $28.0 \pm 0.9\text{‰}$ [Alexander et al., 2004; B. Alexander, personal communication]. Assuming this $\Delta^{17}\text{O}$ and utilizing the $\delta^{18}\text{O}$ of NO_3^- for our samples from *P. aureofaciens*, we estimate $\delta^{17}\text{O}$ and use this to correct our $\delta^{15}\text{N}$ data. This correction results in an overall mean change of -0.6‰ to the $\delta^{15}\text{N}$ of NO_3^- determined with *P. chlororaphis*.

[11] Nitrate concentration ($[\text{NO}_3^-]$) 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 $[\text{NO}_3^-]$ above the instrument’s reported detection limit of $<0.003 \mu\text{mol l}^{-1}$. Nitrite concen-

trations were negligible compared to nitrate concentrations ($<0.3\%$ of $[\text{NO}_3^-]$); therefore, nitrite is not considered separately in the isotope analysis. The snowpit samples from August 2001 were analyzed for $\delta^{18}\text{O}$ of H_2O (snow) at University of Washington using standard CO_2 equilibration [e.g., Craig, 1961].

2.3. Seasonal Binning

[12] The NO_3^- isotope data were grouped into seasonal bins based on snow accumulation, surface height change, and density profiles for Summit, Greenland, collected during 2000 and 2001 (J. E. Dibb and M. Fahnestock, Snow accumulation, surface height change, and firn densification at Summit, Greenland: Insights from 2 years of in situ observation, submitted to *Journal of Geophysical Research*, 2004). Each 1 m snowpit from August represents approximately 5.5 seasons (i.e., ~ 1.5 years) of snow, and the bins are described in Table 1. Based on the seasonal binning, the top of the March snowpits should be located at approximately 0.33 m in the snowpits that were collected in August (Table 2). We have not attempted to precisely date the snowpits, and our seasonal binning of the isotope data makes the assumption that there has been no migration or re-organization of NO_3^- within the snowpack. Therefore, our assignments of season and the seasonal averages are susceptible to uncertainties. However, the $\delta^{18}\text{O}$ of snow, which is highly correlated with seasonal temperatures in Greenland [e.g., Grootes and Stuiver, 1997], qualitatively corroborates the seasonal binning for winter and summer, respectively (see Results section).

3. Results

3.1. $[\text{NO}_3^-]$ in the Snowpack

[13] The range and seasonality in $[\text{NO}_3^-]$ 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]. $[\text{NO}_3^-]$ in the August and March snowpit samples ranges from 0.8 to $5.9 \mu\text{mol l}^{-1}$ (Figure 1a). Overall, average $[\text{NO}_3^-] \pm 1$ SD for the two August snowpits is $1.9 \pm 0.7 \mu\text{mol l}^{-1}$ and $2.5 \pm 1.3 \mu\text{mol l}^{-1}$ 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 $[\text{NO}_3^-]$ is very similar to $[\text{NO}_3^-]$ data collected by Burkhart et al. [2004] for 10 snowpits sampled in July of 1998. Based on the seasonal binning described above, $[\text{NO}_3^-]$ 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 Burkhart et al. [2004] find no clear seasonality in $[\text{NO}_3^-]$.

3.2. The $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of NO_3^- in the Snowpack

[14] The $\delta^{15}\text{N}$ of NO_3^- for all of the snowpit samples collected in August and March ranges from -15.3‰ to $+16.7\text{‰}$ versus atmospheric N_2 (Figure 1b). There is some spatial heterogeneity in the $\delta^{15}\text{N}$ 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 $[\text{NO}_3^-]$, the $\delta^{15}\text{N}$ of NO_3^- is not significantly different between the August snowpits. Considering the large range and spatial heterogeneity in $\delta^{15}\text{N}$, comparison of the March and August

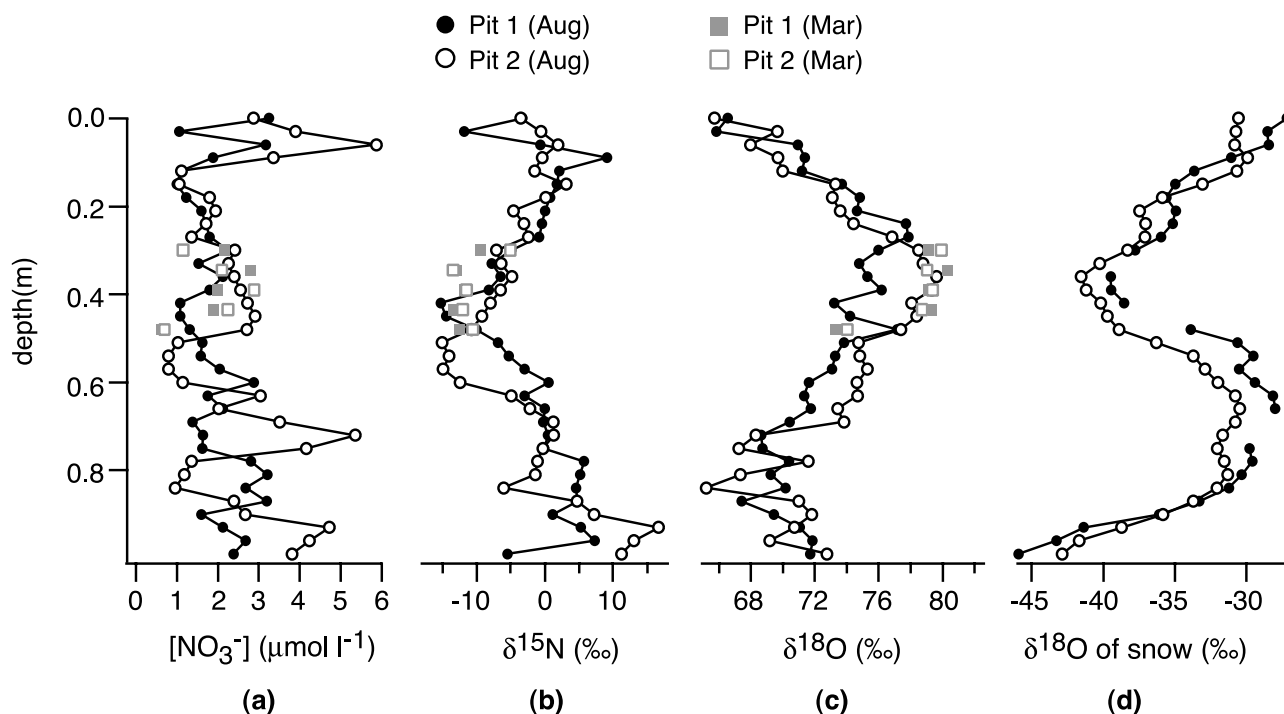


Figure 1. Profiles of (a) nitrate concentration ($[\text{NO}_3^-]$ in $\mu\text{mol l}^{-1}$), (b) $\delta^{15}\text{N}$ of NO_3^- (‰ versus atmospheric N_2), (c) $\delta^{18}\text{O}$ of NO_3^- (‰ versus VSMOW), and (d) $\delta^{18}\text{O}$ of snow (‰ versus SMOW) from two 1 m snowpits sampled every 3 cm in August 2001. Also shown are results from two shallow snowpits sampled at 6 cm resolution in March 2001 (gray squares). The March samples are located starting at 0.33 m (based on our seasonal binning) to compare with the “same” snow in August.

samples shows that the $\delta^{15}\text{N}$ of NO_3^- does not change significantly between the time of initial deposition and subsequent burial by more snowfall (Figure 1b).

[15] The overall average $\delta^{15}\text{N}$ of NO_3^- from surface snow samples collected in various locations near Summit camp is $-5.5 \pm 1.1\text{‰}$ ($n = 14$, Table 3). Fresh snow collected on 7 August has a $\delta^{15}\text{N}$ of -6.9‰ , which is very similar to surface snow (-6.4‰) collected the next day. This similarity is also seen for the $\delta^{18}\text{O}$ 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 $\delta^{15}\text{N}$ 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 $\delta^{15}\text{N}$ ($+5.9\text{‰}$) in 2000, but in 2001 the spring $\delta^{15}\text{N}$ of NO_3^- is similar to that found in summer. The fall $\delta^{15}\text{N}$ average is -9.2‰ , similar to that of wintertime snow.

[16] Overall, the $\delta^{18}\text{O}$ of NO_3^- in the upper meter of snow ranges from 65.2 to 79.6‰ versus VSMOW (Figure 1c). As with the $\delta^{15}\text{N}$ of NO_3^- , the $\delta^{18}\text{O}$ of NO_3^- profiles show some spatial variability between the different snowpits, but their difference is not significant. The $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ of NO_3^- of $66.9 \pm 2.2\text{‰}$ ($n = 14$, Table 3). The gradual changes found in the $\delta^{18}\text{O}$ of NO_3^- profile (Figure 1c) and the observation that fresh snow has a similar $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ of NO_3^- to be driven much lower than observed (see $\delta^{18}\text{O}$ of snow in Figure 1d). In contrast to the $\delta^{15}\text{N}$ of NO_3^- , the average $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ of NO_3^- in Surface Snow

[17] 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 $[\text{NO}_3^-]$ for these six samples ranges from 1.2 to 1.7 $\mu\text{mol l}^{-1}$, increasing by 0.5 $\mu\text{mol l}^{-1}$ 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 $[\text{NO}_3^-]$, the isotopes exhibit marked changes during the sampling period. The $\delta^{15}\text{N}$ of NO_3^- in these surface samples ranges

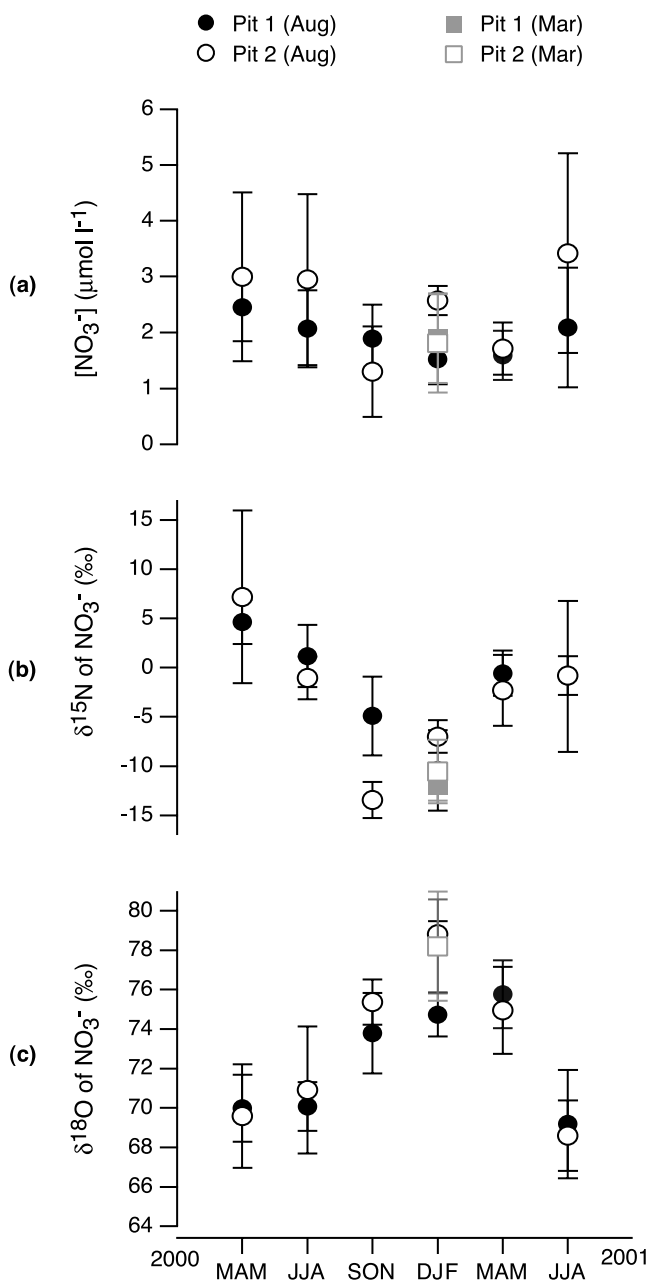


Figure 2. Seasonal averages of (a) $[\text{NO}_3^-]$ ($\mu\text{mol l}^{-1}$), (b) $\delta^{15}\text{N}$ of NO_3^- (‰ versus atmospheric N_2), and (c) $\delta^{18}\text{O}$ of NO_3^- (‰ versus VSMOW) for the August snowpits. Seasonal bins are described in Table 1. Shown for comparison with the August 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 $\delta^{15}\text{N}$ of NO_3^- in the snow at night appears to be much lower than during the day (Figure 3b). $\delta^{15}\text{N}$ 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 $\delta^{15}\text{N}$ 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 $\delta^{18}\text{O}$ of NO_3^- (Figure 3c) behaves like the $\delta^{15}\text{N}$ for the first five sample times, but then increases by 0.5 ‰ between midday and night on August 5th, while $\delta^{15}\text{N}$ decreases by 3.9 ‰. Overall, the amplitude of variation in $\delta^{18}\text{O}$ is smaller than in $\delta^{15}\text{N}$ of NO_3^- . From these few samples, it appears that both the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ 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.

[18] 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

[19] Several studies have measured a flux of NO_x 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; Röthlisberger *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 $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of NO_3^- in surface snow from night into day fits this qualitative expectation (Figure 3b). However, the subsequent decrease in $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ on the night of August 4th suggests that the NO_x (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 $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ on the night of the 5th is somewhat surprising. However, the $\delta^{18}\text{O}$ 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 oxygen isotopic composition 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_x 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_x emission was matched by HNO_3 deposition.

[20] 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

Table 2. Overall Seasonal Averages (± 1 Standard Deviation) for NO_3^- Concentration, $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ of NO_3^- , and $\delta^{18}\text{O}$ of Snow

Season ^a	$[\text{NO}_3^-]$, $\mu\text{mol l}^{-1}$	$\delta^{18}\text{O}$ of NO_3^- , ‰ vs VSMOW	$\delta^{15}\text{N}$ of NO_3^- , ‰ vs air N_2	$\delta^{18}\text{O}$ of Snow, ^b ‰ vs SMOW
Spring 2000	2.7 ± 1.1	69.8 ± 2.1	5.9 ± 6.2	-36.7 ± 2.6
Summer 2000	2.5 ± 1.2	70.5 ± 2.4	0.1 ± 2.8	-30.2 ± 1.8
Fall 2000	1.6 ± 0.7	74.6 ± 1.8	-9.2 ± 5.4	-32.8 ± 3.1
Winter ^c 2000–01	2.0 ± 0.7	77.5 ± 2.4	-10.0 ± 3.2	-40.1 ± 1.0
Spring 2001	1.7 ± 0.4	75.4 ± 1.9	-1.4 ± 3.0	-36.1 ± 1.5
Summer 2001	2.8 ± 1.5	68.9 ± 2.1	-0.8 ± 5.3	-30.4 ± 1.3

^aSeasons are as described in Table 1.

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

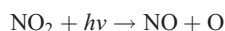
^cWinter includes the wintertime snow from both August and March snowpits.

(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 $[\text{NO}_3^-]$ measurements in snow from Summit, *Burkhart 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 $[\text{NO}_3^-]$.

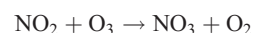
4.2. Controls on the $\delta^{18}\text{O}$ of NO_3^-

[21] Since surface processing of NO_3^- does not appear to dominate the observed seasonal isotopic signals, we will now consider the $\delta^{18}\text{O}$ of NO_3^- in terms of the larger scale tropospheric chemistry that produces HNO_3 from NO_x , prior to deposition at Summit. The range in $\delta^{18}\text{O}$ 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_x in the atmosphere [*Hastings et al., 2003; Michalski et al., 2003*]. The high $\delta^{18}\text{O}$ of atmospheric NO_3^- results from NO_x interactions with O_3 , the $\delta^{18}\text{O}$ of which is in the range of ~ 90 to 122‰ (versus VSMOW) [*Johnston and Thiemens, 1997; Krankowsky et al., 1995*]. The $\delta^{18}\text{O}$ 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:



[23] In the resulting HNO_3 , OH dilutes the high $\delta^{18}\text{O}$ signal imparted on NO_2 by O_3 . In the winter, we expect HNO_3 to be primarily produced via hydrolysis of N_2O_5 [*Stroud et al., 2003; Tie et al., 2003; Yang et al., 1995*]:



This pathway of HNO_3 production is only important in winter and early spring (polar night) because NO_3 and N_2O_5 are rapidly destroyed by photolysis. We expect HNO_3 produced from N_2O_5 hydrolysis to result in a higher $\delta^{18}\text{O}$ 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 3. NO_3^- Concentration, $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ of NO_3^- in Surface Snow Samples Collected in August 2001

Sampling Date and Time ^a	$[\text{NO}_3^-]$, $\mu\text{mol l}^{-1}$	$\delta^{18}\text{O}$ of NO_3^- , ‰ vs VSMOW	$\delta^{15}\text{N}$ of NO_3^- , ‰ vs air N_2	
<i>Surface Snow</i>				
8/2 17:00	4.5	69.5	-4.4	
	4.7	69.4	-4.6	
	4.5	69.1	-4.4	
8/3 09:00	3.7	68.4	-4.7	
	3.4	69.3	-4.5	
	20:00	3.5	68.5	-5.2
8/4 07:30	3.4	68.8	-4.5	
	13:00	3.4	65.0	-7.9
	19:30	4.6	64.9	-5.8
8/6 15:00	3.5	64.4	-6.9	
	5.8	65.9	-5.4	
	5.9	64.9	-6.4	
8/8 15:00	5.9	64.2	-6.5	
	5.3	64.7	-6.2	
	Average ± 1 SD	4.4 ± 1.0	66.9 ± 2.2	-5.5 ± 1.1
<i>Fresh Snow^b</i>				
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	

^aReplicate samples were collected at the same time in separate bottles.

^bThis refers to snow collected just after (8/7) and during (8/11) a snowfall event (see section 2.1).

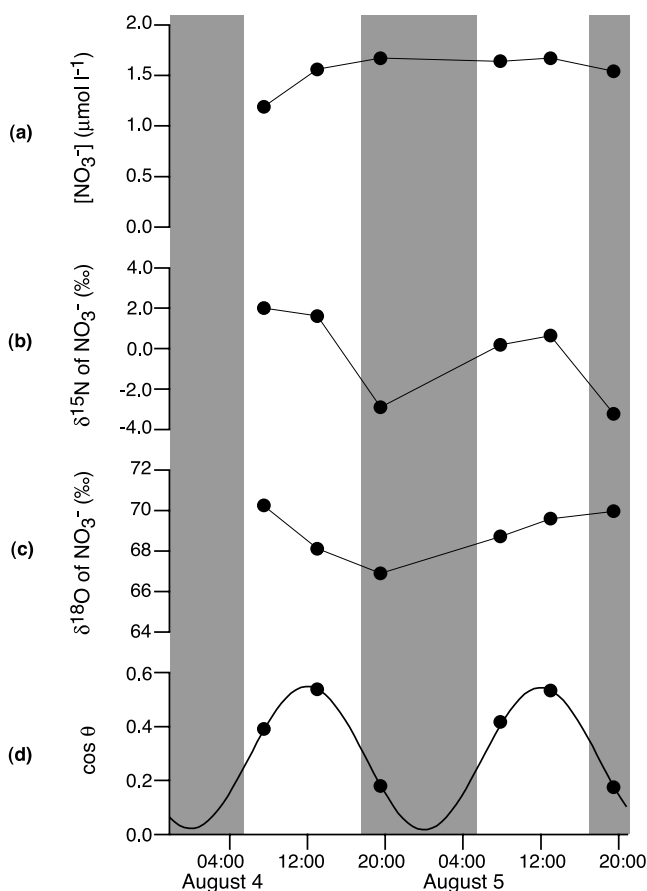


Figure 3. Results of (a) $[\text{NO}_3^-]$ ($\mu\text{mol l}^{-1}$), (b) $\delta^{15}\text{N}$ of NO_3^- (‰ versus atmospheric N_2), and (c) $\delta^{18}\text{O}$ of NO_3^- (‰ versus VSMOW) for six near-surface snow samples collected in the morning (07:30 LT), midday (13:00 LT), and night (19:30 LT) 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 ($\cos \theta$) 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_2O_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 $\delta^{18}\text{O}$ of NO_3^- corresponding to these two end-member mechanisms of HNO_3 production can explain the entire amplitude of the observed seasonal $\delta^{18}\text{O}$ change [Hastings *et al.*, 2003]. The $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ of NO_3^- in spring 2001 implies that production of HNO_3 in this season is a mix of N_2O_5 hydrolysis and the reaction of NO_2 with OH, and confirms that hydrolysis of N_2O_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 $\delta^{18}\text{O}$ of NO_3^- and the difference found between the two spring seasons captured in the snowpits suggest that the contribution of N_2O_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 photolysis and high temperatures can act to destroy PAN, NO_3 and N_2O_5 .

[24] It is interesting to compare the range and seasonal pattern in $\delta^{18}\text{O}$ of NO_3^- in snow at Summit to that observed in Bermuda rain. At Bermuda, Hastings *et al.* [2003] find a range in $\delta^{18}\text{O}$ of 60.3 to 86.5‰, with a significantly higher average $\delta^{18}\text{O}$ observed in cool season NO_3^- deposition ($76.9 \pm 6.3\%$) in comparison to that found in the warm season ($68.6 \pm 3.6\%$). The difference between the average winter ($77.5 \pm 2.4\%$) and summer ($69.8 \pm 2.4\%$ for 2000 and 2001) $\delta^{18}\text{O}$ in Summit snow is similar to that found in Bermuda rain, although a smaller range (65.2 to 79.6‰) and less variability in $\delta^{18}\text{O}$ of NO_3^- is found in Summit snow. From the Bermuda study, it appears that the $\delta^{18}\text{O}$ of NO_3^- may be sensitive to [OH]. The similarity between summertime $\delta^{18}\text{O}$ 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 $10\text{--}20 \times 10^5$ molecules cm^{-3} for the northern high latitudes and 20×10^5 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 ratios of OH and O_3 .

[25] For the winter, we might have expected to find higher $\delta^{18}\text{O}$ of NO_3^- in Greenland than Bermuda since both the OH and N_2O_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 $\delta^{18}\text{O}$ 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 [Krankowsky *et al.*, 1995; Johnston and Thiemens, 1997]. Based on the $\delta^{18}\text{O}$ of NO_3^- measurements, we might infer that the $\delta^{18}\text{O}$ of O_3 influencing NO_x 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 $\delta^{18}\text{O}$ of O_3 (see Brenninkmeijer *et al.* [2003] for a review).

4.3. Controls on the $\delta^{15}\text{N}$ of NO_3^-

[26] The $\delta^{15}\text{N}$ 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 $\sim 30\%$ range in $\delta^{15}\text{N}$ 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 $\delta^{15}\text{N}$ of NO_3^- data from Summit exhibit a range from -5 to $+3\%$ in 8 snowpack samples, with a slight preference for positive $\delta^{15}\text{N}$ 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_x . For example, Freyer *et al.* [1993] find that the cyclic interconversions of NO and NO_2 affect the $\delta^{15}\text{N}$ of NO_2 (and therefore of HNO_3). The Freyer *et al.* study was of an

urban, polluted site in Jülich, Germany where the concentration of NO_x often exceeds that of O_3 . Their explanation for higher wintertime $\delta^{15}\text{N}$ of NO_2 is based largely on the observation of a large equilibrium isotope effect ($\alpha = 1.028$ at 25°C) between NO and NO_2 [Begun and Melton, 1956], which works to increase the $\delta^{15}\text{N}$ of NO_2 and decrease that of NO . Freyer et al. argue that because NO and NO_2 are of comparable concentrations during the winter at Jülich, the $\delta^{15}\text{N}$ of NO_2 can deviate significantly from the mean $\delta^{15}\text{N}$ of NO_x , such that the $\delta^{15}\text{N}$ of NO_2 would be $\sim 14\%$ higher than that of NO_x if the NO_2/NO_x ratio is 0.5. Higher O_3 levels in the summer lead to nearly complete conversion of NO to NO_2 such that the $\delta^{15}\text{N}$ of NO_2 must be, by mass balance, equivalent to the mean $\delta^{15}\text{N}$ of NO_x , explaining the lower summertime $\delta^{15}\text{N}$ of NO_2 .

[28] Although direct measurements are limited, the ratios of NO_x to O_3 and NO to NO_2 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 $\delta^{15}\text{N}$ of NO_3^- at Summit is opposite of that at Jülich, with higher $\delta^{15}\text{N}$ in the summer. Nevertheless, given the large nitrogen isotope effect considered by Freyer et al., it is possible that the higher $\delta^{15}\text{N}$ of NO_3^- during summer results from a lower NO_2/NO_x ratio at that time, as the $\delta^{15}\text{N}$ of NO_2 could be significantly higher than that of NO_x under these conditions. A few summertime studies have shown boundary layer average $[\text{NO}_x]$ and $[\text{O}_3]$ 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] (O_3 data for Summit also provided by NOAA/CMDL, available at www.cmdl.noaa.gov). There is little to no information on $[\text{NO}_x]$ during winter at Summit. However, with a lack of photolysis and typical surface O_3 concentrations of >40 ppbv, we expect NO_x to exist primarily as NO_2 , so that the $\delta^{15}\text{N}$ of NO_2 should equal that of NO_x (O_3 data for Summit provided by NOAA/CMDL, available at www.cmdl.noaa.gov). Assuming no change in the $\delta^{15}\text{N}$ of NO_x , one would thus predict a lower $\delta^{15}\text{N}$ of NO_2 in the winter, which agrees at least qualitatively with the observation of lower $\delta^{15}\text{N}$ of NO_3^- in wintertime snow.

[29] The above scenario focuses on local processing of NO_x as a possible influence on the $\delta^{15}\text{N}$ of NO_2 , which is subsequently converted to HNO_3 . However, this explanation for the seasonal $\delta^{15}\text{N}$ signal assumes a constant $\delta^{15}\text{N}$ for NO_x 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 NO_x loss process. While the short lifetime of NO_x makes this assumption credible, this then implies that most of the NO_x being supplied to Summit is deposited there. In this case, partitioning between NO and NO_2 would have little impact on the $\delta^{15}\text{N}$ of HNO_3 being deposited at Summit. In addition, Bermuda rain shows a similar seasonal variation in the $\delta^{15}\text{N}$ of NO_3^- , where the NO_2/NO_x 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/NO_2 partitioning explanation for the $\delta^{15}\text{N}$ of NO_3^- change in Summit snow. Finally, if NO/NO_2 partitioning were the sole driver of the seasonal $\delta^{15}\text{N}$ change, the same global models would

predict the highest $\delta^{15}\text{N}$ during the summer (the season with the lowest NO_2/NO_x ratio), whereas the Summit 2000 data show a maximum in the spring (Figure 2 and Table 2).

[30] Long-range transport of NO_x 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 NO_x . More generally, there is an obvious need to determine the isotopic relationships among important reactive nitrogen oxides (e.g., NO , NO_2 , PAN, NO_3 , N_2O_5). 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 NO_x sources in determining the $\delta^{15}\text{N}$ of atmospheric NO_3^- . In any case, given current knowledge, photochemical processing of NO_x cannot be ruled out as a contributor to the $\delta^{15}\text{N}$ of atmospheric NO_3^- , 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 NO_x is the most straightforward explanation for the seasonal changes in $\delta^{15}\text{N}$ of NO_3^- at Summit. Several studies have inferred that the $\delta^{15}\text{N}$ of NO_3^- contains NO_x source signatures [Freyer, 1978, 1991; Garten, 1996; Russell et al., 1998; Xiao and Liu, 2002; Hastings et al., 2003]. The $\delta^{15}\text{N}$ of NO_x from a few emission sources has been determined. Heaton [1990] reports measurements of the $\delta^{15}\text{N}$ of NO_x from vehicle emissions (-13 to -2% , varying with vehicle load) and coal combustion ($+6$ to $+9\%$) in South Africa. Hoering [1957] finds that the $\delta^{15}\text{N}$ of NO_x from electrical discharges (analogous to lightning) is between -0.5 and $+1.4\%$. No direct measurements exist for $\delta^{15}\text{N}$ of NO_x from biomass burning, biogenic soil emissions, or stratospheric injection. However, measurements of $\delta^{15}\text{N}$ of NO_3^- in pre-industrial ice suggest that natural sources of NO_x have positive $\delta^{15}\text{N}$ source signatures: Freyer et al. [1996] find that the $\delta^{15}\text{N}$ of NO_3^- in pre-1950 ice at Summit is much higher ($+12$ to $+18\%$) in comparison to post-1950 (-5 to $+5\%$), and measurements of the $\delta^{15}\text{N}$ of NO_3^- in the GISP2 ice core show positive values throughout the pre-industrial Holocene [Galanter et al., 2001; Hastings, 2004]. Thus, the higher $\delta^{15}\text{N}$ of NO_3^- found in spring and summer snow at Summit could be due to a seasonal increase in the contribution from sources of NO_x 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 NO_x from biomass burning and soils are important [Miller et al., 2002]. In fact, biomass burning is the dominant contributor to summertime total surface NO_x 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 $\delta^{15}\text{N}$ between spring 2000 and 2001 might then be explained by a difference in the contribution of these NO_x 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 $\delta^{15}\text{N}$

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 $\delta^{15}\text{N}$ NO_x [Hastings *et al.*, 2003]. The range of Summit wintertime $\delta^{15}\text{N}$ also falls in the range of previous measurements of NO_x from vehicle emissions, although this range is admittedly large [Heaton, 1990].

5. Conclusions

[32] We observe diurnal variation in the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ 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 $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ 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^- . Nor does it appear to cause major deviation in the $\delta^{15}\text{N}$ of NO_3^- archived in the accumulated snow from the $\delta^{15}\text{N}$ of NO_3^- deposited six months prior.

[33] Using snowpits to reconstruct the seasonal cycle, we find higher $\delta^{15}\text{N}$ and lower $\delta^{18}\text{O}$ of NO_3^- in summer than in winter snow. The lower $\delta^{18}\text{O}$ of NO_3^- in summer is the result of reaction between NO_2 and OH to produce HNO_3 , which dilutes the high $\delta^{18}\text{O}$ signature of O_3 in NO_2 . In winter, hydrolysis of N_2O_5 is expected to dominate HNO_3 formation, leading to higher $\delta^{18}\text{O}$ of NO_3^- because of a larger contribution from O_3 . In addition, the high $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ 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 $\delta^{15}\text{N}$ of NO_3^- is based on seasonal variation in the relative contributions of different NO_x sources. The higher $\delta^{15}\text{N}$ found in spring and summer snow might be explained by an increased contribution of NO_x from sources such as biomass burning, biogenic soil emissions, and lightning. The lower fall and winter $\delta^{15}\text{N}$ agree with the range observed for $\delta^{15}\text{N}$ of NO_x 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 $\delta^{15}\text{N}$ of NO_3^- .

[35] The isotopic composition of NO_3^- offers a new tool for the investigation of NO_x 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 changes in atmospheric chemistry, oxidizing capacity of the atmosphere and fluctuations in the sources of NO_x with climate change. It is interesting to note that both the concentration and $\delta^{15}\text{N}$ of NO_3^- in Antarctic snow (Dome C) suggest significant fractionating loss of NO_3^- , due to photolysis and/or evaporation [Floch and Blunier, 2004].

This marked difference between Summit and Dome C may be associated with their differences in accumulation rate, through its affect 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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