

Glacial/interglacial changes in the isotopes of nitrate from the Greenland Ice Sheet Project 2 (GISP2) ice core

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[1] The $^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$ ratios of nitrate in the Greenland Ice Sheet Project 2 (GISP2) (Summit, Greenland) ice core are much higher in ice from the last glacial period than in the pre-industrial Holocene, despite the lack of a significant glacial/interglacial change in nitrate concentration. While both the $^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$ records are anticorrelated with snow accumulation rate, neither is satisfactorily explained by accumulation changes or post-depositional processes. The similarity in the glacial/interglacial change in $^{15}\text{N}/^{14}\text{N}$ from several different Greenland ice cores and the large amplitude of this change relative to observed seasonal variation raise the possibility that the isotopes of nitrate in ice cores indicate a large-scale glacial/interglacial change in the isotopic composition of atmospheric NO_x . The glacial/interglacial change in $^{18}\text{O}/^{16}\text{O}$ is best explained by a greater contribution of HNO_3 production from hydrolysis of N_2O_5 , which has implications for reconstruction of past atmospheric oxidant levels. Although isotope effects associated with NO_x photochemistry and nitrate scavenging have not been fully characterized, the $^{15}\text{N}/^{14}\text{N}$ data may indicate glacial/interglacial changes in the relative contributions from different natural sources of NO_x on a hemispheric or global scale.

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1. Introduction

[2] Nitrate (NO_3^-) is one of the major anions found in snow, and many profiles of NO_3^- from alpine and polar ice cores exist. A major motivation in studying ice core records of NO_3^- concentration is to reconstruct past levels of nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$), the precursor of deposited NO_3^- . Because NO_x interacts with the major oxidant cycles of the atmosphere, reconstruction of NO_x dynamics in the atmosphere would provide powerful constraints on tropospheric chemical composition and oxidizing capacity in the past atmosphere [Dibb *et al.*, 1998]. However, interpretation of NO_3^- concentration in the ice core record is difficult, and the contributions of different natural sources to the pre-industrial NO_x budget remain elusive [Legrand and Kirchner, 1990; Mayewski *et al.*, 1994; Wolff, 1995; Yang *et al.*, 1997; Legrand and Mayewski, 1997]. Since the atmosphere was acidic during the Holocene in comparison to the more alkaline glacial period, different

scavenging processes are expected to impact the concentration of NO_3^- that is deposited [e.g., Röthlisberger *et al.*, 2000; Yang *et al.*, 1997; Fuhrer and Legrand, 1997; Legrand *et al.*, 1988, 1999]. Additionally, post-depositional processes such as loss by sublimation and photolysis in surface snow can impact the NO_3^- concentrations that are ultimately archived in the ice core record [Dibb *et al.*, 1998, 2002; Honrath *et al.*, 2002; Röthlisberger *et al.*, 2002; Davis *et al.*, 2001; Jones *et al.*, 2000; Fischer *et al.*, 1998; Legrand and Kirchner, 1990].

[3] The isotopic composition of NO_3^- offers a tool to complement studies of ice core NO_3^- concentration. The isotopic composition of NO_3^- reflects the sources and chemical processing of atmospheric NO_x [Freyer, 1978; Heaton, 1986; Freyer *et al.*, 1993; Russell *et al.*, 1998; Xiao and Liu, 2002; Hastings *et al.*, 2003; Michalski *et al.*, 2003; Heaton *et al.*, 2004]. A recent study of the isotopic composition of NO_3^- in surface snow at Summit, Greenland reveals seasonal variation in both $^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$ of NO_3^- [Hastings *et al.*, 2004]. This study concluded that variation in the $^{18}\text{O}/^{16}\text{O}$ of NO_3^- reflects a seasonal change in the oxidation chemistry that converts NO_x to HNO_3 in the atmosphere, while the $^{15}\text{N}/^{14}\text{N}$ of NO_3^- most likely varies with seasonal changes in the contribution of different NO_x source emissions. The Summit study revealed that photo-

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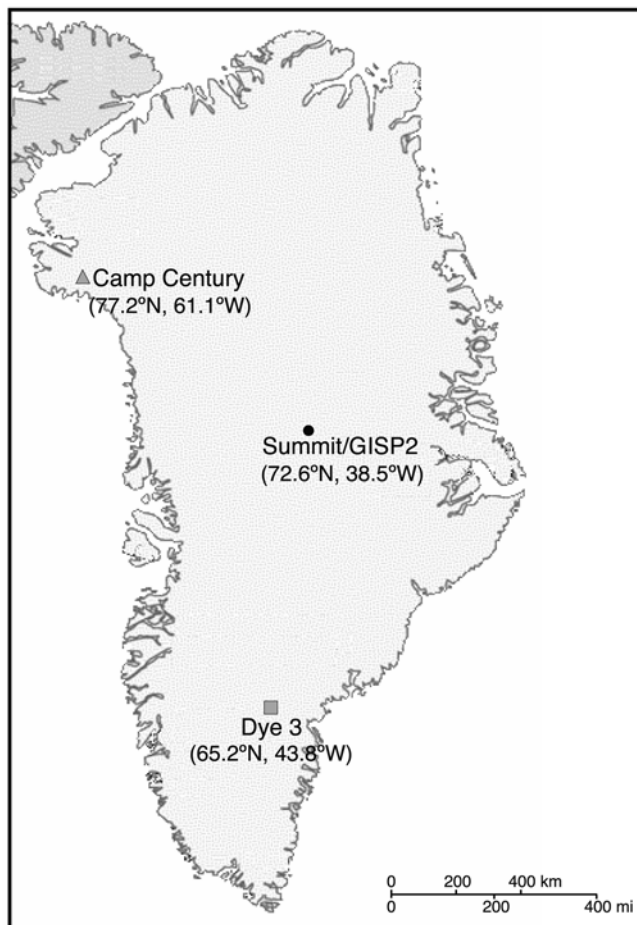


Figure 1. Location of ice cores from Camp Century (77.2°N, 61.1°W, 1880 m, 0.35 m ice yr⁻¹ accumulation), Dye 3 (65.2°N, 43.8°W, 2491 m, 0.54 m ice yr⁻¹), and GISP2 (72.6°N, 38.5°W, 3200 m elevation, 0.24 m ice yr⁻¹).

lytic or evaporative loss is not contributing to significant post-depositional enrichment in the isotopes of NO₃⁻. However, a study of Antarctic surface snow (Dome C) indicated a loss of NO₃⁻ from the snowpack that left the snow NO₃⁻ enriched in ¹⁵N (and presumably ¹⁸O as well) [Blunier *et al.*, 2005; Floch and Blunier, 2004] [see also Freyer *et al.*, 1996]. It is not yet known what process is responsible for the isotopic fractionation during NO₃⁻ loss from snow at Dome C. This type of NO₃⁻ loss appears to be much less important under the high accumulation conditions at Summit, Greenland. Despite the lower accumulation rate in Greenland during the last glacial period, which may enhance photolytic or evaporative loss of NO₃⁻, the association of calcium (Ca²⁺) and NO₃⁻ in glacial ice is expected to make NO₃⁻ less sensitive to post-depositional processing [Wolff, 1995; Fuhrer and Legrand, 1997; Legrand *et al.*, 1999; Röthlisberger *et al.*, 2000].

[4] Here we report measurements of the ¹⁵N/¹⁴N, ¹⁸O/¹⁶O, and concentration of NO₃⁻ in samples from the Greenland Ice Sheet Project 2 (GISP2) ice core, covering the last 36,000 years. To constrain the cause of observed glacial/interglacial changes, we also analyze samples

corresponding to the Holocene (from the last 10,000 years) and last glacial (prior to 18,000 years ago) from the Dye 3 and Camp Century ice cores in Greenland (Figure 1).

2. Methods

2.1. Sample Collection

[5] The ice core samples from the GISP2 ice core (72.6°N, 38.5°W, 3200 m elevation, 0.24 m ice yr⁻¹ accumulation) were cut for gas extraction and analysis in the laboratory of Michael Bender at Princeton University [Blunier *et al.*, 2002]. The meltwater from these samples was saved for NO₃⁻ isotope analysis. The parts of the apparatus that came in to contact with the sample water were thoroughly rinsed with deionized water prior to use and between samples. The sample vessels were also thoroughly cleaned between uses. Periodically, to check for NO₃⁻ contamination, blanks were collected by running deionized water through the entire process.

[6] Samples from Dye 3 (65.2°N, 43.8°W, 2491 m, 0.54 m ice yr⁻¹) and Camp Century (77.2°N, 61.1°W, 1880 m, 0.35 m ice yr⁻¹) were obtained from the National Ice Core Laboratory in Denver, CO (Figure 1). In Princeton, the outer layer of the ice samples was cut with a bandsaw at -30°C and discarded to avoid contamination that may have occurred during the drilling process and/or subsequent handling and transport. The ice was then placed directly into clean HDPE bottles and melted at room temperature for NO₃⁻ concentration and isotope analysis.

2.2. Nitrate Concentration and Isotope Analysis

[7] Nitrate concentration ([NO₃⁻]) was determined by reduction of NO₃⁻ (and nitrite, NO₂⁻) to nitric oxide (NO) followed by chemiluminescence detection of NO [Braman and Hendrix, 1989]. NO₂⁻ concentrations are typically negligible compared to [NO₃⁻] [e.g., Legrand and DeAngelis, 1995], and NO₂⁻ is not considered separately in the isotope analysis. Typical [NO₃⁻] for the GISP2 samples is 1.2 μmol L⁻¹ (μM), and repeated measurements indicated a standard deviation of ±0.2 μM.

[8] A sensitive method is critical for the high-resolution study of the isotope ratios of NO₃⁻ in ice cores since [NO₃⁻] is low and ice core samples are precious. The isotope ratios (¹⁵N/¹⁴N and ¹⁸O/¹⁶O) of NO₃⁻ were determined using the denitrifier method [Sigman *et al.*, 2001; Casciotti *et al.*, 2002]. This method requires as little as 10 nmol N (i.e., 10 mL of a 1 μM sample), utilizing denitrifying bacteria that lack nitrous oxide (N₂O) reductase to convert NO₃⁻ to N₂O, which is then measured on a DeltaPlus IRMS in continuous flow mode to determine δ¹⁵N and δ¹⁸O (delta (δ) notation in units of “per mil” (‰): δ¹⁵N_{sample} = ((¹⁵N/¹⁴N)_{sample} / (¹⁵N/¹⁴N)_{reference} - 1) × 1000‰ and δ¹⁸O_{sample} = ((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)). In this study, the standard deviation indicated by repeated measurements of δ¹⁵N and δ¹⁸O is 0.2‰ and 0.4‰, respectively.

[9] Referencing of ¹⁵N/¹⁴N to atmospheric N₂ and of ¹⁸O/¹⁶O to VSMOW is done via comparison to the potassium nitrate (KNO₃) reference material IAEA-N3, with an assigned δ¹⁵N of +4.7‰ [Gonfiantini *et al.*, 1995] and

Table 1. Mean (and Standard Deviation/ \sqrt{n}) for Concentration, $\delta^{15}\text{N}$, and $\delta^{18}\text{O}$ of NO_3^- in Holocene and Glacial Ice Samples From the GISP2 Ice Core

	$[\text{NO}_3^-]^a$		$\delta^{15}\text{N}$		$\delta^{18}\text{O}$	
	μM	n^b	‰	n	‰	n
Holocene ^c	1.32 (0.10)	16	9.7 (0.7)	17	62.7 (1.8)	14
GISP2 $[\text{NO}_3^-]^d$	1.29 (0.06)	16				
Glacial ^c	1.30 (0.12)	9	28.4 (1.1)	10	75.3 (2.1)	10
GISP2 $[\text{NO}_3^-]$	1.32 (0.08)	9				

^aDoes not include two outliers (see section 3.1).

^bNumber of samples included in mean.

^cHolocene defined here as ~ 500 – $10,000$ yrs BP; Glacial as $\sim 18,000$ – $36,000$.

^dGISP2 mean is from *National Snow and Ice Data Center* [1997] for samples that correspond (based on depth) to the samples in this study.

reported $\delta^{18}\text{O}$ of $+22.7$ to $+25.6\text{‰}$ [Böhlke et al., 2003; Révész et al., 1997; Silva et al., 2000]. We adopt here a $\delta^{18}\text{O}$ of 22.7‰ [Révész et al., 1997; Silva et al., 2000] for consistency with previous work and awaiting greater certainty in the $\delta^{18}\text{O}$ of IAEA-N3. The large uncertainty in the O isotopic difference between NO_3^- reference IAEA-N3 (and indeed all NO_3^- references) and VSMOW is not addressable with the denitrifier method, which can only indicate isotopic differences among NO_3^- samples. If we were to assume the highest estimate for the $\delta^{18}\text{O}$ of IAEA-N3 (25.6‰ [Böhlke et al., 2003]), then the $\delta^{18}\text{O}$ of all of our samples would increase by $\sim 2.9\text{‰}$. The uncertainty in the isotopic difference between IAEA-N3 and VSMOW is an unfortunate source of uncertainty in our reported values. However, our focus here is on the variation of NO_3^- $^{18}\text{O}/^{16}\text{O}$, not its relationship to the isotope ratios found in other O-bearing materials. Moreover, where comparisons to O_2 , O_3 , and H_2O are made, the current uncertainty in IAEA-N3 does not significantly affect the interpretation.

[10] Isotopic measurements of N_2O at masses 44, 45, and 46 must be corrected for the contribution of $^{14}\text{N}^{14}\text{N}^{17}\text{O}$ at mass 45 to determine $\delta^{15}\text{N}$. The standard correction assumes a mass-dependent relationship between $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$, which does not necessarily hold for N_2O produced from atmospheric NO_3^- (see Hastings et al. [2003] for a detailed discussion), so that it could overestimate the “true” $\delta^{15}\text{N}$ of NO_3^- by as much as 1 – 2‰ [Sigman et al., 2001]. A more appropriate correction, similar to that presented in Hastings et al. [2004], is applied here. This correction takes into account the “mass-independent” behavior of the $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ of atmospheric NO_3^- , quantified by $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$ [e.g., Michalski et al., 2002, 2003, and references therein]. Alexander et al. [2004] find a $\Delta^{17}\text{O}$ of $27.9 \pm 0.9\text{‰}$ ($n = 31$) for NO_3^- in Greenland ice covering the time period 1692–1976 AD. Assuming this $\Delta^{17}\text{O}$ and utilizing our $\delta^{18}\text{O}$ of NO_3^- data, we determine $\delta^{17}\text{O}$ and use this to correct our $\delta^{15}\text{N}$ data. This correction results in a mean difference of -1.7‰ from the $\delta^{15}\text{N}$ corrected assuming a mass-dependent relationship between $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ (i.e., $\Delta^{17}\text{O} = 0$). The $\Delta^{17}\text{O}$ of NO_3^- may have changed significantly on interglacial/glacial timescales. Using the minimum (20‰) and maximum (30‰) reported $\Delta^{17}\text{O}$ of NO_3^- from measurements in La Jolla, California [Michalski et al., 2003] would result in a mean $\delta^{15}\text{N}$ correction of

between -1.2‰ and -1.8‰ , respectively. We expect that our corrected $\delta^{15}\text{N}$ of NO_3^- is closer to the “true” $\delta^{15}\text{N}$ than suggested by this range since the $\Delta^{17}\text{O}$ of NO_3^- was most likely $\geq 28\text{‰}$ in the last glacial (see section 4).

2.3. Comparison With GISP2 Data

[11] We have matched our sample depths to existing GISP2D data for ice age, $[\text{NO}_3^-]$ and accumulation rate, and we make use of the high-resolution records for the $\delta^{18}\text{O}$ of ice and calcium (Ca) concentration [Grootes et al., 1993; Steig et al., 1994; Meese et al., 1994a, 1994b; Alley et al., 1993; Mayewski et al., 1990, 1997; Taylor et al., 1996; Yang et al., 1995; Cuffey et al., 1995; Cuffey and Clow, 1997; Grootes and Stuvier, 1997; National Snow and Ice Data Center, 1997]. Ages are reported in years before present (BP), where present is 1950 AD. During sample processing, ~ 70 g of ice was consistently collected, representing an ice thickness of ~ 5 cm. In general, our results represent about a single year in the Holocene and as much as ~ 3 years in the glacial period. Direct comparison of $[\text{NO}_3^-]$ measurements with Mayewski et al. [1997] is compromised since our results represent less ice than Mayewski et al.’s measurements, and there is some uncertainty in the depths of our samples (i.e., whether the depths represent the top or bottom of an ice core sample was not recorded). Still, on the basis of a paired t-test, our mean $[\text{NO}_3^-]$ does not differ significantly from the measurements by Mayewski et al. [1990, 1997].

3. Results

3.1. Nitrate Concentration ($[\text{NO}_3^-]$)

[12] $[\text{NO}_3^-]$ varies between 0.7 and $2.7 \mu\text{M}$ (44 – 167 ppb NO_3^- ; $n = 37$) between ~ 500 and $\sim 36,000$ years ago for the samples in this study (Figure 2a). Two samples represent outliers for our concentration data set. The outliers have $[\text{NO}_3^-]$ of 2.3 and $2.7 \mu\text{M}$, and come from 498 and $26,072$ years before present (BP), respectively. However, the isotope results for these samples do not appear anomalous (Figures 2b and 2c). Moreover, no significant NO_3^- contamination was found in periodic procedural blanks. Similar to earlier findings, the average $[\text{NO}_3^-]$ does not vary significantly between the pre-industrial Holocene (defined here as between ~ 500 and $\sim 10,000$ years BP) and the last glacial period ($18,000$ to $\sim 36,000$ BP) (Table 1). The average $[\text{NO}_3^-]$ from corresponding samples of Mayewski et al. [1997] (based on depth) is also shown in Table 1.

[13] No correlation is found between $[\text{NO}_3^-]$ and accumulation rate or between $[\text{NO}_3^-]$ and $\delta^{18}\text{O}$ of ice (i.e., temperature) for the GISP2 samples in this study (Figure 2). The results from analyses of a few samples from the Dye 3 and Camp Century ice cores are shown in Table 2 (also see Figure 1). The present accumulation rate at the GISP2 coring site (Summit, Greenland) is $0.24 \text{ m ice yr}^{-1}$, in comparison to $0.35 \text{ m ice yr}^{-1}$ for Camp Century and $0.54 \text{ m ice yr}^{-1}$ for Dye 3 [e.g., Ohmura and Reeh, 1991]. Among the three Greenland sites, $[\text{NO}_3^-]$ in Holocene ice tends to increase with decreasing accumulation rate such that $\text{GISP2 } [\text{NO}_3^-] > \text{Camp Century } [\text{NO}_3^-] > \text{Dye 3 } [\text{NO}_3^-]$ (Tables 1 and 2). These results ((1) the lack of a temporal correlation between $[\text{NO}_3^-]$ and accumulation rate in

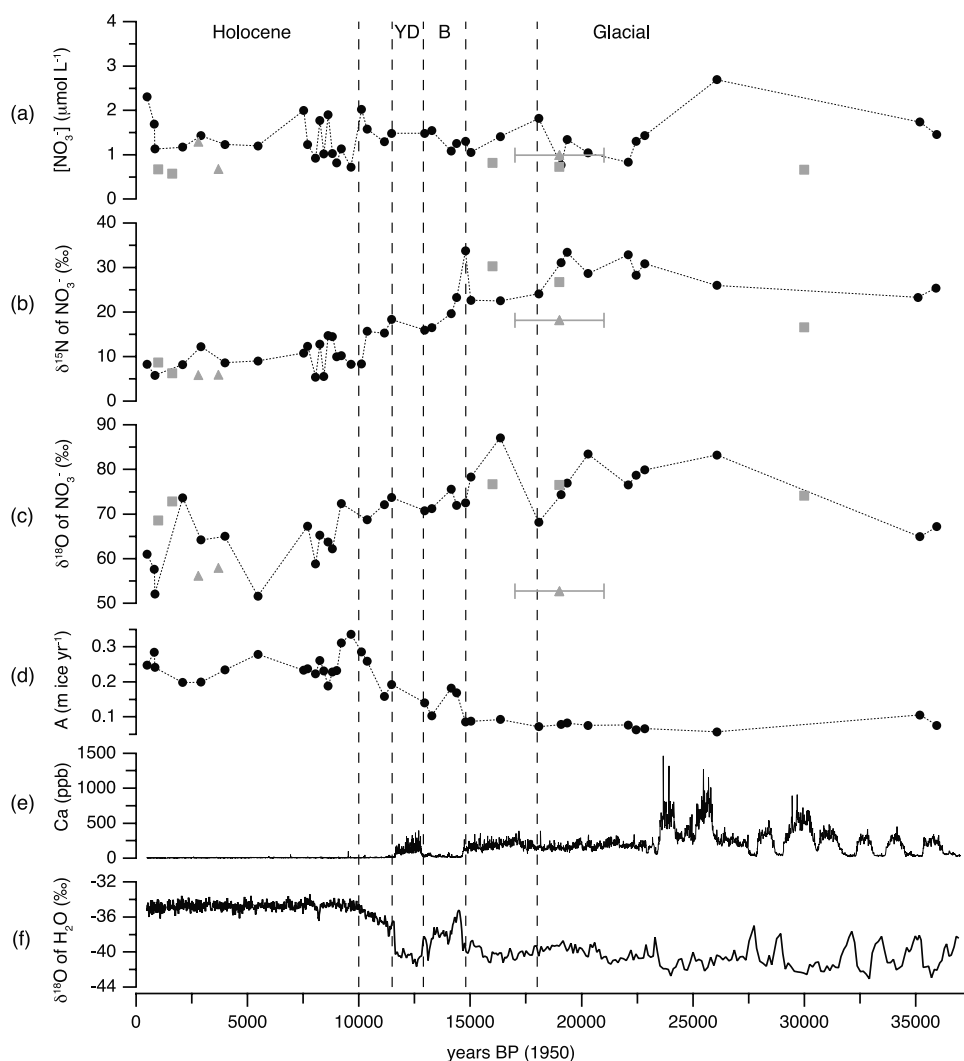


Figure 2. Results from measurements on GISP2 ice core samples of (a) NO_3^- concentration (μM), (b) $\delta^{15}\text{N}$ of NO_3^- (‰ versus N_2), and (c) $\delta^{18}\text{O}$ of NO_3^- (‰ versus VSMOW). (d) Accumulation rate (m ice yr^{-1}) corresponding to the NO_3^- measurements, and high-resolution records of (e) calcium concentration (ppb), (f) $\delta^{18}\text{O}$ of ice (‰ versus SMOW), and age (x axis) are from *National Snow and Ice Data Center* [1997]. Gray symbols represent samples from Dye 3 (squares) and Camp Century (triangles). The error bar on the Camp Century sample represents the estimated time the sample covers (see Table 2). Dashed lines mark important climate transitions the Holocene, Younger Dryas (YD), Bølling-Allerød (B), and the last glacial period [see e.g., *Grootes and Stuvier*, 1997, and references therein].

GISP2, and (2) the presence of a spatial correlation among Greenland sites with different accumulation for Holocene ice) fit with earlier observations [Yang *et al.*, 1996; Röthlisberger *et al.*, 2002].

3.2. The $\delta^{15}\text{N}$ of NO_3^- in GISP2

[14] The $\delta^{15}\text{N}$ of NO_3^- ranges from +5.4 to +33.7‰ versus atmospheric N_2 ($n = 37$) between ~500 and 36,000 years BP (Figure 2b). The $\delta^{15}\text{N}$ of NO_3^- in pre-industrial ice is higher than typically observed in modern precipitation around the world [e.g., *Hastings et al.*, 2003; *Russell et al.*, 1998; *Kendall*, 1998; *Freyer*, 1991, and references therein]. The $\delta^{15}\text{N}$ of pre-industrial NO_3^- in the

GISP2 core is also higher than the mean $\delta^{15}\text{N}$ found in the present annual snowpack at Summit, Greenland ($-2.0 \pm 6.8\text{‰}$, $n = 68$) [*Hastings et al.*, 2004] and Svalbard ($-10.6 \pm 1.0\text{‰}$, $n = 13$, spring/winter snow only) [*Heaton et al.*, 2004]. Higher $\delta^{15}\text{N}$ in pre-industrial NO_3^- at Summit was also found by *Freyer et al.* [1996], who report $\delta^{15}\text{N}$ of NO_3^- ranging between +12 to +18‰ ($n = 4$) for samples dated between ~1730 and 1950 AD.

[15] In contrast to $[\text{NO}_3^-]$, the $\delta^{15}\text{N}$ of NO_3^- changes significantly ($P < 0.01\%$) between the pre-industrial Holocene and last glacial, increasing from a mean of 9.7‰ to one of 28.4‰ (Figure 2b, Table 1). The $\delta^{15}\text{N}$ of NO_3^- from Dye 3 and Camp Century is also significantly higher in

Table 2. Results From Dye 3 and Camp Century Ice Cores

Depth, m	[NO ₃ ⁻], μM	δ ¹⁵ N, ‰	δ ¹⁸ O, ‰	Estimated Age (Years BP) ^a
<i>Dye 3</i>				
488.86–489.16	0.67	8.7	68.5	early Holocene (1000)
714.17–714.37	0.57	6.3	72.9	early Holocene (1620)
1818.61–1818.91	0.82	30.3	76.7	near glacial (16,000)
1831.78–1832.00	0.73	26.7	76.6	glacial (19,000)
1979.54–1979.89	0.66	16.6	74.2	glacial (>25,000)
<i>Camp Century</i>				
708.41–708.91	1.29	5.8	56.2	mid-Holocene (2900)
799.58–799.90	0.99	6.0	57.9	mid-Holocene (3700)
1210–1246	1.17	18.2	52.7	glacial (17–21,000)

^aEstimated age based on work of *Hammer et al.* [1978] for Camp Century and E. J. Steig and S. Johnsen (personal communication, 2004) for Dye 3.

glacial samples than in the Holocene (Figure 2b, Table 2). The results from Dye 3 are very similar to GISP2 with δ¹⁵N of 6.3 and 8.7‰ in Holocene samples, and 26.7 and 30.3‰ near the last glacial maximum (~18,000 years ago). The amplitude of the change in δ¹⁵N between two Holocene (5.9‰) and one glacial (18.2‰) sample from Camp Century is smaller than the other two sites. The δ¹⁵N of NO₃⁻ in the GISP2 ice core is anti-correlated with accumulation rate ($r = -0.87$; Figure 3b).

3.3. The δ¹⁸O of NO₃⁻ in GISP2

[16] The δ¹⁸O of NO₃⁻ in the GISP2 ice core ranges from +51.6 to +87.1‰ versus VSMOW (Figure 2c). This range is similar to that found in modern precipitation [e.g., *Hastings et al.*, 2003; *Michalski et al.*, 2003; *Williard et al.*, 2001]. The δ¹⁸O of NO₃⁻ in recent measurements of snow at Summit, Greenland, varies seasonally, ranging from 65.2 to 79.6‰, with an overall mean of 72.6 ± 3.6 ‰ ($n = 68$) for the upper meter of snow [*Hastings et al.*, 2004]. The results

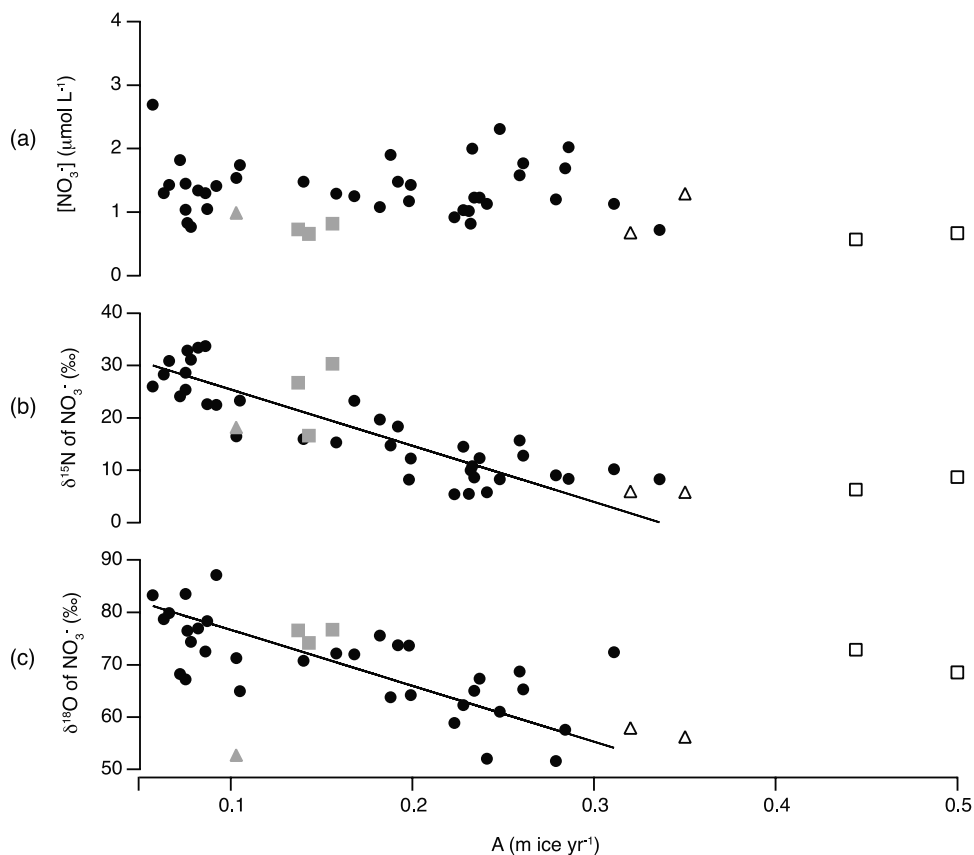


Figure 3. (a) NO₃⁻ concentration (μM), (b) δ¹⁵N of NO₃⁻ (‰ versus N₂), and (c) δ¹⁸O of NO₃⁻ (‰ versus VSMOW) plotted against accumulation rate. Results from GISP2 are shown as black circles. Open symbols represent Holocene samples from Dye 3 (squares) and Camp Century (triangles) for which age and accumulation rate are well constrained. Accumulation rate is estimated for the glacial samples from Dye 3 (gray squares) and Camp Century (gray triangles) by scaling present accumulation based on the ratio of accumulation change from the GISP2 ice core. NO₃⁻ concentration shows no relationship with accumulation rate. The regressions for the GISP2 data in Figures 3b and 3c are based on the reduced major axis (line of organic correlation) method [e.g., *Miller and Kahn*, 1962]. The correlations found for (Figure 3b) δ¹⁵N and accumulation rate ($r = -0.87$) and (Figure 3c) δ¹⁸O and accumulation rate ($r = -0.69$) are highly significant ($P < 0.05\%$).

presented here are the first reported measurements of $\delta^{18}\text{O}$ in pre-industrial NO_3^- . These measurements counter the previous suggestion that the high $\delta^{18}\text{O}$ of atmospheric NO_3^- precipitation might be a reflection of an anthropogenic pollution source [Kendall, 1998].

[17] Similar to the $\delta^{15}\text{N}$ of NO_3^- , the $\delta^{18}\text{O}$ is significantly higher ($P < 0.01\%$) in the last glacial than Holocene. However, the glacial/interglacial change is not as striking for $\delta^{18}\text{O}$ because there is additional variability in the record. Since the ~ 5 cm samples of GISP2 ice (section 2.3) could represent less than a year of snow in the Holocene, the apparently greater variability of $\delta^{18}\text{O}$ of NO_3^- in the Holocene samples relative to the glacial samples may be related to the seasonality of $\delta^{18}\text{O}$ captured in these samples. The $\delta^{18}\text{O}$ of NO_3^- increases from a mean of 62.7‰ in the Holocene to a mean of 75.3‰ in the glacial period (Table 1). The $\delta^{18}\text{O}$ of NO_3^- in the GISP2 ice core is anticorrelated ($r = -0.69$) with accumulation rate, though not as strongly as is $\delta^{15}\text{N}$ (Figure 3c). The $\delta^{18}\text{O}$ of NO_3^- in the two Holocene samples from Dye 3 (68.5 and 72.9‰) tends to be higher than that found in the Holocene at GISP2 (Figure 2b). A more subtle increase in $\delta^{18}\text{O}$ is found between the Holocene and glacial (77‰) samples from Dye 3 than in GISP2 (Tables 1 and 2). The two Holocene samples from Camp Century have a lower mean $\delta^{18}\text{O}$ of NO_3^- than GISP2 and Dye 3 (57‰). The $\delta^{18}\text{O}$ of NO_3^- at Camp Century decreases slightly from the Holocene to glacial (52‰). While this is based on only one glacial sample, that sample covers ~ 4000 years (Table 2).

4. Discussion

4.1. Post-Depositional Processing

[18] In light of the anticorrelation of $\delta^{15}\text{N}$ of NO_3^- (and to a lesser extent $\delta^{18}\text{O}$) with accumulation rate in the GISP2 ice core (Figures 2b and 2c), we must consider the role that accumulation rate can play in the isotopic variations we observe. Accumulation rate may dilute the concentration of NO_3^- in polar snow, based on the observation that $[\text{NO}_3^-]$ decreases with increasing accumulation rate among sites in Greenland and Antarctica [Röthlisberger et al., 2002]. We do not expect this to impact the isotopic composition of NO_3^- . Since snow crystals and water droplets efficiently scavenge gaseous HNO_3 , we expect the isotopic composition of HNO_3 in snow and rain to reflect that of atmospheric HNO_3 , and thus not to be affected directly by precipitation rate [e.g., Diehl et al., 1995; Abbatt, 1997]. This is supported by the lack of correlation between precipitation rate and $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of NO_3^- in samples from Bermuda [Hastings et al., 2003], Greenland [Hastings et al., 2004], and Hawaii [Houlton et al., 2004]. The correlation between $\delta^{15}\text{N}$ of NO_3^- and accumulation rate in the data reported here could involve the seasonality of both accumulation and/or NO_x sources; this is discussed below. Our main concern here is to consider the variation in the isotopic composition of NO_3^- in terms of post-depositional processing, since post-depositional processing of NO_3^- will vary with accumulation rate [Röthlisberger et al., 2002].

[19] $[\text{NO}_3^-]$ in surface snow can be impacted by photolysis [e.g., Dibb et al., 2002; Honrath et al., 2002, 2000; Jones et al., 2000] or by the gaseous loss of HNO_3 from the

snow surface [e.g., Dibb et al., 1998; Mulvaney et al., 1998]. These losses of NO_3^- are expected to be greatest at low accumulation sites [e.g., Röthlisberger et al., 2000, 2002]. We expect that a loss of NO_3^- from the surface snow would increase both the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of NO_3^- left behind in the snow. In fact, snow NO_3^- enriched in ^{15}N , associated with loss of NO_3^- from the snow, has been measured at the very low accumulation site of Dome C, Antarctica [Floch and Blunier, 2004], and Blunier et al. [2005] determined a fractionation factor of 11.7‰ for $\delta^{15}\text{N}$ due to photolysis of NO_3^- in snow. In contrast, our study of the isotopes of NO_3^- in recent snow at Summit did not reveal a significant impact of post-depositional processing [Hastings et al., 2004]. Additionally, despite significant differences in accumulation rate at Summit, Camp Century and Dye 3, the $\delta^{15}\text{N}$ of NO_3^- in Holocene ice is similar at all three sites (Tables 1 and 2). Finally, the $\delta^{18}\text{O}$ of Holocene NO_3^- is highest at Dye 3, where accumulation rate is the highest among the three sites, which is in the opposite sense to the expected effect of post-depositional loss. Thus we do not expect that post-depositional processing is determining the isotopic composition of NO_3^- in recent ice.

[20] Nonetheless, with the much lower accumulation of snow in Greenland during the last glacial (Figure 2d) [Cuffey and Clow, 1997; Johnsen et al., 1995], we need to consider whether post-depositional processing can explain the earlier (ice age) part of the record. Although the accumulation in Greenland during the last glacial period was still greater than at sites such as Dome C today, the increased potential for post-depositional loss would apply to Summit, Camp Century and Dye 3. The higher $\delta^{15}\text{N}$ in glacial ice at all three sites follows qualitatively the expectation that post-depositional loss would enrich ^{15}N of NO_3^- (Figure 2b). However, while the $\delta^{18}\text{O}$ of NO_3^- in Dye 3 and GISP2 increases in the glacial, Camp Century ice shows little change or a decrease in $\delta^{18}\text{O}$ of NO_3^- (Figure 2c, Table 2).

[21] Other considerations also suggest that post-depositional processing of NO_3^- should be less important during the last ice age. The $\sim 15^\circ\text{C}$ lower average temperature in Greenland during the glacial period [e.g., Johnsen et al., 2001] would decrease the potential for gaseous loss of HNO_3 from the snow surface (e.g., Thibert and Dominé [1998] show that the solubility of HNO_3 on ice increases by about a factor of 2 or more for this magnitude of temperature change). Moreover, glacial ice is alkaline in comparison to Holocene ice [Wolff, 1995; Yang et al., 1997], and it has been suggested that the association of NO_3^- with Ca^{2+} in glacial ice should prevent post-depositional loss of NO_3^- in snow [Fuhrer and Legrand, 1997; Legrand et al., 1999; Röthlisberger et al., 2000]. Overall, there is not a compelling case for post-depositional processing of NO_3^- to be the primary cause of the glacial/interglacial changes in $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of NO_3^- .

4.2. NO_3^- Scavenging

[22] We can now consider what changes may have occurred prior to NO_3^- deposition to explain the glacial/interglacial change observed in the isotopes of NO_3^- . One possibility is that different isotope effects are associated with different scavenging mechanisms between the Holo-

cene and glacial periods. We expect that HNO_3 is primarily taken up by water and/or ice surfaces during the Holocene, whereas glacial HNO_3 was primarily taken up by alkaline dust particles that contain Ca^{2+} to produce $\text{Ca}(\text{NO}_3)_2$. Unlike the uptake of HNO_3 onto ice, which is not completely irreversible [Abbatt, 1997; Dibb *et al.*, 1998; Röthlisberger *et al.*, 2000], the formation of $\text{Ca}(\text{NO}_3)_2$ is a unidirectional reaction that was probably limited by the amount of HNO_3 in the glacial atmosphere [Laskin *et al.*, 2005]. Therefore we expect a kinetic isotope effect is more likely to be important for the unidirectional uptake of nitrate onto dust (i.e., glacial conditions). This type of effect would result in particulate NO_3^- that is isotopically lighter than the gas-phase HNO_3 . This is counter to the higher $\delta^{15}\text{N}$ (and $\delta^{18}\text{O}$) observed during the glacial period (Figures 2b and 2c). If the uptake of HNO_3 is reversible and there is an isotope effect associated with loss from the particle, then ^{15}N and ^{18}O enrichment in the particulate phase could occur, producing the direction of change observed between the Holocene and glacial. Given the magnitude of glacial/interglacial change in $\delta^{15}\text{N}$, a large isotope effect would have to be associated with loss from the particulate phase, and this would have to be more important for NO_3^- associated with dust than with ice. As mentioned above, the loss of HNO_3 from dust is very unlikely, especially in the case of $\text{Ca}(\text{NO}_3)_2$ formation on CaCO_3 -containing dust [Laskin *et al.*, 2005]. Finally, although our data set is limited, it is interesting to note that there does not appear to be direct evidence for an association between $\delta^{15}\text{N}$ (or $\delta^{18}\text{O}$) and Ca^{2+} concentration in the GISP2 ice core (Figure 2e). For instance, at $\sim 15,000$ years BP there is an abrupt increase in Ca^{2+} concentration (Figure 2e) that is approximately coincident with a large increase in $\delta^{15}\text{N}$ of NO_3^- (Figure 2b). However, while the Ca^{2+} concentration remains high, the $\delta^{15}\text{N}$ decreases significantly and stabilizes between $\sim 15,000$ and $18,000$ yrs BP. In addition, the two oldest samples near $35,000$ and $36,000$ yrs BP occur during a local minimum and maximum in Ca^{2+} concentration, respectively, but their $\delta^{15}\text{N}$ only differ by 2.1% . In short, while we cannot rule out a scavenging explanation for the ^{15}N enrichment of glacial nitrate, there is currently no support for it.

4.3. Seasonal Accumulation

[23] Seasonal variations in the isotopic composition of NO_3^- are observed in modern snow at Summit [Hastings *et al.*, 2004]. Therefore seasonal and/or spatial changes in accumulation may affect the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of NO_3^- archived in the GISP2 ice core. At Summit today, the mean $\delta^{15}\text{N}$ of NO_3^- is higher in summer (-0.3%) than winter (-10.0%), most likely because of seasonal changes in the sources of NO_x emissions. The lower mean $\delta^{18}\text{O}$ of NO_3^- observed in summer (69.8%) snow than in winter (77.5%) is best attributed to seasonal changes in the oxidation chemistry that converts NO_x to HNO_3 in the atmosphere. In this context, changes in the seasonality of accumulation might drive isotopic differences by virtue of their correlation with seasonal changes in NO_x sources and chemistry (section 4.4).

[24] Since the source regions and transport pathways are similar for Summit and Dye 3 [Kahl *et al.*, 1997; Davidson

et al., 1993], we can directly compare these two sites. A weak maximum in present-day accumulation in the northern interior (GISP2/Summit) of Greenland occurs in August in comparison to a maximum of October for the south (Dye 3) [Bromwich *et al.*, 1993]. On the basis of the seasonality in the NO_3^- isotopes found at Summit today [Hastings *et al.*, 2004], one would expect the mean $\delta^{15}\text{N}$ to be higher in Holocene ice from GISP2 than Dye 3, and the $\delta^{18}\text{O}$ to be lower, both of which appear to be the case (Figure 2b, Tables 1 and 2). Thus the differences in $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of NO_3^- between GISP2 and Dye 3 Holocene samples may well be related to the seasonality of accumulation at each site.

[25] We must also consider whether seasonal changes in accumulation can explain the glacial/interglacial change in $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of NO_3^- . Accumulation in Greenland under glacial conditions is expected to mostly represent summertime snow since low temperatures and a lack of moisture would have reduced precipitation during the winter months [Werner *et al.*, 2000; Krinner *et al.*, 1997; Steig *et al.*, 1994]. If the seasonal variation in $\delta^{15}\text{N}$ in the pre-industrial atmosphere is similar to that at present, then it is possible that this difference in seasonal accumulation could explain the glacial/interglacial sense of change in $\delta^{15}\text{N}$. However, the amplitude of the change in $\delta^{15}\text{N}$ ($\sim 20\%$) is much larger than any seasonal change observed today. Moreover, the increase in $\delta^{18}\text{O}$ of NO_3^- from the Holocene to glacial samples in both GISP2 and Dye 3 are of the opposite sense to what one would expect based on the above seasonality argument. Therefore larger-scale phenomena most likely determine the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of NO_3^- .

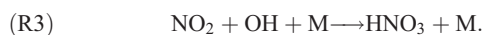
4.4. NO_x Sources and Chemistry

[26] At present, it is unclear whether the $\delta^{15}\text{N}$ of NO_3^- predominantly reflects variability in the long-range transport of NO_x and/or fractionation associated with the cycling and subsequent conversion of NO_x to HNO_3 . Freyer *et al.* [1993] find an overall isotope effect of $\sim 18\%$ associated with NO/NO_2 cycling (see reactions (R1)–(R2) below) based on measurements of NO_x , O_3 , and the $\delta^{15}\text{N}$ of NO_2 in an urban environment. However, this isotope effect does not provide an adequate explanation for the observed seasonal changes in $\delta^{15}\text{N}$ of NO_3^- at Summit [Hastings *et al.*, 2004], Ny Ålesund [Heaton *et al.*, 2004], or Bermuda [Hastings *et al.*, 2003]. In fact, recent calculations using this isotope effect and the assumptions made in the Freyer *et al.* [1993] study can explain less than half of the seasonal variability in $\delta^{15}\text{N}$ of NO_3^- at Summit [Jarvis *et al.*, 2004] (also J. Jarvis *et al.*, Controls on the isotopic composition of NO_x and HNO_3 at Summit, Greenland, submitted to *Atmospheric Environment*, 2005).

[27] Several studies suggest that the $\delta^{15}\text{N}$ of NO_3^- most likely reflects the N isotopic composition of NO_x sources [Freyer, 1978, 1991; Garten, 1996; Russell *et al.*, 1998; Xiao and Liu, 2002; Hastings *et al.*, 2003; Heaton *et al.*, 2004]. The important pre-industrial sources of NO_x include biomass burning, biogenic soil emissions, lightning, and stratospheric injection [e.g., Wolff, 1995; Legrand and Kirchner, 1990]. The $\delta^{15}\text{N}$ of NO_x from biomass burning, soil emissions and the stratosphere has not been directly measured, whereas Hoering [1957] found that the $\delta^{15}\text{N}$ of

NO_x produced from electric discharges (comparable to lightning) is between -0.5 and $+1.4\%$. Since lightning appears to be near 0% , the positive $\delta^{15}\text{N}$ of NO_3^- throughout the pre-industrial record (Figure 2b) suggests that other NO_x emission sources, with positive $\delta^{15}\text{N}$ source signatures, make important contributions. Current study of the isotopic composition of NO_3^- in Greenland has yet to reveal whether the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ signals reflect local to regional or global scale NO_x production and chemistry. However, with the change in transport patterns, higher wind speeds, lower temperatures and a more well-mixed atmosphere during the glacial period [e.g., *Mayewski et al.*, 1994; *Yang et al.*, 1997], it is likely that the $\delta^{15}\text{N}$ of NO_3^- in ice from the glacial period reflects NO_x emissions sources on a hemispheric to global scale. On the basis of measurements of the isotopic composition of N_2O in the upper troposphere and the isotope effects associated with N_2O oxidation, the NO produced from N_2O oxidation in the stratosphere most likely has a low $\delta^{15}\text{N}$ ($\sim -1\%$) [*Kaiser et al.*, 2002] (see *Heaton et al.* [2004] for discussion). *Heaton et al.* [2004] also suggest that the stratosphere may provide a source of very negative $\delta^{15}\text{N}$ via recycling of HNO_3 associated with polar stratospheric cloud particles. If the $\delta^{15}\text{N}$ of lightning NO_x is near 0% and that for stratospheric production of NO_x and HNO_3 is negative, then the large and positive $\delta^{15}\text{N}$ in glacial ice suggests that biomass burning and biogenic soil emissions are important contributors to the NO_x budget in the last ice age. Direct measurements of the $\delta^{15}\text{N}$ of NO_x from these sources are needed to further constrain this hypothesis.

[28] On the basis of our present knowledge, the down core changes in $\delta^{18}\text{O}$ of NO_3^- are best explained by changes in the major pathway of HNO_3 production in the atmosphere. HNO_3 is typically produced, during the day (or arctic summer), by the reaction of NO_2 with OH ,



During night (arctic winter), HNO_3 is primarily produced via N_2O_5 hydrolysis [*Dentener and Crutzen*, 1993; *Stroud et al.*, 2003; *Tie et al.*, 2003],



Production of HNO_3 via N_2O_5 hydrolysis (reaction (R6)) is of minor importance in the presence of sunlight because NO_3 (reaction (R4)) is readily lost via photolysis. The $\delta^{18}\text{O}$ of atmospheric NO_3^- depends upon the oxidation processes

that produce HNO_3 from NO_x . Owing to rapid exchange with water vapor, the $^{18}\text{O}/^{16}\text{O}$ of OH in the troposphere is much lower than that of O_3 [*Dubey et al.*, 1997; *Röckmann et al.*, 1998]. Globally, the $\delta^{18}\text{O}$ of tropospheric water vapor is typically much less than 0% versus VSMOW, while the reported range in $\delta^{18}\text{O}$ of tropospheric ozone is ~ 90 to 120% versus VSMOW [*Krankowsky et al.*, 1995; *Johnston and Thiemens*, 1997]. For HNO_3 produced via reactions (R1)–(R3), two out of the three oxygen atoms in HNO_3 result from exchange with O_3 , while the third comes from OH . On the other hand, five out of the six oxygen atoms in the 2HNO_3 produced from reactions (R1) and (R4)–(R6) come from O_3 . Thus the OH pathway of HNO_3 production results in a lower $\delta^{18}\text{O}$ of NO_3^- relative to the N_2O_5 hydrolysis pathway [*Hastings et al.*, 2003].

[29] The higher $\delta^{18}\text{O}$ of NO_3^- in the last glacial period most likely reflects an increase in the fraction of HNO_3 produced via N_2O_5 hydrolysis (as opposed to reaction of NO_2 with OH). The equilibrium in reaction (R5) is strongly temperature dependent, with lower temperatures favoring the production of N_2O_5 [*Sander et al.*, 2000]. The reaction rate for the hydrolysis of N_2O_5 (R6) can be approximated as $k_{R6} = (\gamma/4)\nu A$, where γ is the uptake coefficient, $\nu = [8kT/m]^{1/2}$ is the molecular mean speed of the gas at temperature T and mass m , A is the aerosol surface area per unit volume, and k is the Boltzmann constant (see *Hanson et al.* [1994], *Jacob* [2000], and references therein for a more thorough discussion). Thus the lower temperatures and higher aerosol loading of the glacial atmosphere [*Mayewski et al.*, 1994] could increase the probability of HNO_3 production via N_2O_5 hydrolysis. On the basis of the model of *Michalski et al.* [2003], we expect that future measurements will reveal a higher $\Delta^{17}\text{O}$ of NO_3^- in glacial ice as well, reflecting this increase in production of HNO_3 from N_2O_5 hydrolysis.

[30] The hydrolysis of N_2O_5 in winter in the present Northern Hemisphere high latitudes represents a significant loss of NO_x , which subsequently impacts the budgets of O_3 and OH [e.g., *Stroud et al.*, 2003; *Tie et al.*, 2003; *Dentener and Crutzen*, 1993]. We can attempt to quantify the amount of N_2O_5 hydrolysis needed to produce the observed $\delta^{18}\text{O}$ of NO_3^- by estimating the $\delta^{18}\text{O}$ of OH and O_3 . For example, if we assume a $\delta^{18}\text{O}$ of OH of -30% and a $\delta^{18}\text{O}$ of O_3 in the middle of the reported range (105% ; see above), then $\sim 55\%$ of the HNO_3 deposited to Greenland today must come from the N_2O_5 pathway to explain the annual mean $\delta^{18}\text{O}$ of NO_3^- of 72.6% at Summit. This agrees favorably with predictions for the Northern Hemisphere from the modeling studies of *Tie et al.* [2003] and *Dentener and Crutzen* [1993]. For a glacial $\delta^{18}\text{O}$ of NO_3^- of 75.3% , we calculate that $\sim 75\%$ of the HNO_3 deposited to Greenland must be produced via N_2O_5 hydrolysis if we assume a $\delta^{18}\text{O}$ of OH of -40% and $\delta^{18}\text{O}$ of O_3 of 105% . (Note that our estimate of the $\delta^{18}\text{O}$ of OH is based on the $\delta^{18}\text{O}$ of ice and snow found in the Northern Hemisphere and the observation by *Grootes and Stuvier* [1997] that the $\delta^{18}\text{O}$ of snow is in equilibrium with the $\delta^{18}\text{O}$ of water vapor.) It is unclear at present whether the $\delta^{18}\text{O}$ of NO_3^- deposited in Greenland is sensitive to regional, hemispheric or global scale oxidation processes. On a hemispheric to global scale, an increase in the production of HNO_3 from N_2O_5 hydrolysis might also

suggest that O_3 concentrations were higher during the last glacial than the pre-industrial Holocene (favoring reactions (R4)–(R5)) and/or that OH concentrations were lower. While several modeling studies suggest that, on a global basis, average O_3 concentrations were lower and OH concentrations were higher in the last glacial than the pre-industrial Holocene [e.g., Valdes et al., 2005; Martinerie et al., 1995; Thompson et al., 1993], at least one modeling study finds the opposite [Karol et al., 1995]. In addition, Valdes et al. and Martinerie et al.'s results suggest a fair amount of spatial heterogeneity in both O_3 and OH concentrations, and Martinerie et al. [1995] show higher glacial O_3 concentrations in the high northern latitudes. Further measurements of the oxygen isotopic composition of HNO_3 under different atmospheric conditions are needed to assess the sensitivity of the oxygen isotopes of NO_3^- to O_3 and OH concentrations. Nevertheless, confirmation of our predicted increase in production of HNO_3 via N_2O_5 hydrolysis during the last glacial may have important implications for determining past NO_x chemistry and atmospheric oxidant levels.

5. Conclusions

[31] The isotopes of NO_3^- offer a new tool for the study of NO_3^- preserved in ice cores. In contrast to $[NO_3^-]$, the $\delta^{15}N$ and $\delta^{18}O$ of NO_3^- in the GISP2 ice core show a significant change between the Holocene and last glacial period. The mean $\delta^{15}N$ and $\delta^{18}O$ in Holocene ice are 9.7‰ and 62.7‰, respectively. Both $\delta^{15}N$ and $\delta^{18}O$ are higher in glacial ice, averaging 28.4‰ and 75.3‰, respectively. Comparison of the GISP2 results with measurements of ice from Dye 3 and Camp Century suggest that accumulation rate and/or post-depositional processing are not the primary factors determining the isotopic composition of NO_3^- . Further studies are needed to constrain possible isotope effects associated with the scavenging of HNO_3 or chemical processing of NO_x , but at present this also does not appear to explain the changes observed in the ice cores. The $\delta^{15}N$ and $\delta^{18}O$ of ice core NO_3^- most likely reflect changes in the isotopic composition of NO_3^- generated in the atmosphere and deposited in snow. Although we cannot conclusively discern whether the isotopes of NO_3^- reflect local, regional, or global scale processes, the large amplitude of change in $\delta^{15}N$ in glacial ice and the similarity among the different Greenland ice cores suggests that the isotopic composition of NO_3^- reflects large-scale changes in NO_x .

[32] It is possible that the observed glacial/interglacial change in $\delta^{15}N$ of NO_3^- represents a change in the proportional contributions of natural NO_x sources. On the basis of our current understanding of the $\delta^{15}N$ of NO_x from lightning and the stratosphere, the relatively high $\delta^{15}N$ of NO_3^- in the ice core record implies that NO_x from biomass burning and biogenic soil emissions have positive $\delta^{15}N$ source signatures. Direct determination of the $\delta^{15}N$ of NO_x from these different emission sources is needed to test this inference and constrain their importance in the last ice age. Nevertheless, the much higher $\delta^{15}N$ of NO_3^- in glacial ice suggests a significant change in the atmosphere's reactive N cycle.

[33] The $\delta^{18}O$ of NO_3^- is higher in the last glacial period, most likely owing to an increase in HNO_3 production via N_2O_5 hydrolysis. Compared to HNO_3 produced via reaction

of NO_2 and OH, HNO_3 produced via N_2O_5 hydrolysis has more O atoms from O_3 , which has a very high $\delta^{18}O$. This interpretation should be tested further by determination of $NO_3^- \Delta^{17}O$. A greater amount of heterogeneous loss of NO_x during the last ice age has implications for past concentrations of O_3 and OH. High-resolution measurements over important climate transitions as recorded in the GISP2 ice core (e.g., Younger Dryas, Bølling-Allerød, Dansgaard-Oeschger events) will make it possible to more fully characterize changes in the isotopes of NO_3^- and their relationship to climate change. Incorporation of the isotopes of NO_x and NO_3^- into chemical transport models will allow for quantitative estimates of past atmospheric chemistry and possibly NO_x source changes.

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