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

Meredith G. Hastings and Daniel M. Sigman
Department of Geosciences, Princeton University, Princeton, New Jersey, USA

Eric J. Steig
Department of Earth and Space Sciences, University of Washington, Seattle, Washington, USA

Received 3 March 2005; revised 23 September 2005; accepted 26 October 2005; published 24 December 2005.

1. Introduction

Nitrate ($\text{NO}_3^-$) is one of the major anions found in snow, and many profiles of $\text{NO}_3^-$ from alpine and polar ice cores exist. A major motivation in studying ice core records of $\text{NO}_3^-$ concentration is to reconstruct past levels of nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$), the precursor of deposited $\text{NO}_3^-$. Because $\text{NO}_x$ interacts with the major oxidant cycles of the atmosphere, reconstruction of $\text{NO}_x$ 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 $\text{NO}_3^-$ concentration in the ice core record is difficult, and the contributions of different natural sources to the pre-industrial $\text{NO}_x$ 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 $\text{NO}_3^-$ 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 $\text{NO}_3^-$ 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].

The isotopic composition of $\text{NO}_3^-$ offers a tool to complement studies of ice core $\text{NO}_3^-$ concentration. The isotopic composition of $\text{NO}_3^-$ reflects the sources and chemical processing of atmospheric $\text{NO}_x$ [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 $\text{NO}_3^-$ 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 $\text{NO}_3^-$. This study concluded that variation in the $^{18}\text{O}/^{16}\text{O}$ of $\text{NO}_3^-$ reflects a seasonal change in the oxidation chemistry that converts $\text{NO}_x$ to $\text{HNO}_3$ in the atmosphere, while the $^{15}\text{N}/^{14}\text{N}$ of $\text{NO}_3^-$ most likely varies with seasonal changes in the contribution of different $\text{NO}_x$ source emissions. The Summit study revealed that photo-

\[1\] 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) 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 match in nitrate concentration. While both the $^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$ records are higher in ice from the last glacial period (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 match 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 $\text{NO}_x$. The glacial/interglacial change in $^{18}\text{O}/^{16}\text{O}$ is best explained by a greater contribution of $\text{HNO}_3$ production from hydrolysis of $\text{N}_2\text{O}_5$, which has implications for reconstruction of past atmospheric oxidant levels. Although isotope effects associated with $\text{NO}_x$ 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 $\text{NO}_x$ on a hemispheric or global scale.

lytic or evaporative loss is not contributing to significant post-depositional enrichment in the isotopes of NO\textsubscript{3}. However, a study of Antarctic surface snow (Dome C) indicated a loss of NO\textsubscript{3} from the snowpack that left the snow NO\textsubscript{3} enriched in $^{15}$N (and presumably $^{18}$O 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 NO\textsubscript{3} loss from snow at Dome C. This type of NO\textsubscript{3} 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 NO\textsubscript{3}, the association of calcium (Ca\textsuperscript{2+}) and NO\textsubscript{3} in glacial ice is expected to make NO\textsubscript{3} less sensitive to post-depositional processing [Wolff, 1995; Fuhrer and Legrand, 1997; Legrand et al., 1999; Röthlisberger et al., 2000].

Here we report measurements of the $^{15}$N/$^{14}$N, $^{18}$O/$^{16}$O, and concentration of NO\textsubscript{3} 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\textsuperscript{-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 NO\textsubscript{3} 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 NO\textsubscript{3} 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\textsuperscript{-1}) and Camp Century (77.2°N, 61.1°W, 1880 m, 0.35 m ice yr\textsuperscript{-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 $-30^\circ$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 NO\textsubscript{3} concentration and isotope analysis.

2.2. Nitrate Concentration and Isotope Analysis

[7] Nitrate concentration ([NO\textsubscript{3}]) was determined by reduction of NO\textsubscript{3} (and nitrite, NO\textsubscript{2}) to nitric oxide (NO) followed by chemiluminescence detection of NO [Braman and Hendrix, 1989]. NO\textsubscript{3} concentrations are typically negligible compared to [NO\textsubscript{2}] [e.g., Legrand and DeAngelis, 1995], and NO\textsubscript{2} is not considered separately in the isotope analysis. Typical [NO\textsubscript{3}] for the GISP2 samples is 1.2 µmol L\textsuperscript{-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 NO\textsubscript{3} in ice cores since [NO\textsubscript{3}] is low and ice core samples are precious. The isotope ratios ($^{15}$N/$^{14}$N and $^{18}$O/$^{16}$O) of NO\textsubscript{3} 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 (N\textsubscript{2}O) reductase to convert NO\textsubscript{3} to N\textsubscript{2}O, which is then measured on a DeltaPlus IRMS in continuous flow mode to determine $^{15}$N ($^{14}$N) and $^{18}$O ($^{16}$O) notation in units of “per mil” (‰): $^{15}$N\textsubscript{sample} = ($^{15}$N/$^{14}$N\textsubscript{sample})/(100% × $^{15}$N/$^{14}$N\textsubscript{reference}) × 1000‰ and $^{18}$O\textsubscript{sample} = ($^{18}$O/$^{16}$O\textsubscript{sample})/(100% × $^{18}$O/$^{16}$O\textsubscript{reference}) × 1000‰, where the $^{15}$N/$^{14}$N reference is N\textsubscript{2} in air and the $^{18}$O/$^{16}$O reference is Vienna Standard Mean Ocean Water (VSMOW)). In this study, the standard deviation indicated by repeated measurements of $^{15}$N and $^{18}$O is 0.2‰ and 0.4‰, respectively.

[6] Referencing of $^{15}$N/$^{14}$N to atmospheric N\textsubscript{2} and of $^{18}$O/$^{16}$O to VSMOW is done via comparison to the potassium nitrate (KNO\textsubscript{3}) reference material IAEA-N3, with an assigned $^{15}$N of +4.7‰ [Gonfiantini et al., 1995] and
reported $\delta^{18}O$ of $+22.7$ to $+25.6\%$ [Böhlke et al., 2003; Révész et al., 1997; Silva et al., 2000]. We adopt here a $\delta^{18}O$ of $22.7\%$ [Révész et al., 1997; Silva et al., 2000] for consistency with previous work and awaiting greater certainty in the $\delta^{18}O$ 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 $\delta^{18}O$ of IAEA-N3 ($25.6\%$ [Böhlke et al., 2003]), then the $\delta^{18}O$ of all of our samples would increase by $\sim2.9\%$. 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$_3^-$ $^{18}O$/$^{16}O$, not its relationship to the isotope ratios found in other O-bearing materials. Moreover, where comparisons to O$_2$, O$_3$, and H$_2$O are made, the current uncertainty in IAEA-N3 does not significantly affect the interpretation.

3. Results

3.1. Nitrate Concentration ([NO$_3^-$])

[12] [NO$_3^-$] varies between 0.7 and 2.7 $\mu$M (44-167 ppb NO$_3^-$; $n = 37$) between $\sim$500 and $\sim$36,000 years ago for the samples in this study (Figure 2a). Two samples represent outliers for our concentration data set. The outliers have [NO$_3^-$] of 2.3 and 2.7 $\mu$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 [NO$_3^-$] does not vary significantly between the pre-industrial Holocene (defined here as between $\sim$500 and $\sim$10,000 years BP) and the last glacial period (18,000 to $\sim$36,000 BP) (Table 1). The average [NO$_3^-$] from corresponding samples of Mayewski et al. [1997] (based on depth) is also shown in Table 1.

[13] No correlation is found between [NO$_3^-$] and accumulation rate or between [NO$_3^-$] and $\delta^{18}O$ 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 m ice yr$^{-1}$, in comparison to 0.35 m ice yr$^{-1}$ for Camp Century and 0.54 m ice yr$^{-1}$ for Dye 3 [e.g., Ohmura and Reeh, 1991]. Among the three Greenland sites, [NO$_3^-$] in Holocene ice tends to increase with decreasing accumulation rate such that GISP2 [NO$_3^-$] > Camp Century [NO$_3^-$] > Dye 3 [NO$_3^-$] (Tables 1 and 2). These results ((1) the lack of a temporal correlation between [NO$_3^-$] and accumulation rate in
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 δ15N of NO3− in GISP2

[14] The δ15N of NO3− ranges from +5.4 to +33.7‰ versus atmospheric N2 (n = 37) between ~500 and 36,000 years BP (Figure 2b). The δ15N of NO3− 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 δ15N of pre-industrial NO3− in the GISP2 core is also higher than the mean δ15N found in the present annual snowpack at Summit, Greenland (−2.0 ± 6.8‰, n = 68) [Hastings et al., 2004] and Svalbard (−10.6 ± 1.0‰, n = 13, spring/winter snow only) [Heaton et al., 2004]. Higher δ15N in pre-industrial NO3− at Summit was also found by Freyer et al. [1996], who report δ15N of NO3− ranging between +12 to +18‰ (n = 4) for samples dated between ~1730 and 1950 AD.

[15] In contrast to [NO3−], the δ15N of NO3− 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 δ15N of NO3− from Dye 3 and Camp Century is also significantly higher in

Figure 2. Results from measurements on GISP2 ice core samples of (a) NO3− concentration (μM), (b) δ15N of NO3− (% versus N2), and (c) δ18O of NO3− (%o versus VSMOW). (d) Accumulation rate (m ice yr−1) corresponding to the NO3− measurements, and high-resolution records of (e) calcium concentration (ppb), (f) δ18O of ice (%o 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 Stuiver, 1997, and references therein].
glacial samples than in the Holocene (Figure 2b, Table 2). The results from Dye 3 are very similar to GISP2 with \( \delta^{15}N \) 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 \( \delta^{15}N \) between two Holocene (8.9\%) and one glacial (18.2\%) sample from Camp Century is smaller than the other two sites. The \( \delta^{15}N \) of NO\(_3^-\) in the GISP2 ice core is anti-correlated with accumulation rate (\( r = -0.87 \); Figure 3b).

### 3.3. The \( \delta^{18}O \) of NO\(_3^-\) in GISP2

The \( \delta^{18}O \) of NO\(_3^-\) 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 \( \delta^{18}O \) of NO\(_3^-\) 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

---

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

<table>
<thead>
<tr>
<th>Depth, m</th>
<th>[NO(_3^-)], ( \mu )M</th>
<th>( \delta^{15}N ), %</th>
<th>( \delta^{18}O ), %</th>
<th>Estimated Age (Years BP)*</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dye 3</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>488.86–489.16</td>
<td>0.67</td>
<td>8.7</td>
<td>68.5</td>
<td>early Holocene (1000)</td>
</tr>
<tr>
<td>714.17–714.37</td>
<td>0.57</td>
<td>6.3</td>
<td>72.9</td>
<td>early Holocene (1620)</td>
</tr>
<tr>
<td>1818.61 – 1818.91</td>
<td>0.82</td>
<td>30.3</td>
<td>76.7</td>
<td>near glacial (16,000)</td>
</tr>
<tr>
<td>1831.78 – 1832.00</td>
<td>0.73</td>
<td>26.7</td>
<td>76.6</td>
<td>glacial (19,000)</td>
</tr>
<tr>
<td>1979.54 – 1979.89</td>
<td>0.66</td>
<td>16.6</td>
<td>74.2</td>
<td>glacial (&gt;25,000)</td>
</tr>
<tr>
<td><strong>Camp Century</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>708.41–708.91</td>
<td>1.29</td>
<td>5.8</td>
<td>56.2</td>
<td>mid-Holocene (2900)</td>
</tr>
<tr>
<td>799.58–799.90</td>
<td>0.99</td>
<td>6.0</td>
<td>57.9</td>
<td>mid-Holocene (3700)</td>
</tr>
<tr>
<td>1210–1246</td>
<td>1.17</td>
<td>18.2</td>
<td>52.7</td>
<td>glacial (17–21,000)</td>
</tr>
</tbody>
</table>


---

**Figure 3.** (a) NO\(_3^-\) concentration (\( \mu \)M), (b) \( \delta^{15}N \) of NO\(_3^-\) (% versus N\(_2\)), and (c) \( \delta^{18}O \) of NO\(_3^-\) (% 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. NO\(_3^-\) 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) \( \delta^{15}N \) and accumulation rate (\( r = -0.87 \)) and (Figure 3c) \( \delta^{18}O \) and accumulation rate (\( r = -0.69 \)) are highly significant (P < 0.05%).

---

5 of 11
presented here are the first reported measurements of $\delta^{18}O$ in pre-industrial NO$_3$. These measurements counter the previous suggestion that the high $\delta^{18}O$ of atmospheric NO$_3$ precipitation might be a reflection of an anthropogenic pollution source [Kendall, 1998].

[17] Similar to the $\delta^{15}N$ of NO$_3$, the $\delta^{18}O$ is significantly higher ($P < 0.01\%$) in the last glacial than Holocene. However, the glacial/interglacial change is not as striking for $\delta^{18}O$ because there is additional variability in the record. Since the $\sim 5$ cm samples of GISP2 ice (section 2.3) could represent less than a year of snow in the Holocene, the apparently greater variability of $\delta^{18}O$ of NO$_3$ in the Holocene samples relative to the glacial samples may be related to the seasonality of $\delta^{18}O$ captured in these samples. The $\delta^{18}O$ of NO$_3$ increases from a mean of 62.7$\%$o in the Holocene to a mean of 75.3$\%$o in the glacial period (Table 1). The $\delta^{18}O$ of NO$_3$ in the GISP2 ice core is anti-correlated ($r = -0.69$) with accumulation rate, though not as strongly as is $\delta^{15}N$ (Figure 2c). The $\delta^{18}O$ of NO$_3$ in the two Holocene samples from Dye 3 (68.5 and 72.9$\%$o) tends to be higher than that found in the Holocene at GISP2 (Figure 2b). A more subtle increase in $\delta^{18}O$ is found between the Holocene and glacial (77$\%$o) samples from Dye 3 than in GISP2 (Tables 1 and 2). The two Holocene samples from Camp Century have a lower mean $\delta^{18}O$ of NO$_3$ than GISP2 and Dye 3 (57$\%$o). The $\delta^{18}O$ of NO$_3$ at Camp Century decreases slightly from the Holocene to glacial (52$\%$o). While this is based on only one glacial sample, that sample covers $\sim 4000$ years (Table 2).

4. Discussion

4.1. Post-Depositional Processing

[18] In light of the anticorrelation of $\delta^{15}N$ of NO$_3$ (and to a lesser extent $\delta^{18}O$) 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 [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; Abbott, 1997]. This is supported by the lack of correlation between precipitation rate and $\delta^{15}N$ and $\delta^{18}O$ 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 $\delta^{15}N$ of NO$_3$ and accumulation rate in the data reported here could involve the seasonality of both accumulation and/or NO$_3$ 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] [NO$_3$]$_i$ 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 $\delta^{18}N$ and $\delta^{18}O$ 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 [Floh and Blunier, 2004], and Blunier et al. [2005] determined a fractionation factor of 11.7$\%$o for $\delta^{15}N$ 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 $\delta^{15}N$ of NO$_3$ in Holocene ice is similar at all three sites (Tables 1 and 2). Finally, the $\delta^{18}O$ 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) [Caffey 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 $\delta^{15}N$ 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 $\delta^{18}O$ of NO$_3$ in Dye 3 and GISP2 increases in the glacial, Camp Century ice shows little change or a decrease in $\delta^{18}O$ 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 $\sim 15^\circ$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 $\delta^{15}N$ and $\delta^{18}O$ 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 HNO3 is primarily taken up by water and/or ice surfaces during the Holocene, whereas glacial HNO3 was primarily taken up by alkaline dust particles that contain Ca2+ to produce Ca(NO3)2. Unlike the uptake of NO3 onto ice, which is not completely irreversible [Abbott, 1997; Dibb et al., 1998; Röhlisberger et al., 2000], the formation of Ca(NO3)2 is a unidirectional reaction that was probably limited by the amount of HNO3 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 NO3 that is isotopically lighter than the gas-phase HNO3. This is counter to the higher δ15N (and δ18O) observed during the glacial period (Figures 2b and 2c). If the uptake of HNO3 is reversible and there is an isotope effect associated with loss from the particle, then 15N and 18O 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 δ15N, a large isotope effect would have to be associated with loss from the particulate phase, and this would have to be more important for NO3 associated with dust than with ice. As mentioned above, the loss of HNO3 from dust is very unlikely, especially in the case of Ca(NO3)2 formation on CaCO3-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 δ15N (or δ18O) and Ca2+ concentration in the GISP2 ice core (Figure 2e). For instance, at ~15,000 years BP there is an abrupt increase in Ca2+ concentration (Figure 2e) that is approximately coincident with a large increase in δ15N of NO3 (Figure 2b). However, while the Ca2+ concentration remains high, the δ15N decreases significantly and stabilizes between ~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 Ca2+ concentration, respectively, but their δ15N only differ by 2.1‰. In short, while we cannot rule out a scavenging explanation for the δ15N enrichment of glacial nitrate, there is currently no support for it.

4.3. Seasonal Accumulation

[25] Seasonal variations in the isotopic composition of NO3 are observed in modern snow at Summit [Hastings et al., 2004]. Therefore seasonal and/or spatial changes in accumulation may affect the δ15N and δ18O of NO3 archived in the GISP2 ice core. At Summit today, the mean δ15N of NO3 is higher in summer (~0.3‰) than winter (~10.0‰), most likely because of seasonal changes in the sources of NO3 emissions. The lower mean δ18O of NO3 observed in summer (69.8‰) snow than in winter (77.5‰) is best attributed to seasonal changes in the oxidation chemistry that converts NO3 to HNO3 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 NO3 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 NO3 isotope found at Summit today [Hastings et al., 2004], one would expect the mean δ15N to be higher in Holocene ice from GISP2 than from Dye 3, and the δ18O to be lower, both of which appear to be the case (Figure 2b, Tables 1 and 2). Thus the differences in δ15N and δ18O of NO3 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 δ15N and δ18O of NO3. 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 δ15N 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 δ15N. However, the amplitude of the change in δ15N (~20‰) is much larger than any seasonal change observed today. Moreover, the increase in δ18O of NO3 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 δ15N and δ18O of NO3.

4.4. NO3 Sources and Chemistry

[26] At present, it is unclear whether the δ15N of NO3 predominantly reflects variability in the long-range transport of NO3 and/or fractionation associated with the cycling and subsequent conversion of NO3 to HNO3. Freyer et al. [1993] find an overall isotope effect of ~18‰ associated with NO/NO2 cycling (see reactions (R1)–(R2) below) based on measurements of NO3, O3, and the δ18O of NO2 in an urban environment. However, this isotope effect does not provide an adequate explanation for the observed seasonal changes in δ15N of NO3 at Summit [Hastings et al., 2004], Ny Alesund [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 δ15N of NO3 at Summit [Jarvis et al., 2004] (also J. Jarvis et al., Controls on the isotopic composition of NO3 and HNO3 at Summit, Greenland, submitted to Atmospheric Environment, 2005).

[27] Several studies suggest that the δ15N of NO3 most likely reflects the N isotopic composition of NO3 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 NO3 include biomass burning, biogenic soil emissions, lightning, and stratospheric injection [e.g., Wolff, 1995; Legrand and Kirchner, 1990]. The δ15N of NO3 from biomass burning, soil emissions and the stratosphere has not been directly measured, whereas Hoering [1957] found that the δ15N of
NO\textsubscript{3} produced from electric discharges (comparable to lightning) is between \(-0.5\) and \(+1.4\%\). Since lightning appears to be near \(0\%\), the positive \(^{15}\text{N}\) of NO\textsubscript{3} throughout the pre-industrial record (Figure 2b) suggests that other NO\textsubscript{3} emission sources, with positive \(^{15}\text{N}\) source signatures, make important contributions. Current study of the isotopic composition of NO\textsubscript{3} in Greenland has yet to reveal whether the \(^{15}\text{N}\) and \(^{18}\text{O}\) signals reflect local to regional or global scale NO\textsubscript{3} 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 \(^{15}\text{N}\) of NO\textsubscript{3} in ice from the glacial period reflects NO\textsubscript{3} emissions sources on a hemispheric to global scale. On the basis of measurements of the isotopic composition of N\textsubscript{2}O in the upper troposphere and the isotope effects associated with N\textsubscript{2}O oxidation, the NO produced from N\textsubscript{2}O oxidation in the stratosphere most likely has a low \(^{15}\text{N}\) [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 \(^{15}\text{N}\) via recycling of HNO\textsubscript{3} associated with polar stratospheric cloud particles. If the \(^{15}\text{N}\) of lightning NO\textsubscript{3} is near \(0\%\) and that for stratospheric production of NO\textsubscript{3} and HNO\textsubscript{3} is negative, then the large and positive \(^{15}\text{N}\) in glacial ice suggests that biomass burning and biogenic soil emissions are important contributors to the NO\textsubscript{3} budget in the last ice age. Direct measurements of the \(^{15}\text{N}\) of NO\textsubscript{3} from these sources are needed to further constrain this hypothesis.

On the basis of our present knowledge, the down core changes in \(^{18}\text{O}\) of NO\textsubscript{3} are best explained by changes in the major pathway of HNO\textsubscript{3} production in the atmosphere. HNO\textsubscript{3} is typically produced, during the day (or arctic summer), by the reaction of NO\textsubscript{2} with OH,

\begin{align*}
(R1) & \quad \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2, \\
(R2) & \quad \text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O}_3, \\
(R3) & \quad \text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M}.
\end{align*}

During night (arctic winter), HNO\textsubscript{3} is primarily produced via N\textsubscript{2}O\textsubscript{5} hydrolysis [Dentener and Crutzen, 1993; Stroud et al., 2003; Tie et al., 2003],

\begin{align*}
(R4) & \quad \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2, \\
(R5) & \quad \text{NO}_3 + \text{NO}_2 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M}, \\
(R6) & \quad \text{N}_2\text{O}_5 + \text{H}_2\text{O} (\text{surface}) \rightarrow 2\text{HNO}_3.
\end{align*}

Production of HNO\textsubscript{3} via N\textsubscript{2}O\textsubscript{5} hydrolysis (reaction (R6)) is of minor importance in the presence of sunlight because NO\textsubscript{3} (reaction (R4)) is readily lost via photolysis. The \(^{18}\text{O}\) of atmospheric NO\textsubscript{3} depends upon the oxidation processes that produce HNO\textsubscript{3} from NO\textsubscript{3}. 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 OH, \(^{18}\text{O}^{16}\text{O}\) is between \(0.5\%\) and \(+1.4\%\). Globally, the \(^{18}\text{O}\) of tropospheric water vapor is typically much less than \(0\%\) versus VSMOW, while the reported range in \(^{18}\text{O}\) of tropospheric ozone is \(75\%\) to \(120\%\) versus VSMOW [Krankowsky et al., 1995; Johnston and Thiemens, 1997]. For HNO\textsubscript{3} produced via reactions (R1)–(R3), two out of the three oxygen atoms in HNO\textsubscript{3} result from exchange with O\textsubscript{3}, while the third comes from OH. On the other hand, five out of the six oxygen atoms in the 2HNO\textsubscript{3} produced from reactions (R1) and (R4)–(R6) come from O\textsubscript{3}. Thus the OH pathway of HNO\textsubscript{3} production results in a lower \(^{18}\text{O}\) of NO\textsubscript{3} relative to the N\textsubscript{2}O\textsubscript{5} hydrolysis pathway [Hastings et al., 2003].

The higher \(^{18}\text{O}\) of NO\textsubscript{3} in the glacial period most likely reflects an increase in the fraction of HNO\textsubscript{3} produced via N\textsubscript{2}O\textsubscript{5} hydrolysis (as opposed to reaction of NO\textsubscript{3} with OH). The equilibrium in reaction (R5) is strongly temperature dependent, with lower temperatures favoring the production of N\textsubscript{2}O\textsubscript{5} [Sander et al., 2000]. The reaction rate for the hydrolysis of N\textsubscript{2}O\textsubscript{5} (R6) can be approximated as \(k_{R6} = (\gamma/4)nA\), where \(\gamma\) is the uptake coefficient, \(v = [8kT/m]\) 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 Hansson 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\textsubscript{3} production via N\textsubscript{2}O\textsubscript{5} hydrolysis. On the basis of the model of Michalski et al. [2003], we expect that future measurements will reveal a higher \(^{17}\text{O}\) of NO\textsubscript{3} in glacial ice as well, reflecting this increase in production of HNO\textsubscript{3} from N\textsubscript{2}O\textsubscript{5} hydrolysis.

The hydrolysis of N\textsubscript{2}O\textsubscript{5} in winter in the present Northern Hemisphere high latitudes represents a significant loss of NO\textsubscript{3}, which subsequently impacts the budgets of O\textsubscript{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 NO\textsubscript{3} hydrolysis needed to produce the observed \(^{18}\text{O}\) of N\textsubscript{2}O\textsubscript{5} by estimating the \(^{18}\text{O}\) of OH and O\textsubscript{3}. For example, if we assume a \(^{18}\text{O}\) of OH of \(~30\%\) and a \(^{18}\text{O}\) of O\textsubscript{3} in the middle of the reported range (105%); see above), then \(~55\%\) of the HNO\textsubscript{3} deposited to Greenland today must come from the N\textsubscript{2}O\textsubscript{5} pathway to explain the annual mean \(^{18}\text{O}\) of NO\textsubscript{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 \(^{18}\text{O}\) of NO\textsubscript{3} of 75.3%, we calculate that \(~75\%\) of the HNO\textsubscript{3} deposited to Greenland must be produced via N\textsubscript{2}O\textsubscript{5} hydrolysis if we assume a \(^{18}\text{O}\) of OH of \(~40\%\) and \(^{18}\text{O}\) of O\textsubscript{3} of 105%. (Note that our estimate of the \(^{18}\text{O}\) of OH is based on the \(^{18}\text{O}\) of ice and snow found in the Northern Hemisphere and the observation by Grootes and Stuiver [1997] that the \(^{18}\text{O}\) of snow is in equilibrium with the \(^{18}\text{O}\) of water vapor.) It is unclear at present whether the \(^{18}\text{O}\) of NO\textsubscript{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\textsubscript{3} from N\textsubscript{2}O\textsubscript{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$_2$O$_5$ 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$_3$ sources. On the basis of our current understanding of the $\delta^{15}N$ of NO$_3$ from lightning and the stratosphere, the relatively high $\delta^{15}N$ of NO$_3$ in the ice core record implies that NO$_3$ from biomass burning and biogenic soil emissions have positive $\delta^{15}N$ source signatures. Direct determination of the $\delta^{15}N$ of NO$_3$ 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$_2$O$_5$ hydrolysis. Compared to HNO$_3$ produced via reaction of NO$_3$ and OH, HNO$_3$ produced via N$_2$O$_5$ 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$_3$ 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$_3$, NO$_2$, and NO into chemical transport models will allow for quantitative estimates of past atmospheric chemistry and possibly NO$_3$ source changes.

[34] Acknowledgments. We thank Michael Bender for access to the GISP2 samples; Bruce Barnert, Thomas Blunier, and Joe von Fischer for sample collection; Greg Cane for analytical assistance; Julia Jarvis and Joel Thompson for useful discussions; and two anonymous reviewers for helping to significantly improve this manuscript. We also thank the National Ice Core Laboratory for the samples from Dye 3 and Camp Century. M. G. H. acknowledges support from the Department of Energy Graduate Research Fellowship (GCEP GREF). Additional support was provided by U.S. NSF through grants OCE-9981479, OCE-0081686, and OCE-0136449 to D. M. S., as well as by British Petroleum and Ford Motor Company through the Princeton Carbon Mitigation Initiative.

References


Dibb, J. E., R. W. Talbot, J. W. Munger, D. J. Jacob, and S. M. Fan (1998), Air-snow exchange of HNO3 and NOy at Summit, Greenland, J. Geo-

Environ., 36, 2501–2511.


Chem., 1010, 1494–1500.

Fischer, H., D. Wagenbach, and J. Kipfstuhl (1998), Sulfate and nitrate firm concentrations on the Greenland ice sheet: 2. Temporal anthropogenic deposition changes, J. Geo-

Union, Nice, France.

Freyer, H. D. (1978), Seasonal trends of NH4 and NO3 nitrogen isotope composition in rain collected at Jülich, Germany, Tellus, 30, 83–92.


Freyer, H. D., D. Kley, A. Volz-Thomas, and K. Kobel (1993), On the interpretation of isotopic exchange processes with photochemical reactions in the atmospheric oxides of nitrogen, J. Geo-


Fuhrer, K., and M. Legrand (1997), Continental biogenic species in the Greenland Ice Core Project ice core: Tracing back the biosphere history of the North American continent, J. Geo-


Gonfiantini, R., W. Stichler, and K. Rozanski (1995), Standards and inter-
Energy Agency, Vienna.

Groote, P. M., and M. Stuiver (1997), Oxygen 18/16 variability in Green-
land snow and ice with 103 and 105-year time resolution, Nature, 366, 552–554.


compose of ancient atmosphere: A model study constrained by atmospheric cycle (160,000 years), Atmos. Environ., 39, 624 – 629.

Heaton, T. H. E. (1986), Isotopic studies of nitrogen pollution in the hy-


Houltou, B. Z., M. Arsenault, and L. O. Hedin (2004), 15N/14N as a proxy for gaseous nitrogen losses across a forest rainfall gradient, paper pre-
mitted at the 98th Annual Meeting, Ecot. Soc. of Am., Portland, Ore.

Jarvis, J. E. (2000), Heterogeneous chemistry and tropospheric ozone, Atmos.
Environ., 34, 2131–2159.


Kahl, J. D. W., D. A. Martinez, H. Kuhs, C. I. Davidson, J. L. Jaffe, and J. M. Harris (1997), Air mass trajectories to Summit, Greenland: A 44-year climatological and some episodic events, J. Geo-

Kaiser, J. C., M. A. Brenninkmeijer, and T. Röckmann (2002), Intramole-
cular 15N and 14N fractionation in the reaction of N2O with O3 and its implications for the stratospheric N2O isotope signature, J. Geo-

Karl, I. L., V. A. Frolikis, and A. A. Kiselev (1995), Radiative-photochemi-
cal modeling of the annually averaged composition and temperature of the global atmosphere during the last glacial and interglacial periods, J. Geo-


Kanowski, D. F., B. J. Krueger, V. H. Grassian (2005), Laskin, A., T. W. Wietsma, B. J. Krueger, and V. H. Grassian (2005), Heterogeneous chemistry of individual mineral dust particles with nitric acid: A combined CCEM/EDX, ESEM, and ICP-MS study, J. Geo-

carboxylic acids in polar precipitation, J. Geo-

Legrand, M., and S. Kirchner (1997), Origins and variations of nitrate in south polar precipitation, J. Geo-

Laskin, A., T. W. Wietsma, B. J. Krueger, and V. H. Grassian (2005), Heterogeneous chemistry of individual mineral dust particles with nitric acid: A combined CCEM/EDX, ESEM, and ICP-MS study, J. Geo-

carboxylic acids in polar precipitation, J. Geo-

Martinierie, P., G. P. Braseur, and C. Granier (1995), The chemical-
composition of ancient atmosphere: A model study constrained by ice core data, J. Geo-


Mayewski, P. A., L. D. Meeker, M. S. Twickler, W. Whitlow, Q. Yang, W. B. Lyons, and M. Prentice (1997), Major features and forcing of high-
latitude Northern Hemisphere atmospheric circulation using a 110,000-
year-long glaciochemical series, J. Geo-


M. G. Hastings, Joint Institute for the Study of the Atmosphere and Ocean and Department of Atmospheric Sciences, University of Washington, Box 351310, Seattle, WA 98195-1640, USA. (mhasting@atmos.washington.edu)

D. M. Sigman, Department of Geosciences, Princeton University, Guyot Hall, Princeton, NJ 08544, USA.

E. J. Steig, Department of Earth and Space Sciences, University of Washington, Box 351310, Seattle, WA 98195-1310, USA.