

## Seasonal accumulation timing and preservation of nitrate in firn at Summit, Greenland

John F. Burkhart and Manuel Hutterli<sup>1</sup>

Department of Hydrology and Water Resources, University of Arizona, Tucson, Arizona, USA

Roger C. Bales

School of Engineering, University of California, Merced, California, USA

Joseph R. McConnell

Division of Hydrologic Science, Desert Research Institute, Reno, Nevada, USA

Received 17 February 2004; revised 19 May 2004; accepted 4 June 2004; published 2 October 2004.

[1] In a yearlong investigation of the air-snow transfer function for nitrate ( $\text{NO}_3^-$ ) at the Greenland Environmental Observatory, Summit (3203 m above sea level), surface snow concentrations measured every other day were compared with levels measured in 10 snow pits dug adjacent to accumulation stakes. Concentrations in the surface snow ranged from 0.4 to 34  $\mu\text{M}$  with a mean of  $2.9 \pm 1.9 \mu\text{M}$ . Measured firn profiles in the snow pits had a maximum  $\text{NO}_3^-$  concentration of 12  $\mu\text{M}$  and a mean of  $2.7 \pm 0.5 \mu\text{M}$ . Reconstructed profiles from surface snow observations and accumulation data closely matched the observed profiles. The small difference in preserved concentrations from observed surface snow concentrations gives evidence of only 7% postdepositional loss at this site (mean annual accumulation  $\sim 23 \text{ g cm}^{-2} \text{ yr}^{-1}$ ). Removing the three highest outliers (which may originate from local sources) of surface snow concentration drops the mean to 2.7  $\mu\text{M}$ , further demonstrating preservation. Results indicate that at this site accumulation is the most significant process affecting preservation of nitrate in the firn. Other rapid postdepositional processes may impact surface snow concentrations, but do not appear to significantly change the preserved record. The inverse analysis of converting preserved records to surface snow concentrations provides equivalent evidence of the same preservation. **INDEX TERMS:** 0312 Atmospheric Composition and Structure: Air/sea constituent fluxes (3339, 4504); 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 1854 Hydrology: Precipitation (3354); 1863 Hydrology: Snow and ice (1827); 3344 Meteorology and Atmospheric Dynamics: Paleoclimatology; **KEYWORDS:** nitrate preservation, snow and ice, Greenland

**Citation:** Burkhart, J. F., M. Hutterli, R. C. Bales, and J. R. McConnell (2004), Seasonal accumulation timing and preservation of nitrate in firn at Summit, Greenland, *J. Geophys. Res.*, 109, D19302, doi:10.1029/2004JD004658.

### 1. Introduction

[2] Ice cores as high-resolution archives of paleoatmospheric conditions have given the scientific community a valuable tool to understand natural variability of the atmosphere at timescales from annual to 100 kyr. More recent drilling projects have dated recovered ice with annual and even subannual accuracy [McConnell *et al.*, 2002a; Hutterli *et al.*, 2001]. The recent documentation of rapid climate change [Alley *et al.*, 2003; National Research Council, 2002] further highlights the importance of high temporal resolution climate records. A higher-resolution record enables a more complete understanding of the transfer

function for the constituent of interest, and the possibility to separate actual atmospheric change from noise resulting from variability in the deposition or preservations of species recorded in ice cores.

[3] As a reversibly deposited species in the snow, the transfer function for  $\text{NO}_3^-$  involves multiple processes. Recent work [Munger *et al.*, 1999; Jones *et al.*, 1999, 2000; Beine *et al.*, 2002; Dibb *et al.*, 2002; Honrath *et al.*, 1999, 2000, 2002; Wolff *et al.*, 2002] has shown that  $\text{HNO}_3$  in the surface snow is recycled in a photochemical cycle between the boundary layer, surface snow, and interstitial air. Negative fluxes of  $\text{NO}_x$  in the boundary layer, and net positive fluxes of  $\text{NO}_3^-$  in the snow have been observed, suggesting that the snowpack is ultimately a source for  $\text{NO}_x$  while acting as a sink for  $\text{NO}_3^-$  [Honrath *et al.*, 2002].

[4] Preservation of  $\text{NO}_3^-$  in polar snow and ice is thought to be determined by (1) snow accumulation, (2) temperature, (3) in situ physiochemical reactions, (4) temperature-

<sup>1</sup>Also at Climate and Environmental Physics, University of Bern, Bern, Switzerland.

dependent partitioning between the air and ice, and (5) pH-dependent mobility of the ion in ice [Bales, 1995; Bales and Choi, 1996; Röthlisberger *et al.*, 2000a, 2002]. Recent studies of Röthlisberger *et al.* [2002] provide evidence for a strong correlation of the  $\text{NO}_3^-$  concentration in snow with temperature, given sufficient accumulation ( $>5 \text{ g cm}^{-2} \text{ yr}^{-1}$ ) to preserve the  $\text{NO}_3^-$  in Antarctica and Greenland. They also show that  $\text{NO}_3^-$  concentrations may be strongly affected by the pH of the snow at the time of deposition. Further demonstrating the effect of snow pH are the results of Beine *et al.* [2003] that show increased alkalinity of the snow may reduce the availability of nitrate in the snowpack to postdepositional physical exchange or photochemistry. Results from a coastal Antarctic station with low accumulation demonstrated the cause for postdepositional loss of  $\text{NO}_3^-$  in the near surface snow to be likely controlled by an equilibrium process with atmospheric concentrations [Beine *et al.*, 2003; Mulvaney *et al.*, 1998]. In contrast, Yang *et al.* [1995] did a linear regression of annual mean concentration with annual accumulation in the GISP II core and concluded that  $\text{NO}_3^-$  concentrations at Summit, Greenland, are independent of accumulation. Their study of five northern hemispheric ice cores, however, does show a clear relationship between the flux of  $\text{NO}_3^-$  and accumulation. An earlier study of south polar snow had similar results, finding that  $\text{NO}_3^-$  concentration was independent of accumulation while flux strongly depended on accumulation [Legrand and Kirchner, 1990]. All of these findings are contradictory to the initial work of Herron [1982], who suggested higher accumulation resulted in a dilution of  $\text{NO}_3^-$ .

[5] Accumulation on the Greenland Ice Sheet is sufficient in most regions to adequately preserve the annual signal of  $\text{NO}_3^-$ . Research described in this paper focused on the postdepositional changes of  $\text{NO}_3^-$  during the first year following snow deposition. Specifically, we asked, (1) Can year-round surface snow concentrations be accurately estimated from the concentrations preserved in the firn, and (2) what components of the transfer function for  $\text{NO}_3^-$  most affect the preserved profiles?

## 2. Methods

[6] Three sets of measurements were used in this analysis: field observations of snow accumulation, nitrate concentrations measured in surface snow samples collected year-round, and nitrate concentrations in snow pit samples collected at the end of the year-round period. Observations of snow accumulation were made during three periods when personnel were on-site year-round at the Greenland Environmental Observatory (GEOSummit) located at the summit of the Greenland Ice Sheet (3203 m above sea level (masl)). The spatial variability of snow accumulation was measured approximately twice a week from June 1997 to May 1998 and again from August 2000 to August 2002 at 100 1.5-m-long bamboo poles set in a square array, 10 stakes to a side, with 10-m spacing. An additional single measurement of the array was made in August of 1999. A datum was set at the top of each  $\sim 1.5 \text{ m}$  stake initially, and the distance from the datum to the snow surface was recorded to within 0.5-cm. Once or twice a year the snow stakes were reset as snow accumulated. The measurements represent net snow accumulation for the period between measurements.

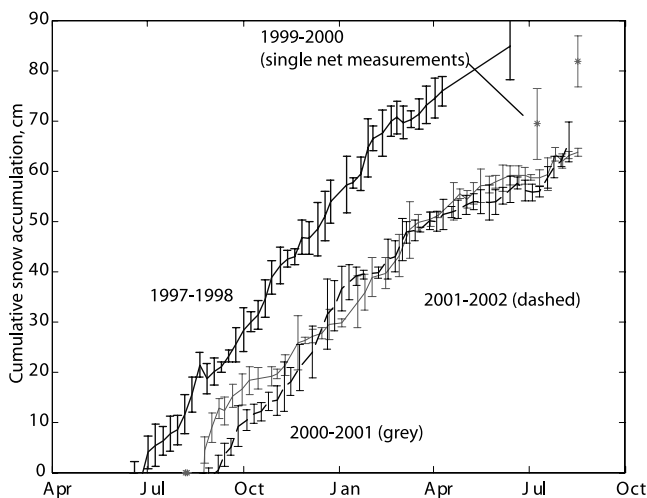
[7] During the year-round campaigns, personnel also collected surface snow scrapes from the topmost homogeneous layer every other day and during fresh snow events wearing polyethylene gloves and a Tyvek® suit and using stainless steel or Plexiglas scrapers to collect enough volume of the surface snow layer to fill a 100-mL Schott bottle. The bottles were stored and shipped frozen to our laboratory for analysis. Snow samples were collected approximately 100 m northeast of the accumulation array in an area that has been designated “no traffic” and is upwind of local pollution sources. Descriptions of the snow age and texture were recorded.

[8] In July 1998, 1.2-m snow pits were sampled at 1-cm resolution beside 10 of the stakes around the periphery of the accumulation array. Snow pits were excavated by personnel wearing polyethylene gloves and a Tyvek® suit to minimize contamination using a clean aluminum hand shovel. The sampled wall was carefully scraped using a stainless steel sheet and observations of stratigraphy and temperature were recorded. Snow samples were taken at 1-cm intervals with a stainless steel trowel measuring  $5.5 \times 6 \times 1 \text{ cm}$  ( $33 \text{ cm}^3$ ) that had been prerinsed in milli-Q water. Care was taken that no grains were able to cross contaminate samples. Samples were weighed and stored in Whirl-pack bags and shipped frozen to our laboratory. The weight variability of 100 Whirl-pack bags was less than 0.05 g, well below the observed standard deviation of sample weights (0.15 g) and the range for sample measurements within the pits.

[9] Once received in our lab, the surface snow and snow pit samples were stored frozen at  $-15^\circ\text{C}$  until analyzed. Two hours prior to analysis, each sample was thawed in a clean glass bottle with aliquots transferred by syringe for injection into a Dionex® DX-100 IC ion chromatograph system. All samples were analyzed with a standard sample injection volume of 4 mL. Standards were used to calibrate the IC prior to and following sample analysis [Littot *et al.*, 2002].

## 3. Results

[10] The mean annual snow accumulation for the entire observation period was 74.4 cm snow with a standard deviation of 8.1 cm. Using a surface snow density of  $0.31 \text{ g cm}^{-3}$  (GEOSummit, unpublished data, 1997–1998, 2000–2003), the mean annual accumulation is equivalent to  $23.1 \text{ g cm}^{-2}$  water. Accumulation during the 1997–1998 winter was  $26.0 \text{ g cm}^{-2}$ , 13% greater than the mean (Figure 1). This winter appears to be unique from the other two years showing a more linear growth pattern. During the 2000–2002 seasons, one can see some seasonal changes in the slope of the cumulative accumulation record (Figure 1). From the individual monthly averages of all years, it is apparent there is seasonality (Figure 2), with the lowest accumulation occurring during the months of April, May, and June. This trend is consistent in individual monthly averages of the gross accumulation (sum of positive measurements). Additionally, the seasonal cycle of the net accumulation appears to be enhanced because of increased loss during the summer months. While it is tempting to label the loss sublimation, other processes such as enhanced densification during the summer or redistribution of the

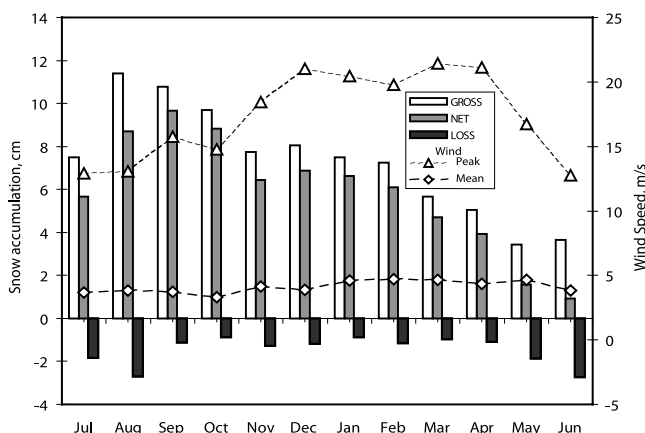


**Figure 1.** Cumulative mean accumulation and standard deviation for the 100-stake field at Summit, Greenland. Note that only two net measurements were made for the 1999–2000 year.

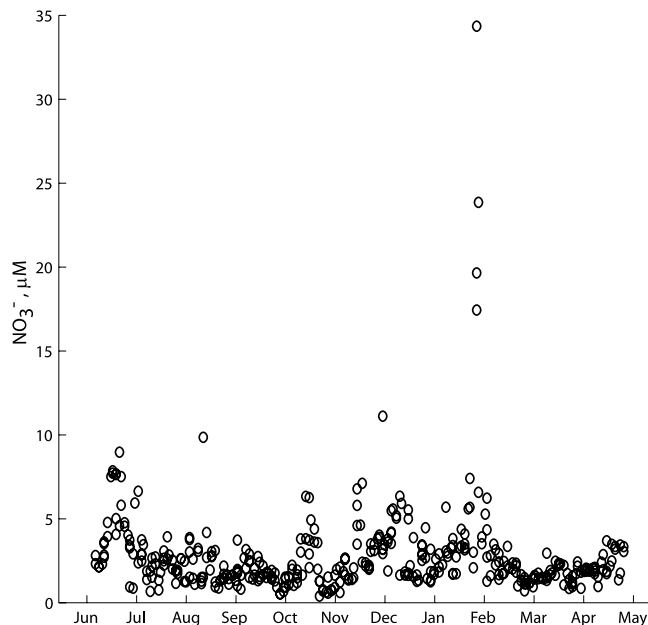
surface snow from wind must be considered. However, there does not appear to be a clear relationship between the mean or peak wind speeds with the height change variability (Figure 2). For the 3 years of cumulative snow height measurements, there is an average gross loss of 20%.

[11] Of 398 samples of surface snow collected between June 1997 and May 1998,  $\text{NO}_3^-$  concentrations ranged from 0.4 to  $34.4 \mu\text{M}$ , with 85% of the values being less than  $5 \mu\text{M}$  (Figure 3). Mean concentration was  $2.9 (\pm 1.9) \mu\text{M}$ . There is variability in the record; however, there is no clear seasonality. Some of the “spikey” variability may likely be from local camp pollution.

[12] Snow pits sampled to 1-m depth with a 1-cm resolution had a mean annual concentration of  $2.7 (\pm 0.5) \mu\text{M}$  (Table 1). The maximum concentration recorded in any of the pit samples was  $12 \mu\text{M}$ , observed in pit i-10, which in general had a higher degree of variability than the other pits. Flux for the snow pits was calculated as the sum of



**Figure 2.** Monthly snow accumulation (gross, net, and loss) averaged over the 100-stake field for all 3 years. Mean and peak wind speeds are shown for concurrent measurement periods.



**Figure 3.** Surface snow concentrations from 1997–1998 year-round measurements.

cumulative layer inventories during 1 year using the relationship between concentration (converted to  $\text{g m}^{-3}$ ) and accumulation:

$$F_l = C_l \times A_l,$$

where  $F_l$  is flux for individual layer ( $\text{g m}^{-2}$ ),  $C_l$  is concentration of layer ( $\text{g m}^{-3}$ ), and  $A_l$  is accumulation for individual layer (meters water equivalency). Average nitrate flux over a 1-year period for the 10 snow pits was  $0.05 (\pm 0.01) \text{ g m}^{-2} \text{ yr}^{-1}$ .

[13] Concentration versus depth profiles for each stake were constructed from the single-year set of surface snow concentrations (Figure 3) and the stake-specific change in snow height ( $dh/dt$ ) measurements of (Figure 4). A concentration was assigned to each preserved layer using averages of the surface snow concentrations for the 2-week period in which the accumulation occurred. Only those layers that had subsequent burial (i.e., positive  $dh/dt$ ) were assumed to be preserved. During periods of negative or zero accumulation, it was assumed that there was no preservation of  $\text{NO}_3^-$ . Additionally, if a loss of snow occurred during a 2-week period exposing the previous layer(s),  $\text{NO}_3^-$  was assumed lost and a new layer thickness was calculated for the old layer. Neither the concentration profiles constructed from the snow-stake and surface snow concentrations nor those observed in the 10 snow pits collected after the 1997–1998 year-round season showed distinct seasonal patterns (Figure 5).

[14] The results of  $t$  tests performed both on the observed and reconstructed concentration values for each pit show that with a confidence of 95% the values in the reconstructed pits are not statistically different from the observations with the exception of pit c-1 (Table 1). To examine whether the constructed profiles had the same sample distribution as the observations, Kolmogorov-Smirnov (KS) tests were conducted. For all but two pits, c-1 and j-6, there was no

**Table 1.** Results From Observations, Reconstructions, and Statistical Analysis of 10 Snow Pits<sup>a</sup>

	Pit Identification										Standard Deviation
	a-5	a-9	c-1	g-10	h-1	i-10	j-1	j-10	j-6	j-7	Mean
Mean observed concentration, $\mu\text{M}$ (standard deviation)	2.80 (0.2)	2.74 (0.2)	1.89 (0.15)	2.90 (0.23)	2.91 (0.34)	3.56 (0.68)	2.73 (0.11)	2.44 (0.70)	2.09 (0.11)	2.81 (0.07)	2.69
Mean constructed concentration, $\mu\text{M}$ (standard deviation)	2.79 (0.24)	2.91 (0.34)	2.93 (0.37)	2.55 (0.20)	2.58 (0.79)	2.90 (0.09)	2.38 (0.84)	2.23 (0.83)	2.30 (0.81)	2.83 (0.37)	2.64
<i>t</i> test for observed versus constructed concentration $h(p)$	0 (0.95)	0 (0.83)	1 (0.01)	0 (0.47)	0 (0.59)	0 (0.25)	0 (0.22)	0 (0.32)	0 (0.26)	0 (0.94)	–
KS test for observed versus constructed concentration $H(p)$	0 (0.52)	0 (0.49)	1 (0.01)	0 (0.16)	0 (0.19)	0 (0.26)	0 (0.40)	0 (0.27)	1 (0.00)	0 (0.12)	–
Annual flux observed, $\text{g m}^{-2}$ (underestimate from improper dateline)	0.05 (–3%)	0.04 (–8%)	0.03 (–14%)	0.03 (–4%)	0.06 (–2%)	0.06 (0%)	0.05 (–2%)	0.04 (–1%)	0.04 (–1%)	0.05 (0%)	0.05
Annual flux constructed, $\text{g m}^{-2}$	0.05	0.04	0.04	0.03	0.06	0.05	0.05	0.04	0.04	0.05	0.05
Depth observed, m snow	–0.895	–0.735	–0.755	–0.65	–0.97	–0.775	–0.925	–0.82	–0.94	–0.835	–0.83
Depth constructed, m snow	–0.925	–0.8	–0.86	–0.68	–0.99	–0.775	–0.95	–0.83	–0.945	–0.835	–0.86
Accumulation observed, $\text{g cm}^{-2} \text{ yr}^{-1}$	29.1	25.5	26.4	20.6	32.2	26.2	32.5	26.7	32.2	27.4	27.9
Accumulation constructed, $\text{g cm}^{-2} \text{ yr}^{-1}$	28.5	23.7	23.4	19.6	31.5	26.6	31.6	26.4	31.2	27.7	27.0
											4.0

<sup>a</sup>Means of observations are calculated from a depth based on the gross accumulation for the year.

statistical difference between the reconstructed and observed distributions.

[15] Flux calculations were made using the concentration profiles, available density profiles, and depth timescales for each pit. The reconstructions generally followed the observations for seven of the 10 pits with the exceptions of pits c-1, g-10 and i-10 (Figure 6). These differences likely resulted from differences in whether or not spikes were preserved. In c-1, a large spike at 30-cm depth was not evident in the pit. This spike created an overestimate of flux that was proliferated throughout the depth of the pit ultimately overestimating the flux by 50%. The reverse is the case for g-10, a peak in the pit was not reflected in surface snow, leading to an underestimate by 15% of the annual flux. In pit i-10, an underestimate also results though by 15%. Several peak events were evident in the pits, yet the surface snow only exhibited one major peak, which occurred in the late winter.

## 4. Discussion

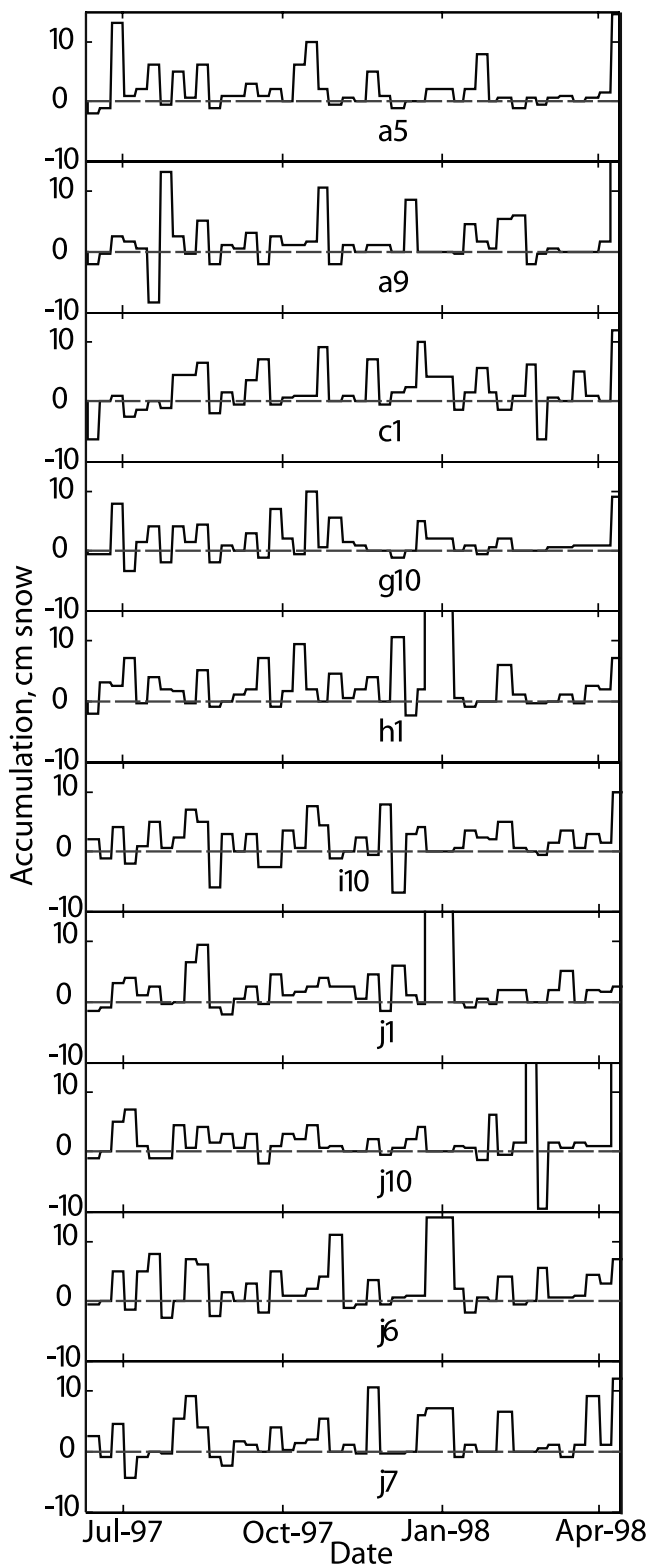
### 4.1. Characterization of Preserved Nitrate Record

[16] The importance of accumulation for the preservation of reversibly deposited species has been demonstrated in numerous studies. *Steig et al.* [1994] showed the concentration of seasonally varying species in an ice core record is largely sensitive to the temporal distribution of accumulation events. In a physically based model of atmosphere-to-firm transfer of  $\text{H}_2\text{O}_2$  and  $\text{HCHO}$ , *Hutterli et al.* [2003] demonstrated that the greatest uncertainty in paleoatmospheric mixing ratios developed from proxy records of preserved profiles is a function of the seasonality and timing of accumulation.

[17] Accumulation records for the 3 years of measurement exhibited large interannual variability (Figure 1). In particular, 1997–1998 had a 13% greater accumulation rate than the two later years. This particular year was an El Niño year and it is possible the accumulation at Summit was affected by the climate anomaly. Another difference is the linear nature of accumulation during the 1997–1998 season. The latter 2 years of measurements from 2000 to 2002 showed a higher degree of nonlinearity, consistent with the pattern presented by *Bromwich et al.* [1993].

[18] Reconstructions of the firm nitrate profiles demonstrate the importance of understanding accumulation variability when reconstructing paleosurface snow concentrations from preserved records. In part, because our biweekly accumulation measurements were not as frequent as the surface snow measurements of nitrate, which were 3–4 times per week, the reconstructed depth profiles failed to match many of the concentration spikes in the preserved pits in a one-to-one basis. Surface snow concentrations exhibited considerable day-to-day variability, owing to both fresh and blowing snow (Figure 3). However, there are some qualitative similarities in the profiles. In a few of the pits (a-9, c-1, j-10), there are sections where there is almost an exact match between the reconstructions and the observations. It can be seen that for pit a-9, the high-concentration surface snow event was captured in both profiles. In other pits this event was either not captured, or smoothed by postdepositional processes. However, nine of 10 pits are statistically indistinguishable to the observed profiles





**Figure 4.** Stake-specific snow height measurements from Summit, Greenland, 1997–1998.

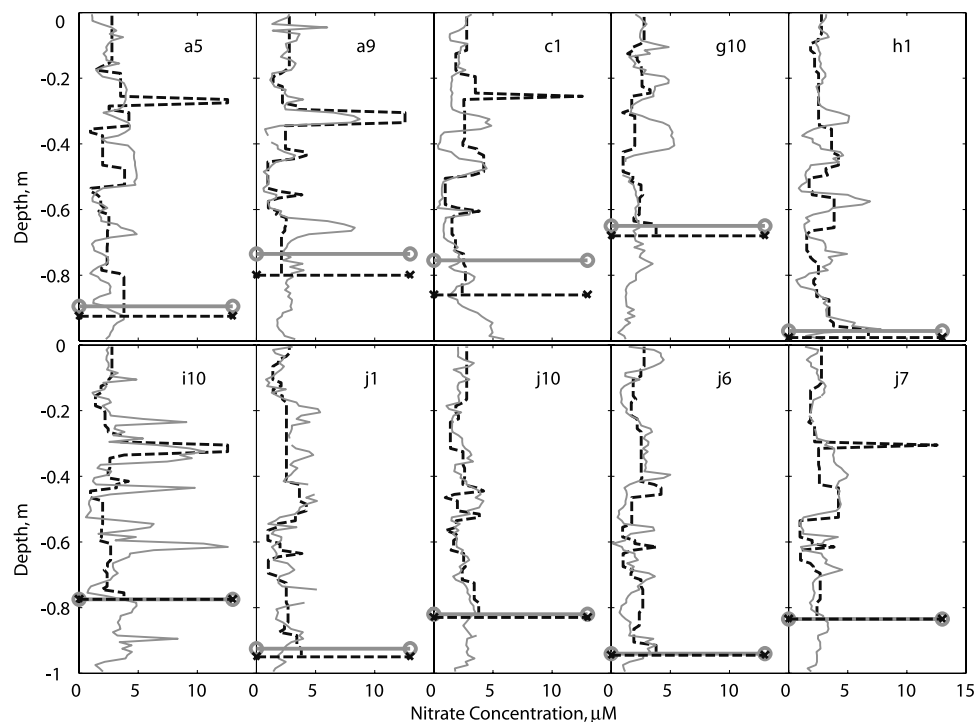
(Table 1,  $t$  tests) and eight of 10 pits have a consistent distribution (Table 1, KS tests). Visually, the mismatch in profiles appears to be due to a combination of concentration spikes and small offsets in timing, both of which could reflect wind redistribution of snow. Similarly, the mismatch in

average concentration in pit c-1 appears to be due to differences in one main event.

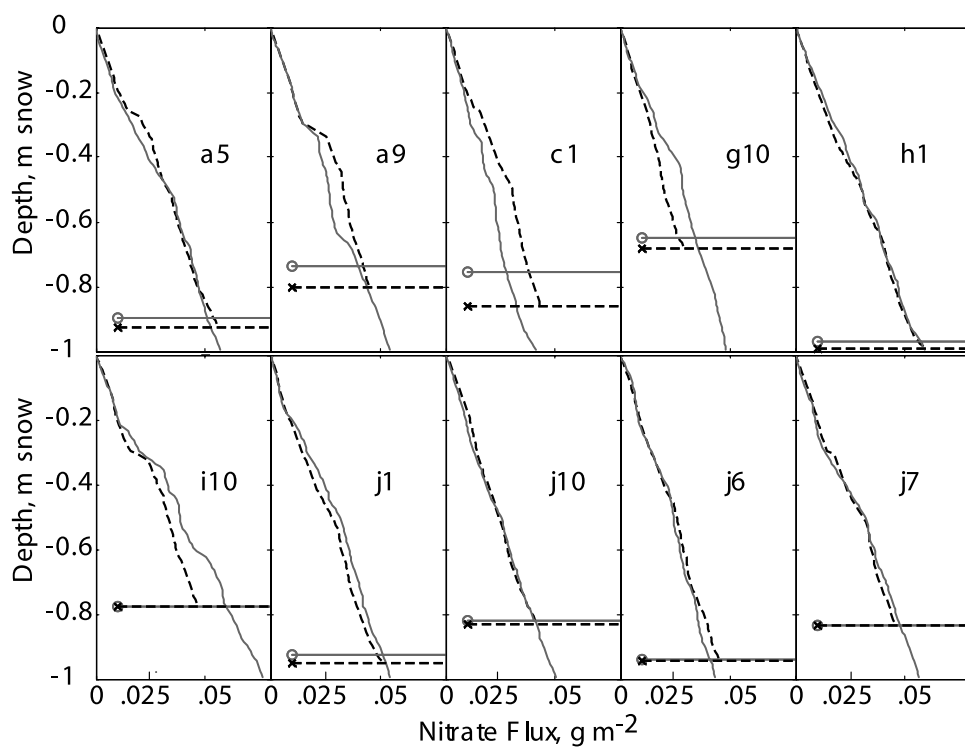
[19] Assuming an average annual snowfall at Summit of  $\sim 70$  cm, the 1-cm pit sampling gave an average resolution of more than one sample per week or twice as frequent as the reconstruction based on biweekly observations. However, because of sublimation and wind-driven snow redistribution, the actual age of layers in the pits varies and they are neither uniform nor sequential. It is common to measure accumulation at stake arrays assuming a starting point datum, and measuring the net accumulation at some point in time afterward. This approach yields a similar result to picking annual indicators in ice cores. When calculating nitrate flux for individual snow pits, we compared using the net accumulation to establish the depth for the 1-year interval and the depth based on the reconstruction. When constructing the snow pits, weekly snow height changes are either added or subtracted from an initial datum. In some cases, the surface level of the snow drops below the initial datum because of sublimation or physical removal. In these cases the actual depth of the pit for the year exceeds that measured by net accumulation. The depth based on the reconstruction is the actual depth of the 11 June 1997 layer; however, using this value will bias the results to overestimate accumulation, and thus flux, as it includes a component of the gross accumulation the net stake measurements miss. Note that datum for the reconstructions in most cases are within 3% of the net dateline. However, in two of the pits (a-9 and c-1) they differ by 8% and 14% (Table 1 and Figures 5 and 6). Lacking high-resolution seasonal markers it is common to simply assume uniform annual accumulation over the year [Beer *et al.*, 1991]. Using high-resolution continuous flow analysis [e.g., Röthlisberger *et al.*, 2000b; McConnell *et al.*, 2002b] one can infer seasonal markers and thus improve the accuracy of time-depth calculations.

[20] The empirical reconstructions do not account for chemical postdepositional processes. Differences in profiles (e.g., i-10, Figure 5) most likely result from surface snow redistribution, as well as the net effect of nitrate loss from surface snow to the atmosphere and dry deposition of  $\text{HNO}_3$  to surface snow. Nine of the 10 pits had similar stratigraphy; however, that of i-10 was unique from the other pits, with excessive hoar layers at 30 and 60 cm depths. In a study of structure and microphysics of arctic snowpack in Alert, Domine *et al.* [2002] described intense sublimation and condensation cycles leading to the formation of hoar layers. Using acetone as an example, they show that major releases of the compound may be induced with increases in temperature and physical restructuring of the snow surface area. Changes have also been documented in formaldehyde and hydrogen peroxide concentrations during snow metamorphism. [Hutterli *et al.*, 1999, 2001; McConnell *et al.*, 1997].

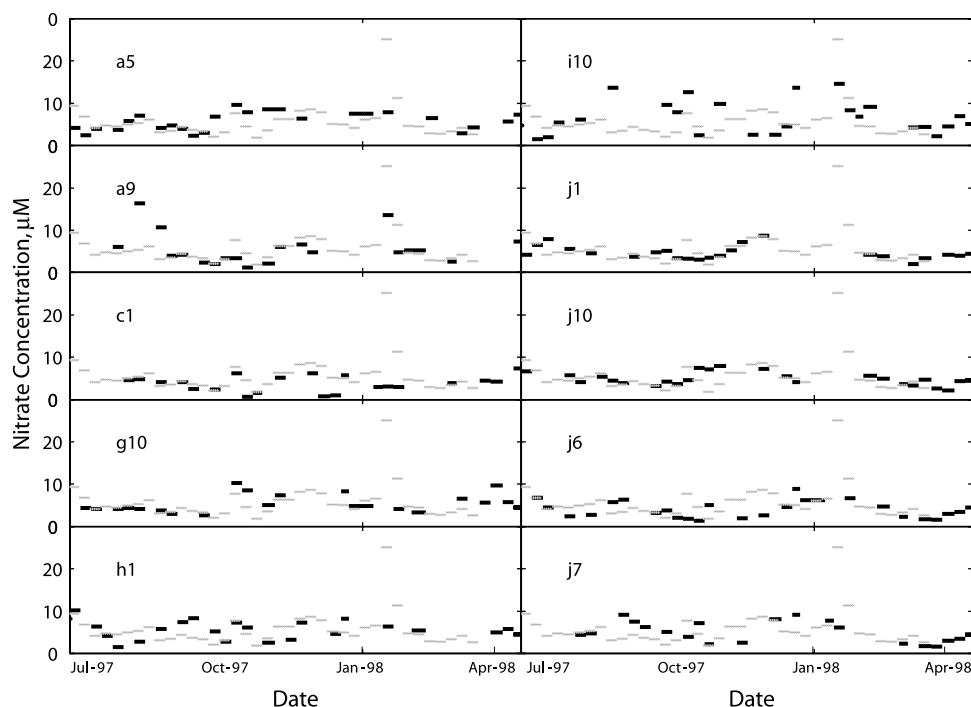
[21] The linear characteristic of the cumulative flux profile suggests that flux is uniform with accumulation. Whether or not the flux is uniform throughout the year is a function of the timing of the accumulation and concentrations in the surface snow. On average across the stakes, accumulation was linear through the 1997–1998 season (Figure 1). However, this may not be the case for all years or for other regions of the ice sheet [Bromwich *et al.*, 1999]. The ability of the reconstructions to mirror the measured flux observations demonstrates how large a role



**Figure 5.** Observed (vertical shaded) and reconstructed (vertical dashed) snow pit profiles of nitrate concentrations. The 1-year dateline of 11 June 1997 from cumulative accumulation observations is shown as a horizontal shaded line. The reconstructed maximum depth is shown as a vertical dashed line. The vertical scale is snow depth, measured as collected.



**Figure 6.** Observed (shaded) and reconstructed (solid) snow pit cumulative nitrate flux profiles. The 1-year dateline of 11 June 1997 from cumulative accumulation observations and from the reconstructions is also shown.



**Figure 7.** Observed (shaded) biweekly surface snow concentrations and reconstructed (black) surface snow concentrations from preserved layers in the snow pits.

accumulation variability and timing play in the preservation of  $\text{NO}_3^-$ . In cases where there are not strong postdepositional alterations in the pits, one can accurately estimate the total flux from concentrations accounting for accumulation alone. Accounting for accumulation alone successfully captures the statistical nature of the annual deposition. However, in cases that have high-resolution variability of the  $\text{NO}_3^-$  record in the snow, or if one is looking at seasonal variability, a more rigorous approach to the transfer function is required. In recent decades there is no obvious seasonal cycle in  $\text{NO}_3^-$  concentrations (e.g., Figures 3 and 5). However, prior to anthropogenic influences on  $\text{NO}_3^-$  definite peaks in spring are apparent [e.g., Anklin *et al.*, 1998], resulting in a slightly higher spring flux.

[22] Conditions at Summit are very good for the preservation of nitrate as a result of the consistently cold temperatures and the relatively high accumulation. In areas of lower accumulation such as Dome-C, postdepositional processes will play a greater role in the preserved record [Wolff *et al.*, 2002; Röthlisberger *et al.*, 2000a]. Rapid losses have been observed at Dome C, which exceed estimates of nitrate photolysis in the snowpack. Other measurements of South Pole surface snow samples of nitrate exhibit up to 90% losses (J. McConnell, unpublished data, 2000). To accurately characterize the nitrate record in lower accumulation conditions will require a physically based transfer function model.

[23] This study demonstrates that deposition of nitrate through the winter is largely irreversible but closely related to the timing of snowfall events. The results of correlation analysis of the mean values from the snow pit observations show a stronger relationship between flux with concentration ( $\rho = 0.73$ ) and flux with accumulation ( $\rho = 0.55$ ). With respect to the observations, between the two components

concentration and accumulation; about 25% and 35%, respectively, of the variability of flux can be explained. While this explains more than half of the variability in the observations, it demonstrates that there is still a large component of unexplained variability that likely results from postdepositional processes. Interestingly, there is very little correlation between concentration and accumulation alone within the 10 snow pits. This is consistent with the results of Yang *et al.* [1995], who found that there was no clear correlation between these two variables, in a multi-century analysis of the GISP core which was also drilled at Summit.

[24] As an argument that postdepositional transformations are occurring only to  $\text{NO}_3^-$  in the snow, Yang *et al.* [1995] conducted normality tests on chemical concentration data in four ice cores. Nitrate was the only compound for which annual means were normally distributed. Their argument concluded that the normal distribution was a result of postdepositional transformation that did not alter other ions in the snow. Normality tests conducted on all pits in this study had varied results. Only two of the observed profiles were normally distributed. The same is true for the reconstructed pits, with the exception of the two that failed the KS test, j-1 and j-10. However, these results do not necessarily differ from those of Yang *et al.*, as the timescale of the observations is very different. Their tests were conducted on annual average values whereas ours are conducted on irregularly spaced data within a snow pit spanning 1 year. Postdepositional processes for  $\text{NO}_3^-$  may, and likely would, continue for longer than 1 year. What is important to note, is the similarity of the two distributions within each pit. One could argue that preservation resulting from high accumulation, rather than postdepositional processes, is accounting for a large portion of the variability

**Table 2.** Statistics for Surface Snow Samples and Reconstructed Surface Snow Time Series

	Mean of Surface Snow Observations	Pit Identification										Mean of Pits	Standard Deviation
		a-5	a-9	c-1	g-10	h-1	i-10	j-1	j-10	j-6	j-7		
Mean concentration, $\mu\text{M}$	2.90	2.91	3.27	1.78	2.46	3.05	3.65	2.42	2.44	2.11	2.85	2.70	0.56
Standard deviation	1.97	1.09	2.59	0.88	1.02	1.43	2.08	0.92	0.72	0.90	1.02	1.27	0.60
Maximum concentration, $\mu\text{M}$	11.65	4.81	8.33	3.35	4.55	5.62	8.01	4.50	4.02	3.69	4.67	5.16	1.71
Minimum concentration, $\mu\text{M}$	0.92	1.14	1.01	0.40	0.95	0.65	0.71	1.00	1.30	0.94	1.11	0.92	0.26
$t$ test for observed versus constructed concentration $h(p)$	–	0 (0.64)	0 (0.88)	1 (0.02)	0 (0.98)	0 (0.72)	0 (0.48)	0 (0.95)	0 (0.88)	0 (0.44)	0 (0.18)	–	–

within the first year of deposition, as the reconstructions capture the statistical nature of the distribution for both individual pits and spatially looking at all 10 pits.

#### 4.2. Inversion of Pit Record

[25] To understand the importance of the high-resolution variability, we have examined back calculations of surface snow concentrations from the observed pit profiles. One of the greatest challenges to the proper interpretation of ice core proxies is inverting the record to a meaningful record of the “time of deposition” conditions. The inversion of preserved snow or ice profile to surface snow concentrations is one step in a multistep process of inverting an ice core record to an atmospheric concentration.

[26] Using only the observed snow pit concentration profiles, and the depth-age relationship generated from the reconstructions, a time series of surface snow concentrations was estimated from the pit measurements. The calculations assumed 100% preservation of  $\text{NO}_3^-$  in snow that accumulated. In other words, if the layer of fresh snow was preserved in the pit, all of the  $\text{NO}_3^-$  was also preserved.

[27] Time series of surface snow concentration generated from the pit profiles along with weekly average time series from the winter-over observations are shown together in Figure 7. In general the agreement is quite good, however, as with reconstructing the firn profiles, it is clear some of that variability is not captured, leading to an underestimate or overestimate of the surface snow concentrations at different points throughout the year. Surface snow reconstructions from preserved layers in the pits pass  $t$  test comparisons with surface snow from the same period of time with the exception of pit c-1 (Table 2). To conduct the  $t$  test the populations of concentration from preserved layers are compared with a population of concentration from observed surface snow during the same period that the preserved layers represent. The means of all the time series ( $2.7 \mu\text{M}$ ) is  $\sim 7\%$  lower than mean surface snow observations ( $2.9 \mu\text{M}$ ), as can be seen in Table 2. However, the mean of the surface snow observations drops to  $2.7 \mu\text{M}$  simply by removing the three highest concentration events in the surface snow record. This evidence of rapid postdepositional loss is shown by the fact that none of the inverted pit observations generates a surface snow concentration equivalent to the maximum observed concentration and that the mean concentrations match when those spikes are removed. The physical process of wind redistribution smoothing the surface snow record may explain these rapid losses, however, one must not exclude the possibility of

other physical or chemical processes occurring in the surface snow.

#### 5. Conclusions

[28] Concentration profiles developed using only observed accumulation and mean surface snow concentration closely matched the observed pit profiles. Though there was not a strong correlation between annual accumulation and concentration, it is clear accumulation is critical to the preservation of  $\text{NO}_3^-$  and that by accounting for accumulation and surface snow concentrations the variability of nitrate flux may be adequately captured at Summit, Greenland. The ability to reconstruct pit profiles indicated that postdepositional processes controlling  $\text{NO}_3^-$  preservation at Summit are mainly driven by accumulation variability and wind redistribution. Over 90% of the measured nitrate in the surface snow is preserved in the pits indicating that photochemistry and temperature-dependent uptake and release from the snow do not play as important a role with preservation at Summit as has been indicated for Antarctic sites. Estimating surface snow concentrations from snow pits was also successful, using knowledge of the timing of snow accumulation. These results suggest that inverting a preserved record in a longer core to reproduce past conditions and estimating annual fluxes based on knowledge of the accumulation timing should be feasible. The use of statistical rather than time series accumulation data should be further analyzed.

[29] **Acknowledgments.** This research was conducted under the National Science Foundation's Office of Polar Programs research grants: 9813442 and 9813311 and a NASA Earth System Science Fellowship. M. H. was partly funded by the EC project PACLIVA (EVR1-2002-000413). Research at Summit is made possible with the generous permission of the Danish Polar Centre and Greenland Home Rule Ministry of Environment and Nature. Without the support of year-round staff at the Greenland Environmental Observatory ([www.geosummit.org](http://www.geosummit.org)) and the logistical support of VECO Polar Resources, none of this work would be possible. In addition, special thanks to J. Dibb for access to the year-round surface snow chemistry data analyzed at UNH and to K. Wolff, K. Young, and the 1998 crew at Summit for their field support.

#### References

- Alley, R. B., et al. (2003), Abrupt climate change, *Science*, 299, 2005–2010.
- Anklin, M., R. C. Bales, E. Mosley-Thompson, and K. Steffen (1998), Annual accumulation at two sites in northwest Greenland during recent centuries, *J. Geophys. Res.*, 103, 28,775–28,783.
- Bales, R. C. (1995), Nitric acid in firn: Discussion, in *Ice Core Studies of Global Biogeochemical Cycles*, NATO ASI Ser., Ser. I, vol. 30, edited by R. Delmas, pp. 241–245, Springer-Verlag, New York.
- Bales, R. C., and J. Choi (1996), Conceptual framework for interpretation of exchange processes, in *Chemical Exchange Between the Atmosphere*



- and Polar Snow, *NATO ASI Ser., Ser. I*, vol. 43, edited by E. Wolff and R. Bales, pp. 319–338, Springer-Verlag, New York.
- Beer, J., et al. (1991), Seasonal variations in the concentration of Be-10, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, H<sub>2</sub>O<sub>2</sub>, PB-210, H-3, miner dust, and Delta-18O in Greenland snow, *Atmos. Environ.*, **25**, 899–904.
- Beine, H. J., F. Domine, W. Simpson, R. E. Honrath, R. Sparapani, X. L. Zhou, and M. King (2002), Snow-pile and chamber experiments during the Polar Sunrise Experiment 'Alert 2000': Exploration of nitrogen chemistry, *Atmos. Environ.*, **36**, 2707–2719.
- Beine, H. J., F. Domine, A. Ianniello, M. Nardino, I. Allegrini, K. Teinila, and R. Hillamo (2003), Fluxes of nitrates between snow surfaces and the atmosphere in the European high arctic, *Atmos. Chem. Phys.*, **3**, 75–106.
- Bromwich, D. H., F. M. Robasky, R. A. Keen, and J. F. Bolzan (1993), Modeled variations of precipitation over the Greenland Ice Sheet, *J. Clim.*, **6**, 1253–1268.
- Bromwich, D. H., Q. S. Chen, Y. F. Li, and R. I. Cullather (1999), Precipitation over Greenland and its relation to the North Atlantic Oscillation, *J. Geophys. Res.*, **104**, 2103–2115.
- Dibb, J. E., M. Arsenault, M. C. Peterson, and R. E. Honrath (2002), Fast nitrogen oxide photochemistry in Summit, Greenland snow, *Atmos. Environ.*, **36**, 2501–2511.
- Domine, F., A. Cabanes, and L. Legagneux (2002), Structure, microphysics, and surface area of the Arctic snowpack near Alert during the ALERT 2000 campaign, *Atmos. Environ.*, **36**, 2753–2765.
- Herron, M. (1982), Impurity sources of F, Cl, NO<sub>3</sub>, and SO<sub>4</sub><sup>2-</sup> in Greenland and Antarctic precipitation, *J. Geophys. Res.*, **87**, 3052–3060.
- Honrath, R. E., M. C. Peterson, S. Guo, J. E. Dibb, P. B. Shepson, and B. Campbell (1999), Evidence of NO<sub>x</sub> production within or upon ice particles in the Greenland snowpack, *Geophys. Res. Lett.*, **26**, 695–698.
- Honrath, R. E., S. Guo, M. C. Peterson, M. P. Dziobak, J. E. Dibb, and M. A. Arsenault (2000), Photochemical production of gas phase NO<sub>x</sub> from ice crystal NO<sub>3</sub><sup>-</sup>, *J. Geophys. Res.*, **105**, 24,183–24,190.
- Honrath, R. E., Y. Lu, M. C. Peterson, J. E. Dibb, M. A. Arsenault, N. J. Cullen, and K. Steffen (2002), Vertical fluxes of NO<sub>x</sub>, HONO, and HNO<sub>3</sub> above the snowpack at Summit, Greenland, *Atmos. Environ.*, **36**, 2629–2640.
- Hutterli, M. A., R. Röthlisberger, and R. C. Bales (1999), Atmosphere-to-snow-to-firm transfer studies of HCHO at Summit, Greenland, *Geophys. Res. Lett.*, **26**, 1691–1694.
- Hutterli, M., J. R. McConnell, R. W. Stewart, H.-W. Jacobi, and R. C. Bales (2001), Impact of temperature-driven cycling of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) between the air and snow on the planetary boundary layer, *J. Geophys. Res.*, **106**, 15,395–15,404.
- Hutterli, M. A., J. R. McConnell, R. C. Bales, and R. W. Stewart (2003), Sensitivity of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and formaldehyde (HCHO) preservation in snow to changing environmental conditions: Implications for ice core records, *J. Geophys. Res.*, **108**(D1), 4023, doi:10.1029/2002JD002528.
- Jones, A. E., R. Weller, A. Minikin, E. W. Wolff, W. T. Sturges, H. P. McIntyre, S. R. Leonard, O. Schrems, and S. Bauguette (1999), Oxidized nitrogen chemistry and speciation in the Antarctic troposphere, *J. Geophys. Res.*, **104**, 21,355–21,366.
- Jones, A. E., R. Weller, E. W. Wolff, and H. W. Jacobi (2000), Speciation and rate of photochemical NO and NO<sub>2</sub> production in Antarctic snow, *Geophys. Res. Lett.*, **27**, 345–348.
- Légrand, M. R., and S. Kirchner (1990), Origins and variations of nitrate in South Polar precipitation, *J. Geophys. Res.*, **95**, 3493–3507.
- Littot, G. C., R. Mulvaney, R. Röthlisberger, R. Udisti, E. W. Wolff, E. Castellano, M. De Angelis, M. Hansson, S. Sommer, and J. P. Steffensen (2002), Comparison of analytical methods used for measuring major ions in the EPICA Dome C (Antarctica) ice core, *Ann. Glaciol.*, **35**, 299–305.
- McConnell, J. R., R. C. Bales, J. R. Winterle, H. Kuhns, and C. R. Stearns (1997), A lumped parameter model for the atmosphere-to-snow transfer function for hydrogen peroxide, *J. Geophys. Res.*, **102**, 26,809–26,818.
- McConnell, J. R., G. W. Lamorey, and M. A. Hutterli (2002a), A 250-year high-resolution record of Pb flux and crustal enrichment in central Greenland, *Geophys. Res. Lett.*, **29**(33), 2130, doi:10.1029/2002GL016016.
- McConnell, J. R., G. W. Lamorey, S. W. Lambert, and K. C. Taylor (2002b), Continuous ice-core chemical analyses using inductively coupled plasma mass spectrometry, *Environ. Sci. Technol.*, **36**(1), 7–11.
- Mulvaney, R., D. Wagenbach, and E. W. Wolff (1998), Postdepositional change in snowpack nitrate from observation of year-round near-surface snow in coastal Antarctica, *J. Geophys. Res.*, **103**, 1021–1031.
- Munger, J. W., D. J. Jacob, S. M. Fan, A. S. Colman, and J. E. Dibb (1999), Concentrations and snow-atmosphere fluxes of reactive nitrogen at Summit, Greenland, *J. Geophys. Res.*, **104**, 13,721–13,734.
- National Research Council (2002), *Abrupt Climate Change: Inevitable Surprises*, Natl. Acad. Press, Washington, D. C.
- Röthlisberger, R., M. A. Hutterli, S. Sommer, E. W. Wolff, and R. Mulvaney (2000a), Factors controlling nitrate in ice cores: Evidence from the Dome C deep ice core, *J. Geophys. Res.*, **105**, 20,565–20,572.
- Röthlisberger, R., M. Bigler, M. Hutterli, S. Sommer, B. Stauffer, H. G. Junghans, and D. Wagenbach (2000b), Technique for continuous high-resolution analysis of trace substances in firn and ice cores, *Environ. Sci. Technol.*, **34**, 338–342.
- Röthlisberger, R., et al. (2002), Nitrate in Greenland and Antarctic ice cores: A detailed description of post-depositional processes, *Ann. Glaciol.*, **35**, 209–216.
- Steig, E. J., P. M. Grootes, and M. Stuiver (1994), Seasonal precipitation timing and ice core records, *Science*, **266**, 1885–1886.
- Wolff, E. W., A. E. Jones, T. J. Maring, and T. C. Grenfell (2002), Modeling photochemical NO<sub>x</sub> production and nitrate loss in the upper snowpack of Antarctica, *Geophys. Res. Lett.*, **29**(20), 1944, doi:10.1029/2002GL015823.
- Yang, Q., P. A. Mayewski, S. Whitlow, M. Twickler, M. Morrison, R. Talbot, J. Dibb, and E. Linder (1995), Global perspective of nitrate flux in ice cores, *J. Geophys. Res.*, **100**(D3), 5113–5121.

R. C. Bales, School of Engineering, University of California, Merced, CA 95344, USA.

J. F. Burkhart and M. Hutterli, Department of Hydrology and Water Resources, University of Arizona, Tucson, AZ 85721, USA. (johnny@hwr.arizona.edu)

J. R. McConnell, Division of Hydrologic Science, Desert Research Institute, Reno, NV 89512, USA. (joe.mcconnell@dri.edu)