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Global Perspective of Nitrate Flux in Ice Cores

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Global perspective of nitrate flux in ice cores

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Abstract. The relationships between the concentration and the flux of chemical species (Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}) versus snow accumulation rate were examined at GISP2 and 20D in Greenland, Mount Logan from the St. Elias Range, Yukon Territory, Canada, and Sentik Glacier from the northwest end of the Zanskar Range in the Indian Himalayas. At all sites, only nitrate flux is significantly ($\alpha = 0.05$) related to snow accumulation rate. Of all the chemical series, only nitrate concentration data are normally distributed. Therefore we suggest that nitrate concentration in snow is affected by postdepositional exchange with the atmosphere over a broad range of environmental conditions. The persistent summer maxima in nitrate observed in Greenland snow over the entire range of record studied (the last 800 years) may be mainly due to NO_x released from peroxyacetyl nitrate by thermal decomposition in the presence of higher OH concentrations in summer. The late winter/early spring nitrate peak observed in modern Greenland snow may be related to the buildup of anthropogenically derived NO_y in the Arctic troposphere during the long polar winter.

Introduction

Ice core records from polar regions provide a unique record of environmental and climatic change [e.g., *Dansgaard and Oeschger*, 1989; *Lorius et al.*, 1989; *Mayewski et al.*, 1993a, 1994] and illustrate the influence of anthropogenic emissions on the chemistry of the remote atmosphere [e.g., *Neftel et al.*, 1985; *Mayewski et al.*, 1986, 1990a; *Mayewski and Legrand*, 1990]. They have also contributed to our understanding of atmospheric chemistry, atmospheric circulation and biogeochemical cycling [e.g., *Legrand et al.*, 1988, 1991; *Delmas and Legrand*, 1989; *McElroy*, 1989; *Mayewski et al.*, 1993a, 1994].

Nitrate is one of the major chemical species in polar snow. As such, measurements of nitrate in ice cores may provide information for understanding the complex atmospheric nitrogen cycle [e.g., *Neubauer and Heumann*, 1988; *Legrand and Kirchner*, 1990; *Mayewski and Legrand*, 1990; *Mayewski et al.*, 1990a; *Mulvaney and Wolff*, 1993]. However, the sources, transport pathways, and scavenging processes of nitrate deposited on glaciers are not well understood [*Wolff*, 1995]. Understanding these relationships will improve our interpretation of nitrate data retrieved from worldwide ice cores.

The relationships between snow accumulation rate and nitrate concentration/flux are important because they can be used to asses the dominant processes of nitrate incorporation into snow. The seasonal variation of nitrate concentration in snow is presumably related to the source of nitrate precursor in the atmosphere.

Previous studies conducted by *Herron* [1982], *Legrand and Delmas* [1986], and *Legrand and Kirchner* [1990] investigated relationships between nitrate concentration and flux versus snow accumulation rate in Greenland and Antarctica. However, there is a discrepancy in their conclusions. *Herron* [1982] concluded that nitrate concentration decreased with increasing snow accumulation rate, whereas *Legrand and Delmas* [1986] and *Legrand and Kirchner* [1990] found that nitrate concentration was independent of snow accumulation rate. In this paper we reevaluate this relationship using high-resolution snow chemical series from central Greenland as well as other series from southern Greenland, northwest Canada, and central Asia.

Annual nitrate summer peaks in snow have been reported for both Greenland and Antarctica [*Finkel et al.*, 1986; *Mayewski et al.*, 1987, 1990b; *Davidson et al.*, 1988; *Neubauer and Heumann*, 1988; *Legrand and Kirchner*, 1990; *Whitlow et al.*, 1992; *Mulvaney and Wolff*, 1993]. However, the cause for the timing of the peak is not yet well understood. We investigated cause(s) for the peak in Greenland snow to improve our understanding of the relationship between seasonal variations of nitrate measured in snow and possible sources of NO_x in the atmosphere.

Methodology

In this paper we first examine the relationship between the concentration of major cations and anions

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(Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}) and their flux versus snow accumulation rate using 36 detailed sections (averaging 10 samples per year over sections ranging from 2 to 10 years) sampled from the GISP2 core located at Summit, Greenland, to see if nitrate behaves differently from other major ions. The same analysis is performed on several other glaciochemical series, namely, 20D from southern Greenland; Mount Logan from the St. Elias Range; Yukon Territory, northwest Canada; and Sentik Glacier from the northwestern end of the Zanskar Range in Ladakh, Indian Himalayas. Ice core sites and some basic information about sites and sampling details are presented in Figure 1 and Table 1. Although the Sentik Glacier nitrate time series is shorter than the others, it is the only continuous high-resolution chemical record available from a low-latitude/high-elevation site.

Samples retrieved from GISP2, 20D, and Mount Logan were processed in a cold room at temperatures that did not exceed $-12°C$ by individuals wearing precleaned polyethylene gloves, nonparticulating clean suits, and particle masks. All tools and containers used for sampling were precleaned in ultrapure water. Container blanks prepared on a frequent basis showed that these containers were free of contamination. All analyses were performed by ion chromatography using a Dionex^{TM} model 4040 with techniques described previously [e.g., *Mayewski et al.*, 1990b; *Buck et al.*, 1992]. Samples retrieved from Sentik Glacier were processed in the field, and nitrate was measured using a Technicon Auto Analyzer^{TM} system [*Lyons and Mayewski*, 1983; *Mayewski et al.*, 1984].

Each core was dated by using a variety of different seasonal indicators (e.g., major anions and cations, stable isotopes), historically documented volcanic events plus total beta activity signatures related to known nuclear fallout events. Maximum dating error is ±1 year throughout most of the cores [*Lyons and Mayewski*, 1983; *Holdsworth and Peake*, 1985; *Mayewski et al.*, 1986, 1993b]. Flux (F) of each chemical species is calculated based on that individual annual mean concentration (C) times snow accumulation rate (A) of the same year ($F = C \times A$).

Results and Discussion

Chemical Concentration/Flux versus Snow Accumulation Rate

The relationship between chemical (Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}) concentration ($\mu g/kg$) and snow accumulation rate ($kg\ m^{-2}\ yr^{-1}$) was examined using the GISP2 chemical data sets (exclusive of the anthropogenic period) (Figure 2). On the basis of the data shown in Figure 2, we examined each individual species using statistical methods of polynomial and linear regression to determine if there is a relationship. From Figure 2 it is clear that none of the concentration series of chemical species are statistically related to snow accumulation rate. This suggests that the annual mean concentration of chemical species in snow is independent of the annual snow accumulation rate at Summit, Greenland.

In Figure 3 we compare chemical flux ($kg\ km^{-2}\ yr^{-1}$) versus snow accumulation rate ($kg\ m^{-2}\ yr^{-1}$). A table of t values (Table 2) provides the significance of the slope coefficients for all chemical flux versus snow accumulation rate relationships in Figure 3. Nitrate has the highest t value and correlation coefficient (r value). For the other species, t values exceed the critical value of 1.645 (significance level $\alpha = 0.05$), but their r values are lower than 0.4, suggesting that less than 20% of to-
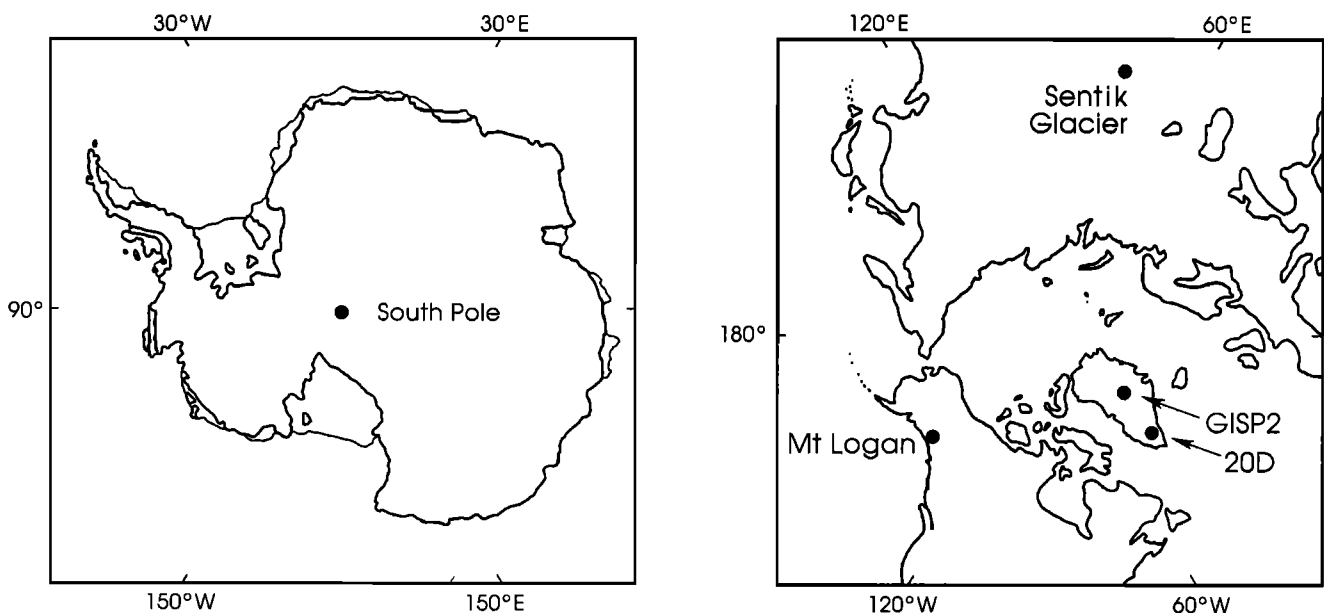

Figure 1. Location map showing the sampling sites at Summit, Greenland; 20D, south Greenland; Mount Logan; Sentik Glacier; and south pole.

<u>**Table 1. Ice Core Site Details**</u>

	GISP2	20D[a]	Core Mount Logan[b]	Sentik Glacier[c]	South Pole[d]
Location	72.58°N, 38.47°W	65.01°N, 44.87°W	60.63°N, 140.50°W	35.00°N, 76.01°E	90.00°S
Elevation, meters above sea level	3207	2616	5340	4908	2880
Accumulation rate, m yr^{-1}, water equivalent	0.23	0.41	0.33	0.60	0.085
Mean annual temperature, °C	-31.5	-20.2	-28.9	-3	-50
Total samples analyzed	1524	1357	1853	103	759
Sampling resolution, samples/year	~10	~6.3	~6.4	~6.2	~4.3
Period covered by core (AD)	1989-1200[e]	1984-1767	1980-1688	1980-1963	1980-1805

[a]*Mayewski et al.* [1986, 1990a].
[b]*Holdsworth and Peake* [1985].
[c]*Mayewski et al.* [1984], *Lyons and Mayewski* [1983].
[d]*Legrand and Kirchner* [1990].
[e]Represented by 36 uniformly distributed sections throughout the period. Each section ranges from 3 to 10 years.

tal flux variance can be explained by a linear fit to the relationship. Only nitrate flux has a statistical linear relationship with snow accumulation rate over the range measured (120 to 350 kg m^{-2} yr^{-1} water equivalent and 9.3 to 25.6 kg km^{-2} yr^{-1} of NO$_3^-$).

The best fit linear regression of nitrate flux to snow accumulation rate for Summit, Greenland is

$$F = 0.75 + 0.071A \qquad (r = 0.81) \qquad (1)$$

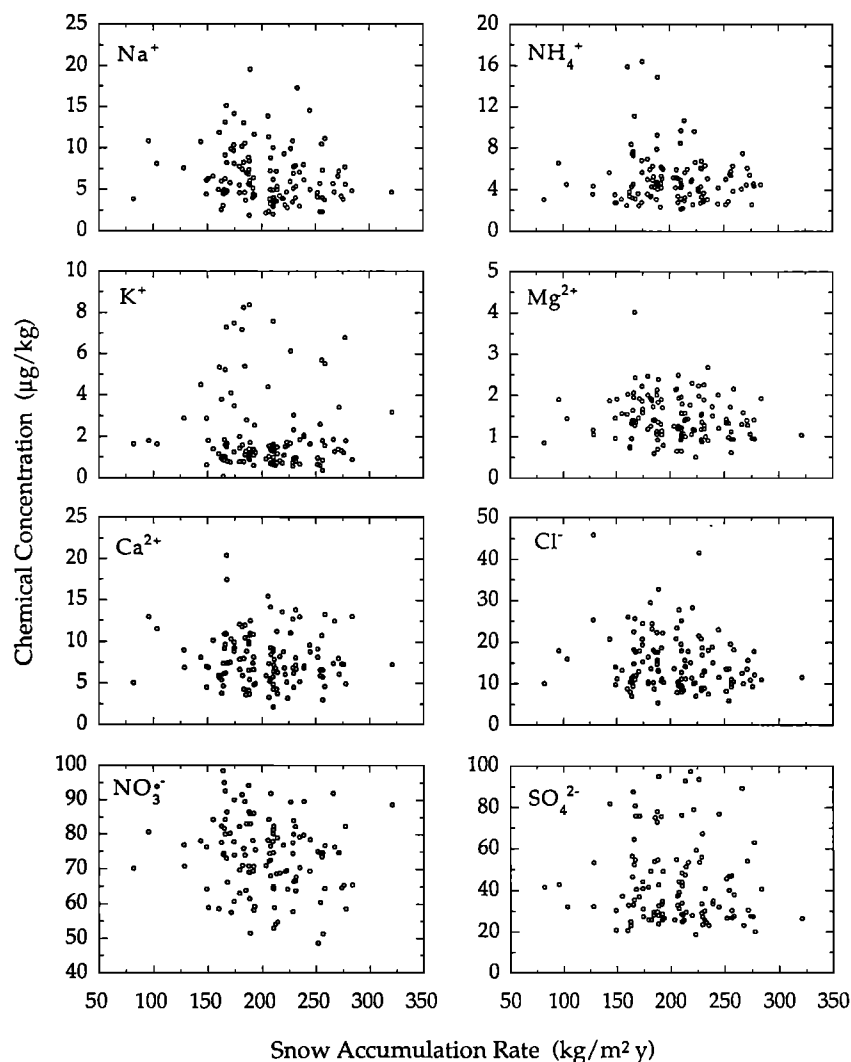where F is nitrate flux in kg km^{-2} yr^{-1}, and A is the snow accumulation rate in kg m^{-2} yr^{-1}.

Figure 2. Chemical concentration (Na$^+$, NH$_4^+$, K$^+$, Mg^{2+}, Ca^{2+}, Cl$^-$, NO$_3^-$, SO$_4^{2-}$) versus snow accumulation rate for the GISP2 detailed sections.
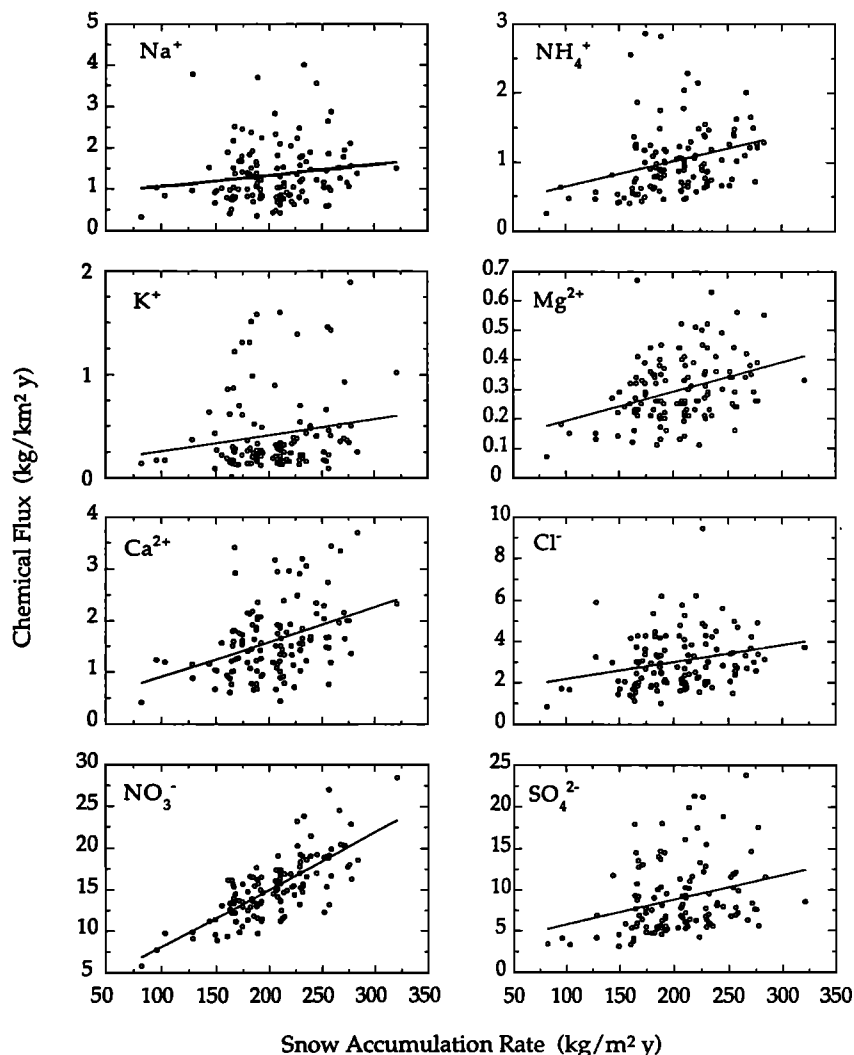
Figure 3. Chemical flux (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-}) versus snow accumulation rate for the GISP2 detailed sections. The solid line is the least squares fitted regression line to each species.

Herron [1982] investigated snow pits and ice cores recovered from different sites in Greenland and Antarctica and suggested that the relationship between nitrate concentration and snow accumulation rate may be expressed as

$$NO_3^- = CA^{-\frac{1}{2}} \qquad (2)$$

where C is a constant, and A is the snow accumulation rate in $kg\ m^{-2}\ yr^{-1}$.

Legrand and Delmas [1986] and *Legrand and Kirchner* [1990] found a discrepancy in *Herron*'s [1982] relationship for Antarctica. Their data suggested that

nitrate concentration was not related to snow accumulation rate, but nitrate flux was related to snow accumulation rate by the following expression:

$$F = 0.99 + 0.082A \qquad (r = 0.92) \qquad (3)$$

Our data sets (Figure 2) show that nitrate concentration is independent of snow accumulation, in harmony with the findings of *Legrand and Delmas* [1986] and *Legrand and Kirchner* [1990]. Furthermore, we found that the relationship between nitrate flux and snow accumulation at Summit, Greenland, agrees closely with the relationship at south pole [*Legrand and Kirchner*, 1990].

Table 2. Calculated t-Distribution Values and Correlation Coefficients (r) for the Regression Lines Displayed in Figure 2

		Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}
GISP2	n=117								
t value		1.71	2.78	1.75	4.22	4.67	2.92	12.54	3.13
r		0.15	0.3	0.16	0.36	0.39	0.25	0.82	0.28

n, Data points used in regression.

To investigate the apparent uniqueness of the GISP2 nitrate data compared to other chemical species, we examined their concentration probability plots [*Looney and Gulledge*, 1985]. The "straightness" of the probability plot is tested by using their correlation coefficients [*Looney and Gulledge*, 1985; *Minitab*, 1993]. Nitrate is the only species whose concentration data are normally distributed at a significance level of 95% in Greenland snow (Table 3).

To test if a similar relationship between nitrate flux and snow accumulation rate exists at our other study sites, we used chemical data series from three additional sites: 20D (exclusive of the anthropogenic portion of the record), Mount Logan, and Sentik Glacier. At all three sites the relationship between nitrate flux and snow accumulation rate has the highest correlation coefficient (significant at the 95% level) of any of the species (Table 4).

The best fit linear regression equations of nitrate flux to snow accumulation rate at the three sites are

20D :	$F = 1.3 + 0.053A$	$(r = 0.71)$	(4)
Mount Logan :	$F = -1.9 + 0.054A$	$(r = 0.79)$	(5)
Sentik Glacier :	$F = 1.8 + 0.080A$	$(r = 0.74)$	(6)

Since there is a relatively strong linear relationship between nitrate flux and snow accumulation rate at all three sites, we investigated the distributions of nitrate concentration versus the other chemical species concentration at these sites. The normality of chemical concentration probability plots from 20D, Mount Logan, and Sentik Glacier were tested as described for the GISP2 data set (Table 3). Nitrate is the only chemical species for which the correlation coefficient is higher than the critical value (at significance level of 95%) for each of the data sets.

Nitrate concentrations in snow at these sites are distinct from the other chemical species concentrations in that they are normally distributed. A recent surface snow chemistry study at Summit, Greenland [*J. Dibb*, unpublished data, 1994] indicates that the summer surface snowpack loses nitrate at some time after deposition, as has been reported for lower accumulation sites

in Antarctica [*Mayewski and Legrand*, 1990]. The normally distributed nitrate concentration may be a consequence of postdepositional alteration, potentially via exchange between the surface snow and the atmosphere [*Neubauer and Heumann*, 1988]. Hence we suggest that the exchange of nitrate between the snow and the atmosphere results in sufficient smoothing of the series to make them normally distributed (Table 3).

Two depositional styles dominate the incorporation of chemical species into snow, namely, wet and dry [*Barrie*, 1985; *Davidson*, 1989]. Equations (1) and (4)-(6) have small (<10%) y-intercept values relative to the individual mean nitrate flux of 17, 24, 17, and 74 kg km^{-2} yr^{-1} in the snow at GISP2, 20D, Mount Logan, and Sentik Glacier, respectively. If the value of the y intercept of these equations reflects the flux contributed by dry depositional processes [*Legrand and Kirchner*, 1990], then nitrate is incorporated into snow predominantly by wet deposition at these sites. However, as discussed previously, the nitrate mean annual concentration is affected by the postdepositional processes. For nitrate the y- intercept value may not be an indication of the contribution of dry deposition in snow.

Since the annual mean concentration of nitrate is independent of snow accumulation rate at our study sites and at south pole [*Legrand and Kirchner*, 1990], the presence of a statistically significant linear relationship between nitrate flux and snow accumulation rate suggests that the supply of atmospheric nitrate is large enough so that it is never depleted over the accumulation range studied here. If this is the case, we would suggest that annual mean nitrate concentration in snow is proportional to its annual mean concentration in the atmosphere despite postdepositional process, as long as the depositional environment does not vary significantly.

Sources for Nitrate Summer Peak

As mentioned previously, one of the important characteristics of nitrate concentrations in Greenland and Antarctic snow is that there is a persistent nitrate summer peak [*Finkel et al.*, 1986; *Mayewski et al.*, 1987, 1990b; *Neubauer and Heumann*, 1988; *Steffensen*, 1988;

Table 3. Normality Tests for Chemical Concentration Data Distribution

	Na$^+$	NH$_4^+$	K$^+$	Mg^{2+}	Ca^{2+}	Cl$^-$	NO$_3^-$	SO$_4^{2-}$
GISP2 n-117 r critical=0.988[a]								
r 0.903		0.717	0.831	0.966	0.909	0.931	0.996	0.907
20D n=174 r critical=0.990								
r 0.926		0.822	0.649	0.935	0.916	0.917	0.991	0.954
Mount Logan n=220 r critical=0.992								
r 0.683		0.825	0.847	0.884	0.834	0.954	0.995	0.955
Sentik Glacier n=16 r critical=0.942								
r 0.893		*	*	*	*	0.915	0.965	*

n, Data points used in test. Asterisk, species not measured.
[a](After Table 13.1 in *Minitab Reference Manual* [1993].

Table 4. Calculated t-Distribution Values and Correlation Coefficients (r) Between Chemical Flux and Snow Accumulation Rate at 20D, Mount Logan, and Sentik Glacier

	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}
20D n=174								
t value	6.98	2.22	2.38	6.59	5.66	7.81	12.88	7.39
r	0.43	0.15	0.16	0.41	0.36	0.47	0.66	0.45
Mount Logan n=220								
t value	4.95	6.21	6.4	4.95	5.48	6.79	18.89	11.29
r	0.32	0.39	0.4	0.32	0.35	0.42	0.79	0.61
Sentik Glacier n=16								
t value	1.59	*	*	*	*	2.01	4.26	*
r	0.38	*	*	*	*	0.46	0.74	*

n: Data points used in regression. Asterisk, species not measured.

Davidson, 1989; *Whitlow et al.*, 1992; *Mulvaney and Wolff*, 1993]. However, the mechanism(s) that causes this peak is not well understood. To investigate the source of the nitrate in snow, we start our investigation of the cause(s) for the annual nitrate summer peak in Greenland snow by examining controls on the formation of seasonal variations in nitrate in the atmosphere.

Nitric acid (HNO_3) is formed primarily by the reaction of NO_2 + OH in the presence of sunlight and is well known as a main sink for atmospheric NO_x [*Logan*, 1983; *Warneck*, 1988; *Ehhalt et al.*, 1992]. HNO_3 is also formed by the nighttime reaction between N_2O_5 and H_2O [*Russell et al.*, 1986; *Mozurkewich and Calvert*, 1988]. Various processes and sources can contribute to the nitrate budget at high latitude, including combustion of fossil fuel (especially in the northern hemisphere [*Logan*, 1983; *Ehhalt et al.*, 1992]), biomass burning, lightning, ammonia oxidation and soil exhalation, in addition to processes acting within the stratosphere (galactic cosmic rays, N_2O oxidation [*Levy et al.*, 1980]). A few scientists have investigated the possible origin of nitrate in polar precipitation, suggesting an important role for lightning and N_2O stratospheric oxidation [*Legrand and Kirchner*, 1990; *Wolff*, 1995] and sometimes processes acting in the high atmosphere [*Parker and Zeller*, 1979; *Zeller et al.*, 1986]. Using a modeling approach, *Legrand et al.* [1989] suggested that lightning, soil exhalation, and N_2O stratospheric oxidation are likely major contributors to the natural Antarctic nitrate budget. The major sources of NO_x in the northern hemisphere troposphere are combustion of fossil fuels, lightning formed at high altitude/low latitude, and NO exhalation from soils [*Logan*, 1983; *Legrand and Kirchner*, 1990; *Mayewski et al.*, 1990a].

With the rather short residence time of NO_x in the troposphere (less than a day in summer and a few days in winter [*Singh*, 1987]), it is unlikely that it is directly transported from primary sources to interior central Greenland. Most of the nitric acid and particulate nitrate is believed to be removed during transport [*Barrie*, 1985; *Lyons et al.*, 1990; *Bottenheim et al.*, 1993]. However, the formation of peroxyacetyl nitrate (PAN) has recently received considerable attention as a carrier

and reservoir of NO_x for the northern high latitudes due to its longer residence time (up to months in winter) and strong thermal decomposition characteristics [*Cox and Roffey*, 1977; *Singh*, 1987; *Honrath and Jaffe*, 1992; *Singh et al.*, 1992a]. *Singh and Hanst* [1981], and *Singh and Salas* [1983] suggested that PAN not only is associated with polluted air but also is an important constituent of the natural atmosphere. The production rate of OH radicals varies seasonally, with a maximum in summer in the troposphere [*Warneck*, 1988]. *Honrath and Jaffe* [1992] reported a well-defined seasonal cycle of NO_y, with a maximum (560-620 parts per trillion, by volume) in early spring and minimum (median 70 parts per trillion, by volume) in summer at Barrow, Alaska. The transition occurs sharply in April, when a sevenfold to eightfold decrease in NO_y concentration was observed. *Davidson et al.* [1993] also conclude that the minima in summer of atmospheric CO and CH_4 at Dye-3, Greenland, is caused in part by high concentrations of OH which are related to relatively high airborne concentrations of NO_x and O_3.

To explain the summer peak seen in nitrate concentration in polar snow we propose the following: During the winter, cold temperature and low insolation at middle to high latitudes favor long distance transport of PAN into polar regions. Further, since there is no sunlight during the polar winter, the secondary sources of NO_x and OH are limited. Under such conditions, snow falling during the polar winter has low nitrate concentrations due to a lack of NO_x and OH. With the appearance of sunlight and increasing atmospheric temperatures during the polar spring, the NO_x released from PAN reacts with OH to form HNO_3, yielding a summer nitrate peak in Greenland snow.

The less pronounced summer nitrate peaks at Mount Logan and Sentik Glacier may be a consequence of the types of air masses reaching these sites. Air masses reaching Mount Logan and Sentik Glacier are pristine free troposphere due to high elevations [*Monaghan and Holdsworth*, 1990, *Mayewski et al.*, 1993b; *Wake et al.*, 1993]. Additionally, these sites maintain some sunlight during winter so that the nitrate formed/released from PAN is deposited throughout the year.

As reported by *Finkel et al.* [1986] and *Whitlow et al.* [1992], our snow pit chemistry study around the GISP2 site reveals that there is sometimes a late winter/early spring nitrate peak in modern Greenland snow. Since this earlier peak has not been observed from our GISP2 detailed sections and *Finkel et al.*'s [1986] data before the year 1900 A.D., it may result from the input of anthropogenic material. In general, any NO_y species (NO, NO_2, HO_2NO_2, HNO_3, the PANs, HNO_2, N_2O_5, NO_3, and gaseous nitrates [*Singh*, 1987]) may end up as nitrate to be removed from the atmosphere. PAN concentrations are elevated in the polluted air [*Singh*, 1987; *Warneck*, 1988] which is transported and accumulated in "Arctic haze" during winter. PAN has also been reported to be a significant component of NO_y in the Arctic boundary layer during spring [*Barrie and Bottenheim*, 1991]. But NO_x released from PAN is restricted in the polar regions due to lower temperatures in late winter/early spring [*Singh et al.*, 1992b].

In addition to the role of NO_x and PANs, N_2O_5 chemistry may also play a role in the formation of the modern spring nitrate peak in Greenland snow since the low light to dark conditions favor the formation of N_2O_5 [*Calvert et al.*, 1985; *Leaitch et al.*, 1988]. There are two potential ways for N_2O_5 to yield nitrate spring peaks in snow. First, NO_2 is released from N_2O_5 due to an increased temperature in spring [*Atkinson et al.*, 1986], and it then reacts with OH to form HNO_3. Second, N_2O_5 scavenges to HNO_3 on aqueous aerosols in late winter/spring [*Calvert et al.*, 1985; *Mozurkewich and Calvert*, 1988]. Although there are no N_2O_5 data sets available from the ambient Greenland atmosphere and we are unable to provide quantitative relationship between nitrate in snow and N_2O_5 in the atmosphere, these two processes may also be important in explaining the difference between the preanthropogenic nitrate summer peak and the anthropogenic era nitrate spring peak.

Conclusions

By examining the GISP2, 20D, Mount Logan, and Sentik Glacier ice core chemical species, we find that the mean annual concentrations of all chemical species are independent of the annual snow accumulation rate. Only the nitrate concentration data series reveal a normally distributed pattern. Based on previous work [*Neubauer and Heumann*, 1988; *Mayewski and Legrand*, 1990], we suggest that the cause of this pattern is post-depositional alternation. As a consequence, nitrate flux has a relatively strong linear relationship to the rate of snow accumulation at all sites studied.

The presence of a nitrate summer peak for the past several thousand years in Greenland snow is believed to be associated with the higher OH radical concentrations and an available NO_x source released from PAN in summertime.

The observed nitrate peak in early spring in modern (anthropogenic era) Greenland snow may be due to the buildup of NO_y as Arctic haze in the troposphere dur-

ing the long polar winter. NO_x released/formed from a component of NO_y (N_2O_5, PAN, HO_2NO_2) reacting with OH to form HNO_3 in the atmosphere is believed to cause this peak.

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