

## Factors controlling nitrate in ice cores: Evidence from the Dome C deep ice core

Regine Röthlisberger, Manuel A. Hutterli,<sup>1</sup> and Stefan Sommer

Climate and Environmental Physics, University of Bern, Bern, Switzerland

Eric W. Wolff and Robert Mulvaney

British Antarctic Survey, Natural Environment Research Council, Cambridge, England

**Abstract.** In order to estimate past changes in atmospheric  $\text{NO}_x$  concentration, nitrate, an oxidation product of  $\text{NO}_x$ , has often been measured in polar ice cores. In the frame of the European Project for Ice Coring in Antarctica (EPICA), a high-resolution nitrate record was obtained by continuous flow analysis (CFA) of a new deep ice core drilled at Dome C. This record allows a detailed comparison of nitrate with other chemical trace substances in polar snow under different climatic regimes. Previous studies showed that it would be difficult to make firm conclusions about atmospheric  $\text{NO}_x$  concentrations based on ice core nitrate without a better understanding of the factors controlling  $\text{NO}_3^-$  deposition and preservation. At Dome C, initially high nitrate concentrations (over 500 ppb) decrease within the top meter to steady low values around 15 ppb that are maintained throughout the Holocene ice. Much higher concentrations (averaging 53 ppb) are found in ice from the Last Glacial Maximum (LGM). Combining this information with data from previous sampling elsewhere in Antarctica, it seems that under climatic conditions of the Holocene, temperature and accumulation rate are the key factors determining the  $\text{NO}_3^-$  concentration in the ice. Furthermore, ice layers with high acidity show a depletion of  $\text{NO}_3^-$ , but higher concentrations are found before and after the acidity layer, indicating that  $\text{NO}_3^-$  has been redistributed after deposition. Under glacial conditions, where  $\text{NO}_3^-$  shows a higher concentration level and also a larger variability, non-sea-salt calcium seems to act as a stabilizer, preventing volatilization of  $\text{NO}_3^-$  from the surface snow layers.

### 1. Introduction

Considering the importance of  $\text{NO}_x$  ( $\text{NO}$  and  $\text{NO}_2$ ) for tropospheric chemistry and taking advantage of  $\text{NO}_x$  being a precursor of  $\text{NO}_3^-$ , attempts have been made to reconstruct past atmospheric  $\text{NO}_x$  by  $\text{NO}_3^-$  measurements in polar ice cores. Polar ice sheets are well-established archives of paleoclimatic information. While some species measured in ice cores can be used to infer directly past atmospheric composition, it is more difficult to draw conclusions for those particulate and reactive gas species where depositional and postdepositional processes overlay the changes in the atmosphere (e.g.,  $\text{HNO}_3$ ).

<sup>1</sup>Now at Department of Hydrology and Water Resources, University of Arizona, Tucson.

Copyright 2000 by the American Geophysical Union.

Paper number 2000JD900264.  
0148-0227/00/2000JD900264\$09.00

Although  $\text{NO}_3^-$  data from polar ice cores already exist, it remains difficult to interpret them [Wolff, 1995]. Some features in the  $\text{NO}_3^-$  records can be explained, for example, the clear increase since 1940 seen in Greenland ice cores, which is attributed to  $\text{NO}_x$  emissions from industrialized countries. Others, such as the difference in Greenland and Antarctic  $\text{NO}_3^-$  records, are only vaguely understood.

Many sources for  $\text{NO}_x$  and therefore  $\text{NO}_3^-$  have been discussed [Legrand and Kirchner, 1990; Wolff, 1995]. Meteorite impacts, supernovae, and solar modulation (sunspot cycle, solar proton events) seem to have a minor impact on  $\text{NO}_3^-$  in Antarctica.  $\text{NO}_x$  production in the stratosphere and tropospheric lightning are considered to be the main sources [Wagenbach *et al.*, 1998]. However, recent studies of atmospheric  $\text{NO}_y$  ( $\text{NO}_x$ ,  $\text{HNO}_3$ ,  $\text{N}_2\text{O}_5$ , particulate and organic nitrates) concentrations showed considerable amounts of organic nitrate [Jones *et al.*, 1999; Dibb *et al.*, 1998], which further complicates the interpretation of ice core  $\text{NO}_3^-$  data.

Before past changes in atmospheric chemistry can be derived from  $\text{NO}_3^-$  records, the preservation of  $\text{NO}_3^-$  in ice cores has to be examined. Recent studies have shown that depositional and postdepositional processes have a strong influence on  $\text{NO}_3^-$  concentrations preserved in snow [Neubauer and Heumann, 1988a; Wolff, 1995; Mulvaney et al., 1998]. Substantial postdepositional losses have been reported from low-accumulation sites [Wagnon et al., 1999; Legrand et al., 1996]. Also, an influence of high sulfuric acid ( $\text{H}_2\text{SO}_4$ ) concentrations, originating from volcanic eruptions, has been found in both Antarctic and Greenland ice cores [Laj et al., 1993; Legrand and Kirchner, 1990; Wolff, 1995], leading either to less formation of  $\text{NO}_x$  (a precursor of  $\text{NO}_3^-$ ) in the atmosphere or to a displacement of  $\text{NO}_3^-$  after deposition in the ice. On the other hand, an irreversible deposition of  $\text{NO}_3^-$  related to high levels of continental dust has been suggested for ice of the Last Glacial Maximum (LGM) [Legrand et al., 1999]. However, no detailed study with high-resolution data has been done so far.

Deposition and preservation mechanisms of  $\text{NO}_3^-$  in snow can be analyzed through direct studies of the atmosphere and of the air-snow transfer [Mulvaney et al., 1998; Dibb et al., 1998; Munger et al., 1999] combined with transfer models. However, studies of the way in which  $\text{NO}_3^-$  in ice cores changes under different conditions can also give clues about the processes involved.

Here we present high-resolution data from Dome C (75°06'S, 123°24'E, 3233 m above sea level, -53.5°C mean annual temperature), a low-accumulation site (2.7 g cm<sup>-2</sup> yr<sup>-1</sup>) on the East Antarctic plateau, that allow a more detailed study of the different mechanisms involved in  $\text{NO}_3^-$  deposition and conservation. The core was drilled in the frame of the European Project for Ice Coring in Antarctica (EPICA) during the 1997/1998 and 1998/1999 field seasons. Of the 786.4 m recovered, 585.2 m have been processed, and they cover approximately 30,000 years. The remaining 200 m of ice was too brittle to be processed yet and therefore has been left in a storage container at Dome C for later analyses.

## 2. Methods

The high resolution of the data is achieved by continuous flow analysis (CFA) [Röthlisberger et al., 2000]. Measurements were done in a processing line at Dome C during 1997/1998 and 1998/1999 field seasons. Along the whole core, subsections of 3.2 × 3.4 cm<sup>2</sup> and 1.1 m length were melted slowly from one end, and the melt-water was continuously drained off into a heated laboratory for online analysis.  $\text{NO}_3^-$  was measured using an absorption spectrometry method developed by McCormack et al. [1994], based on reduction of  $\text{NO}_3^-$  to  $\text{NO}_2^-$  (nitrite) with copperized cadmium and subsequent diazotization with sulfanilamide and naphthylethylenediamine (NED) to form a colored complex. Thus the measured concentrations include both  $\text{NO}_3^-$  and  $\text{NO}_2^-$ .

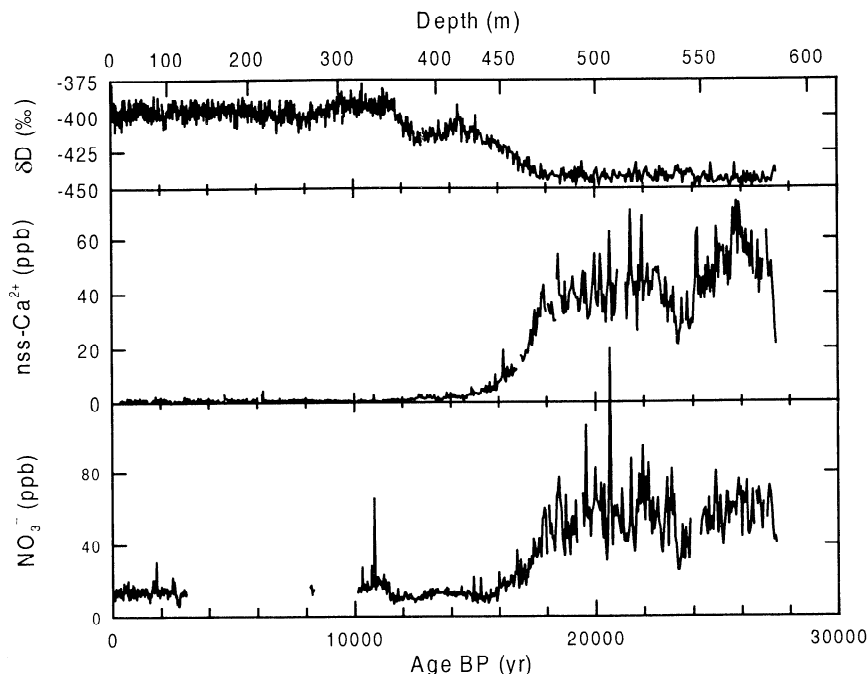
However, owing to the low  $\text{NO}_2^-$  concentrations in polar snow [Legrand and De Angelis, 1995], the influence of  $\text{NO}_2^-$  is negligible. The resolution is approximately 1 cm with a detection limit of 1 ppb ( $\mu\text{g}/\text{kg}$ ) and a linear range exceeding 1000 ppb, which is ample for Antarctic ice samples. The analytical procedure is described in more detail by Röthlisberger et al. [2000]. Owing to technical problems, no  $\text{NO}_3^-$  data are available in the depth interval from 123 to 320 m.

## 3. Results

The whole  $\text{NO}_3^-$  record obtained from the EPICA ice core is shown in Figure 1, together with non-sea-salt  $\text{Ca}^{2+}$  (nss- $\text{Ca}^{2+}$ ), calculated as  $[\text{nss-Ca}^{2+}] = [\text{Ca}^{2+}] - 0.038[\text{Na}^+]$  using the seawater ratio of 0.038 [Bowen, 1979]. We used total  $\text{Na}^+$  for this calculation, although some  $\text{Na}^+$  is of crustal origin during the LGM. Thus nss- $\text{Ca}^{2+}$  is slightly underestimated. Even so, over 90% of the total  $\text{Ca}^{2+}$  is nss- $\text{Ca}^{2+}$  in the LGM, so that  $\text{Ca}^{2+}$  is considered to be a reliable tracer of continental dust during this period. As an indicator of climatic stages, deuterium data (J. Jouzel et al., A new 27 kyr high-resolution East Antarctic climate record, submitted to *Geophysical Research Letters*, 2000) are added to the plot. The isotope record shows the gradual increase in temperature from the last glacial maximum (LGM) toward the Holocene, while nss- $\text{Ca}^{2+}$  shows a strong decrease from the LGM to the Holocene, opposite to the isotope record. The dating of the record is based on flow modeling and comparison of reference horizons with other well-dated records (J. Schwander et al., A tentative chronology of the EPICA Dome Concordia ice core, submitted to *Geophysical Research Letters*, 2000).

As seen in other ice cores of the East Antarctic plateau (e.g. Vostok [Legrand et al., 1988], Dome F [O. Watanabe et al., 1999]), the mean  $\text{NO}_3^-$  concentration was several times higher during the LGM than during the Holocene. However, this change in concentration does not necessarily reflect a corresponding change in atmospheric  $\text{NO}_3^-$  load, but rather a change in the depositional and postdepositional mechanisms. Present  $\text{NO}_3^-$  concentration in summer surface snow exceeds the highest concentrations seen in the LGM, but only a minor fraction is preserved. The high surface levels drop within the top 5 to 10 cm depth to values slightly above the mean Holocene concentrations and reach mean Holocene concentrations by a depth of approximately 50 cm (Figure 2). Possible processes for this substantial loss are volatilization of  $\text{HNO}_3$  from the surface snow layer and photolytic decomposition [Neubauer and Heumann, 1988b; Honrath et al., 1999].

Another prominent feature of the high-resolution data is the high variability of the  $\text{NO}_3^-$  concentration and the coincidence of high  $\text{NO}_3^-$  peaks with high nss- $\text{Ca}^{2+}$  peaks (Figure 3). This is observed clearly in ice of the LGM, when nss- $\text{Ca}^{2+}$  concentrations and variability were high. Also in the Holocene and the transition, nss-



**Figure 1.**  $\text{NO}_3^-$ ,  $\text{nss-Ca}^{2+}$  and  $\delta\text{D}$  record (bag averages) from Dome C. Owing to technical problems during 1997/1998 field season, no  $\text{NO}_3^-$  data are available from 123 to 320 m.

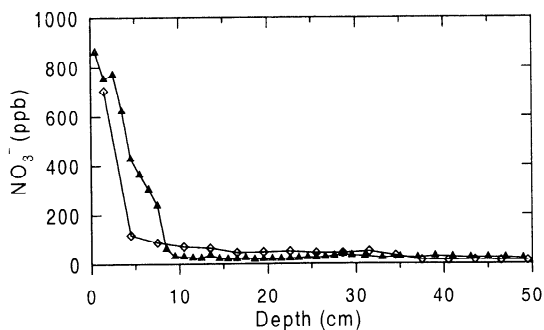
$\text{Ca}^{2+}$  peaks coincide with  $\text{NO}_3^-$ , but due to the missing data from 123 to 320 m, only a few events have been recorded. A relation between  $\text{nss-Ca}^{2+}$  and  $\text{NO}_3^-$  has been suggested recently by *Legrand et al.* [1999], who proposed that  $\text{nss-Ca}^{2+}$  prevents  $\text{NO}_3^-$  from being lost. This hypothesis will be discussed with respect to the high-resolution data presented here.

#### 4. Discussion

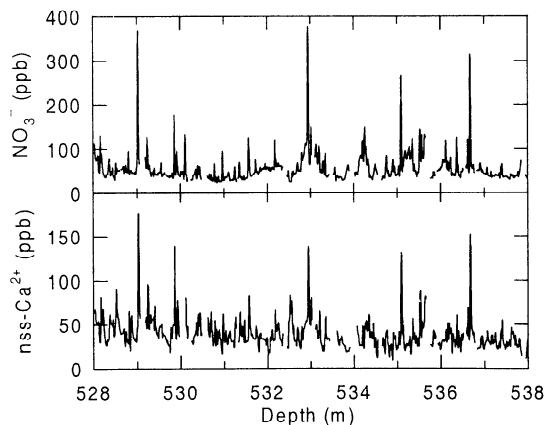
In order to investigate possible processes influencing  $\text{NO}_3^-$  concentrations in ice, the high-resolution  $\text{NO}_3^-$  record was considered in the light of the various parameters that may affect it, namely, accumulation rate, temperature, and the major impurities found in the ice [Legrand and Mayewski, 1997]. A possible effect of al-

titude on  $\text{NO}_3^-$  concentrations in Antarctic snow cannot be distinguished from the effects of accumulation rate and temperature. However, the relationship between  $\text{NO}_3^-$  and altitude [Mulvaney and Wolff, 1994] is weaker than that of  $\text{NO}_3^-$  versus temperature. Since there is also a simple physical mechanism for a temperature effect on nitrate concentrations, we treat it as a more important determinant, while accepting that altitude could also play a role.

Particular features that must be explained are the much higher concentrations in the LGM, the high vari-



**Figure 2.**  $\text{NO}_3^-$  concentration profiles of the top 50 cm at Dome C. The squares and triangles correspond to two different pits, excavated and analyzed in January 1999.



**Figure 3.** High-resolution  $\text{NO}_3^-$  and  $\text{nss-Ca}^{2+}$  data (one data point every 2 mm). According to a tentative timescale (J. Schwander et al., A tentative chronology of the EPICA Dome Concordia ice core, submitted to *Geophysical Research Letters*, 2000), this interval corresponds to almost 900 years at 23,000 years B.P.

**Table 1.** Nitrate Concentrations and Holocene Accumulation Rates for Different Antarctic Sites

Station	Holocene, ppb	LGM, ppb	Accumulation Rate, $\text{g cm}^{-2}\text{yr}^{-1}$	Reference
Dome C	15	53	2.7	this study
Dome C	19	39	3.4	[ <i>Legrand and Delmas, 1988</i> ]
Vostok	16	87	2.3	[ <i>Legrand et al., 1988</i> ]
Dome Fuji	20	80	2.8	[ <i>O. Watanabe et al., 1999</i> ]
Byrd	38	49	10	[ <i>Palais and Legrand, 1985</i> ]
Taylor Dome	51/25	19*	6.5	CCRC <sup>†</sup> (unpublished data, 1996)
South Pole	100		8.0	[ <i>Legrand and Kirchner, 1990</i> ]
Dronning Maud Land	82		7	BAS <sup>‡</sup> (unpublished data, 2000)
Dronning Maud Land	44		15.5	BAS <sup>‡</sup> (unpublished data, 1993)
Berkner Island	56		23	BAS <sup>‡</sup> (unpublished data, 1998)

Nitrate concentrations at Taylor Dome show major concentration changes from the early to the late Holocene, presumably due to considerable changes in accumulation rate. The values given are calculated for the period from 0 to 6000 years B.P. and 9000 to 11,500 years B.P., respectively.

\*Concentrations during the LGM vary from 15 to 60 ppb. Data are available at <http://www.ngdc.noaa.gov/paleo/icecore/antarctica/antarctica.html>.

<sup>†</sup>Climate Change Research Center, University of New Hampshire

<sup>‡</sup>British Antarctic Survey, Cambridge, England

ability, and the difference between Dome C and other Antarctic sites.

#### 4.1. Accumulation Rate

Under present-day conditions,  $\text{NO}_3^-$  concentrations in polar snow seem to be related to the accumulation rate. At low-accumulation sites such as Dome C, the typical  $\text{NO}_3^-$  profile of the top meter shows a sharp decrease with depth and stable concentrations with little variation thereafter (Figure 2) [*Mayewski and Legrand, 1990*]. *Munger et al.* [1999] hypothesized that changes in surface/volume ratio contributed to release of  $\text{HNO}_3$  in deeper snow layers and subsequent uptake by the fine-grained snow at the surface. However, the concentration of fresh snow at Dome C is unknown, leaving the source of the abundant  $\text{NO}_3^-$  in surface snow unclear. The decrease in  $\text{NO}_3^-$  concentration in the upper snow layers is attributed to postdepositional concentration changes (uptake and release and/or photolytic decomposition). At sites with higher accumulation rates, the typical pit profile looks quite different [*Legrand and Kirchner, 1990; Isaksson, 1994; Mulvaney et al., 1998*]; the surface concentrations are lower than in the low-accumulation sites, but they decay less, so that generally higher mean concentrations and annual fluctuations are seen below the surface layer. In analogy to  $\text{H}_2\text{O}_2$ , which shows a similar behavior, one would expect that less  $\text{NO}_3^-$  is lost with higher accumulation rates [*Bales, 1995; McConnell et al., 1998*].

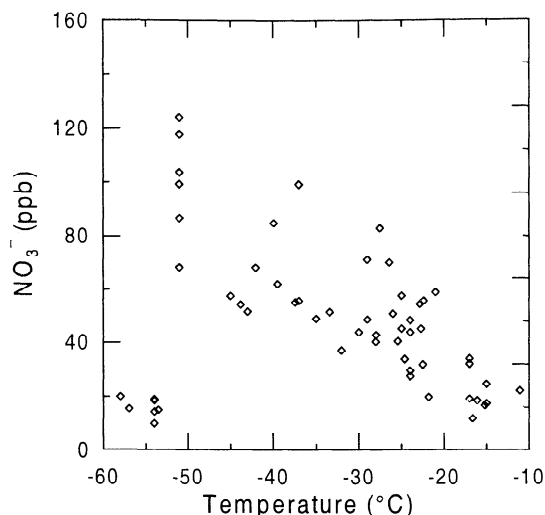
If we apply this in a qualitative way to the Dome C record, the low accumulation rate of the LGM ( $1.5 \text{ g cm}^{-2} \text{ yr}^{-1}$ , (J. Schwander et al., A tentative chronology of the EPICA Dome Concordia ice core, submitted to *Geophysical Research Letters*, 2000)) should then lead

to lower  $\text{NO}_3^-$  concentrations during the LGM than in the Holocene ( $2.7 \text{ g cm}^{-2} \text{ yr}^{-1}$ ), that is, to a completely different shape of the  $\text{NO}_3^-$  record. Although accumulation rate and presumably seasonality of precipitation are involved in the processes of  $\text{NO}_3^-$  deposition under present-day conditions, they cannot explain the high  $\text{NO}_3^-$  concentrations of the LGM. However, the large difference between Holocene and LGM concentration levels is seen at low-accumulation sites only (Table 1). It is not seen at Byrd Station with a much higher accumulation rate.

An interesting intermediate case is that of Taylor Dome. This site shows a strong decrease in concentrations between about 7 and 12 kyr, in line with a strong reported decrease in accumulation rate; in the early Holocene the  $\text{NO}_3^-$  concentration is as low as 10 ppb when the accumulation rate falls below about  $3 \text{ g cm}^{-2} \text{ yr}^{-1}$  according to estimates based on  $^{10}\text{Be}$  data [*Steig et al., 2000*]. It appears as if  $\text{NO}_3^-$  at Taylor Dome is not subject to major loss under present-day accumulation rates, but was so in the early Holocene. The values then increase back up in the late glacial period, but show much variability.

#### 4.2. Temperature

Another factor which potentially influences  $\text{NO}_3^-$  concentration in snow is temperature. At colder temperatures the ice-air concentration ratio of  $\text{HNO}_3$  is shifted toward higher snow concentrations at a given atmospheric concentration [*Abbatt, 1997*], that is, a tendency of higher uptake at lower temperatures. In addition, colder temperatures decrease the exchange of  $\text{HNO}_3$  between ice and interstitial air, leading to a higher variability preserved in the ice. Figure 4 shows that tem-



**Figure 4.**  $\text{NO}_3^-$  concentrations from different Antarctic sites versus present-day mean annual temperature. The data points at temperatures below  $-53^\circ\text{C}$  correspond to low-accumulation sites such as Dome C, Dome F, and Vostok. Data are from *Mulvaney and Wolff* [1994], *O. Watanabe et al.* [1999], *K. Watanabe et al.* [1999], *Stenberg et al.* [1998], *Kreutz and Mayewski* [1999], and *Curran et al.* [1998], as well as British Antarctic Survey (unpublished data, 2000).

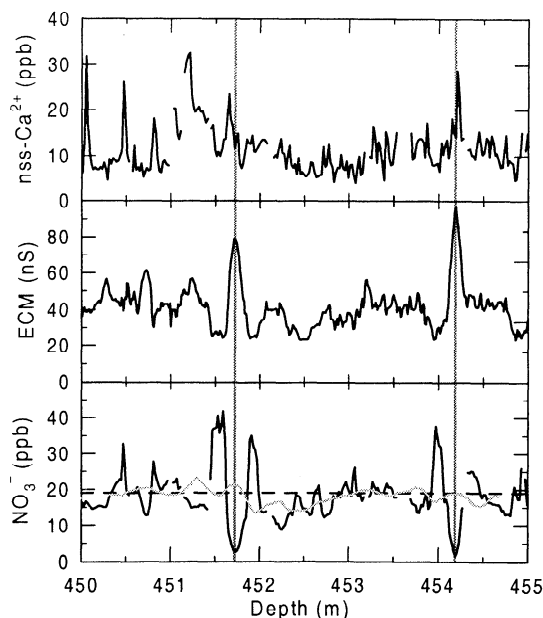
perature is a very strong indicator for  $\text{NO}_3^-$  concentrations in present-day Antarctic snow, as long as the accumulation rate is high enough to limit postdepositional losses. It seems as if, under present conditions, the effect of lowering the accumulation rate dominates the effect of lowering temperature at accumulation rates below  $5\text{ g cm}^{-2}\text{ yr}^{-1}$ .

Another reversibly deposited species, formaldehyde (HCHO), showed an elevated concentration level as well as high peaks during the last glacial period in the Greenland Ice Core Project (GRIP) ice core [*Fuhrer et al.*, 1993]. Transfer studies showed a strong temperature dependence of the HCHO concentration in ice, which probably accounted for a large part of the higher concentration level in the glacial period, but whether the high HCHO peaks in the glacial period are solely an effect of the colder temperatures remains still unclear [*Hutterli et al.*, 1999; *Hutterli*, 1999]. Analogous to HCHO, transfer studies for  $\text{NO}_3^-$  are required to estimate the importance of temperature on the high  $\text{NO}_3^-$  concentrations during the LGM (Figure 3). We could imagine that the lower temperatures of the last glacial were at least partially responsible for an enhanced uptake of  $\text{NO}_3^-$ , overcoming the effect of lower accumulation rate, and therefore leading to higher concentrations of  $\text{NO}_3^-$  in the ice. However, the detailed shape of the temperature changes seen at sites such as Vostok and Taylor Dome does not support this as the only factor, since  $\text{NO}_3^-$  changes significantly during the earlier parts of the glacial with only small temperature changes.

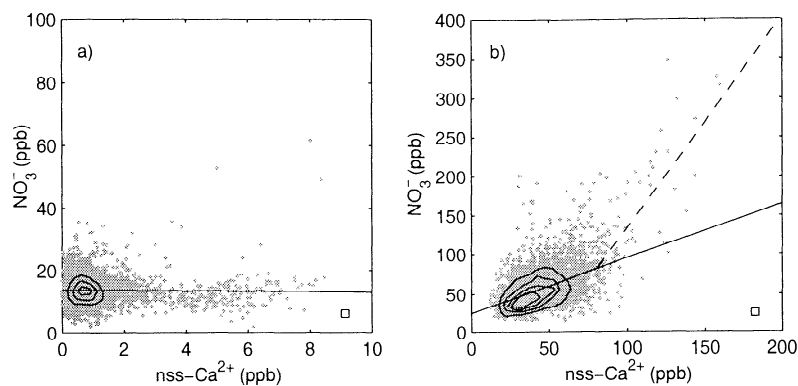
### 4.3. Impurities

In relation to  $\text{NO}_3^-$ , sea salt (mainly  $\text{Na}^+$  and  $\text{Cl}^-$ ) shows a different general shape (R. Röthlisberger et al., manuscript in preparation, 2000), as well as no correlation of the peaks. The only similarity between sea salt and  $\text{NO}_3^-$  is a substantial postdepositional loss of  $\text{Cl}^-$  and  $\text{NO}_3^-$  in surface snow at low-accumulation sites [*Wagnon et al.*, 1999; R. Röthlisberger et al., manuscript in preparation, 2000], although for  $\text{Cl}^-$  it is less pronounced. Thus sea salt seems to have no significant influence on  $\text{NO}_3^-$  in polar ice.

$\text{SO}_4^{2-}$ , the only anion occurring in high concentration apart from  $\text{Cl}^-$  and  $\text{NO}_3^-$ , offers no obvious mechanism influencing the  $\text{NO}_3^-$  concentration either. The  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  records have no similarities. Both the long-term trend and the high peaks are fairly different in shape and timing. On a large scale, the same also applies to acidity (inferred from the electrical conductivity measurements (ECM) and dielectric profiling (DEP) records). However, on a short scale, high acidity, which is usually related to  $\text{H}_2\text{SO}_4$  peaks of volcanic origin, seems to coincide with low  $\text{NO}_3^-$  levels (Figure 5). The same has been reported for volcanic events recorded at other sites, for example, in the GRIP ice core [*Clausen et al.*, 1997]. Two hypotheses have been proposed to explain this phenomenon. Less  $\text{NO}_3^-$  production in the atmosphere after volcanic eruptions or the mobilization of  $\text{NO}_3^-$  in the snowpack after deposition could be the reason for the low  $\text{NO}_3^-$  concentration levels during vol-



**Figure 5.** Example of the low  $\text{NO}_3^-$  concentrations in the presence of high acidity, indicated by the peaks in the electrical conductivity measurement (ECM) record. In the lower plot the dashed line indicates the mean concentration level and the shaded line the running mean over 62 cm.



**Figure 6.** Plots of  $\text{NO}_3^-$  against  $\text{nss-Ca}^{2+}$ : (a) Holocene (0 to 310 m), (b) Last Glacial Maximum (LGM) (490 to 590 m). Each data point is a 2 cm average. A linear fit is shown for the Holocene. For the LGM, a linear fit for  $\text{nss-Ca}^{2+}$  ranging from 20 to 80 ppb (solid line) and one for  $\text{nss-Ca}^{2+}$  from 80 to 200 ppb (dashed line) are shown. To improve visibility of the data points, the data were gridded and contoured; grid size is indicated by the square in the lower right angle. For Holocene data, grid boxes are 0.25 ppb horizontally and 2.5 ppb vertically. Contours are 100, 200, and 300 points per box. For the LGM, grid boxes are 5 ppb horizontally and 10 ppb vertically. Contours are 25, 50, 75, and 100 points per box.

canic events. Volcanic eruptions with emission of large amounts of  $\text{SO}_2$  have a large impact on atmospheric chemistry in reducing the concentration of oxidants. Assuming that the oxidation of  $\text{NO}_x$  is a major  $\text{NO}_3^-$  source, formation of  $\text{NO}_3^-$  would be reduced after volcanic eruptions [Yang *et al.*, 1996; Laj *et al.*, 1993]. However, other reactions that are enhanced by high  $\text{SO}_4^{2-}$  concentrations (conversion of  $\text{N}_2\text{O}_5$  to  $\text{HNO}_3$ ) might compensate or even overcompensate this [Wolff, 1995]. The second hypothesis considers processes occurring in the snowpack to be responsible for the effect observed. Wolff [1995] suggested that atmospheric  $\text{NO}_3^-$  concentration was not affected, but that during and/or after recrystallisation,  $\text{NO}_3^-$  was mobilized and pushed to the sides of the  $\text{SO}_4^{2-}$  peak, leaving a  $\text{NO}_3^-$  dip coincident with the  $\text{H}_2\text{SO}_4$  peak and slightly increased  $\text{NO}_3^-$  concentrations on the shoulders of the  $\text{H}_2\text{SO}_4$  peak. A similar effect is also seen for fluoride [De Angelis and Legrand, 1994]. The high-resolution  $\text{NO}_3^-$  data of the Dome C ice core reveal several events that support this hypothesis, while the first hypothesis seems less plausible due to the fact that  $\text{NO}_3^-$  levels are enhanced before and after the acidity peak (Figure 5).

Of the major impurities in polar ice,  $\text{nss-Ca}^{2+}$  (i.e., dust) is the only species that is remarkably similar to  $\text{NO}_3^-$  with respect to the general trends and the high spikes during the LGM (see Figures 1 and 3). Additionally, the trends in the two species are very similar in the earlier parts of the glacial recorded at Vostok, with both varying strongly together in periods when variability in other parameters was subdued. The  $\text{nss-Ca}^{2+}$  (or more generally dust) might lead to more efficient scavenging of  $\text{NO}_3^-$  and thus to more  $\text{NO}_3^-$  deposition or to a reaction of  $\text{NO}_3^-$  and dust particles, which prevents postdepositional  $\text{NO}_3^-$  losses. The lat-

ter seems more appropriate, since the high surface snow concentrations under present-day conditions imply efficient deposition even in the absence of  $\text{nss-Ca}^{2+}$ . However, it is not clear whether such reactions occur in the atmosphere or in the snowpack. If they happen in the atmosphere, one would expect to see a coincidence of  $\text{nss-Ca}^{2+}$  and  $\text{NO}_3^-$  peaks all over Antarctica, since  $\text{nss-Ca}^{2+}$  originates from quite far north and is rather well mixed in the Antarctic atmosphere. Furthermore, most  $\text{NO}_3^-$  sources are expected to lead to a fairly uniform concentration over Antarctica, giving a common basis for reaction of  $\text{NO}_3^-$  and dust for all Antarctic sites. Unfortunately, there are no high-resolution data from other sites going back into the LGM that would allow a comparison and support the assumption of atmospheric processes.

Recently, Legrand *et al.* [1999] established a relationship between  $\text{nss-Ca}^{2+}$  and  $\text{NO}_3^-$  in the Vostok ice core. Based on 54 samples of the last glacial period which contained more than 20 ppb  $\text{nss-Ca}^{2+}$ , they derived  $[\text{NO}_3^-] = 4.0 \text{ ppb} + 1.542 [\text{nss-Ca}^{2+}]$  with  $r^2 = 0.65$ . If we apply the same criterion to our data (2 cm averages, 4117 data points), we obtain a different relationship ( $[\text{NO}_3^-] = 12 \text{ ppb} + 1.0 [\text{nss-Ca}^{2+}]$ ) and also a weaker correlation ( $r^2 = 0.37$ ).

Plots of  $\text{NO}_3^-$  versus  $\text{nss-Ca}^{2+}$  are presented in Figure 6. As discussed above, the climatic conditions may have a strong influence on the  $\text{NO}_3^-$  concentrations preserved in ice. Therefore we examine the relationship between  $\text{nss-Ca}^{2+}$  and  $\text{NO}_3^-$  for two different climatic regimes. Figure 6a shows 2 cm averages of the Holocene, Figure 6b shows 2 cm averages of the LGM. During the Holocene, there is no correlation between  $\text{nss-Ca}^{2+}$  and  $\text{NO}_3^-$ . Irrespective of the  $\text{nss-Ca}^{2+}$  concentration,  $\text{NO}_3^-$  concentrations are around 15 ppb. In the LGM

the slope of a linear relationship increased with higher thresholds of the  $\text{nss-Ca}^{2+}$  chosen. With  $\text{nss-Ca}^{2+}$  concentrations ranging from 20 to 80 ppb, we obtain a linear relationship with a slope of 0.7, which seems to fit the data reasonably well. However, with higher  $\text{nss-Ca}^{2+}$  concentrations, we obtain a slope of 2.7, which is close to the stoichiometric ratio of  $\text{Ca}(\text{NO}_3)_2$ .

## 5. Conclusions

To summarize, we found that under present-day conditions, which are characterized by low  $\text{nss-Ca}^{2+}$  (a few parts per billion) in Antarctic snow, accumulation rate and temperature control  $\text{NO}_3^-$  preservation. At sites with accumulation rates higher than  $\sim 5 \text{ g cm}^{-2} \text{ yr}^{-1}$ , mean  $\text{NO}_3^-$  concentrations are higher than at sites with low snow accumulation, although the  $\text{nss-Ca}^{2+}$  concentration is comparable to the one seen at Dome C (see Table 1). Given a sufficient accumulation rate preventing  $\text{NO}_3^-$  from being lost, colder temperatures lead to higher mean  $\text{NO}_3^-$  concentrations (Figure 4). While the detected vast loss of  $\text{NO}_3^-$  in the top meter of the snowpack at Dome C can be explained by volatilization and/or photochemical decomposition, the origin of the abundant  $\text{NO}_3^-$  in surface snow has still to be determined.

Snow layers with high acidity of volcanic origin lead to  $\text{NO}_3^-$  redistribution in the firn, occurring regardless of accumulation rate. The acid layer shows a depletion in  $\text{NO}_3^-$  and the layers above and below show an enhancement. The redistribution has to occur in the top few meters, since the effect is already seen at a depth of 12 m, where the Tambora eruptions are recorded in the Dome C ice core.

In the LGM, lower temperatures and the reaction of  $\text{NO}_3^-$  with  $\text{nss-Ca}^{2+}$  (or dust) reduce or prevent  $\text{NO}_3^-$  loss despite lower accumulation rates, leading to higher mean concentrations as well as higher variability. However, the reaction of  $\text{NO}_3^-$  with  $\text{nss-Ca}^{2+}$  seems to be more efficient at higher  $\text{nss-Ca}^{2+}$  levels. So far, it remains unclear whether this reaction takes place in the atmosphere or in the snow.

Although the factors favoring loss or retention of  $\text{NO}_3^-$  in polar ice have been identified, further studies are needed to quantify the contribution of each of them and the interplay of all of them. Only when the effect of all these processes can be determined and accounted for will it be possible for information on past  $\text{NO}_x$  concentrations to be extracted from ice core nitrate data.

**Acknowledgments.** We thank T. Stocker and B. Stauffer for valuable discussions. This work is contribution 17 to the “European Project for Ice Coring in Antarctica” (EPICA), a joint ESF (European Science Foundation)/EC scientific programme, funded by the European Commission under the Environment and Climate Programme (1994–1998) contract ENV4-CT95-0074 and by national contributions from Belgium, Denmark, France, Germany, Italy, Netherlands, Norway, Sweden, Switzerland, and the United

Kingdom. The Swiss contribution is funded by the “Bundesamt für Bildung und Wissenschaft” project 97.0417 and the Swiss National Science Foundation.

## References

- Abbatt, J. P. D., Interaction of  $\text{HNO}_3$  with water-ice surfaces at temperatures of the free troposphere, *Geophys. Res. Lett.*, *24*(12), 1479–1482, 1997.
- Bales, R. C., Nitric acid in firn: Discussion, in *Ice Core Studies of Global Biogeochemical Cycles*, edited by R. Delmas, NATO ASI Ser. I, vol. 30, pp. 214–245, Springer-Verlag, New York, 1995.
- Bowen, H. J. M., *Environmental Chemistry of the Elements*, Academic, San Diego, Calif., 1979.
- Clausen, H. B., C. U. Hammer, C. S. Hvidberg, D. Dahl-Jensen, J. P. Steffensen, J. Kipfstuhl, and M. Legrand, A comparison of the volcanic records over the past 4000 years from the Greenland Ice Core Project and Dye 3 Greenland ice cores, *J. Geophys. Res.*, *102*(C12), 26,707–26,723, 1997.
- Curran, M. A. J., T. D. van Ommen, and V. Morgan, Seasonal characteristics of the major ions in the high-accumulation Dome Summit South ice core, Law Dome, Antarctica, *Ann. Glaciol.*, *27*, 385–390, 1998.
- De Angelis, M., and M. Legrand, Origins and variations of fluoride in Greenland precipitation, *J. Geophys. Res.*, *99*(D1), 1157–1172, 1994.
- Dibb, J. E., R. W. Talbot, J. W. Munger, D. J. Jacob, and S. M. Fan, Air-snow exchange of  $\text{HNO}_3$  and  $\text{NO}_y$  at Summit, Greenland, *J. Geophys. Res.*, *103*(D3), 3475–3486, 1998.
- Fuhrer, K., A. Neftel, M. Anclin, and V. Maggi, Continuous measurements of hydrogen peroxide, formaldehyde, calcium, and ammonium concentrations along the new GRIP ice core from Summit, central Greenland, *Atmos. Environ.*, *27A*(12), 1873–1880, 1993.
- Honrath, R. E., M. C. Peterson, S. Guo, J. E. Dibb, P. B. Shepson, and B. Campbell, Evidence of  $\text{NO}_x$  production within or upon ice particles in the Greenland snowpack, *Geophys. Res. Lett.*, *26*(6), 695–698, 1999.
- Hutterli, M., *Luft-Firn Transferstudien von HCHO und H<sub>2</sub>O<sub>2</sub> zur Interpretation von Eisbohrkerndaten*, Ph.D. thesis, Univ. Bern, Bern, Switzerland, 1999.
- Hutterli, M. A., R. Röthlisberger, and R. C. Bales, Atmosphere-to-snow-to-firn transfer studies of HCHO at Summit, Greenland, *Geophys. Res. Lett.*, *26*(12), 1691–1694, 1999.
- Isaksson, E., *Climate records from shallow firn cores, Dronning Maud Land, Antarctica*, Ph.D. thesis, Stockholm Univ., Stockholm, Sweden, 1994.
- Jones, A. E., R. Weller, A. Minikin, E. W. Wolff, W. T. Sturges, H. P. McIntyre, S. R. Leonard, O. Schrems, and S. Bauguutte, Oxidized nitrogen chemistry and speciation in the Antarctic troposphere, *J. Geophys. Res.*, *104*(D17), 21,355–21,366, 1999.
- Kreutz, K. J., and P. A. Mayewski, Spatial variability of Antarctic surface snow glaciochemistry: Implications for palaeoatmospheric circulation reconstructions, *Antarct. Sci.*, *11*(1), 105–118, 1999.
- Laj, P., J. M. Palais, J. E. Gardner, and H. Sigurdsson, Modified  $\text{HNO}_3$  seasonality in volcanic layers of a polar ice core: Snow-pack effect or photochemical perturbation, *J. Atmos. Chem.*, *16*, 219–230, 1993.
- Legrand, M., and M. De Angelis, Origins and variations of light carboxylic acids in polar precipitation, *J. Geophys. Res.*, *100*(D1), 1445–1462, 1995.
- Legrand, M., and R. J. Delmas, Soluble impurities in

- four Antarctic ice cores over the last 30,000 years, *Ann. Glaciol.*, *10*, 116–120, 1988.
- Legrand, M., and S. Kirchner, Origins and variations of nitrate in South Polar precipitation, *J. Geophys. Res.*, *95* (D4), 3493–3507, 1990.
- Legrand, M., and P. Mayewski, Glaciochemistry of polar ice cores: A review, *Rev. Geophys.*, *35*(3), 219–243, 1997.
- Legrand, M., C. Lorius, N. I. Barkov, and V. N. Petrov, Vostok (Antarctica) ice core: Atmospheric chemistry changes over the last climatic cycle (160,000 years), *Atmos. Environ.*, *22* (2), 317–331, 1988.
- Legrand, M., A. Leopold, and F. Domine, Acidic gases (HCl, HF, HNO<sub>3</sub>, HCOOH, and CH<sub>3</sub>COOH): A review of ice core data and some preliminary discussions on their air-snow relationships, in *Chemical Exchange Between the Atmosphere and Polar Snow*, edited by E. Wolff and R. Bales, *NATO ASI Ser. I*, vol. 43, pp. 19–43, Springer-Verlag, New York, 1996.
- Legrand, M., E. Wolff, and D. Wagenbach, Antarctic aerosol and snow fall chemistry: Implications for deep Antarctic ice core chemistry, *Ann. Glaciol.*, *29*, 66–72, 1999.
- Mayewski, P., and M. Legrand, Recent increase in nitrate concentration of Antarctic snow, *Nature*, *346*, 258–260, 1990.
- McConnell, J. R., R. C. Bales, R. W. Stewart, A. M. Thompson, M. R. Albert, and R. Ramos, Physically based modeling of atmosphere-to-snow-to-firn transfer of H<sub>2</sub>O<sub>2</sub> at South Pole, *J. Geophys. Res.*, *103*(D9), 10,561–10,570, 1998.
- McCormack, T., A. R. J. David, P. J. Worsfold, and R. Howland, Flow injection determination of nitrate in estuarine and coastal waters, *Anal. Proc.*, *31*, 81–83, 1994.
- Mulvaney, R., and E. W. Wolff, Spatial variability of the major chemistry of the Antarctic ice sheet, *Ann. Glaciol.*, *20*, 440–447, 1994.
- Mulvaney, R., D. Wagenbach, and E. W. Wolff, Postdepositional change in snowpack nitrate from observation of year-round near-surface snow in coastal Antarctica, *J. Geophys. Res.*, *103*(D9), 11,021–11,031, 1998.
- Munger, J. W., D. J. Jacob, S. M. Fan, A. S. Colman, and J. E. Dibb, Concentrations and snow-atmosphere fluxes of reactive nitrogen at Summit, Greenland, *J. Geophys. Res.*, *104*(D11), 13,721–13,734, 1999.
- Neubauer, J., and K. G. Heumann, Nitrate trace determinations in snow and firn core samples of ice shelves at the Weddell Sea, Antarctica, *Atmos. Environ.*, *22*(3), 537–545, 1988a.
- Neubauer, J., and K. G. Heumann, Determination of nitrate at the ng/g level in Antarctic snow samples with ion chromatography and isotope dilution mass spectrometry, *Fresenius Z. Anal. Chem.*, *331*, 170–173, 1988b.
- Palais, J. M., and M. Legrand, Soluble impurities in the Byrd Station ice core, Antarctica: Their origin and sources, *J. Geophys. Res.*, *90*(C1), 1143–1154, 1985.
- Röthlisberger, R., M. Bigler, M. Hutterli, S. Sommer, B. Stauffer, H. G. Junghans, and D. Wagenbach, Technique for continuous high-resolution analysis of trace substances in firn and ice cores, *Environ. Sci. Technol.*, *34*, 338–342, 2000.
- Steig, E. J., D. L. Morse, E. D. Waddington, M. Stuiver, P. M. Grootes, P. A. Mayewski, M. S. Twickler, and S. I. Whitlow, Wisconsinan and Holocene climate history from an ice core at Taylor Dome, western Ross Embayment, Antarctica, *Geogr. Ann.*, in press, 2000.
- Stenberg, M., E. Isaksson, M. Hansson, W. Karlén, P. A. Mayewski, M. Twickler, S. I. Whitlow, and N. Gundestrup, Spatial variability of snow chemistry in Western Dronning Mand Land, Antarctica, *Ann. Glaciol.*, *27*, 378–384, 1998.
- Wagenbach, D., M. Legrand, H. Fischer, F. Pichlmayer, and E. W. Wolff, Atmospheric near-surface nitrate at coastal Antarctic sites, *J. Geophys. Res.*, *103*(D9), 11,007–11,020, 1998.
- Wagnon, P., R. J. Delmas, and M. Legrand, Loss of volatile acid species from upper firn layers at Vostok, Antarctica, *J. Geophys. Res.*, *104*(D3), 3423–3431, 1999.
- Watanabe, K., K. Satow, K. Kamiyama, H. Motoyama, and O. Watanabe, Non-sea-salt sulfate and nitrate variations in the S25 core, near the coastal region, East Antarctica, *Polar Meteorol. Glaciol.*, *13*, 64–74, 1999.
- Watanabe, O., K. Kamiyama, H. Motoyama, Y. Fujii, H. Shoji, and K. Satow, The palaeoclimate record in the ice core at Dome Fuji station, East Antarctica, *Ann. Glaciol.*, *29*, 176–178, 1999.
- Wolff, E. W., Nitrate in polar ice, in *Ice Core Studies of Global Biogeochemical Cycles*, edited by R. Delmas, *NATO ASI Ser. I*, vol. 30, pp. 195–224, Springer-Verlag, New York, 1995.
- Yang, Q., P. A. Mayewski, G. A. Zielinski, M. Twickler, and K. C. Taylor, Depletion of atmospheric nitrate and chloride as a consequence of the Toba volcanic eruption, *Geophys. Res. Lett.*, *23*(18), 2513–2516, 1996.

M. A. Hutterli, Department of Hydrology and Water Resources, University of Arizona, Tucson, AZ 85721. (manuel@hwr.arizona.edu)

R. Mulvaney and E. W. Wolff, British Antarctic Survey, Natural Environment Research Council, High Cross, Madingley Road, Cambridge CB3 0ET, England. (rmu@bas.ac.uk; ewwo@bas.ac.uk)

R. Röthlisberger and S. Sommer, Climate and Environmental Physics, Physics Institute, University of Bern, Sidlerstrasse 5, 3012 Bern, Switzerland. (regine@climate.unibe.ch; sommer@climate.unibe.ch)

(Received March 2, 2000; revised April 26, 2000; accepted April 28, 2000.)