Sulfate and nitrate firn concentrations on the Greenland ice sheet
1. Large-scale geographical deposition changes

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Abstract. Eleven shallow firn cores and three deeper ice cores drilled along a meridional line over the Greenland ice sheet from 71° to 80°N have been specifically evaluated for their nitrate and sulfate concentrations. Recent average annual sulfate concentrations strongly increase from around 100 ppb in central Greenland to 175 ppb in the northeastern part of the ice sheet, while nitrate levels remain essentially constant at around 150 ppb. Recent sulfate firn concentrations exhibit a distinct seasonal cycle with maximum concentrations in spring. The seasonal amplitude is 5 times higher over the northern ice sheet compared to the central Greenland region. The corresponding nitrate cycle is only weakly defined with a tendency toward higher summer concentrations. Application of a macroscopic deposition model, developed for irreversibly deposited sulfate as well as reversibly deposited nitrate, shows that geographical variations in sulfate and nitrate firn concentrations can be explained largely by the spatial change in snow accumulation rate over the entire interior of the Greenland ice sheet both for recent and for preindustrial conditions. The recent wet sulfate deposition flux has increased by a factor of 2 since preindustrial times, while the dry deposition flux has risen by a factor of 5. In the case of nitrate, depositon fluxes have increased by a factor of 2 both for wet and for dry deposition. On the basis of the empirically determined model parameters, up to 50% of the initially deposited nitrate appears to be remobilized from the firn column.

1. Introduction

Polar ice sheets represent unique archives of environmental and climate change [*Johnsen et al.*, 1992; *O'Brien et al.*, 1995; *Raynaud et al.*, 1993]. In this context, sulfate and nitrate ice core records from the Greenland ice sheet (the latter being affected by the long range transport of industrial emissions (e.g. NO_x, SO_2) from middle latitudes) have been shown to mirror anthropogenically induced changes during this century [*Neftel et al.*, 1985; *Mayewski et al.*, 1990]. The interpretation of such records in terms of atmospheric concentration changes, however, is strongly impaired by the still limited knowledge of the air/snow-transfer of aerosols and water-reactive trace gases [*Bergin et al.*, 1995; *Dibb*, 1996; *Dibb and Jaffrezo*, 1997; *Jaffrezo et al.*, 1995]. In particular, local climatological conditions (e.g., the local snow accumulation rate, which controls the relative contribution of wet and dry deposition to pollutant removal) may strongly affect firn concentrations [*Legrand*, 1995; *Fischer and*

Wagenbach, 1996]. Furthermore, nitrate, which is present in the Greenland atmosphere in the form of gaseous species like HNO_3 and organic nitrogen compounds [*Dibb et al.*, 1998; *Silvente and Legrand*, 1995], was found to be partly reemitted to the atmosphere from the Greenland snowpack [*DeAngelis and Legrand*, 1995]. The influence of this reevaporation effect on mean nitrate firn concentrations is expected to depend on the local snow accumulation rate as indicated by the extraordinarily high nitrate losses encountered in the low accumulation areas of central Antarctica [*Mayewski and Legrand*, 1990].

Quantification of such effects on the deposition of aerosols and water-reactive trace gases is a prerequisite for reliable comparison of chemical long-term ice core records from different climatological regions on the Greenland ice sheet as well as between different climatic stages in the past. In order to help resolve this problem, we attempted in this study to "simulate" changing deposition conditions on the ice sheet with a spatially well resolved ice core study covering a large range of different accumulation conditions and to interpret the results according to a macroscopic deposition model. We emphasize here that this approach cannot give insight in the highly variable aerosol and trace gas scavenging processes operating on a synoptical timescale but is designed to extract the major effects relevant on a timescale which can be resolved in ice core records (typically months to years).

In the following paper we will concentrate on the geographical and seasonal variation of sulfate and nitrate firn

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concentrations. By developing an easy macroscopic model approach for both the irreversible deposition of sulfate aerosol and the reversible deposition of gaseous nitrate precursors, the influence of geographical changes in snow accumulation will be assessed for recent and preindustrial conditions. Detailed evaluation of the temporal anthropogenic changes in sulfate and nitrate firn concentrations will be presented in part 2 of *Fischer et al.* [this issue] where reasons for the geographically varying extent of these changes in different regions of the Greenland ice sheet will be addressed.

2. Samples and Methods

Ice cores for this study were drilled during the years 1993-1995 in the so far little investigated area of northern Greenland (see Figure 1). Along the North Greenland Traverse, more than 40 shallow firn core drillings and pit studies were performed and 13 deeper (100-200 m) ice cores drilled. Here we will present the findings along a meridional subsection of the traverse from 71° to 80°N (hereinafter referred to as NGT; see enlargement in Figure 1). Along this line, 25 pit studies, 11 shallow firn cores, and 3 deeper ice cores (B16, B18, B21, covering the time span from approximately 1400 A.D. to present) were analyzed for $\delta^{18}O$ as well as for their major and trace ion content. On the one hand, this study represents an extension of the chemical, isotopical, and glaciometeorological surface study along the longitudinal EGIG-line (Expédition Glaciologique Internationale au Groenland), central Greenland, [*Fischer et al.*, 1995; *Fischer and Wagenbach*, 1996] to the vast low accumulation area of northern Greenland. On the other hand, the extended time span covered by the deeper NGT ice cores

enables us to reconstruct the preindustrial variability in isotopic [*Fischer et. al.*, 1998] and chemical records as well as anthropogenic changes over the last century representative for the northern Greenland ice sheet [*Fischer et al.*, this issue].

Snow pit profiles and shallow firn cores were sampled at high resolution (approximately 8 samples/year) covering the top 10-30 years at each site, whereas the deeper ice cores were sampled at coarse resolution (1-4 years/sample) over the time span 1400 A.D to present. All ice core samples were thoroughly decontaminated under clean room conditions in our cold labs using an electromechanical plane with adjustable speed to ensure fast and reliable removal of potential surface contamination, even for low density firn core sections.

All samples were analyzed in Heidelberg by autosupressed ion chromatography and evaluated for their methanesulfonate (MSA), Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, Mg^{2+}, and Ca^{2+} concentrations. Cation concentrations were determined isocratically using a Dionex 4500i chromatography module equipped with a Dionex CG12/CS12 column combination. 2.2 mL of each sample were preconcentrated on a Dionex TCC-LP1 column to avoid matrix effects previously encountered [*Preunkert*, 1994] when using large sample loop volumes. Anion concentrations were determined without preconcentration using a gradient run on a Dionex 300 module equipped with a Dionex AG11/AS11 column pack. Average concentrations of process blank samples made from frozen deionized water which was subjected to the entire decontamination and analytical procedure (as listed in Table 1) were well below the average ice core concentrations for all species except NH_4^+ where significant NH_3 contamination by ambient lab air occurred. No blank correction was applied for any species. As seen in Table 1, the relative reproducibility error RE (defined as 2 times the standard deviation divided by the mean of fivefold replicate measurements) is higher at the lower end of the ice core concentration range, reflecting the higher influence of the blank variability for such samples. For the nitrate and sulfate concentrations discussed here the reproducibility error is always less than 5%.

The $\delta^{18}O$ measurements were performed in Heidelberg on all high-resolution pit samples as well as on the coarse-resolution samples of core B16, B18, and B21. Additionally, five bulk samples covering the top 15 years of each shallow firn core were analyzed to obtain a temporal representative average in $\delta^{18}O$ for each site. The overall accuracy of $\delta^{18}O$ for an individual sample is better than 0.2 ‰.

The high-resolution ion profiles revealed distinct seasonal cycles for nearly all species (see Figure 2). Calcium showed a clear seasonal maximum in spring relative to the $\delta^{18}O$ record in our snow pit profiles. Since calcium, which is mainly derived by long-range transport of mineral dust aerosol onto the Greenland ice sheet [*Steffensen*, 1988], is not subject to migration in the ice, the shallow firn cores were dated with an accuracy better than ±1 year by counting annual layers in the high-resolution Ca^{2+} records (see Figure 2). Water-weighted annual concentration averages for sulfate and nitrate have been determined according to this dating with single years defined from one Ca^{2+} maximum to the next. In order to avoid overrepresentation of single years subject to extraordinarily high concentrations (as for example caused by volcanic deposits in the sulfate record) the median of all years and the median of absolute deviations [*Bloomfield and Steiger*, 1983;
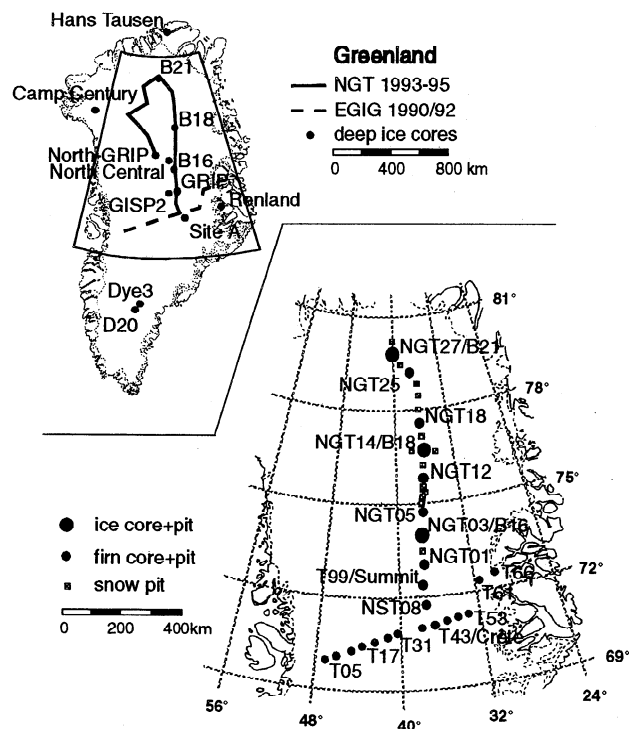

Figure 1. Overview: route of the North Greenland and EGIG Traverses performed during the years 1990-1995 and locations of major deep ice core drillings performed on the Greenland ice sheet. Enlargement: geographical location of the sampling sites along the NGT and EGIG lines.

Table 1. Summary of Accuracy in the Ion Chromatographic Analysis of Ice Core Samples

	MSA	Cl⁻	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	Mg^{2+}	Ca^{2+}
Process blank ppb	0.3±0.1	3.5±3.2	0.9±1.0	1.8±1.9	2.5±1.9	6.3±4.8	1.5±1.2	0.5±0.7
Sample range ppb	0.5-5	5-160	30-300	20-600	3-120	5-30	0.5-20	1-40
Reprod. error %	20-7	10-3	5-2	5-3	20-5	60-15	15-7	15-10

Average and standard deviation of process blank samples, typical concentration range of the high-resolution ice core samples and the maximum and minimum reproducibility error (see text) at the lower and upper end of the sample concentration range, respectively.

Fischer et al., this issue] instead of arithmetic mean and standard deviation were determined for the time span 1992-1983 in each core. This period is covered by all firn cores and is comparable to the time interval investigated along the EGIG line. In order to derive average annual concentration cycles, the median of seasonal averages has been calculated with individual seasons determined by dividing the depth interval between adjacent Ca^{2+} maxima into four equidistant parts. Average preindustrial concentrations over the time span 1500-1850 A.D. were determined from the long-term NGT records after removal of singular (volcanic) events in the sulfate record. Details concerning dating, data reduction, and time series analysis of the deeper ice cores are given in part 2 of *Fischer et al.* [this issue].

3. Results

The geographical variations of recent sulfate and nitrate firn concentrations, together with the variation in surface topography and glaciometeorological parameters (isotope temperature, snow accumulation rate), are displayed in Figure 3. For comparison, both the new results along the meridional NGT as well as the previously published results along the longitudinal EGIG line, central Greenland [*Fischer et al.*, 1995; *Fischer and Wagenbach*, 1996], are presented.

As illustrated in Figures 3a and 3b, recent sulfate and nitrate concentrations in central Greenland range between 70-110 ppb and 110-150 ppb, respectively, with a ~30% increase from west to east for both species as well as slightly enhanced firn concentrations at the westernmost positions T05 and T09. Going north along the NGT, a 100% increase in sulfate levels

with maximum concentrations around 170 ppb is encountered. In contrast, nitrate shows rather constant concentrations of approximately 150 ppb throughout the NGT.

The seasonal variations in recent sulfate and nitrate concentrations along the NGT are plotted in Figures 4a and 4b. Nitrate firn concentrations show a very subdued seasonal cycle along the NGT with a tendency to slightly enhanced levels in summer and possibly spring which is more prominent in the central ice sheet region. In contrast, sulfate firn concentrations exhibit a clear seasonal cycle with maximum concentrations in spring. Spring levels increase from south to north by a factor of 4, while summer and autumn concentrations remain essentially constant throughout the investigated line. Accordingly, the seasonal sulfate amplitude increases from ~50 ppb in central Greenland to more than 250 ppb in the northern parts of the ice sheet.

These findings, taken at face value, could be interpreted as evidence of an increase in sulfate air concentration from central to northern Greenland, possibly linked to an enhanced influence of Arctic haze air masses during spring. However, any interpretation of the geographical variations in firn concentrations in terms of an atmospheric signal must consider the overall change in geographical and glaciometeorological (temperature, snow accumulation) parameters, which may cause systematic changes in aerosol and trace gas deposition. The altitude increases from ~1800 m at the westernmost position of the EGIG-line (T05) to ~3200 m at the Greenland Summit, while average $\delta^{18}O$ decreases from approximately -26‰ at T05 to a minimum of -37‰ at 75°N. The latter translates to a decline in mean
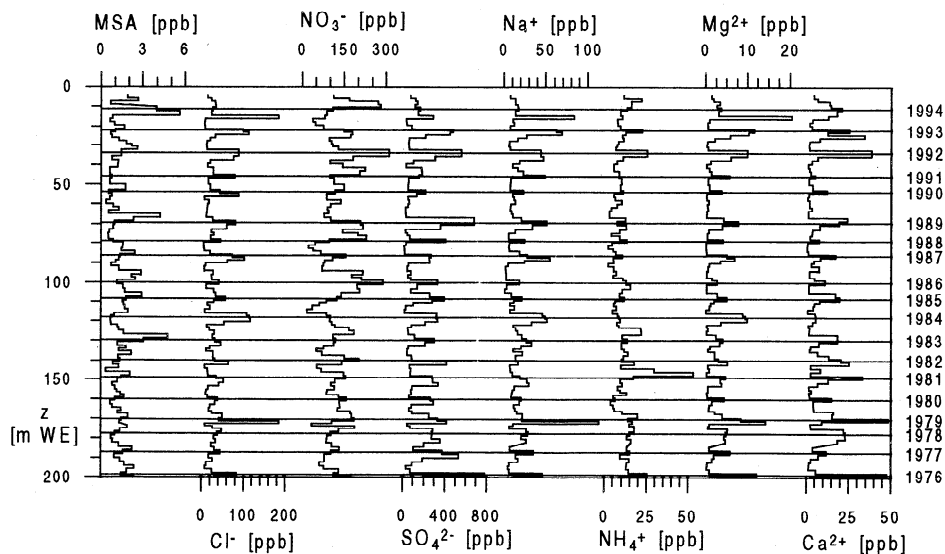

Figure 2. Example for high-resolution profiles of the MSA, Cl⁻, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, Mg^{2+}, and Ca^{2+} concentrations in the shallow core at position NGT27.
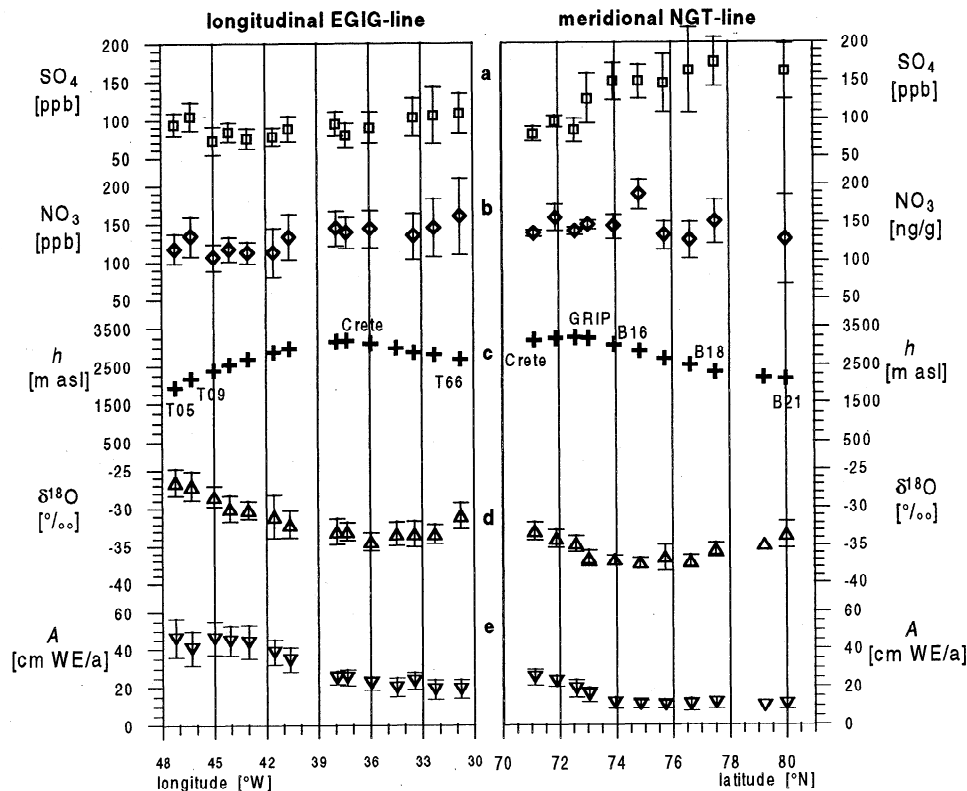
Figure 3. Geographical variation of (a) sulfate firn concentration, (b) nitrate firn concentration, (c) altitude, (d) $\delta^{18}O$, and (e) snow accumulation rate along the NGT and EGIG lines. Plotted are average annual means ± standard deviation (error bars) of all parameters except for sulfate and nitrate concentrations along the NGT. Here the median of annual concentrations ± median of absolute deviations (error bars) are given (see text).

annual temperature from -18°C to -35°C when applying the recent spatial $\delta^{18}O$/temperature relationship ($\delta^{18}O=0.67T$ [°C] -13.7 in ‰) for the Greenland ice sheet given by *Johnsen et al.* [1989]. Again, these topographical and glacio-meteorological changes are connected with a strong decrease in the annual snow accumulation rate from 46 cm water

equivalent (WE)/year at the west coast to values as low as 10 cm WE/a for most of the northeastern Greenland ice sheet.

4. Deposition Model

4.1. Irreversible Sulfate Deposition

The more than 400% variation in snow accumulation rate covered in this study is expected to influence strongly average annual firn concentrations, due to the accompanying change in the relative contributions of wet and dry deposition fluxes. In order to take such accumulation-induced changes into account, a macroscopic model for the irreversible deposition of aerosols like sulfate has been previously discussed and applied to the firn concentrations along the EGIG line [*Fischer and Wagenbach*, 1996]. In this model the firn concentration of conservative species (if averaged over a sufficiently long time and number of precipitation events) can be described as the sum of an average annual fresh snow concentration C_{snow} and the average annual total dry deposition flux J_{dry}^{tot}, which is uniformly diluted by the average snow accumulation rate A:

$$C_{firn} = C_{snow} + \frac{J_{dry}^{tot}}{A} \qquad (1)$$

(where J_{dry}^{tot} comprises all processes not associated with substantial precipitation such as dry deposition of aerosol, fog deposition, or snowdrift scavenging). In view of the very low and geographically relatively uniform temperature distribution (between -25°C and -35°C for most of the area investigated) a primary connection between mean annual temperatures and average sulfate firn concentrations seems to be unlikely on the ice core timescale investigated in this study. This assumption
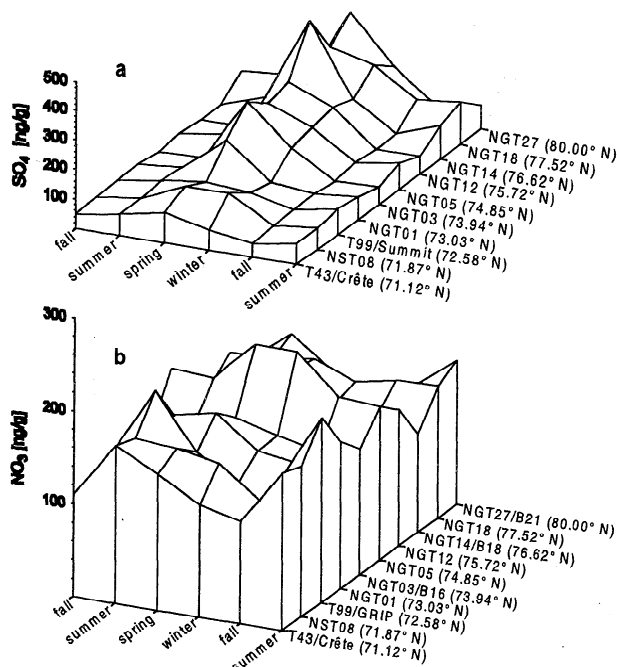

Figure 4. Average seasonal cycle of (a) sulfate and (b) nitrate firn concentrations along the NGT.

seems reasonable for most of the dry snow area investigated with the exception of positions T05 and T09 in the west where occasionally surface melting occurred during summer. On shorter timescales, i.e., when considering snow formation temperatures during single precipitation events, a temperature effect on aerosol and trace gas scavenging is expected [*McConnell et al.*, 1997b]. However, average annual temperatures, as can be resolved in the $\delta^{18}O$ record, are not representative for the temperature during snow formation and, accordingly, are not taken into account in our model.

According to equation (1), a linear increase of firn concentrations with inverse snow accumulation rate is expected if C_{snow} and J_{dry}^{tot} are essentially constant throughout the investigated area. Also assuming that wet scavenging is essentially independent of the precipitation rate for the snow accumulation range considered here implies that the atmospheric near-surface sulfate concentration would be geographically uniform. Conversely, geographical net changes in the atmospheric aerosol concentration can only be resolved from spatial variations in firn concentrations if they cause a significant deviation from this implicit linear relationship.

4.2. Reversible Nitrate Deposition

In the case of nitrate, equation (1) appears not to be applicable since reevaporation of gaseous nitrate species like HNO_3 may cause a net loss of initially deposited nitrate. Such losses were previously observed in fresh snow studies [*De Angelis and Legrand*, 1995] on the Greenland ice sheet and were also indicated by extraordinarily high nitrate concentrations (up to several hundred ppb) confined to the top centimeters of some of our snow pit profiles along the NGT. In contrast to the scavenging of gaseous H_2O_2, where modeling efforts of air concentrations and H_2O_2 deposition were rather successful [*McConnell et al.*, 1997a; *McConnell et al.*, 1997b], the microscopic processes of nitrate deposition and remobilization are so far not well understood [*Wolff*, 1995] and defy a quantitative description. Furthermore, the relative contributions of different gaseous nitrogen precursors to the total nitrate firn content are not sufficiently known [*Dibb et al.*, 1998]. Therefore we developed a macroscopic model approach which describes nitrate firn concentrations simply as a budget of deposition and evasion to evaluate the influence of snow accumulation on nitrate firn concentrations on the Greenland ice sheet. Such a model is not dependent on the actual speciation of gaseous nitrate precursors. Accordingly, it cannot give insight into the microscopic deposition and reevaporation processes, but it is essential for the interpretation and comparison of long-term ice core records from different climatological regions on the ice sheet. Also, a temperature dependence of the nitrate remobilization process, as possibly related to a temperature dependent recrystalization process in the snowpack, has not been explicitly incorporated in our macroscopic model. However, the extraordinary nitrate loss of surface snow in the ultralow accumulation areas of the Antarctic plateau [*Mayewski and Legrand*, 1990] despite extremely low temperatures in this region indicates that temperature is not so important as accumulation rate in the control of nitrate evasion.

We assume that the snowpack has essentially the same texture throughout the dry snow zone implying that the evasion process of gaseous nitrate species is comparable at all sites. Secondly, we divide the near surface firn column into two boxes: (1) a convective upper box of thickness Δz, where

remobilized nitrate may be effectively removed to the atmosphere, e.g., by firn ventilation caused by wind pumping at small-scale perturbations of the surface topography [*Waddington and Cunningham*, 1996]; (2) a diffusive box beneath, where further smoothing of nitrate records might occur but no net transport to the atmosphere via the upper convective box.

In the most simple approach we assume the net nitrate transfer from the ice matrix to the open pore space to be of first order and governed by a rate constant λ, hence

$$\frac{dC_{firn}(t)}{dt} = -\lambda \cdot C_{firn}(t) \qquad (2)$$

Since the upper (ventilated) box is considered to be well mixed (i.e., maintaining a uniform gas phase nitrate concentration similar to the atmospheric surface concentration throughout the box), the degree of nitrate loss of a single snow layer (which is assumed to be thin compared to the depth of the upper box) is dependent on the residence time Δt of the strata in the convective box. With $\Delta t = \Delta z/A$, where Δz denotes the thickness of the upper box and A the average snow accumulation rate (both in water equivalent), C_{firn}^* at the bottom of the convective box becomes

$$C_{firn}^* = C_0 e^{-\lambda \cdot \Delta t} = C_0\, e^{\frac{\lambda \cdot \Delta z}{A}} \qquad (3)$$

with C_0 the initially deposited surface firn concentration, expressed according to equation (1). Note that equation (3) implies an exponential depth profile in the convective box with a characteristic depth scale of $\Delta z' = A/\lambda$ and is only valid for limited residence times, hence a limited range of snow accumulation rates, since the snowpack cannot be arbitrarily depleted in nitrate. For practical reasons, equation (3) may be expanded to first order, leading to a second-order polynomial in inverse accumulation rate:

$$C_{firn}^* = \left(C_{snow} + \frac{J_{dry}^{tot}}{A}\right)\left(1 - \frac{\lambda \cdot \Delta z}{A}\right)$$

$$= C_{snow} + \left(J_{dry}^{tot} - \lambda \cdot \Delta z \cdot C_{snow}\right)\frac{1}{A} - \lambda \cdot \Delta z \cdot J_{dry}^{tot}\frac{1}{A^2} \qquad (4)$$

Equation (4) is equivalent to a constant loss rate and thus to a linear decline in snow concentration over the entire residence time. According to equation (4) an approximately second-order polynomial dependence of average firn concentration and inverse snow accumulation rate is expected if C_{snow}, J_{dry}^{tot}, and $\lambda\Delta z$ are essentially constant throughout the investigated area.

5. Discussion

5.1. Sulfate

In order to investigate the accumulation effect on sulfate firn concentrations, we applied the deposition model in equation (1) on the spatial distribution of snow accumulation and sulfate firn concentration found on the Greenland ice sheet. Accordingly, recent sulfate concentrations along the NGT as well as the EGIG line are plotted in Figure 5a versus inverse snow accumulation rate. For comparison, average preindustrial levels derived from the deeper NGT cores B16, B18, B21, and preindustrial data found in the literature for D20 (southern Greenland), Site A, GISP2 (central Greenland),
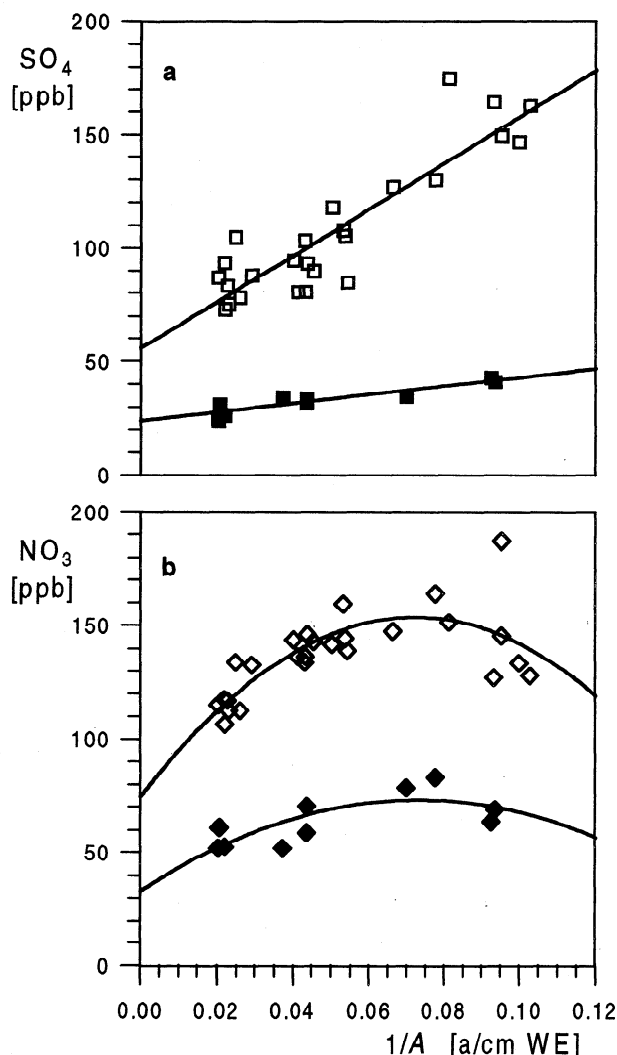
Figure 5. Average firn concentrations versus inverse average snow accumulation rate for (a) sulfate and (b) nitrate. Open squares represent values for recent conditions determined along the NGT and EGIG lines, solid squares represent average preindustrial levels as determined from core B16, B18, B21, as well as preindustrial values reported in the literature (see text). Also plotted are polynomial fits in $1/A$ (first-order for sulfate, second-order for nitrate) as suggested by the respective macroscopic deposition model.

Table 2. Sulfate Model Parameters for Recent and Preindustrial Conditions

SO_4^{2-}	C_{snow} ng/g	J_{dry}^{tot} ng/cm^{2}a	A_{crit} cm WE/a
Recent	56±6	1020±100	18
Preindustrial	24±2	190±30	8
Rise factor	2.3	5.4	2.3

Average fresh snow concentration C_{snow} and average total dry deposition flux J_{dry}^{tot} together with their standard errors as determined by linear regression according to equation (1).

concurrent change in snow accumulation. On the basis of our model we conclude that average annual sulfate firn concentrations are governed largely by the change in local snow accumulation rate and that a rather uniform geographical distribution of atmospheric sulfate concentrations over the entire interior of the Greenland ice sheet can be assumed. This conclusion is also supported by the absence of a clear latitudinal gradient in average annual sulfur concentration reported from ground-based aerosol measurements at various sites along the Greenland coast [Heidam, 1984], although the seasonal amplitude in sulfur concentrations is significantly higher at the northern Greenland coast compared to other Greenland stations [Heidam et al., 1993]. Also, model calculations by Christensen [1997] for air pollution of the Arctic atmosphere show rather low latitudinal gradients in sulfur dioxide and sulfate air concentrations over the Greenland ice sheet.

Comparison of the empirically determined C_{snow} and J_{dry}^{tot} for recent and preindustrial conditions in Table 2 shows that the recent average fresh snow concentration for sulfate exceeds the preindustrial level by 100%, while the average dry deposition flux increased by approximately 500% over this century. This drastic rise clearly illustrates the dominating anthropogenic impact on recent Greenland sulfate levels. Most interesting here is the difference in the rise factor of wet and dry deposited sulfate aerosol which indicates that anthropogenic changes are not equally reflected by wet and dry deposition. This difference may be attributed to the previously observed change in the seasonal cycle of sulfate firn concentrations in Greenland during this century [Finkel et al., 1986; Mayewski et al., 1987]. While during preindustrial times sulfate firn concentrations were maximum during summer/spring, anthropogenic sulfate aerosol is episodically transported onto the ice sheet with a well-defined seasonal maximum in early spring as seen in our results for the northern ice sheet region and in previous studies in southern and central Greenland [Davidson et al., 1993; Whitlow et al. 1992]. Precipitation in the northern and central interior of the ice sheet is mainly expected in summer [Chen et al., 1997] and therefore anthropogenically polluted air masses in spring are not necessarily accompanied by precipitation events during that time of the year and, accordingly, are not equally reflected by wet deposition.

Another interesting parameter given in Table 2 is the critical accumulation rate, defined as the snow accumulation rate where wet equals dry sulfate deposition. The values of A_{crit} in Table 2 imply that for recent and especially preindustrial conditions, dry deposition comprises a significant contribution to the total sulfate content only in the low accumulation area of northeastern Greenland, while wet deposition controls the major part of the ice sheet.

and North Central (northern Greenland) [Herron, 1982; Laj et al., 1992; Mayewski et al., 1990; Whitlow et al., 1992] are plotted in Figure 5a as well. In general, a linear relationship (with r significantly different from zero on the 1 ‰ level) between firn concentrations and inverse snow accumulation rate is very well obeyed both for recent and for preindustrial conditions. According to equation (1) the linear regression parameters of the fits in Figure 5a (as summarized in Table 2) represent the average fresh snow concentration C_{snow} and the total dry deposition flux J_{dry}^{tot}. The value for J_{dry}^{tot} is approximately 60% higher than values determined in the same manner for the longitudinal EGIG-line only [Fischer and Wagenbach, 1996], while C_{snow} is 30% lower. This is either due to the greater range of accumulation covered by the present study or by systematic higher atmospheric sulfate concentrations in northern Greenland. However, based on the high coefficient of determination of the linear regression, 70-80% of the data variance can be explained solely by the

5.2. Nitrate

The corresponding picture for nitrate (Figure 5b) shows significantly lower nitrate firn concentrations in the low accumulation area of northern Greenland than what would be expected for conservative aerosol deposition given in equation (1). Although a northward decrease in air concentrations cannot be excluded, we attribute this finding to enhanced remobilization of nitrate from the firn column in the low accumulation areas. A second-order polynomial fit of inverse snow accumulation in Figure 5b, corresponding to equation (4) of the reversible deposition model, fits the geographical trend in nitrate firn concentrations very well (r significantly different from zero on the 5% level both for recent and for preindustrial conditions). We therefore conclude that the geographical variation in average annual nitrate concentrations can be explained largely by the change in local snow accumulation rate as well. The coefficients of determination show that according to our model, close to 60% of the variance in the data can be attributed to the change in snow accumulation. The competing processes of higher contribution of dry nitrate deposition and enhanced nitrate loss in the low accumulation areas cause a typical maximum in average annual nitrate firn concentrations at sites with the moderately low accumulation rate of ~ 14 cm WE/a both for recent and for preindustrial conditions. This agreement for both periods indicates that the remobilization process is rather independent from the total nitrate level or the speciation of the gaseous nitrate precursors which has most probably changed from preindustrial to recent conditions. Instead, nitrate evasion out of the snowpack seems to be controlled by inherent glaciological parameters (e.g., residence time in the convective box, strength of firn ventilation, snow texture, and recrystalization).

Given in Table 3 are the average fresh snow concentration C_{snow}, average total dry deposition flux J_{dry}^{tot}, and the nitrate evasion velocity $v_{evasion} = \lambda\Delta z$ for recent and preindustrial conditions which were derived according to equation (4). In contrast to sulfate, wet and dry nitrate deposition both increased by approximately 100% since the preindustrial era. Comparing the evasion velocity in Table 3 of 5-6 cm WE/a with the low accumulation rates encountered in northeastern Greenland (A~10 cm WE/a), a loss of more than 50% of the initially deposited nitrate from the snowpack is indicated. Also remarkable is the unexpectedly high value of the total dry nitrate deposition flux derived in our model, which results in a critical accumulation rate of more than 30 cm WE/a. This means that nitrate concentrations are governed by efficient dry deposition of HNO_3 [*Johansson and Granat*, 1986] and/or

organic nitrate precursors onto the snow surface over large parts of the Greenland ice sheet.

6. Summary and Conclusions

Extensive traverse studies over the central and northern Greenland ice sheet allowed us to investigate the spatial distribution of sulfate and nitrate firn concentrations in geographically high resolution over an extraordinarily wide range of accumulation conditions. In order to evaluate this distribution with respect to geographical net changes in atmospheric concentrations, a simple macroscopic model approach for the deposition of particulate sulfate aerosol as well as gaseous nitrate species was developed (taking reemission of nitrate species from the snowpack into account). Application of this model reveals that geographical variations in sulfate and nitrate firn concentrations can be attributed largely to the change in local snow accumulation rate. On the basis of the model outcome, recent sulfate concentrations are governed by wet deposition over large parts of the ice sheet, while in the case of nitrate, dry deposition appears to be as important as wet deposition. Considering the approximately 50% lower accumulation rates during the Pleistocene [*Alley et al.*, 1993], a much higher contribution of dry deposited sulfate aerosol to the total sulfate deposition has to be considered during glacial conditions.

Comparison of our model results for preindustrial and recent conditions shows, that dry sulfate deposition has recently increased by a factor of 5 compared to the preindustrial period, more than twice the respective increase in wet sulfate deposition during this century. This implies that the extent of the long-term anthropogenic increase in sulfate firn concentrations archived in Greenland ice cores is dependend on the geographic position of the drill site, solely due to the relative contributions of wet and dry deposition fluxes to total sulfate deposition which are controlled by the local snow accumulation rate. This spatial effect is clearly observed in our long-term records [*Fischer et al.*, this issue] where northern Greenland ice cores show a more than twofold larger increase in 20th century sulfate firn concentrations compared to southern and central Greenland drill sites.

In the case of nitrate, both wet and dry deposition fluxes increased by 100% from preindustrial to recent conditions, accordingly, no discrepancy in the temporal nitrate record is expected for different drill sites. However, the more than 50% loss of initially deposited nitrate from the firn column in the low accumulation area of northeastern Greenland further complicates the reconstruction of atmospheric concentrations of gaseous nitrate precursors.

Table 3. Nitrate Model Parameters for Recent and Preindustrial Conditions

NO_3	C_{snow} ng/g	J_{dry}^{tot} ng/cm²a	$v_{evasion}$ cm WE/a	A_{crit} cm WE/a
Recent	75±12	2620±430	5.8±1.6	34
Preindustrial	35±12	1290±490	5.8±3.9	37
Rise factor	2.1	2.0	1	0.9

Average fresh snow concentration C_{snow}, average total dry deposition flux J_{dry}^{tot} and the effective evasion velocity $v_{evasion}$ as determined by a second-order polynomial fit according to equation (4). Error limits were calculated by propagation of the standard errors of the regression parameters.

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