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Glacio-chemical study spanning the past 2 kyr on three ice cores from Dronning Maud Land, Antarctica
2. Seasonally resolved chemical records

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Abstract. The ammonium, calcium, and sodium concentrations from three intermediate depth ice cores drilled in the area of Dronning Maud Land, East Antarctica, have been investigated. Since all measurements were performed by a high-resolution Continuous Flow Analysis system, for the first time seasonal signals of chemical trace species could be obtained from the interior of central Antarctica over a period of approximately 2 millennia. Although the elevation as well as the accumulation rate differ between the drilling sites, similar values were obtained by comparing mean concentrations spanning the last 900 years. However, a distinct lack of intersite correlation was found on decadal timescales. Despite a noticeable accumulation change, apparent in one core, no significant concentration change of all three species has occurred. All the measured ions show clear seasonal signals over the whole records. While the sea-salt-related component sodium peaks simultaneously with calcium, the maximum ammonium concentration occurs in the snow with a time lag of 2 months after the sea-salt peak. More than 60% of the calcium concentration can be attributed to an ocean source. Elevated sodium concentrations were found within this millennium compared to mean values of the whole records, but the spatially varying shape of the increase suggests that a possible climatic signal is biased by local deposition effects.

1. Introduction

Polar ice sheets represent unique archives of past climate and environmental variations. Ice core analyses provide information about local temperature and precipitation, but also offer the possibility of reconstructing the past atmospheric composition [*Stauffer*, 1999]. Several deep ice core drillings have already been performed, in both the northern and southern hemispheres. While in Greenland ice core records reach back about one glacial-interglacial cycle [e.g., *Dansgaard et al.*, 1993; *Mayewski et al.*, 1997], data from Antarctica span up to 420,000 years [*Petit et al.*, 1999]. In order to improve our understanding of the mechanisms controlling the natural climate variability, two further deep drillings will be carried out in the framework of the European Project for Ice Coring in Antarctica (EPICA).

The ionic composition of the ice provides an excellent resource for investigating changes in the source strength and pathway of chemical species in the atmosphere [*Legrand and Mayewski*, 1997]. Because glacio-chemical results from Antarctic ice cores have been obtained so far by measuring discrete samples e.g., [*Legrand and Delmas*, 1988a; *Legrand*

et al., 1988], the depth resolution of these data is far below some high-resolution Greenland records, where continuous methods for ion analyses were used [*Fuhrer et al.*, 1996, 1999]. In order to enable a more detailed insight also into Antarctic glacio-chemical data, the EPICA ice core measurements will be partially performed by an improved Continuous Flow Analysis (CFA) system [*Röthlisberger et al.*, 2000a]. The first results from the newly drilled Dome Concordia (Dome C) ice core show already the advantage of such high-resolution data records from the southern hemisphere [*Mulvaney et al.*, 2000; *Röthlisberger et al.*, 2000b].

Ammonium and calcium analyses, carried out on Greenland ice cores, have provided a wealth of information about past climate. Ammonium records allowed the reconstruction of the history of forest fires from the boreal zone [*Legrand et al.*, 1992]. Additionally, background ammonium level, free from sporadic biomass burning events, is mainly related to continental biogenic emissions from soil [*Fuhrer et al.*, 1996]. On the other hand, high-resolution calcium records were used to quantify the atmosphere dust load of the northern hemisphere during different climatic stages [*Fuhrer et al.*, 1999]. Little attention, however, has been paid so far to the ammonium and calcium content in Antarctic snow during the Holocene time period, mainly due to the low concentration level of both chemical species. In particular, little is known of the ammonium cycle within Antarctica, because no accurate ammonium results are available in high depth resolution due to contamination problems during the measuring procedure of discrete samples [*Legrand et al.*, 1998]. Thus no seasonal ammonium signal has so far been found in central Antarctica.

In order to establish an unambiguous link between chemical concentrations in air and snow, the exact

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understanding of deposition processes is a prerequisite. However, even for irreversibly deposited species, where the transfer from the atmosphere to the snow may occur by dry, wet, or fog deposition [Bergin et al., 1995], the knowledge of the mechanisms involved is still very limited. Because ion concentrations in ice may be influenced additionally by postdepositional effects, such as ventilation of the surface snow [Waddington et al., 1996], or the transformation of snow characteristics by blowing snow [Pomeroy and Jones, 1996], concentration variations appearing in glacio-chemical time series may not be attributed exclusively to atmospheric concentration changes. One way to reduce the deposition noise by ignoring microscale effects is to investigate the spatial variability of chemical concentrations in the ice [Fischer et al., 1998a, 1998b]. While several snow pit studies were carried out in Antarctica in order to study the variability on annual timescales [Legrand and Delmas, 1985; Minikin et al., 1994; Stenberg et al., 1998], only a few ice cores, covering longer time spans, have been compared so far. Reusch et al. [1999], for example, investigated the spatial distribution of chemical trace species on 40-year long records, obtained from four ice cores drilled in West Antarctica.

In this paper we focus on chemical records of ammonium, calcium, and sodium, obtained from three intermediate depth ice cores (115-150 m). The cores were drilled within a few 100 km of each other in the area of Dronning Maud Land (DML), East Antarctica (see Figure 1), at altitudes between 2670 and 3160 m above sea level (asl). Owing to an accumulation rate of about 60 mm H_2O yr^{-1} and the excellent depth resolution of our CFA system, for the first time annually resolved ion data could be routinely obtained from the interior of central Antarctica. On the basis of the precise dating of the cores, presented in detail by Sommer et al. [this issue], a well-defined experimental field could be developed in order to study the spatial and temporal variability in seasonal resolution of (1) the unknown ammonium signal, (2) the comparatively well-known crustal signal (nss-calcium), and (3) the very well-known sea-salt signal (sodium). Because

the records reach back nearly 2000 years, long-term variations may be expected. Their spatial behavior allows evidence about the representativeness of single records.

2. Methods

High-resolution chemical measurements of the three DML ice cores were performed by a CFA system [Röthlisberger et al., 2000a] at Neumayer several days after drilling. Ammonium and calcium analyses were obtained by well established fluorescence methods [Sigg and Neftel, 1991; Fuhrer et al., 1996, 1999], each with an accuracy of better than 10%. Sodium was measured for the first time with a novel absorption technique, described in more detail by Röthlisberger et al. [2000a]. Because this technique shows a linear behavior only in a limited concentration range (1-100 ppb), a nonlinear calibration procedure has to be used to quantify higher Na^+ values. Since this was not applied during the DML field season, all sodium values higher than 100 ppb are underestimated on average by 10-20%. Less than 2% of all data have Na^+ values above 100 ppb, and therefore mean concentrations are not significantly influenced. A specially designed firn melt head was used, which prevented meltwater rising through the porous firn driven by capillary forces [Röthlisberger et al., 2000a], and thus allowed a contamination-free melting process even in the upper part of the cores. Because of a very slow melt rate, the depth resolution for all chemical components could be reduced to 0.7 cm of ice. A more detailed description of the analysis procedure is given by Sommer et al. [this issue].

In this paper, we focus particularly on seasonally resolved data. However, for discussing the variability on longer timescales (decades to centuries), the records were smoothed by using a robust spline [Meeker et al., 1995] to produce filtered time series, which are not influenced by large sporadic events.

The timescales of the three ice cores and inherent accumulation records are discussed comprehensively by Sommer et al. [this issue]. The most important conclusions relevant for this study can be summarized as follows: the dating of the DML cores was established by using seasonal signals of sodium, calcium, and ammonium, in combination with the identification of historic volcanic horizons via non-sea-salt electrolytical conductivity records and the use of a densification model [Schwander et al., 1997]. Owing to the well-known volcanic chronology during the last 9 centuries, maximum errors between 5 and 8 years, depending on the accumulation rate, could be obtained. However, dating uncertainties are higher within the first millennium. While for the last 9 centuries the mean accumulation rates at B31 and B32 are quite similar (63 mm and 61 mm H_2O yr^{-1}), there is a lower value at B33 (44 mm H_2O yr^{-1}). Though all records show high temporal variations, which describe nearly white noise time series, there is neither a trend nor a periodicity on longer timescales detectable. Constant accumulation rates can be observed also during the first millennium, as recorded in cores B32 and B33. However, at B31 a distinct change has occurred somewhere around 1000 AD, where the layer thickness has increased from 38 to more than 60 mm H_2O yr^{-1}. This change may result from either a low accumulation area upstream of the drilling site, or surface waves, which influence the deposition pattern in that region.

0°

45° W   45° E

B32
B33
B31   Dome F

South Pole
90° W   90° E
Byrd   Vostok

Dome C

135° W   135° E

180°
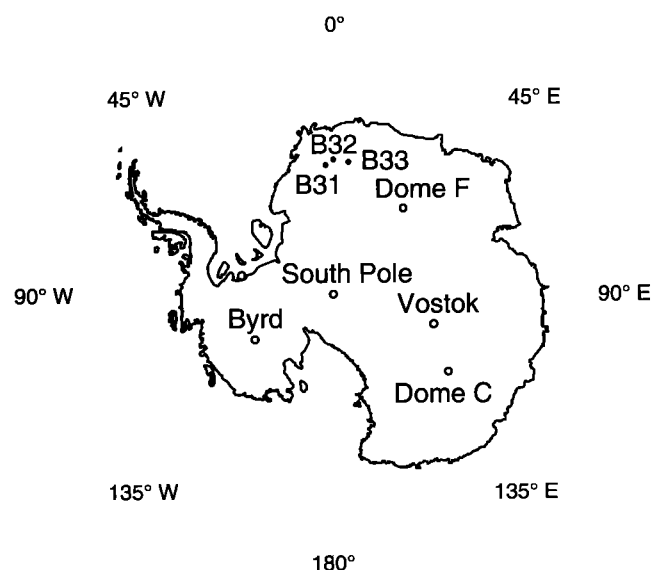
Figure 1. Geographical locations of the drill sites of the DML cores B31, B32, and B33, together with major deep ice core drillings of Antarctica.
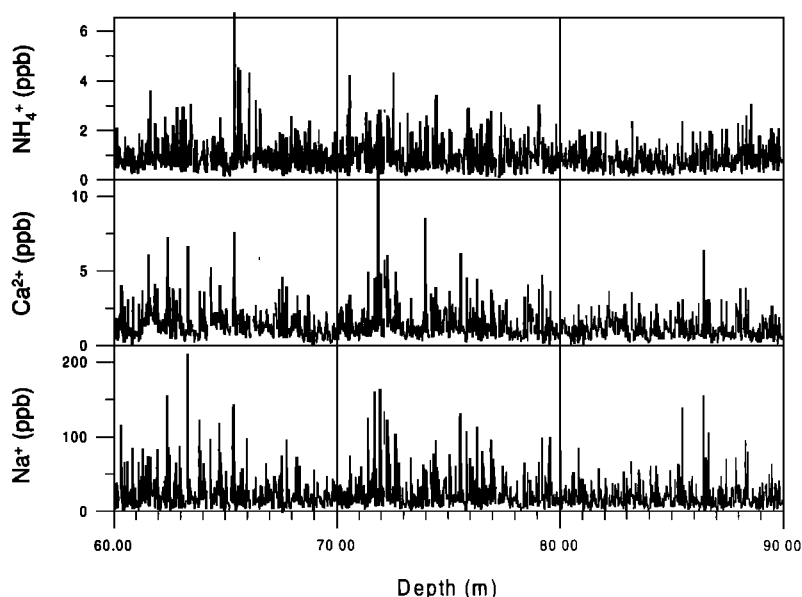
Figure 2. Annually resolved data of ammonium, calcium, and sodium versus depth at B32, covering the time period between 1031 and 1416 AD.

3. Results

Almost 400 m of ice cores were analysed in total, covering approximately 1536 (B31), 1855 (B32), and 2140 years (B33). Since the measurements were performed continuously, the raw data are available in 2 mm steps, except for breaks and cuts where no data exist. The results from a 30 m section of core B32 are shown in Figure 2, spanning approximately 385 years. A more detailed view in high-resolution can be seen in Figure 3. According to the depth-age scale of the core this part represents the period between 1200 and 1213 AD. With a mean accumulation rate of 61 mm H_2O yr^{-1}, the layer thickness at a depth of 76 m is about 77 mm. The records of

all three chemical components show approximately 12-13 peaks, which can be attributed therefore to seasonal variations. Averaged concentrations, obtained from two different time periods within the last 2 millennia, are given in Table 1, together with the standard deviation, calculated from annual mean values.

3.1. Chemical Characteristics

All our ammonium data show a very clear seasonal signal, which is characterized by regular peaks with values usually between 1 and 3 ppb and minima around 0.5 ppb. While for coastal sites the recent ammonium concentrations in snow
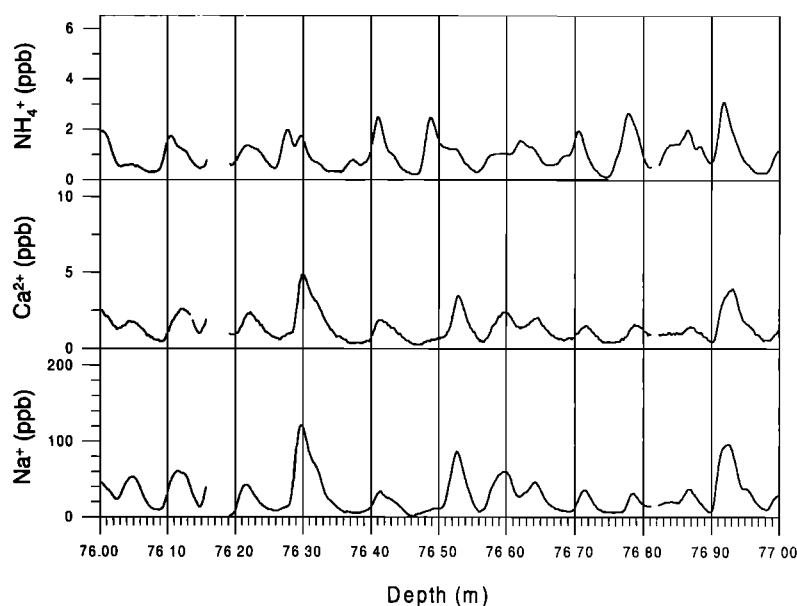
Figure 3. Sequence of ammonium, calcium, and sodium versus depth at B32 in high-resolution, covering the time period between 1200 and 1213 AD.

Table 1. Mean Concentrations of Ammonium, Calcium, Sodium, and nss Calcium (See Text) During Two Different Time Periods[a]

Time period, year AD	Core	NH_4^+		Ca^{2+}		Na^+		$nss\text{-}Ca^{2+}$
		Mean, ppb	Variation, %	Mean, ppb	Variation, %	Mean, ppb	Variation, %	Mean, ppb
1100-1980	B31	0.9	55	1.5	59	24.3	58	0.6
	B32	1.0	44	1.5	50	25.6	62	0.5
	B33	1.0	39	1.5	56	25.7	54	0.5
500-900	B31	1.1	54	1.4	62	19.4	68	0.6
	B32	0.9	41	1.3	66	19.7	47	0.5
	B33	1.1	39	1.2	51	21.2	54	0.4

[a]Variation is given in one standard deviation from annual mean.

have mean values between 2.4 (Berkner Island) and 7.5 ppb (Neumayer) [*Legrand et al.*, 1998], the ammonium content of ice at higher elevation is much lower. In a South Pole snow pit, covering the years 1955-1988, *Whitlow et al.* [1992] measured 1.2 ppb. At the same site, *Kirchner and Delmas* [1988] reported 0.5 ppb over the last 1000 years. From a part of an ice core located close to Dumont D'Urville, where the ice originated from an elevation up to 2000 m asl, *Legrand et al.* [1998] found a concentration of 0.9 ppb. All these values, obtained from the Antarctic plateau, are in good agreement with our results.

As with ammonium, calcium concentrations in Antarctic snow are also very low during the Holocene. Our average calcium concentrations compare well with results from *Isaksson* [1994], obtained from a 20 m core in DML, who measured a mean value of 1.2 ppb. At Dome C and Vostok, mean concentrations between 1.8 and 2.0 ppb were found during different periods in the Holocene [*Legrand and Delmas*, 1988a; *Legrand et al.*, 1988].

Our sodium data show the most distinct seasonallity within the three components reported here. While the minimum concentrations are in general around 5 ppb, the maximum values vary over a large concentration range from 30 up to more than 200 ppb, resulting in mean concentrations of about 25 ppb over the last 9 centuries. In contrast to ammonium and calcium, a variety of Na^+ records are available from different areas of the Antarctic plateau. Mean concentrations at Dome C, Vostok, and Dome F vary between 20 and 28 ppb during the Holocene [*Legrand and Delmas*, 1988a; *Legrand et al.*, 1988; *Watanabe et al.*, 1999]. A lower value (13.5 ppb) measured by *Isaksson* [1994] in a 20 m long DML ice core differs significantly from our data, but the discrepancy may be explained by the high spatial and temporal variability found in the sodium results, as will be discussed later. Sodium analyses on discrete samples by ion chromatography (IC) performed about 60 km south of B31 gave a mean value of 27 ppb (unpublished data), which is quite consistent with our value of 25 ppb. Thus we do not expect any systematic difference between CFA and measurements by IC.

3.2. Spatial Variability

Comparing mean concentrations between the three drilling sites spanning the last 9 centuries, there is no spatial trend apparent. Although the accumulation rate as well as the

altitude differ between each location, similar values were obtained over distances of a few 100 km. However, by investigating the intersite variability on smaller timescales a different finding is obtained. Neither the annually resolved data nor decadal variations show a correlation between the three cores. In particular within the sodium records, which are characterized by the highest temporal variability, no intersite similarity is apparent. Even single distinct peaks, present in the sea-salt records in a large number, could not be identified simultaneously in the well-dated cores. Hence, of all the measured trace species, only the hydrogen peroxide measurements, presented by *Sommer et al.* [this issue], show a significant correlation between the three cores.

Studies of the spatial variability of chemical concentrations within Antarctica show decreasing sea-salt concentrations with increasing elevation and distance inland [*Mulvaney and Wolff*, 1994; *Kreutz and Mayewski*, 1999]. However, the relationship seems to be apparent only up to a threshold distance inland of 500 km from the coast [*Kreutz and Mayewski*, 1999]. Our results, obtained from ice cores at least 500 km away from the ice edge, agree well with these findings. Because intersite correlation of chemical records on decadal, or even shorter timescales, requires well-dated ice cores, only a few studies were performed so far in Antarctica. By comparing four 40-year records, *Reusch et al.* [1999] also found a distinct lack of similarity between different locations for all aerosol related chemical species investigated.

3.3. Accumulation Rate Dependence

Following *Bergin et al.* [1998], the relationship between the concentration of irreversibly deposited species in the air and snow is, among others, linearly dependent on the inverse of the accumulation rate [*Fischer et al.*, 1998b]. Hence a dependence of the measured concentrations on the accumulation rates may be assumed. However, within the three cores no significant correlation was found when comparing the accumulation rates with the concentration records of NH_4^+, Ca^{2+}, and Na^+, even by smoothing the time series with filter lengths up to 30 years. In order to exclude the deposition noise as far as possible, mean values for two different time periods were calculated in each core, spanning the years between 1100-1980 AD, and 500-900 AD, respectively. Thus systematic accumulation differences between the regimes of B31/32 and B33, respectively, as well
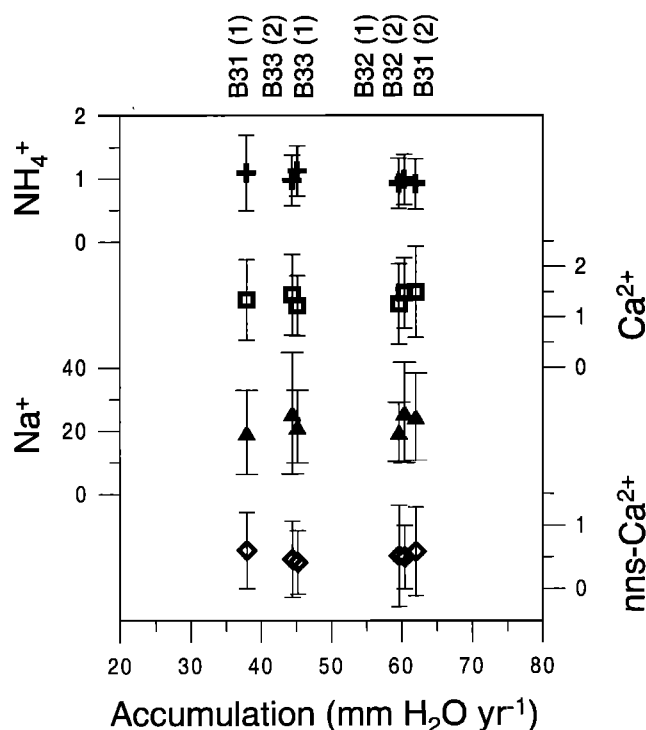
Figure 4. Mean concentrations of ammonium (cross), calcium (square), sodium (triangle), and nss calcium (diamond) in ppb as a function of average accumulation rates. The different time periods are indicated as (1) 500-900 AD and (2) 1100-1980 AD. Variation is given in one standard deviation from annual mean.

as the temporal accumulation change around 1000 AD in B31 could be used to test the accumulation dependence. As Figure 4 indicates, the long-term mean concentrations calculated in this manner do not show a clear relationship with accumulation rates varying between 38 to 62 mm H_2O yr^{-1}. Therefore it seems that the fraction of dry deposition has only a minor influence on the total amount of NH_4^+, Ca^{2+}, and Na^+. However, the high spatial variability of both the accumulation rate and the concentration of chemical species allows also the conclusion that redistribution by wind may have been masked a possible relationship of both parameters.

A similar result is reported also by *Reusch et al.* [1999], who found no relationship between changes in concentration of chemical species and changes in accumulation rate in his

four West Antarctic firn cores. Because concentrations appear to be independent over the limited range in accumulation rate in our records, for further discussions we will therefore use the concentration records, instead of fluxes.

4. Discussion

After presenting our results and addressing the issue of spatial variability in respect of deposition mechanisms, we will focus on three main points, extracted from the large amount of data available. Since our ammonium measurements are the first with a subannual resolution, we will, along with a presentation of a whole record, investigate the seasonal timing of the ammonium deposition in relation to relatively well-known chemical trace species. We then construct a non-sea-salt (nss) calcium record to discuss terrestrial dust events. Finally, we investigate sodium changes on longer timescales (decades to centuries) since only the sodium records show a significant long-term variability over the whole time period.

4.1. Seasonal Ammonium Timing

While there are seasonal measurements available of ammonia in aerosols at coastal locations [*Legrand et al.*, 1998], there is a distinct lack of ammonium measurements along Antarctic ice cores with seasonal resolution. Thus the knowledge about this component in inland Antarctica is very limited. Neither the controlling sources nor the transport mechanisms of ammonium are well understood. According to *Legrand et al.* [1998], three potential sources are possible. (1) The Antarctic penguin population is indeed one, but its emission is not large enough to influence the concentration in the interior of Antarctica. Thus only coastal sites, situated close to penguin colonies, show this biological signal. (2) Ammonium may originate from marine biogenic sources. Because the emission is generally favoured by high biological activity and high seawater temperatures, enhanced concentrations are expected during summer. (3) A long-range transport of ammonium produced over continents cannot be excluded.

Because the high-resolution ammonium data of all three ice cores are comparable, we only present the entire record of core B33 (see Figure 5), which spanning the longest time period. Although there are several high peaks appearing at irregular time intervals, mean values of the three records do not show a significant variability on longer timescales. On the contrary, the relatively small variation, obtained from annual mean concentrations, show a regular behavior of the
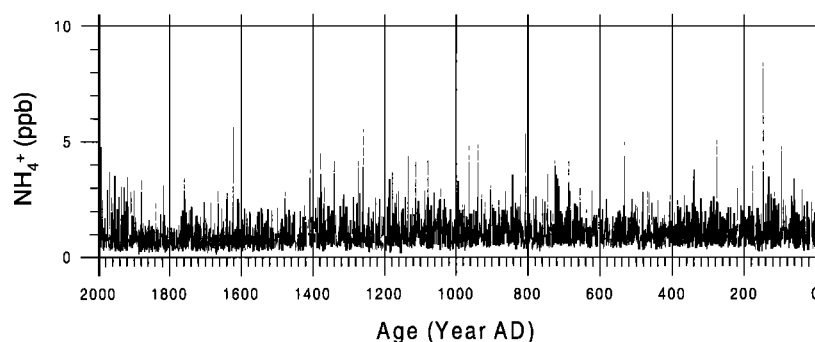
Figure 5. Ammonium concentrations of core B33 spanning the last 2 millennia, based on the timescale deduced from annual layer counting (until 1100) and from the calculated depth-age scale. Mean values are shown corresponding to 1 month, or to a depths interval of about 4 mm of ice, respectively.
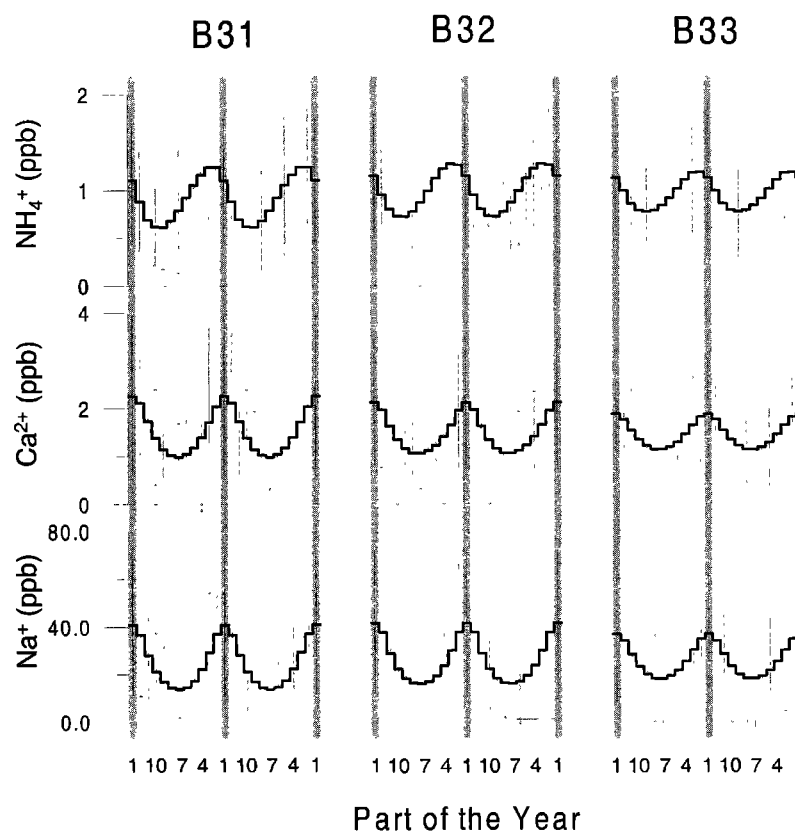
Figure 6. Mean seasonal variations of ammonium, calcium, and sodium during the time period between 1100 and 1980 AD, shown over 2 years. The emphasized bar indicates the sea-salt peak; 1 year is divided linearly into 12 sequences in relation to depth. Note that month number 1 occurs approximately during winter/spring, but is not equivalent to January (see text).

ammonium signal over the past 2 millennia. In relation to the seasonal sea-salt peak seen in sodium and calcium, the ammonium maxima occur somewhat later (see Figure 3 for an example). In order to quantify the timing behavior of the ammonium signal we calculated mean values for 12 identical depth intervals between the year marks, obtained by the dating procedure based on annual layer counting [*Sommer et al.*, this issue]. Although the snow accumulation distribution is probably not constant throughout the year, the few field data and model results available suggest a fairly constant input of precipitation to this region throughout the year with perhaps a tendency to slightly higher precipitation in late spring. *Noone et al.* [1999] present mean daily model precipitation fields from reanalysis runs of the European Centre for Medium-Range Weather Forecasts (ECMWF) data set for a grid box that includes the ice cores sites reported in this work. They show precipitation occurring regularly throughout the year. Additionally, *Noone et al.* [1999] show 1 year of measured surface accumulation in the DML area which again shows precipitation throughout 1 year including one particularly high event in late spring, though this could be affected by drift. Therefore we will assume a constant accumulation rate through the year for our sites, and for further discussion we will thus define the individual intervals as months. While the subannual timing uncertainty for single years may be enormous, the accuracy of this method increases by analyzing a large number of years. A possible systematic dating error may result from the CFA data processing due to

the different passage times of Ca^{2+}, NH_4^+, and Na^+ through their analysis lines, but this effect is less than ±1 month for each component. In Figure 6 the seasonal variations of ammonium, calcium, and sodium is shown over the period between 1100 and 1980 AD. It is clear that the sea-salt peak leads the one of ammonium by about 2 months. By investigating this time lag over different time periods, for example, during the last few decades, the same picture is obtained. We can therefore rule out a migration of the ammonium signal relative to sodium in the firn after deposition, at least for depths below 4 m. Owing to bad core quality in the uppermost layers and no pit studies performed with accurate ammonium results, it is not possible to discuss this problem for the most recent 20 years (0-4 m depth).

Because the calculation of the nss conductivity [*Sommer et al.*, this issue], representing mainly the concentration of nss-SO_4^{2+}, is influenced by relatively high uncertainties which do not allow an interpretation of the seasonal nss signal, the seasonal apportionment of our ammonium peak is possible only by comparing the timing of sodium peaks with other locations. At South Pole there is clear evidence that the sodium maximum in ice appears during September/October [*Legrand and Delmas*, 1984; *Legrand and Delmas*, 1988b; *Whitlow et al.*, 1992]. These findings are confirmed by atmospheric measurements performed there by *Tuncel et al.* [1989], who reported maximum sea-salt concentrations during southern hemisphere spring. On the assumption that the atmospheric influence at South Pole and DML is comparable,

our ammonium signal would therefore occur in late spring/early summer. This appears to display a similar timing to ammonium in aerosol measured at Neumayer, where on the average a broad peak is centered around January [*Legrand et al.*, 1998]. However, two questions remain:

1. Does the sodium peak in DML really occur during spring, as at South Pole? Since atmospheric measurements from Neumayer [*Wagenbach et al.*, 1998], as well as ice core analysis from Berkner Island [*Wagenbach et al.*, 1994] show a seasonal sea-salt peak during southern hemisphere midwinter, one cannot exclude a priori a different atmospheric influence at South Pole and at DML. If we take the earlier timing of the sea-salt input, then our ammonium peak would be displaced toward early spring.

2. Is the ammonium peak coupled with nss sulfate, as suggested by *Legrand et al.* [1998]? Assuming the nss sulfate peaks in summer due to the biogenic source, our late spring/early summer ammonium signal would briefly match.

Unfortunately, due to the lack of a clear summer reference signal in our records and no high-resolution sulfate measurements it is not possible at present to find reliable answers to these two questions. However, we have presented, for the first time, high-resolution ammonium measurements from the interior of Antarctica and demonstrated that a clear seasonal cycle is preserved in the snow, which in further studies may help to localize potential ammonium sources.

4.2. Crustal Calcium

Crustal calcium is expected to originate primarily from neighboring continental areas [*Delmas and Petit*, 1994] and is therefore transported to Antarctica over long distances. Hence nss calcium may be used as an indicator for the variability of the strength and efficiency of the long-range transport.

As can be clearly seen in Figure 3, both calcium and sodium records show very similar signals even at high depth resolution. Correlation coefficients around 0.80, obtained by

analyzing the whole records, prove this qualitative assessment. Thus the two chemical species appear to be significantly influenced by the same source. Because the origin of sodium is mainly sea salt and a terrestrial contribution is negligible during the Holocene [*Legrand and Delmas*, 1988b], a considerable amount of calcium must also be derived from sea-salt aerosols. In order to calculate the crustal fraction we subtracted the sea-salt contribution of calcium by using the sodium concentration and the seawater ratio of major ions [*Legrand and Mayewski*, 1997]. By doing this, mean concentrations of nss calcium between 0.5 and 0.6 ppb were obtained, compared to the mean total Ca^{2+} of 1.5 ppb. Thus more than 60% of the total calcium input have to be attributed to sea-salt aerosols. Similar values of nss calcium were reported also from Dome C (0.6 ppb) [*Legrand and Delmas*, 1988a] and Vostok (1.2 ppb) [*Legrand et al.*, 1988].

The analytical uncertainty in the calculation of nss calcium significantly exceeds the long-term variability in each of the three cores. Therefore nss calcium is not suitable for investigating the variability of the long-range transport of crustal aerosols to Antarctica during Holocene time periods. However, in contrast to the background variation, the distinct nss calcium peaks are obviously less affected by the analytical uncertainty. Neither the height of the peaks nor the frequency of their appearance show any characteristics, but in a few cases the peaks could be observed in all three cores contemporaneously, notwithstanding the dating uncertainties. One such peak occurred simultaneously with an unknown volcano at 1270 AD, as shown in Figure 7. Maximum nss calcium concentrations between 9 and 13 ppb are a strong indicator of a dust peak, which may be of volcanic origin. The occurrence of four volcanoes, erupted in the second half of the thirteenth century, has already been shown in several ice cores [*Langway et al.*, 1995]. While the most prominent of them, dated to the year 1259 AD, is considered to be a significant bipolar time marker, the other three volcanic layers
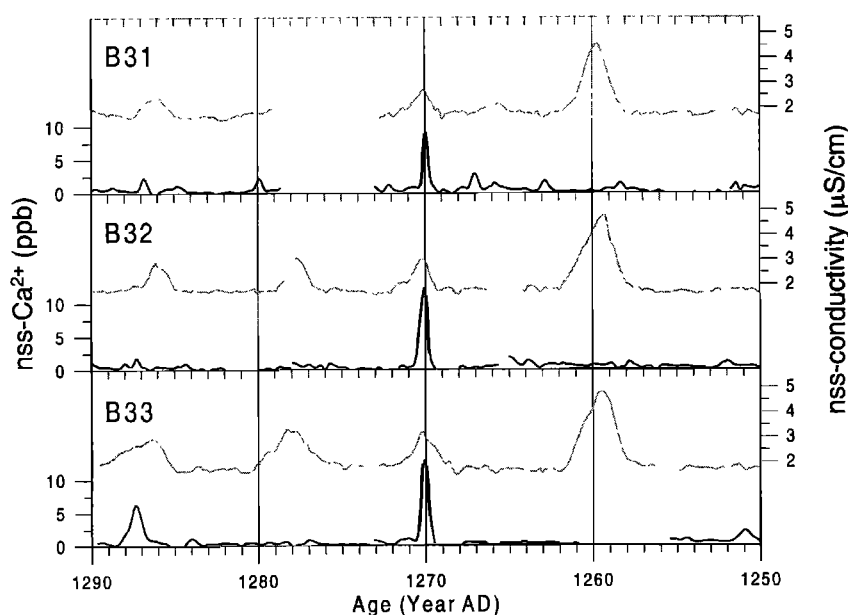
Figure 7. Nss calcium concentrations (black line), together with the nss conductivity data (grey line) of all three ice cores during the volcanic sequence of 1259 AD. Simultaneously to the unknown volcano at 1270 AD high terrestrial calcium content can be seen.

have not always been detected in Antarctic ice core acidity records [*Delmas et al.*, 1992; *Moore*, 1991]. We can suggest that our significant nss calcium peak, which was found also in the new Dome C core (R. Röthlisberger, personal communication, 2000), may be an additional reference horizon for Antarctic ice cores. Moreover, a more detailed investigation of the dust content for possible volcanic glass shards [*Palais et al.*, 1992] may perhaps provide the first evidence about the true origin of one of these unknown volcanic horizons within this sequence.

4.3. Long-Term Sea-Salt Trend

Except for the hydrogen peroxide records, presented by *Sommer et al.* [this issue], in our data only sodium concentrations show also significant temporal variations on decadal to century timescales. This can be seen in Figure 8, where the annually resolved records are presented together with smoothed curves, representing approximately 30 and 100 year filtered data. The high spatial variability of the sodium results on smaller timescales, discussed above, is obvious by comparing the three records over the whole time period. On the other hand, the 100 year filtered curves show a slight trend, with increasing values towards the present. While during the first millennium the sodium mean concentrations hardly exceed 21 ppb, they are around 25 ppb in the time period between 1100 and 1997 AD (see Table 1). Although the trend can be described also as a concentration change with two different plateaux, the timing of the onset does not occur simultaneously within all three cores. While at B33 the rate of change reaches highest values around 1000 AD, the increase of B32 lasts longer and is thus less steep, and at B31 it occurs about 200 years later. Moreover, the sodium concentration starts to decrease again within the last century at B32 and B33, whereas it stays stable at B31. Increasing sodium concentrations extending over the entire Holocene are also

seen in the Dome F [*Watanabe et al.*, 1999] and Dome C (R. Röthlisberger, personal communication, 2000) chemical records. The high-resolution sodium data of the newly drilled Dome C core shows minimum mean concentrations around 10,400 years BP of 15 ppb, with an increasing trend to recent values of 26 ppb (R. Röthlisberger, personal communication, 2000).

Provided that the Na^+ change would reflect an atmospheric signal, both, a long-term trend in the sea-salt source strength and in the transport efficiency of maritime air masses onto the Antarctic plateau may be assumed. An increased source strength would imply higher storminess over the southern oceans if the sea-salt particles are (as usually) produced at the sea surface (bubble bursting and wave crust disruption). Adopting, however, mobilization of brine from (growing) sea ice areas as controlling sea-salt source [*Wagenbach et al.*, 1998], an increased sea ice cover, both, in area and seasonal extent, may be suggested in addition. It is presently not know, however, if the brine-derived sea-salt particles seen up to some hundred kilometres inland and up to 1000 m height [*Wagenbach et al.*, 1998] constitute a significant source to the central Antarctic sea-salt budget as well.

Inspection of the sodium enhancement period indicates that it is mainly driven by the higher frequency of strong Na^+ spikes rather than by generally higher values. This would be in favor of an increased frequency of frontal passages associated with moist maritime air mass advections [*Hogan and Barnard*, 1978]. If true, we may expect a higher snow accumulation rate as well [*Bromwich*, 1988], which is not corroborated, however, by the ice core records discussed by *Sommer et al.* [this issue].

Assuming local glacio meteorological effects to be responsible for the sodium trend, we may again expect an associated change in the snow accumulation or in its seasonal distribution, which, however, has not been observed during
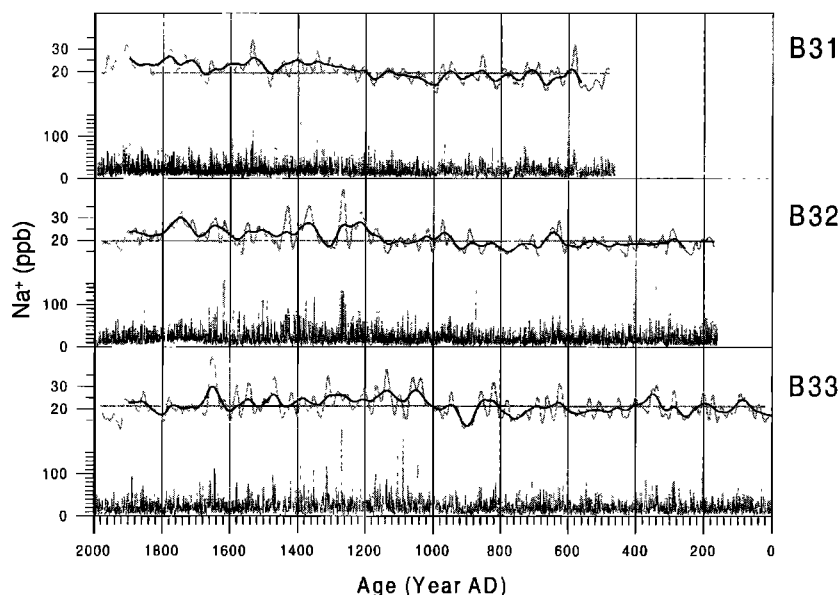
Figure 8. Sodium concentrations of all three ice cores, based on the timescale deduced from annual layer counting (until 1100) and from the calculated depth-age scale. Thin lines indicate annually resolved measurements; thick lines are smoothed curves [*Meeker et al.*, 1995], representing approximately 30 (grey) and 100 year (black) filtered data. The latter curves are shown on a different vertical axe, together with the mean value of the period between 500 and 900 AD.

the period in question. In conclusion, although statistically significant, no clear reason for the enhanced sodium level can be presently discerned.

A similar increase of sodium concentrations within the last millennium has already been reported by *Kreutz et al.* [1997]. In a coastal Antarctic ice core, drilled at Siple Dome, a statistically significant change was found around 1400 AD. The authors explain this rise by an intensified air mass transport to the drilling site, which they ascribe to climatic conditions of the Little Ice Age (LIA). Although the timing of the concentration change is out of phase by about 200-400 years compared to the three DML cores, a change of atmospheric circulation patterns cannot ruled out. However, the varying characteristics of all trends in our DML data as well as the fact that no correlation is apparent between these records suggest that sodium signals are additionally biased by local deposition processes. On the basis of the knowledge obtained from our study, the climatic interpretation of a simultaneous northern and southern hemisphere response to the LIA derived from a comparison between the Holocene sodium data of a Greenland ice core with that of the Siple Dome core [*Kreutz et al.*, 1997], performed also on decadal timescales, has to be questioned.

5. Conclusions

The first ion analyses on Antarctic medium depth ice cores from the DML area determined by CFA in high depth resolution enables us to do the following: (1) to discuss the seasonal cycles of ion species routinely over the total core depths of up to 150 m, (2) to perform accurate annual layer counting for dating purposes, and (3) to obtain the first results while still in the field.

While a high spatial variability of ammonium, calcium, and sodium concentrations was found on annual to decadal timescales, mean values covering 900 years are remarkably similar between all three cores. Thus, over centennial timescales, DML may be characterized by a robust deposition system. Although mean accumulation rates vary systematically between 38-63 mm H_2O yr^{-1}, an accumulation rate dependence on concentrations of all investigated species in ice could not be found, neither spatially, nor temporally. This is in contrast to an expected inverse relationship between accumulation and concentration particularly at low accumulation areas due the relatively high dry deposition flux. Both the reasons for the high and uncorrelated spatial variability on short timescales as well as for the absent link between concentration and accumulation remain unclear. Thus detailed air-to-firn transfer studies at DML are needed to tackle these questions.

A seasonal ammonium cycle was found with a small time lag of approximately 2 months toward summer, with respect of the sodium peak, which is considered in central Antarctica as a southern hemisphere winter/spring time marker. The very regular ammonium signals indicate that neither the source strength, nor the transport efficiency or the deposition process of ammonium was subject of considerable variations in the past 2000 years. However, identification of the controlling source responsible for the ammonium input on the Antarctic plateau was not possible based on this study, due to the lack of high-resolution measurements of other biogenically related species.

In contrast to Greenland, where calcium is considered to be an ideal tracer for dust input [*Angelis et al.*, 1997; *Fuhrer et al.*, 1999], this ion is influenced in Antarctica during the Holocene to more than 60% by sea-salt aerosols. Because the analytical uncertainty in calculating nss calcium concentrations is large, it will be important for further ice core studies to perform additional analysis of another entirely crustal trace element, such as the total aluminium or silicium content in high depth resolution, in order to investigate the behavior of continental dust particles, at least during climatically stable periods.

Increasing sodium concentrations are seen in all three records, superimposed by high temporal variations. The trend fits in general with the rising sodium level observed in other Antarctic ice cores (in particularly extending over the entire Holocene at Dome C). Although an obvious concentration change appears in all three cores, the timing of the onset ranges over about 200 years. Because the sodium records do not show any correlation on decadal to century timescales, the question arises, what information may be obtained by these time series? On the one hand, the sea-salt change may be caused by varied pathways of mesoscale cyclones. Thus the records would represent a more local signal. On the other hand, the spatially similar signal may have been biased by deposition noise, caused mainly by redistribution of snow or various postdepositional effects. A distinct lack of intersite similarity is apparent also by comparing the accumulation rate records of the three cores [*Sommer et al.*, this issue], but the correct explanation likely lies in a combination of both processes. However, the understanding of the mechanisms responsible for the higher sodium concentrations within this millennium, as well as the increasing trend during the whole Holocene found in several ice cores on both hemispheres, will be a challenge of Holocene climate research. However, its understanding requires not only the collection of as many well-dated ice cores as possible, but also the transfer characteristics and postdepositional effects have to be studied in more detail.

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