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Michel Legrand, C. Hammer, M. de Angelis, J. Savarino, R. Delmas, et al.. Sulfur-containing species (methanesulfonate and SO<sub>4</sub>) over the last climatic cycle in the Greenland Ice Core Project (central Greenland) ice core. *Journal of Geophysical Research. Oceans*, 1997, 102 (C12), pp.26663-26679. 10.1029/97JC01436 . hal-04418165

**HAL Id: hal-04418165**

**<https://hal.science/hal-04418165v1>**

Submitted on 26 Jan 2024

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## Sulfur-containing species (methanesulfonate and SO<sub>4</sub>) over the last climatic cycle in the Greenland Ice Core Project (central Greenland) ice core

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**Abstract.** A high-resolution profile covering the last two centuries and a discontinuous study spanning the complete last glacial-interglacial cycle of methanesulfonate (MSA) (CH<sub>3</sub>SO<sub>3</sub><sup>-</sup>) and sulfate were obtained along Summit (central Greenland) ice cores. MSA concentrations were close to  $4 \pm 1.4$  ng g<sup>-1</sup> from 1770 to 1870 A.D. and 3 ng g<sup>-1</sup> in 1900, and exhibited a well-marked decreasing trend from 1945 to the present. These changes of Summit snow MSA concentrations between 1770 and 1945 are discussed in terms of possible modulation of dimethylsulfide (DMS) marine emissions influencing the Greenland Ice Sheet by past climatic fluctuations in these regions. The decrease of MSA levels in Summit snow layers deposited since 1945 suggests either a decline in marine biota at high northern latitudes or a changing yield of MSA from DMS oxidation driven by modification of the oxidative capacity of the atmosphere in response to increasing anthropogenic NO<sub>x</sub> and hydrocarbon emissions. While interglacial ice concentrations of MSA and sulfate are close to  $2.9 \pm 1.9$  ng g<sup>-1</sup> and  $27 \pm 10$  ng g<sup>-1</sup>, respectively, reduced MSA ( $1.2 \pm 0.7$  ng g<sup>-1</sup>) and enhanced sulfate ( $55 \pm 19$  ng g<sup>-1</sup>) levels characterized the early Holocene stage (9000 to 11,000 years B.P.). MSA concentrations in glacial ice remain similar to the ones observed during interglacial stages. In contrast, sulfate levels are strongly enhanced ( $243 \pm 84$  ng g<sup>-1</sup>) during the last glacial maximum (14,400 to 15,700 B.P.) compared with the interglacial ones. These variations of sulfur-containing species in response to past climatic conditions are similar to those found in other Greenland cores. In contrast, they are different from those revealed in the Antarctic Vostok ice core, where colder climates were associated with an increase by a factor of 5 and 2 in MSA and sulfate concentrations, respectively. These glacial-interglacial changes are discussed in terms of present and past contributions of marine DMS emissions versus other sulfate sources such as volcanic emissions and continental dust to the Greenland precipitation.

### 1. Introduction

Along with major biogenic cycles of nitrogen and carbon, the sulfur cycle is important to the chemical composition of our atmosphere and climate. The conversion of reduced sulfur gases into submicronic sulfuric acid aerosols is an important process because of the potential interaction of such aerosols with incoming solar radiation and their effects on the cloud albedo [Charlson *et al.*, 1987]. In return, climatic conditions can affect biological processes controlling sulfur biogenic

emissions [Shaw, 1983]. Present-day anthropogenic emissions of SO<sub>2</sub> represent 84% to 50% of the sulfur budget in the northern and southern hemispheres, respectively [Spiro *et al.*, 1992]. Sulfur gases are also emitted within the atmosphere by various sources (marine and terrestrial biosphere, volcanoes, and biomass burning), among which oceanic emissions, mainly in the form of dimethylsulfide (DMS) (CH<sub>3</sub>)<sub>2</sub>S, dominate [Bates *et al.*, 1992a]. Interactions between climatic conditions and the rate of marine sulfur emissions are complex. For instance, the roles of insolation, sea and surface air temperatures, sea-ice cover, and nutrient supply in marine DMS emissions are poorly documented.

Some of these questions can be investigated by studying sulfur-derived species in polar ice cores. Indeed, assuming proper knowledge of the relation linking the sulfate and MSA concentrations of the snow with those of the atmosphere at the time of deposition, polar ice cores offer the unique opportunity to investigate the natural variability of the sulfur cycle over different time periods, from the last decades back to the last climatic cycle. In this paper a discontinuous study of MSA and sulfate along the entire Greenland Ice Core Project (GRIP) core is presented. This record depicts qualitatively how the climate modulated the sulfur cycle at high northern latitudes during the last 150,000 years. The

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Paper number 97JC01436  
0148-0227/97/97JC-01436\$09.00

high-resolution study of a Summit core spanning the last two centuries may serve to examine the temporal variability of DMS emissions from the ocean and to identify factors controlling these biogenic emissions including climatic conditions (temperature and sea-ice production) and possibly man-made activities. Finally, these data permit one to estimate the role of biogenic versus nonbiogenic sources contributing to the sulfur budget over Greenland.

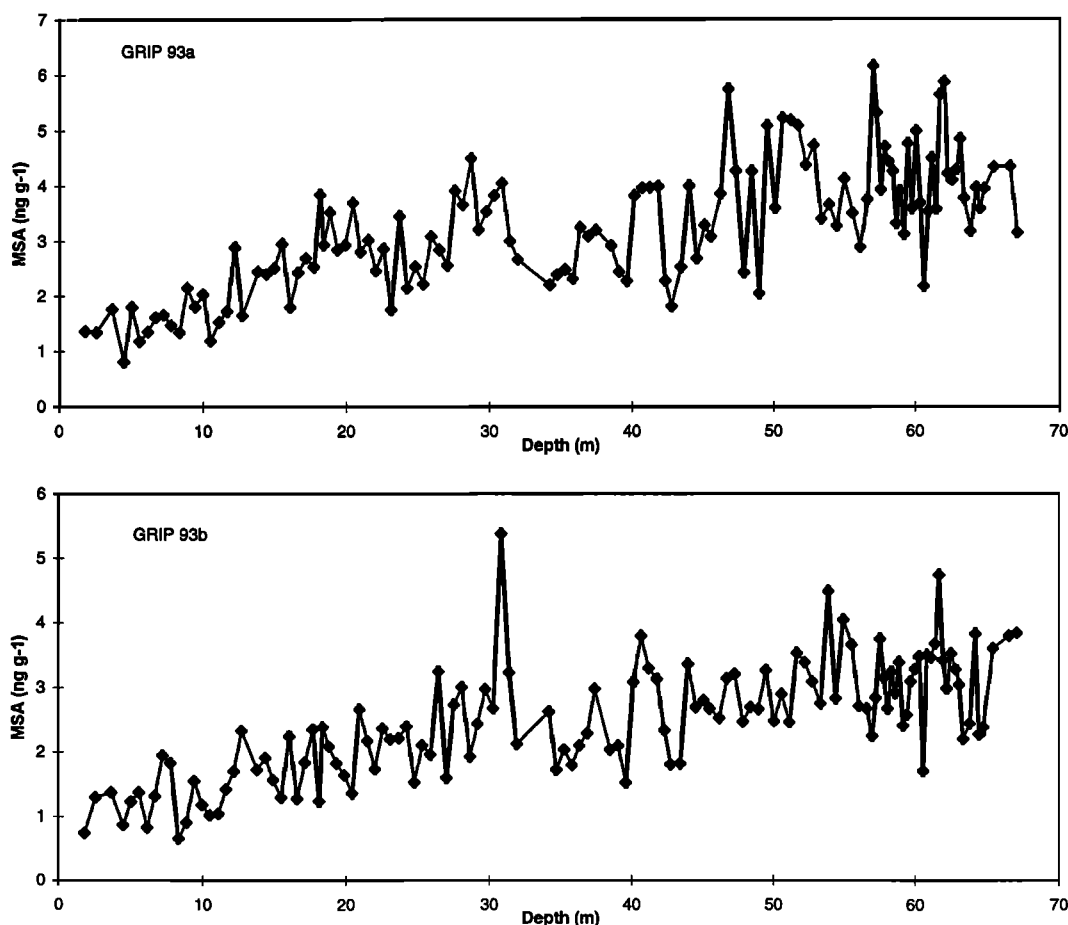
## 2. Sampling and Analyses

The analyses reported in this study were performed on samples from a snow pit, firn cores and ice cores collected at Summit, central Greenland (72°34'N, 37°38'W, 3240 m above sea level), in the framework of the European GRIP and Eurocore projects.

In June 1993, two firn cores covering the last two centuries were extracted. To remove the outer part of these firn core sections, which were contaminated during the drilling procedure, we shaved off the outer part using a lathe, as was successfully tested by *Legrand et al.* [1993]. The first one, a 73-m-long firn core (GRIP 93a) covering the 1767-1993 A.D. time period, which was mainly dedicated to the study of carboxylic acids, was processed in the field 1 or 2 hours after core recovery in order to avoid contamination during the

storage in plastic bags [*Legrand and De Angelis*, 1996]. The remaining cleaned sections were cut into 9-cm-long pieces (i.e., a total of 732 samples, with a sampling frequency of two to six samples per year). The second one, a 67-m-long firn core (GRIP 93b), extracted 2 m away from the preceding one, covering the 1790-1993 time period, which was dedicated to the study of total and black carbon [*Pertuisot et al.*, 1994], was packed and stored at -15°C in sealed plastic bags until the decontamination procedure was applied in Grenoble. This core was cut into 55-cm-long pieces (i.e., a total of 120 samples, with a sampling frequency of a half to two samples per year).

Several studies suggested movement of MSA in firn and ice [*Mulvaney et al.*, 1992; *Wolff*, 1996]. *Legrand et al.* [1992] found that MSA can migrate from the inner to the outer part of deep ice cores during the washing of ice sections with ultrapure water. Processes driving such a high mobility of MSA being not yet elucidated, we have here examined whether such a migration can proceed in firn core sections during several months of storage at -15°C. As seen in Figure 1, the two MSA profiles exhibit a similar pattern (correlation coefficient of 0.7 for 140 samples), with a steady decrease from 30 m depth to near the surface. Such a good agreement between the two profiles indicates that, if it had occurred, the migration of MSA from inner to outer parts of GRIP 93b firn sections during storage at -15°C remained a very limited phenomenon.



**Figure 1.** Methanesulfonate (MSA) depth profiles of two Summit firn cores, Greenland Ice Core Project (GRIP) 93a and GRIP 93b, which were sampled in the field and after 9 months of storage at -15°C. Given the lower sampling frequency achieved along the GRIP 93b core (55 cm) compared with the GRIP 93a core (9 cm), the GRIP 93a data have been averaged over six samples.

The dating of the GRIP 93a core has been established by using seasonal variations of calcium and ammonium in addition to the identification of well-known volcanic horizons by using the sulfate profile, as detailed by *Legrand and De Angelis* [1996]. On the basis of this information, we assumed possible errors of 1 year between the surface and 40 m depth and of 2 years farther down. Owing to the poor quality of the cores near the surface (0 to 5 m depth, i.e., the 1985–1993 years), we have used data previously published by *Legrand and De Angelis* [1995] on 99 samples collected in a snow pit of 3.7 m depth covering the 1985–1991 time period.

Along the main Eurocore, 300-m depth core that was extracted at Summit in 1989, a high-resolution sequence (i.e., 47 samples) was studied between 182.0 and 184.5 m depth (i.e., 1274 to 1285 A.D. [*Savarino*, 1996]) in order to investigate seasonal variations of sulfate during the preindustrial time period.

Along the GRIP core a discontinuous study was achieved between 100 and 3015 m depth (257 depth levels). At each depth level a 55-cm-long ice section was cut into 9-cm-long pieces (i.e., 1557 samples), as detailed by *Legrand and De Angelis* [1995]. Owing to ice flow phenomenon and the subsequent thickening of annual layers with depth, a 9-cm-long piece corresponds to half a year near the surface, 1 year at 1500 m depth, and around 10 years near the bottom of the core. The dating of the GRIP core was established by *GRIP Members* [1993]. However, discrepancies in the lowermost parts of the GRIP and the Greenland Ice Sheet Project 2 (GISP 2) (a U.S. program) Summit records casted doubt on the validity of the stratigraphy below 2740 m depth (i.e., 105,000 years B.P.) [*Taylor et al.*, 1993].

On each sample the concentrations of sulfur species ( $\text{CH}_3\text{SO}_3^-$  and  $\text{SO}_4^{2-}$ ) as well as those of other ions such as  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ ,  $\text{F}^-$ , or  $\text{NO}_3^-$  were determined by ion chromatography using the working conditions detailed by *Legrand et al.* [1993]. Non-sea-salt sulfate (i.e., excess sulfate, denoted  $\text{SO}_{4\text{exc}}^{2-}$ ) is calculated by subtracting the sea-salt contribution using the bulk seawater  $\text{Na}^+/\text{SO}_4^{2-}$  weight ratio (0.25) from the total sulfate concentrations. As discussed by *De Angelis et al.* [this issue], the sodium measured along the entire GRIP core is mainly marine in origin, the sodium crustal contribution remaining very weak, even in the glacial ice where a huge amount of dust was present. With mean sodium content of  $5.4 \pm 2.0$  and  $59 \pm 20 \text{ ng g}^{-1}$  over warm and cold climatic stages, respectively, the sea-salt sulfate component represents 5% and 6% of the total sulfate level (29 and  $250 \text{ ng g}^{-1}$ ) during interglacial stages and the ice age, respectively.

Throughout this paper we use the MSA fraction (i.e.,  $\text{MSA}/(\text{MSA} + \text{SO}_{4\text{exc}}^{2-})$ ), which, as argued by *Whung et al.* [1994], is more adequate than the commonly used  $\text{MSA}/\text{SO}_{4\text{exc}}^{2-}$  ratio to discuss the contribution of marine biogenic sulfur emissions to the total sulfur budget of the atmosphere in high-latitude regions.

### 3. Recent Time Period (1770–1990) at Summit

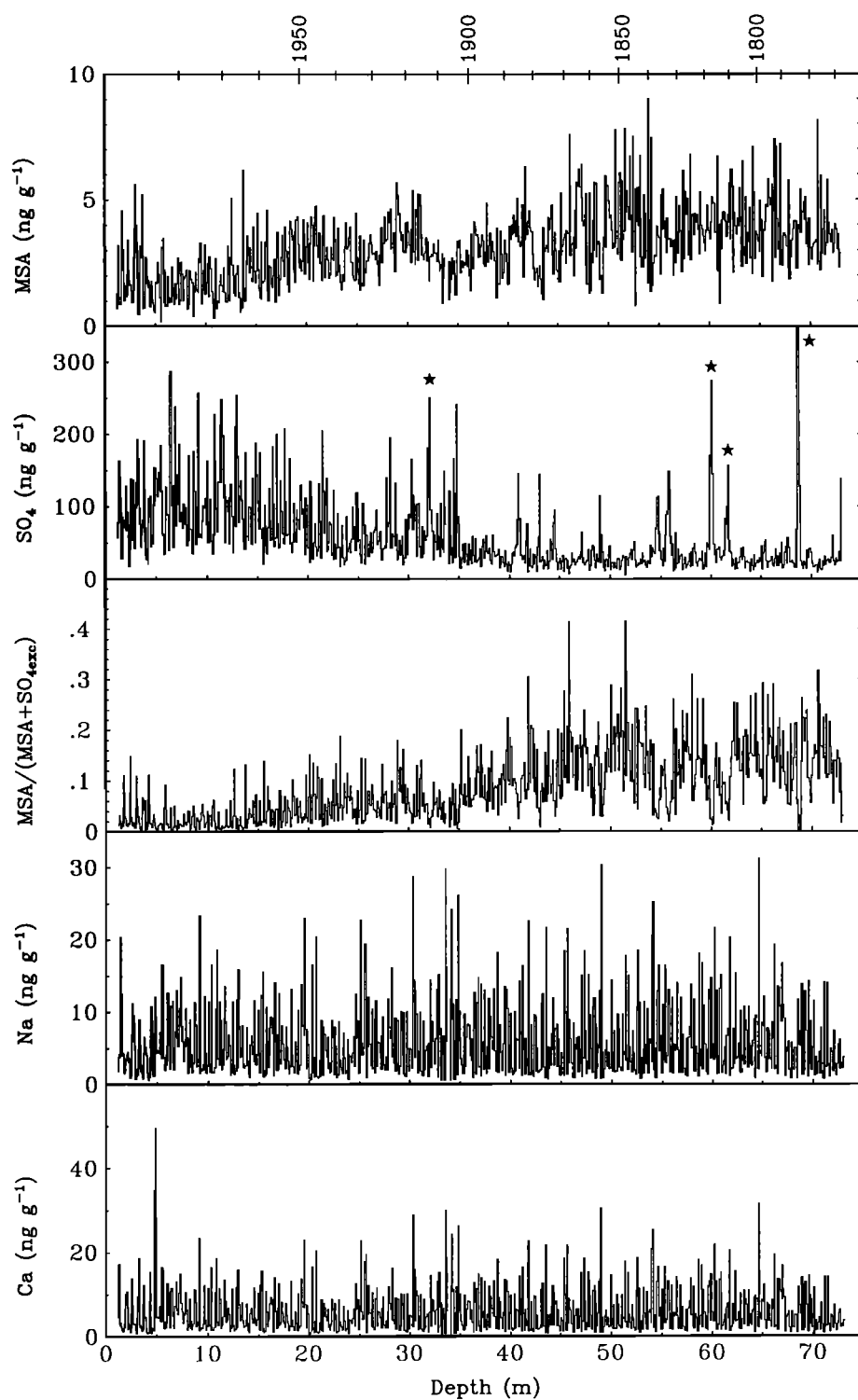
The high-resolution (GRIP 93a) profiles of MSA,  $\text{SO}_4^{2-}$ , and  $\text{MSA}/(\text{MSA} + \text{SO}_{4\text{exc}}^{2-})$  ratio covering the last two centuries are shown in Figure 2. In contrast to sodium and calcium, for which no temporal trend is seen over this time period, MSA and sulfate levels as well as the MSA fraction exhibit large changes since 1900. In agreement with previous studies in

south and central Greenland ice, a sharp increase in sulfate concentrations had occurred at the turn of the last century, as a consequence of growing  $\text{SO}_2$  fossil-fuel-burning emissions in the northern hemisphere [*Neftel et al.*, 1985; *Mayewski et al.*, 1986, 1990, 1993]. From 1770 to 1870 the mean MSA level remained quite stable at  $4 \pm 1.4 \text{ ng g}^{-1}$ , a value closed to the mean one observed over the last 9000 years ( $2.9 \pm 1.9 \text{ ng g}^{-1}$ ; see Table 1). After 1920 the mean MSA level became lower than  $4 \text{ ng g}^{-1}$ , with a decrease down to  $1.7 \pm 1.7 \text{ ng g}^{-1}$  during the 1960–1970 decade. Such a general trend of MSA concentrations has also been detected along another Greenland core extracted at D20 (South Greenland, 2615 m elevation), with a steady decrease from the turn of this century ( $4.1 \pm 2.0 \text{ ng g}^{-1}$ ) to the 1964–1984 time period ( $2.34 \pm 1.63 \text{ ng g}^{-1}$ ) [*Whung et al.*, 1994]. Although both the D20 and Summit profiles show higher values before 1900 than over this century, decadal fluctuations are not similar along the two records, MSA concentrations reaching a maximum from 1880 to 1899 at D20 and from 1845 to 1850 at Summit.

#### 3.1. Modulation of Summit MSA Levels by Climatic Conditions

Referring to the possibility that DMS emissions may be modulated by the climate [*Shaw*, 1983], we examine the relationship between air temperatures and MSA levels in Greenland (Figure 3). The 1950–1985 time period during which MSA levels may have been influenced by man-made activities (section 3.2) is discarded from this comparison. Surface air temperatures in the Greenland sea region were generally colder before 1930 than those over the 1930–1950 time period [*Kelly et al.*, 1982]. A similar temperature change is also exhibited by the global northern hemisphere temperature record [*Jones et al.*, 1986] which is available for the 1861–1985 time period. In the Greenland sea region a long and well-marked cold period started after 1900, ended during the 1920 decade, and was followed by a gradual increase of temperatures until 1938. MSA concentrations were close to  $2.3 \pm 0.6 \text{ ng g}^{-1}$  from 1900 to 1910 (52 points), reached  $3.6 \pm 0.9 \text{ ng g}^{-1}$  from 1910 to 1925 (44 points), and dropped to  $2.6 \pm 0.7 \text{ ng g}^{-1}$  from 1928 to 1939 (45 points). Before 1910, several other years were characterized by cold temperatures, in particular, from 1895 to 1899 and in 1893 (Figure 3). Although they are more difficult to identify because of the dating uncertainty ( $\pm 2$  years), the 1895–1899 cold years correspond to MSA values higher than  $3 \text{ ng g}^{-1}$  ( $3.24 \pm 0.64$ , 20 points). This intercomparison of mean Summit MSA levels with the Greenland sea temperature for the 1870–1950 time period shows a reverse relationship. This conclusion is in agreement with the 20D (south Greenland) core study achieved by *Whung et al.* [1994].

The precursor for DMS in the surface seawater is DMSP, an osmoregulator in plankton cells. High salinity in brine pockets of sea ice may involve an increase in DMSP production [*Gibson et al.*, 1990] and an increased sea-ice extent may cause higher DMS emissions in the atmosphere. Some previous studies of Antarctic ice cores have suggested that MSA concentrations were enhanced when severe sea-ice conditions had occurred in the past in these regions. *Welch et al.* [1993] observed a positive correlation between the MSA content of snow deposited in a coastal antarctic site (1600 m elevation, near the Ross Sea) and the sea-ice extent over the last 2 decades. In another coastal Antarctic site, located near the Weddell Sea, *Peel and Mulvaney* [1992] found a strong



**Figure 2.** High-resolution profiles of MSA,  $\text{SO}_4^-$ , MSA fraction,  $\text{Na}^+$ , and  $\text{Ca}^{++}$  along the GRIP 93a core. Stars denoted the well-known volcanic eruptions of Katmai (1912-1913 A.D.), Tambora (1815), the eruption of 1807, and Laki (1783).

inverse relationship between the sulfate content of snow and the annual duration of sea ice in this region over this century. However, the authors found a large positive correlation over the 1970-1980 decade. Marine source regions for MSA reaching the Greenland ice cap likely include both local oceans such as Greenland Sea in summer and oceans located

at more temperate latitudes in spring [Jaffrezo *et al.*, 1994]. This is confirmed by the presence of two distinct maxima of MSA levels, in spring and in summer, detected in a 4-m-deep snow pit dug at Summit and covering the 1985-1991 time period (Figure 4). Such a detailed examination of the seasonality of MSA concentrations in deeper snow layers is

**Table 1.** Mean Background Values of Methanesulfonate (MSA), Non-Sea-Salt Sulfate ( $\text{SO}_{4\text{exc}^-}$ ), Non-Sea-Salt Calcium ( $\text{Ca}_{\text{exc}^{++}}$ ), and the MSA Fraction of Summit Ice Calculated Over Successive Climate Stages

Depth Interval, m	Stage	[MSA], $\text{ng g}^{-1}$	$[\text{SO}_{4\text{exc}^-}]$ , $\text{ng g}^{-1}$	$[\text{Ca}_{\text{exc}^{++}}]$ , $\text{ng g}^{-1}$	MSA Fraction, %
0-1450	Holocene	$2.9 \pm 1.9$	$27 \pm 10$	$7 \pm 6$	$11 \pm 7$
1450-1617	early Holocene	$1.2 \pm 0.7$	$55 \pm 19$	$8 \pm 4$	$3.2 \pm 2.3$
1628-1673	Younger Dryas	$1.7 \pm 0.9$	$108 \pm 53$	$112 \pm 86$	$1.8 \pm 1.3$
1683-1750	Alleroed/ Boelling	$2.1 \pm 1.1$	$78 \pm 37$	$35 \pm 36$	$3.4 \pm 2.0$
1800-2000	last glacial maximum	$2.8 \pm 0.8$	$243 \pm 84$	$298 \pm 143$	$1.3 \pm 0.6$
1800-2585	late Weichsel	$2.8 \pm 0.8$	$146 \pm 99$	$188 \pm 169$	$3.3 \pm 2.7$
2585-2740	early Weichsel	$2.7 \pm 0.9$	$54 \pm 31$	$47 \pm 47$	$5.7 \pm 2.5$

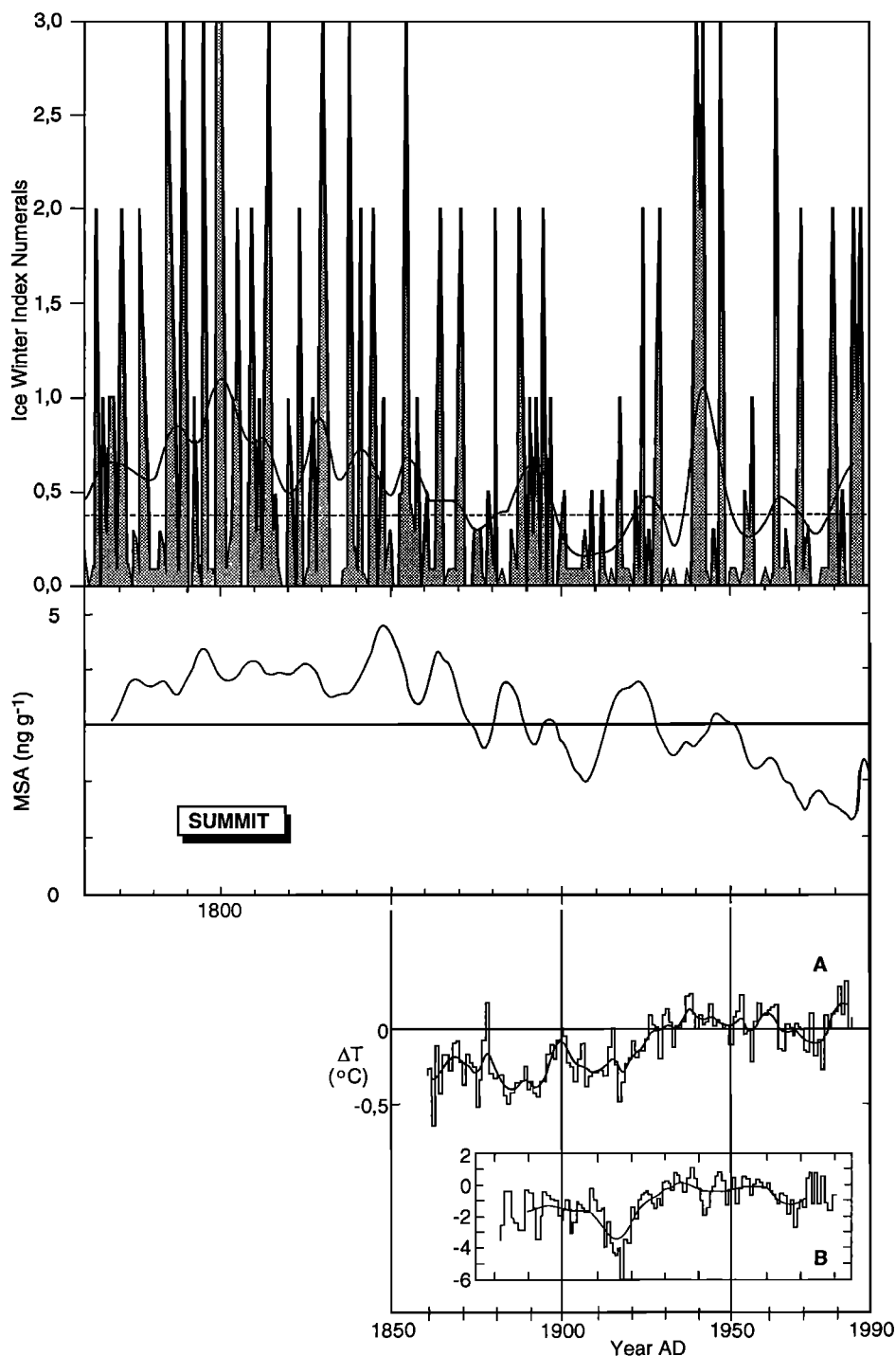
Samples containing sporadic volcanic inputs have been discarded from calculations.

useful to investigate the past variability of both spring and summer MSA inputs over Greenland. However, it appears that such a study is not possible at Summit. Indeed, whereas MSA concentrations exhibit minimal values of less than  $1 \text{ ng g}^{-1}$  in winter snow layers between the surface and 4 m depth (Figure 4), MSA minima remain close to  $1 \text{ ng g}^{-1}$  down to 10 m depth and exhibit a steady increase with depth below 15 m depth (Figure 2). No trend of sodium maxima, which correspond to the winter snow layers [Whitlow *et al.*, 1992], is seen in the Summit profile (Figure 2). The increase of MSA winter values is therefore not related to a reduced temporal definition with depth. Above 10 m depth, sodium and MSA levels exhibit a reverse relationship ( $\text{MSA} = 3.6 - 0.30 \text{ Na}^+$ ,  $r = 0.52$ , 66 points), with MSA levels being minima in winter layers. In the lowest sections of the Summit firn core a phase relationship between MSA and sodium levels is observed ( $\text{MSA} = -0.40 + 0.67 \text{ Na}^+$ ,  $r = 0.42$ , 204 points), indicating the presence of MSA maxima in winter layers. Since this firn core was subsampled in the field, it is very likely that there was a partial relocation of the MSA from summer to winter layers during the diagenesis of firn. A similar shift of MSA minima between upper layers and deeper layers has previously been observed for Antarctica by Mulvaney *et al.* [1992] and for South Greenland by Whung [1991]. Thus the investigation of the role of sea ice on DMS emissions using the MSA deposits at Summit can only be achieved by examining mean annual MSA concentrations versus sea ice over various source regions. The number of weeks per year since 1800 when ice affected the coast of Iceland has been reconstructed [Mysak *et al.*, 1990]. These data are thought to be representative of a large area of the northern North Atlantic sector [Kelly *et al.*, 1987], an oceanic region that may represent a local source of biogenic emissions for Greenland. Heavy sea-ice conditions were less frequent during the 1900-1950 period ( $3.2 \pm 1.7$  weeks of ice) than over the preceding century ( $8.7 \pm 2.5$  weeks) around Iceland [Mysak *et al.*, 1990]. A reconstruction of the ice winter severity since 1701 is available for the western Baltic Sea (Figure 3), and it also indicates less frequent occurrence of heavy sea-ice conditions over this

century with respect to the 1800-1900 period. Decadal fluctuations appear similar in these two regions. For instance, very light sea-ice conditions have prevailed both around Iceland ( $1.4 \pm 1.7$  weeks) and in the Baltic Sea (Figure 3) during the 1930-1940 decade. They were followed by heavier sea-ice conditions from 1940 to 1945 both in the Baltic Sea (Figure 3) and around Iceland ( $6.0 \pm 2.7$  weeks). However, a large discrepancy in sea-ice conditions appears for the 1840-1850 decade, which was characterized by very light sea-ice conditions ( $3.1 \pm 6.4$  weeks) around Iceland [Mysak *et al.*, 1990], while heavy sea-ice conditions took place in the Baltic Sea (Figure 3). As seen in Figure 3, high MSA levels are observed at Summit, when severe sea-ice conditions had occurred, in particular, throughout a main part of the preceding century. Although difficult, this intercomparison between MSA levels at Summit and sea-ice conditions prevailing in the past in the northern North Atlantic as well as at lower latitudes supports the idea of a positive role of sea ice on DMS marine emissions.

### 3.2. Possible Effect of Man-Made Activities on Summit MSA Levels

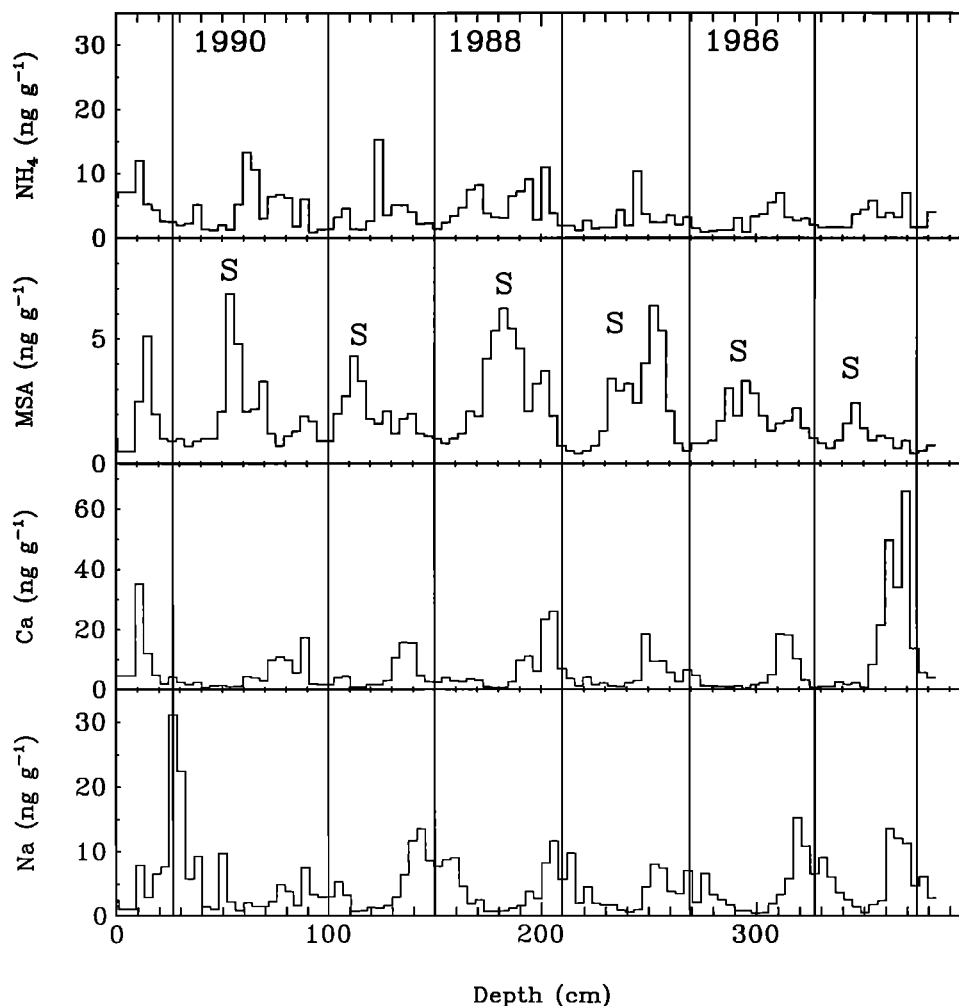
As seen in Figure 3, over the last four decades (1950-1990), MSA concentrations exhibited a strong decreasing trend, which cannot be explained by a further increase in temperatures or a marked absence of sea-ice severity. A recent atmospheric study conducted at Alert (Canadian Arctic) has also detected a decreasing trend of MSA over the 1980-1990 time period [Li *et al.*, 1993], in particular, at the beginning of the period. As seen in Figure 5, the MSA trend in Summit ice is not accompanied by significant changes of the level of sodium, a good tracer of sea salt, and of calcium, a good tracer of dust. This suggests that no dramatic changes in the atmospheric circulation had taken place in the Greenland regions over the last four decades. Another possibility may be that either the sea-air transfer of DMS has been reduced or the DMS production by marine phytoplankton has decreased over the last decades. Although we cannot exclude the possibility that increasing pollution of sea surface



**Figure 3.** (top to bottom) Ice winter index in the western Baltic Sea (see details given by *Koslowski and Glaser [1995]*) from 1760 to 1990, smoothed ( $p = 10^{-4}$ ) MSA profile (GRIP 93a) at Summit spanning the 1770-1990 time period, and air surface temperatures  $\Delta T$  as a departure from the 1951-1980 reference years in the northern hemisphere [*Jones et al., 1986*] (curve A) and over the Greenland Sea [*Kelly et al., 1982*] as a departure from the 1946-1960 period (curve B).

water (ship traffic, pollution of rivers) limits the transfer of DMS from the surface ocean to the atmosphere, the Summit drop of MSA coincides with the decline in algae populations observed in the North Pacific Ocean over the last 40 years [*Roemmich and McGowan, 1995*]. Finally, the drop of MSA over the last few decades is also in phase with a 100%

increase of nitrate concentrations, which reflects the growing anthropogenic  $\text{NO}_x$  emissions at high northern latitudes (Figure 5). These growing  $\text{NO}_x$  emissions after World War II were accompanied by a large enhancement of methane and carbon monoxide concentrations, leading to modification of the level of several oxidants including ozone, hydrogen



**Figure 4.** Seasonal variations of  $\text{NH}_4^+$  (spring and summer maxima), MSA (spring and summer maxima),  $\text{Ca}^{++}$  (spring maxima), and  $\text{Na}^+$  (winter maxima) in a Summit snow pit covering the 1985-1991 period. Vertical lines denote winter layers (minima of ammonium and maxima of sodium; see text), S refers to summer layers.

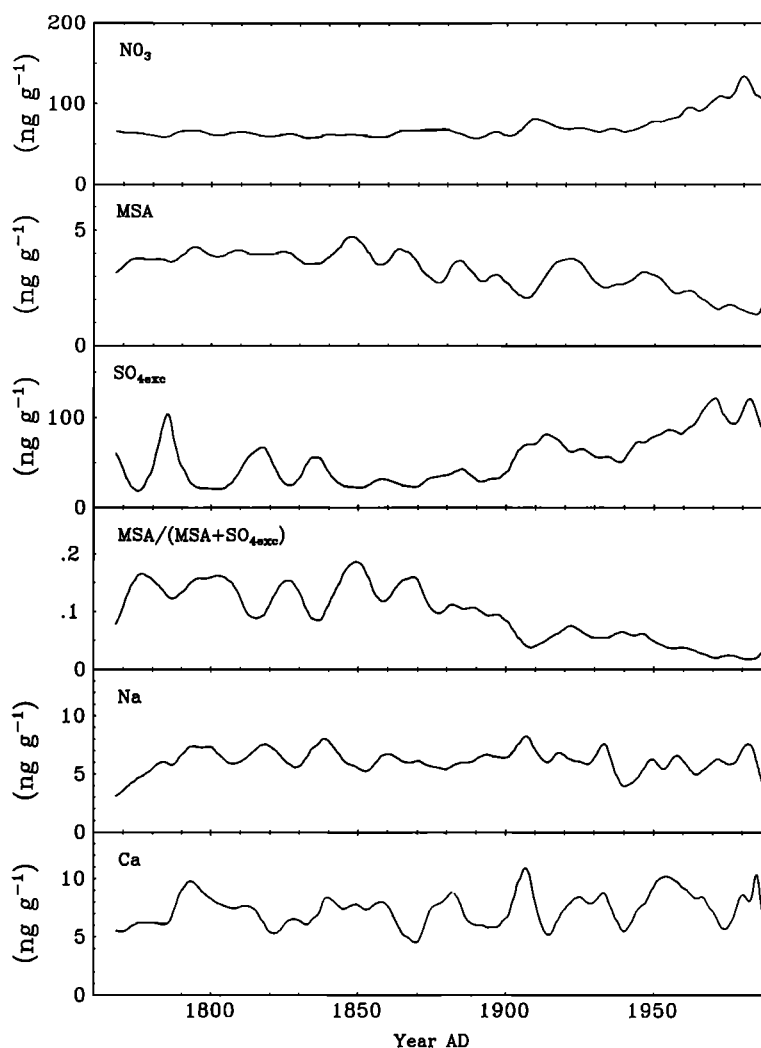
peroxide, OH, and nitrate radicals. For instance, an increase by 50% of the hydrogen peroxide content has been identified in recent Summit snow layers by *Sigg and Neftel* [1991]. The recent changing oxidative capacity of the atmosphere is complex and likely depends on regions and seasons [Thompson, 1995]. Because the reaction pathways of DMS oxidation are not yet fully understood (for a review, see *Saltzman* [1995]), it is difficult to say if the changing oxidation capacity of the atmosphere could lead to a decrease of MSA in central Greenland snow layers. In the D20 core, *Whung et al.* [1994] did not observe a change in the rate of decrease during the 1960s, when the nitrate level rapidly increased. Since the  $\text{NO}_x$  increase is of global concern in these high-latitude regions of the northern hemisphere, the different MSA trend recorded at Summit and D20 does not support the assumption of a causal relationship between MSA levels in Greenland snow and the growing  $\text{NO}_x$  emissions. In conclusion, the rapid decrease of MSA level detected in Summit snow layers since 1950 may be related to a decreased level of DMS emissions from marine biota.

The MSA fraction in Summit snow layers deposited prior to 1900 ranges between 10% and 20% (Figure 5). Over this period the MSA fraction occasionally dropped below 5% in relation to volcanic inputs (Figure 2). From 1900 to 1910 the MSA fraction suddenly decreased from 10% to 4%. From 1910 to the present a steady decrease of the MSA fraction occurred, reaching a minimum value of 2% during the 1960-1970 decade (Figure 5). Whereas the cause of the decreasing MSA fraction is mainly related to the increasing anthropogenic sulfate input, the decrease of MSA over this century still contributed to the trend.

#### 4. Holocene Record and Greenland Sulfate Origins Under Present-Day Climate

The MSA and  $\text{SO}_{4\text{exc}}^-$  levels of ice deposited at Summit over the last 11,500 years (the Holocene stage) have implications for investigating the origin of sulfate in Greenland ice. Over this warm stage, mean values of  $2.9 \pm$

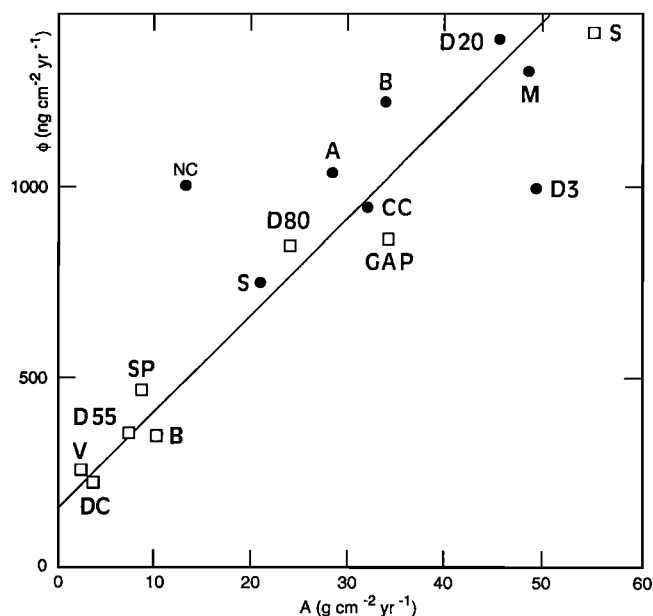




**Figure 5.** Smoothed ( $p = 5 \times 10^{-7}$ ) variations of  $\text{NO}_3^-$ , MSA, non-sea-salt sulfate (denoted  $\text{SO}_{4\text{exc}}$ ), MSA fraction,  $\text{Na}^+$ , and  $\text{Ca}^{++}$  in snow layers deposited at Summit since 1770.

1.9 and  $28.5 \pm 10.5 \text{ ng g}^{-1}$  are observed for MSA and excess sulfate, respectively. The MSA fraction remains close to  $11\% \pm 7\%$  over a main part of the Holocene stage (Table 1). Jaffrezo *et al.* [1994] observed the same MSA fraction in snow and in the boundary layer in Greenland. Thus it is legitimate to compare MSA fraction observed in Summit snow with atmospheric values. In particular, the comparison with atmospheric values observed in the marine boundary layer of the southern hemisphere where non-sea-salt sulfate is predominantly of marine origin may be useful in discussing the origin of sulfate at Summit. The MSA fraction observed in the southern hemisphere marine boundary layer ranges from 5% at  $20^\circ\text{S}$  to 10% at  $40^\circ\text{S}$ , and reaching 30% at  $65^\circ\text{S}$  [Whung *et al.*, 1994; Bates *et al.*, 1992b]. The MSA fraction at Summit therefore suggests that if non-sea-salt sulfate is mainly of marine origin, high (north of  $65^\circ$ ) and low (south of  $40^\circ$ ) marine biota emissions contribute in similar proportions to the sulfate budget of central Greenland. However, such an explanation requires that a significant transport of air masses occurs between  $40^\circ\text{N}$  and the Greenland ice cap. More reasonable assumptions may be that air masses reaching the ice cap originate mainly from north of  $50^\circ\text{N}$  and that other

sources, in addition to the marine one, contribute to the central Greenland sulfate budget. An argument in favor of this second possibility merges from the examination of Antarctic and Greenland sulfate content of ice deposited during the present climatic conditions. Because of the dependence of concentrations in ice on the snow accumulation rates [Legrand, 1995], such a comparison requires examination of fluxes at various sites. In Figure 6, we summarize non-sea-salt sulfate deposition fluxes observed for present-day climatic conditions (preindustrial time period) at various Greenland and Antarctic sites. When sites characterized by a similar annual snow accumulation rate are considered, a very similar sulfate deposition fluxes is observed in Greenland and in Antarctica (Figure 6). Given the expected lower biogenic marine biota emissions at high northern latitudes ( $23 \times 10^9$  moles of sulfur per year between  $50$  and  $85^\circ\text{N}$ ) compared with the southern ones ( $54 \times 10^9$  moles of sulfur per year between  $50$  and  $85^\circ\text{S}$ ) [Bates *et al.*, 1992a], the observed similar sulfate deposition fluxes over both Greenland and Antarctica suggest that nonbiogenic sources of sulfate have to be considered at high northern latitudes in order to compensate the lower marine biogenic source.



**Figure 6.** Annual deposition fluxes of non-sea-salt sulfate  $\phi$  (in nanograms per square centimeter per year) observed in ice deposited at various Greenland and Antarctic locations under present-day climatic conditions as a function of annual snow accumulation rates  $A$  (in grams per square centimeter per year). Samples suspected to be influenced by volcanic eruptions have been discarded. Antarctic sites (squares) are Vostok (V), Dome (DC), South Pole (SP), Byrd (B), D55 and D80 (Adélie Land), Siple (S), and Gomez (GAP), Antarctic Peninsula). Greenland sites (circles) are North Central (NC), Milcent (M), Summit (S), Camp Century (CC), sites A and B (A and B), 20D, and Dye 3 (D3). The solid line is the regression between annual deposition fluxes of non-sea-salt sulfate and snow accumulation rate. Adapted from Legrand [1995].

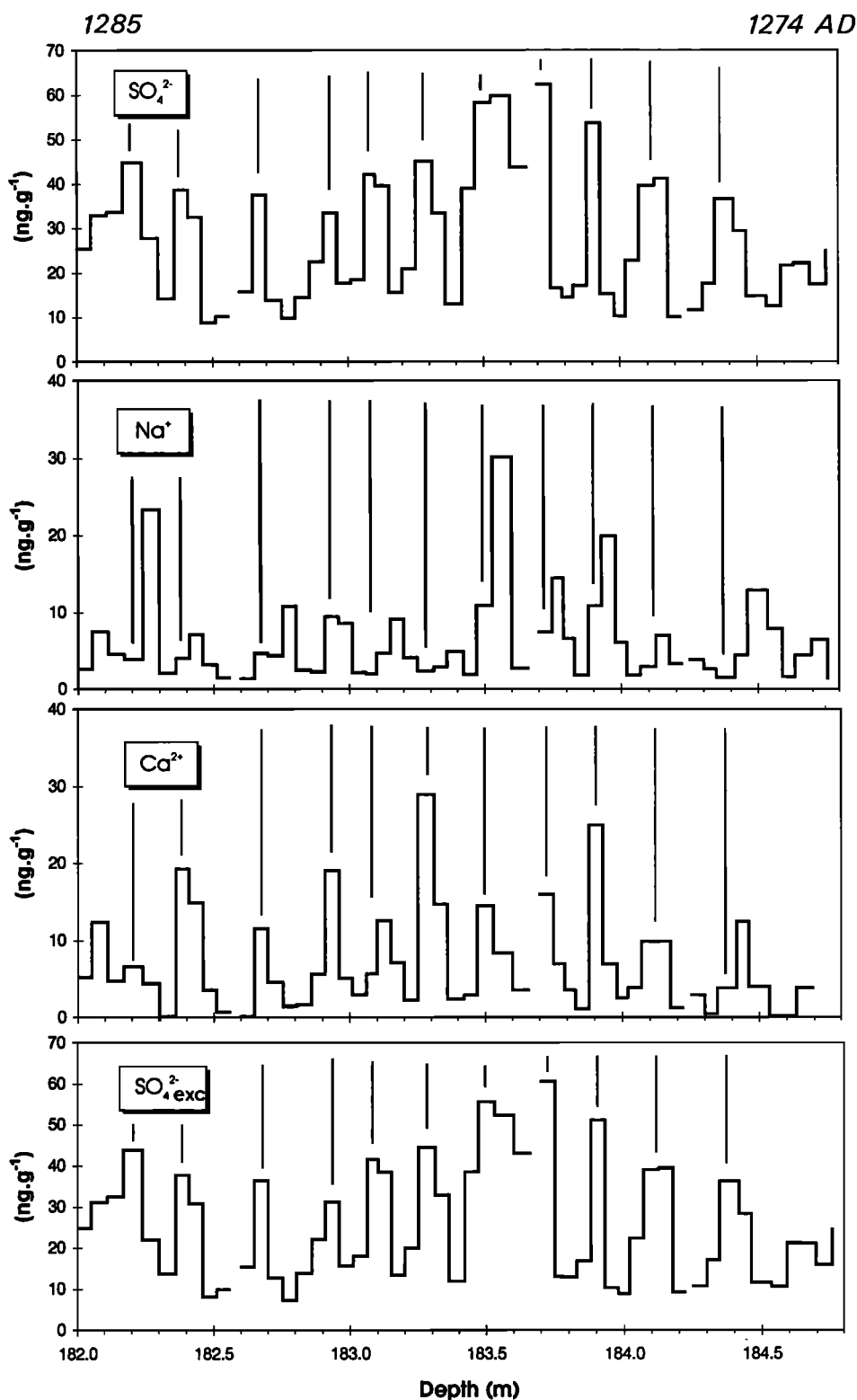
Other sulfur sources include terrestrial biogenic emissions, continental dust, and volcanic emissions. Noneruptive volcanic emissions are important in some subarctic regions (Kamchatka, Iceland, and Aleutians) ( $45 \times 10^9$  moles of sulfur per year between  $50$  and  $85^\circ\text{N}$  [Bates *et al.*, 1992a]), in contrast to those at high southern latitudes ( $1 \times 10^9$  moles of sulfur per year between  $50$  and  $85^\circ\text{N}$  [Bates *et al.*, 1992a]). Seasonal variations recorded at Summit during the preindustrial time period (1274–1285 A.D.) reported in Figure 7 can serve to estimate the noneruptive volcanic contribution to the sulfate Greenland budget. With a mean annual concentration of  $26.0 \pm 15.0 \text{ ng g}^{-1}$ , non-sea-salt sulfate profile exhibits maxima in spring and minima in winter (Table 2). The spring sulfate input corresponds to calcium carbonate emissions hereafter neutralized in the atmosphere into  $\text{CaSO}_4$  and to direct dust emissions in the form of gypsum. The sulfate to calcium weight ratio corresponding to a direct sulfate terrestrial emissions is close to 18% (section 6). As previously discussed (section 3.1), because of the remobilization of MSA in firn, MSA levels in winter snow layers at Summit have no atmospheric significance over the 1274–1285 A.D. time period. However, as suggested by the MSA values close to zero seen in winter layers near the surface (Figure 4), marine biogenic inputs to the Summit snow

layers are minima in winter. The upper limit of the noneruptive volcanic contribution can therefore be estimated from the mean non-sea-salt sulfate winter concentrations, after subtracting the possible gypsum contribution using the calcium winter levels. We thus obtain  $12.3 \text{ ng g}^{-1}$  of non-sea-salt sulfate, which may represent the volcanic contribution (i.e., 57% of the mean annual non-sea-salt sulfate concentration). This picture fits rather well with our present knowledge of volcanic versus marine biogenic emissions at high northern latitudes.

## 5. Early Holocene Time Period

A detailed examination of the last deglaciation time period is presented in Figure 8. While the calcium level reached low typical values of the Holocene ( $7 \pm 5 \text{ ng g}^{-1}$ ) above 1620 m depth (i.e., 11,500 years B.P.), MSA levels are low ( $1.2 \pm 0.7 \text{ ng g}^{-1}$ ) until 1430 m depth (9100 years B.P.), instead of  $2.99 \pm 1.9 \text{ ng g}^{-1}$  between the surface and 1430 m depth (Table 1). More generally, low MSA values characterized the entire transition period including the Allerød/Boelling interstades (12,700 to 14,450 years B.P., i.e., 1683 to 1750 m depth) and the Younger Dryas (11,500 to 12,700 years B.P., i.e., 1628 to 1673 m depth) (Table 2). Such a large delay in the recovery of typical warm-stage MSA values at the beginning of the Holocene suggests a slow setup of the current marine biota after the last great climatic transition. This may be related to the input in the surface ocean of fresh water provided by the melting of continental ice built up during the ice age. The study of the sea level record from Bard *et al.* [1990] and modeling predictions of the contribution of North America (the Laurentide Ice Sheet) to the sea level rise was suggested to be very important between 15,000 and 9000 years B.P. [Peltier, 1994]. A possible consequence of this input of fresh water may have been a reduced DMS production by marine biota due to lower salinity in the high northern latitude oceans. This possibility is also supported by the examination of the profile of formate to acetate weight ratio shown in Figure 8. Legrand and De Angelis [1996] previously discussed the carboxylic acid variations along the GRIP core. They showed that formate levels were close to  $1 \text{ ng g}^{-1}$  at 20,000 years B.P., started to increase after 14,000 years B.P., and exhibited maxima of  $12 \text{ ng g}^{-1}$  during mid-Holocene time, as a result of the setup of vegetation over North America. The timing of acetate changes was quite different from that of formate, with an increase by a factor of 2 between the ice age and the Holocene stage. From this difference, authors suspected that in addition to vegetation emissions, marine biogenic emissions of alkenes may provide acetate to the Greenland ice. Furthermore, the recovery of acetate levels did not occur before 9000 years B.P., leading to a maximum of the formate to acetate ratio between 1600 and 1450 m depth (i.e., 9000 to 11,000 years B.P.; Figure 8). Low acetate levels with respect to the formate ones over this depth interval may reflect that the increasing contribution of vegetation emissions has been counteracted by a decreased level of marine biogenic emissions at this time.

The non-sea-salt sulfate profile also exhibits some difference at the beginning of the Holocene stage with respect to typical Holocene conditions. Discarding depth levels for which a high standard deviation is observed (see vertical bars in Figure 8), for which a sporadic input of sulfate related to a volcanic eruption can be suspected, we observe a mean non-sea-salt



**Figure 7.** Seasonal variations of sulfate, sodium, calcium, and non-sea-salt sulfate in Summit ice between 182 and 184.5 m depth (i.e., 1274–1285 A.D.). Vertical bars refer to spring layers (maxima of calcium).

sulfate background level of  $55.1 \pm 19.4 \text{ ng g}^{-1}$  between 1460 and 1620 m depth, compared with  $28.5 \pm 9.8 \text{ ng g}^{-1}$  for full Holocene conditions (from the surface to 1460 m depth). As seen in Figure 8, fluoride concentrations also exhibit higher values over this depth interval ( $0.14 \pm 0.13 \text{ ng g}^{-1}$ ) with

respect to the mean Holocene value ( $0.06 \pm 0.05 \text{ ng g}^{-1}$ ). As discussed by *De Angelis and Legrand* [1994], such a change of fluoride is not related to enhanced dust fluoride contribution, as suggested by the absence of calcium change and which likely corresponds to greater volcanic activity at

**Table 2.** Mean Seasonal Concentrations of Sodium, Calcium and Non-Sea-Salt Sulfate of Summit Snow Layers Deposited between 1274 and 1285 A.D.

Season	Na <sup>+</sup> , ng g <sup>-1</sup>	Ca <sup>++</sup> , ng g <sup>-1</sup>	SO <sub>4exc</sub> <sup>-</sup> , ng g <sup>-1</sup>
Summer/fall	2.3 ± 0.7	2.4 ± 1.8	21.6 ± 10.6
Spring	6.0 ± 2.9	15.6 ± 6.0	41.4 ± 9.6
Winter	12.4 ± 8.0	4.6 ± 2.0	15.7 ± 12.0

See Figure 7.

high northern latitudes, particularly from Iceland. These observations suggest that at the beginning of the Holocene stage, noneruptive volcanic emissions were strengthened. Zielinski *et al.* [1994] found more frequent sulfate peaks during the early Holocene, suggesting that eruptive volcanism was also enhanced at this time. Such an increase of both eruptive and noneruptive volcanic activity at the beginning of the Holocene stage may be related to loading and unloading of ice and water masses that accompanied the retreat of continental ice following the last climate change [Rampino *et al.*, 1979; Chappel, 1975].

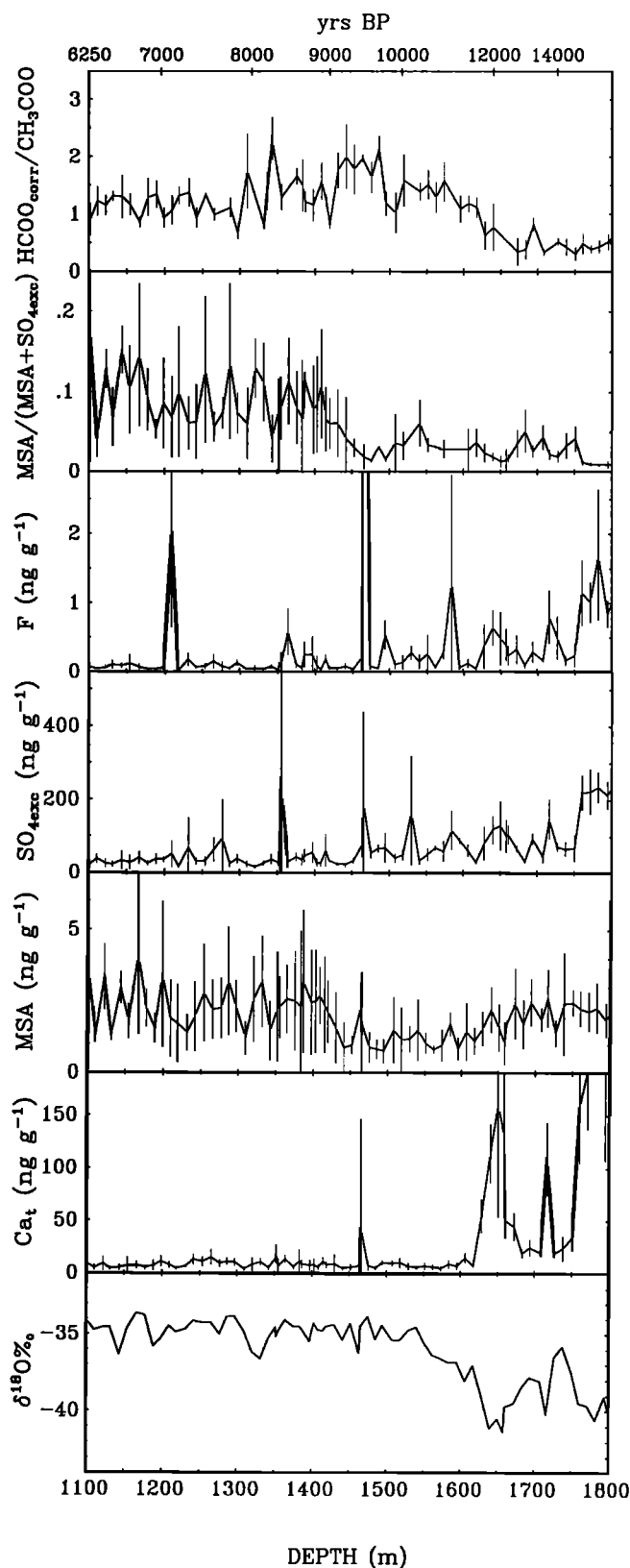
The time period corresponding to the beginning of the Holocene stage was therefore marked by reduced marine biogenic emissions, while noneruptive volcanic emissions were enhanced, leading to a significant changes of the sulfate origin with respect to mid-Holocene conditions. Under full Holocene conditions, noneruptive volcanic emissions contribute to 57% of the mean background of non-sea-salt sulfate of 27 ng g<sup>-1</sup> (i.e., 15 ng g<sup>-1</sup>), terrestrial emissions of 1 ng g<sup>-1</sup>, and marine biogenic of 11 ng g<sup>-1</sup> (along with a mean MSA level of 2.9 ng g<sup>-1</sup>). During the early Holocene the MSA values were close to 1.2 ± 0.7 ng g<sup>-1</sup>, lower than those observed during full Holocene conditions (2.9 ± 1.9 ng g<sup>-1</sup>). Assuming no dramatic changes of the MSA fraction corresponding to marine biogenic emissions at this time, such a decreased MSA value corresponds to a marine biogenic contribution of 4.5 ng g<sup>-1</sup> of non-sea-salt sulfate. This calculation leads to the conclusion that during the early Holocene stage, only 10% of non-sea-salt sulfate (55 ng g<sup>-1</sup>) was of marine origin and that the noneruptive volcanic input was enhanced by a factor of 3 with respect to full Holocene conditions.

## 6. Ice-Age Record

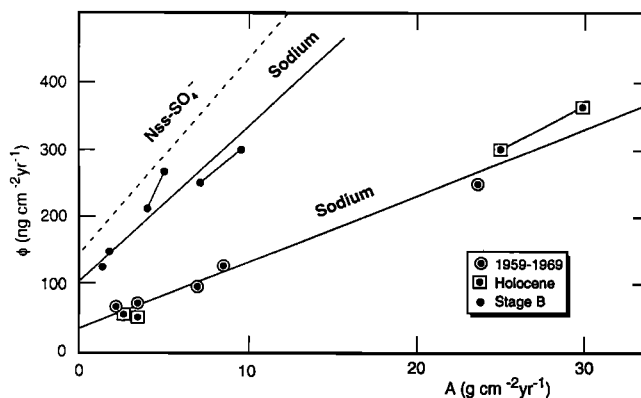
As previously discussed [Legrand, 1995], non-sea-salt sulfate concentrations vary inversely with the accumulation rate, both in Greenland and in Antarctica. The snow accumulation rate dependence of SO<sub>4exc</sub><sup>-</sup> concentrations is strong at low accumulation rates, reflecting the dilution of the dry-deposited amount of sulfate by the increasing amount of snow. In sites characterized by very low accumulation rates such as Vostok in East Antarctica a main part of sulfate is dry deposited and the variations of depositional fluxes therefore represent a better estimate of atmospheric paleoconcentrations [Legrand, 1995]. Oppositely, if a species is mainly wet deposited, the examination of ice concentrations would depict correctly the past atmospheric changes. It is therefore crucial to evaluate the relative importance of wet versus dry

deposition for species of concern at Summit. For non-sea-salt sulfate deposited during the preindustrial time (Figure 6), the deposition fluxes  $\phi$  (in nanograms per square centimeter per year) is related to the snow accumulation rate  $A$  (in grams per square centimeter per year) by  $\phi = 28 A + 154$ . This relationship suggests that under present climatic conditions (preindustrial time period), 154 ng cm<sup>-2</sup> of non-sea-salt sulfate are annually dry deposited. Figure 6 also indicates that at a given site the total flux minus the dry flux is proportional to the snow accumulation rate. At summit the dry flux accounts for some 20% of the total amount of non-sea-salt sulfate deposited under present climatic conditions. It is therefore necessary to correct concentrations observed along the GRIP core from the change of the accumulation rates which were 3 times lower during very cold climate compared with the Holocene one [Johnsen *et al.*, 1992]. Such a calculation requires the examination of the relationship between fluxes and snow accumulation rates for the ice age in Greenland ice. At present, sulfate levels in Greenland glacial ice are not well documented. However, as shown in Figure 9, for sodium, available data allow one to examine the relationships for sea salt in Antarctic ice deposited under present-day climatic conditions as well as during the ice age. As seen in Figure 9, the two regression lines for sodium and the one for non-sea-salt sulfate have a very similar  $x$  intercept, close to -5 g cm<sup>-2</sup> yr<sup>-1</sup>. In the case of sodium both the slope and the  $y$  intercept are enhanced during the ice age with respect to the present climate. This reflects the increase of atmospheric sodium concentrations between the ice age and a warm stage which enhanced the wet and dry fluxes. Assuming that this remains valid for non-sea-salt sulfate, ice concentrations can be corrected from the effect of changing accumulation in the past, as detailed by De Angelis *et al.* [this issue], and the corrected values are more representative of past atmospheric concentration changes. For MSA, not enough data are available to establish the relationship between MSA deposition fluxes and snow accumulation rates in various Greenland sites. Nevertheless, from the examination of deposition fluxes along the 20D core, Whung *et al.* [1994] concluded that dry deposition of MSA is not an important contributor to the total flux.

The entire set of data obtained along the entire GRIP core is presented in Figure 10. Along the Holocene part of the core, some sporadic spikes of excess sulfate corresponding to volcanic inputs are clearly seen. With the aim of discussing the background level of non-sea-salt sulfate, we have discarded samples for which we suspect an input of sulfate related to a volcanic eruption. Such samples are easily identified over the Holocene stage. As discussed by De Angelis and Legrand [1994], over the warm stages of the



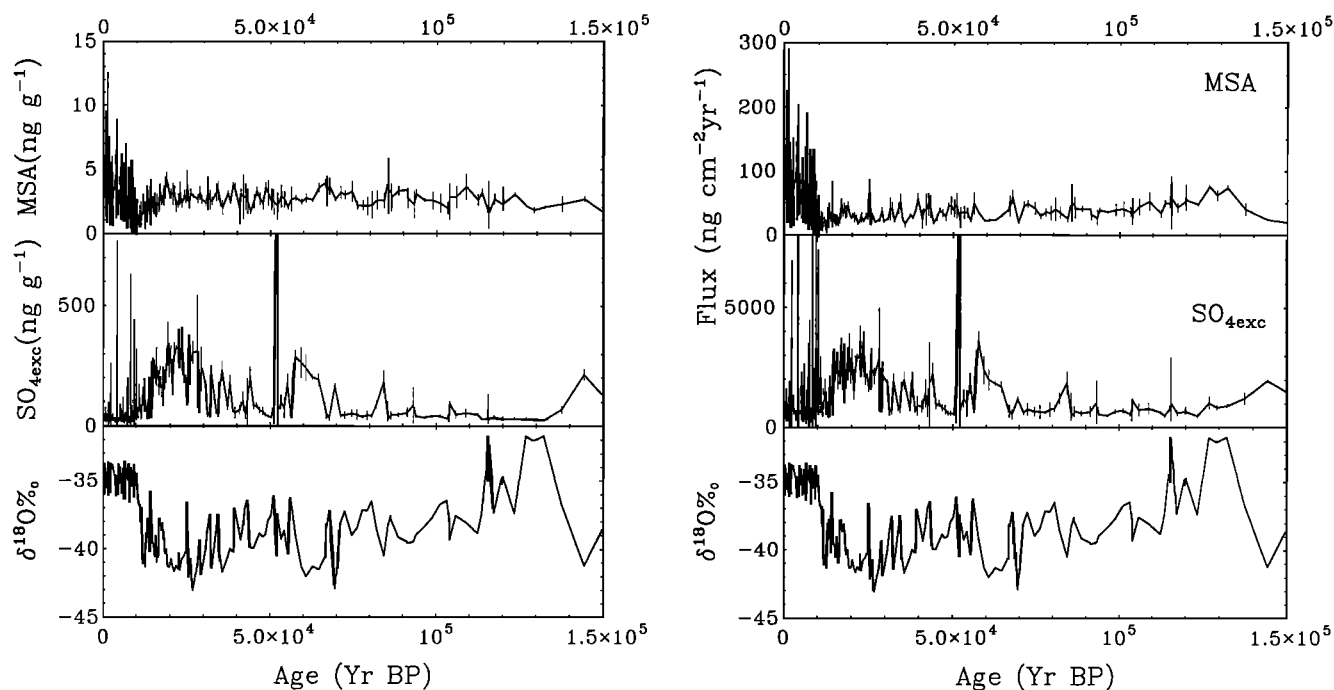
**Figure 8.** Discontinuous depth profiles from 1100 and 1800 m depth along the GRIP core: formate to acetate weight ratio, for which we take into account the effect of changed acidity of the ice over this time period, as detailed by *Legrand and De Angelis* [1996]; MSA fraction; fluoride, non-sea-salt sulfate, and calcium concentrations; and  $\delta^{18}\text{O}$  profile from *Johnsen et al.* [1992]. The timescale from *Johnsen et al.* [1992] is reported on the top.



**Figure 9.** Annual deposition fluxes of sodium  $\phi$  (in nanograms per square centimeter per year) versus snow accumulation rates  $A$  (in grams per square centimeter per year) in ice deposited over the Antarctic Plateau under present-day climate and at 18,000 years B.P. (stage B) [*Legrand and Delmas*, 1988]. The dashed line refers to the deposition fluxes of non-sea-salt sulfate observed under present climatic conditions over both Greenland and Antarctica (see Figure 6). Note the similar  $x$  intercept for the three lines.

GRIP core we have discarded samples containing more than  $100 \text{ ng g}^{-1}$  of non-sea-salt sulfate. Over the ice age, because of higher sulfate background concentrations, it is more difficult to identify samples contaminated by volcanic inputs. Following the previous study of *De Angelis and Legrand* [1994], we characterize the ice-age samples containing volcanic inputs as having unusually high levels of sulfate with respect to those of calcium and, generally, also as containing anomalously high fluoride levels. Using such criteria, we remove 162 of 1557 samples and calculated new mean values and standard deviations.

Figure 11 depicts variations of the background non-sea-salt sulfate and MSA levels over the entire climate cycle, concentrations of both species having been corrected similarly to changes of snow accumulation rates in the past. As discussed above, the correction is perhaps not legitimate in the case of MSA. Even if it exists, the dry flux of MSA represents a weak fraction of the overall deposition at Summit, and the corrected MSA profile (Figure 11) exhibits, in fact, a very similar picture to the rough profile (Figure 10). Except between 9000 and 14,000 years B.P., MSA concentrations remained quite stable along the whole profile and concentrations (or corrected concentrations) over the ice age remained quite stable and close to those observed over the Holocene stage (Figures 10 and 11). The large increase of the sodium level of the Summit glacial ice with respect to the Holocene one [*Mayewski et al.*, 1994; *De Angelis et al.*, this issue] suggests an enhancement of the primary marine aerosol content of air masses reaching the Greenland ice cap at this time. Marine emissions of sea salt and sulfur biogenic from the North Atlantic regions were very likely strongly reduced during the ice age [*COHMAP Members*, 1988]. As discussed by *De Angelis et al.* [this issue], the enhanced sea salt input over Greenland, particularly during the second part of the ice age (20,000 to 70,000 years B.P.), reflects enhanced emissions from the North Pacific, where the main surface of the high-latitude ocean remained free of ice. Furthermore, the



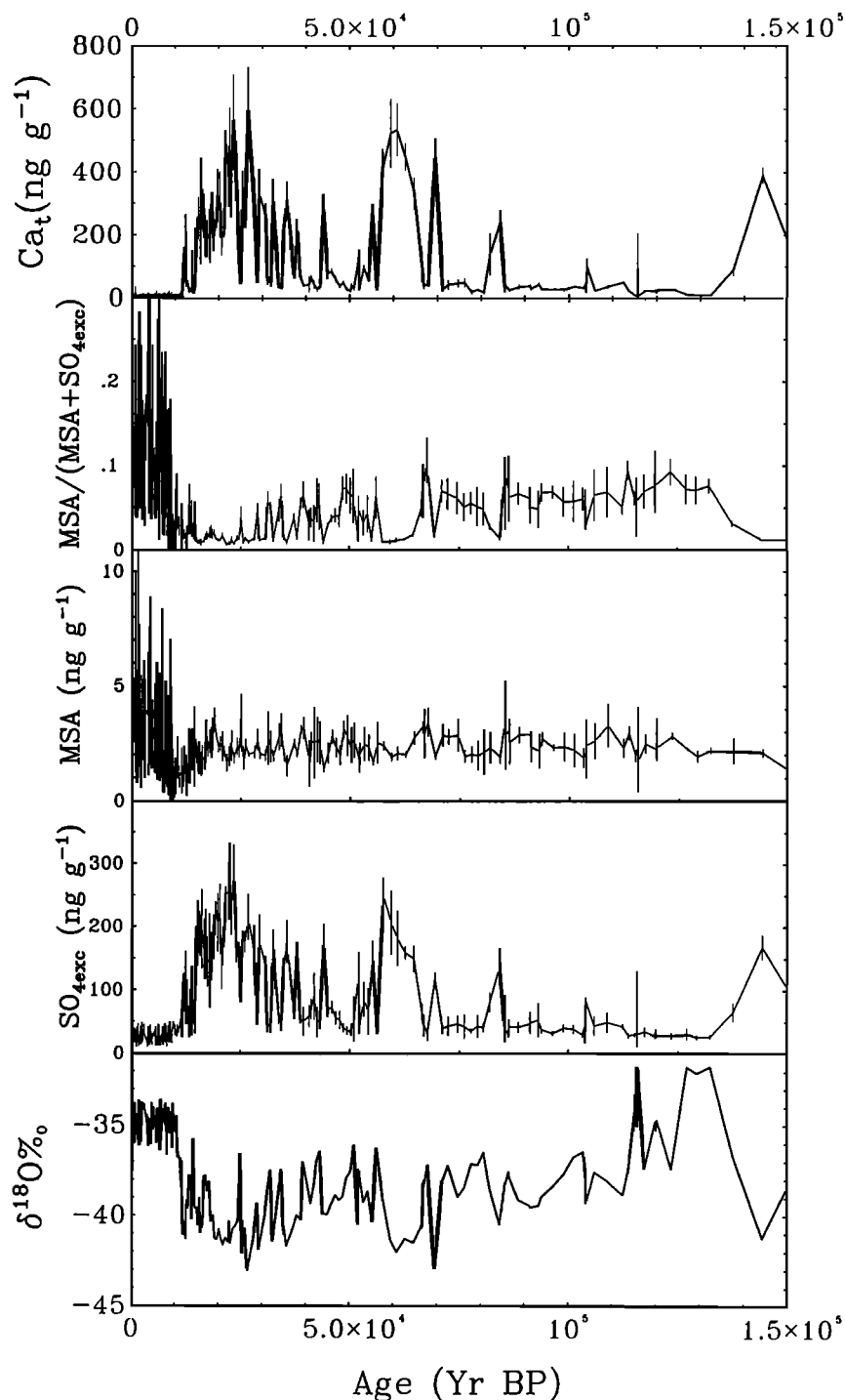
**Figure 10.** Discontinuous profiles of MSA and non-sea-salt sulfate along the entire GRIP core of (left) concentrations and (right) deposition fluxes. Samples contaminated by sporadic volcanic input are included in these profiles. The timescale from *Johnsen et al.* [1992] is reported at top. Vertical bars denote standard deviations observed at each level.

very fast transport between the North Pacific region and the Greenland ice cap relates to a possible split of the jet stream, of which the north branch was able to transport efficiently sea salt toward Greenland. If correct, the lack of MSA response to past climatic conditions suggests lower DMS emissions from the North Pacific Ocean with respect to present ones in the North Atlantic Ocean.

In contrast to MSA, sulfate levels were strongly enhanced during the ice age, in particular, at 25,000 and 60,000 years B.P. The large enhancements of non-sea-salt sulfate contents are accompanied by a large increase in the dust input, as suggested by the calcium profile (Figure 11). On the basis of both fine-fraction mineralogy and Sr and Nd isotopes, *Biscaye et al.* [this issue] concluded that the most likely source of dust at 25,000 years B.P. for the Summit (GISP core study) was similar to that of the loess in China. *De Angelis et al.* [this issue] concluded that large enhancements of calcium would correspond to dust injected by storms at 400 mPa, hereafter brought by the north branch of the westerly stream. The sulfate changes that were not accompanied by MSA changes lead to large changes of the MSA fraction, which reached 1% during very cold climatic conditions. The common feature of non-sea-salt sulfate and calcium levels during the ice age suggests a terrestrial origin for sulfate (gypsum emissions, for instance) during the ice age. However, the relationship between calcium and non-sea-salt sulfate levels is nonlinear (Figure 12). When very large amounts of calcium are present in Summit ice, the sulfate to calcium weight ratio is similar to the one observed in soils (18% [Vinogradov, 1959]) and in aerosols collected over China [Winchester et al., 1981]. Oppositely, when calcium levels are weaker, the sulfate to calcium weight ratio in Summit ice is enhanced and becomes close to the calcium sulfate molar ratio. The nonlinear

relationship between non-sea-salt sulfate and calcium suggests that at the emission stage, only part of the calcium is emitted in the form of gypsum, the remaining part being emitted as calcium carbonate. Since the dust input remained quite weak (calcium concentrations lower than 100 ng g<sup>-1</sup>), the calcium carbonate emitted in the atmosphere was efficiently neutralized by sulfuric acid or SO<sub>2</sub> and the final composition in Summit ice looked like a gypsum emission (Figure 12). For higher calcium emissions, either not enough acidic compounds were available in the atmosphere to neutralize such a large amount of alkaline material or the transport time between the source region and the Greenland ice cap was too short. However, an intriguing observation lies in the absence of MSA change in rich calcium ice. Because MSA is a strong acid, one would suggest dust plumes to adsorb MSA as well as sulfate during the transport. This suggests that the dust plumes were transported in regions of the atmosphere where sulfate was far more abundant than MSA. In the free troposphere over the oceans, lower MSA fractions have been observed compared with those in the boundary layer [Berresheim, 1987]. Furthermore, as previously discussed, noneruptive volcanic emissions of SO<sub>2</sub> dominate the sulfate budget in these high-latitude regions. Our data therefore suggest that during the transport toward Greenland, the calcium carbonate was mainly in contact with atmospheric layers where SO<sub>2</sub> dominates MSA.

The study of the Renland (east Greenland) core that covers the entire climate cycle exhibits a similar pattern with decreased MSA and increased sulfate levels during the ice age [Hansson and Saltzman, 1993]. Long-term records of sulfate and MSA have also been obtained along Antarctic deep ice cores (D10 and Dome C [Saigne and Legrand, 1987] and Vostok [Legrand et al., 1991]), revealing that MSA and



**Figure 11.** Discontinuous GRIP profiles of non-sea-salt calcium (denoted  $\text{Ca}_t$ ), MSA fraction, concentrations of MSA, and non-sea-salt sulfate after correction for changed accumulation rates of snow (see text), along with the  $\delta^{18}\text{O}$  profile from *Johnsen et al.* [1992]. Samples suspected to be contaminated by sporadic volcanic input were discarded (see text). Vertical bars denote standard deviations observed at each level.

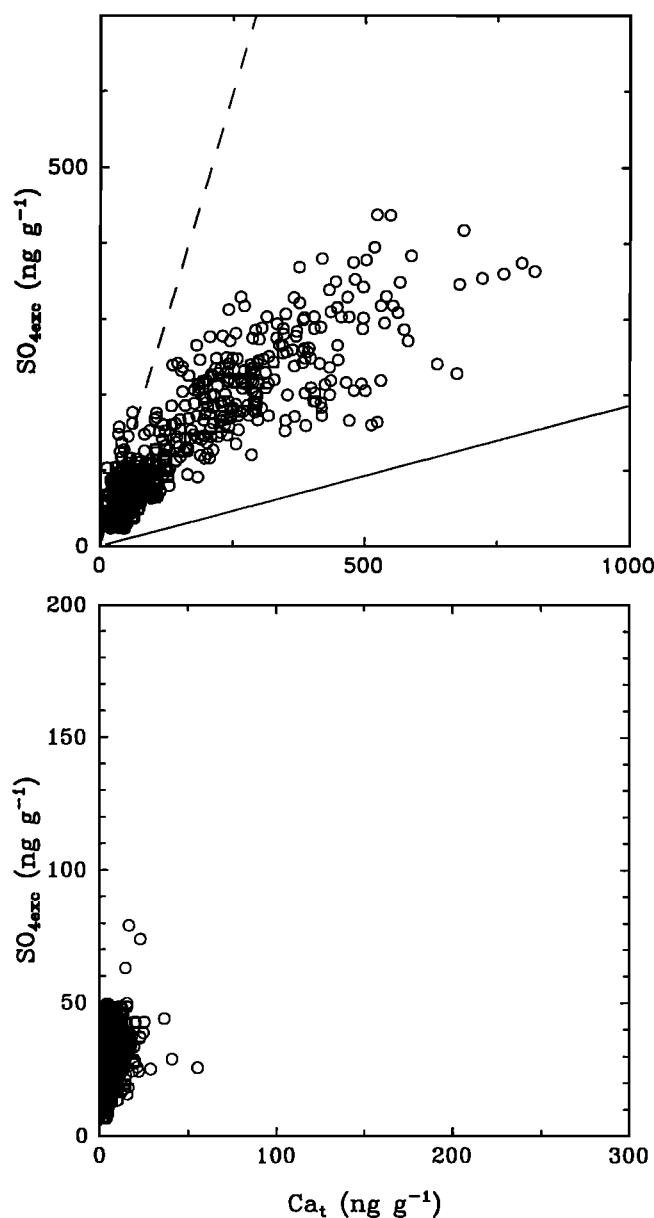
sulfate levels were 5 and 2 times higher, respectively, under warm compared with cold climate. These long-term records suggest that the Southern Ocean responded differently than the North Atlantic Ocean to past climatic conditions.

## 7. Conclusions

The study of Summit snow layers deposited over the industrial period indicates that, in contrast to the increasing

trend of sulfate related to growing man-made  $\text{SO}_2$  emissions, a decreasing trend of MSA has started during recent decades. This MSA trend may be due to weakened atmospheric DMS emissions from the surface ocean.

The Summit records of MSA and sulfate over the preindustrial time period confirm that under present climatic conditions, the Greenland natural budget of sulfate is dominated by noneruptive volcanic emissions and DMS emissions from marine biota in similar proportions. Cold



**Figure 12.** Non-sea-salt sulfate as a function of non-sea-salt calcium concentrations observed in GRIP samples free of sporadic volcanic input (see text) for (top) ice age and (bottom) Holocene stage. The solid line refers to the mean sulfate to calcium weight ratio in soils [Vinogradov, 1959]; the dashed line corresponds to the presence of calcium sulfate.

surface air temperatures at high northern latitudes correlate with MSA deposits at Summit. Although not yet clearly established, our data suggest a possible connection between positive sea-ice anomalies and high MSA levels at Summit. Reversely, biogenic sulfur emissions were reduced at the beginning of the warm Holocene stage, during which the input of fresh water to the surface ocean provided by the melt of continental ice had taken place. The noneruptive sulfur emissions were likely strengthened at the beginning of the Holocene stage, in response to unloading of ice that accompanied the retreat of continental ice.

The GRIP record indicates that colder climates were characterized by higher levels of sulfate than were warm periods. The strong increase of sulfate in glacial ice reflects enhanced terrestrial inputs (direct gypsum emissions and calcium carbonate, hereafter neutralized in the free troposphere by sulfuric acid). Except for a decrease at the beginning of the Holocene, the MSA levels remained quite similar over cold and warm climatic stages. Given the large increase of sea salt during the cold climate, it is likely that marine biogenic emissions at high northern latitudes were depressed during the ice age.

**Acknowledgments.** This work is a contribution of the Greenland Ice Core Project (GRIP) and the Eurocore project organized by the European Science Foundation. We thank CNRS (programme "Atmosphère Polaire" du PACB) and Danish National Science Research Council for financial support. We thank E. Saltzman and P.-Y. Whung for helpful discussions during the Wolfboro meeting. We also thank the two reviewers for their valuable comments on the manuscript.

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(Received February 10, 1996; revised January 20, 1997; accepted January 27, 1997.)