

Ice-core records of atmospheric sulphur

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SUMMARY

Sulphate and methanesulphonate (MSA), the two major sulphur species trapped in polar ice, have been extensively studied in Antarctic and Greenland ice cores spanning the last centuries as well as the entire last climatic cycle. Data from the cores are used to investigate the past contribution of volcanic and biogenic emissions to the natural sulphur budget in high latitude regions of both Hemispheres. Sulphate concentrations in polar ice very often increased during one or two years after large volcanic eruptions. Sulphate records show that fossil fuel combustion has enhanced sulphate concentrations in Greenland snow by a factor of four since the beginning of this century, and that no similar trend has occurred in Antarctica. At present, sulphate in Antarctic snow is mainly marine and biogenic in origin and the rate of dimethyl sulphide (DMS) emissions may have been enhanced during past developments of El Niño Southern Oscillations (ENSO). Marine biota and non-eruptive volcanic emissions represent the two main contributors to the natural high northern latitude sulphur budget. While these two sources have contributed equally to the natural sulphate budget of Greenland ice over the last 9000 years B.P., non-eruptive volcanic emissions largely dominated the budget at the beginning of the Holocene. A general negative correlation is observed between surface air temperatures of the Northern Hemisphere and Greenland snow MSA concentrations over the last two centuries. Positive sea-ice anomalies also seem to strengthen DMS emissions. A steady decrease of MSA is observed in Greenland snow layers deposited since 1945, which may either be related to decreasing DMS emissions from 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 these regions. Slightly reduced MSA concentrations are observed in Greenland glacial ice with respect to interglacial levels. In contrast, sulphate and calcium levels are strongly enhanced during the ice age compared to the present day. These long-term variations in Greenland cores are opposite in sign to those revealed by Antarctic ice cores. Such a difference suggests that climate changes led to a quite different sulphur cycle response in the two Hemispheres.

1. INTRODUCTION

Along with the cycles of nitrogen and carbon, the sulphur cycle is one of the major biogenic cycles of interest for the chemical composition of our atmosphere. Indeed, sulphuric acid, a major oxidation product of reduced sulphur species via SO_2 oxidation, contributes to a large extent to the acidity of the atmosphere. The oxidation of reduced sulphur gases into submicrometre sulphuric acid aerosols is an important process because of the potential interaction of such aerosols with incoming solar radiation, and of their role on cloud microphysics (Charlson *et al.* 1987). In addition to present-day anthropogenic SO_2 emissions, these sulphur gases are released into the atmosphere by various sources (marine and terrestrial biosphere, volcanoes, and biomass burning) among which oceanic emissions, mainly in the form of dimethyl sulphide ($(\text{CH}_3)_2\text{S}$), are predominant (Bates *et al.* 1992*a*). Climatic conditions can affect biological processes controlling sulphur biogenic emissions (Lovelock & Kump 1994). However, the roles of insolation, sea and surface air temperatures, sea-ice

cover and nutrient supply on DMS emissions are still poorly documented. We urgently need to clarify the mechanisms which could link the biota and climate of the Earth in the natural environment and evaluate, for both Hemispheres, the respective contribution of present man-made SO_2 emissions to the atmospheric sulphate burden.

Certainly, ice-core data can help to elucidate some of these key questions. Indeed, assuming a good knowledge of the relationship linking the sulphate and MSA concentrations of the snow with those of the atmosphere at the time of deposition, polar ice cores offer the unique possibility of reconstructing atmospheric concentrations of these species over different time periods from the last decades back to the last climatic cycle. They permit investigations of the natural sulphur cycle over the past, in particular the evaluation of the contribution of marine emissions compared with other natural sources (volcanic, for instance).

Here, sulphate and methanesulphonate (MSA) data available from both Greenland and Antarctic cores are reviewed. Greenland records spanning the last century are discussed in terms of the effect of increasing SO_2

from fossil fuel burning emissions, and a possible decline in marine biota emissions. Antarctic and Greenland records spanning the pre-industrial era highlight the role of marine biogenic and volcanic emissions which influence the sulphur budget in different ways at high northern and southern latitudes. The possible influence of temperature, sea ice and ENSO developments on DMS emissions are discussed. Finally, a very different response of these sulphur species to major climatic changes in the past is revealed by Greenland and Antarctic deep ice cores. Such an inter-Hemispheric difference is of importance for future climate modelling studies.

2. STATE-OF-THE-ART

Studies of sulphate in polar ice were first initiated by the pioneering study of Hammer (1977) which revealed that numerous volcanic eruptions are recorded as 'acid layers' in the Greenland ice. Since then, numerous studies have provided detailed records of past volcanic activity. More recently, ice core studies have been extended to measurements of MSA which, after sulphate, is the second most important oxidation product of DMS, but in contrast to sulphate, DMS oxidation is the only known atmospheric source of MSA. Simultaneous studies of sulphate and MSA can help to distinguish biogenic from non-biogenic sulphur inputs reaching polar ice caps.

Using a modern ion chromatographic system, it is easy to measure sulphate and MSA which are present in most polar precipitations at 10–200 ng g⁻¹ and at 1–30 ng g⁻¹ levels, respectively. Using working conditions detailed in Legrand *et al.* (1993), it is possible to measure MSA and SO₄²⁻ in a 5 ml sample with an accuracy of less than 5% in the range of 1–10 ng g⁻¹. Ice coring, handling, and storage of ice cores create high contamination on the external part of the cores. Surface contamination can be removed either by washing cores with ultrapure water at room temperature or shaving off the exterior of cores with a lathe in a cold room. Difficulties were sometimes encountered during the washing procedure for MSA measurements (Legrand *et al.* 1992), and Mulvaney *et al.* (1992) suggested a possible high mobility of MSA in firn or ice cores. All data presented here have been obtained by shaving off the ice sections.

A fraction of sulphate present in the atmosphere comes from direct emissions of sea salt, by the bursting of bubbles at the ocean surface. The remaining part of sulphate (i.e. the non-sea salt contribution of sulphate, so called 'excess-sulphate', denoted either SO₄^{2-_{exc.}} or SO₄^{2-*}) corresponds to various chemical species. As an initial approximation, sodium can be used to evaluate the sea salt content of both Greenland (De Angelis *et al.* 1997) and Antarctic (Legrand *et al.* 1988) ice. Excess sulphate, therefore can be estimated by subtracting the sea salt contribution, calculated on the basis of the sodium content, from the total sulphate content. One of the excess sulphate species, CaSO₄ (gypsum) can be introduced directly into the atmosphere (primary aerosol) from continental surface. All other excess sulphate species are derived from gaseous

SO₂, and sulphuric acid which is produced within the atmosphere by the oxidation of SO₂. Sulphuric acid and/or SO₂ can react with primary aerosols (sea salt and soil dust), or with alkaline gaseous compounds like NH₃, to form Na₂SO₄, CaSO₄, (NH₄)₂SO₄ or NH₄HSO₄. SO₂ itself is either directly introduced into the atmosphere during volcanic eruptions, or by man-made activities, or produced by the oxidation of various S-compounds among which OCS and DMS are the most important. From this complex picture, it is obvious that the interpretation of sulphate ice records requires a comprehensive study of soluble species in order to reconstruct the initial associations between sulphate and various cations (Ca²⁺, H⁺, Na⁺, NH₄⁺). After these associations are estimated, it becomes more easy to discuss possible sources which can explain the recorded sulphate variations in ice cores (Legrand 1995).

Recent studies dealing with simultaneous measurements in falling snow and in the atmosphere at the times of deposition indicate a reasonable correspondence for sulphate and MSA contents (Jaffrezo *et al.* 1994), giving confidence in interpreting such depth profiles in terms of sulphate content of the past atmosphere.

3. THE IMPACT OF MAN-MADE ACTIVITIES

The first sulphate records extracted in South Greenland show that sulphate concentrations have recently increased because of the long-range transport of pollution from middle and high northern latitudes (Neftel *et al.* 1985). In agreement with this, the high resolution central Greenland profile of sulphate covering the last two centuries shows that a sharp increase of concentrations occurred at the turn of the last century (figure 1). In contrast, Antarctic sulphate profiles covering the last decades revealed no similar trend (§5). MSA levels, as well as the MSA fraction, exhibit large changes since 1900 in Greenland ice (figure 1). Over the last decades (1950–1990), MSA concentrations exhibit a strong decreasing trend which cannot be explained by an increase of temperature or a marked absence of sea ice severity (§4). Atmospheric studies carried out at Alert (Canadian Arctic) have also detected a decreasing MSA trend over the 1980–1990 time period (Li *et al.* 1994). This drop in MSA in recent Greenland snow layers coincides with the decline in algae populations observed in the North Pacific Ocean over the last 40 years (Roemmich & McGowan 1995), which is attributed to an increase in sea surface temperature of 1.5 °C over the same time period. The decrease in the rate of deposition of MSA in Greenland is also in phase with an increase by a factor of two of nitrate concentrations (figure 1), which results from the growing NO_x emissions originating from fossil fuel burning in automobile traffic. These enhanced NO_x emissions were accompanied by increases of methane and carbon monoxide concentrations, leading to a change in the level of several oxidants including ozone, hydrogen peroxide, OH and nitrate radicals. The recent changing oxidative capacity of the atmosphere is complex, and probably

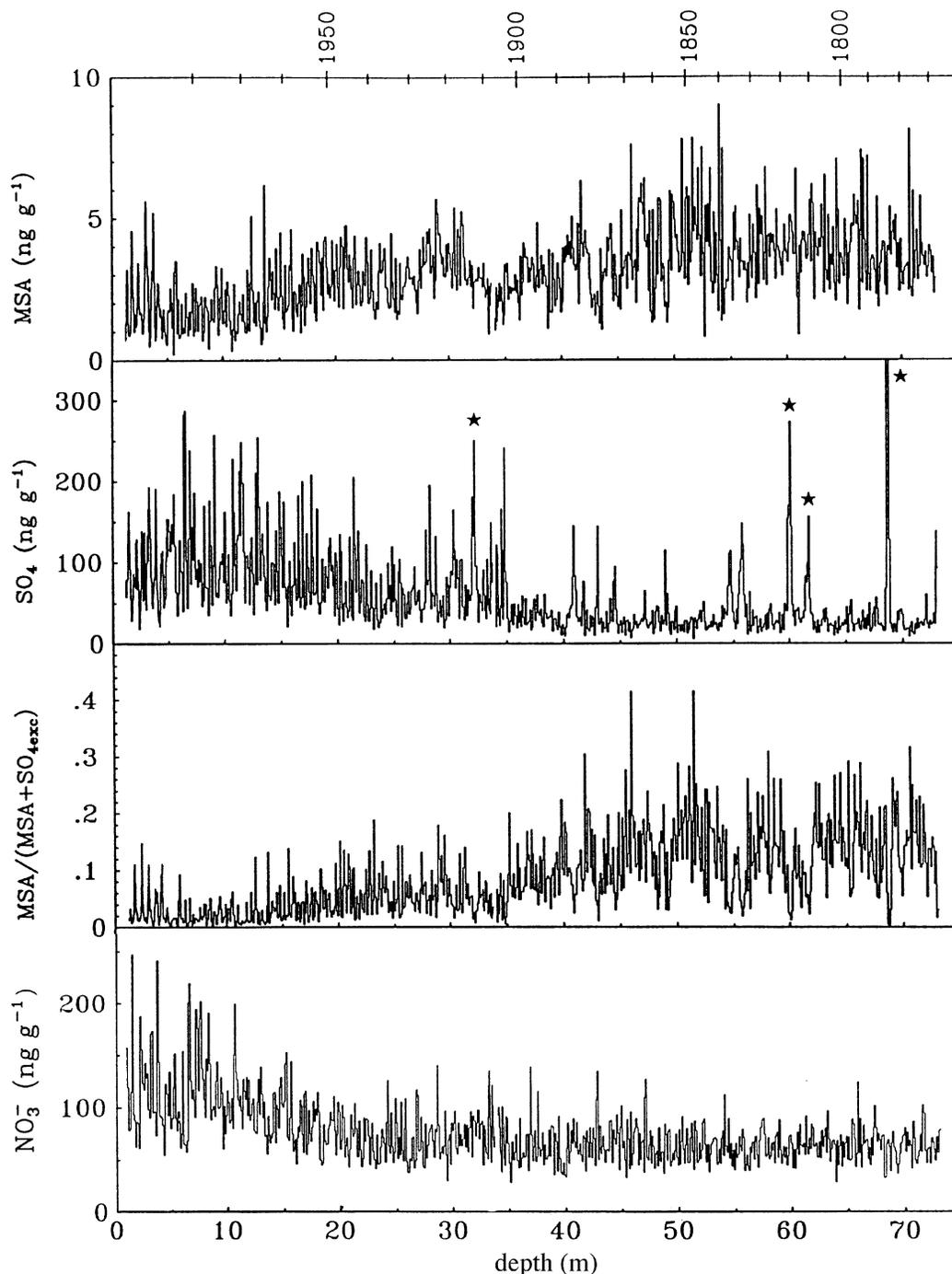


Figure 1. High-resolution profiles of MSA, SO_4^{2-} , MSA fraction, and NO_3^- along a Summit (central Greenland) ice core. Stars denote the well-known volcanic eruptions of Katmai (1912), Tambora (1815), the eruption of 1807, and Laki (1783). Reproduced with permission (Legrand *et al.* 1997).

varies with regions and seasons (Thompson 1995). Because the reaction pathways of DMS oxidation are not yet fully understood (reviewed in Saltzman 1995), it is still difficult to assess whether or not the very recent decrease of MSA in central Greenland snow layers is related to a change in DMS oxidation at high northern latitudes over this period.

4. THE NATURAL SULPHUR BUDGET IN GREENLAND AND ANTARCTICA

There is a general consensus among researchers that sulphate in Antarctica mainly originates from marine

DMS emissions while the stratospheric contribution remains weak. The volcanic eruption of Mt Agung (1963) emitted some 3 Mt of H_2SO_4 into the atmosphere and debris of this eruption have, after a period of six-months travel within the stratosphere, been deposited in Antarctica (Legrand & Delmas 1987) leading to 11 kg km^{-2} of H_2SO_4 being deposited in South Polar snow. Using these data, it can be estimated that the annual downward transport of sulphate from the stratosphere to the troposphere in the Southern Hemisphere (0.15 Mt , Turco *et al.* 1980) during a non-volcanic time period would provide only a $0.8 \text{ kg km}^{-2} \text{ yr}^{-1}$ sulphate deposition at the South Pole.

Compared to the measured $4.6 \text{ kg km}^{-2} \text{ yr}^{-1}$ total sulphate deposition in South Polar snow layers, this value suggests that the stratospheric reservoir, built up by both upward transport of SO_2 and *in situ* oxidation of OCS, delivers less than 20% of the total SO_4 deposition in Antarctic ice. In the last years, studies have started to investigate the role of marine biogenic versus other emissions through simultaneous measurements of MSA and sulphate. Indeed, next to SO_4 , MSA is the second most important oxidation product of DMS, but in contrast to sulphate, DMS oxidation is the only source of MSA. However, it rapidly appeared that the use of the MSA to non-sea salt sulphate ratio (R) to deconvolute sulphate signals in terms of marine biogenic and non-biogenic sources is more intricate than expected. Indeed, a study of R values in marine boundary layers achieved at high southern latitudes showed high values (up to 80%) compared to values of about 5% previously reported for mid-latitudes (Bates *et al.* 1992*b*). These authors observed a very good, but nonlinear, relationship between atmospheric temperatures and R values, colder temperatures favouring the appearance of MSA and thus high R values.

Reviewing sulphate data available in Greenland and Antarctic ice, Legrand (1995) found a remarkably similar amount of sulphate deposited in Greenland and Antarctic snow over pre-industrial time periods. Given the lower biogenic marine emissions at high northern latitudes (23×10^9 moles of sulphur per year between 50° and 85° N) compared to the southern ones (54×10^9 moles of sulphur per year between 50° and 85° S) (Bates *et al.* 1992*a*), the observed similar sulphate input over both Greenland and Antarctica suggests that non-biogenic sources of sulphate exist at high northern latitudes which compensate the lower marine biogenic source. Non-eruptive volcanic emissions are important

in some sub-Arctic regions (Kamchatka, Iceland, and Aleutians) (45×10^9 moles of sulphur per year between 50° and 85° N, Bates *et al.* 1992*b*), in contrast to those taking place at high southern latitudes (1×10^9 moles of sulphur per year between 50° and 85° N). Checking sulphate and MSA seasonal variations in central Greenland ice from the pre-industrial era (table 1), Legrand *et al.* (1997) estimated the non-eruptive volcanic contribution to the sulphate Greenland budget. With a mean concentration of $26.0 \pm 15.0 \text{ ng g}^{-1}$, excess sulphate exhibits maxima in spring and minima in winter. In winter, marine biogenic emissions are minimal, as suggested by MSA values close to zero seen in winter layers near the surface (figure 1). The upper limit of the non-eruptive volcanic contribution can therefore be estimated from the mean non-sea salt sulphate winter concentrations. The authors thus obtain 12.3 ng g^{-1} of excess sulphate which may represent the volcanic contribution (i.e. 57% of the mean annual content). This picture fits rather well with our present knowledge of volcanic versus marine biogenic emissions at high northern latitudes.

The picture of Greenland presented above has changed over the last 10000 years. As shown in table 2, at the beginning of the Holocene stage, MSA levels exhibit low levels ($1.2 \pm 0.7 \text{ ng g}^{-1}$) until 9100 years B.P. instead of $3.0 \pm 1.9 \text{ ng g}^{-1}$ during the main part of the Holocene. Such a large delay in the recovery of typical warm stage MSA values at the beginning of the Holocene suggests a slow setup of marine biota after the last great climatic transition which may be related to the input in the surface ocean of freshwater provided by the melting of continental ice built up during the ice age (Legrand *et al.* 1997). This input of freshwater may have reduced marine biota activity due to lower salinity in the high northern latitude oceans. Excess sulphate content also exhibits some change at the beginning of the Holocene stage with respect to typical Holocene conditions. We observe a mean excess sulphate level of $55.1 \pm 19.4 \text{ ng g}^{-1}$ at the end of the last great climatic transition instead of $28.5 \pm 9.8 \text{ ng g}^{-1}$ over full Holocene conditions (table 2). As discussed by De Angelis & Legrand (1994), 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 a result of enhanced volcanic activity at high northern latitudes, particularly from Iceland. These observations suggest that at

Table 1. Mean seasonal concentrations of sodium, calcium and excess sulphate in Summit snow layers deposited between 1274 and 1285 AD. Reproduced with permission (Legrand *et al.* 1997)

season	Na ⁺ (ng g ⁻¹)	Ca ²⁺ (ng g ⁻¹)	SO ₄ ²⁻ _{exc} (ng g ⁻¹)
summer/ autumn	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

Table 2. Mean background values of MSA, excess sulphate, non-sea salt calcium, and MSA fraction in Summit ice calculated over successive climate stages. Samples containing sporadic volcanic inputs have been discarded from calculations. Reproduced with permission (Legrand *et al.* 1997)

depth interval (m)	age Kyrs	[MSA] (ng g ⁻¹)	[SO ₄ ²⁻ _{exc.}] (ng g ⁻¹)	[Ca _{exc.} ²⁺] (ng g ⁻¹)	MSA fraction (%)
0–1450	0–9	2.9 ± 1.9	27 ± 10	7 ± 6	11 ± 7
1450–1617	9–11.5	1.2 ± 0.7	55 ± 19	8 ± 4	3.2 ± 2.3
1628–1673	11.7–12.9	1.7 ± 0.9	108 ± 53	112 ± 86	1.8 ± 1.3
1683–1750	13.1–14.4	2.1 ± 1.1	78 ± 37	35 ± 36	3.4 ± 2.0
1800–2000	15.0–25.0	2.8 ± 0.8	243 ± 84	298 ± 143	1.3 ± 0.6
1800–2585	25.0–72.5	2.8 ± 0.8	146 ± 99	188 ± 169	3.3 ± 2.7
2585–2740	72.5–100.0	2.7 ± 0.9	54 ± 31	47 ± 47	5.7 ± 2.5

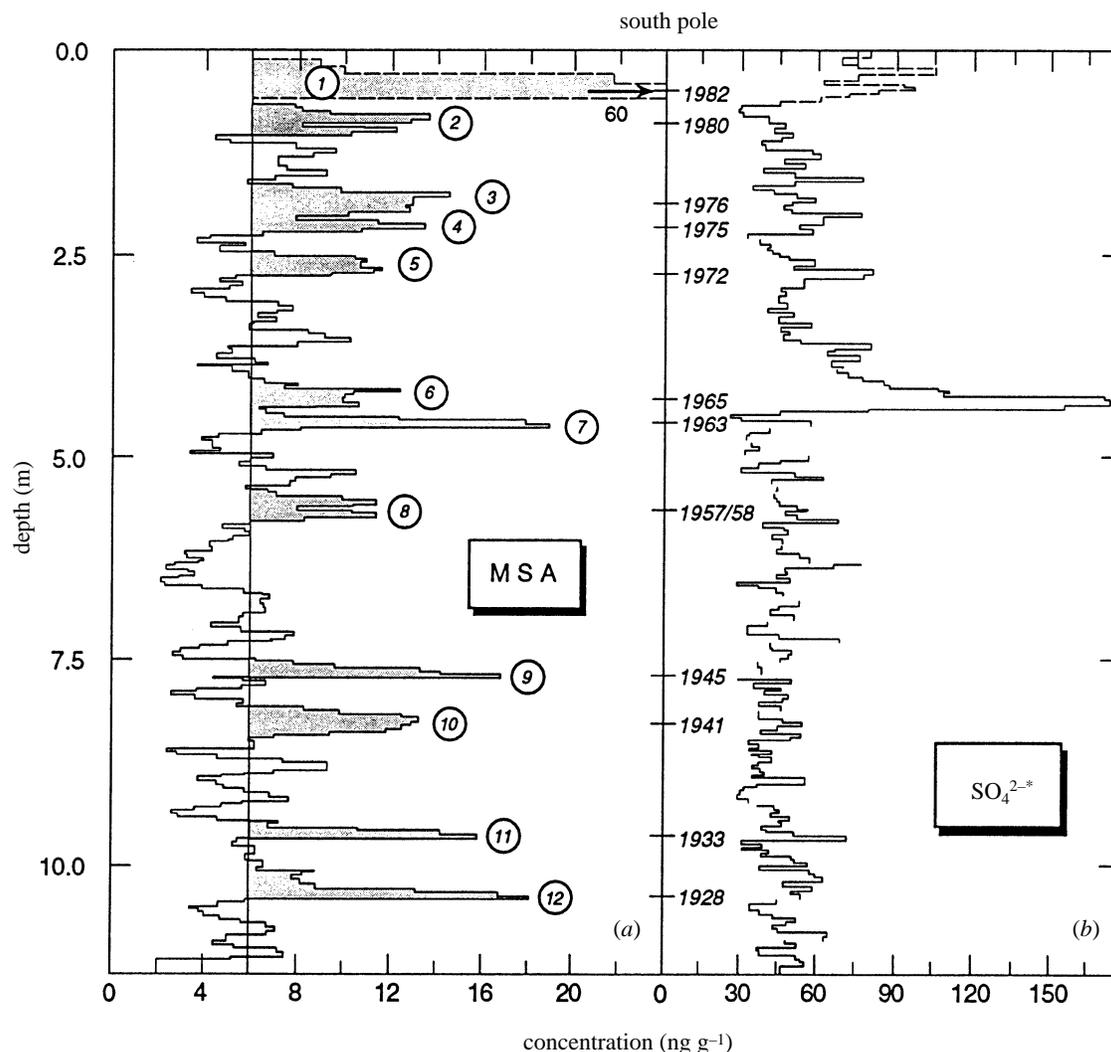


Figure 2. Excess-sulphate (SO_4^{2-*}) and MSA concentrations in South Polar snow layers (1922–1984 time period). Reproduced with permission (Legrand & Feniet-Saigne 1991).

the beginning of the Holocene stage, non-eruptive volcanic emissions have been strengthened, possibly due to loading and unloading of ice and water masses which accompanied the retreat of continental ice following the last climate change (Chappel 1975; Rampino *et al.* 1979). Under full Holocene conditions, non-eruptive volcanic emissions contribute to 57% of the mean background of excess sulphate of 27 ng g^{-1} (i.e. 15 ng g^{-1}), and marine biogenic to 12 ng g^{-1} (along with a mean MSA level of 2.9 ng g^{-1}). During the early Holocene, the MSA values were reduced by a factor of 2.4. Assuming no dramatic changes of the MSA fraction at this time, such a decreased MSA value corresponds to a marine biogenic contribution of 4.5 ng g^{-1} of excess sulphate. This calculation leads to the conclusion that during the early Holocene stage only 10% of excess sulphate (55 ng g^{-1}) was of marine origin, and that the non-eruptive volcanic input was enhanced by a factor of three.

5. NATURAL VARIABILITY OF DMS MARINE EMISSIONS

A few Antarctic ice studies have shown that the content of sulphur-derived species has changed over

the last century, possibly in response to changes in meteorological conditions at high southern latitudes. First, Legrand & Feniet-Saigne (1991) found a good correlation between the occurrence of El Niño Southern Oscillations (ENSO) and high MSA concentrations in South Polar snow layers deposited over the last 60 years. Indeed, as shown in figure 2, the excess sulphate content of South Polar snow layers deposited over the 1922–1982 time period remained rather stable except for short-term increases after the Mt Agung (1963) and El Chichon (1982) eruptions. In contrast, the MSA profile shows several sporadic increases which, taking into account the uncertainty of dating snow layers, seem to be correlated to major ENSO events of the last 60 years (1925–1926: peak 12, 1941: peak 10, 1957–1958: peak 8, 1972–1973: peak 5, and 1982–1983: peak 1, figure 2). The high R values which accompanied these MSA perturbations suggest that enhanced MSA concentrations during these years could reflect an enhanced contribution of high latitude marine biogenic emissions. Legrand & Feniet-Saigne (1991) suggested that these MSA peaks are related to enhanced DMS concentration of the Antarctic marine atmosphere, possibly resulting from higher windspeed at the sea surface leading to a more efficient

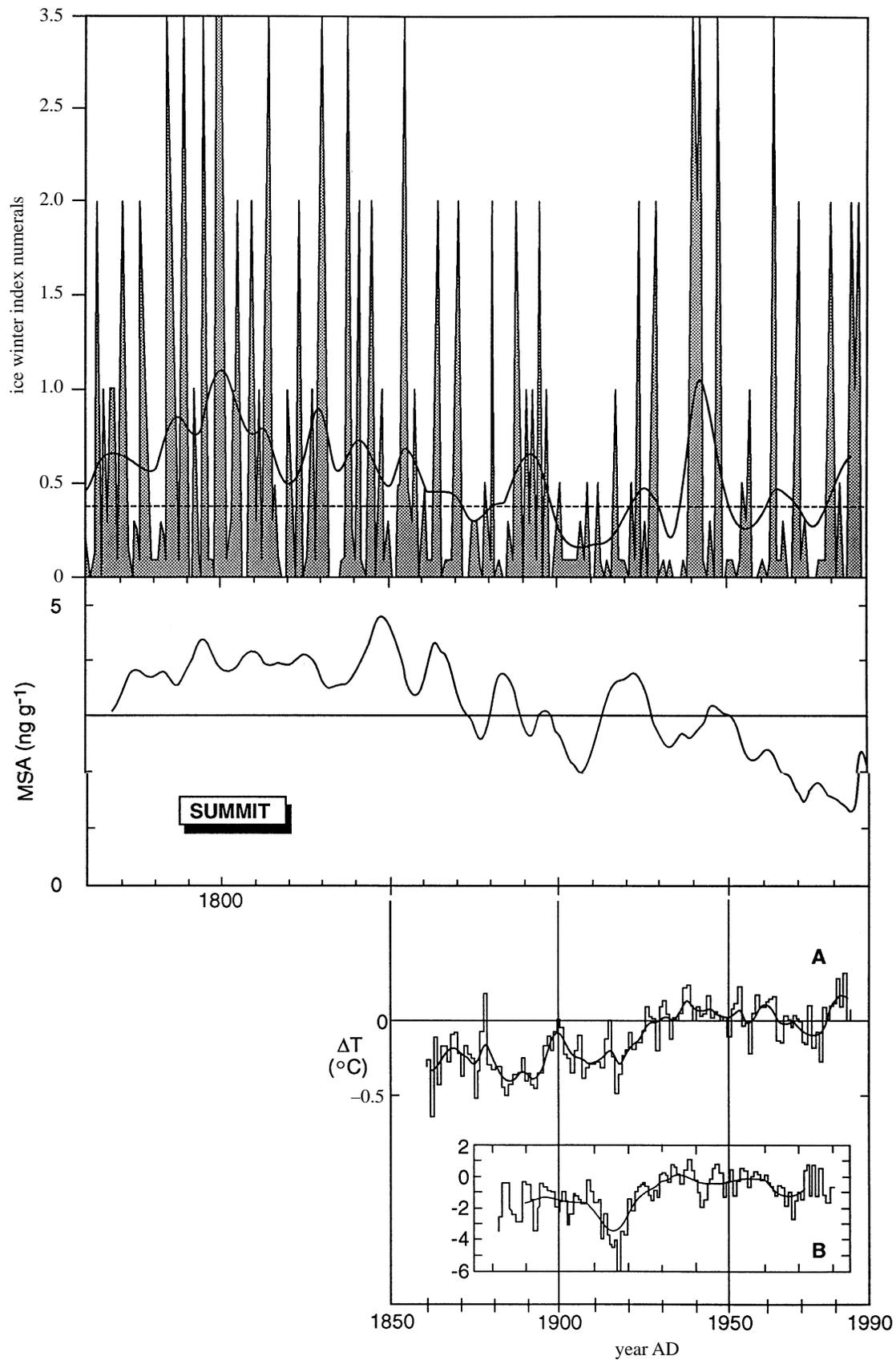


Figure 3. From top to bottom: Ice winter index in the western Baltic sea (Koslowski & Glaser 1995) from 1760 to 1990. Smoothed ($\rho = 10^{-4}$) MSA profile at Summit spanning the 1770–1990 time period. Air surface temperatures (ΔT), as departure from the 1951–1980 reference years in the Northern Hemisphere (Jones *et al.* 1986) (curve A) and over the Greenland sea (Kelly *et al.* 1982) as departure from the 1946–1960 years (curve B).

air–sea exchange of DMS. Many other plausible explanations can be invoked. For example, the precursor of DMS in the surface sea water 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 increased sea ice extent or duration during ENSO events could, therefore, cause higher DMS emissions at high southern latitudes. Studies of coastal Antarctic ice have also shown that the content of sulphur species had fluctuated over the last century in response to ENSO events and sea ice extent (Peel & Mulvaney 1992; Welch *et al.* 1993; Pasteur *et al.* 1995).

In Greenland ice, the MSA level remained quite stable between 1770 and 1870, close to the mean level observed over the last 9000 years ($2.9 \pm 1.9 \text{ ng g}^{-1}$, table 2). After 1920, the mean MSA level fell below 4 ng g^{-1} , with a decrease to $1.7 \pm 1.7 \text{ ng g}^{-1}$ during the 1960–1970 decade. The general pattern of the Summit MSA profile is quite similar to the one obtained in south Greenland by Whung *et al.* (1994), with a steady decrease from the turn of the last century to the most recent decades. Referring to the possibility that DMS emissions may be modulated by the climate, we have examined (figure 3) the relationship between air temperatures and MSA levels in Greenland. As seen in figure 3*b*, surface air temperatures in the Greenland sea region were generally colder before 1930 than those over the 1930–1985 time period, with cold decades in 1910–1920 and to a lesser extent in 1880–1890. High mean MSA values are recorded at Summit during these cold periods. Similar temperature changes are also detected in the global Northern Hemisphere temperature record which is available for the 1861–1985 time period, and reveals the very warm year in 1878 (low MSA values in Summit snow layers). There is therefore a general negative correlation between surface air temperatures and mean MSA concentrations of Summit snow layers. The occurrence of heavy sea ice conditions at high northern latitudes is extremely variable, depending on the considered region, which makes the investigation of the role of sea ice on DMS emissions a complex task. We have therefore compared our MSA record with the temporal variability of sea ice extent in two different regions around Iceland (Mysak *et al.* 1990) since 1800 and in the western Baltic Sea since 1701. One common feature of both data sets is the less frequent occurrence of heavy sea ice conditions over this century with respect to the 1800–1900 period. However, decadal fluctuations appear quite different in these two regions. For instance, prior to 1900, the 1840–1850 decade, which corresponds to high MSA levels in Summit ice (figure 3), was characterized by very light sea ice conditions around Iceland (Mysak *et al.* 1990), while heavy sea ice conditions took place in the Baltic Sea. Conversely, the 1870–1880 decade, over which we observe a drop in MSA levels in Summit ice (figure 3), was marked by light sea ice conditions in the Baltic Sea and heavy sea ice conditions around Iceland (Mysak *et al.* 1990). Over the last century, light sea ice conditions have prevailed both around Iceland and in the Baltic Sea during the 1930–1940 decade, and these correspond to

decreased MSA values in Summit ice. They were followed by heavier sea ice conditions during 1940–1950, during which we observe a partial recovering of MSA values at Summit. However, sea ice severity occurred between 1900 and 1910 around Iceland while the Baltic Sea was free of ice during this period. Our data tend to suggest that heavy sea ice conditions in the Baltic Sea influence the MSA input of the central Greenland region.

6. THE ICE AGE RECORD

Over longer time periods, concentrations of sulphur species of central Antarctic deposits have been modulated by past climatic conditions. For instance, the excess sulphate content of the Vostok core shows glacial-interglacial changes from 100 ng g^{-1} during the two warm stages to $210\text{--}240 \text{ ng g}^{-1}$ during the three very cold stages (figure 4). The variations in the MSA profile strongly correlate with the climate, increasing from 5 ng g^{-1} over warm stages to $25\text{--}31 \text{ ng g}^{-1}$ during very cold climate (Legrand *et al.* 1991). This covariance of MSA and excess sulphate contents in the Vostok core strongly suggests that excess sulphate present in precipitation on the high Antarctic plateau is primarily derived from DMS emissions. The relative magnitude of the glacial-interglacial changes in MSA are greater than those of excess sulphate, resulting in an increase of the ratio R during cold climate. Such changes of the partitioning between MSA and non-sea salt sulphate in the past are still difficult to explain because of the previously mentioned lack of understanding of present-day latitudinal variations of R in the marine boundary layer. Two explanations can be invoked to explain R values in the past. First, as a result of lowered temperatures during the Glacial Age, the ratio increased. Second, the increase of R values could reflect a greater contribution of high latitude DMS emissions to the high Antarctic plateau sulphate budget during colder climatic periods in the past, as a result of increased wind velocity at the ocean surface and/or an increase in biological productivity. Although we cannot yet say what R values really mean, Antarctic ice studies suggest that sulphate is mainly marine in origin during present-day conditions as well as during colder climatic periods in the past, and that there is a link between the ocean–atmosphere sulphur cycle and the climate.

Figure 5 depicts the background level of excess sulphate and MSA over the entire last climatic cycle in a central Greenland ice core. Except between 9000 and 14000 years B.P., MSA concentrations remained quite stable along the whole profile and concentrations over the ice age remained fairly stable and close to those observed over the Holocene stage. The large increase in the sodium level of the Summit glacial ice with respect to the Holocene (Mayewski *et al.* 1994; De Angelis *et al.* 1997), suggests an enhancement of the primary marine aerosol content of air masses reaching the Greenland ice cap at this time. The lack of MSA response to past climatic conditions suggests lower DMS emissions from the Arctic Ocean with respect to present ones. In contrast to MSA, sulphate levels were

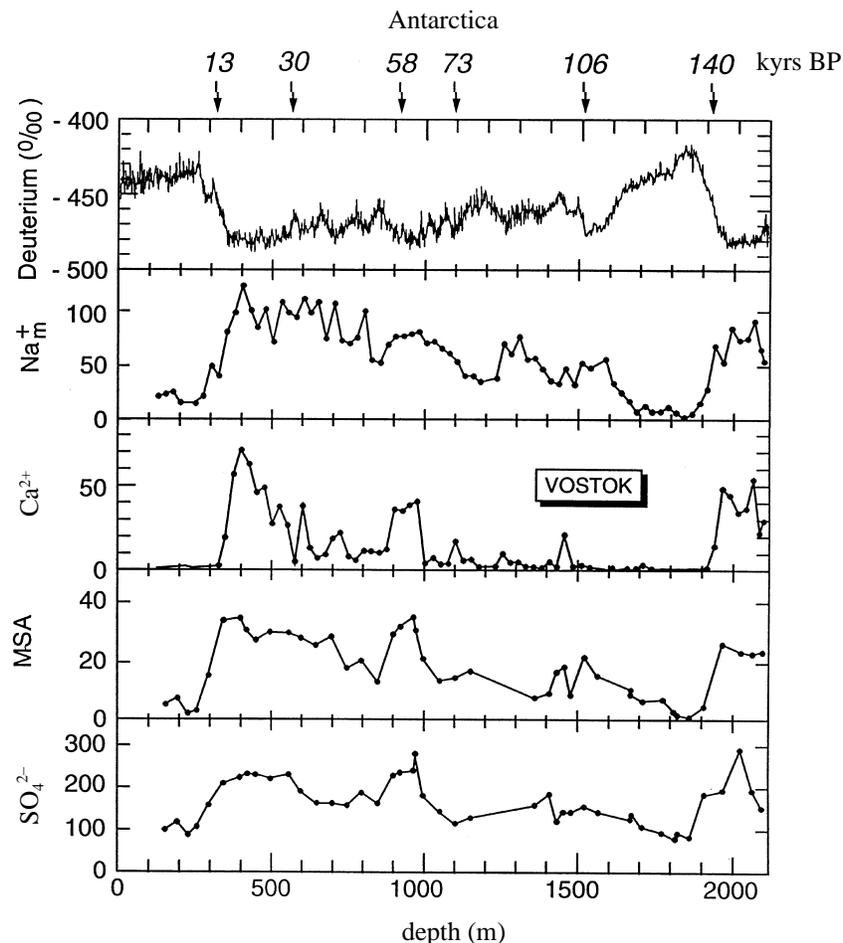


Figure 4. Vostok (central Antarctica) ice core profiles. From top to bottom: deuterium profile (in ‰); marine sodium (Na_m^+), excess calcium (Ca^{2+*}), MSA and excess sulphate (SO_4^{2-*}) in ng g^{-1} . Adapted from Legrand *et al.* (1988) and Legrand *et al.* (1991).

strongly enhanced during the ice age, in particular at 25000 and 60000 years B.P., leading to large changes of the MSA fraction which reached 1% during very cold climatic conditions. As seen in figure 5, the large enhancements of excess sulphate contents are accompanied by a large increase in dust input, as suggested by the calcium profile. Based on both fine-fraction mineralogy and Sr and Nd isotopes, Biscaye *et al.* (1997) concluded that the most likely source of dust at 25000 years B.P. for the Summit was similar to the loess in China. The common feature of excess sulphate and calcium levels during the ice age suggests a terrestrial origin for sulphate (gypsum emissions, for instance) during the ice age. When very large amounts of calcium are present in Summit ice, the sulphate to calcium weight ratio is similar to the one observed in soils (18%, Vinogradov 1959). In contrast, when calcium levels are weaker, the sulphate to calcium weight ratio in Summit ice is enhanced and comes close to the calcium sulphate molar ratio. The nonlinear relationship between non-sea salt sulphate and calcium suggests that at the emission stage, only 7.5% of calcium is emitted in the form of gypsum, the remaining part being emitted as calcium carbonate. As long as the dust input remained quite low (calcium concentrations lower than 100 ng g^{-1}), the calcium carbonate released into the atmosphere was efficiently neutralized by

sulphuric acid or SO_2 , and the final composition in Summit ice looks like a gypsum emission (figure 4). 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 changes in rich calcium ice. As MSA is a strong acid, that would suggest that dust plumes were transported within regions of the atmosphere where sulphate was far more abundant than MSA. Our data therefore suggest that the transport of calcium carbonate from China towards Greenland during the ice age mainly occurred at quite high altitudes where SO_2 dominates MSA. That implies a larger influence of volcanic emissions with respect to biogenic ones in these regions of the atmosphere at high northern latitudes.

7. CONCLUSIONS

A large amount of data concerning MSA and sulphate concentrations in polar ice exists providing useful information which increases our knowledge of the atmospheric sulphur cycle. Marine biogenic DMS emissions probably dominate the sulphur cycle at high southern latitudes under present-day climatic con-

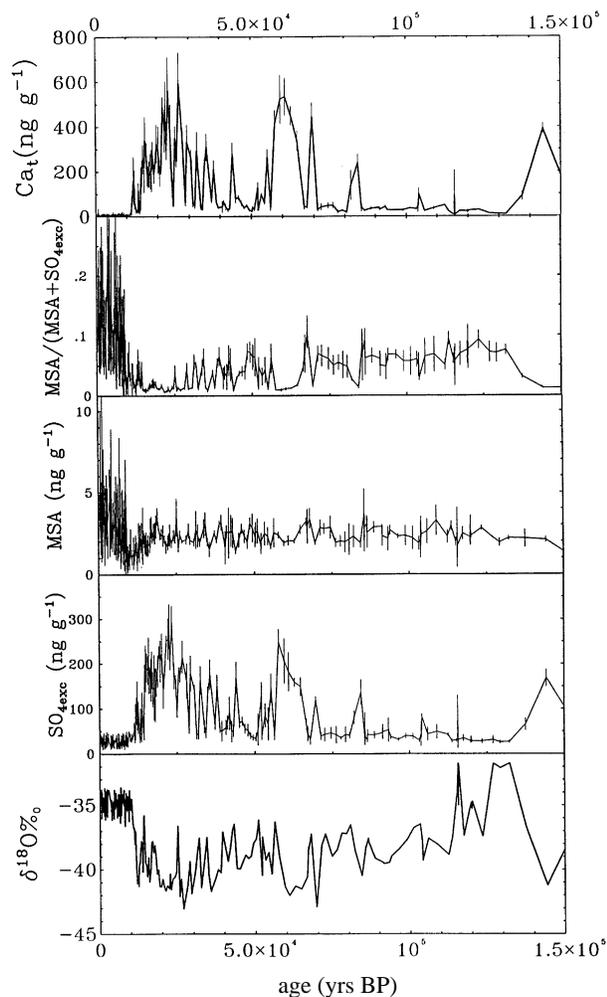


Figure 5. Discontinuous GRIP (central Greenland) profiles of excess calcium (denoted Ca_t), MSA fraction, MSA and excess-sulphate (SO_4^2-) concentrations along with the $\delta^{18}\text{O}$ profile from Johnson *et al.* (1992). Samples suspected of being contaminated by eruptive volcanic input have been discarded. Reproduced with permission (Legrand *et al.* 1997).

ditions as well as during past colder time periods. Such studies also suggest that DMS marine emissions are sensitive to short-term climatic fluctuations induced by ENSO events. However, an in-depth interpretation of these changes having occurred in the past in terms of meteorological conditions (sea ice cover, wind speed, insolation and temperatures) still remains limited because a major gap remains in our knowledge of the oxidation of DMS at high southern latitudes. In contrast to the Antarctic sulphate level which remained unchanged over the last two centuries, those of Greenland ice exhibit an increase since 1900–1910, as a consequence of increasing SO_2 fossil fuel burning emissions in the Northern Hemisphere. In contrast, a decreasing trend of MSA, which started in very recent decades, may be due either to weakened DMS emissions resulting from the depleted algae population in the high northern latitude ocean, or to a change in the yield of MSA from DMS oxidation driven by the changing oxidative capacity of the atmosphere. The central Greenland records of MSA and sulphate over the pre-industrial era show that under present climatic conditions, the Greenland natural sulphate budget is

dominated by non-eruptive volcanic emissions and DMS emissions from marine biota in similar proportions. Cold surface air temperatures and sea ice anomalies encourage marine biogenic sulphur emissions. Conversely, biogenic sulphur emissions declined at the beginning of the warm Holocene stage during which freshwater, provided by melting of continental ice, was added to the surface ocean. The non-eruptive sulphur emissions were probably strengthened at the beginning of the Holocene stage in response to the unloading of ice which accompanied the retreat of continental ice. Central Greenland deep ice cores indicate that colder climates were characterized by lower levels of MSA and higher levels of sulphate than during warm periods. It is suggested that marine biogenic emissions at high northern latitudes were depressed during the ice age. The strong increase of sulphate in glacial ice reflects enhanced terrestrial inputs (direct gypsum emissions and calcium carbonate subsequently neutralized in the free troposphere by sulphuric acid).

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