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Authors

Mulvaney, Robert
Pasteur, Elizabeth C
Peel, David A
et al.

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The ratio of MSA to non-sea-salt sulphate in Antarctic Peninsula ice cores

By ROBERT MULVANEY, ELIZABETH C. PASTEUR and DAVID A. PEEL, *British Antarctic Survey, Natural Environment Research Council, Madingley Road, Cambridge, CB3 0ET, UK*, ERIC S. SALTZMAN and PAI-YEI WHUNG, *Rosentiel School of Marine and Atmospheric Science, Division of Marine and Atmospheric Chemistry, 4600 Rickenbacker Causeway, Miami, Florida 33149-1098, USA*

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ABSTRACT

Methane sulphonic acid (MSA) in an ice core from Dolleman Island (70°35'S, 60°56'W) shows significantly high concentrations (typically 1–2 μM , but up to 5 μM) compared to values recorded in ice cores and in snowfall from elsewhere in Antarctica. MSA data from two other higher altitude Antarctic Peninsula ice cores, Dyer Plateau (70°31'S, 65°01'W) and Gomez Nunatak (74°01'S, 70°38'W), show that the high concentrations measured at Dolleman Island are not representative of the Peninsula region as a whole. However the mean molar MSA/nss-SO₄²⁻ ratios at the three sites are similar (Dolleman Is, 0.46; Gomez, 0.37; Dyer, 0.32). Exceptionally high concentrations observed at Dolleman Island may be related to its proximity to the biologically productive Weddell Sea, an important source of dimethyl sulphide (DMS), the precursor of MSA. The MSA data from this site are further unusual in that in deeper sections of this core they demonstrate a well defined seasonal maximum in winter rather than in summer and are out of phase with non sea-salt sulphate, another product of the decomposition of DMS. In contrast, in a near-surface section, MSA variations are in phase with non sea-salt sulphate, with a maximum concentration in the summer layer. A change in the season of deposition of MSA from winter to summer in the recent past is not considered likely. An alternative explanation is that there has been a relocation of the MSA from summer to winter layers during burial.

1. Introduction

The possible influence of oceanic dimethyl sulphide (DMS) on the number of cloud condensation nuclei, and on global climate through a cloud albedo feedback mechanism, has been discussed by Charlson et al. (1987). Whilst the connection between DMS and atmospheric aerosol particle populations has been demonstrated (Bates et al., 1987), Schwartz (1988) has questioned the link between DMS, albedo and climate. He argues that SO₂ should have the same effect, but in the northern hemisphere, where man-made SO₂ emissions exceed marine DMS emissions, there appears to be no correlation between albedo or temperature and anthropogenic SO₂. In the remote southern hemisphere, the influence of anthropogenic SO₂ is low, and attempts have been made to compare DMS emissions with past

climate changes. As instrumental time-series records of DMS do not exist, the proxy records available in ice cores have been used. DMS is oxidised in the atmosphere to either methane sulphonic acid (MSA) or to sulphuric acid. Legrand et al. (1991) have measured both MSA and sulphuric acid (as sulphate) over the last climatic cycle and conclude that the ocean-atmosphere sulphur cycle is sensitive to climate change.

As MSA is exclusively derived from the oxidation of marine biogenic DMS, it could act as useful indicator for past biological activity in the oceans surrounding the Antarctic. However, DMS is also converted to sulphate in the atmosphere by a competing reaction mechanism. The relative importance of the alternative reaction pathways varies with temperature, and hence will vary spatially. It is therefore crucially important both to understand the processes involved during transport and the

Table 1. *Characteristics of the three ice cores*

	Dolleman Island	Gomez Nunatak	Dyer Plateau
Physical properties			
position	70°35'S 60°56' W	74°01'S 70°38' W	70°31'S 65°01' W
elevation m asl	398	1130	1900
10 m temperature (°C mean annual air temperature)	-16.8	-17.3	-21.7
accumulation (m water/a)	~0.34	~0.88	~0.48
date collected	Jan. 1986	Jan. 1981	Jan. 1989
samples/annum	~12	~16	~12
Chemical properties			
mean MSA (μM)	0.85	0.11	0.09
mean nssSO ₄ ²⁻ (μM)	1.86	0.30	0.28
mean SO ₄ ²⁻ (μM)	2.55	0.44	0.36
MSA/nssSO ₄ ²⁻	0.46	0.37	0.32
nssSO ₄ ²⁻ /tot SO ₄ ²⁻	0.73	0.68	0.78
(ratios are ratios of the two means)			

mechanisms by which MSA is incorporated into snowfall, and subsequently into ice cores, if we are to evaluate unambiguously the past levels of biological activity in the oceans from ice core analysis.

Ayers et al. (1991) have demonstrated that DMS, MSA and non sea-salt sulphate in air at a remote marine site (Cape Grim, Tasmania) have a seasonal cycle, with the peak concentration of all three species in summer. MSA data from aerosol measurements in Antarctica, collected at monitoring stations at both Mawson (Prospero et al., 1991), and Neumayer (A Minikin and D Wagenbach, personal communication) show a clear annual cycle with the maximum MSA measured during the summer period. Similar timing is reported for the measurement of MSA in Antarctic ice cores from Law Dome (Ivey et al., 1986). In stark contrast, the first analyses on the Dolleman Island ice core (details of this site are given in Table 1) showed that MSA apparently peaks in the winter period, and concentrations may be 10 times greater than measured elsewhere in the Antarctic. Clearly this result appears to challenge the established seasonal pattern of MSA deposition. In this paper, we present the anomalous results and compare these results with other sections of the same core, together with sections taken

from cores collected elsewhere in the Antarctic Peninsula to establish if this is an anomaly or a local or regional phenomenon.

2. Collection and analysis of the ice cores

We compare here the MSA profiles from sections of three Antarctic Peninsula ice cores taken from Dolleman Island on the east coast, a low altitude (398 masl) site close to the Weddell Sea, the Dyer Plateau at a higher altitude (1900 masl) on the spine of the Peninsula but at a similar latitude, and Gomez Nunatak at an intermediate altitude (1130 masl) on the spine but 500 km further south. Table 1 shows the physical details of the three sites, and Fig. 1 shows their location in the Peninsula. At Dolleman Island, the warmest site, summer melting is limited and only very rarely do ice layers exceed 1 cm thickness. During an exceptionally warm summer event (1984-85) observations of pit stratigraphy showed that percolation was contained within the upper snow layers of the previous winter. The two plateau sites showed negligible evidence of summer melting; even mm-thick ice layers are a rare occurrence. All three cores were collected by electromechanical drill and stored in the field in snow pits, trans-

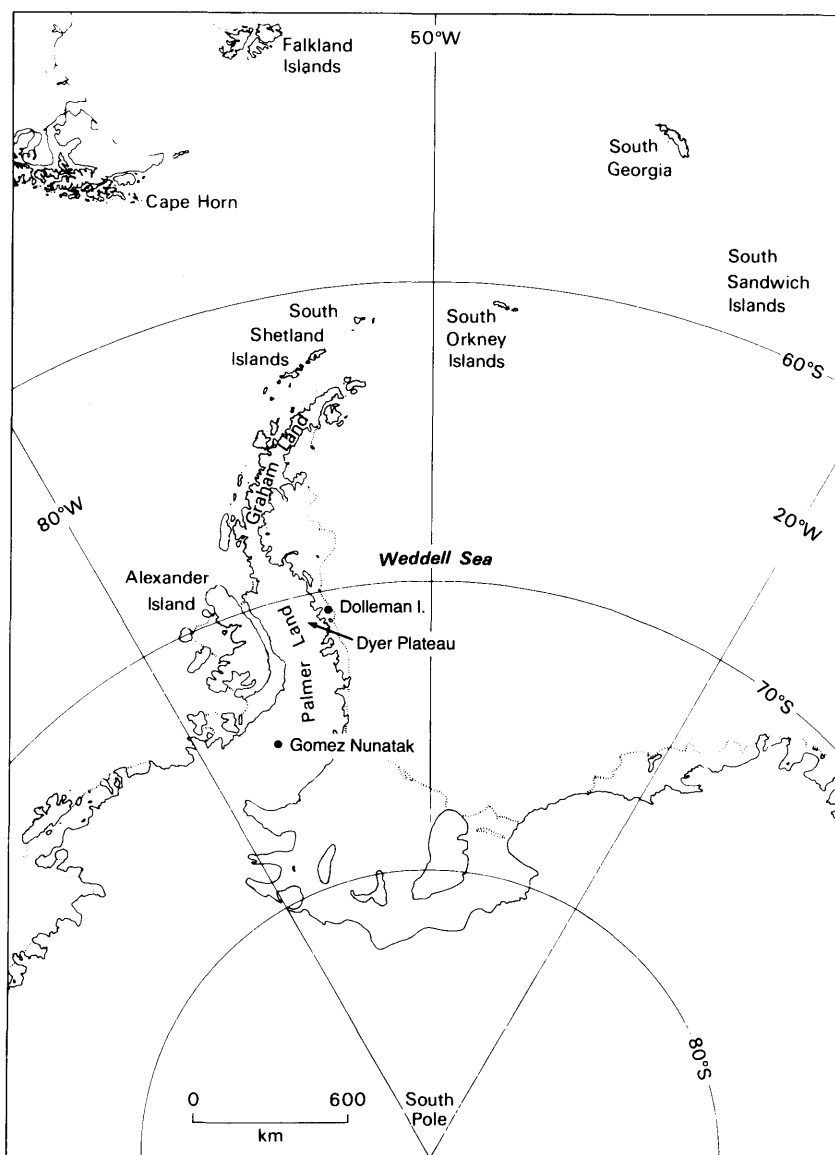


Fig. 1. Map of the Antarctic Peninsula region and the Weddell Sea showing the location of the three ice cores.

ported to the UK in a cold storage container at -22°C , and kept deep frozen in a large commercial frozen storage facility (-20°C) until subsampling and melting for analysis. The cores are not likely to have experienced temperatures warmer than the ambient in the storage pits in the field (which at the warmest site, Dolleman Island, would have reached about -10°C for short

periods). Stringent precautions were taken at all stages of the sample handling to avoid contamination, and all sample containers were scrupulously pre-cleaned in a multi-stage wash procedure with final rinses in 18 Mohm ultra-pure water. Each core was cut by band-saw to give, on average, at least 12 samples per annual accumulation layer. The outside of each core section was removed to

avoid including contamination from the drilling process, either by sub-coring or by cutting off the outer layer with a band-saw.

Analyses for MSA were conducted at University of Miami (Fig. 2a), and at BAS (Fig. 2b and Figs. 2a-c). At University of Miami, analyses were carried out using AG4/AS4 columns with sodium hydroxide eluants and a preconcentrator column. The detection limit was $0.1 \mu\text{g}/\text{kg}$ ($0.001 \mu\text{M}$). At

BAS, analyses were carried out on a Dionex 2010 ion chromatograph using an AS4A separator column and an isocratic eluent of 5 mM sodium tetraborate, degassed and kept under a blanket of helium to avoid absorption of carbon dioxide. Sample injection was via a $200 \mu\text{l}$ loop, which gave a detection limit of about $1 \mu\text{g kg}^{-1}$ ($0.01 \mu\text{M}$). The sulphate, chloride and nitrate ions were separately measured using the same columns but with the standard eluent and regenerant conditions, and using a concentrator column to achieve a sample size of 2 ml. The detection limit for these ions is similar to the MSA. Sample container blank levels were measured and found to be undetectable for MSA and at about the detection limit for the standard anions. The relative reproducibility for MSA determinations ranged from 10.9% at $0.13 \mu\text{M}$ to 5.0% at $2.6 \mu\text{M}$; for chloride 10.6% at $0.85 \mu\text{M}$ to 4.2% at $25.4 \mu\text{M}$ and for sulphate 7.7% at $0.31 \mu\text{M}$ to 3.6% at $9.4 \mu\text{M}$.

A series of 14 samples ranging in concentration of MSA from 6 to $119 \mu\text{g}/\text{kg}$, was analysed at both University of Miami and BAS. The difference between the two series of measurements (relative standard deviation 10.8%), was not significant at the 95% confidence level.

The cores were dated primarily by the oxygen isotope stratigraphy, although reference was also made to the strong seasonal cycle in nss-SO_4^{2-} (Mulvaney and Peel, 1988), which in places allowed confirmation of rather weak isotopic minima as true winter minima. Isotope data on the lower sections of both the Dyer Plateau and Dolleman Island cores are not yet available, so these sections are undated, but annual cycles can clearly be seen in the non sea-salt sulphate signal. The seasonality of the MSA and nss-SO_4^{2-} species along the core is considered relative to the oxygen isotope profile. Analysis of an 11-year sequence of mean monthly snowfall collections at Faraday ($65^\circ 15' \text{S}$, $64^\circ 16' \text{W}$) on the western side of the Peninsula (Peel et al., 1988) has shown a consistent, in-phase correlation ($R = 0.61$) between the stable isotope ratio and the mean monthly air temperature, with the annual isotopic minimum corresponding to early August (1 month). Similar behaviour is evident in corresponding data from Halley ($75^\circ 30' \text{S}$, $26^\circ 30' \text{W}$) situated adjacent to the Weddell Sea (International Atomic Energy Agency 1964-87). Snow accumulation throughout the Peninsula region is generally associated with

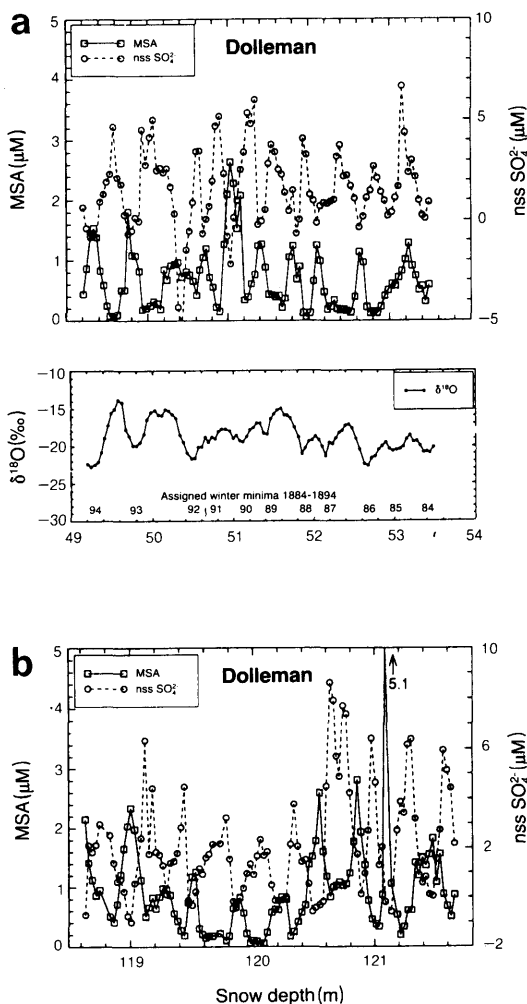


Fig. 2. Sections of Dolleman Island ice core: (a) from just above pore close off, the assigned winter minima in $\delta^{18}\text{O}$ is taken to be dated July of the year shown under the profile; (b) from well below pore close off, $\delta^{18}\text{O}$ not yet available.

frequent cyclonic activity, and at Faraday this results, on average, in snowfall occurring during 40% of 3-hourly meteorological observations throughout the year. Snowfall is distributed throughout the year, although as evident at Faraday there may be some increase during the equinoctial periods when there is an increase in cyclonic activity. Because the relatively large annual accumulation rate at the three ice core sites is deposited throughout the year by weather systems which also influence conditions at Faraday and Halley, we consider that the broad seasonal characteristics of the isotopic deposition pattern, especially the calendar month of the occurrence of the isotopic minima should be similar. In the following discussion, snow layers deposited around the time of the isotopic minima are considered to have fallen during the winter period.

3. Results

For each core, non sea-salt sulphate concentration has been calculated relative to chloride for which a comparable data set is available. In the case of Dolleman Island, a series of 1124 samples along the core give a mean molar Cl/Na ratio of 1.38 compared to the sea water ratio of 1.17, suggesting that there is no large-scale departure of chloride from the sea water ratio e.g., by volatilization in the presence of acids. We have assumed that similar behaviour applies at both Gomez and Dyer Plateau, where data for Na are unavailable. There is evidence for partial fractionation of the sea salt aerosol in the derived nssSO_4^{2-} data which show negative values during some of the winter troughs, most noticeable in the Dolleman Island core but also occasionally detected in the Gomez core. This behaviour does not affect the overall seasonal pattern of deposition which is considered in this paper.

Fig. 2 compares MSA with non sea-salt sulphate (nssSO_4^{2-}), calculated here as $[\text{SO}_4^{2-}]_{\text{nss}} = [\text{SO}_4^{2-}]_{\text{total}} - 0.052[\text{Cl}^-]$ (in mols l^{-1}), for two sections of Dolleman Island core. In both of these sections, one from just above pore close off, and one from well below close off, the MSA data are

out of phase with the nssSO_4^{2-} data. The 49–54 m section shows that nssSO_4^{2-} peaks in the summer period defined by $\delta^{18}\text{O}$, as is normal in Peninsula ice cores (e.g., Mulvaney and Peel, 1988; Mosley-Thompson et al., 1991) and elsewhere in Antarctica: e.g., Neumayer (Wagenbach et al., 1988), South Pole (Legrand and Delmas, 1984), Mawson (Prospero et al., 1991), and Law Dome (Ivey et al., 1986). However, in this section MSA peaks in the winter period. The antiphase relationship between MSA and nssSO_4^{2-} is even more clearly demonstrated in the lowest section where in several summer periods the MSA signal is essentially flat, while rising to very sharp winter peaks. This is a phenomenon not reported before, and appears to be anomalous.

Compared to the deeper sections, the phase relationship between the nssSO_4^{2-} and MSA in a near-surface section of the Dolleman core (Fig. 3a) is confused. In this section, there are peaks which are in phase (e.g., the two very large MSA peaks in the summers of 1975/76 and 1976/77) and others where the phase relationship is not clear. We have checked that this section of core has not suffered damage by partial melting during its storage history by measuring a short sequence of the same age in a separate short core from Dolleman Island and found identical results.

The profile of MSA, nssSO_4^{2-} and oxygen isotopes in Figs. 3b and c for Gomez Nunatak and the Dyer Plateau cover a similar period of time to the upper Dolleman profile, each having at least the years 1972 to 1975 in common. The section of the Gomez Nunatak core shows MSA concentrations of about a tenth of the values at Dolleman Island with peaks in summer, as defined by $\delta^{18}\text{O}$. Results from the upper section of the Dyer Plateau core show similar concentrations to Gomez and again demonstrate the peaks in MSA during the summer.

These two sets of results suggest that the out of phase character of MSA at Dolleman Island may be a localised phenomenon, and due perhaps in some way to its location very near to the biologically productive Weddell Sea region, or the high sea-salt flux experienced at this site. However, data from three short sections of deeper ice from the Dyer Plateau (Fig. 4), each representing approximately 1–2 years of snowfall, seem to display a slight departure from the in-phase relationship found in the upper section.

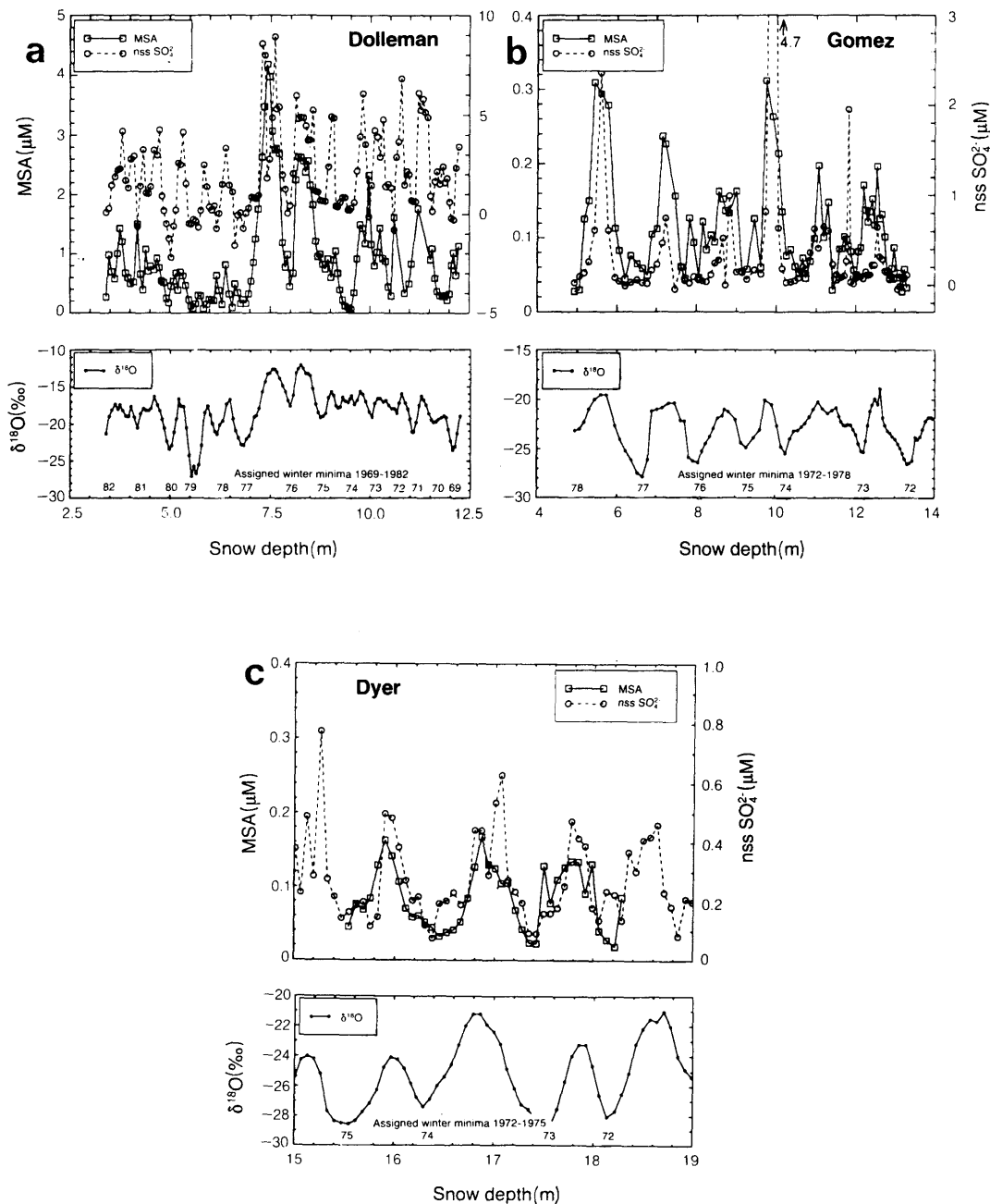


Fig. 3. Comparison of MSA (left-hand scale) and nssSO_4^{2-} (right-hand scale) in near surface sections of: (a) Dolleman Island; (b) Gomez Nunatak; (c) Dyer Plateau. In each case the assigned winter minima in $\delta^{18}\text{O}$ is taken to be dated July of the year shown under the profile.

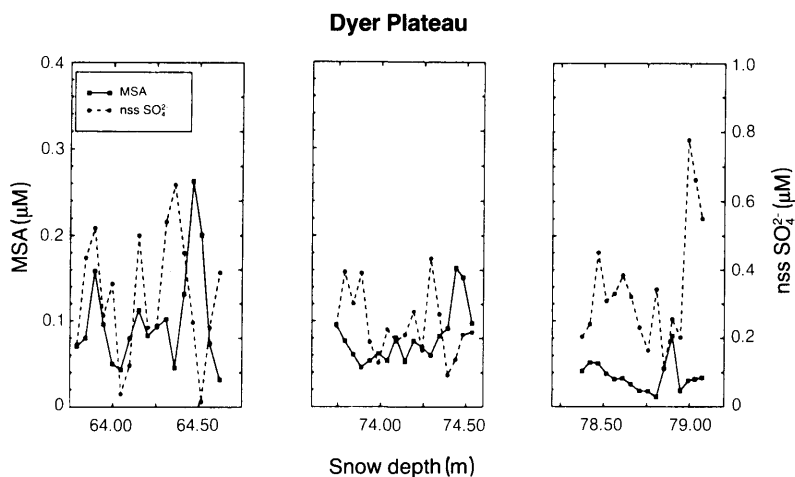


Fig. 4. Short sections of the Dyer Plateau core with 1–2 years snowfall represented in each case. $\delta^{18}\text{O}$ data not yet available.

4. Discussion

The oxidation of DMS in the atmosphere can be initiated by reactions with either OH or NO_3 , but in the unpolluted marine environment, the low levels of NO_3 mean that the OH radical is the primary route (Winer et al., 1984). Reaction of DMS with OH can proceed via either addition, or abstraction of a hydrogen atom, and either branch could lead to SO_2 or MSA (Yin et al., 1986). The abstraction route is thought to favour SO_2 (Barnes et al., 1988), which is subsequently oxidised to SO_4^{2-} , while addition may favour MSA (Hynes et al., 1986). Laboratory studies (Hynes et al., 1986) of the reaction kinetics have shown that the branching mechanism is strongly temperature dependent, with a 1:1 ratio of abstraction to addition at 285 K, while at colder temperatures the addition mechanism is preferred (about 3:1 in favour of addition at temperatures typical of the Antarctic Peninsula). Field experimental evidence for this is strong: in the warm South Pacific the molar ratio of MSA to nssSO_4^{2-} is approximately 0.06–0.07 (Prospero et al., 1991). In comparison, Berresheim (1987) found the average aerosol MSA/ nssSO_4^{2-} molar ratio to be 0.60 in air at sea level in the Gerlache Strait on the west of the Antarctic Peninsula and 1.01 in the Drake Passage in late summer, while at Mawson, a coastal Antarctic station, Prospero et al. (1991) found that

the ratio was 0.22. In ice cores, Ivey et al. (1986) found a ratio of 0.39 with a mean MSA concentration of $0.077 \mu\text{M}$ from an ice core collected at Law Dome. Here we have found the mean molar MSA/ nssSO_4^{2-} ratio to be between 0.3 and 0.5 (see Table 1), though note that particularly for Dolleman Island, the ratio can vary greatly at sub-annual resolution since the two are out of phase. The table suggests that the concentration of MSA and nssSO_4^{2-} falls off with altitude (or distance from source).

The Dolleman MSA data are clearly out of phase at depth with both the oxygen isotope and nssSO_4^{2-} data, with MSA reaching a maximum in the winter layer, but this is not the case near the surface. A similar phenomenon has been observed in deep ice from the 1989 Byrd Station core (K Osada, personal communication). It appears then that there may be evidence for movement of MSA within an ice core. The three Dolleman sequences suggest that this continues at least until pore close off, and perhaps further. As discussed earlier, the ratio of MSA to SO_4^{2-} can vary depending on temperature, and it may be tempting to speculate that Dolleman Island is a special site with a year-round flux of DMS, converted to MSA during the winter and SO_4^{2-} during the summer. However, the evidence is that this cannot be the case in the near surface section, and this alternative explanation seems improbable.

What mechanism could be the driving force behind such a redistribution of MSA during the diagenesis of ice? It is unlikely to be diffusion since this would tend to broaden the MSA peaks, nor presumably can it be driven by a concentration gradient since the evidence of change between the near pore close off section and the deepest Dolleman section is that the winter peak is becoming more sharply defined with increasing age, and the summer ice becomes more depleted in MSA.

Legrand et al. (1991) found that MSA was removed from sections of deep ice cores by washing the ice with ultra-pure water. The implication is that MSA was solubilized by the drilling fluid and may be more mobile than other ions under certain circumstances. Indeed, the solubility of MSA has been found to be extremely high in water, where it forms a very strong acid with a dissociation constant K_a of 73 mol l^{-1} (reported in Clegg and Brimblecombe, 1985). Although the freezing point of pure MSA is 20°C , eutectic compositions of strong acids commonly freeze substantially below 0°C , with many remaining liquid at well below the temperature of Antarctic ice. Mulvaney et al. (1988) showed that in the case of sulphuric acid, a large part of this acid found in ice cores could be located at grain boundaries. Depending on the bulk concentration of the sulphuric acid, these boundaries may form a series of interlinked veins of liquid in the ice. At a particular temperature, the concentration of the liquid in the veins is at the composition determined by the freezing point curve, if the temperature changes, either water freezes out or ice melts in order to maintain this composition. In effect, within the veins there is no concentration gradient, only a change in vein diameter to reflect changes in bulk composition. Like sulphuric acid, MSA also has a eutectic temperature substantially below zero: Berthoud (1929) reported a eutectic temperature of about -75°C at a composition of 16.4% mol MSA.

Thus, if MSA is located within veins at a eutectic composition, a mechanism exists for moving MSA against an apparent gradient in bulk concentration if necessary. However, this mechanism may not be very effective within the firn where the ice grains are not sufficiently well compacted to form a completely interlinked network of veins. We are also left with the problems of why the MSA should

move at all, and what causes it to concentrate within the winter layer. The latter may well be answered by a study of the reactions with the sea salt components at low temperatures since it is a characteristic of the ice core from Dolleman Island that the concentrations of the sea salt components are high ($\sim 12.6 \mu\text{M Na}$, $\sim 1.5 \mu\text{M Mg}$). For example, although the sodium salt of MSA is hygroscopic and readily dissolves in water, ruling out solid precipitation on contact with NaCl, the freezing temperature of $\text{CH}_3\text{SO}_3\text{Na}$ may be sufficiently above the local temperature for freezing to take place, effectively removing MSA from the liquid phase. We are not aware of any data showing freezing point curves for solutions of the Na or Mg salts of MSA; measurement may reveal a freezing point above the temperature within the ice pack.

5. Conclusion

At this stage, much of the argument is conjecture, and more effort is needed to confirm whether the MSA is indeed deposited during the summer period at Dolleman Island only to relocate during diagenesis to the winter ice layer, and at what depth or density this is taking place. We must also consider whether the processes leading to an out-of-phase relationship between MSA and non sea-salt sulphate are also significant for other constituents. However, MSA may be a special case because it is a strong acid with a low eutectic temperature. Careful seasonal analysis of other sections of the three cores studied here and of ice cores from areas with similar annual mean temperatures are needed. Unfortunately, until we understand the processes involving MSA in the ice, it is difficult to begin to use ice core evidence to deduce the mechanisms governing the ratio of DMS converted to MSA and non sea-salt sulphate in the Antarctic region before deposition in snowfall.

Irrespective of the mobility of MSA in ice at these relatively warm sites, the long term trend should be conservatively maintained, and the usefulness of MSA as a marine biological activity indicator should not be compromised. Data from ice cores in this region, where high accumulation rates allow annual or sub-annual resolution, should reveal a valuable record of the flux of

MSA and sulphate from the surrounding oceans over the last few centuries. The comparison with palaeoclimate data derived from the same ice cores

will be important in understanding the link between marine biological activity and climate change.

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