

Methanesulphonate and non-sea salt sulphate in aerosol, snow, and ice on the East Antarctic plateau

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Abstract: This investigation reports the first simultaneous measurement of methanesulphonate (MSA) and non-sea salt sulphate (NSSS) in aerosols, surface snow, and ice core samples for a continental site in Antarctica (78°S, 139°E, elevation 2849 m). Aerosol MSA concentrations ranged from 0.09–0.43 nmol m⁻³ STP (median 0.14 nmol m⁻³) and were generally lower than those observed at coastal Antarctic sites. NSSS concentrations varied from 0.66–1.32 nmol m⁻³ stp (median 0.88 nmol m⁻³), comparable to those reported for other continental Antarctic locations. Whereas the MSA:NSSS molar ratio in aerosol samples was in the range 12.7–32.5% (median 17.0%), the ratio down a snow pit and ice profile varied from 1.14–55.6% (median 3.50%), reflecting the variability to be expected over a period of a decade. The chemical composition and low MSA content suggests an origin of aerosols consistent with long range transport from mid-latitudes.

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Introduction

The hypothesis that dimethylsulphide (DMS) can exert an influence on global climate (Charlson *et al.* 1987) and the hydrological cycle (Mészáros 1988) still intrigues many and is the impetus for much sulphur research, including the present study. Primarily of marine biogenic origin, DMS evades to the atmosphere and can be oxidized to form methanesulphonate (MSA) and non-sea salt sulphate (NSSS). These constituents aggregate to form aerosols, known as condensation nuclei (CN) and cloud condensation nuclei (CCN) (Andreae *et al.* 1995). The consequent formation of clouds in the marine troposphere influences the planetary albedo and can cause a cooling effect which may offset the current trend in global warming. Both the magnitude and sign of the proposed climate stabilizing mechanism are, however, still controversial (Kiehl & Briegleb 1993). Since notable uncertainties at each stage of the mechanism make stepwise testing difficult, researchers have looked to ice core records, and particularly the MSA:NSSS ratio (Legrand *et al.* 1988, Legrand & Feniet-Saigne 1991), for evidence of changes in DMS-derived species during periods of stable and changing climate as an overall test of the so-called CLAW (Charlson *et al.* 1987) hypothesis. Additionally, the climate related interpretation of these ratios in ice is still controversial because of uncertainty about the representativeness of their concentrations over the polar plateau, sources of these sulphur-containing aerosols, and untested assumptions about the similarity of size distributions between MSA and NSSS both at the deposition sites and along their transport pathways.

Although the principal aerosol end product of DMS oxidation is NSSS, enough MSA is formed to make the MSA:NSSS ratio an attractive method for apportioning the sulphate burden amongst its possible sources: DMS, volcanoes, and anthropogenic SO₂. However, the yield of MSA from DMS oxidation is highly variable. A MSA:NSSS ratio of about 6–7% has been observed in tropical regions (Savoie & Prospero 1989, Bates *et al.* 1992, Pszenny 1992, Huebert *et al.* 1993, Huebert *et al.* 1996). In the mid-latitudes MSA formation is apparently slightly more efficient, generating an MSA:NSSS ratio of 6–12% in unpolluted areas (Savoie & Prospero 1989, Ayers *et al.* 1991, Huebert *et al.* 1996). Polar regions, however, are strikingly different with various studies observing values to be about 60% (Pszenny *et al.* 1989), 40–100% (Berresheim 1987), 15–40% (Savoie *et al.* 1992) and in the range 7–40% with a median of 30% (Wylie *et al.* 1993). At the coastal site of Mawson, Prospero *et al.* (1991) found the mean MSA:NSSS ratio to be *c.* 22%. Similarly, elevated MSA:NSSS ratios have been observed in aerosols and snow over the Greenland ice sheet during summer, consistent with high latitude source regions (Jaffrezo *et al.* 1994). This much higher ratio near the poles has been attributed to a strong temperature-dependence of branching ratios in the DMS oxidation mechanism (Hynes *et al.* 1986). Although a latitudinal gradient exists in the MSA:NSSS ratio, temperature alone can not explain the variation (Ayers *et al.* 1991, Bates *et al.* 1992). Furthermore, Jaffrezo *et al.* (1994) found the relationships between sea level and the ice sheet were very different for NSSS and MSA. These authors

emphasized the importance of making aerosol measurements at the altitude of the ice, such as have been performed in this study, for understanding both depositional processes and the potential for post-depositional changes.

There have been relatively few studies of aerosol MSA and NSSS in Antarctica, and most have been confined to coastal regions. A comprehensive investigation of aerosol MSA and NSSS concentrations has been carried out at the coastal stations of Mawson (Prospero *et al.* 1991, Savoie *et al.* 1993) and Georg von Neumayer (Minikin & Wägenbach 1990). Both locations have clearly revealed a distinct seasonal trend in concentrations and inferred a local marine biogenic source for these aerosols. In addition, short term studies of aerosol MSA and NSSS concentrations in the marine troposphere of the Antarctic Peninsula region have been conducted (Berresheim 1987, Pszenny *et al.* 1989). To date, aerosol MSA and NSSS concentrations have been observed not to differ much between coastal sites such as Mawson (Prospero *et al.* 1991) and Georg von Neumayer (Minikin & Wägenbach 1990), nor even at Cape Grim (41°S) (Ayers & Gras 1991), implying similar aerosol sulphur chemistry over a wide region in the Southern Hemisphere.

MSA and NSSS deposition on the Antarctic plateau has been investigated at relatively few sites. These continental sites have included Vostok (Legrand *et al.* 1988), Dome C (Saigne & Legrand 1987), Byrd station (Langway 1991) and the South Pole (Legrand & Feniet-Saigne 1991). In these studies, MSA concentrations have been observed to vary from a background level at the detection limit of $0.01 \mu\text{eq l}^{-1}$ up to $0.62 \mu\text{eq l}^{-1}$. Elevated MSA concentrations, as high as $2.08 \mu\text{eq l}^{-1}$, have been observed at maritime locations such as Dolleman Island in the Antarctic Peninsula region (Mulvaney *et al.* 1992). Additionally, MSA concentrations from 0.01 – $0.28 \mu\text{eq l}^{-1}$ (mean $0.07 \mu\text{eq l}^{-1}$) have been observed at the coastal Antarctic site of Law Dome (Ivey *et al.* 1986). MSA concentrations in falling snow samples at the coastal site of Dumont d'Urville have been reported in the range from 0.01 to $0.46 \mu\text{eq l}^{-1}$ (median $0.04 \mu\text{eq l}^{-1}$) (Maupetit & Delmas 1992). The MSA:NSSS molar ratio in ice cores exhibits significant spatial variations with elevation and/or with distance from the coast. Coastal regions can exhibit a wide range in ratios, from values <10% (Savoie *et al.* 1993) up to 100% (Maupetit & Delmas 1992). MSA:NSSS ratios *c.* 40% (Ivey *et al.* 1986), between 30–50% (Mulvaney *et al.* 1992) and in the range 4–44% (Legrand *et al.* 1988) have been measured in Antarctic ice cores. MSA:NSSS ratios observed at Antarctic plateau sites are generally much lower relative to values for coastal sites, reflecting the long range transport and sporadic input of sulphur compounds to the remote Antarctic interior. Legrand & Feniet-Saigne (1991) presented ice core MSA:NSSS data over the last glacial-inter-glacial cycle that showed clearly higher ratios during the colder climatic periods; however, these values are lower than recent aerosol literature suggest for high latitude regions.

Measurements for sulphur species in Antarctica remain

relatively limited, especially for aerosol MSA and NSSS at plateau sites. This investigation reports the first simultaneous measurement of MSA and NSSS in aerosols and surface snow for a continental site in Antarctica. We also present measurements for a short ice core in order to have an appreciation of variations in MSA:NSSS molar ratios at this site during the past decade. Other ions have been analysed, but they are discussed here only in so far as they validate analytical results. Such studies are important in order to understand better the source apportionment of biogenic sulphur in Antarctic aerosols.

Methodology

Sample collection

High volume aerosol, surface snow, snow pit and firn core (5.17 m length) samples were collected at a site ($78^{\circ}1.5'S$, $139^{\circ}48.2'E$, elevation 2849 m) on the East Antarctic plateau. Figure 1 shows the location of this site, together with other locations in Antarctica that have been used for the study of MSA and NSSS in snow or aerosols. The nearest coastline was *c.* 600 km to the east. Sampling was carried out between 24 November 1990 and 26 January 1991. The prevailing winds were continental in origin, predominately from the direction of Vostok (Fig. 2). Wind speeds were typically $<5 \text{ m s}^{-1}$, consistent with a weak surface wind gradient due to the down slope flow characteristic of the high central plateau (Parish 1988). Persistent inversion winds over the Antarctic plateau during the summer months depend on the orientation of the surface topography (Schwerdtfeger 1984). The surface topography at this site was characterized by low lying, southerly orientated sastrugi with light drifting and blowing snow being regular events. Cloud coverage was minimal,

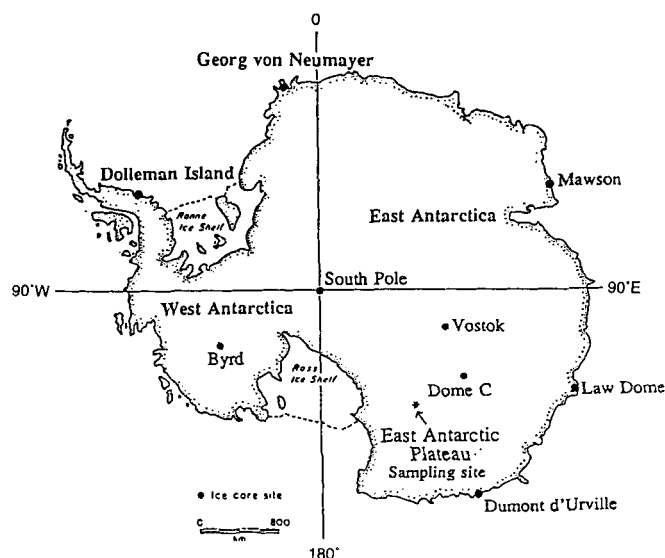


Fig. 1. Location of the sampling site on the East Antarctic plateau.

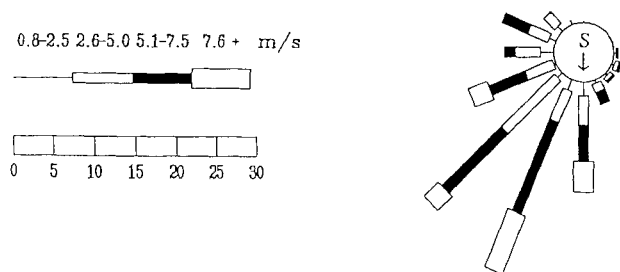


Fig. 2. Wind rose at the sampling site for the period 24 November 1990–26 January 1991.

usually < 2/8 cirrus, due to the inherently low atmospheric water content present over the cold polar plateau. The air temperature was low, ranging from -27 to -13.5°C with a mean of -22.7°C . Diamond dust appeared to be the main form of precipitation.

Concerned about potential contamination (Legrand *et al.* 1984, Saigne & Legrand 1987), special safeguards were taken both in the field and laboratory (see Wylie 1993 for details). Snow and ice sampling was conducted 2 km upwind from the aircraft landing site. During all sample handling procedures, personnel wore clean room clothing and used pre-washed teflon tools and associated sampling equipment. The ice core and snow pit samples were handled in specially excavated pits in order to protect samples from blowing snow.

Surface snow samples ($n = 3$) were collected directly into pre-washed (Milli-Q water) 2 l low density polyethylene (LDPE Nalgene) bottles which were then capped and sealed in double LDPE bags. Snow pit samples ($n = 41$) were taken by pushing a pre-cleaned stainless steel tube through the shaven face of the pit wall. Snow samples were taken every c. 5 cm from the surface down to 2.35 m. A series of random samples ($n = 6$) was also taken throughout the pit face as replicates for analysis of major constituents. Snow pit samples were transferred directly into pre-washed 250 ml LDPE bottles with screw cap lids which in turn were sealed in pre-washed LDPE bags. An ice core was obtained adjacent to the snow pit using a SIPRE hand auger. Although a core 5.17 m in length was obtained, the upper 2.05 m was abandoned as it was brittle and consequently would shatter upon cutting. The ice core was cut sequentially into lengths (typically 4–6 cm) on site, and then put into pre-washed LDPE bottles and bagged. All snow and ice samples were kept frozen (c. -18°C) until analysed in New Zealand. Sample bottle blanks were always included in each sampling series.

High volume aerosol sampling was conducted at a clean site 200 m upwind from the camp only when the wind speed exceeded 5 m s^{-1} from the sector 80° through south to 260° . Bulk aerosol samples were collected on pre-washed Whatman 41 filters at a flow rate of c. $0.9 \text{ m}^3 \text{ min}^{-1}$ STP (face velocity, $V_f \sim 32 \text{ cm s}^{-1}$) with a collection efficiency of 90% (Savoie

et al. 1989, Wylie 1993). Operational filter blanks ($n = 3$) were obtained by pumping through the filter for only a few minutes and the results are presented in Table I. After sampling, exposed filters were immediately placed into pre-cleaned petri dishes and sealed in LDPE bags. All aerosol and ice core samples were stored in the field and returned to New Zealand frozen at c. -18°C .

Chemical analyses

Analytical precautions ensured that sample preparation was performed within a class-100 laminar flow bench. This included ultrasonic extraction of the soluble aerosol ions into Milli-Q water and melting of all snow and ice samples in a pre-cleaned desiccator. An atmosphere of oxygen free nitrogen, which had been passed through molecular sieve 4A to remove water vapour and oxalic acid scrubbers to remove base contaminants, was used to purge the desiccator. Each 4–5 cm sub-sampled ice core and snow pit sample typically yielded >5 ml of melt water.

The major soluble ion species present in the atmospheric aerosol extracts and snow samples were analysed by ion chromatography (IC) with conductivity detection (Wylie 1993). Whereas anions were analysed within one week of melting, cations were determined within 24 h to prevent atmospheric contamination. In all cases, care was taken to equilibrate solutions to ambient room temperature prior to analysis. A Dionex Model QIC (Sunnyvale, CA, USA) IC instrument equipped with an HPIC AS4A analytical column and an HPIC AS4G guard column was used for the isocratic separation of the anions. Cations were analysed using a Dionex Model 2000i/SP IC system equipped with Fast Sep I and II separator columns in combination with a column switching technique. Fresh standard solutions were prepared after about every 50 sample analyses. The calibration curve entered into the integrator was checked using standard solutions after every 15–20 samples. From replicate injections, the analytical precision was $\pm 6\%$ for most analytes.

The observed ion detection limits are presented in Table I. Further details of technique validation and consideration of blanks is available elsewhere (Wylie 1993). A detection limit of $0.02 \mu\text{eq l}^{-1}$ was obtained for MSA, SO_4^{2-} and Na^+ in melted ice and aerosol extracts. This corresponded to a detection limit of 0.02 nmol m^{-3} for these species in a typical 400 to 500

Table I. Blanks and detection limits

	Na^+	Cl^-	SO_4^{2-} ($\mu\text{eq l}^{-1}$)	NSSS	MSA
Detection limit	0.09	0.06	0.04	0.02	0.02
R.S.D (%)	7	9	6	7	7
Snow sample container blanks	<0.09	0.06	0.04	<0.02	<0.02
Milli-Q blank	0.10	<0.06	<0.04	<0.02	<0.02
Aerosol detection limit ^A	0.05	0.04	0.02	0.005	0.004

^A All concentrations in nmol m^{-3}

m³ aerosol sample. An indication of the reproducibility of the snow pit sampling technique was obtained from MSA, NSSS and Na⁺ concentrations at various random depths. Considering the surface to 2.05 m snow pit samples, there were no significant differences in concentrations for MSA and NSSS in the random and soft snow layers when compared with the concentrations measured in the sequentially sampled snow.

NSSS calculations

NSSS concentrations for aerosol and snow samples were calculated by assuming that Na⁺ was a conservative indicator of marine origin using:

$$[\text{NSSS}] = [\text{SO}_4^{2-}] - 0.060 [\text{Na}^+]$$

where 0.060 is the mole ratio SO₄²⁻:Na⁺ for sea water. Na⁺ content has been used in preference to Cl⁻ concentrations because the latter can be volatilized following the reaction of sea salt with acid (Legrand & Delmas 1988). Inter-element ratios for the ice and snow samples provided evidence of the volatilization of chlorine. Although the mean Cl⁻/Na⁺ ratio of 1.05 was similar to that for sea water ratio, namely 1.18, the Cl⁻/Na⁺ ratio values ranged from 0.26–10.4. In contrast to previous studies (Legrand *et al.* 1984), the relatively minor crustal contribution has not been subtracted as the Al content of the Antarctic snow was not determined.

Results and discussion

Aerosols

The chemical composition of high volume aerosol samples ($n = 7$) is indicated in Table II. The low concentrations of aerosol constituents were typical of pristine Antarctic regions (Savoie *et al.* 1992). This observation was consistent with the katabatic winds typical of a continental interior rather than from close proximity to the open ocean. In particular, low Na⁺ concentrations (mean 0.27 nmol m⁻³) were comparable to summer Na⁺ concentrations observed at the South Pole (mean 0.30 nmol m⁻³) rather than the elevated concentrations (3.85 nmol m⁻³) common at coastal sites such as at Georg von Neumayer (Wägenbach *et al.* 1988).

Aerosol MSA concentrations, shown in Fig. 3, ranged from 0.09–0.43 nmol m⁻³ (median 0.14 nmol m⁻³). A single elevated value occurred during 5–6 January 1991, coincident with a period of no cloud cover and light ($c. 2.5 \text{ m s}^{-1}$) variable winds ranging in direction from an easterly (coastal) through south to a westerly sector. In contrast, the lowest aerosol MSA concentration (1–2 January) corresponded with steady winds ($c. 6 \text{ m s}^{-1}$) from the south with 1/8 stratus cloud coverage. As shown in Table III, the observed range (0.09–0.43 nmol m⁻³) in aerosol MSA concentrations at the site was comparable aerosol MSA concentrations (mean 0.22 nmol m⁻³) found over the ocean in subantarctic regions (Berresheim 1987) and was also similar to the lowest values

Table II. Composition of atmospheric aerosols collected on the Antarctic plateau.

	Na ⁺	Cl ⁻	SO ₄ ²⁻	NSSS	MSA	% MSA/ NSSS
	(nmol m ⁻³)					(mol/mol)
5–6/12/90	0.35	0.16	0.68	0.66	0.12	18.2
10–11/12/90	0.14	0.26	0.73	0.72	0.11	15.2
16–17/12/90	0.17	0.11	0.89	0.88	0.15	17.0
20–21/12/90	0.31	0.17	0.95	0.93	0.21	22.5
1–2/1/91	0.33	0.10	0.73	0.71	0.09	12.7
5–6/1/91	0.29	0.10	1.34	1.32	0.43	32.5
14–15/1/91	0.31	0.30	1.12	1.10	0.14	12.7
Median	0.33	0.16	0.89	0.88	0.14	17.0
Maximum	0.35	0.30	1.34	1.32	0.43	32.5
Minimum	0.14	0.10	0.68	0.66	0.09	12.7
South Pole ^A	0.31			0.86		
South Pole ^B		2.80				
Mawson ^C	3.70	3.05	0.44	2.40	0.47	19.6

A, B & C aerosol values are summer means from ^A(Tuncel *et al.* 1989), ^B(Gras 1983), ^C(Prospero *et al.* 1991).

(0.05–0.81 nmol m⁻³) typically observed in regions of the equatorial Pacific marine troposphere (Saltzman *et al.* 1983). The values are somewhat lower than summertime aerosol MSA concentrations at coastal Antarctic sites such as Mawson (mean 0.31–0.63 nmol m⁻³, Prospero *et al.* 1991), Georg von Neumayer (mean 0.63 nmol m⁻³, Minikin & Wägenbach 1990) and Ross Island (1.80 nmol m⁻³, Wylie *et al.* 1993).

Aerosol NSSS concentrations, ranging from 0.66–1.32 nmol m⁻³ with a median value of 0.88 nmol m⁻³ (Table II), varied in a similar manner to aerosol MSA concentrations (Fig. 3). The mean aerosol NSSS concentration, 0.90 nmol m⁻³ (Table III), was a factor of about two lower than the summertime aerosol NSSS concentrations reported for the

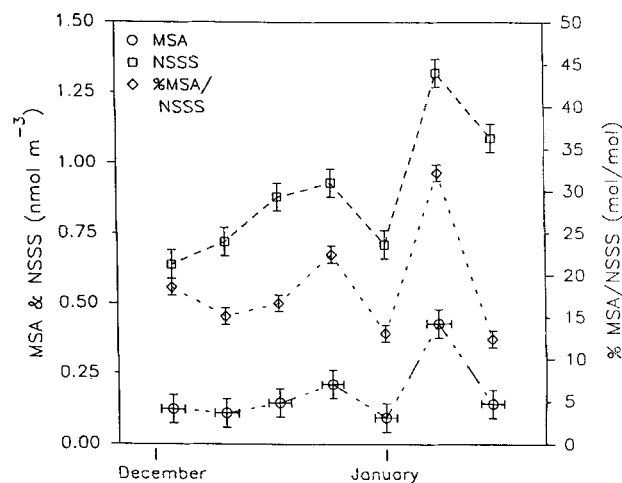


Fig. 3. Methanesulphonate and non-sea-salt sulphate concentrations (nmol m⁻³) and the ratio of MSA:NSSS (%) for aerosol samples from the Antarctic plateau.

Table III. Comparison of sulphur species concentrations in Antarctic aerosols.

Location	MSA (nmol m ⁻³)	NSSS (nmol m ⁻³)	% MSA:NSSS (mol:mol)	References
Subantarctic Peninsula Region (50–65°S)	0.06–0.36 A (0.22)	-1.17–0.34 A (0.34)	47–56 A (53)	(Pszenny <i>et al.</i> 1989)
Mawson (68°S, 63°E)	0.02–0.03 W 0.31–0.63 S (0.20)	0.07–0.09 W 2.19–2.60 S	15–40 S (22)	(Prospero <i>et al.</i> 1991)
Georg von Neumayer (70°S, 8°W)	0.03 W 0.63 S	0.41 W 2.50 S		(Minikin & Wägenbach 1990)
McDonald Beach (77°S, 166°E)	0.60–3.46 S (1.80)	3.05–11.6 S (6.77)	7–40 S (27)	(Wylie <i>et al.</i> 1993)
East Antarctic plateau (78°S, 139°E)	0.09–0.43 S (0.18)	0.66–1.32 S (0.90)	13–33 S (19)	(this study)
South Pole (90°S)		0.44 W 1.79 S		(Cunningham & Zoller 1981) (Tuncel <i>et al.</i> 1989)

A, S and W refer to Autumn, Summer and Winter. Concentrations and ratios are ranges with means in parenthesis.

South Pole, namely 1.79 nmol m⁻³ (Tuncel *et al.* 1989). Still higher summer aerosol NSSS concentrations have been reported at Mawson, mean 2.40 nmol m⁻³ (Prospero *et al.* 1991), and Georg von Neumayer, mean 2.5 nmol m⁻³ (Minikin & Wägenbach 1990). The aerosol NSSS concentrations at this continental Antarctic position were also lower, by at least a factor of two, than those measured in equatorial or South Pacific marine regions (Savoie & Prospero 1989).

A plot of the aerosol MSA:NSSS molar ratios is shown in Fig. 3 and the results are presented in Table II. The aerosol MSA:NSSS molar ratio ranged from 12.7–32.5% (median 17.0%). The aerosol MSA:NSSS ratio trended with the observed aerosol MSA and NSSS concentrations. Although these ratios were significantly higher than values <10% considered typical of equatorial and South Pacific ocean regions (Saltzman *et al.* 1983, Wylie & de Mora 1996), a similar summer MSA:NSSS ratio of 16% has been observed at Cape Grim (Ayers *et al.* 1991). Also, aerosol MSA:NSSS ratios ranging from 6.54–40.4% (median 30%) have been observed at a coastal site on Ross Island during the summer (Wylie *et al.* 1993). Several factors can influence the MSA:NSSS molar ratio. Firstly, it should be noted that non-marine NSSS input is generally regarded as being weak over the Antarctic plateau (Delmas 1992a) but volcanic eruptions can elevate the background NSSS content for a period of between 2–3 years. Although Mount Erebus (77°S, 167°E) is the only significant continuous sulphur producer south of 60°, it is generally concluded that this volcano represents only a minor contributor (<5%) to background sulphur concentrations over the Antarctic plateau (Delmas *et al.* 1982, Rose *et al.* 1985). Major volcanic eruptions, such as Mount Agung (8°S, 115°E) in 1963 and Mount Krakatoa (6°S, 105°E) in 1883, have made significant sporadic contributions to the NSSS content of Antarctic snow and can consequently be used to date ice core horizons (Delmas

1992a). Secondly, an investigation of the size distribution of aerosol MSA and NSSS in the McMurdo Sound region has shown that aerosol NSSS was incorporated into fine and coarse particles, the later being subject to deposition near the coast (Wylie *et al.* 1993). In contrast, aerosol MSA was predominately located on sub-micron particles which can be more efficiently transported to the plateau. Thirdly, colder temperatures are likely to enhance production of MSA. According to the experimentally determined relative OH addition and H abstraction rates (Hynes *et al.* 1986), a temperature decrease from c. 0°C (coastal Antarctic regions) to -23°C (this plateau site) should result in a factor of about 7.7 increase in the branching ratio of addition to abstraction. However, the observed median high volume aerosol MSA:NSSS molar ratio relative to coastal sites was only 3.6 higher.

Whereas in coastal regions of Antarctica local emissions of biogenic DMS are accepted as the prime source of sulphur in aerosols, the origin of sulphur aerosols in the continental atmosphere remain subject to debate. Comprehensive studies at Mawson (Prospero *et al.* 1991) and Georg von Neumayer (Minikin & Wägenbach, 1990) have revealed a distinct seasonal trend in aerosol MSA and NSSS concentrations with a summer maximum, consistent with a seasonal cycle in marine biogenic productivity and photochemistry. Savoie *et al.* (1992) used a regression analysis to conclude that most of the NSSS at Mawson was biogenic, but that a significant fraction, even at this coastal site, was of a continental origin. Legrand *et al.* (1992) argued that the atmosphere of coastal Antarctica was supplied by local DMS emissions, but that the high polar plateau was influenced by DMS oxidation products from more temperate regions, transported through the mid to upper troposphere. Other authors believe that coastal sources are responsible for most of the sulphur found in the ice, reasoning that transport in the lower- to mid-troposphere

delivers gases and aerosols from the surrounding Southern Ocean to the polar plateau (Gras 1983, Shaw 1979, Hogan 1986). It is clear that mid-latitude air moves toward the poles throughout much of the year. Mroz *et al.* (1989) presented tracer evidence of the rapid (several days) transport of gases and aerosols from the mid-latitudes to the surface of the polar plateau during the summer months. In October, a tracer released into the marine boundary layer at 64°S reached the South Pole in just a few days. Therefore, it is evident that conclusions extrapolated from variations in the MSA and NSSS content of Antarctic ice core samples is controversial primarily because of the lack of spatial MSA and NSSS data, and the variety of assumptions, including a similarity of transport and aerosol size distributions over climatically very different areas. Observations presented here are important in contributing to the sparse data available for the Antarctic plateau, but are not unequivocal in its interpretation. The chemical composition and low MSA content suggests an origin of aerosols consistent with long range transport from mid-latitudes. Given the similarity of MSA:NSSS ratio between this site and Ross Island (Wylie *et al.* 1993), a coastal Antarctic source cannot be discounted but circumstances seem to mitigate against this interpretation. Whereas the lower concentrations in the interior could be explained by depositional losses along the transport path, the aerosol MSA and NSSS at Ross Island exhibited markedly different size distributions which would certainly be subject to differential settling during transport.

No direct measurements of MSA or NSSS were made in falling surface snow, and hence, a deposition velocity using the respective aerosol and surface snow concentrations for this species cannot be made. However, an estimate of the dry deposition rate of aerosol MSA and NSSS has been calculated using a deposition velocity of 0.005 m s⁻¹ (Savoie & Prospero 1989). The median aerosol MSA and NSSS concentrations in Table II have been used. The estimated median dry deposition rates for aerosol MSA and NSSS are 0.06 μmol m⁻² d⁻¹ (0.70 mg S m⁻² y⁻¹) and 0.38 μmol m⁻² d⁻¹ (4.43 mg S m⁻² y⁻¹), respectively. The mean daily flux, representing a summertime deposition rate, is predominately in the form of NSSS. The total sulphur flux corresponded to 5.13 mg S m⁻² y⁻¹, with MSA representing only about 14% of this figure. Thus, aerosol MSA deposition was a relatively minor sink for biologically derived sulphur at the site. Comparison with other sites is difficult in that there is a distinct lack of MSA and NSSS dry deposition rates reported for Antarctica. Estimated dry deposition rates are 0.09 and 1.50 μmol m⁻² d⁻¹ for aerosol MSA and NSSS, respectively, in coastal Antarctic regions (Pszenny *et al.* 1989). The sulphate deposition rate at the South Pole was calculated to be 1.36 mg S m⁻² y⁻¹ (Delmas 1992b). For the Southern Hemisphere, NSSS dry deposition rates ranged from 6–33 mg S m⁻² y⁻¹ (Varhelyi & Gravenhorst 1983). Thus, NSSS and MSA dry deposition values for this plateau site appear reasonable.

Surface snow

The median concentration of MSA in surface snow (Table IV) was 0.07 μeq l⁻¹, in good agreement with background MSA concentrations measured down a 2700 m ice core at Vostok over the last climatic cycle (Legrand *et al.* 1988) and MSA concentrations (mean 0.06 μeq l⁻¹) measured in snow at the South Pole (Legrand & Feniet-Saigne 1991). Similarly, MSA levels in coastal Antarctic precipitation ranged from 0.06–0.09 μeq l⁻¹ (Maupetit & Delmas 1992, Pszenny *et al.* 1989). MSA was a relatively minor contribution to the total sulphur deposition. The NSSS concentration measured in surface snow was much larger, with the median NSSS concentration of 1.78 μeq l⁻¹ being comparable to previous Antarctic studies (Legrand & Delmas 1984, Pszenny *et al.* 1989).

The surface snow MSA:NSSS molar ratio of 7.8% is in good agreement with values reported for remote Pacific marine sites (Saltzman *et al.* 1983), and also with background ratios of about 6% reported for coastal Antarctic regions (Maupetit & Delmas 1992, Pszenny *et al.* 1989). The MSA:NSSS molar ratio in surface snow was significantly lower than that observed in the aerosol (median 17.0%). This result was surprising as the MSA and NSSS content of the deposited snow is assumed to be closely related to the chemical composition of the atmospheric aerosols. As blowing snow events were common at this site, it is possible that the surface snow samples were collected *in situ* with aged blowing snow. However, the driving air/snow fractionation mechanisms remain poorly understood and it is hard to resolve the low surface snow MSA:NSSS molar ratio with the higher ratio observed in the aerosol.

Snow pit and ice core

A short firn core was collected and analysed primarily for comparison of MSA:NSSS ratios with those measured in the aerosols and to obtain a record of the inputs of these two sulphur components in the recent past. Concentrations of MSA and NSSS in the ice core, snow pit and surface snow samples are presented in Table V and, together with Na⁺, are depicted in Fig. 4. The Na⁺ depth profile can be used to indicate the frequency of marine air masses injected over the Antarctic continent (Legrand & Kirchner 1988). The Na⁺

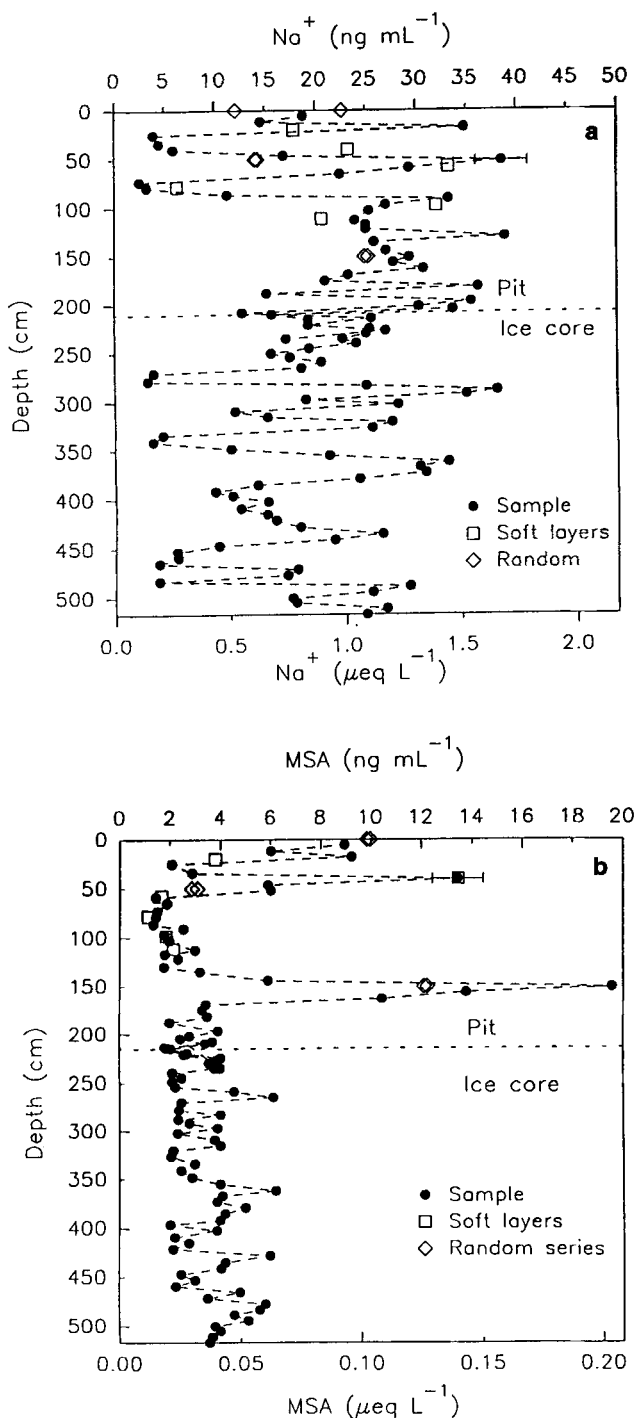
Table IV. Comparison of the composition of surface snow.

	Na ⁺	Cl ⁻	SO ₄ ²⁻	NSSS	MSA	%MSA: NSSS
			(μeq l ⁻¹)			(mol:mol)
This work (14/1/91)	0.36	0.83	1.84	1.80	0.07	7.8
South Pole ^A	0.63	1.25	1.50	1.04	0.06	12.0
South Pole ^B	0.17	0.11	0.89	1.59	0.15	9.43

^A (Legrand & Delmas 1984), ^B (Legrand & Feniet-Saigne 1991)

profile (Fig. 4a) does not exhibit a well defined seasonal cycle as has been previously observed at other polar plateau sites (Delmas 1992a). The median Na^+ concentration was $1.09 \mu\text{eq l}^{-1}$ with a minimum and maximum of 0.10 and $3.92 \mu\text{eq l}^{-1}$, respectively. The solute concentrations reported here are in good agreement with other ice core studies in Antarctica (Legrand & Delmas 1984).

The MSA profile (Fig. 4b) can be described as having a



baseline value of about $0.03 \mu\text{eq l}^{-1}$ with occasional large peaks up to $0.20 \mu\text{eq l}^{-1}$. The MSA distribution down the ice core presented here appeared to follow a weak seasonal cycle corresponding to about 46 cm of snow depth. This observation agreed well with oxygen isotope data which indicated an annual deposition of about 45 cm of snow per year (Harvey unpublished data). The apparent seasonal pattern of MSA was similar to that of NSSS (Fig. 4) with a maximum presumably during summer which is linked to elevated marine biogenic activity and atmospheric photochemical processes. A factor of about 20 difference between the maximum and minimum MSA values is lower than the factor of 30 sometimes recorded for coastal Antarctic sites (Maupetit & Delmas 1992). This observation is consistent with East Antarctic Plateau sites often being isolated from the penetration of large scale meteorological disturbances. The snow profile revealed that hard ice layers, which are probably indicative of summer melt, corresponded to MSA peaks at about 20, 50 and 150 cm (Fig. 4b). At a snow depth of about 148 cm, MSA concentrations increased steadily to peak at $0.20 \mu\text{eq l}^{-1}$ which was a factor of about 6 higher than the median background MSA level ($0.03 \mu\text{eq l}^{-1}$). From Table V, MSA represents a relatively minor (median 0.7%) portion of the total anion and total sulphur burden throughout the length of the core. Generally, MSA concentrations here are in agreement, although slightly lower than those reported by (Legrand & Feniet-Saigne 1991, Legrand *et al.* 1992) and similar to levels observed at Vostok and Dome C (Table VI).

As evident in Fig. 4c, NSSS was detected throughout the

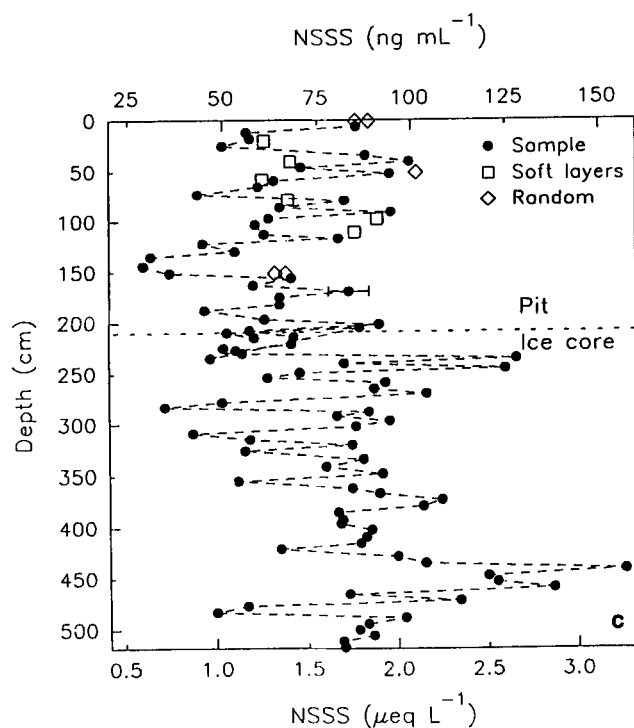


Fig. 4. Concentrations of a. Na^+ , b. MSA and c. NSSS in the ice core, snow pit and surface snow samples.

Table V. Comparison of sulphur species concentrations in aerosol and ice samples.

	Aerosol	Surface snow	Snow pit 0–2.05 m	Ice core 2.05–5.17 m
<i>MSA</i>	(nmol m ⁻³)	(μ eq l ⁻¹)	(μ eq l ⁻¹)	(μ eq l ⁻¹)
median	0.14	0.07	0.03	0.04
mean	0.18	0.08	0.05	0.04
range	0.09–0.43	0.07–0.09	0.01–0.20	0.02–0.06
<i>NSSS</i>	(nmol m ⁻³)	(μ eq l ⁻¹)	(μ eq l ⁻¹)	(μ eq l ⁻¹)
median	0.88	1.80	1.35	1.75
mean	0.90	1.72	1.40	1.76
range	0.66–1.32	1.51–1.85	0.60–2.10	0.60–3.26
% <i>MSA</i> : <i>NSSS</i> (mol:mol)				
median	17.0	7.8	4.70	3.70
mean	18.7	5.96	8.20	4.62
range	12.7–32.5	4.86–7.75	1.14–55.6	1.60–12.0

profile ($n = 55$) at concentrations ranging from 0.60–3.26 μ eq l⁻¹. The median *NSSS* value, 1.85 μ eq l⁻¹, represented about 44% of the total ionic budget. The lack of a relationship between *NSSS* and marine tracers such as sodium and chloride agrees with previous measurements in ice core samples (Legrand & Delmas 1988). *NSSS* concentrations in the ice core displayed no clear seasonal cycle. However, some of the lowest *NSSS* levels were associated with hard ice layers believed to be indicative of summer accumulation. The *NSSS* profile was characterized by sporadic inputs of *NSSS* interpreted to be due to either volcanic eruptions or a marine biogenic source when coincident with an *MSA* peak. The median *NSSS* concentration (2.79 μ eq l⁻¹) was higher than the background *NSSS* concentration considered typical for the Antarctic plateau (Table VI). In previous studies of remote and coastal Antarctic regions, the *NSSS* concentrations have ranged from 0.6–2.5 μ eq l⁻¹, with an overall mean and standard deviation given as 1.2 \pm 0.5 μ eq l⁻¹ (Galloway 1985).

The *MSA*:*NSSS* molar ratio from the surface to 5.17 m (Fig. 5) varied between 1.14–55.6%, with a median of 3.50% (Table V). The range was slightly greater than that observed in the aerosol samples (Table V). Low *MSA*:*NSSS* ratio values have been observed in snow pit and ice core samples presented here are comparable to the low ratios reported elsewhere in Antarctica (Legrand *et al.* 1992) and to the background marine aerosol ratio reported for remote marine regions (Saltzman *et al.* 1983). However, on occasion there can be quite elevated *MSA*:*NSSS* ratios, up to 30% as evident in Fig. 5. Variations of *MSA* in snow samples from the South Pole were interpreted to manifest changes in DMS emissions from the Southern Ocean as a result of large scale meteorological events such as El Niño phenomena (Legrand & Feniet-Saigne 1991). Thus, the large increase in the *MSA*:*NSSS* ratio appearing here at a depth of about 148 cm probably corresponded to the 1987–88 El Niño event. The concurrent *MSA* peak exhibited no enhancement with respect to either *NSSS* or Na⁺. However, the peak that should

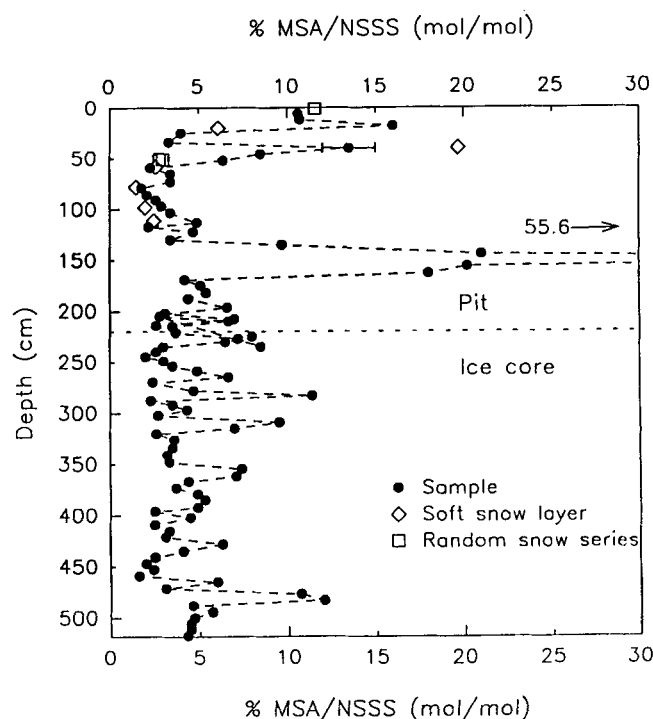
Table VI. *MSA* & *NSSS* concentrations (means with ranges in parenthesis) and *MSA*:*NSSS* molar ratio (%) in snow pit and ice core samples. Observations from previous studies are given for comparison.

Location	<i>MSA</i> (nmol m ⁻³)	<i>NSSS</i> (nmol m ⁻³)	% <i>MSA</i> : <i>NSSS</i> (mol:mol)
Law Dome ^A (66°S, 113°E)	0.08 (0.006–0.28)	0.39 (-0.4–2.4)	
Dumont d'Urville ^B (66°S, 140°E)	0.04 (0–0.46) falling snow	0.50 (<0–10.8) falling snow	6 (0–36) falling snow
Dome C ^C (74°S, 124°E)	0.06 (0.02–0.13)	1.48	(3–44)
East Antarctic plateau (78°S, 139°E)			
Pit (surface to 2.05 m)	0.03 (0.01–0.20)	1.35 (0.60–2.10)	5 (1–56)
Ice core (2.05–5.17 m)	0.04 (0.02–0.06)	1.75 (0.72–3.26)	4 (2–12)
Vostok ^D (78°S, 130°E)	0.06	2.25	5 (3–44)
South Pole ^E (90°S)	0.06 (0.02–0.62)	1.04 W 1.46 S	12 (17–50)

^A(Ivey *et al.* 1986), ^B(Maupetit & Delmas 1992), ^C(Legrand & Saigne 1988), ^D(Legrand *et al.* 1988), ^E(Legrand & Feniet-Saigne 1991)

correspond to the 1982 event is less apparent.

Although *MSA* and *NSSS* peaks generally coincided, there was no significant correlation ($r^2 = 0.15$) between *MSA* and *NSSS* concentrations for the combined snow pit and ice core

**Fig. 5.** The % *MSA*:*NSSS* molar ratio throughout the length of the snow pit and ice core.

sample set (Fig. 6). This result was similar to observations at Law Dome (Ivey *et al.* 1986) and in South Pole snow samples (Legrand & Feniet-Saigne 1991). The lack of a covariation between MSA and NSSS concentrations in the ice core and pit samples (Fig. 6) can result from several processes pertaining to varying source strengths, differential deposition mechanisms over the Antarctic plateau, or via diagenetic effects. Sporadic volcanic input of NSSS has already been mentioned (Delmas 1992a). Udisti *et al.* (1993) found a poor correlation between MSA and NSSS in snow at Terra Nova Bay on the Ross Sea, interpreted as evidence for NSSS derived from a source other than DMS. Alternatively, Mulvaney *et al.* (1992) observed decoupling of MSA and NSSS profiles deep within ice cores which was interpreted to be caused by the diagenetic migration of MSA from summer layers into winter layers. However, this last mechanism is not likely to be a factor in the short firn core considered here. Such studies highlight the complexities in sulphur geochemistry in Antarctica and that the origin of sulphur is difficult to establish on the basis of ice core data alone. Further investigations of aerosol composition as a function of size distribution at continental Antarctic sites are necessary to determine the source apportionment of sulphur.

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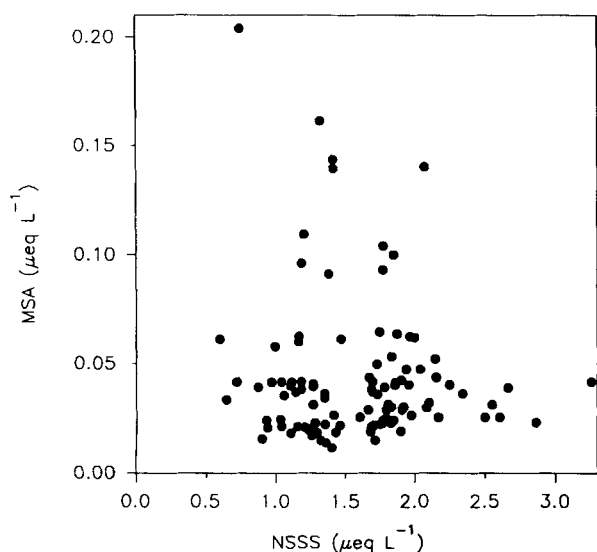


Fig. 6. Plot of MSA versus NSSS concentrations (nmol m^{-3}) in the ice core and snow pit samples.

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