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Spatial distribution and seasonal pattern of biogenic sulphur compounds in snow from northern Victoria Land, Antarctica

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ABSTRACT. A study of the spatial and temporal distribution of methane sulphonic acid (MSA) and $nssSO_4^{2-}$ concentrations in snow-pit samples was performed to determine the main and secondary sources, transport effects and seasonal pattern of biogenic sulphur compounds. Four snow pits, about 3 m deep, excavated at the same time at different altitudes (870–2960 m a.s.l.) in northern Victoria Land, Antarctica, gave coherent information about the effect of altitude and seasonality on the snow chemical composition. A progressive, well-defined decreasing concentration trend is shown as altitude increases, with the biggest effect in the first 1000 m a.s.l. At higher altitudes, biogenic sources make the most important contribution to the total sulphate balance with respect to sea-spray input. Particular attention was paid to the relationship between MSA and $nssSO_4^{2-}$ by using MSA as a univocal biogenic marker. The $nssSO_4^{2-}$/MSA ratio was evaluated with respect to altitude and seasonality to determine the effect of transport mechanisms (such as long-range transport and fractionation) or non-dimethyl sulphide sources on $nssSO_4^{2-}$ snow content.

INTRODUCTION

In the Antarctic coastal area, the total sulphate concentration in the snow collected at low-altitude stations is mainly correlated with primary aerosol (sea-spray) inputs (Piccardi and others, 1994, 1996a, b). As altitude increases, the contribution of secondary atmospheric aerosol becomes dominant. In unpolluted marine-dominated areas such as Antarctica, because of the low impact of other aerosol sources, the sulphur-cycle secondary aerosol is closely related to biogenic activity. The main source of sulphur compounds is the dimethyl sulphide (DMS) emitted by phytoplanktonic activity and which is oxidised in the atmosphere mainly to methane sulphonic acid (MSA) and H_2SO_4 (Andreae and Raemdonck, 1983; Saltzman, 1995). These substances may be important in the climate control of remote marine regions as principal factors in cloud-condensation nuclei formation (Charlson and others, 1987; Ayers and Gras, 1991).

In Antarctica, the main contribution to $nssSO_4^{2-}$, at least during summer, comes from the oxidation of biogenic DMS (Legrand and others, 1991; Delmas, 1994; Saltzman, 1995; Wagenbach, 1996) rather than from other postulated sources such as volcanic input, crustal origin and long-range transport effect (Legrand and Delmas, 1987; Shaw, 1988). At high latitudes, the annual cycle of solar irradiation imparts a sharp seasonal character to the DMS production, with concentration maxima during and immediately after the phytoplanktonic bloom (Saltzman, 1995; Wagenbach, 1996). For the studied area, this period is January–February (full-late austral summer). The seasonality of the biogenic $nssSO_4^{2-}$ input has been shown by snow measurements (Ivey and others, 1986; Mulvaney and others 1992; Piccardi and others, 1994; Udisti 1996; de Mora and others, 1997) and aerosol measurements (Ayers and others, 1991; Prospero and others 1991; Saltzman, 1995; Wagenbach, 1996; de Mora and others, 1997).

MSA derives only from oxidative processes of phytoplanktonic DMS. Because of its univocal origin, this compound can be employed as a reliable indicator of biological marine activity (Savoie and Prospero, 1989; Ayers and others, 1991; Legrand and others 1991; Udisti, 1996; de Mora and others, 1997). The seasonal trend of this compound is normally in phase with $nssSO_4^{2-}$ (assuming similar atmospheric transport mechanisms), with concentration maxima during late summer. Some authors, however, report evidence of dephasing between these two compounds, probably due to post-depositional phenomena (Mulvaney and others, 1992; Minikin and others, 1994). In our previous measurements on firn-core and snow-pit samples collected in northern Victoria Land such dephasing was never found. MSA summer maxima were shown by snow measurements (Mulvaney and others, 1993; Udisti and others, 1993) and aerosol measurements (Ayers and others 1991; Saltzman, 1995; Wagenbach, 1996; de Mora and others, 1997). Because of its sharp seasonality, MSA has been used to date successive snow layers (Piccardi and others, 1994; Udisti, 1996).

Evaluation of the different contributions to the sulphur balance and study of the distribution of the species originating from DMS in Antarctic snow can give useful information about past and present climatic conditions, phyto-planktonic activity and global-change phenomena. In fact, MSA and $nssSO_4^{2-}$ can be considered near-stable in the glacial ice cap (Legrand and others, 1991; Saltzman, 1995).

Moreover, the study of the spatial and vertical variation of the MSA/$nssSO_4^{2-}$ ratio, with particular attention to altitude effects (related to dimensional atmospheric aerosol classes) and to seasonality, can explain short and global-scale transport mechanisms and fractionating phenomena.

SAMPLING AND ANALYTICAL METHODS

Sampling stations

During the 1993–94 Italian Antarctic campaign, snow samples were obtained from four snow pits (about 3.0 m depth) excavated at different altitudes and distances from the sea. Figure 1 and Table 1 show the locations and altitudes of the sampling stations. Northern Victoria Land is a region with different orographic and glaciological characteristics, in which the proximity to the sea of the Transantarctic Chain and the presence of the valleys of the outlet glaciers are responsible for the confluence of katabatic winds (Bromwich and Kurtz, 1984). The sampling area was accurately prospected by remote-sensing analysis (based on satellite photos) to identify aeolian morphologies linked to ablation (blue-ice area, sastrugi, wind scoop) or different accumulation processes (snowdrift, drift plume). In this way it was possible to find (personal communication from B. Stenni and others, 1997) areas not influenced by such morphologies where snow accumulation seems not to be influenced by katabatic wind effects (erosion, transport, redistribution). The minimum station altitude (870 m a.s.l.) was accurately chosen to avoid any possibility of summer snow-layer melting. No ice crusts were detected in the sampled snow pits.

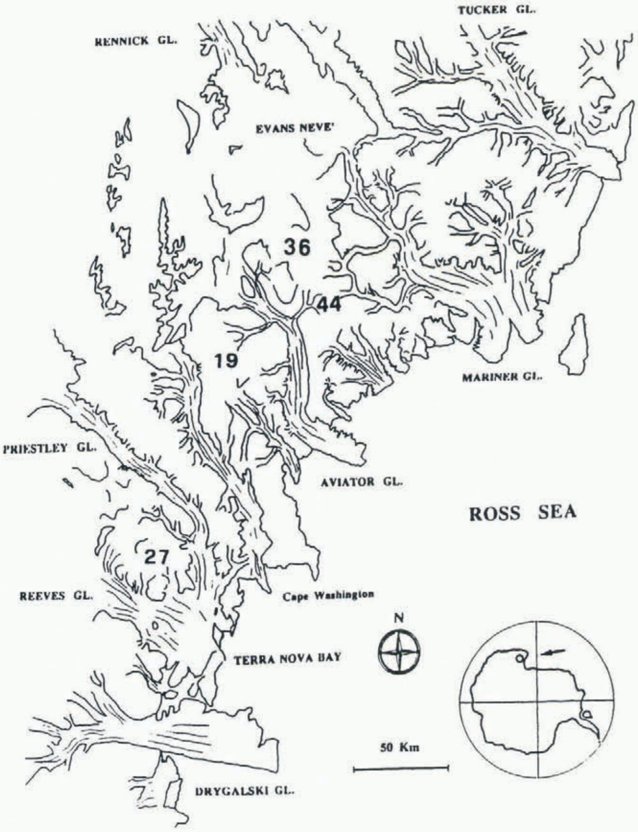

Fig. 1. Map of northern Victoria Land showing locations of sampling stations.

Sampling procedures and analytical methods

All the samples were collected by using a sampling protocol (Udisti and others, 1991, 1994; Piccardi and others, 1994) to minimise contamination. The snow pits were hand-excavated by personnel wearing clean-room clothing, and the snow walls were cleaned by removing a 5–10 cm layer with a stainless-steel scraper just before the sampling. Pre-cleaned polypropylene vials were inserted in the vertical snow walls with a snow-layer resolution of 35 mm. After removal, each sampling vial was sealed in a double polyethylene bag.

Table 1. Locations and altitudes of sampling stations

Station No., name	*Lat.* °S	*Long.* °E	*Height* m a.s.l.	*km from coastline*
27. McCarthy Ridge	74°36′	163°03′	870	40
19. Styx Glacier	73°52′	163°42′	1660	50
44. Pilot Glacier	73°16′	165°31′	2100	60
36. Hercules Névé	73°06′	165°28′	2960	90

The determinations of MSA and of those compounds necessary to calculate nssSO$_4^{2-}$ (total sulphate and sodium) were performed by ion chromatography (IC).

A system of three Dionex ion chromatographs (4000i, 4500i and DX 500) with conductivity detector was used for all measurements. The separation columns were Dionex AS12A (inorganic anions), AS11A (organic anions plus fluoride) and Dionex CS12A (cations) followed by electrochemical micro-membrane conductivity suppressors. All the components were analyzed as soon as possible after melting (generally 30 min). A 1 ml sample loop was sufficient to determine the lowest concentrations of the compo-

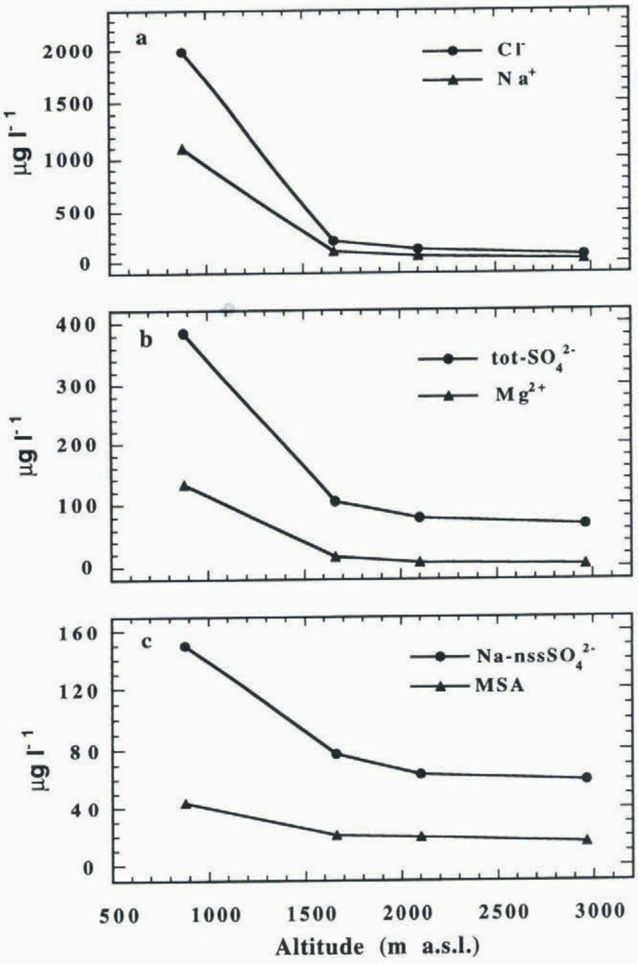

Fig. 2. Mean concentration values of Cl$^-$ and Na$^+$ (a), totSO$_4^{2-}$ and Mg^{2+} (b), nssSO$_4^{2-}$ and MSA (c) as function of altitude at the four sampling stations.

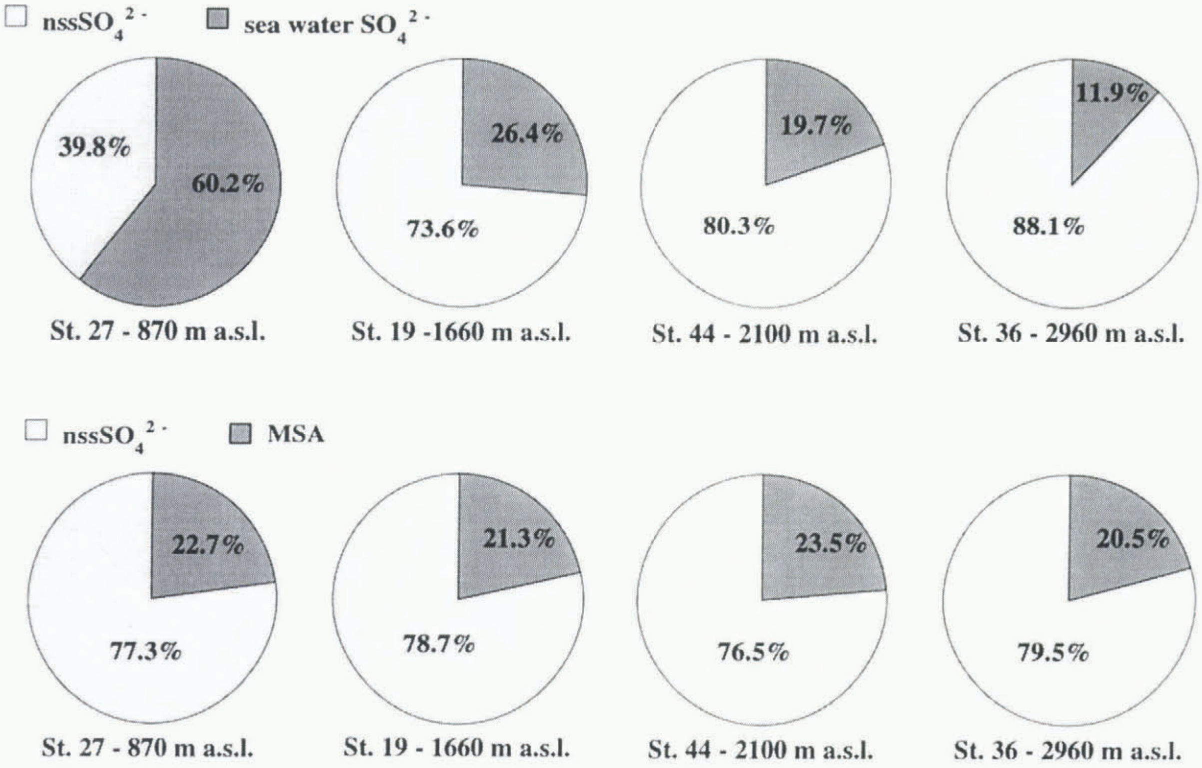

Fig. 3. Relative contributions of $nssSO_4^{2-}$ to total sulphate budget (upper pies) and of MSA and $nssSO_4^{2-}$ to total amount of non-sea-salt oxidised sulphur compounds (MSA + $nssSO_4^{2-}$) (lower pies) for all sampling stations.

nents without pre-concentration, to avoid contamination risk. For the same reason, sample manipulation was minimised. The sealed samples were melted under a class 100 laminar hood, and the sample was filtered on a 0.45 μm Teflon membrane just before analysis. The blank control procedures, sample treatment and IC methods have been described in previous papers (Udisti and others, 1991, 1994; Piccardi and others, 1994; Udisti, 1996).

RESULTS AND DISCUSSION

$nssSO_4^{2-}$ calculation

The term $nssSO_4^{2-}$ refers to the contribution of sulphates not coming from sea spray. For each sample, the $nssSO_4^{2-}$ concentration was calculated using the formula (Maupetit and Delmas, 1992):

$$[nssSO_4^{2-}] = [SO_4^{2-}]_{tot} - 0.253[Na^+]$$
$$\text{or} - 0.139[Cl^-](w/V)\,.$$

Previous $nssSO_4^{2-}$ measurements on samples collected in the same region indicated that either Cl^- or Na^+ could be used as a sea-spray indicator (Udisti, 1996). Nevertheless, the use of Cl^- gives relatively high errors when the primary marine contribution is very low (Piccardi and others, 1996a). For this reason, Na^+ concentration has been used as the sea-spray marker. Since $nssSO_4^{2-}$ measurement is obtained from the difference between two experimental data, the analytical error is greater with respect to MSA determination (Keene and others, 1986; Hawley and others, 1988; Udisti, 1996). Moreover, the uncertainty (not quantifiable) of the calculation hypotheses must be evaluated assuming (i) the $([SO_4^{2-}]/[X])_{\text{sea water}}$ is considered known and constant, (ii) the concentration of Na^+ or Cl^- in the sample is attributed to sea spray only and (iii) there is an absence of selective fractionating processes or post-depositional effects.

The main evidence of incorrect evaluations of the above factors is provided by negative $nssSO_4^{2-}$ values, usually found in snow precipitation characterised by high sea-spray and/or low $nssSO_4^{2-}$ content. These situations occur principally at coastal and low-altitude stations in the winter period (Maupetit and Delmas, 1992; Piccardi and others, 1996a, b; Wagenbach, 1996). For the samples analyzed here, negative $nssSO_4^{2-}$ values were found only for McCarthy Ridge. In order to obtain a reliable data comparison among the four snow pits, only positive values were considered.

Spatial and vertical distribution

From the preliminary data, the altitude was the dominant factor in the snow chemical composition in northern Victoria Land (Piccardi and others, 1996a). To confirm this, four snow pits were sampled at stations located at different altitudes (870–2960 m a.s.l.). Such altitude variation makes it possible to identify main and secondary aerosol sources and to point out the fractionating aerosol phenomena related to different aerosol dimensional classes. Moreover, the snow-composition data can be reliably compared because the snow pits were sampled at the same time and the samples came from similar annual snow layers.

Figure 2 shows the decrease of mean concentration values as altitude increases. Each mean value refers to about 60–90 samples. There is a similar behaviour for all substances: a very large concentration decrease occurs in the range 870–1660 m a.s.l.. A slower decreasing trend is still visible for the range 1660–2100 m a.s.l., but for higher altitudes the concentration values remain fairly constant. At Hercules Névé station (2960 m a.s.l.) $\mu g\,l^{-1}$ or sub-$\mu g\,l^{-1}$ concentration levels were found for almost all the compo-

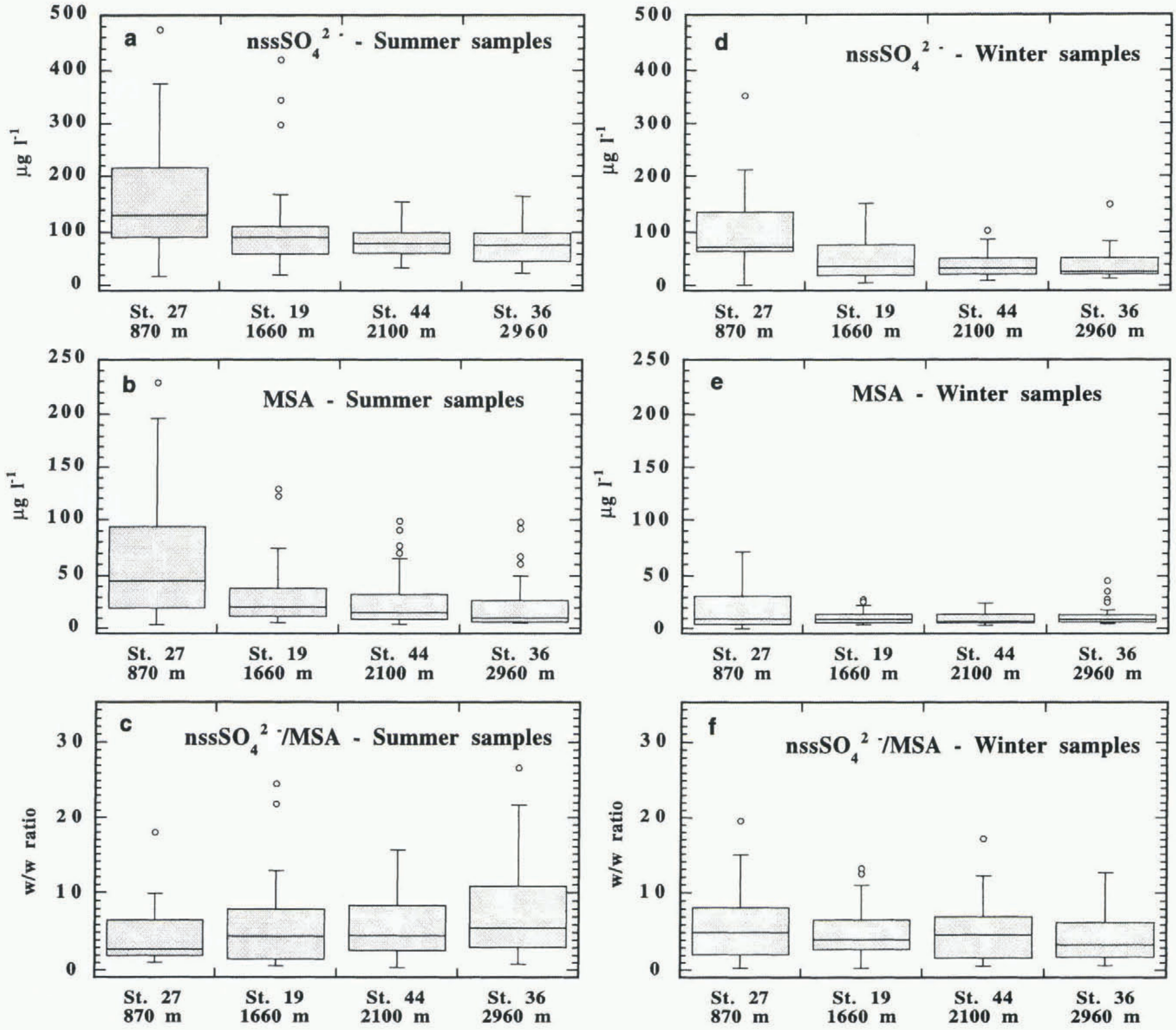

Fig. 4. Distribution plots of nssSO_4^{2-}, MSA and w/w nssSO_4^{2-}/MSA ratio for the four sampling stations. The plots are separated as summer (a, b, c) and winter (d, e, f) samples. Each box contains 50% of the data, with the median value displayed as a line. The top and bottom of the box mark the limits of ±25% of the variable population (25th and 75th percentiles). The lines extending from the top and bottom of each box mark the minimum and maximum values that fall within an acceptable range (1.5 times the box width). Any value outside this range (outlier) is shown as an individual point.

nents. The most dramatic decrease is shown by the sea-spray components (Na^+, Cl^-, Mg^{2+} and totSO_4^{2-}; Fig. 2a and b). Cl^- shows the highest concentration decrease, with mean concentration values at stations 27, 19, 44 and 36, respectively, of 1991, 215, 126 and 73 $\mu g\,l^{-1}$ (St. 36/St. 27 = 3.7%). The totSO_4^{2-} (Fig. 2b) and the nssSO_4^{2-} (Fig. 2c) show a lower decrease from station 27 to station 36: totSO_4^{2-} from 386 to 68 $\mu g\,l^{-1}$ (St. 36/St. 27 = 18%); nssSO_4^{2-} from 176 to 79 $\mu g\,l^{-1}$ (St. 36/St. 27 = 45%). Comparing Cl^-, totSO_4^{2-} and nssSO_4^{2-} altitude trends, it is evident that the SO_4^{2-} contribution from sea spray is partially counterbalanced by the presence of biogenic sources, which becomes more important as the altitude of the sampling station increases. The smaller decrease of the biogenic contribution with altitude, with respect to decrease of sea-spray sources, is confirmed by the MSA trend (Fig. 2c). The mean concentration values of MSA are 44, 21, 19 and 16 $\mu g\,l^{-1}$ at stations 27, 19, 44 and 36, respectively, with a percentage ratio of 48% at the first step

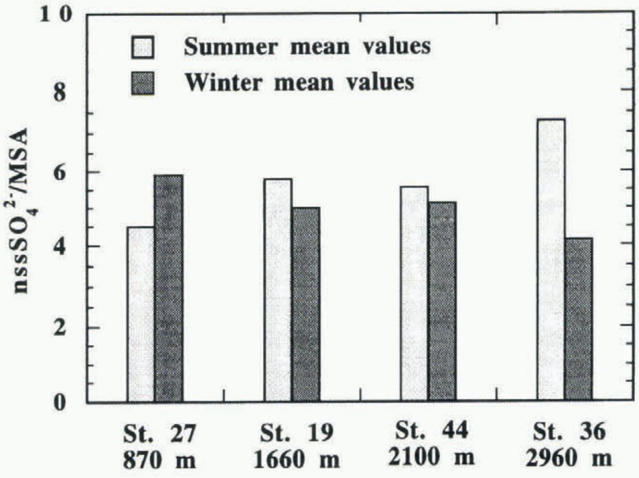

Fig. 5. nssSO_4^{2-}/MSA ratio mean values in summer and winter periods plotted for all sampled stations.

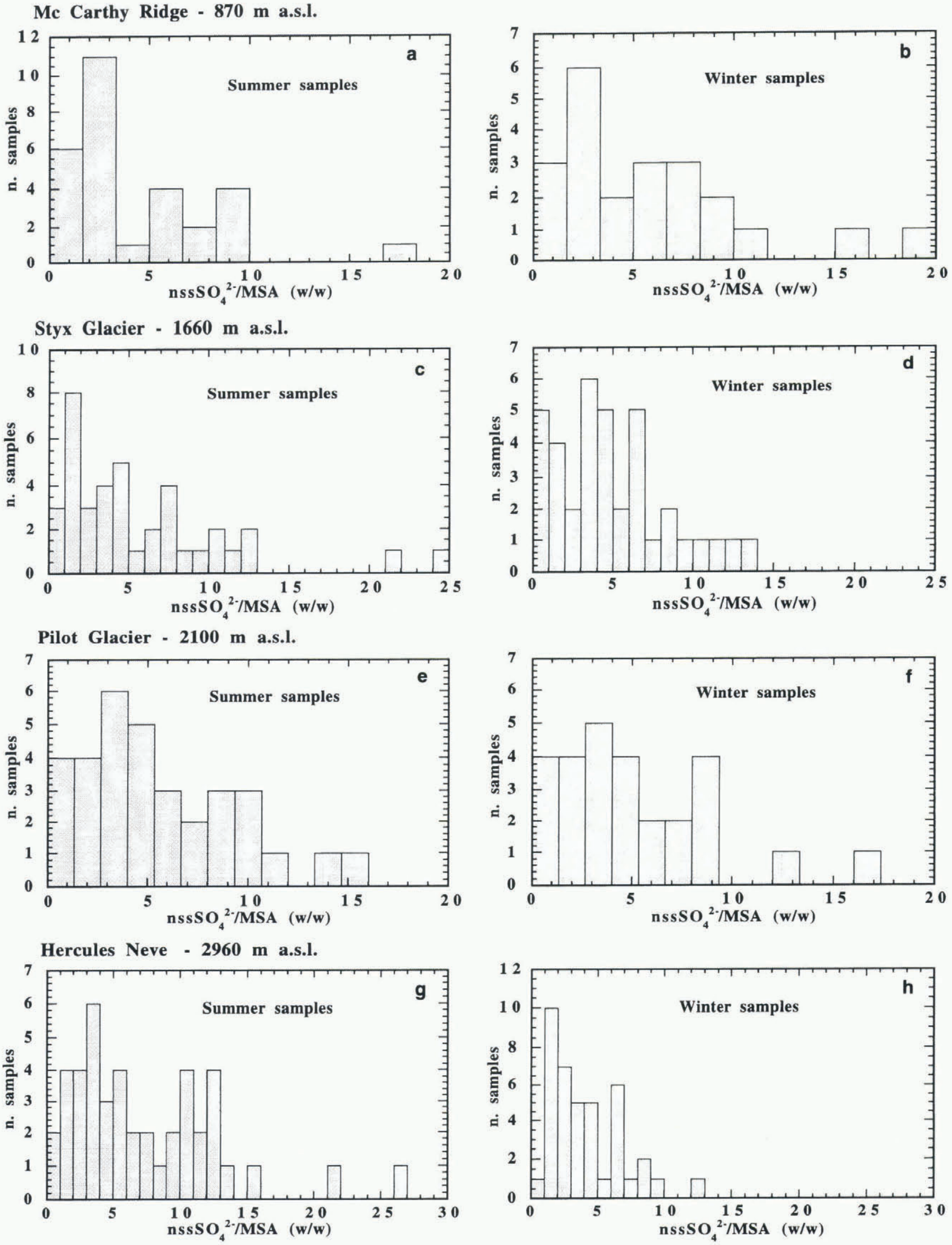

Fig. 6. Distribution frequencies for MSA, $nssSO_4^{2-}$ and their (w/w) ratio of summer (a, c, e, g) and winter samples (b, d, f, h) for all sampling stations. The frequency steps for McCarthy Ridge and Pilot Glacier stations are wider than those of Styx Glacier and Hercules Névé for the lower sample number.

(St. 19/St. 27) and 84% at the last (St. 36/St. 44). Such variations are similar to those of $nssSO_4^{2-}$.

The relative contributions of sea-salt and non-sea-salt sulphate to the total sulphate balance are shown in Figure 3. A very large depletion of sea-salt sulphate occurs when the altitude increases. At the Hercules Névé station, the $nssSO_4^{2-}$ contribution represents about 88% of the total sulphate. By contrast, the relative contributions of $nssSO_4^{2-}$ and MSA to the non-sea-salt sulphur budget are near-constant and independent of altitude:

mean MSA fraction = MSA/(MSA + nssSO_4^{2-}) ≅ 0.22 w/w. This value is consistent with Berresheim's (1987) and Pszenny and others' (1989) aerosol measurements over circum-Antarctic oceans where MSA fractions were as high as 0.5 with a mean value of 0.3.

Seasonal nssSO_4^{2-} and MSA pattern

The seasonal pattern of the phytoplanktonic DMS emissions requires a seasonal characterisation of the snow-pit samples in order to determine the MSA and nssSO_4^{2-} distributions and relationships at the different stations. The snow-pit dating was performed using a multiparametric method based on a normalisation of the concentration/depth profiles of H_2O_2, nssSO_4^{2-} and MSA (Udisti, 1996). The dating results are reported elsewhere (Piccardi and others, 1995). In this way, 5, 6, 4 and 8 annual layers were found, respectively, for snowpits 27 (depth 286 cm), 19 (depth 277 cm), 44 (depth 223 cm) and 36 (depth 321 cm).

Based on this dating, a seasonal characterisation of the samples is performed here. The seasonal concentration and distribution data are given in Table 2. Graphical representations of the MSA and nssSO_4^{2-} distribution are given in the box plots shown in Figure 4. Each box contains 50% of the data, with the median value displayed as a line. From the mean data of Table 2 and distribution plots of Figure 4a, b, d and e, some generalisations can be made about the distributions of MSA and nssSO_4^{2-} in summer and winter samples with respect to altitude.

> The mean and median concentrations of the two components at all the stations are higher in summer than in winter. Therefore, the biogenic contribution from DMS is dominant for all altitudes. The seasonal concentration trends of mean and median values confirm the trend evidenced by general mean values: a sharp decrease is evident in the first altitude step (870–1660 m a.s.l.). A lower but progressive decrease is shown when the altitude increases.
>
> In both seasons, the data dispersion is higher for the stations at lower altitude. This is graphically shown by the box height and numerically indicated by the concentration range between the 25th and 75th percentiles. In particular, McCarthy Ridge station shows very high data dispersion, especially in summer, for MSA and nssSO_4^{2-}. This agrees with the fact that the sea is the principal source of their precursor DMS, even though its oxidation takes place in the atmosphere.
>
> The median values are not symmetrical with respect to the data distributions. This is shown by the position of the median line in the box plots and by the difference between the mean and median values. Generally the median line is shifted to the bottom of the box and, consequently, the mean values are higher than the median ones. This result indicates that there are a few snow precipitation events with high MSA and nssSO_4^{2-} concentrations rather than a larger number of events with lower contributions. This is especially evident in winter at McCarthy Ridge, where the proximity of the sea and the low altitude make this station more subject to isolated and intense atmospheric disturbances (such as salt storms).
>
> nssSO_4^{2-} negative values occur at the lowest station only, and almost all occur in winter (27% of winter data). Only one negative value is found in summer. All these values coincide with intense sea-spray contributions. The underestimation of sea-spray contribution to sulphate budget (due to an incorrect $\text{SO}_4^{2-}/\text{Na}^+$ sea-spray ratio or to transport fractionation) seems, therefore, to be a fundamental factor for nssSO_4^{2-} calculation. This error becomes more evident when the other nssSO_4^{2-} contributions (DMS) are lower. At higher stations, the sulphate sea-spray contribution is lower (Fig. 2) and this misinterpretation is "hidden" by the dominant contribution of nssSO_4^{2-} to the total sulphate budget.

nssSO_4^{2-}/MSA ratio

A different behaviour is shown by the nssSO_4^{2-}/MSA ratio (Fig. 4c and f). The data dispersions and median values increase with altitude in summer samples, while these values remain fairly constant in winter samples.

In summer, the 50% data range changes from 2.0–6.6 $\mu g\,l^{-1}$ at McCarthy Ridge to 3.1–10.9 $\mu g\,l^{-1}$ at Hercules Névé, with relative median values of 4.5 and 7.3 $\mu g\,l^{-1}$. In winter, 50% of the samples have nssSO_4^{2-}/MSA ratios ranging from 2.1 $\mu g\,l^{-1}$ (bottom value at Pilot Glacier) to 8.1 $\mu g\,l^{-1}$ (top value at McCarthy Ridge), with the median value in the narrow range from 3.5 $\mu g\,l^{-1}$ (Hercules Névé) to 5.0 $\mu g\,l^{-1}$ (McCarthy Ridge). For each station, the nssSO_4^{2-}/MSA ratios show a smaller nssSO_4^{2-}/MSA variation of median value between summer and winter with respect to single substances. The variation in values and trends of the nssSO_4^{2-}/MSA ratios with seasonality shows the low significance of their general (all-station) or annual mean values, usually reported in the literature. The same general mean MSA fractions reported here (Fig. 3) render us unable to distinguish stations that have different nssSO_4^{2-}/MSA seasonal patterns. In fact, the mean ratios show an opposite seasonal trend at the lowest station to that at the higher ones (Fig. 5). At McCarthy Ridge (790 m a.s.l.) the nssSO_4^{2-}/MSA ratio increases in winter; at all the other stations, this ratio reaches the highest values in summer (particularly at Hercules Névé). This behaviour can be explained by the distribution frequencies shown in Figure 6 where a quasi-bimodal distribution of the ratio values during summer and winter can be observed. Relatively high sample frequencies are bunched in two value ranges: around the nssSO_4^{2-}/MSA value of 2 and around 5 or higher. At the lowest station, the ratio distribution varies according to the season; more samples have higher values during winter. At the intermediate stations, the distributions are very similar (Pilot Glacier) or compensating (Styx Glacier), so that the mean ratio assumes similar values in the two seasons. At Hercules Névé, the mode located at values around 10 in summer is missing in the winter period. For this reason, the mean nssSO_4^{2-}/MSA ratio is lower in winter here.

Seasonal variation of transport processes and/or fractionation such as marine aerosol inputs from lower latitudes (with a different nssSO_4^{2-}/MSA ratio) due to atmospheric circulation changes may explain this seasonal and altitude-induced trend in the nssSO_4^{2-}/MSA ratio.

The nssSO_4^{2-}/MSA ratio as a function of MSA concentration, used as a univocal biogenic indicator, is shown in Figure 7. The ratio tends to values around 2 for the highest MSA concentrations. To better evaluate the summer behaviour of nssSO_4^{2-}/MSA ratio, superficial summer snow

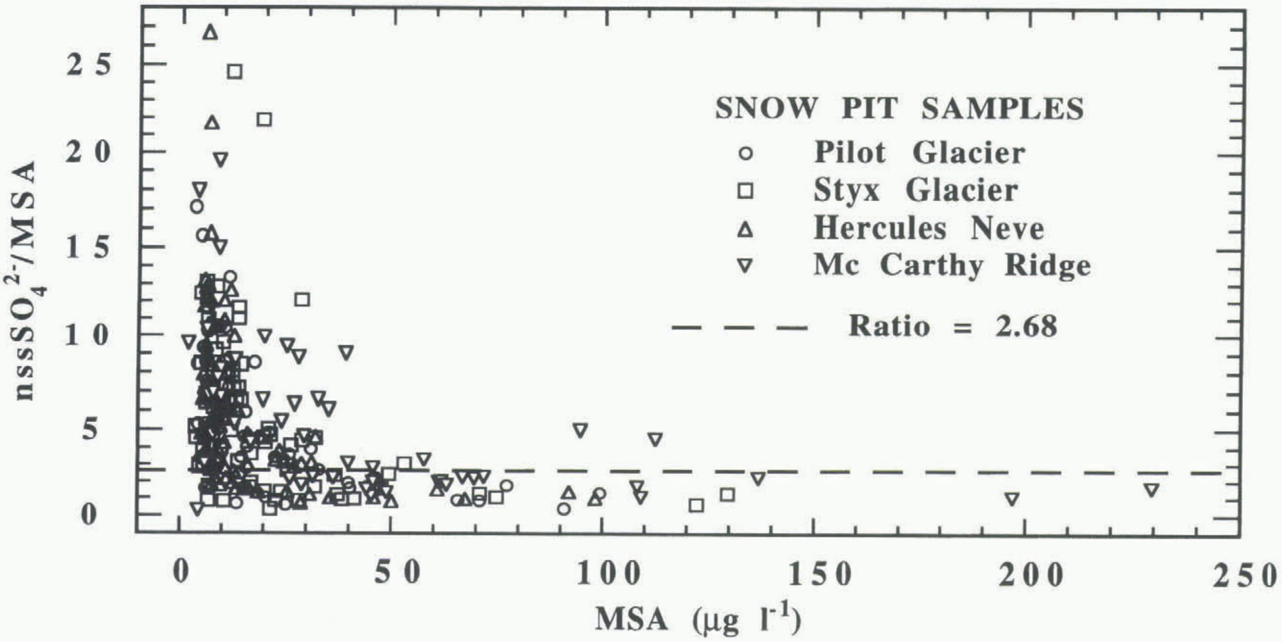

Fig. 7. All samples' nssSO_4^{2-}/MSA ratios plotted vs MSA concentration in the four snow pits. The dashed line shows the value 2.68 found for summer "fresh" snow samples.

was sampled at about 20 stations within a 200 km radius of the snow-pit stations. The time between the snowfall and the sampling was as short as possible so that the samples could be considered as "fresh" snow samples, affected as little as possible by post-depositional processes. These samples, collected in November–January, are representative of typical summer snowfalls. A good correlation ($R = 0.81$, $n = 88$) between nssSO_4^{2-} and MSA was obtained, with a slope (indicating the summer mean nssSO_4^{2-}/MSA ratio) of 2.68. This result agrees with the nssSO_4^{2-}/MSA ratio found for snow-pit samples with high MSA concentration. When the MSA concentration decreases, the nssSO_4^{2-}/MSA ratio quickly increases to values higher than 20 (Fig. 7). This occurs mainly for winter samples and for the higher stations.

Such behaviour can be explained by the presence of other possible nssSO_4^{2-} sources, by sea-spray or biogenic sulphur compounds fractionation or by long-range transport of marine aerosol characterised by different nssSO_4^{2-}/MSA ratios. In fact, the nssSO_4^{2-}/MSA ratio is strongly latitude-affected (Bates and others, 1992). At the highest latitudes, as in Antarctica, the nssSO_4^{2-}/MSA aerosol ratio can reach a value close to 1 (Berresheim, 1987; Pszenny and others, 1989), but this ratio increases very quickly with decreasing latitude. At mid- to low latitudes, the nssSO_4^{2-}/MSA ratio reaches values ten times higher than in polar regions (Saltzman, 1995). In winter, when sea ice constitutes a very large belt around Antarctica and the sealine is 500–1500 km away from the coastline, two concomitant effects could contribute to an increase in the nssSO_4^{2-}/MSA ratio: more intense fractionation of sea spray, and long-range transport of oceanic air from lower latitudes. Similar transport processes can also be assumed in summertime for high-altitude stations (above 1500 m a.s.l.) where usually only the lower-dimensional aerosol classes can arrive. In fact, the aerosol transport from southern mid-latitudes appears more effective at the upper tropospheric level (Wagenbach, 1996).

A background nssSO_4^{2-} contribution (volcanic or crustal) that becomes more evident when the biogenic source decreases (low MSA concentrations in winter and at the highest stations) is another possible explanation of the nssSO_4^{2-}/MSA trend.

CONCLUSIONS

The two major contributions to sulphates in northern Victoria Land, sea spray and DMS, are important. The latter contribution predominates for seasonal inputs (high phytoplanktonic activity in summer) or when the former decreases (altitude increase, absence of events such as salt storms). Further work is needed to obtain a correct evaluation of nssSO_4^{2-} (original aerosol SO_4^{2-}/Na^+ ratio and fractionation during air-mass transport).

Altitude is a fundamental parameter for the distribution of components coming from sea spray as well as from marine biogenic activity. Fractionating aerosol phenomena, related to aerosol dimensional classes, have an important effect.

MSA and nssSO_4^{2-} concentrations in the snow show a clear seasonal pattern due to the production of their principal source (DMS of phytoplanktonic origin).

The MSA/nssSO_4^{2-} trend with altitude and seasonality and its relationship with MSA, used as a univocal biogenic indicator, reveal the importance of long-range transport effects or the presence of other nssSO_4^{2-} sources which are more evident in winter precipitation and in the snow collected at higher altitudes.

The low significance of the MSA/nssSO_4^{2-} mean ratio calculated on all-station samples as well as on annual periods should be noted. Only a seasonal study can give reliable information about the trend of this ratio.

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