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Study of the MSA, nssSO_4^{2-} concentration and MSA to nssSO_4^{2-} ratio in the snow/ice and atmospheric aerosols of the regions surrounding the Weddell Sea

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Abstract The MSA and nssSO_4^{2-} concentration data from the ice cores and from atmospheric aerosols of the regions surrounding Weddell Sea have been analyzed in the present paper. The results suggest that the high concentration of biogenic sulphur in the snow and ice as well as in the atmospheric aerosols reflects the proximity of the Weddell Sea even though a distinct strength discrepancy exists in the productivity among the areas. The snow/ice shows that the production seems to be higher in the middle of the Antarctic Peninsula than near the Filchner-Ronne ice shelf. Despite the factors impacting on the transportation and deposition processes of biogenic surlphur, the concentration of MSA and nssSO_4^{2-} in snow and ice shows a regular spatial distribution: decreasing with the distance from the open sea and the altitude above sea level. Nevertheless, below a certain height, the "altitude effect" is no longer significant. The "displacement" of seasonality for MSA concentration observed in ice cores of the regions has been discussed. The "out of phase" pattern in surface layer is attributed to the modification by prevailing meteorological condition to the transport and deposition process; while "relocation" in the deep layers may be caused by migration, a mechanism for which is to be further investigated. The comparative study of the atmospheric and snow/ice samples implies that at the high altitude like the Weddell Sea the atmospheric signal of SO_4^{2-} and MSA could be somewhat muted in the snow samples. But the seasonal variations in the airborn sulphate and MSA are reasonably well reproduced in the surface snow, for temporal and spacial distribution. The very close ratio of MSA to nssSO_4^{2-} (or to SO_4^{2-}) of atmospheric aerosol and snow/ice sample is indicative of weak, if any, fraction between the two species during the scavenging and deposition processes. This could serve as the internal cause to explain the relative stable MSA/nssSO_4^{2-} ratio, both for atmosphere and snow, an important regional specificity for the study of marine biogenic sulphur.

Key words Weddell Sea, snow/ice, aerosol, MSA, nssSO_4^{2-}.

1 Introduction

It is now well recognized that the oceanic biogenic sulphur cycle plays an important role in the forcing of global climate. Dimethylsulphide(DMS) derived from the planktonic algae in sea water oxidizes in the marine atmosphere to form sulphonate aerosols, serving as the major source of the cloud condensation nuclei (CCN). A rise in the CCN

population may cause an increase of the albedo of marine clouds, lowering the incident solar radiation, thus affecting the Earth's radiation budget. This mechanism proposed by Charlson *et al.* (1987) includes another by-product of the DMS oxidation, methanesulphonate acid (MSA), effective as CCN also in the remote marine atmosphere. Unlike sulphate with various sources (terrestrial, volcanic, anthropogenic, oceanic) among which oceanic emissions take the dominant position (mainly by DMS, and denoted usually as non-sea salt SO_4^{2-}, $nssSO_4^{2-}$, to distinguish it from that of sea salt contribution) (Bates *et al.* 1992), whereas MSA is exclusively produced by the above mechanism. Therefore it could act as useful tracer for biological activity in the remote marine environment, such as the oceans surrounding Antarctic continent. Both MSA (as methanesulphonate) and sulphuric acid (as sulphate), as proxy records of DMS, have been measured in ice cores from central Antarctic and the relationship of these species to the climate change has been demonstrated for Antarctica (Legrand and Feniet-Saigne 1991).

Recent studies have demonstrated a reasonable correspondence of sulphate and MSA concentration in atmosphere, in fresh snow and in snowpit samples (Jeffrezo and Davidson 1994), which not only provides information concerning the biogenic sulphur studies of snow and ice conducted so far in polar regions, but also gives confidence in interpreting depth-profiles in terms of the sulphate and MSA content of the past atmosphere. However, to enhance our knowledge of the sulphur cycle and its global budget, and to evaluate unambiguously the past levels of biological activity in the oceans by means of deep ice core analysis, it is crucially important to investigate the current spatial and temporal variation of sulphur species, particularly in the high-latitude region which are very sensitive to the climate change and are expected to have large primary productivity (El Sayed *et al.* 1983). The Weddell Sea, one of such regions, is surrounded by the Antarctic Peninsula in the west, Drake Passage in the north, and Filchner-Ronne (or, for short, F-R) Ice Shelf in the south. The concentration measurements of marine biogenic surlphur both for the atmosphere and the snow/ice since the 1980's (Berresheim 1987; Mulvaney *et al.* 1992; Savoie *et al.* 1993; Pasteur *et al.* 1995; Minikin *et al.* 1994; Wagenbach *et al.* 1994) made in the region have brought us the most abundant data. In this paper we present the MSA and sulphate concentration of an ice core from the King George Island near the north end of the Antarctic Peninsula to make comparison with the data from other sites of the region. The preliminary aim is to describe the temporal and spatial distribution of marine biogenic sulphur; to seek factors affecting the production of DMS and its oxidation to MSA and sulphate, as well as their transportation and deposition processes. And finally, the mechanism for altering the vertical location of MSA in snow/ice will be discussed.

2 The geography and physical feature of the sampling sites

Fig. 1 illustrates the location of the sampling sites. Among them the aerosol sampling for Drake Passage and Gerlache Strait was done during the period from March 20 to April 28, 1986 (Berresheim 1987), and for Palmer Station (64.77°S, 64.05°W) from April 3, 1990 to June 17, 1991 (Savoie *et al.* 1993). The geographical position, sampling date and the most important physical features for the major ice coring sites are

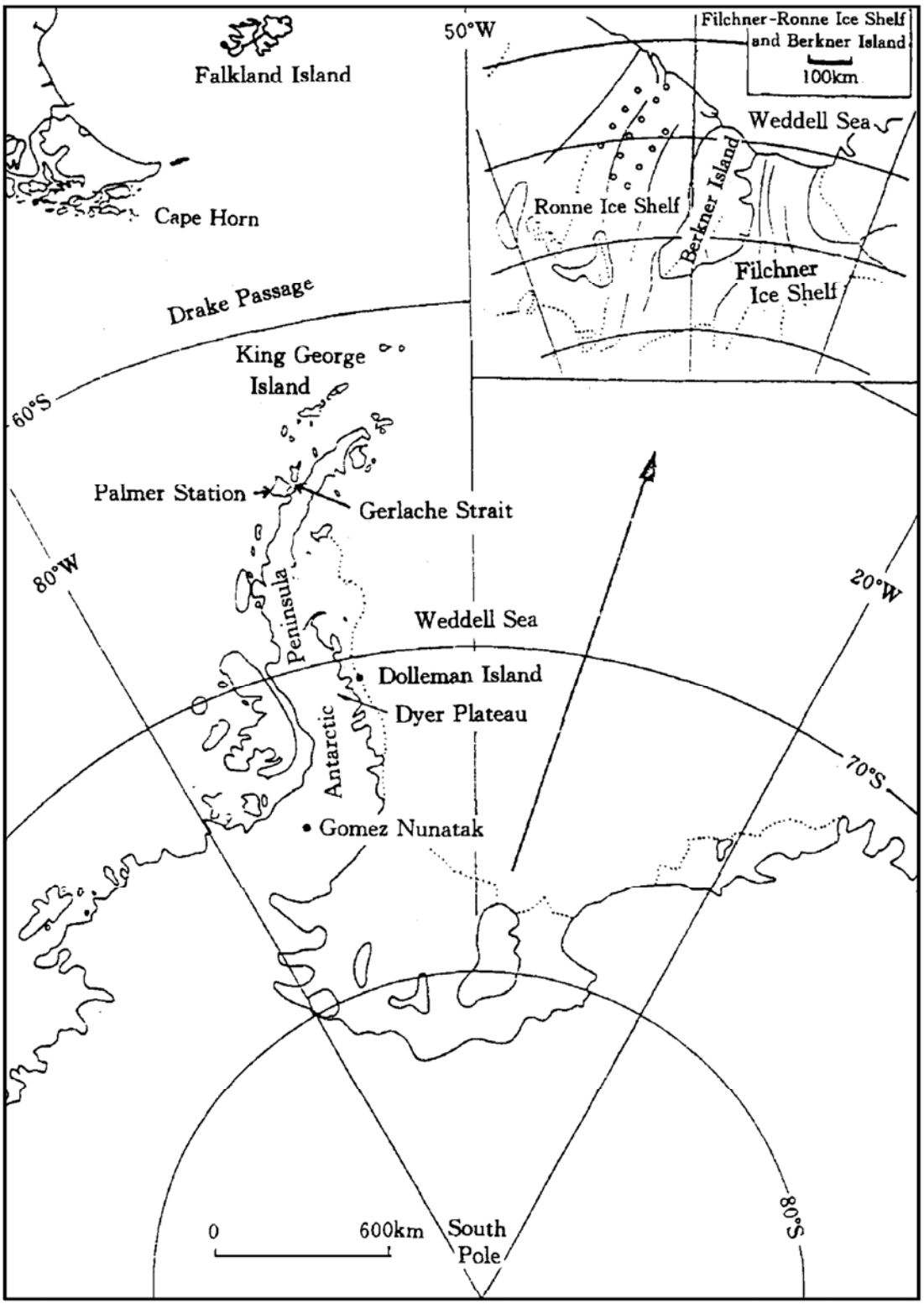

Fig. 1. Map of Weddell Sea and the Surrounding area showing the sampling sites.

listed in Table 1.

Among the places of ice sampling in the Antarctic Peninsula the Gomez Nunatak (G. N.) on the ridge is at the most south; the Drey Plateau at the north, 500 km from G. N. , has the highest altitude of 1900 m a. s. l. ; the Dolleman Island on east side of the Peninsula is the closest to the Weddell Sea; and the King George Island where our sampling was taken is at the northern end of the Peninsula. The former three listed above were studied by Britain glaciologists in the period of 1981-1989, where ice cores at

a depth of 133 m were achieved. According to Mulvaney *et al.* (1992) and Pasteur *et al.* (1995), the galciers in the central Peninsula showed weak surface melting even in the summer, with few of ice layers on the snow stratigraphy of the pit walls. While in comparison, the Collins Ice Cap, King George Island suffers from percolation of melt water due to the higher summer temperature on the surface. The ice layers in various thicknesses were displayed both on the pit walls and the firn cores extracted. However, benefiting from the high coring site at the summit, 702 m a. s. l., and the high accumulation rate, 4 m about in snow, the 1991 - 1992 cores exhibited distinct variation of chemical species for the top 10 m (Han *et al.* 1993). The ice cores of F-R Ice Shelf extending to the north for about 500 km from the Antarctic continent were drilled by the Germany scientists during 1985 - 1992. 14 shallow cores were drilled along two major flow lines which covered the central area of the shelf. The coring at two sites with distance of about 100 km on the high dome of the Berkner Island provided the samples for the investigation of snow chemistry in wider spatial dimensions.

Table 1. The characteristics of the major drilling sites

Site	King George Island	Dolleman Island	Gomez Nunatak	Dyer Plateau	Berkner Island	
					North Dome	South Dome
Position	62°10′S 58°50′W	70°35′S 60°56′W	74°01′S 70°38′W	70°31′S 65°01′W	78°18′S 46°17′W	79°36′S 45°37′W
Altitude /m a. s. l.	702	398	1130	1900	730	940
Mean annual temperature/ C	−9.3	−16.8	−17.3	−21.7	−22.5	−24.6
Accumulation rate/(m water equivalent/a)	2.4	0.34	0.88	0.48	0.23	0.17
Coring date	Dec. 1991	Jan. 1986	Jan. 1981	Jan. 1989	Jan. 1990	Jan. 1990
Data resources	this paper	Mulvaney *et al.* (1992)			Wagenbach *et al.* (1994)	

The atmospheric aerosol samplings collected so far could not correspond to that of ice corings one-by-one in places. But the quoted ones in the present paper offered the regional materials for the comparison of atmospheric content of marine biogenic sulphur with that of ice cores. And the comprehensive study in the regions surrounding the Weddell Sea surely helps the investigation of their relationships.

3 Data and analysis

The ice core data, mean MSA and nssSO_4^{2-} as well as the MSA/nssSO_4^{2-} ratios, will be examined first (Table 2). The equation for calculating nssSO_4^{2-} is:

$$[SO_4^{2-}]_{nss} = [SO_4^{2-}]_{Total} - k \times [X]$$

Where X denotes the measurement of Cl^- or Na^+ (Mg^{2+} sometimes), k is the ratio of SO_4^{2-} to X (in eq/L mostly) for sea water in mean. As mentioned, the MSA/ nssSO_4^{2-} ratio is regarded as the indicator with the regional specificity usually.

Table 2. Chemical features of ice core

Site	King George Island	Dolleman Island	Gomez Nunatak	Dyer Plateau	Berkner Island		F-R Ice Shelf	
					North Dome	South Dome	North	South
Mean MSA(μeq/L)	0.17	0.85	0.11	0.09	0.2	0.17	0.20	0.12
Mean nssSO_4^{2-}(μeq/L)	0.85	3.72	0.60	0.56	1.17	0.88	1.00	0.82
MSA/nssSO_4^{2-}	0.20	0.23	0.18	0.16	0.17	0.20	0.20	0.15
Data resource	This paper	Mulvaney *et al.* (1992)			Wagenbach *et al.* (1994)		Minikin *et al.* (1994)	

A regular spatial distribution of the variables could be found. With the increasing distance from the Weddell Sea, the MSA and SO_4^{2-} concentation decreases. Minikin *et al.* (1994) reported the decreasing gradient for F-R Ice Shelf is 25%/(100 km) for MSA, and 10%/(100 km) for nssSO_4^{2-}. The examination for the Berkner Island showed similar varying trend. It is interesting to see the close concentration for the sites with similar distances to the sea but different elevation (about 1000 m apart) above sea level for the cores from the F-R Ice Shelf and the Berkner Island. The MSA/nssSO_4^{2-} ratios for the two areas are also similar. This suggests their common source region of the mass, on the one hand, the negligible effect of the elevation, within a certain of altitudes, on the transportation and deposition of biogenic sulphur species on the other. In contrast, the Dyer Plateau in the central Peninsula shows a great difference both in MSA and SO_4^{2-} concentrations from those of the nearby Dolleman Island, but a closer similarity to those of Gomez Nunatak 500 km away. The cause for this discrepancy is ascribed, probably, to the elevation of 2000 m a.s.l. of the Dyer Plateau. Without consideration of the different distance to the sea for Dolleman Island and the Dyer Plateau, and assuming their same mass source, the decreasing gradient is 6.7%/(100 m) for MSA and 6.3%/(100 m) for nssSO_4^{2-}, showing synchronous variation. It seems that the Weddell Sea which influences the snow chemistry of the Gomez Nunatak at about 1000 m a.s.l. not by the elevation, but by the distance to the open sea water, is similar in the situation to the Berkner Island. There is probably a critical altitude above which the deposition of marine biogenic sulphur is dropping dramatically with raising elevation, and below that the effect could be neglected while only the distance effect should be taken into account.

All the above analyses strongly support the view that the Weddell Sea is the source of the marine biogenic sulphur included in snow and ice of the studied region, extending even to the West Antarctic Continent. The MSA/nssSO_4^{2-} ratio, close to 0.20, may be considered to be characteristic of the region. The distinguished MSA concentration of the Dolleman Island from other sites indicates the quite changeable biogenic sulphur, bigger in the Peninsula than in the F-R Ice Shelf. However, the similar value for the King George Island and the F-R Ice Shelf, 2000 km apart from each other, indicates the productivity for the whole Weddell Sea may be closer to that of F-R Ice Shelf.

Along with the spatial regularity of snow/ice concentration of biogenic sulphur, the ice cores exhibited vertical distribution different from some of the Antarctic ice cores, such as those from Neumayer (Wagenbach *et al.* 1988), South Pole (Legrand and Delmas 1984) and Mawson (Prospero *et al.* 1991). The seasonality of those cores in MSA and SO_4^{2-} concentration fits that of the atmosphere, that is, high in summer and low in winter. The "out of phase" seasonality of the core from the King George Island was shown in the MSA profile (Fig. 2) which displays the peaks to be associated not exactly

with the summer snow, but with that of fall as referred from the summer deposition by the $\delta^{18}O$ maximum. Other cores from the studied regions showed the migration of MSA from summer layers to winter's in deep parts in spite of that they were in phase on the surface sections, i.e. MSA, $nssSO_4^{2-}$ and $\delta^{18}O$ all varying pace by pace: summer is the highest and winter is the lowest. To show it explicitly, the observation from F-R Ice Shelf by Minikin *et al.* (1994) was given in Fig. 3. The thick line is assigned to a near surface interval, corresponding to the year of 1989 - 1983, and the thin line to a low depth interval, to 1976 - 1970, for δD, MSA and $nssSO_4^{2-}$ in monthly mean respectively. The three parameters on the top show high value in summer and low value in winter simultaneously, whereas in the depth of 1976 - 1970 where δD and $nssSO_4^{2-}$ still keeps same seasonality as were on the top even with smaller concentration, MSA shows the up-down distribution of the peaks and troughs: winter with high value and summer with low value. What is the mechanism behind those unexpected "out of phase" seasonality, it is worth of further investigation.

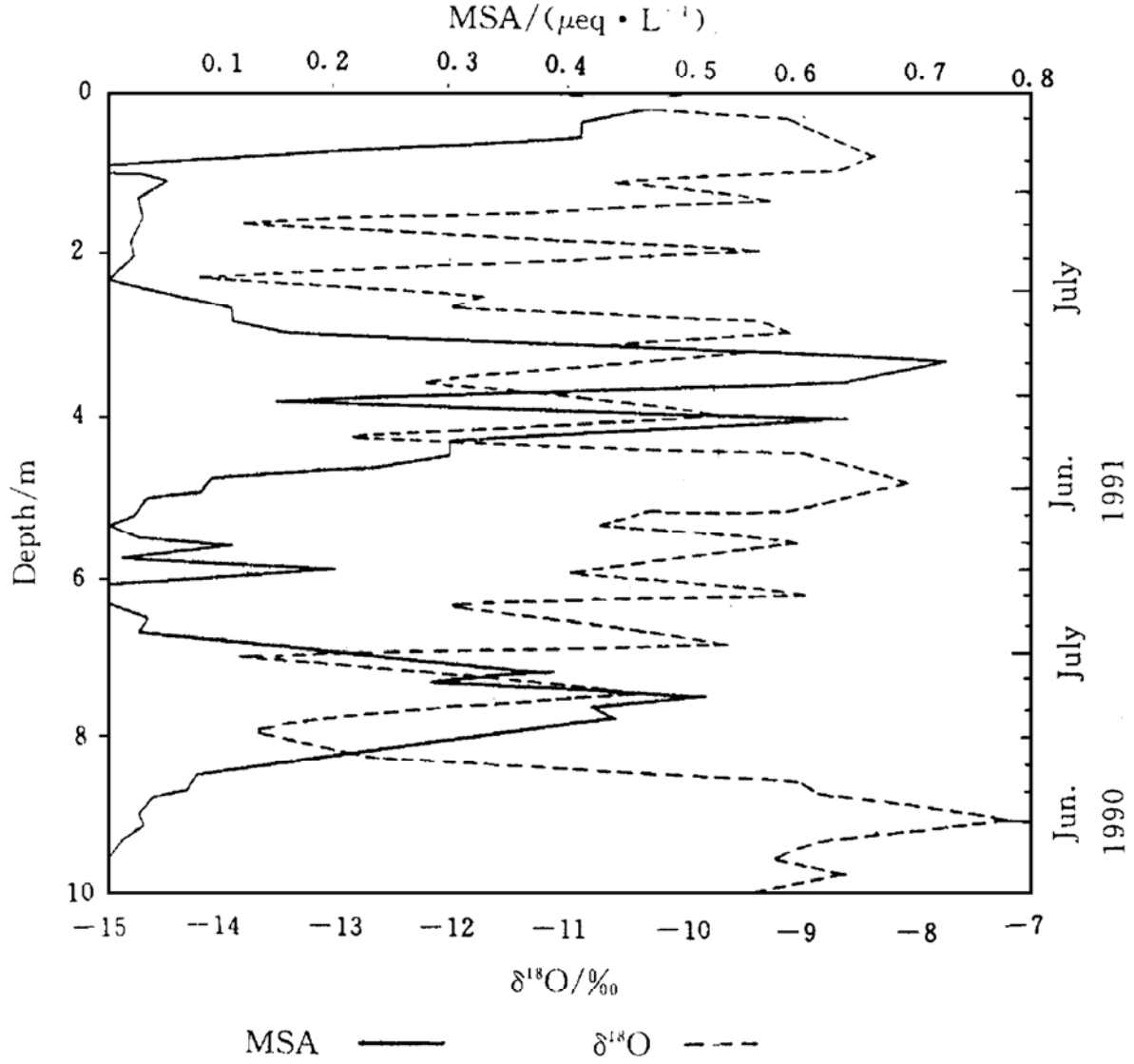

Fig. 2. MSA concentration in comparison with $\delta^{18}O$ variation against depth for the ice core of the King George Island.

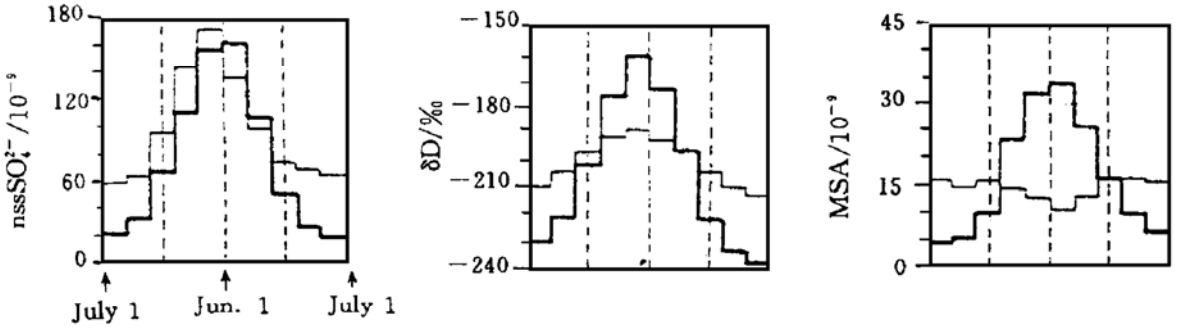

Fig. 3. Mean annual cycle of δD, MSA and nssSO_4^{2-} for a firn core drilled at F-R ice shelf. The thick line is assigned to a near-surface interval (corresponding to the years 1989 - 1983) and the thin line to a lower depth interval (1976 - 1970). (from Minikin *et al.* 1994).

The representative time sequence must be considered when examining the biogenic sulphur in the atmospheric aerosols individually. The data for Palmer Station are for over year observation, and others just for occasional sampling. Only the former, in the sense of present study, can be comparable with core data. The atmospheric aerosols of Palmer showed the same seasonality of MSA and SO_4^{2-} as that of the surface snow, and the similar MSA/nssSO_4^{2-} ratio. The listed results for other two sites (Table 3) in sampling season of autumn implicates that the Weddell Sea and the surrounding regions keep the high MSA/nssSO_4^{2-} ratio caused by the "surprising" high MSA concentration in the atmosphere (Berresheim 1987), which is in fitness with the results coming from the King George Island ice core analysis.

Table 3. Chemiscal features of atmospheric aerosols

Site	Palmer Station	Gerlache Strait	Drake Passage
Mean MSA/(ng·m^{-3})	48.8	18	32
Mean nssSO_4^{2-}/(ng·m^{-3})	98.5	33	29
MSA/nssSO_4^{2-} *	0.25	0.30	0.55
Data resources	Sovoie *et al.* (1993)	Berresheim(1987)	Berresheim(1987)

* :Sulphur equivalent ratio(to obtain molar ratio, multiply figure by 2).

4 Discussion

(1) The formation of the source region of productive biogenic sulphur in the Weddell Sea. The DMS concentration of the surface seawater is not directly connected to the production, as it also determined by emission and removing of DMS which relying heavily on the ventilation of the sea surface, and also on the decomposition of DMS and microbes in the water column. Welch *et al.* (1993) reported the correlation between the MSA concentration and the sea ice extent in the sampling place, believing the high possibility that the sea ice is suitable to the growth of oceanic photoplankton.

In this sense, the Weddell Sea probably possesses advantages over other Antarctic Seas. With the long shore of the Peninsula and the vast ice shelves in the south providing the quantitative amount of icebergs and floating ice, and frequent passing cyclones speeding up the air circulation, as well as the proper temperature condition favorable the photo-chemical reaction in the atmosphere (Mulvaney *et al.* 1992), the Weddell Sea must

be as a productive region of marine biogenic sulphur. As far as the discrepancy among areas is concerned, it may be the consequence of the combination of various affecting factors, on which we will not mention too much here.

(2) The regular spatial distribution of biogenic sulphur in the snow pack. The nssSO_4^{2-} and MSA produced by DMS are able to affect the CCN due to their high solubility, essentially, into the water. When they moving with the air mass after formation, small water droplets could be formed through absorption of vapor. More CCN could be formed in the case of high concentration of the MSA and nssSO_4^{2-}, hence the weight, for which raindrop required could be easily formed. This could serve as the reason for the high biogenic sulphur content in the low elevation and in the offshore area.

When the air moves further to inland and to higher altitudes, the reduction of the CCN requires more vapor to be absorbed to form a drop for a CCN, then the number of CCN in a drop declined, so only the lower concentration of MSA and nssSO_4^{2-} could be observed for the snowfall deposited in the higher sites and in the places far from the open seawater.

(3) The displacement of the MSA seasonal signals in the cores. The correspondence of the MSA peak to the autumn deposition exhibited by the King George ice core does not exclude the possibility that the summer is also the season with high MSA concentration in the atmosphere. The high content of the fall snow may be caused by the extra supplementation of the MSA from the Weddell Sea (Han *et al.* 1998) combined with other mechanism. The migration of MSA in the deep cores from the central Peninsula is probably the common phenomenon existing in deeper cores, deserving further investigation.

(4) The correlation and the discrepancy of the ice and atmospheric MSA concentration. There are both yearly summer and winter data for Palmer Station which share the aerosol sampling (Berresheim 1987), the ratio of summer to winter is about 30; while for the Dolleman Island the ratio of ice core records for 40 a is less than 20 (Pasteur *et al.* 1995). It suggests the "muting" of the atmospheric signals in the snow and ice. But one fact could not be negligible: the variation trend and the seasonality of the atmosphere were traced in the surface snow/ice. So it is reasonable to explain the profiles of cores in terms of atmospheric change even great caution has to be taken in interpretation. The close ratios of MSA to nssSO_4^{2-} (or to SO_4^{2-}) for atmosphere and snow/ice present us the confidence that the disassociation of the two species is very limited in the procedure when they fell from the air onto the snow. That is why the MSA/nssSO_4^{2-} both for snow and aerosols could be treated as the regional specificity.

5 Conclusion

In summary, the MSA and nssSO_4^{2-} concentration data from the ice cores and from atmospheric aerosols of the region surrounding the Weddell Sea have been analyzed in the present paper. The results suggest that the high concentration of biogenic sulphur in the snow and ice as well as in the atmospheric aerosols reflects the proximity of the Weddell Sea even though a distinct strength discrepancy exists in the productivity among the areas. The snow/ice shows that the production seems to be higher in the middle of the Antarctic Peninsula than near the F-R Ice Shelf. Despite factors impacting on the transportation and deposition processes of biogenic sulphur, the concentration of MSA and nssSO_4^{2-} in snow and ice shows a regular spatial distribution: decreasing with the

distance from the open sea and the altitude above sea level. Nevertheless, below a certain height, the "altitude effect" is no longer significant. The "displacement" of seasonality for MSA concentration observed in ice cores of the region has been discussed. The "out of phase" pattern in surface layer is attributed to the modification by prevailing meteorological condition to the transportation and deposition processes; while "relocation" in the deep layers may be caused by migration or a mechanism, which needs to be further investigated.

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References

Bates TS, Charlson RJ, Gammon RH(1987): Evidence for the climatic role of marine biogenic sulphur. Nature, 329:319 - 321.

Berresheim H (1987): Biogenic sulfur emissions from the subantarctic and Antarctic Oceans. J. Geophys. Res., 92:13245 - 13262.

Charlson RJ, Lovelock JE, Andreae MO *et al.* (1987): Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. Nature, 326:655 - 661.

El Sayed SZ, Bigg DC, Holm-Hansen O(1983): Phytoplankton standing crop, premary productivity and near-surface nitrogeneous nutrient fields in the Ross Sea, Antarctica Deep Sea Res., 80:871 - 886.

Han JK, Kang JC, Wen JH *et al.* (1993): Concentration characteristics of soluble impurities in the surface snow of Collions Ice Cap, King George Island, Antarctica. Antarctic Research, 4(2): 29 - 35.

Han JK, Xie ZC, Mayewski PA *et al.* (1998): Seasonal distribution of MSA in the snow/ice of a subantarctic glacier. J. Glaciology and Geocryology, 20(4):343 - 347.

Jeffrezo JL, Davidson CI (1994): Sulphate and MSA in the air and snow on the Greenland Ice Sheet. J. Geophys. Res., 99:1241 - 1253.

Legrand MR, Delmas RJ (1984) The ionic balance of Antarctic snow: a 10-year detailed record. Atmos. Environ., 18: 1867 - 1874.

Legrand M, Feniet-Saigne C (1991): Strong EI Nino Revealed by methanesulphonic acid in South Polar snow layers. Geophys. Res. Lett., 18:187 - 190.

Minikin A, Wagenbach D, Grat W *et al.* (1994): Spatial and seasonal variations of the snow chemistry at the central Filchner-Ronne Ice Shelf. Antarctic. Ann. Glaciol., 20: 283 - 290.

Mulvaney R, Pasteur EC, Peel DA (1992): The ratio of MSA to non-sea-salt sulphate in Antarctic Peninsular ice cores. Tellus, 4413: 295 - 303.

Pasteur EC, Mulvaney R, Peel DA *et al.* (1995): A 340-year record of biogenic sulphur from the Weddell Sea area, Antarctic. Ann. Glaciol., 21:169 - 174.

Prospero JM, Savoie DL, Saltzman ES *et al.* (1991): Impact of oceanic sources of biogenic sulphur on sulphate aerosol concentrations at Mawson, Antarctic. Nature 350:221 - 223.

Savoie DL, Prospero JM, Larsen RJ *et al.* (1993): Nitrogen and sulfur species in Antarctic aerosols at Mawson, Palmer Station, and Marsh (King George Island). J. Atmospheric Chemistry, 17:95 - 122.

Wagenbach D, Gorlach U, Moser K *et al.* (1988): Coastal Antarctic aerosol: the seasonal pattern of its chemical composition and radionuclide content. Tellus, 40B: 426 - 436.

Wagenbach D, Graf W, Minikin A *et al.* (1994): Reconnaissance of chemical and isotopic firn properties on top of Berkner Island, Antarctica. Ann. Glaciol. 20,307 - 312.

Welch KA, Mayewski PA, Whitlow SI (1993): Methanesulfonic acid in coastal Antarctic snow related to sea-ice extent. Geophys. Res. Lett., 20:443 - 446.