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## SPATIAL AND TEMPORAL VARIATIONS OF METHANESULFONIC ACID AND NON SEA SALT SULFATE IN ANTARCTIC ICE

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**ABSTRACT.** A simultaneous glaciochemical study of methanesulfonic acid (MSA) and non-sea-salt sulfate ( $\text{nss-SO}_4^-$ ) has been conducted on the Antarctic plateau (South Pole, Vostok) and in more coastal regions. The objective was to investigate marine sulfur emissions in very remote areas. Firstly, our data suggest that MSA and  $\text{nss-SO}_4$  present in antarctic ice are mainly marine in origin and that DMS emissions have been significantly modulated by short term (eg. El Nino Southern Oscillation events) as well as long term climatic changes in the past. Secondly, our study of spatial variations of these two sulfur species seems to indicate that the atmosphere of coastal antarctic regions are mainly supplied by local DMS emissions whereas the atmosphere of the high plateau is also influenced by DMS emissions from more temperate marine latitudes. Thirdly, our study of the partitioning between MSA and  $\text{nss-SO}_4$  suggest that the temperature could have been an important parameter controlling the final composition of the high southern latitude atmosphere over the last climatic cycle ; colder temperature favoring the formation of MSA. However, our data also support a possible role played by changes in the transport pattern of marine air to the high antarctic plateau.

**Key words :** Antarctica, snow chemistry, sulfur cycle.

### 1. Introduction

DMS emissions from the oceans may affect Earth's climate through the production of submicrometer sulfate particles which may act as cloud condensation nuclei and modify the marine cloud albedo (Charlson et al., 1987). Although it is now clear that marine biogenic DMS emissions represent the major source of such aerosol in marine remote areas, some important gaps in our knowledge remain in the sulfur cycle at high latitudes.

First, there have been few DMS studies in the marine boundary layer and in surface water of

these high latitude regions where relatively high primary marine productivity is expected (El-Sayed and Weber, 1982). Until now, only a few measurements have been carried out on DMS oxidation products in the marine boundary layer south of about 40° S (Berresheim, 1987 ; Pszenny et al., 1989) and such studies generally have covered very short time periods.

A second knowledge gap relates to the fate of the DMS within the atmosphere at high latitudes. Indeed methanesulfonic acid ( $\text{CH}_3\text{SO}_3\text{H}$ , abbreviated as MSA) and sulfur dioxide (converted in the atmosphere into non sea-salt sulfate,  $\text{nss-SO}_4$ ) are two major end products from the atmospheric oxidation of DMS provided by the marine biota. Molar MSA/ $\text{nss-SO}_4$  ratios (R) ranging from 3 to 10 % have been generally observed in marine remote area at mid and low latitudes (Saltzman et al., 1983 ; 1986) but this ratio seems to increase at higher latitudes (Berresheim, 1987 ; Pszenny et al., 1989 ; Savoie et al., 1989 ; Savoie et al., 1990 ; Minikin and Wagenbach, 1990). It is therefore important to increase our understanding of the sulfur cycle in these very remote areas.

Polar ice cores can provide a unique record of environmental changes and be therefore useful to obtain information on the variability of marine DMS emissions in the past and on the fate of DMS in the high latitude atmosphere. Only a few studies have investigated MSA and  $\text{nss-SO}_4$  content of polar ice. Legrand et al. (1991) have suggested that DMS emissions of southern hemisphere oceans have been modulated by the climate in the past. In a recent study, Legrand and Feniet-Saigne (1991) suggest that DMS emissions from the antarctic oceans were enhanced during ENSO developments. In this paper we investigate MSA and  $\text{nss-SO}_4$  content of snow and ice deposited in various antarctic stations (coastal as well as central antarctic), over different time periods.

## 2. Experimental

On each sample, we have determined MSA, sulfate, sodium and calcium contents using an ion chromatograph (Dionex 4000 i). Using a gradient pump system, an  $\text{AS}_5$  separator column and a sodium hydroxide eluant (carbonation prevented by a continuous helium flow), it is possible (as shown in Figure 1) to measure MSA and  $\text{SO}_4$  on the same sample. At the beginning of the analysis, a weak NaOH concentration ( $5 \cdot 10^{-4}$  N) is used to obtain a good separation between formate ( $\text{HCOO}$ ) and methanesulfonate ( $\text{CH}_3\text{SO}_3$ ) ions (Figure 1). Later on, we increase the NaOH concentration (up to  $3 \cdot 10^{-2}$  N) to elute the  $\text{SO}_4$  ion within less than fifteen minutes. As far as we prevent our sample from formate contamination (such a contamination occurs when liquid samples are stored in polyethylene bags for instance, see Legrand and Saigne, 1988 ; Saigne et al., 1987), the accuracy is 5 % (at 95 % confidence level) in the range 1 to 20  $\text{ng} \cdot \text{g}^{-1}$  of MSA with a 5 ml sample volume. Cation measurements were performed using working

conditions reported elsewhere (Saigne et al., 1987) with an accuracy of 10 %.

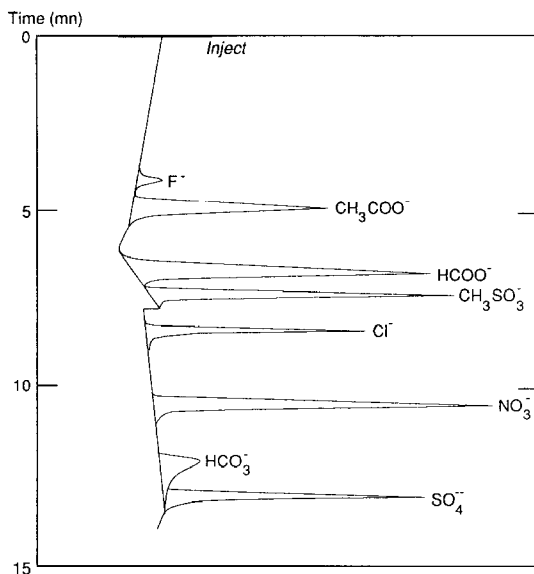


Figure 1 : Typical ion chromatogram:  $F^-$  ( $0.4 \text{ ng.g}^{-1}$ ),  $CH_3COO^-$  ( $7 \text{ ng.g}^{-1}$ ),  $HCOO^-$  ( $10 \text{ ng.g}^{-1}$ ),  $CH_3SO_3^-$  ( $8 \text{ ng.g}^{-1}$ ),  $Cl^-$  ( $30 \text{ ng.g}^{-1}$ ),  $NO_3^-$  ( $90 \text{ ng.g}^{-1}$ ),  $SO_4^-$  ( $100 \text{ ng.g}^{-1}$ ). Sample volume  $5 \text{ ml}$ , meter setting  $3 \mu\text{S}$  from  $F^-$  to  $CH_3SO_3^-$ ,  $30 \mu\text{S}$  from  $Cl^-$  to  $SO_4^-$ .

Ice coring, transport and storage of ice cores create high contamination levels on the external part of the cores. To remove surface contamination, two procedures can be used: 1) washing cores with ultrapure water at the room temperature ( $\sim 20^\circ\text{C}$ ) or, 2) mechanically removing the exterior of cores in cold room ( $-15^\circ\text{C}$ ). In their first MSA study along the deep Dome C ice core, Saigne and Legrand (1987) washed ice core sections with ultrapure water. This method successfully employed for the analysis of mineral species (successive fractions from the outer to the inner part of the core exhibit high values on the exterior of the core and then a constant value further inside, see Figure 2a) appeared to be adequate for MSA study along the Dome C (Figure 2b<sub>1</sub>) core. When using this procedure on the Vostok core, we observed a rather slight but persistent decrease of MSA concentrations to the center of the core (Figure 2b<sub>2</sub>). Note that, in contrast to the Dome C core, the Vostok core sections were stored during 24 hours at  $-3^\circ\text{C}$  to prevent breakage of this core which appeared to be extremely fragile.

When using the washing procedure on an ice core section close to the firm ice transition (Figure 2b<sub>3</sub>), the exterior-interior profile exhibits a more dramatic picture. Because corresponding profiles obtained for mineral species (not reported here) do not exhibit such an exterior-interior trend, it is difficult to explain by a weak contamination dragged by the washing procedure to the interior of these cores.

Subsequently we have designed an ice core lathe equipped with a stainless steel knife to mechanically remove the outer part of the core until 95 % of the ice volume was discarded. Using this procedure which does not require any previous storage of ice at temperature close to  $0^\circ\text{C}$ , the exterior-interior profiles for mineral species as well as for MSA exhibit a plateau

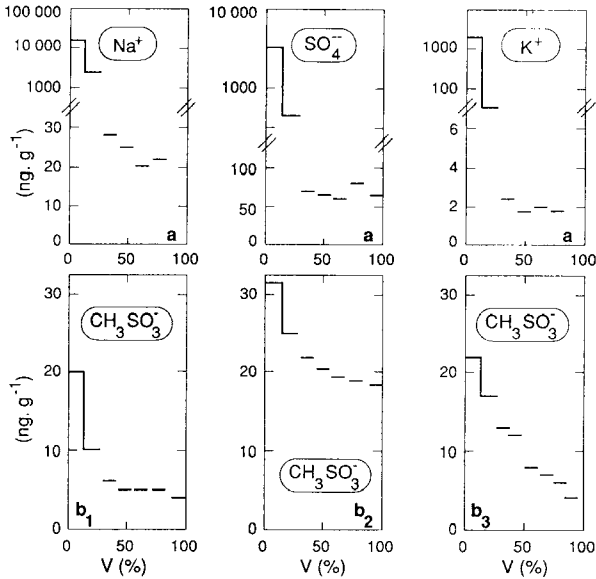


Figure 2 : Decontamination of ice sections by washing with ultrapure water :

a) For mineral species (Na,  $\text{SO}_4$ , K) on a 250-m depth Dome C core section

b<sub>1</sub>) For  $\text{CH}_3\text{SO}_3^-$  on the same core section

b<sub>2</sub>) For  $\text{CH}_3\text{SO}_3^-$  on a Vostok core section

b<sub>3</sub>) For  $\text{CH}_3\text{SO}_3^-$  on a D10 core section

Concentration (in  $\text{ng.g}^{-1}$ ) are reported as a function of the melted fraction of ice volume (%V).

(Figure 3). It also becomes clear that in contrast to the mineral species, no dramatic MSA contamination is observed on the outer part of the Vostok core.

The importance of the choice of the decontamination procedure is clearly demonstrated in Figure 4 on which we report  $\text{SO}_4$  and MSA values observed along the Vostok core at similar depths by the washing procedure and by using the lathe.  $\text{SO}_4$  data obtained using the two procedures agree rather well whereas we can observe systematically lower MSA values by washing Vostok core sections. Although it remains unclear why MSA and mineral species seem to have very different behaviours when ice cores are washed with ultrapure water, our data strongly recommend using the mechanical procedure in future MSA studies along deep ice cores.

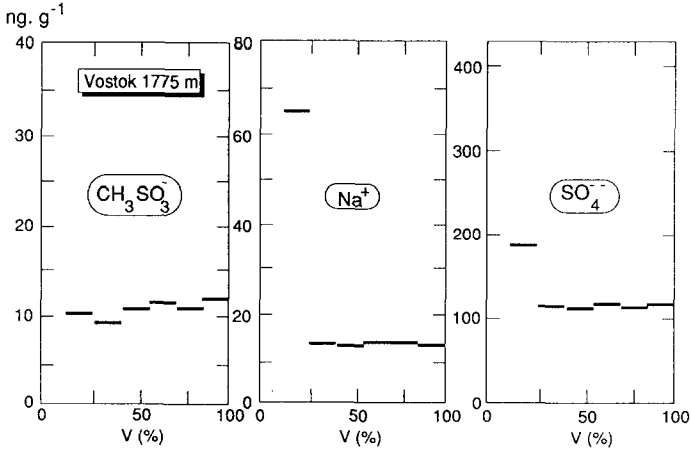


Figure 3 : Demonstration of the external contamination of an ice core section (Vostok at 1775 m depth) for mineral species ( $\text{Na}^+$  and  $\text{SO}_4^-$ ). At the opposite, no contamination is observed for MSA.

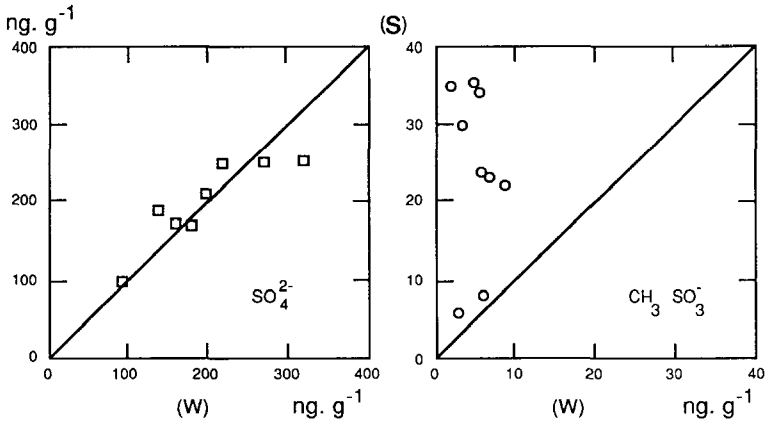


Figure 4 :  $\text{SO}_4$  and MSA values obtained at similar depths along the Vostok ice core by washing (W) and by subcoring (S) with a lathe (see text) ice core sections.

3. Results and discussion

3.1. SPATIAL VARIATIONS OF THE MSA/nss-SO<sub>4</sub> RATIO (R)

MSA and nss-SO<sub>4</sub> have been measured in snow and ice deposited under present climatic conditions (recent years as well as the Holocene stage) at various antarctic locations (South Pole, Dome C, and Vostok) of the high plateau and in more coastal area (the Mirny-Vostok traverse, James Ross Island and Law Dome).

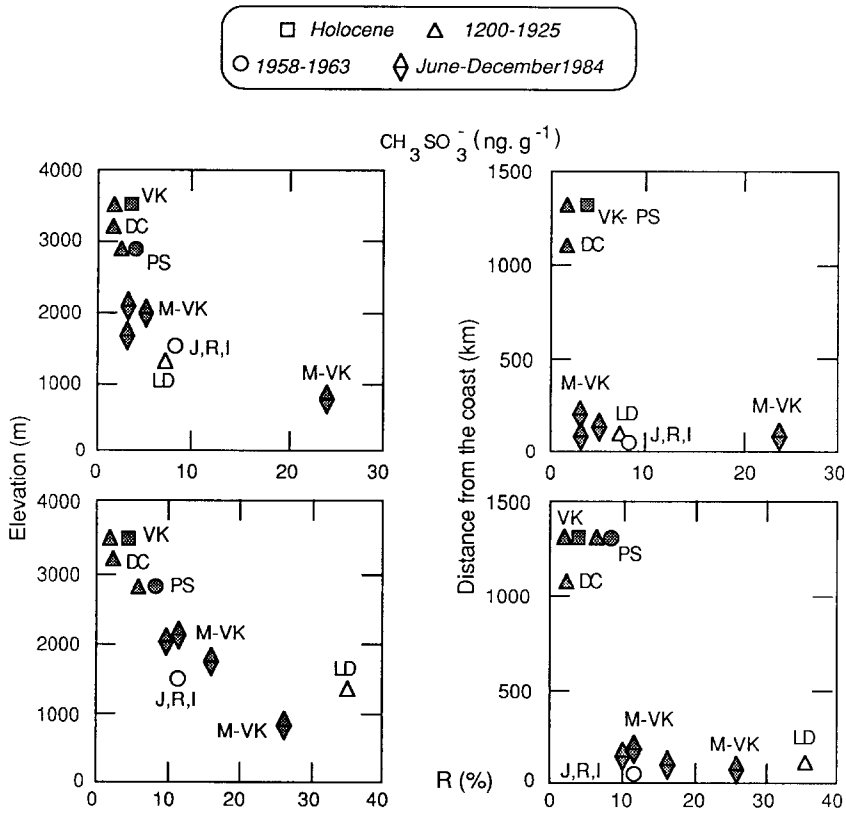


Figure 5 : MSA (in ng.g<sup>-1</sup>) and MSA/nss-SO<sub>4</sub> molar ratio R (in %) in snow deposited at several antarctic sites under present climatic conditions.

VK abbreviates Vostok, DC Dome C, PS South Pole, LD Law Dome, JRI James Ross Island, and M-VK the traverse Mirny-Vostok.

JRI data are from A. Aristarain (personal communication), LD data from Ivey et al. (1986).

The MSA to non sea-salt sulfate molar ratio (R) (Figure 5) exhibits significant spatial variations with the elevation or with the distance from the coast. Indeed high antarctic plateau (~ 3000 m elevation or more) precipitation exhibits low R values (3 to 10 %) whereas higher R values are observed near the coast. This picture confirms data previously obtained by Saigne et al. (1987) along a coastal deep ice core.

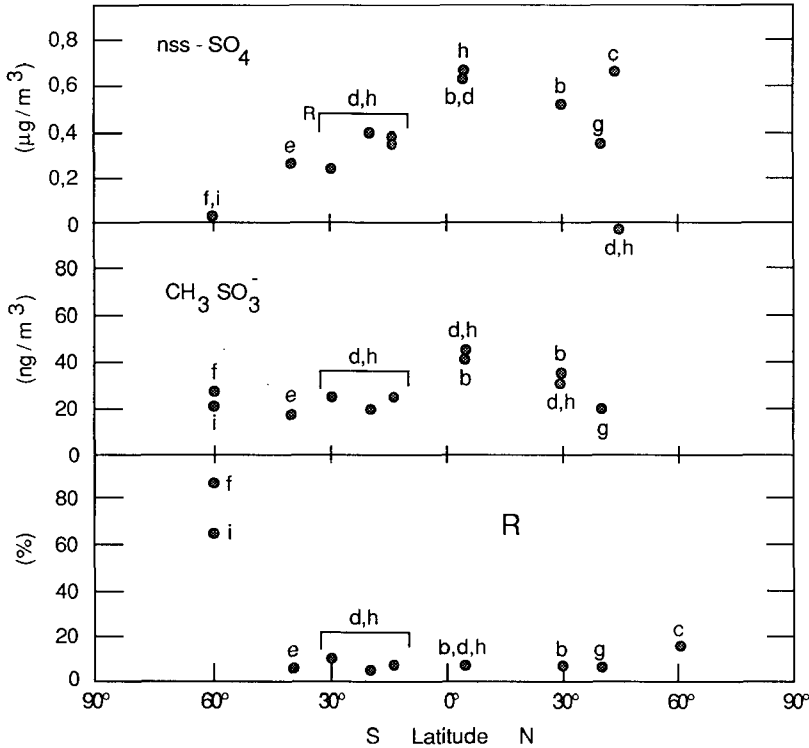


Figure 6 : Atmospheric variations with latitude of nss-SO<sub>4</sub>, MSA concentrations and R ratios reported by several studies : (b) from Saltzman et al. (1983), (c) Prospero et al. (1985), (d) Saltzman et al. (1986), (e) Ayers et al. (1986), (f) Berresheim (1987), (g) Andreae et al. (1988), (h) Savoie et al. (1989), (i) Pszenny et al. (1989).

In the marine boundary layer, low R values are generally observed at low latitudes (Figure 6) but recent studies (Berresheim, 1987 ; Pszenny et al., 1989) reported a strong increase of this ratio (60 to 80 %) at 60° S. In this way, ratios observed in coastal antarctic precipitation are in rather good agreement with atmospheric observations at high southern latitudes. More questionable are the lowered ratios observed in high antarctic plateau precipitation and several



possible explanations can be suggested. First, we can invoke the input of a non-marine  $\text{SO}_4$  source acting more efficiently over the antarctic plateau than in coastal areas. The stratospheric input has historically been presented as a possible contribution to the  $\text{SO}_4$  budget of central Antarctica. There is now a general agreement that this contribution is weak (see Legrand and Delmas, 1990) except after large volcanic eruptions (Legrand and Delmas, 1987). Second, if we assume that end products (MSA and nss- $\text{SO}_4$ ) present in central as well as in coastal antarctic regions both originate from the same high latitude marine DMS emissions, our data could suggest a different branching ratio ( $\text{DMS} \rightarrow \text{SO}_2$ ,  $\text{DMS} \rightarrow \text{MSA}$ ) related to different photochemical conditions occurring over the central plateau and over the surrounding ocean. For instance, the relative content of  $\text{NO}_3$  and OH radicals of the atmosphere over the ocean and over the continent could modify the DMS oxidation scheme, but due to a present lack of knowledge of possible DMS oxidation schemes occurring under polar conditions, it remains difficult to assess such a explanation. More recently, a size distribution study (Pszenny, 1990) has shown that MSA particles have a larger size range than have that of nss- $\text{SO}_4$ . It may be therefore possible that the lowering of R over the antarctic plateau reflects a more efficient uptake of MSA by sea salt particles near the coast. On the other hand, the study from Minikin and Wagenbach (1990) reveals an underestimation in evaluating the nss- $\text{SO}_4$  at high latitudes in connection with a possible sea salt fractionation phenomena which can lead to some important errors in the calculation of R in these regions.

Finally, to explain lowering R values towards the high antarctic plateau, Saigne and Legrand (1987) suggested that these regions are mainly supplied by end products of DMS emitted at more temperate latitudes thereafter long-range transported in the middle troposphere.

### 3.2. Temporal variations of MSA and R

3.2.1. *Short term variations.* Seasonal variations of MSA and nss- $\text{SO}_4$  in snow may help to unravel the origin of these species. As previously discussed (Legrand and Delmas, 1988) the South Pole is a very suitable location for such studies. In this section, we examine the years 1976-1983 at the South Pole. This was a period during which seasonal variations were particularly well recorded, as evidenced by the sodium profile (Figure 7) .

The Na profile exhibits a mean value of  $10 \text{ ng.g}^{-1}$ , with maxima ( $16 \text{ ng.g}^{-1}$ ) in winter and minima ( $3 \text{ ng.g}^{-1}$ ) in summer. Atmospheric aerosol measurements at the South Pole (Cunningham and Zoller, 1981 ; Tuncel et al., 1989) show similar seasonal sodium variations with marked maxima in winter. These variations arise from the more frequent advection of marine air masses over the high antarctic plateau in winter. Nss- $\text{SO}_4$  exhibits seasonal cycles which are smaller in amplitude than those of sodium, with weak maxima in summer and minima in winter. These variations differ markedly from that in coastal antarctica, where the amplitude of seasonal variations in nss- $\text{SO}_4$  is very large, in fact much larger that of sodium (Savoie et al.,

1990).

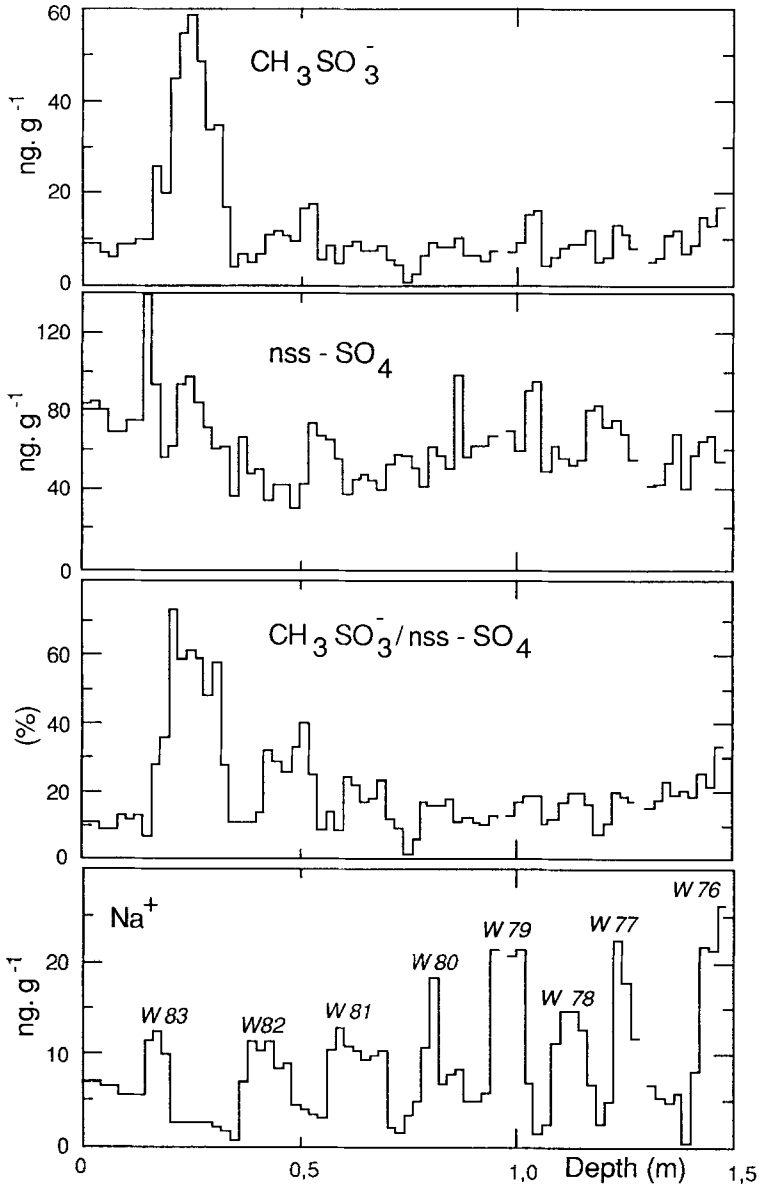


Figure 7 : Seasonal variations of MSA, nss-SO<sub>4</sub>, R, and Na content of south polar snow deposited between 1976 and 1983. W denotes winters seasons.

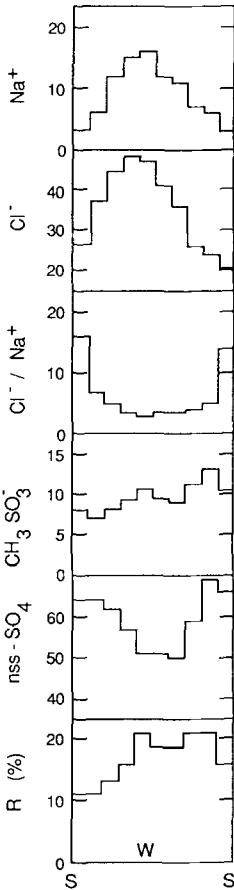


Figure 8 : Mean seasonal signals of sodium, chloride, Cl/Na weight ratio, MSA, nss-SO<sub>4</sub>, and R molar ratio in south polar snow layers over the 1976-1981 time period. W denotes winter (Na maxima) and S summer (Cl/Na maxima) seasons (Legrand and Delmas, 1988).

Wintertime concentrations of nss-SO<sub>4</sub> at South Pole are comparable or 6 times greater than in coastal areas (Table 1).

In contrast to Na, MSA exhibits very weak seasonality in South Pole snow, with slight maxima occurring during the early spring (Figure 8). Again, this weak seasonal cycle differs from that observed in coastal Antarctica, where winter to summer variations in MSA are as large as a factor of 30 (Table 1). As a consequence of the different seasonal cycles of MSA and nss-SO<sub>4</sub> at South Pole, the ratio R (MSA/nss-SO<sub>4</sub>) also exhibits seasonality, with a fall-winter maximum of 15-21% and a spring-summer minimum of 10-15%.

The marked differences between the seasonality observed at South Pole and that in coastal aerosols suggest that the high latitude coastal source may not dominate the sulfur budget of the high antarctic plateau. One might expect that transport between the coast and plateau would be most efficient during the winter (as evidenced by the sodium seasonality) but during this time, there is little atmospheric nss-SO<sub>4</sub> and MSA available in the coastal air masses for transport. The

TABLE 1 : Mean concentrations of constituents measured at the South Pole (in snow and in the atmosphere) and in coastal antarctic regions over winter (W) and summer (S)

Stations	Na	nss-SO <sub>4</sub>	MSA	References
South Pole (air)	34 ng/m <sup>3</sup> (W) 7 ng/m <sup>3</sup> (S)	42 ng/m <sup>3</sup> (W) 172 ng/m <sup>3</sup> (S)	- -	Cunningham and Zoller (1981) Tuncel et al. (1989)
South Pole (snow)	16 ng g <sup>-1</sup> (W)	50 ng g <sup>-1</sup> (W) 70 ng g <sup>-1</sup> (S)	7 to 13 ng g <sup>-1</sup> (maxima early spring)	This work
G.v. Neumayer (air)		40 ng/m <sup>3</sup> (W) 240 ng/m <sup>3</sup> (S)	3 ng/m <sup>3</sup> (W) 60 ng/m <sup>3</sup> (S)	Mimikin and Wagenbach (1990)
Mawson (air)		6-8 ng/m <sup>3</sup> (W) 210-250 ng/m <sup>3</sup> (S)	2-3 ng/m <sup>3</sup> (W) 30-60 ng/m <sup>3</sup> (S)	Savoie et al. (1990)

R ratios observed at South Pole throughout the year are surprisingly low, well below the 30% expected for the coastal antarctic source region. This suggests that the source regions are located at low to mid latitudes and that the long-range transport plays a major role in the sulfur budget at the South Pole. Of course, the possibility must also be considered that the ratio of MSA to nss-SO<sub>4</sub> in South Pole precipitation has been altered from that at the source region due to selective deposition of MSA relative to nss-SO<sub>4</sub> as a result of particle size differences. The particle size distributions of MSA and nss-SO<sub>4</sub> over Antarctica are unknown at present and further investigation of this point is needed.

As depicted in Figure 7, a large increase of MSA occurred in 1982 and 1983. This MSA increase is accompanied by a small nss-SO<sub>4</sub> change, resulting in a large increase of the R ratio  $R=45\%$ . Referring to high R values observed at high latitudes, our data suggest an enhanced contribution of high latitude DMS emissions towards the antarctic plateau during this event. We tentatively have tried to reconstitute MSA and nss-SO<sub>4</sub> origins at the South Pole in terms of local and more temperate DMS emissions. Concerning background levels, we assume that almost a half of MSA originates from local DMS emissions, an other half from north of 40°S. Using R values of 6% and 100% for temperate and high latitude emissions respectively (as suggested by the figure 6), we can expect a mean nss-SO<sub>4</sub> content of about 55 ng.g<sup>-1</sup> and a mean R of 15% over the high antarctic plateau (Figure 9). Such a picture is in rather good agreement with our

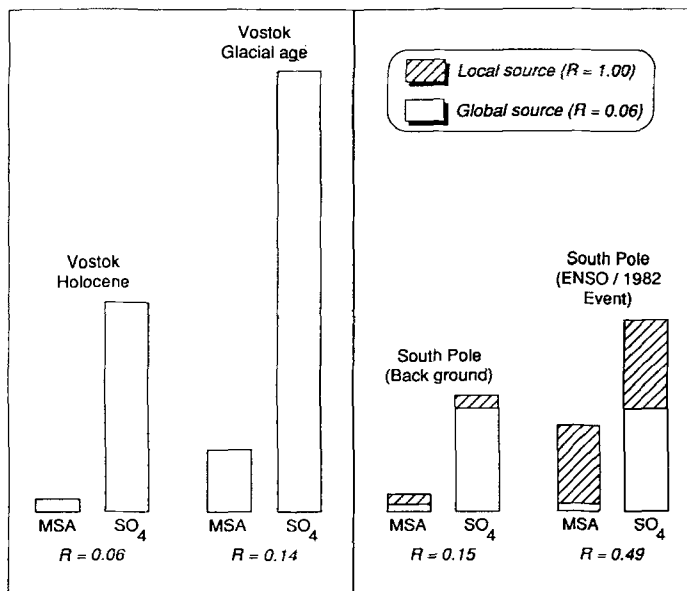


Figure 9 : Relative contribution of local and global DMS emissions to the MSA and sulfate content of snow deposited at Vostok and South Pole (see text).

data (Figure 8). For the 1982-1983 event, the large increase of MSA is mainly linked with local emission increase as reflected by the small change of  $\text{nss-SO}_4$  (Figure 9). This enhanced contribution of the local DMS source suggests a more efficient transport between the central area and surrounding oceans or enhanced high latitude DMS emissions during these years. Because the 1982 perturbation is not accompanied by higher Na content (Figure 7), we can therefore conclude (as Legrand and Feniet-Saigne, 1991) that the perturbation reflects enhanced DMS emissions at high latitudes. Such perturbations appear rather often further down in south polar snow layers and it was recently suggested that they coincide with years of strong ENSO development (Legrand and Feniet-Saigne, 1991). The physical link between ENSO event and high latitude DMS emissions is not still elucidated and further studies are required.

3.2.2. *Long term variations.* MSA and  $\text{nss-SO}_4$  depth profiles along the Vostok ice core have been recently examined by Legrand et al. (1991). Under present climatic conditions, with mean MSA and  $\text{nss-SO}_4$  levels of 6 and 100  $\text{ng.g}^{-1}$  respectively, the Vostok site seems to be mainly influenced by DMS emissions from mid latitudes (see Figure 9). This absence of input from high latitude DMS emissions at Vostok (as opposed to South Pole) could be explained by the more continental position of the Vostok station : 3400 m elevation at the top of the East antarctic plateau where a quasi-permanent high pressure probably limits invasion of local marine air masses.

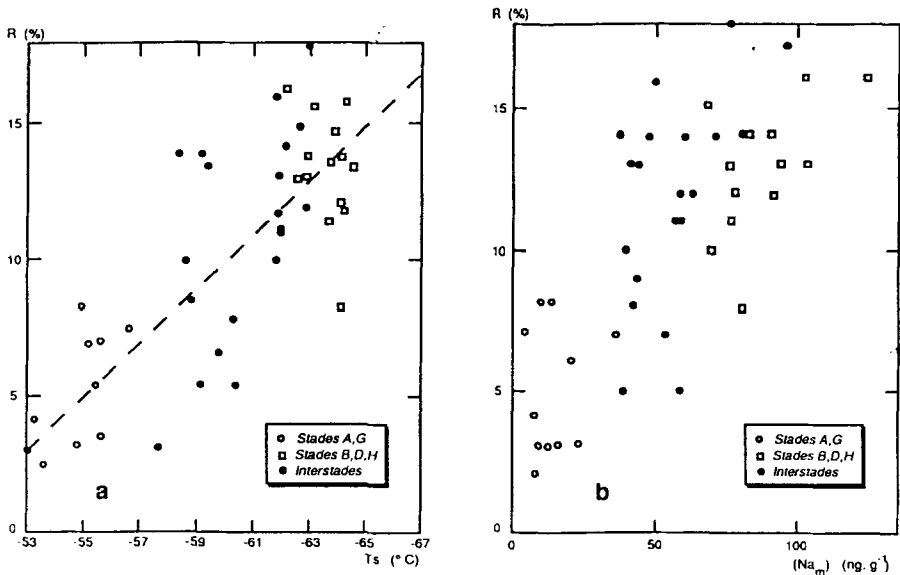


Figure 10 : Temporal variations of R along the Vostok ice core (the last climatic cycle) :

a) as a function of surface Vostok temperatures ( $T_s$ ).

b) as a function of the Na content of the ice ( $\text{Na}_m$ ).

Stades A to H are defined in Legrand et al. (1991).

One of the notable features of these MSA and nss-SO<sub>4</sub> records over the last climatic cycle is that both species increase during glacial ages. These data suggest that during very cold time periods over the last climatic cycle, DMS emissions of the southern hemisphere oceans have been significantly enhanced. Moreover, the R ratio itself seems to be modulated by the climatic conditions as reflected (Figure 10 a) by the good relationship ( $r=0.78$ ) with the temperatures (Ts) at Vostok in the past. Such a good correlation between R and the climate (colder temperature being favouring MSA formation) may be indirect evidence for temperature dependence of the branching ratio of the DMS oxidation process. Indeed, as suggested by laboratory experiments (Hynes et al; 1986), the temperature dependence of OH addition (MSA formation) versus H abstraction (SO<sub>2</sub> formation) during the DMS oxidation by OH should increase the MSA production at colder temperatures. However our Vostok data suggest that other explanations are possible as well. Indeed, as shown in Figure 10 b, R values are also well correlated with the Na content ( $r=0.73$ ). Such a correlation could be the result of the good correlation between Na content and the climate (cold climate leading enhanced sea salt production, Legrand et al., 1987) or the reflect of a more efficient transport of MSA on sea salt particles to the central antarctic. We need therefore further studies to understand this link between the climate and the MSA/nss-SO<sub>4</sub> ratios during the past.

#### 4. Conclusions

This study of spatial and temporal variations of MSA and nss-SO<sub>4</sub> contents of antarctic snow and ice provides some useful information on the sulfur cycle at high latitudes. Our data show that the atmosphere of the East antarctic plateau contains sulfur species (MSA and sulfate) in similar proportion than in the mid latitude marine atmosphere and that its sulfur content is strongly modulated by climatic conditions in the past. At the South Pole, the MSA budget seems to be additionally influenced by more sub-antarctic DMS emissions, especially during years corresponding to ENSO developments. Finally, coastal regions are more exposed to local DMS emissions which seems to be characterised by relatively rich MSA content.

Further works are needed to evaluate the relative contributions of local and global DMS emissions to the sulfur budget of snow deposited in various antarctic regions.

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