

Evidence for the loss of snow-deposited MSA to the interstitial gaseous phase in central Antarctic firn

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ABSTRACT

We have examined several MSA (methanesulfonic acid) records from the upper 200 m of the Antarctic ice sheet and in particular the new Dome F profile. At all the four sites studied, concentration profiles exhibit similar patterns as a function of depth. They suggest that snow metamorphism and solid phase migration are responsible for a marked release of gaseous MSA to interstitial firn air as well as probably to the free atmosphere, in particular at extremely low accumulation sites. Snow acidity can also modify MSA concentration. It is proposed that, below the upper few metres where the communication with the free atmosphere is possible, gaseous MSA may remain in the firn layers and be entrapped later in air bubbles at pore close-off, i.e. when firn is transformed into ice. Chemical measurements on the firn core do not take into account the MSA released to the gaseous phase, but this fraction is measurable in ice samples. In spite of these alterations occurring in the firn layers, relative changes of the atmospheric MSA concentration in the past are probably still there deep within the Antarctic ice sheet. However, for glacial periods, different processes have to be considered in relation to modified aerosol properties.

1. Introduction

Dimethyl sulfide (DMS) is produced in the ocean, but its major environmental effect is observed in the atmosphere given that this gas is the most significant natural source of atmospheric sulfur (Nguyen et al., 1978; Andreae, 1986; Charlson et al., 1987; 1989). Sulfate (non-sea-salt sulfate or nss-SO₄) and methanesulfonic acid (MSA) are the two most important compounds formed in the complex oxidation processes affecting DMS in the atmosphere (Hynes et al., 1986; Turnipseed and Ravishankara et al., 1993; Saltelli and Hjorth, 1995). MSA is specific to marine biogenic activity and, for this reason, its concentrations in the remote troposphere have been a subject of great interest over the last decade. In ice core studies, particularly,

MSA has become a species of primary importance: it has been proposed as a tool for reconstructing the past history of major El Niño events (Legrand and Feniet-Saigne, 1991) and documenting past variations of marine productivity related to climate changes (Legrand et al., 1991; 1992).

The determination of MSA in polar ice is a relatively recent field of investigation (Saigne and Legrand, 1987; Saigne et al., 1987) and not free of analytical difficulties (Legrand et al., 1992). Moreover, there are indications that MSA ice records may suffer post-deposition modifications (Mulvaney et al., 1992; Pasteur and Mulvaney, 2000), and laboratory experiments show that the methane sulfonate ion is able to migrate in the firn, most probably via liquid drainage, according to Pasteur and Mulvaney (1999). It has been proposed from a study carried out at Vostok, central Antarctica, that MSA could be deposited on the snow as a gas, or at least that a gaseous species is involved in the formation of its records in ice (Wagnon

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et al., 1999). Measurements suggest that 80–90% of this compound may leave the ice matrix in the very first metres, in relation probably to the metamorphism of snow. The marked decrease in MSA concentration is similar to the trend observed in Vostok snow for species known to be partly (Cl) or nearly totally (NO₃) deposited as gases. This finding may cast doubt on the validity of MSA records in polar ice. What is the actual significance today of MSA concentrations in ice cores?

The answer to this question is important when reconstructing the past atmospheric sulfur cycle from ice cores. It may question the augmentation of marine productivity during glacial climatic stages and the link between MSA concentrations and El Niño events mentioned earlier.

Firn is the interface between the polar atmosphere and the ice. Once deposited, snow undergoes metamorphic changes, including compaction, sublimation and sintering. These processes are likely to have a significant effect on the concentrations of chemicals contained in firn, and consequently on the formation of ice records.

For all these reasons, we have decided to re-examine MSA data from Antarctic records covering the firn layers and the firn/ice transition, taking into account the hypothesis of gaseous MSA in polar firn.

2. Study sites, sampling and experimental methods

Discussions will be focused mainly on snow, firn and ice data from four Antarctic locations: Vostok and Dome Fuji (extremely low accumulation sites), and Amundsen–Scott (South Pole Station) and Byrd Station (low accumulation sites). Major features of the study sites are reported in Table 1.

2.1. Vostok samples

A 32-m firn core covering nearly the last 800 yr was collected at Vostok (East Antarctic Plateau) in

December 1991 and cut in the field into 1-m lengths (Wagnon et al., 1999). 269 samples (48% of the total length of the core) were analyzed 15 months later in the laboratory. Major ions and methane sulfonate concentrations were measured by ion chromatography at the ppb (ngg⁻¹) to sub-ppb level. The core was accurately dated on the basis of nss-SO₄ spikes corresponding to major volcanic eruptions: Krakatoa (1884) at 6.6 m, Tambora (1816) at 9.85 m and the 1259 unknown (Langway et al., 1988) at 30.15 m.

A snowpit was sampled in great detail (every 2 cm) from December 1989 to January 1990 for chemical and grain size measurements. Snow samples for chemistry were stored in individual Accuvettes[®] containers and transported in the solid state to Grenoble for analysis (Feniet, 1990), whereas grain size was determined in the field (Lipenkov, personal communication).

2.2. Dome Fuji samples

Dome Fuji is located in Dronning Maud Land, on the high Antarctic Plateau. Study samples (220 in all) were selected along the depth range 6.6–200 m of an ice core collected at this site from 1993 to 1995. The first 112.6 m were recovered in 1993 using a dry electromechanical technique (Dome-F Deep Coring Group, 1998a) and transferred in 1994 to the cold laboratory in Tokyo. One year later, 10-cm lengths were selected along the ice core approximately every metre and analyzed by ion chromatography (Watanabe et al., 1997a). Below 112.6 m, drilling was continued in 1995 after pouring a fluid into the bore hole. Chemical analyses on this part were carried out in 1996 in Tokyo (Dome-F Deep Ice Core Research Group, 1998b). The age at 200 m depth has been estimated to be 5000 ± 500 BP using a combination of dating methods (Watanabe et al., 1997b).

2.3. Amundsen–Scott Base samples

The geographical South Pole is located at the edge of the East Antarctic Plateau (Table 1). Several firn

Table 1. Some key features of the four central Antarctic sites discussed in this paper

Site	Latitude	Elevation (m)	Temperature (°C)	Accumulation (g cm ⁻² yr ⁻¹)
Dome F	77° 19' S	3810	-58	2.7
South Pole	0° S	2835	-51	8
Byrd Station	80° 01' S	1530	-28	10–12
Vostok Station	78° 28' S	3490	-56	2.2

cores were recovered at this site during the 1983–84 summer season (PS1, PS8, PS12, PS13 and PS14) and kept frozen until analysis. PS11 snow samples were collected in a pit and each sample stored in its individual plastic bag. These samples were analyzed 4–5 yr later by ion chromatography. Details concerning analytical procedures and dating have been reported elsewhere (Saigne et al., 1987; Saigne and Legrand, 1987; Legrand and Feniet-Saigne, 1991).

2.4. Byrd Station samples

The samples were selected along the main ice core (164 m) drilled in November 1989 at New Byrd Station, West Antarctica (Langway et al., 1994). Age was determined by counting the annual acidity peaks. Prominent volcanic levels were found and used to adjust dating: the reference horizon 1259 AD at 97.8 m and Tambora (1816) at 28.57 m. The firn to ice transition is located at about 52 m depth, i.e. 330 yr before 1989.

The MSA record (discontinuous) covers the last 1360 yr. Over this period, the mean MSA concentration is 8 ng g^{-1} for 74 distinct depth-levels each representing average values from individual 1 m core increments (Langway et al., 1994).

3. MSA records and discussion

3.1. Vostok Station and Dome Fuji data

Two key environmental parameters, mean annual temperature and snow accumulation rate, are relatively similar at Vostok and Dome F sites (Table 1). They are typical of central Antarctic conditions. MSA data from these two locations have therefore been plotted together in Fig. 1. As the detailed MSA record of Vostok being limited to the upper 32 m, Dome Fuji data (Dome-F Ice Core Research Group, 1998b) have been used to document deeper firn layers and more precisely the close-off zone where air bubbles are definitively entrapped in the ice. In this way, a display of MSA changes from the surface to 200 m depth is obtained, assuming that atmospheric concentrations of this compound are relatively similar at both locations. Vostok and Dome F data overlap discontinuously in the depth range 7–32 m. In central Antarctic regions, the slow transformation of snow into firn and ultimately ice spans over several millennia. Pore close-off (i.e. the transition between firn and ice) can be considered as

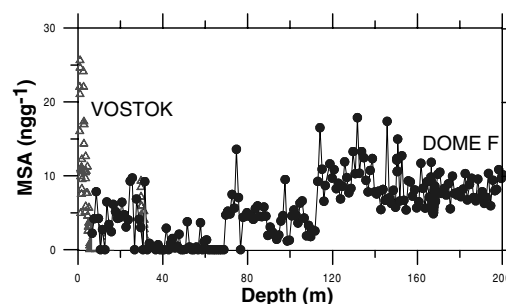


Fig. 1. Methane sulfonate concentration (ng g^{-1}) at Vostok [triangles (Wagon et al., 1999)] and Dome Fuji [solid circles (Dome-F Ice Core Research Group, 1998b)] sites as a function of depth (m). Pore close-off can be considered to be terminated at around 100 m depth at these sites.

fully terminated below 100 m depth (Watanabe et al., 1997c), i.e. at an age of about 2400 and 3400 BP at Vostok (Barnola et al., 1991; Petit et al., 1999) and Dome F (Watanabe et al., 1997b), respectively.

The depth profile (Fig. 1) shows relatively high MSA values in the upper first metres (Vostok data), then a marked decrease down to 70 m, thereafter progressively higher values again, particularly below 120 m (Dome-F data). At around 5.5 m, concentrations reach 2 ng g^{-1} (Wagon et al., 1999). Mean concentrations in the first 6 m and between 6–32 m are 10.4 ± 7.1 and $1.7 \pm 1.4 \text{ ng g}^{-1}$, respectively. Concentration spikes of short duration (1–3 yr), as high as 8 ng g^{-1} , are still observed in the deepest part of this core (30–32 m). Below this depth, in the ice, higher mean values [8.5 ng g^{-1} from 120 to 200 m at Dome F and $5 \pm 2 \text{ ng g}^{-1}$ between 100 and 400 m at Vostok (Legrand et al., 1991; 1992)] are observed. Note the marked shift at Dome F in mean MSA concentrations around 112 m, i.e. when passing from the upper to the lower part of the sampling. At 112.6 m there was a change in the electromechanical drilling technique at Dome F: a dry method was used down to this depth and a fluid-filled bore hole below (see section 2).

Interestingly, a snowpit study at Vostok (Fig. 2, data from Feniet, 1990) reveals that NO_3 and MSA concentrations exhibit different patterns in the upper 2 m: the former start to decrease close to the surface, whereas the latter show no clear change (mean concentration for this data set: $17.6 \pm 5.9 \text{ ng g}^{-1}$). The drop is observable below 2–3 m (Wagon et al., 1999). This suggests that, at first sight, the post-deposition processes that affect HNO_3 and MSA are not similar.

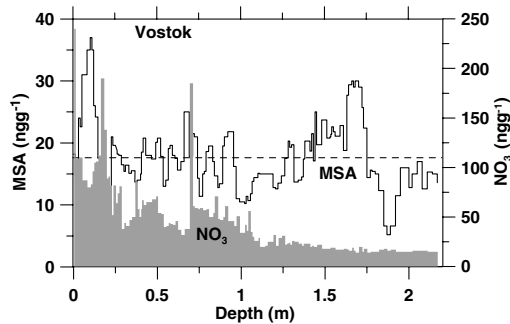


Fig. 2. MSA (continuous line) and NO_3 (shadowed area) concentrations in a snowpit study at Vostok. Concentrations are in ng g^{-1} . The horizontal stippled line shows the mean MSA concentration (17.6 ng g^{-1}) of this profile.

The decreasing trend found in upper firn layers at Vostok was interpreted by Wagnon et al. (1999) as proof that gaseous MSA is released from the solid phase to the interstitial air and that this MSA is lost (and therefore not measured) during ice core transport and storage. On the other hand, measurements do not formally demonstrate that MSA is deposited as a gas. Once in the interstitial phase, gaseous MSA may leave the snow layers and return to the free atmosphere, be partly redeposited in the snow layers or just remain in the interstitial air. It is impossible to estimate the fraction returning to the atmosphere just from the data presently available. The deposition mechanism itself is unknown for this gas, even less documented than for other acid species like HCl or HNO_3 , two species known to be deposited in gaseous form in the Antarctic.

Wagnon et al. (1999) put forward snow metamorphism as a possible explanation for the postdeposition artefacts pointed out at Vostok site for acid gases. It is therefore of interest to examine the impact of this process on the physical properties of the upper snow layers and to tentatively connect MSA concentration changes to these physical modifications. Field measurements of the firn physical properties are very scarce. By chance, grain size measurements were carried out at Vostok in the snowpit where it was sampled for chemistry (data reported in Fig. 2). The data set obtained by Lipenkov (personal communication) for the upper snow layers indicates that crystal section increases by one order of magnitude in the very first metre (from 0.08 mm^2 close to the surface to 0.8 mm^2 at 1 m depth), due probably to several water vapour distillation/condensation cycles within the snowpack in relation with seasonal

temperature oscillations. A detailed description of this phenomenon is proposed by Nakamura et al. (2000) for the Dome F site. Below this depth, the measurements are few and the observed changes are less marked (in the range $0.6\text{--}1.1 \text{ mm}^2$). The changes are linked to metamorphism. After being deposited, snow undergoes densification and recrystallization according to processes similar to metallic sintering (Sommerfeld and LaChapelle, 1970; Maeno and Ebinuma, 1983). It has been found by Gow (1969) that the velocity of the transformations depends on temperature, and that the crystalline structure of the snow changes rapidly in the very first metres, thereafter slower until pore close-off.

The comparison of MSA and crystal size data are inconclusive, since MSA concentrations remain relatively stable just in the layers (the upper first metre) where crystals strongly reorganize. MSA concentration decreases below, in possibly relation to the migration process recently pointed out by Pasteur and Mulvaney (1999).

It is observed that MSA concentrations reach very low values (sometimes not even measurable) in the depth range 20–50 m but increase again in deeper firn layers. The mean concentration between 20 and 100 m is 3.2 ng g^{-1} (calculated for 106 samples, Watanabe et al., 1997a). The increase starts at around 70–75 m. It is related to the development of the close-off process, but terminates only at around 115 m, i.e. below the estimated end of the pore close-off process (assumed to be fully achieved at around 100 m depth). This difference of 15 m could be related to the time needed to consolidate the ice structure and the airtightness of the bubbles. Microcracks in the ice could also cause a loss of gaseous MSA. The Dome-F Ice Core Research Group (1998b) calculated a mean concentration of about 10 ng g^{-1} between 100 and 400 m (8.5 ng g^{-1} between 120 and 200 m, see above), i.e. a level lower than the mean concentration determined in the upper 2 m of snow (13.9 ng g^{-1}). At Vostok, mean concentration in the upper 2 m and for the Holocene is 17.3 ng g^{-1} (Fig. 2) and 6 ng g^{-1} (Legrand et al., 1992), respectively. This suggests that a significant amount of MSA is lost between the time it is deposited in the snow and the time it is entrapped in the ice. The presence of gaseous MSA in the central Antarctic atmosphere has been discussed by Wagnon et al. (1999). Several arguments make it plausible to assume a significant gaseous-phase contribution to central Antarctic MSA, even if this gas has not yet been detected in the atmosphere. This compound is predominately present in the fine-particle mode (Berresheim, 1987)

but recent measurements have demonstrated the presence of gaseous MSA and nss-SO₄ in the marine atmosphere (Berresheim and Eisele, 1998; Mauldin et al., 1999). If the oxidation of DMS occurs in the dry, cold and pristine Antarctic free troposphere, a much longer lifetime for gaseous MSA can be expected in comparison to those at other latitudes and altitudes.

Model studies of trace gases having no interaction with ice (like CO₂ or CH₄) show that gas exchange with the free atmosphere is easy until about 10 m, but increasingly difficult below this depth until close off, where it ceases definitively (Schwander et al., 1988). The case of MSA is different, since the release of this gas to the interstitial air is linked partly to (a) snow metamorphism, a process which slows down rapidly with depth, and (b) diffusion in ice grains, a process which takes time to develop. Once in the gaseous phase, MSA could stagnate in the firn due to its high density (3.7) and finally be entrapped in bubbles at pore close-off. It is suggested that most of the loss of gaseous MSA from the interstitial phase could occur during transportation and storage, i.e. not in natural conditions. This sequence of processes would explain why measured concentrations are very low until pore close-off level and increase again in the ice below.

After pointing out the serious changes of MSA concentrations observed in the upper firn layers in central Antarctic snow, we will now discuss the significance of MSA records in central Antarctic snow.

How reliable are temporal changes of MSA concentrations recorded in firn layers? This issue is particularly important since MSA concentrations in South Pole snow were suggested several years ago (Legrand and Feniet-Saigne, 1991, see below) to be linked to El Niño events. In other words, is there still a chance that records of strong El Niño events of the past may be reconstructed by analyzing polar ice cores?

To document this issue, the detailed study of Wagon et al. (1999) at Vostok is particularly useful, at least for an initial picture. Strong signals have been detected along MSA profiles, even below 10 m depth. These spikes may represent atmospheric changes or be randomly distributed and caused by the post-deposition processes discussed above. Their occurrence simultaneously or just after a volcanic eruption suggests that they could be real phenomena, i.e. not artefacts. We propose that this effect is linked to acidity changes, MSA moving from volcanic to less acidic adjacent firn layers. The effect has been pointed out by Wagon et al. (1999), and is also observed for other acid gases such as HCl and HNO₃. It is presently

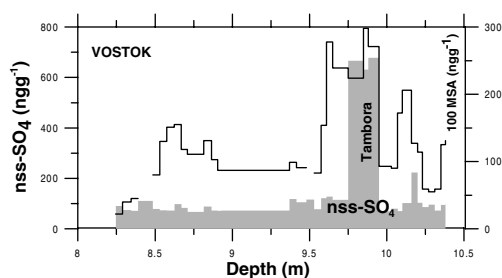


Fig. 3. MSA (solid line) and nss-SO₄ (shaded area) concentration changes in Vostok firn layers around the time of the Tambora eruption, 1815 AD. NssSO₄ (non-sea-salt sulfate) peaks are volcanic.

not fully explained, but we can speculate that it may be linked to the decrease of the solubility of MSA in ice caused by high acidity levels. Such an effect is well known in aqueous-phase chemistry: the solubility of acids in water is pH-dependent. As the phenomenon is very slow in the solid phase (it takes centuries to develop), it occurs at depth, i.e. in dense firn layers, and a large part of the gas is redeposited locally, forming a spike. However, the occurrence of an atmospheric MSA signal (e.g. triggered by an ENSO event) cannot be excluded. This is particularly the case for the 1818 Tambora eruption (Fig. 3), which is historically known to have been followed by a major El Niño event (Chenoweth, 1996). The atmospheric aftermaths of older eruptions, e.g. the 1259 eruption, are much less documented.

Dome F data are not detailed enough to be helpful in this issue. Nevertheless, the Dome F MSA profile exhibits marked short-term variations which could be related to atmospheric changes, suggesting that MSA spikes are not entirely levelled off in central Antarctic ice by post-deposition diffusion processes. This will be further discussed below for South Pole studies.

Finally, we examined the possible role of marine aerosol (as an alkalinity provider) in retaining MSA (as proposed by Mulvaney et al., 1992). By plotting Na and MSA concentrations for Dome F samples between 120 and 200 m depth, we attempted to demonstrate that MSA concentrations in the ice could be linked to sea salt concentration due to the redeposition phenomenon but the correlation found ($r^2 = 0.2$) is too weak to be decisive. In conclusion, Vostok and Dome F profiles depict the post-deposition changes that affect MSA concentrations in the firn layers at sites with extremely low accumulation rates. This species is only

partly released to the interstitial air during snow metamorphism. The transfer to the gas phase seems to occur later in depth, where MSA can move slowly within ice grains and leave the ice phase of firn. Data suggest that gaseous MSA could become entrapped in air bubbles. In the ice, it is therefore most probably located in the air enclosures rather than in the solid phase. MSA concentration in ice most likely depends on acidity, this parameter influencing the solubility of MSA in ice.

3.2. South Pole and Byrd Station

At Amundsen–Scott (South Pole) and Byrd Stations, snow accumulation rates (in the range $8\text{--}11\text{ g cm}^{-2}\text{ yr}^{-1}$) are 2–3 times higher than at the sites studied above. Are significant post-deposition effects on MSA concentration also observed at these sites? To answer this question, we have re-examined South Pole data from Feniet (1990) and Legrand and Feniet-Saigne (1991), some of them unpublished, and the Byrd Station record from Langway et al. (1994).

Six data sets are available at South Pole (see section 2). MSA concentrations obtained from the longest discontinuous record (PS-1, Fig. 4) decrease from the upper layers until 15–20 m and then start to increase again until the end of the record. This indicates that a post-depositional effect on MSA concentrations is probable. Concentrations in the ice (in the range $4\text{--}6\text{ ng g}^{-1}$ between 100–120 m) are lower than in the upper first metres (range $5\text{--}30\text{ ng g}^{-1}$, Fig. 5), which suggests that there is probably an overall loss of MSA from the firn layers at this location as earlier mentioned for Dome F and Vostok sites. The gaseous MSA formed during snow metamorphism is partly redeposited and partly stored in the interstitial air. The redeposition of

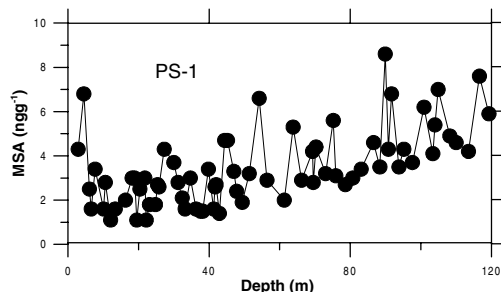


Fig. 4. Methane sulfonate concentration (ng g^{-1}) at the South Pole (PS-1 ice core) as a function of depth (m) (data from Feniet, 1990).

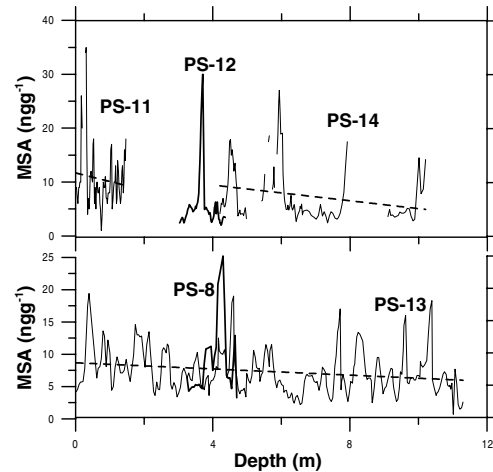


Fig. 5. MSA concentration (ng g^{-1}) at the South Pole (PS-13 + PS-8, PS-11, PS-12 and PS-14 firn cores) as a function of depth (m) (Legrand and Feniet-Saigne, 1991). PS-8 (in bold) was analyzed in 1999 by Patris (Patris et al., 2000). The broken line was calculated using PS-13 data only.

gaseous MSA is likely, as suggested by the absence of seasonal variations of MSA concentrations, even close to the surface (Legrand et al., 1992), whereas Mulvaney et al. (1992) observed a migration of MSA from summer to winter layers only at depth (after a few decades) at a site where accumulation is four times higher than at the South Pole. More recent measurements confirm this effect (Langway et al., 1994; Minikin et al., 1994; Kreutz et al., 1998).

Measured MSA concentrations in the upper firn layers do not appear to be entirely reliable. This conclusion results from the comparison of the various data sets (from several firn cores) recovered during the same campaign at the South Pole (PS 11, PS 12, PS 13 and PS 14, see Table 2). On the other hand, PS 8,

Table 2. Mean MSA concentrations at the South Pole obtained from various samplings

Sample	Depth (m)	MSA (ng g^{-1})
PS-1	2.9–14	2.86 ± 1.8
PS-1	100–120	5.5 ± 1.2
PS-8	3.25–4.7	8.6 ± 5.4
PS-11 (pit)	0–1.5	12.8 ± 11.3
PS-12	3–4.8	4.8 ± 5.2
PS-13	0–4	8.0 ± 3.3
PS-13	4–11.3	6.9 ± 3.4
PS-14	4.2–10.2	7.6 ± 5.2

analyzed some 10 yr later than the others, does not exhibit unusual MSA concentrations (Patris et al., 2000). This suggests that major metamorphic changes developed during sampling and transport from Antarctica to Grenoble (rather than during storage) in addition to the processes naturally affecting firn structure in situ. Marked declining trends of MSA concentrations as a function of depth are found for the longest upper firn records (PS-11, PS-13 and PS-14, Fig. 5), confirming that MSA long-term records obtained from these cores were affected by post-depositional changes, and that the changes are more marked at depth than in upper layers.

On the other hand, perturbations on shorter time scales (a few years) seem to be conserved at South Pole. In particular, Legrand and Feniet-Saigne (1991) detected large concentration changes that they attributed to the impact of El Niño events on the production or transport of MSA from the sub-antarctic ocean to inner Antarctica. Figure 5 shows that the changes attributed to El Niño are superimposed on the general decreasing trend of MSA profiles in the upper firn layers at South Pole. Part of the MSA initially deposited escapes probably to the atmosphere. The MSA/nss-SO₄ ratio calculated over 385 samples (PS 12 + PS 13 + PS 14) has a mean value of 0.13, a figure within the range of *R* values obtained in the sub-Antarctic marine atmosphere (Legrand and Pasteur, 1998). The decrease observed at South Pole is clearly marked but less steep than the decrease found at Vostok by Wagnon et al. (1999). It spans over more metres at South Pole than at Vostok, probably in relation to the different snow accumulation rates at the two locations.

A major issue is the record of El Niño events discovered at South Pole and never confirmed elsewhere. May this record be questioned by the post-deposition artefact we point out in this paper? The record shown by Legrand and Feniet-Saigne over the last 60 yr (upper 12 m of firn) is located in the part of the MSA record where the decreasing trend is particularly well marked (mean value at 30–50 m depth: $2.6 \pm 2.9 \text{ ng g}^{-1}$, in comparison with the mean value of $9.2 \pm 2.9 \text{ ng g}^{-1}$ at 1–2 m depth). On the other hand the fluctuations of concentrations are not totally obliterated, although they are probably mitigated at depth. At Vostok, where the concentration decrease is much more clearly marked than at South Pole, sharp MSA peaks seem to be conserved even at 30 m depth (see above). Dome F sampling, which is discontinuous, does not allow us to draw definite conclusions. An unbroken 2 m

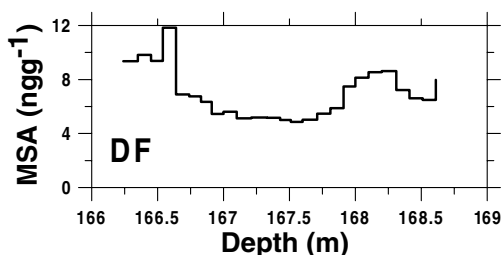


Fig. 6. Dome F: MSA concentration along a 2.2-m-long continuous ice core section around 167 m depth.

sequence (25 samples) around 166 m exhibits marked MSA fluctuations which could be related to El Niño events (Fig. 6).

At Byrd Station (accumulation $10 \text{ g cm}^{-2} \text{ yr}^{-1}$), Langway et al. (1994) observed a marked sag (by a factor of 3–4) in MSA concentrations from about 350 to 150 yr BP (i.e. about 50–30 m depth, Fig. 7). The minimum of MSA is found around 110 BP. This depth range agrees with those where measured MSA concentrations decreased in the other firn cores discussed in this paper. Note that pore close-off at Byrd is around 52 m, i.e. at the lower limit of the depth range where MSA concentration is low. This agrees well with our proposal that MSA may be located partly in the gaseous phase in the firn and that this part is lost from firn samples during core storage. The record compares satisfactorily with the PS1 profile shown in Fig. 4.

4. Concluding remarks

This review shows that the formation of MSA records in polar ice is not a simple process. Measurements carried out in firn layers at different central polar sites suggest that this species is deposited reversibly. MSA re-emission to the gaseous phase is linked to (1) the reorganisation of the snow flakes after deposition (so-called snow metamorphism), (2) the migration of MSA in the firn and its release to the interstitial air, and (3) the pH of the ice, probably due to decreasing solubility of MSA in the ice as a function of acidity.

At Dome F, the increase observed for MSA concentration in the depth range where air bubble close-off occurs is quite consistent with the proposal that gaseous MSA is present in central Antarctic firn layers: MSA released from the snow matrix into the gaseous phase in the upper firn layers (as proposed by Wagnon et al., 1999) is entrapped in the air bubbles at greater depths. The gaseous MSA present in firn samples in the

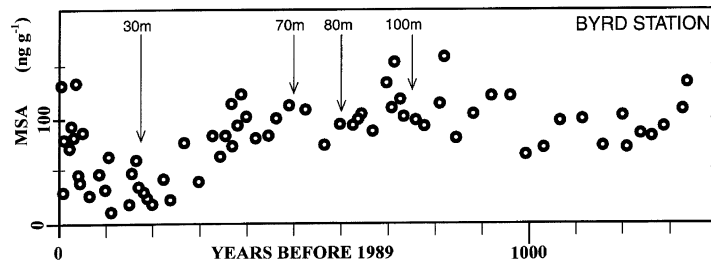


Fig. 7. Byrd Station (Langway et al., 1994). A marked low (by a factor of 3–4) is observed along the MSA profile for 30–50 m depth.

20–50 m depth range is lost during sample storage and is consequently not measured. This loss does not occur under natural conditions.

Some of the gaseous MSA in the firn can be expelled to the free atmosphere, but the quantity involved is uncertain. It has been proven that the remaining gas may be partly redeposited on winter layers, due to their low acidity. Acidity is therefore a crucial parameter, as confirmed by the expulsion of MSA from acidic volcanic layers.

At depth, short-term variations (El Niño type) are conserved, but probably not quantitatively, as demonstrated by measurements carried out at the South Pole. This is encouraging for the determination of past El Niño events but inconclusive regarding the quality of MSA levels. Of particular importance is the explanation concerning the origin of the MSA peaks found in deep firn. Are they simply glaciological artefacts or are they linked to real atmospheric concentration changes during those periods? A clear answer to this challenging question would require the analysis of MSA fluctuations in two parallel firn cores.

The development of a model valid for gases (in particular acids like HCl, HNO₃ and MSA) interacting with the ice matrix has to be encouraged. Modelling

has to take into account the various physical and chemical processes mentioned in this paper. Unfortunately, in-situ measurements and observations concerning firn layers are scarce and few property data exist, in particular for MSA.

Finally, under ice-age conditions, it may be assumed that MSA was not deposited as an acid, but rather as a salt, due to its probable fixation on alkaline particles (of marine or continental origin) during long-range aerosol transport to polar areas. Changes of snow alkalinity or/and temperature, combined with accumulation changes, could explain MSA variations over the last 100 000 yr. This point requires further investigation.

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REFERENCES

- Andreae, M. O. 1986. The ocean as a source of atmospheric sulfur compounds. In: *The role of air-sea exchange in geochemical cycling*. (ed. P. Buat-Menard) D. Reidel Dordrecht, 331–361.
- Barnola, J.-M., Pimienta, P., Raynaud, D. and Korotkievitch, Y. S. 1991. CO₂ climate relationship as deduced from the Vostok ice core: a re-examination based on new measurements and on a re-evaluation of the air dating. *Tellus* **B43**, 83–91.
- Berresheim, H. 1987. Biogenic sulfur emissions from the Subantarctic and Antarctic oceans. *J. Geophys. Res.* **92**, 13245–13262.
- Berresheim, H. and Eisele, F. 1998. Sulfur chemistry in the Antarctic troposphere experiment: an overview of project SCATE. *J. Geophys. Res.* **103**, 1619–1627.
- Charlson, R. J., Lovelock, J. E., Andreae, M. O. and Warren, S. G. 1987. Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. *Nature* **326**, 655–661.
- Charlson, R. J., Lovelock, J. E., Andreae, M. O. and Warren, S. G. 1989. Sulphate aerosols and climate. *Nature* **340**, 437–438.
- Chenoweth, M. 1996. Ship's logbooks and "The year without a summer." *Bull. Am. Meteorol. Soc.* **77**, 2077–2093.

- Dome-F Deep Coring Group. 1998a. Deep ice-core drilling at Dome Fuji and glaciological studies in east Dronning Maud Land, Antarctica. *Ann. Glaciol.* **27**, 333–337.
- Dome-F Ice Core Research Group. 1998b. Preliminary investigation of paleoclimate signals recorded in the ice core from Dome Fuji station, east Dronning Maud Land, Antarctica. *Ann. Glaciol.* **27**, 338–342.
- Feniet, C. 1990. Methanesulfonic acid in Antarctic precipitation: implications for the high latitude sulfur cycle. *Thesis, Université Joseph Fourier, Grenoble*, 260 pp (in French).
- Gow, A. J. 1969. On the rates of growth of grains and crystals in South Polar firn. *J. Glaciol.* **8**, 241–252.
- Hynes, A. J., Wine P. H. and Semmes, D. H. 1986. Kinetics and mechanisms of OH reactions with organic sulfides. *J. Phys. Chem.* **90**, 4148–4156.
- Kreutz, K. J., Mayewski, P. A., Whitlow, S. I. and Twickler, M. S. 1998. Limited migration of soluble ionic species in a Siple Dome, Antarctica, ice core. *Ann. Glaciol.* **27**, 371–377.
- Langway, C. C., Jr., Clausen, H. B. and Hammer, C. U. 1988. An inter-hemispheric volcanic time-marker in ice cores from Greenland and Antarctica. *Ann. Glaciol.* **10**, 102–108.
- Langway, C. C., Jr., Osada, K., Clausen, H. B., Hammer, C. U., Shoji, H. and Mitani, A. 1994. New chemical stratigraphy over the last millennium for Byrd station, Antarctica. *Tellus* **46B**, 40–51.
- Legrand, M. and Feniet-Saigne, C. 1991. Strong El Niño revealed by methanesulphonic acid in South Polar snow layers. *Geophys. Res. Lett.* **21**, 187–190.
- Legrand, M. and Pasteur, E. C. 1998. Methanesulfonic acid to non-sea-salt sulfate ratio in coastal Antarctic aerosol and surface snow. *J. Geophys. Res.* **103**, 10991–11006.
- Legrand M., Feniet-Saigne, C., Saltzman, E. S., Germain, C., Barkov N. I. and Petrov, V. N. 1991. Ice-core record of oceanic emissions of dimethylsulphide during the last climate cycle. *Nature* **350**, 144–146.
- Legrand, M., Feniet-Saigne, C., Saltzman, E. S. and Germain, C., 1992. Spatial and temporal variations of methanesulfonic acid and non sea salt sulphate in Antarctic ice. *J. Atmos. Chem.* **14**, 245–260.
- Maeno, N. and Ebinuma, T. 1983. Pressure sintering of ice and its implication to the densification of snow at polar glaciers and ice sheets. *J. Phys. Chem.* **87**, 4103–4110.
- Mauldin R. L., III, Tanner, D. J., Heath, J. A., Huebert, B. J. and Eisele, F. L. 1999. Observations of H₂SO₄ and MSA during PEM-Tropics-A. *J. Geophys. Res.* **104**, 5801–5816.
- Minikin, A., Wagenbach, D., Graf, W. and Kipfstuhl, J. 1994. Spatial and seasonal variations of the snow chemistry at the central Filchner-Ronne Ice Shelf, Antarctica. *Ann. Glaciol.* **20**, 283–290.
- Mulvaney, R., Pasteur, E. C., Peel, D. A., Saltzman, S. and Whung, P.-Y. 1992. The ratio of MSA to non-sea-salt sulphate in Antarctic Peninsula ice cores. *Tellus* **44B**, 295–303.
- Nakamura, K., Nakawo, M., Ageta, Y., Goto-Azuma, K. and Kamiyama, K. 2000. Post-depositional loss of nitrate in surface snow layers of the Antarctic ice sheet. *Bull. Glaciol. Res.* **17**, 11–16.
- Nguyen, B. C., Gaudry, A., Bonsang, B. and Lambert, G. 1978. Re-evaluation of the rôle of dimethyl sulphide in the sulphur budget. *Nature* **275**, 637–639.
- Pasteur, E. C. and Mulvaney, R. 1999. Laboratory study of the migration of methane sulphonate in firn. *J. Glaciol.* **45**, 214–218.
- Pasteur, E. C. and Mulvaney, R. 2000. Migration of methane sulphonate in Antarctic firn and ice. *J. Geophys. Res.* **105** (D9), 11 525–11 534.
- Patris, N., Delmas R. J. and Jouzel, J. 2000. Isotopic signatures of sulfur in shallow Antarctic ice cores. *J. Geophys. Res.* **105**, 7071–7078.
- Petit, J.-R., Jouzel, J., Raynaud, D., Barkov, N. I. and coauthors, 1999. Climate and atmospheric history of the past 420 000 years from the Vostok ice core, Antarctica. *Nature* **399**, 429–436.
- Saigne, C. and Legrand, M. 1987. Measurement of methanesulphonic acid in antarctic ice. *Nature* **330**, 240–242.
- Saigne, C., Kirchner, S. and Legrand, M. 1987. Ion chromatographic measurements of ammonium, fluoride, acetate, formate and methanesulphonate ions in antarctic ice. *Anal. Chim. Acta* **203**, 11–21.
- Saltelli, A. and Hjorth, J. 1995. Uncertainty and sensitivity analyses of OH-initiated dimethylsulphide (DMS) oxidation kinetics. *J. Atmos. Chem.* **21**, 187–221.
- Schwander, J., Stauffer, B. and Sigg, A. 1988. Air mixing in firn and the age of the air at pore close off. *Ann. Glaciol.* **10**, 141–145.
- Sommerfeld, R. A. and LaChapelle, E. 1970. The classification of snow metamorphism. *J. Glaciol.* **9**, 3–17.
- Turnipseed, A. A. and Ravishankara, A. R. 1993. The atmospheric oxidation of dimethylsulphide: elementary steps in a complex mechanism. In: *Dimethylsulphide: oceans, atmosphere, and climate*. (eds G. Restelli and G. Angeletti), Kluwer Academic Publishers, Dordrecht 185–195.
- Wagnon, P., Delmas, R. J. and Legrand, M. 1999. Loss of volatile acid species from upper firn layers at Vostok, Antarctica. *J. Geophys. Res.* **104**, 3423–3431.
- Watanabe, O., Kamiyama, K., Motoyama, H., Igarashi, M., Matoba, S., Shiraiwa, T., Yamada, T., Shoji, H., Kanamori, S., Kanamori, N., Nakawo, M., Ageta, Y., Koga, S. and Satow, K. 1997a. Preliminary report on analyses of melted Dome Fuji core obtained in 1993. *Proc. NIPR Symp. Polar Meteorol. Glaciol.* **11**, 14–23.
- Watanabe, O., Fujii, Y., Motoyama, H., Furukawa, T., Shoji, H., Enomoto, H., Kameda, T., Narita, H., Naruse, R., Hondoh, T., Fujita, S., Mae, S., Azuma, N., Kobayashi, S., Nakawo, M. and Ageta, Y. 1997b. A preliminary study of ice core chronology at Dome Fuji Station, Antarctica. *Proc. NIPR Symp. Polar Meteorol. Glaciol.* **11**, 9–13.
- Watanabe, O., Shimada, W., Narita, H., Miyamoto, A., Tayuki, K., Hondoh, T., Kawamura, T., Fujita, S., Shoji, H., Enomoto, H., Kameda, T., Kawada, K. and Yokoyama, K. 1997c. Preliminary discussion of physical properties of the Dome Fuji shallow ice core in 1993, Antarctica. *Proc. NIPR Symp. Polar Meteorol. Glaciol.* **11**, 1–8.