

## Migration of methane sulphonate in Antarctic firn and ice

Elizabeth C. Pasteur and Robert Mulvaney

British Antarctic Survey, Natural Environment Research Council, Cambridge, England, United Kingdom.

**Abstract.** We investigate the seasonal relationship of the sulphur-bearing anions methane sulphonate ( $\text{MSA}^-$ ) and non-sea-salt sulphate ( $\text{nssSO}_4^{2-}$ ) in sections of firn and ice cores from the Antarctic Peninsula and Weddell Sea region of Antarctica. In cores from Dolleman Island and Berkner Island,  $\text{MSA}^-$  has clearly migrated from the summer snow layer, where it is initially deposited, to become concentrated in the winter layer. A similar behavior is evident in a core from the Dyer Plateau, though in deeper layers. Cores from Gomez Nunatak and Beethoven Peninsula show little evidence of relocation of  $\text{MSA}^-$ , though migration at greater depth in the ice sheet cannot be ruled out. In contrast, in all these cores, non-sea-salt sulphate remains in the summer layer. From comparisons between the ice core characteristics and the migration behavior at these sites, we conclude that the movement of  $\text{MSA}^-$  does not occur via percolation and refreezing of meltwater. Simple concentration-driven diffusion is also not a factor, as the  $\text{MSA}^-$  peaks are sharp in the winter layer. The data presented indicate that the movement of  $\text{MSA}^-$  in firn is likely to be linked to the concentration of other ionic species in the snowpack and to the snow accumulation rate. A possible mechanism for the migration of  $\text{MSA}^-$  in the snowpack is via an initial diffusion in the liquid or vapor phase, which is halted by trapping in the winter layer when the  $\text{MSA}^-$  forms a salt with a cation.

### 1. Introduction

It has been suggested that oceanic emissions of dimethyl sulphide (DMS) could affect the climate [Charlson *et al.*, 1987] via the role of its oxidation products, particularly sulphate ( $\text{SO}_4^{2-}$ ), as cloud condensation nuclei. This has raised interest in the history of DMS oxidation products in the atmosphere over time, and ice core analysts have responded by routinely measuring the two main products, sulphate and methane sulphonate ( $\text{MSA}^-$ ), as indicators of past marine DMS emissions. Studies have linked the seasonal non-sea-salt sulphate ( $\text{nssSO}_4^{2-}$ ) and  $\text{MSA}^-$  to short- and long-term climate effects such as El Niño and sea ice extent [Legrand *et al.*, 1991; Welch *et al.*, 1993; Pasteur *et al.*, 1994].

Seasonal variations of  $\text{MSA}^-$  and  $\text{nssSO}_4^{2-}$  have been studied in aerosol samples from coastal locations [Wagenbach *et al.*, 1988; Savoie *et al.*, 1993; Wagenbach, 1996; Minikin *et al.*, 1998]; both species exhibit clear maxima in the summer layer and minima in the winter. However, in a study of several Antarctic Peninsula firn cores, Mulvaney *et al.* [1992] found that, although  $\text{MSA}^-$  was at a maximum in the summer layer in the upper few meters, at greater depth the highest concentration was in the winter layers. They suggested that this change in seasonality may be due to migration of the  $\text{MSA}^-$  in firn or ice. Later, it became evident that this behavior was common in other Antarctic ice cores, such as those from Berkner Island [Minikin *et al.*, 1994], a site on the Filchner-Ronne ice shelf [Wagenbach *et al.*, 1994], Byrd on the continental plateau [Langway *et al.*, 1994], and Siple Dome [Kreutz *et al.*, 1998]. In an experiment to test the migration of  $\text{MSA}^-$  in natural firn but under laboratory-controlled conditions, Pasteur and Mulvaney [1999] found evidence that  $\text{MSA}^-$  could migrate on the

centimeter scale over periods of less than a year in firn kept at  $-5^\circ\text{C}$ , a condition that could exist during the summer at near-coastal Antarctic sites. However, not all ice cores display migration of  $\text{MSA}^-$ : in the high-accumulation Dome Summit South (DSS) core, the  $\text{MSA}^-$  tends to remain in the summer layer, though with anomalous years where the summer  $\text{MSA}^-$  is missing [Curran *et al.*, 1998]. In order to use the proxy palaeoenvironmental information, it is usually assumed that the chemical species are stable in the ice core. If species do migrate or are modified postdeposition, it is important to understand why, how far, and by what mechanism. In this study, we investigate in detail sections of firn and ice cores from several locations in the Antarctic and from different depths in an effort to understand the factors controlling the migration of  $\text{MSA}^-$ .

### 2. Sample Collection and Analysis

The cores used in this study are from the Antarctic Peninsula and Weddell Sea sector of Antarctica. Site details are summarized in Table 1, and the locations are shown in Figure 1. After transport to the United Kingdom, stored in  $-20^\circ\text{C}$  freezers, the cores were subsampled in a cold room by band saw into precleaned polythene containers at a resolution of around 12 samples per year. During processing, clean room clothing with masks and long polythene gloves were worn to minimize contamination of samples.

Analysis of anions was by ion chromatography using either a Dionex AS4A column system and isocratic elution (1.8 mM  $\text{Na}_2\text{CO}_3$ /1.7 mM  $\text{NaHCO}_3$  eluent with a concentrator column for  $\text{SO}_4^{2-}$  and 5 mM sodium tetraborate eluent and 200  $\mu\text{L}$  sample loop for  $\text{MSA}^-$ ) or a Dionex AS11 column system with gradient elution (0.5–28 mM  $\text{NaOH}$  eluent and 200  $\mu\text{L}$  sample loop). The detection limit for  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , and  $\text{MSA}^-$  varies depending on which method is used and on the sample volume but is usually around 0.01  $\mu\text{eq L}^{-1}$ .  $\text{Na}^+$  and  $\text{Mg}^{2+}$  were analyzed using atomic absorption spectrometry using a Pye Unicam SP9 atomic absorption

**Table 1.** Locations of Drilling Sites and Details of Core Sections Studied

Drilling Site	Date of Collection	Location	Accumulation Rate, m w.e.	Surface Elevation, m	Distance From Coast, km	10 m Temperature, °C	Pore Close Off, m w.e.
Dyer Plateau	1988-1989	S70°39', W065°01'	0.48	1943	190	-21.7	45
Dolleman Island	1985-1986 1992-1993	S70°35', W060°56'	0.34	398	20	-16.8	42
Beethoven Peninsula	1992-1993	S71°53', W074°34'	1.2	580	16	-12.5	45
Gomez Nunatak	1980-1981	S74°01', W070°38'	0.88	1130	135	-17.3	32
Berkner Island North	1994-1995	S78°18', W046°17'	0.20	730	50	-22.5	43

Here, m w.e. is water equivalent depth, derived from the snow depth and the density profile.

spectrophotometer. Samples and standards were acidified to 100  $\mu\text{M}$  using HCl to reduce the effect of ionization contamination.

$$[\text{SO}_4^{2-}]_{\text{nss}} = [\text{SO}_4^{2-}]_{\text{total}} - 0.103 [\text{Cl}^-] \quad \text{in } \mu\text{eq L}^{-1}$$

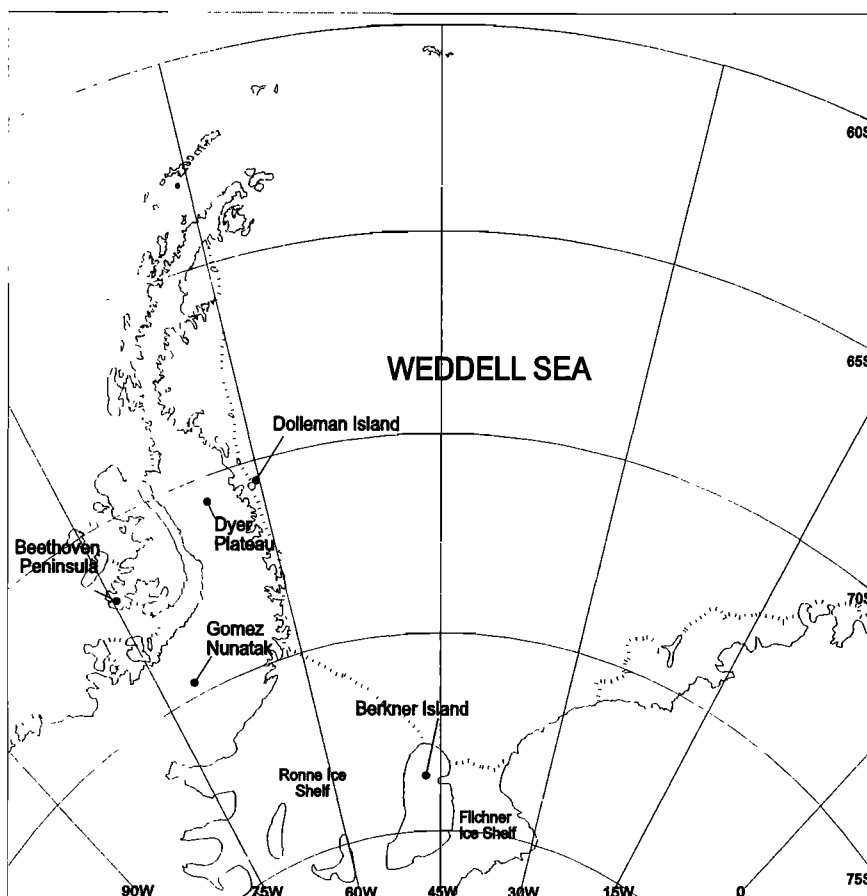
$$[\text{SO}_4^{2-}]_{\text{nss}} = [\text{SO}_4^{2-}]_{\text{total}} - 0.12 [\text{Na}^+] \quad \text{in } \mu\text{eq L}^{-1}$$

### 3. Results

#### 3.1. Calculation of $\text{nssSO}_4^{2-}$

Non-sea-salt sulphate ( $\text{nssSO}_4^{2-}$ ) is calculated from total  $\text{SO}_4^{2-}$  by subtracting the calculated sea salt component of the  $\text{SO}_4^{2-}$  from the total  $\text{SO}_4^{2-}$  using one of the following expressions:

This method of calculating  $\text{nssSO}_4^{2-}$  can give rise to negative values, particularly at coastal sites [Mulvaney *et al.*, 1992; Minikin *et al.*, 1994]. This is likely to be due to the precipitation of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  in seawater solution at high latitudes during cold winter temperatures. Methods have been devised to adjust the calculation of  $\text{nssSO}_4^{2-}$  in aerosol and surface snow samples, taking



**Figure 1.** Map of the Antarctic Peninsula and Weddell Sea area, showing the location of Dolleman Island, Dyer Plateau, Beethoven Peninsula, Gomez Nunatak, and Berkner Island (North Dome) ice core sites.

this depletion into account [Wagenbach *et al.*, 1998]. However, for ice cores, separating winter layer and summer layer concentrations is uncertain, and making corrections for this could therefore lead to inaccuracies in the data. In this work the principle aim is to look at trends in the data and not absolute values. The  $\text{nssSO}_4^{2-}$  values are therefore presented without correction for winter depletion of sodium sulphate.

### 3.2. Near-Surface Sections of the Firn Cores

Aerosol measurements of  $\text{MSA}^-$  and  $\text{nssSO}_4^{2-}$  carried out at coastal stations show that both species have distinct maxima during the austral summer, coincident with the period of maximum biogenic production of DMS from the ocean and winter minima [Wagenbach *et al.*, 1988; Savoie *et al.*, 1993; Wagenbach, 1996; Minikin *et al.*, 1998]. In this section we investigate sections of firn cores from the upper 15 m of the ice sheet at five sites to determine if the seasonality of  $\text{MSA}^-$  and  $\text{nssSO}_4^{2-}$  is maintained in the recent snowpack.

At the high-altitude inland sites Dyer and Gomez,  $\text{MSA}^-$  and  $\text{nssSO}_4^{2-}$  both have clear seasonal cycles with maxima in the summer (Figure 2; in all core profiles we have converted the firn depth to a water equivalent depth scale using the density profiles). The winter layers, which have been chosen by reference to the minima in oxygen isotopes and  $\text{nssSO}_4^{2-}$  signals, are marked with a vertical line. The section from Dyer Plateau represents snow which is around 13-15 years old. The concentrations of  $\text{MSA}^-$  and  $\text{nssSO}_4^{2-}$  are highest in the summer snow layer, fall to a minimum in the winter layer, and are positively correlated at the 99% level ( $r=0.64$ ,  $n=40$ ). At Gomez in a section from 2 to 5 m (2 to 5 years old), coincident summer peaks for both species are also evident, though the two signals are not as well correlated. There is no sign of any diffusion or relocation of  $\text{MSA}^-$  in the near-surface firn at these inland sites.

In a shallow core section from Dolleman Island (2.5 - 4.5 m, 6-9 years old) the relationship between  $\text{MSA}^-$  and  $\text{nssSO}_4^{2-}$  is more confused (Figure 2). The two largest peaks for both species at around 3.5 and 4 m are in phase, but otherwise the phase relationship is not clear. A section from the upper 4 m (0-4 years old) of the Beethoven core (Figure 2) shows clear in-phase seasonality for  $\text{MSA}^-$  and  $\text{nssSO}_4^{2-}$ , with very low winter  $\text{MSA}^-$  concentrations. In a short core section collected from the surface at Berkner Island (Figure 2),  $\text{MSA}^-$  and  $\text{nssSO}_4^{2-}$  are clearly in phase. However, it should be noted that this section represents only the top 0.6 m of the core (0-3 years). Wagenbach *et al.* [1994] showed that the seasonality of the  $\text{MSA}^-$  signal becomes less clear below about 4 m in a section of core from Berkner Island. It appears that, close to the surface (within the first few years of snowfall), each of these sites shows the  $\text{MSA}^-$  and  $\text{nssSO}_4^{2-}$  in phase and in the summer layer, though we note at one site (Dolleman) there are years with low summer  $\text{MSA}^-$ .

### 3.3. Deeper Sections of the Firn Cores

Sections of core from Dyer, Gomez, and Beethoven (Figure 3, showing ice with ages of 100, 40, and 27 years, respectively, from these sites) show  $\text{MSA}^-$  and  $\text{nssSO}_4^{2-}$  profiles are generally in phase during and at a maximum in the summer layer. However, in the section from Dyer there are two higher  $\text{MSA}^-$  peaks which occur in the winter layer at 51.8 and 53 m. These may correspond to the initial stages of the relocation of  $\text{MSA}^-$ .

In deeper sections from Dolleman Island, almost all of the  $\text{MSA}^-$  peaks are in the winter snow layer defined by  $\delta^{18}\text{O}$  and out of phase with the  $\text{nssSO}_4^{2-}$  peaks (Figure 4), the only exception being the peak at 35.5 m. These sections are from around 100 and 290 years prior to drilling. Similarly, at Berkner (Figure 5), even at a

depth of around 13 m (~62 years old), the  $\text{MSA}^-$  profile is clearly out of phase with  $\text{nssSO}_4^{2-}$ , and this is also seen in deeper sections at around 24 m (~106 years old) and 38 m (~170 years old).

In summary,  $\text{MSA}^-$  and  $\text{nssSO}_4^{2-}$  are still apparently in phase in the cores from Dyer, Beethoven, and Gomez although there are  $\text{MSA}^-$  spikes in winter in some sections from the Dyer core which may be the start of migration. Dolleman and Berkner cores both show a clear change in the location of the  $\text{MSA}^-$  from the summer to winter layers. Table 2 shows a summary of the predominant location of  $\text{MSA}^-$  maxima in the core sections, together with depths and ages of the sections and mean  $\text{MSA}^-$  and  $\text{nssSO}_4^{2-}$  at the sites. The lengths of the core sections summarized in Table 2 are longer than those presented in Figures 2 to 5, where the number of years shown was reduced for clarity.

## 4. Discussion

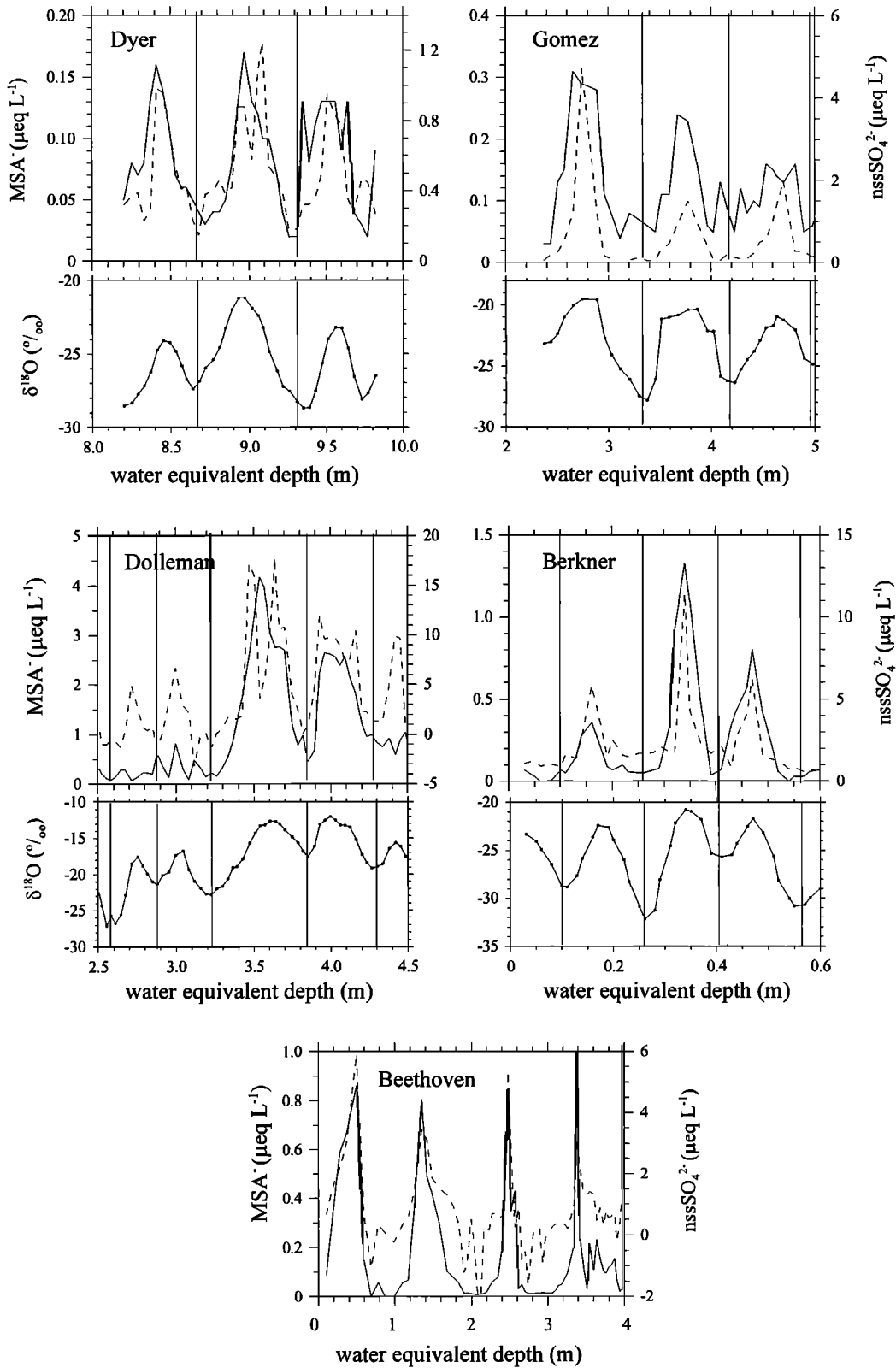
$\text{MSA}^-$  maxima are present in the winter snow layer in ice cores from some sites, yet it is clear from aerosol and surface snow measurements that  $\text{MSA}^-$  is deposited predominantly during the summer, when DMS is emitted from the ocean and sunlight is available for the photochemical oxidation to  $\text{MSA}^-$ . To have become concentrated in the winter layer,  $\text{MSA}^-$  must have migrated after deposition.

Smoothing of the seasonal signal of some species by vapor phase diffusion is observed: both  $\text{H}_2\text{O}_2$  [e.g., Sigg and Nefel, 1991] and  $\delta^{18}\text{O}$  [e.g., Whillans and Grootes, 1985] are examples. In contrast, when  $\text{MSA}^-$  migrates, the peaks remain well defined, and there is no sign of any smoothing of the  $\text{MSA}^-$  signal which would indicate diffusion in the snow layers. In Figures 4 and 5, at Dolleman and Berkner, the winter  $\text{MSA}^-$  peaks appear to become sharper with depth with lower summer minima in deeper sections. Simple diffusion of  $\text{MSA}^-$  driven by a concentration gradient can therefore be ruled out as a mechanism for movement of  $\text{MSA}^-$ .

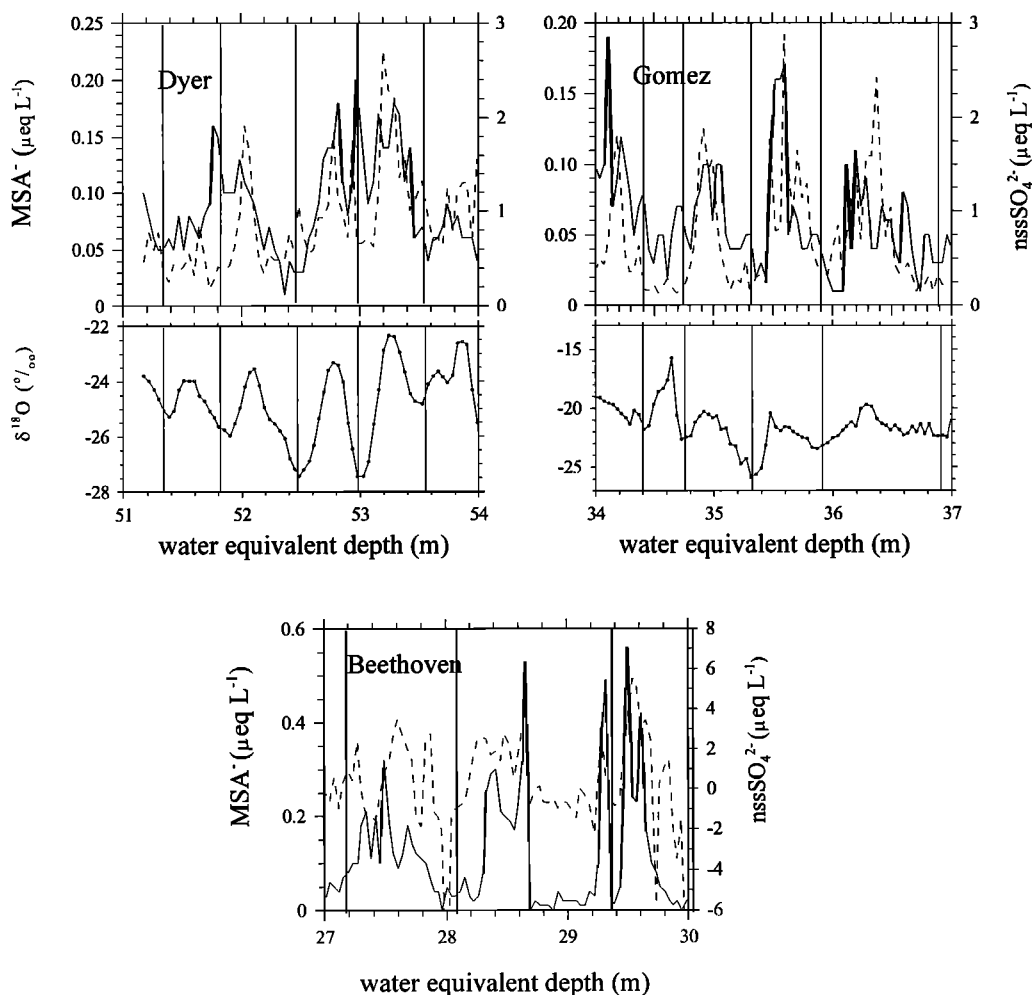
Contaminants in snow may be incorporated inside snow crystals as condensation nuclei when snow forms in clouds, deposited on the outside of the crystals by scavenging as snow falls, or deposited by riming. Snow crystals start to change very soon after deposition: the snow grains change shape to reduce their surface area and become more spheroidal. Grain boundaries migrate, causing ions to move to the area between the snow grains or to the air-snow interface. In a laboratory study growing ice columns containing dilute solutions of  $\text{MSA}^-$  and  $\text{nssSO}_4^{2-}$ , Gross *et al.*, [1992] found that <0.01% of solute was located in the ice lattice, implying that it must be present at grain boundaries and between snow grains. Mulvaney *et al.* [1988] showed that a large part of the sulphuric acid found in ice from Dolleman Island was located at grain boundaries. The acid may have been sufficiently concentrated to remain liquid and hence form a network of submicron veins through the ice [Wolff and Mulvaney, 1990]. Smaller molecules such as HF, HCl, and  $\text{NH}_3$  may become incorporated into the ice lattice via substitution with water molecules [Wolff, 1996]. Species such as  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{MSA}^-$  would be too large or complex to substitute into these sites.

$\text{MSA}^-$  is very soluble, forming a strong acid with dissociation constant  $K_a$  of  $73 \text{ mol L}^{-1}$  [Clegg and Brimblecombe, 1985]. The freezing point of pure  $\text{MSA}^-$  is  $20^\circ\text{C}$ , but a eutectic mixture containing  $\text{MSA}^-$  would remain liquid well below  $0^\circ\text{C}$  (Figure 6). There may therefore be a mechanism for  $\text{MSA}^-$  to move as a liquid along grain boundaries driven by gravity or by capillary pressure.

An alternative mode of transport for  $\text{MSA}^-$  could be via the vapor phase. Relocation of  $\text{MSA}^-$  at Dolleman and Berkner occurs above the level of pore close off. Any vapor transport through firn would be partially blocked by layers caused by summer melt or



**Figure 2.** Comparison of  $\text{MSA}^-$  (left-hand scale, solid line) and  $\text{nssSO}_4^{2-}$  (right-hand scale, dashed line) in near-surface sections from Dyer, Gomez, Dolleman, Berkner, and Beethoven. The assigned winter minima are marked with vertical lines. The  $\delta^{18}\text{O}$  values below the main plots show seasonal cycles ( $\delta^{18}\text{O}$  not available for Beethoven).  $\text{MSA}^-$  summer layer maxima are observed for Dyer, Gomez, Beethoven, and Berkner at the depths shown. In the Dolleman section the  $\text{MSA}^-$  shows two large summer peaks at 3.5 and 4 m, but otherwise the seasonality is not clear.



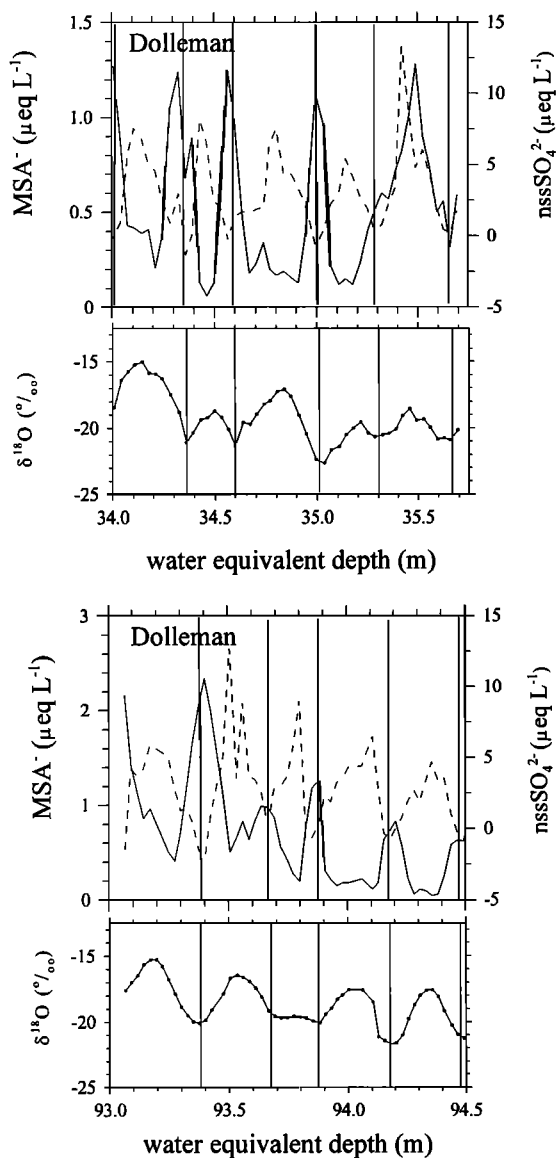
**Figure 3.** Comparison of  $\text{MSA}^-$  (left-hand scale, solid line) and  $\text{nssSO}_4^{2-}$  (right-hand scale, dashed line) in deeper sections from Dyer, Gomez, and Beethoven. The assigned winter minima are marked with vertical lines. The  $\delta^{18}\text{O}$  values below the main plots show seasonal cycles ( $\delta^{18}\text{O}$  not available for Beethoven).  $\text{MSA}^-$  maxima occur in the summer layer at all sites, but note winter layer peaks in the Dyer section at 51.8 and 53.0 m.

wind crust which are characteristic to a greater or lesser extent at all of the sites studied. At Berkner, there is diffusion of the isotope signal through vapor transport as this site remains constantly below freezing and does not have large blocking ice layers. Vapor phase transport of  $\text{MSA}^-$  at Berkner may therefore be possible. Dolleman is a warmer site and the core has around five ice layers in each year, which would restrict vapor phase migration of  $\text{MSA}^-$ . Therefore, while vapor phase transport cannot be ruled out, it is unlikely that it is the main mechanism for the movement of  $\text{MSA}^-$ .

Having discussed the possible mechanism for the movement of  $\text{MSA}^-$ , we turn to the site-specific factors that govern whether movement takes place: the temperature of the ice, accumulation rate, and chemical matrix. Movement of  $\text{MSA}^-$  in the snowpack may be influenced by the temperature of the site, and we might expect  $\text{MSA}^-$  to move more readily in firn at higher temperatures. Table 1 gave the 10 m temperatures at each site, providing an estimate of the mean annual temperature. The two sites which show clear  $\text{MSA}^-$  relocation are Dolleman and Berkner, the second warmest and the coldest sites, respectively. At Dolleman, air temperatures during December and January may rise slightly above freezing, and cores collected from this site show occasional ice

layers caused by melt which are up to 30 mm thick. At Berkner, however, the temperatures remain well below freezing throughout the year, and even millimeter-scale ice layers are rare. We conclude that temperature is not the main factor influencing the relocation of  $\text{MSA}^-$  to the winter layer. However, temperature would have a greater influence at much warmer sites (such as temperate glaciers), and we cannot rule out the effect of seasonal temperature contrasts at very cold sites.

The amount of snowfall at a site may be a controlling factor on  $\text{MSA}^-$  movement. At high accumulation sites, there is a greater distance between the summer and winter snow, which may be important if  $\text{MSA}^-$  was mobile only over a short distance in the pack. In this study, at sites with higher accumulation (greater than  $\sim 0.4$  m water equivalent), no relocation is observed. We also note that in the high-accumulation (0.64 m water equivalent (w.e.)) Law Dome DSS core,  $\text{MSA}^-$  appears to remain in the summer snow layer [Curran *et al.*, 1998]. Berkner has the lowest accumulation rate (0.2 m w.e.) and is the core in which  $\text{MSA}^-$  appears to migrate most readily. Dolleman also has lower accumulation than the other sites in this study (0.34 m w.e.). Low accumulation means that there is less distance for the  $\text{MSA}^-$  to move within the firn in order



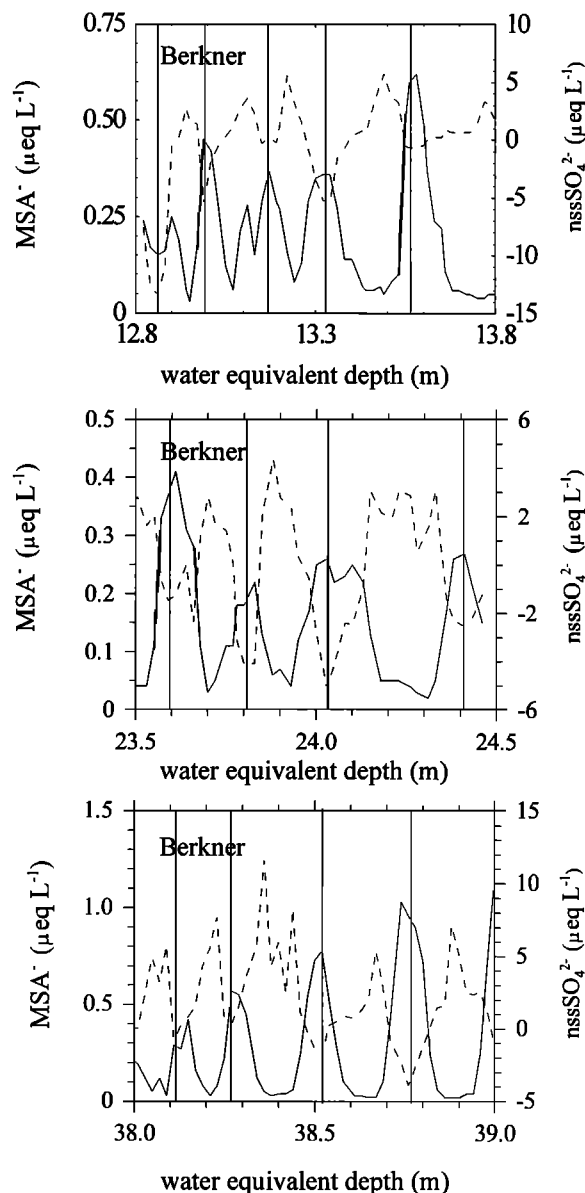
**Figure 4.** Comparison of  $\text{MSA}^-$  (left-hand scale, solid line) and  $\text{nssSO}_4^{2-}$  (right-hand scale, dashed line) in deep sections from Dolleman. The  $\delta^{18}\text{O}$  values below the main plots show seasonal cycles, and assigned winter minima are marked with vertical lines. Winter layer  $\text{MSA}^-$  maxima are clearly seen in both sections, with the exception of the summer layer  $\text{MSA}^-$  peak at 35.5 m.

to relocate to the winter layer. In a core drilled at Byrd,  $\text{MSA}^-$  migration is evident in the upper 3 m of the core, which has a low accumulation rate (around 0.1 m w.e. [Langway et al., 1994]).

Concentrations of  $\text{MSA}^-$  are highest at Dolleman and Berkner with mean annual values of 0.79 and 0.28  $\mu\text{eq L}^{-1}$ , respectively. The high concentrations are a result of the close proximity of the biologically productive Weddell Sea and are also partly a result of the concentration effect of lower accumulation rates, particularly at Berkner.  $\text{MSA}^-$  is a large molecule and is likely to be excluded from the ice lattice to the grain boundaries during crystal growth. With greater concentrations we can speculate that the likelihood of liquid migration is higher. However, we note that the mean  $\text{MSA}^-$  concentration at Byrd, which also shows relocation, is 0.08  $\mu\text{eq L}^{-1}$ . This is the same mean concentration as at Dyer and Gomez, which

do not show significant  $\text{MSA}^-$  relocation. Concentration alone may therefore not determine whether the  $\text{MSA}^-$  migrates, but a combination of factors, including concentration, could be relevant.

Sea salt ions  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , and  $\text{Ca}^{2+}$  all have winter maxima with the highest flux to the ice sheet during winter storms. We suggest that insoluble  $\text{MSA}^-$  salts could be formed between liquid  $\text{MSA}^-$  in veins and a sea-salt cation which would then precipitate out. Mobilization of  $\text{MSA}^-$  in a liquid film at grain boundaries in the summer layer could allow movement of  $\text{MSA}^-$  into the winter layer, where it would become "fixed" by combination with a sea-salt cation. Comparing concentrations of  $\text{MSA}^-$  with concentrations of  $\text{Na}^+$  and  $\text{Mg}^{2+}$  from the deeper sections in the Dolleman core with  $\text{MSA}^-$  (Figure 7) shows that the three species all generally have maxima in winter. The concentrations of the cation species are in excess compared to the



**Figure 5.** Comparison of  $\text{MSA}^-$  (left-hand scale, solid line) and  $\text{nssSO}_4^{2-}$  (right-hand scale, dashed line) in deep sections from Berkner. The assigned winter minima are marked with vertical lines and are here based on the minima in the  $\text{nssSO}_4^{2-}$ .

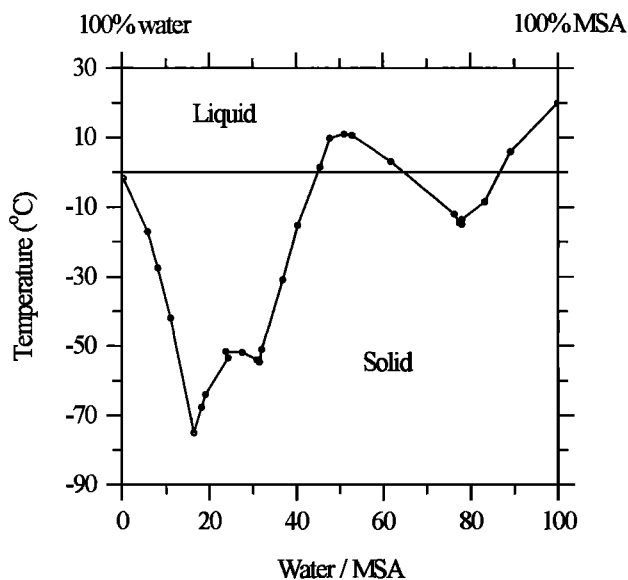
**Table 2.** Summary of Seasonality of MSA<sup>-</sup> in Core Sections in This Study, With Depths of Sections, Approximate Ages, and Mean Concentrations of MSA<sup>-</sup> and nssSO<sub>4</sub><sup>2-</sup> at Each of the Sites

Core Section m w.e.	MSA <sup>-</sup> Maxima Season	Approximate Age of Section, years	Mean MSA Concentration, μeq L <sup>-1</sup>	Mean nssSO <sub>4</sub> <sup>2-</sup> Concentration, μeq L <sup>-1</sup>
Dyer				
8-10	summer	13-15	0.08	0.81
51-56	summer	94-103		
Dolleman				
1-5	summer	3-12	0.79	3.64
32-36	winter (except one)	91-101		
93-96	winter	289-297		
Beethoven				
0-6	summer	0-5	0.13	0.62
26-30	summer	25-28		
Gomez				
2-8	summer	2-8	0.08	0.67
33-37	summer	37-42		
Berkner				
0-0.8	summer	0-2	0.28	0.88
13-14	winter	57-61		
23-24	winter	101-106		
37-39	winter	165-174		

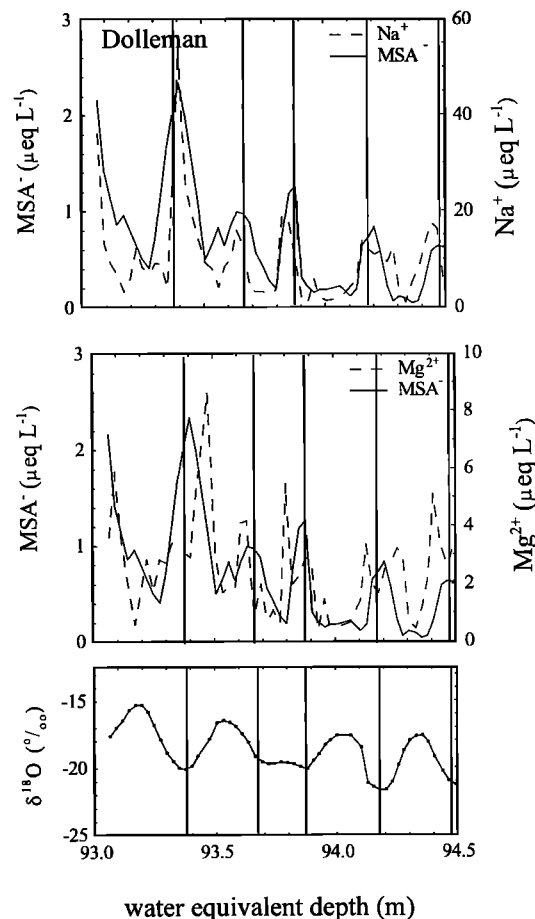
MSA<sup>-</sup> concentration, so a direct relationship may not be expected. However, it should be noted that the high MSA<sup>-</sup> peak at 93.4 m corresponds to a high concentration of Na<sup>+</sup> and Mg<sup>2+</sup>. The high cation concentrations may determine the direction in which the MSA<sup>-</sup> moves through the firm.

**4.1. Comparison of Two Cores From Dolleman**

There is a time lag between the deposition of the sulphur species MSA<sup>-</sup> and nssSO<sub>4</sub><sup>2-</sup> in the snow and the relocation of MSA<sup>-</sup> to the winter snow layer. Comparison of the profiles from several sites



**Figure 6.** Phase diagram for MSA<sup>-</sup>/water mixtures. Data from Stephen and Stephen [1963].



**Figure 7.** Comparison of MSA<sup>-</sup> (left-hand scale, solid line) with Na<sup>+</sup> and Mg<sup>2+</sup> (right-hand scales, dashed lines) in deep core sections from Dolleman. Maximum concentrations of cation species and MSA<sup>-</sup> generally occur in the winter layer.

has shown that the depth at which movement takes place is variable. It is not immediately apparent whether depth or time since deposition is more important. In order to test whether time or depth governs the onset of  $\text{MSA}^-$  movement, we returned to a site where relocation takes place in the upper few tens of meters of the snowpack and collected a second core 7 years later.

Two cores drilled at locations ~1 km apart on Dolleman Island in 1985-1986 (D1) and 1992-1993 (D2) season have been analyzed at subannual resolution (12 samples per year) back to the year 1948. Thinning of the layers due to ice deformation has not been taken into account as it is not significant at this depth in the ice sheet.

The mean concentrations of  $\text{MSA}^-$ ,  $\text{nssSO}_4^{2-}$ , and  $\delta^{18}\text{O}$  are compared for the overlapping sections of D1 and D2 in Table 3. D2 has slightly higher anion concentrations and a lower mean  $\delta^{18}\text{O}$ . Mean annual concentrations were calculated by taking the average of the data between the winter minima for each year in both cores. *T* tests were carried out to compare the mean annual concentrations for each species in D1 and D2. Taking a null hypothesis that the two cores give the same chemical signal, for  $\text{MSA}^-$  and  $\text{nssSO}_4^{2-}$  the null hypothesis is retained and for  $\delta^{18}\text{O}$  the null hypothesis is rejected. The D1 and D2  $\delta^{18}\text{O}$  data were measured at different laboratories, and the shift in values may be due to different equipment used or a difference in the standard used as reference. It should be noted that the annual average  $\delta^{18}\text{O}$  data are well correlated ( $r=0.81$ ) for the cores, with correlations significant at the 99% level. Good correlations were also measured between the two cores for  $\text{MSA}^-$  and  $\text{nssSO}_4^{2-}$  (Table 3).

Chemistry data from the D1 and D2 cores (shown in Figure 8) overlap for the period 1984-1948. Owing to the year-on-year variability in accumulation for the two cores, the depths do not match perfectly. In the upper part of both cores, the  $\text{MSA}^-$  peak is in the summer layer. From 1992-1984, the concentrations of  $\text{MSA}^-$  in the D2 core are always highest in the summer layer, with minima in the winter layer. The first overlapping period of the D1 and D2 cores is 1983-1984, the  $\text{MSA}^-$  peaks for both cores are clear and broad, and the  $\text{nssSO}_4^{2-}$  and  $\delta^{18}\text{O}$  peaks in both cores are similar. For the following 6 years the  $\text{MSA}^-$  signal becomes quite low, and the variations in the signals of the two cores are similar. In the winter layer assigned to 1975, there is an  $\text{MSA}^-$  peak in the D2 core, but not in D1, but for 1973-1971 both cores have  $\text{MSA}^-$  winter layer maxima. In the layer corresponding to summer 1966-1967 there are sharp  $\text{MSA}^-$  peaks in both cores. However, winter  $\text{MSA}^-$  maxima are more frequent in both cores at this depth, and often there are maxima in both winter and summer layers. Below 1954 the maximum concentration in both cores appears more established in the winter layer.

The first sign of  $\text{MSA}^-$  migration in the D1 core is at a depth of 1.9 m (4 years after deposition). In the D2 core the first sign of

relocation occurs at a depth of 5.4 m (11 years after deposition), which corresponds to the same calendar year as the winter peak in the D1 core (1979). If the top 5 m of each core is compared, in the D1 core there are three clear winter layer peaks, while in the D2 core there are none at all. We conclude that the  $\text{MSA}^-$  migration does not occur at a given depth below the surface or at a specific time after deposition.

Dolleman sometimes experiences temperatures  $>0^\circ\text{C}$  in December and January, and there is some occasional slight melting and percolation of water, resulting in clear ice layers which are up to 30 mm thick. In Figure 8 we plot the ice layers for D1, measured at the time of drilling. The ice layers are not limited to the summer deposited snow layer as some percolation occurs in the firn at this site. The location of the ice layers and the occurrence of  $\text{MSA}^-$  peaks and  $\text{MSA}^-$  migration do not appear to be related. At Berkner, where there is clear relocation of  $\text{MSA}^-$  to the winter layer in the core, there is no significant summer melting. Taken together, these observations imply that melting and gross percolation of meltwater are not the mechanisms of  $\text{MSA}^-$  migration.

The seasonal signals in the two cores are very similar, with only three major differences over a period of 37 years, and relocation to the winter layer occurs for the same years in both cores. The only exceptions are D1 has no  $\text{MSA}^-$  peak corresponding to the winter layer in 1975 and in 1965 and 1959 there are peaks in the winter layers in D1 and not in D2. Relocation appears to increase with time before 1984, but this is not a gradual progression, and there is no clear point at which the  $\text{MSA}^-$  is completely established in the winter layer.

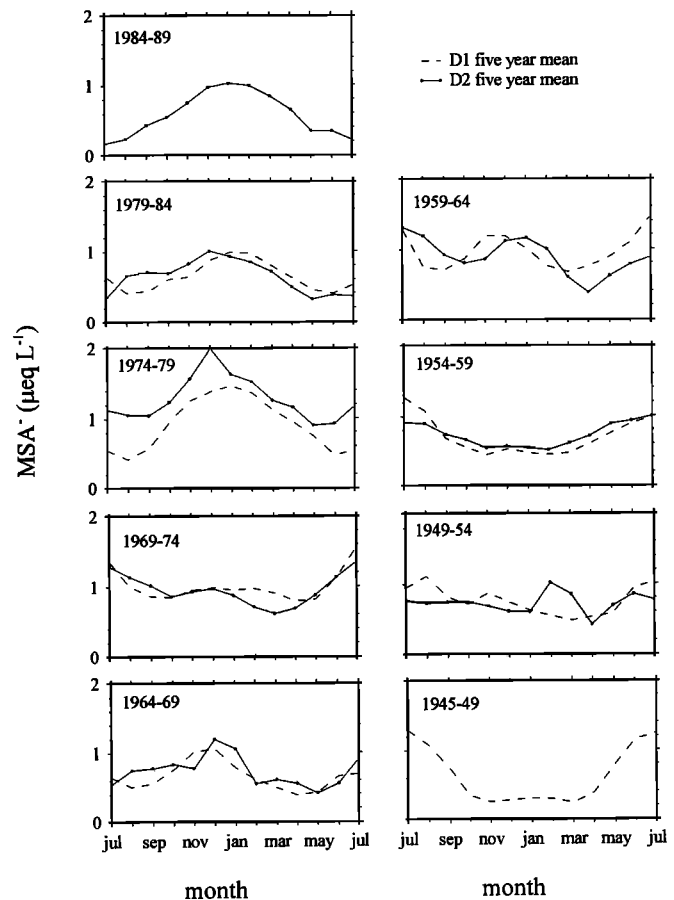
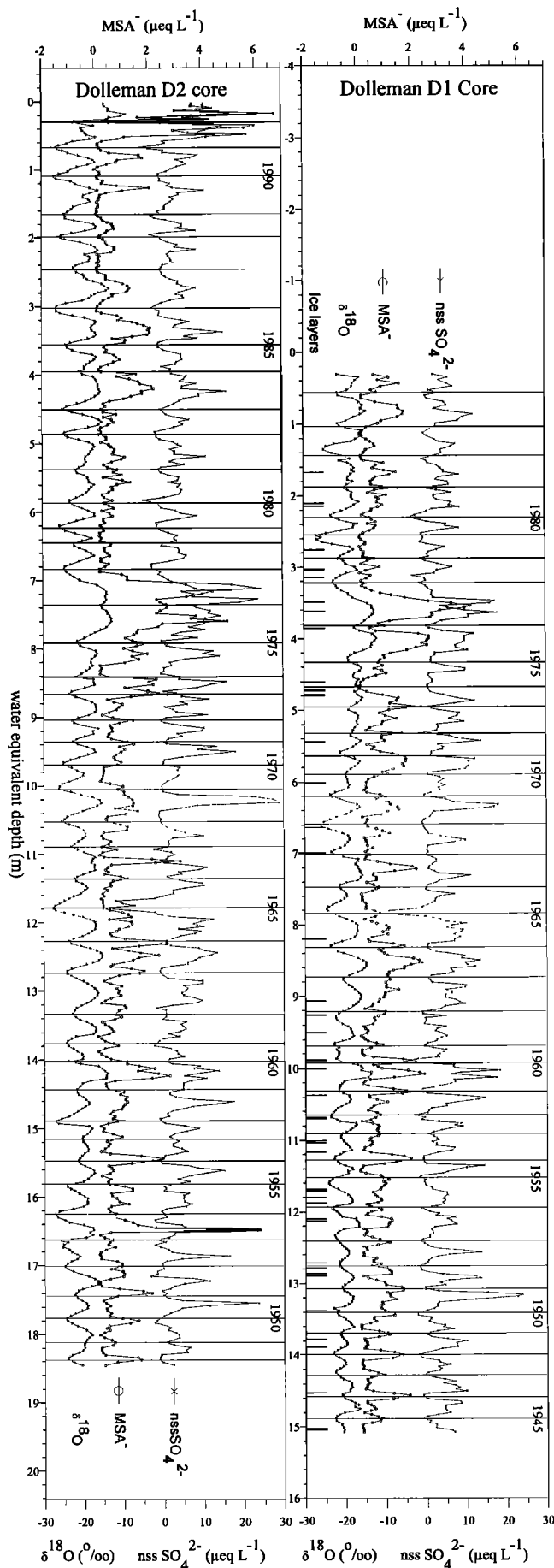
#### 4.2. Comparison of Average Seasonal Cycles for the D1 and D2 Dolleman Cores

By calculating mean annual cycles for each core, we can analyze the data in a more systematic way. Each year is interpolated into 12 equal parts broadly corresponding to months, taking the winter minimum in  $\delta^{18}\text{O}$  as July of each year. This calculation does not take into account the variations in snow accumulation throughout the year and is therefore not a true representation of monthly concentrations. However, it provides an indication of the annual cycles of the different species and can be used to compare the variations over different time periods. In Figure 9 we calculate a series of these mean annual cycles over 5-year periods for each of the two Dolleman cores. The two cores show broadly similar patterns. In the periods 1979-1984 and 1984-1989, the  $\text{MSA}^-$  seasonal cycle is summer based. In the 20 years before this, there is evidence of the increasing influence of winter  $\text{MSA}^-$ , while sufficient  $\text{MSA}^-$  remains in the summer layers to make the annual profile bimodal. In the 10 years 1949-1959, there is less influence

**Table 3.** Mean Concentrations of Anion Species and  $\delta^{18}\text{O}$  in D1 and D2 Cores and Correlations Between the Data for the Two Cores

Species	Mean D1 (s.d.)	Mean D2 (s.d.)	Correlation Coefficient <i>r</i>	<i>T</i> statistic, %
$\delta^{18}\text{O}$	-19.38 (2.72)	-20.11 (3.08)	0.81	99
$\text{MSA}^-$	0.81 (0.64)	0.88 (0.80)	0.80	99
$\text{nssSO}_4^{2-}$	3.71 (4.48)	3.93 (5.36)	0.82	99
Number of samples	422	390	-	-





**Figure 9.** Mean 5-year average seasonal concentrations of  $MSA^-$  for D1 (dashed lines) and D2 (solid lines) cores for the period from 1989 to 1945.

on the annual profile from  $MSA^-$  remaining in the summer (with the exception of the February-March peak in the D2 profile, peak is caused by the large summer  $MSA^-$  peak in 1953-1954, which is not seen in the D1 core; if this peak is removed from the calculations, then a clear cycle with a winter  $MSA^-$  maximum is observed.). By 1945-1949 the annual profile is dominated by the  $MSA^-$  located in the winter layer.

Both D1 and D2 show a very similar progression from summer  $MSA^-$  peak in the upper part of the core through stages when there are summer and winter maxima to a point where the  $MSA^-$  is predominantly located in the winter layer, despite the fact the D2 core was collected 7 years later. The relocation effect appears not to be well related to the passage of time since snowfall and may therefore be more dependent on the impurity concentrations and the ice fabric, which are similar for the two cores.

**Figure 8.** Comparison of  $MSA^-$  (left-hand scale), and  $nssSO_4^{2-}$  and oxygen isotope (right-hand scale) signals for D1 and D2 cores from Dolleman Island. The cores were drilled 1 km apart with a 7-year time difference between the drilling of each core. Winter minima are marked with vertical lines, and assigned years are marked every 5 years. Ice layers which were recorded at the time of drilling have also been marked to scale on the plot.

## 5. Conclusions

MSA<sup>-</sup> migrates from the summer snow layer where it was initially deposited to the winter layer in cores from Dolleman and Berkner. At Dyer, there is some indication of relocation in one section we studied, but the pattern is less clear. Migration of MSA<sup>-</sup> was not observed in cores from Beethoven and Gomez, but relocation deeper in the ice sheet at these sites cannot be ruled out. We do not observe migration of  $\text{nssSO}_4^{2-}$ . We have considered the characteristics of the ice core sites in order to explain our observations of the migration of MSA<sup>-</sup>. We do not consider that the mean annual temperature of the site determines whether MSA<sup>-</sup> is able to migrate since we observe the clearest changes in our coldest and our second warmest sites. Dolleman and Berkner are characterized by a relatively high concentration of MSA<sup>-</sup> and lower accumulation and these may be the factors governing which sites display the unusual behavior of MSA<sup>-</sup>.

The relocation process begins in the upper 5 m of one firm core from Dolleman and becomes more established deeper in the core. The change from summer to winter MSA<sup>-</sup> peaks does not occur at a fixed depth or time after deposition, but there is an overall gradual change from mainly summer layer to mainly winter layer MSA<sup>-</sup> peaks. Peaks in MSA<sup>-</sup> are generally observed only in summer snow (where they are deposited) and winter snow (where they migrate) rather than in spring and autumn snow. In two cores drilled at Dolleman, the changes in the seasonal MSA<sup>-</sup> behavior generally occur for the same years, and the pattern of relocation is the same. This is a remarkable result, as the cores were drilled at an interval of 7 years. Relocation is therefore not directly related to depth below the surface or time after deposition. The similar behavior in the two cores suggests that the movement of MSA<sup>-</sup> in firm is linked to specific factors in the core, such as local impurity concentrations and ice fabric, which are similar for the two cores.

We have discounted gross melting and percolation as a mechanism for the mobility of MSA<sup>-</sup> since Berkner, our coldest site, shows no evidence of ice layers, and at Dolleman, where ice layers are visible, they are not related to MSA<sup>-</sup> concentration. Simple diffusion along a concentration gradient can also be discounted since this would lead to a smoothing out of the seasonal cycle, whereas we observe that the MSA<sup>-</sup> peak, once it has appeared in the winter layer, tends to sharpen with depth. A possible mechanism for the migration of MSA<sup>-</sup> in the snowpack is via an initial diffusion in either the vapor or liquid phase which is halted by precipitation in the winter layer when the MSA<sup>-</sup> forms an insoluble salt with a cation. The eutectic temperature of MSA<sup>-</sup>/water mixtures is sufficiently low that mixtures would remain liquid at ice sheet temperatures if the MSA<sup>-</sup> was concentrated at grain boundaries. We suggest that an investigation of the relationship of MSA<sup>-</sup> with ions in firm and ice and the formation of salts with sea-salt cations at low temperatures may confirm this mechanism.

**Acknowledgments.** The authors would like to thank the many people involved in the collection and subsampling of the cores used in this work.

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E.C. Pasteur and R. Mulvaney, Ice and Climate Division, British Antarctic Survey, Natural Environment Research Council, Madingley Road, Cambridge, CB3 0ET, England, U.K. (r.mulvaney@bas.ac.uk)

(Received October 14, 1999; revised December 20, 1999; accepted December 30, 1999.)