MICROPARTICLES, MARINE SALTS AND STABLE ISOTOPES IN A SHALLOW FIRN CORE FROM THE ANTARCTIC PENINSULA

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ABSTRACT. Variations in the concentration of stable oxygen isotopes, marine salts and microparticles have been measured in a 6–m firn core which was recovered from the Antarctic Peninsula plateau (lat. 70°53′S, long. 64°57′W) in January 1977. The marine salts profile shows a regular periodicity which follows the seasonal pattern of stable isotope variations. Maximum concentrations tend to occur during the autumn, being associated with the minimum extent of sea ice.

Microparticle concentrations show no simple periodicity although on the average, main peaks occur at a frequency of between 0.5 and 1.0 a^{-1}. General trends along the profile match the record of gale occurrences at Faraday station in the Antarctic Peninsula.

The analysis of marine salt profiles may therefore provide useful stratigraphic information for dating ice cores from the region, particularly where oxygen isotope data cannot be interpreted. A combination of marine salt and microparticle analyses of ice cores should give important information relating to the extent of sea ice and cyclonic activity in the past.

EVIDENCE for past climatic change in the Antarctic Peninsula is being sought from studies of ice cores (Swithinbank, 1973). Data from a network of 10-m cores distributed throughout the region (Peel and Clausen, 1982) has shown a promising correlation between mean annual air temperature and oxygen isotope ratio ($\delta^{18}O$). This must now be tested over longer time sequences by comparing data from deeper cores with instrumental weather records from the nearest manned stations. For such studies it is essential to establish an ice-core chronology, preferably accurate to one year. Although in recent firn an absolute chronology can be established at horizons in artificial radio-activity, stratigraphic methods must be used to achieve a year-by-year dating and to extend the record beyond the earliest fission-product horizon (1955). Analysis of the 10-m cores has shown that seasonal variations in oxygen isotope ratios can be identified reliably only in limited areas of the Antarctic Peninsula. Alternative methods must be sought if we are to extend the area. This study forms part of an attempt to evaluate marine salts and mineral microparticles as seasonal stratigraphic markers.

Seasonal variations in Na and Cl⁻ in Greenland have been well documented (e.g. Murozumi and others, 1969; Langway and others, 1977). There, distinct maximum concentrations correlate with minima in the oxygen isotope ratio (isotopic winter). Some indication of a similar periodicity in Antarctica has been found by Herron and Langway (1979). Pit and shallow-core sequences from the Ross Ice Shelf showed a periodicity for Na consistent with an annual layer thickness obtained from fission product dating methods and from stake measurements. There was evidence that sea salt maxima occurred initially in winter and in early spring, which agrees with an earlier suggestion by Warburton and Linkletter (1978) using data obtained from 2-m pits on the Ross Ice Shelf. However, these authors could find no direct link between high concentration values and specific stratigraphic features. Recent data from James Ross Island (Aristarain and Delmas, 1981) also shows a seasonal variation in sea-salt deposition but with peaks occurring between summer and winter layers.

An annual periodicity in microparticle concentrations has been detected consistently in Greenland ice cores (e.g. Hamilton and Langway, 1967; Hammer and others, 1978) with a maximum concentration during spring demonstrated by comparison with parallel oxygen isotope ratio ($\delta^{18}O$) profiles. Several sites in Antarctica also appear to exhibit annual cycles in microparticle concentrations. At South Pole, Dome C and Byrd Station recent snow accumulation rates estimated by counting successive microparticle peaks agree with values derived from independent dating methods (e.g. Hamilton, 1969; Thompson, 1977, Thompson and others, 1981). Two 7-m cores from the Byrd strain network, which were also analysed for $\delta^{18}O$ (Thompson, 1977) indicated that the microparticle peaks were associated with summers.

This is consistent with the seasonal variation in the near-surface total aerosol at the South Pole reported by Hogan (1976).

Earlier data from the Antarctic Peninsula (Gliozzi, 1966) interpreted against stratigraphic observations, indicated that at Eights Station (lat. 75°15′S, long. 77°07′W) and site 'K' (lat. 74°27′S, long. 67°07′W) there may be a two-year cycle in microparticle concentration. The interpretation for Eights Station was substantiated by stake measurements and later by $\delta^{18}O$ stratigraphy. In contrast, Hamilton and O'Kelly (1971), who analysed a 7-m core from a neighbouring site (site 'C'; lat. 75°S, long. 73°W) concluded that there was an annual cycle of dust accumulation at this site although their interpretation was based on stratigraphic observations alone. More data are evidently required to establish the extent to which microparticle fluctations can provide reliable stratigraphic horizons in the Antarctic Peninsula.

Here we attempt to compare several potential stratigraphic dating methods along a single 6.4-m core retrieved from the central plateau region of northern Palmer Land. Na, Mg, Cl– and microparticle concentrations have been measured at a frequency of approximately 20 samples per accumulation year and the data evaluated in comparison with a parallel sequence of $\delta^{18}O$ measurements. Meteorological data from an Antarctic Peninsula coastal station, Faraday, combined with estimates of sea-ice extent from satellite imagery are used to interpret general features of the impurity profiles.

COLLECTION AND SUB-SAMPLING OF CORE

In January 1977 a 6.44-m firn core (90 mm diameter) was recovered from the central plateau of northern Palmer Land (lat. 70°53′S, long. 64°57′W; Fig. 1) using an aluminium hand auger. The site (station 25 in Peel and Clausen, 1982), at an altitude of 1 835 m a.s.l. (determined barometrically) is 170 km from the Weddell Sea to the east and 220 km from the South Pacific Ocean to the north-west. The nearest exposed rock is 18 km distant and the prevailing northerly winds come from an area generally free from exposed rock. The mean annual air temperature is −20.2°C (temperature at 10 m depth) and no sign of melt layers was observed in the core.

Clean-room garb was worn by the investigators whilst the core was drilled and sealed in polyethylene tubing. This was in turn placed in cardboard cylinders for shipment to the laboratory at storage temperatures below −10°C.

50-mm segments of the core were sub-sampled in a class-100 laminar flow work station in a cold (−22°C) laboratory using a PTFE-coated freezer knife. This had been pre-cleaned by leaching with 1:6 'Analar' grade nitric acid (12 h) followed by soaking (24 h) in ultra-pure water obtained from a Millipore 'Milli-Q' water system supplied with deionised and double distilled water. Three central plugs (diameters 15 mm, 15 mm and 35 mm) were removed from each segment using a pre-cleaned stainless steel subcorer. One plug was placed in a glass beaker, covered, then transported to an adjacent class-100 clean-air laboratory for melting and subsequent microparticle analysis. The two remaining plugs were each placed in 20-ml polyethylene scintillation vials which had been cleaned in 1:6 nitric acid followed by repeated rinsing with ultra-pure water. These were analysed for marine salts. The remainder of each core segment was placed in a polyethylene bag and melted prior to transfer to polyethylene vials in which they were shipped to the Geophysical Isotope Laboratory, Copenhagen for $\delta^{18}O$ analysis. Clean-room clothing and polyethylene overgloves were worn at all times.

ANALYTICAL PROCEDURES

Marine salts

Chloride concentration was analysed with an Orion specific ion electrode, the reliability of which deteriorates below concentrations of about 50 ng/g although it has a detection limit of about 5 ng/g. Sodium concentration was determined by flame atomic emission spectrometry and magnesium by flameless atomic absorption spectrometry using a graphite boat atomizer. A
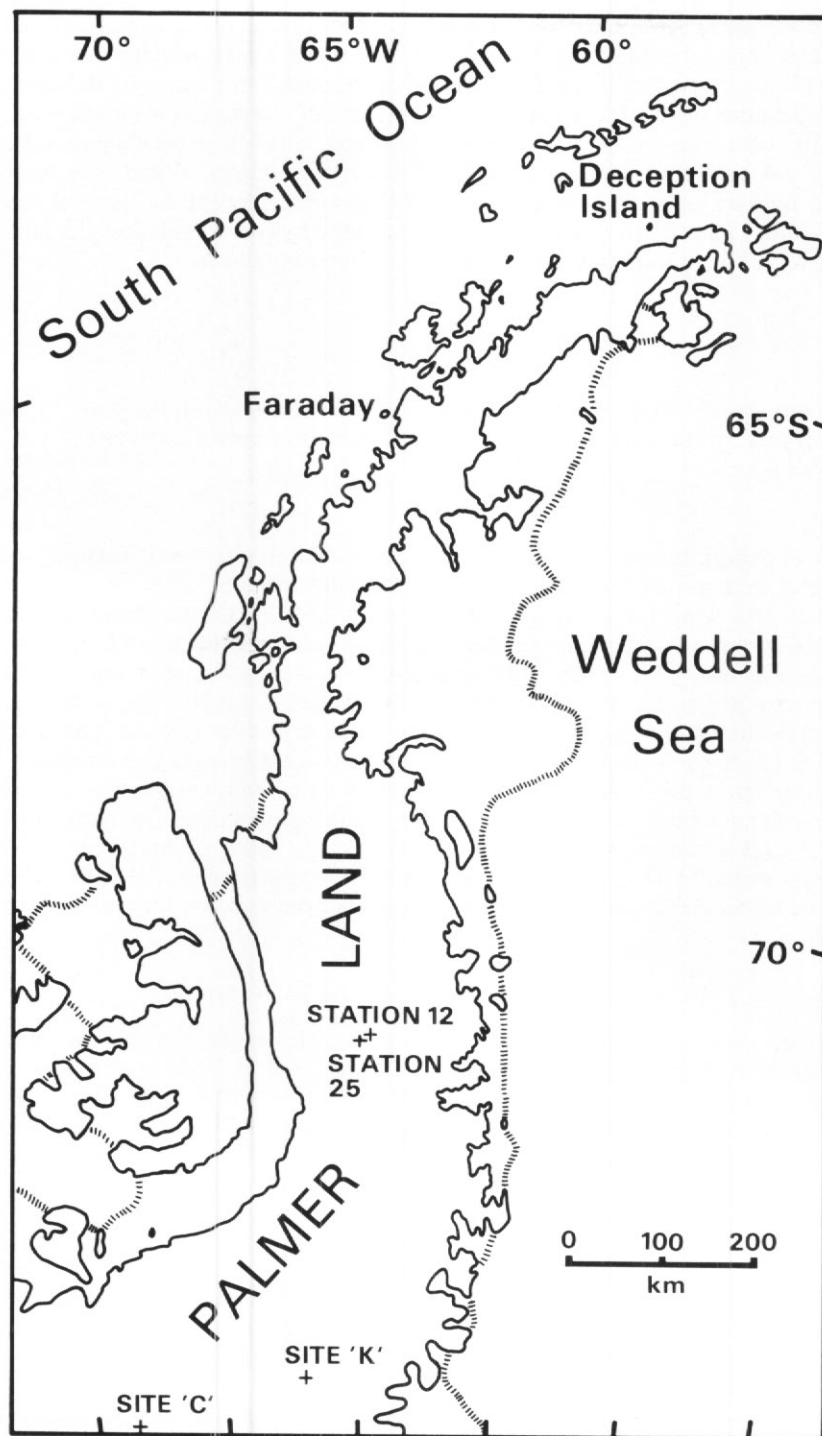
Fig. 1. Firn sampling sites in the Antarctic Peninsula.

Baird Atomic A5100 spectrometer was used. Calibrations for all the analyses were made using mixed standards containing Na, Mg, Ca, K and Cl⁻ in ocean water proportions. The procedure was checked by the method of standard additions for selected snow samples. Before analysis all samples and standards were acidified to pH 1.5–2 with BDH 'Aristar' grade nitric acid.

Procedural blanks were measured on ultra-pure water which had been subjected to the full sub-sampling and analysis routine employed for authentic samples. Water was frozen in pre-cleaned glass beakers and the stainless steel corer ground into the ice several times. After melting, the sample was transferred to a pre-cleaned polyethylene scintillation vial and analyzed in the normal way. The following blank concentrations were obtained;

$$Cl^- \sim 6 \pm 32 \text{ ng/g}$$
$$Na \quad 4.6 \pm 9 \text{ ng/g}$$
$$Mg \quad 0.8 \pm 0.4 \text{ ng/g}$$

These values are smaller than the lowest concentrations determined in the core. In view of the standard deviation of the blank values, a blank has not been subtracted from reported concentrations in snow.

Microparticles

Microparticle concentrations and size distributions in eleven size bands between 0.6 μm and 6.0 μm diameter were measured using a Model ZB Coulter Counter fitted with a 30-μm orifice tube, essentially following the procedure of Thompson (1977). Concentrations in procedural blanks were determined using similar methods to those employed for the marine salts with the exception that the ultra-pure water was passed through an additional final filtration stage (0.1 μm). The data presented relate to particle diameters larger than 0.6 μm since microparticle counts below this diameter are subject to errors arising from electronic noise. The concentration of microparticles is given as the total number of particles with diameters greater than 0.6 μm per 0.038-ml sample since this number is less susceptible to contamination than an estimate of microparticle volume which is biased to a relatively small proportion of particles in the larger size ranges. A procedural blank measurement of 3 362 ± 2 098 particles per 0.038 ml was obtained, which includes 978 ± 670 particles from the ultra-pure water and 340 ± 270 particles from the added brine. Reported concentrations have not been corrected by the counts obtained from the blank.

SNOW ACCUMULATION RATE AT THE SAMPLING SITE

Station 25 lies near the northerly limit of the region within which it is possible to identify seasonal cycles in $\delta^{18}O$ unambiguously (Peel and Clausen, 1982). A 10-m core was drilled at a topographically similar site 18 km away (station 12; lat. 70°50′S, long. 64°27′W, altitude 1 987 m a.s.l., 10-m temperature −21.4°C) during December 1974. Fig. 2 shows the $\delta^{18}O$ and total β-activity profiles obtained from this core. The horizon in total β-activity at 4.2 m water equivalent (WE) depth is associated with radioactive fallout from a series of Soviet nuclear weapons tests in the northern hemisphere which created a broad peak in activity in Antarctic snows in 1964/65 (Clausen and Dansgaard, 1977) that we have identified throughout the Antarctic Peninsula. The periodicity in the stable isotope profile fits quite well with the absolute dating of this horizon. Interpretation of cycles below 2 m WE depth improves because transient fluctuations which tend to complicate the record in the upper snow layers become smoothed by diffusion processes during firnification. An annual accumulation rate of 0.44 m water was derived for station 12.

The $\delta^{18}O$ profile for station 25 is given in Fig. 3. The core was insufficiently long to reach the 1964/65 horizon in total β-activity, therefore successive winter snow layers have been identified as minima in the $\delta^{18}O$ profile by analogy with the profile from station 12. This leads to an annual
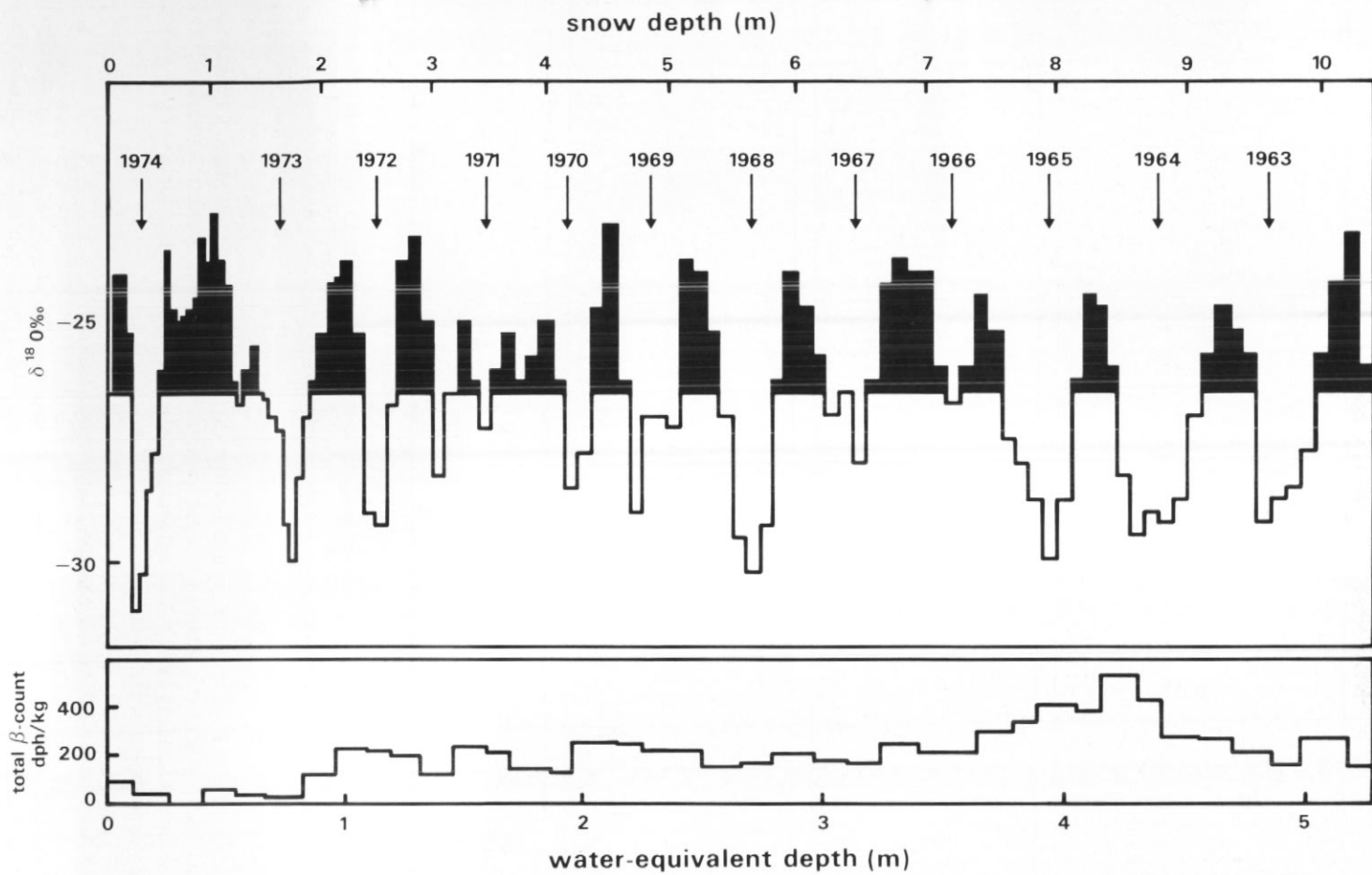
snow depth (m)

Fig. 2. Oxygen isotope ratio and total β-activity profiles down a 10-m firn core from station 12 (lat. 70°50′S, long. 64°27′W). Shaded areas are isotopically heavier than the mean. The arrows mark assigned isotopic winter layers.
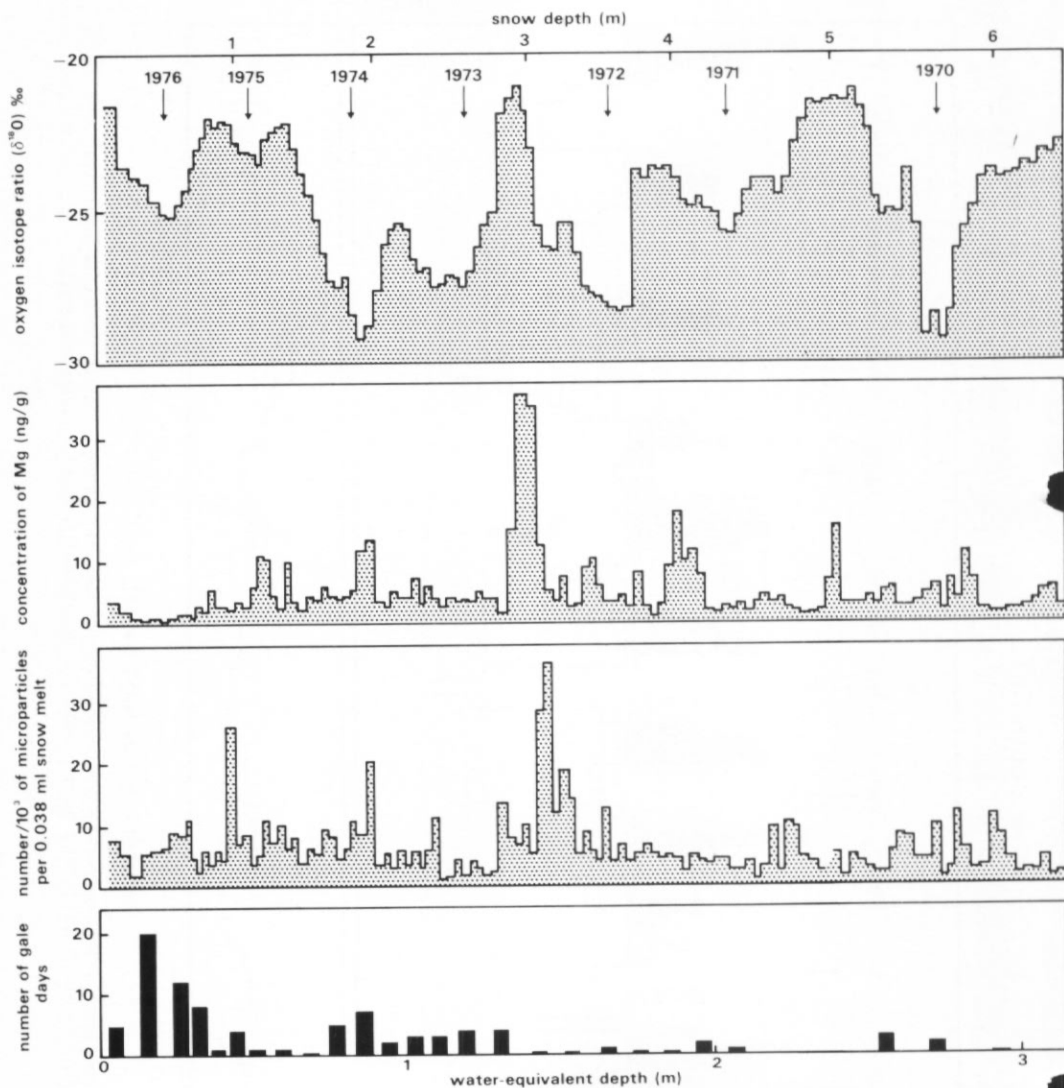
Fig. 3. Distribution of oxygen isotopes, magnesium and microparticles (diameters greater than 0.6 μm) down the 6.4 m firn core from station 25 (lat. 70°53′S, long. 64°57′W) in comparison with the number of gale days per season at Faraday. Arrows mark assigned isotopic winter layers.

accumulation rate of 0.42 m water, which is close to the value obtained at station 12 and to the mean value (0.51 ± 0.11 m) obtained at eight stations on the plateau between latitudes 65°S and 74°S (Peel and Clausen, 1982). The agreement between derived accumulation rates indicates that the dates assigned in Fig. 3 are accurate to ±1 a.

MARINE SALT VARIATIONS

The mean concentrations of Na, Mg and Cl⁻ in the core are given in Table I and the detailed profile for Mg in Fig. 3. The profiles for Na and Cl⁻, which are not presented, parallel the Mg

TABLE 1. MEAN MARINE ION CONCENTRATIONS AND CONCENTRATION RATIOS AT STATION 25

Ion	Mean Concentration (ng/g)	Point by point correlation with Mg (123 points)	$\dfrac{\text{Mean ion concentration}}{\text{Mean Na concentration}}$ in core	$\dfrac{\text{Mean ion concentration}}{\text{Mean Na concentration}}$ in sea water
Sodium	42.0	0.87 ($T = 19.0$)	1	1
Chloride	61.5	0.84 ($T = 17.2$)	1.46	1.80
Magnesium	5.5	1	0.13	0.12

profile very closely (correlation coefficients between these profiles are given in Table I) supporting a marine origin for these ions. Additional evidence is provided by the relative abundances of these elements, which lie close to those found in ocean water (Table I).

The variation of marine salt concentration with depth is clearly periodic and maximum concentrations in general coincide with summer or autumn snow layers identified isotopically. A similar correspondence was noted by Peel (1976) for snow-melt conductivity profiles in a series of 2-m pits sampled inland of Halley Bay. The snow layers in this case were characterized stratigraphically. If the peaks in marine salt concentration are assumed to be annual, Fig. 3 leads to an annual accumulation rate of 0.46 m water at station 25, which agrees satisfactorily with that deduced from the oxygen isotope ratio profile. The Mg concentration peaks are evidently much sharper than the smoothed features in the oxygen isotope profile and may indicate that marine salts are injected during discrete storm events.

Two main processes, or a combination of them (Peel, 1976; Warburton and Linkletter, 1978) probably control the concentration of marine salts deposited in snow within a few hundred kilometers of the Antarctic coastline:

i) Seasonal variations in the extent of sea ice control the distance between the marine aerosol source and the deposition site. Within 300 km of the coast the concentration of marine salts is strongly dependent on the distance from sea water thus seasonal variations in this distance may be expected to produce a parallel fluctuation in marine salt deposition.

ii) Cyclonic activity can provide a mechanism both for generating greater concentrations of sea salt nuclei at the ocean surface and for transporting a greater proportion of large nuclei to the deposition site.

The variation of sea salt concentration as a function of the distance from the coast has been studied in several parts of Antarctica including profiles along the axis Mirny-Vostok (Boutron and others, 1972), between Dumont d'Urville and Dome C (Boutron, 1978), and on the Ross Ice Shelf (Warburton and Linkletter, 1977; Herron and Langway, 1979). In general the concentration (C) appears to vary exponentially with distance (D) from the coast according to the following expression (Herron and Langway, 1979):

$$C = C_0 \exp (D/D_0) \tag{1}$$

where C_0 is the concentration at the coast and D_0 is a scale distance.

A best fit for annually averaged data from the Ross Ice Shelf is obtained with $D_0 = 250$ km and with C_0 values ranging between 600 and 300×10^{-9} g/g (expressed as a Na concentration). A similar regression for combined data from East (Greater) Antarctica taken along the axis Mirny–Vostok between 45 and 1 030 km from the coast and along the Dumont d'Urville–Dome C traverse between 5 and 500 km from the coast gave a scale distance, D_0, of 306 km and a C_0 value of 77×10^{-9} g/g. The C_0 values reflect the mean annual aerosol composition near the geographical coastline and will be sensitive to the distance of this position from the mean position of the sea ice edge and to different patterns of transport of aerosol from the source

region. The similarity of the D_o values in both regions, which exhibit contrasting meteorological and topographic regimes, suggests that within a few hundred kilometres of the coastline, distance from open water dominates any influence of altitude on the scale distance.

Assuming that the seasonal marine salt deposition in the Antarctic Peninsula decays with distance inland according to a similar scale distance we can estimate the ratio of maximum (C_{max}) to minimum concentrations (C_{min}) which should occur at a fixed site as a result of seasonal movement of the sea ice boundary:

$$C_{max}/C_{min} = \exp[(D_{max} - D_{min})/D_o] \tag{2}$$

where D_{max} and D_{min} are the distances between the sampling site and the maximum and minimum positions of the sea ice edge respectively.

The U.S. Navy FLEWEAFAC ice charts have been used to plot the distance of the sea ice edge from station 25 on a monthly basis during the period 1974–76. These data together with mean monthly temperature observations from Faraday are given in Fig. 4. Inspection of the NOAA satellite photographs for the period before 1973 showed a similar pattern for all the years spanned by the core (1970–76). For 2–3 months during late summer/autumn (Feb/April) open water extends near to the west coast of the peninsula approximately 220 km from station 25. At the winter maximum extent of sea ice, open water is approximately $1\,000 \pm 140$ km away.

Putting these distance limits into Equation 2 together with scale distances of 250 and 306 km gives C_{max}/C_{min} in the range 12.8 to 22.6. The data for Mg from station 25, with the exception of a snow layer at a water equivalent depth of 1.30–1.45 m, show a mean peak concentration of $13.1 \pm 2.3 \times 10^{-9}$ g/g and a mean minimum concentration of $1.3 \pm 0.9 \times 10^{-9}$ g/g. These concentrations have been corrected for the blank. The resulting ratio C_{max}/C_{min} is 10.1 ± 7.6 in satisfactory agreement with that predicted from Equation 2.

Absolute values for the peak and minimum concentrations estimated from Equation 1 and incorporating both the parameters C_o and D_o obtained on the Ross Ice Shelf are also compatible
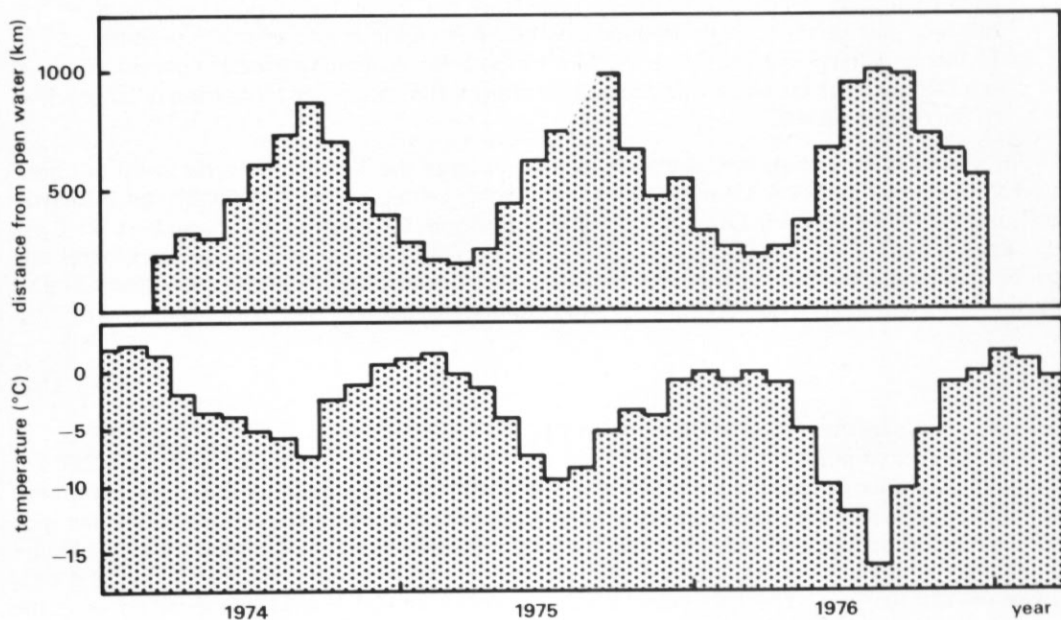

Fig. 4. Mean monthly minimum distance of sea-ice edge from station 25 and surface temperatures at Faraday for the period 1974–76.

with the measured values. The Mg concentrations, derived from Na concentrations calculated from Equation 1 by using the ionic ratios in Table I, are $12-32 \times 10^{-9}$ g/g (peak) and $0.5-1.4 \times 10^{-9}$ g/g (minimum). It seems therefore that much of the variability in marine salts observed at station 25 can be accounted for by seasonal variations in the extent of sea ice.

The unusually high concentration of marine salts in the 1.30–1.45 m WE depth layer coincides with both a large dust concentration and an isotope maximum. It seems likely that this was associated with an unusual meteorological event, that could be linked with the intense cyclonic activity that occurred during March/April 1973 (Limbert, 1977). The lowest mean monthly pressures for at least 8 years were recorded at all BAS meteorological stations during this period.

Although further work on longer cores is needed to confirm an unequivocal seasonal signal in marine salt concentrations in this area, this short core sequence gives ground for optimism that it may provide a convenient dating method. It is also possible that secular variations in the extent of sea ice could be estimated from changes in marine salt maximum and minimum concentrations, although these may also be linked with changes in cyclonic activity.

MICROPARTICLE VARIATIONS

The profile for dust concentration (particle diameters greater than 0.6 μm) is given in Fig. 3. Evidently, annual layers are not uniformly associated with a microparticle peak and on the average a periodicity of between one and two years is indicated. This lends some support to the earlier observations by Gliozzi (1966) in the southern part of the peninsula. In general the microparticle peaks do not coincide with peaks in marine salt concentration or with a particular isotopic season, with the exception that substantial peaks do not occur at the depth of isotopic winter.

The coincidence of the dominant peak at 1.3–1.45 m snow depth with an unusually large peak for Mg, which our dating indicates may be associated with extreme cyclonic activity, suggests that winds and storm events may be important factors controlling the supply of microparticles to the Antarctic Peninsula. The general level of cyclonic activity in the region can be assessed from wind-speed data recorded at coastal stations. Fig. 3 shows the seasonal incidence of gale days (wind speed > 32 knots) at Faraday (lat. 65°15'S, long. 64°16'W). This station is generally free from local katabatic winds and the records should reflect behaviour on a scale that is larger than that recorded by stations closer to the mainland. The period 1969–72 was the calmest period since records began in 1946. Corresponding sections of the core contain no major dust concentration maxima, in contrast to the upper section of the core which was deposited under a much windier regime.

It is of interest to note that a minor volcanic eruption on Deception Island which occurred in August 1970 did not cause a detectable increase in dust in the corresponding section of the core. Most of the ash fall in the larger size range from this eruption was deposited under a south-westerly wind and directed away from Palmer Land (Baker and others, 1975). However, our data relate to microparticles in a size range which would remain suspended in the atmosphere for up to several days following an eruption and hence may become included in the regional atmosphere circulation. The absence of a signal in the ice core suggests that such indirect input from local volcanism does not contribute significantly to the small-sized microparticle deposition in Palmer Land. Future cores spanning the larger eruptions of 1967 and 1969 on Deception Island should help to confirm this.

CONCLUSIONS

The variation in concentrations of marine salts down a firn core from a remote site in the Antarctic Peninsula appears to be a periodic function, with maxima occurring at annual

intervals. If more widely confirmed this could be exploited as a chemical stratigraphic dating method. The concentration ranges of maximum and minimum values generally relate to seasonal fluctuations in the distance of open ocean water from the snow deposition site. With more core data spanning the period for which accurate sea ice records from satellite imagery are available (1968 onwards) it may, in the future, be possible to estimate sea ice conditions for earlier periods from marine salt variations down deeper cores. However, simultaneous cyclonic activity also has to be taken into account.

Microparticle analyses indicate that there is no simple annual periodicity in the variation of dust concentration with depth, but there appears to be a general link with the incidence of storm events rather than volcanism. Together with the marine salt and stable isotope data (whose link with air temperature has already been established) dust measurements on cores will provide valuable information for studies on past climate in the Antarctic Peninsula. Such studies are vital to our understanding of changes in the atmospheric circulation system in the sub-Antarctic zone which have important implications for world climate.

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