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Time-trends in the pattern of ocean-atmosphere exchange in an ice core from the Weddell Sea sector of Antarctica

By D. A. PEEL and R. MULVANEY, *British Antarctic Survey, Natural Environment Research Council, High Cross, Madingley Road, Cambridge, CB3 OET, UK*

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ABSTRACT

The east coast of the Antarctic Peninsula is strongly influenced by air masses that have traversed the Weddell Sea zone. A continuous record of annual-average values for $\delta^{18}O$, δD, Cl^- and non sea-salt SO_4^{2-} in snowfall deposited since 1795, has been obtained on an ice core drilled on Dolleman Island (70°35.2′S, 60°55.5′W). Chemical changes along the ice core seem to be linked to changes in the concentration of the ice cover in the marginal ice zone. In the period since 1956, these variations appear to be coupled to the atmospheric circulation, as indexed by the atmospheric pressure gradient across the marginal ice zone. The largest anomaly in the 200-year sequence occurs in the period 1820–1880, during the final stages of the Little Ice Age. Exceptionally high concentrations of Cl^-, low concentrations of biologically-derived sulphate, and high deuterium excess suggest that at this time there was a dense, compacted marginal ice zone with cyclones tracking more frequently than normal across ocean areas to the north of the ice edge. During the past century, there has been a marked decrease in deuterium excess of about 4 ‰, which implies that there has been a progressively increasing contribution to precipitation from moisture sources at lower temperature, probably from within the marginal ice zone. The implication is that there may have been significant weakening of the ice cover in this zone during the past century, despite satellite evidence which reveals no significant change in the position of the ice edge, at least since 1973.

1. Introduction

The Antarctic marginal ice zone, in which the Weddell sea forms a large element, is an important component of the global climate system (Budd, 1991). The global radiative energy budget is affected directly by the extent of ice cover owing to its high albedo. Various secondary feedback processes involving exchanges of heat, moisture and dissolved gases (e.g., the downdraw of CO_2) between ocean and atmosphere may also be connected with changes in the ice cover. The sub-polar zones are also believed to be major source regions for organic sulphur species due to high levels of biological activity (Prospero et al., 1991). Charlson et al. (1987) have suggested that there is potential for feedback into the climate system through interference with cloud condensation nuclei (CCN) concentrations by sulphuric acid aerosol, an oxidation product of these species. So far, however, analysis of satellite imagery of the sea ice margin around Antarctica has failed to detect any significant change in extent during the period 1978–87 (Gloersen and Campbell, 1991). This study represents an attempt to detect changes in the ice level of the Weddell Sea during the past two centuries, by identifying changes in the chemistry of air masses that have travelled for long distances across the marginal ice zone. The chemistry of the air masses is inferred from chemical changes in snowfall as recorded in an ice core drilled adjacent to the region. This study came about because large and apparently non-temperature-related signals had previously been reported by Peel and Mulvaney (1990) and Peel (1992) in time series of stable isotopes for several ice cores drilled in the vicinity of the Weddell Sea. It was suggested that this anomalous behaviour could be linked to important changes over time, in the sources of moisture from which the precipitation was derived; a variable contribution from sources within the marginal ice zone was suspected.

2. Characteristics of the sampling site

Table 1 summarizes the principal features of the sampling site on Dolleman Island. The site lies on the eastern side of a major climate divide (Fig. 1) along the axis of the Antarctic Peninsula, separating a relatively warm, maritime cyclonic regime on the western side from a colder more continental regime to the east, strongly influenced by the semi-permanent ice cover of the Weddell Sea (Schwerdtfeger, 1984). The climate at this low altitude site is dominated by prevailing winds from

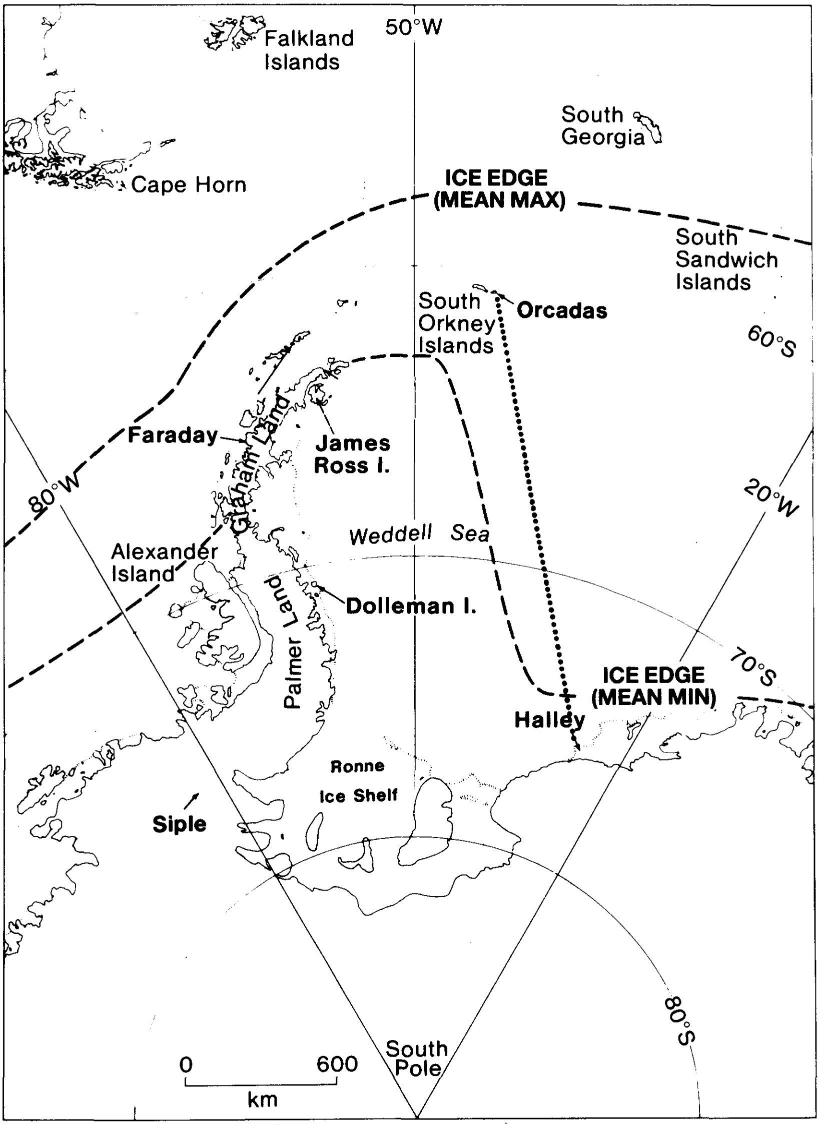

Fig. 1. Map of the Antarctic Peninsula region and the Weddell Sea showing the location of the ice core drilling site and weather stations referred to in this work. The mean positions of the seasonal maximum and minimum positions of the sea-ice edge are marked. The bold stippled line marks the axis across which the pressure gradient has been calculated to index atmospheric forcing on the Weddell sea ice cover.

Table 1. *Physical characteristics of the ice core sampling site at Dolleman Island*

position	70°35′S, 60°56′W
site type	dome
elevation	398 masl
ice thickness	~460 m
accumulation rate	0.42 m water/a
10 m temperature	−16.8°C
drilling date/depth	1986/133 m

the south and east, forced by the geographical obstruction of the steep mountain range (~2000 m altitude) of the Antarctic Peninsula in the prevailing easterly flow of cold, stably-stratified air crossing the Weddell Sea; air that has flowed for several hundreds of km over the marginal ice zone. A relatively large snow accumulation rate at the site has ensured that the annual cycles in several chemical constituents (including $\delta^{18}O$, SO_4^{2-}, Cl^-) in the ice core are well preserved, and a maximum dating error of ±5 years can be estimated back to 1795 (Peel et al., 1988; Peel, 1992). Peel et al. (1988) discussed the recent oxygen isotope ($\delta^{18}O$) record at the site from a 133 m ice core collected in 1986, in comparison with temperature records from neighbouring weather stations. The results are summarized in Fig. 2, where the data have been smoothed by a 5-year binomially-weighted filter to suppress noise arising from local spatial variations in the isotope record. Whilst the overall increase in temperature since about 1950 seems to be reflected in a general increase in $\delta^{18}O$, there was an important anomaly in the period 1973–77 which clearly had no relation to temperature. Moreover, as discussed by Peel (1992) the most significant feature of the longer-term record since 1795 shows a general decrease in $\delta^{18}O$ up to 1960 following a broad maximum in the mid-19th century, a period corresponding with the final stages of the Little Ice Age event. Simple interpretation of these features in terms of a temperature shift poses problems: whilst there is evidence for a similar broad maximum in stable isotopes at James Ross Island (Aristarain et al., 1990), on Ronne Ice shelf

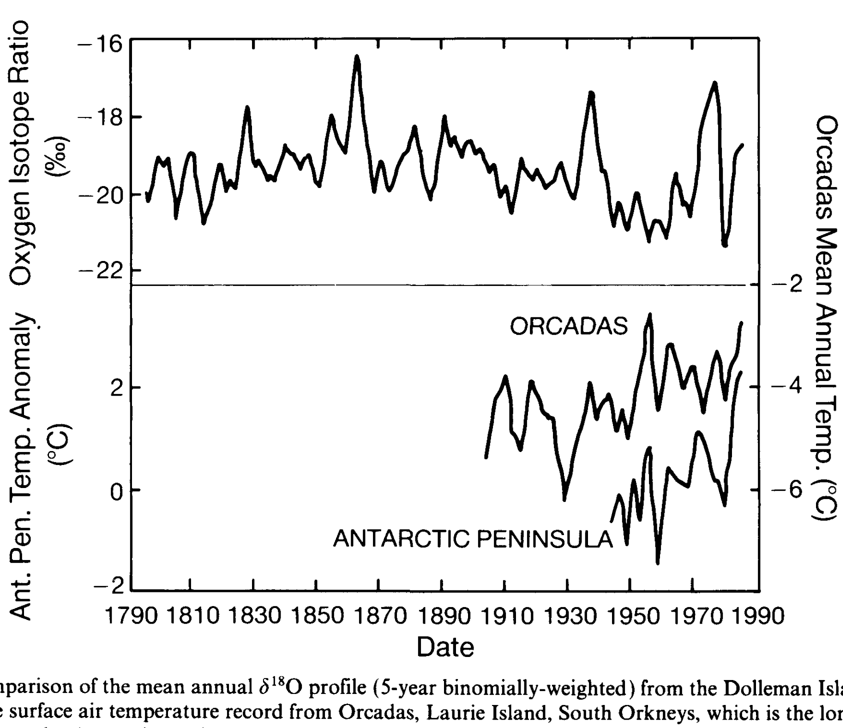

Fig. 2. Comparison of the mean annual $\delta^{18}O$ profile (5-year binomially-weighted) from the Dolleman Island ice core with: (i) the surface air temperature record from Orcadas, Laurie Island, South Orkneys, which is the longest record available from the Antarctic Peninsula region; (ii) an average temperature time-series for the Antarctic Peninsula region computed by Limbert (1984).

(Graf et al., 1990) and at Siple station (Mosley-Thompson and Thompson, 1990), other isotopic evidence from ice cores drilled in the interior of Antarctica from Law Dome (Morgan, 1985), South Pole (Mosley-Thompson and Thompson, 1990) and Dome C shows a corresponding isotopically cold period. In addition, Clapperton and Sugden (1988) give supporting evidence for broadly synchronous behaviour in the South American Andes, South Georgia and from South Shetlands and South Orkneys in the sub-Antarctic, which indicates that glaciers reached advanced positions during this period. On the basis of comparisons between the $\delta^{18}O$ record from Dolleman Island and a record of δD from James Ross Island, Peel (1992) argued that the isotopic profiles at these sites may have been affected by changes in the moisture source regions of the precipitation. Such changes could be traced using co-isotope analysis on the ice core in order to follow kinetic isotope effects.

3. Ice-core tracers of atmospheric circulation

This study examines the behaviour of three parameters in the Dolleman ice core in an effort to characterize either changes in the ice cover of the Weddell Sea or possibly associated changes in the atmospheric circulation.

3.1. Deuterium excess

There is a strong body of evidence reviewed by Robin (1983), both empirical and based on physical models, to support the idea that temporal variations in $\delta^{18}O$ and δD along an ice core are broadly determined by the temperature gradient from the moisture source regions to the deposition site, following the Rayleigh condensation process. However, non-equilibrium effects, especially during both the evaporation stage and the condensation stage, can influence the isotope fractionation process (Dansgaard, 1964). Johnsen et al. (1989) give evidence that the behaviour at low altitude sites, can be highly sensitive to changes in the temperature of the moisture source. Hence the interpretation of temperature change at the condensation point can be ambiguous. There is a growing interest in the application of measurements of deuterium excess, the differential behaviour of $\delta^{18}O$ and δD, to help elucidate this problem.

The deuterium excess (d) is computed as:

$$d = \delta D - 8 \times \delta^{18}O,$$

where the scaling factor of 8 is based on the Meteoric Water Line obtained for precipitation on a global scale (Craig, 1961). d is most sensitive to kinetic factors in the isotope fractionation process, including temperature, relative humidity, and possibly wind speed (hence evaporation rate) in the source area(s) (Johnson et al., 1989; Petit et al., 1991). Modelling studies for both Greenland (Johnsen et al., 1989) and Antarctica (Petit et al., 1991), support the idea that at coastal, low altitude stations, low d values indicate that a considerable part of the precipitation is derived from moisture evaporated from a cold source. Fisher (1990) has developed a semi-empirical global model of the zonal contributions of moisture sources extending from the tropics through to the Polar oceans, to the isotopic composition of polar snowfall. This model also predicts a deep minimum in d for precipitation deposited around 70° S, mainly arising from a large contribution of moisture from the cold southern oceans. We have determined d along the Dolleman ice core to identify areas with exceptionally low d values, which might indicate periods when there were important sources of moisture within the body of the pack ice zone.

3.2. Non sea-salt sulphate and chloride

The non sea-salt sulphate (nss-SO_4^{2-}) content of the snow at Dolleman Island is believed to be derived mainly from atmospheric oxidation of dimethyl sulphide (DMS), a product of marine biogenic activity (Prospero et al., 1991). Superimposed on this background may be sporadic short-term increases due to volcanic eruptions (Legrand and Delmas, 1987; Legrand et al., 1991), which are most clearly seen in the low snow-accumulation areas in the continental interior. These influences are probably negligible at Dolleman Island, a low elevation, near-coastal site with high snow accumulation rate, where there is a particularly strong seasonal cycle in nss-SO_4^{2-} showing a maximum in the austral summer (Mulvaney and Peel, 1988). Further support comes from James Ross Island, a site with comparable snow accumulation rate yet at considerably greater elevation (1660 masl), where even the major eruptions such as Agung (1963) could not be detected in a firn core (Aristarain et al., 1982). Our nss-sulphate measurements at Dolleman also show no sign of a significant positive perturbation during the three years following this eruption. Combined measurements of methane sulphonic acid (MSA) and nss-SO_4^{2-} at Mawson, which are highly correlated (Prospero et al., 1991), have added support to the proposition that biological processes in the Southern Ocean strongly influence sulphur chemistry in the Antarctic atmosphere, and may be predominant at near-coastal sites. Indeed, concentrations of MSA reported by Mulvaney et al. (1992) from Dolleman Island are amongst the highest recorded anywhere in the world. Even major volcanic events are unlikely to perturb significantly the background concentrations of sulphur compounds at Dolleman Island arising from biogenic emissions.

We have determined nss-SO_4^{2-} relative to Cl^- along the Dolleman core using ion chromatography (Mulvaney and Peel, 1988). At this stage, a complete data set is available for Cl^- but not for Na^+. Nevertheless, 1124 samples from the core have been analysed for both ions, giving a mean molar Cl/Na ratio of 1.38 compared with the sea water ratio of 1.17. Whilst there was evidence for significant deviations from these average values for individual samples (sampling rate averaged 12 samples per year), the mean annual values throughout were consistent with the longer-term average. This indicates that when considering the longer term trends there is no major departure of Cl from the sea water ratio, e.g., by volatilization in the presence of acids, and hence that at this site Cl may be used as a reference for the marine aerosol produced from sea spray over the open ocean. Moreover, we find no evidence throughout the record for any year during which there has been a net overall deficit of sulphate relative to sea-water composition. Major year-round deficits have been reported by Gjessing (1989) for three near-coastal sites less than 10 km from the sea, but the phenomenon seems to be restricted to sites that are extremely close to open water. The drilling site in the centre of Dolleman Island will normally have a minimum distance to heavy pack ice of around

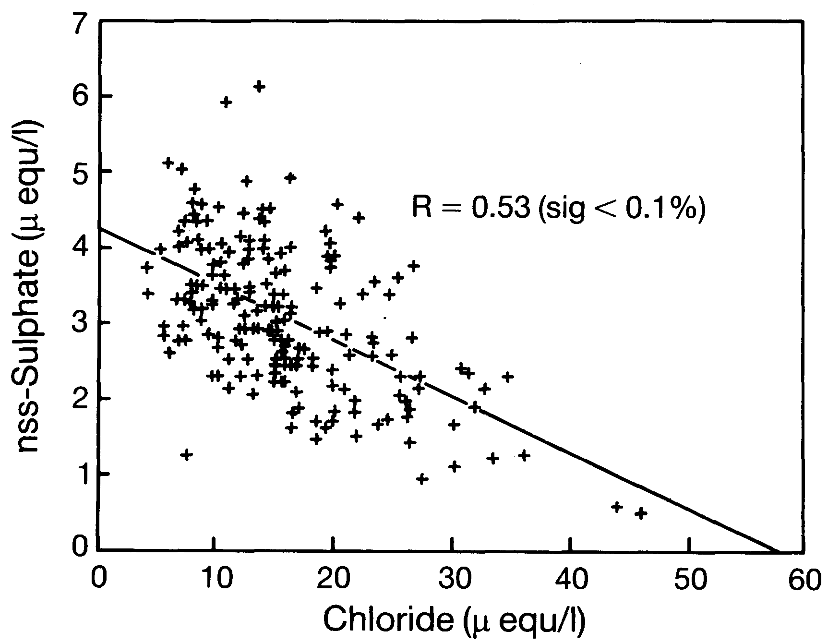

Fig. 3. Scattergram of 5-year binomially-smoothed mean annual concentrations of chloride and nss-SO_4^{2-} (using chloride as marine salt reference) from the Dolleman core (1795–1982) shows a strong inverse relationship. The inference is that different sources and transport processes are frequently involved in the mobilisation of these components of the atmospheric aerosol reaching the east coast of the Peninsula.

50 km, and distance to "open water" will normally be at least several hundred km, even during the summer.

Fig. 3 compares annual mean values of chloride and nss-SO_4^{2-} along the Dolleman core since 1795. There is a highly significant negative correlation. Indeed, there are cases where for entire years one species is almost totally dominant to the exclusion of the other. This not only suggests that different sources are involved but also indicates that the atmospheric transport pathways for these species differ. In exceptional cases there is almost no inut of nss-SO_4^{2-} yet Cl^- concentrations remain very high.

Clearly, during these years, efficient transport of marine aerosol from the Southern Ocean was a regular occurrence, yet the air masses involved generally contained only small quantities of nss-SO_4^{2-}. The implication is that the open areas of the Southern Ocean may not be a major source of the biogenic sulphur reaching Dolleman Island. Conversely, where nss-SO_4^{2-} concentrations are large and Cl^- concentrations suppressed, we suggest that the SO_4^{2-} signal is primarily a product of sulphurous emissions picked up by the air mass as it transects the pack ice zone. Whilst an air mass can efficiently absorb any gases emitted from leads and polynyas within the ice zone, due to the small "reach" of open water and the damping action of extensive pack ice there will be very limited production of sea spray, and hence no significant uptake of Cl^- by the air mass since it left the open ocean.

Further evidence, which may point more directly to the importance of marine biological activity within the marginal ice zone as a source, comes from a comparison of the nss-SO_4^{2-} profile at Dolleman and a record of sea ice variation from Orcadas, Laurie Island (60.7°S, 44.7°W) since 1903 compiled by Mayes (1981) from meteorological observations kept by the Argentinian Meteorological Service that record the dates in which Scotia Bay was closed by ice and the dates of opening each year. A long ice-season reflects extensive production of pack ice within the Weddell Sea, and in turn, a correspondingly colder than average temperature field (Mayes, 1981, p. 295). Fig. 4 shows that from 1902 to the late 1960's, the main features in the Cl^- and sea ice-extent-profiles are anti-phase, suggesting that when there is prolonged ice coverage in the NW corner of the Weddell Sea the production and transport of nss-SO_4^{2-} towards the east coast of the Peninsula is suppressed. The implication is that the area of ocean within the marginal ice zone is a major source area for nss-SO_4^{2-} reaching Dolleman Island. By contrast, a large positive anomaly in nss-SO_4^{2-} around 1972–76 appears to coincide with a period of somewhat higher ice production in the Weddell Sea. Whilst we cannot account for this anomaly, Schwerdtfeger (1976) has reported that there was a very significant change in atmospheric circulation during that period compared with the 29-year average since the start of meteorological observations, with a sharp increase in warm air advection from the

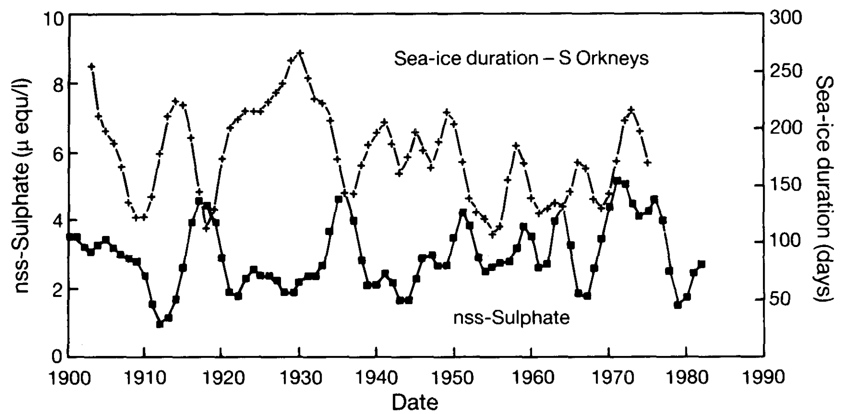

Fig. 4. nss-SO_4^{2-} at Dolleman Island generally shows a strong inverse relationship with the record of annual duration of sea ice from Orcadas, Laurie Island, South Orkneys (Mayes, 1981).

south-eastern Pacific Ocean towards the western side of the Peninsula. The Weddell Polynya was also an exceptional feature during this period (Carsey, 1980).

3.3. Link with atmospheric circulation since 1956

On the basis of arguments presented above, we have assumed a priori that high chloride levels in the Dolleman core are primarily associated with air masses that have tracked fairly directly towards the site from the open ocean, although the actual concentrations will be a function both of the wind speed (and hence sea-spray production) in the source areas, and the distance tracked over sea ice where, due to lack of breaking waves there will be no further opportunity to collect more sea salt aerosol. Low chloride levels would indicate that, on average, air masses have tracked for long distances over sea ice or over calm water where chloride has been depleted by precipitation and dry deposition. Periods characterized by high nss-SO_4^{2-}, normally associated with low Cl^-, should indicate that on the average, air masses have travelled extensively over a region of high marine biological activity, such as the marginal ice zone suggested above. If such behaviour is systematic then it should be possible to detect latitudinal shifts in the atmospheric circulation pattern from the differential behaviour of Cl^- and nss-SO_4^{2-}.

Fig. 5 makes a comparison between the ice core parameters and an index of the atmospheric circulation in the region of the marginal ice zone calculated from weather records available since 1956 (Jones and Limbert, 1987). The index is based on the sea level pressure difference between Orcadas and Halley (Fig. 1). This vector transects a major part of the seasonal sea ice zone in the area of interest and the pressure gradient reflects the atmospheric forcing on the pack ice. The pressure difference will respond to changes in both the depth and the latitudinal position of the circumpolar trough in the Weddell Sea region. High values for the index should generally correspond to periods of more southerly penetration of cyclonic systems, and displacement of the circumpolar trough deep within the marginal ice zone. Lower values for the index would correspond to periods where the circumpolar trough is shifted northwards, conditions under which cyclones will be able to track over open water for a higher proportion of the year. In Fig. 5, the index has been calculated across the winter half-year (May through October), which spans the period of most extensive ice cover, where any changes are likely to have a maximum impact on the chemistry of advecting air masses. The corresponding profile for the index based on the overall annual averages is similar, both in terms of interannual variations and the longer-term trends, but its correlation with the ice core parameters is somewhat weaker.

No firm dependence has been established between cyclone frequency and the strength of the zonal circulation or ice production/extent. However, extensive analysis of available pressure records in the Antarctic Peninsula region by Mayes (1981) indicates that periods such as the early 1960's with a more poleward trough position and a peak of cyclonic activity in the Weddell Sea correspond with a strengthening of the westerly circulation. At the same time, on a decadal time scale, during periods of strong westerlies (e.g., 1959–64) ice duration at Laurie Island fell significantly below average and conversely, the period with the longest annual duration of ice (1920–32) corresponded to a period of weaker westerlies. The winter advance of the ice front near Orcadas seems to be strongly influenced by the strength of the prevailing westerlies.

Against this background, it is possible to suggest factors that may have helped to shape the profiles of chloride, nss-SO_4^{2-} and d since 1956. In Fig. 5, the profiles of the ice core parameters have been lagged by 1–2 years in order to achieve the maximum correlation with the pressure index (the correlograms are inset). This time-lag may represent the period needed by the sea ice cover to adjust to a change in atmospheric pressure regime. nss-SO_4^{2-} shows some positive correlation with the pressure index; the concentration is highest when the circumpolar trough is shifted polewards. Such a relationship would be consistent with Gordon and Taylor (1975) who suggested that cyclonic activity over sea ice will tend to cause divergence of the ice due to Ekman-drift related transport, where the wind-driven layer tends to move to the left of the wind under the action of Coriolis forces. This process will encourage the formation of leads and polynya where phytoplankton growth, and hence biogenic sulphur emission could reach the level of the extremely productive ice-edge zone (Sakshaug and Skjoldal, 1989;

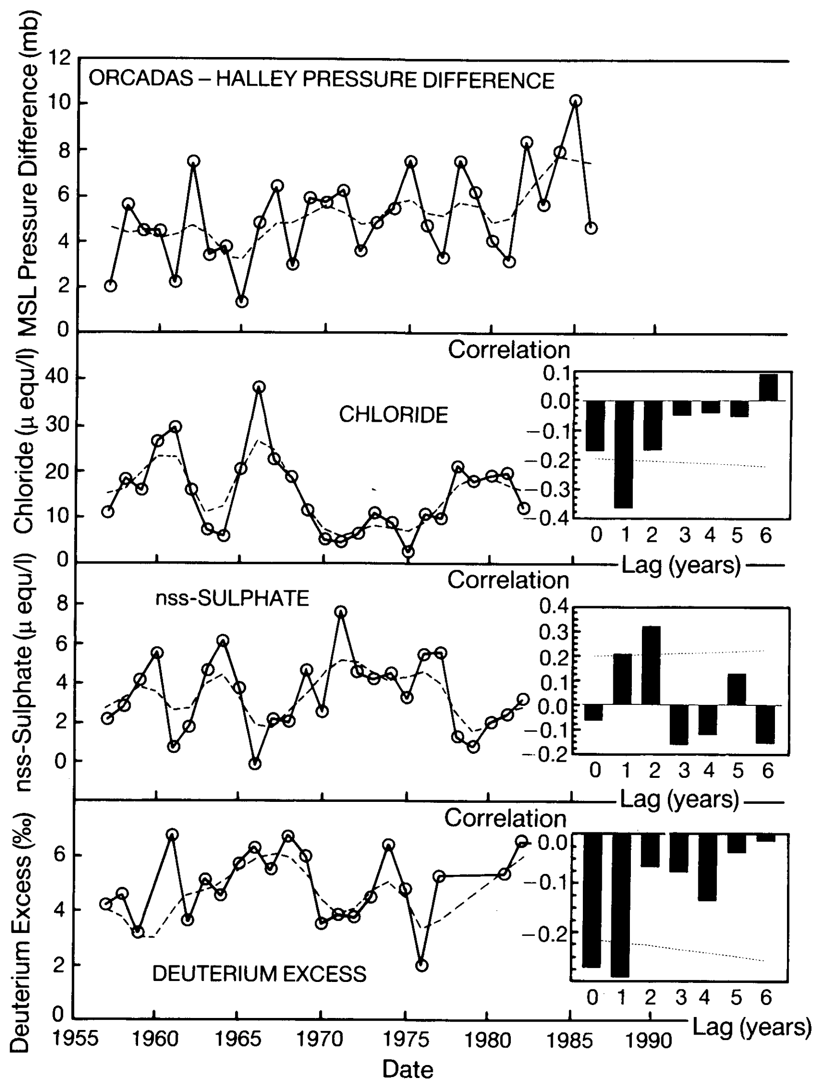

Fig. 5. Mean annual values of the MSL pressure difference between Orcadas and Halley (averaged over the winter 6-months, May–October) in comparison with constituents from the Dolleman core. The stippled curves are 5-year binomially weighted data. Correlograms relate to cross-correlation of the un-smoothed species and pressure gradient profiles. The species profiles have been displaced by 1–2 years to achieve the best match according to the correlograms.

Ackley et al., 1979). At the same time the presence of open water channels within the pack ice would allow uptake of water vapour from a cold source into an advecting air mass. This will lead to a reduction in the deuterium excess (d) in the water vapour and in precipitation derived from it. Modelling studies (Petit et al., 1991) show that the d value of the evaporating water is reduced by approximately 0.3 per mil per °C decrease in the sea surface temperature. Furthermore, riming was observed frequently whilst Dolleman Island was occupied, in association with ground-level stratus cloud. Low-level inversion conditions over the surrounding sea ice may be relatively common, particularly during the winter months, and indeed may be an important factor in establishing the lower temperature regime on the east coast of the Peninsula. Under these circumstances, evaporation from water bodies within the ice zone is likely to occur under conditions of high relative humidity (rh). This would lead to a further reduction in *d*. Petit et al. (1991) calculate a reduction of approximately 0.3 per mil per cent increase in rh for the evaporating vapour. A combination of these processes can explain why the strongest features of the profile of *d* tend to show a negative correlation both with nss-SO_4^{2-} and with the pressure index.

The major peaks in chloride tend to occur the pressure index is low, where the circumpolar trough is shifted northwards. Under these conditions, cyclones will track more frequently across open ocean areas to the north of the ice edge. At the same time, the cyclones may help to suppress sea ice extension both by wave action and by divergence in the surface water due to Ekman transport. These conditions will favour the pick-up of sea salt aerosol by air masses tracking into the Weddell Sea zone, and at the same time inhibit formation of open water bodies within the pack ice with its characteristic signature in nss-SO_4^{2-} and *d*.

4. Evidence for changes in ocean/atmosphere exchange since 1795 AD

Fig. 6 compares the profiles of the stable isotope constituents $\delta^{18}O$ and *d* against the trends in

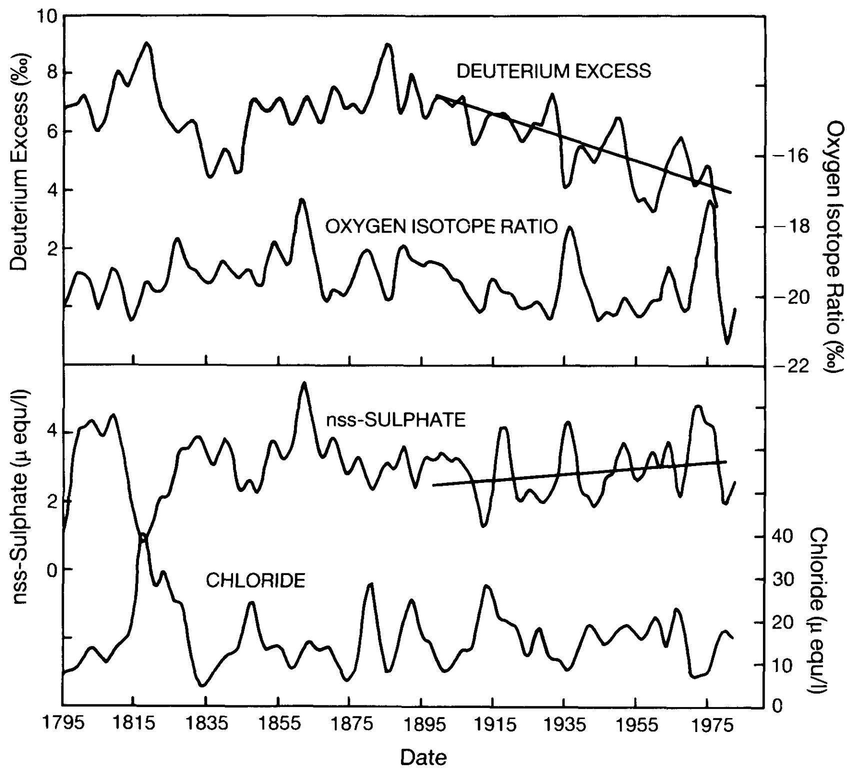

Fig. 6. 9-year binomially-weighted average concentrations of constituents in the Dolleman core. Trend lines during the past century suggest important decreases in deuterium excess which may reflect the development of weaknesses within the pack-ice zone and an increasing ocean/atmosphere exchange in this area. The increasing trend in nss-SO_4^{2-} may support this inference. Note the large fluctuations in deuterium excess, nss-SO_4^{2-}, and chloride during the period 1800–1850, in the final stages of the Little Ice Age, which most likely relate to major changes in the atmospheric circulation.

nss-SO_4^{2-} Cl^- since 1795. On the basis of the recent behaviour of the ice core parameters relative to the circulation index, we can hypothesize on the origin of some of the main features of the longer record.

4.1. Influence of local moisture sources on the stable isotope record

Fig. 6 shows a highly significant correlation between $\delta^{18}O$ and nss-SO_4^{2-} throughout the 200 year period over both short period events and longer trends ($r = 0.59$, sig $= < 0.1$ %). If nss-SO_4^{2-} is related to biological emissions from open water features within the body of the pack ice zone, then a parallel response in $\delta^{18}O$ might be expected if these water bodies also make a significant contribution to the water vapour from which the snowfall at Dolleman is derived. For a given air temperature at the deposition site, snowfall containing moisture from a colder source within the ice zone will tend to have a higher $\delta^{18}O$ value than normal owing to the reduced temperature gradient between the source and the deposition point. Isotopically "warm" features will then occur during periods where there is significant input of moisture from cold water sources. This mechanism would also explain why the isotopically "warm" anomalies generally match negative anomalies in deuterium excess, which also characterise low temperature sources. It seems that at this site the isotopic record is strongly influenced by changes in the contribution of moisture to precipitation from local moisture sources. The link between air temperature and isotope content may even be a secondary phenomenon, with the likelihood that there is a link between temperature along the east coast of the Peninsula and the occurrence of water within the pack ice zone.

The strong periodicity of these records is striking. The most recent "event", spanning the period 1974–76 coincides with the occurrence of the Weddell Polynya, when 300,000 km^2 of open water persisted throughout the winter months of 1974–76 (Carsey, 1980). Clearly, this feature was a major source of moisture for the Weddell Sea zone, with sea surface temperatures around 8°C colder than source areas north of the polar frontal zone; at the same time it was probably highly productive biologically. It is possible that this feature and similar features around 1935, 1885, 1860 and 1825 are associated with large polynya events.

The most striking feature in the isotopic records is the very marked decrease in deuterium excess during the past century, an overall reduction of around 4 ‰. The magnitude of the shift is comparable with the change reported by Dansgaard et al. (1989) in the Dye 3 core in South Greenland at the termination of the Younger Dryas. This latter shift has been linked to a dramatic retreat of the sea ice cover which exposed vast areas of relatively cold sea surface. Whilst it is possible that a change in the precipitation process (e.g., more frequent occurrence of riming/precipitation from low-level stratus) could have amplified the trend observed at Dolleman Is, the most probable explanation is that there has been a significant weakening of the pack ice cover of the Weddell Sea during the past century, with lines of weakness opening up within the sea ice zone allowing ocean/atmosphere exchange to occur. Since around 1965, there has been a marked increase in the pressure gradient across the Weddell Sea between Halley and Orcadas, which we interpret as indicating a poleward shift in the position of the circumpolar trough. Such a pressure distribution would encourage the opening of small leads and polynya within the sea ice cover. Hence we suggest that a change in atmospheric circulation may have been responsible for at least part of the decrease in *d*.

Whatever the reason, important changes in the concentration of sea ice within the pack ice zone are indicated. This suggestion contrasts with recent analyses of the trends in Antarctic sea ice extent (Jacka, 1990; Gloersen and Campbell, 1991) which show, at most, a very weak retreat in the ice margin since systematic mapping from satellite imagery started in 1973. Indeed the ice margin seems to be an insensitive indicator of climate change. Parkinson (1990) has failed to find any evidence of a significant change in ice extent during the LIA period from reported positions of the ice margin in the records of ship's voyages. Allison (1989) suggested that the position of the ice edge may be controlled primarily by ice drift; in the case of the Weddell Sea margin, the protrusion of the Antarctic Peninsula into the westerly circulation is likely to be the major contraint. In this case, the position of the ice front probably bears little relation to the thickness or concentration of ice inside the margin which is of greater significance for ocean/atmosphere exchange processes. The resolution of satellite imagery currently being used for studying the ice margin (ca. 30 km) is probably too coarse to detect a network of relatively fine leads and polynya which may be responsible for generating the chemical signals from the marginal ice zone that we are detecting in the Dolleman ice core.

4.2. The late Little Ice Age signal

The largest anomaly in the 200-year sequence occurs in the period 1810–1820 during the final stages of the Little Ice Age period (16th to mid-19th centuries as documented in many regions of the Northern Hemisphere). Exceptionally high concentrations of Cl^-, low concentrations of nss-SO_4^{2-} and very high values for deuterium excess indicate, by analogy with behaviour during the post-1956 period, that at this time there was a dense pack ice zone with a weak circumpolar trough displaced northwards of its average position, so that cyclone systems were tracking frequently along pathways in the open ocean zone to the north of the ice edge. Exceptionally high values for d at this time tend to support the idea that the effective source of the precipitation moisture was displaced well to the north of its long-term average position. A reversal to extremely low chloride concentrations, high nss-SO_4^{2-} and low d in the mid-1830's may have been linked to a major southward displacement of the circumpolar trough, possibly associated with a strengthening of the westerly circulation. Consequent divergence within the pack ice zone, with associated local moisture production may then have contributed to the generally high values of $\delta^{18}O$ observed during the mid-19th century period. The implication is that this isotopically "warm" period on the east coast of the Peninsula may not actually reflect true climatic warming. Further work is needed to determine whether records from higher altitude sites in the area influenced by weather systems tracking across the Weddell Sea are affected, such as that from James Ross Island (Aristarain et al., 1990).

5. Conclusions

Ice core data from low latitude sites such as Dolleman Island are sensitive to processes occurring within a range of tends to hundreds of kilometres, and at first sight may appear to provide a rather narrow depth of field with respect to the detection of large-scale changes in climate and environment. However, this limitation can be turned to advantage in terms of understanding specific processes, if by careful selection of site we can focus on critical parts of the sea-ice/ocean/atmosphere system. Dolleman Island is unusual in the sense that it predominantly samples air that has travelled for long distances over sea ice and at times may have spent up to several days in contact with the ice cover. Snowfall deposited on Dolleman Island therefore contains a very concentrated signal of chemical species involved in ocean/atmosphere exchange within the marginal ice zone. Comparison of the behaviour of nss-SO_4^{2-}, Cl^-, and d with an index of the pressure gradient across the marginal ice zone available since 1956 suggests that it is possible to detect shifts in the position of the circumpolar trough, which in turn influences lead and polynya production and hence water vapour release and marine algal production in the sea ice zone. A substantial decrease in deuterium excess during the past century may be associated with a progressive weakening of the ice cover in the Weddell Sea zone. How extensive this is, is still a matter for conjecture. That there is a contradiction with time tends observation of satellite images of the ice edge which show virtually no trend since 1973, may simply reflect the insensitivity of the ice edge to climate change. It may be possible to develop much more effective indices of sea ice concentration based on the chemistry of the atmosphere and of ice cores collected around the marginal ice zone, in order to achieve a more realistic impression of the interaction of the pack ice zone and climate.

6. Acknowledgements

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