Tellus (1993), 45B, 179–187
Printed in Belgium – all rights reserved

TELLUS
ISSN 0280–6509

The fractionation of sea salt and acids during transport across an Antarctic ice shelf

By ROBERT MULVANEY, GUY F. J. COULSON and HUGH F. J. CORR, *British Antarctic Survey, Natural Environment Research Council, Madingley Road, Cambridge, CB3 OET, UK*

(Manuscript received 18 September 1991; in final form 10 August 1992)

ABSTRACT

Analyses of Cl^-, NO_3^-, SO_4^{2-}, Na and Mg made on a series of surface snow samples, collected at 4 km intervals along a 116 km traverse of the Fimbul Ice Shelf in Dronning Maud Land, show that fractionation of some of the sea salt species has taken place. There is depletion of Mg compared to Na in the coastal part of the traverse, but the bulk sea water ratio is maintained further inland. Evidence for Cl^- fractionation is less clear, with a depletion in some sections and an enrichment in others compared to Na. Taken over the whole data-set of 120 samples, the bulk sea water ratio between the marine ions Na, Mg and Cl appears to be conservatively maintained. For all of the sea-salt components, the general trend in concentration was an increase from the ice shelf front to a maximum value approximately 45 km inland, before decreasing to a value of 10% of the maximum by the end of the traverse. Non sea-salt sulphate followed a similar trend to 45 km, but the subsequent decrease in concentration was less rapid, suggesting a greater residence time for sulphate derived from marine biogenic activity than for sea-salt aerosol. Relatively high concentrations of nitrate were found in all of the surface snow samples in comparison to samples taken from shallow pits at each end of the traverse. This may be an indication of a post depositional loss of nitrate from the snow surface.

1. Introduction

Analysis of ice cores often shows that the relative composition of ionic species of marine origin differs significantly from that found in bulk sea water. In a near coastal site, Aristarain et al. (1982) showed enrichments in potassium and calcium, and at the South Pole the ratio of sodium to chloride departs from that found in sea water, the dominant source of both species (Legrand and Delmas, 1984). Legrand and Delmas (1988) remarked that in central Antarctica, 50% of sea-salt may be fractionated. They report that the Cl/Na ratio may be greater than that found in bulk sea water and suggest that this could be due to the reaction of sodium chloride and sulphuric acid in the atmosphere producing gaseous HCl.

Non sea-salt sulphate (derived from the break-down of dimethyl sulphide of marine biogenic origin) is usually calculated by subtracting from the total sulphate the sulphate attributable directly to sea-salt using bulk sea water ratios. In some sections of high resolution ice cores (e.g., Mosley-Thompson et al., 1991) this may result in a negative value, indicating a deficit of sulphate. In near-coastal snow pits the shortfall in sulphate can be substantial; Gjessing (1989) measured a deficit of 29 $\mu eq\, l^{-1}$ compared to sea water sodium. Measurements of sea-salt and sulphate in coastal aerosols also demonstrate periods where a deficit of sulphate occurs (Wagenbach et al., 1988). Since it is common when reporting ice core analyses to calculate non sea-salt sulphate with respect to sodium, it is clearly of importance to be aware of the extent that fractionation of the sea-salt component could affect the sea-salt sulphate to sodium ratio.

Here, we examine whether these observations can be explained by fractionation during transport from open water to the deposition site. Previous studies (e.g., Delmas and Boutron, 1978; Legrand and Delmas, 1985) of the variation of sea water components along a series of close spaced sites from the coast to a point well inland have

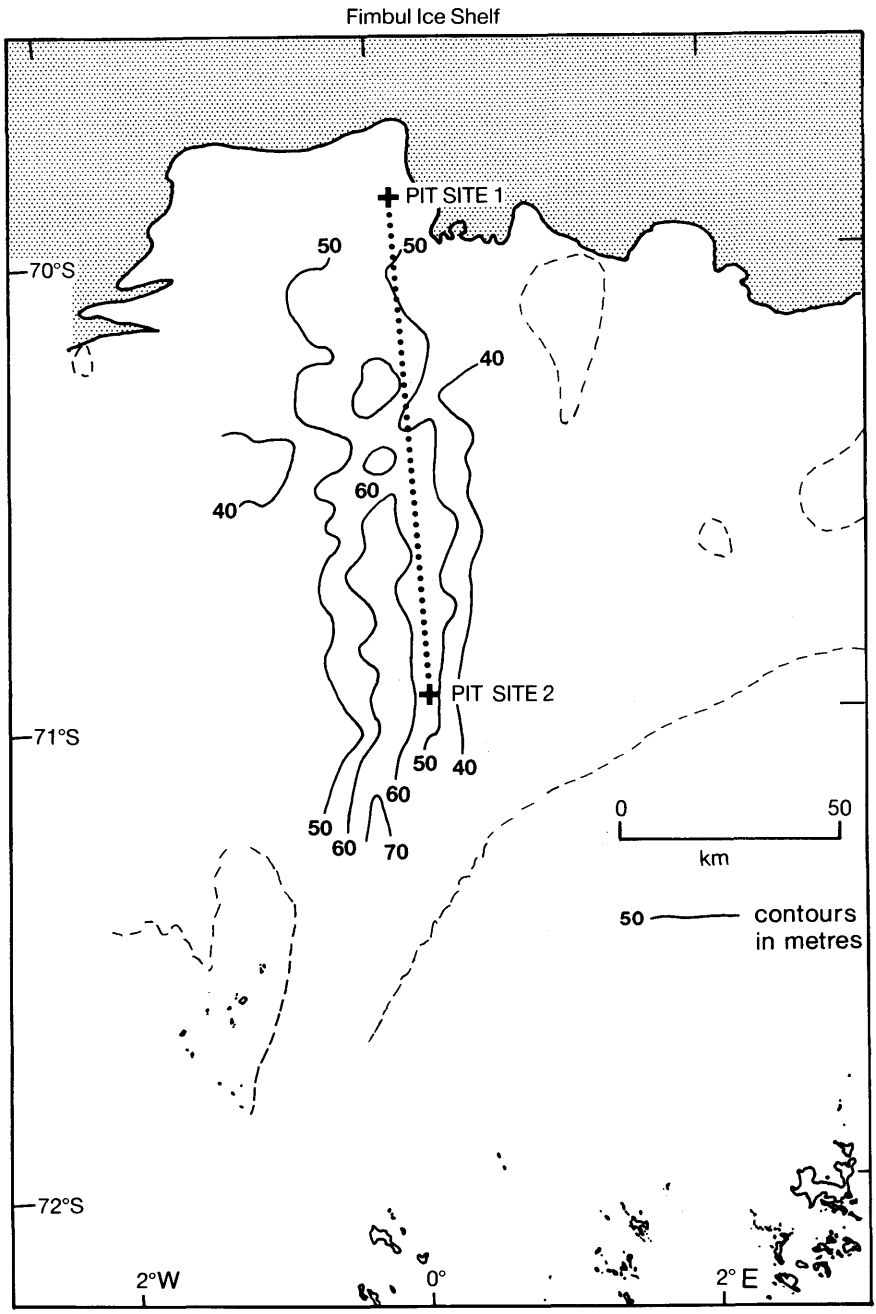

Fig. 1. Map of the Fibulisen showing the route taken by the 116 km surface snow sampling traverse approximately along the 50 m contour, and the location of the two shallow snow pits. Elevations in metres are from Seasat altimetry (Zwally et al., 1987).

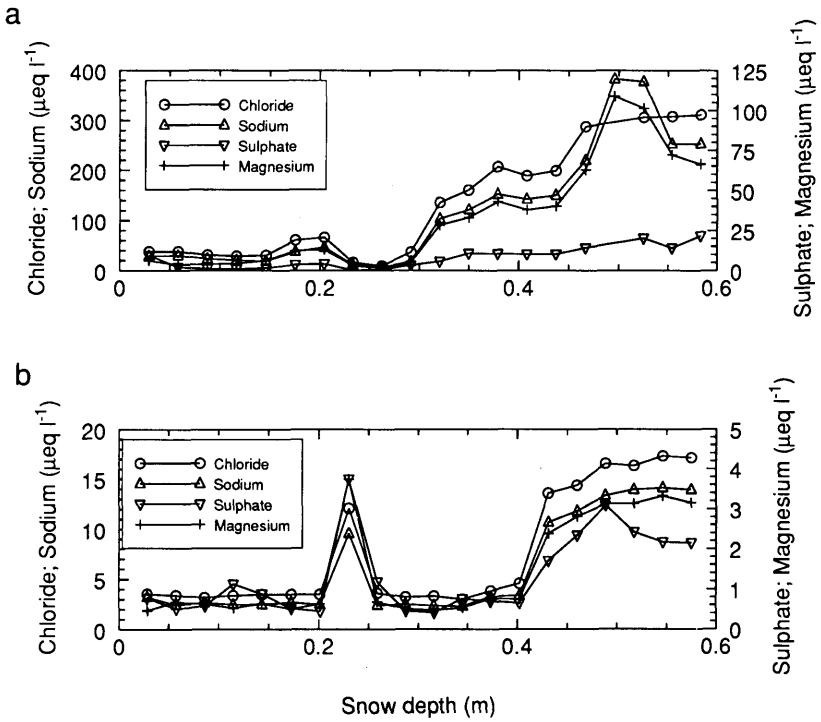

Fig. 2. The major anions and cations in the two snow pit profiles: (a) pit 1, 7 km from the coast; (b) pit 2, the inland end of the traverse.

measured samples that have integrated between 1 and 4 years of snowfall. In this study, by collecting only the surface layer of snow during a 20-hour traverse across an ice shelf with little change in altitude, we are able to examine the influence of distance from the coast on the composition of recent snowfall.

2. Sample collection and analysis

In January 1990, a series of surface snow samples was collected along a traverse of the Fimbul Ice Shelf in Dronning Maud Land during the 1989/90 Norwegian Antarctic Research Expedition (Fig. 1 shows the traverse route). The accumulation in the previous year was estimated by visual pit stratigraphy to be 0.6 m water (J.-G. Winther, personal communication). At the first site (69°55.6′S, 0°06.8′W), 7 km from the ice shelf front, and at the last site (70°58.7′S, 0°12.1′E) approximately 123 km inland, shallow pits were dug to allow sampling through about 0.6 m of snowfall at a resolution of about 30 mm. Between these sites, four separate samples of the surface layer (to a depth of about 10–15 mm) were collected at sites every 4 km, along a direct line that approximately follows a 50 m contour. The time taken to complete the whole traverse and collect all surface samples was 20 h. The weather for the period of 7 days preceding the traverse had been light variable winds, with persistent warm and foggy conditions and light snowfall. During the sampling period, the wind was about 0–3 knots from the west, the sky was largely cloudless, there was no snowfall and no drifting was observed. The surface layer over the whole of the traverse route was of unconsolidated snow over a slightly firmer base at about 20–50 mm depth. The data from the pit profiles (Fig. 2) show that the upper 100 mm of the snow pack had consistent chemistry. We consider therefore that the surface samples collected are of recent snowfall.

At surface sites, and at both pits, samples were

scraped directly into hard polystyrene ("Coulter" type) accuvettes which had been scrupulously pre-cleaned in the laboratory by repeated 24-hour soaks in 18 Mohm ultra-pure water. Once collected, the accuvettes were double-bagged and shipped in cold storage back to the UK for analysis. Precautions were taken to avoid contaminating the samples in the field, including wearing disposable polyethylene gloves and ensuring that the sample area was at least 100 m upwind of the travel party. Once returned to the laboratory, the samples were melted, transferred to pre-cleaned polyethylene vials and stored frozen until analysis. Handling of the samples in the laboratory was carried out in a laminar flow cabinet wearing a clean room coat and disposable polyethylene gloves. Cl^-, NO_3^- and SO_4^{2-} were measured using a Dionex 2010 ion chromatograph with an AS4A column and standard eluent conditions. Na and Mg were measured by flameless atomic absorption spectrometry, using a Pye SP9 spectrophotometer with a pyrolytically coated graphite furnace. Since the sampling procedure generated only about 4 ml of liquid, aliquots of the samples were diluted 4-fold for the chromatography and 20-fold for the AAS using 18 Mohm ultra-pure water. Results presented here have been corrected for dilution. Blank levels for all species measured were of the order of $<5\ \mu g\ kg^{-1}$ after correcting for dilution. Analytical precision was of the order of ± 5–10% for the anions and Mg and better than ± 5% for Na.

3. Post depositional loss of nitrate

The mean nitrate concentration for the traverse is $3.5\ \mu eq\ l^{-1}$, which is considerably higher than is common in ice cores where concentrations of between 0.2 to $2\ \mu eq\ l^{-1}$ are normal (e.g., Legrand and Delmas, 1984; Mulvaney and Peel, 1988; Mosley-Thompson et al., 1991). The high nitrate in the surface layer could be a consequence of the co-condensation of nitric acid with surface hoar in the foggy conditions prior to sampling. The mean nitrate concentration from the two snow pits (ignoring the surface value in each case) is $0.17\ \mu eq\ l^{-1}$ for pit 1 and $0.58\ \mu eq\ l^{-1}$ for pit 2, similar to typical values reported for ice cores and substantially lower than any of the 120 surface samples collected (Fig. 3a). In both pits (Fig. 3b and 3c), the nitrate concentration falls rapidly from high values in the surface layer to a lower and consistent value below 0.05 m. These observations suggest that the surface nitrate concentration may not be representative of the concentration that will ultimately be incorporated into the snow-pack. Neubauer and Heumann (1988a, b) report that freshly fallen snow has a nitrate concentration well above that found both in old snow surfaces, and at depth in ice pits. They conclude that there must be a re-emission of nitrate from surface snow during aging and the early stages of burial, but were unable to determine whether this was due to re-evaporation of HNO_3 or to a photochemical decomposition. Our finding here of the persistently high values measured at the surface compared with the snow pits certainly supports their findings, but cannot confirm the mechanism. More work is needed to deduce the mechanism of post depositional loss of nitrate and to determine why clear annual cycles in nitrate can still be seen in ice core profiles.

4. Trends along the traverse

Analyses for chloride, nitrate, sulphate, sodium and magnesium were made on each of the four separate surface samples taken at each traverse site. The results of the replicate samples were remarkably consistent, with typical relative standard deviations in the range 3 to 15% for all species. At the sites 31 and 35 km from the ice shelf front, two samples were taken from the peak and two from the trough of 0.1 m sastrugi; analysis showed no significant bias in the concentration of any of the species measured, as is evident from the error bars shown in Fig. 4 for these two sites. This is good evidence of the lack of drifting in the period immediately before and during sampling.

The general trend shown in Figs. 4 and 5 for the components of sea-salt origin is an increase in concentration from the coast inland, reaching a maximum at about 43 km from the ice shelf front, before falling at a somewhat slower rate to approximately 10% of the maximum value by 123 km. We are not able to say conclusively that the snowfall originated from a single air-mass moving inland from the coast.

We have chosen to calculate the expected values of chloride, magnesium and sulphate based on

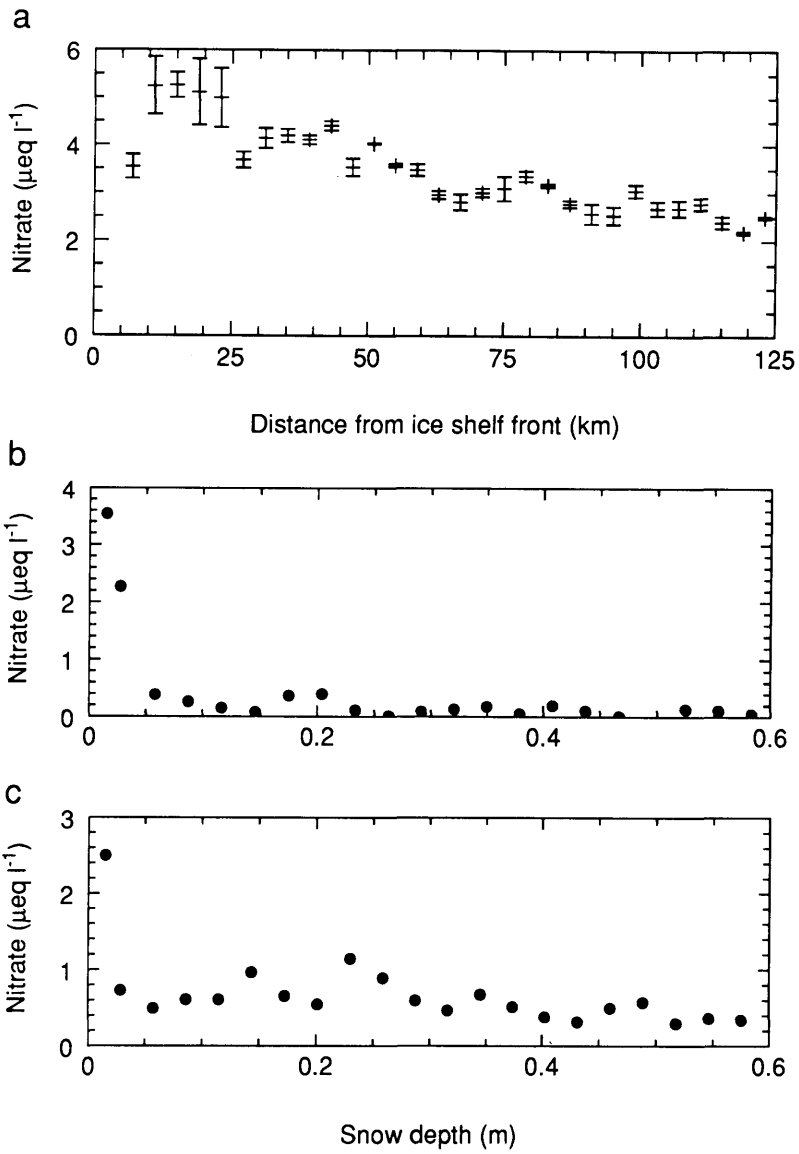

Fig. 3. Nitrate in surface snow samples collected at 4 km intervals along the 116 km traverse, and taken from shallow pits dug at each end: (a) the mean of 4 samples collected at each site, error bars show the standard error of the mean; (b) pit 1, 7 km from the coast; (c) pit 2, the inland end of the traverse.

measured sodium values in order to calculate the relative enrichment or depletion of these species. We do not imply that the sodium is the conservative reference specie but are following the convention in ice core chemistry of using it as the marine reference.

4.1. Chloride

Clegg and Brimblecombe (1985) modelled the behaviour of the H_2SO_4/NaCl system at 25°C and concluded that most of the hydrogen ions in acidic sodium chloride aerosol would be lost as HCl.

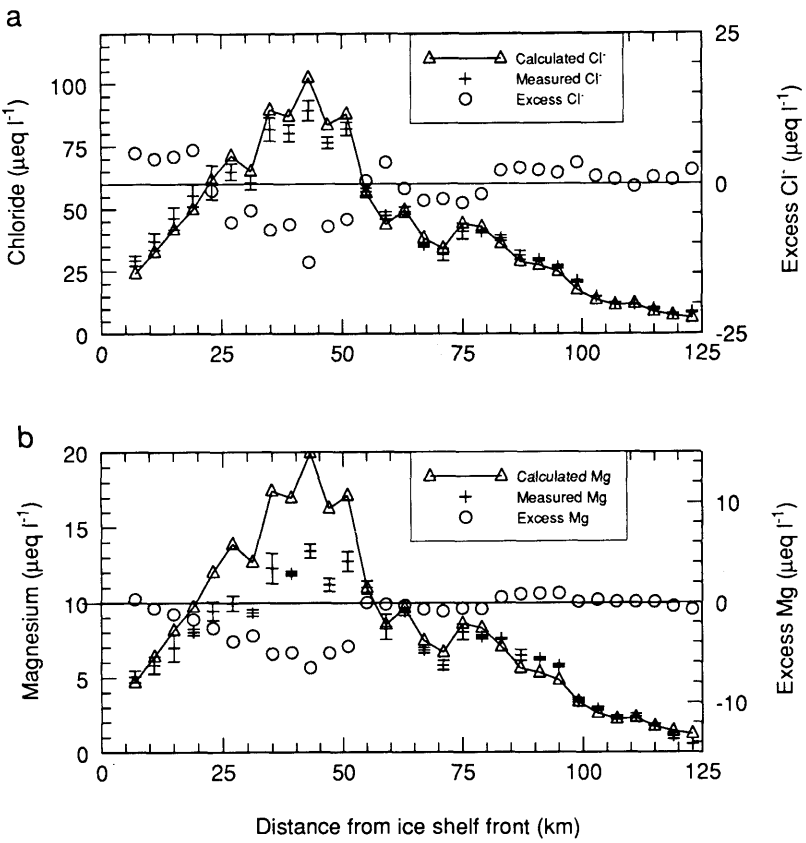

Fig. 4. Comparison of the measured values for the major marine ions with the calculated value based on their bulk sea water ratios with sodium: (a) chloride; (b) magnesium. Error bars show the standard error of the mean of 4 samples taken at each site, and for Cl^- and Mg the residual or "excess" over the sea water composition in shown (right-hand scale).

While it is not clear to what extent this mechanism is relevant at Antarctic temperatures, the result suggests that in the case of near coastal snowfall in the Antarctic, with its abundance of both Cl^- from sea water and H_2SO_4 from the oxidation of biogenic sulphurous gases, the fractionation of the sea-salt ions by loss of HCl is possible. However, the results from our traverse do not show a significant overall depletion of Cl^-. In Fig. 4a, the data for Cl^- are compared to the values calculated from the bulk sea-water Na/Cl ratio using

$$[Cl^-]_{calc} = 1.165[Na]_{meas} \text{ (in } \mu eq\ l^{-1}).$$

Over the whole data-set of 120 samples, the mean Na and Cl^- concentrations were 37.2 and 42.5 μeq l^{-1}. The slight average deficit of 0.8 μeq l^{-1} Cl^- is less than 2% of the total Cl^- and this is indistinguishable from experimental error.

The generally low degree of fractionation in this near coastal area is consistent with results reported by Legrand and Delmas (1988) who found a near sea water Cl/Na ratio in samples taken within 200 km of the coast. However, further inland, and particularly at higher altitudes (above 2000 m), they found significant fractionation, with Cl/Na ratios of about 2.0 (compared to 1.165 in sea water) at South Pole and Dome C. Martens et al. (1973) measured the Na/Cl ratio in captured marine aerosol particles, and found a very marked variation in the Cl/Na ratio with particle size, with increased depletion of Cl at smaller particle size.

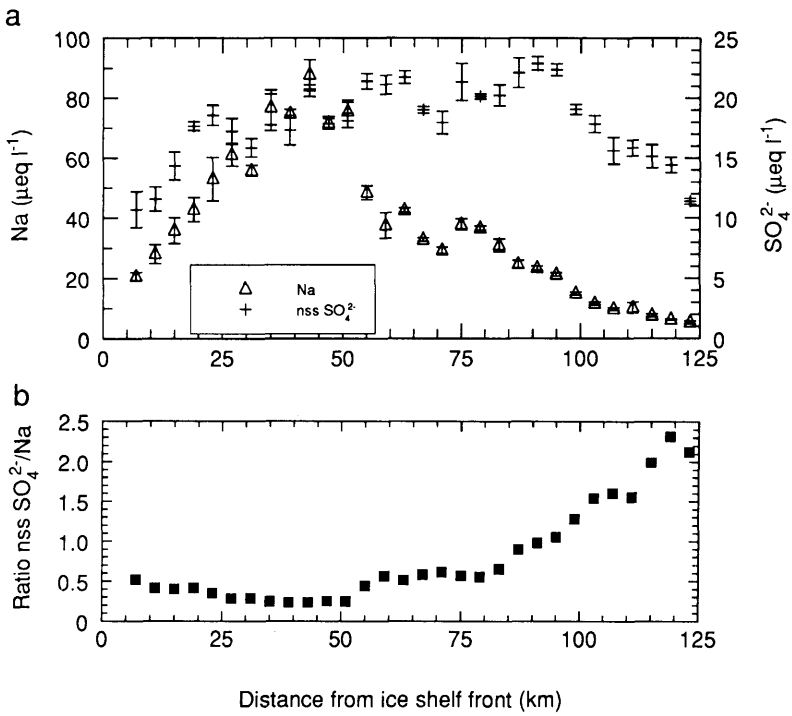

Fig. 5. (a) Non sea-salt sulphate and sodium in the surface snow samples, with error bars for the standard error of the mean; (b) ratio of non sea-salt sulphate to sodium.

This supports the observation of increasing NaCl fractionation with distance from the coast and altitude as the larger particles are progressively removed from the aerosol, leaving smaller particles more prone to fractionation by the HCl loss mechanism. Further, data from the thermodynamic model of Clegg and Brimblecombe (1985) show a very marked reduction in the loss of HCl from the H_2SO_4/NaCl system for larger particles at 25°C and ~100% relative humidity. The warm, foggy conditions during the period prior to our sampling would appear from this result to indicate a low loss of HCl. We can also note from the results for the acidic non sea-salt sulphate (Fig. 5) that the reaction of NaCl with H_2SO_4 will be more effective further inland as the ratio of H_2SO_4/NaCl rises due to the more rapid deposition of sea-salt particles. Finally, the observation of excess Cl^- in central Antarctic sites (Legrand and Delmas, 1988) may imply that the residence time of HCl is greater than Na_2SO_4.

From these observations, we can suggest the following scenario for the fractionation of NaCl by reaction with H_2SO_4. Close to the coast, particularly in relatively warm, humid conditions, little fractionation of NaCl takes place, but the larger sea-salt particles are lost from the aerosol by wet or dry deposition. As the aerosol mass moves inland, the progressively smaller sea-salt particles lose HCl by reaction with H_2SO_4, with the resulting Na_2SO_4 precipitated from the aerosol. HCl remains in the air mass and is transported further inland before deposition.

4.2. Magnesium

The comparison (Fig. 4b) of measured Mg with calculated Mg (from $[Mg]_{calc} = 0.227[Na]_{meas}$) shows a significant departure from sea water composition in the early part of the traverse. Weisel et al. (1984) found no fractionation of Mg relative to Na at the sea/air interface, so the result here suggests fractionation during transport. The overall mean deficit in the early part of the magnesium profile (7 to 51 km from the ice shelf front) is 3.3 μeq l^{-1} (mean Na 57.0, mean Mg 9.7 μeq l^{-1}, Mg/Na 0.170) whereas from 55 to 123 km the Na

Tellus B/45/2-7

and Mg are in sea water ratio (mean Na 23.9, mean Mg 5.4 μeq l^{-1}, Mg/Na 0.226).

Although the overall Cl/Na ratio reported above is close to that found in sea water, the section in the coastal part of the traverse shows a departure from the sea water ratio. We note that the general shape of the deficit in Mg with respect to Na is similar to that of Cl^-. This is due in part to the calculation of both against Na, but it suggests that the two species are related in the aerosol, presumably as $MgCl_2$ (excess Mg and excess Cl^- are well correlated, with a correlation coefficient of 0.962, significant at the 0.001 level, for the section 7 to 51 km). The mean deficit of Cl^- from 7 to 51 km is 2.7 μeq l^{-1}, compared to 3.3 μeq l^{-1} for Mg, apparently in broad agreement, though the section 7 to 19 km does not follow the trend. There is also likely to be a contribution to the fractionation of Mg in the form of $MgSO_4$ due to the conditions of excess SO_4^{2-} prevailing in the aerosol, but this is difficult to quantify from this data set.

Reactions taking place involving sea-salt particles are inter-related and will not necessarily reach equilibrium in the dynamic atmospheric conditions. However, if any specie is lost from the system completely (for example the loss of HCl gas), this will clearly affect the progress of the related reactions. Over the whole of the data set, the balance of the marine ions Cl^-, Mg and Na is close to the bulk sea water composition. We conclude that, despite the local fluctuations in the ratios of these species, the system appears to have remained conservative in this near coastal region.

4.3. *Sulphate*

The mean sulphate concentration for the whole traverse is 22.5 μeq l^{-1}, compared to the mean sodium of 37.2 μeq l^{-1}. Assuming all the sodium present in the snowfall directly originated from sea water, the sea-salt sulphate component would have a mean value of 4.5 μeq l^{-1}. Thus the excess, or non sea-salt sulphate ($nssSO_4^{2-}$), calculated as $[SO_4^{2-}]_{nss} = [SO_4^{2-}]_{total} - 0.12[Na]$, has a mean value of 18.0 μeq l^{-1} or 80% of the total sulphate deposited. Fig. 5 demonstrates that the $nssSO_4^{2-}$ concentration increases at a similar rate to the Na in the initial part of the profile, before flattening out at about 55 to 95 km. Further inland, the concentration falls more slowly than Na.

The difference in the pattern of deposition of the $nssSO_4^{2-}$ compared to the sea-salt components is to an extent governed by the differing source regions involved. Sea-salt is produced by wind action over the open ocean surface, while $nssSO_4^{2-}$ is derived from biological activity and is thus a part of the background aerosol, though the marginal sea-ice zone is a particularly productive source (during the sampling period, the marginal sea-ice zone extended approximately 10–20 km from the coast). We can suggest an explanation for our $nssSO_4^{2-}$ results. The $nssSO_4^{2-}$ in this near coastal area is mainly derived from the partial oxidation to H_2SO_4 of dimethyl sulphide (DMS), excreted by marine phytoplankton during respiration. The initial slow rise in the $nssSO_4^{2-}$ could be due to its relatively slow production by the reaction of DMS with the hydroxyl radical, reported to take at least 14 hours (Hewitt and Davison, 1988). We propose that the oxidation of DMS was incomplete close to the coast but that the reaction moved towards completion as the air mass moved inland, with, perhaps, production matching deposition over the 55 to 95 km section. Further inland, $nssSO_4^{2-}$ concentrations fall more slowly than sea-salt indicating the shorter residence time of the sea-salt particles, and the possible contribution to $nssSO_4^{2-}$ from longer range sources.

4.4. *Nitrate*

Nitrate (in Fig. 3a) shows a general decrease in concentration with distance from the coast. Little can be inferred about the scavenging of NO_3^- from these data since the trend observed may reflect progressive aging of the freshly fallen snow since deposition, owing to a post depositional loss mechanism as discussed previously. It is perhaps worth noting that Chan and Chung (1986) found that NO_3^- and HNO_3 are slightly more effectively scavenged by snowfall than SO_4^{2-}, yet between about 95 to 123 km the concentration of SO_4^{2-} falls by half while NO_3^- remains almost constant, suggesting that the aerosol is depleted more readily in SO_4^{2-} than NO_3^-.

5. Summary

The concentration of sea salts in individual snowfalls is not simply an inverse function of the distance from the coast, particularly in near coastal regions.

Fractionation of sea-salt ions apparently takes place during transport, with evidence of a deficit in both Cl^- and Mg over short sections of our data. However, taken over the whole data-set, the bulk sea water composition for Na, Mg and Cl^- appears to be maintained.

The profile of non sea-salt sulphate concentration in snowfall differs in character to that of the sea-salt derived species reflecting the different source distribution. It does not decrease as rapidly with distance from the open ocean as do the sea-salt ions, and this may be governed by the rate of oxidation of the gaseous sulphur precursors to sulphuric acid.

There is evidence that the fresh surface concentration of nitrate is considerably higher than seen in ice cores and in aged firn. This indicates that a post depositional re-emission process removes nitrate from the snow.

6. Acknowledgements

We would like to thank the Norwegian Antarctic Research Expedition 1989/90 for inviting Hugh Corr to participate, and Jan-Gunnar Winther of the Norsk Polarinstitutt for his assistance in the field.

REFERENCES

Aristarain, A. J., Delmas, R. J. and Briat, M. 1982. Snow chemistry on James Ross Island (Antarctic Peninsula). *J. Geophys. Res. 87*, 11004–11012.

Chan, W. H. and Chung, D. H. S. 1986. Regional-scale precipitation scavenging of SO_2, SO_4, NO_3 and HNO_3. *Atmos. Environ. 20*, 1397–1402.

Clegg, S. L. and Brimblecombe, P. 1985. Potential degassing of hydrogen chloride from acidified sodium chloride droplets. *Atmos. Environ. 19*, 465–470.

Delmas, R. and Boutron, C. 1978. Sulfate in antarctic snow: spatio-temporal distribution. *Atmos. Environ. 12*, 723–728.

Gjessing, Y. 1989. Excess and deficit of sulfate in polar snow. *Atmos. Environ. 23*, 155–160.

Hewitt, C. N. and Davison, B. M. 1988. The lifetimes of organosulphur compounds in the troposphere. *Applied Organometallic Chemistry 2*, 407–415.

Legrand, M. R. and Delmas, R. J. 1984. The ionic balance of Antarctic snow: a 10-year detailed record. *Atmos. Environ. 18*, 1867–1874.

Legrand, M. and Delmas, R. J. 1985. Spatial and temporal variations of snow chemistry in Terre Adelie (East Antarctica). *Ann. Glaciol. 7*, 20–25.

Legrand, M. R. and Delmas, R. J. 1988. Formation of HCl in the Antarctic atmosphere. *J. Geophys. Res. 93*, 7153–7168.

Martens, C. S., Wesolowski, J. J., Harriss, R. C. and Kaifer, R. 1973. Chlorine loss from Puerto Rican and San Francisco Bay area marine aerosols. *J. Geophys. Res. 78*, 8778–8791.

Mosley-Thompson, E., Dai, J., Thompson, L. G., Grootes, P. M., Arbogast, J. K. and Paskievitch, J. F. 1991. Glaciological studies at Siple Station (Antarctica): potential ice-core paleoclimatic record. *J. Glaciol. 37*, 11–22.

Mulvaney, R. and Peel, D. A. 1988. Anions and cations in ice cores from Dolleman Island and the Palmer Land plateau, Antarctic Peninsula. *Ann. Glaciol. 10*, 121–125.

Neubauer, J. and Heumann, K. G. 1988a. Determination of nitrate at the ng/g level in Antarctic snow samples with ion chromatography and isotope dilution mass spectrometry. *Fres. Z. Anal. Chem. 331*, 170–173.

Neubauer, J. and Heumann, K. G. 1988b. Nitrate trace determinations in snow and firn core samples of ice shelves at the Weddell Sea, Antarctica. *Atmos. Environ. 22*, 537–545.

Wagenbach, D., Görlach, U., Moser, K. and Münnich, K. O. 1988. Coastal Antarctic aerosol: the seasonal pattern of its chemical composition and radionuclide content. *Tellus 40B*, 426–436.

Weisel, C. P., Duce, R. A., Fasching, J. L. and Heaton, R. W. 1984. Estimates of the transport of trace metals from the ocean to the atmosphere. *J. Geophys. Res. 89*, 11607–11618.

Zwally, H. J., Stephenson, S. N., Bindschadler, R. A. and Thomas, R. H. 1987. Antarctic ice-shelf boundaries and elevations from satellite radar altimetry. *Ann. Glaciol. 9*, 229–235.