

ATMOSPHERIC PROCESSES AND THE CHEMISTRY OF SNOW ON THE ROSS ICE SHELF, ANTARCTICA

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ABSTRACT. Correlations between chemical profiles (Na, K and Mg) in three 2 m deep pits, separated by hundreds of kilometers on the Ross Ice Shelf, suggest that the passage of major storm systems is often recorded as peaks in cationic concentration in the snow-pack on the Ice Shelf. The magnitude of the peaks appears to be a function of both storm intensity and the extent of sea ice adjoining the Ross Ice Shelf. Samples were collected from a network of 21 shallow pits on the Ice Shelf. Although concentration of impurities in the snow varies as a function of distance from the sea on northern portions of the Ross Ice Shelf, a more complex relationship exists in the interior of the Shelf. A distinct chemical zone south of Roosevelt Island may reflect the presence of a "cyclone graveyard". Non-marine cationic ratios in the southern portion of the Ice Shelf suggest the significant influence of a fractionated marine aerosol and the presence of a second, continental aerosol source. Ionic ratios in rime deposited on the Ross Ice Shelf during periods of fog are interpreted as reflecting the production of fog droplets from the chemically-enriched surface microlayer of the ocean. Diffusionally grown snow crystals also have non-marine ratios. In contrast, snowfall associated with peaks in chemical concentration in particular, and the snow-pack on northern portions of the Ross Ice Shelf in general, yield near-marine ionic ratios. This indicates that the chemistry of snow which is near the coast and snow from major storms is dominated by large droplet riming and the associated presence of a high proportion of sea-salt particles.

RÉSUMÉ. *Processus atmosphérique et chimie de la neige dans le Ross Ice Shelf, Antarctique.* Les corrélations entre les profils chimiques (Na, K et Mg) trouvés dans trois forages de 2 m de profondeur, séparés par des centaines de kilomètres sur le Ross Ice Shelf, font présumer que les passages des principaux systèmes de perturbations sont souvent enregistrés comme des pointes dans la concentration en cations dans les manteaux neigeux sur le Shelf. L'importance de ces pointes semble être une fonction à la fois de l'intensité de la perturbation et de l'importance de la glace de mer attenante au Ross Ice Shelf. Les échantillons étaient rassemblés dans les forages peu profonds dans une grille des 21 points à travers le Shelf. Bien que la concentration en impuretés dans la neige varie comme une fonction de la distance à la mer dans les parties nord du Ross Ice Shelf, une relation plus complexe s'établit à l'intérieur de la banquise. Une zone chimique distincte au sud de Roosevelt Island peut refléter la présence d'un "cimetière de cyclones". Des teneurs en cations "non marins" dans le sud du Ice Shelf révèlent l'influence significative d'une dispersion de l'aérosol marin et de la présence d'une source secondaire d'aérosol continental. Les rapports ioniques dans le givre déposé sur le Ross Ice Shelf au cours de périodes de brouillard sont interprétés comme le résultat de la production de gouttelettes de brouillard à partir de la microcouche superficielle, chimiquement riche, de l'Océan. Les cristaux de neige crus par diffusion ont nettement des concentrations non marines. Bien que les chutes de neige associées à des maximum de concentration chimique, en particulier et que les manteaux neigeux des régions Nord de l'Ice Shelf, en général, donnent des concentrations ioniques de type marines. Ceci indique que la chimie des neiges subcôtières et celle des neiges des grands épisodes perturbés sont dominées par un fort givrage des gouttelettes et, corrélativement, par la présence d'un forte proportion de particules de sel marin.

ZUSAMMENFASSUNG. *Atmosphärische Vorgänge und der Chemismus des Schnees auf dem Ross Ice Shelf, Antarktika.* Zusammenhänge zwischen chemischen Profilen (Na, K, und Mg) in drei 2 m tiefen Schächten, die hunderte von Kilometern auf dem Ross Ice Shelf auseinander liegen, lassen darauf schliessen, dass der Durchzug grösserer Zykklonen sich oft durch Maxima der Kationen-Konzentration in der Schneedecke des Schelfeises äussert. Die Grösse der Maxima scheint eine Funktion sowohl der Sturmstärke als auch de angrenzende Meeris Ross Ice Shelf der Ausdehnung des an das zu sein. Die Proben wurden einen Netzwerk von 21 flachen Schächten auf dem Schelfeis entommen. Zwar ändert sich die Konzentration an Verunreinigungen im Schnee in Funktion des Meeresabstandes in den nördlichen Teilen des Ross-Schelfeises, doch herrscht eine kompliziertere Beziehung im Innern des Schelfeises. Eine bestimmte chemische Zone südlich des Roosevelt Island mag das Vorhandensein eines "Zyklonen-Friedhofs" andeuten. Nicht-marine Kationen-verhältnisse im Südtel des Schelfeises deuten auf den wesentlichen Einfluss eines fraktionierten marinen Aerosols und das Vorhandensein einer zweiten, kontinentalen Aerosolquelle hin. Aus Ionenverhältnissen im Reif, auf dem Ross Ice Shelf abgelagert während Nebelperioden, lässt sich die Produktion von Nebeltröpfchen aus dem chemisch angereicherten Oberflächenfilm des Ozeans annehmen. Schneekristalle, die durch Diffusion gewachsen sind, haben ebenfalls ausgeprägt nicht-marine Verhältnisse. Im Gegensatz dazu ergeben Schneefälle, verbunden mit Maxima der chemischen Konzentration, im besonderen und die Schneedecke auf den nördlichen Teilen des Schelfeises im allgemeinen fast-marine Ionenverhältnisse. Dies deutet darauf hin, dass der Chemismus küstennahen Schnees und der des Schnees aus grösseren Stürmen durch Reifbildung aus grossen Tropfen und — damit verbunden — durch das Vorhandensein eines hohen Anteils an Meeressalzpartikeln bestimmt wird.

INTRODUCTION

Snow and ice in glaciers contain particles which have been carried to the surface by falling snow. Additional impurities are added by sedimentation processes. In the high-polar regions, where there is an almost complete absence of melting, the ice sheets contain a long-term record of such depositions and chemical analysis of the snow and ice will reveal the nature of the particles. If the atmospheric processes which control the concentration and composition of these impurities are understood, then it may be possible to use the chemical record to discover certain aspects of the climatic history of the region.

Since the pioneering work of Junge (1960) at Site 2, Greenland, there have been several studies into the chemistry of impurities contained in polar snow and ice. In Antarctica, geographic variations of major and trace elements have been revealed through investigations of samples collected on traverses (e.g. Boutron and others, 1972; Briat and others, 1974). Temporal variations in the chemical content have been studied using ice cores (Langway, 1967; Linkletter, 1970, 1973; Ragone and Finelli, 1972; Langway and others, 1974, 1975). Although there is evidence of anthropogenic components to the chemistry, it has been clearly demonstrated that the marine aerosol is the dominant source of impurities in Antarctic snow and ice (Murozumi and others, 1969; Boutron and others, 1972).

So far, little attention has been given to the roles of the fundamental precipitation processes and their influence on the observed chemical variations (except for general considerations of the seasonal distribution of cyclonic storms and their large-scale movement).

During the southern summer of 1971–72, Warburton observed that the relative proportions of accretional and diffusional growth found in ice crystals and snowflakes falling to the surface in Antarctica varied with location. At stations near the coast there was a significantly high proportion of crystals grown by accretion; however, at the South Pole growth was almost entirely by diffusion. These two dominant mechanisms involve different physical processes and operate at very different rates, and so Warburton suggested that their temporal and spatial variations might influence the amounts and composition of impurities incorporated into the polar ice sheets.

The Ross Ice Shelf was chosen as a region devoid of large orographic features where an investigation of the relationships between the chemical composition of the snow and the precipitation forms could be made. This paper presents some results from the first year of this program.

SAMPLING AND LABORATORY PROCEDURES

Sheets of nylon net were used to collect samples of falling snow during storms, and rime and hoar during periods of supercooled fog at C7 and the Ross Ice Shelf Project (RISP) Base Camp (Fig. 1). The nylon nets on which the precipitation was collected, and all the other equipment with which the samples came into contact, were cleaned by a series of leachings in extremely pure solutions of nitric acid. This treatment was followed by several rinses and leachings in doubly-distilled, de-ionized water. All the equipment was then sealed in polyethylene bags for transport to the Antarctic. Samples were taken from the nets with a scoop once a sufficient quantity had accumulated, they were then stored in tightly-sealed polyethylene bags and kept frozen until analysis.

The snow-pack was intensively sampled in pits of 2 m depth at C7, RISP Base Camp and Roosevelt Island Camp (RIC), in addition, three or four samples were collected from each of 21 shallow pits at sites which we visited with RISP glaciologists (Fig. 1). After the pits had been excavated, 5–10 cm of snow was scraped from the wall which was to be sampled using a carefully cleaned, long-handled scraper made from "Teflon". The samples were collected by inserting wide-mouthed polyethylene jars (of capacity 500 ml and diameter

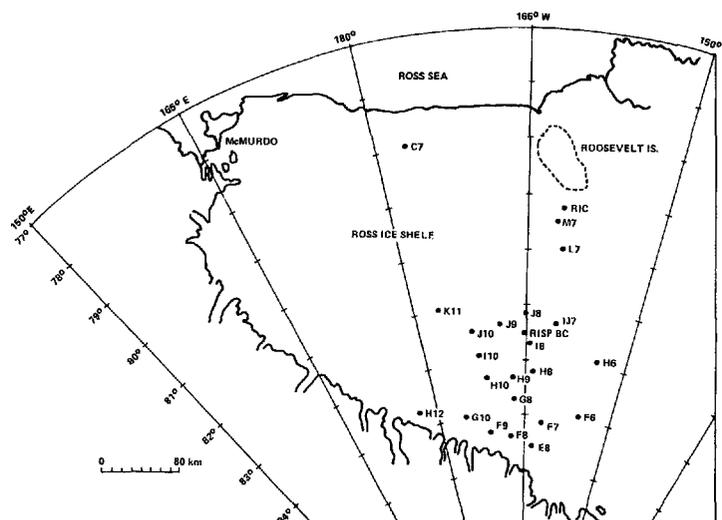


Fig. 1. 2 m deep pits were intensively sampled at C7, RISP BC, and RIC. Three or four snow samples were collected from the other 21 Ross Ice Shelf locations indicated on the map.

10 cm) into the pit wall. The jar screw tops were replaced, and the jars were sealed in polyethylene bags. Each sample covered a depth range of 10 cm.

All sample preparation and analyses were conducted in the clean room facility of the Desert Research Institute. Elemental analyses were made using atomic absorption techniques: flame techniques for Na and Mg analysis, flameless techniques for K and low concentrations of Na and Mg. Matrix standards (Na : Mg : K = 5 : 2 : 1) were used to establish reference levels. Each standard and sample analysis was repeated three to five times for each element, depending on the consistency of the machine response. The analytical procedure produced concentration values which have a typical uncertainty of 5–10%.

RESULTS

Table I shows the concentrations of Na, Mg, and K, and their ratios in Antarctic snow and ice which have been determined in both this and other work. Whereas most of the concentrations and the ratios found on the Ross Ice Shelf fall within the range of values reported by others, the cationic ratios at the sites on the Shelf farthest from the coast (E, F and G sites) show significant departures from the proportions generally reported at similar distances from the open sea. These results are discussed in greater detail later in the paper.

TABLE I. RESULTS OF CHEMICAL ANALYSIS OF SNOWS FROM VARIOUS SITES

Location	Chemical analysis			Ionic ratios			
	Na p.p.b.	Mg p.p.b.	K p.p.b.	Na/Mg	Mg/K	Na/K	
Little America ice, 52–84 m depth	325	42.0	21.0	7.7	2.0	15.5	Langway and others (1974)
Mirny (45 km from coast, 820 m a.s.l.)	48	7.1	2.1	6.8	3.4	22.9	Boutron and others (1972)
“Byrd” Station	31	4.0	1.5	7.8	2.7	20.7	Murozumi and others (1969)
C7 pit (sea-level), Ross Ice Shelf	196	22.0	8.0	8.9	2.8	24.5	Warburton and Linkletter (1977)
Base Camp pit (sea-level), Ross Ice Shelf	98	14.0	4.0	7.0	3.5	24.5	Warburton and Linkletter (1977)
E, F and G site pits, Ross Ice Shelf	48	8.5	6.8	5.6	1.2	7.1	Warburton and Linkletter (1977)
Sea-water				8.3	3.3	27.8	

(a) *Temporal variations*

Figure 2 shows the variations in concentrations of Na, Mg, and K with depth (i.e. time) down to 1.6 m at the C7, RISP Base Camp, and RIC sites (see Fig. 1 for locations). At all three sites the concentrations vary markedly with depth. The *average* maximum-to-minimum ratios for the three sites are 7 : 1 for Na, 10 : 1 for Mg, and 9 : 1 for K; maximum-to-mean ratios average 2.3 : 1, 2.6 : 1, and 2.2 : 1 for Na, Mg, and K respectively. Except for Mg, the variability is greater at the Base Camp site than at sites nearer the ocean.

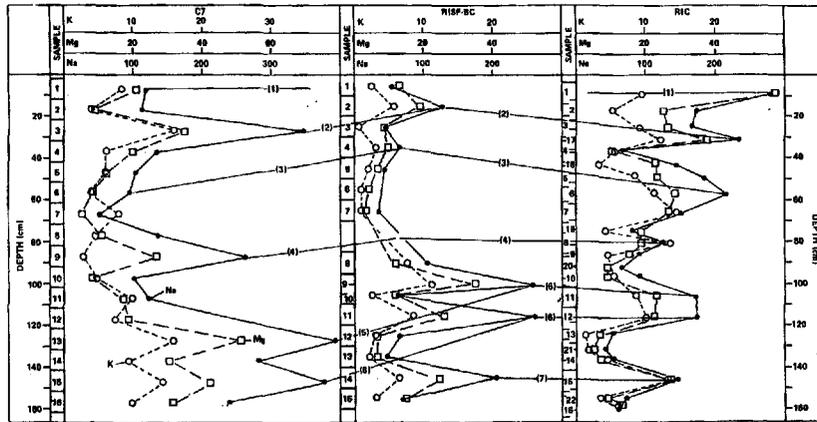


Fig. 2. Temporal variations in Na, Mg, and K concentration peaks have been correlated both on the basis of the pattern and spacing of peaks and of the mean annual snow accumulation at the three sites.

At any one site, the distinctive high-concentration peaks generally occur at the same depths for the three elements. Also, as was reported in an earlier comparison of the C7 and Base Camp profiles (Warburton and Linkletter, 1977), the ratio of the depths of the well-defined peaks at both sites was 1.4 : 1 (C7 : BC), a figure which is in agreement with the average accumulation ratio for the sites (Crary and others, 1962). Peak number 4 at the C7 site did not have a counterpart at the Base Camp because no sample was collected at the appropriate depth. Peak number 7 at the Base Camp site did not have a C7 counterpart because it would have occurred below the maximum depth sampled at C7.

Although the correlations of concentration maxima at RIC with those at C7 and Base Camp are not so compelling as those between C7 and Base Camp, a reasonable correlation does exist. On the basis of the data of Crary and others (1962), it is expected that the accumulation at RIC will be similar to that at the RISP Base Camp and the proposed correlation of chemical features fits this assumption.

It is important to note that, although the mean values of the ionic ratios at the three sites are on the order of 10% lower than the sea-water values, the ionic ratios for the concentration peaks are generally quite close to the sea-water ratios. This fact is important in a consideration of the possible origins of these concentration maxima.

(b) *Geographic variations*

The geographic distribution of the mean concentrations and the concentration ratios of the Na, Mg, and K ions at 24 sites on the south-eastern portion of the Ross Ice Shelf are indicated in Figure 3. The data presented on these maps have been contoured to suggest the general pattern of variation. Data points are often widely spaced, and alternative contour

schemes are possible. The data for the region south of Roosevelt Island suggests the existence of a zone marked by low concentrations and high ratios of Na : K, Na : Mg, and Mg : K.

Whereas the pits at C7, Base Camp, and RIC were continuously sampled with depth, the other 21 shallower pits were not. It is possible that the *mean* concentrations determined from these two sampling procedures may not be strictly comparable. The ratio of maximum-to-minimum concentrations for the shallow pits are, on average, half the value of the ratios found in the three deeper pits, whereas maximum-to-mean concentration values average 0.7 of those of the deeper pits. In spite of these limitations, the clusters of similar values and the

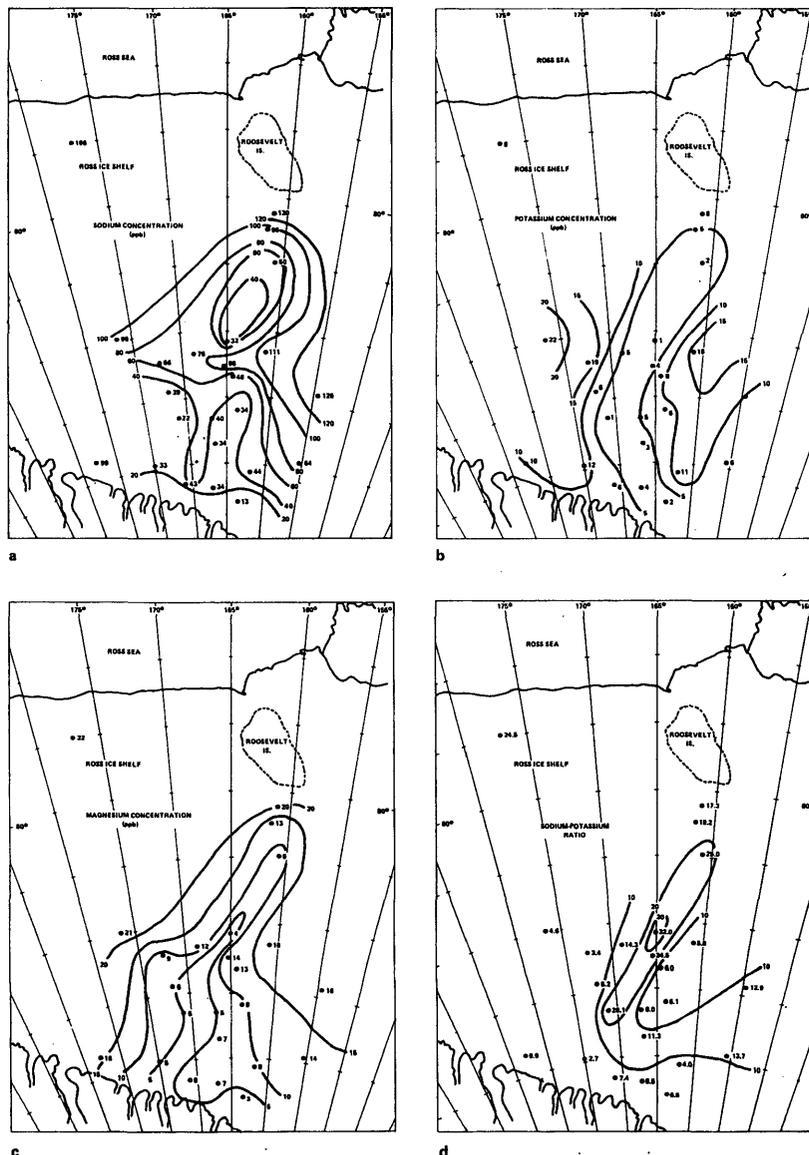


Fig. 3a-d. The geographic variations of Na, Mg, and K concentrations and their ratios are not a simple function of distance from the sea. Although alternative contouring schemes are possible, all seem to show a feature in the region south of Roosevelt Island.

sequential spatial variations on the maps indicate that the two data sets can be used together to give a general view of the geographic variability. In no cases do the data from the more intensively sampled sites (C7, Base Camp, and RIC) distort the distributional patterns. The two-dimensional diagrams of concentrations and ratios are discussed below in terms of possible causes and origins.

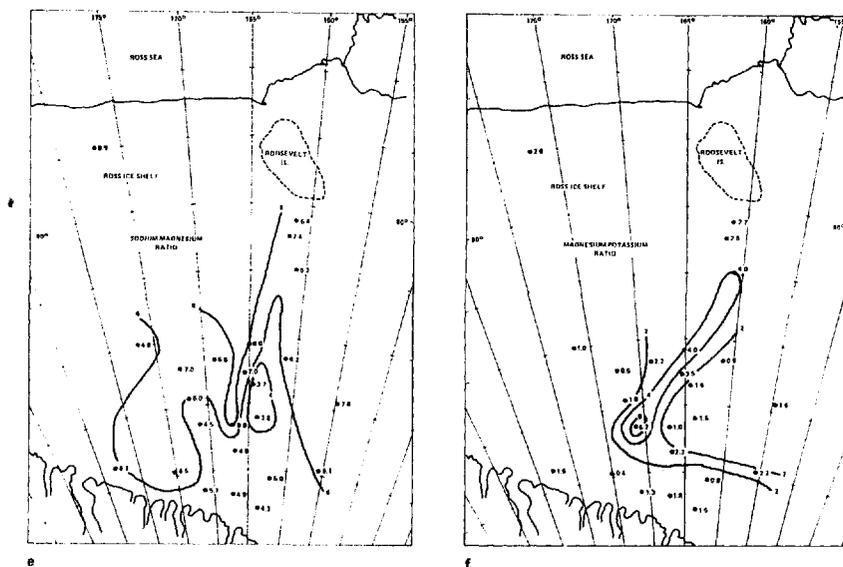


Fig. 3e and f. The geographic variations of Na:Mg and Mg:K ratios.

(c) *Chemical variations with precipitation type*

The most common form of precipitation which occurred at C7 and RISP Base Camp during November and December 1974 was a form of diffusional ice deposition on the nylon nets which occurred in supercooled fog conditions. C7 experienced fog for 29% of the time during its two-month occupation. It has been estimated that this diffusional deposition (often in the form of hoar frost) accounts for 5–10% of the annual accumulation on the Ross Ice Shelf (Linkletter and Warburton, 1976). Little snowfall occurred at C7 and only two significant snowfalls were experienced at Base Camp during the observation period.

The mean values for Na, Mg, and K concentrations and their ratios in diffusional growth are listed in Table II together with the mean values for the total accumulated snow from the pits at the same sites. The relationship of the elemental concentrations in the diffusional depositions to those of the pit snows differ at the two camps. However, the cationic ratios in

TABLE II. RESULTS OF CHEMICAL ANALYSIS OF SNOWS FROM C7 AND BASE CAMP

	Chemical analysis			Ionic ratios		
	Na p.p.b.	Mg p.p.b.	K p.p.b.	Na/Mg	Mg/K	Na/K
C7 site (70 km from edge of Ross Ice Shelf)						
Average values in pits	196	22	8	8.9	2.8	24.5
Average values in diffusional fog deposition	237	36	17	6.6	2.1	13.9
Base Camp site (450 km from edge of Ross Ice Shelf)						
Average values in pits	98	14	4	7.0	3.5	24.5
Average values in diffusional fog deposition	47	11	4	4.3	2.8	11.8
Predominantly diffusional growth snowfall	54	14	12	3.9	1.2	4.5

the diffusional-growth ice at both sites are consistently lower than the coastal water values found in the pits. Also listed in Table II are concentrations and ratios for samples collected during a snowfall at the Base Camp site. The cationic ratios in these samples of diffusionaly grown snow are also significantly lower than sea-water ratios.

DISCUSSION

(a) *Temporal variations*

A general correlation has been suggested among the chemical records found in the C7, Base Camp, and RIC pits even though the sites are separated by hundreds of kilometers. Although Clausen and Dansgaard (1977) have suggested that the accumulation estimates of Crary and others (1962) for the southern portion of the Ross Ice Shelf are too large, there is no evidence that the relative variations from place to place are significantly different from those indicated by the earlier work. Because only the Crary and others data cover the area where the pits were located, those data were used here.

The accumulation data indicate that the original correlations, based on the patterns and relative spacings of the peaks, are reasonable in terms of the variations in mean annual accumulation among the three sites. A detailed record of the stratigraphy was made only for the C7 pit and it has not been possible to establish the exact periods of the year in which the concentration peaks occur, solely on the basis of the C7 stratigraphy. However, oxygen-isotope data from a site near our Base Camp pit (personal communication from W. Dansgaard) suggest that many of the peaks in cation concentration represent fall and early winter periods. It is clear, however, that the high concentration values are not regularly associated with specific stratigraphic features.

Possible causes of the observed concentration peaks include:

- (1) Extended periods of dry fallout of marine aerosols over the Ice Shelf. The stratigraphic record does not support this possibility because high concentrations are not associated with radiation crusts, wind crusts, or other features which would be indicative of a given layer having resided at the surface for an extended period of time.
- (2) Periods of storm activity. Three factors make this a possibility: (i) Increased wind velocities associated with storms would increase the proportion of the ocean surface occupied by breaking waves leading to an increased production of sea-salt nuclei (Blanchard and Woodcock, 1957). Toba (1961) estimated that an increase in wind velocity from 8.7 to 12.1 m/s would increase the number of sea-water droplets of less than 50 μm diameter entering the atmosphere by a factor of 40. (ii) During periods of high-velocity winds, the chemically-enriched surface microlayer of the ocean would be broken up and mixed into the deeper water layers. Hence, droplets entering the atmosphere would contain salts of typical sea-water proportions. The ionic ratios in the higher concentration peaks are closer to marine ratios than are those in samples with lower concentrations. (iii) As the maximum water content of the atmosphere is limited by the temperature of the cold Antarctic atmosphere, storm conditions might be expected to produce a proportionally larger increase in sea-salt particles than in liquid-water content for the clouds in which the snow is forming. This could lead to higher salt concentrations in the snowfall occurring during larger storms.
- (3) Seasonal (or longer-term) minima in sea-ice extent leading to the closer proximity of large areas of open water directly offshore from the Ross Ice Shelf. By shortening the spacing between the aerosol source and the sampling sites, the observed increases in ionic concentrations could readily be produced (Lodge, 1955; Rossknecht and others, 1973). Recent work by Gordon and Taylor (1975) has shown that the pack ice surrounding the Antarctic continent undergoes large seasonal fluctuations.
- (4) A combination of (2) and (3).

The peaks appear to be the products of large-scale meteorological events occurring over the Ice Shelf, and their chemistry indicates that the aerosols which contribute to the peaks are predominantly of marine origin.

(b) *Two-dimensional variations*

Information into the geographic distribution of the impurities in Antarctic snow which was previously available was based on essentially linear arrays of sampling sites because the samples were collected either during traverses (e.g. Boutron and others, 1972) or at fixed bases. An earlier presentation of chemical data from the Ross Ice Shelf which we have made (Warburton and Linkletter, 1977) also took variations along a line of sampling points, and discussion centered on variations with distance from the sea. Data from the present two-dimensional array of sites (Fig. 3) presents a more complex picture.

The broad, flat surface of the Ross Ice Shelf is a region where one might expect to find a rather regular variation of chemistry with distance from the sea. However, Figure 3 makes it clear that the observed distribution is not a simple function of distance from the primary aerosol source. The geographic variations of both concentrations and ratios show a distinct discontinuity to the south of Roosevelt Island. At the moment, the spacing of data points limits our ability to define the overall extent and character of this feature in other than a general way.

The presence of this discontinuity is further suggested by the results of a study into the relationship between mean annual accumulation at sites studied by Clausen and Dansgaard

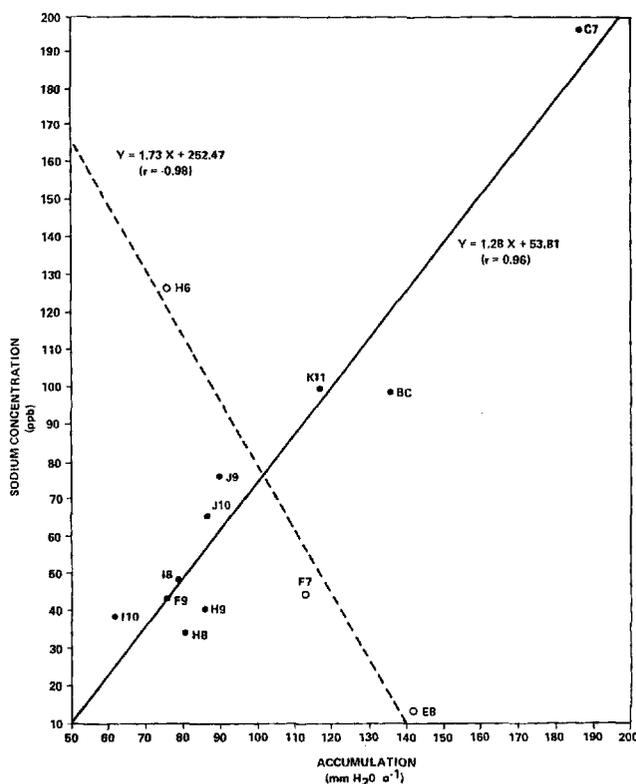


Fig. 4. The presence of two chemistry-accumulation regimes on the eastern portion of the Ross Ice Shelf is suggested by the two distinct relationships indicated.

(1977) and the sodium content of snow collected at the same sites by the present authors (Fig. 4). Whereas the sodium content increases with accumulation between F9 and C7, along the line between H6 and E8 an inverse relationship exists. This result suggests the existence of two zones having different meteorological or accumulation characteristics.

The physiographic and meteorological setting of the Ice Shelf has several features of interest for the present discussion. Both the narrow tongue of higher accumulation (Fig. 5b (1)) and the elongated zone of higher mean annual temperature (Fig. 5c (1)), which cut across the topographic grain of Marie Byrd Land and the polar plateau, appear to reflect the preferred tracking of storm systems across Marie Byrd Land (Fig. 6). The high accumulation zone along the inner edge of the Ice Shelf (Fig. 5b (2)) is caused by the orographic lifting of air masses as they approach the Transantarctic Mountains. This lifting leads to deeper cloud development and to higher precipitation rates and amounts. This effect, extending some distance out onto the Ice Shelf, was observed by the authors on several occasions during the 1974–75 field season. A secondary contribution to this accumulation zone comes from snow transported from the East Antarctic plateau by katabatic winds which probably also produce a slightly warmer zone (Fig. 5c (2)) through the influence of the adiabatically-warmed air which descends through the mountains from the plateau.

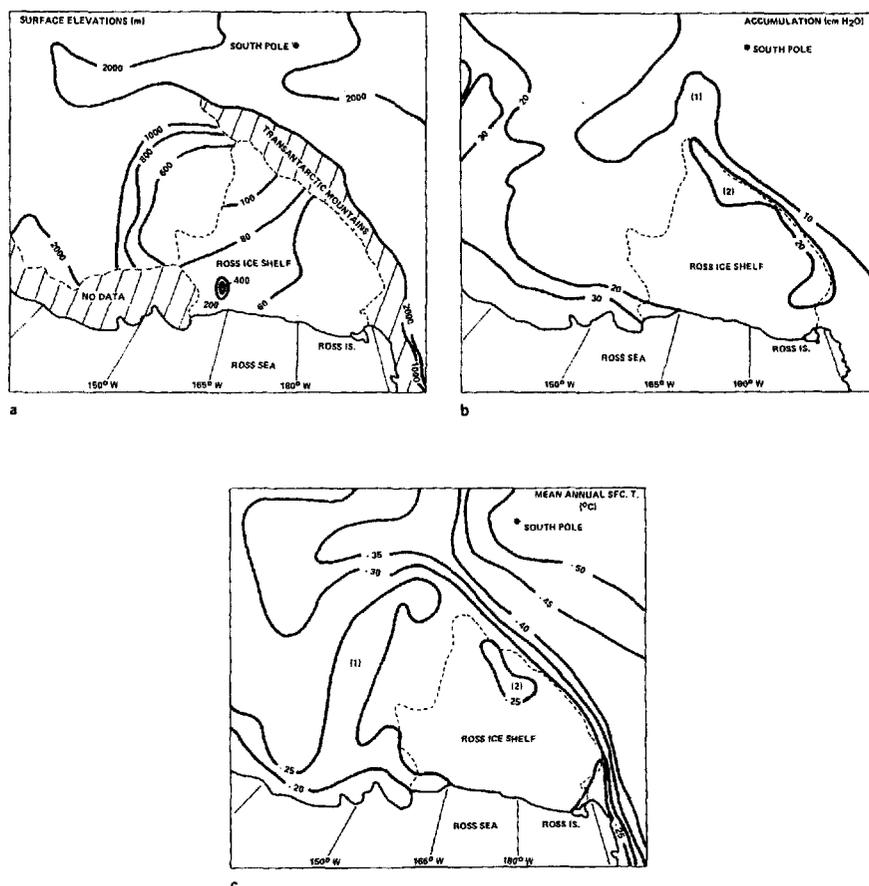


Fig. 5. The physiographic and meteorological setting of the Ross Ice Shelf. 5b(1) and 5c(1) are thought to reflect an important storm track with its associated increased incidence of snowfall and advected warmer marine air. The high accumulation zone on the Shelf (5b(2)) is produced by the orographic effect of the Transantarctic Mountains. Adiabatically warmed air carried to the Ice Shelf by katabatic winds is probably responsible for 5c(2). (Maps after Bentley and others, 1962.)

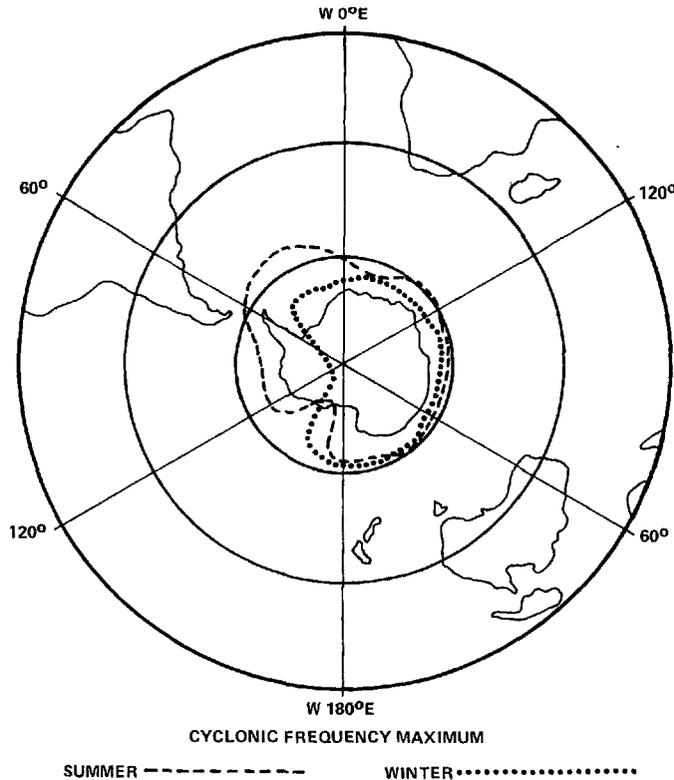


Fig. 6. Cyclonic frequency maxima (Taljaard, 1972) illustrated here, total cloudiness, and the distributions of cyclonic and anticyclonic centers, all indicate that most storms which affect the Ross Ice Shelf initially penetrate the Shelf in the vicinity of Roosevelt Island and the Marie Byrd Land coast.

The distributions of total cloudiness (van Loon, 1972), cyclonic and anticyclonic centers, and cyclonic frequency maxima (Taljaard, 1972) during all seasons show clearly that most storms affecting the Ross Ice Shelf pass near its north-east corner in the vicinity of Roosevelt Island. The winds recorded at Ice Shelf stations and camps reflect this. Some of the storms continue across Marie Byrd Land, but many move along the west slope of Marie Byrd Land (leading, we believe, to the features shown in Figures 5b and c), either to penetrate towards the South Pole or to curve back across the interior of the Ross Ice Shelf.

Figure 7 shows the distributions of four parameters on the Ross Ice Shelf as determined by Cray and others (1962). Mean annual temperature, snow hardness, and snow density all have their lowest values in a broad zone south of Roosevelt Island. Although recent work by Clausen and Dansgaard (1977) suggests lower values and a slightly different pattern for accumulation on the southern portion of the Ice Shelf, the overall picture remains basically the same.

The distributions of chemical, meteorological, and glaciological features studied so far may be summarized as follows: Along the lines from C7 to F9, and from RIC to L7 there is a general decrease in concentration of the cations studied. Although accurate accumulation data are not available for the RIC to L7 sites, there is a positive relationship (correlation coefficient $r = 0.96$) between accumulation and Na concentration for the C7-F9 sequence. It appears that the general decrease in both snow and chemical accumulation found in the region near to the coast does not hold in the interior of the Ice Shelf where chemical variations

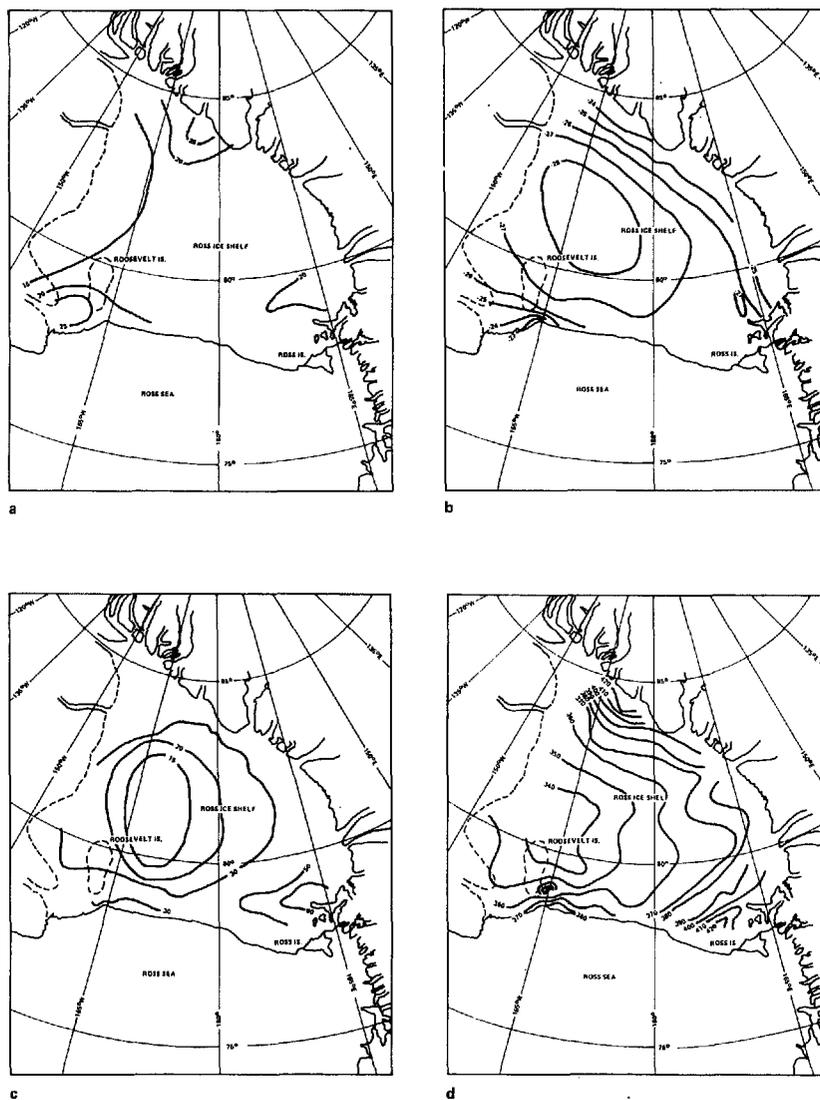


Fig. 7. The variations in (a) average annual accumulation (g/unit area), (b) average annual surface temperature ($^{\circ}\text{C}$), (c) average snow hardness (kg), and (d) average snow density ($\text{Mg}/\text{m}^3 \times 10^3$) were measured by Cary and others (1962). All parameters have their lowest values in the interior of the Shelf. The patterns south of Roosevelt Island may reflect the movement of storms near and over the Ross Ice Shelf.

are more irregular. However, the positive relationship between accumulation and chemical concentration prevails in at least part of the central region.

We suggest that storm intensity is the dominating and controlling factor from the coast across the center of the Ice Shelf. Warmer, more vigorous storms will not only penetrate further across the Ice Shelf but will contain more liquid water (hence more snowfall) and will have accumulated more marine aerosols while still over open water in the Ross Sea. The positive relationship between accumulation and chemistry suggests that the aerosol content undergoes a proportionally larger increase than does liquid-water content as storm intensity increases, probably due to the limit imposed by temperature on liquid-water content. In

addition, the chemical data reflect the efficiency with which the precipitation processes clean aerosols from the air and produce a more rapid decrease in chemical concentration than in snowfall, thus accentuating the deviation from a simple 1 : 1 relationship. Low enrichment factors for both Mg and K (relative to Na) at C7 and RIC indicate that a relatively undiluted, unfractionated marine aerosol predominates near the sea.

A different picture emerges for the southernmost portion of the Ice Shelf. Along the line from H6 to E8, snow accumulation and Na concentration (both with significant gradients) are inversely related ($r = 0.98$). The accumulation gradient appears to be much affected by the orographic effect of the Transantarctic Mountains. The chemical gradient is determined by the direction of storm movement through this area, the progressive cleansing of the air by precipitation, and dilution of the aerosol by the rapidly increasing snowfall near the mountains.

The ionic ratios at the southern sites are very different from the coastal ratios to the north. The greatest deviation occurs for the Na : K ratio which averages approximately 30% of the sea-water value along the E, F, and G lines of sampling sites. The Mg : K averages 45% and the Na : Mg 65% of marine ratios at these sites. Although these values may arise only from fractionation of the marine aerosol, the proportionally greater increase in K concentration required to yield such a marked change in ratio suggests a second aerosol source. Whereas Na and Mg are generally considered to be of marine origin, K can be indicative of a continental aerosol (Langway, 1967). The proximity of exposed rock and glacial deposits in the Transantarctic Mountains suggests a possible local source for an aerosol which is relatively rich in K. In addition, upper tropospheric and stratospheric dust which has traveled long distances enters the Antarctic lower troposphere under subsidence conditions over the interior plateau (Hogan and Nelson, 1975; Hamilton and O'Kelley, 1971). This aerosol, which could be carried to areas of the Ross Ice Shelf by katabatic winds, would be expected to have lower Na : K and Mg : K ratios than does sea-water.

The general coincidence of the zone of low chemical concentrations with low values for mean annual temperature, snow density, and snow hardness south of Roosevelt Island are intriguing. Although cationic concentrations are low, their ratios are near to oceanic values. The low concentrations may indicate a tendency for cyclonic disturbances to "die" in this region, as most of the aerosol removal would have already been accomplished. The high incidence of cyclonic centers near this area may be attributable to this "graveyard effect" (Taljaard, 1972). The low values for Cray's measured factors may be interpreted in a similar way. The slightly lower temperature may reflect a somewhat reduced advection of marine air across this part of the Ice Shelf whereas the lower density and snow hardness suggest a less windy character in addition to the lower temperature.

(c) *Chemical variations with precipitation type*

One aim of the 1974-75 field season was to collect falling snow during storms in order to study the relationship between snow growth mechanisms and chemical composition. This met with only limited success because the incidence of storms was low. Nevertheless, some information which bears on this problem was gathered.

As mentioned above, the most common form of precipitation which occurred at C7 and Base Camp during the 1974-75 field season was riming in supercooled fogs. The fog condition was generally associated with relatively warm air moving across the Ice Shelf in winds of low velocity. The distinctly cellular character of the air masses was indicated by frequent temperature oscillations of up to 5°C, which occurred at rates as rapid as 0.5°C/min. The fogs are associated with the advection of maritime air across the cold snow surface when there are no storms.

The mean concentrations for Na, Mg, and K and their ratios in the rime which formed in these fog conditions are listed in Table II. Although the air masses in which the fog formed

were thought to be of marine origin, the Na : K and Na : Mg ratios are significantly lower than sea-water values. They are also distinctly different from the average ratios found in the snow taken from the pits at C7 and Base Camp. A fractionated marine aerosol is suggested as the cause for the K and Mg enrichments. Enrichment factors of 2.4 for potassium and 1.2 for magnesium are in agreement with Komabayasi (1962). The small size of the fog droplets (around 20 μm diameter) and associated low wind velocities indicate that the enrichment may occur in association with the production of small water droplets from the chemically-enriched surface micro-layer of the ocean. The coastal values for the ionic ratios in the pit samples of snow suggest that the bulk of the accumulation at these sites is from snowfall which contains larger frozen water drops or sea-salt particles introduced into the atmosphere during storm periods when the sea surface is in a more turbulent state.

The apparent importance of the large drop and sea-salt particle contributions to the chemistry of the Ross Ice Shelf, is also supported by the results of chemical analyses of predominantly diffusional-grown snowfall collected at the Base Camp site. Although only three samples were collected, all showed marked departures from sea-water ratios (Table II).

CONCLUSIONS

The chemical features of snow collected from pits, 2 m deep, on the Ross Ice Shelf have been correlated between three locations separated by hundreds of kilometers. The peaks in concentration, averaging 7 to 10 times the background values, are probably produced when major cyclonic storm systems move, first across the Ross Sea acquiring moisture and marine aerosols, and then over the Ross Ice Shelf where the snow and chemicals are deposited. The magnitude of the concentration peaks may be influenced by the intensity of the storm system and the extent of the sea ice in the Ross Sea.

Although geographic variations in the chemistry of snow on the Ross Ice Shelf are not a simple function of distance from the sea, such a relationship does appear to exist on the northern portions of the Shelf. While the zone of low concentrations immediately south of Roosevelt Island probably reflects the presence of a "cyclone graveyard" in that area, the irregularities in chemistry further south are thought to mark the confluence between a region dominated by storms which have tracked over westernmost Marie Byrd Land and those which have moved directly over the Ice Shelf. The southern portion of the Shelf possesses low concentrations and ionic ratios which are very different from sea-water ratios. Whereas the concentrations reflect the progressive wash-out of aerosols and the dilutional effect of increasing snowfall near the mountains, the ratios suggest a second aerosol source superimposed on a fractionated marine aerosol. The strong katabatic flow from the high plateau onto the Shelf may very well be the dominant low-level transport mechanism for such an aerosol source.

Ionic ratios in rime deposited on the Ross Ice Shelf differ significantly from sea-water ratios. This may be caused by the small droplets in the supercooled fogs which deposit the rime which is produced from the chemically-enriched surface microlayer of the ocean under conditions of low wind velocity. The reason for the snow which is diffusional grown having ionic ratios which differ markedly from marine values is less clear. The diffusional growth process may produce a fractionation in the atmosphere by the preferential collection of aerosols of certain chemical compositions. In any case, because the ionic ratios on the northern portion of the Shelf are close to those of sea-water, it appears that the accumulation there is dominated by snowfall which has a significant amount of large droplet riming and which contains a higher proportion of sea-salt particles. The increasing importance of diffusional growth processes which is apparent toward the interior of the Ice Shelf (as indicated by the changing ratios, is in agreement with our earlier observations of the increasing proportion of diffusional against accretional growth with distance from the coastline.

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