A CHEMICAL COMPARISON OF SNOWS FROM MT RUAPEHU, NEW ZEALAND AND THE POLAR PLATEAU, EAST ANTARCTICA.

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ABSTRACT

The chemistry of surface, snowpit and ice core samples from Mt Ruapehu, New Zealand, was compared to surface snow samples from Mt Egmont-Taranaki, New Zealand, and to snowpit samples from the Polar Plateau, East Antarctica. Na^+, K^+, Ca^{2+}, and Mg^{2+} were determined by atomic absorbtion spectrophotometry, and the anion contribution of Cl^-,Br^-, NO_3^-, PO_4^{3-}, and SO_4^{2-} was determined by ion chromatography using a Dionex QIC II.

Marine aerosols dominate in Antarctic snow, with significant enrichment of Ca from crustal sources, consistent with the location at the head of the Dry Valleys.

On Mt Ruapehu, a marine background with superimposed volcanically derived concentrations of SO_4^{2-} is present in precipitation, with enrichment of all ions with phreatomagmatic and major phreatic activity, and enrichment of Ca^{2+} and SO_4^{2-} associated with minor phreatic activity. Na^+ and Cl^- concentrations are significantly increased during southerly and westerly winds, but are also increased by volcanic activity. All New Zealand samples are enriched in K^+ relative to bulk sea water, consistent with a crustal input.

On Ruapehu, the dominant mechanisms of concentration are dry deposition and adsorbtion of gases for the volcanic components, and in-cloud scavenging of the marine components; while in Antarctica, the coastal region is dominated by scavenging and the Plateau is dominated by dry deposition and adsorbtion of gases.

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CHAPTER ONE

SNOW CHEMISTRY

1.1 INTRODUCTION

Mt Ruapehu is an active, multivent, composite volcano situated at the south-west end of the Taupo Volcanic Zone, New Zealand at 39°17'S 175°34'E. It is the highest mountain in the North Island, at 2797 metres and is glaciated by six major glaciers and a number of ice tongues extending from the summit area to as low as 2000 metres. These glaciers feed three skifields and 4 major rivers, namely Whakapapa, Tongariro, Whangaehu and Manganuioteao, and a number of lesser streams, many of which are diverted into the Tongariro Power Development - (TPD) (Hackett & Houghton,1987). The glaciation has been present since the Pleistocene-Holocene period and has greatly modified the summit region, with cirques and moraines evident. The glaciers are currently retreating, presently occupying less than 4 km^2, - a recession of about 240 m in 40 years (Otway, pers.comm.). While some have been separated from their source (Mangaehuehu, Wahianoa and Whakapapa) others remain intact. The Summit Plateau, the site of a number of inactive vents, is covered in ice, in places to a depth of >130 metres (Holdsworth, pers.comm.).

The crater lake at the summit of Mt Ruapehu has fluctuated in composition and temperature from 9.0°C to 46.7°C over the last three years (Otway,1987-1990), in response to fumarolic or magmatic emissions at the bottom of the lake. Many of the added chemical components dissolve in the lake or take part in secondary reactions, but others pass through the lake to the atmosphere without influencing the chemistry. Some of the vapours emitted 'dissolve' in precipitation and are deposited with or on the snow, or are 'scavenged' by already deposited snow.

Two important consequences stem from the contamination of the snow on active volcanic peaks. Firstly, contamination affects the water quality of rivers and streams derived from snow melt. This has potentially far reaching effects as most of the streams and rivers on the north and eastern sides of Mt Ruapehu, are diverted into the Tongariro Power Development Scheme (TPD) for production of electric power for the National Grid. Pollution of Lake Rotoaira, a trout fishery, which is fed from waters entering the TPD is another possibility; this occurred during the 1975 eruption of Mt Ruapehu. Water from local rivers and streams is also used for irrigation of crops and watering of livestock down river. Secondly, contamination of snow can be used to study the active state of the volcano and is useful in determining the past eruption sequence in old snow profiles and ice (Delmas et al,1985; Kyle et al,1982; Palais and Kyle,1988).

In order to determine the chemical composition of snow on Mt Ruapehu, recent snow samples from around the crater lake and ice cores from the Summit Plateau (North Crater) were taken. Snow samples from Mt Egmont-Taranaki were used as a control to establish background marine levels for snow from a similar latitude. Polar snow from the Plateau, East Antarctica was also collected and analysed to determine global background levels.

This study aims to predict the dominant mechanism for the concentration of chemical components in snow and to estimate the proportion of marine, volcanic and continental aerosols in temperate and polar snow.

The following chapters describe the sampling locations and techniques used on Mt Ruapehu, Mt Egmont-Taranaki and in East Antarctica, the results obtained, interpretations of the data, and possible origins of the components and mechanisms of concentration.

1.2 PHYSICS AND CHEMISTRY OF SNOWFALL

1.2.1 Formation of Ice Crystals

Water from the ocean evaporates, and as the air mass rises, it expands and cools to temperatures lower than that of the surrounding air. Condensation then occurs, forming clouds of water vapour. Three main conditions give rise to the formation of clouds: i) widespread gradual lifting associated with low pressure areas and frontal systems; ii) orographic lifting associated with mountain ranges; and iii) convective lifting, from heating of the lowest layer of the atmosphere (Richards,1973). Water evaporated from inland water bodies, soil and plant matter, may also significantly contribute to the air mass as it moves inland (Schemenauer et al, 1981).

For condensation to occur, a high degree of supersaturation is required (about four times its saturation value in a pure environment), unless there are very small particles (aerosols) present, which form condensation nuclei (Richards,1973). The aerosols may be sea salt particles formed from the breaking of waves, continental dust particles, or nuclei formed from combustion or chemical reactions, e.g., sulphur, ammonia, oxides of nitrogen, chlorine and sodium, and organic vapours (Richards,1973), and are larger than 0.1 µm in radius (Junge, 1977).

Particulate matter, such as clay silicates, (dominantly kaolinite) can also act as nuclei for the formation of ice crystals, reducing the degree of supercooling necessary for freezing from -40°C to -5°C (Richards,1973). Once formed, these tiny ice crystals continue to grow either by direct sublimation, scavenging aerosols less than 0.1µm in radius (Junge,1977), or by aggregation through collision with other ice crystals (Schemenauer et al, 1981).

During impaction, aerosols larger than 1 µm may be scavenged (Junge,1977). This scavenging process within the cloud is termed snowout or rainout (Schemenauer et al, 1981).

Snowflakes continue to increase in size as the air mass descends, exhibiting a variety of shapes dependent on the temperature and humidity of formation, attaining a maximum size at 0°C. Above this temperature, melting occurs (Schemenauer et al,1981).

1.2.2 Precipitation

Continued scavenging of aerosols occurs below the cloud base, and this is termed washout (Schemenauer et al,1981). Chemical species scavenged, include HCO_3^-, SO_4^{2-}, Cl^-, Ca^{2+}, Na^+, K^+, Mg^{2+}, silicas and clays (Richards,1973).

The chemical composition of precipitation is affected by the greater scavenging efficiency of aerosols by snow and ice crystals than by liquid water. This is dependent on the shape and motion of the ice crystals as they fall, and the water vapour transfer in clouds (Podzimek, 1987). The fall velocity of snow particles is less than rain and has lead some authors to propose snow to be a more reliable indicator of aerosol concentration in the atmosphere than rain (Schemenauer et al, 1981).

The total amount of aerosol removed is closely related to the residence time of water vapour in the cloud, and is dominated by the nuclei of condensation and of crystallisation, and the aerosols removed by sublimation (Richards, 1973; Junge,1977). Once precipitation begins, the removal of aerosols is dependent on the rate, the water content and the raindrop size, more being removed by the larger drops (Podzimek, 1987). No preferential scavenging or fractionation during the scavenging process in a 'clean air' environment is evident (Dick & Peel,1985).

The proportions of chemical constituents in falling snow are dependent on: i) air mass origin, whether the ocean, having dominantly sea spray aerosols, or dominantly continental dusts;

ii) physiographic effects, especially the decrease of sea salt aerosols with increasing altitude over the ocean;

iii) local climate, since more aerosols result in dry climatic regimes compared to humid ones;

iv) local sources, such as volcanoes and industry; and

v) lightning, meteoric dust and solar thermal-nuclear reactions (Richards,1973).

Of particular importance is the ageing of continental aerosols through coagulation in the upper troposphere. These comprise up to 80% of the troposphere's background aerosols, having a uniform distribution. In addition, the physiographic effect over the ocean results in low concentrations of sea salt aerosols at heights of around 2 km and above so that in the mid and upper troposphere, continentally derived aerosols are dominant. This has important connotations for the polar ice sheets and some temperate glaciers which are usually higher than 2 km above sea level (Junge,1977).

1.2.3 Metamorphism of the Snowpack

The chemistry of the snow is modified after emplacement as a snowpack by the addition of aerosols through dry deposition, and by evaporation and sublimation. The structure of the snowpack is modified by freezing rain, wind and diurnal melting and refreezing at the surface.

Dry Deposition

The deposition of aerosols directly onto the snow surface contributes a significant proportion of the total constituents in the snowpack, although less than the wet deposition (aerosols incorporated into snow before or during precipitation) (DeWalle,1987; Cadle & Dasch,1987). The rate of deposition is expressed as a deposition velocity (Bales et al, 1987).

Deposition of the larger aerosols is controlled by the deposition velocity, which decreases with particle size and temperature (Cadle & Dasch,1987), while the smaller aerosols move by diffusion to the surface (Junge, 1977). Downdrafts induced by precipitation have been found to be an important mechanism for the transport of particulates to the snow surface (Podzimek,1987).

Although in the Southern Hemisphere it can be expected that snowpacks oriented to the south will experience lower temperatures than those facing north, it has been found that the evolution of the snowpack is independent of slope orientation where slopes are not steep, and that the difference in temperature has no effect on the snowpack chemistry prior to melt (Page,1987).

Chemicals deposited by dry deposition include SO_4^{2-} from SO_2 and particulate SO_4^{2-}; Cl^- from HCl and particulate Cl^-, of which HCl deposition dominates; NO_3^- from particulate NO_3^-, HNO_3, NO_2, and NO, of which HNO_3 probably dominates; and Ca, Mg, Na and K all from particulate matter (Cadle & Dasch, 1987). Dry fallout originates particularly from local industrial sources (Richards, 1973), and is also likely to be enhanced by volcanic outputs.

Of particular importance for the snows surrounding Mt Ruapehu's Crater Lake is the uptake of sulphur from the oxidation of SO_2 to sulphate and subsequent deposition. This is strongly dependent on the liquid water content of the snow (the deposition velocity increasing significantly with liquid-water content), the SO_2 concentration, and the rate of oxidation of S(IV) to S(VI), since most uptake is of S(VI) as sulphate. Deposition velocities decrease as pH decreases, since SO_2 solubility and the S(IV) oxidation rate decline with pH. Thus, deposition velocities decrease at high SO_2 concentrations and decrease with time as sulphuric acid accumulates in the snowpack through oxidation (Bales et al, 1987).

In a study of the chemical evolution of a seasonal snowpack (Page,1987), it was discovered that the concentrations of all ions were higher in the surface and top 10 cm of the snow profile (consistent with dry deposition, evaporation or sublimation), decreased in the body of the profile, and increased and decreased in the last 10-20 cm above the soil. In this way, the body of the snowpack acts as a preferential filter, with migration of ions down through the pack (Gjessing,1977; Page,1987) and up from the soil by upward movement of pellicular water (Page,1987; Jonasson,1973).

Drifting Snow

A substantial modification of the snowpack occurs when winds speeds are sufficient to overcome the cohesive forces between the snow grains. The threshold force in loose unbonded snow of 3-8 m sec^{-1} is dependent on the size, shape and weight of new snow grains, while in developed snowpacks, hardness and wetness increase the threshold force required to greater than 30 m sec^{-1} (Male,1980; Kind,1981).

Blowing snow is an important feature of snowpacks as it not only redistributes the snow, but also distributes continental dusts and foreign vegetative matter (DeWalle,1987), and aids evaporation (Junge,1977), modifying the chemistry. Drifting snow is also an important source of accumulation for glaciers and a factor in avalanche formation (Male,1980).

Snow melt and Rainfall

In a temperate snowpack, diurnal melting and refreezing of the surface layers is common. This leads to a complex structure of ice layers alternating with coarse textured, low density, highly permeable layers (Male & Gray,1981).

In polar snowpacks, a similar structure is evident, although the individual layers may be annual rather than individual storm events. This arises from vapour transfer in response to temperature gradients which are negative in summer and positive in winter. In summer evaporation occurs at the surface giving lower densities and larger grained deposits and the vapour recrystallises at depth, increasing the thickness of the existing ice lens from the previous year (Taylor,1965). Conversely, in winter condensation occurs at the surface, giving smaller grains and higher densities (Stephenson,1967). The formation of wind crusts from prolonged winds also sets up temperature gradients in the top few millimetres of the snow and causes vapour condensation to occur at or very close to the surface (Stephenson,1967). Temperature gradients can cause the complete loss of all gases from the snow profile, during evaporation and recrystallisation (Sigg et al,1987) but as temperatures remain well below freezing for most of the year in the polar environment, precipitation and evaporation are low, and water vapour transfer is confined to the snow profile.

In temperate zones, where seasonal snow cover predominates, precipitation of both snowfall and rainfall is high. As the season progresses, melting increases due to higher temperatures and the occurrence of rain on the snowpack increases. The effect of rainfall on the snowpack is to raise the average temperature of the snowpack and therefore to increase the rate of melting, although rainfall will refreeze at depth if the average temperature of the snowpack remains below 0°C (Male & Gray,1981).

Percolation of water through the snowpack proceeds in a highly irregular manner and is dependent on the variations in the snowpack structure and thickness (Krimmel et al,1973). Initially percolation is slow (2-60 cm/min) (Male & Gray,1981), but as the liquid water content of the snow increases, percolation increases, with coarse grained snow acting as flow channels. Water movement is generally vertical, although the presence of relatively impermeable ice layers impedes this flow and forces lateral movement (Male,1980).

On reaching the ground surface, the water either infiltrates or moves laterally in a slush layer at 10-60 cm/min, and faster once drainage channels form (Male & Gray,1981).

The metamorphism of the snowpack caused by melting and rainfall modifies the shape of the snow crystals on the ground (Male,1980), and tends to concentrate the impurities onto the surface of the crystals from whence they are easily leached. In this way, there is fractionation of the solute in the meltwater relative to the snow composition, with up to 80% of the snowpack impurities being lost in the first 30% of melt (DeWalle,1987; Tranter et al,1987).

In addition, there appears to be a preferential elution of SO_4^{2-} and NO_3^- relative to Cl^- from the snowpack (DeWalle,1987), leading to a pH drop in streamwater. Thus, the composition of streamwater fed from alpine catchments is most extreme at the onset of snow melt, when proportions of SO_4^{2-} and NO_3^- are highest (Tranter et al, 1987).

It has been demonstrated through oxygen isotope studies, that ~50% of peak stream discharge and ~60% of total discharge is composed of 'old' water, melt from a previous season that has been refrozen in or below the snowpack in winter, while the remainder is water added from the current runoff-producing season (Obradovic & Sklash,1987). Even in a highly responsive catchment in South Westland, a four month residence time for runoff was observed (Pearce et al, 1986). Therefore, dramatic events, such as volcanic eruptions, may not significantly affect melt stream chemistry for some time afterwards.

1.3 SOURCES OF AEROSOLS

1.3.1 Polar Snow

Aerosols in Antarctic precipitation are mainly composed of sea-salt and gas-derived secondary aerosols composed of mineral acids. Within the first 40 km from the coast, the sea-salt contribution dominates, with deposition of the coarsest sea-salt particles through rapid scavenging and dry deposition, while inland the acid contribution dominates (Legrand & Delmas, 1985). The dominant cations, Na^+, K^+, Mg^{2+}, H^+, are balanced in Antarctic precipitation by the dominant anions, Cl^-, NO_3^- and SO_4^{2-}. Total Ca, both soluble and insoluble, is always less than 2 ng/g and is thus considered unimportant for the ionic balance. NH_4^+ also plays a negligible role in the chemical budget (Legrand & Delmas,1984).

Sea-salt Aerosols

Storms over the ocean provide a major source of aerosols to the Antarctic atmosphere. Stronger more vigorous storms increase the proportion of the ocean surface occupied by breaking waves, and thereby increase the production of sea-salt nuclei. The stronger the storm, the higher the concentrations of marine trace ions and the closer is their ratio to the bulk sea water ratio (Molenar & Warburton, 1980; Gjessing,1984).

The sea-salt contribution decreases sharply inland with distance (Boutron & Lorius,1977; Legrand & Delmas,1985) and altitude (Junge,1977).

On the Ross Ice Shelf, the transition between snow characteristic of the ice shelf and the inland regime occurs at around the 500 m elevation contour (Herron & Langway,1979), while the elevation barrier is thought to lie between 850 m and 1730 m, some 50-100 km inland, in Adélie Land East Antarctica (Boutron & Lorius,1977; Legrand & Delmas,1985).

Peaks in concentration of marine ions can be linked to i) periods of large storms; ii) minima in sea ice extent; and iii) periods of increased dry deposition, although the latter is thought to be unlikely (Warburton & Linkletter,1977). The concentration of ions can vary greatly, even by orders of magnitude, over such events (Molenar & Warburton,1980).

The dominant marine ions are Na^+, K^+, Mg^{2+}, and Cl^-, with a small contribution of Ca^{2+} and SO_4^{2-}. Of these, Na^+ is the best reference element, with a marine contribution of greater than 90% (Boutron & Lorius,1977) and is used in preference to Cl^- which shows some enrichment inland.

Seasonal variations of Na and Cl are similar, and peak in summer to late winter, in accordance with the penetration of storms into the Antarctic continent (Legrand & Delmas,1984). However, owing to the altitude effect of sea-salt aerosols, dry deposition of Na^+ at elevations above 2000 metres is low, and relatively constant with time, and fractionation of the Cl/Na ratio, from the bulk sea water ratio of 1.18 (1.8 by weight), is significant above this level (Legrand & Delmas,1988). The fractionation is slightly affected by location; there are slightly higher concentrations of Na^+ in West Antarctica (30 ng/g Na), compared to East Antarctica (10 ng/g Na) (Herron & Langway,1979).

Where the Cl/Na ratio deviates from that of the bulk sea water ratio, excess Cl (values greater than 1.18) or excess Na (values less than 1.18) is present. The latter case is rare in polar environments but has occurred during the last glacial maximum when large areas were ice-free and Na was contributed from a crustal source (Legrand & Delmas,1988).

The Mineral Acids

The excess Cl (from atmospheric HCl) is formed by the reaction of sulphuric acid with sea-salt particles as indicated by the reaction:

$$\boxed{H_2SO_4 + 2NaCl <==> Na_2SO_4 + 2HCl}$$

The amount of total choride deposited as [Cl]ex can be expressed as:

$$\boxed{[Cl]_{ex} = [Cl]_{tot} - 1.18\,[Na]_{tot}}$$

where Cl/Na in bulk sea water equals 1.18 (Palais & Legrand,1985).

This results in a non-uniform distribution over the surface of the continent (Legrand & Delmas,1988), with summer maxima of the Cl/Na ratio linked to the availability of H_2SO_4 in the troposphere and to quiet weather conditions in summer (Legrand & Delmas,1984).

Although primary SO_4^{2-} of marine origin is present, and this component dominates at coastal sites, sea-salt SO_4^{2-} comprises only 10% of the total SO_4^{2-} deposited in East Antarctica (usually in the order of 50-100 ng/g SO_4) between 150-200 km inland (Delmas & Boutron,1978; Delmas et al,1982). As there is no observed decrease in SO_4^{2-} with distance from the coast (Legrand & Delmas,1985), the immediate source of the background SO_4^{2-} is unlikely to be marine (Herron,1982).

The 'excess' or 'non-marine' sulphate is generally in the form H_2SO_4, ammonium sulphate or methanesulphonate and is probably formed from the biogenic oxidation of gaseous precursors to SO_2 and thence to H_2SO_4 (Delmas et al,1982), occurring on freshly precipitated snow or at or near the ice sheet surface (Herron,1982) or by atmospheric photo-oxidation of dimethylsulphide (Ivey et al,1986; Saigne & Legrand,1987). It has an inverse relationship with accumulation (as the flux of particles is constant) and exhibits summer maxima, consistent with the strong temperature dependence of a biogenic source (Herron,1982) and the aerosol maximum from easy vertical mixing of the troposphere (Legrand & Delmas,1984).

The amount of total sulphate deposited as H_2SO_4 equals the total SO_4^{2-} minus the sea-salt SO_4^{2-}:

$$\boxed{[SO_4^{2-}]_{ex} = [SO_4^{2-}]_{tot} - 0.125\,[Na]_{tot}}$$

where SO_4/Na in bulk sea water equals 0.125 (0.25 by weight).

The dominant mineral acid, often exceeding $[SO_4^{2-}]$ by weight, is NO_3^- (Herron,1982). Unlike $[H_2SO_4]$, which remains constant with distance inland, $[HNO_3]$ in snow increases (Legrand & Delmas,1985). This trend is also evident in soil salt from the Transantarctic mountains where Cl^- remains the dominant anion, but the proportion of nitrate increases with increasing distance inland (Campbell & Claridge,1987). $[NO_3^-]$ exhibits seasonal variations with narrow summer peaks and broad winter lows (Laird et al,1987) and exhibits decreasing concentration with age, from fresh surface snow (~206 ng/g), to old surface snow (~146 ng/g), down to the winter depositional layer (~61 ng/g in firn cores), with considerably less pronounced peaks corresponding to summer layers (Neubauer & Heumann,1988b; Laird et al,1987). This is suggested to be from re-emission of NO_3^- into the atmosphere after deposition, by evaporation and photochemical decomposition of HNO_3 (Neubauer & Heumann, 1988a; 1988b).

A dilution effect with accumulation, similar to that of non-marine SO_4^{2-} is evident, but is not as pronounced. This is thought to result from two mechanisms of concentration: gas to particle reactions and dry deposition (Herron,1982), although the former is more efficient (Neubauer & Heumann,1988a).

Spatial variability of peak concentrations is also evident, and Laird et al (1987) attribute this to individual sastrugi that have been rapidly filled and sealed with summer snow before mixing can occur. Spikes of NO_3^- would not correlate with other cores if this is the case.

The source of NO_3^- in Antarctic precipitation is still unidentified, though many theories have been proposed. However, the absence of a Na/NO_3 correlation (Legrand & Delmas,1984), the low concentration of NO_3^- in sea water (Parker et al,1982; Legrand & Delmas,1986), and the absence of NO_3^- salts in coastal deposits (Keys & Williams,1981), excludes a marine origin. Anthropogenic, continental or volcanic sources are also unlikely (Legrand & Delmas,1986).

NO_3^- may be formed from an NO_x precursor, the possible sources of which include: 1) N-fixation by lightning (Legrand & Delmas,1986);

2) induced fixation by aurorae (Parker & Zeller,1980);

3) fixation by galactic cosmic rays (GCR) (Parker & Zeller,1980);

4) induced fixation by giant solar flares (Stothers,1980);

5) fixation by meteoroids (Parker & Zeller,1980); and

6) N-fixation by supernovae gamma- and X-rays (Rood et al, 1979).

Although lightning is absent at high latitudes (Parker et al,1982), lightning at tropical and mid latitudes, with tropospheric transport, is thought to contribute 1.3×10^{12} g NO_3^- to the Antarctic NO_3^- budget (Legrand & Delmas,1986).

The auroral origin implies that during periods of low solar activity and associated auroral activity, notably the Maunder and Spörer Minimums of 1645-1715 AD and 1400-1510 AD respectively, $[NO_3^-]$ is also reduced (Zeller & Parker,1981; Laird et al,1982). Spikes of $[NO_3^-]$, also associated with giant solar flares, exhibit a periodicity of 11 and 22 years, correlated to the solar maxima and the alternating solar magnetic field reversal (Parker et al,1982). The galactic cosmic ray hypothesis shows an inverse effect, with increased $[NO_3^-]$ during low solar activity and associated higher cosmic ray flux (Parker et al, 1982).

No evidence for any of the solar related hypotheses could be found in cores taken in Greenland, where similar trends should be evident (Herron,1982; Risbo et al,1981), nor evidence of two peaks of intense solar activity in 1778-1788 and 1947-1959 in cores from Adélie Land, Antarctica (Zanolini et al,1985). Hence, it can be concluded that [NO_3^-] is independent of solar activity.

No 'nuclear' nitrate, or meteoric nitrate from the huge Tunguska event in 1908 was found in ice cores from Antarctica. This suggests that either nuclear and meteoric sources have no impact on the stratospheric budget of nitrogen compounds, or the stratospheric contribution is negligible in the deposition of nitrogen in Antarctica. Nitrogen fixation may also occur in the stratosphere, although there is no evidence to suggest that it is important (Legrand & Delmas,1986).

Spikes corresponding to the 1604 and 1572 Kepler and Tycho supernovae are evident in a number of cores from Antarctica (Zanolini et al,1985). As these are Northern Hemisphere phenomena, the concentration levels should be higher there. No evidence of enhanced NO_3^- was found in the years of any of the five historical supernovae or in the following years in the Greenland cores (Risbo et al,1981). It has been concluded therefore, that peaks in NO_3^- in the Antarctic cores are not derived from the effects of supernovae (Herron,1982).

Volcanic Sources

Sporadic, intense volcanic activity in the Southern Hemisphere (Delmas et al,1985) seems to affect the chemistry of Antarctic precipitation by enhancing SO_4^{2-} and F^- and occasionally Cl^- concentrations . NO_3^- concentrations are unaffected by volcanic activity (Herron,1982; Risbo et al,1981).

Major explosive eruptions eject large amounts of acids, mainly H_2SO_4 and HCl into the stratosphere. Fluoride, a good indicator of volcanic activity, increases 100-fold from the detection limit of 0.2 ng/g to over 20 ng/g in Antarctic snow at the onset of large eruptions (Herron,1982) while SO_2 is slowly converted to H_2SO_4 in the stratosphere and has a residence time of 2-3 years (Legrand & Delmas,1987a), so the F^- peak precedes the SO_4^{2-} peak by about one year. The decrease in [SO_4^{2-}] following an eruption is evident and further supports the stratospheric source (Herron, 1982).

For example, background concentrations of SO_4^{2-} are in the order of 0.5-2.0 μeq l^{-1} (25-100 ng/g) at inland locations (Herron,1982), and these rose by 1-2 μeq l^{-1} (50-100 ng/g) for two years after the Mt Agung eruption in 1963 (Delmas & Boutron,1978). Acidity increased by 3-4 μeq l^{-1} in the same time period (Delmas et al,1985).

It is likely that the active volcanoes in Antarctica, namely Mt Erebus and Mt Melbourne (Giggenbach et al,1973), play a negligible role in the Antarctic sulphate budget. Although the total sulphate emissions of the most active, Mt Erebus, 0.42 x 10^5 tons yr^{-1}, are significant when compared to the estimated SO_4 budget of Antarctica of 1.3-2.0 x 10^5 tons yr^{-1}, comprising up to 32 % (Radke,1982), they are insignificant when compared to the total flux of sulphur transported over the continent of 1.5 x 10^6 tons yr^{1} (Delmas,1982).

Volcanically derived species in Antarctica, are better defined in the interior than in the coastal regions, for example, 420-560 μg l^{-1} in the Vostok core (Kyle et al,1982), compared to 180-250 μg l^{-1} SO_4^{2-} in the Byrd Station ice core. This may be a result of enhanced volcanic debris fallout from the stratosphere to central areas, or more likely is an effect of greater accumulation and hence dilution in the coastal regions (Legrand & Delmas,1987a).

Crustal or Continental Aerosols

Continental aerosols comprise up to 80% of the background aerosols in the troposphere (Junge,1977). They are uniformly distributed and are not of local origin, although they are increased during periods of low sea level during periods of extensive glaciation (Legrand & Delmas,1988).

Although continental aerosols form the dominant background aerosol, it is unlikely that they are significantly enriched above this level in places other than the Dry Valleys, although calcium, derived from soil dust (primarily $CaCO_3$), does show a weak enrichment inland (Gjessing,1984).

In the Dry Valleys, the close correlation between rock type and the composition of soil salts indicates that most of the cations, with the exception of Na, are derived from mineral weathering of local rock material (Claridge & Campbell,1987; Keys & Williams,1981). Soils formed from dolerite contain a high proportion of Ca and Mg from the weathering of ferromagnesian minerals, while soils from granite contain high proportions of K from the weathering of feldspars, mainly orthoclase(Claridge & Campbell,1987) and relatively lower proportions of Ca and Mg from the weathering of biotite(Claridge & Campbell,1977).

As the prevailing wind in the Taylor and Wright Valleys is up-valley (an easterly) (Claridge,1965), it is likely that some enrichment of crustal derived ions will be present in the snows at the head of these valleys.

Anthropogenic Aerosols

Anthropogenic aerosols include emissions from combustion of fossil fuels, particularly from coal and vehicular emissions, and from industrial activity. As 90% of the anthropogenic emissions occur in the Northern Hemisphere (Herron,1982), and the equator is considered to be an effective barrier for interhemispheric exchanges (Gjessing,1984), it is estimated that precipitation in Antarctica is likely to have about 10% of the anthropogenic contaminant exposure of Greenland (Herron,1982). For SO_4^{2-}, this amounts to 5-8 ng/g, which is less than the natural variability of SO_4^{2-} in Antarctica. No anthropogenic NO_3^- is evident above the natural variability either (Herron,1982). Hence, the anthropogenic inputs into Antarctic precipitation of the ions determined are thought to be negligible, although significant contamination by Pb, Cd, Cu and Zn (Wolff & Peel,1985), may be present.

1.3.2 Temperate Snow

The main differences between polar snow and temperate snow chemistry have been attributed to: 1) anthropogenic emissions which increase the concentration of the mineral acids (Herron,1982); 2) the shorter lifetime of aerosols at mid latitudes owing to higher deposition rates (Legrand & Delmas,1988; Delmas,1982); 3) the decreased vertical mixing compared to high latitudes (Legrand & Delmas,1986); and 4) the larger contribution from crustal sources.

In New Zealand, anthropogenic influences are small (Ayers et al,1986; Holden & Clarkson,1986), so the increased contribution of marine and continental aerosols relative to polar precipitation are likely to be the controlling factors in the background levels of ions.

Snow, although falling more slowly, has a similar composition to rainfall in New Zealand (Fish,1976). Relatively few studies have been carried out on the chemistry of precipitation in New Zealand and these involve the study of a few major ions only (Fish,1976; Stevenson,1980; Holden & Clarkson,1986; Ayers et al,1986; Harvey & Clarkson,1988). Precipitation in New Zealand can be classified into one of two categories - coastal or inland.

Marine sites are dominated by the marine aerosols containing sodium, chloride and to a lesser extent magnesium, potassium and sulphate. These make up around 90% of the total ionic composition. As precipitation moves inland, the mean sea salt content of rain is significantly reduced within several tens of kilometres, so that the marine content at inland sites is only about 40% of the ionic composition (Harvey & Clarkson, 1988).

A substantial non-marine component, largely sulphate, ($NMSO_4^{2-}$) with some ammonia and nitrate, exists at both coastal and inland sites. This component is present in approximately equal concentrations at both sites (Harvey & Clarkson, 1988). The $NMSO_4^{2-}$ is derived from pyrogenic sources or biogenically reduced sulphur from the oceans being oxidised to acidic sulphur gas, and further oxidised to sub-micron SO_4^{2-} aerosol, which owing to its size, is transported more readily than the larger sea salt aerosol. Thus at inland sites, the majority of sulphate deposited is non-marine sulphate, while at coastal sites only about half of the sulphate is non-marine (Harvey & Clarkson, 1988).

Soluble atmospheric trace gases, NH_3, HNO_3, and SO_2, although at concentrations less than 5 μeq l^{-1} (<300 ng/g), play an important role in precipitation mechanics. Water vapour nucleates onto the trace gases, a ubiquitous component of the background aerosol, to form cloud droplets (Ayers et al,1986).

Incorporation of soil-derived aerosols into clouds and snow also has a marked effect on the chemistry of precipitation. Incorporation of soil dust and soil organic material, composed of Na, K, Ca, and Mg, gives rise to a progressive enrichment in K and Ca relative to Na and Mg in precipitation, with increasing distance from the coast (Ayers et al,1986).

While there is a large seasonal difference in the precipitation at coastal sites, the difference at inland sites is much less pronounced. Acidity, [$NMSO_4^{2-}$], [NO_3^-] and [PO_4^{3-}] are all higher in summer compared to winter. [$NH4^+$] is also higher then and this is due to the larger biogenic flux into the atmosphere. Summer rainfall is also higher than in winter, suggesting a higher deposition in summer of the non-marine components (Harvey & Clarkson, 1988). The increased amount and frequency of rainfall are suggested to be more important parameters than time or season at inland sites, with high rainfall areas receiving greater amounts of dissolved substances from rain, than low rainfall areas (Fish,1976).

Volcanic components affect the chemical composition of precipitation, with increased SO_4^{2-}, NO_3^-, and F^-. Large scale changes are seen during periods of activity, while a background level of elevated SO_4^{2-} is evident during quiescent periods (Kyle et al,1982).

The pH of snow is thus a balance between the background trace gases, $NMSO_4^{2-}$ and NO_3^-, the biogenically produced NH_4^+, and an added source of alkalinity, the continental soil dust (Ayers et al,1986), on which atmospheric CO_2 has a minor buffering effect, shown in the following equilibrium equation:

$$\boxed{CO_2 + H_2O \Longleftrightarrow H_2CO_3 \Longleftrightarrow H^+ + HCO_3^-}$$

The equilibrium pH of this reaction is 5.6 (Holden & Clarkson,1986), and although this represents a somewhat mythical pH for natural waters, it was found to be very close for coastal precipitation in New Zealand, mean pH of 5.5 (Holden & Clarkson,1986). Owing to the reduced concentrations of SO_4^{2-} aerosol at inland sites, higher pHs are evident (Charlson & Rodhe,1982), up to 6.1 in winter precipitation (Harvey & Clarkson,1988). The acidity of volcanically affected snow is likely to be much higher, with increased concentrations of SO_4^{2-}, shown by the mean pH of 5.2 for Rotorua (Holden & Clarkson,1986).

Marine Snow

The marine component of coastal snow is high, with 90% of the ionic composition attributed to it (Harvey & Clarkson,1988). A significant non-marine contribution is present, plus a small continental contribution of added alkalinity (Ayers et al,1986).

Seasonal differences are large in the coastal areas and these are reflected in the chemical composition of the precipitation. Greater mean wind speeds of the southerly rain-bearing winds in winter entrain more sea salt into the atmosphere and this is washed out in the local rain (Harvey & Clarkson,1988). During these peak times the ion ratios of precipitation approach that of seawater (Miller,1961); the sea salt component being enriched by a factor of two in winter rainfall compared to in summer rainfall, in spite of 1.5 times more rain occurring in winter (Harvey & Clarkson,1988).

During the non-peak times, the proportions of Mg, SO_4^{2-} and especially of K and Ca are increased relative to seawater, with the inclusion of terrestrial dust in precipitation (Miller,1961).

A previous study of the precipitation at New Plymouth (Ayers et al,1986), found mean NH_4^+ and NO_3^- to be about 2-3 $\mu eq\ l^{-1}$ (54 ng/g and 186 ng/g) and $NMSO_4^{2-}$ to be about 10 $\mu eq\ l^{-1}$, (~480 ng/g) which should produce a pH of ~5.0. A pH of 5.6 was measured, necessitating an added source of alkalinity, proposed to be soil dust containing $CaCO_3$.

Mt Egmont-Taranaki was chosen as a control to establish concentrations of marine ions at a similar latitude to Mt Ruapehu. It is a non-active volcanic cone, situated on a peninsula on the west coast of the North Island, New Zealand, 39°18'S 174°4'E. It is particularly susceptible to marine influences, with the ocean no more than 23 km from the summit on three sides (Marcus & Moore,1983). At 2517 metres, it is the second highest peak in the North Island and has a seasonal snow cap with the snow line descending to about 1000 metres in winter (Thompson,1981), but disappearing in most summers (Marcus & Moore,1983). Precipitation on the western slopes is dominantly from the west from the Tasman Sea, while the eastern slopes are affected by the southeasterly airstream from the Cook Strait (Marcus & Moore,1983).

CHAPTER TWO

SITE LOCATIONS : ENVIRONMENT AND SAMPLING TECHNIQUES

2.1 ANTARCTIC SAMPLES

The initial intention of this study was to compare the snows of Mt Erebus, Antarctica and Mt Ruapehu, New Zealand with the aim of classifying the volcanic gaseous emissions entering the snow profile. The proposal to the Ross Dependency Research Committee for the 1988-1989 season to sample Mt Erebus snow was unsuccessful and so the opportunity was taken to sample snows on the polar plateau. The primary objective of the NZARP event (K092), was to determine mercury levels in snow and hence a remote location on the Antarctic Plateau, near Mt Fleming was chosen. The results of this study have been submitted for publication (Sheppard et al, in prep).

2.1.1 The Polar Plateau

Snows of the Antarctic Polar Plateau have little contamination from terrestrial, marine, volcanic or anthropogenic sources. The concentrations of ions vary in the range 10^{-7} to 10^{-12} g/g of snow (Delmas et al,1982), and present serious difficulties in sampling without significant contamination, and in analysis.

Site Location

For the primary task of the Antarctic programme, the site had to be within an approximate 160 km range of Scott Base to be within helicopter range and had to be within sight of bare rock for navigational purposes. The site had to be upwind of rock material in the prevailing winds, and had to be in a low accumulation zone where annual increments were small in order to sample pre-industrial snow in a pit of ~4 metres depth, as was the intention. To reduce potential contamination the snow texture had to be appropriate for excavation using hand tools, rather than machinery.

The site selected was on the plateau between the heads of the Upper Wright and Taylor Glaciers, Victoria Land, East Antarctica and was about 40km from Vanda Station, 160km from Scott Base, and approximately 6 km southwest of Horseshoe Mountain at approximately 77°35'S 159°50'E (Fig 2.1).

The campsite was set downwind of the laboratory igloo, used for Hg determinations, and the sample pit was 100 metres further upwind from the laboratory, along a flagged route. Surface snow samples were taken at the same location (Fig 2.2).

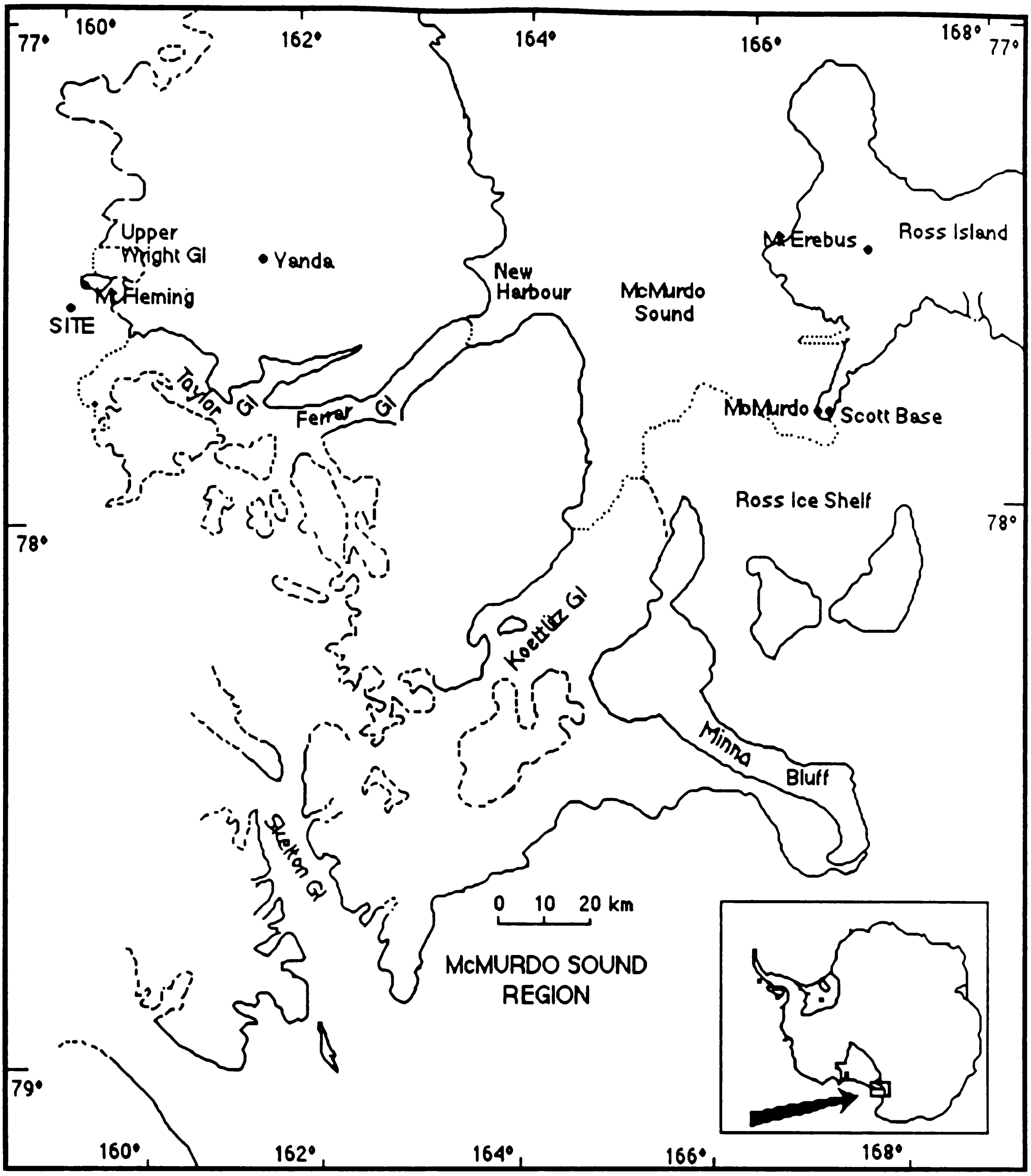


Fig 2.1 Location of sampling site on the edge of the Plateau, at the head of the Wright and Taylor Valleys.

The sampling location was 95km west of the nearest coast, and is therefore likely to have had minimal marine contribution, owing to the prevailing wind being W-SW, and to rapid scavenging and dry deposition of sea salt particles in the first tens of kilometres from the coast (Delmas et al,1982; Herron & Langway,1979; Legrand & Delmas,1985). Situated within 100 km of the coast and above the Transantarctic Mountains, this site may have characteristics of both interior and coastal regions.

Fig 2.2 Campsite at the head of the Wright and Taylor Valleys, taken from the sample pit.

Weather

Antarctica, with an average surface elevation of two kilometres, is the Earth's highest, driest and coldest continent (Stearns & Wendler,1988). Extremes of both temperature and wind speed are common. Temperatures as low as -89.2°C have been recorded at Vostok Station in 1983, and near-surface winds in coastal areas of East Antarctica are known for their intensity, frequently gusting to 50 m/s (180 km/h) during Mawson's 1911-1914 Australasian Antarctic Expedition recorded at Cape Denison (Parish,1988).

Topography is the dominant controlling factor of the temperature and wind regime. The continent is a large ice dome with slopes of 10^{-3} in the interior of the ice sheet, increasing to 10^{-2} within 100 km of the coast and locally to 10^{-1} at the coastal perimeter. An albedo of 70-80% (Parish,1988) ensures a strong radiative deficit exists for much of the time over the ice surface. This gives rise to a strong temperature inversion, greater than 20°C at the South Pole (Schwerdtfeger,1984), with a cold dense air layer close to the ground which flows under the influence of gravity down the slope and is termed the 'katabatic wind' (Stearns & Wendler,1988).

Mean wind speeds increase steadily from the interior of the continent towards the coasts, reaching a maximum some distance from it (Stearns & Wendler,1988). However the drainage of cold air does not follow a radially outward pattern but becomes concentrated in particular areas of topographically induced enhanced cold air supplies which feed the katabatic winds. Examples of these confluence zones in East Antarctica are Beardmore Glacier, Byrd Glacier, Terra Nova Bay and Dumont D'Urville (Parish,1988).

Although the sample site at the head of the Taylor and Wright Valleys fell between confluence zones, it retained the coastal characteristic of having moderate katabatic winds, ranging from calm, to about 50 knots (average of ~10 m/s), in the three weeks of December-January that were measured. Winds were dominantly W-SW-S, consistent with the katabatic winds, with the exception of one brief spell of an easterly breeze. Temperatures were characteristic of the plateau interior rather than the coastal sites (Schwerdtfeger,1984), ranging from -12° to -23°C.

The katabatic winds are stronger in winter than in summer, and are responsible for drifting snow. The entrainment of particles of snow by the wind occurs at a threshold speed of 10 m/s, while at 18 m/s total whiteout conditions exist (Stearns & Wendler,1988). Drifting snow was a major feature of the site, with snow drifts of over a metre deposited around the tents within three weeks. These were largely deposited during the blizzard days, of which there were two 4-day blizzards separated by approximately 6 days of fair-moderate weather. During the blizzard conditions, visibility was reduced to about 15 metres.

Sample Pit

The sample pit was dug to a depth of 4.6 metres, using steel and aluminium shovels and subsequently covered with snow blocks and the excavated snow. Protective clothing was donned to prevent contamination of the snow pit and a fresh surface was exposed using a PTFE scraper.

The pit contained 33 distinct alternating layers defined by density and hardness variations in firn, ranging in depth from 3-35 cm and these were assumed to be annual layers. Subsequent isotope analyses of 2cm strips of firn taken at 5cm intervals in the pit over three depth intervals, suggest that these are more likely to be wind storm events superimposed upon annual layers, and give annual accumulation rates of greater than 50 cm a^{-1} (Fig 2.3) (Sheppard et al, in prep). This is atypical of the interior, where accumulations are in the order of less than 20 g cm^{-2} $year^{-1}$ but accords with the coastal sites where annual accumulations range up to 71 g cm^{-2} $year^{-1}$ recorded at Casey (66.3°S 110.5°E) (Schwerdtfeger,1984).

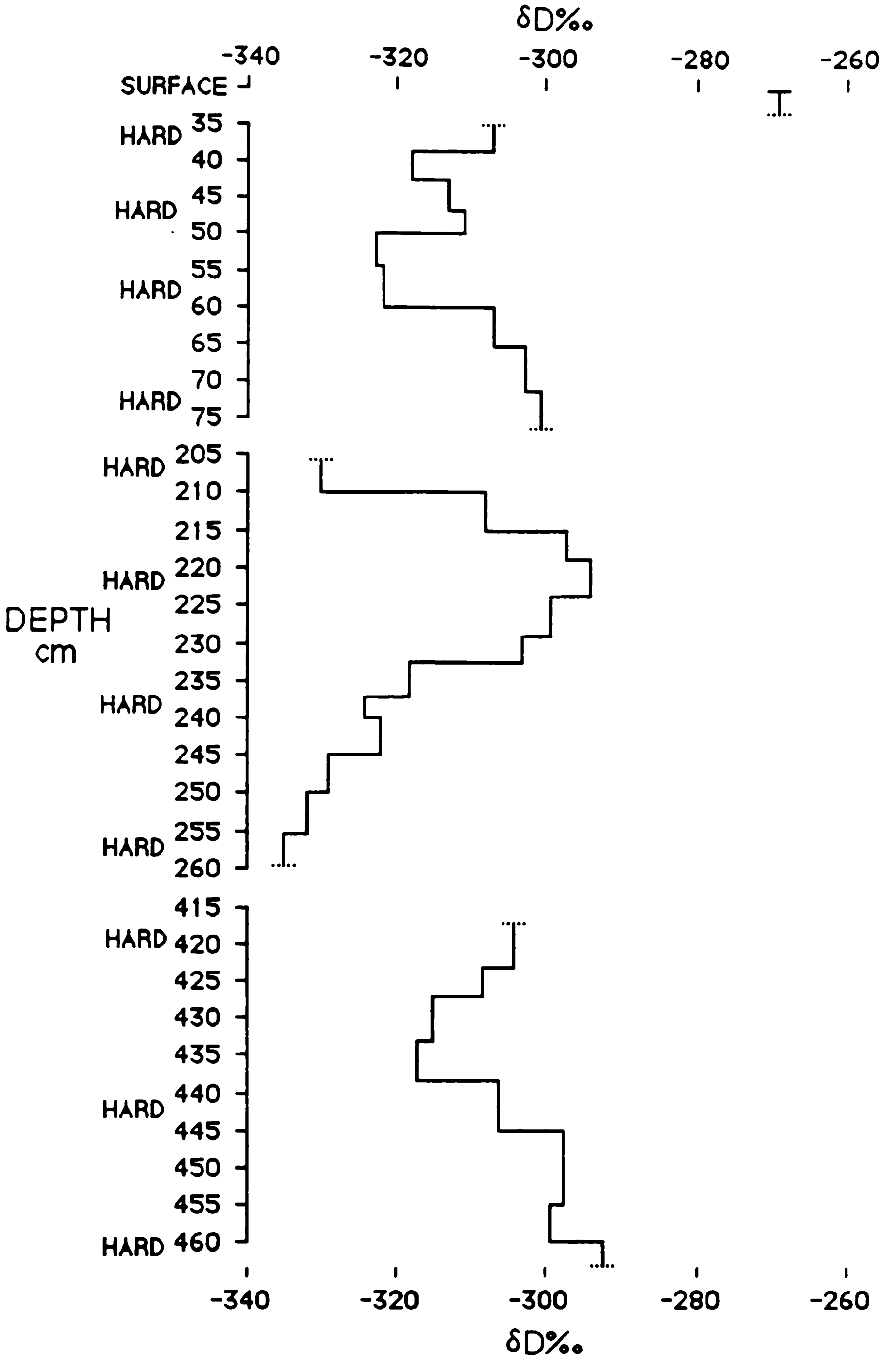


Fig 2.3. Variation in the δD values of the polar firn core, showing the hard layers initially presumed to be annual layers (Sheppard et al, in prep).

2.1.2 'Clean' Sampling Techniques

Contamination occurring during sampling or during transport and storage can cause large deviations in the determinations of trace ions in polar snow, which are often in the 1-100 ng/g range. The use of 'clean' sampling techniques is thus required.

Sampling Equipment

In glaciological pits, to depths of less than 10 metres, a good method for snow sampling is to push cleaned plastic vessels directly into the walls by hand. Blank values are generally less than the detection limit, providing pre-cleaned equipment and 'clean' clothing are used (Legrand et al,1984).

Pre-cleaning of sampling tools and containers, involving multiple steps of rinsing with deionised water (resistivity > 18 MΩ) and desorption of ions by periods of heating in a microwave oven, and storage for periods of 24 hours, followed by rinsing, drying and sealing in polyethylene envelopes is recommended (Boutron,1979; Legrand & Delmas,1987b).

A PTFE corer and scraper and one litre polyethylene pottles were used for sampling; these had been pre-cleaned in dilute nitric acid, followed by the rinsing and desorption steps. This practice is not recommended as even after multiple cycles of rinsing and desorption, non-negligible quantities of acid may be desorbed into the sample, especially from teflon which acts as a 'veritable acid sponge' (Legrand & Delmas,1987b). Nitrate analyses from this part of this study must be suspect.

Protective clothing, consisting of hooded antistatic nylon coverall, polyethylene boot covers, and shoulder length veterinary gloves (unpowdered) (Dick et al, 1990), was worn when sampling or attending to the pit. The pit was sealed with snow blocks after sampling to prevent snow drift accumulation in the pit. The suits were sufficiently large enough to wear with full survival gear underneath to guard against the bitterly cold winds (Fig 2.4).

Sample Collection

The 460 cm deep pit was composed of 33 layers which were numbered from the bottom of the pit. A clear temperature profile in the walls of the pit was evident from -25°C at 0.6m to -28°C at -1.6m, attaining a constant value of -31°C from 2.6m downwards. Each of the 33 layers in the pit was sampled, with two samples taken in layer 24 and 27 where the depth exceeded 30 cm or the hard layer was sufficiently thick to sample. Two surface samples and two blanks were also taken (Table 2.1). The blank containers were opened to the atmosphere, and were sealed without the inclusion of a sample. In the laboratory, the blank containers were filled to the same level as the rest of the pottles with deionised water of known concentration, and this was analysed in the same manner as the rest of the samples.

Sampling was begun at the base of the profile in order to avoid contamination from infill. The surface was scraped clean to a depth of one centimetre with the PTFE scraper and where possible, pottles were pushed directly into the snow (Fig 2.5). Where the snow was firmer, a PTFE corer was knocked into place using a cleaned high density polyethylene mallet and the snow core was dropped into the sample pottles. Pottles were immediately closed and were taped, and sealed in polyethylene bags within 24 hours.

Fig 2.4 'Clean' clothing used for sampling including polyethylene coverall, gloves, boot bags, and snorkel with gold ball trap (Photo: J.E. Patterson).

Table 2.1 Antarctic snow samples and their corresponding depths.

Sample No	Depth (cm)	Sample No	Depth (cm)	Sample No	Depth (cm)
1	438.5-460.5	15	269-283.5	27 Hard	89.5-95
2	417-438.5	16	255.5-269	27 Soft	83.5-89.5
3	399.5-417	17	239-255.5	38	80.5-83.5
4	384-399.5	18	219-239	29	71.5-80.5
5	370-384	19	205.5-219	30	54.5-71.5
6	358-370	20	181.5-205.5	31	46.5-54.5
7	343-358	21	170.5-181.5	32	35-46.5
10	330-343	22	160.5-170.5	33	25-35
11	322-330	24A	145-160.5	34	Blank
12	309-322	24B	126-145	35	Blank
13	290-309	25	109.5-126	36	Surface
14	283.5-290	26	95-109.5	37	Surface

Fig 2.5 Sampling directly into sample pottles from pit wall (Photo: J. Patterson).

Contamination

Post-sampling contamination largely occurs as a result of melting and exposure to the atmosphere. Samples should thus be kept frozen and sealed, refrozen and stored at -15°C between determinations (Legrand et al,1984). Unintended melting of the samples occurred en route to New Zealand.

Contamination by ambient gases such as ammonia has been demonstrated (Legrand et al,1984; Legrand & Delmas,1987b). To overcome this problem, the air volume inside the sample container should be minimized by filling the sample container, and the cations are analysed at the first melt (Legrand & Delmas,1987b). As NH_4^+ is unlikely to be in significant proportions in polar snows (Legrand & Delmas,1984), analysis was not attempted. In addition, snow samples having melted en route, would likely have given erroneous results.

2.2 NEW ZEALAND SAMPLES

The volcanic influence on snow chemistry was studied on Mt Ruapehu, an intermittently active andesitic volcano. Mt Egmont-Taranaki, to the west of Mt Ruapehu, was chosen as a control.

2.2.1 Mt Ruapehu

Crater Lake

The single active vent on Mt Ruapehu is occupied by a 0.16 km^2 crater lake (Hackett & Houghton,1987), at an altitude of ~2530 metres. The lake is currently roughly circular, with an average diameter of 500m and a depth of greater than 200 metres (Otway,1983). The lake depth and volume have varied greatly over the time span given in Table 2.2, and are dependent on the intrusion of magma at the lake bottom. A depth of 300 m was measured, giving an estimated volume of 10^7 m^3 in 1966 (Giggenbach,1974), followed by intrusion of magma during the 1966, 1968 and 1969 eruptions, giving a depth of 78 m in 1970, a reduction in volume of 40% (Giggenbach & Glover,1975). The infill was subsequently ejected in the 1971 and 1975 eruptions, the depth estimated at >200 m in 1983 (Otway,1983).

The lake has an outlet at the southern end where it enters an icecave and flows into the Whangaehu River. Because of its direct source to Crater Lake, with associated low pH, the Whangaehu River is not diverted into the TPD (Carr,1978).

The colour of the lake varies from a pale blue-green during quiescent periods to a dark grey during active periods and usually has an area of upwelling in the centre of the lake, marked by yellow spongy masses of bubbles or black slicks of highly plastic sulphur. The bubbles are thought to be formed by gases slowly percolating through a layer of liquid sulphur underlying the lake (Giggenbach,1974).

Submerged fumaroles maintain the lake temperature at 15-35°C, rising to >60°C (Nairn & Wood,1987), although periods of freezing have been recorded in 1896 and 1926 (Giggenbach & Glover,1975; Otway,1981).

Chemistry of Crater Lake

Crater Lake waters are well mixed and largely homogeneous throughout, as shown by the lack of a concentration gradient for chloride (Giggenbach & Glover,1975). The suspended sediment is dominantly fine-grained (<20μm) amorphous silica, cristobalite, sodic alunite, gypsum and unaltered andesite particles (Giggenbach,1974).

Two processes are responsible for the chemical composition of the lake water, introducing different components: i) volatile components enter in the gaseous phase from fumarolic activity arising from *degassing of a magma* ; and ii) metallic ions and silica are derived from the interaction of acidic water and andesitic material, especially after *intrusion of a magma body* (Giggenbach,1974).

Degassing of a magma - The species that enter as volatile components are H_2O, CO_2, HCl, HF, HBr, H_2S, SO_2, NH_3, H_2, N_2 and CH_4. Of these CO_2, H_2, N_2, and CH_4 pass through the lake because of its low pH and reducing conditions, and are likely to be responsible for the prevention of temperature and concentration gradients in the lake, through turbulence of rising gases. The remaining volatiles are virtually completely absorbed into the lake, some remaining in solution - (HCl, HBr and NH_3), and others participating in secondary reactions (Giggenbach,1974). Gaseous emissions from Mt Ruapehu's Crater Lake therefore, have low concentrations of the reactive gases, SO_2 and HF, and high concentrations of CO_2 and CH_4, owing to their interaction with water (Giggenbach,1982).

One important secondary reaction is the oxidation of H_2S by SO_2 or atmospheric oxygen, forming elemental sulphur. Because it has a specific gravity of around two, the sulphur is thought to accumulate at the bottom of the lake in a distinct layer, covered by less dense sediment of amorphous hydrated silica. This inhibits the dissipation of heat to the lake water, so that the sulphur is able to melt and coalesce into large liquid sulphur pools, as indicated by the spongy masses of yellow sulphur bubbles at the surface (Giggenbach,1974).

SO_2 is also oxidised to SO_4^{2-}, although some SO_2 must escape, as is evident by the pungent odour. The concentration of SO_4^{2-} is limited by the formation of secondary minerals, for example, alunite and gypsum (Giggenbach,1974).

Intrusion of a magma body - The leaching of rock or debris in the crater basin is thought to be a minor source of silica and metallic cations, the dominant source being interaction of acidic water with high temperature material (Giggenbach,1974). Of the species not limited by solubility, (e.g. Mg, Li, and to some extent Na), increases in concentration occur solely during active eruptive periods, while decreases in concentration occur by dilution with meteoric and fumarolic waters. This suggests that the lake water is largely inert to reactions with andesitic material, being saturated or supersaturated with cations at these temperatures. This is supported by the observance of unaltered andesite particles in the suspended sediment (Giggenbach,1974).

Variation in pH of the lake waters, which varies between 0.8 and 2.0 at the surface (Sheppard, pers comm), is brought about by the addition or partial neutralisation of the acids HCl and HSO_4^- by oxidic constituents of the magma, e.g., according to the reaction:

$$\boxed{\text{`}CaO\text{'} + 2H^+ \Longleftrightarrow Ca^{2+} + H_2O}$$

This leads to an increase in pH which causes a large drop in concentration of the secondary minerals, despite an increase in the amount of andesitic material dissolved. Thus, the concentrations of SO_4^{2-}, Ca, Al, K, and to some extent Na, are controlled by the precipitation of gypsum, $CaSO_4.2H_2O$, and alunite $(K,Na)Al_3(SO_4)_2(OH)_6$ owing to variations in SO_4^{2-} concentration in response to pH:

$$\boxed{HSO_4^- \Longleftrightarrow SO_4^{2-} + H^+}$$

(Giggenbach,1974).

No secondary reactions are known to involve Mg or Cl at these low pHs and increases are solely related to dissolution of hot andesitic material (Mg), or fumarolic HCl from degassing (Cl). The ratio of Mg/Cl is therefore, a good indicator of volcanic activity, rising with intrusion of magma, and decreasing with fumarolic activity. Both [Mg] and [Cl] reach their peak after the maximum lake temperature is reached, since the water : rock interaction continues for up to 6 months after injection. A good precursor to ash eruptions appears to be constant Mg/Cl ratios for up to 6-12 months, caused by a decrease in fumarolic activity owing to blockage of the conduits (Giggenbach & Glover,1975).

In tephra eruptions, much water is carried as droplets on mineral grains and on deposition, this significantly alters the chemical composition of the snow. Concentrations of the major constituents in the lake water, recorded over the period December 1970 to February 1973 (Giggenbach,1974) show the variation in concentration with magmatic input and fumarolic degassing. Mg concentrations range from 1030 - 2420 μg/g, reaching a maximum 5 months after the 1971 active period, while Cl concentrations show a gradual increase from 9450 μg/g (two months prior to the eruption), to 13710 μg/g, several months afterwards. [Na] ranges from 725-1575 μg/g peaking two months after the eruption, followed by a gradual decrease caused by secondary reactions. Ca, K, and F all reach maxima in concentration long after the phreatomagmatic activity has ceased, with ranges of 1120-1580 μg/g, 77-202 μg/g and 145-340 μg/g, respectively. [SO_4^{2-}] is significantly affected by secondary reactions occurring soon after the magmatic input. Concentrations decrease during the eruption and remain at low levels (5020 μg/g) for 7 months afterwards and then gradually increase, peaking 22 months afterwards at 16800 μg/g (Giggenbach, 1974).

Eruptive History

Since the European record commenced in 1861, all eruptions of Mt Ruapehu have been observed from the present crater where the lake has existed continuously, except for a period in 1945 when a lava tholoid displaced the lake (Nairn & Wood,1987).

The majority of eruptions are of two types:

i) phreatic eruptions, where fumarolic activity at the base of the lake, generates eruption columns of less than 100 metres, and base surge collars of ash-poor steam and water; and

ii) phreatomagmatic eruptions, where injection of fresh andesite magma interacts with water and hot rock and leads to violent Surtseyan-type eruptions. These larger scale eruptions produce primary base surges and secondary surges on column collapse, and eject mud, indurated lake sediment, assorted vent debris and a minor content of juvenile ash and lava bombs (Nairn & Wood,1987), and have displaced 3 x 10^6 m^3 of lake water and generated large lahars (Hackett & Houghton,1987).

A third eruption type has been observed once; the violent Plinian-type eruption of 1945, where a dome building phase was followed by intermittent violent eruptions that showered ash as far south as Wellington with the prevailing wind. Although greater than 10^7 m^3 of magma was extruded, few permanent deposits remain (Hackett & Houghton,1987).

A summary of the major volcanic events of Mt Ruapehu, from 1945 to 1977, is shown (Table 2.2), while a detailed account of the eruption history from 1980-1990 is given in Table 2.3. There were 16 probable phreatic eruptions from 1861-1945, although little is known about them (Nairn & Wood, 1987).

Table 2.2 Eruptive history of Mt Ruapehu 1945-present (Nairn & Wood,1987; Hackett & Houghton,1987).

Year	Type	Notes	Wind
1945, 22 July	plinian	Dome building, intermittent violent explosions in Aug. Peaks of eruptive violence in Sept and Nov. 10^7 m^3 magma extruded.	?
1968, 26 April	phreatomagmatic	lahar down Whangaehu River	
1969, 22 June	phreatomagmatic	lahars in 4 major valleys, ballistic blocks 4m diam. around crater, smaller rocks up to 1.2km away, 1.9×10^6 m^3 ejecta, many polluted streams.	SE/SW
1971, 8 May	phreatomagmatic	sequence of eruptions from 8-16 May, generated lahar down Whangaehu	W
1975, 24 April	phreatomagmatic	lahars in all major valleys, pyroclastic surges external to summit area, 1.6×10^6 m^3 ejecta many polluted streams, affected TPD.	NW
1977, 2 Nov.	phreatomagmatic	moderate size eruption, pyroclastic surges confined to crater lake area, lahar in Whangaehu.	SW

Table 2.3 Recent eruptive events of Mt Ruapehu (Otway,1980-1990).

Date	Type	Notes
29 Jan - end May 1980	small-moderate phreatic	frequent eruptions ranging from sudden upwellings to occasional ash eruptions
18 Oct 1980	small phreatic	fine layer of lake sediment ejected to Tahurangi
10 Oct 1981 - mid April 1982	small-moderate phreatic	2 small ash eruptions confined to Crater Lake in Oct & Nov, low S, regular phreatic events at 4-127 min intervals in Jan, ejecta plumes of black muddy water to 100 m above lake, geysering
21 May - 9 June 1985	small phreatic	many hydrothermal events at roughly hourly intervals, updoming to c.15 cm, surging
31 Oct - 15 Nov 1985	v. small phreatic	series of sudden convective overturns, upwelling to c.5 m, associated surging
8-9 Feb 1986	small phreatic	several events, muddy water to c.5 m, surging, steam column to >150 m
24-30 Aug 1987	small phreatic	waves and steam plumes, jets of muddy water to >10m
20 Mar - 21 May 1988	small phreatic events	updoming, and jets to c.15m, surging 2m above surface in March. Activity decreasing to low in April, elevated lake temp till mid May, few very small eruptions.
8 Dec 1988	moderate phreatic	block-size ejecta of altered andesite leaving 1m diam impact and melt craters in ice. Thin veneer of ash to Cathedral Rocks (strong SW). Mudflow on Whangaehu
27 Jan - 28 Feb 1989	v. small phreatic events	Many passive events of upwelling and occasional updoming, steam clouds often witnessed
1-24 July 1989	small phreatic	sporadic eruptions accompanied by surges 2-3 m higher than lake level and 200 m high steam columns
7 Jan - 1 Feb 1990	small phreatic	jets of steam and water to 50-60 m, steam clouds to ~280 m, tide marks to 10 m above shore

Site Location

The criteria for sampling snow on Mt Ruapehu were simple. The sites had to be in close proximity to Crater Lake where plume contaminants could be deposited with falling snow, or scavenged by the snow particles. In order to sample ice cores, other factors influenced the site location. As the cores were also to be used for isotope determination, a position removed from the summer melt streams was necessary as percolation of melt water affects the isotope ratio (Schotterer et al,1977). Another problem was discovered on the first attempt to core in mid-winter, when the frozen 1969/1975 eruption debris layer proved to be an insurmountable barrier to the sipre corer, resulting in cores of less than 3 m length.

A position on the Summit Plateau at the base of the Te Heu Heu ridge, (Fig 2.6), was chosen for the second attempt, where accumulation is higher and/or ablation is less, as even in the record ablation summer of 1988-1989 (Otway,1988; 1989), this area was covered in snow, compared to the rest of the plateau where there was but a hummocky terrain, covered in debris and surrounded by summer melt streams and lakes (Fig 2.7). The core site is at an altitude of 2595 m and is 1.26 km from the lake edge.

Fig 2.7 The Summit Plateau, Mt Ruapehu, taken on the 21/3/89 (Photo: F.West).

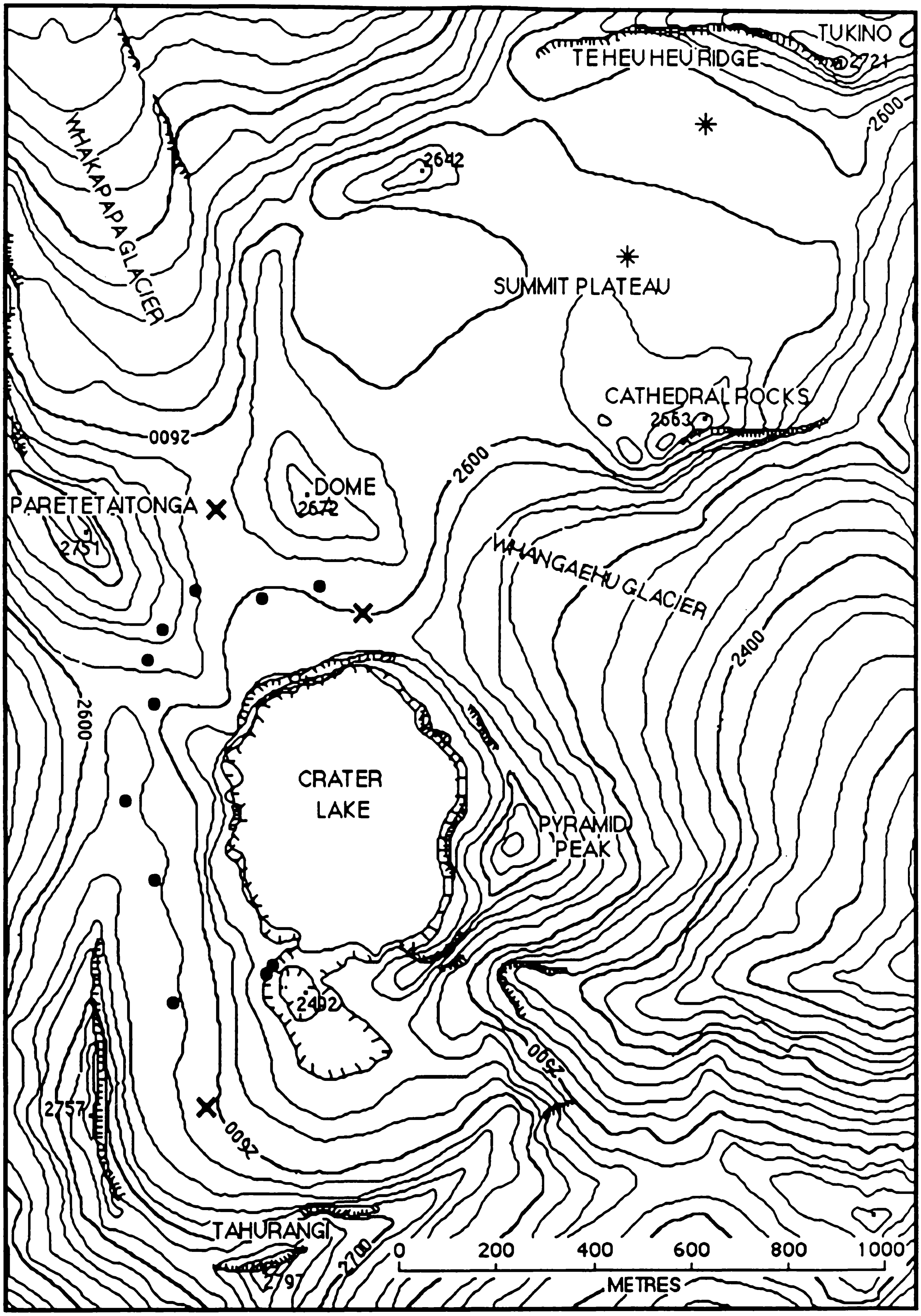


Fig 2.6 Location of sampling sites at the summit of Mt Ruapehu, showing pit samples ✕, surface snow samples ●, and ice core locations ✳.

It is interesting to note that the core site by Te Heu Heu ridge is at a lower elevation than the rest of the plateau, despite the apparent decreased ablation. As this depression alongside Te Heu Heu also coincides with the lowest sub-glacial terrain (Holdsworth, pers comm), it may be that melt water streams underlie this area, and flow out through the Mangatoetoenui Glacier, causing slumping in the overlying ice.

Most surface samples and pit samples were collected from : 1) the dome site (10°N from Crater Lake) at an altitude of 2600m and 60m from the lake edge; 2) the col site between the Dome and Paretetaitonga (340°N from Crater Lake), at an altitude of 2605m and 260m from the lake edge; and 3) Tahurangi site, at the base of the summit (200°N from Crater Lake), above the lake outlet, 2590m altitude and 440m from the lake (Fig 2.6). The surface samples were taken at sites between the pit locations.

Sampling Methods

Owing to the higher concentration of components in temperate snow compared to Antarctic snow, contamination from sampling techniques is insignificant. For this reason, stringent contamination-free sampling techniques were not necessary and fewer precautions were taken.

Polyethylene sample pottles were rinsed several times in deionised water, left to soak overnight for desorbtion of impurities and then stored until use.

In the field, sample pits were dug using a garden spade, the stratigraphy recorded (Fig 2.8a) and the faces cleaned back two centimetres with a polyethylene scraper. Sample pottles were rinsed with snow from the pit (Fig 2.8b), and were pushed directly into the pit wall or surface layer, followed by immediate capping of the pottles. Polyethylene lab gloves were worn, but no other precautions were taken.

In order to sample ice cores, a sipre corer was used. This comprises a stainless steel auger with tungsten carbide cutters and aluminium extension rods. Stainless steel augers are recommended for use in temperate regions, where multiple ice layers are encountered (Legrand & Delmas,1987). The cores were extruded onto a length of PVC piping and slid into sample pottles from there (Fig 2.9a,b). Unfortunately when the first cores were taken, the sample pottles available, were not sufficient to accommodate the full diameter of the core (8cm), and the cores had to be trimmed using a stainless steel knife. Larger sample pottles were used during the second sampling trip.

Fig 2.8a Recording the stratigraphy (Photo: T. Naish).

Fig 2.8b Rinsing the pottles with snow, prior to sampling (Photo: T. Naish).

Fig 2.9a Extruding the ice core from the sipre corer onto clean PVC piping.

Fig 2.9b Pottling, measuring, taping and recording (Photo: C. Hendy).

Weather

The prevailing airflow in the region is from the west (Thompson,1984), although the wind at the summit is largely topographically controlled. High wind speeds are common at elevations of greater than 2000 metres, with wind speeds over 30 knots occurring 20% of the time, and gale force winds, 10% of the total time (Thompson,1984). Wind speed data at the higher elevations is scarce, with most meteorological records taken at the Chateau Tongariro at an elevation of 1119 metres a.s.l. Wind roses for Chateau Tongariro (1119 m), and The Chalet (1997 m), both situated on the northern slopes of the mountain, the latter sheltered on the eastern side by Pinnacle Ridge; and Ohakune Junction (600 m), and Turoa skifield (1620 m), both on the southeastern flank (Fig 2.10) show the variation in wind direction. This suggests that wind direction at the summit will be even more varied with small scale topography having a large effect. Although the frequency of wind is higher at Turoa, represented by the percentage of calm days, no wind speed data was available for this site. The wind speed data at the remaining sites shows greater wind speed at higher elevations, as seen in the comparison of Chateau Tongariro and The Chalet.

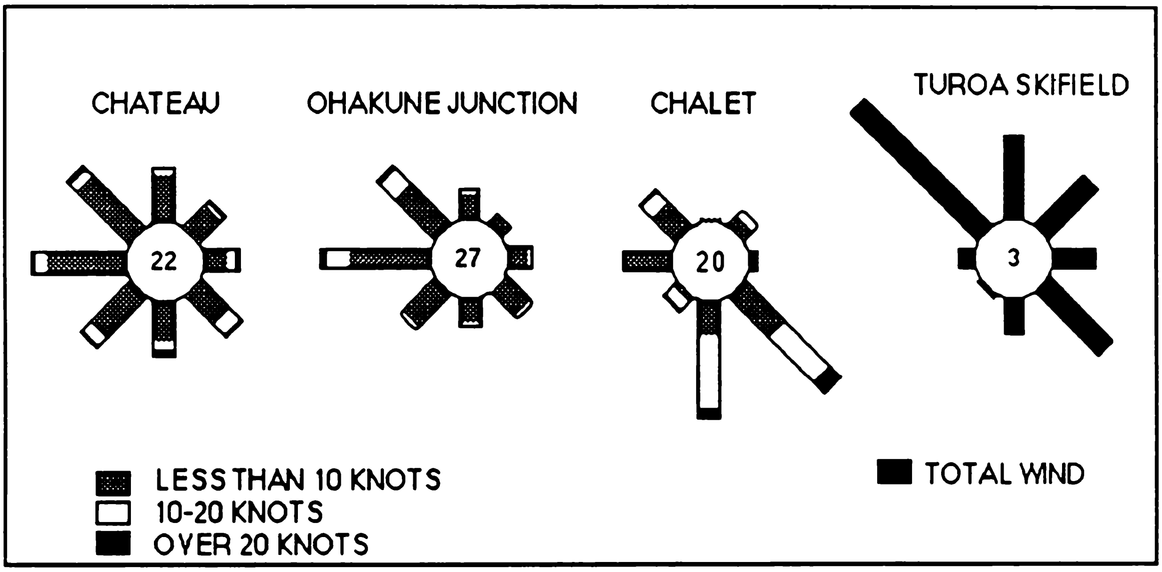


Fig 2.10 Frequency of wind direction (%) at Chateau Tongariro from 1972-1980, 2666 observations; Ohakune Junction from 1974-1978, 1348 observations (NZ Met Obs); The Chalet, 1989 (winter months only) 93 observations (Ruapehu Alpine Lifts Mountain and Skifield Weather Observations); and Turoa Skifield, for the period 1977-1978 (Thompson,1984). The frequency of calm weather is represented in the centre of the rose.

Temperatures at the higher elevations are also poorly documented. The mean monthly temperatures at Chateau Tongariro (Fig 2.11) show the characteristic temperature range for a 'continental' type climate of about 12°C to 13°C in summer and 9-10°C in winter. However, daily temperature variations are controlled largely by cloudiness and altitude and so with increasing altitude and hence increased cloud cover, the temperature and temperature range decreases (Thompson,1984) (Fig 2.12).

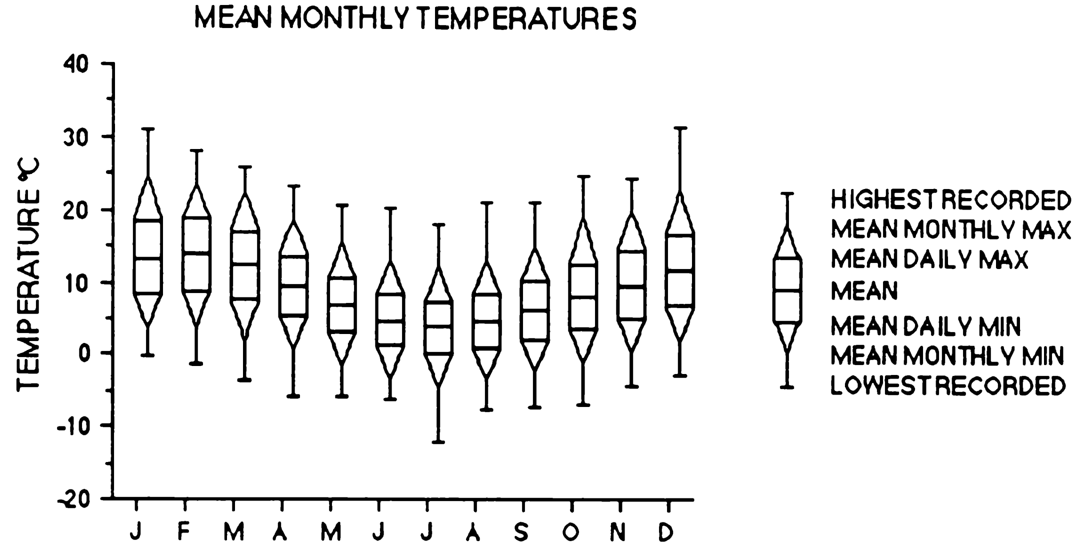


Fig 2.11 Mean monthly temperatures (°C) for Chateau Tongariro from 1930-1980 (NZ Met Obs).

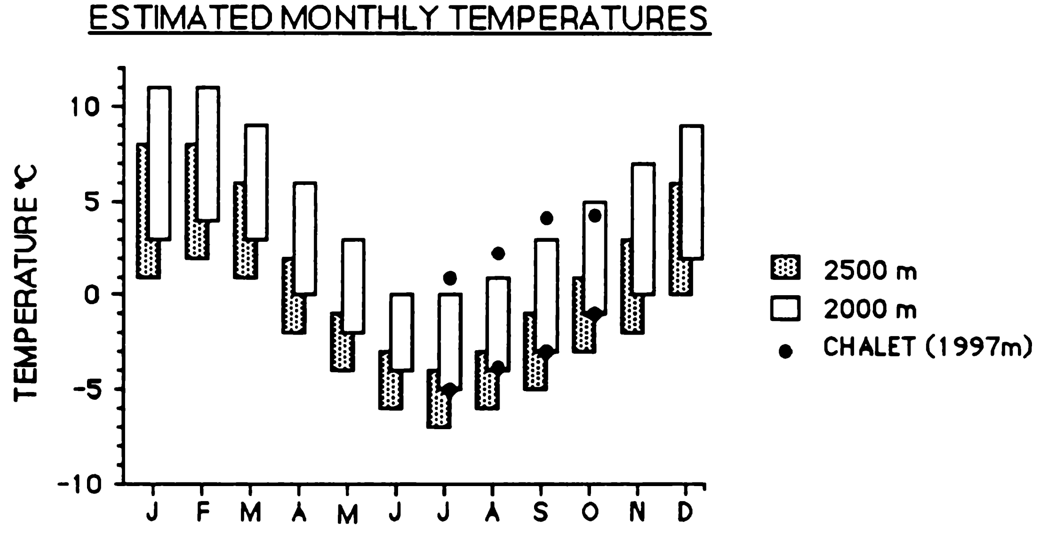


Fig 2.12 Estimated mean daily maxima and minima (°C) at 2000 m and 2500 m (Thompson, 1984) and superimposed data from The Chalet (Ruapehu Alpine Lifts Mountain and Skifield Weather Observations, 1989). The top of the bar represents the mean daily maximum and the bottom, the mean daily minimum.

Thus at the more elevated sites, temperatures remain below freezing for much of the year, with a mean daily range of 7°C in summer and about 3°C in winter. Temperature estimates for the higher elevations (Thompson,1984) show good agreement with recorded data from the Chalet, 1997 metres elevation, for the winter months of 1989. Mean daily maxima and mean daily minima at the Chalet are: July, 1.0, -4.9; August, 2.2, -3.8; September, 4.1, -2.9; and October, 4.3, -1.0, respectively (RAL Mountain and Skifield Weather Obs, 1989) (Fig 2.12).

During the cold months of July, August and September, the majority of the snow falls that forms the skifields. Although a substantial amount may fall in June, as the temperatures would suggest, evaporation is high and snow does not remain on the ground for long. In July, August and September, deposition exceeds evaporation and the snow base builds up. Snowfall data recorded at the Chalet for the years 1984, 1985, 1986, 1987 and 1989 (Fig 2.13) shows the mean maximum snow base occurs in September and attains a depth of about 120 cm. At higher elevations, this trend is expected to extend in both directions, with deposition adding to the snowpack from June to October.

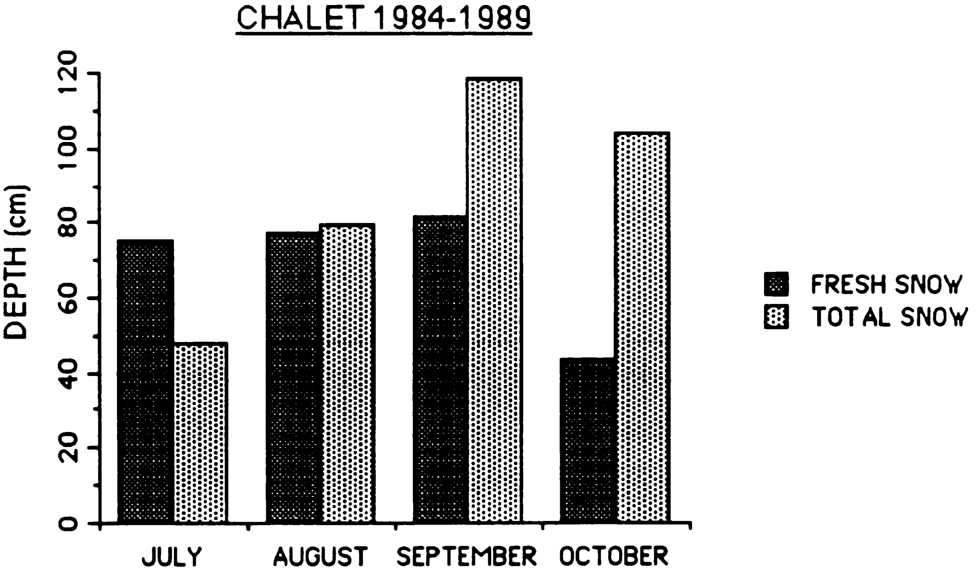


Fig 2.13 Snowfall at the Chalet 1984-1989 (Ruapehu Alpine Lifts Mountain and Skifield Weather Observations,1984-1989). Fresh snow indicates freshly precipitated snow while total snow indicates the snowpack depth, both recorded on a daily basis.

Much blowing snow is evident on Mt Ruapehu with the dominant southerly winds in the Whakapapa area, carrying much of the snow deposited at the higher altitudes to lower levels on the skifield (Heine,1962). Wind-blown snow may give erroneous precipitation values but obviously contributes to the snow pack.

2.2.2 Mt Egmont-Taranaki

Weather

Winds on Mt Egmont-Taranaki are markedly affected by the local terrain, particularly the location relative to the mountain and the orientation to the coast (Thompson,1981). Wind roses for the sites North Egmont (955 m), Stratford Mountain House (846 m) and Stratford Demonstration farm (311 m) are given (Fig 2.14) and show the variation in dominant wind direction on the eastern side of the mountain.

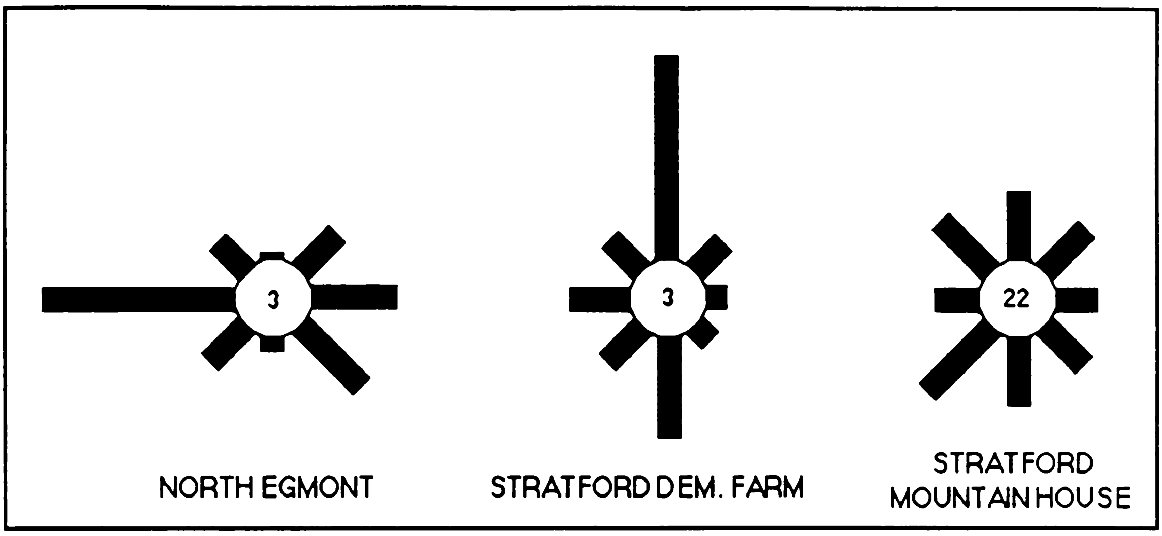


Fig 2.14 Wind roses for North Egmont, 1094 observations, Stratford Demonstration Farm, 1458 observations, and Stratford Mountain House, 1460 observations (NZ Met Obs).

North Egmont, (39°16.3'S 174°5.6'E), has predominant westerlies with the southerly winds deflected by the mountain to a southeasterly direction. Stratford Mountain House has a uniform wind distribution although Stratford Demonstration Farm, on the plain to the east of the mountain, by Stratford township, and Egmont East, (1037 m) above the Mountain House, both have a high proportion of northerly and southerly winds, - the prevailing westerly wind being deflected around the mountain to appear as a northerly flow.

Temperatures on the plains surrounding Mt Egmont-Taranaki are mild and are dominated by the influence of the sea; however, temperatures inland and at higher elevations are much colder with temperatures often below 0°C (Thompson,1981).

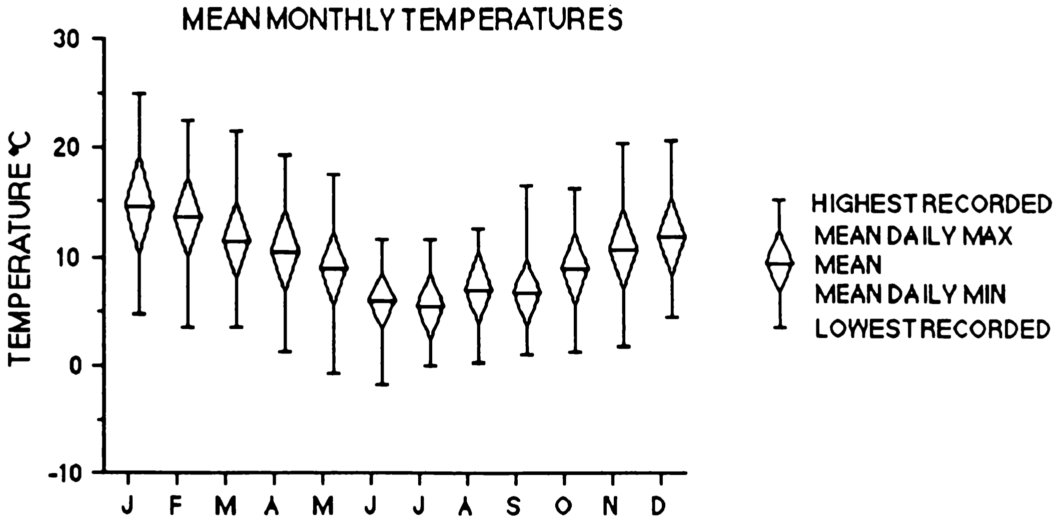


Fig 2.15 Mean monthly temperature data for North Egmont 1987-1988 (NZ Met Obs).

The mean monthly temperature range is about 9°C, with a mean daily temperature range of 10°C in summer and about 5°C in winter at North Egmont, resembling that at a similar altitude on Mt Ruapehu (Fig 2.15). Mean temperatures decrease with altitude by approximately 0.6°C/100m and from this, estimates of temperatures at higher elevations are possible (Table 2.4).

Table 2.4 Estimated mean monthly temperatures (°C), at 1500 m and 2000 m on Mt Egmont-Taranaki from 1966-1973 (Thompson,1981).

Altitude	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
1500m	9.4	9.6	8.9	5.4	3.3	1.5	0.3	1.2	2.2	3.8	6.3	8.1
2000m	6.4	7.7	6.6	3.0	1.2	-0.7	-1.7	-1.0	-0.6	1.1	3.2	4.8

Snowfall at coastal sites like Mt Egmont-Taranaki is highly variable from year to year, usually occurring when a trough of low pressure or a depression over or east of the North Island is present with a strong cold south to southwesterly airstream over the southern districts of the North Island (Thompson,1981). At Stratford Mountain House, there is an average 18 days of snow per year, with 26 days in 1977 and only 7 days in 1973 (Thompson,1981).

Three important factors control the amount and structure of the snowpack on Mt Egmont-Taranaki. These are the variation of precipitation with elevation, the variation of melt with elevation and the elevation of the rain-snow boundary, correlated to the freezing level (Marcus & Moore,1983).

Mean annual rainfall increases with altitude up to an elevation of about 1200 metres. Above this level, precipitation either increases or remains constant (Thompson,1981; Marcus & Moore,1983).

Variation of the freezing level by 1000-2000 metres in rainy weather is a common occurrence at Mt Egmont-Taranaki, suggesting that throughout the winter, most of the mountain experiences temperatures above freezing and the occurrence of rain on snow. This causes much snowmelt and prevents the formation of a deep snowpack (Marcus & Moore,1983). As the elevation increases, however, the temperature rises less frequently above zero and a greater proportion of precipitation falls as snow, therefore increasing the snowpack depth with elevation (Marcus & Moore,1983).

The structure is affected markedly by the rain-snow boundary causing the formation of ice bands. Two conditions give rise to their formation: (1) freezing of condensation onto the snow surface on cold clear nights, caused by radiative cooling of the snow surface followed by advection of a warm humid air mass; and (2) percolation of rain or meltwater down to an impermeable layer in the snowpack where it freezes into the ice matrix. This layer could be a buried surface ice crust, a buried ice sheath, or a boundary between two snow layers. Thick ice bands, up to 10 cm, are indicative of percolation of rain or meltwater after each major snowfall (Marcus & Moore,1983), a feature of the snowpack on Mt Egmont-Taranaki and on Mt Ruapehu.

Site Location

Snow samples were collected from Mt Egmont-Taranaki from two separate locations (Fig 2.16). The first was from the Stratford side in the Manganui Gorge, an area prone to avalanches (Marcus & Moore,1983), where a large avalanche had come to rest. Avalanched snow was still sufficiently clean to sample. Five samples were taken at varying sites across the 30 metre wide avalanche, all at depths greater than 10 cm below the surface, where clean snow was found.

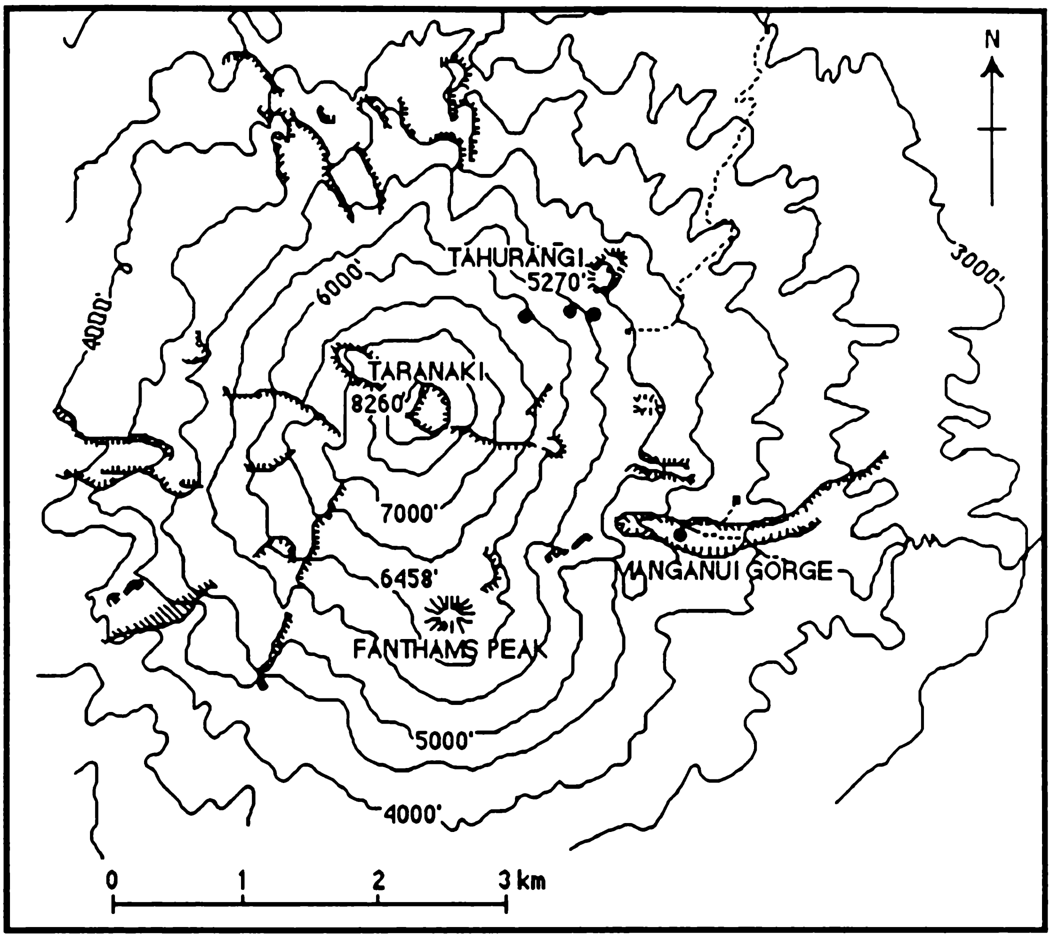


Fig 2.16 Location of sample sites, •, on Mt Egmont-Taranaki. Altitude and spot heights are in feet.

The second location was on the North Egmont side, where a series of samples were taken above the Tahurangi Lodge on the Summit track, at altitudes of 1645 m, 1710 m and 1845 m, corresponding to two positions on the wooden staircase and at the base of Snow Valley.

Surface snow samples were collected using the same techniques as the Mt Ruapehu samples, with the same precautions taken to avoid contamination.

CHAPTER THREE

ANALYTICAL TECHNIQUES

3.1 ANTARCTIC SAMPLES

Samples were transported back from Antarctica packed in polystyrene lined wooden boxes and therefore had thawed on arrival. They were refrigerated at 4°C until analysis, which was carried out within 112 days for sodium and potassium, and 192 days for calcium and magnesium, while the anion determinations had to be repeated, and this occurred within a year of sampling. The initial anion determinations showed the relative insignificance of F^-, Br^-, and PO_4^{3-} (all below the detection limit), and hence, these were not determined in the repeat analyses.

3.1.1 Ion Chromatography

The use of ion chromatography in the detection of trace and ultratrace levels of ions in polar snow and ice is widespread (Legrand et al,1984; Ivey & Davies,1987; Saigne et al,1987). The advantages are high precision, simultaneous detection, and high sensitivity with relatively small volumes (10^{-10}g g^{-1} detection using a 10ml sample). The relatively short elution time of 12 minutes per sample is another advantage.

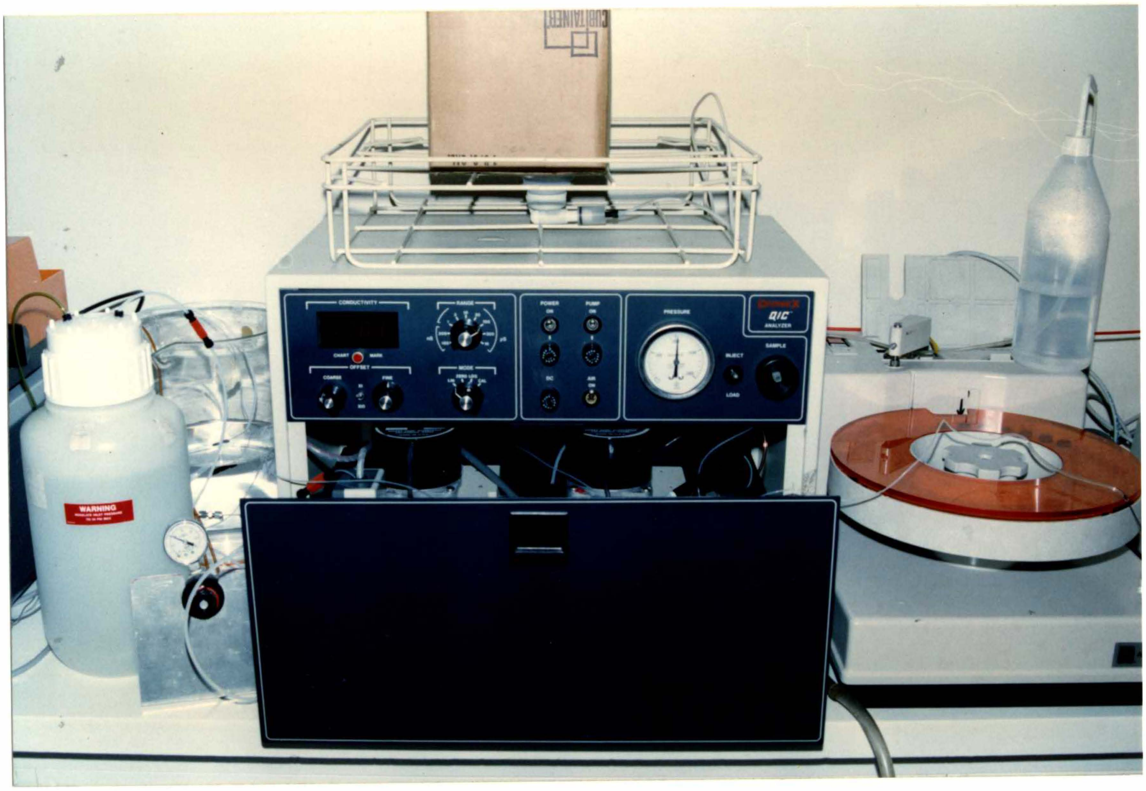


Fig 3.1 The Dionex QIC II

An ion chromatograph typically consists of an eluent reservoir, a pump, a sample inlet, a separator column, with guard columns often preceding it, a suppressor device, a detection cell and a chart recorder often linked to a computer. The ion chromatograph used in this study is a Dionex QIC II IonChrom Analyzer (Fig 3.1), located at Chemistry Division, DSIR, Gracefield, Lower Hutt.

The schematic diagram (Fig 3.2) represents the flow of the sample. Initially eluent from the eluent reservoir flows through a bubble trap, which prevents air entering the pump and columns, and is pumped into the injection valve. From the injection valve the eluent enters the separator column, the suppressor device, and then the flow-through conductivity cell. The sample is meanwhile loaded via a separate sample pump into the sample loop or concentrator column. There is provision for syringe loading of the system although loading was by direct aspiration from the sample containers. The sample is then switched into the eluent flow stream on the inject cycle of the system, and the sample is deposited on the top of the separation column. From here it is carried with the eluent to the suppressor and then to the conductivity cell. The regenerant flows directly to the suppressor and out to waste (Dionex Operators Manual,1984).

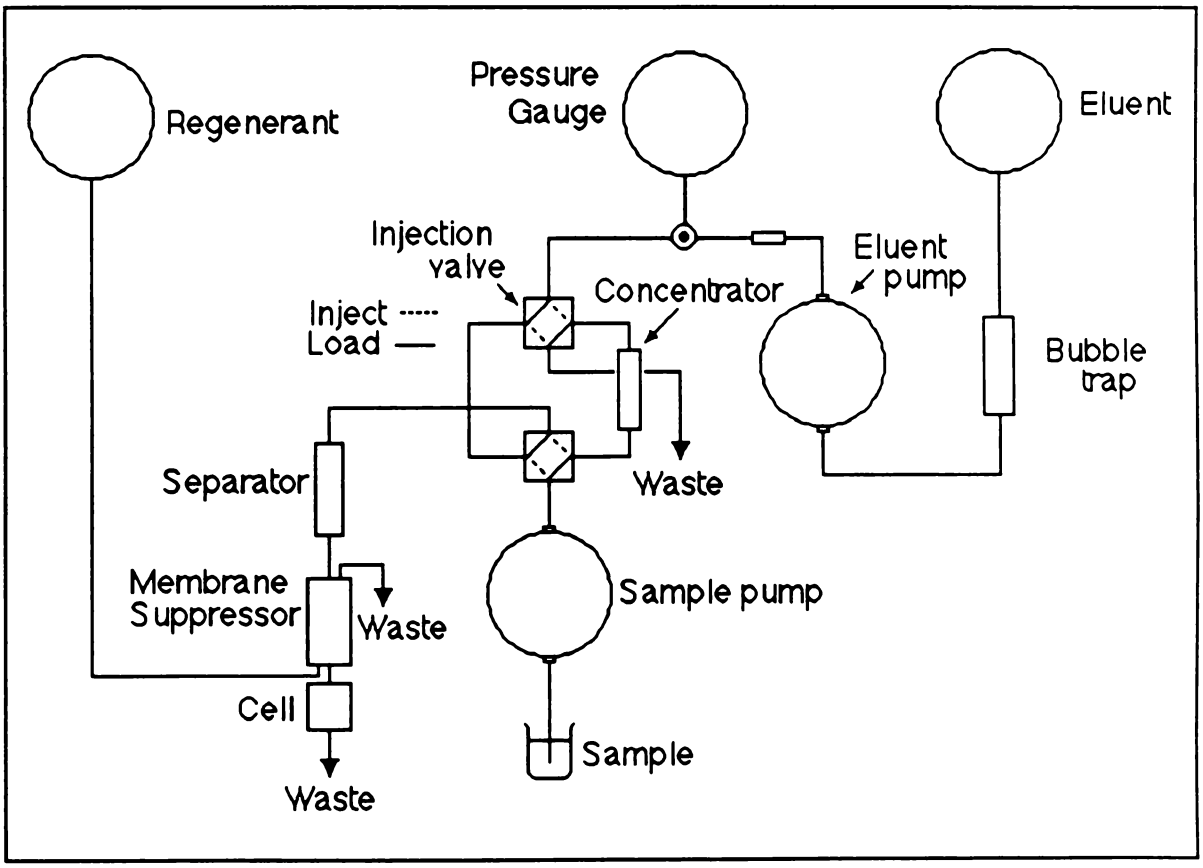


Fig 3.2 A schematic diagram of fluid flow (Dionex Operators Manual,1984).

The Eluent

The choice of eluents for suppressor use must meet 2 requirements: (1) it must be able to displace anionic species from the separator column and (2) it must undergo an exchange reaction in the suppressor to form water or a weakly ionized acid with a low conductivity (Gjerde & Fritz,1987). The eluent used in this study is a weak bicarbonate-carbonate eluent. This is a commonly used eluent as it separates both monovalent and divalent anions in a single injection in a few minutes and the strength of the eluent is easily modified by altering the ratio of HCO_3^-/CO_3^{2-} (Dionex Operators Manual,1984). The eluent concentration was 0.75 mM HCO_3^- and 2.2 mM CO_3^{2-} which was made by dissolving 0.25g reagent grade $NaHCO_3$ and 0.933g Na_2CO_3 in 4 litres of deionised water. The eluent was made directly in a collapsible 4 litre plastic reservoir. The separation obtained using this eluent initially gave retention times of about 1.87 minutes F^-, 2.84 min Cl^-, 5.34 min Br^-, 6.06 min NO_3^-, 8.91 min PO_4^{3-}, and 11.15 min SO_4^{2-}, but this was dependent on the state of the separator columns, and as these deteriorated with age, the retention times became shorter.

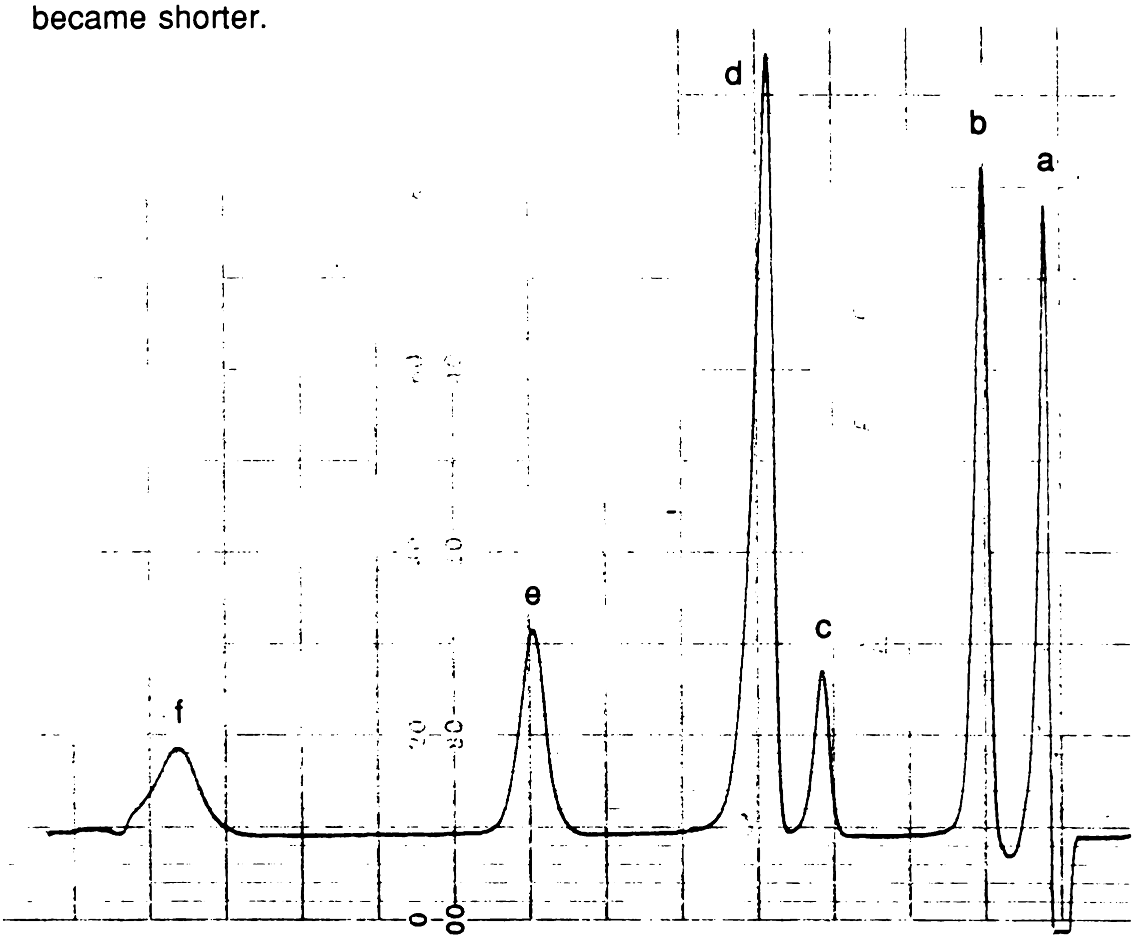


Fig 3.3 Sample chromatogram showing the relative position of a) fluoride, b) chloride, c) bromide, d) nitrate, e) phosphate and f) sulphate.

Concentrator Column

The standard sample loop on the Dionex QIC II has a 50 µl volume. This volume is insufficient to detect the low levels of anions in the Antarctic snows, so initially the TAC-1 concentrator was used. Concentrator columns are short separator columns whose function is to strip ions from a large measured volume of sample and inject them as a sample, effectively lowering the detection limit by 1-2 orders of magnitude thereby allowing routine analysis, at the ppb (ng/g) level. However, there are limitations to their use. The main limitation appropriate to this study is the capacity of concentrator columns.

As with all exchange resins, the concentrator column has a finite capacity. If this is exceeded, the stripping of ions from water becomes non-quantitative. This dynamic capacity of the concentrator is estimated to be about 50% of the total static capacity as the ions are flowing and therefore have less chance to interact with the resin. This corresponds to about 6 µeq and it is important that the column should not be loaded beyond this level (Dionex Tech Note 8R). When the concentration is close to or exceeds the dynamic capacity, sulphate or nitrate, owing to their high affinity for the resin, can act as an eluent , displacing chloride from the resin. Therefore, it may be difficult to analyse ng/g levels of chloride in the presence of µg/g levels of other anions (Gjerde & Fritz,1987).

Although dynamic capacity was likely not exceeded in the analyses of the samples, the calibration using a 50 ng/g standard is certain to have exceeded the capacity, giving inaccurate results. Hence, the analyses were repeated using a large sample loop (2 ml). Large sample loops (5-10 ml) are commonly used in preference to concentrator columns in the detection of ultratrace ions in polar snow and ice (Legrand et al,1984; Ivey & Davies,1987).

The use of a large sample loop also has its limitations with respect to the size of the 'water dip'. The 'water dip' (Fig 3.3) is a negative deflection at the front of the chromatogram caused by the water in the sample having a lower conductivity than the weakly dissociated H_2CO_3 (Dionex Manual,1984). The shape, size, and elution time of the water dip is dependent on the pH of the solution, the size of the suppressor column, and the volume of sample injected (Dionex Tech Note 8R). By altering the concentration of the eluent and therefore the pH, the chloride peak fell after the 'water dip' enabling quantitative determination.

Guard Column

Guard columns are used primarily as a protection for the more expensive analytical columns they precede. They are usually short versions of the analytical columns, and act as filters for any particulate matter from the eluent or sample, and traps for the strongly retained ions which 'poison' the column. The guard column on the instrument used is an NG-1, an MPIC guard column appropriate for use where the sample matrix may contain large hydrophobic organic contaminants such as surfactants, humic acids, aromatic organics or very high affinity ions such as ClO_4^-, or metal cyanides (Dionex Tech Note 2R).

Separation Column

The Dionex separation columns utilize a binary pellicular anion exchange resin. This surpasses the conventional ion-exchange resins both in its speed of separation and in column efficiency (Gjerde & Fritz,1987). The core of the resin particle is a polystyrene divinylbenzene. Surrounding this is a sulphonated layer which is reacted with an anion exchange material consisting of 0.5 µm latex particles. The latex particles bond to the sulphonated layer by electrostatic attraction and form another thin shell. Owing to the large number of ionic interaction sites between the latex and the resin, the process is essentially an irreversible one and hence the resin is very stable (MacDonald, 1985). The separator used is an HPIC-ASA4, a high performance separator. This separates the anions as they compete with the eluent ions for the functional groups on the ion exchange resin by the equilibrium reaction:

$$\boxed{\underline{(\text{Solute})^-} + \underline{(\text{Eluent})^-}.\text{NR4-Resin}^+ \ <==> \ \underline{(\text{Solute})^-}.\text{NR4-Resin}^+ + \underline{(\text{Eluent})^-}}$$

The counterion in this case is HCO_3^-. The distribution coefficient for the above reaction depends on ionic charge, ionic size, ionic strength, pH and resin type. In general, monovalent ions elute before divalent, before trivalent. Ions with large ionic radii are strongly attracted to the resin so fluoride elutes first, then chloride, then bromide and lastly iodide. The choice of eluents is important as this dictates the relative position of the eluted ions. For example, by changing the ratio of the HCO_3^-/CO_3^{2-} in the eluent and thus lowering the pH, phosphate will elute before the less strongly retained divalent SO_4^{2-} (Gjerde & Fritz,1987). Essentially, the higher the equilibrium constant the stronger is the affinity of the ion and the longer will be its retention time.

Suppressor Unit

The suppressor unit contains a strongly acidic cation exchange membrane in the hydronium form. The eluent flowing through the suppressor is neutralized and its conductivity reduced. At the same time, sample anions with pK_a values smaller than 7 are converted to ionized highly conductive acids. This technique allows the detection of anions in a low background conductivity (Gjerde & Fritz,1987).

Consider a system where a sample solution of chloride, nitrate and sulphate (potassium salts) is injected into a stream of HCO_3^-/CO_3^{2-} eluent. The ions are separated on the analytical column and exit at different times. As the solution enters the suppressor two important reactions occur:

(1) Eluent: $Na_2CO_3 + 2R\text{-}SO_3^-.H^+ \text{-->} 2R\text{-}SO_3^-.Na^+ + H_2CO_3$

$NaHCO_3 + R\text{-}SO_3^-.H^+ \text{-->} R\text{-}SO_3^-.Na^+ + H_2CO_3$

(2) Sample ions: $K^+Cl^-, K^+NO_3^-, K_2{}^+SO_4^{2-} + R\text{-}SO_3^-.H^+ \text{-->}$

$R\text{-}SO_3^-.K^+ + HCl + HNO_3 + H_2SO_4$

The highly ionized and conducting acids enter the conductivity cell in a stream of weakly conducting carbonic acid. This not only reduces background conductivity but also enhances the detection sensitivity (Dionex Operators Manual,1984).

Modern suppressors typically consist of ion-exchange membranes. The column effluent passes between the sulphonated polyethylene sheets and while the eluent and sample anions do not penetrate the membranes owing to Donnan exclusion forces, the cations do (Fig 3.4). On both sides of the unit the 0.025 N H_2SO_4 regenerant flow replaces the converted Na_2SO_4 and carries the cationic salts to waste. The suppressor is constantly regenerated and needs no downtime and can be operated for indefinite periods of time (Gjerde & Fritz,1987). Another advantage over the packed bed suppressor is that the movement of the 'water dip' is eliminated.

The highly efficient AMMS-1 membrane suppressor is an ultra high capacity dynamic suppressor that allows suppression of concentrated eluent to a background conductivity of less than 18-24 µS (Gjerde & Fritz,1987). The background conductivity is dependent on the flow rate and composition of both the eluent and regenerant. With eluent flow rates of approximately 2 ml/min the optimum conditions seem to apply (Dionex Tech Note 14R).

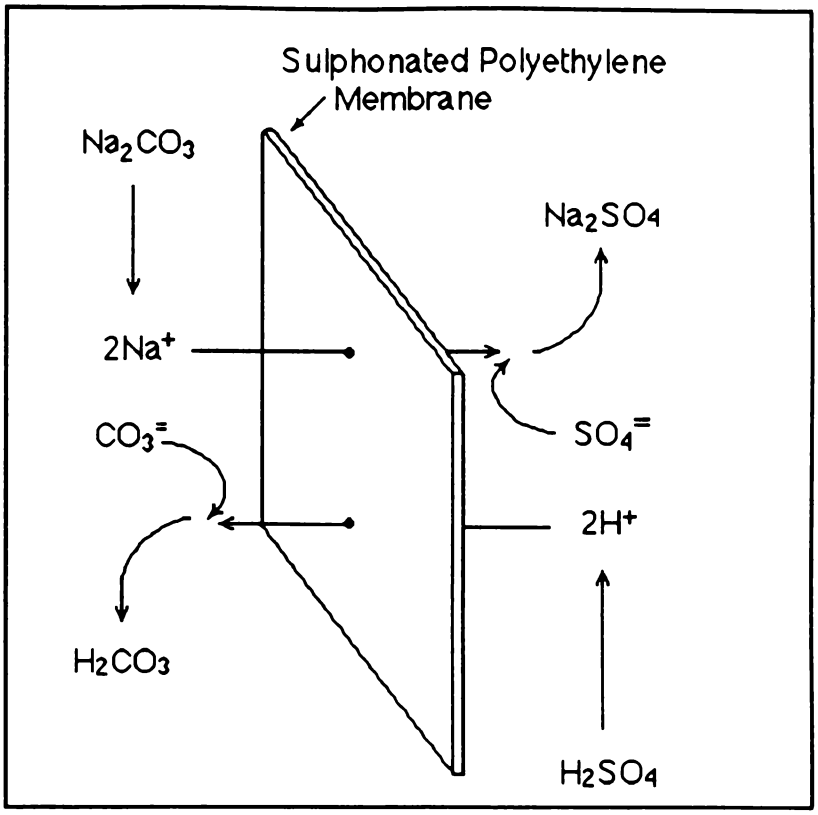


Fig 3.4 Theory of operation of the micromembrane suppressor (adapted from Gjerde &Fritz,1987).

Conductivity Detection

Conductance increases with total ionic concentration. Deviations can occur with changes in temperature or equilibration processes in the analysed solution, especially the formation of ion-pairs in solution affecting the mobility of the ions (Dionex Tech Note 9R). The use of a suppressor device tends to minimize these problems.

Standards

The samples were analysed for chloride, nitrate, and sulphate, assuming that these would be within a detectable range.

1000 μg/g stock solutions containing 2.1028 g KCl, 7.2175 g KNO_3, and 1.8156 g K_2SO_4 were used to make up standards. Both stock solutions and standards were made using deionised water directly from the deionising unit as the reservoir tanks have been soaked in dilute HNO_3, and NO_3^- tends to leach from the plastic.

A mixed working standard of 500 ng/g SO_4^{2-}, 100 ng/g Cl^- and 100 ng/g NO_3^-, and 20% and 40% dilutions thereof, were used to calibrate the Dionex as the calibration curve below 500 ng/g SO_4^{2-} and 100 ng/g Cl^- and NO_3^- was found to be linear. Fresh standards were made every day to avoid deterioration of the standard at the low ng/g levels, although stored correctly, the standards are claimed to be stable for up to 8 days (Dionex Technical Note 8R). All samples were aspirated directly into the Dionex without filtering and were measured and calculated from the trace of the chart recorder used.

3.1.2 Atomic Absorption Spectrophotometry (AAS)

Initially cation analysis was attempted on the samples with the Dionex Ion Chromatograph, utilising the cation separation columns and the associated concentration column. However, difficulty was encountered in choosing the concentration of the eluent to elute the species within an acceptable time. Instead, the samples were concentrated by a factor of five times using the Dionex TCC-1 cation concentrator column, and then were measured by AAS, adjusting for the eluent. The elution time of 1.5 minutes using a 26 mM HCl eluent proved later to be insufficient to elute calcium and magnesium and so these were subsequently analysed using the unconcentrated samples. The concentrated samples, stored in 8 ml Nalgene vials, gave results within ± 5% of expected concentrations for sodium and potassium.

1000 µg/g stock solutions were made using 1.002 g Mg ribbon, 2.492 g $CaCO_3$, 1.905 g KCl and 2.548 g NaCl. The stocks were subsequently diluted to make mixed standards of 100 & 200 ng/g which were also concentrated to test the accuracy of the concentration method.

Potassium, calcium and magnesium were analysed using a Perkin-Elmer 305B atomic absorption spectrophotometer using emission (AES) for calcium and potassium and AAS for magnesium, while sodium was analysed using a Hitachi Z6000 Polarized Zeeman AA in the emission mode.

3.2 NEW ZEALAND SAMPLES

3.2.1 Ion Chromatography

Snow samples were left to thaw, and stored at room temperature. Analysis of the anions took place on completion of the cation analyses (3.2.2) and were performed on the Dionex. This occurred within 20 days of collection with the exception of the 10/1/90 samples which were completed within 50 days.

Owing to the higher concentrations of the dominant ions in the New Zealand snow samples compared to the Antarctic samples, the concentrator column was not used although a larger sample loop of 0.62ml was used (usually 50 µl), and the autosampler and integrator were used. These consist of a Technicon® AutoAnalyzer® II and a Spectraphysics SP4270 integrator. This had the advantage of saving time and replaced manual measuring techniques with computer integrated measurements. This was ideal for all but the chloride peaks, as the computation of the baseline made these concentrations greater than normal, due to the negative 'water dip', accentuated by the larger sample loop. This necessitated measurement of the chloride peaks by hand.

The anion stock solutions mentioned previously, were used to make a standard of 10 µg/g Cl^-, 10 µg/g SO_4^{2-}, 1.1 µg/g F^-, and 0.1 µg/g Br^-, NO_3^- and PO_4^{3-}. A 50% dilution of this standard was used to calibrate the Dionex and dilutions of 20%, 10% & 5% were used to check the calibration. Blanks were also repeated for detection limit determination.

3.2.2 Atomic Absorption Spectrophotometry (AAS)

Analysis of the cations took place within 8 days of collection, with the exception of the samples collected on 10/1/90 which were analysed within 3 weeks.

A Phillips Pye Unicam spectrophotometer was used for analyses using AAS for all elements. In retrospect, this may not have been ideal, for under AES sensitivity might have been enhanced.

Generally, samples were aspirated into the flame directly without filtering or dilution, with the exception of the ice core samples containing rock material. Where filtration was necessary, the filter paper was 'rinsed' in the sample solution, before the remainder of the sample was filtered to ensure that no contaminants from the filter paper were introduced.

Calibration was carried out using working standards of 0, 50, 100, 250, 500, & 1000 ng/g, made from the stock solutions previously mentioned. These same standards were used as 'dummy' standards throughout the run. A low concentration sample was repeatedly analysed in order to calculate detection limits for each element.

3.2.3 Isotopic Analysis

The measurement of isotopes in snow, firn and ice cores in the polar regions has for many years been used to determine age and net accumulation, and in more recent years has been used to elucidate climatic information, especially temperature (Müller et al,1977). In temperate regions, however, the interpretation of isotopic data is more complicated, with problems of percolation of meltwater, and disturbance of snow deposits by high winds causing an overall smoothing of the isotope variations (Schotterer et al,1977). In a dry snow area, signatures remain extensively unaltered, while in the percolation zones, deterioration of the signature occurs over a number of decades. In the soaked snow zone profiles can become homogenised during a single melt season (Krouse et al,1977). Snows from the Summit Plateau of Mt Ruapehu are expected to fall within the percolation zone and should therefore retain an isotopic signature for several seasons.

The isotopic signature is affected by two factors: the average temperature during precipitation, and the distance from the coast (Moser et al, 1973). It does not reflect the signature of the water from which it evaporates, as mixing of locally evaporated water and fractionation of the source water occurs (Schriber et al,1977).

Isotope fractionation is the depletion or enrichment of the heavy isotopes and it occurs in many processes. During evaporation liquid water becomes progressively enriched with the heavy isotopes, and in condensing and freezing, the heavy isotopes are enriched in the water relative to the water vapour. The lower the temperature of the phase transformation, the greater the fractionation (temperature effect). However, this is small compared to the progressive enrichment due to progressive removal of water (amount effect). In a body of water vapour, each removal of water by precipitation removes the heavier isotopes preferentially so that the remaining vapour is progressively depleted in ^{18}O, resulting in more negative δ values (Dansgaard,1964). Consequently, as distance from the coast and altitude increases, the heavy isotope becomes depleted in precipitation (Moser et al, 1973). A seasonal effect arises, with more precipitation and lower temperatures in winter resulting in more negative $\delta^{18}O$ peaks in winter snow layers. Dansgaard (1964) found the temperature relationship to be:

$$\boxed{(d\delta^{18}O/dt) \approx 0.70\ ‰\ /^{\circ}C}$$

It is expected that an annual range of ~ 8 ‰ (Fig 2.11) might be evident in the ice cores taken from Mt Ruapehu, where a continuous depth profile was sampled.

It follows that during the evolution of a seasonal snowpack, progressive enrichment of the heavier isotopes through evaporation, and through fractionation and exchange with percolating melt water and rain water, will also be evident (Arnason et al, 1973; Krouse & Smith,1973; Martinec et al,1977). This is caused by recrystallisation and isotopic exchange between the liquid and solid phase, and may result in an overall smoothing of the isotopic signature (Arnason et al, 1973).

The method used to measure the $^{18}O/^{16}O$ ratio of the samples was the CO_2 equilibration method (Epstein & Mayeda,1953) and described in detail by Dunbar (1980), in which a known mass of CO_2 is added to a 10ml sample of water, then left to equilibrate at 25°C.

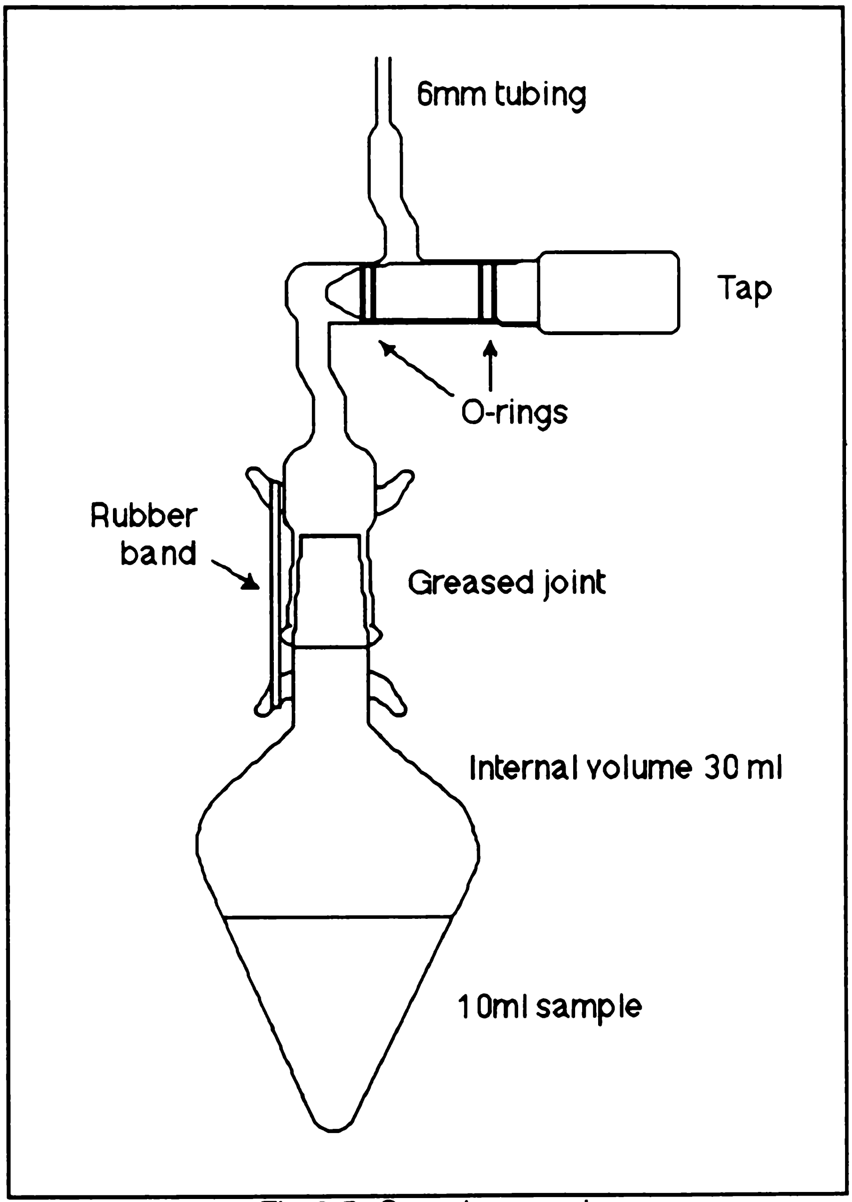


Fig 3.5 Sample vessel.

Equilibration of the oxygen isotopes is reached by the following equation:

$$\boxed{C^{16}O_2 + H_2{}^{18}O \iff C^{16}O^{18}O + H_2{}^{16}O}$$

after which the carbon dioxide reflects the $\delta^{18}O$ ratio of the sample water. Complete isotopic equilibrium should be reached after 18 hours (Dunbar,1980), although the samples were left in the water bath for at least 44 hours.

Sample Preparation

A 10ml sample was pipetted into the sample vessel (Fig 3.5), and with the tap greased in place was fitted onto the vacuum line (Fig 3.6).

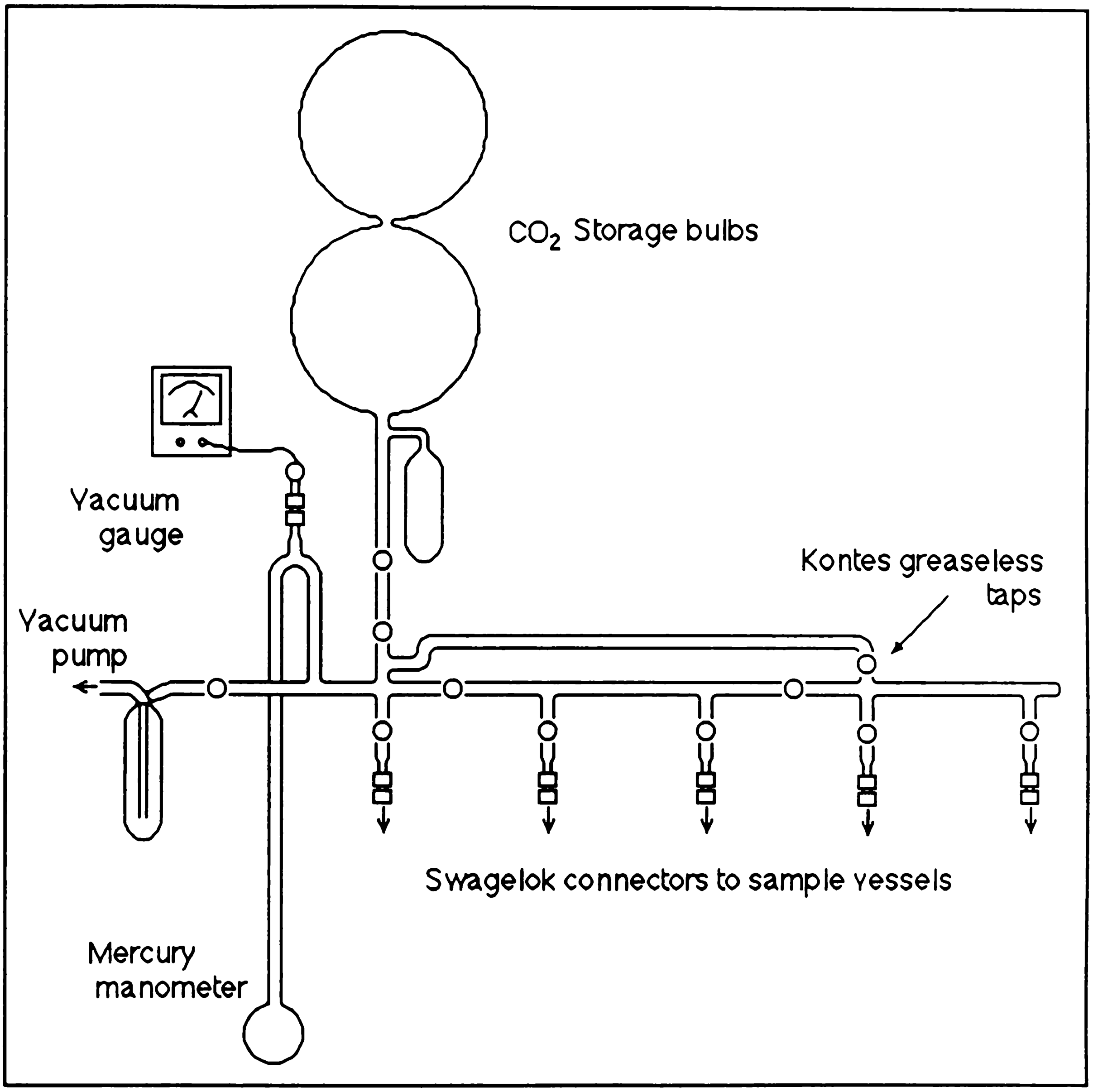


Fig 3.6 Vacuum line 1.

The sample was frozen down with liquid nitrogen for 10 minutes, and with all taps open, the air space was evacuated. With the taps closed, the sample was thawed, in order to release any gas trapped in the solid matrix into the evacuated headspace. The sample was then refrozen and the air pumped off again. Degassing twice was found to be sufficient for water samples (Dunbar, 1980).

After degassing, 3 aliquots (~ 9 cm^3) of CO_2 of a known isotopic composition were added to the sample vessel from a 10 litre storage bulb on the vacuum line. Addition of the CO_2 was carried out while the samples remained frozen, after which the samples were immediately evacuated to remove any pressure remaining in the line, caused by a slow leak or gas other than CO_2 in the storage bulbs.

Sample vessels were then removed from the line and equilibrated in a 25°C waterbath for 48 hours, submerged above the tap to ensure complete partitioning (Dunbar,1980). The samples were removed from the waterbath and transferred to the second vacuum line (Fig 3.7) for purification of the CO_2.

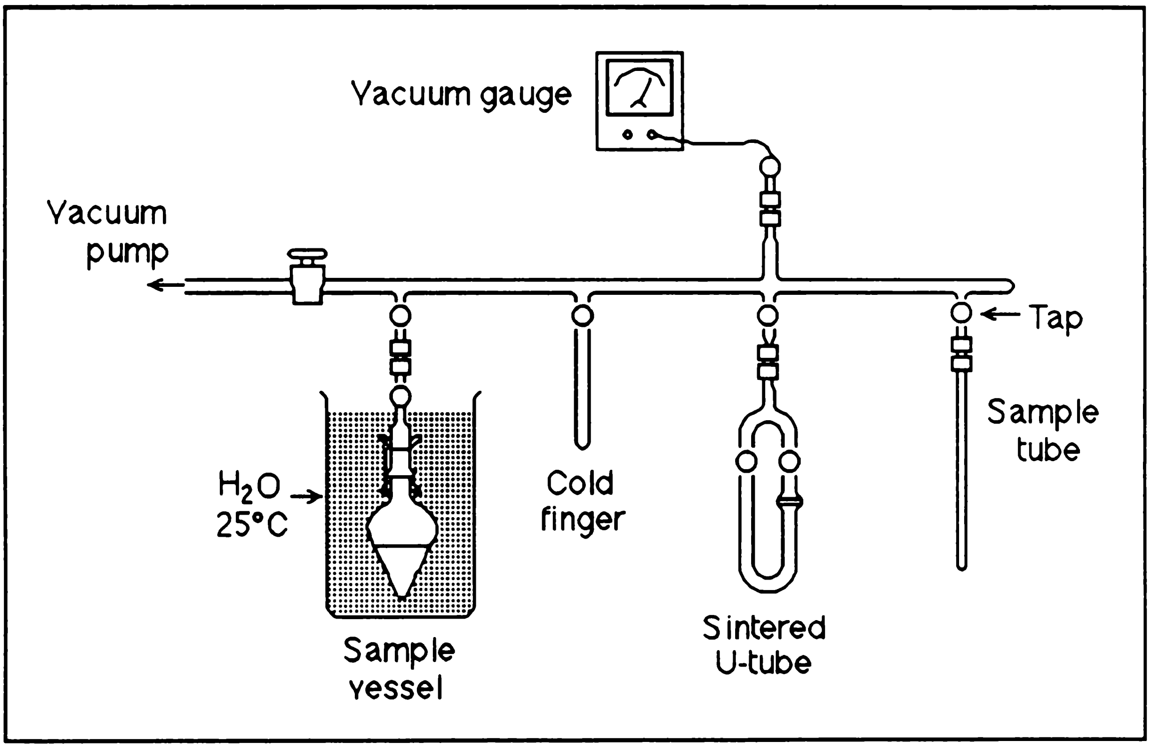


Fig 3.7 Vacuum line 2.

This consisted of a wet slug of CO_2 being released from the sample vessel and frozen with liquid nitrogen into the cold finger. The liquid nitrogen was then replaced with a 50:50 ethanol: isopropanol slush bath (-95°C) and the liquid nitrogen was placed over the sintered U-tube, the right tap of which was shut.

This allowed the CO_2 to distill off the cold finger and condense into the U-tube. Once the pressure had dropped, the cold finger tap and the left tap of the U-tube was shut, and the right, sintered side of the U-tube was opened. With the liquid nitrogen dewar still in place the line was evacuated. The liquid nitrogen was then moved onto the sample tube and replaced by the slush bath, allowing the passage of the purified CO_2 through the sinter. Once the pressure had fallen the sample tube was sealed off with a gas torch at the constriction point. CO_2 samples could be stored in these sealed glass tubes for many weeks without any change in the $\delta^{18}O$ values (Grinsted,1977).

Isotopic Measurement

The $\delta^{18}O$ ratios were measured on an Isotope Micromass 602E mass spectrometer. This is a double collector 6.2cm radius, 90° deflection, permanent magnet instrument. Routinely, an absolute accuracy to 95% confidence, of better than 0.1‰ overall enrichment for ^{18}O and ^{13}C is attained (Bridger et al,1973).

The inlet system is a twin type where the sample is fitted to one side and the reference gas, Waikato Limestone Standard (WLS), is fed into the other. Within a contained bellows the sample tube is broken and the gas is fed through a stainless steel capillary to the changeover valve. An identical capillary carries the reference to the changeover valve. While one gas flows to the mass spectrometer, the other flows to waste, and a changeover alternates this. A series of 12 changeovers and readings are taken in each run, with the pressures balanced as nearly as possible, from which the delta values (δ), are calculated and displayed on a digital recorder. This nomenclature is used as it is possible to determine the difference in the ratio of $^{18}O/^{16}O$ between a sample and a standard to 1 in 10^5, whereas it is very difficult to measure absolute ratios to better than 1 in 10^3. Thus, $\delta^{18}O$ is defined as :

$$\left(\frac{(^{18}O/^{16}O)_{sample} - (^{18}O/^{16}O)_{reference}}{(^{18}O/^{16}O)_{reference}} \right) X\ 1000$$

with units of per mil (‰).

The internationally accepted reference for analysis of water samples is SMOW (Standard Mean Ocean Water), distributed by IAEA (Vienna), and for ^{13}C is PDB (Peedee Belemnite), which in turn is calibrated against secondary standards distributed by US National Bureau of Standards.

CHAPTER FOUR

RESULTS AND INTERPRETATIONS

4.1 ANTARCTIC SAMPLES

4.1.1 Collection of Data

For the anions, peak heights were measured from the chromatogram, calculated from the calibration curve, and the raw data (with the exception of NO_3^- concentrations), were adjusted for the concentrations of the blanks (Table 4.1). The concentration of all the anions in both the blanks had increased over the year between the intitial and repeat analyses, and this is an effect either of storage or the initial inaccurate analyses. The initial blank concentrations (measured within 50 days of collection), averaged 45 ng/g NO_3^- and were below the detection limit for Cl^- and SO_4^{2-}.

NO_3^- values were not adjusted for the blank, as in both the initial and repeat analyses, the blank concentrations were higher than many of the sample concentrations. If this results from ineffective washing of the sample pottles and the subsequent desorption of acid, then the concentrations of NO_3^- (Appendix I) can only be regarded as maximum values.

Sodium and potassium concentrations were read directly from the AAS printout and were adjusted for the eluent and divided by the concentration factor before being adjusted for the blank. Calcium and magnesium analyses did not require a concentration step and so required only the blank adjustment.

Discrepancies between the two blank concentrations for Na^+, Cl^- and SO_4^{2-} are significant (Table 4.1), although the cause is unknown. The concentration of the cations in the blanks, measured within 6 months of collection, are significantly lower than the anions measured within 15 months.

Table 4.1 Blank concentrations and detection coefficients and limits for Antarctic snow samples from the repeat analyses. 34 and 35 refer to pottle numbers.

Sample No	Na^+ ng/g	K^+ ng/g	Ca^{2+} ng/g	Mg^{2+} ng/g	Cl^- ng/g	NO_3^- ng/g	SO_4^{2-} ng/g
Blank (34)	-	-	-	-	187	139	24
Blank (35)	20	-	-	-	108	135	-
Detection Coeff.	1	12	13	4	8	4	5
Detection Limit	2	25	25	8	16	7	10

The detection coefficient and detection limit are statistical parameters, approved by the Testing Laboratory Registration Council, below which, concentrations should not be accepted (Table 4.1).

Detection limits are calculated from the difference between replicate analyses of low concentration samples or blanks.

$$\text{The coefficient of detection} = \frac{t \,.\, \sqrt{2} \,.\, S_R}{\sqrt{n}}$$

$$\text{and the limit of detection} = \frac{2t \,.\, \sqrt{2} \,.\, S_R}{\sqrt{n}}$$

where n = number of analyses for each sample

t = single-sided t-factor for 5% probability (95% confidence level)

S_R = standard deviation of results

$$S_R^2 = \frac{1}{2p} \sum_{i=1}^{p} [y_1 - y_2]^2$$

where $[y_1 - y_2]$ = the difference between duplicates

p = number of replicates.

As the t-factor is dependent on the number of analyses, with fewer data the factor increases and the detection limit increases. In the calculation of the detection limits for the cations (Appendix I), few duplicate analyses were available and the limits are not as low as could be expected. Concentrations less than the detection limit are represented by < detection limit, while concentrations less than the coefficient of detection are represented by a dash (-). For example, owing to the small number of duplicates, the detection limit for potassium is 25 ng/g, so the 4 concentrations which exceeded 12 ng/g but were less than 25 ng/g are recorded as <25, while the remainder are recorded as a dash (Appendix I).

Calculation of terms

Concentrations of the respective elements in polar precipitation are given in Appendix I. In addition, the total ionic charge for cations (ΣC), and for anions (ΣA) are given in units of μeq l^{-1}, derived from division of the ionic charge by the molecular weight Also shown are excess chloride [Cl]ex, and excess sulphate $[SO_4]$ex concentrations in μg/g (Section 1.3.1).

Where pH is not known and all the dominant cations and anions have been determined, the imbalance between ΣC and ΣA approximates pH:

$$\boxed{H^+ = \Sigma C + \Sigma A}$$

Ca concentrations are likely to have been overestimated, due to very low sensitivity, resulting in the cation charge exceeding the anion charge in all but the samples where Ca concentrations are high - the significance of the low sensitivity decreases with increasing concentration. As pH rarely exceeds 6.1 in New Zealand precipitation, this approximation is not valid for these analyses.

pH can also estimated from the total concentration of anions which are theoretically linked to protons in the mineral acids:

$$\boxed{H^+ = [Cl]ex + [NO_3] + [SO_4]ex}$$

This calculated pH agrees well with measured values of pH in other polar precipitation studies (Palais & Legrand,1985; Legrand & Delmas,1985), and as it involves only the acid component, calculated from Na^+, Cl^-, NO_3^- and SO_4^{2-} (Section 1.3.1), it is independent of the Ca concentration.
As pH was not measured in any of the snow samples, this approximation in $\mu eq\ l^{-1}$, is given, related by the equation: $pH = -\log_{10} [H^+]$ (Table 4.2).

Table 4.2 Equivalent pH values derived from the sum of the mineral acids, displayed as $[H^+]$.

pH	$[H^+]$ $\mu eq\ l^{-1}$
7.0	0.1
6.5	0.3
6.0	1
5.5	3.16
5.0	10
4.5	31.6
4.0	100
3.5	316
3.0	1000
2.5	3160

4.1.2 Antarctic Snows

The 4.5 metre deep snowpit contained 33 alternating layers of coarse grained, low density firn and fine grained high density ice layers (Fig 4.1) which increased in density with depth. It was initially presumed that the ice layers were annual layers; however, after consideration of the δD content of sections of the profile (Fig 2.3) and the seasonal variations of the Cl/Na ratio, it is suggested that they are probably storm events, occurring several times a year, superimposed on the annual layers.

The comparison of δD and the Cl/Na variations, although somewhat offset, show some agreement with each other, and are consistent with, or greater than the annual δD variations in the Vostok core of <20‰ (Jouzel et al,1987; Legrand et al, 1988) and in the South Pole core of ~50‰ (Jouzel et al,1983). The Cl/Na ratio may indicate that between five and ten years accumulation are represented in this profile, giving an accumulation rate of between 46 cm and 92 cm/year.

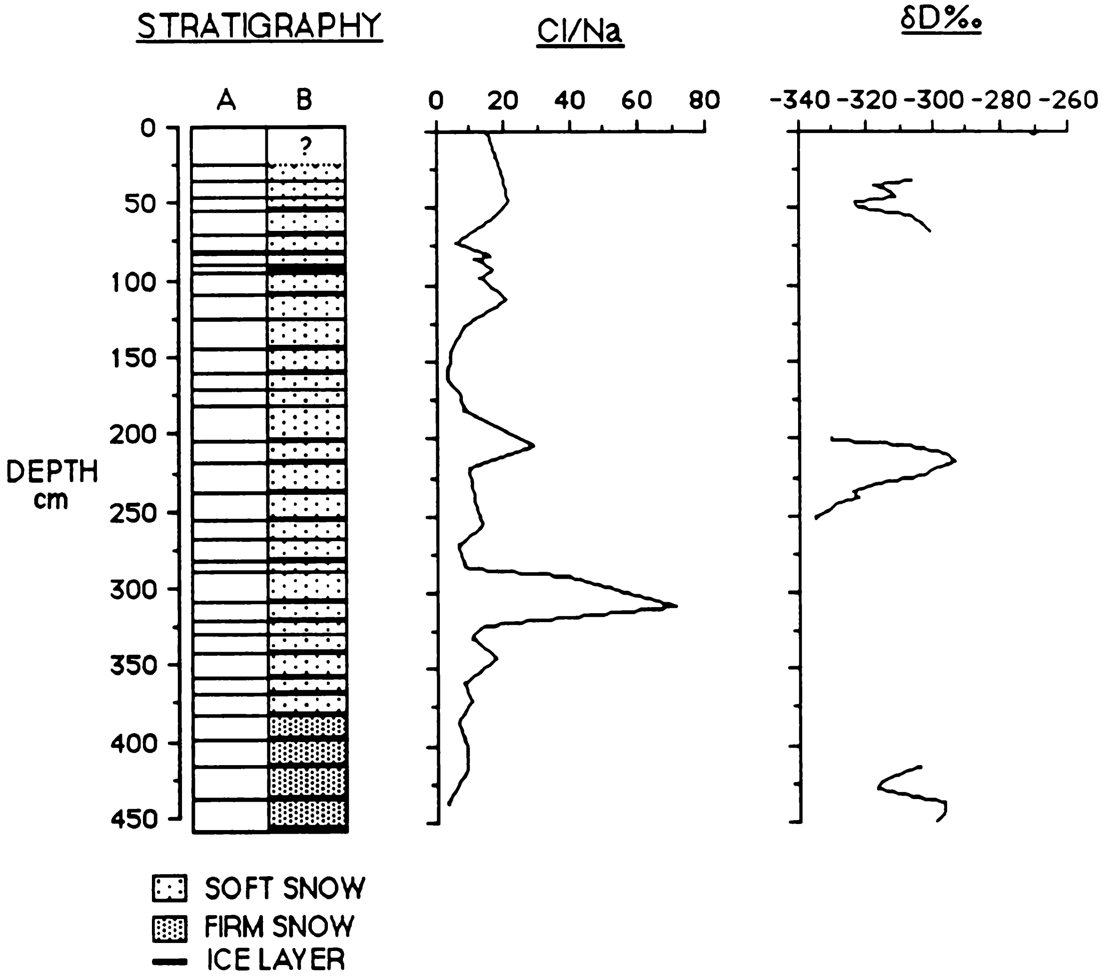


Fig 4.1 Antarctic snow stratigraphy, showing the alternating coarse-fine bands, with the Cl/Na ratio and the δD isotope variations in the segments analysed.

The calculated pH of the snow profile varies around 4.96 and is most closely correlated to the fluctuations of $[Cl^-]$ (Fig 4.2) with some influence from $[SO_4^{2-}]$(Fig 4.3). The close correlation between pH and [Cl] (Fig 4.2) suggests that atmospheric HCl is the dominant source of acidity at this site, with relative contributions to the bulk acidity of on average 74% HCl, 16% HNO_3 and 10% H_2SO_4. The very high [Cl]ex contrasts with snow from the interior, where HNO_3 and H_2SO_4 are in almost equal proportions while HCl contributes only ~15% (Legrand & Delmas, 1984), and to the coastal regions where H_2SO_4 contributes 64% and HNO_3 36% (Legrand & Delmas,1985). At sites intermediate to the coast and interior regions, HCl is also present but at lower concentrations than H_2SO_4 and HNO_3 (Legrand & Delmas,1985). The relative contributions of the mineral acids vary with time (Legrand & Delmas, 1984) but the evidence from this study also suggests a large spatial distribution as the concentration of HCl is high relative to other polar precipitation studies (Legrand & Delmas,1984;1985; Herron,1982). The cause of the large contribution of HCl is unknown although it may be related to the proximity of the Dry Valleys.

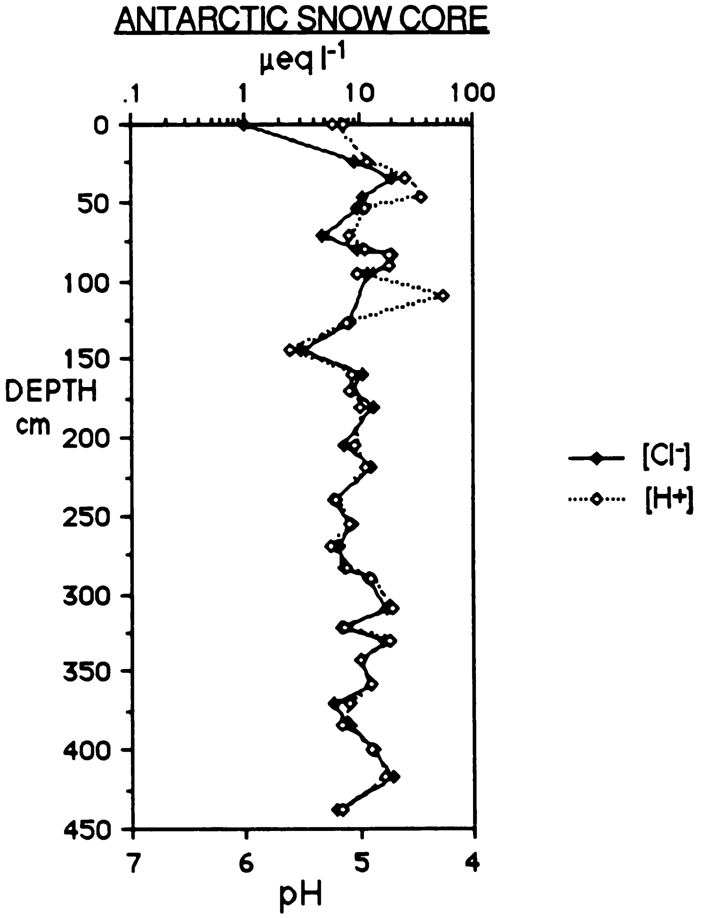


Fig 4.2 Variations of H^+ and total Cl^- (in μeq l^{-1}) with depth in the Antarctic snow profile.

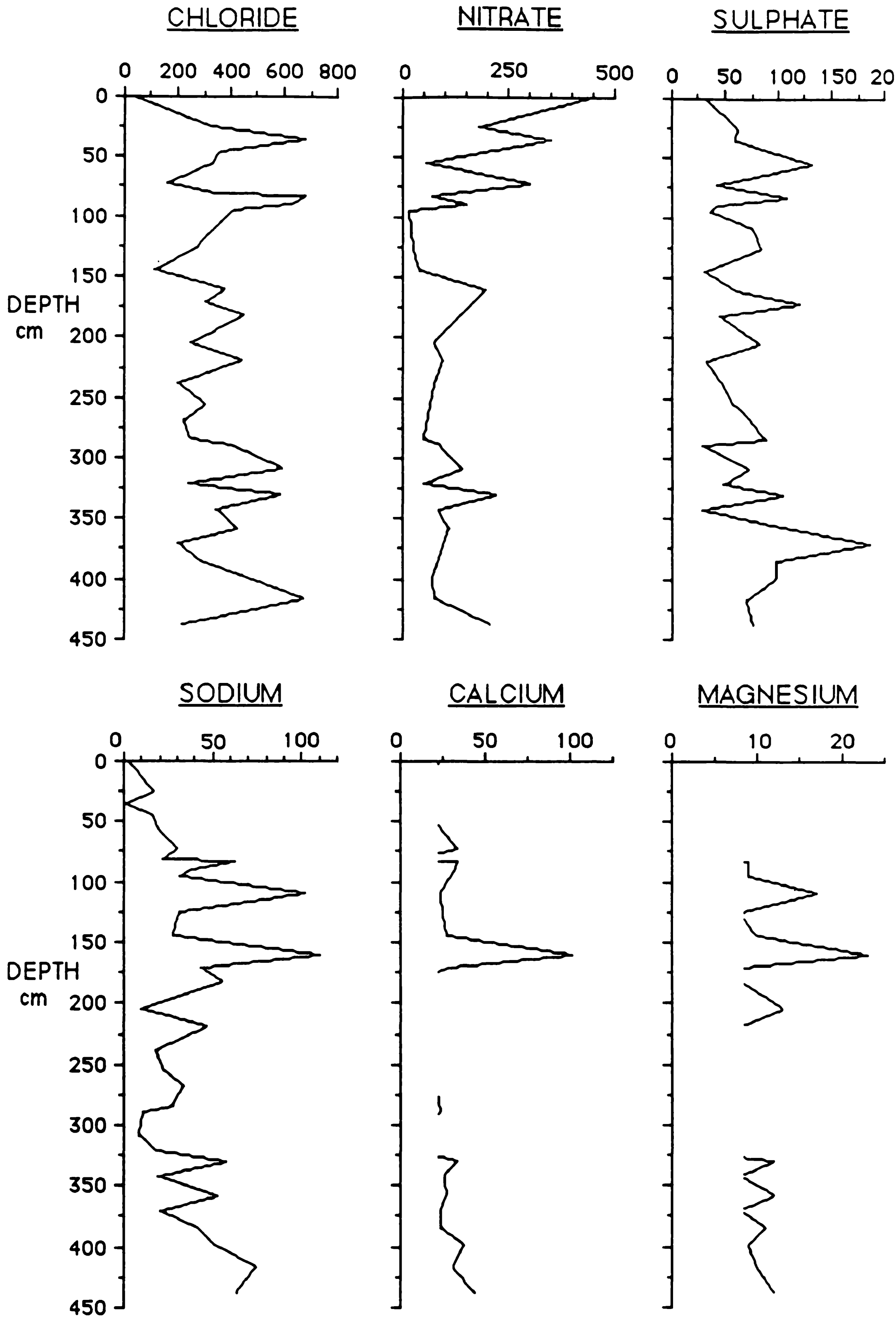


Fig 4.3 Concentrations of major ions (ng/g) in Antarctic snow. Nitrate concentrations have not been adjusted for the blank and can only be considered as maximum values. Calcium and magnesium profiles show only the concentrations above the detection limit.

The variation of the major ions with depth (Fig 4.3) is inferred to be seasonal, with storm events superimposed. Fine grained, high density ice layers associated with winter and wind packing events characteristically have low concentrations of the major ions, with the exception of the species derived from sea salt aerosols, while coarse grained, low density firn layers associated with summer and quiet weather conditions (when evaporation predominates at the surface), show increased concentrations (Stephenson,1967; Legrand & Delmas,1984). This trend is not particularly well represented in the analyses where only one sample containing solely hard ice was taken, number 38 at 80.5 cm depth. At this depth all ions (except NO_3^-) are at low concentrations. The remainder of the samples incorporated hard layers with soft layers.

Chloride concentrations are high, averaging 350 ng/g and peaking at 681 ng/g. Most correspond with peaks in Na (averaging 38 ng/g), consistent with locations within 100 km from the ocean (Legrand & Delmas,1985), and therefore of dominantly marine origin. The correlation of the Na and Cl peaks suggests that a contribution of marine Cl is present but may not be the dominant source.

Sulphate concentrations are slightly higher than the concentrations expected at 100 km inland, averaging 60 ng/g and peaking at 174 ng/g. This is inferred to be dominantly non-marine sulphate as indicated by the SO_4 ex (Appendix I), averaging 58 ng/g, consistent with the proportion of non-marine sulphate to total sulphate at inland locations (Legrand & Delmas,1985).

Over half of the Mg and Ca concentrations fall below the detection limit, averaging 8 ng/g and 24 ng/g respectively and peaking at 23 ng/g and 101 ng/g. The magnesium concentrations are also higher than the expected concentrations at ~100 km from the ocean of ~2 ng/g (Legrand & Delmas,1985). Calcium concentrations, rarely determined in Antarctic precipitation because of their insignificance, are high at this location and are consistent with a large crustal input, probably derived from the Dry Valleys.

Nitrate concentrations, averaging 107 ng/g without adjustment for blank concentrations, show a distinct trend of decreasing concentration with depth - from 445 ng/g at the surface to an average of ~75 ng/g from one metre downwards.

Ratios of the respective ions were compared with that of seawater and crustal rock and were classed accordingly (Table 4.3). Enrichment factors of ions relative to Na were also calculated:

$$\boxed{E_{Na}(x) = \left(\frac{x}{Na}\right)_{SNOW} \Big/ \left(\frac{x}{Na}\right)_{SW}}$$

where x/Na is the mass ratio of ion x to Na in snow or seawater (Gjessing,1984).

Layers where the enrichment factors approached unity were classed as marine. The above techniques were used together to determine the overall signature of the individual firn layers, as the ratios and enrichment factors often showed varying trends.

Table 4.3 Ratios of ions by weight and enrichment values relative to sea water, in sea water[a], crustal rocks[a], and polar snow[b].

Ratios	Sea Water[a]	Crust[a]	Snow[b]	Range[b]
Cl/Na	1.8	0.0082	12	1.5 - 54
Mg/Na	0.12	1.2	0.25	0.14 - 0.33
Ca/Na	0.037	2.2	0.71	0.44 - 1.4
Cl/SO_4	7.0	0.21	6.0	1.0 - 14
E_{Na} (Cl)	1	0.0045	7.8	1.0 - 39
E_{Na} (Mg)	1	10	2.6	1.2 - 12
E_{Na} (Ca)	1	59	22	11 - 36

[a] Constants from Kaye (1973).
[b] Ratios calculated in this study.

Four layers were classed as crustal and occur at 71.5, 145, 205.5 and 343 cm depth. E_{Na}(Ca) values were high throughout the profile averaging 21, while the enrichment in 3 of the 4 layers averaged 31. The fourth layer was classed as crustal by an E_{Na}(Mg) value of 12, averaging 1.9 in the rest of the profile. The remainder of the layers were dominantly of marine origin or substantially influenced by marine aerosols, characterised by E_{Na}(Cl) of less than 5, E_{Na}(Mg) of less than 2.0, and Cl: SO_4 of 5.5 to 8.5. This included the surface layer and layers at depths of 83.5, 109.5, 160.5, 239-283.5, 322-330, 358, 399.5 and 438.5 cm, corresponding to both peaks and troughs in the profiles.

Snow Composition of Sample Site

At sites ~100 km from the ocean with the prevailing wind seaward, low concentrations of the marine ions are expected with background concentrations of 23-50 ng/g Na, 4-8 ng/g Mg (Boutron & Lorius,1977; Boutron & Martin,1980) and [Cl^-] about five times greater than [Na^+] by weight (Delmas et al,1982). Peaks above this level are associated with the penetration of storms into the continent (Boutron & Martin,1980).

Reduced scavenging of aerosols in the Dry Valleys, owing to low precipitation, and the increased scavenging efficiency of snow on the plateau, have the effect of compressing the lateral trend of decreasing concentration with distance, causing elevated concentrations of marine ions at locations bordering the Dry Valleys, more consistent with locations within ~30 km from the ocean.

This may also explain the elevated concentrations of excess Cl at this site, as this is formed from the reaction of seasalt with tropospheric H_2SO_4, and the respective air masses, the prevailing easterly in the Dry Valleys (Claridge,1965) and the prevailing westerly at the Plateau site, converge at the edge of the plateau.

The signature of snow samples collected at the plateau site are thus dominated by the marine influence, with significant additions of crustal components from both a tropospheric source and from locally derived sources in the Dry Valleys.

4.2 NEW ZEALAND SAMPLES

4.2.1 Collection of Data

The anion concentrations were read directly from the ion chromatograph integrator and adjusted, where necessary, for the concentration of the deionised water used to make up the standards. This approximated 1 ng/g Br^-, 2 ng/g NO_3^-, 0 ng/g PO_4^{3-} and 14 ng/g SO_4^{2-}. Cl^- concentrations were calculated by measuring the peak heights and calibrating against standards, as the calculation of the baseline by the integrator gave erroneous concentrations.

The cation concentrations were read directly from the monitor without adjustment as distilled water was used to 'autozero' the AAS.

Detection coefficients and limits for both the anions and cations are shown in Table 4.4.

The low sensitivity experienced in detection at low concentrations and the deterioration of the Ca-Mg hollow cathode lamp causes the high detection limit for Ca. To increase the sensitivity, a N_2O flame was used in the later analyses and this gave a detection coefficient and limit of 16 ng/g and 33ng/g respectively from 7 duplicates. This pertains only to the analysis of the A2 and B2 ice cores.

Table 4.4 Detection coefficients and limits for New Zealand samples and the number of duplicates used in the calculation.

	Na ng/g	K ng/g	Ca ng/g	Mg ng/g	F ng/g	Cl ng/g	Br ng/g	NO_3 ng/g	PO_4 ng/g	SO_4 ng/g
No of duplicates	14	15	11	18	3	21	20	20	10	20
Detection Coeff.	9	18	46	5	27	9	2	4	2	17
Detection Limit	18	35	93	11	53	18	4	8	4	33

The very low sensitivity is also probably responsible for over-estimation of Ca concentrations at low levels, and hence, little importance can be attached to ratios involving Ca so these are sparingly used in the estimation of source in this study.

Isotopic Analysis

The mean delta values (δ) for mass 45 and mass 46 were read from the digital recorder and were used in the following calculations of $\delta^{18}O$ and $\delta^{13}C$.

$$\boxed{\begin{array}{c}\delta^{18}O = 0.999.\delta 46 + 0.0098.\delta 45 - 1.78 \\ \delta^{13}C = 1.063.\delta 45 \; - \; 0.034.\delta 46 - 4.50\end{array}}$$

The constant 1.78 in the $\delta^{18}O$ equation is derived from $\delta 45$ and $\delta 46$ values of SMOW, Standard Mean Ocean Water where $\delta^{18}O_{SMOW} = 0‰$, and the mean $\delta 45$ was 22.65 and the mean $\delta 46$ was 2.00 (Fig 4.4).

Two other standards were also measured frequently and these are Standard Light Antarctic Precipitation, SLAP which had an average $\delta^{18}O$ of -55.95‰ and Waikato water, WW with an average $\delta^{18}O$ of -6.46‰ (Fig 4.4). Normalization, the stretching or shrinking of the isotope scale so that a second reference value is set, is common practice and is carried out to ensure that the per mil difference remains constant. Oxygen isotope ratios are always expressed relative to SMOW on scales normalized so that $\delta^{18}O_{SLAP} - \delta^{18}O_{SMOW} = -55.5‰$ (Coplen, Kendall and Hopple,1983; Coplen,1988). All $\delta^{18}O$ values have thus been divided by the normalization factor of 1.008. The WW standard was used as an internal standard and attains a value of -6.41‰ after normalization.

Several processes may have operated to cause variations in the δ determinations:

1) If alkaline waters were encountered, significant fractions of the equilibrating CO_2 would be converted to HCO_3^-, which is enriched by about 8‰ compared to CO_2. This would result in the $\delta^{13}C$ becoming more negative without affecting the $\delta^{18}O$ (Hendy, pers comm).

2) If at any stage of the handling of the CO_2 incomplete transfer occurred, a kinetic partitioning of the CO_2 would result with the lighter molecules transferring through constrictions faster and freezing slower than the heavier molecules. This would result in a shift of both $\delta^{13}C$ and $\delta^{18}O$, with the change in $\delta^{18}O$ being twice as great as the change in $\delta^{13}C$. A test for this is demonstrated in Fig 4.4, where δ_{M45} values for standards are plotted against δ_{M46} values. It can be seen that the majority of samples lie within a tight cluster, but a few outliers (circled) appear to have been kinetically fractionated (Hendy, pers comm).

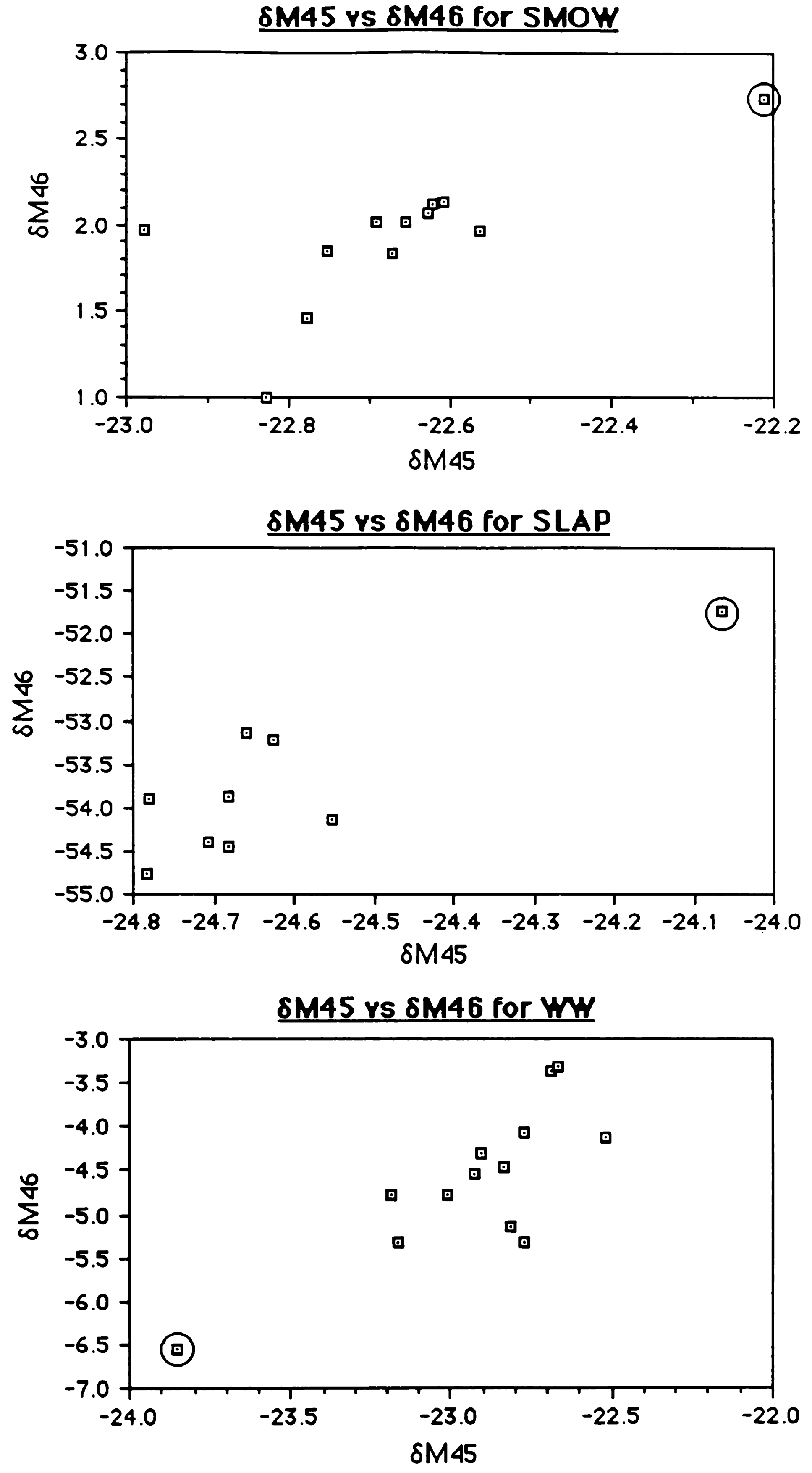


Fig 4.4 δ45 and δ46 values of the O isotope standards SMOW, SLAP and WW before normalization. Circled points were excluded from calculations of means and standard deviations.

As insufficient duplicates can be run of samples to employ these techniques, all samples with $\delta^{13}C$ shifts greater than two standard deviations from the mean $\delta^{13}C$ have been excluded (Appendix IV). Separate means and standard deviations were calculated for each data set as A1 and B1 were collected at different times to A2 and B2, and B2 was analysed after an overhaul of the mass spectrometer. 2σ limits for $\delta^{13}C$ values of A1 & B1 were from -27.39 to -29.99, from -27.88 to -29.44 for A2, and from -28.02 to -29.44 for B2.

4.2.2 Mt Egmont-Taranaki

By taking samples from Mt Egmont-Taranaki, it was hoped to establish a level of marine ions below which concentrations on Mt Ruapehu would vary. However, this is complicated by the variation of concentration of the marine ions with distance and altitude. This trend is evident in the samples taken from North Egmont (Appendix II) where at 1645 metres altitude, concentrations of Na and Cl are 228 and 468, at 1710 m 146 and 302, and at 1845 m 106 and 230 ng/g respectively (Fig 4.5). The snow comprising the avalanched material sampled at Manganui at 1315 m.a.s.l. with average concentrations of 117 ng/g Na and 301ng/g Cl may have originated from snowfields from 1680 m to ~1900 m a.s.l. Were this trend with altitude to continue we could expect negligible Na or Cl of marine origin on Mt Ruapehu at ~2530 metres.

No samples were taken on the seaward side of Mt Egmont-Taranaki and so the marine content of the snow may be underestimated.

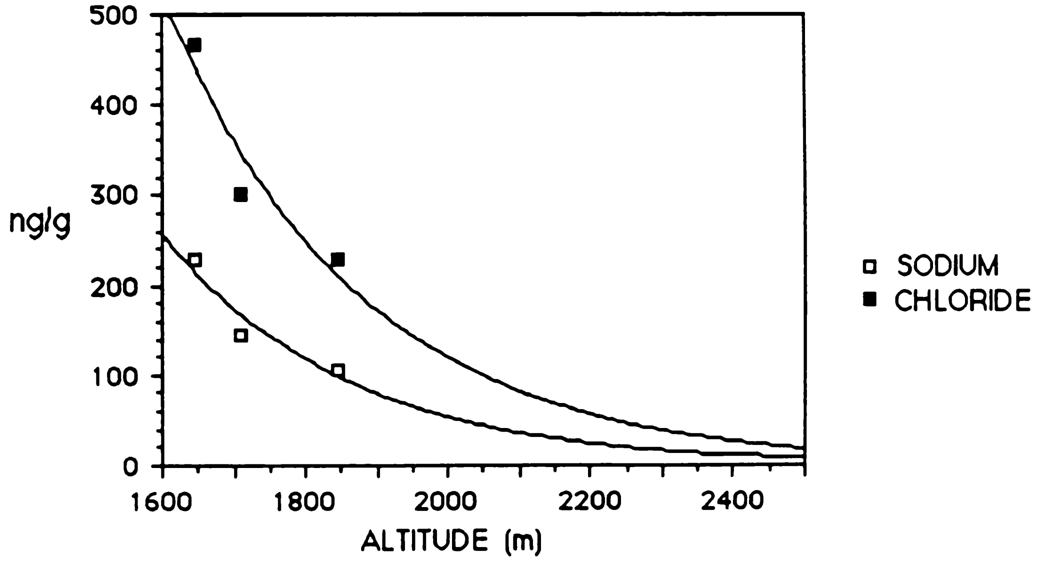


Fig 4.5 Variation of Na and Cl concentrations with altitude on Mt Egmont-Taranaki. $R^2 = 0.893$ Cl and $R^2 = 0.916$ Na.

Potassium and magnesium concentrations are low and close to the detection limit averaging 40 ng/g and 12 ng/g respectively. Mg/Na ratios (1:11) are slightly depleted in Mg relative to seawater giving E_{Na} (Mg) of 0.71. Sulphate concentrations are also low (53 ng/g) and are almost solely derived from a marine source giving Cl/SO_4 ratios of 6, whereas in seawater the ratio is 7. The non-marine SO_4 accounts for <34 ng/g of SO_4.

The enrichment of Cl relative to Na (E_{Na} (Cl) = 1.27) gives excess chloride concentrations of ~66 ng/g, somewhat unusual for coastal sites. Snow on the western and southern sides of the mountain may have a lower excess choride concentration as the excess chloride is thought to form from the reaction of sulphuric acid with sea salt particles in the marine atmosphere (Palais & Legrand,1985).

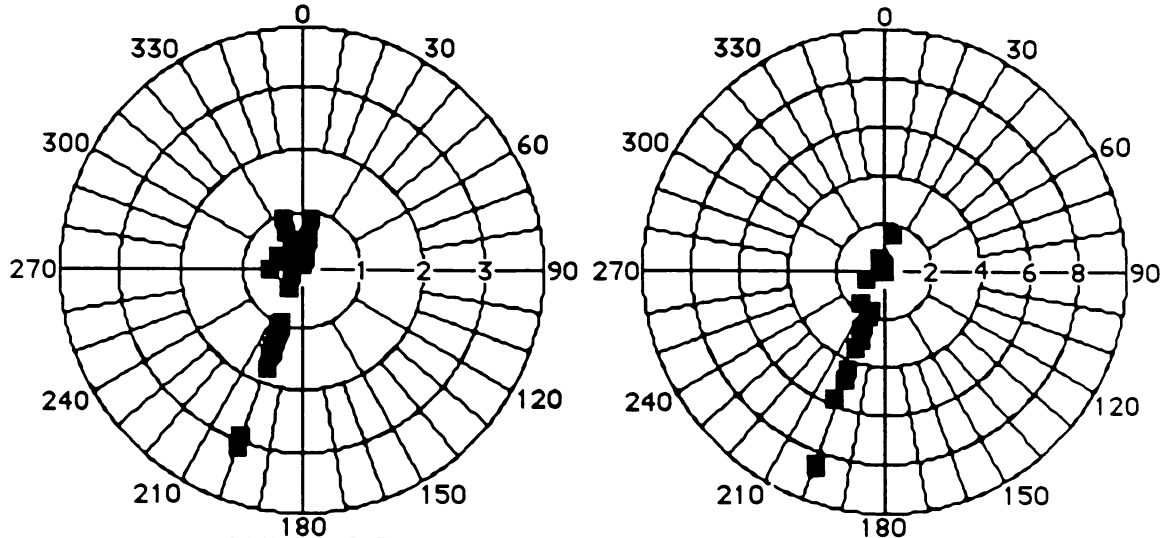
Calcium concentrations are high (143 ng/g) and give enrichment values for E_{Na} (Ca) of 29. This suggests that there is an inherent error in calculation of Ca or that Ca is enriched significantly from a crustal source. If the latter were the case, we would expect to see a decrease with altitude owing to the decreased input of continental dust from ploughing on the Taranaki lowlands and/or an increase in the Manganui avalanched snow through incorporation of debris. Neither of these trends is discernible.

The calculated values of the hydrogen ion concentration (~2.31 μeq l^{-1}) equates to a pH range of 5.4 to 6.6 (Table 4.2), perhaps in keeping with a slightly increased source of alkalinity from continental dust, namely Ca.

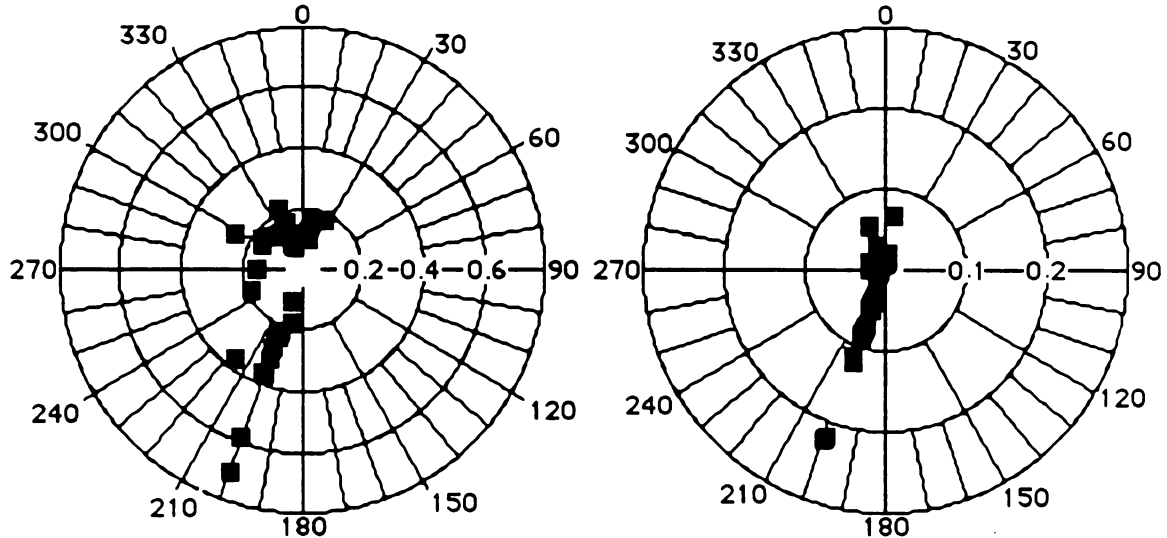
4.2.3 Mt Ruapehu Snows

The emphasis on the snow sampling was to quantify the volcanic effect on sites around the Crater Lake. As only two of the sampling trips skirted the lake, one largely unsuccessful, and the remainder were to sites 'assumed' to be affected by winds off the lake, the time period represented by the data may be as little as two months, September and October of 1989. This is unlikely to be representative of the snows on the summit area but gives some idea of the concentrations to be expected during small hydrothermal eruptions and in the other areas probably affected by past eruption activity (Table 2.2 and Table 2.3).

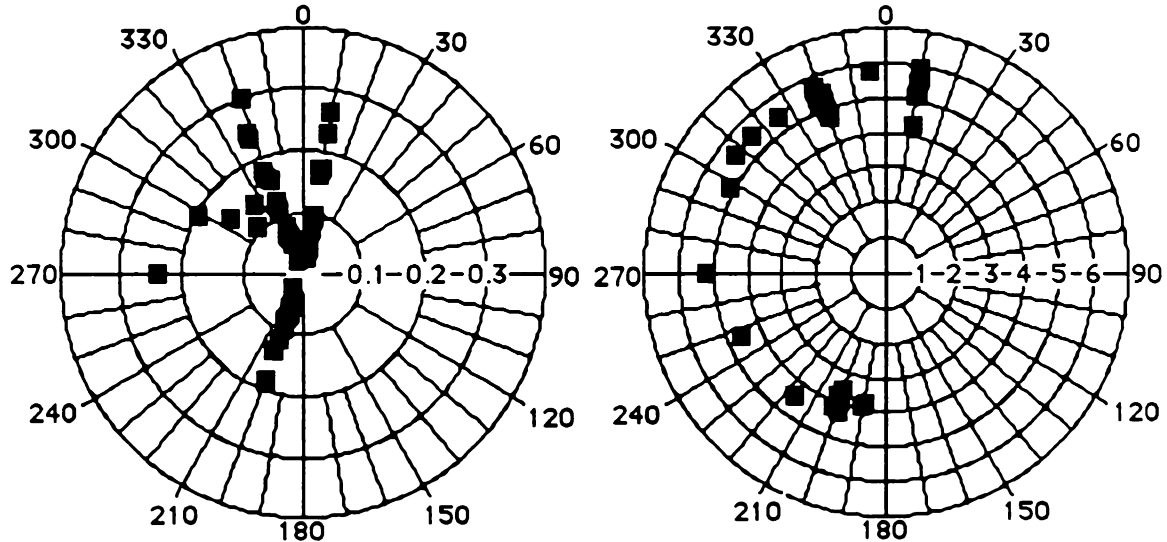
The duplicate samples collected at four sites around the Crater Lake during the initial sampling trip on 15/7/88 were left for over a year before analysis took place. The first set was stored in Lower Hutt at room temperature, the second in Hamilton at ~10°C. Large discrepancies arose probably resulting from temperature dependent leaching from the plastic and temperature dependent evaporation, affecting the first set more. These data have been excluded from all diagrams and calculations but remain in Appendix II.



CHLORIDE SULPHATE



CALCIUM MAGNESIUM



SODIUM pH

Fig 4.6 Concentrations of major ions (µg/g) and direction from Crater Lake (°N) of Mt Ruapehu snow samples.

The snow sample concentrations are shown relative to the direction from Crater Lake (Fig 4.6), while the positions of the sample sites are given in Fig 2.6. There are four main groupings of data, evident from the Na concentrations.

The Tahurangi site at 200°N is directly above the outlet of Crater Lake. As the prevailing westerly winds are known to eddy up around the outlet (Otway,1982), this is probably the dominant site for deposition of volcanically derived aerosols and gases. The snowpit sampled at this site (Fig 4.7) has higher concentrations in every element, except Na, than all other sites around Crater Lake. SO_4 and Ca are particularly high in this profile: SO_4 fluctuates around 2977 ng/g and peaks at 8593 ng/g, while Ca fluctuates around 266 ng/g and peaks at 586 ng/g. Similar variations in concentration profiles are seen in Na, Mg and Cl, with background levels of 74, 266, and 1355 ng/g and peaks of 186, 713, and 3143 ng/g respectively.

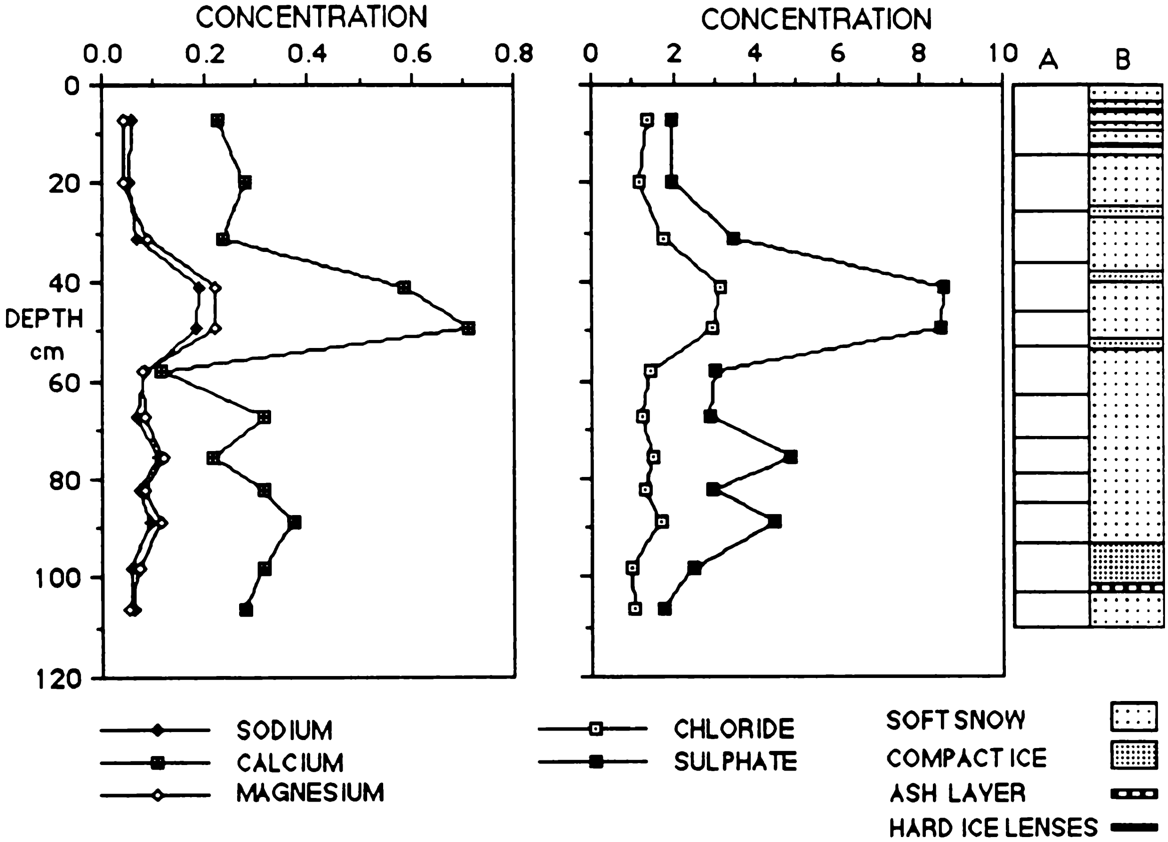


Fig 4.7 Concentration of major ions (µg/g) and the stratigraphy of Pit 1, Tahurangi. 'A' represents the sample divisions while 'B' represents the stratigraphy.

The pH is low, between 3.6 and 4.2 and this is attributable to the extremely high non-marine sulphate, comprising 99% of the total SO_4, and the high excess chloride, comprising 91% of the total Cl. Nitrate was not significant in the pit with all analyses falling below the detection limit.

The small scale fluctuations in the background levels are likely to be the result of passive degassing during precipitation or periods of ablation, further concentrating the components. All ions are significantly enriched above the normal background marine values with an average Cl/SO_4 ratio of 0.38 (6 in Mt Egmont-Taranaki snow). The tephra at 93-103 cm is likely to be reworked tephra as no significant increase in component concentrations, consistent with lake water carried as droplets on the surface of tephra particles, is evident.

The concentration peak occurring at 36-53 cm was probably not caused by wind off the lake but by a small hydrothermal eruption, as all ions show a 4-fold increase in concentration at this depth. Both snow flake scavenging during precipitation and dry deposition are processes that may be responsible for the concentration.

Samples collected at the outlet constitute an extension of the Tahurangi site. These samples have a similar chemical composition to the Tahurangi samples but generally have higher concentrations. They form a distinct group on the polar plots (Fig 4.6) at 202°N, separated slightly from the Tahurangi samples.

The second main group on the polar plots, moving clockwise around the lake, is the surface samples occurring at 217, 247, 270, 298, 307, 315 and 325°N. These generally show a progressive decrease in the volcanic components and an increase in the marine components, also evident by the pH rise.

The third group of samples is the col site at 340°N. Three pits were sampled from this location on separate sampling trips, collecting 24 samples in total. The snow profile from the third sampling trip (3/11/89) is shown in Fig 4.8.

Compared to the Tahurangi site, concentrations of all components are low. The dominant ions are Na^+ and Cl^-, both showing a progressive decrease in concentration from 246 and 686 ng/g at the top of the profile, to 51 and 95 ng/g at the bottom. Cl remains enriched relative to Na ($Cl/Na = 2.4$) although the enrichment relative to seawater is not high ($E_{Na}(Cl) = 1.4$). The mean excess chloride concentration is 88 ng/g, 25% of the total Cl, a modest increase from 20% at Mt Egmont-Taranaki. This is unlikely to be of volcanic origin as concentrations of Ca and SO_4 remain low in this profile with a Cl/SO_4 ratio more characteristic of marine aerosols than volcanic components ($Cl/SO_4 = 4$).

A proportional increase in non-marine sulphate relative to Mt Egmont-Taranaki is also evident, with 60% of total SO_4 (85 ng/g) being non-marine compared to 33% in the marine snows. Marine SO_4 of 35 ng/g in marine snows on Mt Egmont-Taranaki decreases to 34 ng/g on Mt Ruapehu. Non-marine Cl also shows a similar trend with a proportional increase in concentration inland but a slight increase in absolute concentration of marine Cl from 253 ng/g to 262 ng/g. A slight decrease in Na concentration is evident inland with ~140 ng/g at the coast and 135 ng/g at the Col site.

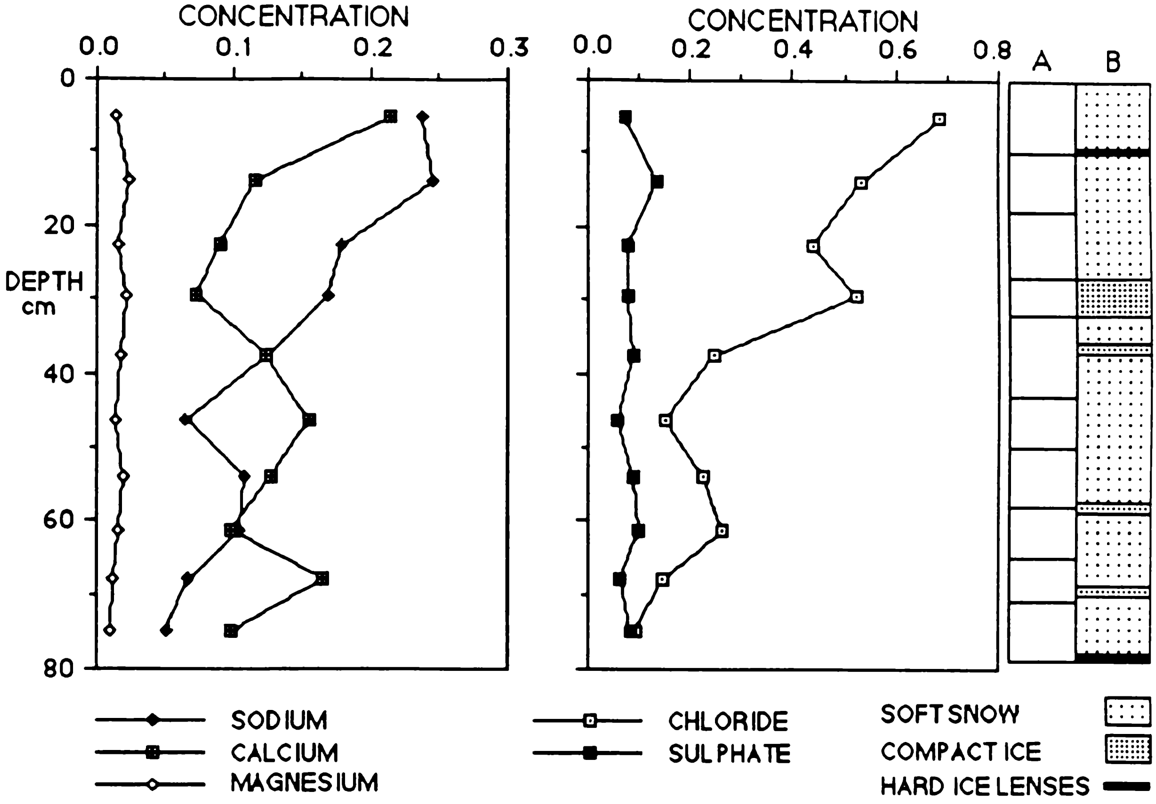


Fig 4.8 Concentration of major ions (µg/g) and stratigraphy of Pit 3, Col.

Magnesium concentrations are likely to be dominantly of marine origin at this site with an increase in absolute concentration from 12 ng/g to 16 ng/g compared to marine snows, but giving a Mg/Na ratio of 8.4, characteristic of marine snows.

The marine component in snows on Mt Ruapehu appears to be similar to that of the sampled sites on Mt Egmont-Taranaki, with no substantial decrease in concentration inland.

Ca concentrations are again likely to be affected by the low sensitivity in detection and are likely to be overestimated in this profile.

The $[H^+]$ at this site equates to a pH range of 5.1-5.7 in the 3/11/89 data, extending to 4.7 in samples taken from this site on 7/6/89 with acompanying SO_4 concentrations of up to 584 ng/g. Although no record of eruptive activity exists at this time (Otway,1990), small phreatic events were recorded throughout July so the possibility of an unrecorded event influencing snow at this site should not be discounted. In addition, there appears to be a small volcanic input at the base of the 3/11/89 profile with Cl/SO_4 varying markedly from the ratio in marine snows.

From the concentration peaks of Na and Cl at 28-34 cm and at the surface, and the accompanying stratigraphy, it is evident that concentration of ions occurs by scavenging by falling snow crystals, but is significantly increased through dry deposition on the surface layers in association with ablation.

More efficient dry deposition occurs when the surface layer is wet, either through ablation or rain on snow as is evident by the presence of ice at 28-34 cm.

The fourth group of data (Fig 4.6) are the Dome samples at 10°N, very similar in composition to the Col samples. The marine component is usually dominant at this site, carried by the prevailing westerly winds blowing through the gap between Paretetaitonga and Tahurangi. On occasions this area is significantly affected by volcanic inputs, as the frequency of eruption debris, especially from the larger eruptions, reaching to Cathedral Rocks and to the head of the Whangaehu Glacier is high. Normal passive degassing of the lake is not likely to influence the chemical composition greatly but a pH range of 4.3 to 5.8 suggests some volcanic input.

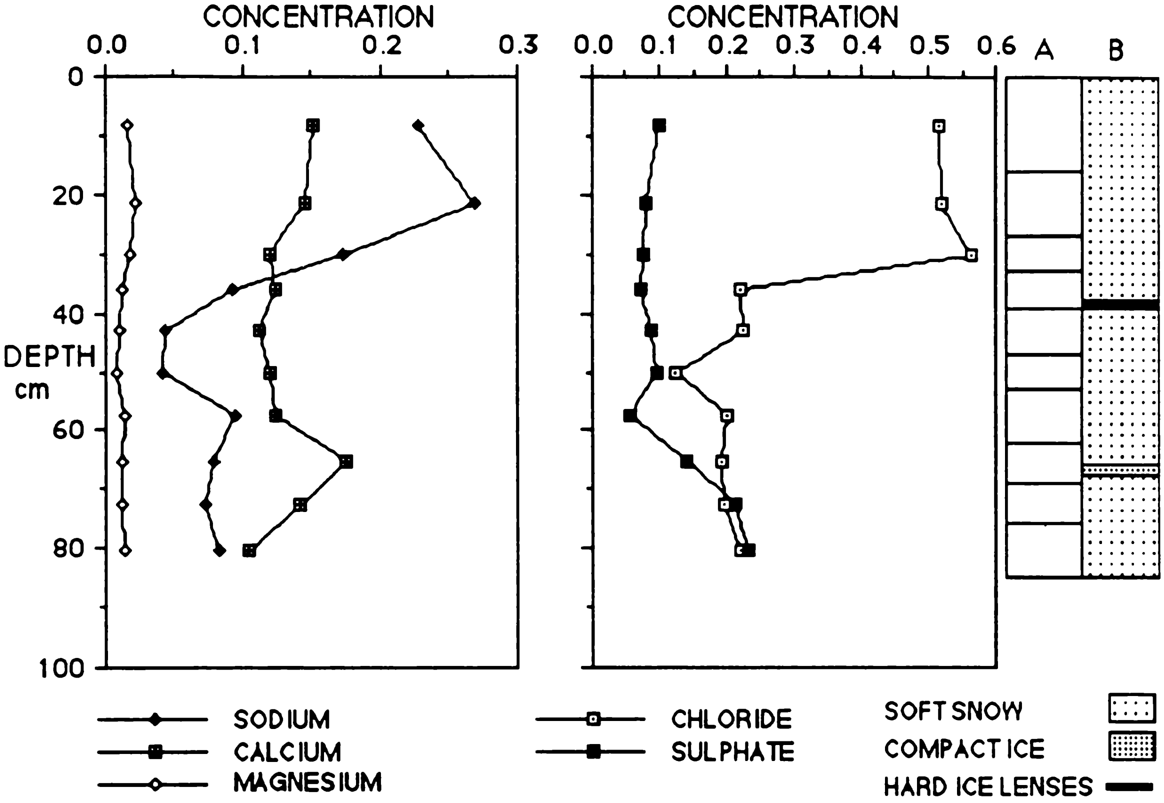


Fig 4.9 Concentration of major ions (µg/g) and stratigraphy of Pit 2, Dome.

Na and Cl concentrations at Dome (Fig 4.9) are similar to the Col site, averaging 117 and 298 ng/g respectively, giving Cl/Na ratios of 2.5 and E_{Na} (Cl) = 1.4, the same as at the Col. Excess chloride concentrations of 87 ng/g comprise 29% of the total Cl, with a reduction in the absolute concentration of marine Cl to 211 ng/g. The proportion of non-marine SO_4 is also greater than the Col site, 75% of total SO_4 with a reduction in absolute concentration of the marine SO_4 to 29 ng/g. Cl/SO_4 ratios are characteristically marine in the upper 40 cm of the profile, but significant volcanic input reduces this ratio to 0.95 at the base of the profile.

Ca and Mg fluctuate between 103-174 ng/g and from below the detection limit to 22 ng/g, respectively. The average Mg/Na ratio for the profile is 8.4 indicating that the dominant source for Mg at this site is not of volcanic origin but marine.

The prevailing wind at Mt Ruapehu is westerly but this is probably reflected as a north-easterly at Tahurangi site, a westerly at the Dome and a south-westerly at the Col. The wind will carry marine aerosols from the Tasman Sea and may collect volcanic components in the snow downwind of the Crater Lake if the volcano is passively degassing and will certainly concentrate them if small hydrothermal eruptions are occurring.

The southerly winds, which also carry marine aerosols are also likely to affect the area, especially the Dome and the Col. A high concentration of marine components is unlikely to be evident though as the southerlies are the dominant snow-bearing weather system and a dilution effect is likely.

4.2.4 Mt Ruapehu Ice Cores

The first ice cores were sampled on 25/7/89 in the winter following the record ablation season. This proved a major obstacle for the coring efforts as in March (Fig 2.7) a hummocky terrain was evident with uneven distribution of eruption debris from the 1969 and 1975 eruptions. On return to the Summit Plateau in July, the hummocks had been filled with the current season's snow, forming a flat plateau. Three cores were collected to different depths (relative to the position on the hummock) but on each attempt the hardness of the 1969/1975 eruption debris layer proved to be an insurmountable barrier. Continuous sampling of the entire 339 cm A1 core was carried out while the 220 cm B1 core was only sampled in sections to determine conformity (Appendix III). The third core was abandoned on reaching the debris layer at 226 cm depth.

A1 Stratigraphy

The stratigraphy of the A1 core (Fig 4.10) shows two distinct tephra layers, one at 191-197 cm and the second at the base of the core at 334 cm to >339 cm. A third layer of reworked tephra is evident at 240-257 cm. The two major layers are thought to be the 1969 or the 1969 and 1975 eruption debris at the base, and either the 1975 debris at 194 cm or a slumping effect from overlying hummocks in summer. It is likely that both layers are accumulation layers with overlying snow ablating back to this layer in most seasons and meltwater percolating through the deposits in summer.

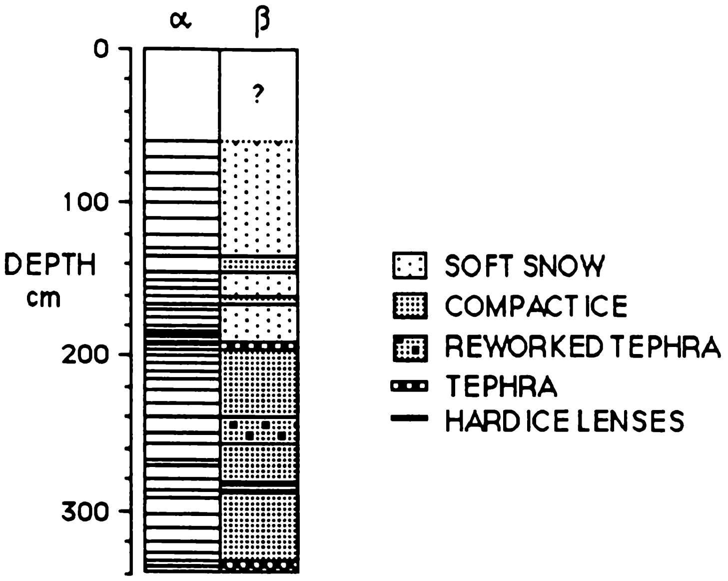


Fig 4.10 Stratigrapy of ice core A1 sampled on 25/7/89. 'α' represents the sample divisions while 'β' represents the stratigraphy.

$\delta^{18}O$ values (Fig 4.11) may indicate that there are one or two seasons' snow layers overlying the first tephra layer and a number of seasons' accumulation below this. The dominance of evaporation and percolation of meltwater has a smoothing effect on the curve and tends to make winter snow layers appear as summer layers (peaks as opposed to troughs). Although the graph between 197 and 340 cm could be construed as one broad peak from one season's snow, it seems more likely that it represents successive infiltration events of meltwater contaminating the original isotopic signature.

Similar results were obtained from the B1 ice core, with the difference that the two tephras may have coalesced through ablation of the intermediate snow to form a single layer of very hard ice-cemented tephra more than 13 cm thick.

Chemical composition

The chemical composition of the major ions in the A1 core are shown in Fig 4.12, plotting concentration on a log scale as the concentration of the tephra peaks were ~100 times more concentrated than the background levels.

On the basis of Cl/SO_4 ratios, the core can be subdivided into three main sections. The upper 187 cm is dominantly marine in origin, with the exception of a small section from 155-165 cm where increased concentrations of SO_4 (3802 ng/g) suggest an input consistent with a small phreatic eruption. From 187-267 cm the core is affected by volcanic components, separated by a small marine segment (267-280 cm) from the remainder of the core (280-339 cm), also of volcanic origin. The continuation of the volcanic influence well below the tephra layer results from percolation of meltwater through the profile, causing leaching from the overlying tephra layer. Peaks in components lower in the profile result from refreezing of the meltwater.

The upper 187 cm is likely to be the only section of the core in an unmodified state, being the current season's accumulation only. The small phreatic peak at 155-165 cm is likely to be the result of one of a series of small phreatic eruptions that occurred from 1-24 July, necessitating a snow accumulation of 1.5 metres in a month.

Concentrations in the upper part of the core are similar to the Col and the Dome site with mean concentrations of 91 ng/g Na; a maximum of 121 ng/g Ca, but mostly below the detection limit; 21ng/g Mg; 347 ng/g Cl; and 128 ng/g SO_4 with the exclusion of the small SO_4 peak. Excess Cl (182 ng/g) comprises 53% of the total Cl, a decrease both proportionally and in the absolute concentration of marine Cl (165 ng/g). This trend is also seen in non-marine SO_4 where 85% of the total SO_4 is non-marine (108ng/g) with marine SO_4 of 28 ng/g. This indicates that the volcanic influence is reasonably high with Cl/SO_4 ratios of 2.7, greatly enriched in SO_4 relative to the marine snows, giving a pH of 5.1 (Fig 4.13). NO_3 concentrations, which were below the detection limit in most other samples, average 15 ng/g with values up to 46 ng/g.

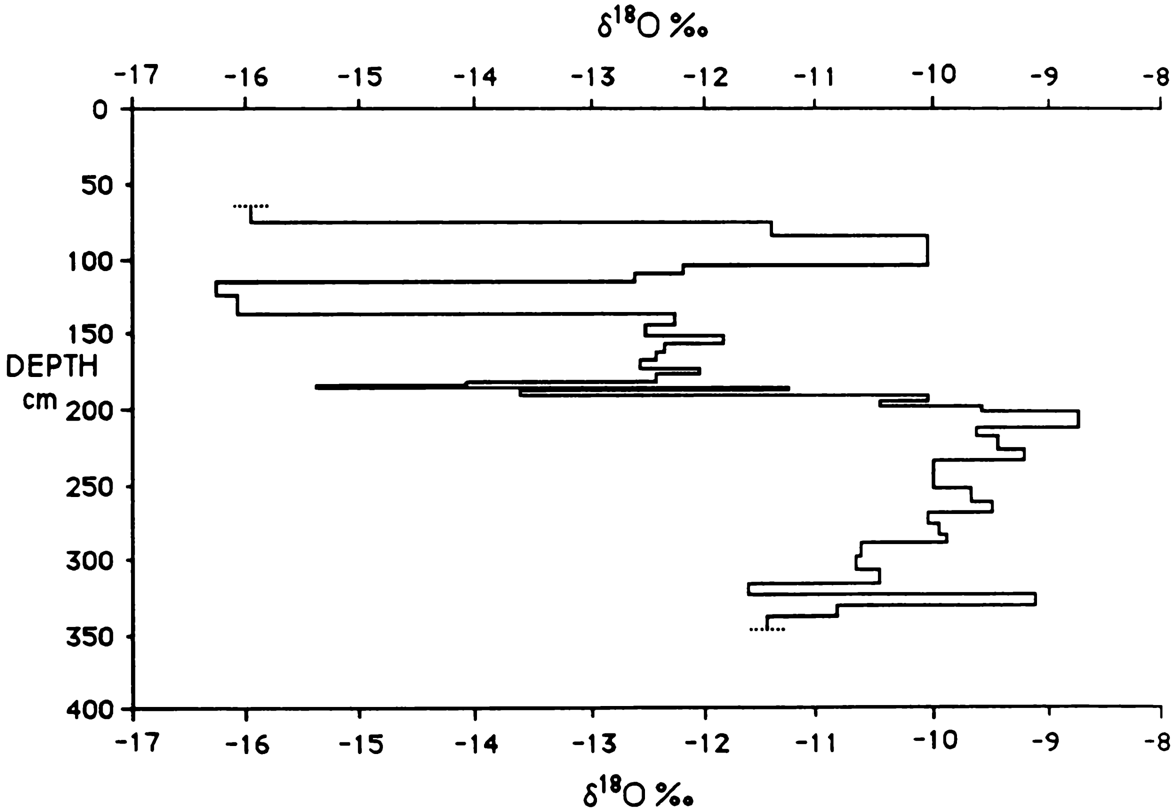


Fig 4.11 $\delta^{18}O$ enrichment values (‰) of ice core A1.

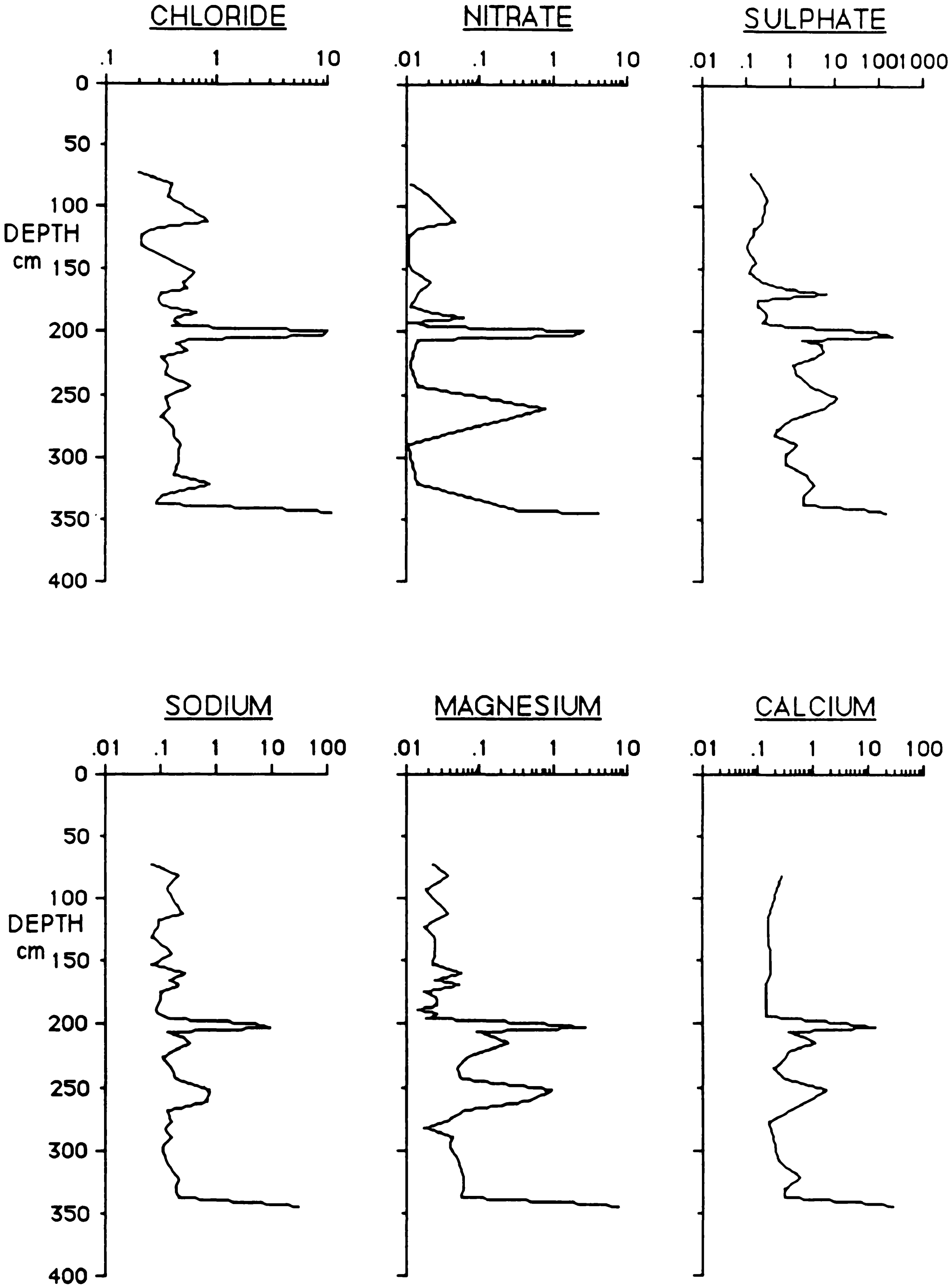


Fig 4.12 Concentration of major ions (µg/g) in ice core A1.

Enrichment in the ions relative to marine snows is significant : E_{Na} (Mg) = 2.5, E_{Na} (Cl) = 2.1 and E_{Cl} (SO4) = 2.2. This indicates that the snow on the plateau has substantial volcanic input in the background levels as well as in the debris layers. Upward movement of pellicular water (Jonasson,1973) may be an important mechanism by which this occurs.

The concentrations in the remaining two sections of the core are similar with an increase in all concentrations in the lower tephra layer, consistent with leaching down or up the profile. Concentrations in the second section are 861 ng/g Na, ~1240 ng/g Ca, 317 ng/g Mg, 1504 ng/g Cl, and 14664 ng/g SO_4. Excess Cl comprises 104 ng/g (30%) of the total Cl in the non-tephra layers and 3150 ng/g (40%) in the tephra layers, while non-marine SO_4 comprises 2209 ng/g (98%) of the total SO_4 in the non-tephra layers and 81760 ng/g (99%) in the tephra layers. This gives non-marine concentrations of 246 ng/g Cl in the snow underlying the tephra layer and 4700 ng/g Cl in the tephra, and 48 ng/g SO_4 in the snow layers and 1140 ng/g SO_4 in the tephra. This indicates that the tephra layers are indeed accumulation layers as marine components are concentrated by a factor of 20 with respect to the underlying snow layers and by a factor of between 30 -40 with respect to the overlying snow, which presumably is characteristic of the snow from which the marine components are derived.

The pH associated with the tephra layer is 2.8, while in the underlying snow the pH is 4.3 (Fig 4.13). This also indicates the leaching effect from percolation of meltwater as the overlying snow has a pH of 5.1.

The third section of the A1 core is also thought to be an accumulation layer, where marine components are concentrated up to 100 times more than those in the overlying snow. Mean concentrations in the snow are 116 ng/g Na, 205 ng/g Ca, 40 ng/g Mg, 390 ng/g Cl, and 1160 ng/g SO_4 while in the tephra accumulation layer mean concentrations are 15180 ng/g Na, 14620 ng/g Ca, 4300 ng/g Mg, 7370 ng/g Cl and 77130 ng/g SO_4. Excess Cl concentrations (184ng/g) comprise 47% of the total Cl in the snow layers.
In the tephra layer Na is enriched relative to marine snow and so there can be no excess Cl present. Non-marine SO_4 (1131 ng/g) comprises 98% of the total SO_4 in the snow layers and 95% (73320 ng/g) in the tephra layer. As the proportion of marine SO_4 remains nearly constant from the overlying snow to the peak but increases dramatically from 29 ng/g to 3810 ng/g in absolute concentration, this must be an accumulation layer.

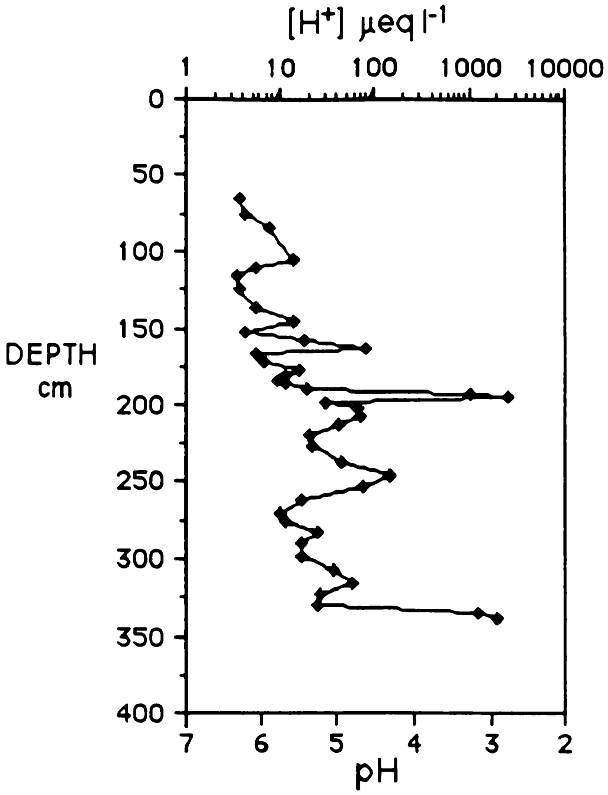


Fig 4.13 [H+], calculated from the sum of the mineral acids and the corresponding pH in the A1 ice core.

Another indication that this is an accumulation layer is the enrichment of Na relative to weight % variations in the proportion of oxides in the calc-alkaline lavas from Mt Ruapehu. CaO is the dominant oxide of the species determined, comprising 4-10 weight % closely followed by MgO 2-8 wt %. Na_2O comprises between 2.59-3.81 wt % while K_2O comprises between 0.58-3.02 wt % (Graham & Hackett,1987). If all components in the tephra layer were solely of volcanic origin, Na concentrations would be much lower, in keeping with the proportions in the lavas.

Core B1 was almost identical to A1 in that layers of snow, near marine in composition, overlay an accumulation layer containing the 1969/1975 eruption debris layer. Concentrations in the debris layer were as high as the 334-339 cm layer in core A1 (Appendix III).

A2 and B2 Stratigraphy

The second attempt to sample ice cores was some 50 metres from the base of Te Heu Heu ridge. Two cores were sampled, the first to a depth of 817 cm from which 914 cm of core was recovered (A2), and the second (B2) to a depth of 577 cm from which 630 cm of core was recovered. The two cores sites were separated by approximately 150 cm and the stratigraphy was almost identical (Fig 4.14).

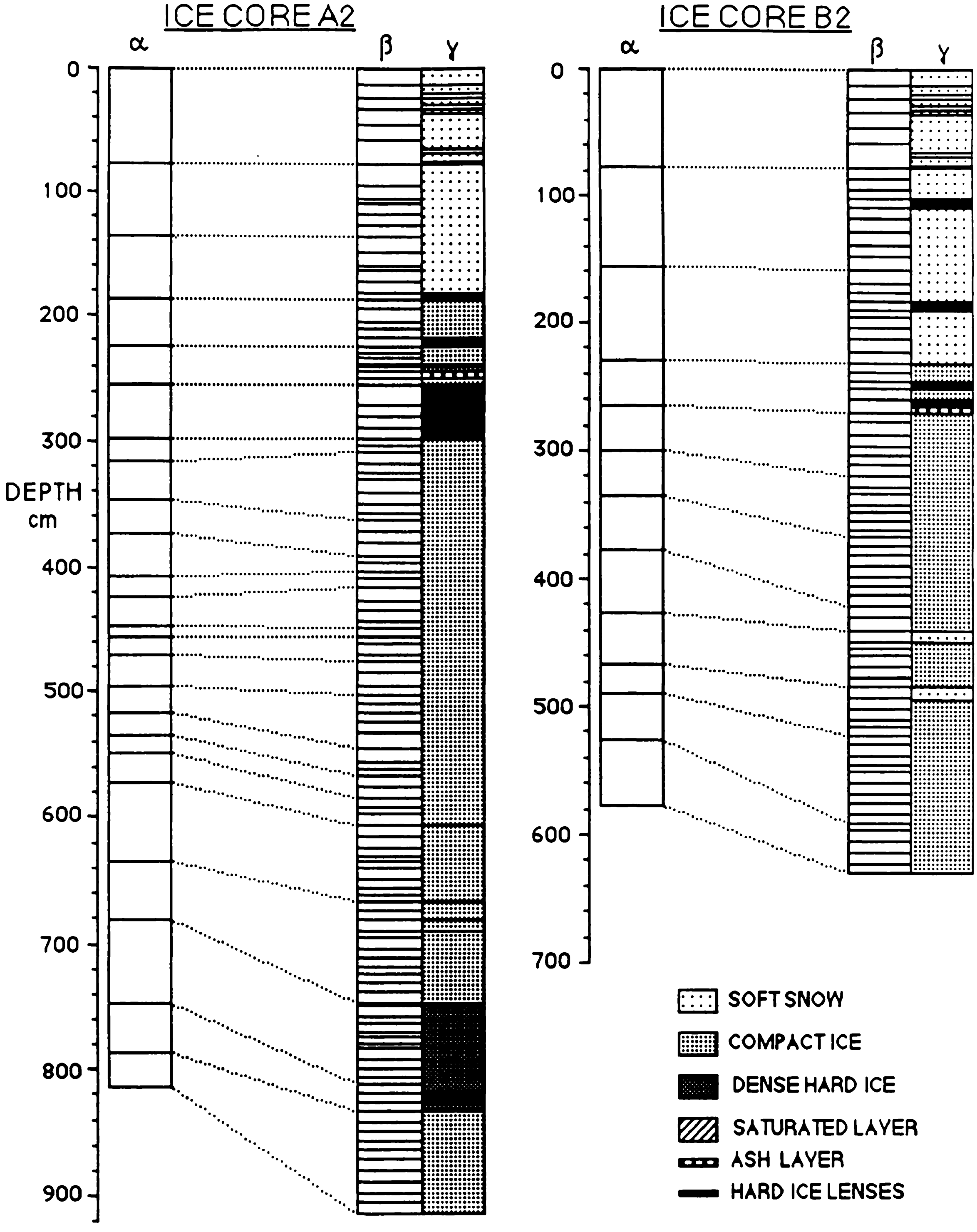


Fig 4.14 Stratigraphy of ice core A2 and B2. 'α' represents the core segments as removed from the sipre corer, 'β' represents the sample divisions of the recovered core, and 'γ' represents the stratigraphy of the recovered core.

The stratigraphy of the A2 and B2 cores bore little resemblance to the A1 or B1 cores; the thick, hard debris layer from the 1969/1975 eruption was not encountered in either of the two cores. A thin, distinct grit layer, assumed to be of volcanic origin, was sampled at 243 cm in the A2 and at 260 cm in the B2 but owing to its thickness (<5mm) and the low concentration of ions in relation to the 1969/1975 eruption layer, this cannot be the same tephra. A progressive increase in density with depth is evident, but few obvious surface layers in the form of buried ice lenses are present.

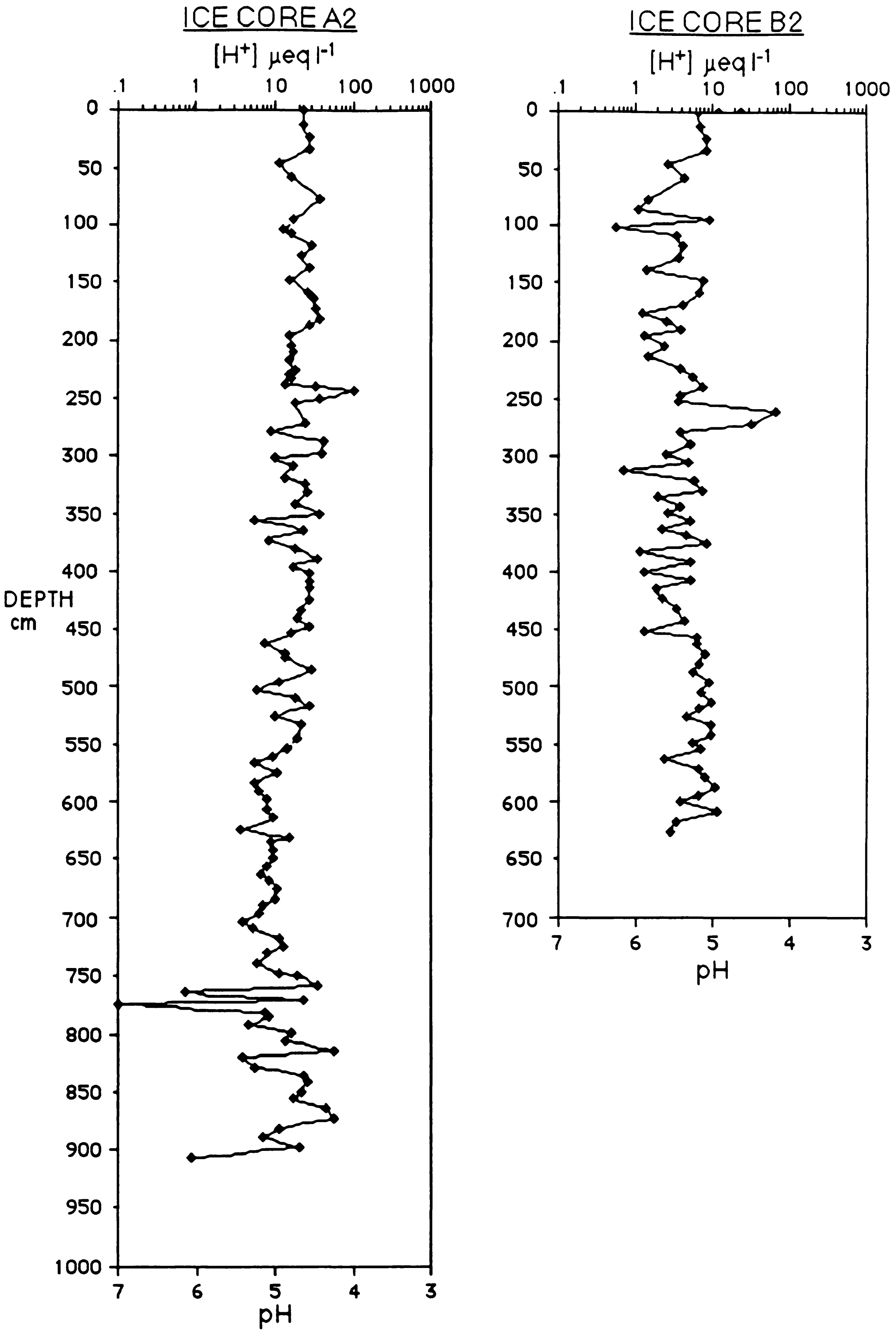
The A2 core was sampled over two consecutive days, the first day to a depth of 606 cm and the second day, the remaining depth to 817 cm. On return to the core site on the second day, the core hole although having been covered, had filled with water from the sides of the core. The first segment to be cored that day was saturated, the water having percolated into it overnight. Successive segments were not saturated but it became progressively more difficult to retrieve the core segments through the water layer and at 817 cm the core was abandoned.

The B2 core was not saturated as may have been expected from its proximity to A2, but the firn in the first 222 cm was particularly soft. A progressive density increase with depth was again evident.

Chemical composition of A2

The profiles of [H+], calculated from the mineral acids, agree closely for A2 and B2 ice cores (Fig 4.15), with pHs of 4.8 and 4.7 respectively.

Profiles of Na, Mg, Cl, Ca and SO4 concentrations with depth are given in Fig 4.16 and Fig 4.17. Na, Mg and Cl are all low averaging 129 ng/g, 25 ng/g and 230 ng/g respectively in the upper 750 cm of the core (Fig 4.16). Below this at 758 cm there is a significant peak of all ions with maxima at 6880 ng/g, 1040 ng/g and 13676 ng/g respectively. The Mg/Na ratio in the upper part of the core is 0.19, giving ENa (Mg) = 2.1, while in the peak area the enrichment is slightly less at 1.7. Excess Cl concentrations (34 ng/g) comprise 15% of the total Cl with a marine component of 196 ng/g, consistent with the Dome and the Col in the overlying snow. At the peak there is an excess Cl of 3043ng/g (22%) with a marine component of 10633 ng/g, a concentration factor of 54 times. There was no obvious stratigraphic marker for the increased concentration, although it corresponds to a broad band of compact ice, extending lower than the peak in concentration.



ICE CORE A2

ICE CORE B2

Fig 4.15 [H+], calculated from the sum of the mineral acids, and the corresponding pH in the A2 and B2 ice cores.

The SO_4 and Ca concentrations fluctuate around 876 ng/g and 226 ng/g in the upper part of the core. The increase in concentration in the lower part of the core is attributable to the marine ions. In the peak at 758 cm, SO_4 increases to 1562 ng/g while Ca and Na peak at 775 cm at 1270 ng/g and 2000 ng/g.

A high correlation between the position of the SO_4 and Ca peaks exists (Fig 4.17). The most pronounced peak is at 243 cm depth associated with a thin tephra layer. Concentrations of Na, Mg and Cl do not increase above the normal background level but Ca increases to 709 ng/g and SO_4 to 5063 ng/g. Non-marine SO_4 (5036 ng/g) comprises 99% of the total SO_4 in this layer with a marine SO_4 component of 27 ng/g. Enrichment of Cl and of Mg relative to marine snow is characteristic of the majority of samples, with values of 1.2 and 2.8 respectively, but E_{Cl} (SO_4) is high at 132.

This peak is presumed to be the result of the moderate phreatic eruption of 8 December 1988 (Table 2.3), the most recent tephra eruption of Mt Ruapehu. By correlating this with the $\delta^{18}O$ data (Fig 4.18) a reference date is set, although it is evident that the summer eruption debris is situated in a winter layer. This can be explained by melt down, where dark objects, particularly tephra will melt into the existing snow layer. The depth of 243 cm in core A2 correlates with winter 1988. For the oxygen isotope data, winter is defined as May to October and summer as November to April, so that November 1988, for example, will be termed as summer 1989.

Non-marine sulphate of 843 ng/g (96%) of total SO_4 in the upper part of the core diminishes to zero in the concentration peak at 758-764 cm, giving a concentration factor of marine SO_4 of 47 times (from 33 ng/g to 1562 ng/g) from the overlying snow. This is certainly a marine layer, with slight accumulation occurring to further concentrate the components. From the $\delta^{18}O$ values (Fig 4.18) it is evident that this is a winter layer. Violent storms are more common during winter and concentrations of similar magnitude have been recorded in rain water after cyclonic events, similar to precipitation following Cyclone Bola, after the initial dilution effect caused by the associated heavy rains (Hendy, pers comm). It is unlikely that this is an error in determination as four separate determinations are required for the cations alone. No evaporation or leakage is known to have occurred from this pottle, although this may be the cause of the high concentration in the subsequent layer (764-771 cm) as this pottle broke on the trip down the mountain in the under-slung load and fractionation of the sample's isotopes may have occurred. There was insufficient sample to determine $\delta^{18}O$ so only chemical analyses were attempted of this layer.

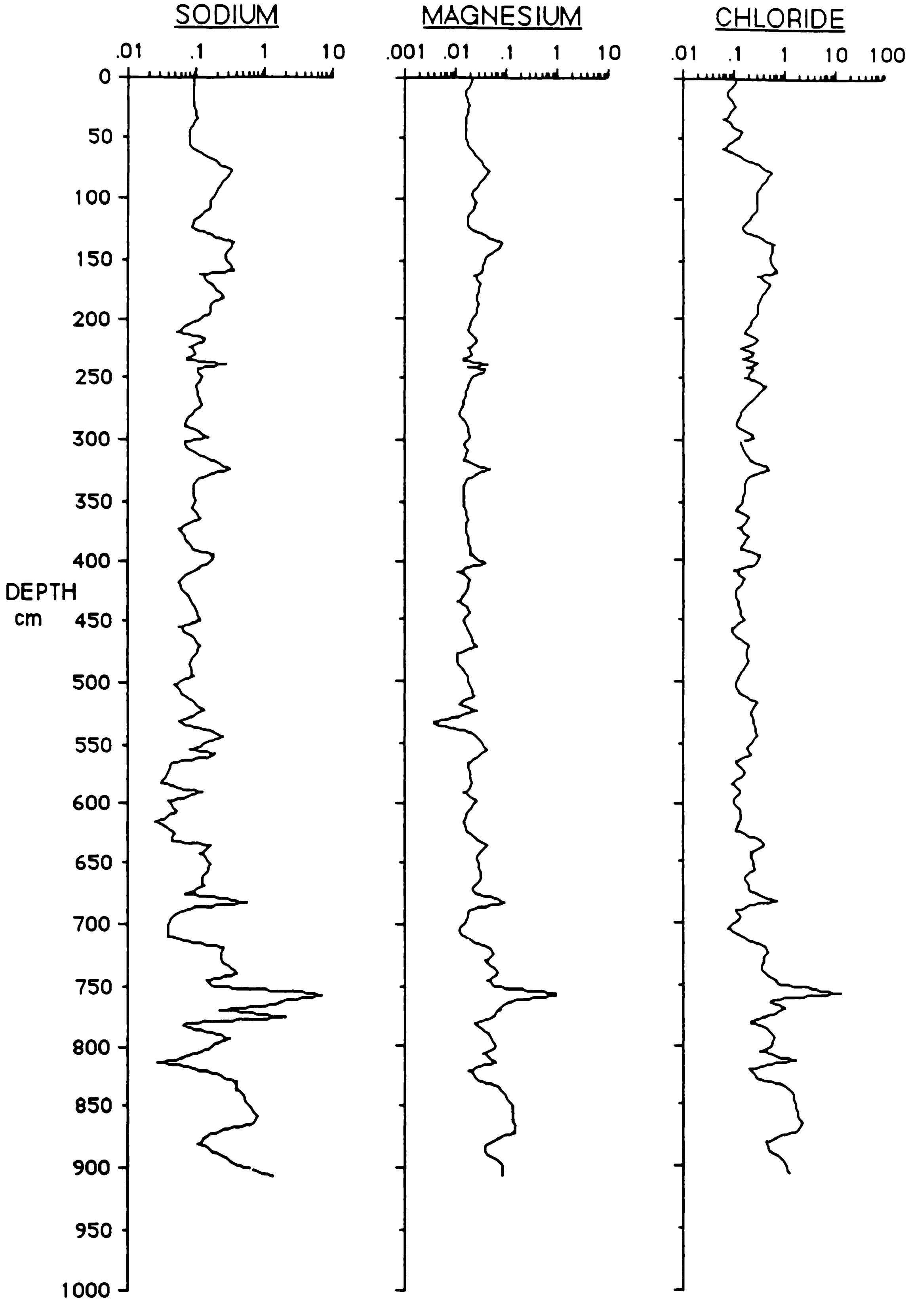


Fig 4.16 Sodium, magnesium and chloride concentrations (µg/g) in the A2 ice core.

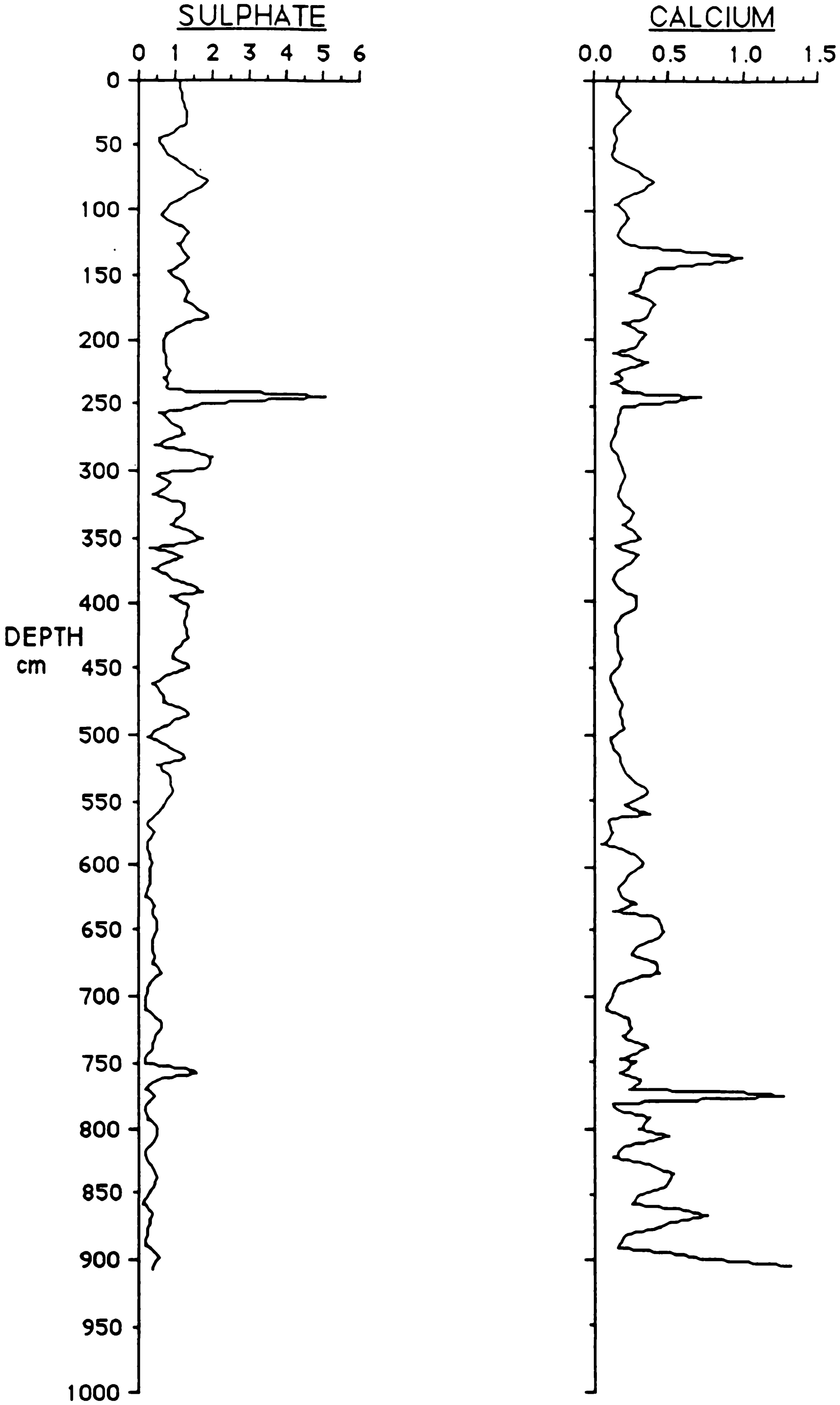


Fig 4.17 Variations in concentration (µg/g) with depth of calcium and sulphate in the A2 ice core.

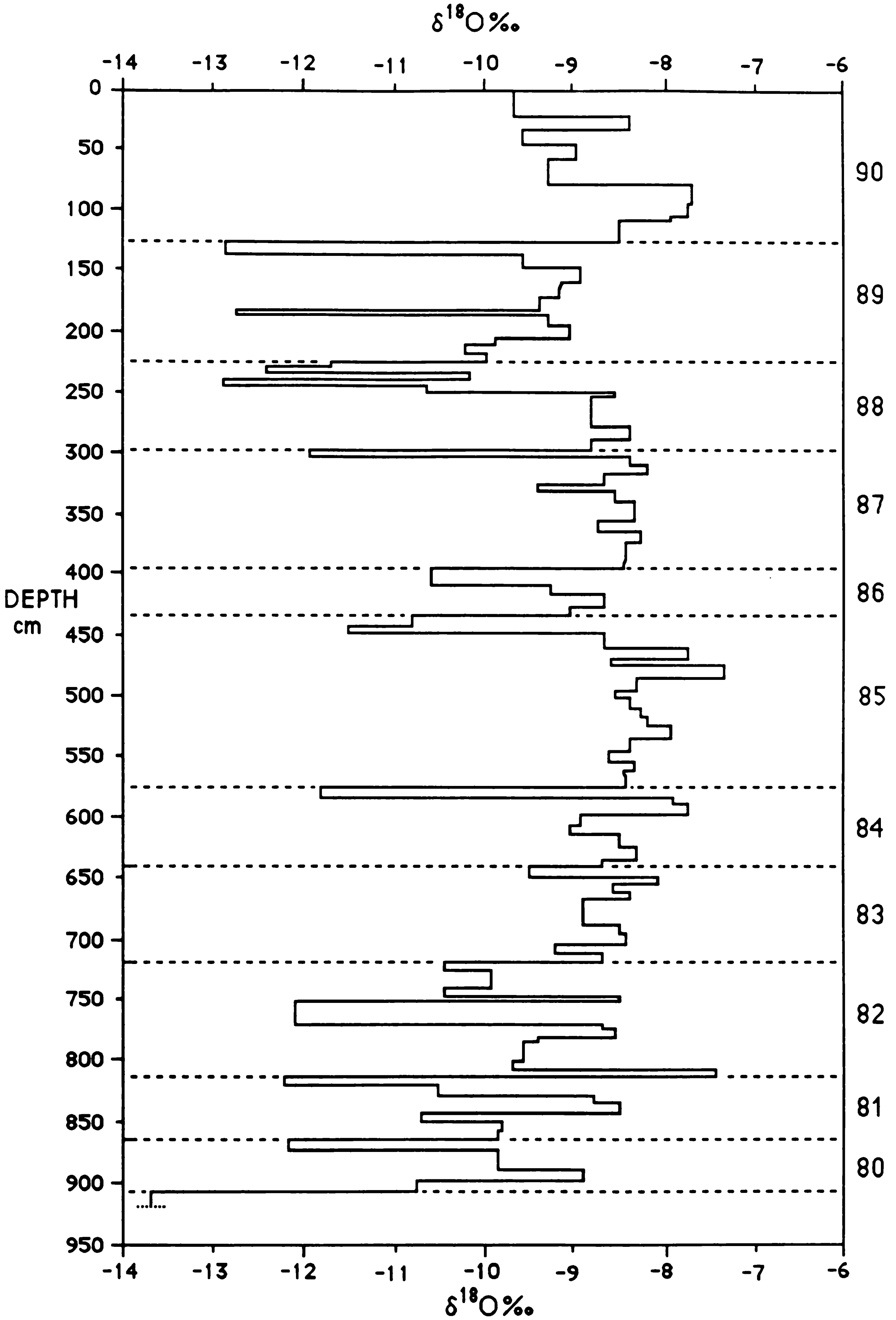


Fig 4.18 $\delta^{18}O$ enrichments (‰) of ice core A2 showing the proposed annual accumulation layers between the dashed line -.

Chemical composition of B2

The chemical composition to the base of the B2 core mirrors that of A2. Unfortunately in the absence of a stratigraphic marker at 758 cm, it was not realised that this would be an important layer and the B2 core was not cored to this depth, probably less than one further metre from the base of the core.

The relative proportions of constituents in core B2 compared to A2 is slightly higher for SO_4 and slightly lower for the remaining elements. Mean concentrations were 109 ng/g Na, 24 ng/g Mg, 174 ng/g Cl (Fig 4.19), 214 ng/g Ca and 890 ng/g SO_4 (Fig 4.20). As in the A2, Na, Mg, and Cl concentrations in B2 show only minor fluctuations and remain low throughout the core with peaks of 263 ng/g Na, 48 ng/g Mg and one peak of up to 1001 ng/g Cl associated with a small Ca peak only. These concentrations are lower than the concentrations from the Col and the Dome and suggest that the marine contribution is very low.

Enrichment values relative to marine snow are slightly higher than in A2 for Mg, but Cl is depleted relative to Na with E_{Na} (Mg) = 2.4, E_{Na} (Cl) = 0.88. The depletion of Cl relative to Na gives excess Cl values averaging 22 ng/g, comprising 13% of the total Cl and thus giving a marine Cl of 152 ng/g.

Ca and SO_4 continue to fluctuate together at concentrations higher than the background marine levels experienced in the Col and the Dome. Non-marine SO_4 is characteristically high, with 824 ng/g comprising 93%. Marine SO_4 measuring 56 ng/g is slightly higher than background levels. The correlation between the position of the Ca and SO_4 peaks is high with Cl/SO_4 values showing a substantial volcanic input giving E_{Cl} (SO_4) = 31. One significantly enriched peak at 260 cm corresponds to the 243 cm tephra peak in A2. Concentration of total SO_4 averages at 4915 ng/g in the peak with non-marine SO_4 comprising 99.6% and marine SO_4 of 21 ng/g. pH in the peak (4.1) is similar to that in A2 (4.2), rather higher than the pH of 2.8 for the tephra layers in the A1 and B1 cores.

The minor fluctuations in the Ca and SO_4 concentrations are attributable to passive degassing of the volcano and small scale phreatic eruptions. The concentration of volcanic components derived from steam is likely to be low; substantial increases coming from contact with the hydrothermal solution only. On contact with water, increases should be evident for all ions, whereas in core B2, situated 1.26 km from the lake edge, this is unlikely to be a major source and the increase in concentration is seen only in Ca and SO_4 alone. Finely fragmented gypsum crystals carried with the steam or hydrothermal fluid are thought to be the cause.

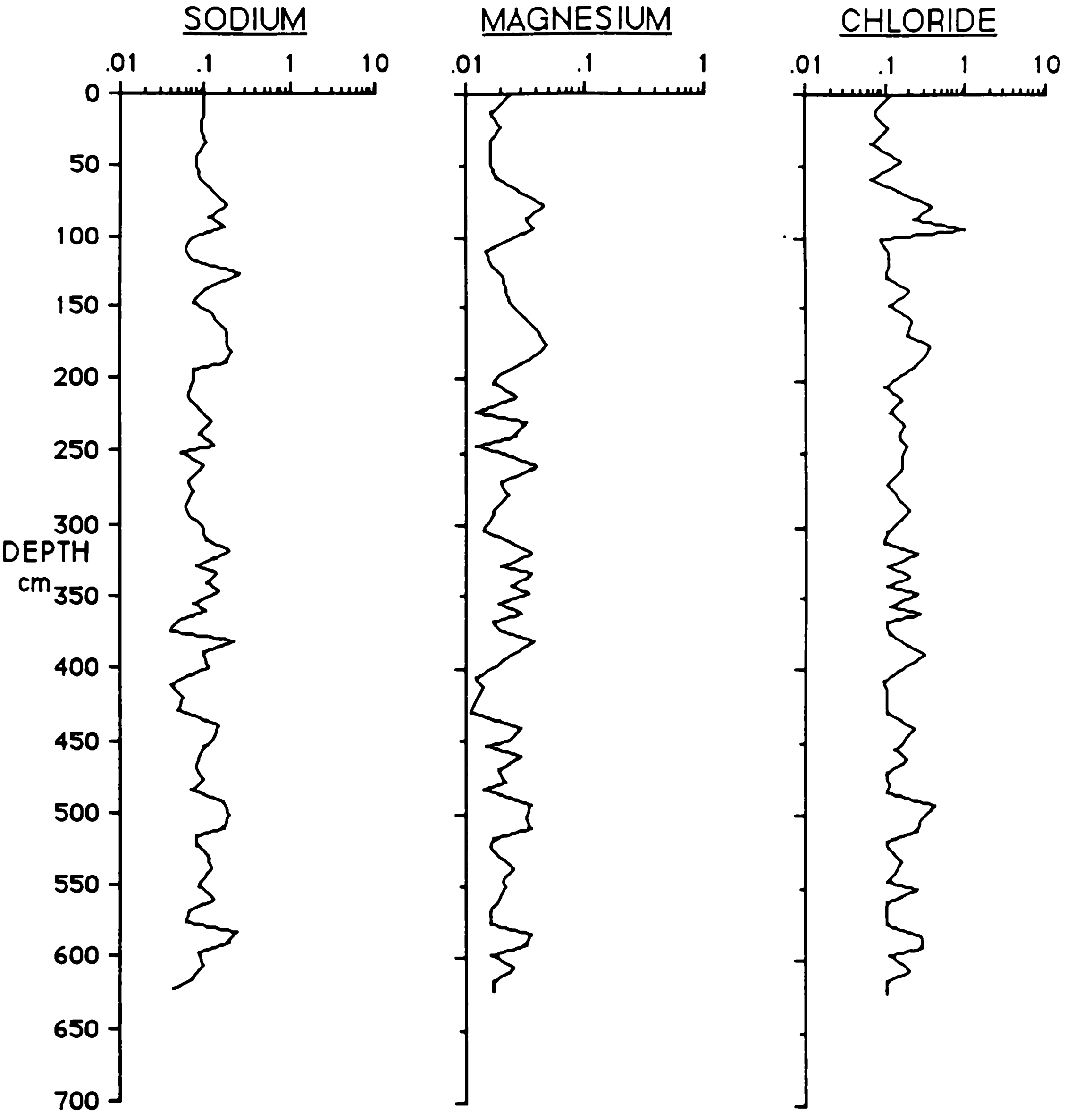


Fig 4.19 Variations in the concentration of sodium, magnesium and chloride (μg/g) with depth in the B2 ice core.

$\delta^{18}O$ values

From the $\delta^{18}O$ values in A2 (Fig 4.18) and B2 (Fig 4.21) it is evident that the ~75% of total precipitation occurs in summer contaminating the underlying winter snow with isotopically heavy rain water, and resulting in the appearance of broad summer peaks and thin winter layers. Recognition of the annual layers may thus be difficult.

The correlation between the Ca and SO_4 peaks in the A2 and B2 cores can be used to fit the $\delta^{18}O$ values of the A2 core to relative positions on the B2 core where not all data was analysed isotopically (Fig 4.21). Correlative peak depths (Table 4.5) and the 1988 tephra marker, establish an accumulation rate of approximately 82 cm/year.

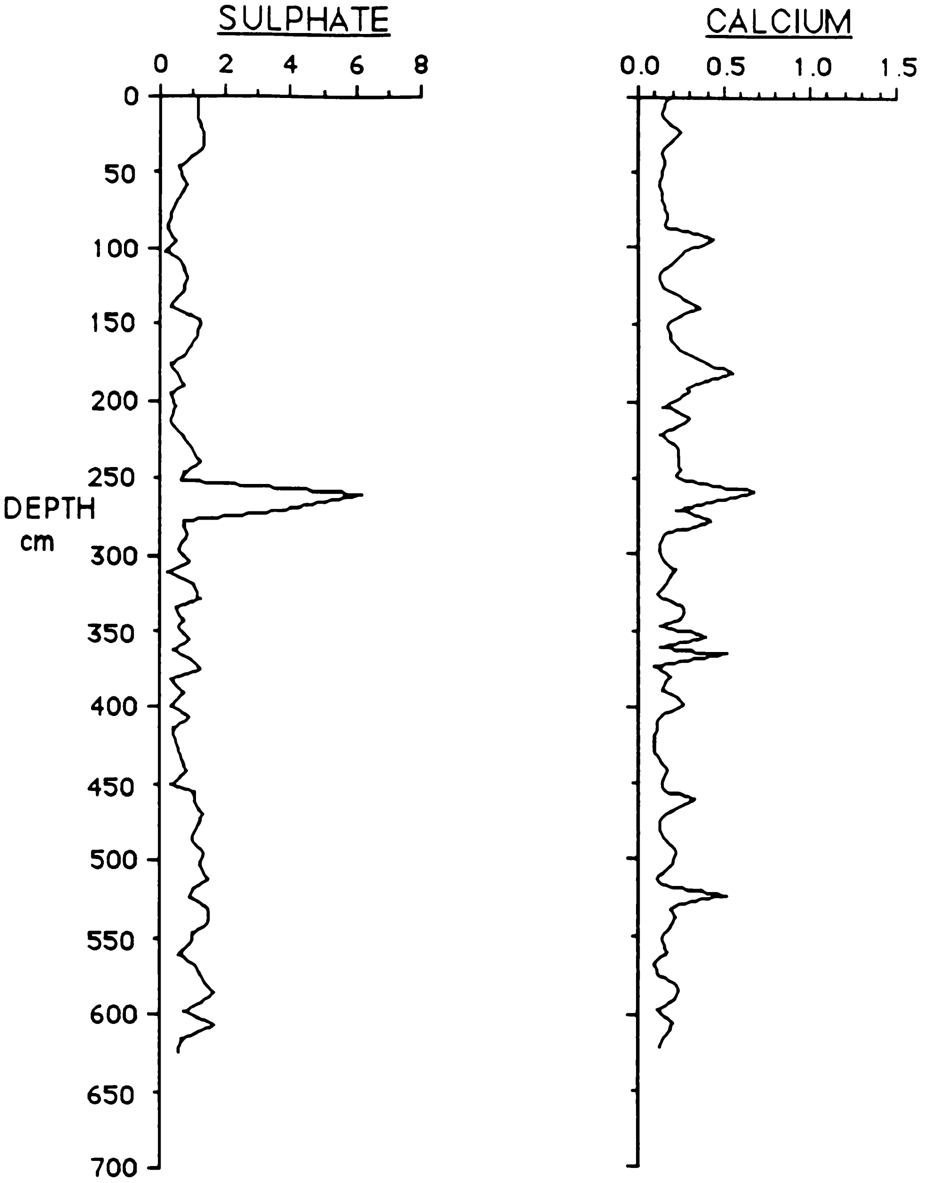


Fig 4.20 Variations in concentration of calcium and sulphate (µg/g) with depth in the B2 ice core.

Table 4.5 Position of corresponding peaks (cm) in the A2 and B2 ice cores

A2	75	110	140	175	243	350	400	545	560	580	675
B2	95	140	175	215	260	350	400	500	525	550	600

An ablation rate of ~100 cm/year is suggested for the centre of the Summit Plateau (Otway,1989). Deposition at Te Heu Heu ridge either exceeds the deposition in the centre of the Plateau, or accumulation is far greater, because in the centre of the Plateau the 1969/1975 eruption debris lies within one metre of the surface with ablation occurring to this level in the 1988 summer. At the Te Heu Heu ridge site, it is likely to be a combination of both increased deposition owing to windblown snow and of lower ablation owing to the position relative to the ridge, where shading occurs for substantial periods of the day in summer and for most of the day in winter. This leads to a more complete accumulation record with proposed annual accumulation layers evident to 1980 in the A2 core and to 1983 in the B2 giving an annual accumulation rate of 82 cm/year. This estimate would be improved if there were a further tephra of known age towards the bottom of the core.

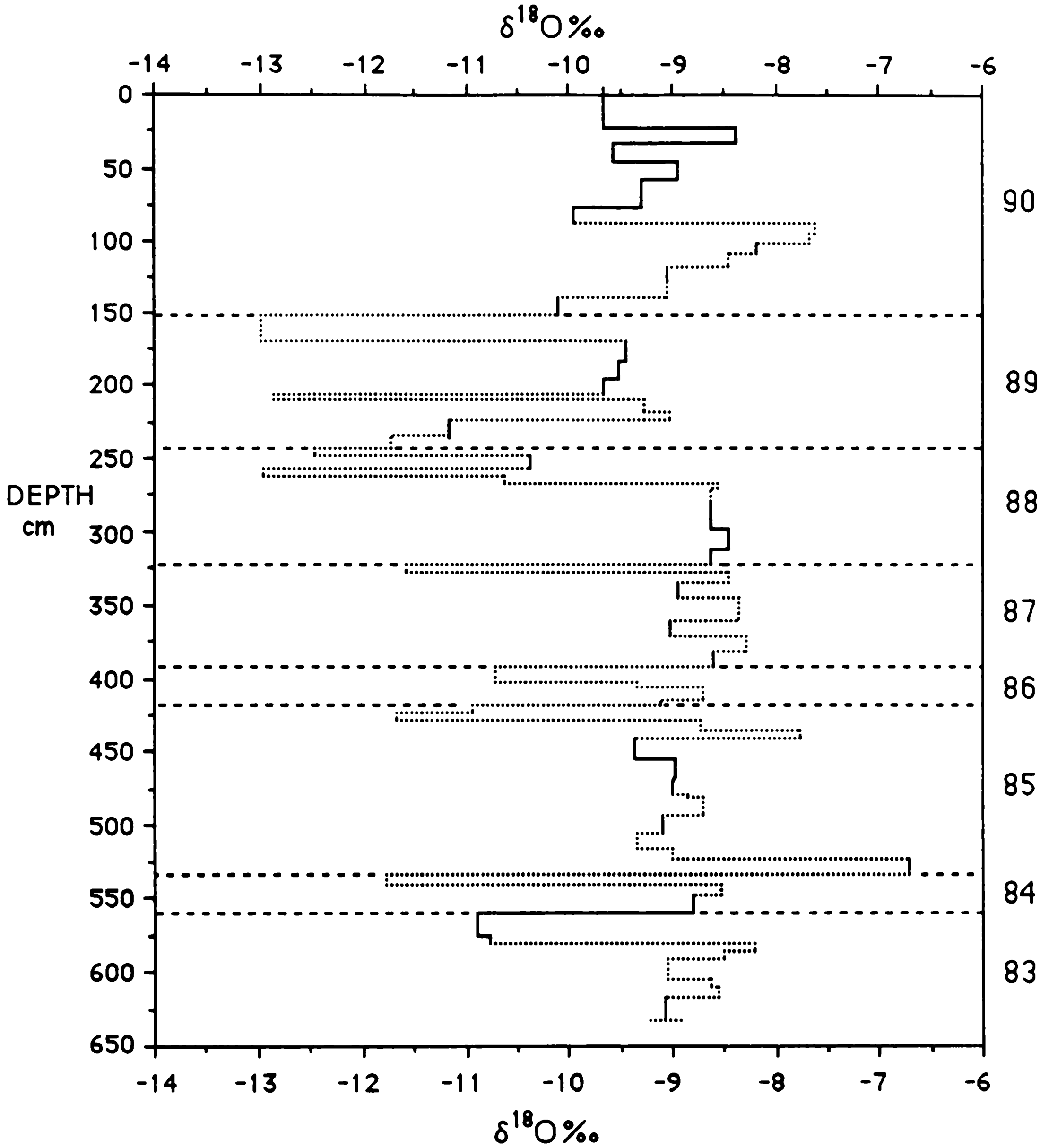


Fig 4.21 $\delta^{18}O$ enrichment values for ice core B2 showing the proposed annual accumulation layers between the dashed lines -. The dotted line indicates areas of the curve where isotopic data for the B2 was unavailable and the correlation of the Ca and SO_4 concentration peaks was used to 'fit' the A2 $\delta^{18}O$ curve to the B2 curve.

4.3 SUMMARY

The dominant source of aerosols contributing to the snow chemistry in East Antarctic Plateau snow is marine with significant contributions from a continental source, both tropospheric and local, the Dry Valleys. Reduced scavenging of aerosols in the Dry Valleys owing to low precipitation and increased scavenging efficiency of snow on the plateau, leads to increased concentrations of the marine components in comparison to other sites at the same distance from source.

Marine snow from Mt Egmont-Taranaki is dominated by marine aerosols, which show a decreasing trend with altitude. An expected decreasing trend with distance inland was not significant, with concentrations of marine Cl and marine SO_4 being the same on Mt Egmont-Taranaki and Mt Ruapehu. However, had snow samples been taken on the seaward slope of Mt Egmont-Taranaki, these may have shown higher concentrations of the marine components and a decreasing trend with distance may have been evident.

Ca concentrations may be enriched relative to seawater consistent with a crustal input, but are likely to have been over-estimated owing to errors in analytical techniques.

Snow samples around the Crater Lake, Mt Ruapehu incorporate marine components from the prevailing westerlies and volcanic inputs from the lake. Snow directly above the outlet on the southern side of the lake (Tahurangi) is most influenced by the volcanic aerosols and gases, with Ca and SO_4 being the dominant ions (with measured concentrations of up to 586 ng/g and 8593 ng/g respectively). Other areas are also likely to be influenced by occasional winds off the lake, especially the snow below the Dome, as is evident by the proportion of volcanic events contaminating the upper Whangaehu Glacier area.

Snow samples affected dominantly by marine components are found on the western and northern sides of the lake where Na and Cl are the dominant ions with background concentrations of 51 and 95 ng/g respectively.

Volcanic input affecting the firns on the Summit Plateau is very high. Eruption debris from the 1969/1975 eruptions is up to three metres below the surface in winter and snow may ablate back to this layer in summer. Concentrations of all components are high, up to 9μg/g Cl, 120 μg/g SO_4, 20 μg/g Na, 6 μg/g Mg and 19 μg/g Ca. The absolute increases in marine components relative to the overlying snow suggests that these are accumulation layers, consistent with ablation and percolation of meltwater through the profile. Underlying snow is also affected, as indicated by the smoothing of the $\delta^{18}O$ curve.

At the edge of the Summit Plateau at the base of the Te Heu Heu ridge, snows remain below 0°C for most of the year, being shaded by the ridge for significant periods of the day in summer and for most of the day in winter. Accumulation may be higher and ablation less than in the central plateau, and a more complete $\delta^{18}O$ profile is preserved. $\delta^{18}O$ values suggest about 10 years accumulation averaging ~82 cm/year at the Te Heu Heu ridge site. This is further supported by the presence of a tephra apparently from the December 1988 phreatic eruption.

The eruption debris from either the 1969 or 1975 eruption is not evident in this location, but is thought to underly the area at depth. Slumping of the ice layers may be caused by underlying melt streams flowing to the Mangatoetoenui Glacier basin.

Ratios of ions and enrichment factors characteristic of the Crater Lake water, volcanically affected snow, from Tahurangi site, and marine snow, from Mt Egmont-Taranaki are given in Table 4.6.

Table 4.6 Ion ratios and enrichment factors of Crater Lake water$_a$, volcanic snow$_b$ and marine snow$_c$.

Ratios	Crater Lake water$_a$	Volcanic snow$_b$	Marine snow$_c$
Cl/Na	11	17	2.3
Mg/Na	1.5	3.8	0.09
Ca/Na	1.3	3.2	1.1
Cl/SO_4	1.0	0.37	6.0
E_{Na} (Cl)	6.2	9.0	1.3
E_{Na} (Mg)	13	32	0.75
E_{Na} (Ca)	35	86	30

a Giggenbach (1974)
b Tahurangi snow measured in this study
c Mt Egmont-Taranaki snow measured in this study

The volcanic influence on the snows of Mt Ruapehu is widespread and substantial. Major phreatomagmatic activity, namely the 1969/1975 eruptions, and some phreatic activity cause increases in concentration of all ions while minor phreatic activity such as the tephra peak in A2 and B2 cause increases in Ca and SO_4 only. This is thought to be from incorporation of tiny crystals of gypsum from the lake water into the steam, and hence into the snow record.

APPENDIX I

ANTARCTIC SNOW 2/1/89

SAMPLE	DEPTH cm	Na ug/g	K ug/g	Ca ug/g	Mg ug/g	ΣC ueq/l	Cl ug/g	NO3* ug/g	SO4 ug/g	ΣA ueq/l	Cl ex ug/g	SO4 ex ug/g	H+ ueq/l
1	438.5	0.065	-	0.044	0.012	6.05	0.217	0.204	0.065	-10.75	0.100	0.049	7.10
2	417	0.076	-	0.031	0.010	5.68	0.669	0.076	0.058	-21.30	0.532	0.039	16.99
3	399.5	0.055	-	0.037	0.009	4.94	0.458	0.071	0.085	-15.82	0.359	0.071	12.73
4	384	0.045	<0.025	<0.025	0.011	4.71	0.277	-	0.086	-9.61	0.197	0.075	7.08
5	370	0.022	-	<0.025	<0.008	2.86	0.199	-	0.174	-9.23	0.160	0.168	7.98
6	358	0.055	-	0.028	0.012	4.76	0.425	0.112	0.100	-15.86	0.325	0.086	12.73
7	343	0.022	-	0.026	<0.008	2.85	0.347	0.087	0.016	-11.51	0.307	0.011	10.26
10	330	0.060	-	0.034	0.012	5.30	0.585	0.218	0.092	-21.93	0.477	0.077	18.51
11	322	0.020	-	-	-	0.88	0.243	0.052	0.035	-8.42	0.207	0.030	7.27
12	309	0.011	-	-	<0.008	1.13	0.590	0.141	0.060	-20.16	0.570	0.058	19.50
13	290	0.013	-	<0.025	<0.008	2.47	0.402	0.090	0.016	-13.10	0.378	0.012	12.34
14	283.5	0.031	-	-	-	1.33	0.249	0.049	0.077	-9.42	0.194	0.070	7.69
15	269	0.037	-	-	-	1.60	0.222	-	0.062	-7.57	0.156	0.053	5.49
16	255.5	0.025	-	-	<0.008	1.76	0.304	-	0.046	-9.52	0.258	0.040	8.08
17	239	0.021	-	-	-	0.90	0.199	0.075	0.036	-7.58	0.162	0.031	6.41
18	219	0.049	<0.025	-	<0.008	3.45	0.437	0.096	0.021	-14.30	0.348	0.009	11.50
19	205.5	0.011	-	-	0.013	1.52	0.248	0.074	0.070	-9.62	0.228	0.067	8.97
20	181.5	0.057	-	-	<0.008	3.15	0.447	-	0.033	-13.28	0.344	0.018	10.04
21	170.5	0.045	-	0.028	<0.008	4.03	0.302	-	0.108	-10.76	0.220	0.097	8.20
22	160.5	0.112	-	0.101	0.023	11.84	0.376	0.195	0.049	-14.76	0.173	0.021	8.45
24A	145	0.029	-	0.028	0.010	3.48	0.108	0.039	0.018	-4.05	0.055	0.011	2.41
24B	126	0.033	-	0.025	0.008	3.32	0.276	0.025	0.073	-9.70	0.217	0.064	7.83
25	109.5	0.104	<0.025	<0.025	0.017	7.80	2.099	-	0.064	-60.52	1.912	0.038	54.51
26	95	0.044	-	0.030	0.009	4.16	0.410	0.017	0.023	-12.34	0.332	0.012	9.86
27Hard	89.5	0.039	-	0.032	0.009	4.04	0.628	0.152	0.030	-20.80	0.557	0.021	18.54
27Soft	83.5	0.064	<0.025	0.034	0.009	5.90	0.681	0.072	0.097	-22.39	0.566	0.081	18.74
38	80.5	0.024	-	-	-	1.04	0.338	0.107	0.083	-12.96	0.295	0.077	11.59
29	71.5	0.032	-	0.034	0.008	3.79	0.163	0.300	0.031	-10.06	0.105	0.023	8.25
30	54.5	0.021	-	<0.025	<0.008	2.83	0.333	0.057	0.121	-12.84	0.295	0.116	11.62
31	46.5	0.019	-	-	-	0.84	0.362	1.528	0.086	-36.60	0.328	0.081	35.49
32	35	0.003	-	-	-	0.14	0.681	0.348	0.049	-25.84	0.675	0.049	25.59
33	25	0.019	-	-	<0.008	1.50	0.320	0.180	0.050	-12.96	0.285	0.045	11.85
36 Surface	0	0.006	-	<0.025	-	1.53	0.058	0.259	0.018	-6.19	0.047	0.017	5.83
37 Surface	0	0.006	-	-	-	0.28	0.009	0.445	0.013	-7.69	0.000	0.012	7.41

* Not adjusted for blank concentrations

ANTARCTIC DETECTION LIMITS

	y1 ug/g	y2 ug/g	(y1-y2)^2	SR^2	Criterion ug/g	Limit ug/g
Sodium	0.017	0.018	0.000001	1.3E-7	0.001	0.002
	0.023	0.023	0			
	0.029	0.029	0			
	0.031	0.031	0			
	0.014	0.014	0			
	0.006	0.005	0.000001			
	0.021	0.021	0			
	0.021	0.021	0			
Potassium	0.136	0.135	0.000001	1.7E-5	0.012	0.025
	0.192	0.189	0.000009			
	0.013	0.024	0.000121			
	0.034	0.032	0.000004			
Calcium	-0.008	-0.002	0.000036	9.3E-6	0.013	0.025
	-0.002	-0.001	0.000001			
Magnesium	-0.001	-0.001	0	1.9E-6	0.004	0.008
	-0.003	0	0.000009			
	-0.002	-0.003	0.000001			
	-0.003	-0.003	0			
	-0.003	0	0.000009			
	-0.002	0	0.000004			
Fluoride	0.019	0.013	0.000036	4.8E-6	0.007	0.013
	0.015	0.015	0			
	0.008	0.009	0.000001			
	0.01	0.011	0.000001			
Chloride	0	0.001	0.000001	8.4E-6	0.008	0.016
	0.043	0.039	0.000016			
	0.002	0.002	0			
	0.006	0.006	0			
	0.004	0.004	0			
	0.104	0.114	0.000100			
	0.125	0.126	0.000001			
Bromide	0.0003	0.0003	0	4.2E-8	0.001	0.001
	0.0002	0.0002	0			
	0.0005	0	0			
Nitrate	0.004	0.002	0.000004	1.9E-6	0.004	0.007
	0.03	0.029	0.000001			
	0.001	0.001	0			
	0.043	0.042	0.000001			
	0.046	0.0495	0.000012			
	0.154	0.152	0.000004			

	y1 ug/g	y2 ug/g	(y1-y2)^2	SR^2	Criterion ug/g	Limit ug/g
Phosphate	0.0012	0.0006	0	9.2E-8	0.001	0.002
	0.001	0.0003	0			
	0.0002	0.0003	0			
	0.0001	0.0004	0			
	0.0009	0.0011	0			
Sulphate	0.001	0.001	0	3.7E-6	0.005	0.010
	0.001	0.004	0.000009			
	0.093	0.087	0.000036			
	0	0.002	0.000004			
	0.004	0.0025	0.000002			
	0.004	0.006	0.000004			
	0.014	0.016	0.000004			
	0.003	0.003	0			

APPENDIX II

SNOW SAMPLES 15/7/88 - 25/7/89

DATE	SAMPLE	DEPTH cm	Na ug/g	K ug/g	Ca ug/g	Mg ug/g	ΣC ueq/l	F ug/g	Cl ug/g	Br ug/g	NO3 ug/g	PO4 ug/g	SO4 ug/g	ΣA ueq/l	Cl ex ug/g	SO4 ex ug/g	H+ ueq/l
15/7/88	1.1*	0	0.968	0.155	0.176	0.219	72.88	<0.053	2.878	0.009	<0.008	0.015	4.358	-175.32	1.136	4.116	117.66
15/7/88	1.2*	0	0.198	0.092	0.185	0.150	32.54	0.080	1.671	0.006	0.011	0.014	5.716	-170.91	1.314	5.667	154.97
15/7/88	1.3*	12.5	0.212	0.048	0.157	0.190	33.92	0.098	2.165	0.008	0.100	0.037	7.205	-218.95	1.783	7.152	200.48
15/7/88	1.4*	15	0.884	0.064	0.157	0.132	58.79	-	1.489	0.009	-	<0.004	0.358	-49.68	0	0.137	2.85
15/7/88	2.1*	0	0.676	0.067	-	0.176	45.60	<0.053	2.855	0.007	-	-	4.038	-167.38	1.638	3.869	126.51
15/7/88	2.2*	0	0.147	0.039	-	0.100	15.62	<0.053	1.319	0.004	<0.008	0.045	4.536	-135.94	1.055	4.499	123.35
15/7/88	2.3*	12.5	0.148	<0.035	-	0.091	14.82	0.100	1.623	0.005	<0.008	0.030	4.246	-140.50	1.357	4.209	125.80
15/7/88	2.4*	15	0.093	0.041	-	0.130	15.79	-	1.739	0.008	0.011	-	0.374	-57.11	1.572	0.351	51.64
7/6/89	COL 1	80	0.053	-	-	0.020	3.95	-	0.267	<0.004	<0.008	<0.004	0.541	-19.09	0.172	0.528	15.93
7/6/89	COL 2	50	0.067	-	-	0.016	4.23	-	0.258	<0.004	-	-	0.320	-13.98	0.137	0.303	10.17
7/6/89	COL 3	40	0.062	-	-	0.015	3.93	-	0.258	-	<0.008	-	0.272	-13.06	0.146	0.257	9.58
7/6/89	COL 4	30	0.056	-	-	0.016	3.75	-	0.233	<0.004	<0.008	-	0.402	-15.11	0.132	0.388	11.91
7/6/89	COL 5	10	0.304	<0.035	-	0.056	18.73	-	0.887	<0.004	0.009	-	0.584	-37.36	0.340	0.508	20.26
25/7/89	DOME 1	14.5	0.163	0.042	-	0.067	13.68	-	0.847	<0.004	0.008	n.d.	1.605	-57.45	0.554	1.564	48.22
25/7/89	DOME 2	32.5	0.028	-	-	0.014	2.37	-	0.170	-	0.012	n.d.	0.161	-8.34	0.120	0.154	6.76
25/7/89	COL 3	20	0.081	<0.035	-	0.020	6.06	-	0.252	-	0.014	n.d.	0.184	-11.16	0.106	0.164	6.62
25/7/89	COL 4	40	<0.018	<0.035	-	0.012	2.67	-	0.131	-	0.011	n.d.	0.144	-6.84	0.099	0.140	5.85
25/7/89	COL 5	50	<0.018	<0.035	-	0.011	2.58	-	0.120	-	<0.008	n.d.	0.066	-5.05	0.088	0.062	3.87
25/7/89	COL 6	60	0.027	-	-	0.012	2.16	-	0.150	-	<0.008	n.d.	0.046	-5.48	0.101	0.039	3.79
25/7/89	COL 7	70	0.028	-	-	0.018	2.70	-	0.114	<0.004	0.009	n.d.	0.067	-4.80	0.064	0.060	3.18
25/7/89	COL 8	100	0.026	<0.035	-	0.014	3.18	-	0.156	<0.004	0.008	n.d.	0.058	-5.78	0.109	0.052	4.27
25/7/89	COL 9	112	0.024	<0.035	-	0.011	2.84	-	0.119	-	0.015	n.d.	0.070	-5.05	0.076	0.064	3.70
25/7/89	COL 10	130	0.160	-	-	0.032	9.59	-	0.349	-	0.013	n.d.	0.158	-13.34	0.061	0.118	4.38

* Error in analyses

n.d. not determined

SNOW SAMPLES 3/11/89

DATE	SAMPLE	DEPTH cm	Na ug/g	K ug/g	Ca ug/g	Mg ug/g	ΣC ueq/l	F ug/g	Cl ug/g	Br ug/g	NO3 ug/g	PO4 ug/g	SO4 ug/g	ΣA ueq/l	Cl ex ug/g	SO4 ex ug/g	H+ ueq/l
3/11/89	Outlet 1	0-5	0.080	0.054	0.365	0.052	27.35	-	0.996	-	0.010	-	5.718	-147.18	0.852	5.698	142.62
3/11/89	2	10-15	0.133	0.085	0.235	0.036	22.65	-	0.942	<0.004	0.009	-	2.693	-82.77	0.703	2.660	75.21
3/11/89	Pit 1 3	110-103	0.064	<0.035	0.279	0.052	21.88	-	1.052	0.004	<0.008	-	1.746	-66.17	0.937	1.730	62.44
3/11/89	Tahurangi 4	103-93	0.058	0.039	0.313	0.073	25.15	-	0.984	<0.004	-	-	2.511	-80.03	0.880	2.497	76.64
3/11/89	5	93-85	0.093	<0.035	0.371	0.115	32.92	-	1.732	0.005	<0.008	-	4.431	-141.20	1.565	4.408	135.77
3/11/89	6	85-79	0.074	<0.035	0.313	0.086	26.81	-	1.276	0.004	<0.008	-	2.939	-97.29	1.143	2.921	92.99
3/11/89	7	79-72	0.112	0.052	0.215	0.120	26.81	-	1.526	0.007	<0.008	0.005	4.863	-144.56	1.325	4.835	137.92
3/11/89	8	72-63	0.067	<0.035	0.313	0.082	26.18	-	1.236	0.004	-	-	2.888	-94.97	1.115	2.871	91.06
3/11/89	9	63-53	0.086	<0.035	0.115	0.078	16.79	-	1.462	0.004	0.008	-	3.030	-104.42	1.307	3.009	99.43
3/11/89	10	53-46	0.185	0.061	0.713	0.222	63.45	0.159	2.934	0.008	<0.008	-	8.482	-267.77	2.601	8.436	248.69
3/11/89	11	46-36	0.187	0.070	0.586	0.219	57.19	0.156	3.143	0.008	-	-	8.593	-275.69	2.807	8.546	256.63
3/11/89	12	36-27	0.070	0.043	0.235	0.091	23.36	-	1.747	0.006	<0.008	<0.004	3.438	-121.10	1.621	3.421	116.82
3/11/89	13	26-14	0.054	0.039	0.279	0.044	20.89	-	1.146	0.004	-	-	1.965	-73.24	1.049	1.952	70.07
3/11/89	14	14-0	0.059	<0.035	0.225	0.043	18.23	-	1.391	0.006	0.016	0.005	1.955	-80.38	1.285	1.940	76.72
3/11/89	Surface 15	0-5	0.028	<0.035	0.365	0.017	21.73	-	0.396	-	0.016	-	1.648	-45.70	0.346	1.641	44.10
3/11/89	16	0-5	<0.018	-	0.179	<0.011	10.62	-	0.214	-	<0.008	-	0.863	-24.11	0.182	0.859	23.09
3/11/89	17	0-5	0.240	0.039	0.151	0.019	20.54	-	0.522	0.005	0.013	<0.004	0.232	-19.94	0.090	0.172	6.32
3/11/89	18	0-5	0.197	<0.035	0.251	0.024	23.96	-	0.431	-	0.016	-	0.287	-18.38	0.076	0.238	7.35
3/11/89	19	0-5	0.150	<0.035	0.165	0.017	17.05	-	0.282	<0.004	0.021	-	0.162	-11.71	0.012	0.125	3.26
3/11/89	20	0-5	0.104	<0.035	0.151	0.016	14.27	-	0.242	-	0.012	-	0.093	-8.95	0.055	0.067	3.13
3/11/89	21	0-5	0.136	<0.035	0.137	0.011	14.55	-	0.346	<0.004	0.010	-	0.082	-11.67	0.101	0.048	4.00
3/11/89	22	0-5	0.062	<0.035	0.091	0.011	9.04	-	0.182	-	0.012	-	0.111	-7.63	0.070	0.096	4.16
3/11/89	23	0-5	0.043	<0.035	0.111	<0.011	9.21	-	0.096	-	0.008	-	0.061	-4.10	0.019	0.050	1.70
3/11/89	Pit 2 24	85-76	0.082	-	0.103	0.013	9.78	-	0.219	<0.004	<0.008	-	0.231	-11.16	0.071	0.211	6.51
3/11/89	Dome 25	76-69	0.072	<0.035	0.141	0.011	11.97	-	0.196	0.005	<0.008	-	0.212	-10.13	0.066	0.194	6.03
3/11/89	26	69-62	0.079	-	0.174	0.011	13.02	-	0.193	<0.004	<0.008	-	0.141	-8.55	0.051	0.121	4.08
3/11/89	27	62-53	0.094	-	0.124	0.014	11.43	-	0.201	-	-	-	0.057	-6.85	0.032	0.034	1.59
3/11/89	28	53-47	0.042	-	0.119	<0.011	8.67	-	0.124	-	<0.008	-	0.096	-5.62	0.048	0.086	3.27
3/11/89	29	47-39	0.043	-	0.111	<0.011	8.31	-	0.226	<0.004	<0.008	-	0.090	-8.42	0.149	0.079	5.95
3/11/89	30	39-33	0.092	<0.035	0.124	0.012	12.07	-	0.220	-	<0.008	-	0.071	-7.81	0.054	0.048	2.66
3/11/89	31	33-27	0.173	-	0.119	0.017	14.86	-	0.563	0.004	<0.008	-	0.077	-17.66	0.252	0.034	7.90
3/11/89	32	27-16	0.268	-	0.146	0.022	20.75	-	0.521	0.005	<0.008	<0.004	0.078	-16.63	0.039	0.011	1.44
3/11/89	33	16-0	0.228	<0.035	0.151	0.016	19.66	-	0.518	<0.004	<0.008	-	0.100	-16.87	0.108	0.043	4.05

SNOW SAMPLES 3/11/89 (CONT)

DATE	SAMPLE	DEPTH cm	Na ug/g	K ug/g	Ca ug/g	Mg ug/g	ΣC ueq/l	F ug/g	Cl ug/g	Br ug/g	NO3 ug/g	PO4 ug/g	SO4 ug/g	ΣA ueq/l	Cl ex ug/g	SO4 ex ug/g	H+ ueq/l
3/11/89	Pit 3 34	79-71	0.051	0.044	0.099	<0.011	9.19	-	0.095	<0.004	0.015	<0.004	0.085	-4.86	0.003	0.072	1.83
3/11/89	Col 35	71-65	0.066	-	0.165	0.011	12.01	-	0.149	-	<0.008	-	0.062	-5.62	0.030	0.046	1.92
3/11/89	36	65-58	0.104	<0.035	0.099	0.015	11.59	-	0.259	<0.004	-	-	0.098	-9.39	0.072	0.072	3.52
3/11/89	37	58-50	0.108	-	0.127	0.019	12.60	-	0.226	-	<0.008	-	0.089	-8.35	0.032	0.062	2.31
3/11/89	38	50-43	0.064	<0.035	0.155	0.013	12.48	-	0.150	-	-	-	0.059	-5.46	0.035	0.043	1.87
3/11/89	39	43-32	0.124	<0.035	0.124	0.018	13.96	-	0.246	0.004	<0.008	<0.004	0.090	-9.11	0.023	0.059	2.00
3/11/89	40	32-27	0.168	<0.035	0.072	0.022	13.61	-	0.525	0.004	-	0.004	0.081	-16.67	0.223	0.039	7.07
3/11/89	41	27-18	0.178	-	0.091	0.016	13.60	-	0.437	0.004	<0.008	0.005	0.077	-14.26	0.117	0.033	4.08
3/11/89	42	18-10	0.246	<0.035	0.115	0.023	19.23	-	0.531	0.004	0.008	<0.004	0.136	-18.11	0.088	0.075	4.16
3/11/89	43	10-0	0.237	<0.035	0.214	0.014	23.04	-	0.686	0.004	0.012	-	0.075	-21.15	0.259	0.016	7.81
Detn Coeff			0.009	0.018	0.046	0.005	3.56	0.027	0.009	0.002	0.004	0.002	0.017	-2.18			
Detn Limit			0.018	0.035	0.093	0.011	7.22	0.053	0.018	0.004	0.008	0.004	0.033	-4.29			

MAJOR ELEMENT CHEMISTRY OF MT EGMONT-TARANAKI

DATE	SAMPLE	ALTITUDE m	DEPTH cm	Na ug/g	K ug/g	Ca ug/g	Mg ug/g	ΣC ueq/l	Cl ug/g	Br ug/g	NO3 ug/g	PO4 ug/g	SO4 ug/g	ΣA ueq/l	Clex ug/g	SO4ex ug/g	H+ ueq/l
1/11/89	Manganui 1	1315	10	0.121	0.039	0.137	0.012	14.08	0.310	<0.004	-	-	0.045	-9.73	0.092	0.015	2.90
1/11/89	Manganui 2	1315	50	0.121	0.039	0.091	0.012	11.79	0.297	<0.004	<0.008	<0.004	0.053	-9.78	0.079	0.023	2.83
1/11/89	Manganui 3	1315	10	0.162	0.053	0.155	0.016	17.45	0.399	<0.004	0.008	0.004	0.075	-13.12	0.107	0.035	3.86
1/11/89	Manganui 4	1315	20	0.103	0.045	0.137	0.013	13.54	0.242	<0.004	0.013	-	0.058	-8.29	0.057	0.032	2.47
1/11/89	Manganui 5	1315	20	0.078	<0.035	0.137	<0.011	12.03	0.259	<0.004	<0.008	<0.004	0.047	-8.59	0.119	0.028	4.03
2/11/89	North Egmont 1	1845	10	0.109	0.042	0.137	<0.011	13.56	0.200	<0.004	-	-	0.036	-6.44	0.004	0.009	0.29
2/11/89	North Egmont 2	1845	10	0.102	<0.035	0.155	<0.011	13.97	0.259	<0.004	<0.008	-	0.041	-8.34	0.075	0.016	2.57
2/11/89	North Egmont 3	1710	12.5	0.155	<0.035	0.165	<0.011	16.78	0.338	0.004	<0.008	-	0.069	-11.15	0.059	0.030	2.42
2/11/89	North Egmont 4	1710	12.5	0.136	0.057	0.155	0.013	16.18	0.265	<0.004	-	<0.004	0.042	-8.52	0.020	0.008	0.73
2/11/89	North Egmont 5	1645	100	0.237	<0.035	0.192	0.014	21.94	0.491	<0.004	-	<0.004	0.055	-15.17	0.064	-0.004	1.72
2/11/89	North Egmont 6	1645	100	0.218	<0.035	0.112	0.015	17.20	0.445	<0.004	<0.008	-	0.059	-13.96	0.053	0.005	1.70

RUAPEHU DETECTION LIMITS

	y1 ng/g	y2 ng/g	(y1-y2)^2	SR^2	Criterion ng/g	Limit ng/g
Sodium	8	9	1	11.67	9	17
	8	10	3			
	12	13	0			
	9	11	3			
	1	11	90			
	2	14	156			
	12	5	42			
	8	11	9			
	45	43	6			
	42	41	1			
	40	42	6			
	43	40	10			
	5	5	0			
	43	42	0			
Potassium	29	18	119	50.85	18	35
	25	15	102			
	38	22	256			
	38	47	88			
	18	15	10			
	10	8	5			
	10	10	0			
	18	25	49			
	29	22	56			
	29	29	0			
	18	24	35			
	64	86	488			
	61	67	38			
	70	54	240			
	64	57	38			
Calcium	37	73	1303	331.77	46	93
	148	105	1849			
	113	130	289			
	130	81	2401			
	6	27	425			
	31	27	19			
	31	16	243			
	6	14	61			
	57	41	262			
	54	54	0			
	36	57	445			
Calcium	32	24	69	39.07	17	34
	32	24	69			
	32	24	69			
	32	32	0			
	41	32	76			
	24	35	125			
	47	35	139			

	y1 ng/g	y2 ng/g	(y1-y2)^2	SR^2	Criterion ng/g	Limit ng/g
Magnesium	15	21	34	4.80	5	11
	13	14	1			
	13	13	0			
	13	7	38			
	18	19	1			
	19	19	0			
	18	19	0			
	11	10	2			
	20	21	1			
	21	20	1			
	7	14	44			
	10	10	0			
	9	9	0			
	5	6	2			
	-4	3	44			
	6	7	2			
	7	8	0			
	5	4	2			

	y1 ug/g	y2 ug/g	(y1-y2)^2	SR^2	Criterion ug/g	Limit ug/g
Fluoride	0.552	0.541	0.000121	0.00006	0.027	0.053
	0.515	0.527	0.000144			
	0.235	0.246	0.000121			
Chloride	0.333	0.284	0.002401	0.00372	0.009	0.018
	0.29	0.286	0.000016			
	0.21	0.263	0.002809			
	0.355	0.4	0.002025			
	0.262	0.266	0.000016			
	0.267	0.262	0.000025			
	0.235	0.246	0.000121			
	0.5	0.391	0.011881			
	0.38	0.402	0.000484			
	0.223	0.291	0.004624			
	0.704	0.508	0.038416			
	0.416	0.518	0.010404			
	0.282	0.283	0.000001			
	0.27	0.222	0.002304			
	0.25	0.248	0.000004			
	0.272	0.279	0.000049			
	0.48	0.501	0.000441			
	0.362	0.363	0.000001			
	0.403	0.273	0.0169			
	0.242	0.491	0.062001			
	0.276	0.313	0.001369			

	y1 ug/g	y2 ug/g	(y1-y2)^2	SR^2	Criterion ug/g	Limit ug/g
Bromide	0.001	0.001	0	0	0.002	0.004
	0.001	0.001	0			
	0.001	0.002	0.000001			
	0.001	0.002	0.000001			
	0.002	0.001	0.000001			
	0.001	0.001	0			
	0	0.002	0.000004			
	0.002	0.001	0.000001			
	0.002	0.002	0			
	0.003	0	0.000009			
	0.003	0.003	0			
	0.001	0.002	0.000001			
	0.003	0.003	0			
	0.003	0.004	0.000001			
	0.002	0.001	0.000001			
	0.003	0.002	0.000001			
	0.002	0.003	0.000001			
	0.001	0	0.000001			
	0.001	0	0.000001			
	0	0.001	0.000001			
Nitrate	0.004	0	0.000016	0	0.004	0.008
	0	0	0			
	0.001	0.001	0			
	0.001	0	0.000001			
	0	0.001	0.000001			
	0.001	0.001	0			
	0.002	0.003	0.000001			
	0	0.001	0.000001			
	0.001	0.002	0.000001			
	0.002	0.001	0.000001			
	0.002	0.002	0			
	0.004	0.003	0.000001			
	0.004	0.003	0.000001			
	0.003	0.007	0.000016			
	0.002	0.002	0			
	0.008	0.003	0.000025			
	0.003	0.001	0.000004			
	0.012	0.015	0.000009			
	0.002	0.001	0.000001			
	0.016	0.011	0.000025			
Phosphate	0.001	0.002	0.000001	0	0.002	0.004
	0.001	0.002	0.000001			
	0.001	0.001	0			
	0.001	0.003	0.000004			
	0.002	0	0.000004			
	0.001	0	0.000001			
	0.002	0.001	0.000001			
	0.001	0.002	0.000001			
	0.001	0.001	0			
	0.001	0	0.000001			

	y1 ug/g	y2 ug/g	(y1-y2)^2	SR^2	Criterion ug/g	Limit ug/g
Sulphate	0.027	0.034	0.000049	0.00005	0.017	0.033
	0.03	0.02	0.0001			
	0.013	0.013	0			
	0.013	0.007	0.000036			
	0.018	0.009	0.000081			
	0.01	0.01	0			
	0.016	0.02	0.000016			
	0.006	0.013	0.000049			
	0.007	0.014	0.000049			
	0.008	0.013	0.000025			
	0.009	0.02	0.000121			
	0.062	0.059	0.000009			
	0.071	0.061	0.0001			
	0.065	0.059	0.000036			
	0.014	0.02	0.000036			
	0.088	0.06	0.000784			
	0.065	0.052	0.000169			
	0.113	0.121	0.000064			
	0.01	0.012	0.000004			
	0.111	0.1	0.000121			

APPENDIX III

ICE CORES 25/7/89

DATE	SAMPLE	DEPTH cm	Na ug/g	K ug/g	Ca ug/g	Mg ug/g	ΣC ueq/l	F ug/g	Cl ug/g	Br ug/g	NO3 ug/g	SO4 ug/g	ΣA ueq/l	Cl ex ug/g	SO4 ex ug/g	H+ ueq/l	O-ISOTOPE %
25/7/89	CORE A1	65	0.049	<0.035	<0.093	0.017	9.07	-	0.163	0.008	<0.008	0.083	-6.6	0.075	0.071	3.70	-15.97
25/7/89		75	0.142	-	0.190	0.029	18.04	-	0.336	0.009	0.009	0.121	-12.2	0.080	0.086	4.18	-11.41
25/7/89		85	0.095	<0.035	<0.093	0.014	10.82	-	0.304	0.009	0.016	0.186	-12.8	0.133	0.162	7.37	-10.03
25/7/89		105	0.174	-	<0.093	0.029	14.60	-	0.704	0.007	0.034	0.149	-23.6	0.391	0.106	13.72	-12.18
25/7/89		110	0.061	0.042	0.113	0.019	10.93	-	0.240	0.004	0.011	0.093	-8.9	0.130	0.078	5.45	-12.61
25/7/89		115	0.062	<0.035	<0.093	0.013	9.30	-	0.175	0.004	0.008	0.088	-6.9	0.063	0.073	3.42	-16.25
25/7/89		125	0.050	-	<0.093	0.018	8.30	-	0.175	<0.004	0.008	0.066	-6.5	0.085	0.054	3.63	-16.08
25/7/89		137.5	0.108	<0.035	<0.093	0.019	11.80	-	0.333	0.006	0.008	0.100	-11.7	0.139	0.073	5.54	-12.25
25/7/89		145	0.050	<0.035	-	0.017	4.47	-	0.525	<0.004	0.010	0.069	-16.5	0.435	0.057	13.56	-12.52
25/7/89		152.5	0.196	<0.035	0.121	0.043	19.00	-	0.416	0.005	0.016	0.149	-15.2	0.063	0.100	4.11	-11.83
25/7/89		157.5	0.100	<0.035	0.113	0.018	12.37	-	0.451	0.005	0.012	0.498	-23.3	0.271	0.473	17.65	-12.34
25/7/89		162.5	0.146	<0.035	0.096	0.039	15.25	-	0.265	0.004	-	3.802	-86.6	0.002	3.766	78.38	-12.42
25/7/89		167.5	0.068	-	<0.093	0.013	8.67	-	0.246	0.005	<0.008	0.114	-9.5	0.124	0.097	5.62	-12.55
25/7/89		172.5	0.070	-	<0.093	0.020	9.33	-	0.278	0.010	0.009	0.115	-10.5	0.152	0.098	6.44	-12.05
25/7/89		177.5	0.061	-	-	0.020	4.30	-	0.543	0.007	0.017	0.170	-19.2	0.433	0.155	15.67	-12.43
25/7/89		181.5	0.060	-	-	0.011	3.52	-	0.364	0.004	0.046	0.169	-14.6	0.256	0.154	11.14	-14.08
25/7/89		184	0.066	<0.035	0.096	0.020	10.20	-	0.345	0.010	0.008	0.136	-12.8	0.226	0.120	8.97	-15.41
25/7/89		186	0.086	<0.035	0.102	0.019	11.29	-	0.374	0.005	0.014	0.239	-15.8	0.219	0.218	10.91	-11.26
25/7/89		189	0.091	-	-	0.014	5.11	-	0.327	0.023	0.014	0.681	-23.9	0.163	0.658	18.50	-13.60
25/7/89		192.5	2.895	0.426	2.074	0.384	271.92	0.74	8.36	0.05	1.94	43.31	-1207	3.15	42.59	1005.5	-10.04
25/7/89		195.5	6.20	1.40	8.80	2.02	910.86	1.27	7.34	0.03	1.35	122.50	-2844	0	120.95	2537.5	-10.45
25/7/89		198.5	0.094	-	0.246	0.068	21.96	-	0.487	0.005	0.011	1.064	-36.1	0.318	1.041	30.75	-9.57
25/7/89		202.5	0.157	<0.035	0.438	0.113	38.88	-	0.355	0.006	<0.008	3.130	-75.3	0.072	3.091	66.45	-8.74
25/7/89		207.5	0.227	0.110	0.733	0.182	64.24	-	0.460	0.009	<0.008	3.353	-83.0	0.051	3.296	70.14	
25/7/89		212.5	0.122	<0.035	0.264	0.095	27.19	-	0.269	0.008	<0.008	2.014	-49.7	0.049	1.984	42.77	-9.60
25/7/89		218.5	0.073	<0.035	0.229	0.053	19.86	-	0.308	<0.004	0.009	0.738	-24.2	0.177	0.720	20.08	-9.44
25/7/89		227	0.111	-	0.132	0.037	14.46	-	0.285	0.006	<0.008	0.928	-27.5	0.085	0.900	21.25	-9.20
25/7/89		236	0.138	<0.035	0.216	0.043	21.22	-	0.482	0.006	0.011	1.877	-52.9	0.234	1.843	45.07	-10.02
25/7/89		245	0.532	1.006	1.153	0.725	166.07	-	0.292	0.004	<0.008	7.077	-155.6	0	6.944	144.56	-10.00
25/7/89		253.5	0.471	0.573	0.502	0.342	88.34	-	0.321	0.006	0.609	3.284	-87.2	0	3.166	75.66	-9.65
25/7/89		262	0.093	-	<0.093	0.046	12.47	-	0.263	0.005	<0.008	0.678	-21.7	0.096	0.655	16.43	-9.48
25/7/89		269.5	0.114	<0.035	0.113	0.026	13.63	-	0.346	<0.004	<0.008	0.317	-16.5	0.141	0.289	10.09	-10.03

ICE CORES 25/7/89 (CONT)

DATE	SAMPLE	DEPTH cm	Na ug/g	K ug/g	Ca ug/g	Mg ug/g	ΣC ueq/l	F ug/g	Cl ug/g	Br ug/g	NO3 ug/g	SO4 ug/g	ΣA ueq/l	Cl ex ug/g	SO4 ex ug/g	H+ ueq/l	O-ISOTOPE %
25/7/89	CORE A1	276	0.081	-	<0.093	0.013	9.23	-	0.349	0.004	<0.008	0.290	-16.1	0.203	0.270	11.45	-9.94
25/7/89		283	0.110	<0.035	0.128	0.033	14.78	-	0.392	0.004	0.008	0.916	-30.3	0.194	0.889	24.06	-9.89
25/7/89		289.5	0.077	<0.035	<0.093	0.030	11.35	-	0.374	0.004	<0.008	0.496	-21.0	0.235	0.477	16.66	-10.63
25/7/89		298	0.080	<0.035	0.152	0.037	15.00	-	0.380	<0.004	<0.008	0.509	-21.5	0.236	0.489	16.93	-10.70
25/7/89		307	0.114	<0.035	0.237	0.044	21.30	-	0.349	<0.004	<0.008	1.535	-41.9	0.144	1.507	35.50	-10.48
25/7/89		315.5	0.149	<0.035	0.408	0.047	31.60	-	0.715	0.004	0.011	2.244	-67.1	0.447	2.207	58.63	-11.60
25/7/89		323.5	0.138	-	0.207	0.045	20.04	-	0.281	0.005	<0.008	1.231	-33.7	0.033	1.197	25.93	-9.10
25/7/89		330.5	0.146	<0.035	0.211	0.042	21.23	-	0.240	<0.004	<0.008	1.189	-31.7	0	1.153	24.10	-10.83
25/7/89		335.5	10.220	2.103	10.068	2.887	1238.3	-	5.55	0.03	0.25	60.26	-1414	0	57.71	1204.4	
25/7/89		338	20.14	4.61	19.17	5.72	2421.4	0.69	9.18	0.03	3.05	94.00	-2300	0	88.97	1899.6	-11.44
25/7/89	CORE B1	75	0.154	0.069	<0.093	0.019	14.67	-	0.670	0.004	0.018	0.108	-21.5	0.393	0.070	12.77	-11.36
25/7/89		140.5	0.111	<0.035	0.136	0.024	14.49	-	0.304	0.005	-	0.087	-10.4	0.104	0.059	4.16	-13.08
25/7/89		156	0.083	-	-	0.023	5.50	-	0.246	0.006	<0.008	0.088	-9.0	0.097	0.067	4.24	-11.31
25/7/89		183	0.077	<0.035	-	0.020	5.89	-	0.237	0.004	<0.008	0.078	-8.5	0.098	0.059	4.12	-10.84
25/7/89		209.5	0.105	<0.035	-	0.024	7.44	-	0.249	<0.004	<0.008	0.105	-9.4	0.060	0.079	3.45	-13.73
25/7/89		213		3.38	n.d.	8.20	n.d.	2.91	2.59	0.02	0.66	569.70	-12087			10.63	-9.93
25/7/89		220	7.59	4.58	18.43	3.87	1685.5	0.96	5.61	0.03	1.09	114.80	-2614	0	112.90	2365.8	-9.53

ICE CORE A2 10/1/90

DATE	DEPTH cm	CORE DEPTH cm	Na ug/g	K ug/g	Ca ug/g	Mg ug/g	ΣC ueq/l	F ug/g	Cl ug/g	Br ug/g	NO3 ug/g	PO4 ug/g	SO4 ug/g	ΣA ueq/l	Cl ex ug/g	SO4 ex ug/g	H+ ueq/l	O-ISOTOPE %
10/1/90	0-13		0.096	<0.035	0.169	0.024	15.48	-	0.117	-	-	-	1.148	-27.18	0	1.124	23.38	-9.59
10/1/90	13-23		0.095	<0.035	0.148	0.016	13.73	-	0.076	-	-	<0.004	1.167	-26.54	0	1.143	23.78	
10/1/90	23-33		0.091	0.048	0.250	0.020	19.31	-	0.114	-	-	-	1.341	-31.11	0	1.318	27.42	-8.32
10/1/90	33-45		0.105	<0.035	0.135	0.016	13.52	-	0.064	-	-	-	1.343	-29.74	0	1.317	27.39	-9.48
10/1/90	45-58		0.078	-	0.152	0.016	12.29	-	0.153	-	-	-	0.550	-15.75	0.013	0.531	11.39	-8.89
10/1/90	58-68		0.083	<0.035	0.119	0.018	11.93	-	0.064	-	-	<0.004	0.809	-18.76	0	0.788	16.40	-9.23
10/1/90	77-95	77-137	0.348	0.238	0.397	0.048	44.99	-	0.548	-	0.013	-	1.888	-54.93	0	1.801	37.67	-7.66
10/1/90	95-105		0.203	0.114	0.144	0.021	20.66	-	0.291	-	0.011	-	0.877	-26.62	0	0.826	17.36	-7.69
10/1/90	105-109		0.162	0.050	0.230	0.025	21.86	-	0.279	-	-	-	0.655	-21.49	0	0.615	12.78	-7.87
10/1/90	109-118		0.167	0.091	0.211	0.024	22.10	-	0.301	-	0.011	-	0.826	-25.85	0	0.784	16.49	-8.41
10/1/90	118-127		0.100	0.043	0.156	0.018	14.72	-	0.205	-	-	-	1.372	-34.32	0.025	1.347	28.72	
10/1/90	127-137		0.084	<0.035	0.196	0.019	15.89	-	0.152	0.004	-	-	1.082	-26.84	0.001	1.061	22.09	-12.76
10/1/90	137-148	137-187	0.377	0.180	0.996	0.088	77.95	-	0.590	-	<0.008	-	1.381	-45.49	0	1.287	26.89	-9.51
10/1/90	148-159		0.271	0.133	0.337	0.040	35.30	-	0.490	-	-	0.004	0.816	-30.92	0.002	0.748	15.63	-8.88
10/1/90	159-164		0.366	0.197	0.314	0.036	39.60	0.237	0.677	-	<0.008	-	1.299	-46.24	0.018	1.208	25.76	-9.07
10/1/90	164-172		0.116	0.036	0.225	0.024	19.17	-	0.276	-	<0.008	-	1.404	-37.12	0.067	1.375	30.62	-9.11
10/1/90	172-182		0.150	0.079	0.403	0.032	31.29	-	0.514	-	0.019	-	1.238	-40.55	0.244	1.201	32.13	-9.28
10/1/90	182-187		0.261	0.094	0.349	0.026	33.31	-	0.344	-	<0.008	-	1.900	-49.35	0	1.835	38.29	-12.64
10/1/90	187-195	187-225	0.169	0.082	0.192	0.029	21.42	-	0.277	-	<0.008	-	1.328	-35.56	0	1.286	26.87	-9.20
10/1/90	195-205		0.168	0.057	0.337	0.026	27.72	-	0.277	-	-	0.004	0.761	-23.77	0	0.719	14.96	-8.97
10/1/90	205-211		0.083	<0.035	0.240	0.019	18.05	-	0.218	-	0.014	-	0.689	-20.70	0.069	0.668	16.05	-9.80
10/1/90	211-217		0.052	0.050	0.119	0.018	10.96	-	0.156	-	-	-	0.771	-20.44	0.062	0.758	17.52	-10.11
10/1/90	217-225		0.137	0.038	0.349	0.025	26.40	-	0.277	-	-	-	0.720	-22.79	0.030	0.686	15.12	-9.88
10/1/90	225-229	225-255	0.079	0.038	0.139	0.018	12.83	-	0.136	-	-	-	0.897	-22.49	0	0.877	18.25	-11.60
10/1/90	229-233		0.098	<0.035	0.183	0.022	16.10	-	0.231	-	-	-	0.697	-21.01	0.055	0.673	15.52	-12.33
10/1/90	233-237		0.077	0.038	0.108	0.014	10.86	-	0.142	-	-	<0.004	0.789	-20.54	0.003	0.770	16.11	-10.06
10/1/90	237-239		0.267	0.061	0.220	0.042	27.61	-	0.284	-	-	-	0.730	-23.19	0	0.663	13.80	
10/1/90	239-243		0.141	<0.035	0.178	0.018	17.39	-	0.178	-	-	-	1.611	-38.53	0	1.576	32.78	-12.79
10/1/90	243-249		0.108	0.053	0.709	0.037	44.48	-	0.234	-	<0.008	-	5.063	-112.04	0.040	5.036	105.99	-10.56
10/1/90	249-255		0.122	0.058	0.192	0.020	18.02	-	0.161	-	-	-	1.866	-43.35	0	1.836	38.18	-8.47

ICE CORE A2 10/1/90 (CONT)

DATE	DEPTH cm	CORE DEPTH cm	Na ug/g	K ug/g	Ca ug/g	Mg ug/g	ΣC ueq/l	F ug/g	Cl ug/g	Br ug/g	NO3 ug/g	PO4 ug/g	SO4 ug/g	ΣA ueq/l	Cl ex ug/g	SO4 ex ug/g	H+ ueq/l	O-ISOTOPE %
10/1/90	255-270	255-297	0.103	0.043	0.174	0.018	15.75	-	0.405	-	0.019	-	0.574	-23.67	0.220	0.548	17.88	-8.74
10/1/90	270-279		0.121	0.046	0.139	0.015	14.61	-	0.172	-	-	-	1.224	-30.31	0	1.194	24.83	-8.75
10/1/90	279-288		0.081	<0.035	0.104	0.012	10.60	-	0.138	-	<0.008	-	0.446	-13.30	0	0.426	8.98	-8.32
10/1/90	288-297		0.072	<0.035	0.161	0.018	13.54	-	0.110	-	-	-	1.998	-44.66	0	1.980	41.18	-8.73
10/1/90	297-303	297-317	0.149	0.061	0.192	0.020	19.27	-	0.235	-	-	0.004	1.887	-46.00	0	1.850	38.47	-11.85
10/1/90	303-309		0.071	0.041	0.201	0.014	15.32	-	0.133	-	-	0.005	0.488	-14.06	0.005	0.470	9.93	-8.32
10/1/90	309-318	317-347	0.083	0.036	0.187	0.018	15.34	-	0.154	-	-	-	0.858	-22.19	0.005	0.837	17.54	-8.10
10/1/90	318-325		<0.017	<0.035	0.161	0.014	10.82	-	0.222	-	-	-	0.391	-14.39	0	0	0	-8.59
10/1/90	325-331		0.317	0.105	0.201	0.048	30.46	-	0.476	0.004	-	<0.004	1.255	-39.70	0	1.176	24.46	-9.32
10/1/90	331-341		0.117	0.036	0.266	0.017	20.68	-	0.181	-	-	<0.004	1.280	-31.85	0	1.251	26.02	-8.47
10/1/90	341-350		0.092	0.048	0.178	0.015	15.35	-	0.156	-	<0.008	-	0.867	-22.56	0	0.844	17.68	-8.26
10/1/90	350-357		0.097	<0.035	0.309	0.015	21.77	-	0.152	-	-	<0.004	1.766	-41.15	0	1.742	36.23	-8.26
10/1/90	357-364		0.088	0.038	0.135	<0.011	12.44	-	0.114	-	-	0.004	0.284	-9.25	0	0.262	5.45	-8.68
10/1/90	364-373	347-376	0.117	<0.035	0.292	0.017	21.96	-	0.193	-	-	<0.004	1.162	-29.74	0	1.133	23.56	-8.20
10/1/90	373-381		0.056	<0.035	0.165	0.016	12.88	-	0.124	-	-	0.004	0.397	-11.88	0.023	0.383	8.62	-8.33
10/1/90	381-390		0.069	0.043	0.119	<0.011	10.95	-	0.198	-	<0.008	-	0.810	-22.56	0.074	0.793	18.69	
10/1/90	390-395	376-407	0.091	<0.035	0.165	0.019	14.65	-	0.138	-	-	-	1.725	-39.77	0	1.702	35.41	-8.40
10/1/90	395-403		0.176	0.068	0.276	0.020	24.82	-	0.322	-	-	-	0.854	-26.84	0.005	0.810	16.99	-10.50
10/1/90	403-409	407-424	0.165	0.036	0.282	0.037	25.22	-	0.284	-	-	0.004	1.359	-36.40	0	1.318	27.41	
10/1/90	409-415		0.085	-	0.187	0.011	13.93	-	0.100	-	-	-	1.336	-30.61	0	1.315	27.35	-9.15
10/1/90	415-426	424-447	0.058	<0.035	0.135	0.020	11.80	-	0.166	-	<0.008	-	1.249	-30.79	0.062	1.235	27.54	-8.58
10/1/90	426-434		0.070	<0.035	0.152	0.016	12.84	-	0.114	-	-	0.004	1.363	-31.69	0	1.346	27.99	-8.95
10/1/90	434-442.5		0.085	<0.035	0.148	0.011	12.88	-	0.117	-	-	0.004	1.053	-25.33	0	1.032	21.46	-10.70
10/1/90	442.5-448		0.107	<0.035	0.183	0.019	16.25	-	0.133	-	-	0.005	0.958	-23.84	0	0.931	19.37	-11.41
10/1/90	448-455	447-455	0.118	0.038	0.169	0.014	15.69	-	0.159	-	-	-	1.390	-33.40	0	1.361	28.30	-8.59
10/1/90	455-462	455-472	0.057	<0.035	0.108	<0.011	9.67	-	0.092	-	-	-	0.781	-18.84	0	0.767	15.95	
10/1/90	462-470		0.080	<0.035	0.131	<0.011	11.82	-	0.104	-	-	-	0.371	-10.65	0	0.351	7.30	-7.67
10/1/90	470-476		0.114	0.041	0.152	0.027	15.82	-	0.191	-	<0.008	-	0.686	-19.78	0	0.658	13.80	-8.79
10/1/90	476-485	472-497	0.108	<0.035	0.187	0.011	15.83	-	0.172	-	<0.008	-	0.675	-19.02	0	0.648	13.61	-7.29
10/1/90	485-496		0.078	<0.035	0.165	0.011	13.43	-	0.193	-	-	-	1.358	-33.69	0.053	1.339	29.32	-8.24
10/1/90	496-503		0.094	0.041	0.201	0.018	16.65	-	0.131	-	-	-	0.575	-15.65	0	0.552	11.47	-8.46

ICE CORE A2 10/1/90 (CONT)

DATE	DEPTH cm	CORE DEPTH cm	Na ug/g	K ug/g	Ca ug/g	Mg ug/g	ΣC ueq/l	F ug/g	Cl ug/g	Br ug/g	NO3 ug/g	PO4 ug/g	SO4 ug/g	ΣA ueq/l	Cl ex ug/g	SO4 ex ug/g	H+ ueq/l	O-ISOTOPE %
10/1/90	503-510	497-517	0.049	0.048	0.104	0.020	10.20	-	0.115	-	-	0.008	0.263	-8.97	0.027	0.251	5.97	-8.31
10/1/90	510-517		0.065	0.043	0.131	0.024	12.44	-	0.131	-	0.008	-	0.891	-22.36	0.014	0.875	18.72	-8.18
10/1/90	517-524		0.091	0.041	0.169	0.012	14.43	-	0.283	-	<0.008	-	1.223	-33.55	0.119	1.200	28.44	-8.11
10/1/90	524-534		0.131	<0.035	0.178	0.027	17.70	-	0.207	-	-	<0.004	0.527	-16.93	0	0.494	10.28	-7.90
10/1/90	534-545		0.057	0.043	0.235	0.004	15.64	-	0.238	-	<0.008	-	0.855	-24.62	0.135	0.841	21.42	-8.32
10/1/90	545-555	517-535	0.253	0.036	0.349	0.030	31.81	-	0.288	0.006	<0.008	-	0.967	-28.36	0	0.904	18.93	-8.53
10/1/90	555-561		0.079	<0.035	0.196	0.042	17.57	-	0.170	-	-	-	0.688	-19.10	0.028	0.668	14.68	-8.29
10/1/90	561-566		0.189	0.041	0.367	0.028	29.89	-	0.209	0.011	-	0.010	0.510	-16.96	0	0.463	9.63	-8.39
10/1/90	566-575	535-550	0.046	0.041	0.090	0.018	9.02	-	0.106	-	-	0.006	0.246	-8.30	0.023	0.235	5.53	-8.34
10/1/90	575-584		0.038	0.077	0.127	0.020	11.61	-	0.154	-	-	0.006	0.407	-13.00	0.086	0.398	10.67	-11.72
10/1/90	584-591	550-572	0.031	<0.035	0.053	0.022	6.70	-	0.089	-	<0.008	<0.004	0.220	-7.34	0.033	0.212	5.48	-7.83
10/1/90	591-598		0.127	-	0.240	0.014	18.65	-	0.136	-	-	0.011	0.331	-11.07	0	0.299	6.22	-7.70
10/1/90	598-606		0.039	0.058	0.320	0.026	21.29	-	0.096	-	-	0.006	0.362	-10.43	0.026	0.352	8.05	-8.87
11/1/90	606-615	572-635	0.053	<0.035	0.245	0.018	16.91	-	0.133	<0.004	<0.008	-	0.335	-10.90	0.038	0.322	7.88	-8.97
11/1/90	615-624		0.025	<0.035	0.156	0.014	10.92	-	0.138	-	<0.008	-	0.318	-10.63	0.093	0.312	9.23	-8.43
11/1/90	624-631		0.049	0.046	0.174	0.017	13.39	-	0.108			0.007	0.160	-6.59	0.020	0.148	3.63	-8.22
11/1/90	631-635.5		0.044	0.091	0.282	0.030	20.78	-	0.328	0.005	-	0.005	0.418	-18.16	0.249	0.407	15.46	
11/1/90	635.5-641.5		0.170	0.043	0.127	0.044	18.45	-	0.391	0.008	<0.008	-	0.354	-18.62	0.085	0.312	9.00	-8.61
11/1/90	641.5-650.5		0.118	0.036	0.435	0.026	29.90	-	0.209	0.006	<0.008	0.004	0.478	-16.17	0	0.449	9.46	-9.43
11/1/90	650.5-656.5		0.171	0.063	0.461	0.028	34.36	-	0.238	0.010	-	0.006	0.497	-17.36	0	0.454	9.45	-8.00
11/1/90	656.5-662		0.154	0.055	0.397	0.031	30.47	-	0.266	-	<0.008	0.006	0.402	-16.18	0	0.364	7.69	-8.51
11/1/90	662-669		0.120	0.066	0.298	0.032	24.41	-	0.154	-	-	0.006	0.344	-11.69	0	0.314	6.53	-8.29
11/1/90	669-676	635-681	0.137	0.038	0.255	0.021	21.39	-	0.189	-	<0.008	0.004	0.427	-14.47	0	0.393	8.30	-8.81
11/1/90	676-683		0.071	0.071	0.416	0.025	27.72	-	0.223	-	-	0.008	0.391	-14.67	0.095	0.373	10.44	
11/1/90	683-689		0.562	0.099	0.428	0.096	56.24	-	0.702	0.004	0.012	-	0.614	-32.81	0	0.474	10.04	-8.84
11/1/90	689-696		0.059	0.046	0.156	0.018	13.01	-	0.113	-	-	0.008	0.335	-10.41	0.007	0.320	6.85	-8.41
11/1/90	696-704		0.042	0.046	0.139	0.017	11.34	-	0.128	-	<0.008	-	0.234	-8.61	0.052	0.224	6.25	-8.33
11/1/90	704-711		0.038	<0.035	0.104	0.012	8.73	-	0.078	-	-	0.008	0.181	-6.22	0.010	0.172	3.84	-9.12
11/1/90	711-719		0.040	<0.035	0.073	0.014	7.43	-	0.118		-	0.009	0.199	-7.75	0.046	0.189	5.22	-8.64
11/1/90	719-725		0.252	0.061	0.235	0.044	27.87	-	0.377	0.004	-	0.004	0.596	-23.20	0	0.533	11.09	-10.33
11/1/90	725-732		0.242	0.071	0.245	0.054	29.01	-	0.444	0.007	-	0.005	0.651	-26.31	0.008	0.591	12.52	-9.86
11/1/90	732-739		0.235	0.053	0.187	0.039	24.12	-	0.381	-	0.010	0.020	0.426	-20.40	0	0.367	7.80	
11/1/90	739-747.5		0.395	0.099	0.355	0.069	43.11	-	0.341	0.011	-	0.007	0.376	-17.80	0	0.277	5.77	-10.34

ICE CORE A2 10/1/90 (CONT)

DATE	DEPTH cm	CORE DEPTH cm	Na ug/g	K ug/g	Ca ug/g	Mg ug/g	ΣC ueq/l	F ug/g	Cl ug/g	Br ug/g	NO3 ug/g	PO4 ug/g	SO4 ug/g	ΣA ueq/l	Cl ex ug/g	SO4 ex ug/g	H+ ueq/l	O-ISOTOPE %
11/1/90	747.5-750.5	681-747	0.143	0.041	0.165	0.044	19.12	-	0.542	0.015	-	0.010	0.179	-19.51	0.285	0.143	10.98	-8.42
11/1/90	750.5-758		0.178	0.043	0.276	0.055	27.14	-	0.862	<0.004	0.015	-	0.207	-28.91	0.542	0.163	18.84	-11.99
11/1/90	758-764		6.88	0.29	0.17	1.04	401.03	-	13.676	0.039	-	<0.004	1.562	-418.76	1.292	0	36.30	
11/1/90	764-771		1.43	0.04	0.31	0.10	87.15	-	0.507	-	-	<0.004	0.394	-22.62	0	0.037	0.76	
11/1/90	771-775		0.223	0.041	0.225	0.069	27.66	-	1.097	0.014	-	0.006	0.205	-35.56	0.696	0.149	22.65	-8.64
11/1/90	775-781.5		2.00	0.08	1.27	0.05	156.51	-	0.507	-	-	0.005	0.455	-23.92	0	0	0	-8.47
11/1/90	781.5-785		0.063	0.041	0.131	0.023	12.22	-	0.221	0.009	-	0.006	0.218	-11.07	0.108	0.202	7.23	-9.31
11/1/90	785-792.5		0.073	0.041	0.135	0.029	13.35	-	0.305	-	-	0.018	0.187	-13.06	0.174	0.169	8.39	-9.50
11/1/90	792.5-800.5		0.324	0.043	0.367	0.050	37.62	-	0.621	0.014	-	0.008	0.258	-23.31	0.038	0.177	4.74	
11/1/90	800.5-807		0.167	0.074	0.292	0.059	28.59	-	0.556	-	-	-	0.495	-25.98	0.255	0.453	16.60	-9.62
11/1/90	807-814		0.099	0.036	0.494	0.034	32.68	-	0.316	-	<0.008	-	0.483	-19.09	0.138	0.458	13.53	-7.35
11/1/90	814-820.5	747-787	0.028	<0.035	0.196	0.063	17.08	-	1.837	0.015	<0.008	0.017	0.311	-59.12	1.786	0.304	56.65	-12.11
11/1/90	820.5-828.5		0.137	<0.035	0.127	0.018	14.67	-	0.195	-	0.014	-	0.204	-9.97	0	0.170	3.76	-10.41
11/1/90	828.5-834.5		0.383	0.036	0.337	0.028	36.70	-	0.284	-	-	0.008	0.356	-15.67	0	0.260	5.41	-8.69
11/1/90	834.5-842.5	787-817	0.391	0.063	0.529	0.094	52.75	-	1.221	0.008	0.013	-	0.503	-45.21	0.518	0.405	23.18	-8.41
11/1/90	842.5-850		0.538	0.041	0.501	0.109	58.42	-	1.652	0.011	<0.008	-	0.438	-55.96	0.684	0.304	25.65	-10.64
11/1/90	850-857		0.618	0.068	0.287	0.144	54.80	-	1.791	0.012	-	0.008	0.310	-57.35	0.678	0.156	22.29	-9.73
11/1/90	857-865		0.791	0.048	0.255	0.153	60.95	-	2.047	0.019	-	0.036	0.153	-62.28	0.623	0	17.51	-9.78
11/1/90	865-872		0.591	0.094	0.758	0.169	79.85	-	2.480	<0.004	0.036	-	0.362	-78.08	1.416	0.214	44.82	-12.08
11/1/90	872-881		0.171	0.071	0.529	0.155	48.41	-	2.072	0.014	0.017	0.026	0.300	-65.94	1.764	0.257	55.20	-9.77
11/1/90	881-890		0.109	0.038	0.215	0.040	19.73	-	0.430	0.005	-	0.004	0.255	-17.62	0.234	0.228	11.31	
11/1/90	890-898		0.213	<0.035	0.148	0.040	20.84	-	0.507	0.006	-	0.007	0.215	-19.07	0.124	0.162	6.84	-8.84
11/1/90	898-906		0.397	0.041	0.594	0.090	55.37	-	1.115	0.009	-	0.006	0.546	-43.10	0.400	0.447	20.54	-10.68
11/1/90	906-914		1.31	0.05	1.31	0.10	131.40	-	1.331	0.009	-	0.010	0.369	-45.63	0	0.042	0.86	-13.57
Detn Coeff			0.009	0.018	0.017	0.005		0.027	0.009	0.002	0.004	0.002	0.017					
Det Limit			0.017	0.035	0.034	0.011		0.053	0.018	0.004	0.008	0.004	0.033					

ICE CORE B2 10/1/90

DATE	DEPTH cm	CORE DEPTH cm	Na ug/g	K ug/g	Ca ug/g	Mg ug/g	ΣC ueq/l	F ug/g	Cl ug/g	Br ug/g	NO3 ug/g	PO4 ug/g	SO4 ug/g	ΣA ueq/l	Cl ex ug/g	SO4 ex ug/g	H+ ueq/l	O-ISOTOPE %
10/1/90	0-13		0.096	<0.035	0.169	0.024	15.48	-	0.117	-	-	-	1.148	-27.18	0	1.124	23.38	-9.59
10/1/90	13-23		0.095	<0.035	0.148	0.016	13.73	-	0.076	-	-	<0.004	1.167	-26.54	0	1.143	23.78	
10/1/90	23-33		0.091	0.048	0.250	0.020	19.31	-	0.114	-	-	-	1.341	-31.11	0	1.318	27.42	-8.32
10/1/90	33-45		0.105	<0.035	0.135	0.016	13.52	-	0.064	-	-	-	1.343	-29.74	0	1.317	27.39	-9.48
10/1/90	45-58		0.078	-	0.152	0.016	12.29	-	0.153	-	-	-	0.550	-15.75	0.013	0.531	11.39	-8.89
10/1/90	58-68		0.083	<0.035	0.119	0.018	11.93	-	0.064	-	-	<0.004	0.809	-18.76	0	0.788	16.40	-9.23
11/1/90	77-86	77-157	0.177	0.082	0.169	0.046	22.02	-	0.383	0.009	<0.008	-	0.304	-17.37	0.064	0.260	7.34	-9.88
11/1/90	86-94		0.115	0.046	0.161	0.032	16.85	-	0.235	-	-	0.004	0.278	-12.54	0.028	0.249	5.97	
11/1/90	94-101		0.173	0.061	0.435	0.038	33.92	0.924	1.001	0.005	0.009	0.011	0.497	-87.72	0.690	0.454	28.96	
11/1/90	101-109.5		0.075	<0.035	0.282	0.024	20.21	-	0.089	-	-	0.007	0.192	-6.72	0	0.173	3.60	-8.12
11/1/90	109.5-118		0.060	<0.035	0.201	0.015	14.77	-	0.110	-	-	0.018	0.686	-17.94	0.002	0.671	14.01	
11/1/90	118-128		0.073	-	0.131	0.016	11.03	-	0.108	-	-	0.005	0.792	-19.68	0	0.774	16.09	-8.97
11/1/90	128-138		0.263	0.036	0.152	0.021	21.68	-	0.103	-	-	0.004	0.777	-19.19	0	0.711	14.79	
11/1/90	138-148		0.104	0.058	0.367	0.022	26.13	-	0.203	-	-	0.007	0.341	-13.04	0.016	0.315	7.00	-10.02
11/1/90	148-158		0.072	0.036	0.165	0.024	14.26	-	0.110	-	-	<0.004	1.22	-28.60	0	1.202	25.00	
11/1/90	158-168	157-232	0.131	<0.035	0.187	0.032	18.56	-	0.207	-	-	<0.004	1.122	-29.30	0	1.089	22.66	
11/1/90	168-176		0.177	0.053	0.245	0.042	24.74	-	0.186	-	-	0.018	0.815	-22.77	0	0.771	16.03	-9.37
11/1/90	176-182		0.178	0.063	0.409	0.048	33.72	-	0.354	0.01	<0.008	0.005	0.308	-16.80	0.034	0.264	6.55	
11/1/90	182-189		0.207	0.079	0.543	0.042	41.58	-	0.327	0.011	-	0.014	0.597	-22.26	0	0.545	11.34	-9.44
11/1/90	189-195		0.185	<0.035	0.276	0.030	25.18	-	0.242	0.011	-	0.006	0.782	-23.46	0	0.736	15.30	
11/1/90	195-203.5		0.072	<0.035	0.298	0.020	20.54	-	0.156	-	<0.008	0.006	0.302	-11.00	0.026	0.284	6.78	-9.58
11/1/90	203.5-212		0.073	<0.035	0.148	0.017	12.86	-	0.096	-	-	-	0.52	-13.52	0	0.502	10.44	
11/1/90	212-222		0.064	<0.035	0.292	0.026	20.39	-	0.154	0.009	-	0.005	0.317	-11.24	0.039	0.301	7.35	
11/1/90	222-230		0.090	0.063	0.127	0.012	12.85	-	0.107	-	-	0.004	0.747	-18.68	0	0.725	15.07	-11.08
11/1/90	230-238	232-265	0.123	<0.035	0.235	0.032	20.61	-	0.166	-	-	-	1.002	-25.52	0	0.971	20.20	
11/1/90	238-245		0.087	0.046	0.240	0.027	19.16	-	0.143	-	-	<0.004	1.251	-30.18	0	1.229	25.57	
11/1/90	245-251		0.130	<0.035	0.250	0.012	20.01	-	0.177	-	-	-	0.763	-20.86	0	0.731	15.19	
11/1/90	251-260		0.053	0.038	0.220	0.021	15.98	-	0.154	-	-	-	0.648	-17.82	0.059	0.635	14.85	-10.29
11/1/90	260-270		0.097	0.058	0.670	0.040	42.43	0.208	0.161	0.007	<0.008	0.004	6.195	-144.68	0	6.171	128.48	
11/1/90	270-278	265-300	0.066	<0.035	0.225	0.020	16.64	-	0.100	-	-	0.01	3.635	-78.74	0	3.619	75.26	
11/1/90	278-288		0.074	<0.035	0.428	0.023	27.37	-	0.136	-	-	0.006	0.743	-19.48	0.003	0.725	15.15	-8.55
11/1/90	288-297		0.062	<0.035	0.148	0.018	12.46	-	0.200	-	-	-	0.806	-22.40	0.088	0.791	18.93	

ICE CORE B2 10/1/90 (CONT)

DATE	DEPTH cm	CORE DEPTH cm	Na ug/g	K ug/g	Ca ug/g	Mg ug/g	ΣC ueq/l	F ug/g	Cl ug/g	Br ug/g	NO3 ug/g	PO4 ug/g	SO4 ug/g	ΣA ueq/l	Cl ex ug/g	SO4 ex ug/g	H+ ueq/l	O-ISOTOPE %
11/1/90	297-303	265-300	0.075	<0.035	0.123	0.016	11.61	-	0.140	-	-	0.009	0.553	-15.73	0.005	0.534	11.25	-8.41
11/1/90	303-311		0.095	<0.035	0.148	0.014	13.57	-	0.105	-	-	0.004	0.92	-22.22	0	0.896	18.64	
11/1/90	311-319		0.107	<0.035	0.225	0.022	18.59	-	0.093	-	-	0.011	0.235	-7.86	0	0.208	4.33	-8.57
11/1/90	319-328	300-337	0.189	0.077	0.165	0.035	21.31	-	0.237	-	-	0.004	1.055	-28.75	0	1.008	20.96	
11/1/90	328-334		0.082	<0.035	0.115	0.020	11.85	-	0.103	-	-	0.011	1.241	-29.07	0	1.221	25.39	
11/1/90	334-342		0.134	0.048	0.271	0.036	23.54	-	0.198	-	-	0.008	0.478	-15.78	0	0.445	9.25	-8.88
11/1/90	342-347		0.106	<0.035	0.260	0.024	20.46	-	0.104	-	-	0.004	0.759	-18.85	0	0.733	15.24	
11/1/90	347-355		0.152	0.050	0.131	0.034	17.23	-	0.242	0.006	-	0.004	0.591	-19.34	0	0.553	11.50	
11/1/90	355-361		0.076	0.043	0.385	0.019	25.18	-	0.113	-	-	0.004	0.931	-22.68	0	0.912	18.97	
11/1/90	361-366		0.105	0.048	0.131	0.029	14.72	-	0.260	0.007	-	0.006	0.422	-16.41	0.071	0.396	10.23	-8.96
11/1/90	366-374	337-378	0.051	<0.035	0.522	0.017	30.56	-	0.103	-	-	0.005	0.828	-20.29	0.011	0.815	17.27	
11/1/90	374-381		0.039	0.038	0.097	0.020	9.16	-	0.112	-	-	0.03	1.267	-30.46	0.042	1.257	27.33	
11/1/90	381-389		0.219	0.061	0.187	0.038	23.55	-	0.172	-	-	-	0.351	-12.15	0	0.296	6.16	-8.54
11/1/90	389-399		0.096	0.036	0.144	0.024	14.26	-	0.312	-	<0.008	<0.004	0.769	-25.05	0.139	0.745	19.54	
11/1/90	399-406		0.110	0.053	0.266	0.017	20.81	-	0.145	-	-	0.005	0.346	-11.44	0	0.319	6.62	
11/1/90	406-412		0.058	<0.035	0.123	0.012	10.54	-	0.094	-	-	-	0.926	-21.91	0	0.912	18.96	
11/1/90	412-421	378-427	0.040	<0.035	0.112	0.014	9.38	-	0.099	-	-	-	0.407	-11.26	0.027	0.397	9.02	
11/1/90	421-430		0.056	<0.035	0.086	<0.011	8.53	-	0.103	-	-	<0.004	0.494	-13.31	0.002	0.480	10.05	
11/1/90	430-440		0.049	<0.035	0.090	0.011	8.42	-	0.104	-	-	0.005	0.664	-16.90	0.016	0.652	14.00	
11/1/90	440-449	427-467	0.145	0.050	0.169	0.029	18.41	-	0.231	-	-	<0.004	0.844	-24.20	0	0.808	16.80	-9.30
11/1/90	449-454		0.130	0.036	0.135	0.022	15.12	-	0.176	-	-	0.01	0.354	-12.64	0	0.322	6.69	
11/1/90	454-460		0.095	0.036	0.144	0.015	13.47	-	0.124	-	-	0.008	1.072	-26.05	0	1.048	21.80	-8.90
11/1/90	460-469		0.093	0.050	0.326	0.030	24.06	-	0.184	-	-	-	1.064	-27.32	0.017	1.041	22.11	
11/1/90	469-478		0.079	<0.035	0.144	0.019	13.08	-	0.105	-	-	0.013	1.301	-30.43	0	1.281	26.65	-8.93
11/1/90	478-484		0.100	<0.035	0.131	0.022	13.59	-	0.110	-	-	<0.004	1.126	-26.65	0	1.101	22.90	
11/1/90	484-493	467-489	0.069	<0.035	0.135	0.014	11.79	-	0.104	-	-	0.005	0.981	-23.50	0	0.964	20.05	
11/1/90	493-502		0.165	0.053	0.215	0.035	22.14	-	0.418	-	<0.008	-	1.287	-38.69	0.121	1.246	29.44	-9.04
11/1/90	502-510		0.201	0.066	0.201	0.033	23.18	-	0.283	-	<0.008	<0.004	1.225	-33.72	0	1.175	24.56	
11/1/90	510-516.5		0.172	0.068	0.108	0.036	17.57	-	0.240	-	-	<0.004	1.493	-37.95	0	1.450	30.16	
11/1/90	516.5-522.5		0.082	<0.035	0.123	0.017	12.00	-	0.106	-	-	-	1.111	-26.10	0	1.091	22.68	

ICE CORE B2 10/1/90 (CONT)

DATE	DEPTH cm	CORE DEPTH cm	Na ug/g	K ug/g	Ca ug/g	Mg ug/g	ΣC ueq/l	F ug/g	Cl ug/g	Br ug/g	NO3 ug/g	PO4 ug/g	SO4 ug/g	ΣA ueq/l	Cl ex ug/g	SO4 ex ug/g	H+ ueq/l	O-ISOTOPE %
11/1/90	522.5-530.5	489-527	0.082	<0.035	0.522	0.016	31.83	-	0.107	-	-	0.016	0.866	-21.54	0	0.846	17.59	-6.66
11/1/90	530.5-538.5		0.116	0.046	0.183	0.020	17.00	-	0.159	-	-	<0.004	1.508	-35.98	0	1.479	30.76	
11/1/90	538.5-545		0.118	0.041	0.215	0.025	18.97	-	0.138	-	-	<0.004	1.481	-34.82	0	1.452	30.19	
11/1/90	545-551		0.106	<0.035	0.183	0.021	16.37	-	0.103	-	-	0.007	0.992	-23.76	0	0.966	20.08	-8.72
11/1/90	551-560		0.085	0.046	0.144	0.022	13.87	-	0.253	-	<0.008	0.007	1.02	-28.70	0.100	0.999	23.71	
11/1/90	560-568		0.125	0.043	0.169	0.019	16.54	-	0.103	-	-	-	0.547	-14.28	0	0.516	10.73	-10.81
11/1/90	568-576		0.069	<0.035	0.097	0.016	10.05	-	0.104	-	-	0.008	1.134	-26.77	0	1.117	23.23	
11/1/90	576-583.5		0.061	<0.035	0.123	0.016	11.00	-	0.103	-	-	-	1.306	-30.07	0	1.291	26.85	-10.68
11/1/90	583.5-590.5		0.233	0.066	0.240	0.036	26.76	-	0.277	-	<0.008	-	1.643	-42.11	0	1.585	33.09	
11/1/90	590.5-597.5	527-577	0.192	0.061	0.225	0.033	23.86	-	0.283	-	-	<0.004	1.158	-32.19	0	1.110	23.09	
11/1/90	597.5-606		0.087	<0.035	0.115	0.016	11.74	-	0.107	-	-	<0.004	0.758	-18.91	0	0.736	15.31	
11/1/90	606-614.5		0.100	0.036	0.196	0.025	17.11	-	0.199	-	<0.008	-	1.64	-39.85	0.019	1.615	34.25	
11/1/90	614.5-622.5		0.074	0.036	0.165	0.017	13.77	-	0.101	-	-	-	0.698	-17.37	0	0.680	14.13	
11/1/90	622.5-630		0.044	<0.035	0.131	0.017	10.75	-	0.099	-	-	0.006	0.577	-14.98	0.020	0.566	12.33	-8.85
Detn Coeff			0.009	0.018	0.017	0.005		0.027	0.009	0.002	0.004	0.002	0.017					
Det Limit			0.017	0.035	0.034	0.011		0.053	0.018	0.004	0.008	0.004	0.033					

APPENDIX IV

ICE CORE A1 AND B1

CORE	SAMPLE	M45	M46	O18	NORMALIZED O18	C13	
CORE A1	60	-23.06	-13.97	-15.97	-15.84	-28.54	
	70	-23.32	-9.41	-11.41	-11.32	-28.97	
	80	-23.05	-8.03	-10.03	-9.95	-28.73	
	110	-23.17	-10.62	-12.61	-12.51	-28.76	
	110	-23.39	-14.25	-16.25	-16.12	-28.88	
	110	-23.00	-10.18	-12.18	-12.08	-28.60	
	120	-23.36	-14.08	-16.08	-15.95	-28.86	
	135	-22.98	-10.26	-12.25	-12.15	-28.58	
	135	-23.84	-10.52	-12.52	-12.42	-29.48	
	150	-22.85	-9.84	-11.83	-11.74	-28.46	
	155	-23.15	-10.34	-12.34	-12.24	-28.76	
	160	-23.51	-10.42	-12.42	-12.32	-29.13	
	165	-23.10	-10.56	-12.55	-12.45	-28.69	
	170	-22.95	-10.06	-12.05	-11.95	-28.55	
	175	-23.18	-10.23	-12.23	-12.13	-28.79	
	175	-23.17	-10.62	-12.62	-12.51	-28.77	
	180	-23.36	-12.08	-14.08	-13.97	-28.92	
	183	-23.27	-13.41	-15.41	-15.28	-28.78	
	185	-23.48	-9.26	-11.26	-11.17	-29.15	
	187	-23.81	-12.16	-14.16	-14.05	-29.40	
	187	-23.46	-11.03	-13.03	-12.92	-29.07	
	191	-22.77	-8.04	-10.04	-9.96	-28.43	
	194	-22.85	-8.46	-10.45	-10.37	-28.51	
	197	-23.36	-7.57	-9.57	-9.50	-29.07	
	200	-22.65	-6.74	-8.74	-8.67	-28.34	
	200	-22.65	-6.74	-8.74	-8.67	-28.34	
	205	-19.40	-5.71	-7.68	-7.62	-24.93	x
	205	-21.35	-3.86	-5.84	-5.80	-27.07	x
	210	-23.18	-7.79	-9.79	-9.71	-28.87	
	210	-23.15	-7.40	-9.40	-9.32	-28.86	
	215	-22.96	-7.43	-9.43	-9.36	-28.66	
	215	-22.95	-7.45	-9.44	-9.37	-28.64	
	222	-23.00	-7.20	-9.20	-9.13	-28.70	
	232	-23.40	-8.02	-10.02	-9.94	-29.10	
	240	-23.20	-8.00	-10.00	-9.92	-28.89	
	250	-22.94	-7.65	-9.65	-9.57	-28.63	
	257	-22.83	-7.48	-9.48	-9.40	-28.52	
	267	-22.96	-8.03	-10.03	-9.95	-28.63	
	272	-23.10	-7.94	-9.94	-9.86	-28.78	
	280	-22.80	-7.90	-9.89	-9.81	-28.47	
	286	-23.33	-8.63	-10.63	-10.54	-29.00	
	297	-22.84	-8.70	-10.70	-10.61	-28.48	
	303	-22.42	-8.49	-10.48	-10.40	-28.04	
	311/1	-23.19	-10.37	-12.37	-12.27	-28.80	
	311/2	-23.43	-9.58	-11.58	-11.48	-29.08	
	311/3	-23.20	-9.62	-11.62	-11.53	-28.83	
	320/1	-22.98	-6.73	-8.73	-8.66	-28.69	
	320/2	-23.25	-7.47	-9.47	-9.39	-28.96	
	320/3	-24.68	-10.56	-12.57	-12.47	-30.38	x
	327	-23.20	-8.83	-10.83	-10.75	-28.87	
	337	-23.38	-9.44	-11.44	-11.35	-29.03	

MEAN	-28.69
STD DEVN	0.65
UPPER LIMIT	-27.39
LOWER LIMIT	-29.99

CORE	SAMPLE	M45	M46	O18	NORMALIZED O18	C13
CORE B1	70	-23.07	-9.37	-11.36	-11.27	-28.71
	139	-23.13	-11.09	-13.08	-12.98	-28.71
	152	-23.17	-9.31	-11.31	-11.22	-28.81
	178	-22.76	-8.85	-10.84	-10.75	-28.39
	207	-22.83	-11.74	-13.73	-13.62	-28.37
	212	-23.02	-7.93	-9.93	-9.85	-28.70

ICE CORE A2

SAMPLE	M45	M46	O18	NORMALIZED O18	C13	
1	-23.00	-7.67	-9.67	-9.59	-28.69	
12	-24.00	-6.76	-8.77	-8.70	-29.78	X
23	-22.94	-6.39	-8.39	-8.32	-28.66	
33	-22.99	-7.56	-9.56	-9.48	-28.69	
48	-22.95	-6.97	-8.96	-8.89	-28.66	
58	-22.99	-7.30	-9.30	-9.23	-28.69	
77	-22.85	-5.72	-7.72	-7.66	-28.60	
95	-22.81	-5.76	-7.75	-7.69	-28.55	
105	-22.80	-5.94	-7.93	-7.87	-28.54	
109	-22.98	-6.48	-8.48	-8.41	-28.71	
118	-22.08	-6.58	-8.57	-8.50	-27.74	X
127	-23.01	-10.87	-12.86	-12.76	-28.59	
137	-22.71	-7.59	-9.58	-9.51	-28.38	
148	-22.30	-6.96	-8.95	-8.88	-27.97	
159	-22.78	-7.15	-9.14	-9.07	-28.47	
164	-22.85	-7.19	-9.18	-9.11	-28.54	
172	-22.85	-7.36	-9.35	-9.28	-28.54	
182	-22.87	-10.75	-12.74	-12.64	-28.44	
187	-22.90	-7.27	-9.27	-9.20	-28.60	
195	-22.74	-7.05	-9.05	-8.97	-28.43	
205	-22.83	-7.88	-9.88	-9.80	-28.49	
211	-22.74	-8.20	-10.19	-10.11	-28.39	
217	-22.85	-7.97	-9.96	-9.88	-28.51	
225	-22.46	-9.71	-11.70	-11.60	-28.04	
229	-23.02	-10.44	-12.43	-12.33	-28.62	
233	-22.99	-8.14	-10.14	-10.06	-28.67	
239	-23.02	-10.90	-12.90	-12.79	-28.60	
243	-22.88	-8.65	-10.64	-10.56	-28.53	
249	-22.88	-6.54	-8.54	-8.47	-28.60	
255	-22.86	-6.81	-8.81	-8.74	-28.56	
270	-22.76	-6.83	-8.83	-8.75	-28.47	
279	-23.54	-6.39	-8.39	-8.32	-29.31	
288	-22.83	-6.80	-8.80	-8.73	-28.54	
297	-23.04	-9.95	-11.94	-11.85	-28.66	
303	-22.75	-6.39	-8.39	-8.32	-28.47	
309	-22.72	-6.17	-8.16	-8.10	-28.44	
318	-22.95	-6.67	-8.66	-8.59	-28.67	
325	-23.00	-7.39	-9.39	-9.32	-28.70	
331	-22.83	-6.54	-8.53	-8.47	-28.55	
341	-22.83	-6.33	-8.32	-8.26	-28.55	
350	-22.85	-6.33	-8.33	-8.26	-28.58	
357	-22.91	-6.75	-8.75	-8.68	-28.62	
364	-22.85	-6.26	-8.26	-8.20	-28.58	
373	-22.82	-6.40	-8.40	-8.33	-28.54	
380	-23.91	-9.09	-11.09	-11.00	-29.61	X
390	-22.88	-6.47	-8.47	-8.40	-28.60	
395	-22.95	-8.59	-10.59	-10.50	-28.60	
403	-24.10	-9.67	-11.68	-11.59	-29.79	X
409	-22.99	-7.23	-9.23	-9.15	-28.69	
415	-22.76	-6.65	-8.65	-8.58	-28.47	
426	-22.94	-7.03	-9.03	-8.95	-28.65	
434	-23.11	-8.79	-10.79	-10.70	-28.77	

MEAN C13	-28.67
STD DEVN	0.38
UPPER LIMIT	-27.88
LOWER LIMIT	-29.44

ICE CORE A2 (CONT)

SAMPLE	M45	M46	O18	NORMALISED O18	C13	
442	-22.94	-9.51	-11.50	-11.41	-28.56	
448	-22.86	-6.66	-8.66	-8.59	-28.57	
455	-23.96	-8.46	-10.47	-10.38	-29.68	X
462	-22.43	-5.74	-7.73	-7.67	-28.15	
470	-22.87	-6.86	-8.86	-8.79	-28.58	
476	-22.75	-5.36	-7.35	-7.29	-28.50	
485	-22.79	-6.31	-8.31	-8.24	-28.52	
496	-22.79	-6.53	-8.53	-8.46	-28.50	
503	-22.85	-6.38	-8.37	-8.31	-28.57	
510	-22.77	-6.25	-8.25	-8.18	-28.50	
517	-22.67	-6.18	-8.17	-8.11	-28.39	
524	-22.80	-5.97	-7.96	-7.90	-28.53	
534	-22.92	-6.39	-8.39	-8.32	-28.65	
545	-22.84	-6.60	-8.60	-8.53	-28.56	
555	-22.96	-6.36	-8.35	-8.29	-28.69	
561	-22.91	-6.46	-8.46	-8.39	-28.63	
566	-22.79	-6.41	-8.40	-8.34	-28.51	
575	-23.10	-9.82	-11.82	-11.72	-28.72	
584	-22.76	-5.89	-7.89	-7.83	-28.50	
591	-22.76	-5.77	-7.76	-7.70	-28.50	
598	-22.91	-6.95	-8.94	-8.87	-28.62	
606	-22.97	-7.05	-9.05	-8.97	-28.68	
615	-22.77	-6.50	-8.50	-8.43	-28.48	
624	-22.91	-6.29	-8.29	-8.22	-28.64	
631	-23.80	-8.72	-10.72	-10.64	-29.50	X
635	-22.92	-6.68	-8.68	-8.61	-28.63	
641	-23.32	-7.50	-9.50	-9.43	-29.03	
650	-22.82	-6.06	-8.06	-8.00	-28.56	
656	-22.79	-6.58	-8.58	-8.51	-28.50	
662	-22.78	-6.36	-8.36	-8.29	-28.50	
669	-22.90	-6.89	-8.88	-8.81	-28.61	
676	-24.17	-9.16	-11.16	-11.07	-29.88	X
683	-23.64	-6.91	-8.91	-8.84	-29.39	
689	-22.81	-6.49	-8.48	-8.41	-28.53	
696	-22.79	-6.40	-8.40	-8.33	-28.51	
704	-23.06	-7.20	-9.20	-9.12	-28.77	
711	-22.85	-6.72	-8.71	-8.64	-28.56	
719	-23.02	-8.42	-10.42	-10.33	-28.69	
725	-22.98	-7.94	-9.94	-9.86	-28.66	
732	-24.20	-10.45	-12.46	-12.36	-29.87	X
739	-22.60	-8.44	-10.43	-10.34	-28.24	
747	-22.77	-6.49	-8.48	-8.42	-28.48	
750	-22.87	-10.09	-12.09	-11.99	-28.47	
758	-23.78	-8.97	-10.97	-10.88	-29.47	X
771	-22.83	-6.71	-8.71	-8.64	-28.54	
775	-22.73	-6.54	-8.54	-8.47	-28.44	
781.5	-22.99	-7.39	-9.39	-9.31	-28.69	
785	-23.07	-7.58	-9.58	-9.50	-28.77	
792	-24.02	-9.78	-11.78	-11.69	-29.70	X
800.5	-23.13	-7.69	-9.69	-9.62	-28.82	
807	-22.27	-5.42	-7.41	-7.35	-27.99	
814	-23.02	-10.21	-12.21	-12.11	-28.62	
820	-23.35	-8.50	-10.50	-10.41	-29.03	

ICE CORE A2 (CONT)

SAMPLE	M45	M46	O18	NORMALIZED O18	C 13	
828	-23.05	-6.76	-8.76	-8.69	-28.77	
834	-22.50	-6.49	-8.48	-8.41	-28.19	
842	-22.90	-8.73	-10.73	-10.64	-28.55	
850	-23.07	-7.82	-9.81	-9.73	-28.76	
857	-23.03	-7.86	-9.86	-9.78	-28.71	
865	-22.97	-10.18	-12.17	-12.08	-28.57	
872	-22.99	-7.85	-9.85	-9.77	-28.67	
881	-23.96	-9.72	-11.72	-11.63	-29.64	X
890	-22.83	-6.92	-8.91	-8.84	-28.53	
898	-23.15	-8.77	-10.77	-10.68	-28.81	
906	-23.18	-11.68	-13.68	-13.57	-28.74	

ICE CORE B2

SAMPLE	M45	M46	O18	NORMALIZED O18	C13	
1	-23.00	-7.67	-9.67	-9.59	-28.69	
12	-24.00	-6.76	-8.77	-8.70	-29.78	X
23	-22.94	-6.39	-8.39	-8.32	-28.66	
33	-22.99	-7.56	-9.56	-9.48	-28.69	
48	-22.95	-6.97	-8.96	-8.89	-28.66	
58	-22.99	-7.30	-9.30	-9.23	-28.69	
77	-23.01	-7.96	-9.96	-9.88	-28.69	
101	-22.87	-6.19	-8.19	-8.12	-28.60	
118	-22.97	-7.04	-9.04	-8.97	-28.68	
138	-23.16	-8.10	-10.10	-10.02	-28.85	
168	-22.98	-7.45	-9.45	-9.37	-28.68	
182	-22.94	-7.52	-9.52	-9.44	-28.63	
195	-23.03	-7.66	-9.66	-9.58	-28.72	
222	-23.02	-9.17	-11.17	-11.08	-28.66	
251	-23.01	-8.38	-10.37	-10.29	-28.67	
279	-22.84	-6.62	-8.62	-8.55	-28.55	
297	-22.94	-6.48	-8.47	-8.41	-28.66	
311	-22.89	-6.65	-8.64	-8.57	-28.61	
334	-22.95	-6.95	-8.95	-8.88	-28.66	
361	-22.97	-7.03	-9.03	-8.96	-28.68	
381	-22.67	-6.61	-8.60	-8.54	-28.37	
412	-24.07	-9.50	-11.51	-11.41	-29.76	X
440	-22.98	-7.38	-9.37	-9.30	-28.67	
454	-22.97	-6.98	-8.98	-8.90	-28.68	
469	-22.95	-7.01	-9.00	-8.93	-28.65	
493	-22.87	-7.11	-9.11	-9.04	-28.57	
522	-23.69	-4.71	-6.72	-6.66	-29.52	
545	-22.89	-6.80	-8.80	-8.72	-28.60	
560	-23.85	-8.90	-10.90	-10.81	-29.55	
576	-23.67	-8.76	-10.76	-10.68	-29.37	
597	-24.17	-9.31	-11.32	-11.23	-29.88	X
622	-22.94	-6.92	-8.92	-8.85	-28.64	

MEAN	-28.84
STD DEVN	0.41
UPPER LIMIT	-28.02
LOWER LIMIT	-29.65

STANDARDS

STANDARD	M45	M46	O18	NORMALIZED O18	C 13			
SMOW	-22.62	2.13	0.12	0.12	-28.62		MEAN	-28.66
SMOW	-22.63	2.07	0.06	0.06	-28.62		STD DEVN	0.18
SMOW	-22.69	2.01	0.01	0.01	-28.69		UPPER LIMIT	-28.29
SMOW 21/12	-22.66	2.02	0.02	0.02	-28.65		LOWER LIMIT	-29.03
SMOW 23/12	-22.61	2.14	0.13	0.13	-28.60			
SMOW 28/12	-22.75	1.85	-0.16	-0.15	-28.75			
SMOW 19/1	-22.78	1.45	0.00	0.00	-28.76			
SMOW 23/1	-22.56	1.96	-0.04	-0.04	-28.55			
SMOW 25/1	-22.83	1.00	-1.00	-0.99	-28.80			
SMOW 27/1	-22.21	2.74	0.74	0.73	-28.20	X		
SMOW 29/1	-22.98	1.96	-0.05	-0.05	-28.99			
SMOW 31/1	-22.67	1.83	-0.17	-0.17	-28.66			
SMOW X	-22.65	2.00	0.00	0.00	-28.64			
SLAP 1	-24.68	-54.45	-56.42	-55.97	-28.89		MEAN	-28.84
SLAP 2	-24.78	-54.77	-56.73	-56.28	-28.98		STD DEVN	0.21
SLAP 3	-24.71	-54.40	-56.36	-55.91	-28.91		UPPER LIMIT	-28.43
SLAP 21/12	-24.55	-54.14	-56.11	-55.66	-28.76		LOWER LIMIT	-29.25
SLAP 23/12	-24.68	-53.87	-55.84	-55.39	-28.91			
SLAP1/1	-24.78	-53.90	-55.86	-55.42	-29.01			
SLAP 23/1	-24.62	-53.21	-55.18	-54.74	-28.87			
SLAP 25/1	-24.07	-51.74	-53.70	-53.27	-28.32	X		
SLAP 27/1	-24.66	-53.15	-55.12	-54.68	-28.90			
WW1	-22.77	-4.07	-6.07	-6.02	-28.56		MEAN	-28.72
WW2	-23.19	-4.78	-6.79	-6.73	-28.98		STD DEVN	0.33
WW3	-23.01	-4.79	-6.79	-6.73	-28.79		UPPER LIMIT	-28.05
WW 21/12	-22.81	-5.14	-7.13	-7.08	-28.58		LOWER LIMIT	-29.38
WW 28/12	-22.91	-4.30	-6.30	-6.25	-28.70			
WW 1/1	-23.17	-5.33	-7.34	-7.28	-28.94			
WW 19/1	-22.92	-4.54	-6.54	-6.49	-28.71			
WW 25/1	-22.52	-4.13	-6.13	-6.08	-28.30			
WW 31/1	-22.69	-3.37	-5.36	-5.32	-28.50			
WW 31/1	-22.67	-3.32	-5.31	-5.27	-28.49			
WW2/2	-23.85	-6.55	-8.56	-8.49	-29.63	X		
WW6/2	-22.78	-5.32	-7.31	-7.25	-28.53			
WW 8/2	-22.84	-4.46	-6.46	-6.41	-28.62			

REFERENCES

Arnason, B., Búason, Th., Martinec, J., and Theordorsson, P., 1973. Movement by water through snow pack traced by deuterium and tritium. In *The Role of Snow and Ice in Hydrology,* (Proceedings of the Banff Symposium, Canada, September 1972), vol.1, IAHS Publ. 107, 299-307.

Ayers, G.P., Gillet, R.W. and Cernot, U., 1986. Chemical composition of rainwater at New Plymouth, N.Z., in 1981-1982. *Clean Air,* 20/3, 89-93.

Bales, R.C., Valdez, M.P., Dawson, G.A. and Stanley, D.A., 1987. Physical and chemical factors controlling gaseous deposition of SO_2 to snow. In *Seasonal snowcovers : Physics, Chemistry, Hydrology,* (Proceedings of the NATO Advanced Institute: Les Arcs, France, July 13-25, 1986). Jones, H.G. and Orville-Thomas, W.J. (Eds), D. Reidel Publishing Co., pp289-297.

Boutron, C. and Lorius, C., 1977. Trace element content in East Antarctic snow samples. In: *Isotopes and Impurities in Snow and Ice,* (Proceedings of the Grenoble Symposium, August-September 1975), IAHS Publ. 118, 164-171.

Boutron, C., 1979. Reduction of contamination problems in sampling of Antarctic snows for trace element analysis. *Analytica Chimica Acta,* 106, 127-130.

Boutron, C., and Martin, S., 1980. Sources of twelve trace metals in Antarctic snows determined by principle component analysis. *Journal of Geophysical Research,* 85, C10, 5631-5638.

Bridger, N.I., Craig, R.D., and Sercombe, J.S.F., 1973. New Mass Spectrometer for Isotopic Analysis of small gas samples. *6th International Mass Spectrometer Conference Proceedings, 10-14 Sept 1973.*

Cadle, S.H. and Dasch, J.M., 1987. The contribution of dry deposition to snowpack acidity in Michigan. In *Seasonal snowcovers : Physics, Chemistry, Hydrology,* (Proceedings of the NATO Advanced Institute: Les Arcs, France, July 13-25, 1986). Jones, H.G. and Orville-Thomas, W.J. (Eds), D. Reidel Publishing Co., pp299-320.

Carr R.G., 1978. An investigation of contamination of the Wahianoa River, Tongariro Power Development. *NZ Geological Survey Engineering Geology Report,* EG300.

Charlson, R.J. and Rodhe, H., 1982. Factors controlling the acidity of natural rainwater, *Nature,* 295, 683-685.

Claridge, G.G.C., and Campbell, I.B., 1977. The salts in Antarctic soils, their distribution and relationship to soil processes. *Soil Science,* 123, 377-384.

Claridge, G.G.C., and Campbell, I.B., 1987. *Antarctica: soils, weathering processes and environment.*. Developments in Soil Science 16, Elsevier Science Publishers, Amsterdam.

Claridge, G.G.C., 1965. The clay mineralogy and chemistry of some soils from the Ross Dependency, Antarctica. *New Zealand Journal of Geology and Geophysics*, 8, 186-220.

Coplen, T.B, 1988. Normalization of oxygen and hydrogen isotope data. *Chemical Geology*, 72, 293-297.

Coplen, T.B., Kendall, C., and Hopple, J., 1983. Comparison of stable isotope reference samples. *Nature*, 302, 236-238.

Dansgaard, W., 1964. Stable isotopes in precipitation. *Tellus* 16, 4, 436-469.

Delmas, R.J., 1982. Antarctic sulphate budget. *Nature*, 299, 677-678.

Delmas, R.J., and Boutron, C., 1978. Sulfate in Antarctic snow: Spatio-temporal distribution. *Atmospheric Environment*, 12, 723-728.

Delmas, R.J., Briat, M., and Legrand, M.R., 1982. Chemistry of South Polar Snow. *Journal of Geophysical Research*, 87, 4314-4318.

Delmas, R.J., Legrand, M.R., Aristarain, A.J. and Zanolini, F., 1985. Volcanic deposits in Antarctic snow and ice. *Journal of Geophysical Research*, 90, D7, 12901-12920.

DeWalle, D.R., 1987. Review of snowpack chemistry studies. In *Seasonal snowcovers : Physics, Chemistry, Hydrology*, (Proceedings of the NATO Advanced Institute: Les Arcs, France, July 13-25, 1986). Jones, H.G. and Orville-Thomas, W.J. (Eds), D. Reidel Publishing Co., pp255-268.

Dick, A.L. and Peel, D.A., 1985. Trace elements in Antarctic air and snowfall. *Annals of Glaciology*, 7, 12-19.

Dick, A.L., Sheppard, D.S., and Patterson, J.E., 1990. Mercury content of Antarctic surface snow: initial results. *Atmospheric Environment*, 24, 4, 973-978.

Dionex Operators Manual, 1984. Dionex Corporation, Sunnyvale, CA.

Dionex technical Note 2R., 1984. Dionex Corporation, Sunnyvale, CA.

Dionex technical Note 8R., 1984. Dionex Corporation, Sunnyvale, CA.

Dionex technical Note 9R., 1984. Dionex Corporation, Sunnyvale, CA.

Dionex technical Note 14R., 1984. Dionex Corporation, Sunnyvale, CA.

Dionex technical Note 16., 1984. Dionex Corporation, Sunnyvale, CA.

Dunbar, J., 1980. *The use of stable isotopes to study biological systems.* unpublished D.Phil. thesis, University of Waikato, New Zealand, 405p.

Epstein, S., and Mayeda, T.K., 1953. Variations in the $^{18}O/^{16}O$ ratio in natural waters. *Geochimica et Cosmochimica Acta*, 4, 213-224.

Fish, G.R., 1976. Nitrogen and phosphorus analyses of rainfall at Rotorua, New Zealand. *Journal of Hydrology (N.Z.)*, 15, 17-25.

Giggenbach, W.F. and Glover, R.B., 1975. The use of chemical indicators in the surveillance of volcanic activity affecting the Crater Lake on Mt Ruapehu, New Zealand. *Bulletin Volcanologique*, 39 (1), 70-81.

Giggenbach, W.F., 1974. The chemistry of Crater Lake, Mt Ruapehu (New Zealand) during and after the 1971 active period. *New Zealand Journal of Science*, 17, 33-45.

Giggenbach, W.F., 1982. The chemistry and isotopic composition of gas discharges from New Zealand andesitic volcanoes. *Bulletin Volcanologique*, 45 (3), 253-255.

Giggenbach, W.F., Kyle, P.R., and Lyon, G.L., 1973. Present volcanic activity on Mt Erebus volcano, Antarctica. *Geology*, 1 (3), 135-136.

Gjerde, D.T., and Fritz, J.S., 1987. *Ion Chromatography*, (2nd Ed), Hüthig, Heidelberg, 283p.

Gjessing, Y.T., 1977. The filtering effect of snow. In: *Isotopes and Impurities in Snow and Ice,* (Proceedings of the Grenoble Symposium, August-September 1975), IAHS Publ. 118, 199-203.

Gjessing, Y.T., 1984. Marine and non-marine contribution to the chemical composition of snow at the Riiser-Larsenisen Ice Shelf in Antarctica. *Atmospheric Environment*, 18, 4, 825-830.

Graham, I.J. and Hackett, W.R., 1987. Petrology of calc-alkaline lavas from Ruapehu volcano and related vents, Taupo Volcanic Zone, New Zealand. *Journal of Petrology*, 28, 3, 531-567.

Grinsted, M.J., 1977. *A study of the relationships between climate and stable isotope ratios in tree rings.* unpublished D.Phil. thesis, University of Waikato, New Zealand, 237p.

Hackett, W.R. and Houghton, B.F., 1987. Active composite volcanoes of Taupo Volcanic Zone. In *Central North Island Volcanism*, New Zealand Geological Survey Record 21, 61-115.

Harvey, M.J. and Clarkson, T.S., 1988. The chemical composition of rain at an inland and a coastal New Zealand site. *Clean Air*, 22/2, 58-63.

Heine, A.J., 1962. Snow structure at Mt Ruapehu. *New Zealand Journal of Geology*, 5, 375-383.

Herron, M. M. and Langway (Jr), C.C., 1979. Dating of Ross Ice Shelf cores by chemical analysis. *Journal of Glaciology*, 24, 345-357.

Herron, M.M., 1982. Impurity sources of F^-, Cl^-, NO_3^-, and SO_4^{2-} in Greenland and Antarctic precipitation. *Journal of Geophysical Research*, 87, C4, 3052-3060.

Holden, R. and Clarkson, T.S., 1986. Acid rain : A New Zealand viewpoint. *Journal of the Royal Society of New Zealand*, 16 (1), 1-15.

Ivey, J.P., and Davies, D.M., 1987. Ion chromatographic determination of selected ions in Antarctic ice. *Analytica Chimica Acta*, 194, 281-286.

Ivey, J.P., Davies, D.M., Morgan, V., and Ayers, G.P., 1986. Methanesulphonate in Antarctic ice. *Tellus*, 38B, 375-379.

Jonasson, I.R., 1973. Migration of trace metals in snow. *Nature*, 241, 447-448.

Jouzel, J., Lorius, C., Petit, J.R., Genthorn, C., Barkov, N.I., Kotlyakov, V.M. and Petrov, V.N., 1987. Vostok ice core: a continuous isotope temperature record over the last climatic cycle (160,000 years). *Nature*, 329, 403-408.

Jouzel, J., Merlivat, L., Petit, J.R. and Lorius, C., 1983. Climatic information over the last century deduced from a detailed isotopic record in the South Pole snow. *Journal of Geophysical Research*, 88, C4, 2693-2703.

Junge, C.E., 1977. Processes responsible for the trace content in precipitation. In: *Isotopes and Impurities in Snow and Ice,* (Proceedings of the Grenoble Symposium, August-September 1975), IAHS Publ. 118, 63-77.

Kaye, G.W.C., 1973. *Table of Physical and Chemical Constants and Some Mathematical Functions*, (14th Ed), Longman, London, 386p.

Keys, J.R., and Williams, K., 1981. Origin of crystalline, cold desert salts in the McMurdo region, Antarctica. *Geochimica et Cosmochimica Acta*, 45, 2299-2309.

Kind, R.J., 1981. Snow drifting. In: *Handbook of Snow Principles, Processes, Management and Use*, Gray, D.M. & Male, D.H. (Eds), Pergamon Press, Canada., pp338-359.

Krimmel, R.M., Tangborn, W.V. and Meier, M.F., 1973. Water flow through a temperate glacier. In *The Role of Snow and Ice in Hydrology,* (Proceedings of the Banff Symposium, Canada, September 1972), vol.1, IAHS Publ. 107, 401-416.

Krouse, H.R. and Smith, J.L., 1973. $^{18}O/^{16}O$ abundance variations in Sierra Nevada seasonal snowpacks and their use in hydrological research. In *The Role of Snow and Ice in Hydrology,* (Proceedings of the Banff Symposium, Canada, September 1972), vol.1, IAHS Publ. 107, 24-31.

Krouse, H.R., Hislop, R., Brown, H.M., West, K., and Smith, J.L., 1977. Climatic and spatial dependence of the retention of D/H and $^{18}O/^{16}O$ abundances in snow and ice of North America. In *Isotopes and Impurities in Snow and Ice,* (Proceedings of the Grenoble Symposium, August-September 1975), IAHS Publ. 118, 242-247.

Kyle, P., Palais, J., and Delmas, R., 1982. The volcanic record of Antarctic ice cores: Preliminary results and potential for future investigations. *Annals of Glaciology,* 3, 172-177.

Laird, C.M., Zeller, E.J. and Dreschhoff, G.A.M., 1987. Nitrate variability in South Pole ice sequences and fossil surface effects. *Antarctic Journal of the United States*, 22, 5, 80-83.

Laird, C.M., Zeller, E.J., Armstrong, T.P. and Parker, B.C., 1982. Solar activity and nitrate deposition in South Pole snow. *Journal of Geophysical Research*, 9, 10, 1195-1198.

Legrand, M.R. and Delmas, R.J., 1984. The ionic balance of Antarctic snow: A 10 year detailed record. *Atmospheric Environment* , 18, 9, 1867-1874.

Legrand, M.R. and Delmas, R.J., 1985. Spatial and temporal variations of snow chemistry in Terre Adélie (East Antarctica). *Annals of Glaciology*, 7, 20-25.

Legrand, M.R. and Delmas, R.J., 1986. Relative contributions of tropospheric and stratospheric sources to nitrate in Antarctic snow. *Tellus*, 38B, 236-249.

Legrand, M.R. and Delmas, R.J., 1987a. A 220 year continuous record of volcanic H_2SO_4 in the Antarctic ice sheet. *Nature*, 327, 671-676.

Legrand, M.R. and Delmas, R.J., 1987b. Experimental protocol for the chemical analysis of snow, firn and ice cores. In *Seasonal snowcovers : Physics, Chemistry, Hydrology*, (Proceedings of the NATO Advanced Institute: Les Arcs, France, July 13-25, 1986). Jones, H.G. and Orville-Thomas, W.J. (Eds), D. Reidel Publishing Co., pp 225-254.

Legrand, M.R. and Delmas, R.J., 1988. Formation of HCl in the Antarctic atmosphere. *Journal of Geophysical Research*, 93, D6, 7153-7168.

Legrand, M.R., De Angelis, M. and Delmas, R.J., 1984. Ion chromatographic determination of common ions at ultratrace levels in Antarctic snow and ice. *Analytica Chimica Acta*, 156, 181-192.

Legrand, M.R., Lorius, C., Barkov, N.I., and Petrov, V.N., 1988. Vostok (Antarctica) ice core: Atmospheric chemistry changes over the last climatic cycle (160,000 years). *Atmospheric Environment*, 22, 2, 317-331.

MacDonald, J.C., 1985. *Inorganic Cromatographic Analysis*, vol.78, Chemical Analysis, John Wiley & Sons, New York, 450p.

Male, D.H., 1980. Seasonal snowcover. In: *Dynamics of Snow and Ice Masses*, Colbeck, S.C. (Ed), Academic Press, New York., pp305-390.

Male, D.H., and Gray, D.M., 1981. Snowcover, ablation and runoff. In: *Handbook of Snow Principles, Processes, Management and Use*, Gray, D.M. & Male, D.H. (Eds), Pergamon Press, Canada., pp360-436.

Marcus, M.G., and Moore R.D., 1983. Snowpack structure and climate, Mount Egmont, New Zealand. *Weather and Climate - Journal of the Meteorological Society of New Zealand (Inc)*, 3/2, 42-51.

Martinec, J., Moser, H., de Quervain, M.R., Rauert, W., and Stichler, W., 1977. Assessment of processes in the snowpack by parallel deuterium, tritium and oxygen-18 sampling. In *Isotopes and Impurities in Snow and Ice,* (Proceedings of the Grenoble Symposium, August-September 1975), IAHS Publ. 118, 220-231.

Miller, R.B., 1961. Chemical composition of rainwater at Taita, New Zealand, 1956-1958. *New Zealand Journal of Science*, 4, 844-853.

Molenar, J.V. and Warburton, J.A., 1980. Temporal variations and correlations in chemistry of snow on Ross Ice Shelf. *Antarctic Journal of the United States*, 14, 72-74.

Moser, H., Silva, C., Stichler, W., and Stowhas, L., 1973. Measuring the isotope content in precipitation in the Andes. In *The Role of Snow and Ice in Hydrology,* (Proceedings of the Banff Symposium, Canada, September 1972), vol.1, IAHS Publ. 107, 14-23.

Müller, F., Stauffer, B. and Schriber, G., 1977. Isotope measurements and firn stratigraphy on ice caps surrounding the North Water polynya. In *Isotopes and Impurities in Snow and Ice,* (Proceedings of the Grenoble Symposium, August-September 1975), IAHS Publ. 118, 188-195.

Nairn, I.A. and Wood, C.P., 1987. Active volcanoes of Taupo Volcanic Zone In: *Active volcanoes and geothermal systems, Taupo Volcanic Zone*, New Zealand Geological Survey Record 22, 60-65.

Neubauer, J. and Heumann, K.G., 1988a. Nitrate trace determination in snow and firn core samples of ice shelves at the Weddell Sea, Antarctica. *Atmospheric Environment*, 22, 3, 537-545.

Neubauer, J. and Heumann, K.G., 1988b. Determination of nitrate at the ng/g level in Antarctic snow samples with ion chromatography and isotope dilution mass spectrometry. *Fresenius Zeitschrift für Analytische Chemie*, 331, 170-173.

New Zealand Meteorological Service Observations, 1968-1986.

Obradovic, M.M., and Sklash, M.G., 1987. An isotopic and geochemical study of seasonal snowmelt runoff in the Apex River watershed. In *Seasonal snowcovers : Physics, Chemistry, Hydrology,* (Proceedings of the NATO Advanced Institute: Les Arcs, France, July 13-25, 1986). Jones, H.G. and Orville-Thomas, W.J. (Eds), D. Reidel Publishing Co., pp643-659.

Otway, P.M., 1980-1990. Ruapehu Crater Lake inspection and survey. *New Zealand Geological Survey Immediate Reports,* T20/501.

Page, Y., 1987. The chemical evolution of a seasonal snowcover at mid-and-high altitudes. In *Seasonal snowcovers : Physics, Chemistry, Hydrology*, (Proceedings of the NATO Advanced Institute: Les Arcs, France, July 13-25, 1986). Jones, H.G. and Orville-Thomas, W.J. (Eds), D. Reidel Publishing Co., pp281-288.

Palais, J.M. and Legrand, M., 1985. Soluble impurities in the Byrd Station ice core, Antarctica: Their origin and sources. *Journal of Geophysical Research*, 90, C1, 1143-1154.

Parish, T.R., 1988. Surface winds over the Antarctic Continent : A review. *Review of Geophysics*, 26 (1), 169-180.

Parker, B.C., and Zeller, E.J., 1980. Nitrogenous chemical composition of Antarctic ice and snow. *Antarctic Journal of the United States*, 14, 80-82.

Parker, B.C., Zeller, E.J., and Gow, A.J., 1982. Nitrate fluctuations in Antarctic snow and firn: Potential sources and mechanisms of formation. *Annals of Glaciology*, 3, 243-248.

Pearce, A.J., Stewart, M.K. and Sklash, M.G., 1986. Storm runoff generation in humid headwater catchments, I: Where does the water come from? *Water Resources Research*, 22, 8, 1263-1272.

Podzimek, J., 1987. Direct scavenging and induced transport of atmospheric aerosols by falling snow and ice crystals. In *Seasonal snowcovers : Physics, Chemistry, Hydrology*, (Proceedings of the NATO Advanced Institute: Les Arcs, France, July 13-25, 1986). Jones, H.G. and Orville-Thomas, W.J. (Eds), D. Reidel Publishing Co., pp209-224.

Radke, L.F., 1982. Sulphur and sulphate from Mt Erebus. *Nature*, 299, 710-712.

Richards, T.L., 1973. Physics and chemistry of snowfall and snow distribution. In: *The Role of Snow and Ice in Hydrology,* (Proceedings of the Banff Symposium, Canada, September 1972), vol.1, IAHS Publ. 107, 1-13.

Risbo,T., Clausen, H.B. and Rasmussen, K.L., 1981. Supernovae and nitrate in the Greenland ice sheet. *Nature*, 294, 637-639.

Rood, R.T., Sarazin, C.L., Zeller, E.J. and Parker, B.C., 1979. X- or γ-rays from supernovae in glacial ice. *Nature*, 282, 701-703.

Ruapehu Alpine Lifts Mountain and Skifield Weather Observations, 1984-1989.

Saigne, C., and Legrand, M., 1987. Measurements of methanesulphonic acid in Antarctic ice. Nature, 330, 240-242.

Saigne, C., Kirchner, S. and Legrand, M., 1987. Ion-chromatographic measurements of ammonium, fluoride, acetate, formate and methanesulphonate ions at very low levels in Antarctic ice. *Analytica Chimica Acta*, 203, 11-21.

Schemenauer, R.S., Berry, M.O. and Maxwell, J.B., 1981. Snowfall formation. In: *Handbook of Snow Principles, Processes, Management and Use*, Gray, D.M. & Male, D.H. (Eds), Pergamon Press, Canada., pp129-152.

Schotterer, U., Finkel, R., Oeschger, H., Siegenthaler, U., Wahlen, M., Bart, G., Gäggeler, H., and von Gunten, H.R., 1977. Isotope measurements on firn and ice cores from alpine glaciers. In *Isotopes and Impurities in Snow and Ice,* (Proceedings of the Grenoble Symposium, August-September 1975), IAHS Publ. 118, 232-236.

Schriber, G., Stauffer, B. and Müller, F., 1977. $^{18}O/^{16}O$, $^{2}H/^{1}H$ and ^{3}H measurements on precipitation and air moisture samples from the North Water area. In *Isotopes and Impurities in Snow and Ice,* (Proceedings of the Grenoble Symposium, August-September 1975), IAHS Publ. 118, 182-187.

Schwerdtfeger, W., 1984. *Weather and Climate of the Antarctic*, Developments in Atmospheric Science 15, Elsevier Science Publishers B.V., Amsterdam.

Sheppard, D.S., Patterson, J.E., Lyon, G.L. and McAdam, M.K., in press.

Sigg, A., Neftel, A. and Zürcher, F., 1987. Chemical transformations in a snow cover at Weissfluhjoch, Switzerland, situated 2500 m.a.s.l. In *Seasonal snowcovers : Physics, Chemistry, Hydrology*, (Proceedings of the NATO Advanced Institute: Les Arcs, France, July 13-25, 1986). Jones, H.G. and Orville-Thomas, W.J. (Eds), D. Reidel Publishing Co., pp269-279.

Stearns, C.R. and Wendler, G., 1988. Research results from Antarctic weather stations. *Reviews of Geophysics*, 26 (1), 45-61.

Stephenson, P.J., 1967. Some considerations of snow metamorphism in the Antarctic Ice Sheet in the light of ice crystal studies. In: *Physics of Snow and Ice*, (Proceedings of International Conference on Low Temperature Science, August 14-19, 1966, Sapporo, Japan). vol 1 pt 2, Bunyeido Printing Co, Japan., pp725-740.

Stevenson, D.J., 1980. The lead content and acidity of Christchurch precipitation. *New Zealand Journal of Science*, 23, 311-312.

Stothers, R., 1980. Giant solar flares in Antarctic ice. *Nature*, 287, 365.

Taylor, L.D., 1965. Glaciological studies on the South Pole Traverse, 1962-1963. Institute of Polar Studies, Report 17, 13p.

Thompson, C.S., 1981. The climate and weather of the Taranaki region. *NZ Meteorological Service Miscellaneous Publication*, 115 (9), 64p.

Thompson, C.S., 1984. The weather and climate of the Tongariro region. *NZ Meteorological Service Miscellaneous Publication*, 115 (14), 35p.

Tranter, M., Abrahams, P.W., Blackwood, I., Davies, T.D., Brimblecombe, P., Thompson, I.P., and Vincent, C.E., 1987. Changes in streamwater chemistry during snowmelt. In *Seasonal snowcovers : Physics, Chemistry, Hydrology*, (Proceedings of the NATO Advanced Institute: Les Arcs, France, July 13-25, 1986). Jones, H.G. and Orville-Thomas, W.J. (Eds), D. Reidel Publishing Co., pp575-597.

Warburton, J.A., and Linkletter, G.O., 1977. Precipitation forming mechanisms and the chemistry of precipitation on the Ross Ice Shelf, Antarctica. In *Isotopes and Impurities in Snow and Ice,* (Proceedings of the Grenoble Symposium, August-September 1975), IAHS Publ. 118, 88-94.

Wolff, E.W., and Peel, D.A., 1985. Closer to a true value for heavy metal concentrations in recent Antarctic snow by improved contamination control. *Annals of Glaciology*, 7, 61-69.

Zanolini, F., Delmas,R.J. and Legrand, M.R., 1985. Sulphuric and nitric acid concentration and spikes along a 200 metre deep ice core at D57 (Terre Adélie, Antarctica). *Annals of Glaciology*, 7, 70-75.

Zeller, E.J., and Parker,B.C., 1981. Nitrate ion in Antarctic firn as a marker for solar activity. *Geophysical Research Letters*, 8, 8, 895-898.