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SALTS AND THEIR DISTRIBUTION IN THE McMURDO REGION, ANTARCTICA

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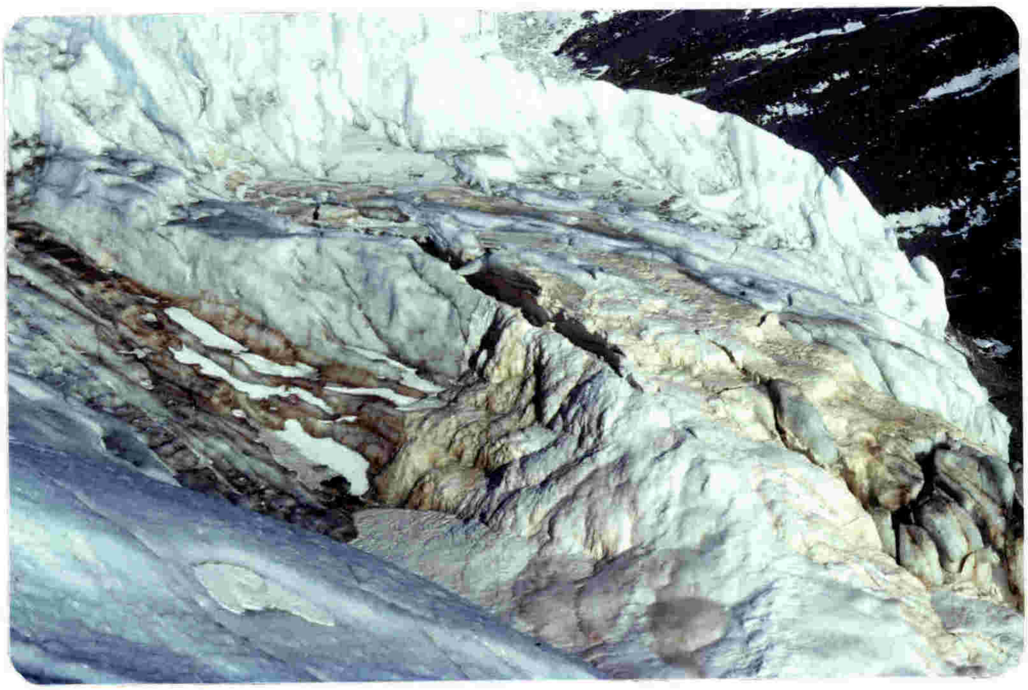
This thesis is dedicated to Karen for her tremendous encouragement and assistance.

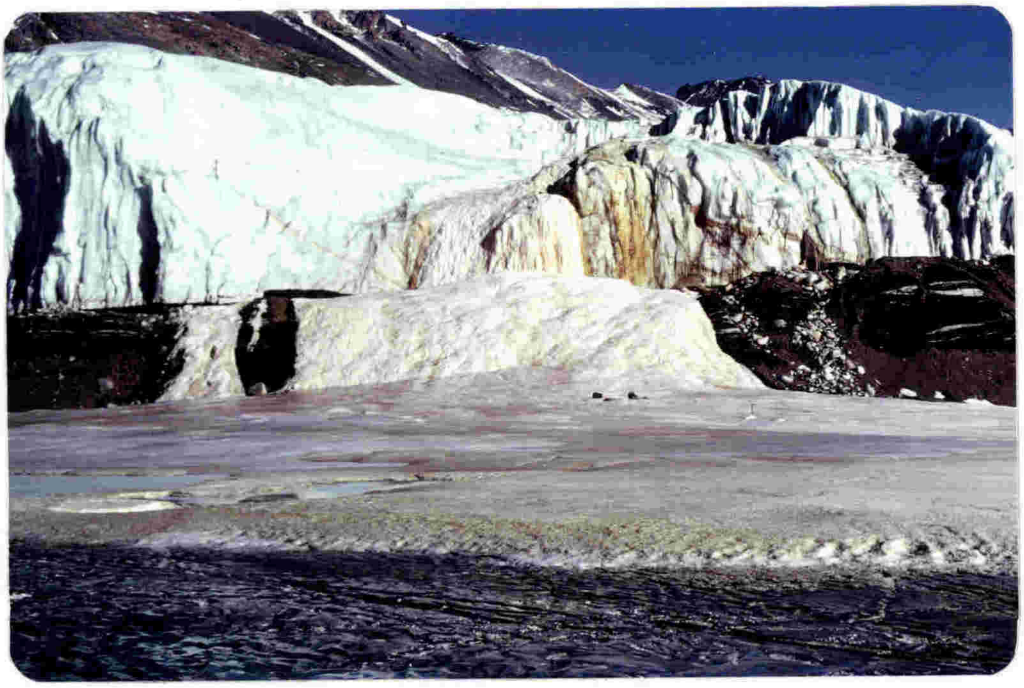
Tamavta tornaqarata ingerdlasa
- may we travel with no evil spirits in our sledge train

Inuit (Eskimo) proverb

FRONTISPIECES



Top: Salty water discharging from a longitudinal crevasse, one metre wide, at the northeastern part of the terminus of Taylor Glacier. The brine, similar in composition to concentrated sea water, is forming a deposit of ice that is white initially but will develop an orange colouration as it ages (24/10/78).



Bottom: The accumulation of saline ice (icing) beside Taylor Glacier being formed during the discharge of 1978 (24/10/78; packs and ice axe for scale).

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ABSTRACT

Salts are widespread in the cold, arid McMurdo region of Antarctica. They exist in a variety of deposit types from massive subglacial and sub-lake deposits containing up to 10^{10} kilograms of salt, down to traces in soil, snow and ice. However, deposits on rock and soil typically amount to a few grams of salt. At least 30 salt phases are known but only 10 of these are widespread. These 10 are thenardite, gypsum, halite, calcite, darapskite, soda nitre, mirabilite, bloedite, epsomite and hexahydrite.

The distribution of salts has been examined on two scales, local and regional. The local scale extends from individual deposits to areas of a few square kilometres. The regional scale covers McMurdo oasis, McMurdo Sound and Ross Island, though areas in McMurdo oasis, and particularly Taylor Valley, receive most attention.

Local distribution is controlled by salt migration and separation. Migration is induced by water and wind, with soil brines moving as thin liquid films, by capillarity and under the influence of gravity. Deflation and asymmetric salt accumulation provide evidence that wind is important.

Separation of phases is a consequence of different physico-chemical properties of salts, and environmental conditions, including site aspect, ambient temperature and humidity. Eutectic temperature is a fundamental salt property but solubility is also important. Several salt deposits containing separated (fractionated) phases have been found in the region. Separation is achieved mainly by fractional dissolution and crystallization and the most evolved product of the general separation sequence is calcium chloride. The separation processes, together with salt migration, obscure the sources of the salts.

Regional distribution of salts has been characterized by determining the relative frequency at which specific phases are encountered at increasing distance from the coast and above sea level. Chloride and sodium phases decrease, whereas magnesium phases increase in frequency away from the coast. Sulphates-to-chloride and nitrates-to-chloride ratios increase with increasing distance. Calcium and carbonate show little change except in Taylor Valley where a marked decrease is apparent.

This regional distribution is mainly dependent on the sources of the salts. The marine source is most important, contributing almost all of the chloride, sodium, sulphate and probably nitrate ions that are present. Chemical weathering is the predominant source of magnesium, calcium and carbonate ions probably via reactions of mafic, ferromagnesian minerals in local rocks and regolith. Biological and volcanic activity are locally significant at eastern Taylor Valley and in the summit area of Erebus Volcano, respectively. The salts have accumulated over the lifetime of the region, that is over less than the last 20-25 Ma or so. There is no evidence that they are relics from earlier, preglacial times, except for very minor amounts of gypsum and calcium carbonate.

There has been a recent influx of sea water into Taylor Valley perhaps between 50,000 and 20,000 years ago, and evaporation of this water has preceded advance of Taylor Glacier over part of the resulting salt deposit. The continuing interaction between glacier and salt is causing basal ice to melt and producing aperiodic discharges of up to a few thousand cubic metres of salty water from the terminus of the glacier.

CHAPTER 1 INTRODUCTION

1.1 The Topic

1.1.1 Introduction to topic:

Salts exist in numerous places in Antarctica. Their presence on the surface of ice- and snow-free ground and in moraine, sediments and lakes, particularly in the McMurdo region, has been known since the early expeditions (Ferrar 1907; Mawson 1915; Jensen 1916; Debenham 1920). Subsequent studies have investigated salts on the ground, within the soil and sediments, in deep drill holes, on the surface of rocks, in streams, ponds and lakes, and in snow and ice. Consequently a wealth of information on salts now exists in the literature, though it is only a small part of the literature pertaining to salts elsewhere in the world.

A simple definition of the class of chemical compounds known as 'salts' is required. Salts are compounds composed of a cation(s) that is, a metal or metal-like radical, and an anion(s);the anion(s) is from an acid after the proton(s) has been partly or wholly replaced from that acid. A salt may contain water of crystallization (structural water). Hydrates and anhydrous forms of a salt are known as phases of that salt; each phase has a mineral name if it has a documented occurrence in nature. In Antarctica, more than thirty different salt phases are known (Appendix 1, Table 1); some are common whereas others are uncommon or rare. Sodium and calcium are the most common cations, and chloride and sulphate the most common anions in these phases. However magnesium, potassium, nitrate, carbonate, and bicarbonate phases are also quite common.

The presence of macroscopic quantities of salt phases containing these ions is a characteristic of desert or semi-desert areas. In other parts of the earth any salts produced are removed in dissolved form by water. Antarctica is a cold desert, not a hot desert like most other arid or semi-arid parts of the world. The difference influences the type and behaviour of salts, because the general salt-water system is temperature dependent.

Various origins or sources have been proposed for the salts in the McMurdo region and a variety of time scales for salt accumulation have been considered. Studies have tended to concentrate on specific salts or elements in those salts, or on specific localities. Such studies cannot lead to valid generalizations of salt origin in the region or in Antarctica as a whole since the accumulation of salts is subject to a number of perturbing processes and is both irregular and sporadic. Migration of salts occurs within the region and is part of the reason why salt deposits vary in space and time. Separation of salts and ions takes place during this migration and causes additional difficulties in interpretation. Therefore to be successful a study of salt origin must first consider salt migration and separation. The study must be based on a large number of samples; analytical results must be subject to averaging processes and where possible to further statistical treatment. Generalizations and conclusions based on one or two samples are unsound.

1.1.2 Scope of the thesis:

The purpose of this thesis is to acquire an understanding of the geochemistry of salts in the McMurdo region. The thesis attempts a synthesis of new data and the literature, mainly pertaining to antarctic salts containing the ions listed earlier. The distribution of salt phases on both local and regional scales is investigated and characterized. Processes of salt migration and separation are examined, and the sources of the salts discussed. Saline lakes are not the main part of this study and are not discussed in detail.

1.1.3 Structure and outline:

This thesis is divided into eight chapters and five appendices. Each chapter has its own introduction and is subdivided into sections and subsections, all numerically labelled. Chapter 1 introduces the topic and describes the field area. Chapter 2 discusses soil temperature and moisture in present-day conditions and briefly over those of the last few million years. The third chapter describes the various salt phases present and the types of salt deposits. Salt distribution on a local scale is portrayed using histograms and rose diagrams. Chapter 4 considers the physical and chemical processes that cause salt migration and separation. Chapter 5 portrays salt distribution on a regional scale using graphs, histograms and statistical analysis. Then, in Chapter 6, the sources of salts, and other influences on regional salt distribution are discussed. The following two chapters are case studies. Chapter 7 deals with salts and their distribution in the summit area of Erebus Volcano. Chapter 8 examines the evolution and composition of brines discharged at the terminus of Taylor Glacier. The conclusion follows.

The appendices of the thesis are referred to throughout the course of Chapters 1 to 8. Appendix 1 contains environmental details and analyses of salt and brine samples, together with numerical summaries of these analyses. Appendix 2 considers sources of error in the data and statistical treatment of the numerical summaries and other data. Appendix 3 is a review of air temperature, wind, precipitation, and humidity in the McMurdo region; without this review it would have been difficult to write this thesis. Appendix 4 lists soil measurements discussed in Chapter 2. Appendix 5 produces physical chemistry data and glaciological background information necessary to Chapter 8 on the saline discharge.

1.2 The Field Area

1.2.1 The area defined:

The fieldwork for this thesis was undertaken in the McMurdo region. This is an area of about 7 x 10^4 km^2 situated at the southern extremity of Victoria Land, East Antarctica (Figs.1.1, 1.2). Victoria Land was the original name applied by Ross (1847) to the land discovered by his expedition in 1841, along the western margin of Ross Sea from the seventieth to the seventy-ninth degree of latitude. This mountainous land, 100-250 km wide, constitutes part of the Transantarctic Mountains and has summits up to 4200 m. It is broken by numerous east-west transverse valleys most of which are occupied by large glaciers discharging ice from the continental ice sheet in the west to Ross Sea in the east.

The McMurdo region consists of two main areas, McMurdo oasis* and Ross Island-McMurdo Sound, that are geographically,

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*The word 'oasis' has been applied since 1939 (Scholes 1953) to extensive areas that are largely free of snow and ice in Antarctica. Individual nunataks, mountains and coastal areas with small amounts of bare ground are not referred to as oases, but may be part of one.

Figure 1.1 Antarctica† showing places mentioned in text and appendices.

geologically and climatologically distinct (Fig.1.2). McMurdo oasis (Clark 1965) comprises a central area of about 1800 km^2 containing Wright and Victoria Valley systems, and numerous other valleys and ice-free areas, the best known being Taylor Dry Valley*. Other well-known parts of the oasis are the Koettlitz dry valleys (northwest of Koettlitz Glacier) and Beacon Valley. Nunataks around Skelton Névé constitute the most western and southern parts of the oasis, Koettlitz dry valleys the eastern, and Convoy Range the northernmost part. In total there are about 3000-4000 km^2

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†Grammatical note: There is a difference between the continent of Antarctica and the south polar or antarctic region, that part of the globe south of latitude 60°S. This thesis uses the lower case 'a' for antarctic when that word is used as an adjective for components or characteristics of the region (e.g. antarctic salt phase, antarctic climate). The upper case 'A' is reserved for named places or features (e.g. Antarctic Circle, East Antarctic Ice Sheet).

*The term 'dry valleys' applies to the predominantly snow- and ice-free valleys of McMurdo oasis. First used by Scott (1905) for his discovery of Taylor Dry Valley in 1903, the term is now generally accepted in both scientific and popular circles.

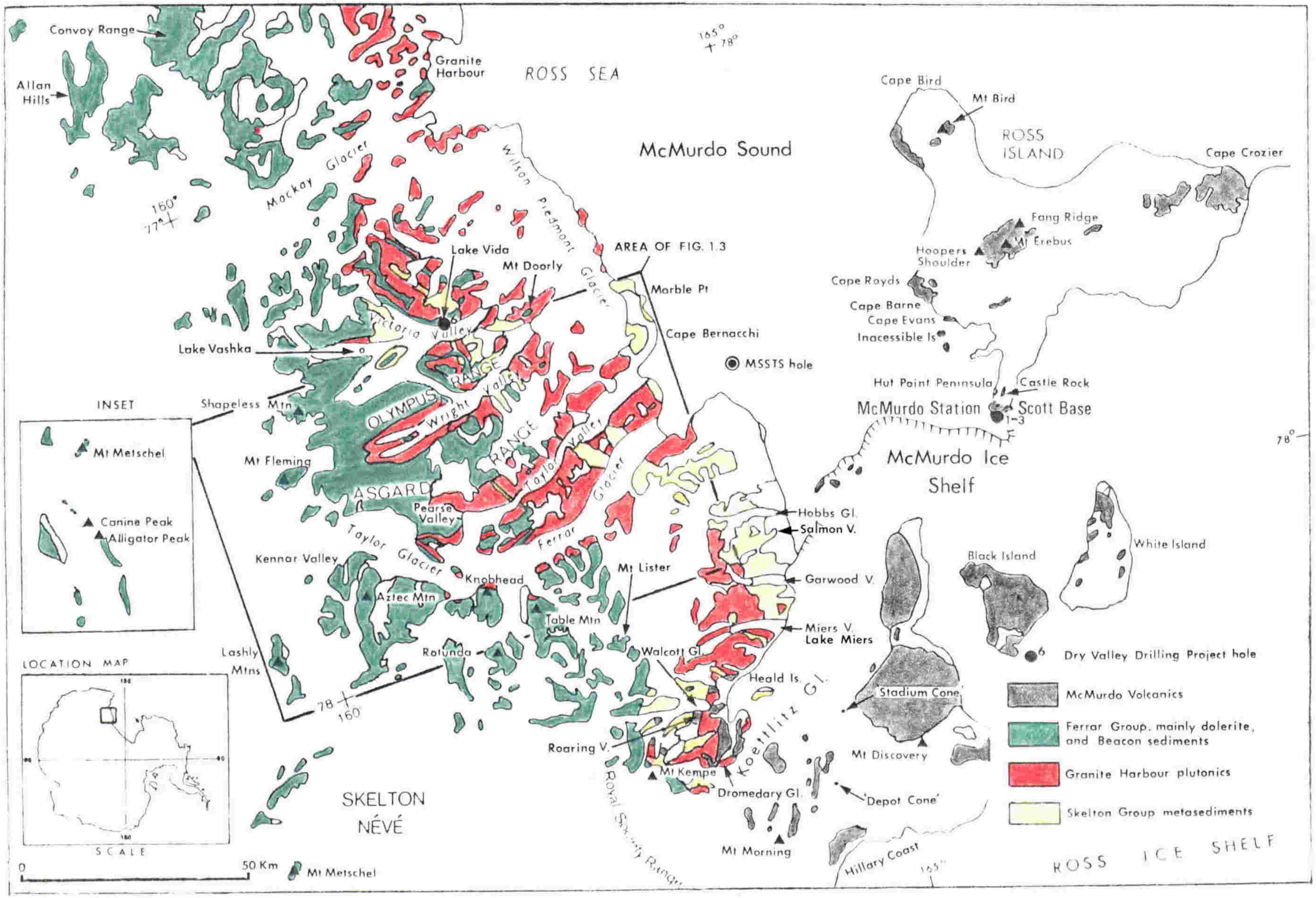

Figure 1.2 The McMurdo region showing bedrock geology (simplified, after Warren 1969).

of snow- and ice-free terrain in McMurdo oasis, which is the largest such area in Antarctica. Ross Island-McMurdo sound area includes Ross Island and areas such as Black Island, White Island, Brown Peninsula, Mts. Discovery and Morning. In this thesis these areas are referred to collectively as McMurdo Sound.

This thesis concentrates on McMurdo oasis (Fig.1.3). In particular, attention has been paid to Taylor Valley which has been studied from New Harbour in the east to Lashly Mountains in the west. In this 80 km long transect through the Transantarctic Mountains, several areas have been sampled in detail to give a representative picture of salt distribution in the valley. The northernmost sampling in the oasis was on Shapeless Mountain, and the southernmost at Alligator Peak. Reconnaissance was made on nunataks immediately south of David Glacier and on areas near Darwin Glacier. Places mentioned in the thesis are shown on Figs.1.1, 1.2, 1.3 and in Appendix 1, Figs.1-5.

In this thesis elevations are assumed to be approximate unless stated precisely. Elevation control and contouring on maps of McMurdo region is still not accurate. The recently published United States Geological Survey 8 map series (1977) (1:50,000) differs from the earlier (1960, 1972) Reconnaissance series 1:250,000 maps by up to 200 m elevation in places, especially on and around Taylor Glacier. Furthermore, spot heights given on maps may not correspond to recent ground survey (e.g. Point 1433 on Solitary Rocks, Taylor Valley, was recently measured as being 1215 m above sea level by New Zealand surveyors; J. Palmer, Lands and Survey Department, personal communication). Where elevations are important to this study, the reference map or article is stated. Generally however the 1:250,000 map series is used. In the oasis elevations range from sea level in the east, to a base level of about 2000 m in the west, with peaks up to 4000 m asl.

1.2.2 Classification of the antarctic climate:

Under the Köppen climate classification system (Strahler 1960) the polar climate of Antarctica as a whole is classed as an 'Ice Climate'. The symbol E is given to such a climate where the monthly mean temperature of the warmest month is colder than +10°C.

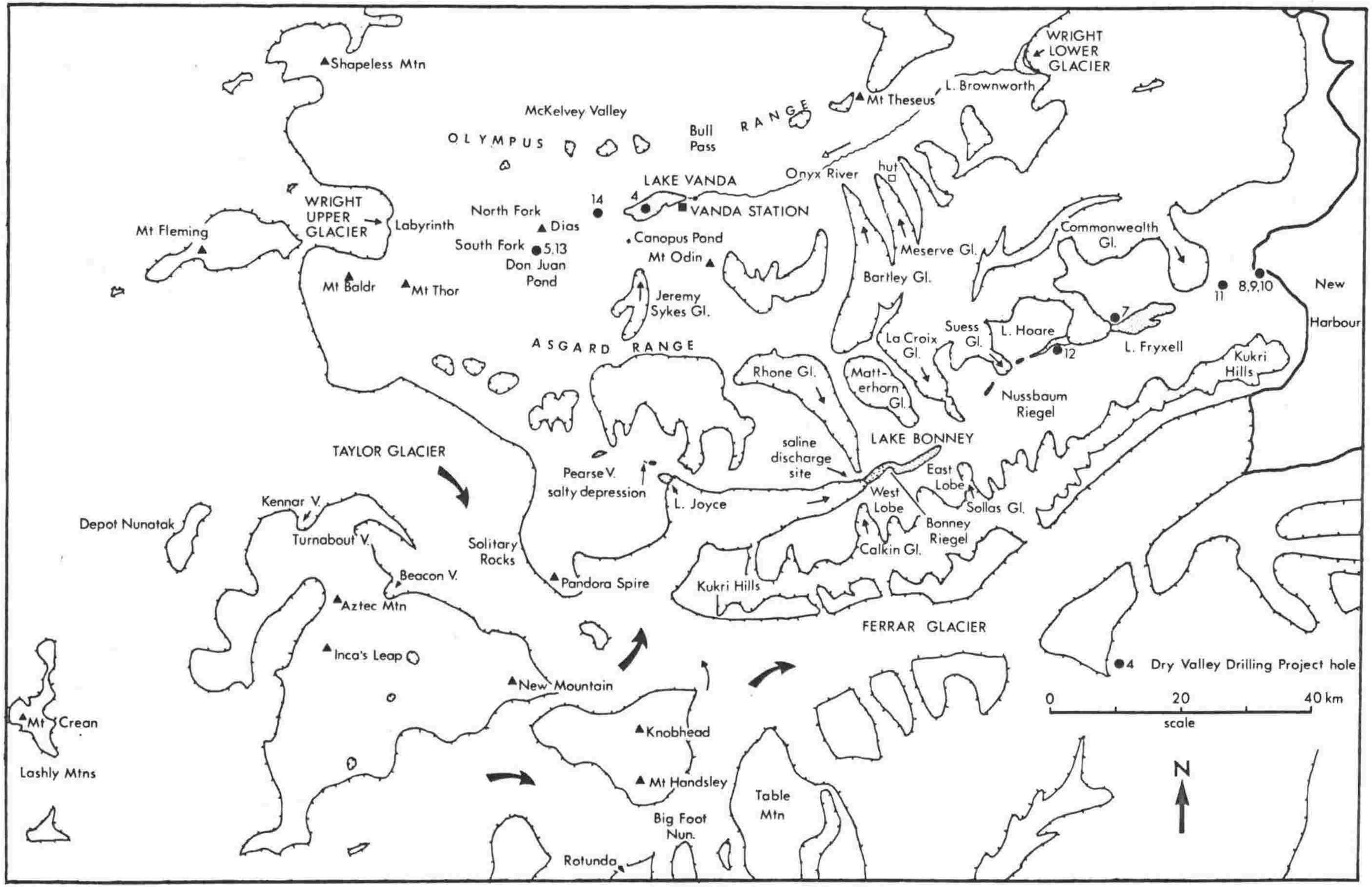

Figure 1.3 Wright, Taylor and Ferrar Valleys, McMurdo oasis.

The more severe 'Icecap Climate' (symbol EF, no monthly mean temperatures above freezing) applies to most of Antarctica, but some localities such as McMurdo oasis do experience positive mean monthly temperatures as high as +1.4°C in summer (Appendix 3, Table 2); there the mean annual air temperature is around -20°C (Thompson et al. 1971a; Appendix 3, Table 4). Antarctica is the earth's coldest continent.

Antarctica is the driest continent also. Mean annual snow accumulation averaged over the whole continent is around 150 mm water equivalent (Bull 1971). This is a reasonable estimate of annual precipitation because ablation is very small in the interior (Appendix 3, section 6.2). Annual precipitation is higher in coastal areas and towards the north, but in the McMurdo region is less than about 200 mm (Appendix 3, Table 14). An arid climate has precipitation less than 250 mm (10 inches) per year (Strahler 1960). Therefore Antarctica is mostly arid, and is often described as a cold desert.

Such a classification is insufficient for the purposes of this study. Temperature and precipitation affect the amount of moisture available for salt migration and in general are strong influences on salt geochemistry in the region. Wind and humidity also affect salt distribution. The frigid, arid climate of Antarctica has been discussed extensively in the literature; Appendix 3 is a review of selected aspects of climate in the McMurdo region, and is referred to extensively throughout the thesis. Chapter 2 discusses maximum and mean surface and subsurface temperatures, and the soil moisture regime in the region.

1.2.3 Bedrock geology:

There are five groups of bedrock exposed at the surface in the McMurdo region. Table 1.1 gives the nomenclature, simplified descriptions, and age relationships, and Fig.1.2 the distribution of in situ exposures of these rocks. The Table also gives useful references, on which much of the following is based.

The bedrock geology of McMurdo oasis consists of a succession of rock types. Metasediments of the Skelton Group are exposed up to 30-40 km inland from the coast and up to 1800 m elevation in Taylor and Wright Valleys; they outcrop up to about 2600 m

Table 1.1 Nomenclature, description and age of bedrock in the McMurdo region. Adapted from Gunn and Warren (1962), McKelvey and Webb (1962), Haskell *et al.*(1965), Neall and Smith (1967), Cole and Ewart (1968), Craddock (1969), Barrett and Webb (1973), Grapes *et al.*(1974), Kyle (1976), Keys *et al.*(1977), Armstrong (1978).

Group		Formation	Description	Age	
				Period	Million years
McMurdo Volcanic Group		Various: Basalts, Trachytes and Phonolites, underlain by pyroclastics	six broad petrographic types of lavas based largely on phenocryst contents; olivine - augite basalts. plagioclase basalts, hornblende basalts, pyroxene trachytes, hornblende trachytes, anorthoclase phonolite	Late Cenozoic	<0.01 (Erebus presently active) ≥15.4
Ferrar Group		Kirkpatrick Basalt	tholeiitic basalt	Jurassic	140
		Mawson Formation	volcanic; sandstones, breccias, mudflows, dykes etc.		
		Ferrar Dolerite	mainly tholeiitic sills and dykes		190
Beacon Super-Group	Victoria Group	Lashly Formation Feather Conglomerate Weller Coal Measures Metschel Tillite	quartzose, arkosic and lithic; sandstones, siltstones, conglomerates etc.; some plant remains including coal; clasts plutonic and metasedimentary in Tillite	Triassic Lower Permian	200 280
	Taylor Group	Aztec Siltstone, Beacon Heights Orthoquartzite, Arena Sandstone, Altar Mountain Formation, New Mountain Sandstone, Terra Cotta Siltstone, Windy Gully Sandstone	sandstones, siltstones, conglomerates, claystones, largely quartzose	Devonian and earlier ?	350
Granite Harbour Intrusive Complex			hornblende, lamprophyre and porphyry dykes	Silurian	400
		Irizar Granite	Medium to coarse, pink homogenous; rich in potassium feldspar phenocrysts.		
		Vida Granite	Similar to Irizar Granite.		
			augite - biotite lamprophyre, porphyry and other dykes and larger bodies		
		Larsen Granodiorite	Coarsely foliated owing to alignment of potassium feldspar phenocrysts and biotite.		
		Dias Granite	Similar to Larsen Granodiorite.		
		Olympus Granite-gneiss	Variable texture depending on contacts; local schistosity	Late Cambrian	500
Ross Super-Group	Skelton Group	Asgard Formation	interbedded, metamorphosed sediments (metasediments): marble, schist, gneiss, quartzite, hornfels	Cambrian to Precambrian	

in Royal Society Range. The plutonics of the Granite Harbour Intrusive Complex are exposed in situ up to 70 km inland and up to 2000 m in the oasis. Beacon sediments and Ferrar Dolerite outcrop most extensively in the west and at higher elevations. The Beacon Supergroup is exposed as far east as Mt. Theseus. Dolerite outcrops further to the east, at Mt. Doorly and in Royal Society Range.

Volcanics, the youngest group, are extensive in the east of the region but become less common towards the west. Ross Island is a composite volcanic pile and contains none of the older rock types in place. Similarly Black and White Islands, Mts. Discovery and Morning are composed entirely of volcanics. Elsewhere, volcanics are common in the south of the Koettlitz dry valleys, and scattered in Taylor and Wright Valleys: in those valleys they have not been found in place further than 40 km inland (Taylor 1922; McCraw 1962; Haskell et al. 1965; Kyle 1976).

1.2.4 Late Cenozoic history and geomorphology:

Successive glaciations, volcanic activity and periglacial processes characterize the Late Cenozoic history of the McMurdo region. The dry valley area was excavated by glaciation, probably during the onset of cooling and glaciation in Antarctica which took place in Late Oligocene to Early Miocene times (20-25 Ma ago, Hayes et al. 1975). Initially at least the glaciation was wet-based (Mayewski 1975). Subsequently three systems of glaciers have affected McMurdo oasis: (1) outlet or valley glaciers flowing east from the East Antarctic Ice Sheet, (2) expansions of Ross Ice Shelf extending westward into the valleys and (3) alpine glaciers descending from small névés in the local ranges into the valleys.

Interactions of the East and West Antarctic Ice Sheets, tectonic uplift, sea level changes and alpine glaciers (Calkin and Bull 1970; Webb and Wrenn 1976) have left a unique record of multiple glaciations in the form of glacial drift and moraine (Péwé 1960; Denton et al. 1971; Everett 1971; Nichols 1971; Stuiver et al. 1980). The age of surface drift which covers much of the flatter parts of the oasis generally increases with elevation; very old surfaces are found towards the west. Taylor Glacier has experienced at least four cycles of advance and retreat and is currently in an advanced stage. Sediments that were deposited mainly in glacio-marine, glacio-fluvial and littoral environments reach thicknesses of greater than 320 m east of Lake Fryxell in Taylor Valley (McKelvey 1975, 1979; Powell 1979). This part of Taylor Valley was a fiord during much of the Late Cenozoic whereas sea water was present in Wright Valley only in Pliocene times (3-4 Ma BP, Webb 1972; Vucetich and Topping 1972; Webb and Wrenn 1976). Terrestrial glaciers and proglacial water bod(ies) deposited the sediments cored by Dry Valley Drilling Project (DVDP) hole 12 at Lake Hoare (Powell 1979). Sediments are thin or non-existent on the valley sides in the oasis.

Some surface rocks and soil in the McMurdo region are older than four million years. Volcanic scoria cones have been erupted since the valleys of McMurdo oasis were excavated. Oldest potassium-argon (K-Ar) dates for such volcanic landforms in the oasis are 4.2 ± 0.2 Ma in Wright Valley (Fleck et al. 1972) and 4.6 ± 0.1 Ma in Taylor Valley (Armstrong 1978). Thus the main excavation of the dry valleys took place more than 4.6 Ma ago. Paleomagnetic and marine fossil records from DVDP holes 8-11 and McMurdo Sound Sediment and Tectonic Studies (MSSTS) hole are consistent with this timing (Park and Barrett 1975; Webb and Wrenn 1976; Brady 1979a; Pyne and Waghorn 1980). Oldest surface volcanics around McMurdo Sound are 15.4 ± 0.5 Ma (base of Mt. Morning), 10.9? ± 0.4 Ma (Black Island), 5.3 ± 0.1 Ma (summit of Mt. Discovery) and 4.5 ± 0.6 Ma (Mt. Bird, Ross Island) respectively (Armstrong 1978).

Soils have developed on the surface in the region. They are not 'normal' soils since they contain almost no organic material. Terrestrial plant and animal life is very restricted in the region; it consists of a sparse distribution of lichens, algae, mosses, fungi, Collembola, mites and microfauna and flora (Boyd et al. 1966; Rudolph 1966; Janetschek 1970), as well as scattered mummified seal and penguin carcasses. Claridge (1965, p.190) considered that the upper part of the regolith (the layer of loose rock material that overlies bedrock) above the permafrost could be described as "true soils in which the influence of living organisms becomes very small". The main soil forming processes are physical weathering by glacial action, freeze-thaw processes and wind abrasion and deposition; however salinization, chemical weathering, leaching, mass wasting and pedogenic clay formation, mainly by hydration of parent micas can also be important (e.g. Ugolini and Bull 1965; Nichols 1966; Tedrow and Ugolini 1966; Claridge 1965; Campbell and Claridge 1967, 1969, 1975; McCraw 1967a; Claridge and Campbell 1968a, 1977; Everett 1971). The oldest soils in the area are much older than 3.5 Ma (Campbell and Claridge 1975) and pedogenic soil mica has been dated at 4.1 ± 0.2 Ma (Jackson et al. 1977).

The asymmetric east-west trending valleys of McMurdo oasis suggest that periglacial processes have long been operative in the area. The north-facing sides of Taylor and Wright Valleys are much lower angled than the steep south-facing sides, whereas north-south oriented valleys such as Beacon Valley and hanging valleys in Asgard Range are symmetrical. Valley orientation and periglacial climates are important factors leading to valley asymmetry (Tricart 1970). Increased freeze-thaw action and cryoturbation on north-facing slopes cause them to become more gentle than south-facing slopes.

There are several landforms and features involving water in the region, despite its aridity. Nichols (1966) has detailed a number of such features, one of the most important being the lakes of McMurdo oasis. The two most important types of lakes are (1) ice-dammed (proglacial) lakes such as Lakes Bonney and Fryxell, and (2) glacial rock basin lakes such as Lakes Vanda and Vida. These lakes are ice-covered for most of the year but a moat of variable width usually develops around the shores in the summer months due to melting and stream inflow. Most of the lakes in the oasis are located in internal drainage basins, a consequence of the frigid, arid climate. The deeper waters of most lakes are saline, density stratified and solar heated up to about +25°C (e.g. Angino et al. 1962, 1964; Wilson and Wellman 1962; Shirtcliffe 1964; Torii et al. 1975). Algae are common, and abundant in places, in their fresh shallow waters (Rudolph 1966) and also in ephemeral melt streams. In the past the levels of most lakes have been both higher and lower than at present (Wilson 1964, 1967; Shirtcliffe 1964; Hendy et al. 1977) and large proglacial lakes have existed in Taylor Valley, dammed by expanded Ross Ice Shelves (Denton et al. 1971; Powell 1979).

1.2.5 A time scale for salt accumulation - a working basis:

A time scale from the present up to at least four million years, but generally less than 20-25 Ma, should be considered when discussing salts in the region. Sea spray is presently adding salts to coastal areas at least (Appendix 3, section 5.5) and measureable concentrations of salts are present in antarctic snowfall (e.g. Boutron et al. 1972; Field 1975); this fallen snow mostly sublimes away leaving minute quantities of salt. Thus salts could have been accumulating on or in surface rocks and soils over the last four million years at least, since leaching is very slow or non-existent in arid, frigid conditions. This is consistent with a general tendency for the salt content of comparable soils to increase with age (e.g. Ugolini and Bull 1965; Campbell and Claridge 1968, 1975; Behling 1972). Significant amounts of soluble salts from warmer, preglacial times are not likely to have survived the wet-based glaciation which commenced 20-25 Ma ago. Therefore the salts of the McMurdo region are mostly younger than this.

CHAPTER 2 SOIL TEMPERATURE AND MOISTURE

2.1 Introduction

2.1.1 Preamble and outline:

Salt distribution is intimately connected with soil temperature and moisture. Some salt phases form in certain temperature ranges only; two double salts, bloedite and darapskite, both widespread in the region (Chapters 3, 5), can crystallize at equilibrium only above a minimum temperature of about +5°C (Cornec et al. 1930; Ericksen and Mrose 1970). Relative humidity of soils affects the distribution of some hydrate phases. In general soil moisture content, availability and movement cause and modify the migration and accumulation of salts.

This chapter discusses specific aspects of soil temperature and moisture. Surface and subsurface temperatures and temperature gradients are discussed to determine maximum and mean surface temperatures, the effect of aspect on temperature, and the maximum depth at which +5°C temperatures could be expected. Soil moisture is then examined. Sources, amounts and availability of this moisture are discussed. Differences between north- and south-facing slopes are considered in detail. The form and movement of soil moisture are examined. All of these climate-related elements of the soil system may have changed substantially at times in the past few million years. Therefore the chapter ends with a brief discussion of past soil temperatures and moisture.

The soil system as a whole is highly complex. Detailed examination of it is outside the scope of this thesis, and semi-quantitative and qualitative approaches are considered here. The geothermally heated soils of Erebus Volcano are not considered.

2.1.2 Classification and general structure of soils in the McMurdo region:

The frigic soils of Antarctica have been classified in a variety of ways, based mainly on work in the McMurdo region summarized by Campbell and Claridge (1969). The most widespread or zonal soils are divided into three on the basis of available moisture, viz. ultraxerous, xerous and subxerous as in Table 2.1 (Campbell-Claridge classification).

The general thermal structure and related terminology for antarctic soils must be defined before discussion can proceed. Antarctic soils

Table 2.1 Classification of zonal soils in Antarctica on the basis of available moisture (mainly after Campbell and Claridge 1969).

Available moisture status	Location of class	Present-day moisture supply	Depth to ice-cemented table
ultraxerous	high elevations, or adjacent to Ice Sheet	negligible or very low and very intermittent	absent or deep (usually > 1 m)
xerous	widespread	mainly from ablation of summer snowfalls but a little from ice-cemented active layer	intermediate, generally between 0.4 and 0.8 m
subxerous	coastal regions and near permanent snow or ice accumulations	melting of snow and ice accumulations, summer snowfalls and ice-cemented active layer	shallow, generally less than 0.3 m

have a level at which the temperature has not risen above 0°C for at least several years. This is the top of the permafrost as defined by Black (1954) and others. The permafrost may or may not be consolidated by ice, depending on the amount of moisture available and in some cases the soil salinity. Above the permafrost level lies the active layer in which the temperature rises above 0°C in the sunlight period. The active layer is capped by a deflation pavement or lag gravel, which covers the soil proper. The base of the active layer will coincide with the top of the permafrost sometime in summer or autumn if the annual thaw is strong enough.

If sufficient moisture is present,the permafrost and that part part of the active layer below 0°C are usually partly or completely cemented with ice. Throughout the year there is a frozen table, below which the soil particles are cemented with ice. It is usually extremely difficult to dig below this. The frozen table sinks during the sunlight seasons and may coincide with the permafrost table at maximum thaw. The permafrost material may be almost pure ice as is the case with ice-cored moraine. In xerous soils the permafrost may be cemented with ice at some considerable depth below the base of the active layer; ice may be absent in ultraxerous soils. During field examination it is often difficult to discern whether the frozen table is in fact the permafrost table although indirect evidence such as depth may sometimes be used to determine this. In most cases in this thesis the problem is avoided by reference to an undifferentiated ice-cemented table.

2.2 Soil Temperature

2.2.1 Surface temperatures:

(i) maximum and mean temperatures

Surface temperatures are dependent on the heat exchange between the soil and the atmosphere. This exchange depends on a number of variables of the soil, climate and soil-air interface including: incoming and outgoing radiation; surface albedo; soil emissivity, specific heat, thermal conductivity, thermal diffusivity and moisture content; slope angle and aspect; wind and turbulent exchange coefficient; and air density, temperature and humidity (Black 1954; Colacino and Stocchino 1975a). Of these, air temperature, insolation and albedo appear to be most important (Davis and Nichols 1968) in affecting soil temperatures in coastal areas of the region, although soil moisture probably has a strong influence in some soils during the thaw period. The ice-free surfaces of Antarctica generally possess a relatively high specific heat and thermal conductivity, and low albedo (10 to 30%) (Rusin 1964; Solopov 1967; Riordin 1973) which may result in considerable surface warming during the sunlight months. It is difficult to model surface temperature because of the large number of variables. However, measurement of maximum surface temperatures requires a long stay at a location and large errors may arise due to practical difficulties. In this study estimates and measurements are combined to gain a semi-quantitative understanding of surface temperatures, in particular maximum and mean summer surface temperatures.

Reliable estimates of mean annual surface temperatures (MAST) of ice-free surfaces can be obtained from estimates of mean annual air temperatures (MAAT). At a particular ice-free location the former is generally close to the latter (Solopov 1967). At Vanda Station in 1970, the mean temperature at 0.08 m depth was -18°C (Thompson et al. 1971b) close to the mean screen temperature of -18.2°C (calculated from NZ Met.S records). MAATs at any location in the region can be obtained by extrapolation from known MAATs at Vanda Station and Scott Base (-20°C) using the topographic lapse rate of 4.0 ± 0.5°C per 1000 m (Appendix 3, Tables 4, 8, 9).

Estimates of maximum surface temperatures (θ_s(max)) at various locations may be obtained from known relationships of MAATs with measured maximum surface temperatures. Some such measurements and corresponding MAATs, reduced from various literature sources are given in Table 2.2. The surfaces at the locations noted are composed of ice-free glacial drift and moraine or possibly a rock outcrop in the Horlick Mountain location. All locations have data for one or part of one summer only. Maximum surface temperatures from spot measurements made at several locations in the McMurdo region are given in Table 2.3. The differences between θ_s(max) and MAATs in this table are generally smaller than those in Table 2.2 which used measurements made over longer time periods. Those in Table 2.3 were made during periods of a few days only which did not usually include the warmest days of the summer.

Surface temperatures may be tens of degrees celsius warmer than mean annual air temperatures. Tables 2.2 and 2.3 suggest that maximum surface temperatures in ice-free locations near the coast are probably 40 to 50 degrees celsius warmer that MAATs. At higher elevations insolation is greater, and more extreme surface temperatures are usually experienced (Geiger 1965); maximum surface temperatures may be as much as 70 degrees warmer than MAATs (Table 2.2). Maximum surface temperatures may be as much as 40 degrees warmer than ambient air temperatures. Mean surface temperatures during the warmest months are probably about 15 to 35 degrees warmer than MAATs, or about 5 to 15 degrees warmer than mean air temperatures.

(ii) aspect

Slope aspect is not a fundamental variable affecting surface temperatures over a 24-hour sunlight period at a particular location in the region. Over 50 measurements of surface temperature were made at different times of the day during November and December 1974, on a variety of soils in McMurdo oasis. No significant correlation was found between aspect and surface temperature.

Time spent facing the sun is more directly important than aspect. Maximum temperatures are attained when the locality is facing the sun, because this is the heating period. Table 2.4 lists surface temperature

Table 2.2 Comparison of surface and air temperatures (°C) in ice-free areas, from literature data (ng. not given; MAAT, mean annual air temperature; θ_s(max), maximum surface temperature during period of measurement; $\bar{\theta}_s$, mean surface temperature; $\bar{\theta}_a$, mean air temperature at two metres, during period; θ_a, air temperature at time of maximum surface temperature).

Location	Max. surface temp., θ_s(max)	Mean surface temp., $\bar{\theta}_s$	Mean air temp., $\bar{\theta}_a$	Air temp. at time of max. surface temp., θ_a	Source of data	MAAT*	θ_s(max) minus MAAT	θ_s(max) minus $\bar{\theta}_a$	θ_s(max) minus θ_a	$\bar{\theta}_s$ minus MAAT	$\bar{\theta}_s$ minus $\bar{\theta}_a$
Bunger oasis	+32.9	+8	+2.2	ng	Rusin (1964); Solopov (1967)	- 8.0	41	31	-	16	6
Cape Hallett	+32.2	c.+7.5	c.-1.5	c.-1	Rudolph (1966)	-15.7	48	34	33	23	9
Marble Point	+20.6	c.+7	c.-3	c.+1	Nichols and Ball (1964)	-18	39	24	20	25	10
Taylor Dry Valley	ng	⩽15†	+0.2	c.-4	Colacino and Stocchino (1975a. b)	-18 to -20	-	-	-	⩽35	⩽15
Eastern Horlicks Mountains	+27.8	ng	ng	⩽-12	Anon. (1962)	-40	68	-	⩽40	-	-

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*MAATS given by Weyant (1967), Rusin (1964) or Appendix 3, section 3.2

†Maximum mean surface temperature in Valley determined by overflight with infrared radiometer

measurements made over 4 days using maximum and minimum thermometers. Three sites were examined on a breached volcanic cone in the saddle between Mts. Discovery and Morning ('Depot Cone', 1000 m asl). The three sites were: A, a small terrace composed of coarse sand on a north-facing slope of 13 degrees; B, a similar, flat site; and C, a similar site on a south-facing slope of 10 degrees. The surface colour at all sites was similar (5R 4/2 - 10R 5/4). The north-facing site A, in the sun for the least time, had the lowest maximum surface temperature, whereas the site in the sun for the longest time (B) had the highest maximum.

Table 2.3 Comparison of measured surface and air temperatures (°C) in selected ice-free areas, McMurdo oasis.

Location	Maximum surface temp. measured θ_s(max)	Air temp. θ_a	Estimated MAAT*	θ_s(max)-MAAT	$\theta_s(\text{max})-\theta_a$
Mt. Kempe	+ 5	-18	-31 ± 3	36 ± 3	23
Table Mountain	+21.1	- 9.5	-26 ± 3	47 ± 3	30.6
Knobhead	+18.0	- 7.0	-25 ± 3	43 ± 3	25.0
Taylor Valley	+21.8	+ 5.5	-20 ± 2	42 ± 2	16.3
Black Island	+15.7	+ 3.5	-20 ± 1	36 ± 1	12.2
'Depot Cone'†	+14.6	c.- 9	-24 ± 2	39 ± 2	c.25

*extrapolated from MAATs at Vanda Station or Scott Base using the topographic lapse rate of 4.0 ± 0.5°C per 1000 m (Appendix 3, Tables 4, 8, 9)

†Mt. Discovery area (Appendix 1, Fig.4C)

Table 2.4 Soil surface temperatures (°C) on Depot Cone. Thermometer bulbs buried 0.5 cm beneath the surface (4-7/12/76).

Site	Aspect	Hours in sun (approx.)	Maximum surface temperature	Minimum surface temperature
A	N	0300 - 2100	+ 9.8	-10.7
B	flat	all day	+14.6	- 9.9
C	S	0700 - 0600	+12.1	- 7.7

Slope aspect is important only if time of day is specified. Three sets of spot temperatures were measured around midday on 10/12/76 at Top Cone, 700 m below the summit of Mt. Discovery. The temperatures were warmest in north-facing slopes (average +6.5°C), followed by those on level ground (average +3.5°C); south-facing slopes were coolest (+0.5°C). Therefore, variables other than aspect dictate surface temperatures over the 24-hour period.

2.2.2 Subsurface temperatures:

The subsurface temperature regime is complex and like surface temperature depends on all the variables listed earlier. Moisture, thermal, density and textural variations between soils mean that temperature modelling is of doubtful merit as has been shown in the literature (Robertson and MacDonald 1962; Weedfall 1963). Here, temperature gradients in the active layer are obtained in order to estimate maximum subsurface temperatures by extrapolation from maximum surface temperatures.

The active layer ranges from about 0.15 to more than a metre thick in the McMurdo region (Black and Berg 1963). At the base of the layer the temperature is 0°C by definition. Although it is difficult to predict the thickness of the layer in a particular location, some generalizations can be made concerning this. Active layers become thinner as the mean annual surface temperature decreases, because of the reduced number of freeze-thaw cycles (Tricart 1970). Therefore, the active layer is probably thickest in some coastal soils and is likely to thin inland and with increasing elevation in McMurdo oasis. Locally, variations in soil properties and topography will cause considerable variations in the thickness. Dry, coarse-grained and rocky soils will have a thicker active layer than finer, clay-rich soils, with a higher moisture content (Ives 1974; Rieger 1974). North-facing slopes tend to have a thicker active layer than south-facing slopes (Legget _et al._ 1961; Rieger 1974), because of greater insolation and extended periods of freeze-thaw action. Ridges tend to have thicker active layers than depressions (McCraw 1967a).

Detailed examples of subsurface temperatures over complete years have been given by Robertson and MacDonald (1962) at Scott Base, Berg and Black (1966) on Hut Point Peninsula and Thompson _et al._

(1971b) at Vanda Station (Figure 2.1). These show the general pattern of subsurface temperatures and temperature gradients. At Vanda (MAAT, -19.8 ± 1.9°C) soil temperatures are positive in the top 0.2 m during December and January; the maximum temperature recorded at 0.08 m depth was +11.6°C (9/1/70); the mean warm peaks at 0.08 m and 0.2 m depths were about +4.5° and +2.4° respectively in January 1970; the active layer is about 0.4 m thick; diurnal fluctuations are barely discernable at 0.46 m (Thompson <u>et al.</u> 1971b). The mean temperature at 0.2 m is close to the mean air temperature for January 1970 (+2.4°C, Thompson <u>et al.</u> 1971a). At Vanda temperature gradients are negative upwards from April to September inclusive and negative downwards on the average from November to February inclusive. Temperature gradients during March and October exhibit differences from year to year. The seasonal dependence of the signs of temperature gradients in other places on the oasis is probably similar to those at Vanda.

The magnitude of the temperature gradient in a particular soil is also dependent on the many variables mentioned earlier. At Vanda in 1969 and 1970 the mean temperatures at 0.08 m depth ranged from about +5 to -39°C, while those at the base of the active layer ranged from 0°C at maximum thaw to colder than -35°C in late winter. Generally gradients from 0.08 m to 0.46 m varied from about 1 to 20°C per metre (from Thompson <u>et al.</u> 1971b). Black and Berg (1963) found that gradients in the active layer of many soils in the region are normally of the order of 10 to 50°C m^{-1} during the course of a year. Gradients may be as high as 100°C m^{-1} or more at shallow depths for short periods. Obviously the gradients in the top few centimetres of the soil will show diurnal reversals and will exhibit very many reversals during the year.

Some subsurface measurements were made during this study. At Knobhead temperatures of +9°C were measured (27/11/74) at 0.005 m depth, and of about 0°C at 0.04 m depth in two dry soils. In this shallow surface layer the temperature gradient was about 250°C m^{-1}. Below 0.04 m the gradients were about 100°C m^{-1} down to the ice-cemented table at a depth of about 0.1 m. At other dry soil sites in the vicinity, gradients of about 20°C m^{-1} were present down to about 0.5 m depth. Gradients of between about 30°C m^{-1} and 130°C m^{-1} were present (9/1/75) in moist sandy soil within the capillary zone beside a stream from Sollas Glacier in Taylor Valley (Fig.2.2). Therefore quite high

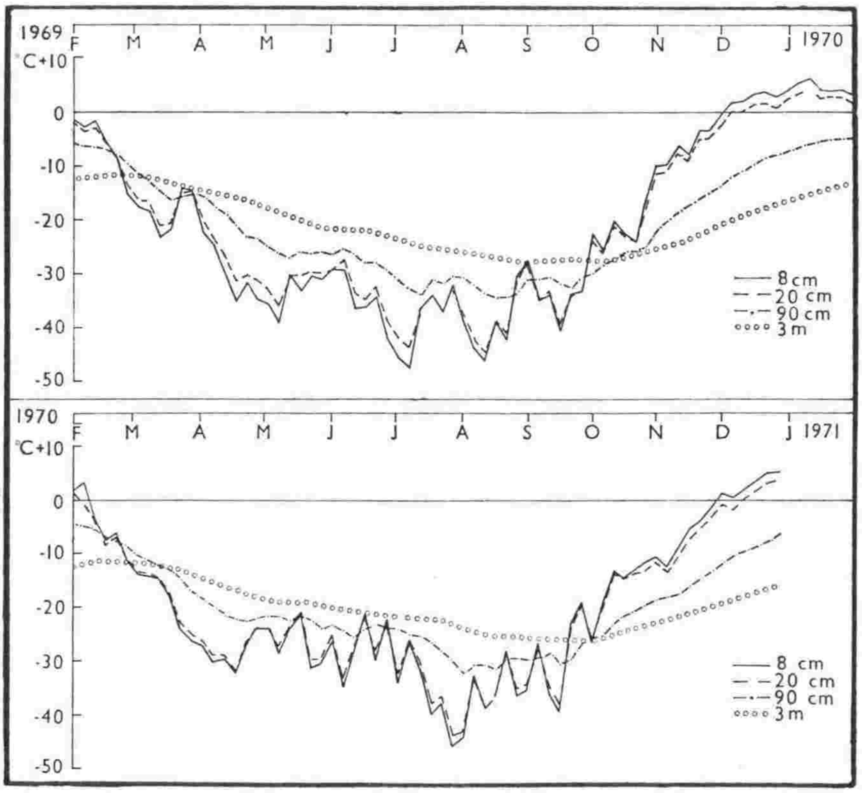

Figure 2.1 Five-day means of soil temperatures at Vanda Station during 1969 and 1970 (after Thompson et al. 1971b).

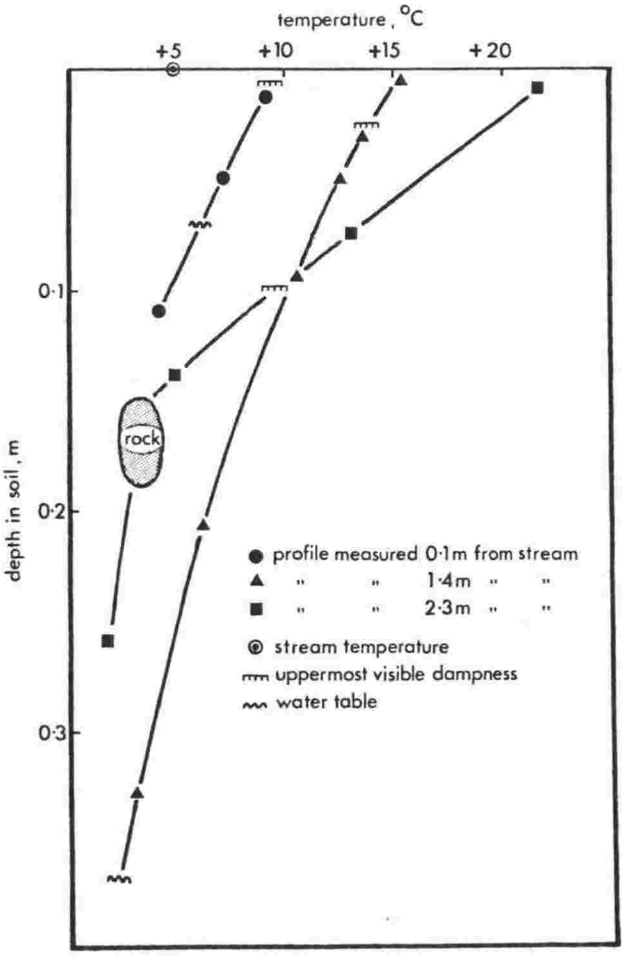

Figure 2.2 Temperature profiles in the capillary zone in aeolian sands beside a melt water stream from Sollas Glacier (measured 9/1/75).

gradients may exist in damp soil despite high heat capacities of such soils (Geiger 1965; Clark 1966) and probable heat loss due to evaporation of moisture at the surface.

2.2.3 Summary of soil temperatures:

The preceding discussions may be summarized to yield estimates of maximum surface and subsurface temperatures at selected localities in the oasis. At Vanda, the maximum summer surface temperature is probably close to +25 ± 5°C (MAAT plus 40 to 50°C). A maximum soil temperature of about +12°C at 0.08 m (January 1970) yields estimates of about 160°C m^{-1} in the active layer below 0.08 m. However, maximum air and probably soil temperatures at Vanda during January 1970 were cooler than some other years (e.g. 1974, see Appendix 3, Table 2). Probably +15 ± 5°C at about 0.1 m is a better estimate of the maximum soil temperature at this depth. This is reasonably consistent with Townsend's (1973) observation that the maximum daily temperature at 0.15 m depth in most soils is similar to the maximum daily air temperature: the extreme maximum daily temperature at Vanda is +15.0°C (Appendix 3, Table 2). This leads to an estimate of 100°C m^{-1} as the corresponding temperature gradient in the upper part of the active layer at this location. Similarly, the active layer probably reaches a maximum thickness of about 0.5 m at Vanda and a corresponding net gradient of about 40°C m^{-1} possibly exists at times in the lower part of the active layer. Under these conditions the soil attains temperatures of +5°C or more down to a depth of about 0.4 m.

Extrapolation to other localities is fraught with difficulties, and the following estimates are subject to errors higher than 100%, in consequence. Due to the increased elevation and lower MAAT and MAST, the active layer at Knobhead is probably significantly thinner than at Vanda. Gradients of 200°C m^{-1} above 0.1 m and 50°C m^{-1} below, are probably reasonable for the active layer in the former more extreme locality. From the MAAT of -25°C determined for Knobhead (Appendix 3, Table 9), the maximum surface temperature there is estimated to be up to about +30°C (MAAT plus 50 to 60°C) and the maximum soil temperature at 0.1 m depth is possibly around +10°C. The soil possibly attains temperatures of +5°C or more down to depths of about 0.2 m. Temperatures at these and other localities are summarized in Table 2.5.

Table 2.5 Maximum soil temperatures and mean surface temperature (°C) estimated for selected localities in McMurdo oasis.

Locality	MAAT	Max. surface temperature	Max. temp. at 0.1 m	Depth where +5°C is max. temp. (m)	Mean surface temp. in summer
Vanda	-20 ± 2	+25 ± 5	+15 ± 5	0.4 ± 0.1	+5 ± 12
west end of Labyrinth	-23 ± 2	+27 ± 10	+12 ± 10	0.3 ± 0.1	+2 ± 12
valley between Knobhead and Mt. Handsley	-25 ± 3	+30 ± 8	+10 ± 8	0.2 ± 0.2	0 ± 13
Kennar Valley	-26 ± 3	+31 ± 8	+11 ± 8	0.2 ± 0.2	-1 ± 13

2.3 Soil Moisture

2.3.1 Moisture content:

(i) sources of moisture

Most soils in Antarctica are dry by most standards for most of the year. Subzero temperatures preclude the presence of abundant water. Extreme maximum air temperatures at Vanda Station are less than 0°C for six months of the year, and mean monthly temperatures for 10 months (Appendix 3, Table 2). However soils may accumulate moisture during November-February when melting occurs; some soils become saturated during this time.

Soil moisture is from three main sources. The largest quantity of melt water is from permanent or semi-permanent snow and ice bodies but this is generally localized in the form of streams and subsurface (suprapermafrost) flows. Thawing of ice in the active layer is a moisture source in subxerous and xerous soils. Ablation of snowfalls is probably the most widespread source. Most fallen snow is dissipated by sublimation but active melting occurs on sun-warmed ground (Appendix 3, section 5.2). Other local moisture sources are the water of lakes and ponds, sea spray and other forms of precipitation near the coast, wind-blown snow and deep ground water. In very dry soils atmospheric water vapour is probably a direct source of soil moisture.

The amount of melt water and moisture available decreases as the MAAT decreases inland and with elevation in McMurdo oasis (Appendix 3, Table 9). This is readily apparent as Taylor Glacier is traversed towards the west. Both stream-cut channels on and beside the glacier, and proglacial lakes, decrease in number and size up glacier. Average ablation (sublimation plus melting) of ice on the glacier surface decreases from 0.43 m a^{-1} at the snout (200 m asl) to 0.16 m a^{-1} up glacier at 1100 m asl opposite Pandora Spire (Robinson 1979). Average ablation is about 0.05 m a^{-1} in the blue ice area at 2000 m elevation west of Allan Hills (Annexstad 1980). The amounts of precipitation (Appendix 3, section 5) and ice in the active layer also decrease towards the west in the oasis (Cameron and Conrow 1969). The snowline ascending towards the west (Appendix 3, 5.2) further indicates a decreasing moisture supply.

Orientation of snow and ice slopes also affects melt water supply (Davis and Nichols 1968). In general, north-facing slopes receive more insolation and hence more melting tends to occur on them. This effect is further examined and discussed in the following subsection. The asymmetry of large "ablation valleys" in Taylor Glacier near the snout shows that ablation is more intense on north-facing slopes than on south-facing slopes. According to Wise and Gressit (1965) favourable biotic environments occur mainly on north-facing slopes. Here a source of moisture is more directly important than insolation.

(ii) amount of soil moisture

Several workers have analysed the in situ moisture content of soils in the McMurdo region. The main method used has been gravimetric, whereby samples are oven dried at 105°C. Two fairly comprehensive but incomplete studies have been made by Berg and Black (1966) and Cameron and Conrow (1969). Additional data have been reported by Black and Berg (1963), Ugolini and Bull (1965), Boyd et al. (1966), Ugolini and Grier (1969) and others. These studies show that the active layer contained zero to about 10% (average 1-4%) moisture (by weight) in McMurdo oasis soils as far west as Beacon Valley. Coastal sites in the region contained from 1% to more than 30% moisture in the active layer. Soils saturated with moisture contain 20 to 35% or more moisture (Townsend 1973). Therefore, most soils in the oasis are well below saturation for most or all of the year.

In the oasis the amount of in situ moisture generally decreases inland away from the coast and increases with depth towards the ice-cemented table. At any site the active layer usually contains much less moisture than the ice-cemented layer which may contain up to 100% moisture by weight in ice-cored moraine (Black and Berg 1963; Ugolini and Bull 1965; Cameron and Conrow 1969).

(iii) relative humidity

In situ relative humidity (RH) is a valuable measure of soil moisture for the present study because it gives an indication of the relationship between soil moisture and soluble salt particles in the soil. Both surface and subsurface RH are of interest here.

The relative humidity at the soil-air interface is influenced by atmospheric and subsurface RHs, turbulent exchange processes between the ground and the air, and by soil properties and snow cover. Solopov (1967) showed that in antarctic oases during summer, the turbulent moisture exchange is mainly upwards from the ground to the atmosphere. This suggests that in comparable snow-free sites the surface RH is largely controlled by soil RH during summer, especially in moister soils. During winter however the opposite occurs and surface RH is largely controlled by atmospheric RH. If a strong wind is blowing the atmospheric influence will be relatively more important during any season, especially in dry soils. Surface RH will be higher in winter than in summer because atmospheric RH is higher in winter (Appendix 3, section 6.1). Diurnal changes of more than 50% may occur during summer (Yoshida and Moriwaki 1972) and snowfalls may create high surface RH for short periods.

Some in situ RH measurements have been made during summer in the present study. Quantitative data were obtained using a Vaisala humidity probe (Appendix 3, section 6.3) covered with a permeable membrane. RHs of 21 ± 1 to 88 ± 1% were measured (7-10/1/75) at a depth of 0.06 m above and within the capillary zone adjacent to the moat of Lake Bonney. Subsurface (0.04 m depth) RHs of 43 ± 1 (cf. atmospheric RH 43 ± 1%) to 100% were measured (12-13/1/75) above and within the capillary zone adjacent to a ponded stream on Black Island. Relative humidities increase towards the ice-cemented table as determined by burial of bimetallic strip hygrometers for hour-long periods.

More complete relative humidity data during summer periods have been reported by Cameron and Conrow (1969). Surface RHs are close to atmospheric RHs in dry soils but as much as 70% (RH units) greater than air in slightly moister soils. Soils at higher elevations tend to have higher RH. Strong positive RH gradients may exist from the surface to the ice-cemented table in dry soils during summer. Gradients are small in moister soils where the RH is as high as 100%. Those active layers with low in situ moisture contents (0.3% by weight) have lower RHs (30 to 60%) while those with higher moisture contents (4, 7% by weight) have higher RHs (80 to 100%). Differences in soil composition and porosity will probably affect these relationships.

Seasonal and diurnal variations are expected. Subsurface RH is probably higher in winter than in summer because temperatures are colder and atmospheric RH is higher (Appendix 3, 6.1). Cameron and Conrow's (1969) data indicated that RH variations of 5 to 10% (RH units) occurred at depths below about 0.1 m during week-long periods. Such variations are probably sufficient to explain diurnal moisture variations of ±1% by weight noted by Ugolini and Bull (1965) in the upper 0.15 m of some dry saline soils. These diurnal variations of up to 50 percent of in situ moisture are believed to be due to adsorption or absorption of atmospheric water vapour, mainly by hygroscopic salts.

2.3.2 Influence of aspect on soil moisture - a study of the depth to the ice-cemented table:

In localized areas some soils have a higher moisture content than others. The moister soils have more liquid moisture available for movement of soluble salts and weathering of soil minerals. In many areas this relative moisture is easily determined by determining the depth to the ice-cemented table. The relationship between moisture content and depth to ice-cemented table in frigic soils, is well known (Campbell and Claridge 1967, 1975; McCraw 1967a; Claridge and Campbell 1968a). The ice-cemented table is shallower in soils with higher moisture contents.

In this study the depth to the ice-cemented table was measured at a large number of sites primarily to determine the influence of aspect on soil moisture. A statistically complete qualitative assessment of the problem can be made more readily in this manner, than by gravimetric determination of soil moisture in a large number of samples. In order to reduce the number of variables, soils of similar age, exposure, texture and surface colour need to be considered wherever possible. Thus, a series of five small volcanic cones in the Mt. Discovery area were chosen (Appendix 1, Figure 4.C) labelled *Depot, Top, Castle,

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*unofficial field names are used here for these five cones

Stadium and Bottom Cones. The soils were examined over a nine-day period and hence seasonal variations were negligible. All sites at each cone are likely to be of similar age (≤5 Ma, 1.2.4) but some age disparity is expected from cone to cone. At each cone the depth to the ice-cemented table was measured as a function of aspect while exposure, texture and surface colour were kept constant or nearly constant. (However, over eighty measurements of surface lightness and depth in McMurdo oasis showed no relationship between these parameters.) Therefore, sites on slopes were examined but not those on ridges or in hollows. Sites adjacent to snow drifts, other snow and ice accumulations and active frost cracks were avoided. Owing to these and terrain constraints, a statistically complete set of measurements were not obtained at every site. The results are tabulated in Appendix 4, Tables A4.1-5. Table A4.6 lists similar data for Table Mountain, a locality where age, exposure, soil texture and colour could not be controlled as easily as at the volcanic sites. The data for the five cones are plotted on Figures 2.3a to e, 2.4 and 2.5. For clarity error bars are not plotted on the figures. These errors range from ±0.003 m to 0.010 m for the depth values (see tables in Appendix 4) and ±10° for the aspect values. Linear regression lines are fitted to all data (Appendix 2, subsection A2.2.2ii).

Strong to non-existent trends are present towards deeper ice-cemented tables for soils with more southerly aspects (Figure 2.3). The trend is best shown at Depot Cone at which the most precise and most voluminous data were collected, and which is furthest from any shading influence by the bulk of Mt. Discovery. Scatter of data for Depot Cone is probably due to unavoidable variations in textural and thermal properties of the soils. The strong trend evident here suggests that slopes with northerly aspects tend to have higher moisture content and hence a greater availability of liquid moisture. Presumably this is due to greater insolation which produces relatively more melting and less sublimation, of blown snow, snowfall and other sources of moisture.

The data for Top, Castle and Stadium Cones are not well correlated Fig.2.3b, c, d). These cones are shaded by the Mt. Discovery massif to the east during a large part of the day for much of the sunlight seasons. Such shading can be expected to reduce any differences in the supply of moisture to slopes of different aspects. This would

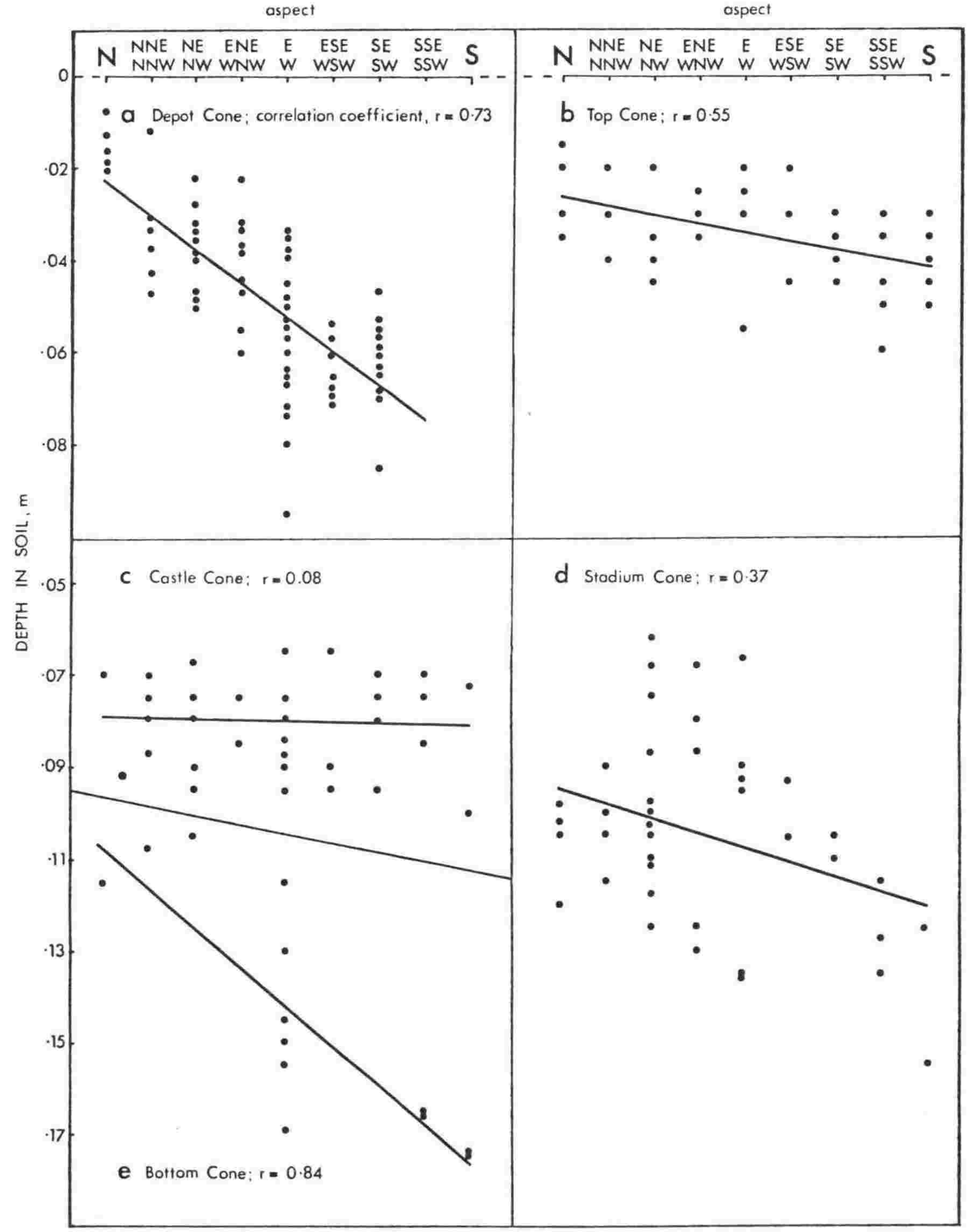


Figure 2.3 Depths to ice-cemented table versus site aspect from north through east and west to south, on five volcanic cones in the Mt. Discovery area. Geographic locations shown in Appendix 1, Fig.4.C. Linear regression lines and correlation coefficients are shown. Error bars have been omitted from data points for clarity and are given in Appendix 4, along with environmental details.

cause flattening of the regression lines, showing less correlation between the data. Castle Cone is situated closer to the bulk of Discovery than Stadium Cone, which is consistent with the greater degree of flattening of the regression line for Castle Cone.

The data can be refitted on an expanded aspect axis. Figure 2.4 has the aspect axis for Top Cone expanded to the full 360° of arc. Curves are fitted to each 180° set of data, that is from north through east to south, and from south through west to north. The data are fitted better than before, although close-fit trends are still not evident ($|r| < 0.7$, Appendix 2). Differential accumulation and subsequent occasional melting of wind blown snow may have affected the data for this cone.

Significant differences are evident between the average depths to the ice-cemented table among the five cones. Comparison of the regression lines for the cones (Fig.2.5) shows that there is a consistent trend towards a shallower ice-cemented table as elevation increases. The trend stands out above the background scatter of data. It is unlikely that the trend is due to consistently decreasing age with elevation although this cannot be entirely discounted; irregular age differences could explain part of the observed difference in depths. It is more likely that much of the trend was due to a higher degree of thaw in the generally warmer ambient air temperatures and longer 'thaw season' at the lower cones. At some sites at Bottom and Stadium Cones, soils were damp from near the surface to the ice-cemented table, at the time of investigation in mid-December. Active thaw was proceeding in these sites at this time. Furthermore, part of the trend is probably due to increased snowfall and fall-out of blown snow at higher elevations leading to a higher moisture content consistent with a shallower ice-cemented table. Considerable moisture is potentially available at such sites, whenever subsurface soil temperatures are warmer than the melting point of the subsurface ice. Evidently, however, melting occurs less commonly at high elevation because there are fewer freeze-thaw cycles there (Campbell and Claridge 1969). The active layer is thinner than nearer sea level.

The trends in relative moisture content and availability in the Mt. Discovery area can be summarized as follows: soils and slopes with northerly aspects have more moisture available than those with southerly aspects. Soils at high elevations may have a higher

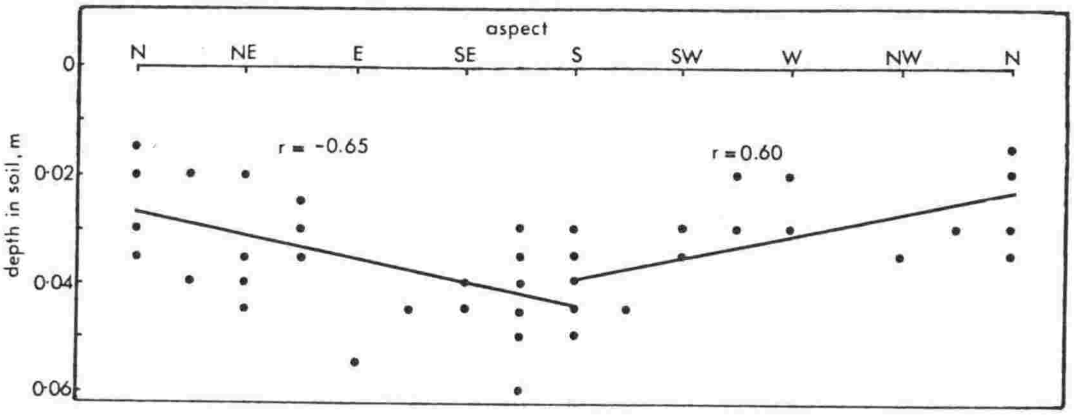


Figure 2.4 Depths to ice-cemented table versus site aspect over 360 degrees of arc at Top Cone. Regression lines fitted to sets of data between north through east to south and south through west to north.

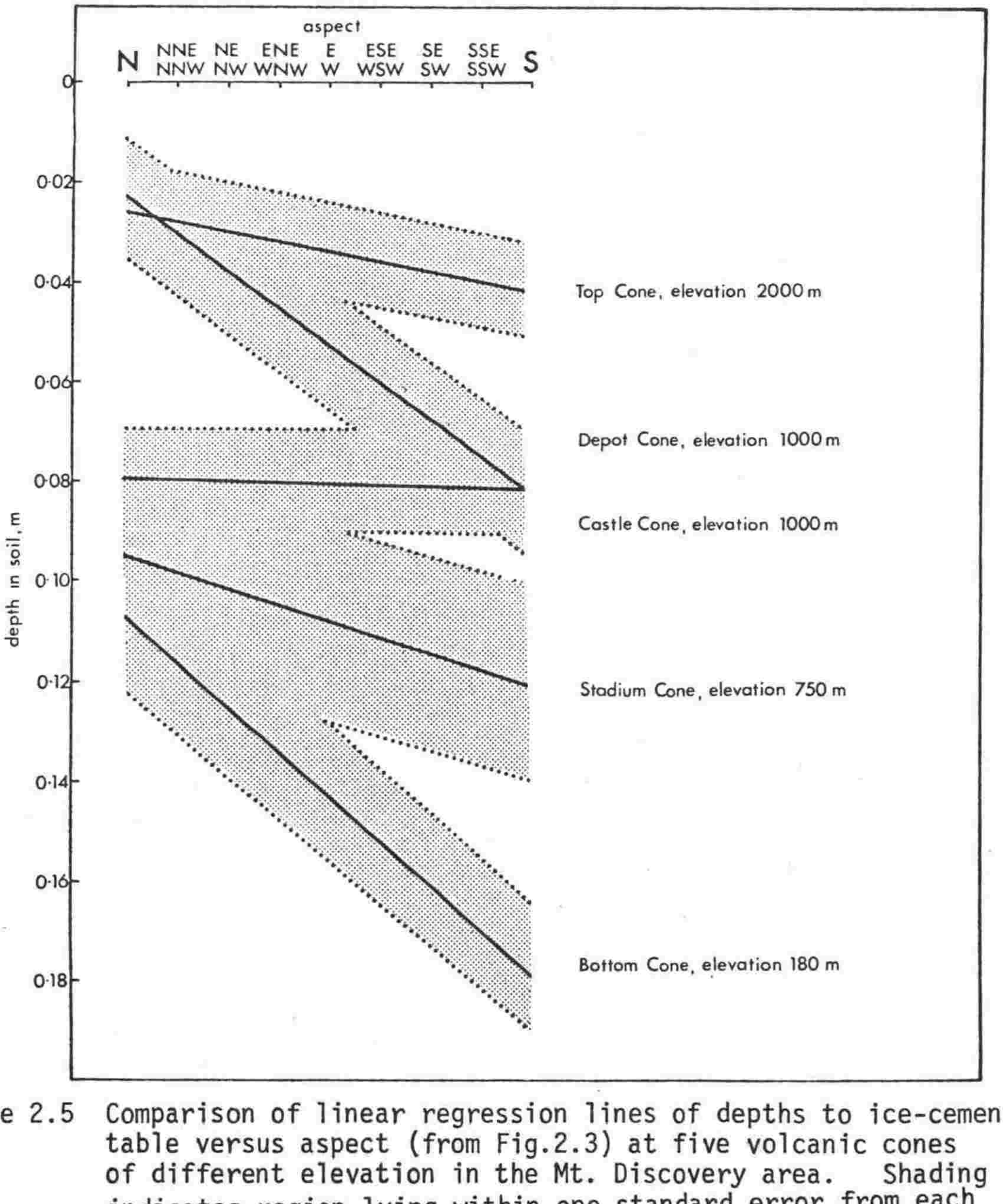


Figure 2.5 Comparison of linear regression lines of depths to ice-cemented table versus aspect (from Fig.2.3) at five volcanic cones of different elevation in the Mt. Discovery area. Shading indicates region lying within one standard error from each line.

moisture content but usually less of this moisture is in an available form. The frequency of occurrence of liquid moisture increases towards sea level as mean air and soil temperatures increase.

The trends evident in the Discovery area should hold in other areas in the McMurdo region. The data for Table Mountain (Appendix 4, Table A4.6) show the same relationship between aspect and depth to the ice-cemented table but the correlation is poor (r = 0.32), due to gross variation in soil properties. A similar trend has been noted at a few sites in Wright Valley by Ugolini and Bull (1965). Probably, however, such a trend will not usually be evident in the arid, high elevation, western parts of McMurdo oasis, where ice-cemented tables are often absent (Claridge and Campbell 1968a; Campbell and Claridge 1969).

2.3.3 Moisture movement:

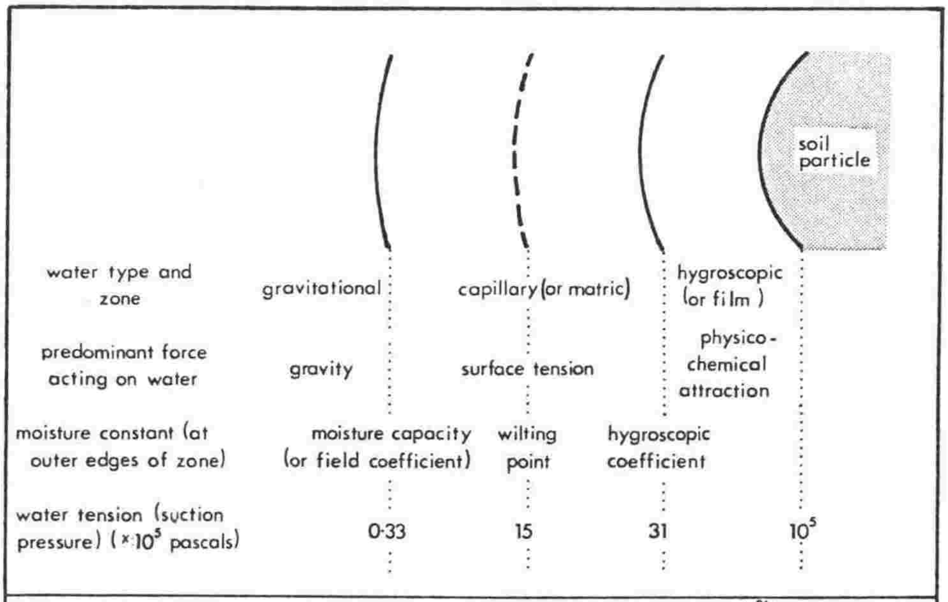
(i) types of soil moisture

There is an extensive literature on the form and movement of moisture in dry soils and in cold temperatures. In such conditions moisture behaviour is controlled by soil composition, texture, particle size, water content, soluble salts, clay content, hysteresis and osmotic effects, and temperature and pressure (e.g. Geiger 1965; Parlange 1973; Townsend 1973; Curtis and Trudgill1974; Scotter 1976). Slope angle, roughness of the ice-cemented table and distance from moisture sources are likely to be important during periods of active thaw. It is not the function of this thesis to fully examine the complex problem but merely to discuss simple soil moisture models and thus gain a basic understanding of moisture movement in antarctic soils. Such movement is basic to the problem of salt migration discussed in Chapters 3 and 4.

The mineral components of soil form a solid but flexible matrix within which pore spaces of different sizes exist. Moisture may be present in these pores in solid, liquid and vapour phases, the liquid phase being held in the soil by surface tension and by physico-chemical attraction to the soil particles. The overall force acting on the liquid and attracting it to the particles can be described in terms of a water tension, suction pressure or soil moisture potential. This force is related to the thickness of a liquid film that can be regarded to exist about the individual soil particles. The film exists at temperatures considerably less than 0°C because the surface energy of the soil particle is a minimum when water molecules are adsorbed on to it (Geiger 1965;

Cary and Mayland 1972; Ugolini 1976). In antarctic saline soils, salts effect a depression of freezing point that potentially allows liquid films to exist at temperatures considerably less than the mean annual soil temperature (Chapter 4).

The liquid film is arbitrarily divided into three main types and zones: gravitational, capillary and hygroscopic. These zones are delineated by moisture constants as in Figure 2.6 (Buckman and Brady 1966 in Curtis and Trudgill 1974). Soil moisture content dictates



regolith	approximate gravimetric water contents, (%)		
clean sand	10	–	2
sandy loam	15	5	3
silt loam	20	–	–
relatively salt free sandy soil, Victoria Valley (1)	20	1	–
salty loamy sand McKelvey Valley (2)	23	8	–

Figure 2.6 Soil water type, content and tension relationships, after Buckman and Brady (1966) in Curtis and Trudgill (1974); Townsend (1973). Footnotes for two soils from McMurdo oasis (after Cameron and Conrow 1969): (1) specific conductance (+25°C) of 1:5 extract was 0.9 mmhos cm^{-2}, *in situ* gravimetric moisture content was 0.3%; (2) specific conductance was 10.5 mmhos cm^{-2}, *in situ* gravimetric moisture content was 1.3%.

the predominant force acting on the liquid. When a soil is saturated (i.e. air is wholly displaced from all pores), the water is moved by gravity which exerts a pressure of 3.3×10^4 pascals (0.33 bars). Capillary action becomes important when gravity-induced free drainage has brought the soil to 'moisture capacity'. As the moisture content is further reduced, the capillary water retracts until a continuous air column is introduced (Townsend 1973). At this stage thin liquid film and water vapour movement become important. Further reduction of moisture causes thinning of the adsorbed film and an exponential increase in the water tension. In very dry conditions the moisture film can be considered as broken and vapour transport is the only means of moisture movement.

The relationship between moisture content and water tension is not straightforward (Curtis and Trudgill 1974). At moisture capacity the water content of salt-free sandy soils is about 10-15% by weight. This value increases with increasing fines (Figure 2.6). The gravimetric moisture content at the 'hygroscopic coefficient' is as low as about 2% for clean sand; soluble salt and clay particles have a large effect on this value because of their strong affinity for water (Figure 2.6).

(ii) transport of moisture in soils of the McMurdo region

Thin film transport of moisture and soil brines is believed to be the most widespread and effective process of moisture movement in soils of McMurdo oasis. At +25°C liquid phase transport in films is dominant in relatively dry sandy loams down to about 5% gravimetric moisture content; it has been detected in the laboratory at 2% moisture content (Scotter 1976). At around 1-4%, moisture transport is dominated by vapour transfer in most soils. Such transport has been detected in laboratory loamy sand whose moisture is more than 8%, and at even higher moisture contents for more clay rich soil (Scotter 1974a, 1976). In McMurdo soils both liquid and vapour phase transport will be operative, as is shown by measurements of soil moisture gravimetric water content (0-30%) and <u>in situ</u> relative humidity of soils (20-100%) (2.3.1). In general thin film movement is probably most important because at low temperatures little moisture is transported by vapour in the conditions of low ambient vapour pressure (Hoekstra 1966; Appendix 3, Figure 6). Thin film transport has been demonstrated in soils in Wright Lower Valley and on Ross Island by Ugolini and Grier (1969) and Ugolini and Anderson (1972). Vapour transfer has been demonstrated by Black and Berg (1963).

The mode and mass (flux) of moisture transport will vary in space and time. Liquid films are probably thickest during summer when most moisture is available. Free drainage and capillarity transport most moisture, and moisture flux will be quite high near sources of moisture in summer. Similarly these processes will be more extensive than normal during summers with more melting than normal (e.g. January 1974, Appendix 3, 2.2). Vapour transfer is likely to become more important in dry soils as their temperature rises in summer. Most transport of moisture and soil brines takes place probably during November to February.

The direction of moisture and dissolved salt movement is mostly influenced by soil moisture potential. Soil water distribution tends to approach a condition of zero potential gradient over a period of time (Townsend 1973). When less water than the moisture capacity is present, the direction of liquid flow is determined by water tension. Flow is from areas of low tension to areas of high tension. Thus, the liquid in thick films generally migrates towards particles carrying thinner films. The flow direction may be upwards, downwards or lateral, away from a source of moisture such as the ice-cemented table, a recent snowfall, melting snow or ice, a water body or the atmosphere. Ugolini and Anderson (1972) have shown that this movement is often upwards in spring and summer, at least in subxerous and xerous soils. In ultraxerous soils film movement will be downwards after snowfalls and during periods with high atmospheric relative humidity.

Temperature has a strong effect on vapour transfer. In a soil with zero gradient of relative humidity the sign of the vapour pressure gradient is the same as the sign of the temperature gradient; thus vapour moves from warm areas to cold areas. In McMurdo oasis vapour transfer probably occurs upwards in permafrosted soils during winter (Everett 1971; Field 1975) and into and out of dry soils during summer (Black and Berg 1963; Ugolini and Bull 1965).

Textural properties of soils significantly influence moisture movement in moister soils (moisture content greater than about 10% by weight, Scotter 1974b). Free drainage of a saturated soil is downwards and is fastest in coarse, well-sorted alluvial or proglacial deposits. Locally, however, this gravitational water may be forced to move laterally or not at all, when drainage is impeded by impermeable obstacles. These include the ice-cemented table, stones, boulders, bedrock or the soil itself if it is rich in fines or water swollen clay particles. In the capillary stage, upward movement from a saturated zone such as a water table may be as high as a metre or more (Townsend 1973; Cooke and Warren 1973). Any process that controls or modifies soil texture has a consequent effect on such moisture movement. Thus the original environment of deposition during sedimentation, and periglacial processes in McMurdo oasis will affect moisture movement in moist soils. Bockheim (1979a) has examined glacial drifts in Wright Lower Valley that have similar ages but are subject to different degrees of frost heaving and sorting. He showed that such periglacial processes may restrict and interrupt salt migration and hence restrict salt accumulation. On the other hand, frost action may promote salt accumulation. Frost heaved layers of fine sandy sediment have been noted (9/1/75) in Taylor Valley (0.5 km east of Lake Bonney), that have caused preferential capillary rise of soil brines and subsequent salt accumulation.

2.3.4 Moisture loss:

Moisture is lost from antarctic soils in a variety of ways. Observations suggest that evaporation is probably the main mechanism for most soils. Run-off and suprapermafrost flow will be important in local areas during the thaw. Freeze-up will immobilize soil moisture in shallow, moist soils; in deeper soils freeze-up will cause some moisture movement to the advancing freezing front (Makeev and Kerzhentsev 1974). Brine expulsion during freezing of soil solutions will allow some salt migration away from the freezing front. Most liquid moisture is lost probably during January and February.

In the oasis, the net transfer of soil moisture from the ice-cemented permafrost table and the soil, upwards to the atmosphere is indicated locally on comparable sites by an increased depth to the ice-cemented table from younger to older soils (Black and Berg 1963; Ugolini and Bull 1965; Claridge and Campbell 1968a; Campbell and Claridge 1975). This moisture transfer is aided by strong turbulent heat exchange processes at the surface of oases (Solopov 1967), and by low atmospheric relative humidities. During summer and early autumn evaporation from warm, moist or saturated soil surfaces into cooler, dry air, may be intense especially in windy conditions. At these times there is adequate energy stored near the soil surface for the evaporation process, and a strong vapour pressure gradient exists across the soil-air interface. Evaporation of water totalling several millimetres per day will occur in favourable circumstances (Rusin 1964; Everett 1971). Atmospheric conditions are probably the main rate determining factor in evaporation from a shallow drying soil (Fuchs and Tanner 1967). However, textural characteristics and hysteresis phenomena become significant in deeper, fine soils during diurnally fluctuating evaporation and later drying stages (Hadas 1975; Hillel and Talpaz 1977). Nevertheless there is a strong tendency for upward movement of soil moisture during the drying stages of antarctic soils. Any salts contained in this moisture will tend to accumulate at or near the surface of the regolith at this time. Thus,surface efflorescences of salt are widespread in the region.

2.3.5 Summary :

Soil moisture content, availability and flux vary throughout McMurdo oasis in ways that can be generalized and summarized for reference in subsequent discussions in the thesis. Figure 2.7 is a model for trends in moisture content through the Transantarctic Mountains in McMurdo oasis. It summarizes data from preceding subsections and from discussions of climate in Appendix 3. Taylor Valley is used as the basis for the model because the patterns there are the simplest of the three major valley systems of McMurdo oasis.

The Figure is divided into two parts. Figure 2.7A shows the variation of climate elements with elevation and with distance inland away from the coast (Appendix 3; 3.3, 5.1, 5.2, 5.4, 6.2). With increasing elevation mean annual air and surface temperatures decrease but precipitation increases. Away from the coast temperature, absolute humidity and precipitation decrease and the elevation of the snowline increases. Figure 2.7A also illustrates the consequent trends in the amounts of melt water and ablation around and on Taylor Glacier (2.3.1).

The second part of the model illustrates the effects that the elements in the first part have on soil moisture (Figure 2.7B). Soil moisture content decreases up valley as a consequence of lower temperatures, precipitation and atmospheric absolute humidity. Similarly

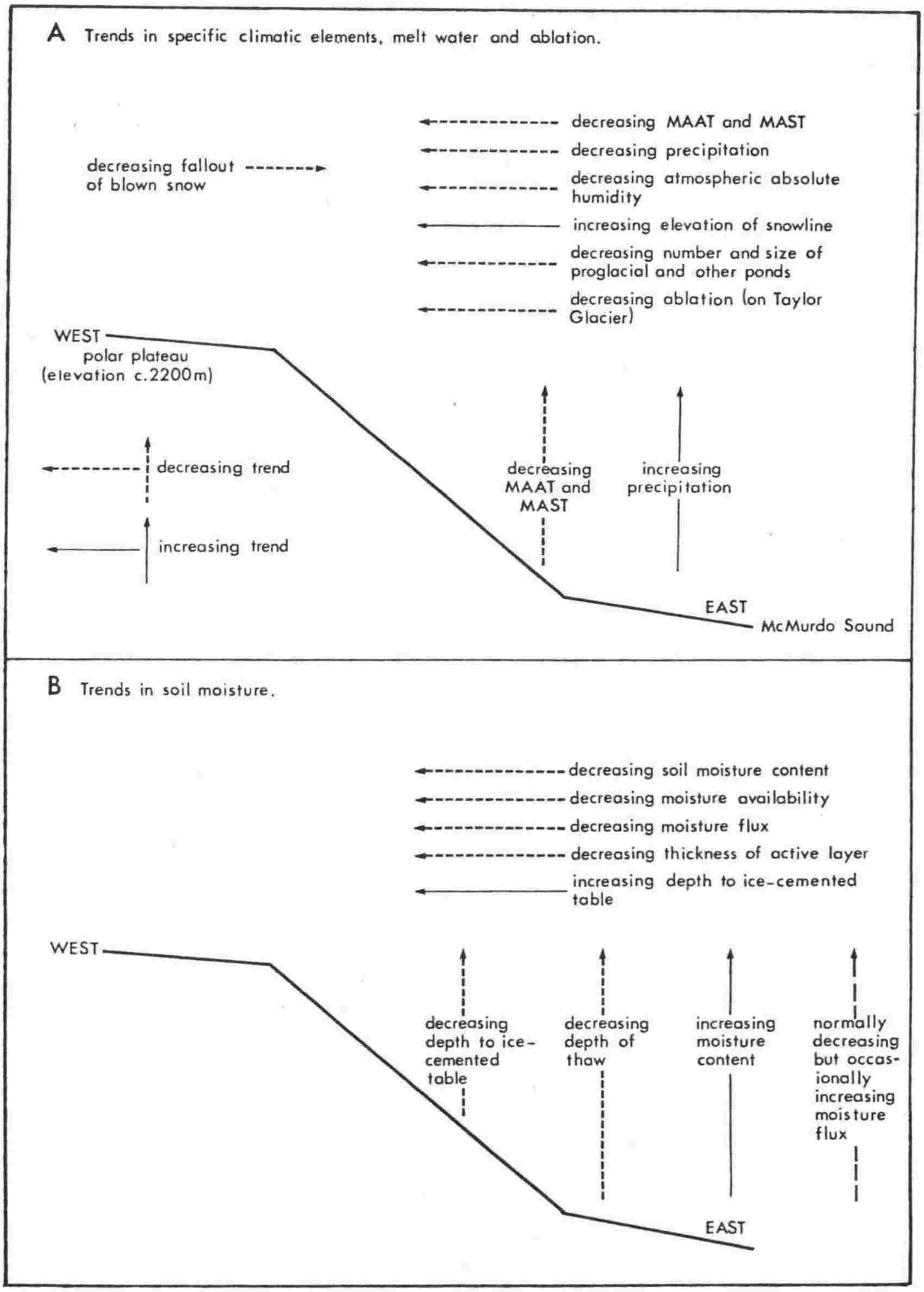


Figure 2.7 Schematic section up Taylor Valley showing A, trends for specific climatic elements, melt water and ablation and B, trends in soil moisture.

the availability of liquid moisture, thickness of liquid films and hence the flux of moisture through soils are likely to generally decrease up valley. The average depth to the ice-cemented table must increase as the moisture content decreases. However, the thickness of the active layer probably decreases up valley as the number of freeze-thaw cycles decreases under the influence of lower surface temperatures. Local exceptions to these trends will be common due to differences in topography, proximity to moisture sources and soil properties including age. Fallout of blown snow may alter the trends immediately adjacent to the plateau.

Trends with increasing elevation at a constant distance inland are more complex. We have seen that the depth to the ice-cemented table decreases with increasing elevation in the Mt. Discovery area (2.3.2). This suggests that the moisture content increases with elevation due to increased precipitation. However, the availability of liquid water generally decreases with elevation as surface temperatures and depth of thaw decrease (Claridge and Campbell 1968a; Campbell and Claridge 1969). In years with average temperatures the thickness of liquid films and moisture flux probably also decrease with increasing elevation. Occasionally, however, extreme warm events in the region (Chinn 1979) probably lead to a temporarily increased amount of liquid moisture at the higher elevations, especially near the coast.

2.4 Effects of Past Climate on Soils

2.4.1 Temperatures:

The surface temperature in Antarctica has not been constant over the last few million years. The sediment record from Ross Sea, Taylor Valley and Ross Ice Shelf Project site J9, show that pronounced cooling began in the area in Late Oligocene to Early Miocene times and reached a climax 4 to 5 million years ago (Hayes et al. 1975; McKelvey 1979; Webb 1979). In the last 0.7 Ma there have been several fluctuations (Blank and Margolis 1975).

More precise estimates of recent changes are possible from isotope records contained in ice cores from the continental ice sheet. Records from the deep core at Byrd Station suggest that surface temperatures have been several degrees colder than at present during the last 10^5 years (Epstein et al. 1971; Whillans 1978). The record at Dome C suggests that surface temperatures were as much as 7°C colder than now at the coldest part of the recent glaciation, 18000 years BP (Lorius et al. 1979). Precipitation was less during these cold periods than it is at present. Temperatures began warming about 16000 years ago, and since about 11000 years ago surface temperatures have at times been one or two degrees warmer than now (Dansgaard et al. 1969; Robin 1976; Lorius et al. 1979). The warmest conditions during this time were experienced from about 11000 to 8000 years BP with other warm periods at 4000-2000 years BP and about 1000 years BP (Lorius et al. 1979).

The isotope record suggests that mean surface temperatures in McMurdo oasis may have been as much as seven degrees colder but no more than two degrees warmer than at present, for the last 10^5 years at least. During these slightly warmer periods, warm and cold temperature extremes were probably little different from now. Evidence for this exists in the beach deposits and shorelines of former lakes. Present-day lakes in the oasis have poorly sorted beach deposits and generally poorly developed shorelines with little change of slope in the valley side. However, strong shorelines with treads of a few metres and steps of a metre or more may develop over a period of a few days given suitable lakeside topography, moat and wind conditions (Hendy 1973; personal observations at Lake Bonney, January 1975). Furthermore, there is good evidence from laminated carbonate "biscuits" in Taylor Valley that lakes there were higher than at present during global warm periods that have occurred in the last 4 x 10^5 years (Hendy et al. 1979). Shoreline development during these and other expanded lakes was similar to present-day development. This indicates that summer ice and moat conditions on the former lakes, and hence summer temperatures, were probably much the same then as now (Denton et al. 1971; Jones et al. 1971). Hence, maximum and mean summer surface and subsurface temperatures in the past were probably similar to those of the present day. In fact, these past temperatures are likely to lie within the range spanned by the errors that are associated with the estimated values of present-day temperatures given in Table 2.5.

2.4.2 Moisture:

Soil moisture conditions may not have been constant in the past. Varied evidence exists for differing conditions.

Changing lake levels suggest changing moisture conditions at least in areas close by. Glacial rock basin lakes, such as Lake Vanda, have been both larger and smaller than at present (Nichols 1966; Wilson 1964, 1967). The expanded lake events occurred at times when more melt water was present than now, due to warmer temperatures, increased precipitation, or some combination of these. About 3000 years ago the level of Lake Vanda was 60 m higher than now, and the lake twice as deep (Wilson 1967; Nakai et al. 1978). About 1000 years ago that lake's depth increased by at least 20 m from a shallow depth of a few metres (Wilson 1964). Both the high level and the rise in level coincide with warm periods detected in the ice core at Dome C (2.4.1). During colder or drier periods the lake was smaller than at present. Similar response to global warm periods have been detected in lakes in Taylor Valley (Hendy et al. 1979). Apparently an increased supply of melt water from Taylor Glacier began filling West Lobe of Lake Bonney about 15000 years ago (Hendy et al. 1977). This is consistent with the onset of warmer surface temperatures indicated by the Dome C isotope record (2.4.1).

The lakes in McMurdo oasis seem to be in a delicate state of balance at present, between inflow of melt water and loss of ice and water by evaporation (Chinn 1979, unpublished). Small changes in inflow or loss drawn out over many tens or hundreds of years could be responsible for marked changes in water level. Lake Bonney is currently rising (about 2 m in the last seven years, Robinson, Ministry of Works and Development, Christchurch, personal communication), with no obvious link to increased soil moisture or specific climatic elements, unless one considers the warming trend evident 100 km away at Scott Base (Appendix 3, section 2.5, Figure 4). However, Lake Vanda's level has dropped about 0.2 m in the last seven years (Robinson, personal communication). Alternatively, larger changes over single seasons, due to a succession of extreme events (Chinn 1979) could lead to significant changes of water level. The largest measured change of the level of Lake Bonney and a large change of Lake Vanda level occurred during the 1973/74 summer (Chinn 1979, unpublished). This summer had the highest recorded air temperature at Vanda Station (Appendix 3, Table 2) and abnormally high melt water flows coincident with high air temperatures (Hoehn et al. 1974; Anderton and Fenwick 1976). Neither of these two climate-based alternatives provides irrefutable evidence that soil moisture conditions in the past were substantially different for significant periods of time from those of the present day (away from the immediate vicinity of the lakes).

There are other possible causes of the current rise of Lake Bonney. These include: present, continual advance or broadening of Taylor Glacier (Hendy et al. 1977); intermittent minor advances (Black and Bowser 1968); or subterranean flow of (1) melt water from the base of Taylor Glacier (Keys 1979; Robinson 1979) and/or (2) fresh water from some other source (Weand et al. 1975). None of these causes appears to have been associated with changes of soil moisture, because this has not noticeably increased in the last seven years.

There is little evidence of widespread unconformities in soil profiles that would indicate significant regional changes in soil forming conditions (Campbell and Claridge 1977), for example during interglacials. Examination of soils from a large number of locations in the Transantarctic Mountains indicated that only a few local changes have occurred, due to local variations such as in moraine deposition, ablation or cryoturbation. From their work, Campbell and Claridge inferred (p.929) that "climatic oscillations in Antarctica have not been of sufficient magnitude to leave an impress on soils, for example by the widespread removal of salts from older soils" at high elevations, by leaching during moist interglacial periods.

However, there is some evidence for increased amounts of moisture at low elevations in the past. Mudflows, alluvial fans, glacio-fluvial deposits and fluvial channels that are predominantly inactive at present are found in McMurdo oasis at elevations mainly below 1000 m (Calkin 1964; Calkin and Bull 1970; Nichols 1971; McSaveney and McSaveney 1972). Field relationships in Wright Lower Valley suggest that such features there are all older than the Alpine II Glaciation (Behling 1972; Behling et al. 1974; Mayewski 1975). K-Ar dates indicate that this glaciation is probably younger than 4 x 10^5 years (Armstrong 1978). A more precise absolute age of 2.4 to 3.2 x 10^5 years was estimated by Behling (1972), using reaction kinetics involving the potassium content of silt-sized soil particles. Total salt content was also used by Behling but gave slightly younger ages, suggesting that some leaching may have occurred in these soils. Possibly Wright Lower Valley did experience significantly moister soil conditions than now prior to about 0.2 Ma ago, probably during interglacial periods.

It is concluded that few soils in Antarctica have been affected by climatic change. Soils at higher elevations, having low mean annual surface temperatures, are insensitive to changes in air or surface temperature. Large warming would be necessary to increase the extent of freeze-thaw activity significantly; there is little evidence for significantly warmer temperatures, at least in the past half million years or so. However, soils at lower elevations may be more susceptible to small changes in climate and there is evidence for moister conditions than now in Wright Lower Valley, prior to about 0.2 Ma ago.

CHAPTER 3 LOCAL DISTRIBUTION OF SALTS

3.1 Introduction

3.1.1 Outline:

This chapter is mainly descriptive. It describes the various crystalline salt phases that have been recognized in the McMurdo region, and discusses the types of deposits in which the salts are formed. The chapter aims at portraying the distribution of the salts on a local scale, that is, from the scale of individual deposits to that about 1 km across (e.g. Labyrinth). The distribution of the common salt phases in various types of deposits is examined and the influence of slope aspect is considered. An important purpose of the chapter is to establish a sequence of relative mobilities of the salt phases. This sequence is used in the following chapter to determine the physico-chemical properties that control migration and separation of the salts.

3.1.2 Sample collection and analysis:

Great variability exists in specific soil properties in sites of similar location, genesis or age (e.g. 2.3.2). This is particularly true for salts, which are "among the most mobile constituents of antarctic soils" (Campbell and Claridge 1975, p.87). Therefore it is necessary to study a large number of salt samples before reliable generalizations can be made.

Sites for salt collection were selected to obtain the best possible picture of local and regional distribution, although topographic obstacles and permanent ice accumulations limited the choice in several areas. To reduce the non-salt component, surface deposits and those beneath surface cobbles and pebbles were the main deposits sampled of the various types of deposits that exist (Table 3.1). After collection, the samples were sealed in plastic bags, normally a sufficient precaution against changes in the hydration state of unstable salt phases (Keys 1972). The antarctic salt phases that are known to be unstable in temperate conditions are detailed in 3.2.2.

X-ray diffraction (XRD) was used for analysis (Appendix 1, Analytical Methods, page 3) because it is a fast, definitive tool. It is especially suitable for analysing large numbers of macroscopic salt deposits. The results can be treated to obtain numerical data for assessing salt trends, by determining the relative number of occurrences of each phase for a particular area, aspect or other property of interest. Therefore, such a qualitative approach is as useful for most purposes as a quantitative one. In fact, quantitative analysis of salt distribution is difficult because of their patchy accumulation. The large numbers of samples required would take an extremely long time to analyse quantitatively. Subsequent presentation of the data would be quite involved. No attempt has been made to estimate or even compare quantities of salts in deposits collected for this study except in Chapter 7. The literature was used for quantitative analyses, mainly from within soils, to supplement the data presented here.

In many cases interpretation of XRD patterns was complicated by peaks due to rock and soil material. In a few instances the parent rock pattern was recorded separately and its contribution to the overall pattern removed. Characteristic peaks due to quartz and clay minerals could be identified and effectively removed from the pattern. After preliminary XRD analysis some important samples were purified by recrystallization. Subsequent XRD showed that such recrystallized salts occasionally contained different amounts of water of crystallization from the original salts (e.g. sodium sulphate) and often double salt structures were affected. However, the purification invariably led to identification of the phases originally present. Peak interference, occasionally a problem, usually could be overcome with experience using the XRD technique. Owing to the inherent limitations of XRD any phase present in concentrations lower than about 5 percent (e.g. iodates) could not be reliably detected.

3.1.3 Data assembly, reduction and presentation:

The results of over 300 analyses, together with site environment details, are assembled in Appendix 1, Tables 3-11. Data from selected tables have been reduced to summary form in Appendix 1, Tables 27-36 (Appendix 1, Notes on Selected Tables, p.7; Appendix 2, subsection A2.2.2i). The different phases are counted in each deposit in which they are present, subject to the constraints depending on the objective of the specific summary involved. The relative number of occurrences or abundance of a specific phase is obtained as a percentage of the total number of all phases counted. This percentage appears in the tables in Appendix 1, and as histograms and rose diagrams here, for each phase or group of phases (e.g. nitrates). The most common phase (hydrate or polymorph) of a salt is considered in each deposit (in most instances) so that no bias is created towards those salts with more than one form. Other sources of error are discussed in Appendix 2 (subsections A2.1.1-3, A2.2.1).

3.2 Composition and Types of Deposits

3.2.1 Salts present:

At least thirty crystalline salt phases have been positively identified from or near the McMurdo region. They are divided here into three groups based on the extent to which they are known (Appendix 1, Table 1, pp.12, 13). Group A comprises the five phases frequently mentioned in the literature, namely halite, thenardite, mirabilite, gypsum and calcite. Group B comprises eleven less widespread or less well-known phases, whereas phases in Group C have been seldom or not previously reported. Zeolites and other late stage hydrothermal alteration minerals are not discussed here, unless they are chemically identical or similar to salts in the region (e.g. calcite, aragonite, dolomite, magnesite).

The existence of Group B phases such as epsomite, hexahydrite, soda nitre, bloedite and darapskite has been known for several years (Gibson 1962; Claridge and Campbell 1968a, b, c; Tasch and Angino 1968). Ericksen and Mrose (1970) doubted the existence of darapskite in Antarctica but subsequent work (Nishiyama 1977; and this thesis) has independently confirmed its widespread presence. Aragonite, a metastable polymorph of calcium carbonate, has often been found in the McMurdo region (Angino et al. 1962; Black et al. 1965; Keys 1972; Browne 1974; Watanuki and Morikawa 1974; Nishiyama and Kurasawa 1975; Hendy et al. 1979). Antarcticite (Plate 3.1) is well known from its presence at Don Juan Pond. The mineral was first identified and named by Torii and Ossaka (1965) but precedence was also claimed by House et al. (1966) who erroneously referred to it as hydrophilite ($CaCl_2$). A calcium chloride phase is present in some arid soils in the region (Kumai et al. 1976). Sylvite, thermonatrite and trona have been known for some time (Browne 1973; Nishiyama and Kurasawa 1975) but are not widespread. All the phases noted above have been detected during this study.

Plate 3.1 Antarcticite ($CaCl_2.6H_2O$) crystals in a deaquation (type 2B) deposit at Don Juan Pond (locality no.218, 11/12/72).

Iodate ions were first found in VUW sample 10567 from near near Lake Vashka (Johannesson and Gibson 1962; Gibson 1962). The iodate was present at the 0.1 percent level in the sample which was analysed as containing 85 percent gypsum and 14 percent calcite, with 0.4 percent sodium ions. Although the iodate was reported in the form $NaIO_3$ it is more probable that it exists as $Ca(IO_3)_2$, (lautarite). This is the iodate containing mineral that occurs with gypsum in the nitrate deposits of Chile (Palache et al. 1951). The trace amounts of iodate in antarctic salts are not detected by most routine analyses including XRD as applied to the present study.

Phases in Group C have been reported no more than twice (see Appendix 1, p.13), and in few cases have there been included X-ray data for the phase in question. This is a serious omission owing to the unusual nature or rare existence of most of these salts. For example, Kumai et al. (1976) using energy dispersion X-ray analysis noted the presence of magnesium chloride but could not specify the salt phases involved. The phase is probably one of either tachyhydrite (tachydrite, $CaMg_2Cl_6.12H_2O$), bischofite or carnallite. Tachyhydrite has recently been reported by Bockheim (1979b) who used X-ray diffraction but did not produce corroborative X-ray data. Bockheim (p.148) believed that tachyhydrite was present in small quantities "commonly associated with samples bearing mirabilite". This seems a most unlikely association since the calcium and sulphate ions present would normally have combined to produce sparingly soluble gypsum; this was found in one sample only. Mirabilite is stable at low temperatures but in warmer (e.g. +20°C) conditions it effloresces (i.e. loses water), dehydrating to thenardite (Dort and Dort 1970). The diffraction peaks of dehydrating mirabilite (Torii et al. 1966) would totally obscure or interfere with all the eight major peaks, at d spacing 2.50 Å or greater, of tachyhydrite (ASTM card number, 1-1092). The writer believes that Bockheim mistook several of the peaks of dehydrating mirabilite for tachyhydrite, which has yet to be confirmed in the McMurdo region.

Of the 17 reported phases of Group C, only four were detected in the present study. Burkeite, melanterite and alunite were possibly first detected for Antarctica during this work but the first-named has recently been reported by Nishiyama (1979) also. The fourth phase detected was nahcolite, first reported by Keys (1972), who also detected the presence of the Group C salt, $Ca_3(PO_4)_2$, from a skua nesting area at Cape Evans. Phase identification was not possible due to the presence of rock material, but it is probably whitlockite. Calcium phosphate was first detected as an antarctic salt by Campbell and Claridge (1966) from an abandoned penguin rookery on Inexpressible Island. These and other Group C phases, plus sylvite, antarcticite, aragonite, thermonatrite, trona and the iodate salt from Group B are excluded from most of the following discussions because they have not been detected in enough samples to make valid generalizations pertaining to local distribution. However, their distribution on a regional scale and their ion sources are discussed in Chapters 5 and 6.

3.2.2 Stability of antarctic salt phases on extraction from the antarctic environment:

All five double salt phases and most single phases detected during this study are quite stable when in the crystalline form in laboratory conditions. In this dry state they show little or no tendency to effloresce, deliquesce (gain water) or change to the stable polymorph. Therefore their collection, extraction from Antarctica, and subsequent analysis pose no problems.

However, hydrates of some single salt phases belonging to Group C are unstable in temperate conditions. They will tend to dehydrate or decompose on extraction from Antarctica. Dihydrohalite tends to dehydrate to halite above +0.15°C (the transition point) in the absence of other phases beside halite (Timmermans 1960; also Fig.4.2), or at lower temperatures if phases containing other ions are present (e.g. as low as -5.9°C in the presence of soda nitre, Chrétien 1929). Hydrates of calcite are unstable above 0°C or colder, and dehydrate rapidly to calcite (Palache et al. 1951). Gaylussite tends to alter to calcite also (Palache et al. 1951). Certain phases that possibly do exist in Antarctica may not have been detected because of decomposition during extraction from the cold, frigid environment. Some such phases that are possible are discussed in Chapter 6.

Other hydrates may be unstable in laboratory conditions but their alteration is slow enough to allow the phase to be identified before or during such alteration. These hydrates include mirabilite which effloresces to thenardite and antarcticite which deliquesces and dissolves.

3.2.3 Deposit types:

The salt phases in the McMurdo region accumulate in a variety of forms or types of deposits most of which are white. Nishiyama and Kurasawa (1975) and Nishiyama (1977) have categorized the various deposits into three types 1, 2, 3. This classification is adopted here and extended by letters and further numbers where necessary. The classification is summarized in Table 3.1. Almost all salt deposits are white in colour (Plates 3.1-3.5) although some are brownish or yellow-brown due to inclusions of quartz, clay minerals, and other rock and soil material. Gypsum is occasionally tinted light orange or green on basaltic substrates due to traces of impurities such as iron.

Surface salt deposits belong to types 1 and 2. On bedrock, boulders and cobbles the salts may be present as: surface encrustations or thin veneers (type 1A, Plates 3.2 and 3.3); accumulations in joints, cracks or behind flakes (1B) (Plate 3.2); or in cavities in bedrock and boulders (1C). On the surface of the regolith throughout the region the types of deposit include: thin, powdery veneers around, immediately downslope of, or in the shelter of soil particles and rocks (Plate 3.3); or

Plate 3.2 Calcite ($CaCO_3$) on the vertical surface (type 1A deposit) and in cracks and joints (type 1B) of Aztec Siltstone at Alligator Peak (locality 183). The deposit is thickest immediately below the ledge where snow lies, whereas salt is absent above the ledge. (14/12/73)

Plate 3.3 Gypsum ($CaSO_4.2H_2O$) and thenardite (Na_2SO_4) in deposits on rock and cobble surfaces (1A deposit, open arrows) and on soil surface around rocks (2A deposits, solid arrows). Tape points downslope (Beacon Valley, locality 129, 6/12/73).

thicker encrustations often partially or completely covering surface pebbles and smaller material (Plate 3.4, also plates in Chapters 4 and 7). Such accumulations are termed efflorescences, or type 2A deposits. Type 2B deposits include all those formed by loss of water, i.e. deaquation, from standing water bodies (Plate 3.1). These deposits include those on the floors of dry or partly dry closed basins (salt covered depressions, salt playas, salinas) or former basins. Some of these deposits are termed evaporites where evaporation was the process of deaquation, as in the classic evaporite sequences in the northern hemisphere (e.g. Kirkland and Evans 1973). In addition 2B deposits include precipitates, those salts precipitated from solution by freezing out (freeze concentration). These deaquation 2B deposits, and 2A deposits, may be indistinguishable in the field. Both may assume a botryoidal shaped surface described as "roundish mammillary shapes" by Nichols (1963) (see also Bowser *et al.* 1970, Fig.4b ; Nishiyama and Kurasawa 1975, Figs.2E, F).

Table 3.1 Main types of salt deposit (extended from Nishiyama and Kurasawa 1975; Nishiyama 1977).

Type of deposit	Type number	Typical salt phase(s)
encrustation on surface of bedrock, boulder or cobble	1A	calcite, gypsum
accumulation or encrustation in joint, crack or behind flake of bedrock, boulder or cobble	1B	calcite, soluble salts
accumulation in cavity in bedrock or boulder	1C	soluble salts
efflorescence or encrustation on surface of regolith	2A	soluble salts
deaquation deposit in enclosed basin	2B	soluble salts
veneer and encrustation on underside of boulder, cobble or pebble	3	calcite
accumulation beneath boulder, cobble or pebble	4	soluble salts
strong salt horizon or nodule in regolith	5	soluble salts

Subsurface deposits belong to types 3, 4 and 5. Veneers of calcite and occasionally gypsum on rock undersides (type 3) (e.g. Nishiyama and Kurasawa 1975, Fig.2G, H) are common in some localities, particularly Taylor Dry Valley. Salt accumulations just beneath surface boulders, cobbles and pebbles and loosely adhering to the undersides of such rocks are very common deposits, here termed type 4 (Plate 3.5 but also plates in Chapters 4 and 7). Within the regolith, salts are sometimes present in massive or crystalline horizons up to several centimetres thick or as nodules, termed type 5, (Plate 3.5).

Specific types of deposit form as a response to moisture availability and transport. In subxerous soils (Table 2.1) salts are found in deposit types 2A, 2B and 3. Above the soil surface 1A, 1B and 1C deposits occur (Campbell and Claridge 1969; Claridge and Campbell 1968b). In xerous soils types 2A, 3 and 4 are present, but most of the salt is disseminated throughout the profile and difficult to examine by XRD. In the most arid (ultraxerous) soils, salts are present in type 5 deposits and type 4 deposits are less common (Claridge and Campbell ibid.; Campbell and Claridge ibid.). However, somewhat moister soils may develop salt-indurated (cemented) horizons if sufficient time has elapsed (Everett 1971; Bockheim 1979b). The existence of types 1, 2, 3, 4 and 5 deposits in the same area (e.g. Table Mountain - Knobhead, Appendix 1, Table 5, pages 21, 22) illustrates the complexity and variability of the soil-moisture-salt system.

It can be shown that examples of most of these types of deposits are actively developing at present, although this development may be very slow. Surface efflorescences (2A) form most summers around standing bodies of water, streams or subsurface moisture movement. Liquid films and capillary action transport subsurface moisture, bearing salts in solution, from the water body to the surface where the moisture is evaporated leaving the salt. Young 2B deposits were studied (Nov. 1972) in Pearse Valley in a dry salty depression (Appendix 1, Table 8, p.32). U.S. Navy aerial photographs show that this depression was filled with ice in December 1970. Very young 1A deposits, still forming in places, have been seen (14-17/12/73) at Alligator Peak, where water containing a small amount of dissolved salt trickled over surface rocks and evaporated to dryness (Appendix 1, p.24, localities 185, 186). On Black Island type 4 deposits were found (6/12/74) that had accumulated beneath boulders

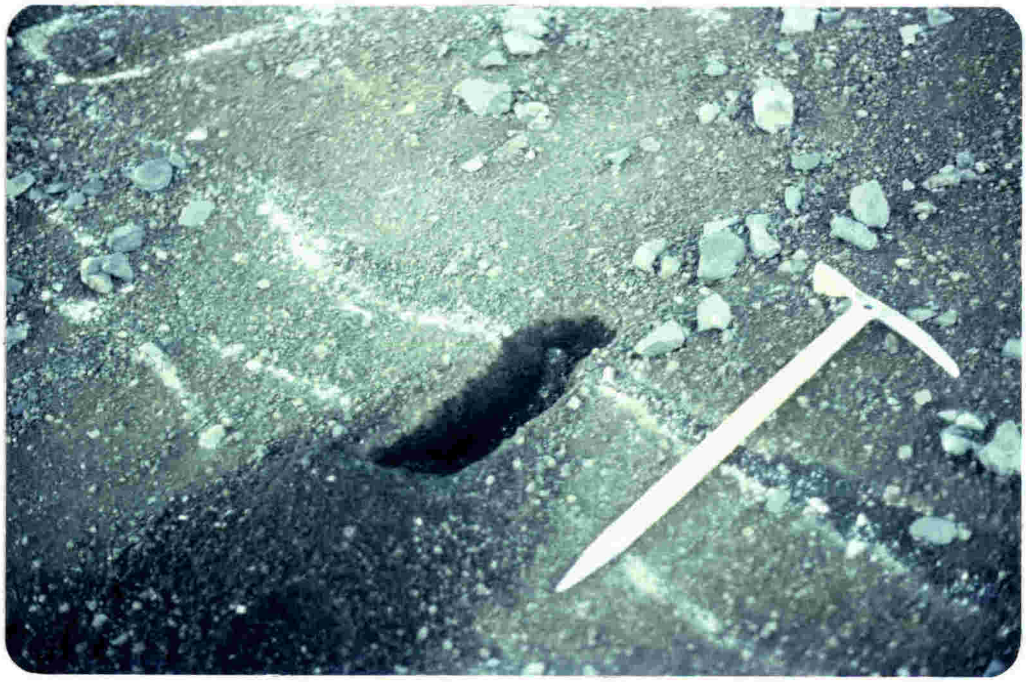


Plate 3.4 Surface encrustation (2A deposit) of salt, Bottom Cone, Mt. Discovery. Fine-grained soil layers dipping into the slope promote capillary action that carries soil brines to the surface where evaporation occurs depositing the salt along the layers. Ice axe points downslope (14/12/76).

Plate 3.5 Subsurface mixed salt deposits of thenardite, halite ($NaCl$), darapskite ($Na_3(NO_3)(SO_4)_2.4H_2O$), bloedite ($Na_2Mg(SO_4)_2.4H_2O$) and gypsum at Pearse Valley (locality 83); deposit types 4 (open arrow) and 5 (solid arrow) are present (23/11/72).

used for anchoring tents in 1964 (Appendix 1, p.30, locality 307). Present-day accumulation of other subsurface salt, especially type 5 deposits, is more difficult to show.

There are several special types of salt deposit that cannot immediately be included in the classification discussed above. In Taylor Valley calcium carbonate "biscuits" are present on the surface in situ, or as lag deposits and as chips within the regolith below about 400 m elevation (Appendix 1, p.15, localities 65, 66). These were deposited from former lakes mainly as a result of depletion of dissolved carbon dioxide by photosynthetic algae (Hendy et al. 1977, 1979). They can be loosely described as 2B deposits. Rarely, soluble salts (mainly nitrates) are found up to a few centimetres inside porous sandstones of the Beacon Supergroup (e.g. Appendix 1, p.17, sample 23837 and J. McPherson, pers.comm.). These endolithic salts have probably migrated in solutions from the rock surface to their present positions as does the moisture that nourishes certain similarly placed endolithic flora (Friedmann 1978). Salts are present on a few rock surfaces inside geothermal ice caves on Erebus Volcano (e.g. localities 343, 344, Appendix 1, p.31). Twinned gypsum crystals are present but are uncommon (Gibson 1962; sample 76/35C, Appendix 1, Table 9, p.33 - interpenetration twin on (101), crystals elongated parallel to the crystallographic a axis and flattened in the ab plane). Such crystals result from some influence on their growth from a seed crystal; this influence is probably chemical, caused by a high concentration of other solutes.

3.3 Local Distribution

3.3.1 Composition of deposit types:

There is a strong tendency for some salt phases to preferentially accumulate in certain types of deposits. Sparingly soluble phases, such as gypsum and calcite predominate in encrustations on rock surfaces, are present in subsurface deposits but are minor phases in deaquation deposits. More soluble phases show opposite trends. Tendencies such as these are the result of differences in physico-chemical properties of the various phases, soil and surface climate, and the supply of ions to the salt-soil system. Before such influences can be examined in this and subsequent chapters, the preferred compositions themselves must be considered.

Histograms provide a convenient summary of deposit composition (Figs.3.1-3.3). Figure 3.1 is a set of four histograms illustrating the composition of deposits in Taylor, Wright, Ferrar Valleys, Skelton Névé and Mt. Kempe. The histograms show occurrences of calcite (least soluble), gypsum (sparingly soluble) and eight more soluble phases combined. (These eight are soda nitre, darapskite, epsomite, bloedite, halite, thenardite, mirabilite and hexahydrite.) Occurrences are given as percentages of total occurrences (Appendix 2, subsection A2.2.2i) of these ten phases in each of four convenient sets of deposit types; rock surface encrustations (1A, 1B, 1C), surface efflorescences (2A), deaquation deposits (2B), and subsurface deposits (3, 4, 5).

The histograms show that different deposit types tend to contain different phases (Fig.3.1). Rock surface encrustations are mainly gypsum and calcite, with very few occurrences of soluble phases. Soluble salts are more evident in the surface efflorescences (2A) studied, which are composed of gypsum and total solubles in approximately equal amounts in this particular treatment. A gap in sampling is evident here, in the absence of calcite in 2A deposits. Evidently calcite is not concentrated sufficiently in such deposits to be conveniently studied by XRD*. It is known that calcium carbonate is concentrated at the surface in some xerous and subxerous soils (e.g. Claridge 1965; McCraw 1967a, b; Claridge and Campbell 1968b; Campbell and Claridge 1969). However the data presented here are sufficient to show the general composition of macroscopic 2A deposits and the differences between them and other deposit types. Deaquation deposits (2B) consist mainly of soluble phases with less frequent occurrences of gypsum and rarely calcite. A similar but less pronounced trend in relative abundance is evident in subsurface deposits. The marked predominance of soluble phases in 2B deposits indicates that salts are brought into salty depressions in inflow waters, and are not originally formed in the depressions.

A few calcite and gypsum deposits that presently are type 1A were once type 3 deposits. They were brought to the surface by rolling of their substrate cobbles during mass movement processes such as gelifluction

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*A better approach may have involved application of dilute acid in the field, but this in turn might lead to preferential sampling of calcite.

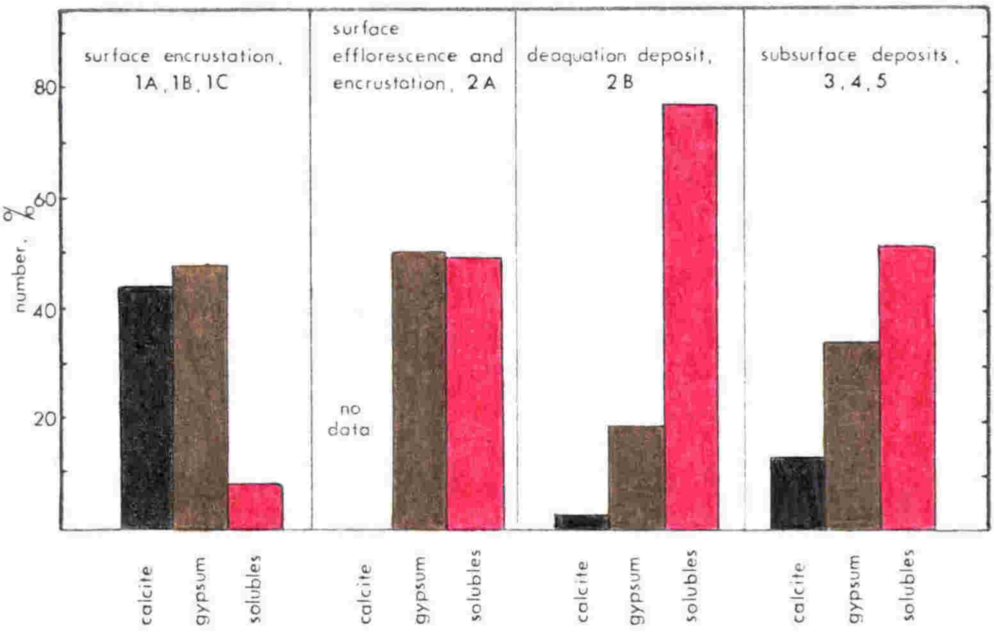

Figure 3.1 Distribution (%) of calcite, gypsum and common solubles in various types of deposits (in Taylor, Wright, Ferrar Valleys, Skelton Névé and Mt. Kempe). Data from Appendix 1, page 47, Table 27a(3).

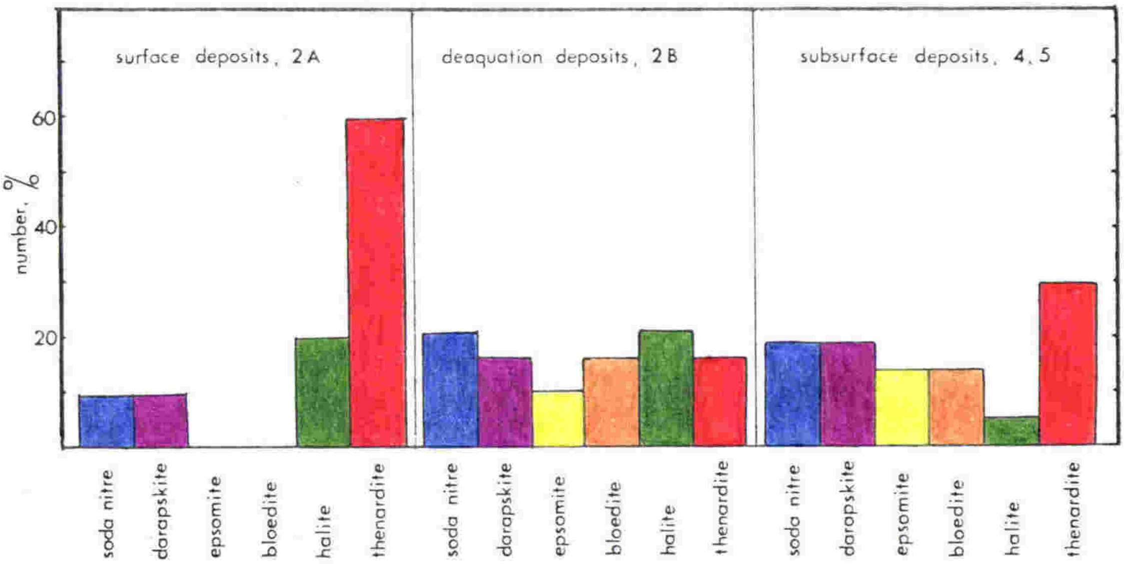

Figure 3.2 Distribution (%) of six major soluble phases in various types of deposits (in Aztec-Kennar and Labyrinth areas only). Data from Appendix 1, page 47, Table 27a(4).

(Nichols 1963 ; McCraw 1967b; e.g. locality 70, Taylor Valley, Appendix 1, p.15; locality 167, sample 72/233, Big Foot Nunatak, Appendix 1, p.22).

The relative abundance of the various soluble phases themselves also vary considerably between deposit types. Figure 3.2 shows a set of three histograms illustrating the composition of deposits of soluble salts in restricted areas of McMurdo oasis. Aztec Mountain, Kennar Valley and Labyrinth areas were chosen because they are at similar distances from the coast of McMurdo Sound (70-80 km) and have similar elevations (800-2200 m). Hence, soils in these areas receive probably similar fallout of marine and continental aerosols (Chapter 6) and are subject to similar amounts of moisture and liquid water (Fig.2.7 and Chapter 4). Further, there are similar lithologies in these areas (mainly dolerite and Beacon Supergroup, Fig.1.2) indicating that any supply of specific ions from rock weathering (Chapter 6) should be approximately the same. Finally, there are sufficient numbers of each deposit type (except type 1) for each of the six major phases in these areas to allow study of deposit composition and salt separation (Appendix 2).

2A deposits most frequently contain thenardite. Halite is of secondary importance followed by nitrates. Magnesium salts are rare in such deposits in the three areas being considered. Deaquation deposits most frequently contain halite and nitrates, with thenardite and magnesium salts being of slightly lesser importance. In subsurface deposits the relative frequency of occurrence is thenardite followed by nitrates, magnesium salts and halite.

Regional perturbations influence local salt distribution. This is shown by considering the types of soluble phases in deposits throughout the region (Fig.3.3A, B), rather than in small areas (Fig.3.2). Halite occurs more frequently in all deposit types in Figure 3.3A than in Figure 3.2 due to an increased abundance of this phase in the more general area (Chapters 5 and 6). Nitrate is absent from McMurdo Sound (Fig.3.3B) for a similar reason.

Single phase hydrates have a subtle distribution. Mirabilite occurs in 2A deposits around the coast and in deaquation and subsurface deposits over the entire region. The apparent lack of this phase in 2A deposits in the oasis is significant. Similarly, hexahydrite occurs in both surface and subsurface deposits near the coast but apparently only in subsurface deposits in the oasis. However, the other phases of these salts, thenardite and epsomite, are present in all deposit types.

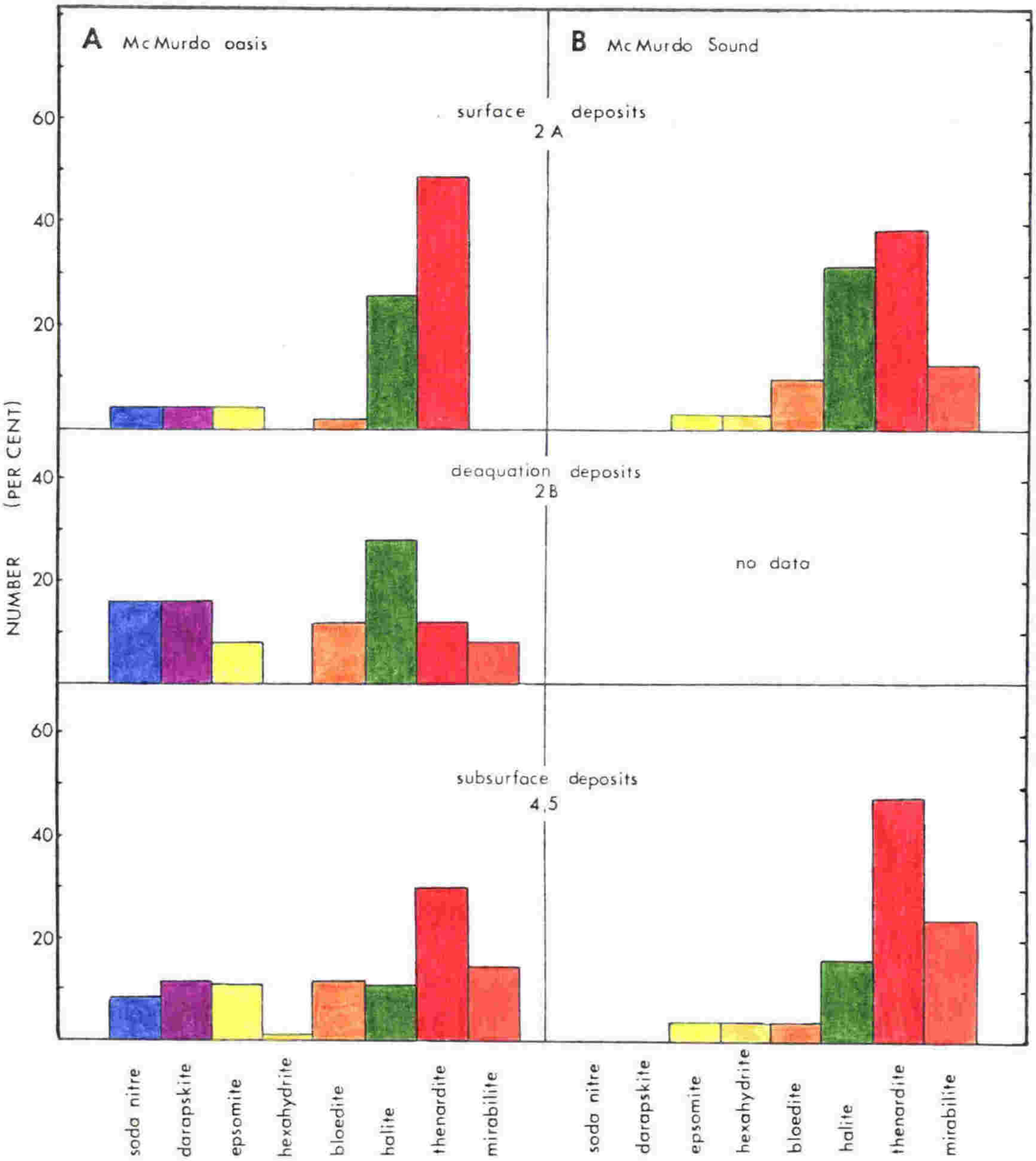

Figure 3.3 Distribution (%) of common soluble phases in various types of deposits: (A) in Taylor, Wright, Ferrar Valleys, Skelton Névé and on Mt. Kempe; (B) on Mts. Discovery and Morning, Black and White Islands, and at Cape Bird and Hoopers Shoulder. Data from Appendix 1, page 46, Table 27a(1) and (2).

3.3.2 Aspect:

It has been seen (2.3.2) that soils and slopes with northerly aspects tend to have more moisture available than those with southerly aspects. Similarly, soils and slopes with northerly aspects have significantly different salt accumulation than those with southerly aspects. The difference is most marked with the sparingly soluble phases. Gypsum and calcite tend to accumulate on north-facing slopes. Generally 2A deposits occur most frequently on north-facing slopes. Deposits on flat terrain and in small scale depressions are excluded from the following discussions.

Rose diagrams are a convenient method of portraying the number of salt occurrences as a function of aspect (Appendix 2, subsections A2.1.2i, A2.2.2 iii). Figure 3.4 presents diagrams for gypsum (Fig.3.4A) and calcite (Fig.3.4B). Each diagram shows the frequency of occurrences of one salt in each of the four main compass points in a specific deposit type. Each diagram has two circles, the radii of which are the 95 and 99 percent significance levels (Appendix 2).

Gypsum and calcite accumulate preferentially on north-facing slopes. In Figure 3.4A for gypsum, there appear to be significantly more type 2A and subsurface (mainly type 4) deposits on slopes with northerly aspects. Such aspect is favoured for 1A, 1B deposits at the 95 percent significance level. Deposits of calcite tend to occur mainly on slopes with northerly aspects (Fig.3.4B). This last tendency is consistent with observations made by Campbell and Claridge (1967) in the Brown Hills area of Darwin Glacier.

Trends are not as strong for specific soluble phases. Two sets of rose diagrams for the six major soluble phases are shown in Figure 3.5. The number of data for most phases in 2A deposits are insufficient for statistical purposes; therefore, data for thenardite, halite, soda nitre, darapskite, epsomite and bloedite are combined in one rose. Figure 3.5A suggests that there is a strong tendency for 2A deposits of soluble salts to preferentially develop on north-facing slopes. Figure 3.5B indicates that any trends are weak in subsurface deposits. There is some tendency for subsurface nitrate salts to preferentially accumulate in soils whose aspect is southerly. This has previously been noted by Campbell and Claridge (1967) who also showed that in such soils, greater amounts of soluble salt accumulated.

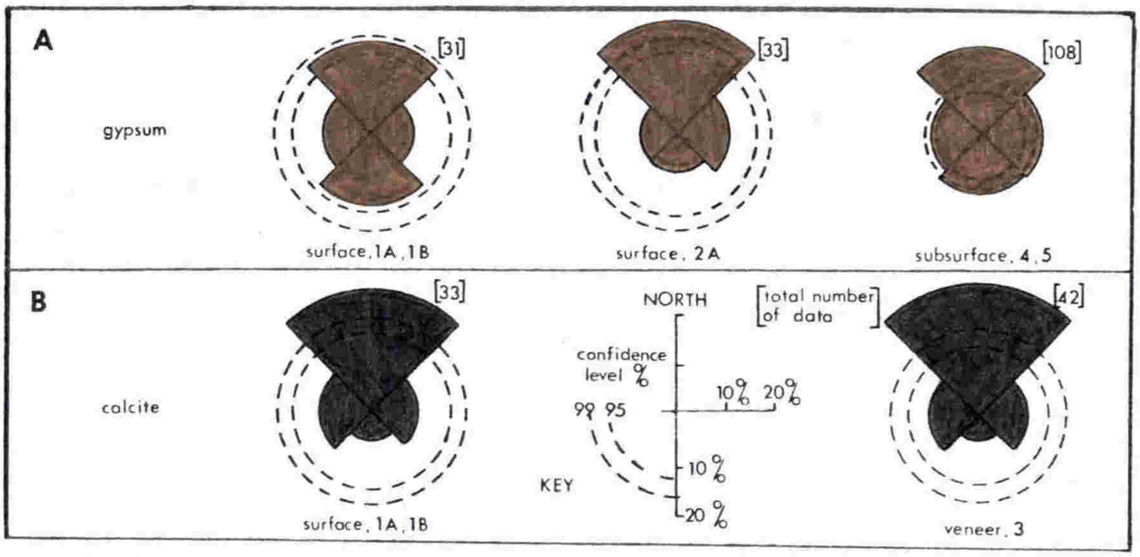

Figure 3.4 Distribution (%) of gypsum and calcite phases in deposits on north, south, east and west facing slopes in various types of deposits, in Taylor, Wright, Ferrar Valleys, Skelton Névé and Mt. Kempe. Data from Appendix 1, Tables 29, 30.

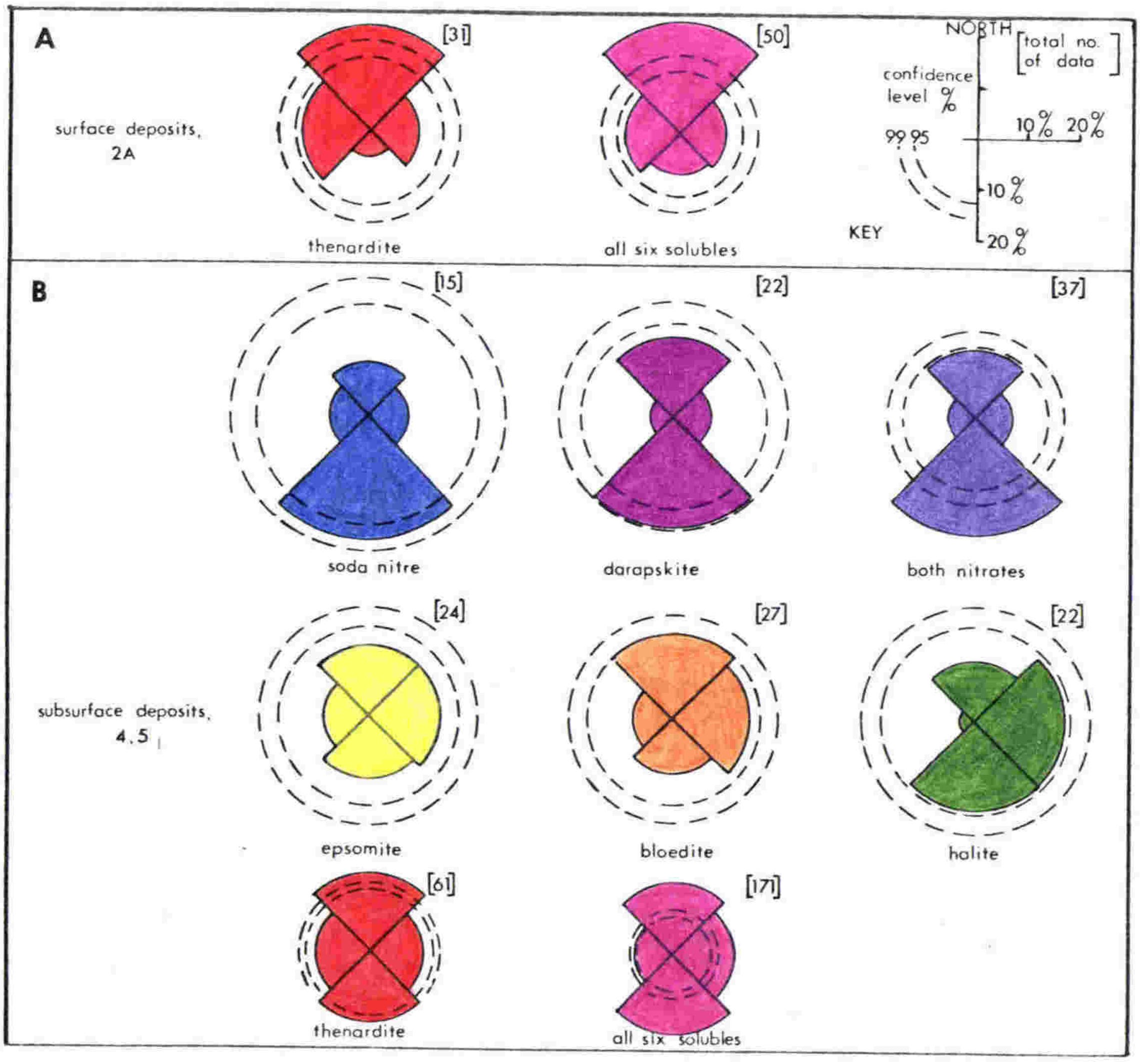

Figure 3.5 Distribution (%) of six major soluble phases in deposits on north, south, east and west facing slopes in (A) surface and (B) subsurface deposits in Taylor, Wright, Ferrar Valleys, Skelton Névé and Mt. Kempe. Data from Appendix 1, Table 28a, b(1).

The rose in Figure 3.5B for subsurface deposits of all soluble phases combined suggests that there is slightly more accumulation in south-facing soils, compared with north-facing soils.

The trends displayed in Figures 3.4 and 3.5 indicate that site aspect does have a significant effect on both salt composition and deposit type. On more frequently moistened north-facing slopes there are more occurrences of gypsum and calcite, and more soluble salts in 2A deposits, than on drier south-facing slopes. However, the latter tend to contain more nitrates in subsurface deposits, suggesting such a response to lack of moisture or specifically lack of leaching.

3.3.3 Separation between salt phases down slopes, and salt mobility:

The inter-phase separation that has developed on slopes in antarctic 'oasis' environments has been known since the work of Glazovskaya (1958, 1968) in Bunger oasis, Wilkes Land (Fig.1.1). Glazovskaya (1968, p.303 et seq.) used this separation to characterize the "geochemical soil sequence" in a series of soils that are linked by downslope migration of salts. She concluded that the least mobile phase is present from the top of the slope while the most mobile phase is present towards the bottom only. This subsection discusses the separation that is apparent in McMurdo oasis. The following chapter discusses the processes and factors leading to this separation.

Glazovskaya (1968) showed that the separation of salts in cold deserts is in the order:

$$CaCO_3,\ Na_2SO_4,\ (NaCl),\ CaCl_2 + MgCl_2.$$

That is, on a series of linked soils $CaCO_3$ is present from higher elevations than is Na_2SO_4, which in turn is present from higher elevations than chloride salts. Keys (1972) characterized the phases present and put gypsum into the sequence to give:

calcite, gypsum, thenardite, halite, antarcticite

as the separation order. Field (1975) and Wilson (1979) confirmed the order of the last three phases and the latter inferred that $MgCl_2$ followed antarcticite. The data of Nishiyama (1977) for eastern Taylor Valley indicate that $NaHCO_3$ and Na_2CO_3 lie between thenardite and halite in the sequence in areas where soluble carbonate phases are abundant (i.e. eastern Taylor Valley). Nishiyama's data also suggest that sylvite comes after halite in the sequence. However, the presence of sylvite with halite in deposits on the south side of Taylor Valley more than 1000 m above Lake Bonney (locality 55, Appendix 1) indicates that in fact the two phases may be close together in the sequence.

The "geochemical soil sequence" must be characterized for as many phases as possible. The following discussion considers the place of $NaNO_3$ as soda nitre and $MgSO_4$ as epsomite in the sequence. Infrequently detected phases such as sylvite, thermonatrite and nahcolite are not considered as there are insufficient data to place them reliably. The common double salts darapskite and bloedite are not considered as they are 'dependent' phases. Their presence depends on the relative concentrations of 'independent' phases such as $NaNO_3$ and Na_2SO_4, and $MgSO_4$ and Na_2SO_4 respectively (4.4.3). The present treatment is not based on a quantitative analysis, which has the following difficulties:

(1) an extended statistical treatment would be necessary to rationalize the analyses and

(2) the multi-component system necessarily involved (Chapter 4) is dependent on supply of ions which changes within the region (Chapters 5 and 6).

However for two sets of linked soils in Brown Hills, the ionic data (Cl/NO_3 ratios) of Campbell and Claridge (1967, p.569) suggest that the mobilities of chloride and nitrate ions are similar and greater than sulphate ions.

The soluble salt phases tend to accumulate in basins at the bottom of linked soil series. This tendency has already been seen in Figure 3.1 and is indicative of the greater mobility of the more soluble phases. The data on which Figure 3.1 is based are rearranged in Appendix 1, page 48, Table 27b(2). The table gives the frequency of various deposit types as a percentage of all deposits of calcite, gypsum and the same eight soluble phases combined. The percent occurrence of 2B deposits, i.e. the mobility of phases, increases in the order:

calcite, gypsum, solubles.

This increased mobility may be quantified by considering ratios of occurrences of specific phases in various deposit types. Mobility can be simply defined as the tendency for a phase to be leached from a soil into a closed basin downslope from that soil. Two mobility ratios can be defined, that is the ratio of occurrences of 2B deposits to (1) subsurface occurrences, i.e. 2B/[(3 +)4 + 5] and (2) 2A, 4 and 5 deposits, i.e. 2B/[2A + 4 + 5]. In Table 27b(2) (Appendix 1) larger values for these ratios for the soluble phases illustrate the greater mobility of such phases.

Similar treatments are performed to obtain ratios for the four major chemical species in the form of major single salt phases soda nitre, epsomite, thenardite and halite (Appendix 1, pp.47, 48, Tables 27a(4) and 27b(3)). Again we refer to Aztec-Kennar-Labyrinth areas as for Figure 3.2, once more enabling control of the two independent variables, ion supply and moisture availability. The same type of data from the more widespread area of the oasis (as for Fig.3.1) are treated in Appendix 1, Table 27b(1), page 47. The sets of ratios in each of these three tables are compared in Table 3.2. In the Aztec, Kennar and Labyrinth areas, both sets of mobility ratios suggest that the mobility increases in the order

thenardite, epsomite, soda nitre, halite

This sequence holds in the more widespread area for the mobility ratio of deaquation deposits to subsurface deposits.

However, the order of mobilities of soda nitre and halite is reversed when 2A deposits are considered in the more widespread area (Table 3.2). The reversal is due mainly to an increased occurrence of halite in surface efflorescences there (Fig.3.3). This suggests that the reversal is an artifact of uncontrolled independent variables.

The mobility ratio that involves occurrence in 2A deposits also measures a tendency for phases to be concentrated at the surface of the soil. This tendency depends on the rate of movement of soil brines to, and rate of evaporation at the soil surface, as well as on moisture availability, salt properties and ion abundance. Figures 2 and 4 in Appendix 1 show that most deposits studied in the more general area of the oasis lie to the east of those in the Aztec-Kennar-Labyrinth areas. More moisture is available for salt migration, and moisture

Table 3.2 Comparison of mobility ratios of four major chemical species as the single salt phases. Mobility ratios are ratios of occurrences (%) of phases in deposit types as shown.

			Phase (species)			
Geographical area	Table in Appendix 1	Mobility ratio	thenardite (Na_2SO_4)	epsomite ($MgSO_4$)	soda nitre ($NaNO_3$)	halite (NaCl)
Aztec, Kennar Labyrinth	27a(4) page 47	2B/[4 + 5]	0.53	0.8	1.1	3.9
"	"	2B/[2A+4+5]	0.44	1.0	1.2	2.5
"	27b(3) page 48	2B/[4 + 5]	0.27	0.4	0.6	2
"	"	2B/[2A+4+5]	0.18	0.4	0.5	1
Taylor, Wright, Ferrar, Skelton, Kempe	27b(1) page 47	2B/[4 + 5]	0.061	0.11	0.29	0.39
"	"	2B/[2A+4+5]	0.042	0.10	0.25	0.21

Table 3.3 Relative frequency (percent) of 2A and subsurface deposits of soluble salts, as a function of increasing distance from the coast. Data for Taylor, Wright, Ferrar Valleys and Skelton Névé for deposits that contain only one deposit type, in Appendix 1, Tables 3, 5, 6.

	Distance from the coast (km)		
Deposit type	20-40	40-70	>70
2A	40	26	19
subsurface (4 + 5)	60	74	81
number of deposits	20	42	37

flux is greater in these more eastern sites (Fig.2.7). However, temperatures are warmer and average relative humidity is less (Appendix 3, sections 3.2, 3.3, 6.1, 6.2); hence, surface evaporation of soil water containing salts (2.3.4) is probably more intense towards the east, especially in the central most sampled parts of the valleys studied. Thus, the frequency of 2A deposits increases from the Aztec-Kennar-Labyrinth area east towards the coast (Table 3.3). Therefore, the ratio 2B/[2A + 4 + 5] will not give a satisfactory measure of the tendency for specific phases to be leached into closed basins if data are taken from a large area.

It is concluded that the ratio 2B/[4 + 5] most reliably defines salt mobility. This ratio indicates that the mobilities increase in the order:

calcite, gypsum, thenardite, epsomite, soda nitre, halite, antarcticite

or

$CaCO_3$, $CaSO_4$, Na_2SO_4, $MgSO_4$, $NaNO_3$, $NaCl$, $CaCl_2$.

This series characterizes the geochemical soil sequence in McMurdo oasis.

CHAPTER 4 LOCAL MIGRATION AND SEPARATION PROCESSES

4.1 Preamble

4.1.1 The role of moisture:

This chapter examines the processes causing salts to migrate and separate on a local scale. It explains the characteristic order of salt mobilities determined in the previous chapter. Soil moisture, particularly water, plays a fundamental role in salt migration. Differences in salt properties cause salt separation, during (a) the initial dissolution stage of salts by moisture, (b) possibly during the migration stage of salt solutions, and (c) during the deaquation stage of solutions. Wind and former lakes also cause migration and separation of salts.

The migration of salts in soil water in oases has been known since the work of Glazovskaya (1958). Since then numerous workers have established that the amount and availability of moisture, particularly water, exert a major control on salt accumulation, and migration (e.g. Claridge 1965; Ugolini and Bull 1965; Tedrow and Ugolini 1966; Campbell and Claridge 1967, 1968, 1969, 1975; Claridge and Campbell 1968a, b, c, 1977; Everett 1971; MacNamara and Usselman 1972). Salt migration is very restricted in the most arid or ultraxerous soils; salts accumulate in such soils to form subsurface deposits (types 4 and 5). As moisture content and availability increase so too does migration of salts; the salts become disseminated throughout the soil so that salt horizons do not develop. The accumulation that does occur is mainly at the surface (2A) and beneath surface cobbles (4). Therefore the tendency for north-facing slopes to have more 2A deposits than south-facing slopes (3.3.2) is probably due to the higher moisture availability on the former (2.3.2); migration appears to be more active on north-facing slopes. Similarly, the increasing frequency of 2A deposits towards the coast in McMurdo oasis (Table 3.3) is due to increased moisture availability towards the east (Fig.2.7). Many observations have shown that the individual salt deposits usually contain much less salt in moister areas than in arid areas; this is because less salt can accumulate in the moister conditions.

It will be shown here that separation of salt phases is achieved at various stages during the migration process largely as a result of different physico-chemical properties of the various phases. These properties cause different salts to respond differently to the moisture present. Obviously, separation can only occur when sufficient moisture is present to allow migration. The amount of moisture that is "sufficient" may be very low.

4.1.2 Previous work:

Some previous work has been done on the processes of antarctic salt migration and separation. The work is briefly discussed to provide a background to this present chapter.

Ugolini and Anderson (1972) proved that migration of salts in thin liquid films occurs in situ in dry antarctic soils; two different ions Cl^- and Na^+ had different migration rates. Field (1975) reviewed literature reporting laboratory studies which suggested that such liquid film transport is the principal means of migration of dissolved salts in unsaturated soils whose temperature is colder than 0°C (Cary and Mayland 1972). The migration is slow and decreases rapidly with decreasing temperature (Hoekstra 1966). Salt diffusion under concentration gradients and water vapour diffusion are less important mechanisms of salt transfer. Salt solubility and cation exchange on active surfaces of soil particles may affect the amount and type of salt migrating; the most mobile salts appear to be the more soluble phases and those whose ions do not enter into exchange.

Selective absorption of water vapour by salts has been proposed to explain their migration and separation in antarctic soils (Wilson 1979). He considered that at high elevations in McMurdo oasis fluctuations of relative humidity at the surface of the regolith and within it "cause some of the more deliquescent salts to slowly percolate downwards through the soil" (ibid. p.207). Hypothetically, the least deliquescent salts are left behind. "The more deliquescent will reach the frozen water table," and slowly migrate downslope along this. In the more arid environment at lower elevations some salts are (hypothetically) no longer deliquescent and crystallize out; supposedly only the most deliquescent salts reach the bottom of the slope. Wilson produced little evidence to support his hypothesis, but did state that the less deliquescent salts (e.g. thenardite, mirabilite) exist at higher elevations, halite at intermediate elevations, and calcium and magnesium chlorides (the most deliquescent) at the lowest elevations in the drainage systems.

This order of relative mobilities is similar to that derived in the previous chapter but that listing did not include magnesium chloride.

There is some other evidence for Wilson's hypothesis. Ugolini and Bull (1965) and Cameron and Conrow (1969) showed that soluble salts in dry antarctic soils do absorb water vapour to some extent. Absorption has also been demonstrated in the laboratory wherein the movement of soluble salts down salt-impregnated strips of chromatography paper and a soil column was studied (Keys 1972). The strips and soil were suspended in atmospheres of different but fixed relative humidities of between 32 and 100 percent at temperatures of mainly +20°C but also at +3°C. The studies showed that at these temperatures at least, water vapour could dissolve soluble salts and cause separation of phases.

In the field, Wilson's process requires three environmental conditions to exist: (1) relative humidities that are high enough for a sufficient length of time to dissolve the more deliquescent salts; (2) temperatures that are warmer than the eutectic temperatures of the aqueous system involved (see below); (3) a negative gradient of relative humidity down slopes. These conditions appear to be often satisfied in summer at least: relative humidities are as high as 100 percent (Appendix 3, section 6.1; also subsection 2.3.1iii); temperatures within the regolith are often warmer than 0°C (2.2.2, Table 2.5); negative humidity gradients exist at times (Appendix 3, Fig.8).

Wilson's hypothesis seems plausible on the basis of the preceding discussions. However, it will be shown by physico-chemical arguments that relative deliquescence is not the fundamental mechanism effecting salt migration and separation in the McMurdo region.

4.1.3 Simplifying assumptions:

The physical chemistry of dissolution, non-isothermal evaporation and freeze-concentration of aqueous multicomponent salt systems is complex. The solubility of specific salts in water and their tendency to absorb water are dependent on temperature and may be strongly influenced by the presence of other phases (Adams and Merz 1929; Berner 1971). This influence is mainly dependent on the nature and the concentration of the phases involved and the temperature diversity, all of which affect chemical equilibria between the ions.

The major ions present in the general, multicomponent antarctic salt system are Na^+, Ca^{2+}, Mg^{2+}, K^+, Cl^-, SO_4^{2-}, NO_3^-, HCO_3^- and CO_3^{2-} (see Appendix 1, Table 1, p.12). The temperature range is from at least as cold as -53°C (the freezing point of Don Juan Pond in December 1971, as determined by Cameron et al. 1972) to at least as warm as +21.1°C (temperature of wet surface sand at Table Mountain on 22/1/74, Table 2.3). No data are available describing the solubility or the ability to absorb water vapour of individual phases in this multicomponent system over this wide range of temperatures. Therefore, a number of simplifications are necessary.

As a first approximation the general multicomponent system can be considered as being composed of three cations (Na^+, Mg^{2+}, Ca^{2+}), three anions (Cl^-, SO_4^{2-}, NO_3^-) and water. In most areas in the McMurdo region HCO_3^-, CO_3^{2-} and K^+ are present in low concentration in salt solutions (e.g. Campbell and Claridge 1967; Bockheim 1979b). Unfortunately, sufficient data do not exist for this simplified system either. This is probably for three main practical reasons. Firstly, any system involving Ca^{2+} and SO_4^{2-} deals with gypsum which requires some weeks to reach equilibrium in solution (Hill and Wills 1938). Secondly, it is difficult to present great mass of solubility data in a diagrammatic fashion for a system of six ions or five independent salt phases and water. Thirdly, the determination of solubilities and vapour pressures for the number of independent salts involved would be a long process indeed.

Sufficient data are not available at most temperatures of interest for all the sixteen ternary systems composed of two independent salts and water, or the higher systems, that comprise the simplified multicomponent system. Therefore, the most simplistic approach of all must be considered - the binary systems of one salt and water, for the salts of interest. This is the approach that was used by Field (1975) and Wilson (1979). Also, the binary approach successfully described separation between phases in ternary systems when absorption of water vapour (relative deliquescence) was examined (Keys 1972).

Some literature data are available for ternary and higher systems. In the following discussions, reference is made to the aqueous systems Na/K/Cl, Ca/Mg/Cl, Ca/Mg/Na/Cl, Na/Mg/SO_4, Na/Cl/SO_4 and Na/Cl/SO_4/NO_3 at certain temperatures, Reference to these systems shows that the binary approach is fairly satisfactory for phases with significantly different solubilities and eutectic temperatures. Until further data are available, the binary model must be used as a basis for the following discussions.

4.2 Dissolution

4.2.1 Physico-chemical controls:

Dissolution is the process of a salt dissolving in sufficient moisture (liquid or vapour) to form a solution. Migration of salts takes place after dissolution has occurred. We have seen that moisture is the primary controller or determining factor for salt migration. If sufficient moisture is available then dissolution and hence salt migration can occur. Separation between salts may occur at the time of dissolution (fractional dissolution) due to differences in physico-chemical properties. For example, if a deposit of several salts is washed by water then the more soluble phases are dissolved and move away in solution, leaving the less soluble phases behind (Glazovskaya 1958; Eugster and Jones 1979).

There are several secondary controls of a physico-chemical nature that, theoretically at least, may be important to the problem of salt dissolution in Antarctica. The eutectic temperature of a salt phase must be considered as well as solubility in the low temperature antarctic environment. The eutectic temperature of a salt phase is the lowest temperature at which the salt can exist in aqueous solution; below this temperature it cannot dissolve but may coexist in the solid form with ice. The salt may dissolve above its eutectic temperature and thus migrate if sufficient moisture is available. Separation would be achieved by differential dissolution. The relative solubilities of phases at their eutectic temperatures may also affect salt separation. The eutectic temperatures and solubilities of salts in binary aqueous subsystems of the Na/Mg/Ca/Cl/SO_4/NO_3/H_2O system plus some other salts are given in Table 4.1 and Figure 4.1.

Temperatures at the surface and within the regolith fluctuate around the eutectic temperatures, which range from 0 to -52°C (Appendix 3, Tables 2, 3; section 2.2, Tables 2.2-2.5). Therefore eutectic temperatures could exert a control on salt migration and separation.

Table 4.1 Eutectic temperatures and concentrations in binary aqueous systems, and solubilities, of some salt phases: from data in International Critical Tables (1926); Smithsonian Inst., (1954); Timmermans (1960); Mellor (1961); Lange (1961); Stephen and Stephen (1963); Hill and Bacon (1927); Kaye and Laby (1958). (Solubilities in kg of anhydrous salt per 100 kg of saturated solution.)

Phase	Eutectic Temperature (°C)	Eutectic Concentration	Solubility -10°C	Solubility 0°C	Solubility +10°C
calcite	0	0.01	-	0.0081	0.0070
nesquehonite	c.0	0.2	-	0.17	0.18
gypsum	c.0	0.2	-	0.176	0.192
mirabilite	- 1.2	3.8	-	4.6	8.2
natron (1)	- 2.1	5.9	-	6.9	12.5
nahcolite	- 2.3	6.3	-	6.5	7.5
epsomite (1)	- 3.9	19.0	-	20.5	23.5
sylvite	-10.8	19.8	19.9	21.8	23.7
soda nitre	-18.5	39	40.2	42.2	44.6
(nitrocalcite) (2)	-20	34	34.2	39.0	42.5
halite (1)	-21.2	23.2	24.8	26.2	26.4
(nitromagnesite) (2)	-31.6	32.3	37.4	38.3	39.8
(bischofite) (3)	-33.6	21.6	33	34.6	34.9
antarcticite	-52	30.5	35.8	37.7	40.0

(1) thermonatrite epsomite and halite are metastable at their respective eutectic temperatures: data are given for the stable phases $Na_2CO_3.10H_2O$, $MgSO_4.12H_2O$ and $NaCl.2H_2O$

(2) calcium and magnesium nitrates have not been detected in Antarctica: nitrocalcite, $Ca(NO_3)_2.4H_2O$ and nitromagnesite, $Mg(NO_3)_2.6H_2O$ are known outside Antarctica (Palache _et al._ 1951)

(3) magnesium chloride has been detected in antarctic soils but bischofite has not been characterized

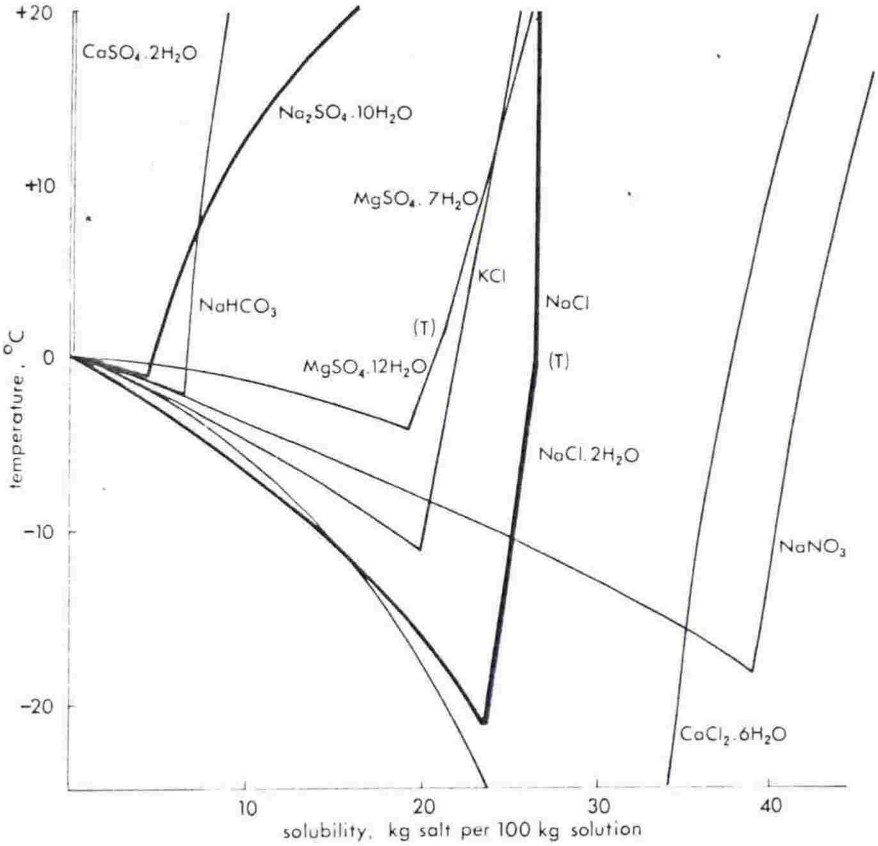

Figure 4.1 Freezing point depressions, eutectic points, and solubilities of some antarctic salts. (T) are transition points.

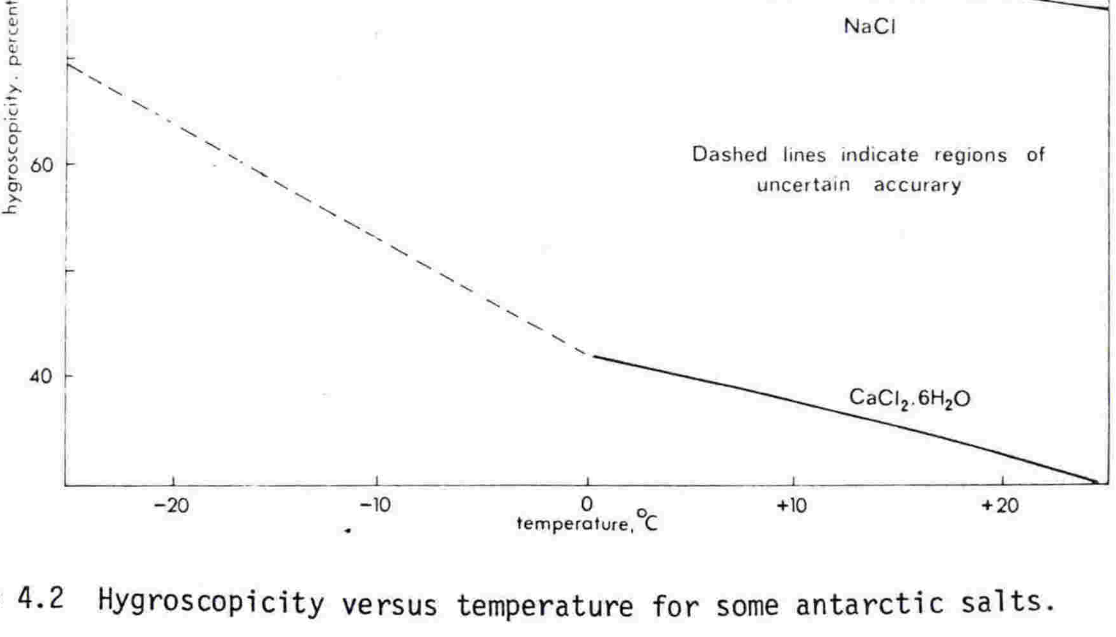

Figure 4.2 Hygroscopicity versus temperature for some antarctic salts.

The least mobile salts would be those with highest eutectic temperatures (e.g. calcite, gypsum) whereas the most mobile would be those with the lower eutectic temperatures (e.g. antarcticite). If solubility controlled the mobility then mobility should increase with increasing solubility; calcite would be least mobile and soda nitre would be most mobile.

A third factor which theoretically effects dissolution and separation is relative deliquescence (Wilson 1979) or the hygroscopicity of a salt (Markowitz and Boryta 1961). The hygroscopicity of a salt is equal to the relative humidity maintained over a saturated aqueous solution of that salt in a closed environment. Like solubility, hygroscopicity is temperature-dependent. If the relative humidity of the atmosphere surrounding the salt is greater than the hygroscopicity of a salt, then that salt will show a thermodynamic tendency to absorb water vapour until it dissolves. In relatively dry soils this salt property causes significant movement of water vapour along the vapour pressure gradient induced by the salt (Scotter 1974a). However, the actual mechanism of dissolution of salt by this process is subject to debate (Parlange 1973; Scotter 1976). In any case, laboratory studies have shown that at temperatures as low as +3°C, at an atmospheric humidity midway between the hygroscopicities of two soluble salts, the one whose hygroscopic point is exceeded will preferentially dissolve and may then migrate away from the other (Keys 1972).

Hygroscopicity data are scattered in the literature and scarce for temperatures colder than 0°C. Interpolation techniques using vapour pressures over saturated solutions were required to derive such data. The hygroscopicity f_s of a salt is related to the spontaneous fugacity or vapour pressure e_s of its saturated solution by the relations

$$f_s = \frac{e_s \times 100}{E_w} \quad (\text{temperature} \geqslant 0°\text{C}) \qquad \ldots\ 4.1$$

and

$$f_s = \frac{e_s \times 100}{E_i} \quad (\text{temperature} < 0°\text{C}) \qquad \ldots\ 4.2$$

where E_w and E_i are the saturation vapour pressures of water and ice respectively (see Appendix 3, Table 16, Fig.6, and section 6.1). At any absolute temperature T (°K) the natural logarithm of e_s is very nearly proportional to the reciprocal of T (Hirschler 1936; West and Menzies 1937); that is

$$\ln e_s = \frac{a}{T} + b \qquad \ldots 4.3$$

(a, b constants) to a good approximation. Furthermore, at the eutectic temperature (Table 4.1) of an aqueous salt system

$$e_s = E_i \qquad \text{or} \qquad f_s = 100\% \qquad \ldots 4.4$$

The interpolation technique for each salt was to (1) plot $\ln e_s$ against $\frac{1}{T}$ (Equation 4.3) for known e_s or f_s (using Equation 4.4 and literature values*); (2) draw the best fit line through the data points; (3) interpolate to obtain values of e_s for temperatures at which it is not known (generally those less than 0°C); (4) convert these e_s to f_s (using Equations 4.1 and 4.2). Table 4.2 and Figure 4.2 summarize data obtained in this way.

The probable effects of these various properties on the salts can now be compared, making an assumption that is basic to the binary model assumed here (4.1.3). The assumption is that if the mobility of a specific salt is dictated by a specific physico-chemical property, then that property will also control relative salt mobility. Thus, the relative order of that specific property (e.g. hygroscopicity) of the various salts should be the same as the observed sequence of salt mobilities. The relative ordering in the properties of various salts are shown in Table 4.3, together with the sequence of salt phase mobilities determined in subsection 3.3.3. The order of eutectic temperatures, and hygroscopicities below about +1°C, are both the same as observed relative mobilities; thus, either of these two properties could control mobility. However,

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*Useful literature: Edgar and Swann (1922), Carpenter and Jette (1923), International Criticial Tables (1926), Leopold and Johnston (1927), Adams and Merz (1929), Hepburn (1932), Shibata and Miwa (1935), Glasstone (1940), Korolev (1940), O'Brien (1948), Carr and Harris (1949), Stokes and Robinson (1949), Rockland (1960), Timmermans (1960), Young (1967).

Table 4.2 Hygroscopic points (percent) of some salt phases.

Phase	Hygroscopic point -10°C	 0°C	 +10°C
calcite	100	100	100
nesquehonite	100	100	-
gypsum	100	100	99
mirabilite	100	98	91
natron	100	>99	99
nahcolite	100	98	96
epsomite	100	96	93
sylvite	99	89	87
soda nitre	91	81	78
halite	87	76	76
nitrocalcite	68	64	60
nitromagnesite	67	61	58
antarcticite	63	52	38
bischofite	34	34	33

eutectics would control mobility over the whole range of soil temperatures experienced (4.1.3). Solubilities in the binary systems do not appear to control salt dissolution and hence separation of phases down slopes.

To determine whether the primary physico-chemical control for salt separation is eutectic temperature or hygroscopicity, other salts may be considered. Near the coast in Taylor Valley (Nishiyama 1977) the relative mobilities of the soluble phases present appear to be

$$Na_2SO_4,\ NaHCO_3 = Na_2CO_3,\ NaCl$$

This is the order of eutectic temperatures (Table 4.1) of these phases but not their hygroscopicities (Table 4.2), which suggests that eutectic temperatures exert the main physico-chemical influence on separation. The position of KCl in the mobility series cannot be used to determine the physico-chemical property controlling separation. With the binary approach used here, both eutectic temperature and hygroscopicity models place sylvite between epsomite and soda nitre (Table 4.3).

Table 4.3 Observed relative mobilities of salt phases compared to relative order of various properties of these salts in binary systems. Phases are shown as anhydrous forms.

Property		Order
observed relative mobilities, increasing (from subsection 3.3.3)		$CaCO_3$, $CaSO_4$, Na_2SO_4, $MgSO_4$, $NaNO_3$, $NaCl$, $CaCl_2$
eutectic temperature, decreasing (Table 4.1)		$CaCO_3$, $CaSO_4$, Na_2SO_4, $MgSO_4$, $NaNO_3$, $NaCl$, $CaCl_2$
hygroscopic point, decreasing (Table 4.2)	-10°C	$CaCO_3 = CaSO_4 = Na_2SO_4 = MgSO_4$, $NaNO_3$, $NaCl$, $CaCl_2$
	0°C	$CaCO_3$, $CaSO_4$, Na_2SO_4, $MgSO_4$, $NaNO_3$, $NaCl$, $CaCl_2$
	+10°C	$CaCO_3$, $CaSO_4$, $MgSO_4$, Na_2SO_4, $NaNO_3$, $NaCl$, $CaCl_2$
eutectic concentration, increasing (Table 4.1)		$CaCO_3$, $CaSO_4$, Na_2SO_4, $MgSO_4$, $NaCl$, $CaCl_2$, $NaNO_3$
solubility, increasing (Table 4.1)	-10°C	- - - - $NaCl$, $CaCl_2$, $NaNO_3$
	0°, +10°C	$CaCO_3$, $CaSO_4$, Na_2SO_4, $MgSO_4$, $NaCl$, $CaCl_2$, $NaNO_3$

Solubilities do influence salt separation, even though they do not control it in the binary model. Nitrates, the most soluble salts, show some tendency to preferentially accumulate on south-facing slopes (3.3.2). This is probably because such slopes are subject to less leaching, having lower moisture availability than north-facing slopes (2.3.2). Campbell and Claridge (1967) illustrated this by considering three soil sites with different aspects in an enclosed basin near Darwin Glacier.

4.2.2 Wilson's argument:

Wilson (1979) believed that hygroscopicity, not eutectic temperature, caused salt separation. His argument was based on

Na/K and Mg/K ratios in freeze-concentrating sea water compared to those in saline ground water and lakes in Wright Valley, particularly around Don Juan Pond. Few antarctic data were presented to support the argument (4.1.2).

The argument is unsoundly based on several counts. The salts in McMurdo oasis are generally not in the same proportion as they are in sea water, and in fact differ widely in composition and concentration (e.g. Morikawa et al. 1975; Claridge and Campbell 1977; Bockheim 1979b; and this thesis). Thus, soil brines also differ in composition and concentration between themselves and from sea water (see also Table 4.5). Such differences together with variable temperatures cause different behaviour of ionic ratios on dissolution and deaquation. Precise behaviour depends on precise conditions, as will be seen in the following subsections. Furthermore, the use of ionic ratios is plagued by ambiguities. Chemical weathering of rock and soil particles may alter Mg^{2+}, Ca^{2+} and K^+ ratios (Claridge and Campbell 1977; and Chapter 6). Ion exchange processes may deplete K^+ (Field 1975; Keys 1979; and 4.3.4). Thus, even if the original source of salts in McMurdo oasis is largely sea water (Chapter 6), fractionation processes obscure changes in ionic ratios; therefore, these must be used with caution when determining ion enrichment or depletion. Wilson (1979) did not consider these problems and so his argument is largely invalid.

4.2.3 Relative mobility of chloride phases:

Multicomponent systems need to be considered to examine the problem of KCl mobility in particular and the other chlorides in general. Aqueous systems can be considered that contain chloride as the only anion: sulphate and nitrate are present in low concentration in Don Juan Pond brine and the suprapermafrost flow of Wilson (1979) (Meyer et al. 1962; Cameron et al. 1972; Field 1975). These are the brines of immediate interest here.

The aqueous ternary system Na /K /Cl is examined. Figure 4.3 illustrates equilibrium concentrations in this system at -22.9°C, which is the ternary eutectic temperature (Cornec and Krombach 1932) and also the crystallization point of dihydrohalite ($NaCl.2H_2O$) in freeze-concentrating sea water (Thompson and Nelson 1956).

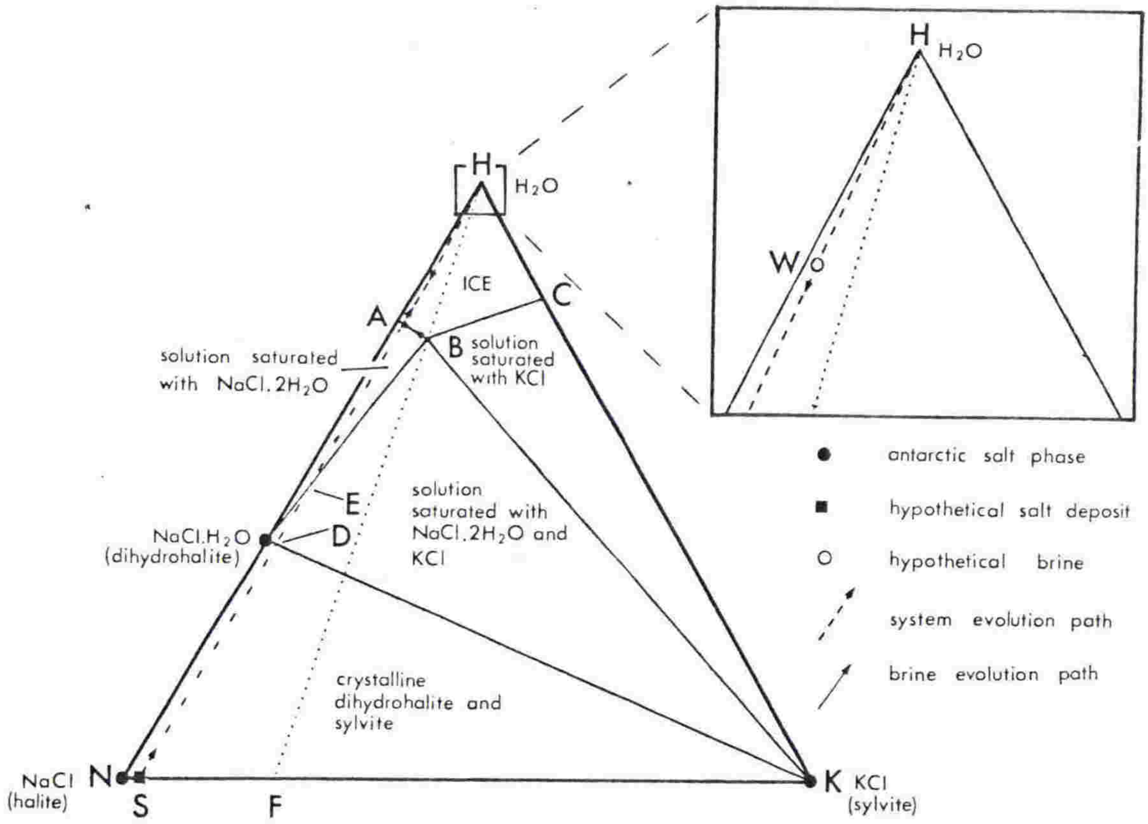

Figure 4.3 The system $Na/K/Cl/H_2O$ at -22.9°C constructed in weight percent from data of Cornec and Krombach (1932) and Mellor (1961). Lines AB, BC are shown straight for simplicity. S represents a salt deposit formed directly from sea water, W an approximation to a sea water brine. The line SDEWH is the path along which the sea salt system evolves during dissolution or deaquation (see text).

The three apexes N, K and H represent points with 100 percent NaCl, KCl and H_2O respectively. Points A and C represent the eutectic concentration of NaCl and KCl respectively in their binary aqueous systems (Table 4.1). B is the univariant point representing the concentrations of NaCl and KCl in the solution saturated with both $NaCl.2H_2O$ and KCl, and in equilibrium with ice, dihydrohalite and sylvite (Cornec and Krombach 1932; Mellor 1961). Lines AB and BC have been straightened for simplicity, this straightening having very little effect on the subsequent arguments. The non-central position of B and the large field for solutions saturated with KCl alone, show that NaCl has greater solubility than KCl in this system. This relationship holds at all temperatures of interest (Mellor 1961).

Isothermal steady state dissolution is considered first. Point S in Figure 4.3 represents the concentrations of NaCl and KCl in a salt deposit formed from deaquated sea water (derived from the sea water ratio Na/K = 27.8, Sverdrup et al. 1942; i.e. approximately 97.4% NaCl, 2.6% KCl as a simplification). A straight line from S towards H represents the path that the system follows when moisture (liquid water or water vapour, RH = 100%) is added at -22.9°C. Between points D and E on this path a solution is present that is (1) saturated with both $NaCl.2H_2O$ and KCl, and (2) in equilibrium with solid dihydrohalite, sylvite and ice. The composition of this solution is given by B. Further addition of moisture at -22.9°C changes the concentrations in the saturated solution along BA. The solution is no longer saturated with KCl; all sylvite originally present in the deposit has been leached from it, and is now in solution. Thus sylvite is more mobile than halite in these conditions.

An opposite sequence can be loosely applied to a sea water brine W hypothetically deaquating isothermally at -22.9°C. The line HWS along which Na/K equals 27.8 is an approximation to the real case. At this temperature in deaquating sea water Na/K would equal about 23 (Thompson and Nelson 1956) due to previous precipitation of mirabilite. The system evolves along line WS, and the saturated solution moves along line AB. Dihydrohalite crystallizes from the solution after that has reached B. This sequence shows why dihydrohalite is crystallized from sea water before sylvite (Thompson and Nelson 1956) even though the latter is less soluble and has a lower eutectic temperature in the binary system (Table 4.1). Brines lying within the triangle HBC, in which the Na/K ratio is less than 2.63 (the univariant composition of B, Cornec and Krombach 1932) will crystallize sylvite first on freeze-concentration at -22.9°C. Similarly halite will be leached from chloride deposits before sylvite if the Na/K ratio is less than 2.63 represented by deposits that would lie along the line FK. These ratios are modified by the presence of other ions and at other temperatures but the basic inequality remains.

From the discussion above it is apparent that after moisture availability, eutectic points and salt solubilities control chloride and other salt separation in multicomponent systems. Temperature and composition exert further controls. This is further illustrated in Table 4.4 which shows the behaviour of Mg/Ca ratios in two aqueous chloride systems at equilibrium. The affect of composition is marked when the brines are in equilibrium with ice. The relative ordering in the apparent mobilities of the end members of the salt series is dependent on these controls.

Table 4.4 Mg/Ca ratios in two aqueous chloride systems (determined from data of Prutton and Tower 1932; Linke 1965).

System	Phases in equilibrium with saturated solution (n = 6, 8, 12 depending on temperature)	Temperature (°C) 0	-15	-30	system eutectic
Ca/Mg/Cl	$CaCl_2.6H_2O$, $MgCl_2.nH_2O$; plus ice at eutectic temperature	1.22	1.59	0.259	0.076 (-52°C)
Ca/Mg/Na/Cl	as above plus $NaCl.2H_2O$	1.2	-	-	0.15 (-58°C)

4.2.4 Relative effectiveness of the dissolution processes:

The process of dissolution is dependent on the presence of moisture. Dissolution is usually diffusion-controlled (Berner 1971). Thus for a particular salt, the rate of dissolution is dependent on the amount and rate of movement of surrounding moisture. Dissolution is slow and separation of phases not very effective, when mass flux of moisture is low, which is normally the case in soils towards the western parts of McMurdo oasis (Fig.2.7). However separation is apparent in places in such areas. Therefore this lack of effectiveness appears to have been offset by the long time that surfaces have been free of ice (1.2.4, 1.2.5).

The largest quantity of water is available during summer. Liquid films are likely to reach their greatest average thickness during this season and therefore most salt is probably dissolved then. In some areas a single extreme melting event (Chinn 1979) probably causes a greater mass of the more soluble salt phases to migrate over a period of several days than would migrate over several years of more normal melting. Relative solubilities may be more important than other properties in such areas. More soluble phases dissolve more rapidly during floods elsewhere in the world (Gorham 1961); such floods are analogous to extreme melting events in McMurdo oasis.

The various physico-chemical properties (e.g. eutectic temperature and hygroscopicity) that may control or influence salt dissolution may cause a particular salt to dissolve at different rates, that is to be of differing effectiveness at causing dissolution. The relative effectiveness of any physico-chemical mechanism of dissolution is assumed to be mainly dependent on the mass and form of moisture available. Liquid films are more important than vapour transfer for the transportation of soil moisture in McMurdo oasis (2.3.3). Dry soils with gravimetric water contents as low as 1% (2.3.1ii), having densities of about 10^3 kg m^{-3} (Metson 1956), contain about 10 kg of water in thin films per cubic metre of soil in summer. This is 4 orders of magnitude larger than the amount of water vapour in a cubic metre of air, whose relative humidity is 60 percent, which is a reasonable value for soil with 1% moisture (2.3.1iii; Appendix 3, section 6.1). Therefore salt properties that affect salt-liquid interactions (e.g. eutectic temperatures, solubilities) are likely to be more important than those properties affecting salt-vapour interactions (e.g. hygroscopicity).

Hygroscopicity gives a measure of the thermodynamic tendency for a phase to absorb water vapour under ambient conditions, but says nothing about the kinetics of the absorption. The rate of absorption probably slows as vapour is absorbed. It is concluded that absorption of vapour, sufficient to cause dissolution, is slow in frigid, arid conditions. Dissolution by thin film water is faster.

4.3 Movement of Brines Within and on Top of the Regolith

4.3.1 Thin films:

The movement of soil moisture has already been discussed in subsection 2.3.3. The main methods of flow of soil brines in order of decreasing mass flux per unit time are: (1) gravity drainage involving overland flow or suprapermafrost flow; (2) capillary action around streams, lakes and channelled flows; and (3) thin liquid films. Any soil brines formed by adsorption of water vapour are likely to form thin films. We have seen that these methods have different spatial and temporal variations depending on location and season. Generally method (3) is probably most widespread in cold xerous, antarctic soils (2.3.3), and is probably most active towards the east during summer.

The movement of salt through antarctic soils was studied in situ by Ugolini and Grier (1969) and Ugolini and Anderson (1972). Radioactive ions $^{36}Cl^-$ and $^{22}Na^+$ were placed at the top of the ice-cemented tables at soils in Wright Lower Valley and at Cape Royds; gravimetric moisture contents of the soils were < 1-3% and 2-7% respectively. At the latter site the radioactive chloride tracer moved 21 cm to the surface in 40 days from 1/11/68 to 10/12/68. In the drier, colder Wright Valley the $^{36}Cl^-$ tracer moved only 7 cm upwards during 25 days of subzero temperatures (Ugolini and Grier 1969). This illustrates that salt movement is by films of liquid moisture; liquid films are thinner and moisture flux is less in the drier Wright Valley soils than at Cape Royds. Comparisons between the positively charged $^{22}Na^+$ ions and the negative $^{36}Cl^-$ ions were made at sites in Wright Lower Valley. The sodium ions moved consistently slower than choride. The difference was explained by Ugolini and Anderson (1972) as being due to adsorption of the positive ions in the thin liquid film, onto negatively charged silicate surfaces in the soils; the migration of chloride is not hindered by such adsorption since it is itself negatively charged.

Differential ion movement may be caused in other ways. Concentration differences in soils may produce differential movement in thin films as salts diffuse down concentration gradients; thermal diffusion (i.e. the Soret effect) is negligible (Cary and Mayland 1972). Generally smaller and monovalent ions diffuse more rapidly than larger polyvalent ions in soils; however, the amount of hydration around the ions influences their effective radius and hence their relative diffusion rates (Savich 1970). In increasingly concentrated solutions complexing between ions becomes important , also affecting ion size and hence movement. Such differential movements may all be obscured by ion exchange or adsorption processes. Ratios between ions need to be examined to investigate this, as is done in subsection 4.3.4.

4.3.2 Free drainage and capillarity:

Flow of brines under gravity through soils appears to be an important local process especially in summer. Plate 4.1 shows three distinct areas of such flow in Taylor Valley near Lake Bonney. These flows represent saline water moving down the surface of the ice-cemented table (suprapermafrost flows). Flow is controlled by the slope of the ice-cemented table rather than the surface slope (Linkletter 1970). Field (1975) estimated a flow rate of about 10^{-4} m^3 min^{-1} in one of the saline flows on the northern bank of Lake Bonney (Plate 4.1), and about 10^{-3} m^3 min^{-1} in a flow towards Don Juan Pond in South Fork, Wright Valley. Such flow systems may be small and several can exist unconnected in close proximity (Cartwright and Harris 1976). These authors consider that none of the suprapermafrost flows in the vicinity of Don Juan Pond or Lake Vanda has a measurable effect on the water budget of the two lakes. In Taylor Valley where there is much more suprapermafrost ground water than in Wright Valley, such contribution is also very minor (Cartwright et al. 1975).

However, these flows may contribute appreciable amounts of salt to the lakes (Field 1975; Wilson 1979). Analyses of the two suprapermafrost flows sampled by Field (1975) are shown in Table 4.5. These are compared with some analyses of streams in the oasis and sea water. Ground water flows are very saline; they transport larger amounts of salt relatively slowly. Surface streams are dilute; they transport small amounts of salt quite swiftly. Most of such movement is likely to be confined to summer although the saline flows with their slow speeds and high concentrations may flow on into autumn; these two flows will commence freezing at -2.5 and -5°C respectively (calculated from Sverdrup et al. 1942). Geographic trends can probably be followed in the compositions of the streams and flows but this would require another study and is outside the scope of this thesis. The possible influence of ion exchange on the compositions is discussed in 4.3.4.

Salts or saline waters may accumulate where surface or subsurface flows are obstructed by bedrock or boulders or where they terminate in closed basins. This is discussed in the following section (4.4). However, the influence of these flows on capillarity is briefly discussed here.

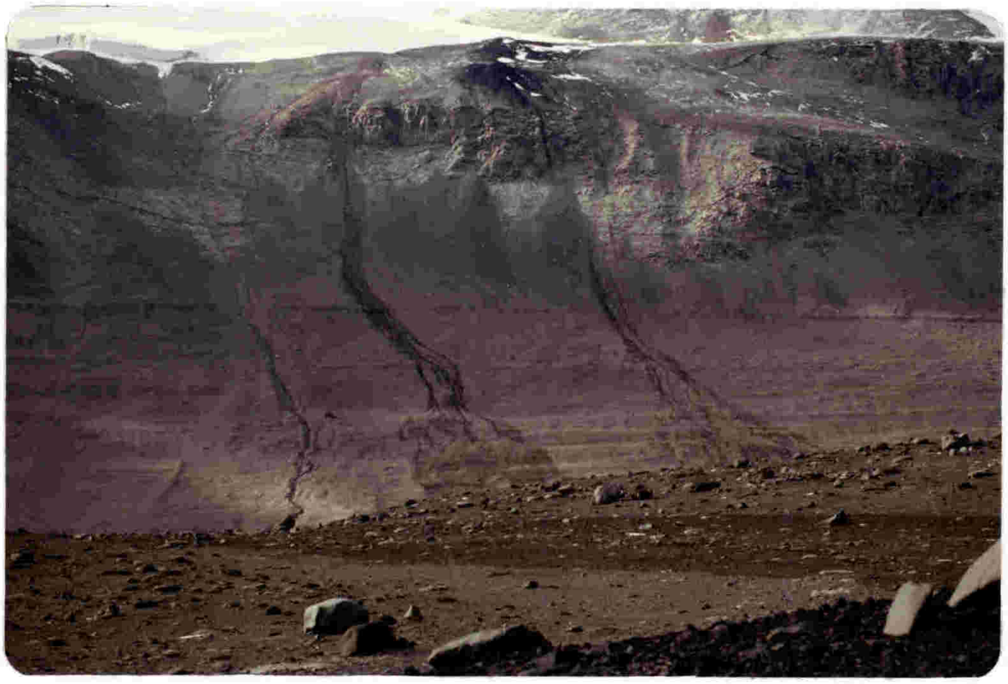

Plate 4.1 Suprapermafrost saline flows near Lake Bonney. Two flows and a dry stream course are visible crossing former lake levels on the north side of Taylor Valley below Matterhorn Glacier. A flow moving slowly from right to left is present in the foreground. (7/1/75)

Plate 4.2 Salt slick on the surface of the regolith on the south side of Taylor Valley, up valley from the terminus of Taylor Glacier. The slick probably marks the position of an inactive saline flow, from which salts were brought to the surface partly or wholly by capillarity. (23/10/76)

Table 4.5 Ionic concentrations in suprapermafrost flows and streams in McMurdo oasis, after Field (1975), Torii *et al.* * (1975), and Yamagata *et al.* † (1967) (Units g m^{-3} ≑ ppm*†).

Location	Na	K	Mg	Ca	Cl	SO_4
Suprapermafrost flows						
north bank, East Lobe Lake Bonney	8560	510	4750	2510	25490	4125
South Fork, Wright Valley	9900	635	6890	18100	61400	11
Surface streams						
south bank, West Lobe Lake Bonney	4.6	2.3	1.4	15.8	5.0	5.8
melt water flowing into Lake Bonney from west*	12.6	1.16	4.0	19.0	12.0	10.7
melt water from Taylor Glacier†	9	1.9	2.9	30.6	20.4	51.2
surface stream flowing into Don Juan Pond from west	83	25	16	75	150	2.5
Onyx River at weir*	6.9	1.27	1.60	9.40	7.5	3.7
Sea water*						
(Sverdrup *et al.* 1942)	10561	380	1272	400	18980	2650

Capillarity is usually an effective mechanism transporting brines laterally or vertically from surface or subsurface flows, from saline ponds and lakes and other localized sources of liquid water such as melting snow drifts. This can be seen in summer where zones of 2A type deposits may accumulate over a period of hours or days on the banks of flows, at the base of slopes, on the shores of standing water bodies and adjacent to melting snow drifts. At other seasons of the year capillarity is inoperative but its effects can be noted. In spring, salt slicks on the surface of the regolith may mark the former position of suprapermafrost flows (Plate 4.2). Zones of 2A deposits surround salt covered depressions and standing brine bodies (see Appendix 1, Figs.6A, 6B), but may be mixed with deaquation (2B) deposits (Plate 4.3). Salt content in soils adjacent to snow drifts may increase away from it over a distance of a few tens of centimetres (Schofield 1971, Fig.6, p.203; also Plate 7.4).

Capillarity may cause selective accumulation of salts due to local differences in soil texture or salt mobility. Plates 3.4 and 4.4 illustrate localized accumulation after preferential movement of soil brines through a fine-grained soil layer. In hot deserts differences in salt composition have been detected through the zone of capillary migration adjacent to saturated soil or brine bodies; the least mobile sulphate ions are concentrated near the moisture source, nitrates at intermediate distances and chlorides farthest from it (Mueller 1968). This sequence is the same as that of relative mobility of salts in McMurdo oasis. Obviously solubility is not the property controlling mobility in this capillary zone, since the order of relative mobilities is not the order of relative solubilities. Ion size and charge are likely to be more important (Savich 1970) which is consistent with the smaller, monovalent ion, Cl^- being the most mobile, and the large divalent ion, SO_4^{2-} being the least mobile. In McMurdo oasis some of the differences in salt composition noted around the fringes of the salty depressions (Appendix 1, Tables 8, 9, 10, 11, pp.32, 33), and in 2A deposits generally (Figs.3.2, 3.3), are probably due to such differences in salt mobility. However these differences are obscured by the superimposition of the developing 2A deposits on previously formed deaquation (2B) deposits, and probably by ion-ion interactions in solution. More detailed study would be needed to resolve these.

4.3.3 Deep ground water:

A different type of subsurface water or brine movement has recently been recognized in McMurdo oasis due to the drilling of Dry Valley Drilling Project holes. These holes have revealed that deep sublake or intrapermafrost ground water flows typical of arid regions exist in the oasis (Cartwright <u>et al.</u> 1974a). Lake Vanda is a local recharge point in such a ground water system whereas Don Juan Pond is a discharge point for a confined aquifer

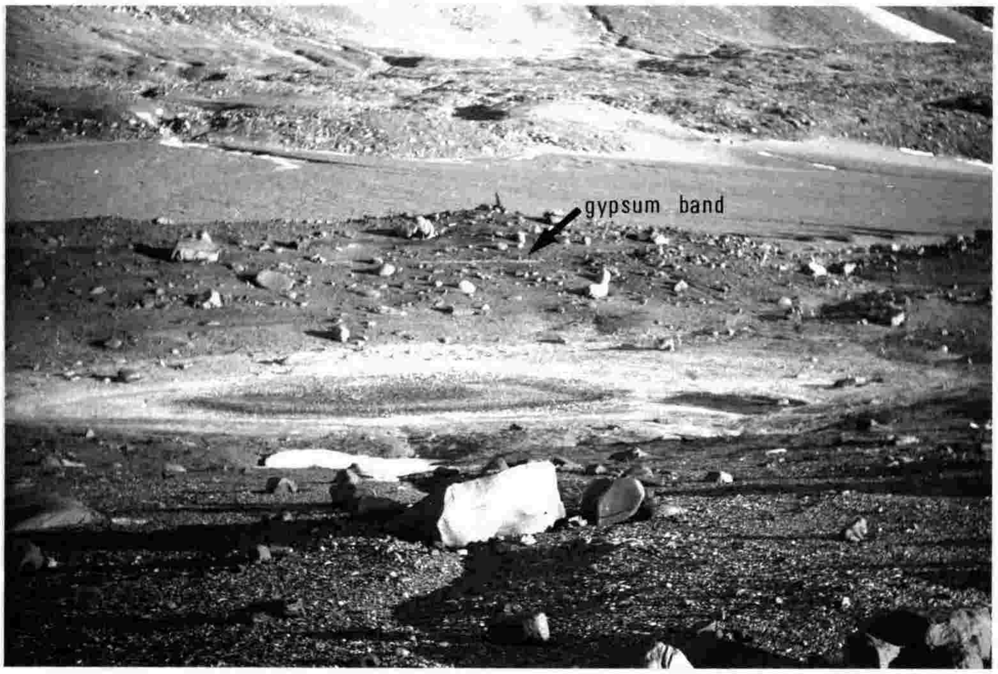

Plate 4.3 Annular rings of salt in a salt-covered depression in Pearse Valley (locality 94). Type 2A and 2B deposits are present here. (28/11/72)

Plate 4.4 White salt accumulating on pebble surfaces in an outcrop of sediments below LaCroix Glacier. Soil brines are preferentially migrating through a fine-grained layer of sediment, and on evaporation at the surface deposit salt in sinuous ridges or zones that mark consecutive periods of migration. (7/1/75)

beneath it (Cartwright et al. 1975; Mudrey et al. 1975).

Deep saline ground water under pressure and permeable zones within permafrosted sediments have also been found in eastern Taylor Valley (Cartwright et al. 1975). Brine has been seen discharging from a source beneath Taylor Glacier at the saline discharge site (Keys 1979; and Chapter 8). No ground water was found in DVDP hole 12 into bedrock near the shores of Lake Hoare/Leon (Cartwright et al. 1975) between New Harbour and Taylor Glacier. This indicates that the ground water systems in these two latter areas are probably unconnected.

The sources and contribution of such subsurface flows to the salt balance of McMurdo oasis are not generally known. However, the ground water upwelling from depth and discharging into Don Juan Pond appears to exert a significant influence on the mass and salt balance of the Pond (Harris and Cartwright 1978). It has been postulated that the source of this water is beneath or at the margins of the East Antarctic Ice Sheet (Cartwright and Harris 1978). However, the $\delta^{18}O$ value of this water, about -16 per mille (Kato et al. 1979) does not confirm this directly, since the $\delta^{18}O$ value of melted ice from the Ice Sheet is around -40 per mille or lighter (Picciotto 1967; Drewry et al. 1980). The source of the brine flowing from under Taylor Glacier is discussed in Chapters 6 and 8.

4.3.4 Ion exchange processes and ionic ratios in saline flows:

(i) the processes

Ion exchange is a possible cause of differential ion movement through the regolith and hence of salt separation. The process is one of the most rapid chemical processes in the weathering cycle elsewhere in the world (Cerling 1979) but does not appear to have been studied systematically throughout McMurdo oasis. For these reasons the process is examined here.

Ions in migrating solutions of any salinity may exchange with other ions adsorbed on surface-active soil particles. Such particles include those composed of some clays, volcanic glass, gels (chemical precipitates), organic material and zeolites (Krauskopf 1967; Berner 1971; Eugster and Jones 1979). Most of these particles have negatively charged active surfaces so that cation adsorption is most important in nature (Berner

1971). This is consistent with Ugolini and Anderson's (1972) observations in Wright Lower Valley, mentioned earlier (4.3.1). Two types of cation exchange can be recognized. They are (1) reversible cation exchange or adsorption and (2) irreversible adsorption or fixation (Berner 1971).

Reversible and irreversible cation exchange reactions are common in soils elsewhere in the world, including desert regions (Krauskopf 1967; Berner 1971; Cooke and Warren 1973). Such reactions proceed to different extents depending on soil water salinity, concentrations and types of ions involved, and the nature of the surface-active particles (Krauskopf 1967; Berner 1971). As salinity or concentration increase so too do exchange and the concentration of a given adsorbed ion. Therefore, saline flows could be expected to reveal ion exchange processes that normally might be obscured in dilute stream waters. Clays such as vermiculite and montmorillonite have high capacity for cation exchange; chlorite and kaolinite usually have little (Berner 1971). It should be noted however that identification of specific clays is not always unambiguous (Berner 1971) and thus problems in interpretation may arise.

Reversible cation exchange often favours specific ions. The tendency is for polyvalent ions to be adsorbed more strongly than monovalent ions, ions forming predominantly covalent bonds to be more readily adsorbed than ions forming predominantly ionic bonds, and smaller ions to more readily exchange than larger ions. However there are many discrepancies, especially from this last tendency, due to differences in ion hydration (Krauskopf 1967; Savich 1970). Generally cation exchange could be expected to result in preferential uptake of Mg^{2+} compared to Ca^{2+} and thus a decrease in the Mg/Ca ratio in the migrating solution. Preferential uptake of Mg^{2+} has been conclusively demonstrated in the laboratory and elsewhere (White 1957; Russell 1970; Berner 1971). Preferential uptake of Na^{+} compared with K^{+} has been demonstrated also (Berner 1971) but so has the reverse (Krauskopf 1967). Thus behaviour of Na/K ratios in migrating solutions may not be a good criterion by which to identify cation exchange in antarctic soils. An increase in Ca/K is often indicative (Field 1975; Eugster and Jones 1979) but this ratio may be affected by precipitation of sparingly soluble calcium salts (Table 4.1). Cation to chloride ratios may be most useful since this anion is generally conserved in migrating solutions (Eugster and Jones 1979).

Irreversible adsorption or fixation of K^+ and Ca^{2+} has been well documented (White 1957; Berner 1971). This fixation results from extended reaction between water and some types of soil particles and rock and is a specific type of weathering process affecting clays and clay-sized material. Irreversible uptake of K^+ in particular may occur from saline water onto clays such as illite, montmorillonite and vermiculite (Mason 1958; Weaver 1958; Johns and Grim 1958; Berner 1971). This loss of K^+ should reflect an increase in Na/K and a decrease in K/Cl in the brine involved.

Surface-active particles are present in the antarctic regolith. Clay-sized particles are not lacking in many soils although the clay content may be far less than in temperate soils (e.g. Glazovskaya 1958; Claridge 1965; Ugolini and Bull 1965; Everett 1971; Linkletter 1971). Montmorillonite and vermiculite type clays may constitute up to 70 percent of the clay-sized fraction which in turn may make up more than 10 percent of some soils (Claridge 1965). These clays were formed mainly from primary micas, by physical comminution and chemical weathering (Claridge 1965; Boyer 1975; Ugolini 1976) and could be expected to have high exchange capacities, initially at least. Wind- or water-sorted volcanic ash is known to occur in thin beds in limited areas of Wright Valley (McSaveney 1973; Jones et al. 1973) and traces of pumice have been detected in old soils in Wright and Taylor Valleys (Claridge and Campbell 1974). Small basaltic cones are quite numerous in Taylor and Wright Valleys (McCraw 1962; Haskell et al. 1965; Denton et al. 1971), and recent ash of basaltic composition has been found in glacier ice in the region (Keys et al. 1977). Therefore, there have been a number of minor inputs of volcanic glass into soils of the region with probably an attendant rise in the number of surface-active particles present. Zeolites formed as late stage alteration products in igneous rocks are not uncommon in the region (Morikawa et al. 1975; Nishiyama 1977; personal observations) and limited amounts have formed from volcanic ash also (Linkletter 1974). Organic material such as algae is lacking in most soils but may be important locally. In summary, it might be expected that soils in the region could have some cation exchange capacity.

(ii) operation in antarctic soils

The extent to which cation exchange and fixation processes operate in antarctic soils is subject to debate but they are probably limited. Everett (1971, 1976) concluded that ion exchange is not important in Wright Valley soils. This was also the view of Simonov and Bonch-Osmolovskaya (1968) who studied saline water in Schirmacher oasis, Dronning Maud Land. The lack of exchange was believed to be due mainly to a lack of surface-active particles or cation exchange capacity. Indeed, this capacity is low in some soils in the McMurdo region and Ross Dependency. Cation exchange capacities as low as 3 and 6 milliequivalents per 100 grams were measured in the Victoria Valley system and Asgard Range (Cameron and Conrow 1969), and up to 27 m.equiv. per 100 g elsewhere (Cameron _et al._ 1971). This low capacity is probably due to the slow rate of formation of active surfaces in antarctic conditions.

Field (1975) and Nakaya _et al._ (1979) believed cation exchange does take place. Nakaya _et al._ based their argument on an initial salt and water content that was assumed to be equivalent to sea water. Knowing the ionic concentrations in the bottom waters of Lakes Bonney and Vanda, they used a 'book-keeping' method to balance the assumed initial composition with the known final composition. The book-keeping method involved: (1) a concentrating stage; (2) hypothetical cation exchange of some magnesium and calcium (in minerals in the regolith and lake sediments) with sodium and potassium (in the water) and (3) precipitation of sparingly soluble phases. This argument stands or falls on the assumption of original composition and the specific types of ions undergoing exchange reactions. Such a book-keeping method does not conclusively demonstrate that ion exchange takes place in the oasis.

The determination of certain ionic ratios in streams in the region may give an indication of the extent to which ion exchange takes place. Recent works have examined the differences in ratios between snow, ice and the streams formed from the melting of this snow and ice. Any such differences can be attributed to processes that modify the composition of the stream water during its passage along its path of drainage. Ion exchange is one modifying process that is possible.

Field (1975) compared Ca/K ratios in nine samples of fresh snow, névé snow and glacier ice from McMurdo oasis with those in two suprapermafrost flows (Table 4.6) and seven streams. He found that the ratio tended to be considerably higher in the flows and streams and attributed this to ion exchange. Field's data also show that SO_4/Cl and K/Cl ratios are less in the flows (Table 4.6); there is a tendency for Na/Cl to decrease as well, and for Na/K to increase. The patterns for Mg/Ca, Mg/Cl and Ca/Cl are quite variable and so no Mg^{2+} depletion is evident. The behaviour of the anion ratio SO_4/Cl cannot be explained by ion exchange since anion exchange is quite limited in nature (Berner 1971). The behaviour of other ratios could be attributed to cation exchange but except for K/Cl the ratios do not show consistent patterns (Table 4.6).

Differences in salt dissolution may also affect these ratios. The different behaviour of the ratios can be explained, in part at least, by differential (fractional) dissolution and migration of present-day salts as discussed in the present work. We have seen that relative mobility appears to be dictated to a large extent by eutectic temperatures (in the binary system model) and also by solubility in multicomponent systems (4.2.1 -3). Saline flows are likely to be enriched in chlorides because these are more easily dissolved than sulphates (Tables 4.1 and 4.3); the decrease of SO_4/Cl, K/Cl, Na/Cl are consistent with this. Similarly the increase in Ca/K and Na/K is consistent with greater mobility of $CaCl_2$ and NaCl compared to KCl, due to lower eutectic temperatures and higher solubilities of the former two salts (Table 4.1). These ratios are all sensitive to environmental temperature and salt composition, which will vary within constraints fixed by phase relations and chemical equilibria (Table 4.4 and Fig.4.3).

Torii et al. (1979) performed a treatment similar to that of Field (1975). A large number (35) of analyses of snow and ice samples from Antarctica were compared with those for seven different stream systems in McMurdo oasis. The analyses plotted onto two separate fields on a ternary diagram. The field for the streams had higher Ca^{2+} and reduced Na^+ and K^+ percentages. Torii et al. attributed the apparent Ca^{2+} enrichment to selective dissolution of the more soluble components of ancient "deposits" in the catchment area.

The differing interpretations of Field (1975), Torii et al. (1979) and that outlined above based on section 4.2 illustrate some of the

Table 4.6 Comparison of ionic ratios in seven snow and two ice samples with those in two saline flows, all from McMurdo oasis (calculated from the data of Field 1975).

Ratio	Ca/K	Na/K	Mg/Ca	Na/Cl	K/Cl	Mg/Cl	Ca/Cl	SO_4/Cl
snow	1.0-7.0	2.3-23	0.17-1.6	0.27-3.6	0.025-0.42	0.024-0.88	0.12-0.45	0.2-9
ice	0.17, 2.9	1.3, 1.8	0.069, 3.0	0.21, 0.40	0.12, 0.30	0.024, 0.15	0.050, 0.34	0.50, 1
Bonney flow	4.92	16.8	1.89	0.336	0.020	0.186	0.0985	0.16
South Fork flow	28.5	15.6	0.38	0.161	0.010	0.112	0.295	1.8×10^{-4}
tendency of ratio to increase or decrease from snow/ice to flows	increase	increase	neither	decrease	consistent decrease	neither	neither	consistent decrease

ambiguities inherent in using ionic ratios. A further problem is that additional ions may be injected into the brines by chemical weathering of soil and rock. Such weathering is known to be a source of Mg^{2+} , Ca^{2+} and K^{+} at least (Claridge and Campbell 1977; also Chapters 5 and 6). As yet the operation of ion exchange is not demonstrated unambiguously. However, the apparently consistent decrease in K/Cl from snow and ice to flows and streams could be due to ion exchange, in part at least.

Cation fixation does appear to operate beneath Taylor Glacier. The saline discharge brines of 1976 and 1978 were both similar to concentrated sea water in terms of bulk chemistry (Appendix 1, Tables 15, 16) as exemplified by (1) ratios between the main ions Cl^{-} and Na^{+}; and (2) the lack of enrichments in Na^{+} and Mg^{2+} compared with these ions in concentrated sea water (Chapter 8). With this interpretation of initial composition, considerable depletion of K^{+} is apparent in the discharge brines (Appendix 1, Table 15; Chapter 8).

Significant amounts of clay-sized material are present beneath the glacier. Robinson (1979) found up to 28 percent (by weight) of material finer than eight phi (4 μm) in basal debris layers in Taylor Glacier. Palmer (1976) found up to 18.5 percent finer than nine phi (2μm). Englacial debris contains less clay-sized material, the mean content finer than eight phi being 8 ± 2% (Robinson 1979). The basal debris was derived from subglacial sediments within a few kilometres of the terminus and the englacial debris was incorporated probably from such sediment also (Robinson 1979).

The clay-sized material consists mainly of unweathered and chemically weathered micas. The englacial clay fraction from Taylor Glacier is composed largely of illite (Scanning Electron Microscope and XRD identification by Palmer 1976). The clay fraction elsewhere in Taylor Valley sediments is comprised mainly of interlayered mixtures of hydrated and non-hydrated micas; montmorillonite and vermiculite are prominent (Claridge 1965; Ugolini et al. 1979).

The depletion of K^{+} in the discharge brines is most likely caused by preferential uptake of the ion from subglacial brines, and fixation into interlayer positions in the clays. As noted earlier (4.3.4i), such uptake has been well documented elsewhere for the types of clay minerals that are inferred to be present beneath Taylor Glacier. Significant amounts of fixation from sea water have been noted within

3 to 14 days in laboratory experiments with clays (Berner 1971). Brines have been discharged from beneath Taylor Glacier intermittently since at least 1958, and probably since 1911 and earlier (Keys 1979; Chapter 8). Therefore, sufficient time has elapsed to allow K^+ fixation beneath the glacier by reaction between subglacial brines and the relatively limited amounts of clay minerals that are present in antarctic sediments.

Similar fixation could explain the behaviour of K/Cl and Na/K ratios around Scott Glacier, central Transantarctic Mountains. Claridge and Campbell (1977) noted that the proportion of K^+ decreased with time in salts from soils derived from granite. Fixation of K^+ during soil formation is consistent with this. However, Claridge and Campbell explained the behaviour as due to differential rates of ion release from the weathering surfaces of K-feldspars, micas and biotites.

Thus, there is mixed evidence for the operation of ion exchange processes in McMurdo oasis. A possible loss of K^+ from soil solutions may be due to such processes. In most areas however, and for most ions, the process is probably not important due mainly to a lack of exchange capacity in the soils. Future work should be done particularly on and around saline flows and their drainage courses. These flows move slowly, and are very saline; thus, there is much contact possibly over several days between cations and soil particles. Any chemical differences should be most developed here.

It is difficult to conclusively show that separation or preconcentration of ions and salts takes place throughout the region during the hypothetical period when they are all in solution and travelling within (or on top of) the regolith. There is some evidence that chloride ion migrates faster than other ions in soil brines (Table 3.2; 3.3.3; 4.3.1). Some separation of anions may occur, with chloride migrating faster or further than nitrate, which moves faster than sulphate, as observed by Mueller (1968) in hot deserts. However, this separation sequence is the same as that produced by eutectic temperature-controlled dissolution and therefore the two processes cannot be distinguished here. Claridge and Campbell (1968b) found no anion separation within dry antarctic soils. Similarly any possible cation separation due to different diffusion rates or ion exchange is probably obscured by this dissolution. In fact, any separation of ions which is apparent in migrating solutions is probably largely inherited from the initial dissolution stage, or due to deaquation subsequent to this dissolution (4,4). K^+ in the saline discharge brines is an exception.

4.4 Deaquation

4.4.1 The process:

The term deaquation refers to loss of water from a brine leading to precipitation or crystallization of a salt. Deaquation occurs when brine temperatures drop and ice forms, or when evaporation of water takes place or a combination of both. It will occur where streams, migrating soil moisture and brines move to an area where evaporation or freezing can take place. This may be in depressions (Plate 4.3), at the surface of bedrock or regolith (Plates 3.2, 3.3, 3.4, 4.2, 4.5), at the ice-cemented table, or elsewhere in the soil (Plate 3.5). Obstacles such as boulders and bedrock may force suprapermafrost flows to reach the surface or close to it (see Plate 4.5). The depth of the ice-cemented table is also critical; where this is shallow, salt accumulation may occur at the surface. Thus, salt deposits of the 2A type are often found at the base of slopes (Gibson 1962; McCraw 1967a).

The evolution of brines and formation of salt deposits during deaquation can only be referred to in a general sense here because of the great number of different brines involved. Detailed general studies of evolution of dilute brines during deaquation by evaporation-concentration have been made for temperate regions (Eugster and Jones 1979). Here we are concerned with more concentrated brines in a frigid environment.

Deaquation is governed by similar physico-chemical properties to dissolution. Deaquation usually causes crystallization of salt from solution when the product of the activities, IAP, of the salt's component ions, exceeds the equilibrium constant (solubility product) K describing the dissolution (also Chapter 8). For a particular salt, K and IAP are dependent on the solubility, type and concentration of all the ions in the brine and on temperature (4.1.3). For dilute solutions the activity of an ion is very similar to its concentration; this relation does not hold for concentrated brines. (Ion activities and deaquation are examined for the saline discharge brines in Chapter 8.) It has been seen (Fig.4.3) that binary eutectic points and solubility give an indication of the tendency of phases to crystallize in sequence from deaquating solutions. This tendency is in the order of the decreasing eutectic temperatures for purely freeze-concentration processes, and increasing solubility for purely evaporation processes. Ion concentration is a controlling factor (Fig.4.3, 4.2.3).

The relative ordering of eutectic temperatures and solubilities of binary systems is different (Tables 4.1, 4.3) primarily because solubility is temperature dependent (Fig.4.1). Therefore, deaquation by a freeze-concentration process produces a different crystallization sequence than does evaporation. For freeze-concentrating sea water the sequence (Thompson and Nelson 1956) is: ($CaCO_3$) (<0°C), $Na_2SO_4.10H_2O$ (-8.2°C), $NaCl.2H_2O$ (-22.9°C), $MgCl_2.12H_2O$ + KCl (-36°C), $CaCl_2.6H_2O$ (-54°C), similar to the order of salt mobilities (3.3.3, Table 4.3). The sequence formed during evaporation of sea water (Kirkland and Evans 1973) is: ($CaCO_3$), $CaSO_4.2H_2O$, NaCl, $MgSO_4$ phase, $KMgCl_3.6H_2O$, KCl or $MgCl_2.6H_2O$, unlike the order of salt mobilities. Many other double salt phases may be formed during this latter process. Minor amounts of $CaCO_3$ tend to precipitate initially in both sequences.

A generalized deaquation sequence involving precipitation from a general brine can be presented, based on salt properties (Table 4.1) and observed salt distribution (Appendix 1, Tables 1, 3-7). This general brine contains Na^+, Mg^{2+}, Ca^{2+}, K^+, Cl^-, SO_4^{2-}, NO_3^-, CO_3^{2-} and HCO_3^- (4.1.3). The first salt to precipitate will often be insoluble $CaCO_3$. Other carbonates are rare in most parts of the region (Appendix 1). Therefore, Ca^{2+} is usually present in excess of CO_3^{2-} and HCO_3^-, which are normally removed by Ca^{2+} from deaquating brines. Where CO_3^{2-} and HCO_3^- are present in excess of Ca^{2+}, other phases such as nesquehonite, or sodium carbonate or bicarbonate phases may crystallize. If Ca^{2+} is still present in sufficient quantities in a deaquating solution, gypsum may be precipitated next, especially during evaporation of sulphate-rich brine. When the concentration of Ca^{2+} is low compared to Na^+, mirabilite (or thenardite) may precipitate out before gypsum, especially from a freeze-concentrating brine.

The deaquation sequence becomes increasingly more difficult to generalize from now on using binary system properties only. In a brine containing unit mole ratios, a phase containing magnesium sulphate would precipitate next. However, normally sulphate would have been depleted by precipitation of other sulphates. In this case halite or dihydrohalite would normally be precipitated before the magnesium sulphate phase, as in the sequences for sea water noted above. If NO_3^- is present in excess of Cl^-, a nitrate phase may precipitate from a freeze-concentrating brine before any of the former phases. The last phases to crystallize from a freeze-concentrating brine will be chlorides of calcium and magnesium; nitrates will usually be last for the evaporation sequence. The apparent absence of calcium and magnesium nitrates in antarctic salt deposits (Appendix 1, Table 1) is significant. This absence suggests that deaquation by evaporation alone is uncommon in those areas where NO_3^- is a prominent ion (Chapter 5), since Ca^{2+} and Mg^{2+} are prominent in those areas also.

The crystallization sequences can be examined more satisfactorily using multicomponent diagrams, especially when the deaquation of a specific brine is being followed. Three of these diagrams are presented in 4.4.3 to illustrate their use and to discuss the formation of double salts. Many such diagrams may be found in the literature; Stewart (1963) has useful illustrations for the $Na/Mg/K/Cl/SO_4/H_2O$ system saturated with NaCl.

4.4.2 Fractional crystallization and fractionation:

The relative orderings of eutectic temperatures and solubilities in Table 4.1 may be loosely applied to sample localities and salt deposits where fractional crystallization has occurred. Fractional crystallization is the crystallization of a specific salt phase, or phases in sequence, from a deaquating brine containing a mixture of dissolved salts. Fractionation refers to the existence of two or more phases that are present separately in a locality or deposit. Fractionated salt deposits indicate that fractional crystallization (or fractional dissolution, 4.2.1) probably occurred during the development of the deposit. These processes may concentrate specific ions, and produce deposits that contain only one or two salt phases. Such macroscopically 'pure' deposits are quite common in the region (Appendix 1, Tables 3-11). The deposit types and localities where fractionation was noted are as follows: (1) a 1A deposit at Alligator Peak (Plate 4.5); (2) salt covered depressions containing 2A and 2B deposits (e.g. Plate 4.3); and (3) a deposit beneath a cobble at Big Foot Nunatak, Ferrar Glacier (Plate 4.6).

1A type deposits are discussed first. Plate 4.5 shows a deposit in which an inner crust is composed of less soluble phases gypsum and calcite (arrow), whereas the outer contains Na^+ and Mg^{2+} as well as Ca^{2+} and SO_4^{2-}. Apparently, fractional crystallization occurred from a deaquating brine which had first been forced to the surface by a dolerite block seated within the ice-cemented regolith. The parent brines moved downwards and outwards from the obvious drainage crack in the rock. Less mobile phases were deposited near the crack followed by the more mobile phases away from it. The amount of calcite present shows that the deposit must have built up over a considerable period. The powdery and less coherent phases at the edge of the deposit probably build up, then fall off or are removed by wind during this period.

A layered surface crust (1A deposit) on basaltic lava from near Walcott Glacier was illustrated by Lindholm et al. (1969). A fractionation sequence is evident from the rock surface outwards in the order: calcite, gypsum, syngenite. This is the order of increasing solubility and eutectic temperatures of these phases (Table 4.1 and Hill 1934), and hence their mobility. Calcite, the first phase to form, developed in thin laminations, and there seemed to be no apparent genetic relationship between it and the sulphate phases. Gypsum was followed by syngenite in the crystallization of these sulphates which are composed of distinct grains and crystals (Lindholm et al. 1969). The deposit as a whole suggests that it was formed by brines moving outwards from the rock or along its surface. Possibly two generations of growth occurred, one dominated by carbonate-bicarbonate anions and the other by sulphate.

In salt-covered depressions annular rings of salt are formed , as specific phases crystallize from deaquating brines in the depressions (Plate 4.3). At depression localities 94 and 223 (Appendix 1, pp.32 and 33) sparingly soluble gypsum crystallized

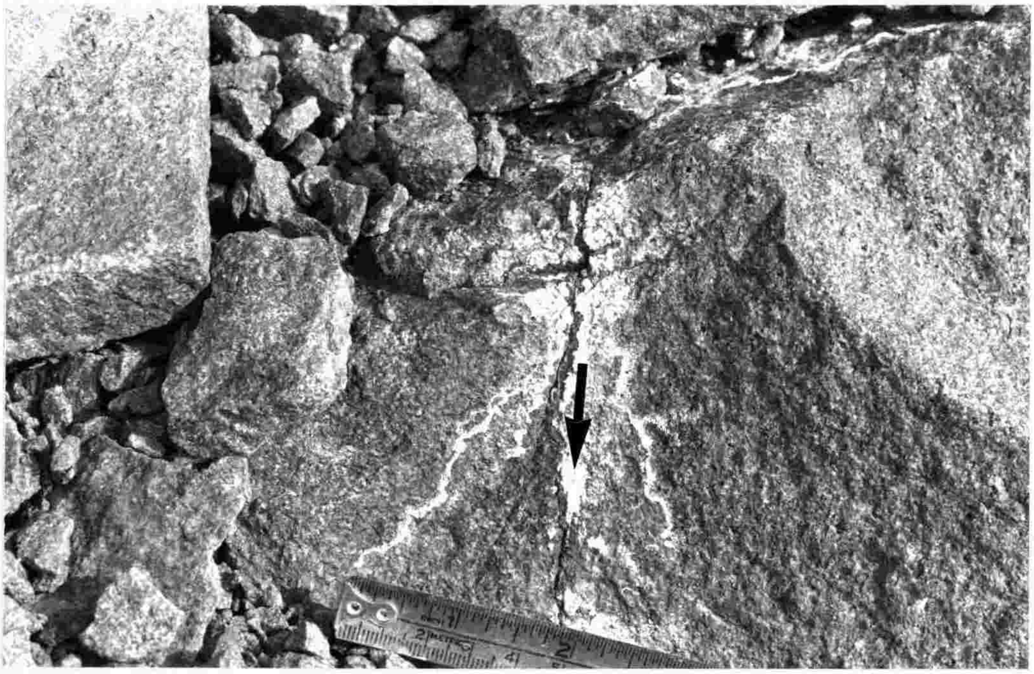

Plate 4.5 Fractionated salt deposit (type 1A) at Alligator Peak (samples 73/178, 73/180, locality 186). Fractional crystallization has occurred separating sparingly soluble phases (gypsum and calcite, arrow) and more soluble phases (thenardite, epsomite as well as gypsum) at the edges of the deposit (15/12/73)

Plate 4.6 Fractionated salt deposit (types 3 and 4) on the underside of a sandstone cobble at Big Foot Nunatak (sample 73/236, locality 167). The cobble has been overturned for display. Fractionation is evident between gypsum (solid arrow) and thenardite (open arrow). (21/12/73)

early from the brines; more soluble phases with lower eutectic temperatures are found in the central areas of these depressions, having crystallized later. In locality 138 (Appendix 1, p.33) mirabilite underlies more soluble salts and those with lower eutectics; mirabilite evidently crystallized first and collected at the bottom of the deaquating pond. Phase relations are complex at locality 230 in Labyrinth, and their elucidation would require detailed examination of the system $Na/Mg/Ca/Cl/NO_3/SO_4/H_2O$ and a knowledge of subsurface topography in the salt-covered depression. Capillarity also causes annular rings of salt to accumulate around deaquating saline ponds and lakes (4.3.2).

The salty depression locality 94 in Pearse Valley (Plate 4.3) has had an interesting recent history. Aerial photographs taken by the United States Navy on 6/12/56 show that the depression was filled with water and ice at the time. Slightly less ice was present when a further set of photos were taken on 1/12/70. At the time of sampling for this study (26/11/72) the depression was free of ice and only subsurface brine was present. Fossil water levels show that the filled pond is 3-4 m deep. By December 1979 the depression was full of ice and water once more (I. Wright, VUW, pers.comm.). Thus the salt deposits studied in this depression, and probably most of the others, were and are young. Extreme melting events (e.g. Jan. 1974, Jan. 1977; Chinn 1979) may fill such depressions with water over a period of a few days; several years of evaporation and sublimation are then required to deaquate them, given ablation rates which are typical for neighbouring Taylor Glacier (0.2 to 0.4 m a^{-1}, Robinson 1979).

Fractionation beneath surface cobbles is probably common. Plate 4.6 shows a sandstone cobble with a type 3 + 4 deposit adhering to its underside, overturned for display. Small accumulations of thenardite and gypsum exist separately in this deposit, within millimetres of each other. During and after the condensation of moisture at the cobble underside (Claridge and Campbell 1968b) fractional crystallization of gypsum and thenardite apparently took place regularly producing such a fractionated deposit. These two salts are common and widespread (3.2.1 and Chapter 5) and have quite different solubilities and eutectic temperatures (Table 4.1); fractionation between them is probably common. Fractionation between salts with different ions was noted beneath cobbles also at localities 116, Aztec Mountain area, and 238, Tyrol Valley (Appendix 1, pp.17, 26). Similar fractionation was also noted in surface efflorescences of the 2A type, for example at locality 211, Mt. Odin (Appendix 1, p.25). Probably, many instances of such fractionation were inadvertently destroyed on sampling.

Obviously, fractionated salt deposits are widespread. Fractionation was caused by fractional crystallization in sequence from deaquating brines, in at least two of the cases studied (Plates 4.3, 4.5). Probably, such fractional crystallization is common also. It is not unreasonable to suppose that the other fractionated deposits, such as that containing syngenite, were formed similarly.

The formation of syngenite at equilibrium requires a high concentration of K^+ in solution, about 9400 ppm at 0°C in the K /Ca/ SO_4 / H_2O system (Hill 1934). This is an order of magnitude more concentrated than the saline flows of Field (Table 4.5) and the ground water of Campbell and Claridge (1967) and three times more concentrated than the deep water of Lake Bonney (Torii et al. 1975). In multi-component brines the K^+ requirement for syngenite formation is not likely to be as high as 9400 ppm, but must still be large. This may indicate preconcentration of K^+ in brines by some process, such as fractional dissolution or crystallization (e.g. 4.2.3, Fig.4.3).

4.4.3 Formation of double salts:

The formation of double salt phases is another type of fractional crystallization. Their crystallization is dependent on temperature and on concentration conditions affecting equilibria in various brine systems during deaquation.

Bloedite, the double salt of sodium and magnesium sulphate is considered in detail as an example. The equilibria describing the formation of bloedite can be represented as follows:

$$2Na^+_{(aq)} + Mg^{2+}_{(aq)} + 2SO_4{}^{2-}_{(aq)} + 4H_2O \rightleftharpoons Na_2Mg(SO_4)_2.4H_2O_{(s)} \quad \ldots \; 4.5$$

The position of the equilibrium is determined by the activities of all species involved, including that of H_2O. The activities and therefore the equilibrium are dependent on the concentrations of these and other ions in the brine, and on temperature. The reaction can also be represented by

$$Na_2SO_{4(aq)} + MgSO_{4(aq)} + 4H_2O \rightleftharpoons Na_2Mg(SO_4)_2.4H_2O_{(s)} \quad \ldots \ 4.6$$

This reduces the number of independent constituents of the left hand side of the equation to three; these constituents can then be simply represented on a ternary diagram.

The phase relations at equilibrium in the ternary aqueous system Na/Mg/SO_4 are shown in Figure 4.4. The three apexes H, N and M represent points with 100 percent water, anhydrous sodium sulphate (Na_2SO_4) and anhydrous magnesium sulphate ($MgSO_4$) respectively. Bloedite may crystallize from this system at temperatures between +20.6°C and +71°C (Blasdale and Robson 1928). Figure 4.4A shows the system at +25°C and Figure 4.4B at 0°C.

Isothermal steady state evaporation at +25°C is considered first. In Figure 4.4A, A and C represent the solubilities of Na_2SO_4 and $MgSO_4$ in binary aqueous systems at +25°C. B1 is the univariant point representing the composition of a solution saturated with both mirabilite (MIR) and bloedite (BL) in equilibrium with both these two solid phases; B2 is the corresponding point for epsomite (EPS) and bloedite. B1 is the point representing 17.8% Na_2SO_4 and 16.6% $MgSO_4$; B2, 13.0% Na_2SO_4 and 21.2% $MgSO_4$ (Archibald and Gale 1924). Bloedite can form only when the relative concentrations of Na_2SO_4, $MgSO_4$ and H_2O in the brine lie on the line B1-B2. Only at these concentrations are conditions at +25°C favourable for the formation of bloedite, by the reaction shown in Equations 4.5 and 4.6 above. For example, an unsaturated brine, of initial composition P, isothermally evaporating, follows the line PD away from H. When it reaches line B2C, the brine is saturated with epsomite. Further evaporation causes epsomite to crystallize out and the brine to 'travel' along the line CB2 towards B2. At B2 the brine is saturated with bloedite as well; further evaporation causes bloedite to crystallize. Mirabilite does not crystallize from brine P evaporating at +25°C, but will do so from brine Q.

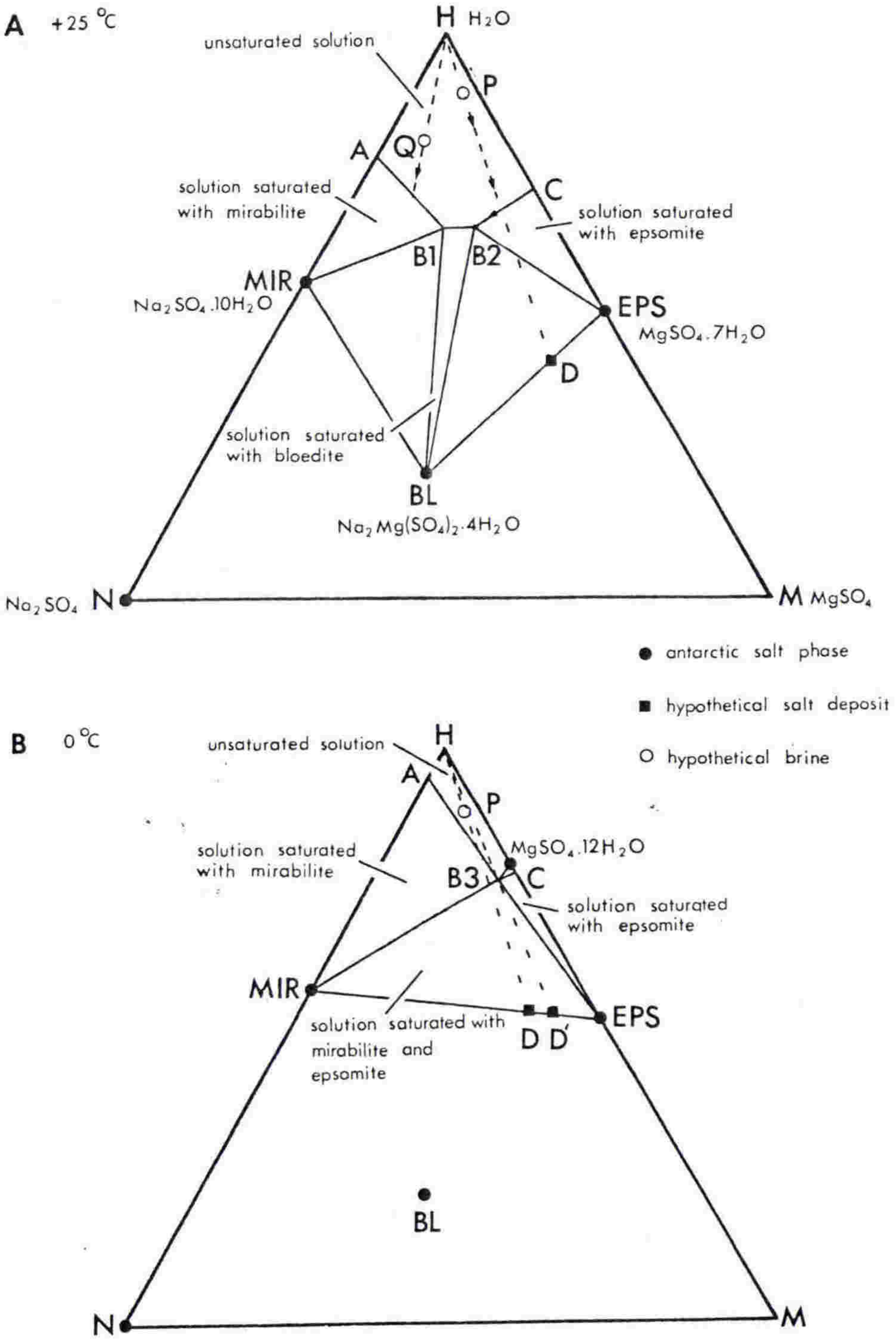

Figure 4.4 Isothermal phase relations in the ternary system Na/Mg/SO_4/H_2O at (A) +25°C and (B) 0°C, constructed in weight percent from data of Blasdale and Robson (1928) and Archibald and Gale (1924). Lines ABi and BiC are shown straight for simplicity. $MgSO_4.12H_2O$ has not been identified in Antarctica but its existence there is probable (Ch.6). Dashed lines show evolution paths of salt systems (see text).

A different crystallization sequence is followed when brine P evaporates and cools simultaneously. In Figure 4.4B, representing the system at 0°C, the bloedite field is absent and B3 is the sole univariant point representing the composition of a saturated solution in equilibrium with both mirabilite and epsomite. For brine P at +25°C evaporating and cooling to 0°C, the precise crystallization sequence is dependent on the rate of temperature decrease compared to the rate of evaporation. Mirabilite, epsomite and bloedite may all crystallize but the latter will not crystallize below +20.6°C. Mirabilite will crystallize first from the brine evaporating isothermally at 0°C just as epsomite did at +25°C. Eventually a saturated solution is attained whose composition is given by B3. Further evaporation at 0°C will cause both mirabilite and epsomite to crystallize.

Figures such as Figure 4.4 can be used for a variety of purposes including examination of the composition of salt deposits during leaching, migration and subsequent deaquation of the leachate. For example on Figure 4.4B, point D represents a salt deposit (say a surface efflorescence) consisting of epsomite, bloedite and thenardite; the Mg/Na ratio is 2.16 in D. Consider moisture from nearby melting ice slowly washing the deposit at 0°C; a small amount of saturated leachate is formed whose equilibrium composition is given by B3, that is Mg/Na = 3.13. If this brine were to migrate away from the depleted deposit and deaquate without coming into contact with other salt, then the Mg/Na ratio in the new deposit D' would be 3.13. Thus the new deposit would be enriched in Mg, while the old would be depleted in Mg, with respect to the original deposit D. Similarly, if the initial ratio in the deposit was greater than 3.13 such a leaching process would cause enrichment of Na in the new deposit and depletion in the old. Other temperatures and ions change these ratios but the inequalities remain. Generally a salt deposit containing bloedite and mirabilite (or thenardite) indicates that the cations are dominated by Na^+; a deposit containing bloedite and epsomite (or hexahydrite) indicates a predominance of Mg^{2+} in the cations.

Another multicomponent aqueous system of interest is the quaternary system $Na/Cl/NO_3/SO_4/H_2O$. Figure 4.5 is the Jänecke diagram showing ratios of salt phases in aqueous solution at +25°C (Ericksen and Mrose 1970). Each phase has a stability or crystallization

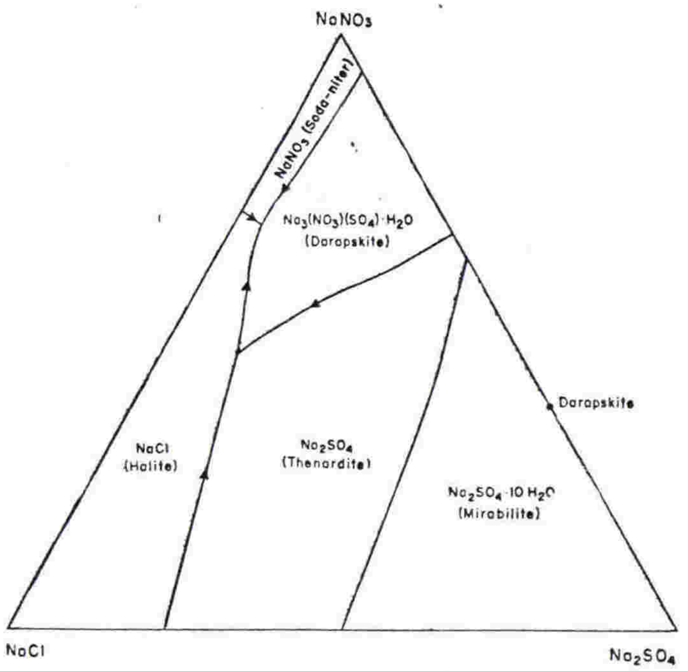

Figure 4.5 Jänecke diagram of the system Na /Cl /NO_3 /SO_4 /H_2O at +25°C, constructed in weight percent (after Ericksen and Mrose 1970).

field as before; darapskite shows incongruent solubility, crystallizing from a brine in which the relative amounts of its component ions differ from those in the mineral itself. Any point on the diagram represents a saturated solution in equilibrium with one, two or three phases. The internal lines represent the locii of saturated solutions in equilibrium with two phases; the arrows on these lines indicate the direction in which the saturated solution evolves on evaporation-concentration at +25°C. In this system darapskite may crystallize from solutions in the temperature interval +7.2° to +71.5°C (Ericksen and Mrose 1970); in the aqueous system Na/NO_3/SO_4 the interval is +13° to 74°C. In the aqueous system Na/K/Cl/NO_3/SO_4 darapskite crystallizes down to +3.4°C (Cornec et al. 1930); thenardite crystallizes down to +11.6°C in the latter system.

Similar data are available in the literature for other double salts found in Antarctica. The temperature intervals for crystallization of most double salts known in

Antarctica are listed in Table 4.7. The lower end of all these temperature intervals is less than present-day maximum surface temperatures in McMurdo oasis (up to +30°C, Table 2.5). Therefore, all of these phases can form at the surface of the regolith in present-day conditions.

Table 4.7 Temperature intervals for crystallization at equilibrium of double salts detected in Antarctica plus phases containing magnesium chloride.

Double salt	Aqueous system	Temperature interval for crystallization (°C)	Remarks	Reference
bloedite	$Na/Mg/SO_4$	+20.6 to 71	see Fig.4.4	Blasdale & Robson (1928)
	$Na/Mg/K/Cl/SO_4$	+ 4.5 to 59.5	-	Palache *et al.* (1951)
darapskite	$Na/NO_3/SO_4$	+13 to 74	-	Ericksen & Mrose (1970)
	$Na/Cl/NO_3/SO_4$	+ 7.2 to 71.5	see Fig.4.5	Ericksen & Mrose (1970)
	$Na/K/Cl/NO_3/SO_4$	+ 3.4 to ?	-	Cornec *et al.* (1930)
trona	$Na/Cl/HCO_3/CO_3$	0 to 195	-	Palache *et al.* (1951)
burkeite	$Na/SO_4/CO_3$	+24 to ?	favoured by low CO_2 activity & moderate salinity & temperature	Jones (1965), Eugster & Smith (1965)
	$Na/Cl/SO_4/CO_3$	+14 to ⩾75		
gaylussite	$Na/Ca/CO_3$	+15 to 40	alters to calcite	Palache *et al.* (1951)
northupite	$Na/Mg/Cl/CO_3$	?	favoured by low to moderate CO_2 activity	Eugster & Smith (1965)
syngenite	$K/Ca/SO_4$	< 0 to >100	large excess K^+ required	Hill (1934)
carnallite	$K/Mg/Cl$	-21 to +168	excess Mg^{2+} required	Palache *et al.* (1951), Thompson & Nelson (1956)
tachyhydrite	$Ca/Mg/Cl$	+22 to ?	-	Igelsrud & Thompson (1936)

Conditions within the regolith are less certain. Darapskite and bloedite can crystallize in present-day conditions probably down to depths of about 0.2 m (at least) below the soil surface. The maximum temperatures at this depth are about +5°C (Table 2.5) similar to the lowest crystallization temperatures of bloedite (+4.5°C) and darapskite (+3.4°C) shown in Table 4.7. Bloedite was found in subsurface deposits down to a depth of about 0.05 m (Plate 3.5) and darapskite to about 0.07 m in the present study. These depths are well within the 0.2 m constraint. Theoretically at least, bloedite and darapskite can crystallize under most cobbles (diameter 0.06 to 0.3 m). However, maximum temperatures under boulders much larger than cobbles would probably be too cold for the formation of these phases. Different thermal conductivities and diffusivities of rock and soil material probably affect the maximum soil depth and rock size for such formation in types 4 and 5 deposits.

The darapskite occurrence noted above was in a salt horizon in pebbly regolith containing very few fines at Knobhead, locality 165 (sample 24872, Appendix 1, p.22). This horizon cannot have formed by upwards capillary action since the regolith contains insufficient fines for such a process. The ice-cemented table was deeper than 0.5 m at this site. The salt horizon probably "represents the limit of water vapour penetration" and thin film movement of soil brines downwards into the soil, mainly "during rare periods of snow cover and melting" (Claridge and Campbell 1968b, p.546; 2.3.3ii). There is no chemical evidence to suggest that the salt in this deposit, or any of the double salts listed in Table 4.7, were formed in conditions warmer than present day.

4.4.4 Effect of soil climate on hydrate phase distribution:

The distribution of hydrate phases in the McMurdo region appears to be largely dependent on their tendency to effloresce. This tendency is strongly influenced by the relationship between the vapour pressure of water in the atmosphere surrounding the hydrate and the dissociation pressure for the system involving that hydrate and its dehydration product. The temperature dependent dissociation reaction, e.g.

$$Na_2SO_4.10H_2O_{(s)} \rightarrow Na_2SO_{4(s)} + 10H_2O_{(v)} \qquad \ldots 4.7$$

will not occur when the ambient vapour pressure is higher than the dissociation pressure. Table 4.8 gives relationships between temperature, dissociation pressure and corresponding relative humidity for the dissociation of four single phase hydrates detected in this study. The ambient vapour pressure or relative humidity required to prevent efflorescence becomes less as the ambient temperature is lowered.

Table 4.8 Dissociation pressure (mm Hg) and temperature relationships for sodium, ferrous and magnesium sulphates, and calcium chloride (interpolated or extrapolated values shown in parentheses).

Temperature (°C)	0	10	20	Data source
water vapour pressure	4.58	9.21	17.54	1
dissociation pressure $Na_2SO_4.10H_2O$-Na_2SO_4 pair	2.78	6.28	13.32	2
corresponding* relative humidity (%)	60.7	68.2	76.0	
equilibrium relative humidity of $FeSO_4.7H_2O$-$FeSO_4.4H_2O$ pair	(60)	(65)	75	3
dissociation pressure $MgSO_4.7H_2O$-$MgSO_4.6H_2O$ pair	(1.7)†	(3.6)	(8.5)	4
corresponding* relative humidity (%)	33	39	48	
dissociation pressure $CaCl_2.6H_2O$-$CaCl_2.4H_2O$ pair	0.60	1.4	3.3	5
corresponding* relative humidity (%)	13	15	19	

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*from Equation 4.1 †value at +1.8°C

1 Weast (1971)
2 from best fit curve of ln (dissociation pressure) versus 1/T (cf. Equation 4.3) fitting data from literature survey (4.2.1), Young (1967), and Maron and Prutton in Dort and Dort (1970): Dort and Dort erroneously listed pressure at 25°C as that for 20°C
3 Ehlers and Stiles (1965)
4 from best fit curve as in 2 above, fitting data of Carpenter and Jette (1923)
5 Timmermans (1960)

The summer climate at the soil surface in McMurdo oasis usually favours the dehydration of mirabilite. Thenardite is the stable phase of sodium sulphate in mean conditions of surface relative humidity and temperature for soils whose gravimetric moisture content is less than about 1-3% (Fig.4.6). Such soils are widespread in McMurdo oasis (2.3.1ii) which is consistent with the lack of mirabilite in 2A deposits there (Fig.3.3A).

Dehydration of mirabilite is retarded within the regolith in the oasis, around McMurdo Sound, and throughout the winter period in the whole region. Higher humidities and lower temperatures in these places and at this time (Fig.4.6) inhibit Reaction 4.7. This is consistent with the occurrence of mirabilite in both 2A and subsurface deposits in McMurdo Sound, and in subsurface deposits in the oasis (Fig.3.3).

Mirabilite and thenardite were found coexisting (or in close proximity to each other) in deposits under stones at more than 25 localities in the region (Appendix 1, Tables 3, 5-7, e.g. localities 60, 61). Equilibrium between the two phases and their subsurface environment had probably been reached in many of these deposits, especially those in xerous or ultraxerous soils of the oasis. The 'phase rule' (Wetmore and LeRoy 1951) dictates that the mean relative humidity and temperature of these deposits lie along the line AB (Fig.4.6) in the binary system. (The presence of other ions, e.g. Cl^-, in the deposits appears to depress line AB by no more than about 10 percent, see line EF on Fig.4.6.) Such conditions are quite probable under cobbles up to 0.2 m or more in diameter.

Mirabilite and thenardite may also coexist in salt-covered depressions (2B deposits, Table 3.3A). Efflorescence of mirabilite is probably slow compared to its rate of crystallization from saline solutions. Similarly, where large masses of mirabilite are present, the layer of thenardite formed on the surface of the mass may physically inhibit further dehydration.

The distribution of other hydrates in Table 4.8 can be rationalized in a similar way. The average atmospheric relative humidity is high (70-100%) on the fringe of the polar plateau in the west of the McMurdo region (Appendix 3, section 6.2). Therefore melanterite at Alligator Peak will seldom have any tendency to dehydrate. Similarly, antarcticite is stable because of its very low dissociation pressure, as well as

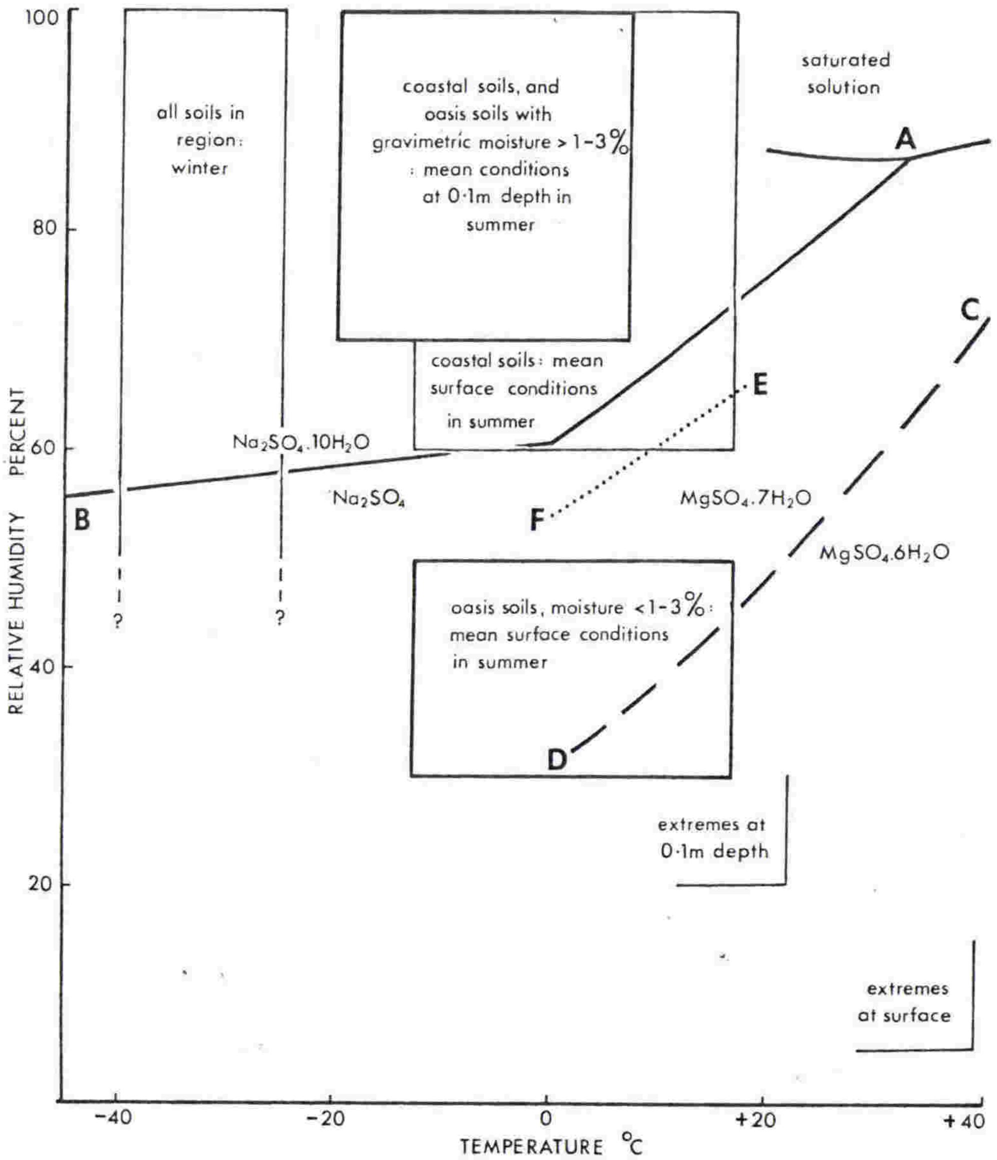


Figure 4.6 Relative humidity and temperature fields (boxes) for soils in the McMurdo region and their relationship to dissociation pressures of mirabilite (solid line, AB, below 0°C approximate only) and epsomite (dashed line, CD) in binary salt systems: lines delineate fields where mirabilite or thenardite (AB), and epsomite or hexahydrite (CD) are the thermodynamically stable phases. Dotted line EF shows probable dissociation pressures of mirabilite in the $Na/Cl/SO_4/H_2O$ system (A and E are quadruple points). Salt data from sources in Table 4.8; soil data from Table 2.5, subsections 2.2.2, 2.2.3, 2.3.1ii, iii, and Appendix 3, Tables 2, 3, section 6.1.

the aridity of the environment. Only in the driest and warmest soil climates (Fig.4.6) would there be any tendency for antarcticite to effloresce. Furthermore epsomite is the prevalent form of magnesium sulphate (Fig.3.3) because of the low dissociation pressure of that phase compared to mean humidity and temperature conditions in soils of the region (Fig.4.6).

The increased frequency of occurrence of hexahydrite in areas around McMurdo Sound (Fig.3.3B) is possibly a kinetic and thermodynamic effect due to the presence of other ions. Coastal 2A deposits with Mg^{2+} as a major component more commonly contain bloedite and thenardite than similar deposits in the oasis (Appendix 1, Tables 3.4, 5.1, 6.6, 7.2). This indicates that high concentrations of other ions such as Na^+ are present in the solutions (containing mainly Mg^{2+} and $SO_4{}^{2-}$) that lead to such coastal deposits. The presence of these other ions lowers the transition temperature between the two hydrates from +48.4°C in the binary aqueous system (i.e. $Mg/SO_4/H_2O$) to as low as +13°C in the sea water system (Carpenter and Jette 1923; Phillips 1947). This lowers the temperature range over which hexahydrite is stable. Hexahydrite is relatively more abundant in coastal areas than in the oasis probably for this reason.

4.5 Effect of Past Changes in the Extent of Lakes and Glaciers

4.5.1 Lakes:

Lakes, both proglacial and in rock-basins, have been more extensive in McMurdo oasis in the past (Nichols 1966; Denton et al. 1971), modifying salt deposits in soils by dissolution and deaquation processes. Above Lake Vanda a pronounced inversion in salt concentration is present between the 56 m and 61 m levels on the elevated strand lines (Nichols 1964 , 1966); the elevation of this inversion is about 150 m above sea level. Field (1975) noted a similar abrupt change on the north side of Taylor Valley above Lake Bonney. The change coincides with a linear feature about 210 m above the present surface of Lake Bonney or about 270 m asl. The linear features and others above and below it have been described as former lake levels (Plate 4.1). These levels belonged to "Glacial Lake Washburn", which was dammed by an expanded Ross Ice Shelf (Péwé 1960; Denton et al. 1971) and to an expanded

Lake Bonney (Hendy et al. 1977, 1979). At both Vanda and Bonney sites, the waters of the expanded lakes have leached salts from the regolith below the high water level.

Salts have accumulated in 2A and 4 deposits near Lakes Vanda and Bonney, below the high water levels of the former lakes (see Appendix 1, pp.14, 15, 25). Therefore these accumulations have developed since the lakes were drained or evaporated. Corrected ^{14}C dates from algae indicate that "Glacial Lake Washburn" reached its full bodied state (300 m asl) about 2 x 10^4 years ago (Denton et al. 1971; Stuiver et al. 1980). The highest lake levels in Lake Vanda are 2000-3000 years old (Wilson 1967; Nakao et al. 1978). Therefore the salt deposits mentioned above are younger than these ages.

The effect of lake expansion on the composition of lake deposits has been described by Morikawa et al. (1975) who studied salts near the present shoreline of Lake Vanda and in elevated areas above 150 m asl (Fig.4.7). These latter areas included the eastern foot of Dias, around Canopus Pond and the southern foot of Bull Pass.

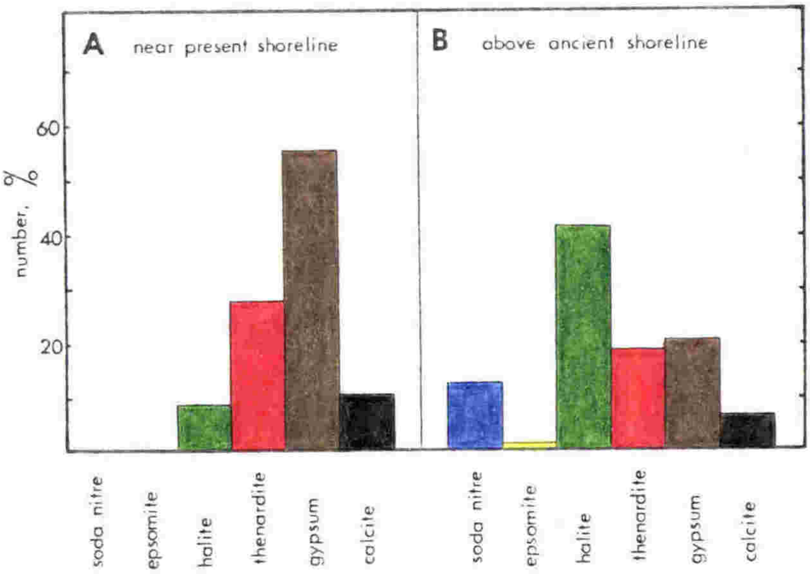


Figure 4.7 Number of occurrences of salt phases in deposits around Lake Vanda. A, near present lake shoreline and B, above ancient shoreline of expanded lake (after Morikawa et al. 1975)

The distribution reveals a tendency for sparingly soluble gypsum to dominate deposits in the shoreline areas but for soluble halite to dominate in the elevated areas. The number of deposits that contain halite is low near the shoreline; here soda nitre does not appear to be present. The salt occurrences noted around Lake Vanda in the present study (Appendix 1, p.25) are consistent with this distribution. The ancient lake waters have probably selectively leached most of the more soluble salts from the regolith in areas below about 150 m asl.

Former ice-dammed lakes have caused salt accumulation as well as leaching. Hendy et al. (1977, 1979) have studied lacustrine carbonates precipitated from expanded lakes in Taylor Valley. Many of these are exposed on the valley sides as carbonate "biscuit" (e.g. localities 65, 66, Appendix 1, p.15). U-Th dates for these carbonates range in ages from the present to greater than 4 x 10^5 years. Bedded mirabilite deposits have been studied in Hobbs Valley and other valleys in the Koettlitz Glacier area by Dort and Dort (1970) and Bowser et al. (1970). Nakai and Mizutani (1977) have sampled mirabilite in layers in bedded 'marine' sediments on Black Island and the Cape Barne locality of David and Priestley (1914). Nakai and Mizutani (1977) and Lyon (1978) sampled gypsum in similarly bedded sediments in Miers Valley. Exposures of crystalline mirabilite are present from near sea level up to an elevation of almost 200 m in Hobbs Valley (Dort and Dort 1970). All these deposits were formed by crystallization of these salts from former water bodies, probably dammed by an expanded Koettlitz Glacier or Ross Ice Shelf (David and Priestley 1914; Bowser et al. 1970; Lyon 1978). Such crystallization of mirabilite has been observed from present-day ponds in the Hobbs Glacier area (Bowser et al. 1970).

4.5.2 Glacier positions:

The former positions of glaciers may not be as well chemically marked by changes in salt concentration as are the former positions of lakes. Table 26.2 in Appendix 1 (pp.45, 46) shows specific conductance in 1:5 water extracts of two sets of soil samples collected on each side of the youngest moraine of the Beacon Valley lobe of Taylor Glacier (Appendix 1, Fig.2). This is one of Black's (1973) sand wedge growth sites in which he attempted to use such wedges to date surfaces. The average specific conductance of three samples from the north (i.e. younger) side of the moraine was 1.50 mmho cm^{-1}, with standard deviation of 0.69. The average of three from the south side was 2.24 mmho cm^{-1}, standard deviation 0.83. The t statistic for the difference between the two average values is

$$t = 0.78 \qquad \text{(from Appendix 2, Equation 5).}$$

At the 80% confidence level (c equals 0.20),

$$t_{c/2} = t_{0.10} = 1.5$$

for $n_{north} + n_{south} - 2 = 4$ degrees of freedom (Freund <u>et al.</u> 1960), and

$$-t_{c/2} \leqslant t \leqslant t_{c/2} \text{ (Appendix 2, A2.2.2iv)}$$

Therefore, there is no significant difference in salt concentrations in the regolith across the moraine. Evidently the glacier lobe caused little differential leaching of the regolith it covered.

4.6 Effect of Wind

4.6.1 Effects noted:

Wind is an important geomorphic agent in the McMurdo region. This is shown by the existence of ventifacts, polished surfaces, windblown sand and pebble ridges, sand dunes, fretted dolerite and englacial and supraglacial windblown sand (David and Priestley 1914; Wright and Priestley 1922; Taylor 1922; McCraw 1967b; Dort 1967; Claridge and Campbell 1968a; Selby <u>et al.</u> 1973, 1974). Deflation has lowered bedrock surfaces by as much as a metre in places as can be seen from the size of some fretted dolerite 'spines' (Claridge and Campbell 1968a).

The localized effect of wind on salt deposits in the McMurdo region has not been extensively studied. Differential supply of windborne sea- and sea ice salt can explain differences between the salinities of lakelets in the Cape Royds area (Mawson 1915). On the north side of Inaccessible Island, McMurdo Sound, small troughs or tracks have developed in a ridge of windblown sand (Taylor 1922). Salt efflorescences are present in these wind-controlled troughs. Black and Berg (1963) thought wind is an important cause of salt movement in McMurdo oasis.

In hot deserts of the world, wind is known to play a significant role in salt transport. Salts are easily blown from salt-covered depressions; fine dust composed partially of salts blown from playas forms a ubiquitous dry fallout in desert areas (Posokhov 1960; Davis and De Wiest 1966; Tsyganenko 1968).

The same is probably true in McMurdo oasis although on a reduced scale because of the relative lack of large playas there. Plate 4.7 shows the localized fallout in the form of salt blown off the saline icing from the Taylor Glacier discharge site (Chapter 8) onto the ice of Lake Bonney. The salts have accumulated preferentially on the windward side of ablation 'dimples' in the lake ice. Plate 4.8 illustrates an efflorescence of the 2A type at locality 285 on 'Depot Cone'. The area of salt immediately to the left of the tape has been deflated by the southerly wind; salt 'tails' extend downwind from basalt fragments, and grooves are present in the deposit. The salt is quite soft and incoherent, and therefore deflates much faster than harder rock.

Similar erosion features have been noted in young efflorescences around the terminus of Taylor Glacier (localities 37-39, Appendix 1, p.21). At locality 37 'windscoops' about 4 mm wide were seen around the upwind end of small pebbles seated in a 2A type crust composed of thenardite and halite. Salt 'tails' and grooves were also seen. Crusts of gypsum are particularly favourable for detecting such signs of wind action.

Two gypsum 'bulbous' deposits from 'Depot Cone' are shown in Plates 4.9A and B. These encrustations have also been shaped and modified by southerly winds. The accumulations are somewhat 'streamlined' and the greater mass of salt is towards the downwind end. Similar deposits exist elsewhere, such as in Taylor Valley west of Lake Bonney at locality 70 (Appendix 1, p.15). The surface of the 'bulbous' deposits is often smooth on the side facing the strongest winds (south or west) but rougher on the leeside. Wind action has apparently shaped these deposits during their slow growth from evaporating soil moisture, and has also smoothed the more exposed surfaces.

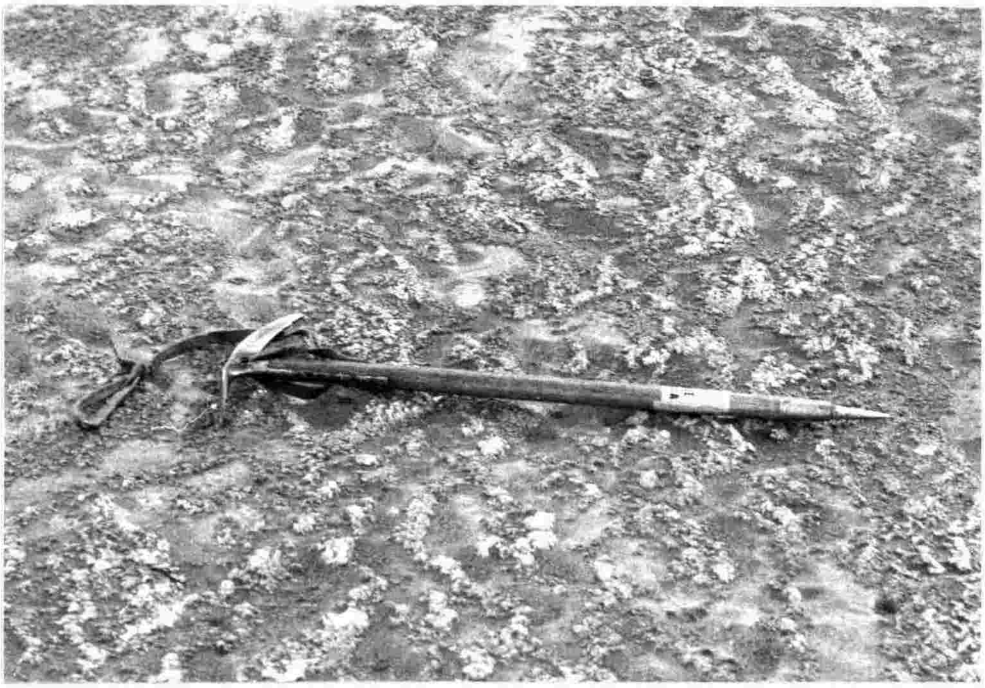


Plate 4.7 Salt, mainly halite, blown off the saline discharge icing from Taylor Glacier onto the moat ice of Lake Bonney. The shaft of the ice axe points in the direction from which the salt was blown. (22/10/76)

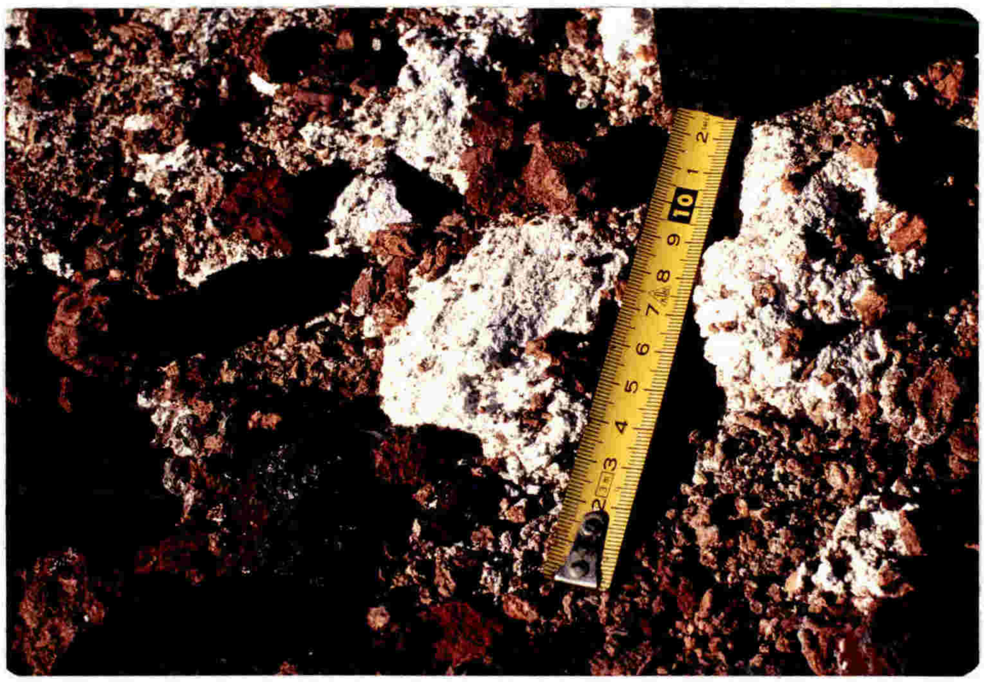
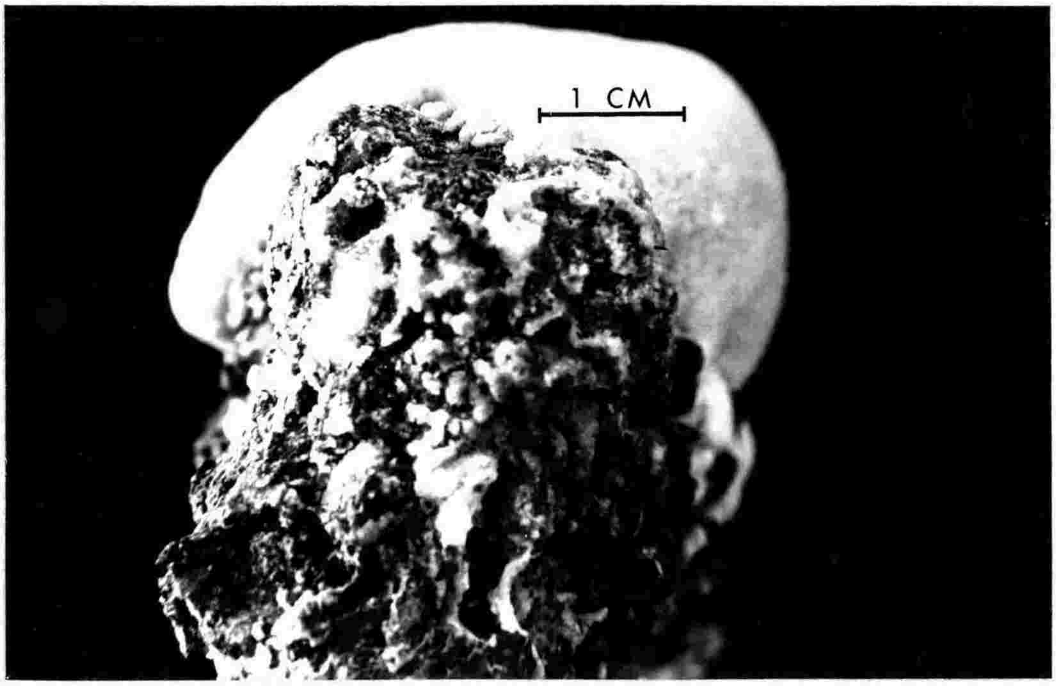


Plate 4.8 Deflated surface efflorescence (deposit type 2A) of epsomite (plus minor gypsum, hexahydrite and bloedite) at Depot Cone, Mt. Discovery area (sample 24813, locality 285). The tape points towards the south, the direction of the strongest wind. Grooves and ridges elongated north-south can be seen in the salt immediately to the left of the tape. (4/12/76)

A



B

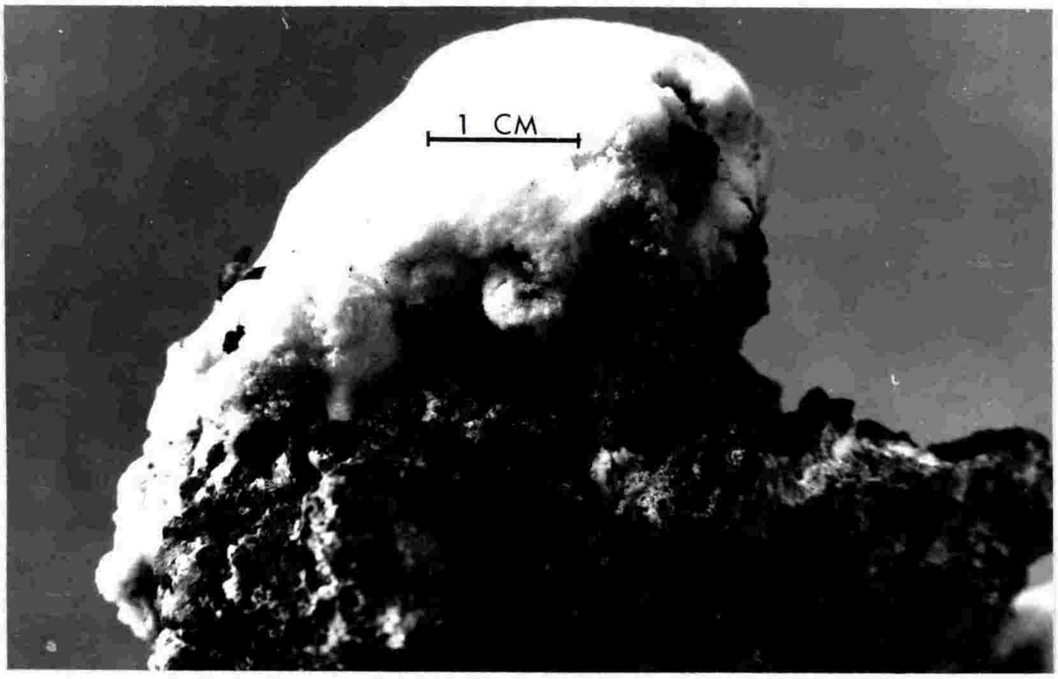


Plate 4.9A & B 'Bulbous' gypsum deposits (types 1A and 2A) encrusting the surface of basalt cobbles and fragments of lava at Depot Cone. Southerly winds blew from left to right across the deposits (5/12/76).

4.6.2 Some theoretical aspects:

Cooke and Warren (1973) have reviewed the factors that may increase wind erosion from soil surfaces and those that may reduce it. The nature of the eroding surface is critical; a smooth dry surface, rich in silt and sand-sized particles, salt and other light material, erodes relatively fast. Salts crystallizing at the surface tend to rework and loosen surface material and render it more liable to removal. Increased cohesion, cementation and surface roughness, wetting, larger material, stone pavements and high clay content, all tend to reduce erosion. Thus, dry incoherent surface efflorescences of soluble sodium and magnesium salts will erode faster than coherent, massive encrustations of gypsum and calcite in Antarctica. Relative cohesion in deposits is probably more important than salt particle density and shape. Thenardite, the most common salt in 2A deposits (Figs.3.2, 3.3) may be the most affected phase.

Wind action is strongest when an abundant supply of wind transportable particles is available. Erosion increases with increased kinetic energy of these particles (Dietrich 1977). Therefore, erosion and subsequent transport of any surface salt will be greatest in localities that are subject to windblown snow and sand and are exposed to strong winds. These localities include areas along the western margin of the ice sheet and those at high elevations (Appendix 3, 5.4).

It is difficult to further quantify the effect of wind on local distribution of salts. More study would need to be made of cohesion in surface salt deposits, and the areal extent of salt-covered depressions. Collection apparatus could be set up to monitor dry fallout of salt. Evidence has been presented which shows that wind has a significant effect on salt deposits. Presumably, wind limits the growth of surface deposits by removal of salt from them. This dislodged salt then migrates downwind for some distance depending on wind strength, surface roughness and topography. Turbulence and other winds with vertical development (Appendix 3, section 4.4) may cause fine salt particles to be carried aloft and travel many kilometres. Larger salt particles will travel a few metres only, before being reincorporated onto the surface of the salt-soil system. Chapters 5-7 further point to the importance of wind to salt distribution in the McMurdo region.

4.7 Summary of Chapters 3 and 4

The purpose of these chapters has been to discuss the various aspects of local distribution of salt. This has included a review of the specific salt phases that have been detected in the region. The 'geochemical soil sequence' down slopes in McMurdo oasis has been characterized and extended. This sequence is:

calcite, gypsum, thenardite, epsomite, soda nitre, halite, antarcticite.

The behaviour of ionic ratios in saline flows appears to reflect this sequence.

The processes responsible for this separation have been examined. These involve separation of salts at various stages of salt migration, the most important stages being dissolution and deaquation. There are several controls on migration and separation: moisture availability is dominant; eutectic temperatures, deposit composition, and solubility are chemical factors; temperature, ambient relative humidity, soil texture, topography and wind are environmental factors. Deaquation of brines has been discussed with examples illustrating the formation of double salts. These salts and deposits can form in present-day conditions.

Migration and separation of salts by the action of water and wind are continuing processes in the McMurdo region. These processes must have been active for a long time now because of the great age of the region (1.2.4) and broadly similar climatic conditions over the past few million years (2.4.2). Salts may accumulate at some distance from where they were first deposited or formed. Purified salt deposits containing only one or two phases are quite common in the region. It is not difficult to envisage that repeated fractional dissolution, migration and crystallization of salt phases, over a period of up to a few million years in an environment with limited moisture, could lead to the development of these purified salt deposits.

CHAPTER 5 REGIONAL DISTRIBUTION OF SALTS

5.1 Preamble

5.1.1 Introduction and previous work:

The regional pattern of salt distribution is useful in helping to determine the salt sources. Trends or gradients in this distribution, for example with increasing distance from the coast, may reveal marine or continental sources. Claridge and Campbell (1977) have already had some success with this approach in soils in the Transantarctic Mountains. In the most comprehensive study to date, they found strong gradients with NO_3/Cl and SO_4/Cl increasing from east to west and from north to south away from the present limits of open sea water. Other conclusions were that soil pH decreases inland, that Ca^{2+} and Mg^{2+} are enriched in soils formed on dolerite, and K^+ in those formed on granites. Also, calcite tends to occur mainly in areas with carbonate-containing rocks, but notable exceptions exist inland and on Hut Point Peninsula.

Nishiyama (1979) also studied regional salt distribution but from a smaller area, namely Taylor Valley east of Taylor Glacier and Wright Valley from east of Labyrinth to below Bull Pass. He, like Keys (1972) and Field (1975) found that sulphate salts tend to exist in higher proportions in elevated areas. A varied suite of soluble carbonate phases exists in eastern Taylor but not in Wright Valley, whereas halite and thenardite are widespread. Other, more limited, regional studies include Bockheim (1979b) who examined soil salts in Wright Lower Valley, and Linkletter (1970) who examined soil salts in the Koettlitz and Taylor Valleys.

5.1.2 Outline:

This chapter describes regional distribution of salts in the McMurdo region with emphasis on McMurdo oasis. East-west and low elevation-high elevation gradients are examined, and the influence of rock type is considered. The three variables, distance from coast, elevation and substrate rock type define the patterns of regional salt distribution. North-south gradients are presented for McMurdo Sound area, and similar gradients on the Ice Sheet are discussed. The saline lakes of McMurdo oasis are briefly examined. The chapter ends with a general discussion covering the distribution of the major and minor phases that are present in the region. The causes of the salt gradients are discussed in the following chapter.

In McMurdo oasis, each of the three variables, distance from coast, elevation and rock type, are interrelated with the other two. For instance, as the average distance from coast increases, so too does average elevation, and the amount of dolerite exposed (Figs.1.2, 2.7). Such interrelationships make it difficult to examine each variable entirely on its own. Here, the problem is overcome to a large extent by placing the salt and rock type data into zones of distance and elevation and examining the influence of one variable at a time. Multiple linear regression analysis was not attempted.

Diagrams, mainly graphs, are used to portray salt distribution. These diagrams show the number of times that specific phases or groups of phases are present in deposits as a percentage of all such numbers of phases or deposits (Appendix 2). Thus the diagrams portray the relative frequency with which specific phases are encountered in an area. The technique assumes that no systematic errors have occurred due to different sampling efficiencies of any phases. However, it is possible that such errors have affected the numbers of gypsum and calcite phases reported, especially in western areas (Appendix 2, A2.1.1). For this reason conclusions comparing these phases with others cannot carry the same weight as those concerning the soluble phases only. Therefore the latter are compared separately on several Tables and Figures (e.g. Tables 5.1, 5.2). Statistical techniques and significance testing are prerequisites for this study to check the validity of the distributions; the applications here (Tables 5.3-12) are based on the treatments noted in Appendix 2, A2.2.2. The complete colour code used in histograms and phase groupings is given in Appendix 2, Table A2.1.

5.2 Regional Distribution

5.2.1 East-west gradients in McMurdo oasis:

(i) common phases

Strong east-west gradients are evident in the distribution of several of the eight common salt phases and their ions (Figs.5.1-5.6). Chloride and sodium phases become less frequent (decrease) towards the west, whereas nitrate and magnesium phases become more frequent (increase) towards the west. Sulphates and calciums tend to increase and carbonate to decrease towards the west, but none of these latter tendencies is strong, over most of the oasis.

These gradients have been determined by counting the phases which comprise those deposits present in two zones of elevation, at map distances between zero and 150 km inland from the present limit of open sea. Surface elevation increases towards the west on average in McMurdo oasis; therefore the influence of this increasing elevation on horizontal east-west salt gradients can be limited by examining the compositions of only those deposits that are present in fixed ranges of elevation. The elevation zones chosen were (1) zero to 1000 metres above sea level (Tables 5.1A, 5.2A) and (2) between 1000 and 2000 m asl (Tables 5.1B, 5.2B). These ranges are large enough to ensure adequate amounts of data but narrow enough to limit the effect of elevation gradients.

Specific phases show distribution trends (Figs.5.1, 5.2). Figure 5.1 examines the distribution of halite, thenardite, gypsum and calcite, as proportions of all numbers of all eight phases. The percentages from Table 5.1A and B are represented on composite Figure 5.1 as single distance points (for clarity). Most data in section a of the figure are scattered mainly due to large but highly variable proportions of calcite, as sampled by Nishiyama (1977). This scatter may be caused by real but relatively local differences in salt distribution or by differing sampling efficiencies (Appendix 2, A2.1). Gypsum is the only phase that can justifiably be fitted to the data in this section. The data in sections b and c are more coherent. Linear regression lines show that halite and thenardite are present less commonly away from the coast, whereas gypsum becomes more common. (A similar gypsum tendency in Dronning Maud Land has been noted by Markov et al. 1970.) The tendency for calcite is to decrease from 30 km inland, but data are variable for this phase and fluctuate about a mean level. Therefore, calcite abundance can be described as a low, approximately constant 'plateau' level of abundance from about 30 km or so inland.

Strong patterns are evident in the distributions of the nitrate and magnesium salt phases (Fig.5.2). The construction of this diagram from data in Table 5.2A, B is similar to the former diagram. None of these phases was found closer than 25 km from the coast. In the distance section 25 - 75 km, salt deposits increasingly contain soda nitre, darapskite, bloedite and epsomite. The trend is continued for epsomite and to a lesser extent soda nitre further west than 75 km (Table 5.2B).

Table 5.1 Distribution (percent) of common salt phases from east to west in McMurdo oasis.

A. From present limit of open sea to 75 km inland in Taylor and Wright Valleys and elevations up to 1000 m asl ; summary of data in Appendix 1, Tables 3, 6 and Nishiyama (1977).

Phase	Map distance inland (km)							
	< 5	5-15	15-25	25-35	25-55*	45-55	55-65	65-75
soda nitre	0	0	0	0	2	3	5	11
darapskite	0	0	0	2	3	3	5	8
epsomite	0	0	0	0	1	1	0	3
bloedite	0	0	0	1	2	2	3	5
halite	19	35	21	40	34	31	30	18
thenardite	15	28	6	26	22	20	12	18
gypsum	2	0	9	11	24	30	30	26
calcite	64	37	63	19	12	8	14	11
total number of phases counted, N	80	97	65	96	277	159	59	38

*Insufficient samples in the range 35-45 km

B. From 25 km to 150 km inland in McMurdo oasis, including Skelton Névé(elevations 1000-2000 m asl); data from Appendix 1, Tables 3, 5,6.

Phase	Map distance inland (km)				
	25-45	45-55	55-75	75-85	130-150
soda nitre	3	0	10	10	9
darapskite	0	14	10	9	4
epsomite	0	3	2	6	17
bloedite	0	6	10	7	4
halite	14	6	5	1	0
thenardite	31	27	22	18	4
gypsum	35	27	34	39	39
calcite	17	17	7	9	22
N	29	36	41	81	23

Table 5.2 Distribution (percent) of six major soluble salt phases from east to west in McMurdo oasis.

A. From present limit of open sea to 75 km inland in Taylor and Wright Valleys (for elevations up to 1000 m asl); summary of data in Appendix 1, Tables 3, 6 and Nishiyama (1977).

Phase	Map distance inland (km)							
	< 5	5-15	15-25	25-35	25-55	45-55	55-65	65-75
soda nitre	0	0	0	0	3	5	9	17
darapskite	0	0	0	3	5	6	9	13
epsomite	0	0	0	0	1	2	0	4
bloedite	0	0	0	1	3	4	6	8
halite	56	56	80	58	54	51	55	29
thenardite	44	44	20	37	34	32	21	29
N	27	61	18	67	177	99	33	24

B. From 25 to 150 km inland in McMurdo oasis, including Skelton Névé (elevations 1000-2000 m asl); data from Appendix 1, Tables 3, 5, 6.

Phase	Map distance inland (km)			
	25-55	55-75	75-85	130-150
soda nitre	3	17	19	c. 22
darapskite	15	17	17	c. 11
epsomite	3	4	12	c. 44
bloedite	6	17	14	c. 11
halite	17	8	2	0
thenardite	56	37	36	c. 11
N	34	24	42	9

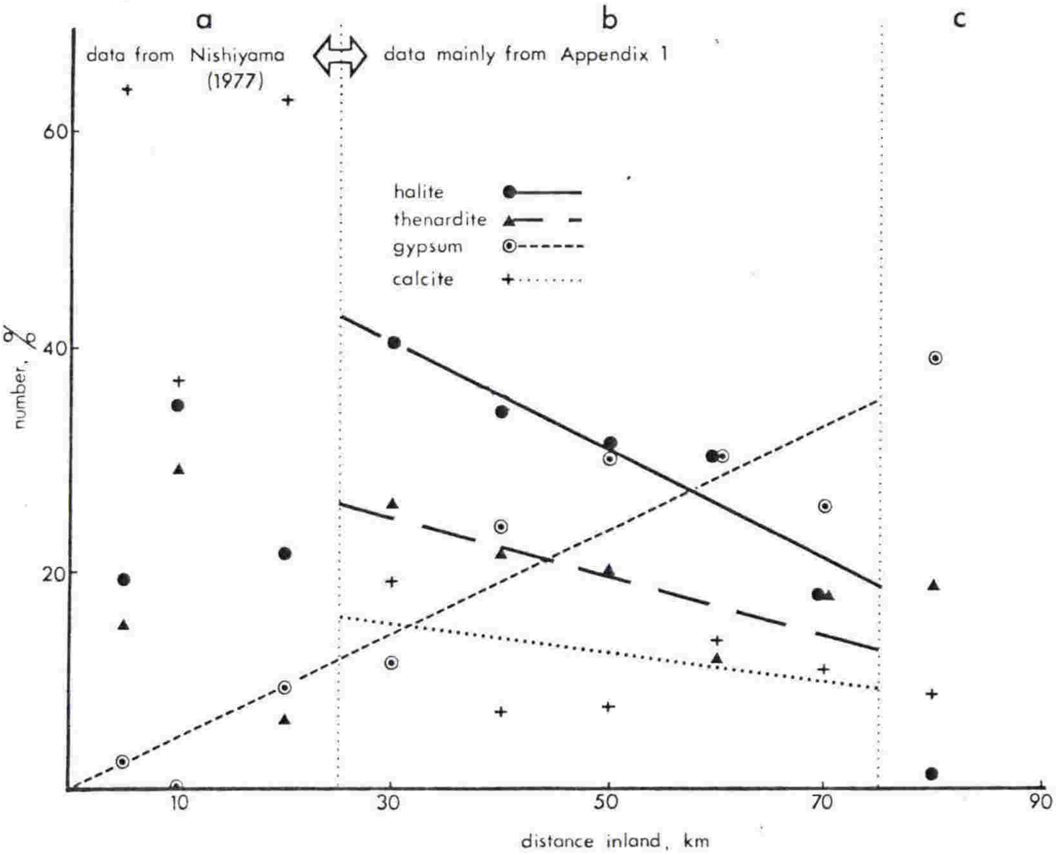


Figure 5.1 Distribution (frequency of encounters, %) of halite, thenardite, gypsum and calcite in deposits with increasing map distance inland (from east to west) in McMurdo oasis (sections a, b, zero-1000 m elevation; c, 1000-2000 m elevation).

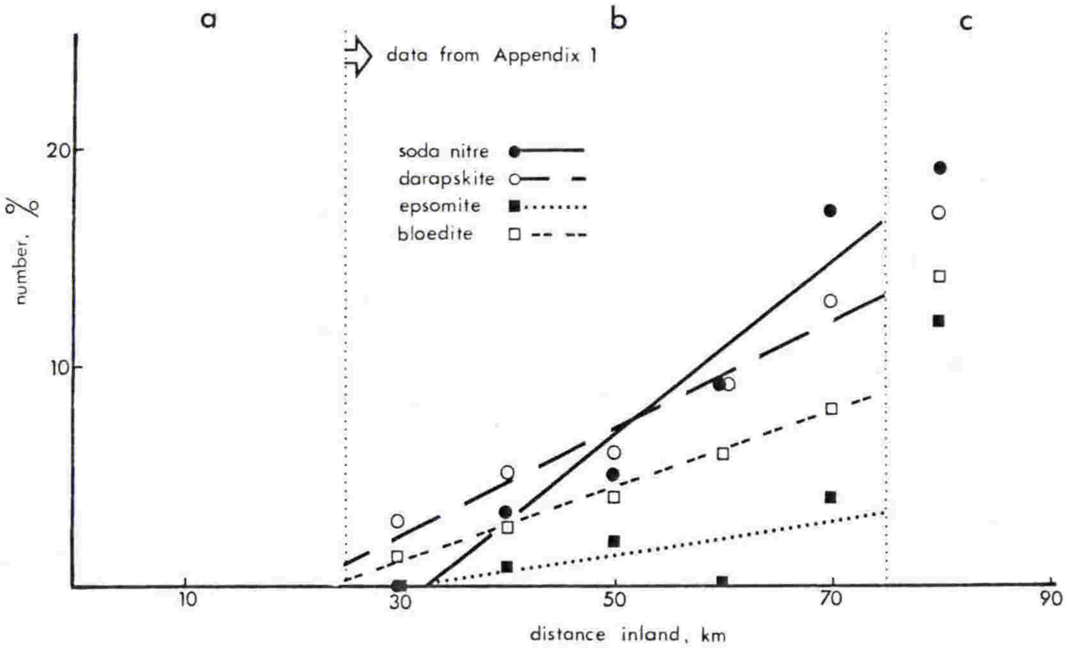


Figure 5.2 Distribution (%) of soda nitre, darapskite, epsomite, bloedite with increasing map distance inland (from east to west) in McMurdo oasis (sections a, b, c as on Fig.5.1).

(ii) ions of common phases

Distribution gradients are more clearly defined when the distribution of specific anions and cations in deposits is examined. A particular 'ion' in a deposit is counted once for each time a phase containing it is present in the deposit; this is a presence or absence test, no account being taken of stoichiometric relationships. Anion distribution is considered first; it is summarized in Table 5.3 and Figure 5.3 for all eight common phases, and in Table 5.4 and Figure 5.4 for the six major soluble phases. In these and subsequent Figures a solid line indicates that a close-fit trend ($c \geqslant 80\%, |r| \geqslant 0.7$, Appendix 2, A2.2.2ii) is apparent, that is a significant correlation is evident from linear regression analysis. The distribution data (%) sum to 100; as one ion increases, another decreases. This trivial 'cause' of gradients is present throughout this and the following subsections, as a consequence of the necessity to maximize the number N of data (Appendix 2).

Strong and significant trends are evident for chloride and nitrate ions (Figs.5.3, 5.4). The increase in nitrate inland is most marked in the lower zone of elevation (Fig.5.3, Table 5.3A). In the higher zone (Table 5.3B) the data can be fitted to two intersecting straight lines whose gradients have opposite signs. The correlations are close and and significant at a high level of confidence, although only three data points are fitted to each line. Nitrate first increases inland, then decreases west of about 75 km. A similar tendency is suggested in the proportions of nitrate in Table 5.4B, though data are limited. Nitrate phases were not found in salt deposits west of Mt. Fleming (Appendix 1, p.27). Deposits sampled in the western areas were almost exclusively of the 2A and 4 types. Furthermore, this decrease in nitrate from soils in inland regions was not noted by Claridge and Campbell (1977). Therefore, it is concluded that (1) the nitrate salts have been unable to accumulate in 2A and 4 deposits and probably (2) have accumulated within the soil such as in salt horizons (type 5) deposits. Such differential accumulation is likely to be due to surficial leaching of nitrate phases. Tendencies are weak for the other anions and statistically unchanging.

Cation distribution shows similar patterns (Tables 5.5, 5.6, Figures 5.5, 5.6). Sodium ion decreases towards the west, similar to chloride. Magnesium ion becomes more commonly distributed at the expense of sodium towards the west. The regression line for calcium ion indicates a slight

Table 5.3 Distribution (percent) of common salt phases as anions, from east to west in McMurdo oasis.

A. From 25 to 75 km inland in Taylor and Wright Valleys (elevations up to 1000 m asl); data from Table 5.1A.

Phases*	Map distance inland (km)					Statistics			
	25-35	25-55	45-55	55-65	65-75	slope of best fit line	t statistic	confidence level (%)	correlation coefficient
chloride	41	34	31	30	18	-0.50	-5.2	97.5	-0.95
nitrates	2	5	7	10	19	0.39	5.0	97.5	0.95
sulphates	38	48	54	46	52	0.26	1.5	< 80	0.65
carbonate	19	12	8	14	11	-0.14	-1.1	< 80	0.52
N	96	277	159	59	38				

B. From 25 to 150 km inland in McMurdo oasis, including Skelton Névé (elevations 1000-2000 m asl); data from Table 5.1B.

Phases*	Map distance inland (km)					Statistics†			
	25-45	45-55	55-75	75-85	130-150	slope of best fit line	t statistic	confidence level (%)	correlation coefficient
chloride	14	6	5	1	0	-0.11	-2.4	90	-0.82
nitrates	3	14	20	18	13	0.57/-0.09	10/-68	90/99	0.99/-1.0†
sulphates	66	63	68	72	65	0.0033	0.070	< 50	0.041
carbonate	17	17	7	9	22	0.057	0.69	< 70	0.37
N	29	36	41	81	23				

*Darapskite included in nitrates, not sulphates

†Data for nitrates fitted to two intersecting straight lines

Table 5.4 Distribution (percent) of six major soluble salt phases as anions from east to west in McMurdo oasis.

A. From 25 to 75 km inland in Taylor and Wright Valleys (elevation up to 1000 m asl); data from Table 5.2A.

Phases*	Map distance inland (km)					Statistics			
	25-35	25-55	45-55	55-65	65-75	slope of best fit line	t statistic	confidence level (%)	correlation coefficient
chlorides	58	54	51	55	30	-0.55	-2.1	88	-0.77
nitrates	3	8	11	18	30	0.64	6.5	99	0.97
sulphates	39	38	38	27	40	-0.088	-0.47	< 60	-0.26
N	67	177	99	33	24				

B. From 25 to 150 km inland in McMurdo oasis, including Skelton Névé (elevation 1000-2000 m asl); data from Table 5.2B.

Phases*	Map distance inland (km)				Statistics			
	25-55	55-75	75-85	130-150	slope of best fit line	t statistic	confidence level (%)	correlation coefficient
chloride	17	8	2	0	-0.15	⩾ -2.4	⩾ 86	-0.86
nitrates	18	34	36	c. 30	-0.078	⩾ 0.64	⩾ 50	0.41
sulphates	65	59	62	c. 70	0.073	⩽ 1.24	< 80	0.66
N	34	24	42	9				

*Darapskite included in nitrates not sulphates

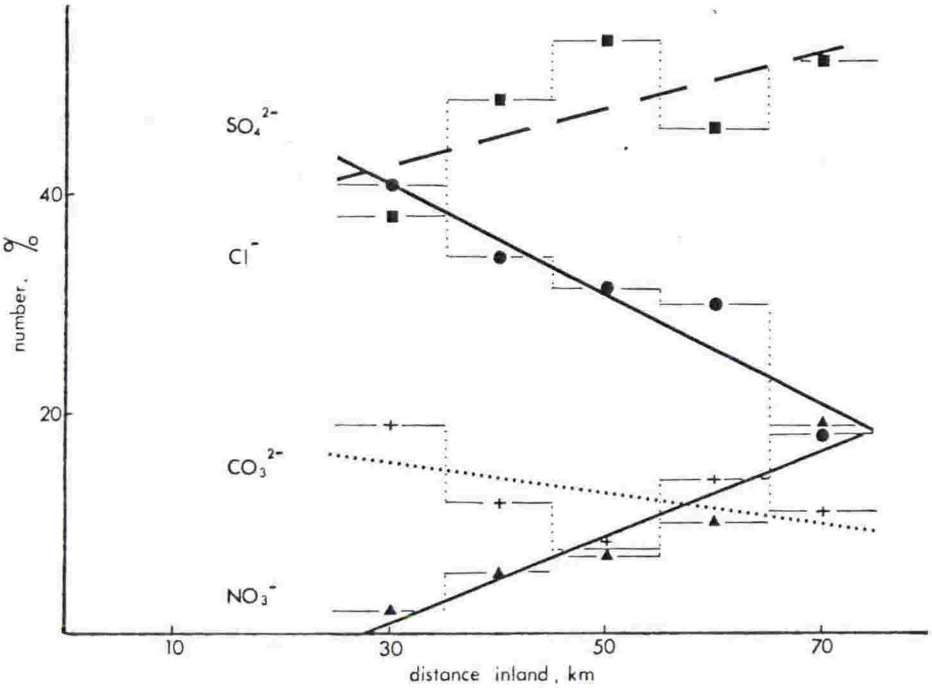


Figure 5.3 Distribution (%) of common salt phases, as anions, with increasing map distance inland (from east to west) in McMurdo oasis; a solid line indicates that a close-fit trend is evident.

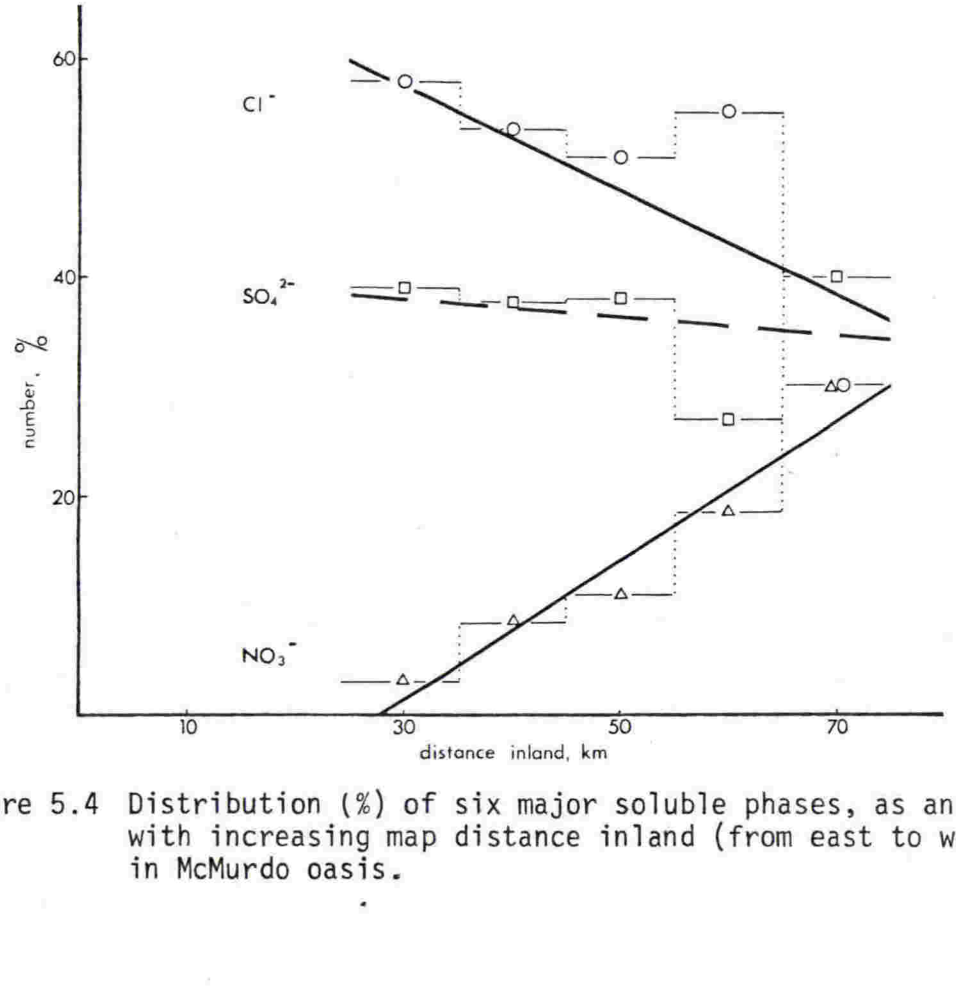


Figure 5.4 Distribution (%) of six major soluble phases, as anions, with increasing map distance inland (from east to west) in McMurdo oasis.

Table 5.5 Distribution (percent) of common salt phases as cations from east to west in McMurdo oasis.

A. From 25 to 75 km inland in Taylor and Wright Valleys (elevations up to 1000 m asl); data from Table 5.1A.

Phases*	Map distance inland (km)					Statistics			
	25-35	25-55	45-55	55-65	65-75	slope of best fit line	t statistic	confidence level (%)	correlation coefficient
sodiums	69	61	58	53	55	-0.36	-4.0	95	-0.92
calciums	30	36	38	44	37	0.22	1.7	82	0.70
magnesiums	1	2	4	3	8	0.15	3.4	95	0.87
N	96	277	159	59	38				

B. From 25 to 150 km inland in McMurdo oasis, including Skelton Névé (elevation 1000-2000 m asl); data from Table 5.1B.

Phases*	Map distance inland (km)					Statistics			
	25-45	45-55	55-75	75-85	130-150	slope of best fit line	t statistic	confidence level (%)	correlation coefficient
sodiums	48	47	47	38	17	-0.32	-7.1	99	-0.97
calciums	52	44	41	48	61	-0.13	-0.76	< 75	-0.68
magnesiums	0	9	12	14	22	0.18	4.6	97.5	0.94
N	29	36	41	81	23				

*Bloedite included in Mg^{2+} phases, not in Na^{+} phases

Table 5.6 Distribution (percent) of six major soluble salt phases as cations from east to west in McMurdo oasis.

A. From 25 to 75 km inland in Taylor and Wright Valleys(elevations up to 1000 m asl); data from Table 5.2A.

Phases*	Map distance inland (km)					Statistics			
	25-35	25-55	45-55	55-65	65-75	slope of best fit line	t statistic	confidence level (%)	correlation coefficient
sodiums	99	96	94	94	88	-0.24	-5.0	97.5	-0.94
magnesiums	1	4	6	6	12	0.24	5.0	97.5	0.94
N	67	177	99	33	24				

B. From 25 to 150 km inland in McMurdo oasis, including Skelton Névé(elevations 1000-2000 m asl); data from Table 5.2B.

Phases*	Map distance inland (km)				Statistics			
	25-55	55-75	75-85	130-150	slope of best fit line	t statistic	confidence level (%)	correlation coefficient
sodiums	91	79	74	c. 40	-0.51	-19	99	-1.0
magnesiums	9	21	26	c. 60	0.51	19	99	1.0
N	34	24	42	9				

*Bloedite included in Mg^{2+} phases, not Na^{+} phases

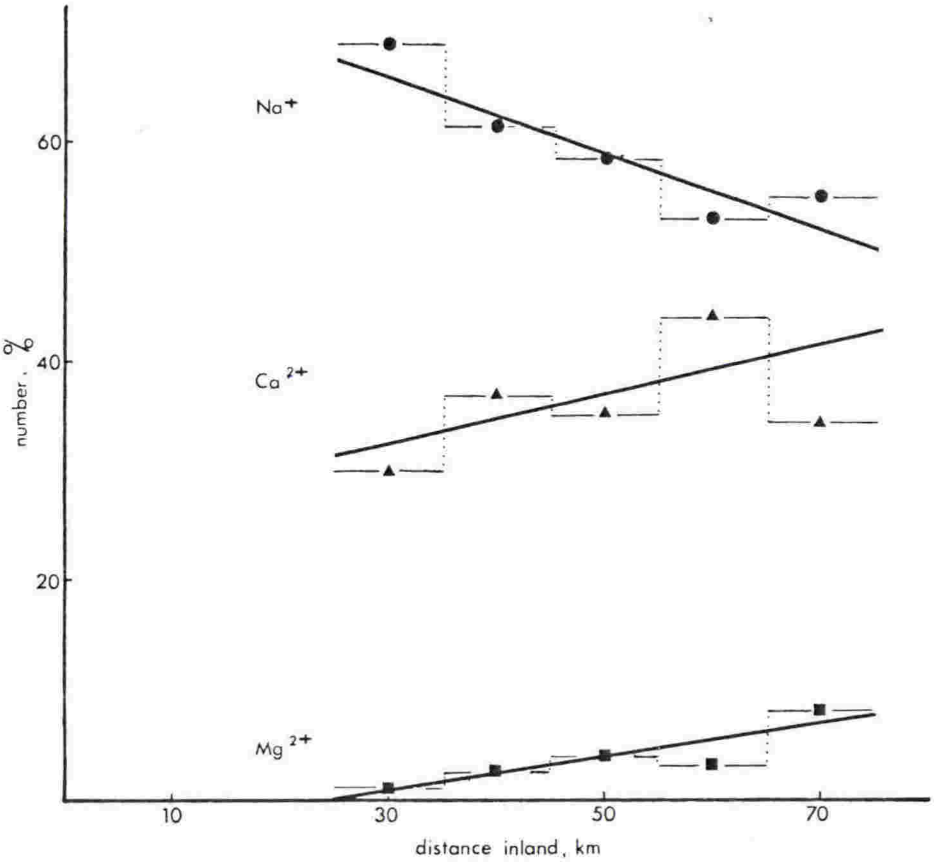


Figure 5.5 Distribution (%) of common salt phases, as cations, with increasing map distance inland (from east to west) in McMurdo oasis.

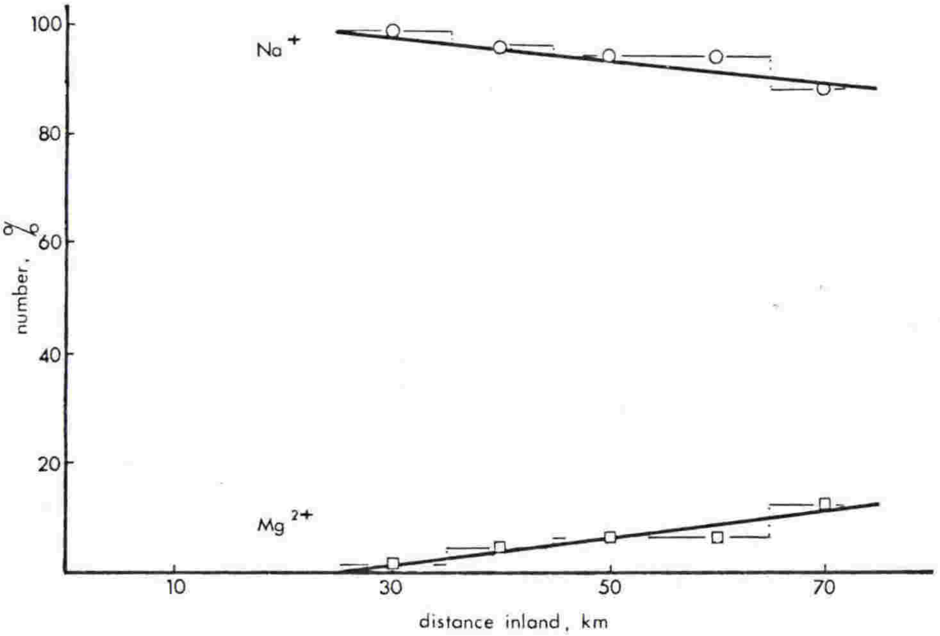


Figure 5.6 Distribution (%) of six major soluble phases, as cations, with increasing map distance inland (from east to west) in McMurdo oasis.

increase towards the west in Figure 5.5; statistical treatment indicates that this trend is significant only at the 82 percent level (Table 5.5A). In the higher elevation zone, calcium ion distribution is statistically unchanging (Table 5.5B).

The distribution patterns of the double salts darapskite and bloedite reflect the relative distributions and relative proportions of their component ions. Towards the east, sodium and sulphate ions dominate magnesium and nitrate ions. Therefore, here thenardite is the major soluble sulphate phase. As the proportions of nitrate and magnesium ions increase towards the west darapskite and bloedite become apparent through reactions among Na^+, SO_4^{2-}, NO_3^- and Mg^{2+}. With a continued rise in the abundance of nitrate and magnesium ions, together with a gradual decrease in Na^+, epsomite and soda nitre become significant, finally becoming the dominant magnesium and nitrate phases towards the west.

These findings can be related to previous quantitative studies. In the present study, nitrate and sulphate tend to become more prominent in deposits towards the west (Fig.5.3) whereas chloride becomes less prominent. Thus the ratios NO_3/Cl and SO_4/Cl for relative distribution of phases increase away from the coast (Figs.5.3, 5.4). The same pattern was observed by Claridge and Campbell (1977) for relative concentrations of ions. This means that the present qualitative-numerical study is consistent with the former quantitative one. Therefore, for a particular phase or ion, the expressions 'encounter frequency' and 'number (percent) of occurrences' are synonymous with 'relative concentration'.

This synonymity is perfectly reasonable. A salt or ion absent (or present in low concentration) in a soil will not be prominent in macroscopic salt deposits. The lack of halite in inland areas and of nitrates near the coast illustrates this, being consistent with the low concentrations of chloride and nitrate respectively, in soils in these areas (Claridge and Campbell 1968a, b, c, 1977). Nitrate is the only ion that shows any noticeable tendency to be concentrated within the soil and not in deposits (especially of the 2A and 4 types). Furthermore this tendency towards differential accumulation is evident only in inland areas. The term 'abundance' is used hereafter to refer to distribution of ions or phases but applies to relative concentration also.

Carbonate is an important anion in eastern Taylor Valley but is much less common inland. Numerous workers have reported the common presence of calcite and aragonite veneers and carbonate-cemented soil material east of Lake Bonney (e.g. Angino et al. 1962; Claridge 1965; McCraw 1967a). The abundance of veneers sharply decreases west from the coast (Nishiyama 1977). Apparently, the average thickness of precipitated calcium carbonate "biscuits" (Hendy et al. 1977) decreases towards the west (Hendy, Waikato University, pers.comm.). Thermonatrite and trona **decrease** rapidly west from the coast in Taylor Valley and do not occur further than 8.5 km from the coast (Nishiyama 1979; Appendix 1, Table 35, p.53). In inland regions calcite deposits are more scattered but are not uncommon. Tasch and Angino (1968) and Claridge and Campbell (1977) reported calcite occurrences in inland areas. Generally the proportion of carbonate phases in salt deposits appears to decrease from the coast to reach an approximately constant or 'plateau' level which extends west of about 30-40 km from the coast. Similar behaviour was noted by Voronov and Spiro (1965) in Enderby Land, and in McMurdo oasis by Linkletter (1970).

The most common salts near the coast in McMurdo oasis are halite, and thenardite plus calcite in places. In inland regions, gypsum and epsomite predominate, followed by thenardite or soda nitre in places.

5.2.2 Gradients with increasing elevation in McMurdo oasis:

Strong gradients are evident in salt distribution with increasing elevation in McMurdo oasis. These gradients are similar to the east-west gradients. Chloride and sodium ions decrease in abundance upwards whereas sulphate and magnesium phases increase upwards (Figs.5.7-5.9). Nitrate phases appear to increase then decrease with increasing elevation. Calcite, calcium and carbonate show no significant trends.

These gradients have been determined by counting the phases which comprise those deposits in two zones at different distances from the coast; within these zones elevations range from about 50 m to 1200 m asl and 800 to 2800 m asl respectively. Such division is necessary to overcome the inherent interference of east-west salt gradients (5.2.1). The distribution of the eight common phases and their ions is illustrated as a series of histograms, one for each elevation increment in Figure 5.7. Similar data for the six major soluble phases and ions are given in Table 5.8 and shown in Figure 5.8. The distribution trends were also examined statistically by regression analysis, the results of which are summarized in Table 5.9 for the Aztec to Shapeless region. Figure 5.9 illustrates the trends and the best-fit lines on a

Table 5.7 Distribution (percent) of eight common salt phases and their ions with increasing elevation in McMurdo oasis; summary of data in Appendix 1, Tables 3, 6.

A. Taylor, Pearse and Wright Valleys from 25 to 65 km inland.

B. Aztec Mountain area, Kennar Valley, Labyrinth, Mt. Fleming, Shapeless Mountain from 65 to 85 km inland.

Phase	Elevation (m asl)						
	0-399	400-799	800-1199	800-1199	1200-1599	1600-1999	≥ 2000
soda nitre	0	2	7	9	18	8	2
darapskite	0	8	7	6	11	8	4
epsomite	0	4	0	3	4	4	17
bloedite	0	4	2	6	4	8	11
halite	40	27	23	16	4	0	0
thenardite	16	22	23	16	15	16	21
gypsum	28	27	33	31	41	41	36
calcite	16	6	5	13	4	14	9
chloride	40	27	23	16	4	0	0
nitrates	0	10	14	15	29	16	6
sulphates	44	57	58	56	64	69	85
carbonate	16	6	5	13	4	14	9
sodiums	56	59	60	47	48	32	27
calciums	44	49	38	44	45	55	45
magnesiums	0	8	2	9	8	12	28
N	25	51	43	32	27	49	47

Table 5.8 Distribution (percent) of six major soluble salt phases and their ions with increasing elevation in McMurdo oasis; summary of data in Appendix 1, Tables 3, 6.

A. Taylor, Pearse and Wright Valleys, from 25 to 65 km inland.

B. Aztec Mountain area, Kennar Valley, Labyrinth, Mt. Fleming, Shapeless Mountain, from 65 to 85 km inland.

Phase	Elevation (m asl)					
	0-399	400-799	800-1199	800-1599	1600-1999	≥ 2000
soda nitre	0	3	11	24	18	4
darapskite	0	12	11	15	18	8
epsomite	0	6	0	6	9	31
bloedite	0	6	4	9	18	19
halite	70	41	37	18	0	0
thenardite	30	32	37	27	36	38
chloride	70	41	37	18	0	0
nitrates	0	15	22	39	36	12
sulphates	30	44	41	42	64	88
sodiums	100	88	96	85	73	50
magnesiums	0	12	4	15	27	50
N	14	34	27	33	22	26

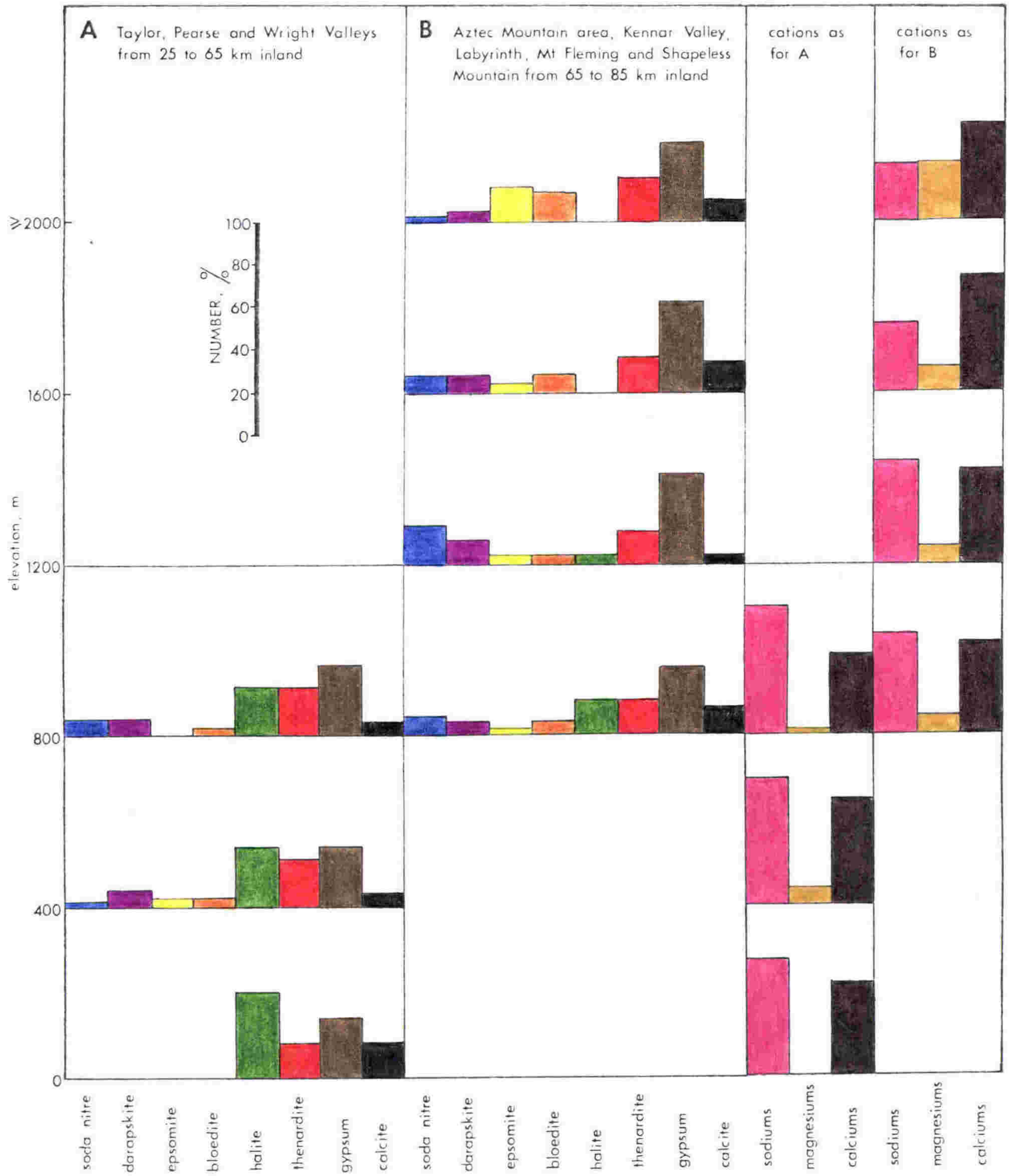


Figure 5.7 Distribution (%) of common salt phases, and of the cations involved, in different elevation ranges in McMurdo oasis.

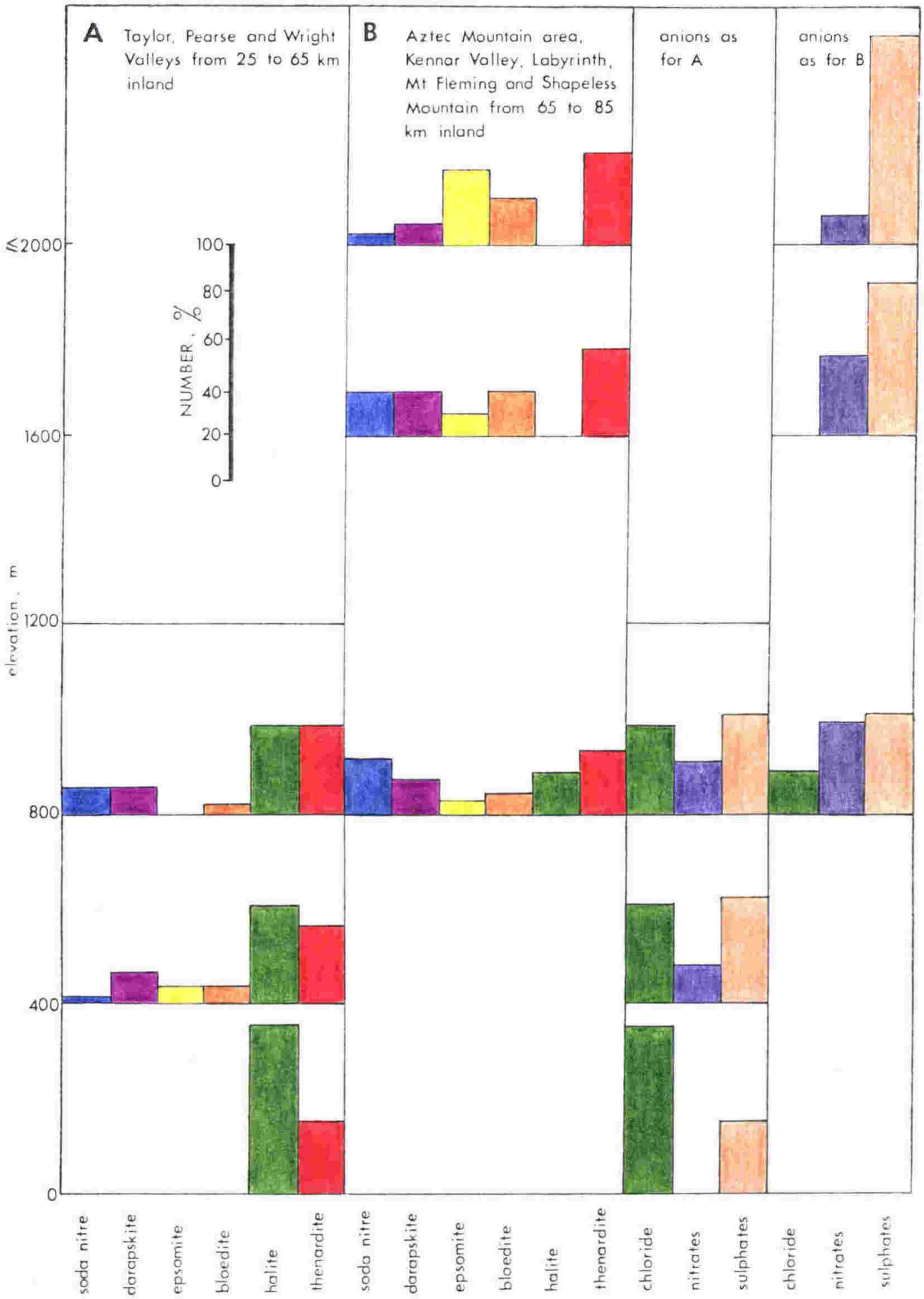


Figure 5.8 Distribution (%) of six major soluble phases, and the anions involved, in different elevation ranges in McMurdo oasis.

Table 5.9 **Statistical significance of trends of salt phases, as ions, with increasing elevation in Aztec Mountain area, Kennar Valley, Labyrinth, Mt. Fleming and Shapeless Mountain from 65 to 85 km inland (processed data from Tables 5.7B and 5.8B)**

Phases	Number of data points	Slope of linear regression line	t statistic	Confidence level (%)	Correlation coefficient	Distribution tendency
a) all eight common phases						
chloride	3	-0.020	-3.5	82	-0.96	decrease
nitrates	4	-0.010	-1.0	< 75	-0.57	(increase
						(then
nitrates	3	-0.026	-8.1	92	-0.99	(decrease
sulphates	4	0.022	6.9	95	0.98	increase
carbonate	4	-0.0005	-0.10	< 55	-0.063	constant
sodiums	4	-0.018	-3.4	92	-0.93	decrease
calciums	4	0.0028	0.43	< 60	0.29	constant
magnesiums	4	0.015	2.5	88	0.87	increase
b) six major soluble phases						
chloride	2	insufficient n				
nitrates	3	-0.025	-1.8	< 80	-0.87	(decrease)
sulphates	3	0.044	8.3	92	0.99	increase
sodiums	3	-0.033	-3.5	82	-0.96	decrease
magnesiums	3	0.033	3.5	82	0.96	increase

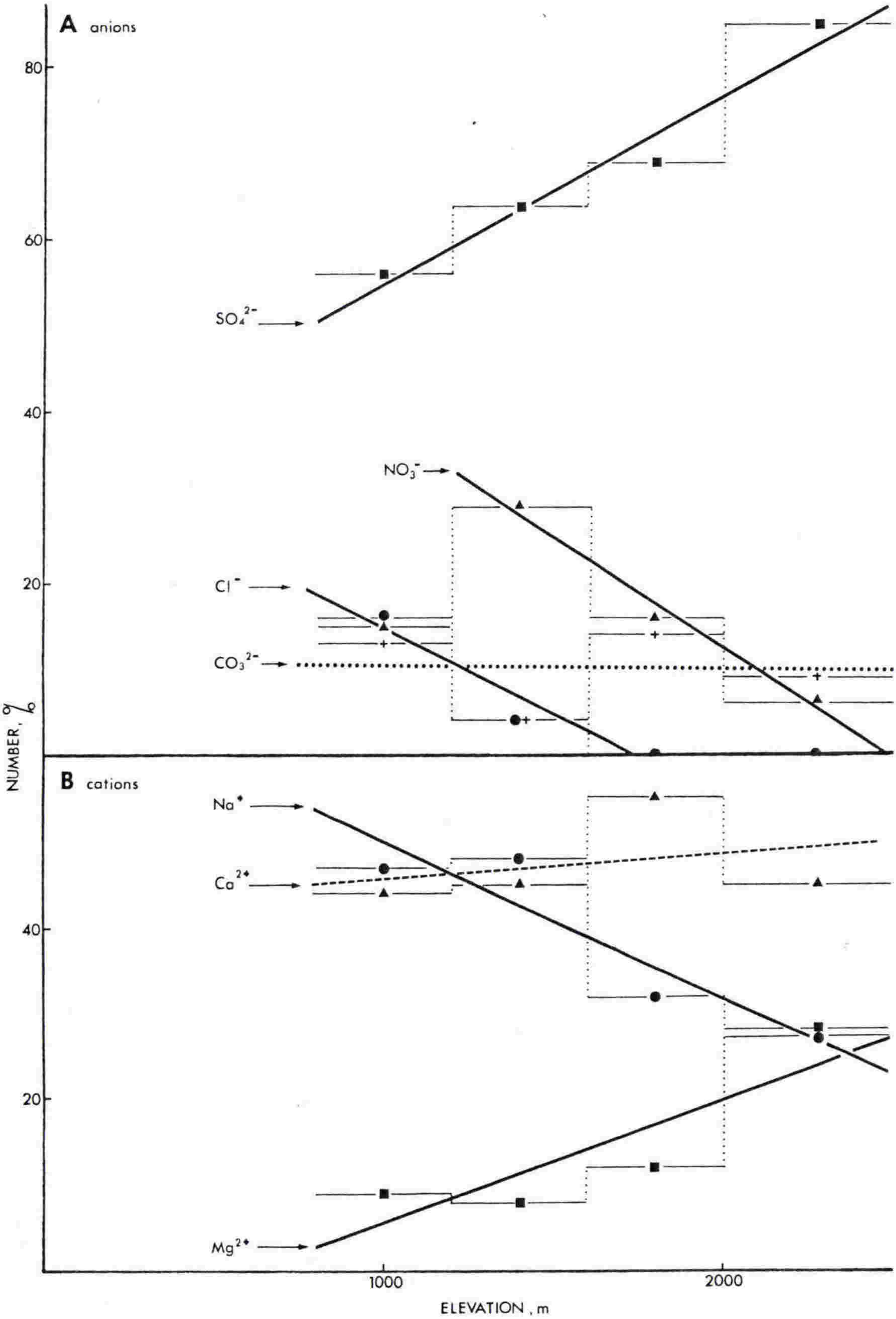


Figure 5.9 Distribution (%) of common salt phases, as ions, with increasing elevation in Aztec Mountain area, Kennar Valley, Labyrinth, Mt. Fleming and Shapeless Mountain.

bivariate plot in which the independent parameter, elevation, is the horizontal axis.

Several salt gradients are evident. Halite is the only phase that shows a continuous decrease in abundance with increasing elevation. Epsomite, bloedite, thenardite and gypsum all tend to increase though the tendency is not strong for thenardite and gypsum. The nitrate phases increase then decrease similar to their behaviour going from east to west at higher elevations (5.2.1). Calcite distribution is variable - no pattern is evident. The decrease of sodium ions upwards is statistically significant (Table 5.9), as are the increases of sulphate and magnesium ions. The decrease of chloride is probably significant also, since the correlation coefficient is close to -1. Lack of data plagues statistical examination here. The statistical significance of nitrate behaviour is difficult to show but the pattern constructed from only three points in Figure 5.9 is significant. Calcium and carbonate distributions are statistically constant with increasing elevation.

These findings are consistent with previous studies. NO_3/Cl and SO_4/Cl ratios increase with elevation as noted by Claridge and Campbell (1977). Mg/Na and Ca/Na ratios also increase with elevation. The proportion of sulphate salts increases with increasing elevation, supporting previous, more limited observations (Keys 1972; Field 1975; Nishiyama 1977). Gypsum is more abundant towards higher elevations in Dronning Maud Land (Markov et al. 1970).

5.2.3 Influence of rock type:

The influence of rock type on local composition of salts has been examined by counting the seven common ions on substrates in which a specific rock type was present on its own, or could be semi-quantitatively assessed as being dominant. Rock types considered were: volcanics (Mt. Erebus summit area excluded), metasediments, acid plutonics (granites, granodiorites, gneisses), dolerite and Beacon Supergroup sediments (Table 1.1). Analyses of salt deposits in many localities cannot be used here, since the regolith is usually composed of more than one lithology. Eastern Taylor Valley is one crucial area where this applies. The number of deposits for metasediments and plutonics is not large (Table 5.10) because pure examples of these types of substrates were less commonly encountered than those of volcanics, dolerite and Beacon sediments. Eight out of the nine deposits on metasediments are from Wright Lower Valley.

Ion proportions are obtained in a different manner from the previous two subsections (Appendix 2, A2.2.2.i). Here, each of the seven common ions is counted in a deposit, one count for each time the ion is present. The relative occurrence or proportion of that ion is obtained as a percentage of the total number of deposits N_D (Table 5.10). Therefore, in the Table percentages do not sum to 100 as before.

Table 5.10 **Salt distribution on substrates of various rock types, arranged in order of increasing distance inland from coast and increasing elevation; distribution in percent occurrences of specific ions in particular deposits.**

Ion	Rock type				
	Volcanics (1)	Metasediments (2)	Plutonics	Dolerite	Beacon sediments
Na^+	88	60	59	53	39
Mg^{2+}	19	0	0	31	0
Ca^{2+}	19	90	59	79	87
Cl^-	58	20	41	11	0
NO_3^-	4	10	6	24	17
SO_4^{2-}	81	80	65	77	85
CO_3^{2-}	8	20	29	25	20
number of deposits, N_D	26	9	17	71	46
mean distance from coast (km)	20	34	37	75	80
mean elevation (m asl)	270	980	1100	1600	2000

(1) Cape Bird, White and Black Islands and Taylor Valley below 760 m asl

(2) Wright and Taylor Valleys

The association of ions with rock types is illustrated in two histograms for each rock type (Fig.5.10A, B). Figure 5.10A clearly shows that magnesium phases are present on dolerite and volcanic substrates only.

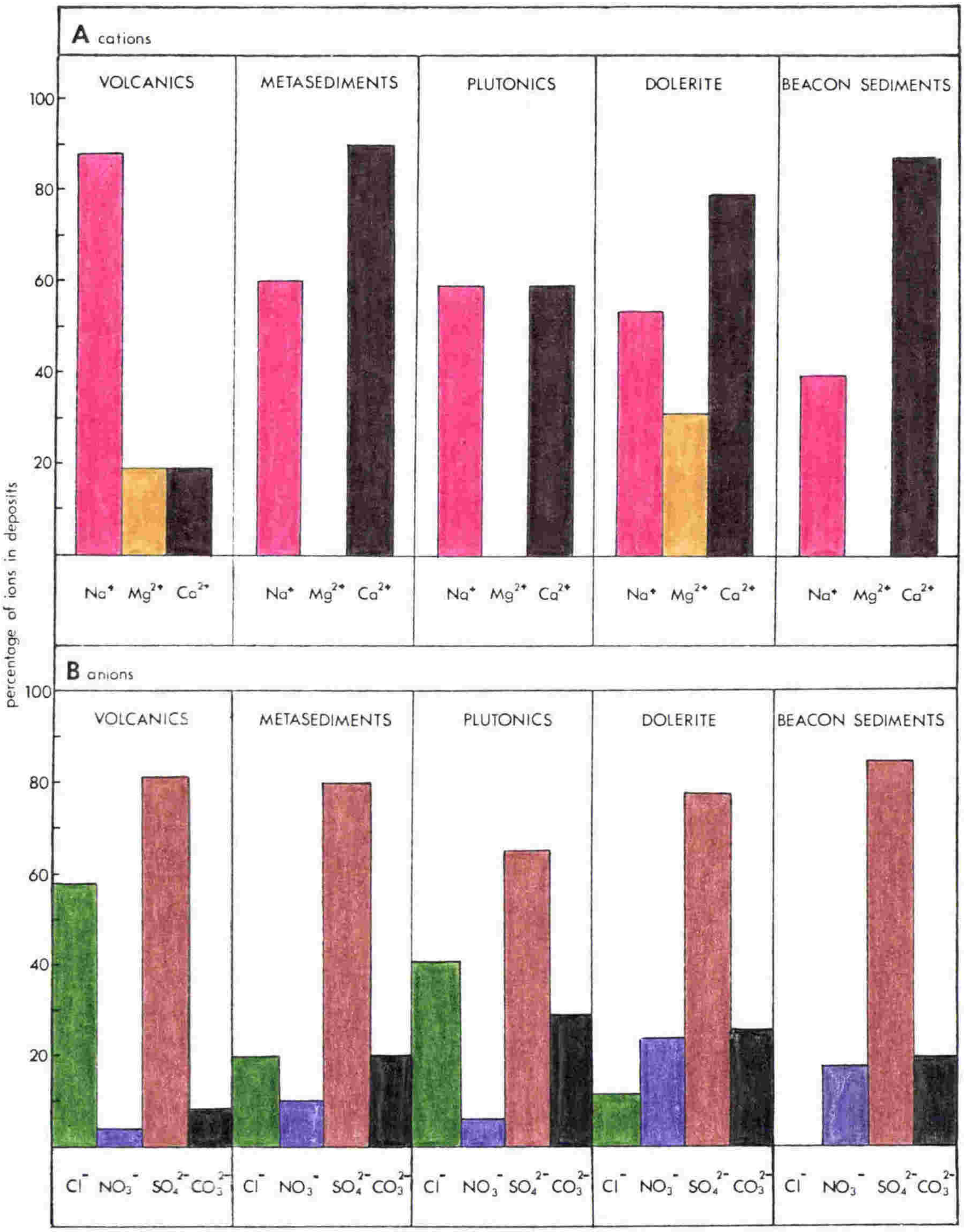


Figure 5.10 Distribution (percent occurrences in deposits) of cations and anions in deposits on substrates of various rock types, arranged in order of increasing distance inland and increasing elevation.

The presence of Mg^{2+} in deposits on volcanics, a substrate that is present near the coast, is counter to regional gradients discussed earlier where magnesium phases did not occur close to the coast. Therefore, it can be concluded that the primary source of magnesium ions is the dolerite and volcanic rocks in the region, similar to the conclusion of Claridge and Campbell (1977). The magnesium gradients inland (5.2.1) and with increasing elevation (5.2.2) can be attributed in part to the more frequent outcropping of dolerite in these areas (Fig.1.2).

All other ions, except chloride are present on all rock types. The common presence of nitrate ion in deposits on dolerite (and other rock types) as well as on sedimentary substrates, indicates that the latter are not the source of nitrates or of salts in general (Claridge and Campbell 1977) as suggested by Gibson (1962) and Linkletter (1970).

The distributions have been arranged in order of increasing distance inland and elevation (Table and Figure 5.10). The arrangement shows that sodium and chloride tend to decrease inland and nitrate to increase, similar to observations noted earlier based on a slightly different approach. Calcium, sulphate and carbonate show no trends on oasis substrates. Earlier it appeared that calcium increased in relative abundance inland and sulphate increased with increasing elevation (Figs.5.5, 5.9); therefore these earlier gradients of Ca^{2+} and SO_4^{2-} are partly a result of the data summing to 100.

The data presented in Figure 5.10 do not reveal any strong influence of rock type on carbonate ion distribution. The slightly higher proportion of carbonate on plutonics is probably due to carbonate variability (5.2.1) and not to a significant positive influence of the substrate. Similarly the proportion of calcium on metasediments is not significantly higher than on dolerite or Beacon sediments.

However, a significant relationship between carbonate-bearing rocks and carbonate salts does exist in Taylor Valley. In that valley large amounts of carbonate-bearing rock outcrop up to 25 km from the coast, with a further thin belt at 37 km (Haskell <u>et al.</u> 1965). This is consistent with the pattern of calcite distribution noted earlier(5.2.1),where calcite dominates salt deposits in eastern Taylor Valley to a distance of about

20 km inland, but from about 30-40 km forms a low plateau level of abundance (Fig.5.1). Furthermore soluble carbonate and bicarbonate salts are common up to 8.5 km from the coast in eastern Taylor Valley (Nishiyama 1977). Claridge and Campbell (1977) considered that the same type of relationship exists in the Koettlitz Glacier area where there are extensive outcrops of marble (Blank et al. 1963).

Further evidence for this carbonate association was obtained by examining the thickness of calcite veneers on regolith composed of dolerite material along the ridge between Kennar and Turnabout Valleys (13/11/76). These veneers appeared to be thickest in the vicinity of veins of hydrothermal calcite in the dolerite (Appendix 1, locality 136, p.18). Therefore, the veins appeared to be a source of the carbonate in the veneers.

There are other controls on carbonate distribution besides the presence of carbonate rocks in the vicinity as indicated by two distribution characteristics. (1) No such rocks exist in the vicinity of volcanic Stadium Cone on Mt. Discovery where soluble carbonate salts are present (Appendix 1, p.29). The existence of carbonatites (carbonate-rich volcanic rocks) was not indicated by an acid test on the basaltic substrate from this cone. The common presence of calcite veneers on the volcanic substrate of Hut Point Peninsula was explained by Claridge and Campbell (1977), as being due to dissolution of carbonate from loess-like dust blown across McMurdo Sound, consistent with Wellman's (1963) evidence of windblown granite and sandstone pebbles. (2) No soluble carbonate salts, nor an **increased** abundance of calcite were found in Wright Lower Valley (Appendix 1, pp.24, 25) on the area of marble-rich metasediments that appear to be a continuation of the Nussbaum Riegel metasediment belt in eastern Taylor Valley (McKelvey and Webb 1962; Haskell et al. 1965). This marked difference in salt chemistry between Wright Lower and eastern Taylor Valleys may be partly due (Chapter 6) to climatic differences.

It has been shown that the rock substrate is the prime determinant of the distribution of magnesium phases. Carbonate and calcium phases may be more common in places near rocks containing calcium carbonate but they are also widespread on other rock types. Rock type has no noticeable effect on the distribution of sodium, chloride, sulphate or nitrate phases.

5.2.4 North-south gradients:

North-south gradients in salt distribution are evident in

McMurdo Sound. Halite decreases in abundance towards the south whereas sulphate ion, calcium phases and gypsum increase towards the south. Magnesium phases have a weak tendency to increase towards the south also (Fig.5.11).

These gradients have been determined by separately counting the numbers of soluble and insoluble phases present in deposits from Cape Bird ice-free area in the north, to Mt. Discovery in the south. Other areas considered were: Capes Royds, Barne and Evans; Hut Point Peninsula; and White and Black Islands. Deposits were considered for elevations up to 1000 m asl. A substrate of volcanic rocks was present throughout.

The distance from Cape Bird ice-free area, south to a particular sample area was used as the independent variable on a bivariate plot (Fig.5.11). The data are expressed as numbers of specific phases as percentages of the total number of phases counted (as in 5.2.1, 5.2.2). These data include those for samples from Capes Royds, Barne and Evans and Hut Point Peninsula as determined by Keys (1972). Bloedite was not identified in that work; therefore errors may arise due to omission of phases that actually are present (Appendix 2, A2.1.3). This would not seriously affect data for halite, thenardite and gypsum which are frequently present, but would affect the apparent distribution of magnesium phases and of calcite. Furthermore, the number of data are low (N = 9-12) for White and Black Islands especially. The absence of magnesium phases in this area is probably due to sampling omissions and not to the lack of such phases. In fact, the magnesium salt magnesite ($MgCO_3$) is known to be present in the area (Watanuki and Morikawa 1974).

Soluble sulphate phases, calcium phases and gypsum all show a close fit increasing trend, whereas halite shows a similar decreasing trend to the south (Fig.5.11). These trends probably reflect increasing SO_4/Cl and Ca/Na ratios in salt deposits towards the south, as noted by Claridge and Campbell (1977). Probably Mg/Na also increases towards the south. The data are variable for thenardite and calcite. The latter appears to be abundant only on Hut Point Peninsula as noted by Claridge and Campbell (1977), although data from other areas are insufficient to be sure of the relative lack of calcite elsewhere. Calcite distribution can best be described as a low 'plateau' type similar to its distribution inland in McMurdo oasis (5.2.1, Fig.5.1).

A high percentage abundance of calcium is evident in the

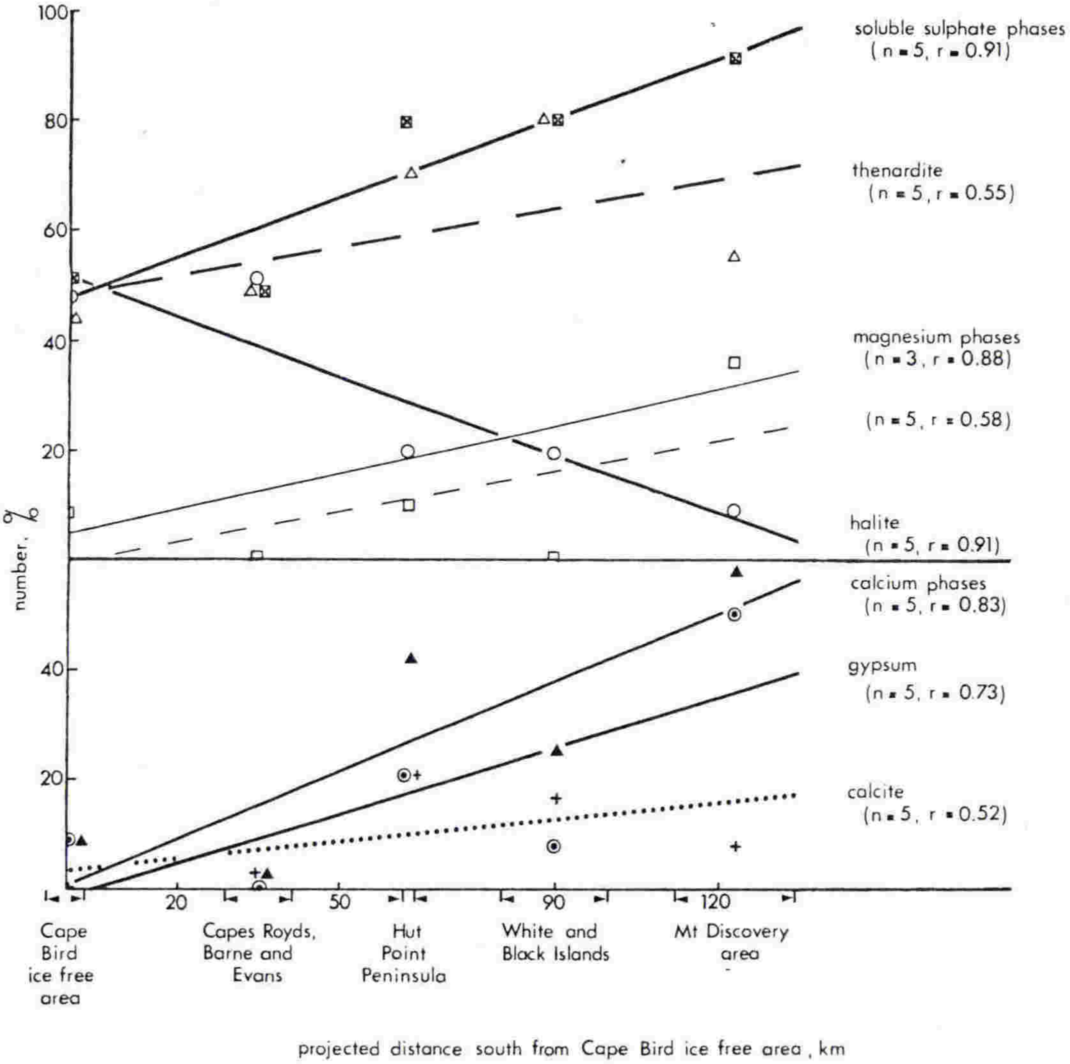


Figure 5.11 Distribution (%) of phases along a north-south transect in McMurdo Sound and areas to the south; distances south of Cape Bird ice-free area are computed by projecting the boundaries of the sampling areas east or west onto the 166° line of longitude which passes through McMurdo Sound; data from Appendix 1, Table 36).

Mt. Discovery area, close to a source of metasediments in the Koettlitz dry valleys (Blank et al. 1963). This could indicate that the calcium in calcite veneers on such volcanic substrates is derived mainly from windblown calcium carbonate-rich dust (see 5.2.3 above, Claridge and Campbell 1977). Apparently however, calcite veneers are less abundant at Mt. Discovery than at Hut Point. This is not consistent with a windblown source for carbonate.

Insufficient data were obtained to determine whether north-south gradients in salt distribution exist in McMurdo oasis. A very large number of samples would need to be collected in Victoria, Wright, Taylor and Koettlitz dry valley areas to enable the influence of the strong east-west and low-high gradients to be taken into account. Such extensive sampling would also even out the effect of different areal extents of dolerite in these areas. With the data available (Appendix 1 , Tables 3, 5, 6) no marked regional differences are evident in the types or abundances of major phases present in Taylor, Ferrar or Wright Valleys.

The Koettlitz and Victoria valley systems have not been sampled in this present study. However, the types and abundances of phases in these areas (Gibson 1962; Torii et al. 1966; Linkletter 1970; Claridge and Campbell 1977; Morikawa et al. 1977) are probably similar to those in Taylor and Wright Valleys. Sulphate phases may be the most common in the Koettlitz system and certainly have received most attention in the literature (e.g. Torii et al. 1966; Bowser et al. 1970; Dort and Dort 1970; Lyon 1978).

The low elevation portions of Taylor and Wright Valleys do exhibit some differences. No nitrate phases were found in salt deposits below 600 m in Taylor Valley above Lake Bonney (Appendix 1, sample 24831, p.15) whereas such phases were found in the lowest deposits sampled in Pearse Valley (450 m, Appendix 1, p.16) and down to 200 m or so in Wright Valley (Morikawa et al. 1975). Soluble carbonates are present in eastern Taylor Valley but are absent from Wright Valley (Nishiyama 1979).

5.2.5 Ion concentration and composition gradients on the ice sheet:

Gradients of ion concentration exist on the continental ice sheet of Antarctica. A general decrease inland from the coast in the concentration of soluble salts in surface snow has been demonstrated by numerous studies (e.g. Wilson and House 1965; Hanappe et al. 1968; Lorius et al. 1969; Markov et al. 1970). The decrease can be subdivided into two. A rapid decrease is evident in the first few hundred kilometres from the coast of East Antarctica (Lorius et al. 1969; Boutron 1978) and an approximately even concentration plateau is reached towards the interior (Boutron et al. 1972; Delmas and Boutron 1978). Analogous behaviour has been measured in ice cores from the Ross Ice Shelf. Deeper portions of the cores consist of ice formed from precipitation in the interior of West Antarctica. This ice contains much lower concentrations of salt than does near-surface firn and ice which formed from precipitation nearer the sea (Gow 1968; Langway et al. 1974; Herron and Langway 1978).

The original source of nearly all the atmospheric water vapour precipitated over Antarctica is the open water of the southern hemisphere oceans (Weyant 1966). Maritime air is transported meridionally towards the centre of the continent by the prevailing circulation in the upper troposphere and stratosphere. In the interior most precipitation is originally deposited from deep cyclonic storms that carry relatively moist maritime air through the troposphere (Rusin 1964; Appendix 3, sections 4.9, 5.1). The greatest snowfalls in coastal regions are produced by similar storms.

A significant amount of sea salt appears to be present in these masses of maritime air. The salt exists as marine aerosols (including condensation nuclei) which are solid or liquid particles of matter about 10^{-2} to 10 µm in diameter (Duce 1967; Kumai 1976; Ohtake 1976). They are small enough to remain dispersed in the atmosphere for several days or weeks. Condensation of water vapour onto them results in the transfer of minute amounts of salt in snowfall and other forms of precipitation (Appendix 3, section 5.5) to the surface. Physical trapping of aerosols by snow particles may be important near the coast where snow particles are larger and grow partly by accretion (Appendix 3, section 5.3).

It has been demonstrated that marine aerosols are in fact the main source of saline impurities in snow in the interior as they are near the coast (Murozumi et al. 1969; Boutron et al. 1972; Ohtake 1976, 1978; Boutron 1979; Boutron and Lorius 1979). Natural and anthropogenic sources of terrestrial aerosols are of relatively little import in antarctic snow.

The general decrease inland in the concentration of impurities in the snow and the existence of the concentration plateau have been linked (Langway et al. 1974) to the decrease inland that normally occurs in the concentration of sea salt constituents in precipitation (Eriksson 1952; Gorham 1961; Junge 1963). Chloride and sodium ions are the ions present in highest concentrations in snow in the first few hundred kilometres from the coast, and are usually found to decrease in concentration in surface snows as distance from the coast increases (Hanappe et al. 1968; Lorius et al. 1969; Boutron et al. 1972). Similar trends may also occur with sulphate, magnesium, calcium and potassium (Vilenskii and Koroleva 1973; Boutron 1978), but are often obscured by other. influences. These include complex meteorological and topographical influences , different precipitation efficiencies of aerosol particles by different forms of precipitation, terrestrial or extraterrestrial sources of ions, contamination and analytical difficulties (Murozumi et al. 1969; Lorius et al. 1969; Boutron et al. 1972; Boutron 1978, 1979; Warburton and Linkletter 1978; Zoller et al. 1978; Boutron and Lorius 1979). Analytical problems and contamination may be most important; recently Boutron and Martin (1978) described a satisfactory procedure for preconcentration and analysis of very dilute solutions (10^{-12} g/g) derived from samples of snow taken from the interior.

Sulphate is the predominant ion in the interior (Delmas and Boutron 1978; Zoller et al. 1978). It forms a concentration plateau in snow of the central part of East Antarctica where SO_4/Cl and SO_4/Na ratios may be much higher than in coastal snows and in sea water (Lorius et al. 1969; Delmas and Boutron 1978). It appears that most of this sulphate originally came from the sea either as sulphate or marine derived sulphur dioxide (Nguyen et al. 1974); however, it is believed that the layer of sulphate that is present in the stratosphere (Junge et al. 1961) (the stratospheric sulphate layer) and volcanic activity are sources of some of the sulphate (Zoller et al. 1974; Lorius and Donnou 1978; Delmas and Boutron 1978; Boutron and Lorius 1979).

Small but significant amounts of other ions are also present in snow of the interior. Nitrate (up to 500 ppb) and ammonium ions are present (Wilson and House 1965; Linkletter 1968; Parker et al. 1978) as they are in the atmosphere (Eriksson 1952). Significant amounts of NH_4^+ and H^+ have been found with SO_4^{2-} in tropospheric aerosols collected in the McMurdo region (Cadle et al. 1968).

It appears that the ratios of nitrogen oxides to ammonia and H^+ to NH_4^+ in aerosols generally increase inland over land masses and with increasing elevation (Lodge and Pate 1966). This is believed to be partly due to oxidation of the ammonia which is primarily of marine origin. It has recently been shown that the concentration of atmospheric aerosols and snow samples at South Pole are closely correlated (Zoller et al. 1978); therefore, little fractionation occurs during the transfer of the aerosolic constituents of the atmosphere at South Pole to the snow surface in such inland regions (Zoller et al. 1978; Boutron 1979). It is likely that the ratios NO_3/Cl and H/Cl in snow in the interior reflect the values of these ratios in aerosols there. The ratios are likely to increase inland, and certainly are higher in the interior than on the coast.

5.2.6 Saline lakes in McMurdo oasis:

The chemistry of saline lakes in Taylor Valley is significantly different from those in Wright Valley. These chemistries and their differences can be considered part of salt distribution in a broad sense, and for that reason are briefly discussed here. The cation concentrations (as equivalents percent) of saline lakes are illustrated in Figure 5.12 (after Torii et al. 1979).

The salt composition of lakes in Taylor Valley is similar to that in sea water (Fig.5.12). Cation ratios in the discharge brines from beneath Taylor Glacier (Appendix 1, Table 15) and in Lake Fryxell closely resemble those in sea water. The deeper waters in both lobes of Lake Bonney appear to have evolved from sea water by deaquation processes involving precipitation of gypsum (West Lobe), and halite, dihydrohalite, gypsum, calcite and aragonite (East Lobe) (Torii et al. 1975, 1979; Hendy et al. 1977).

Other lakes depicted in Figure 5.12 show little resemblance to sea water, having large proportions of calcium ions. Such lakes have been termed "calcium chloride" lakes (Wilson 1967, 1979) due to a predominance of those two ions. Chloride is the predominant anion and sulphate is depleted with respect to sea water in all saline lakes depicted in Figure 5.12 (Yamagata et al. 1967). The lakes also contain nitrogen-containing ions, NO_3^-, NO_2^- and NH_4^+ whose existence and distribution appear to be largely dependent on biogeochemical conditions (Torii et al. 1975).

In general the different lake chemistries do not appear to be closely related to the distribution of salt deposits in the various valleys of McMurdo oasis. Therefore, the lake salts are not derived simply by unfractionated dissolution of salt deposits in their

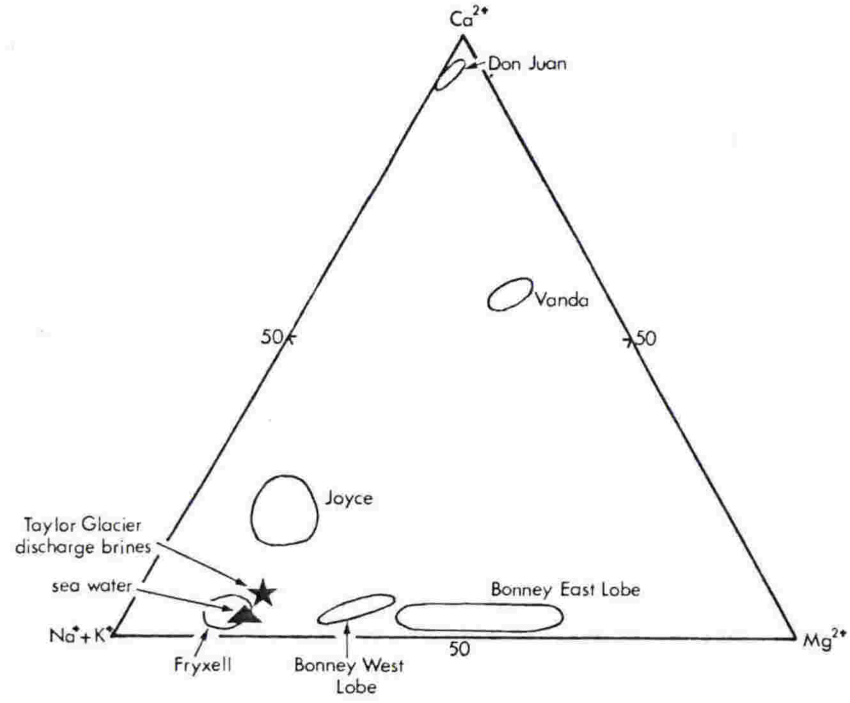


Figure 5.12 Major cation ratios (equivalents percent) for saline lakes in McMurdo oasis (after Torii et al. 1979). Ratios for Taylor Glacier discharge brines calculated from Table 15 in Appendix 1.

catchment areas, nor are those salt deposits derived by redistribution of lake salts.

Lake Fryxell is an exception. The lake contains a large proportion of bicarbonate ion, amounting to about 30-40 percent of total anion content (Angino et al. 1962; Torii et al. 1975). Soluble carbonate and bicarbonate salts (trona and thermonatrite) are widespread in the eastern part of the present lake catchment (Nishiyama 1979) and indicate an excess of CO_3^{2-} plus HCO_3^- over Ca^{2+} in the area. The mole ratio of alkalinity (as HCO_3^-) to Ca^{2+} is 4.9 to 14.1 in the aerobic waters shallower than six metres in the lake (calculated from Torii et al. 1975); this suggests a large excess of HCO_3^- over Ca^{2+}. The ratios are only a few percent less when other contributors to alkalinity are considered, such as HS^-, borate, silicate and phosphate ions. CO_3^{2-} and OH^- are negligible at the ambient pH of 7 to 8. Furthermore, the ratio increases with depth. Other lakes in the oasis have alkalinity-to-Ca^{2+} mole ratios of less than 2.7 (from Torii et al. 1975) and no bicarbonate phases in the salt deposits of their catchments.

There is no evidence for a calcium ion 'sink' that does not include carbonate or bicarbonate ions in the Lake Fryxell area. Gypsum, the most obvious sink of this nature, is absent from surface salt deposits in the area (Nishiyama 1979) and is not present in large amounts in nearby DVDP holes 7-11 (Harris and Mudrey 1974; McKelvey 1975; Ugolini et al. 1979). Sulphate concentration is not high, being 250-460 mg l^{-1} near the bottom of the lake, whose temperature is 0 to +2°C (Angino et al. 1962; Torii et al. 1975). The product of the molal concentrations of calcium and sulphate ions is about 2 to 4 x 10^{-6}, two orders of magnitude less than the solubility product of gypsum at +10°C (Weast 1971). The activity coefficients of Ca^{2+} and SO_4^{2-} are less than unity at this concentration (Berner 1971; also Chapter 8); evidently the lake is undersaturated with gypsum. Therefore, little gypsum can have been precipitated and hence Ca^{2+} cannot have been depleted with respect to HCO_3^- in such a manner in this lake. (Calcium carbonate is currently being precipitated from the lake, as it has been from an expanded Lake Fryxell in the past; Hendy in Selby 1979; Hendy et al. 1979.)

The evidence suggests that there is some specific source or sources that have contributed large amounts of bicarbonate, but not calcium to the lake. Biological activity under anaerobic conditions is such a source (Cole 1975) that is possible for the lake and hence for the soluble carbonate-bicarbonate salts as well (Chapter 6). The carbonate-bearing rocks in eastern Taylor Valley are an additional source of bicarbonate and a source of calcium to the area (5.2.3; Chapter 6).

5.3 Distribution of the Phases that are Present in or near the McMurdo Region

5.3.1 Rare phases:

(i) distribution

Strong tendencies are evident in the distributions of groups of those phases that are known in only one or two localities in the region or in Ross Dependency as a whole. There is a tendency towards occurrence within 40 km of the coast and at elevations less than 750 m or so. Dry Valley Drilling Project (DVDP) holes on Ross Island have contained some of these phases. There is a marked tendency particularly among phases containing carbonate-bicarbonate and magnesium, towards occurrence in volcanic areas. Phosphate phases exist only near bird colonies.

These tendencies have been determined by examining literature reports and known occurrences of rare phases. These are the phases listed as Group C phases in Table 1, Appendix 1, page 13 (which also lists literature reports of these phases). Occurrences of thirteen phases of the eighteen listed salts are presented in a correlation matrix (Table 5.11). This lists occurrences against various generalized environmental details of a regional nature including; area in which the phase occurs, distance from present limits of open sea, elevation, and dominant rock type. Association with a source of guano, near penguin and skua colonies, is considered as a special case. Occurrences are totalled for each group of phases (e.g. carbonates), anions and cations. Insufficient environmental details of a local nature are known for most occurrences of the phases listed in Table 5.11. Statistical treatment is untenable for the low numbers of occurrences in the table.

Several tendencies are clear. The strongest is for phosphate salts to exist near penguin or skua colonies, as has been noticed previously for isolated cases (Campbell and Claridge 1966; Keys 1972). Furthermore, most rare phases occur close to the coast (within 40 km or so) and at low elevations (less than 750 m). Only one rare phase, hydrothermal dolomite from Dias, has been reported (Morikawa et al. 1975) from Wright and Victoria Valleys, despite extensive field work especially in the former. Therefore the observed distribution of rare phases is probably real, not a mere artifact of more extensive field work in any particular area. Rare phases have not been reported from DVDP holes in McMurdo oasis (except anhydrite, see ii below) or on Beacon sediments.

Two rare carbonates occur in eastern Taylor Valley but other areas also contain such phases. Claridge and Campbell's (1977) hypothesis of a windblown carbonate-rich dust source for carbonates at Hut Point and other volcanic areas is not ruled out by this carbonate phase distribution. However, DVDP holes on Ross Island which consists of volcanic rocks contain some rare phases, especially carbonates. In general, the carbonates in Table 5.11 appear to show a strong association with volcanic substrates. The inference is that windblown

Table 5.11 Correlation matrix showing distribution of rare salt phases (● presence; (blank) absence)

Phase	General locality of salt deposit						Distance from coast		Elevation		Dominant rock type							
	McMurdo Sound (incl. White Is.)	Koettlitz Gl. area (incl. Mt. Discovery)	Taylor Valley east of Taylor Gl.	elsewhere in McMurdo oasis	Skelton Névé and North Victoria Land	DVDP Ross Is.	≤ 40 km	> 40 km	≤ 750 m	> 750 m	volcanics	metasediments	plutonics	dolerite	magnetite bed	mixed	bird colony	
a) carbonates																		
nahcolite	●	●					●		●							●		(1)
burkeite		●	●				●●		●●		●					●		(2)
northupite						●	●●		●●		●●							
magnesite	●				●			●		●		●						
nesquehonite						●	●●		●●		●●							
dolomite				●				●		●				●				
monohydrocalcite			●				●		●							●		
siderite						●	●		●		●							
totals (11)	2	2	2	1	1	3	9	2	9	2	6	1	0	1	0	3	0	
b) sulphates																		
burkeite			●				●		●							●		(2)
melanterite		●			●		●	●	●	●	●				●			
syngenite		●					●		●		●							
totals	0	2	1	0	1	0	3	1	3	1	2	0	0	0	1	1	0	
c) chlorides																		
northupite						●	●		●		●							
dihydrohalite			●				●		●							●		
totals	0	0	1	0	0	1	2	0	2	0	1	0	0	0	0	1	0	
d) phosphates																		
$Ca_3(PO_4)_2$	●				●		●●		●●		●		●				●●	(3)
newberyite					●●		●●		●●		●●						●●	(4)
totals	1	0	0	0	3	0	4	0	4	0	3	0	1	0	0	0	4	
anion totals	3	4	4	1	5	4	18	3	18	3	12	1	1	1	1	5	4	
e) sodiums																		
nahcolite	●	●					●		●							●		(1)
burkeite		●	●				●●		●●		●					●		(2)
northupite						●	●●		●●		●●							
dihydrohalite			●				●		●							●		
totals	1	2	2	0	0	1	6	0	6	0	3	0	0	0	0	3	0	
f) magnesiums																		
northupite						●	●		●		●							
magnesite	●				●			●		●		●						
nesquehonite						●	●●		●●		●●							
dolomite				●				●		●				●				
newberyite					●●		●●		●●		●●						●●	(4)
totals	1	0	0	1	3	2	5	2	5	2	5	1	0	1	0	0	2	
g) potassium																		
syngenite		●					●		●		●							
totals	0	1	0	0	0	0	1	0	1	0	1	0	0	0	0	0	0	
h) calciums																		
dolomite				●				●		●				●				
monohydrocalcite			●				●		●							●		
syngenite		●					●		●		●							
$Ca_3(PO_4)_2$	●				●		●●		●●		●		●				●●	(3)
totals	1	1	1	1	1	0	4	1	4	1	2	0	1	1	0	1	2	
i) iron																		
siderite						●	●		●		●							
melanterite					●			●		●					●			
totals	0	0	0	0	1	1	1	1	1	1	1	0	0	0	1	0	0	
cation totals	3	4	3	2	5	4	17	4	17	4	12	1	1	2	1	4	4	

(1) nahcolite from an unspecified locality on Heald Island, collected by D. N. B. Skinner and analysed by G. G. C. Claridge. The island is mainly composed of metasediments and volcanics (Blank et al. 1963).

(2) burkeite in deposit sampled by Nishiyama (1979)

(3) $Ca_3(PO_4)_2$ in salt deposit from skuary at Cape Evans (Keys 1972)

(4) newberyite from Possession Islands, collected by L. Gressitt, and analysed by G. G. C. Claridge

carbonate-rich dust or carbonate-bearing rocks are not the major source of these carbonates.

Other phases have different distributions. Magnesium phases show a strong association with volcanic rocks, consistent with the association noted earlier (Fig.5.10). Four sulphate phase occurrences, one potassium phase occurrence and five occurrences of calcium phases, do not show any strong affinity for specific rock types. The occurrence of one of the two iron (II) phases on a magnetite (Fe_3O_4) bed is not surprising. Similarly the existence of rare chloride and sodium phases close to the coast is not surprising in view of the regional trends in the distribution of these ions (Figs.5.3-6).

(ii) anhydrite and other special cases

Five out of the eighteen listed Group C minerals (Appendix 1, p.13) were not considered in Table 5.11. (1) Gaylussite and (2) vaterite were both found in core recovered from DVDP holes 1 and/or 2. However, both these phases are metastable and may have been formed during drilling by reaction of the drilling fluid (calcium chloride solution) with sodium carbonate from dissolution of thermonatrite that is present (Browne 1973). Therefore, these possible artifacts of drilling were not included in Table 5.11 but it should be noted that their inclusion would strengthen the conclusions formulated above. (3) Magnesium chloride phase (Kumai et al. 1976) was not considered because it has been incompletely identified (by energy dispersion X-ray analysis) and is probably quite widespread (5.3.2). (4) Alunite and other salts on Erebus Volcano were not considered because they are a special case, being volcanogenic (Chapter 7).

Anhydrite ($CaSO_4$) is the fifth phase not considered in Table 5.11. The phase was misreported as a cement in sandstone beds near the top of the Buckley Coal Measures (Beacon Supergroup) in the Beardmore Glacier area (McGregor 1965); subsequent work showed that the cement was prehnite ($Ca_2Al_2Si_3O_{10}(OH)_2.nH_2O$) which has optical properties similar to anhydrite (Barrett 1969). Subsequently, anhydrite has been reported from one depth in DVDP 4 beneath Lake Vanda (Cartwright et al. 1974b) but nowhere else in these or other subsurface sediments. The phase has not been reported in any surficial salt deposits despite the widespread existence of gypsum. This absence of anhydrite is probably due to thermodynamic and kinetic constraints.

Phase equilibria in the gypsum-anhydrite binary and higher aqueous systems have been extensively studied. Considerable debate has centred around the fields of stability of the two phases which are governed by the transition temperature T for the reaction:

$$\underset{\text{gypsum}}{CaSO_4.2H_2O} \rightleftharpoons \underset{\text{anhydrite}}{CaSO_4} + 2H_2O \qquad ...5.1$$

The reaction has considerable importance in the diagenesis of marine evaporites (e.g. Murray 1964). Errors have arisen in the determination of T due to: (1) failure to attain equilibrium (which may take several days or weeks) or saturation during solubility or precipitation experiments; (2) use of imprecise thermodynamic data; (3) incorrect choice of reaction mechanism (Ostroff 1964; Zen 1965). The commonly accepted transition temperature of +40°C in the binary system at one atmosphere (e.g. Palache et al. 1951) is too low; Hardie(1967) determined the value of T as 58°C whereas Ostroff (1964) determined it as 97°C. Other ions reduce the value of T to an extent that is also uncertain. Hardie(1967) determined the stability fields of gypsum and anhydrite as a function of activity of water a_w at one atmosphere total pressure. The activity of water in sea water at the concentration where gypsum becomes saturated is about 0.93 (Berner 1971) at which point T equals 50°C (Hardie1967); at the point of halite saturation a_w equals 0.74 and T equals 18°C. However anhydrite has never been observed to precipitate in the laboratory by evaporation under any temperature and salinity conditions at which it is thermodynamically stable (Berner 1971). Therefore gypsum exhibits metastability above the transition temperature, forming in conditions in which it is not the thermodynamically favoured phase. Anhydrite has been precipitated in the laboratory by mixing calcium chloride and sodium sulphate solutions; Ostroff (1964) considered that T was between 70°C and 90.5°C for solutions containing up to 2.8 moles kg^{-1} of both chloride and sodium ions.

In antarctic soils the saturation point of calcium sulphate is usually reached probably by deaquation of brines. Gypsum will be formed by such a process, and will be further stabilized by removal of the brine phase. Even if saturation were to be reached by admixture of two or more brines, gypsum would be most likely to form; the warmest surface temperatures (+32.9°C) known to have been reached in antarctic soils, outside of geothermal regions (Table 2.2), is well below the transition temperature range determined by Ostroff (1964).

Anhydrite has been reported from DVDP 4 in sediments beneath Lake Vanda, along with gypsum and calcite (Cartwright et al. 1974b). The identification of anhydrite was by optical and/or X-ray diffraction analysis. The salts were contained in organic sand and silt, permeated with H_2S, within 0.1 m of the lake bed in the deepest part of the lake. Gypsum but not anhydrite has been reported from other sediments of this and other lakes (Angino et al. 1964; Nelson and Wilson 1972; Wilson et al. 1974; Hendy et al. 1977) and similarly in other DVDP holes (Browne 1974; Morikawa et al. 1977; Nishiyama 1979).

It is difficult to explain the apparent presence of anhydrite. The maximum temperature in Lake Vanda (+25°C) and its sediments occurs in the bottom waters a few metres above the lake floor (Wilson and Wellman 1962; Yusa 1975). The chloride concentration in the lake is a maximum (2.1 moles kg^{-1}) at the bottom; 3.8 m below the lake floor in DVDP 4 the concentration was about 2.7 moles kg^{-1} (Torii et al. 1975). At the salinities of these brines (110 and 140 per mille respectively, calculated from Torii et al. 1975) the water activity of a concentrated sea water (at +25°C) is about 0.94 and 0.92 respectively (extrapolated from Millero and Leung 1976). Probably, these are reasonable values for Vanda brine because chloride is the major ion present, as in sea water. A 70 m column of brine produces a pressure of about 7×10^5 pascals (7 atmospheres) which has no significant effect on the gypsum-anhydrite transition temperature T (Hardie1967). Therefore +50°C seems a reasonable estimate of the value of T at the bottom of Lake Vanda. This temperature is considerably higher than the bottom temperature; therefore anhydrite is not likely to be stable there or in the sediments, and cannot have formed by diagenesis of gypsum.

The apparent presence of anhydrite can be explained in several ways. Possibly, the phase was misidentified but this is unlikely. Possibly, strong reducing conditions or biological activity could catalyse the dehydration of gypsum at lower temperatures than the predicted transition temperature. However, it is more likely that the phase was formed during drilling through contact of the saline bottom waters with a saturated calcium sulphate brine or gypsum in the sediment. Fine grained metastable anhydrite has been prepared in the laboratory in this way (Palache et al. 1951; Ostroff 1964). Furthermore, calculations suggest that the bottom waters of Lake Vanda are supersaturated with calcium sulphate whereas those in the upper sediments of DVDP 4 may be almost in equilibrium with calcium sulphate (Watanuki and Morikawa 1975). Mixing of these waters could cause precipitation of metastable anhydrite.

5.3.2 Uncommon phases:

Tendencies are evident in the distributions of groups of some relatively uncommon or not frequently reported phases. Such phases have been listed in Appendix 1 (p.12) as Group B phases (along with common magnesium and nitrate phases). These phases are more widespread than the rare phases just discussed although there is a tendency towards occurrence within 50 km or so of the coast and at elevations less than 750 m or so. DVDP cores have contained some of these uncommon phases. In particular carbonate-bicarbonate phases show strong affinities for sites in eastern Taylor Valley and possibly on volcanic substrates.

Carbonates and chlorides are the prominent, less common phases of Group B, but potassium and iodate phases are also significant. Phases of this group that have not been considered in detail so far are: aragonite, thermonatrite, trona, (all carbonates); sylvite, antarcticite (chlorides);and the iodate phase (probably lauterite, see 3.2.1). Aragonite is most common in Taylor Valley, east of Taylor Glacier. It occurs as veneers (Nishiyama 1977), old and recent lake deposits (Angino et al. 1964; Hendy et al. 1977, 1979; Appendix 1, p.15) and as a precipitate from the Taylor Glacier saline discharge brines (Appendix 1, p.20; Black et al. 1965). It has also been found in DVDP holes 1-3 on Ross Island (Browne1974; Morikawa et al. 1977) and in the vicinity of a fault in DVDP 6 at Lake Vida (Watanuki and Morikawa 1974, 1975). Thermonatrite and trona are also most common in eastern Taylor Valley where they occur as surface efflorescences (Nishiyama 1977). They do not occur more than 8.5 km from the present coastline in the valley. Both phases have also been found at one locality (299) at Stadium Cone on Mt. Discovery (Appendix 1, p.29). Thermonatrite was detected in core from DVDP 1 and 2 (Browne 1973). Thus, these carbonate phases appear to show a tendency to occur in eastern Taylor Valley and a weaker tendency to form in drill holes. Volcanic substrates are present for several of the deposits. Calcium ion is not ubiquitous in these carbonates.

Potassium phases tend to occur within 50 km of the coast and/ or in areas affected by acid plutonic rocks. Sylvite is probably quite widespread. The phase has been found in surface efflorescences at seven localities in eastern Taylor Valley and one in Wright Valley near Vanda Station (Nishiyama 1977; Appendix 1, p.14). All these localities are within about 50 km of the coast and except two (localities 55, 57, Appendix 1, p.14) are less than 100 m asl. The salt has also been detected (by X-ray methods) in saline soils in Wright Lower and Beacon Valleys (Kumai et al. 1976). Claridge and Campbell (1977) found potassium to be enriched in soils derived from acid plutonic rocks. In McMurdo oasis such rocks are exposed in situ from the coast to 60-70 km inland, and up to almost 2000 m elevation (1.2.3, Fig. 1.2).This area encompasses the observed sylvite distribution. The presence of KCl in Beacon Valley soils (≥ 70 km from coast) could be explained by the presence of plutonic clasts in the Metschel tillite which is exposed in situ as far west as 150 km, or by up-valley glaciation(s) (Campbell and Claridge 1978). Similarly, the syngenite occurrence on a basalt substrate in Roaring Valley, Koettlitz Glacier area (Lindholm et al. 1969; Table 5.11) could have crystallized from potassium-enriched brines migrating from nearby granites, which are extensive in the area (Blank et al. 1963; Fig.1.2).

Other uncommon phases are probably quite widespread also. Antarcticite is best known for its existence at Don Juan Pond (Torii and Ossaka 1965; Plate 3.1) where it is also present in core from beneath the surface (DVDP 13, Nishiyama 1979). The salt has also been detected in saline, xerous (or subxerous) soils in Beacon, Wright and Victoria Valleys (Claridge 1965; Kumai et al. 1976). Such an occurrence is probably widespread in as much as such saline soils containing large amounts of calcium and chloride are common in the region (Claridge 1965; Morikawa et al. 1977; Bockheim 1979b; and others). Furthermore, similar occurrences of magnesium chloride (Group C salt, reported to be present in Beacon Valley by Kumai et al. 1976) are probably also common, since magnesium ion is abundant in soils. Iodate ion is present as a trace component in many saline soils in the Transantarctic Mountains but appears to be most concentrated in soils in the west (Claridge and Campbell 1968c).

5.3.3 Common phases and major ions - a summary:

It has been shown that the common salt phases have different distributions from each other. Gypsum and thenardite are the most widespread and regionally abundant of the eight common salt phases whose distributions have been examined in detail in this chapter. These two phases are present at both low and high elevations, and in coastal and inland areas. Of the two phases, thenardite is more common in the east near the coast, whereas gypsum predominates in the west. Calcite is also widespread but in most areas is not an abundant phase. Notable exceptions are eastern Taylor Valley, Koettlitz Glacier moraines and Hut Point Peninsula (Claridge and Campbell 1977; Nishiyama 1979). In McMurdo oasis, calcite abundance decreases inland, to what can be described as a 'plateau' level.

The five other common phases have asymmetrical distributions. Halite is the most abundant salt phase near the coast and at low elevations, but is absent in the westernmost parts of the region and at high elevations in McMurdo oasis. Nitrate phases are absent near the coast and at low elevations. These phases increase in abundance towards the west and high elevations, to become prominent soluble phases at distances between about 70 and 80 km from the coast and at elevations of around 1000 m asl. Thereafter they tend to decrease, especially above about 1500 m. Magnesium phases are absent at low elevations and near the coast except on volcanic substrates. They increase in abundance with increasing elevation and distance from the coast.

Two hydrate phases mirabilite and hexahydrite follow the patterns of the more common phases of these two salts. Mirabilite, like thenardite, is widespread (Appendix 1, Tables 3-11). Hexahydrite is not as common but is present in places where epsomite is abundant.

Ion trends are most useful for defining and summarizing salt distribution on a regional scale. Sulphate is the most widespread anion and tends to increase in abundance in salt deposits with increasing elevation. Hence sulphate phases are the most widespread and also increase in abundance with increasing elevation. Chloride ion decreases towards the west in McMurdo oasis and halite distribution closely follows this. Sodium ion trends are similar to chloride but are not so pronounced; sodium is the predominant cation in generalized salt deposits over much of the McMurdo region, whereas chloride predominates only near the coast. Nitrate ion, absent near the coast, increases to a peak towards the west. Calcium ion is widespread in the region and is the predominant cation at high elevations and in inland regions. Magnesium is lacking on most substrates near the coast but increases with increasing distance inland and elevation. The distribution of this ion and hence phases containing it are primarily dependent on the presence of dolerite and volcanic rocks.

The distribution of carbonate ion is not regular. Phases containing carbonate are widespread but in most areas are not locally abundant. The anion shows no strong distribution tendency on the broadest regional scale in the McMurdo region. Previous studies have suggested that the presence of carbonate ion is related to the presence of carbonate-bearing rocks. Certainly, this association is seen in eastern Taylor Valley and in the dry valleys west of Koettlitz Glacier where carbonate phases are abundant. However, some areas in which carbonate rocks are common do not have an unusually large abundance of carbonate salts. Furthermore, rare and uncommon carbonate phases have a significant tendency to occur on areas comprised of volcanic rocks around McMurdo Sound, and a lesser tendency to occur in drill holes. These tendencies are not parallelled by a similar calcium tendency, suggesting that an important source of the carbonate-bicarbonate ion does not involve calcium.

Some of the uncertainty associated with the distribution of carbonate may be due to systematic sampling errors for calcite. Furthermore, calcite and gypsum have strong tendencies to preferentially accumulate on north-facing slopes (3.3.2). This local effect is probably the cause of some of the irregularity evident in the regional distribution of these two phases.

CHAPTER 6 SOURCES OF SALT AND OTHER INFLUENCES ON REGIONAL SALT DISTRIBUTION

6.1 Preamble

6.1.1 Sources of salt:

Several different salt sources have been proposed to account for the salt contained in solid deposits and saline lakes of the McMurdo region. The literature on salt source is quite extensive. A review of that literature shows that by the late nineteen sixties, two schools of thought had developed favouring two different sources. An oceanic or marine source was considered most important by Wilson and co-workers (e.g. Wilson and House 1965; House et al. 1966; Wilson 1967), Nichols and co-workers (e.g. Nichols 1963 ; Ball and Nichols 1960) and many others (e.g. Craig 1966; Yamagata et al. 1967; Neall and Smith 1967). The second school considered chemical weathering of minerals, (including leaching of ancient salt deposits) in the local rocks and soils to be the main source of salts (e.g. Gibson 1962; Claridge 1965; Tedrow and Ugolini 1966; Jones and Faure 1969; Behling and Calkin 1969). An argument used by this group against the former was that the salts are very diverse and often differ in composition from those in sea water. The main arguments used by the group favouring the marine source were (1) the widespread abundance of chloride ion and (2) the slowness of chemical weathering in antarctic conditions compared to physical weathering, as demonstrated by Blakemore and Swindale (1958) and Kelly and Zumberge (1961). At the same time another group of workers considered the salts to be a relic of early, warmer, moister, possibly interglacial or preglacial times (Stephenson 1961; Black and Berg 1963; Faure in Jones and Faure 1969). Still others considered thermal springs or connate (fossil) water as a possible source (e.g. Angino et al. 1962, 1964).

Different pathways of salt transport have been postulated for specific sources. Direct marine incursion (relic sea water), fractional crystallization from trapped sea water, sea spray, salts blown off sea ice, deposition of marine (and other salts) in local snowfall and as dry fallout, sea spray and upper atmosphere circulation are pathways that have been proposed for salts from the marine source. Volcanic activity emitting magmatic gases or producing thermal springs are feasible for the region, which contains both active and inactive volcanic centres. A variety of biological processes may be important in local areas.

6.1.2 Outline

This chapter examines the causes of regional gradients in salt distribution discussed in Chapter 5. Different sources of salts are of major importance. The chapter discusses the marine source using evidence from the previous chapter and the literature including stable isotope studies. Chemical weathering is then examined on a similar basis. Other sources discussed are volcanic and hydrothermal activity, the atmosphere and biological processes. Other influences on regional distribution discussed here involve the relative age of the locality and leaching. The chapter ends with a synthesis that considers the formation of antarctic salt phases.

6.2 The Marine Source

6.2.1 Evidence from salt distribution:

(i) chloride and sodium ions.

The sea is an important source of salts in the McMurdo region, the main lines of evidence being the negative salt gradients inland and with increasing elevation in McMurdo oasis. The clearest evidence is in the gradients involving chloride (Chapter 5, Figures 5.3, 5.4, 5.8 and 5.9A) because this is the major ion in sea water and a very minor ion in acid plutonic, volcanic and sedimentary rocks (Goldschmidt 1954; Taylor 1964). A similar tendency has been shown for sodium ion (Figures 5.5, 5.6, 5.7, 5.9B), and halite and thenardite (Figure 5.1). The existence of these characteristic gradients is due to a marine influence which is strong near the coast but lessens away from it. Similar lessening influences with increasing elevation, and distance south of the Capes Royds-Barne-Evans area are shown by halite distribution in Figures 5.7, 5.8 and 5.11.

Chloride and sodium trends are similar (Figure 5.9) and Na^+ like Cl^-, is derived mainly from the sea. Weathering does not appear to be a significant source for sodium in Antarctica. However, the sodium trends do not decrease inland quite as fast as those for chloride (Figures 5.4, 5.6) suggesting that some Na^+ may be brought into the oasis with another ion besides Cl^- perhaps as Na_2SO_4. The predominance of Na^+ in cation distribution throughout most of the region (Figures 5.5, 5.7) suggests that the marine source is also predominant.

(ii) pH and sulphate ion

Regional gradients of soil pH also point to a marine source. The pH of 1:5 soil-water extracts was studied on a regional basis by Claridge and Campbell (1977). pH is a maximum (9.0) in coastal soils. In McMurdo oasis pH is around 8 but declines towards the west. Xerous and ultraxerous soils at high elevations along the edge of the plateau are acid, having pH as low as 6.0. Low pH in inland soils at Mt. Howe (4.8 - 5.9) and the Pensacolas (6.5 - 7.0) have been reported by Cameron et al. (1971) and Cameron and Ford (1974) also. pH values ranging from 5.0 to 9.0 have been reported in soils from McMurdo oasis and Sound (Boyd and Boyd 1963; Tedrow and Ugolini 1966; Cameron and Conrow 1969;Campbell and Claridge 1978). Claridge and Campbell (1977) found a close correlation ($r = -0.87$) between pH and SO_4/Cl ratio; the lower the pH, the higher the SO_4/Cl ratio.

In antarctic soils, the value of pH is itself a sensitive indicator of salt source (Claridge and Campbell 1977). These soils have very little buffering capacity due to their low clay and negligible organic content. Normally the pH of sea water is 8 to 9 (Sverdrup et al. 1942). Therefore, the high pH of coastal soils and soils from the eastern part of McMurdo oasis reflect the presence of slightly alkaline marine salts (Claridge and Campbell 1977). High pH is not associated with the presence of carbonate rocks (Boyd et al. 1966; Claridge and Campbell 1977) and furthermore is not merely an indication of an absence of leaching, since unleached soils towards the west have low pH.

The low pH and anion composition of inland soils is also indicative of salt source. The predominant ion, sulphate, in snow of the interior (Delmas and Boutron 1978; Zoller et al. 1978) is derived mainly from the sea (Nguyen et al. 1974) via atmospheric aerosols (5.2.5). The pH of precipitation is closely linked with atmospheric sulphuric acid (Likens and Bormann 1974) which accounts for part of this sulphate. Both H/Cl and SO_4/Cl ratios are higher in atmospheric aerosols of inland regions, than those near the coast (5.2.5). Therefore, the pH decreasing inland indicates an increasing contribution of acidic salts derived from atmospheric aerosols, and precipitated in snow such as on the polar plateau (Claridge and Campbell 1977). The predominance of sulphate in anion distribution and the abundance of sulphate phases compared to chloride, increasing away from the coast (5.2.1, 5.2.4, Figures 5.3, 5.4, 5.11), is suggestive of an original marine source for these salts. The close correlation between pH and SO_4/Cl noted by Claridge and Campbell (1977) is consistent with these observations. The presence of traces of iodate in the salts is further evidence of an original marine source. Most iodine in the iodine cycle is derived from the sea (Eriksson 1952); iodate is the stable form (Johannesson and Gibson 1962).

(iii) nitrate ion

Most of the nitrate in salt deposits of the region are probably derived from the sea via atmospheric aerosols. The abundance of nitrate relative to chloride increases from east to west similar to that for sulphate relative to chloride (Figures 5.3, 5.4). This pattern parallels that of the NO_3/Cl ratio in atmospheric aerosols which are mainly of ultimate marine origin (5.2.5). Therefore, most nitrate is probably derived from the sea as concluded by Claridge and Campbell (1968c, 1977). Some nitrate is probably produced by aurora and other ionisation processes in the upper atmosphere (Wilson and House 1965). Fluctuations in the concentrations of nitrate and ammonium ions in a snow pit at South Pole have a period of about 11 years similar to that of sunspot activity (Parker <u>et al</u>. 1977, 1978).

Nitrate is absent, or present in low concentrations in inorganic salt deposits around McMurdo Sound (Appendix 1, Table 36). This absence can be attributed to a lack of nitrate in coastal snowfalls and aerosols (i.e. low NO_3/Cl ratio, 5.2.5) and to leaching in this relatively moist environment (Appendix 3, sections 5.1, 6.1; 2.3.1.i). Nitrates can accumulate only in the absence of leaching and biological activity (Claridge and Campbell 1968c) since they are the most soluble and easily leached salts in the antarctic salt system (Table 4.1).

6.2.2 Isotopic evidence

(i) similarity to isotopic composition of sea water

Stable isotope analysis provides good evidence for the sources and pathways followed by some salts especially those derived from the sea. Literature reports of $^{34}S/^{32}S$, $^{18}O/^{16}O$ and D/H ($^{2}H/^{1}H$) ratios have been examined. These ratios are usually expressed as deviations (δ) in parts per thousand (‰) from the standards SMOW (Standard Mean Ocean Water) for deuterium and oxygen, and CDT (troilite sulphur in the Canyon Diablo meteorite) for sulphur. For example:

$$\delta^{34}S\ (‰) = 10^3 \times \frac{^{34}S/^{32}S(\text{sample}) - {}^{34}S/^{32}S\ (\text{CDT})}{^{34}S/^{32}S\ (\text{CDT})}$$

Numerous analyses of $\delta^{34}S$ in sulphate salts and dissolved sulphate have been published and show that salts of marine origin are widespread. Less numerous are reports of $\delta^{18}O$ in these same sulphates. Stable isotope ratios of sulphates are shown in Figure 6.1 together with the values for sea water and for sulphate contained in rain (Rafter and Mizutani 1967). Other reports of $\delta^{34}S$ values are listed in Table 6.1.

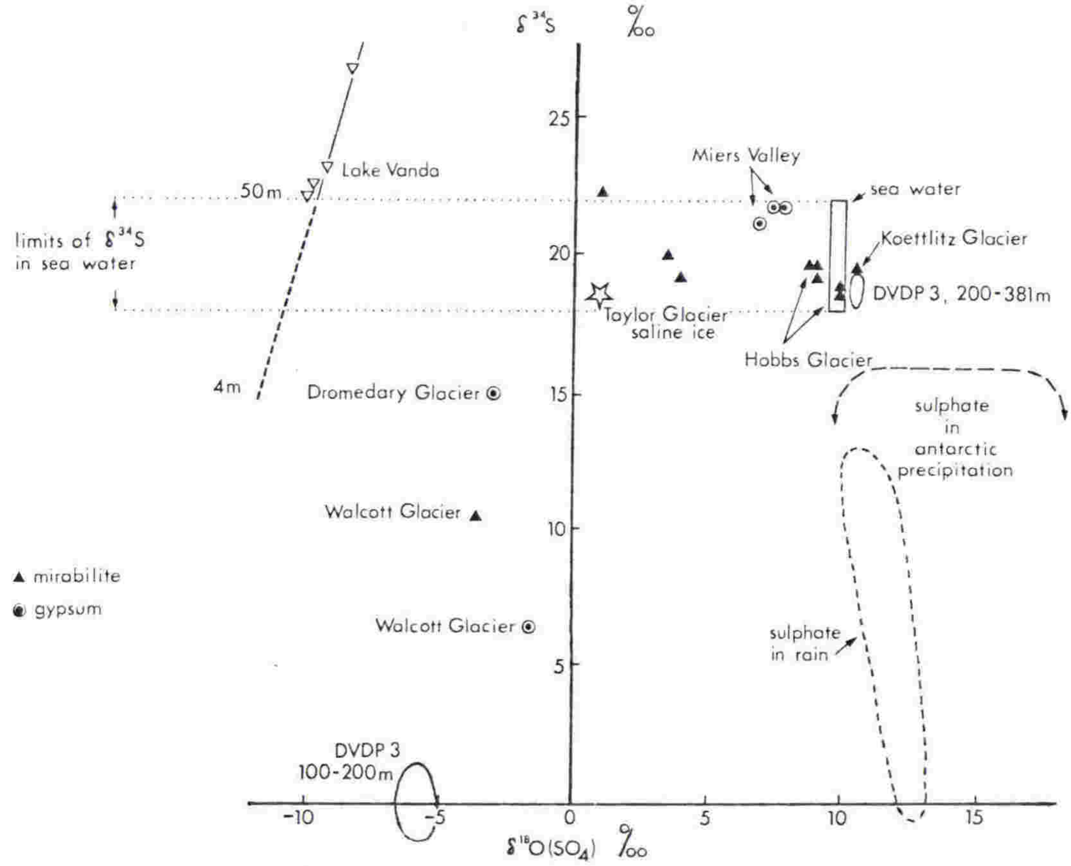


Figure 6.1 Stable isotope ratios of sulphates: $\delta^{34}S_{CDT}$ versus $\delta^{18}O_{SMOW}$. Data from Rafter and Mizutani (1967), Bowser et al. (1970), Lyon (1978) and Nakai et al. (1978).

A close relationship exists between the $\delta^{34}S$ and $\delta^{18}O(SO_4)$ values for sea water sulphate and those for the deepest sulphate in DVDP 3, Miers Valley gypsum, and some mirabilite from Hobbs and Koettlitz Glaciers (Fig.6.1). This implies that these salts have a marine origin (Bowser et al. 1970; Lyon 1978; Nakai et al. 1978). Furthermore, Table 6.1 shows that a similarity exists between marine sulphate and: salt on the sea ice; other mirabilite deposits from Hobbs Glacier and Miers Valley and around McMurdo Sound; saline ice at Taylor Glacier; gypsum in Lake Vanda sediments; some sulphate salts from around the shoreline of Lake Vanda; and some from Taylor Valley. This evidence indicates that marine salts are quite widespread.

Strontium isotopes in salts, soil, lakes and glaciers of the region have been studied by Jones and Faure (1969). Soil and water from the

Lake Fryxell area have $^{87}Sr/^{86}Sr$ ratios similar to this ratio in sea water from McMurdo Sound (0.7094), as does snow and ice from Meserve Glacier. This suggests that the strontium at these locations is derived mainly from the sea.

Table 6.1 $\delta^{34}S$ values for sulphates in salt deposits and dissolved in water in the McMurdo region.

Sample	Location	$\delta^{34}S$ (‰)	Reference
sea water	-	+20 ± 2	Rafter and Muzitani (1967)
mirabilite	Miers Valley, Hobbs Gl area, Black Is, Cape Barne (average of 7 samples)	+20.6	Nakai *et al.* (1975)
salts	shoreline of Lake Vanda	+18.9 to 20.9	Nakai 1974
gypsum	floor of Lake Vanda	+22.4	Nakai *et al.* (1975)
"	DVDP 4 sediment (Lake Vanda)	+20.8	" " "
water	Lake Vanda 4m	+15.0	" " "
	20m	+16.0	" " "
	50m	+18.7	" " "
	55m	+22.0	" " "
	65m	+42.1	" " "
	68m	+46.0	" " "
	DVDP 4 core water 72m	+48.8	" " "
	75m	+39.1	" " "
salts	sea ice (McMurdo Sound)	+18	Wellman and Wilson (1963)
salts	Taylor Valley > 200 m asl on basement rocks	+10.5 to 21.1	Nishiyama and Nakai (1975)
salts	Taylor Valley < 200 m on moraine and glacial drift	+5.2 to 15.0	Nishiyama and Nakai (1975)
salts	Taylor Valley, shorelines of present lakes east of Suess Gl	-27.9 to 19.7	Nishiyama and Nakai (1975)
salts	Dias	+15.0 to 17.6	Nakai 1974
gypsum	Canopus Pond area, salt horizon	+14.1 to 14.4	Nakai 1974

(ii) microbiological activity

Deviations from sea water values of $\delta^{34}S$ and $\delta^{18}O(SO_4)$ are evident for some samples (Fig.6.1 and Table 6.1). The depletion of $^{18}O(SO_4)$ from sulphates in Figure 6.1 has been discussed by Bowser et al. (1970) and Lyon (1978), and attributed to microbiological activity. In anaerobic conditions bacterial reduction of sulphate to hydrogen sulphide, followed by the reoxidation of this in an aerobic part of the system in the presence of light antarctic water, can cause depletion of $^{18}O(SO_4)$ and produce a shift of $\delta^{18}O(SO_4)$ towards negative values. Sulphate reduction by the widespread bacterium Desulfovibrio desulfuricans is recognized as an important part of the global sulphur cycle (Rees 1973); the presence and activity of this bacterium in the McMurdo region has been documented by Barghoorn and Nichols (1961).

The $\delta^{18}O(SO_4)$ can be lowered without change of $\delta^{34}S$ if complete mixing and conservation of sulphur-containing species occurs (Bowser et al. 1970; Lyon 1978). The reduction-reoxidation mechanism is comprised of three main steps (Mizutani and Rafter 1969; Berner 1971):

$$\underset{\text{sulphate}}{SO_4^{2-}} + \underset{\text{organic matter}}{2CH_2O} \xrightarrow{\text{D. desulfuricans}} \underset{\text{hydrogen sulphide}}{H_2S} + \underset{\text{bicarbonate}}{2HCO_3^-} \qquad \ldots\ 6.1$$

$$2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2 \qquad \ldots\ 6.2$$

$$2SO_2 + 2H_2O + O_2 \rightarrow 4H^+ + 2SO_4^{2-} \qquad \ldots\ 6.3$$

Reaction 6.1 leads to enrichment of ^{34}S in the remaining sulphate, and depletion in the sulphur gases; Reaction 6.3 produces SO_4^{2-} whose $\delta^{18}O(SO_4)$ is very similar to that of reactant water (Mizutani and Rafter 1969). Conservation of sulphur gases produces a sulphate product whose $\delta^{34}S$ value is identical to that of the original sulphate. Such closed conditions are inferred for the sulphate in the saline ice at Taylor Glacier and some mirabilite in Hobbs and Miers Valleys which has $\delta^{18}O(SO_4)$ more negative than the sea water value but $\delta^{34}S$ similar to sea water (Fig.6.1).

$\delta^{34}S$ will change in a poorly mixed or open system such as Lake Vanda. Deeper than about 40 m in Lake Vanda, mixing is diffusion controlled and therefore slow (Wilson and Wellman 1962; Wilson 1964). Anaerobic conditions are present and H_2S is being produced under these reducing conditions in the bottom 10 m of the lake (Torii et al. 1975). This is accompanied by an enrichment of ^{34}S in the remaining dissolved sulphate leading to the very positive values of $\delta^{34}S$ (Table 6.1; Mizutani and Rafter 1969 ; Nakai et al. 1975). Some of the H_2S ascends towards the surface and is oxidized, producing isotopically light dissolved sulphate in the presence of light Vanda water ($\delta^{18}O$ about -30 per mille, Mizutani and Rafter 1969). This secondary sulphate lowers the $\delta^{34}S$ of sulphate dissolved in the upper part of the lake (Table 6.1; Nakai et al. 1975). These processes lead to the range of points for Lake Vanda on Figure 6.1.

Similar microbiological activity was invoked by Nishiyama and Nakai (1975) to explain the variation of $\delta^{34}S$ in salts from Taylor Valley (Table 6.1). Salts with $\delta^{34}S$ as low as -27.9 per mille occur at low elevations around present lake shorelines. Repetition of the reduction-reoxidation cycle a number of times was supposed to produce these low values. Similarly, there is evidence to suggest that bacterial activity associated with former high lake levels affected sulphates up to about 200 m elevation. $\delta^{34}S$ values as low as +5.2 per mille are found up to this level (Nishiyama and Nakai 1975). Salt dispersal by wind (4.6) could have obscured these relationships with elevation.

(iii) other causes of ^{34}S depletion

Depletion of ^{34}S from the sea water concentration can be caused by other processes. Figure 6.1 shows a field for sulphate in rain given by Rafter and Mizutani (1967). The field for antarctic precipitation is probably displaced slightly away from the origin due to isotopic fractionation between water and ice. Nakai et al. (1975) gave the $\delta^{34}S$ values for atmospheric sulphate as 0 to +16 per mille. Displacement of $\delta^{18}O(SO_4)$ is probably less than +7 per mille assuming equilibrium fractionation factors similar to those for $\delta^{18}O(H_2O)$ given in Stewart (1975). Figure 6.1 shows what is estimated to be the upper limits of the field for sulphate in the antarctic atmosphere, and the precipitation from it. $\delta^{34}S$ is lowered during aerial transport of marine sulphate and sulphur dioxide, and subsequent mixing with isotopically light atmospheric sulphate. Salts formed from precipitation have lower $\delta^{34}S$ values than does sea water.

Slight depletion of ^{34}S is evident also in salt that has crystallized on the surface of sea ice in McMurdo Sound (Table 6.1). Such salt ('rassol') is a common occurrence in the Sound (Plate 6.1; Evans 1921; Wright and Priestley 1922). Wellman and Wilson (1963) estimated that at least a million tonnes is formed annually there. The amount depends on the rate of sea ice formation (i.e. air temperature) and conditions during freezing.

Plate 6.1 Salt, mainly sodium sulphate, that has crystallized on the surface of young sea ice near Cape Evans, McMurdo Sound. The Siberian term rassol is a synonym for this type of salt occurrence.

Rapid freezing during wind-induced disturbance entraps most brine and causes highest sea ice salinities (Wright and Priestley 1922; Sverdrup et al. 1942; Assur and Weeks 1963; Cherepanov and Kozlovskii 1973). Small amounts of calcium carbonate tend to precipitate from the entrapped brine below -2.2°C (Weeks 1962). Mirabilite crystallizes out onto the surface if the surface temperature is less than -8.2°C; dihydrohalite follows at -22.9°C (Thompson and Nelson 1956). Four analyses of rassol from McMurdo Sound showed that sulphate (as mirabilite and thenardite) is the predominant anion (c.60% of total salt); chloride (c.1%) and calcium carbonate (less than 1%) are very minor constituents (Wellman and Wilson

1963; Keys 1972). This salt and associated saline snow is probably moved by winds greater than about 10 m s^{-1}, which are not infrequent in the area (Appendix 3, section 5.4, Table 11). Therefore, fallout of sulphate from the sea ice, having a $\delta^{34}S$ value of around 18 per mille, must be expected in the McMurdo region.

Above about 200 m in Taylor Valley, the sulphates present have a comparatively narrow range of $\delta^{34}S$ values (+10.5 to 21.1 per mille, Nishiyama and Nakai 1975; Table 6.1). The range suggests that these salts have been aerially transported from open sea water or salt-covered sea ice and some may have been involved in a coastal precipitation stage (Fig.6.1). Analyses of $\delta^{18}O(SO_4)$ for these salts may add further weight to this interpretation of their transport paths.

Three sulphates from near Walcott and Dromedary Glaciers were sampled from salt pans (type 2B deposits) and a 1A deposit at elevations greater than 700 m (Lyon 1978). Their $\delta^{34}S$ and $\delta^{18}O(SO_4)$ values are shown on Figure 6.1. These values indicate that the salts are not derived directly from the sea but are possibly related to weathering of the substrate rocks (Lyon 1978). However it is not possible at present to distinguish between such products of weathering and those deposited from the air and subsequently modified by microbiological activity.

6.2.3 Direct aerial pathways for salts of marine origin:

(i) snowfall

Most marine-derived salts in the McMurdo region appear to have travelled by relatively direct pathways from the sea. This is shown by the similarity between soil and sea water pH (Claridge and Campbell 1977) and the similarity between $\delta^{34}S$ values of sulphates and sea water sulphate. These salts have not undergone long contact with the acidifying and oxidizing environment of the atmosphere experienced by the sulphates further inland. Direct aerial pathways involve coastal and near-coastal snowfall, sea spray and dry fallout, (including salts blown off the sea ice), or combinations of these.

Snowfall is probably the most widespread pathway in McMurdo oasis. The chemical constituents of antarctic snowfall are mainly marine aerosols (5.2.5) and it has been seen that the $\delta^{34}S$ values of these are less than in sea water (6.2.2iii). Relatively moist maritime air and stratus clouds brought up the valleys by easterly winds deposit snow in a pattern that decreases towards the west (Appendix 3, sections 4.2, 4.3, 5.2, 6.2), consistent with the observed decrease of halite towards the west. Vigorous cyclonic storms from the Ross Sea produce the greatest amounts of snowfall; they also contain the largest amounts of marine aerosols and the snow composition is very similar to sea water (Warburton and Linkletter 1978). Snowflakes formed in such conditions are probably large stellar crystals (Appendix 3, section 5.3). Such crystals and the associated precipitation are likely to be more effective at trapping and removing aerosols from the atmosphere than smaller, compact forms produced in drier conditions (5.2.5; Herman and Gorham 1957; Gorham 1961).

Drier snow falling in smaller amounts further from the coast may contain marine aerosols that have been fractionated. K/Na, Mg/Na and Ca/Na ratios may be increased from their bulk sea water values by fractionation processes at the sea-air interface, during aerial transport to the land, or during formation of snow particles and precipitation (Wilson and House 1965; Lorius et al. 1969; Boutron et al. 1972; Warburton and Linkletter 1978). However, Murozumi et al. (1969) and Boutron (1979) have suggested that much of the supposed fractionation that has been reported was due to contamination and analytical error during analysis of samples; certainly such problems are likely given the low concentrations (10^{-8} to $<10^{-10}$ kg kg^{-1}) of soluble constituents in antarctic snow. The only significant proven enrichment is that of potassium within about 100 km of the coast in East Antarctica (Boutron 1979) or perhaps as much as 450 km on Ross Ice Shelf (Warburton and Linkletter 1978). Such fractionated marine aerosols probably contribute to the accumulation of potassium salt phases in McMurdo oasis (5.3.2). Fractionation may also occur between sulphate and chloride since SO_4/Cl ratios in snow tend to increase significantly inland (5.2.5).

(ii) sea spray and dry fallout

Sea spray and salt (rassol) blown off the sea ice seem to be important pathways near the coast of Ross Island. Deposition of sea spray has been observed on Ross Island during periods with open water nearby and strong southerly winds (Appendix 3, section 5.5).

It is reasonable to suppose that most halite in salt deposits at Capes Bird, Royds, Barne and Evans is derived from such deposition (Mawson 1915) rather than from weakly saline snowfalls. However sulphate anion appears to be more widespread than chloride around the western coast of Ross Island (Fig.5.11) in contrast to the situation in eastern Taylor Valley (Figs.5.1, 5.3, 5.4). This suggests that deposition of sea ice sulphate is more important than sea spray chloride on Ross Island.

Chloride abundance sharply decreases between Capes Royds-Barne-Evans and Hut Point Peninsula (Fig.5.11). This implies that the sea spray component decreases between these areas. This may be due to the presence of McMurdo Ice Shelf to the south of the Peninsula and to surrounding sea ice. Under present-day conditions fast sea ice persists for ten or more months per year south of about the latitude of Castle Rock (Evans 1921; Heine 1963). Therefore, south of this there is seldom or never any open water and accordingly deposition of sea spray chloride is likely to be restricted.

A decrease in thenardite corresponding to that of chloride is not evident in Figure 5.11. Local sources of thenardite are probably important south of Ross Island. Extensive bodies of marine-derived mirabilite are known on McMurdo Ice Shelf near Black Island and White Island, Black Island itself, Koettlitz Glacier and Hobbs and Miers Valleys (Debenham 1920; Bowser et al. 1970; Nakai and Mizutani 1977; Brady 1979b).

Sea spray chloride and sea ice sulphate are probably less important in McMurdo oasis than on Ross Island. Old (multi-year) fast sea ice is usually present along the western side of McMurdo Sound (Stonehouse 1967), and breakout to the shore is infrequent. Sea ice loses much of its salt by leaching and brine drainage during its first summer of existence; three-year-old ice is almost salt free (Wright and Priestley 1922; Armstrong et al. 1973). Less rassol can be blown off this western sea ice into the oasis than is blown off generally younger, saltier ice around Ross Island. Since open water is infrequent, sea spray chloride as well will be less important in the oasis than on Ross Island.

Dry fallout of atmospheric salt of marine origin probably occurs from the dry atmosphere over McMurdo oasis, but has not been monitored. Such dry fallout of salt is a significant process elsewhere in the world, especially in dry areas (Gorham 1961). Marine aerosols travelling from the east over McMurdo oasis probably lose moisture to the atmosphere as the relative humidity of this decreases from the east (Appendix 3, section 6.2). This may be accompanied by an increase in dry fallout from the coast towards the central part of the oasis.

6.2.4 Influx of sea water:

(i) evidence

Influx of sea water is also a direct pathway by which salts of marine origin may be incorporated into the salt system in the McMurdo region. This process appears to have been especially important in Taylor Valley. There is both geochemical and geological evidence of sea water influx (variously termed relic or trapped sea water, flooding by sea water, marine incursion).

Best evidence for a sea water influx comes from the Lake Bonney area. At least 15 million tonnes of sodium chloride are present on the floor and in the water of the East Lobe of Lake Bonney; this amount of salt cannot have been produced by weathering without correspondingly large amounts of clay minerals which are relatively sparse in Taylor Valley sediments (Hendy et al. 1977; Ugolini et al. 1979). Several complete specimens and broken fragments of the calcareous foraminifera Globigerina sp. have been found in the bottom of East Lobe (Angino et al. 1964), suggesting transport from marine sources. Furthermore, major and minor ion ratios in the bottom waters of West Lobe are similar to those of sea water (Angino et al. 1964; Torii et al. 1975; Table 6.2), and trace element ratios in the lake are closer to those of sea water than are those of other antarctic lakes (Boswell et al. 1967). In the saline discharge brines from Taylor Glacier, ratios of the major ions that appear not to have been involved in precipitation (Chapter 8) are very similar to ratios in sea water (Table 6.2, Fig.5.12); the high ratio of Na/K that is apparent is probably due to fixation of K^+ by clays (4.3.4). The $\delta^{34}S$ value of saline discharge ice in Taylor Glacier is similar to that of sea water (Bowser et al. 1970; Fig.6.1). The ratios involving Na^+ in Lake Bonney have been lowered with respect to sea water ratios, and that of Mg/Cl raised, mainly by precipitation of sodium sulphate and chloride (Angino et al. 1964; Yamagata et al. 1967; Hendy et al. 1977).

The compositions of present-day streams and saline flows in the Lake Bonney drainage basin are dissimilar to the discharge brines and Lake Bonney water (Fig.6.2, Table 6.2), indicating that the salt in the lake was not derived from these inflows. This assumes that the compositions of the inflows have been the same as now throughout the history of the lake salts, and that the only other processes affecting lake water chemistry have been deaquation and precipitation of specific salt phases. (These are reasonable assumptions based on present knowledge.) The following discussion proves this important point.

The waters of West and East Lobes are chemically distinct from each other (Figs.5.12, 6.2) and are discussed separately. In West Lobe sediments a thin layer of gypsiferous silts overlies subaerially weathered till, and the inference has been made that no other salts apart from calcium carbonate have been precipitated from West Lobe waters (Hendy et al. 1977, 1979). Figure 6.2 shows two analyses of contemporary melt water feeding West Lobe (Field 1975; Torii et al. 1975); a third, from Yamagata et al. (1967, Table 4.5) is not shown but lies between the other two. The dotted arrows show the direction in which these waters would hypothetically evolve during their concentration, and subsequent precipitation of gypsum and calcium carbonate. Such paths lead towards the field of West Lobe waters. However the ratios of the major ions that are unaffected by precipitation of Ca salts(i.e. Na^+, K^+, Mg^{2+}, Cl^-) are markedly different in the stream waters compared to West Lobe waters (Table 6.2). Therefore, the latter cannot have formed by such evolution. Figure 6.2 also shows contemporary analyses of a stream and a saline flow feeding East Lobe (Torii et al. 1975; Field 1975). The dashed arrows show the approximate direction in which these waters would hypothetically evolve during concentration and subsequent precipitation of the minimum of four million tonnes of sodium chloride and minor calcium salts that Hendy et al. (1977) and Hendy (1975) have found in a layer at least 2.2 m thick on the floor of East Lobe. These evolution paths would tend towards the horizontal if large amounts of calcium salts underlie the sodium chloride deposit. East Lobe waters are

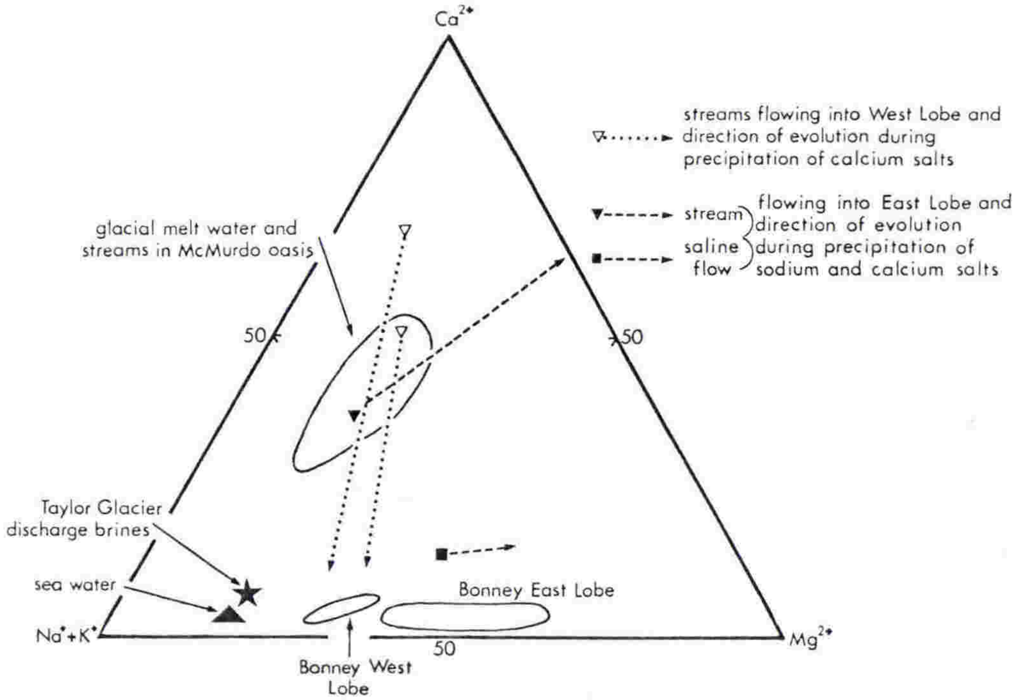


Figure 6.2 Comparison between inflow waters and saline water bodies in Lake Bonney drainage basin. Arrows show hypothetical direction of evolution of inflow waters during deaquation and precipitation of salts. Arrow lengths are schematic and relative only. Fields for Lake Bonney and glacial melt waters after Torii et al. (1979).

Table 6.2 Ratios of sodium, potassium, magnesium and chloride in streams and saline flows in Lake Bonney drainage basin, West Lobe of Lake Bonney, saline discharge brines and sea water.

	Ratio				
Water or brine	Na/K	Na/Mg	Na/Cl	Mg/Cl	Calculated from
streams into West Lobe	2.0 10.9	3.3 3.2	0.92 1.1	0.28 0.33	1 2
stream into East Lobe	6.67	4.3	1.02	0.24	2
saline flow into East Lobe	16.8	1.80	0.336	0.186	1
West Lobe of Lake Bonney					
- whole water column	19-28	2.8-5.5	0.29-0.51	0.093-0.11	2
- bottom (24 m)	28	5.0	0.53	0.108	3
- bottom (29.5 m)	21.8	3.85	0.41	0.107	2
saline discharge brines	35-46	7.2-8.6	0.54-0.57	0.067-0.076	4
sea water	27.8	8.30	0.556	0.067	5

1 Field (1975) and Table 4.5
2 Torii et al. (1975)
3 Angino et al. (1964)
4 Appendix 1, Table 15
5 Sverdrup et al. (1942)

very different from the hypothetical evolved inflows. Saline discharge brines are different from all inflows and their hypothetical evolved forms (Figure and Table 6.2). Therefore, little of the salt in the Lake Bonney drainage basin can have been derived by leaching of salt deposits higher in the basin and input of salt contained in glacial melt waters.

In conclusion, direct incorporation of sea water is the most likely source of the salts in Lake Bonney (Yamagata et al. 1967; Hendy et al. 1977) and beneath Taylor Glacier. The present lake water composition differs from sea water because of precipitation of calcium and sodium salts, together with minor additions of salts from leaching, weathering and marine aerosols (Hendy et al. 1977).

Other lakes and sediment also contain chemical evidence for sea water influx. Major cation ratios in Lake Fryxell, in particular Na/Mg, are very similar to those in sea water (Torii et al. 1975; Fig.5.12), and trace elements also suggest some direct marine influence (Boswell et al. 1967). Pore water from DVDP holes 8, 9 and 10 have ion ratios that are similar to those in sea water (Ugolini et al. 1979). The chemistry of some lakes on the coast of Ross Island and elsewhere in East Antarctica is also suggestive of direct incorporation of sea water (Glazovskaya 1958; Yamagata et al. 1967; Dort and Dort 1970; Ugolini et al. 1979). $\delta^{34}S$ values of mirabilite and gypsum deposits that occur up to 200 m elevation in Hobbs and Miers Valleys (Fig.6.1) and elsewhere (Table 6.1) indicate that the sulphate came from sea water not atmospheric sulphate (6.2.2).

(ii) the process

Sufficient evidence exists to suggest that an influx (or influxes) of sea water has occurred into areas that are now land-locked such as the Lake Bonney drainage basin. A mechanism to account for this influx(es) must explain how:

(1) sea water overflowed the eastern threshold of Bonney basin at the Suess Glacier threshold (elevation 130 ± 20 m asl from USGS 1:50,000 map and Stuiver et al. 1980) but deposited very little recognizably marine sediment in DVDP 12 (Brady 1979b) immediately to the east of Suess Glacier. The sediment threshold beneath Taylor Glacier to the west between Ferrar Fiord

and Bonney basin is about 300 ± 50 m asl (from Stern 1978), which is higher than the Suess threshold and may preclude influx from the west;

(2) salts from sea water (as opposed to aerially transported salts) were deposited at elevations of up to at least 200 m asl in Taylor, Hobbs and Miers Valleys (6.2.2). Relative sea levels have not been this high for two million years or so (Webb 1972) and the Hobbs Valley salts are much younger than this (Bowser et al. 1970). (Kellogg et al. (1980) have refuted Miagkov et al.'s (1976) hypothesis for relative sea levels 150 m above present sea level 50,000 years ago, on both ecological and geomorphological grounds). The water of crystallization of mirabilite and gypsum in Hobbs and Miers Valleys indicates that these marine salts were precipitated from fresh (or brackish) water (Bowser et al. 1970; Lyon 1978). This seems to preclude Debenham's (1920) mechanism of freezing beneath a floating glacier tongue or ice shelf combined with surface ablation to raise sea water salts (mirabilite) to the surface. Furthermore, Debenham's process cannot explain the large quantities of sodium chloride in Lake Bonney.

The problem is examined by considering the salts in Hobbs and Miers Valleys and other areas in which similar salts and their environment have been studied in detail. Bedded, massive mirabilite is found in place at elevations up to 200 m asl near Hobbs Glacier and in Miers Valley (Bowser et al. 1970; Dort and Dort 1970; Nakai and Mizutani 1977). The beds overlie glacial ice and are associated with interstratified sediments and algae, indicating precipitation from standing water bodies. Field relationships including ice foliation and morainal composition indicate that these bodies were dammed by an expanded and grounded Koettlitz Glacier (Bowser et al. 1970).

Stable isotope analyses suggest a non-marine source for these water bodies. Figure 6.3 shows stable isotope ratios of water, ice and snow plus derived salt solutions; δD and $\delta^{18}O$ values for the last named were obtained from the waters of crystallization (paleowater) after the method of Lyon (1978) to account for isotopic fractionation between salt and solution. The close proximity of several different samples of Hobbs Glacier

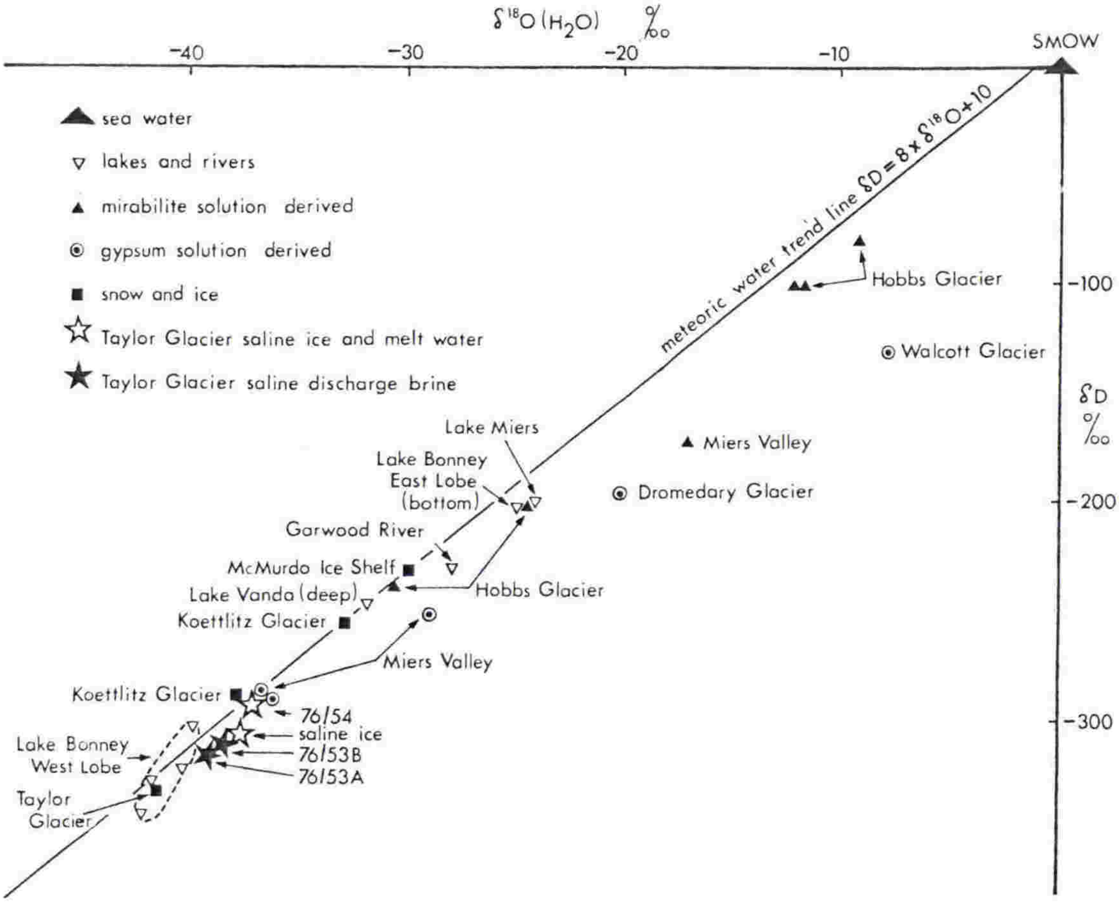


Figure 6.3 Stable isotope ratios of water, ice, snow and derived salt solutions: δD_{SMOW} versus $\delta^{18}O_{SMOW}$. Data from Table 15, Appendix 1 and Bowser et al. (1970), Gow and Epstein (1972), Stewart (1975), Torii et al. (1975), Lyon (1978) and Drewry et al. (1980). The meteoric water trend line of Craig (1961) is shown.

mirabilite and some Miers Valley gypsum to the meteoric water line indicates a non-marine (glacial melt water) source for the water from which these salts were precipitated (Bowser et al. 1970; Lyon 1978). Figure 6.3 also shows that the water in Lakes Bonney and Vanda is glacial melt water not sea water (e.g. Ragotzkie and Friedman 1965; Craig 1966; Ambe 1974; Torii et al. 1975). Similarly the water in the glacier discharge brines is derived from melted Taylor Glacier ice, not sea water.

Fossil records appear to provide conflicting evidence for the water source until they are examined closely. Bedded fossiliferous 'marine' sediments overlie bedded mirabilite at Miers Valley, Black Island and Cape Barne (Nakai and Mizutani 1977) and are present in Salmon Valley (Miagkov et al. 1976). However, Brady (1979b) found non-marine diatoms associated with the 'marine' sediments at Cape Barne, consistent with recent ecological studies by Kellogg et al. (1980). Brady concluded that the sediments had been reworked and raised by an expanding ice shelf. The diatoms formed in non-marine water bodies associated with the expanded ice shelf. Ward (1979) considered that the Cape Barne sediments were raised, lodged and stranded and the associated mirabilite crystallized, between 75,000 and 3,000 years BP.

A process causing influx of sea water to inland areas of the McMurdo region has been proposed by Brady (1979b). He suggested that sea water may be trapped beneath an expanding glacier or ice shelf and forced above the surface by the weight of the glacier as it grounds. Subsequent dilution of this water by glacial melt waters produces a non-marine moat. By this mechanism, bedded mirabilite with marine values of $\delta^{34}S$ and $\delta^{18}O(SO_4)$ but non-marine values of δD and $\delta^{18}O(H_2O)$, could be formed by fractional crystallization from a freeze-concentrating, isotopically light brine body. Such gypsum could be formed by evaporation of similar water, especially if this had been enriched with Ca^{2+} from weathering of marble as suggested by Lyon (1978).

Partially or completely dry lakes may be intermediate stages in the process of salt deposition. The range of water of crystallization plots on Figure 6.3 suggests that various melt waters have been involved, with deaquation stages interposed between them. Similar behaviour in an expanding and shrinking Lake Vanda was inferred by Nakai et al. (1975) from layers of gypsum and calcite in DVDP 4 core. Furthermore, different elevations and amounts of folding of mirabilite beds (Bowser et al. 1970) imply that movement or oscillation of the grounded ice has taken place over a significant time period.

From the preceding discussion it is evident that the highest mirabilite bed (about 200 m asl) would represent the maximum height reached by the expanded glacier, not the maximum former sea level. Carbon-14 dates of algae associated with the mirabilite deposits in Hobbs Valley range from 3,000 to 40,000 carbon-14 years BP (Black and Bowser 1968; Bowser et al. 1970). These dates may be too old due to ^{14}C deficiency in antarctic sea water and isotopic exchange with old bicarbonate in the water bodies containing the algae (Broeker 1963; Black and Berg 1964). However, the error is probably not more than 1,000-2,000 years (Burrows 1979) and does not significantly affect the older date. During the last 40,000 years or so world sea level has been no more than 10 m higher than now (Holmes 1965). Tectonic and glacio-isostatic uplift has occurred in McMurdo oasis during the last three million years at least, at a maximum rate of about 1 x 10^{-4} m a^{-1} (Webb 1972; Drewry 1975). During the last 4 x 10^{4} years such uplift would have amounted to about four metres. The combined maximum relative rise of sea level (14 m) is similar to the highest raised beaches (not lake shorelines) in the McMurdo region (20 m, Nichols 1970) but is much less than a 200 m rise required by Dort and Dort (1970) to explain the mirabilite deposits. Brady's (1979b) hypothesis and the discussion above overcome the major obstacle towards rationalization of the large salt masses in Hobbs and Miers Valleys.

Injection of sub-ice sea water brine into Taylor Valley would account for the composition of salts in Lakes Bonney and Fryxell. The expanded Ross Ice Shelf reached about 300 m asl in eastern Taylor Valley during its most recent advance (i.e. Ross Glaciation I) and apparently about 400 m asl during Ross II (Denton et al. 1971; Stuiver et al. 1980). These levels are higher than both the present 80 m asl threshold east of Lake Fryxell (USGS 1:50,000 map) and the Suess Glacier threshold (130 ± 20 m asl), and similar to the extreme western threshold of Bonney (300 ± 50 m asl). Thus, sea water could have been injected into the basin during the advance of Ross I or II and deposition of unworked sediments need not have occurred. Ross ice reached lower levels to the north (Stuiver et al. 1980); apparently sea water did not penetrate Wright Valley whose eastern sub-ice threshold was about 130-270 m asl (Calkin 1974).

(iii) the timing

Injection of sea water brine into Bonney basin has important implications and it would be useful to place a date on the event(s). Hendy et al. (1977) gave 0.1 to 0.3 Ma BP as the age of the hypothetical event. This is a rough maximum estimate based on assumed rates of both precipitation of snow and inflow of dissolved salts into East Lobe. The estimate does not take into account the precipitation of sodium chloride that has occurred which would have caused enrichment of both magnesium and potassium ions in the lake brine (4.4.1; see also Fig.6.2 for the observed enrichment of Mg^{2+} relative to an initial sea water composition). The minimum age for the injection is probably about 15,500 ± 2,000 years BP, because this is the age of a diffusion cell in West Lobe as well as the apparent ^{14}C age of the bottom waters of the Lobe (Hendy et al. 1977).

The lack of sediment overlying the halite layer at the bottom of East Lobe (Hendy 1975) suggests that the injection took place after the last Taylor Valley glaciation that occupied the basin (Hendy et al. 1977). This is Taylor II of Denton et al. (1971) which apparently just reached as far as East Lobe. Taylor II is poorly dated but must be younger than 1.5 Ma, the maximum age of Taylor III from K-Ar dates on basalt (Armstrong 1978). Hendy et al. (1979) believe that Taylor II is about 0.2 Ma but their argument is indirect, relies on oversimplified drift stratigraphy and has been challenged by Robinson and Keys (in press). The lack of sediment also suggests that the injection postdates 0.1 Ma. At that time alpine glaciers such as Lacroix were more advanced than now, actively depositing sediment and damming melt water isotopically similar to that of the present day from Taylor Glacier (Hendy et al. 1979).

Ross Ice Shelf has advanced probably twice between 15,000 and 0.1 Ma years BP. Ross I reached its maximum extension in Taylor Valley about 20,000 years ago and Ross II possibly about 75,000 years ago (Denton et al. 1971). Therefore, Brady's process of brine injection probably accounts for the sea salt in Bonney basin.

The injection probably predates the period 17,000 to 21,000 ^{14}C years BP. This is the time during which Ross I reached its maximum height and extension in eastern Taylor Valley, damming non-marine Glacial Lake Washburn to a height of 308 m asl (Denton et al. 1971; Stuiver et al. 1980; Kellogg et al. 1980). Probably no brine injection would have occurred after this time because the Ross ice was retreating.

The injection could have occurred between 80,000 and 20,000 years BP during advances of Ross ice into Taylor Valley. Following the onset of global cooling about 80,000 years ago, Ross Ice Shelf probably thickened and grounded further north than now; part of the ice advanced into Taylor Valley reaching a maximum extension (Ross II?) possibly about 75,000 years ago (Denton et al. 1971; Shackleton and Opdyke 1973). A retreat due to slightly warmer conditions may then have occurred, followed by readvance as global temperatures again cooled from about 50,000 to 30,000 years BP. This advance culminated about 20,000 years BP.

It seems more likely that the brine injection occurred during the readvance rather than the initial advance (Ross II?). Between 70-130,000 years BP a lake(s) larger than the present Lake Bonney occupied Bonney basin;

it contained isotopically light water and was dammed by expanded, apparently alpine glaciers (Hendy et al. 1979). These may have prevented significant amounts of sea water brine entering the basin. Therefore the brine may have been injected into Bonney basin between about 50,000 and 20,000 years ago.

6.3 Chemical Weathering

6.3.1 Operation in Antarctica:

Several studies have shown that chemical weathering of rock and soil minerals can take place in antarctic conditions (Blakemore and Swindale 1958; Kelly and Zumberge 1961; Glazovskaya 1958; Claridge 1965; Ugolini and Bull 1965; Behling 1971; Everett 1971; Boyer 1975; Ugolini 1976; Jackson et al. 1977). Intense physical weathering involving freeze-thaw and expansion-contraction processes causes mechanical comminution and micro-fracturing of rock, and soil grains and minerals. Thin liquid films of moisture with high ionic strength surround the grains (Ugolini and Anderson 1972; 2.3.3) enabling a favourable environment for chemical weathering to exist in arid and frigid conditions (Ugolini et al. 1979). Chemical weathering of individual grains has been verified by microscopic examination which showed the presence of iron-stained soil grains and the accumulation of secondary clay residues in fractures in rock and soil minerals (Glazovskaya 1958; Claridge and Campbell 1977); mafic minerals tend to weather most, but plagioclase and alkali feldspars also decay chemically (also Linkletter 1971; Ugolini 1976).

There is no doubt that chemical weathering is taking place at the present time albeit slowly, and has done so for the lifetime of the McMurdo region. The amount of extractable iron and the degree of hydration of micas (to form authigenic clay minerals such as vermiculite), generally increase with time from young soils to those older than four million years (Claridge 1965; Behling 1971; Boyer 1975; Campbell and Claridge 1975, 1978; Ugolini 1976). $^{87}Sr/^{86}Sr$ ratios in river and lake water are very similar to those in soil and sediment in Wright Valley and in and around Lake Bonney (Jones and Faure 1969). This implies that much of the strontium salts in these areas have been derived by chemical weathering during the total lifetimes of the lakes. Thus there is ample evidence to show that chemical weathering is presently active and has been so for the last few million years in the region.

There are two main sets of evidence from the present study for a rock and soil source of salts. These are (1) the close association of magnesium phases with dolerite and volcanic substrates (5.2.3) and (2) the preferential accumulation of calcite and gypsum on north-facing slopes (3.3.2). Other significant evidence discussed here includes calcite and carbonate plus bicarbonate ion distribution.

6.3.2 Magnesium ion:

There is a clear association between magnesium ion and substrates of basic igneous rocks (5.2.3). The association is illustrated in Figure 5.10A and indicates that magnesium ion is derived from minerals in these rocks. Dolerite, the most widespread rock in the western part of McMurdo oasis (Fig.1.2) contains mainly calcic plagioclase feldspars (labradorite) and pyroxenes including hypersthene, augite and pigeonite (McKelvey and Webb 1959). Microscopic examination of thin sections and grain mounts of weathered doleritic material from the Transantarctic Mountains has shown that the pyroxenes (mafic ferromagnesian minerals) are almost completely decayed while feldspars and other minerals are quite fresh (Claridge and Campbell 1977). In moister areas of East Antarctica, Glazovskaya (1958) has found that ferromagnesian minerals show signs of weathering even in relatively fresh rock material. Magnesium ion is released during weathering of such minerals.

Decay of similar minerals in volcanic rocks is likely. Basaltic volcanics are widespread in the region, and are composed primarily of calcic plagioclase (mainly labradorite) and pyroxenes (mainly augite) with phenocrysts of olivine (often abundant), pyroxenes, hornblende, plagioclase and alkali feldspars and other minerals (Haskell et al. 1965; Cole and Ewart 1968; Cole et al. 1971; Kyle 1976). Trachyte occurs in places in McMurdo Sound, and is composed of alkali feldspars, pyroxenes (aegirine-augite), hornblende, plagioclase feldspar, magnetite and accessory minerals (Cole and Ewart 1968; Cole et al. 1971). In these volcanic rocks, the mafic minerals olivine and pyroxenes are probably the main source of magnesium, with hornblende contributing lesser amounts; olivine normally weathers more rapidly than pyroxenes which in turn weather faster than hornblende (Krauskopf 1967; Berner 1971).

Magnesium is produced by chemical weathering in Antarctica probably by two main sets of reactions. One involves oxidation, indicated by the strong orange-brown colour, due to iron oxides, in old dolerite soils. Atmospheric gases including oxygen and carbon dioxide are usually dissolved in natural waters. In antarctic soils these gases are likely to be dissolved in the thin liquid film surrounding soil particles and thus brought into close aqueous contact with the ferromagnesian minerals. In mildly acid conditions at high elevation (6.2.1ii) the reactions describing oxidation of hypersthene and pigeonite can be represented as:

$$\underset{\text{hypersthene}}{n(Mg_{1.4},\ Fe_{0.6})Si_2O_6} \xrightarrow{O_2,\ CO_2,\ H^+} \underset{\text{magnesium ion}}{Mg^{2+}} + \underset{\text{haematite}}{Fe_2O_3} + \underset{\text{bicarbonate ion}}{HCO_3^-} + \text{silicates} \qquad \ldots\ 6.4a$$

$$\text{and} \quad \underset{\text{pigeonite}}{m(Ca_{0.2},\ Mg_{0.9},\ Fe_{0.9})Si_2O_6} \xrightarrow{O_2,\ CO_2,\ H^+} \underset{\text{magnesium ion}}{Mg^{2+}} + \underset{\text{haematite}}{Fe_2O_3} + \underset{\text{calcite}}{CaCO_3} + \text{silicates} \ .\ 6.4b$$

where the ideal compositions are given for examples of the two pyroxenes in dolerites (McKelvey and Webb 1959; Deer *et al.* 1962). It is difficult to write formal, balanced equations for Reactions 6.4 because of (1) uncertain reaction mechanisms(2) uncertainties in the structures of silicate products and (3) the presence of minor amounts of other elements (e.g. aluminium) replacing Si and the metals in the pyroxenes.

In general, however, the weathering of silicate minerals is mainly by hydrolysis (Krauskopf 1967). If olivine is expressed as the end member forsterite, a simplified hydrolysis reaction can be written (Krauskopf 1967) as:

$$\underset{\substack{\text{olivine}\\ \text{(forsterite)}}}{Mg_2SiO_{4(s)}} + 4CO_{2(aq)} + 4H_2O \rightarrow 2Mg^{2+}_{(aq)} + 4HCO^{-}_{3(aq)} + H_4SiO_{4(aq)} \quad \ldots\ 6.5$$

The equilibrium constant for this reaction at +25°C is positive and equal to $10^{2.7}$ (calculated from standard free energy values in Berner 1971), indicating a strong tendency to proceed to the right. Reactions such as 6.5 are likely to be important in volcanic areas near the coast because more moisture is available there than at the small volcanic centres inland in Taylor and Wright Valleys (Fig.2.7).

The magnesium salts have been produced by chemical weathering over the time during which rocks and soil have been exposed. The magnesium gradients inland (Figs.5.5, 5.6) and with increasing elevation (Fig.5.9B) can be mainly attributed to the more common outcroppings of dolerite towards the west and at higher elevations (Fig.1.2). It is expected that magnesium phases will also be found on soils derived from Kirkpatrick Basalt, the extrusive equivalent of Ferrar Dolerite (Table 1.1). The basalt outcrops in the northwest of the region but more extensive outcrops occur to the north and south. The present study did not sample salts on such substrates.

6.3.3 Local accumulation of calcite and gypsum:

Calcite and gypsum show a strong tendency to preferentially accumulate on north-facing slopes and outcrops (Fig.3.4). It has been shown that these are the least mobile of the salt phases studied (Table 4.3), and it is likely that they will accumulate closer to source than the more mobile phases. In some exposed areas strong southerly winds must remove surface salt from south-facing outcrops and slopes but a similar process will operate on other slopes as well. Removal by wind cannot account for preferential subsurface accumulation and therefore wind cannot have produced the tendencies shown in Figure 3.4. It is likely that calcite and gypsum deposits tend to <u>form</u> preferentially on north-facing slopes.

The preferential accumulation of calcium salts is consistent with a greater supply of moisture on such slopes than on slopes of other aspects (2.3.2). Moisture is an important agent of chemical weathering (Krauskopf 1967). Furthermore physical weathering, which creates fresh mineral surfaces, is likely to be more intense on north-facing slopes because of a higher number of freeze-thaw cycles. Temperature itself probably has less direct effect than previously supposed (Tedrow and Ugolini 1966; Tasch and Angino 1968; MacNamara and Usselman 1972) because in general north-facing slopes do not experience significantly warmer maximum temperatures than any others (2.2.1ii). The accumulation tendency for calcite and gypsum is good evidence for calcium ions being released by chemical weathering of rock and soil minerals, for example by reactions such as 6.4b.

Local sources of moisture may assist formation of calcite and gypsum. Plate 3.2 shows a calcite deposit below a ledge in a small bluff at Alligator Peak. The ledge allows snow to accumulate only at this place on the bluff. The thicker accumulation of calcite towards the ledge and the absence of the phase above it indicate that the snow assists salt formation. Moisture released on partial melting of the snow promotes chemical weathering of the bedrock and hence formation and deposition of insoluble calcite.

Calcium phases are widespread, being present on all substrates studied (Fig.5.10A); probably weathering of minerals containing calcium is also widespread. This is consistent with the regional salt gradients for calcium being more poorly defined than those of magnesium (Figs.5.5, 5.9B). Calcium and magnesium ions are significant components of marine and other atmospheric aerosols in Antarctica (Cadle et al. 1968; Boutron 1979), and have similar concentrations in them (Zoller et al. 1978). However, the absence of magnesium on some substrates indicates that aerosols are not a significant source of magnesium in the oasis. Therefore, the widespread distribution of calcium phases is not likely to have been derived from aerosols either.

A small amount of gypsum is derived from lacustrine gypsum of Devonian age in the Beacon Supergroup. Lacustrine gypsum beds, 1 to 3 mm thick, have been noted in the Aztec Siltstone (Table 1.1) at Lashly Mountains (Barrett 1971; McPherson 1978). Gypsum is locally abundant in types 1B and 4 deposits around these beds (localities 142-4, Appendix 1, p.19). The salt appears to be slowly leached from the beds to accumulate in the immediate vicinity. This same process appears to contribute to gypsum in deposits at Table Mountain also (locality 162, Appendix 1, p.22), and presumably in small amounts elsewhere. There is no evidence for other, more soluble salt phases to have formed deposits in this way (Fig.5.10).

6.3.4 Carbonate and bicarbonate phases:

(i) association with carbonate rocks

Carbonate plus bicarbonate phases show two different associations with rock type. Claridge and Campbell (1977), and the data of Nishiyama (1977, 1979) coupled with the present work, show that in places there is an association with carbonate-bearing rocks (5.2.3). Furthermore there appears to be an association between carbonate phases and volcanic substrates (Table 5.11; section 5.3). Generally, however, the most common carbonate, calcite, is widespread but not abundant.

Calcium carbonate (mainly calcite) forms deposits on or beneath the soil, regolith or rocks in many parts of the world. Such deposits have been given many names including calcrete, calcareous duricrusts, calcite veneers, caliche, kunkar and K horizons. The association of such deposits and carbonate-bearing rocks is widely accepted for both hot deserts and arctic regions (Gile 1970; Cooke and Warren 1973; Chapman 1974; Swett 1974). A carbonate source such as limestone or marble is necessary but in some areas a carbonate-rich windblown dust is believed to be the carbonate source. The latter has been proposed by Claridge and Campbell (1977) to account for the abundant calcite veneers at Hut Point Peninsula. Alternating periods of moist and dry conditions are necessary for (1) dissolution or leaching of the carbonate at its source followed by (2) evaporation and precipitation of carbonate. (1) and (2) can be represented by equilibria involving hydrolysis (Krauskopf 1967):

$$\underset{\text{carbonate rock}}{CaCO_3} + H_2O \rightleftharpoons Ca^{2+} + HCO_3^- + OH^- \qquad \ldots 6.6$$

or in mildly acid conditions as:

$$CaCO_3 + H^+ \rightleftharpoons Ca^{2+} + HCO_3^- \qquad \ldots 6.7$$

or:

$$CaCO_3 + H_2O + CO_2 \rightleftharpoons Ca^{2+} + 2HCO_3^- \qquad \ldots 6.8$$

Reaction 6.8 is probably the most important reaction in nature and is usually much more rapid than those involving silicates (Krauskopf 1967; Berner 1971), for example Reactions 6.4 and 6.5.

Carbonate rocks are present in McMurdo oasis. Eastern Taylor Valley, dry valleys near Koettlitz Glacier, Victoria Valley and Wright Lower Valley contain outcrops of Skelton Group metasediments that are rich in marble and extensive in places (Fig.1.2). In Taylor and Wright Valleys these rocks outcrop up to a distance of 30 to 40 km from the coast.

Farther west only minor amounts of carbonate rock material are present regionally, but such material is important locally. Carbonate cement, matrix constituents , nodules (containing more than 85% of fine-grained calcium carbonate), concretions and lenses occur in the Aztec Siltstone (McPherson 1978). Horizons and concretions occur also in the Weller Coal Measures (Pyne 1978; Bradshaw in press). Calcite cement comprising up to 20% of thin section area has been noted in the Weller and Lashly Formations but is absent from most of the Beacon Supergroup (Matz 1968; Pinet 1969). Calcite is present in joints, minor fault zones and veins up to at least 60 mm thick close to or within dolerite sills and dykes (Webb 1963; personal observations).

This distribution of carbonate rocks is consistent with carbonate salt distribution in Taylor Valley and elsewhere, but not in Wright Valley. Carbonate deposits are abundant within about 20 km of the coast in Taylor Valley but are sparse from about 30-40 km inland (Figs.5.1, 5.2, 5.2.1, 5.2.3). In the Koettlitz area and Victoria Valley calcite is also associated with marble (Claridge and Campbell 1977) and bicarbonate and calcium are the dominant ions in fresh Lake Miers (Bell 1967). However, carbonate phases are rare and carbonate in soil salts is negligible in Wright Lower Valley (Appendix 1, pp.24, 25; Bockheim 1979b). It is suggested that this lack is due partly to climatic factors, which exert additional controls on carbonate salt formation. Wright Valley is significantly more arid than Taylor Valley as indicated by the more common presence of suprapermafrost ground water in Taylor Valley (Cartwright et al. 1975; Appendix 3, section 5.2). Taylor Valley and the Koettlitz area are more exposed to moist easterly conditions and snowfall; here alternating moist and dry periods are common in summer. Dry conditions in Wright Valley are likely to inhibit weathering of marbles there (Reactions 6.6 to 6.8).

(ii) calcite in inland areas

The widespread, sparse distribution of calcite in inland areas is probably due to normal weathering processes. Calcite distribution can be described as a low, plateau level in such areas (Figs.5.1, 5.3, 5.9A) which are far from any extensive or significant exposures of carbonate rocks. Atmospheric carbon dioxide dissolved in liquid films promotes reactions similar to 6.4 and 6.5. These can only be very slow, occurring only whenever and wherever moisture conditions are favourable (e.g. Plate 3.2); north-facing slopes are likely to be favoured (2.3.2, 6.3.3). This process is consistent with the macro- and microscopic study of Glazovskaya (1958). She observed calcium carbonate inside and on the surface of silicate minerals and rocks and concluded that it was forming in present-day conditions by 'normal' weathering reactions (Markov et al. 1970, e.g. Reaction 6.4b).

In western areas the minor amounts of carbonate minerals that are present (6.3.4i) probably provide additional local sources of carbonate.

Other considerations do not appear to be necessary to explain this distribution. Swett (1974) and Corbel (in French 1976) suggested that the increased solubility of carbon dioxide at low temperatures (Appendix 5, Table A5.3) may be a partial cause of calcrete crusts in Greenland. However, the pH of dilute solutions in equilibrium with atmospheric CO_2 is 5.6 at both 25° and 0°C (Appendix 5, Table A5.4), and therefore such solutions cannot be more effective agents of chemical weathering in Antarctica than in more temperate areas. Similarly, Smith (1972) showed that dissolution rates of carbonate rocks and minerals are actually slower in high latitudes than in low latitudes. Windblown carbonate dust is not likely to be important inland since the easterly winds are not strong in the west along the fringe of the ice sheet (Appendix 3, sections 4.2, 4.3).

(iii) carbonates on Ross Island and around McMurdo Sound

Normal weathering processes involving dissolved carbon dioxide are probably the source of much of the carbonate in surface or near-surface deposits around McMurdo Sound. The distribution of calcite veneers in McMurdo Sound (Fig.5.11) is not significantly different from that in the inland regions of McMurdo oasis (Fig.5.1 etc., see ii above). Reactions similar to 6.4 and 6.5 are usually important during weathering of igneous rocks (Gorham 1961; Berner 1971; Kozhevnikov 1974) that are the main substrate in this area. Such reactions are likely to be accentuated in moister areas such as eastern Taylor Valley (Appendix 3, section 5.2) and north-facing slopes (2.3.2).

The involvement of aqueous carbon dioxide is consistent with the tendency for carbonates and bicarbonates not always to be associated with calcium ion (Table 5.11, summary in subsection 5.3.3). Northupite, thermonatrite, nesquehonite, and possibly gaylussite are present in places from the surface to 32-70 m in DVDP holes 1-3 (Browne 1973; Morikawa et al. 1977). Browne (1973, 1974) suggested that such near-surface carbonates were formed from evaporated snow via a low temperature brine phase containing atmospheric carbon dioxide dissolved in it. Alternatively, they could have formed after freezing of circulating late-stage hydrothermal fluids having low activity of carbon dioxide.

Other carbonate sources are present around McMurdo Sound that may contribute carbonate to salt deposits in places. Calcium carbonate is a common secondary (e.g. late stage alteration) mineral in volcanic rocks (Palache et al. 1951). Carbonates comprise up to 40% of such surface material (Cole and Ewart 1968; Browne 1973; Luckman 1974; Morikawa et al. 1977).

Fossiliferous marine sediments are a further potential source of carbonates. Two divisions have been formalized, of Pliocene and late Quaternary ages respectively. The older, Scallop Hill Formation contains calcareous marine invertebrates (Speden 1962) and up to 40% aragonite as cement (Eggers 1976). The younger Taylor Formation contains abundant calcareous marine invertebrates (up to 12%, Ward 1979). These sediments have been found up to about 600 m asl and as far as one kilometre inland (Speden 1962). Windblown carbonate dust (Claridge and Campbell 1977) and $CaCO_3$ from the sea ice (6.2.2iii) may be additional sources of carbonate on Ross Island. However, there is little evidence to suggest that any of these three potential sources are in fact significant sources.

6.4 Other Sources of Salt

6.4.1 Biological activity:

Biological activity has an effect on salts in places in the region apart from that concerning sulphate discussed earlier. Phosphate salts, some aragonite and probably monohydrocalcite are formed by biological activity. Bicarbonate and carbonate may be enriched in eastern Taylor Valley as a consequence of biological processes. Generally, however, biological activity is not of regional significance.

Two phosphate salts, calcium phosphate and magnesium hydrogen phosphate, have been mentioned in this thesis (Appendix 1, Table 1). The four documented occurrences are all from penguin or skua rookeries situated on or near outcrops of igneous rock (mainly basaltic volcanics, Table 5.11). Phosphates and uric acid in the guano and other organic material probably cause weathering of mafic minerals in the substrate rock, leading to the formation of phosphate salts of calcium and magnesium. Away from rookeries minor amounts of phosphates may be introduced into the salt systems by skuas and by other organic processes (including human activities, Boyd and Boyd 1963). Weathering of accessory apatites in local igneous rock (Hoehn et al. 1974) is not likely to be a significant source because apatite is probably quite stable (Folk 1968) in antarctic weathering conditions.

Some aragonite is precipitated from lakes after depletion of carbon dioxide by photosynthesis (Hendy et al. 1979). Thinly bedded, fine-grained aragonite 'biscuits' from Taylor Valley have $\delta^{13}C$ values of 0 to +8 per mille, that are consistent with this form of CO_2 depletion. Such by-products of photosynthesis by blue-green algae and bacteria are common elsewhere in the world (Folk 1974) and are forming in Lakes Bonney and Fryxell at present (Hendy et al. 1979; Hendy in Selby 1979).

Other aragonite present on the surface or beneath surface cobbles in the region mainly in Taylor Valley (5.3.2) is nonbiogenic, probably forming in the presence of magnesium, sodium, strontium and other ions. Such ions inhibit the formation of calcite which is the thermodynamically favoured polymorph (Wray and Daniels 1957; Kitano et al. 1962; Rao and Yoganarasimhan 1965; Folk 1974). Large amounts of these inhibiting ions are present in Taylor Valley and associated with the saline discharge (Fig.5.1; Appendix 1, Tables 15 and 22). Loss of carbon dioxide from solutions and rapid evaporation and precipitation probably assist the formation of aragonite rather than calcite (Palache et al. 1951; Kitano et al. 1962; Taft 1969). Dry conditions and low temperatures retard the transformation of metastable aragonite to calcite in the region whereas moist conditions and flushing by fresh water promote it (Wray and Daniels 1957; Taft 1969; Keys 1972; Folk 1974). The morphology of calcium carbonate in DVDP holes (5.3.2) is dictated by similar kinetic factors and also by conditions of pressure and temperature.

Monohydrocalcite is formed probably by biological processes. The phase has been found in one known locality (type 3 deposit) in Antarctica, one kilometre west from the coast and 60 m asl in eastern Taylor Valley (Nishiyama and Kurasawa 1975). Other environmental details are not available. Five other documented natural occurrences of monohydrocalcite from elsewhere in the world have been reviewed by Skinner et al. (1977). All are probably the result of biological activity possibly by specific organisms and/or precise biochemical reactions, involving blue-green algae for example, which is common in eastern Taylor Valley. Low temperatures are likely to stabilize this hydrate once it is formed.

Monohydrocalcite may be an intermediate in the dehydration of hexahydrocalcite to calcite (Palache et al. 1951). Hexahydrocalcite crystallizes out of sea water in small amounts below -2.2°C (Weeks 1962). However, monohydrocalcite would have a more extensive distribution if it was formed in this way in Antarctica because freezing of sea water is common. Hexahydrocalcite has not been reported probably because it readily dehydrates irreversibly above 0°C (Palache et al. 1951; Lippmann 1973).

Biological activity may be the cause of part of the high alkalinity-to-Ca^{2+} ratio in Lake Fryxell (5.2.6) and some of the sodium carbonate-bicarbonate phases in eastern Taylor Valley (5.2.1ii). Microbiological anaerobic reduction of sulphate appears to have been quite widespread in the recent past in eastern Taylor Valley (6.2.2ii). Bicarbonate is usually formed as a by-product of this process as shown in Reaction 6.1 (Berner 1971; Kozhevnikov 1974; Cole 1975). Loss of some carbon dioxide from a reduced sodium sulphate brine either by evaporation or photosynthesis or both would produce sodium carbonate and bicarbonate salts by:

$$2HCO_3^- \rightarrow CO_3^{2-} + CO_2 + H_2O \qquad \ldots 6.9$$

Burkeite could then be formed under specific conditions of concentration, temperature (above about +14°C at equilibrium) and low partial pressures of carbon dioxide (Table 4.7), all of which are reasonable in eastern Taylor Valley. Furthermore there is growing evidence from elsewhere in the world that microorganisms produce soils rich in alkali carbonates (Kutuzova 1973). Such biological activity is more important (Kozhevnikov 1974) elsewhere in the world than the weak tendency for the equilibrium:

$$\underset{\text{calcite, marble}}{CaCO_{3(s)}} + \underset{\text{sulphate brine}}{SO_4^{2-}} + 2H_2O \rightleftharpoons \underset{\text{gypsum}}{CaSO_4.2H_2O_{(s)}} + \underset{\text{carbonate brine}}{CO_3^{2-}} \qquad \ldots 6.10$$

to be displaced towards the right. The equilibrium constant for Reaction 6.10 is small but not particularly so (1.8×10^{-4} at +25°C, calculated from Berner 1971). Reaction 6.10 was proposed by Nishiyama (1979) to account for the abundant sodium carbonate-bicarbonate salts and one occurrence of burkeite in eastern Taylor Valley. If such a reaction was responsible then a considerable amount of gypsum would be present in the area. In fact gypsum is absent at this end of Taylor Valley (Fig.5.1; Nishiyama 1979). Therefore, microbiological activity, not Reaction 6.10, is probably a cause of the abundant soluble carbonates in eastern Taylor Valley. The depletion of sulphate and oxygen in Lake Fryxell, compared to that in sea water, and the large amount of H_2S and NH_4^+ present (Yamagata et al. 1967; Torii et al. 1975) are consistent with a microbiological reduction process causing high alkalinities there.

However, microbiological activity is not of any significance on the broadest scale in the region. The organic component of soils is negligible in most places (Claridge and Campbell 1977). The sparsely distributed lichens do not have large chemical effects on their substrates (Ugolini and Perdue 1968). Biological activity is significant only near the coasts (Glazovskaya 1958) where there is a significant organic component, sufficient moisture or suitable habitats, or combinations of these factors. In Wright Lower Valley biological activity does not appear to have been significant due to a lack of one or more of these factors.

6.4.2 Volcanic and hydrothermal activity:

Alkaline volcanism has been widespread on Ross Island around McMurdo Sound and to a smaller extent in McMurdo oasis during the last 15 million years at least (Kyle 1976; Armstrong 1978). Such activity is normally a source of sulphates and chlorides, and associated hydrothermal activity is a source of carbonates, bicarbonates and silica as well (Krauskopf 1967). However, there is little evidence that volcanogenic anions or cations are widespread. Regional salt distribution has shown that most salt is derived from the sea and by chemical weathering (6.2, 6.3). Early studies of ion ratios and temperature in Lakes Vanda, Bonney and Fryxell suggested that a significant proportion of the salts and the warm lake temperatures (1.2.4) were due to thermal activity (Nichols 1961; Angino et al. 1962, 1964). Subsequent work has shown that the ion ratios have been modified by processes of evolution and that the salts have been derived from the marine source, weathering and leaching (Yamagata et al. 1967; Hendy et al. 1977; Torii et al. 1979; also 6.2.2i, 6.2.4, 6.3.4, 6.4.1). Furthermore, thermal studies have shown that the lakes are heated from above by solar radiation, not from below by high geothermal gradients

(Wilson and Wellman 1962; Shirtcliffe 1964; Hoare et al. 1964, 1965; Wilson et al. 1974; Yusa 1975; Bydder and Holdsworth 1977). Therefore, volcanogenic salts are not quantitatively important in the McMurdo region (also Chapter 7).

Hydrothermal activity has produced some salt in the region. The presence of zeolites and the unusual mineral thaumasite ($CaSiO_3.CaCO_3.CaSO_4.15H_2O$) in DVDP holes on Ross Island indicates that hydrothermal fluids have circulated through the volcanics after they were erupted (Knill 1960; Browne 1973, 1974; Morikawa et al. 1977). A sequence of fluids, progressively cooling and having an increased partial pressure of carbon dioxide, is indicated by the secondary mineral assemblage (Browne 1973, 1974). Browne(1974) also reported siderite, a salt that is formed in reducing conditions and either high partial pressure of CO_2 or low concentrations of $S^{=}$ (Berner 1971). It is not likely to be formed under aerobic surface conditions. This suggests that this and at least some of the other carbonates in these cores were formed from hydrothermal fluids probably towards the end of the sequence of fluid circulation.

Other phases have been formed by hydrothermal processes besides these carbonates. Values of $\delta^{34}S$ and $\delta^{18}O(SO_4)$ for sulphates between 100 m and 200 m depth in DVDP 3 (Fig.6.1) indicate that hydrothermal oxidation of primary sulphide minerals has occurred, consistent with petrological evidence from the volcanics (Nakai 1975; Nakai et al. 1978). Magnesite, found with an unspecified pyroxene mineral at an undocumented site on White Island (Watanuki and Morikawa 1974) was formed possibly by hydrothermal processes. Magnesite is not formed from brines at atmospheric partial pressures of carbon dioxide and earth-surface temperatures (Palache et al. 1951; Lippmann 1973).

However, the presence of magnesite is problematical. The phase has been reported as a type 4 deposit beneath metasedimentary boulders in northern Victoria Land (Dow and Neall 1974). Such a deposit precludes a hydrothermal source here. Generally, the formation of magnesite in earth-surface conditions is not easy to explain (Lippmann 1973). Studies have shown that the thermodynamically favoured reaction

$$Mg^{2+}_{(aq)} + CO_3{}^{2-}_{(aq)} \rightarrow MgCO_{3(s)} \qquad \ldots 6.11$$

(equilibrium constant at 25°C equals $10^{8.1}$) is completely inhibited by kinetic obstacles in earth-surface conditions. The phase may be formed in antarctic conditions by slow conversion of nesquehonite, landsfordite ($MgCO_3.5H_2O$) or hydromagnesite ($Mg(CO_3)_3(OH)_2.3H_2O$), all of which crystallize as metastable phases from low temperature brines (Langmuir 1965; Lippmann 1973). There is evidence that the conversion is accelerated by carbonate ions in a brine in contact with these phases (Lippmann 1973). Nesquehonite has been found in one occurrence in the McMurdo region (in DVDP 3, Morikawa et al. 1977), but the other two phases have not been reported.

Hydrothermal activity has been active beneath the surface in McMurdo oasis. In DVDP hole 6 at Lake Vida, calcite, aragonite, gypsum and zeolites have been produced by hydrothermal activity, some of which was associated with a faulting episode (Watanuki and Morikawa 1974; Morikawa et al. 1977). Zeolites are also present in the bedrock core of DVDP 13 at Don Juan Pond (Nishiyama 1979). Dolomite reported from one locality on Dias is of hydrothermal origin as indicated by stable isotopes ($\delta^{34}S$, $\delta^{13}C$) and association with zeolites (Nakai 1974; Morikawa et al. 1975).

6.5 Salt Mass Balance

6.5.1 Accumulation:

Salts in the McMurdo region have been accumulating for more than four million years. Such long periods of accumulation assist the establishment of salt gradients, although different formation or deposition rates for specific salts or ions may also produce gradients. The present study was not designed to examine the temporal dependence of salt gradients or of salt mass balance in general. These aspects of saline geochemistry in the region are discussed only in general terms here.

Surface rocks and soil in McMurdo oasis have been dated as old as 4.6 ± 0.1 million years (Armstrong 1978; 1.2.4) although the main excavation of the dry valleys occurred long before this time. Comparative soil and glacial studies along the Transantarctic Mountains and in McMurdo oasis have established that the relative ages of surfaces exhibit regional trends as a consequence of this excavation and subsequent glaciations. On a regional basis, the age of surfaces tends to increase from the coast towards the west and towards higher elevations (Denton et al. 1971; Campbell and Claridge 1975). Evidently the salts have been accumulating and migrating for different periods, some for more than four million years.

Numerous studies in McMurdo oasis have shown that the salt content of soils tends to increase with age where leaching is restricted (Ugolini and Bull 1965; Campbell and Claridge 1968, 1969, 1975, 1978; Everett 1971; Behling 1972; Field 1975; Bockheim 1979b). The amount of salt in dry soils ranges from less than 0.1 kg m^{-3} to at least 20 kg m^{-3} with the largest amounts present in the oldest (>> 4 Ma), most arid soils, at high elevations towards the west (Campbell and Claridge 1975, 1978). This relationship indicates that the salts have been accumulating over the last 4 Ma and are not relics of preglacial times.

Salts and ions of direct marine origin are deposited at rates that lessen as distance from the coast increases (5.2.5) counter to the trend in surface age. The deposition rate of chloride decreases from Mirny Station on the coast of East Antarctica towards the interior; the rate is 7×10^{-5} kg m^{-2} a^{-1} 100 km from the coast, decreasing to 3×10^{-5} at 200 km and to 0.2×10^{-5} at 1000 km (Boutron et al. 1972). This decline of chloride inland is consistent with the regional gradient of this ion decreasing inland in McMurdo oasis (Figs.5.3, 5.4). However, in the oasis the deposition rate of chloride probably decreases much faster than inland from Mirny, as very little chloride is found on old, little leached western surfaces (Fig.5.11B; also Claridge and Campbell 1968c, 1977).

6.5.2 Loss:

Salts are lost from soils mainly by leaching. Different salts and ions may be lost at different rates depending on salt mobility, solubility and geographic location. Nitrate appears to be the main ion affected.

Leaching is the major mechanisn of salt loss from soils in the region (Chapter 4). The degree of leaching increases with the amount and availability of moisture, particularly water (4.1.1). Chlorides are the most mobile antarctic salts under average moisture conditions (Table 4.3). However nitrates being the most soluble are susceptible to water action and leaching (3.3.2, 4.2.1, 4.2.4); they accumulate only when leaching is restricted (Claridge and Campbell 1968c).

The amount and availability of moisture vary on a regional basis, generally decreasing from east to west in McMurdo oasis (Fig.2.7). The variation with elevation is more complex (2.3.5); normally moisture availability decreases, but moisture content increases with increasing elevation (Fig.2.7). This complexity has been rationalized into two overlapping and opposite trends with elevation (2.3.5). In years of 'normal' melting the amount of liquid moisture decreases with increasing elevation; in years of extreme melting, perhaps once or twice a decade the amount of water increases with elevation, especially near the coast (Fig.2.7). Leaching, then, may follow certain regional trends for the more mobile ions at least.

The regional distribution of nitrate is influenced by leaching. Nitrate abundance increases inland (Figs.5.3, 5.4; Claridge and Campbell 1977) consistent with decreasing amounts of moisture (Fig.2.7) as well as increasing NO_3/Cl ratios (5.2.5, 6.2.1iii). With increasing elevation nitrate first increases up to 1200-1400 m (Table 5.7), then decreases (Fig.5.9A). This distribution may be explained as a response to changing soil moisture conditions with elevation. At low elevations leaching is relatively common in the warm, moist ambient summer conditions. With an increase in elevation leaching decreases with the accompanying reduction in the number of freeze-thaw cycles (2.3.2). However at the higher elevations extreme melting events periodically flush the soluble nitrates to lower levels, or into the soil.

The elevation below which virtually all nitrate appears to have been leached away varies from place to place in McMurdo oasis. Nitrate is found at lowest elevations (200 m) in Wright Valley, at least as low as 450 m in Pearse Valley but only above 600 m near Lake Bonney (5.2.4). Wright Valley is the most arid of these areas (Appendix 3, section 5.2) whereas Lake Bonney is probably the least arid. Nitrate distribution appears to be an equilibrium between rate of deposition of the ion, and environmental factors governing leaching, mainly soil moisture content. Torii et al. (1975) consider that most nitrate in saline lakes in the oasis is a product of leaching of soil salts.

Less convincing evidence for leaching is displayed by chloride and sodium. The abundances of these ions decrease from low to high elevation (Fig.5.9), but not from east to west (Figs.5.3, 5.5). A similar decline with increasing elevation has been noted for chloride elsewhere in the world and attributed to topographic obstacles that, for example, cause increased precipitation and hence leaching at higher elevations (Gorham 1961). It is not easy here to separate the effects of (1) increased leaching (particularly of the mobile chloride ion) with increasing elevation, from (2) a declining marine influence with increasing distance above the sea. Probably both are important and contribute to the observed distribution.

The distributions of the less mobile anions carbonate and sulphate do not reveal any significant leaching effects. Carbonate exhibits its typical 'plateau' abundance in all three directions (E-W, N-S, low-high). The marked increase of sulphate with elevation (Fig.5.9A) is due to a combination of factors including (1) old surface age, (2) absence of leaching of this anion but significant leaching of nitrate, and (3) relatively slow deposition of chloride. These last 'negative' accumulation tendencies put sulphate accumulation above that of other anions, since the distribution data sum to 100 in Figure 5.9.

Local differences in leaching may indirectly affect regional distribution of salt. These differences are caused by mechanisms that affect the amount of liquid moisture and its movement. Proximity to moisture sources (2.3.1i), aspect (2.3.2), slope, soil texture and periglacial action (2.3.3ii), topography (4.3.2), and former lakes (4.5.1) may all be significant. These combined with regional differences in soil moisture and possible increases in this at low elevations prior to 0.2 Ma BP (2.4.2) create a complex pattern of leaching. This is probably the cause of some of the irregularities in the regional distribution of soluble salts that are evident in places throughout the region (e.g. Fig.5.1 etc.).

Wind has a measurable deflating effect on salt deposits (4.6) and may be a significant mechanism of salt loss. The abundance of surface deposits, particularly dry incoherent efflorescences (2A deposits), wind speed and direction, and the supply of wind transportable material may all influence salt deflation (4.6.2) on a regional scale. The abundance of 2A deposits increases towards the east (Table 3.3). Thenardite is the most common phase in these deposits (Figs.3.2, 3.3) and therefore should be the most affected by wind. Strong west to southwest winds are common in western McMurdo oasis, whereas easterlies predominate and are strongest in the east (Appendix 3, section 4.3). Winds that are strong enough to blow snow and rock particles have speeds of 8-10 m s^{-1} or more; these are mainly westerlies (Appendix 3, Table 11, and sections 4.3, 5.4).

Therefore the distribution of 2A deposits and dominant wind action have potentially opposing effects on salt deflation on a regional scale. Overall the tendency may be for salts, especially thenardite, to be blown towards the centre of the oasis. Such deflation could obscure regional salt gradients to some extent.

Local leaching and deflation effects and local irregularities in salt accumulation indicate that the use of soil salt concentrations for dating purposes (Field 1975; Hendy et al. 1977; Bockheim 1979b) is questionable. There is justification for using these salts for dating only if: (1) the abundance of specific ions can be shown to increase regularly with time (Behling 1972; Behling found that the concentration of K^+ in silt-sized soil particles increased with time); (2) it can be established that no leaching has occurred over the lifetime of the exposed surface (e.g. there should be no evidence of ground water or water movement); (3) extensive sampling and statistical techniques are applied. In general these have not been done in the region.

One example of an irregular relationship between salt accumulation and time has been demonstrated in the present study (Appendix 1, Table 26, p.45). Halite concentrations were measured beneath cobbles on three basaltic cinder cones in Taylor Valley that have been K-Ar dated by Armstrong (1978; and pers. comm.). Flat sites were chosen that had similar soil textures, topography, elevation (1000 m asl) and distance from the coast. No linear relationship with time is evident in the Table. Evidently the concentrations of salt measured here represent net not total accumulation since the times these surfaces were exposed. Probably, sulphate would be a better ion to use for salt dating since it is less mobile than chloride.

6.6 Formation of Salt Phases Present in the Region - a Synthesis

6.6.1 Composition:

There are two main primary physico-chemical influences on the formation of salt phases that occur at or near the surface in the region. These are (1) composition and activity (concentration) of species (including water and carbon dioxide) in parent brines during their deaquation and (2) ambient temperature during deaquation. Dry fallout of salt is of minor importance since most salt deposits are formed from brines. Post-formation conditions that may be important secondary influences include: moisture availability and leaching (4.1.1, 4.2.1-4, 4.5.1, 6.5.2); ambient relative humidity and temperature (4.4.4); and biological activity (6.2.2ii, 6.4.1). These have been discussed in the thesis in the subsections indicated.

The composition and activity of species are regionally dependent on their sources. Salt source has been discussed in sections 6.2 to 6.4. Specific phases form where their component ions are present in sufficient activity to exceed the solubility product of the phases (4.3.1, 4.3.3). Sodium and chloride phases are widespread because the marine source is predominant. These phases become less abundant towards the west because of a decreasing, direct marine influence; halite was found no more than 80 km inland in this study. A less direct marine source is primarily responsible for a widespread distribution of sulphate, iodate and to a lesser extent nitrate phases. Calcium, magnesium and iron phases form as a response to chemical weathering of such ions from rock and soil minerals. Phosphate and hydrogen-phosphate phases form where phosphate ion is locally abundant in or near penguin and skua rookeries. Potassium phases form from combinations of sources of this ion, mainly chemical weathering and to a lesser extent the sea.

The genesis of carbonate phases is more complex (6.3.4). Carbonate in surface deposits is formed during chemical weathering of carbonate and other minerals in local rocks and soils. Atmospheric carbon dioxide appears to be an important source of bicarbonate and carbonate. Some carbonate phases in DVDP holes were formed from hydrothermal solutions.

Localized processes cause additional concentration of species. Evaporation and freeze-concentration are most important (4.4.1). Fractional crystallization, evidence for which is widespread, is probably an important mechanism for concentration of specific ions (4.4.2). Local sources of ions that may be important include hydrothermal or late state alteration, ancient lacustrine gypsum, and biological activity (6.3.3, 6.3.4, 6.4.1, 6.4.2). A greater proportion of rare phases are found relatively close to the coast (Table 5.11) which is probably due to two factors, ion source and fractional crystallization. Significant sources of the ions involved, mainly carbonates, sodium and magnesium, are prominent near the coast. A greater number of fractional crystallization cycles is likely nearer the coast because a larger number of freeze-thaw and wet-dry cycles occurs at low elevation, coastal localities than in high, inland areas.

6.6.2 Ambient temperature:

Temperature influences salt phases forming from deaquating brines. All of the non-hydrothermal phases that have been reported from the surface or near-surface in the McMurdo region can form in present antarctic temperatures. In particular there is no evidence that any salts have formed at temperatures higher than those of the present day. Some phases whose existence in Antarctica is próbable have not been reported.

The temperature-dependent stability of double salts and single salt hydrates has been discussed (Table 4.1, 4.4.3, 4.4.4, 5.3.1ii). Salt phases can only crystallize at equilibrium in specific temperature ranges which are generally lowered by the presence of other ions.

The temperature ranges of formation at equilibrium of antarctic salt phases are shown as horizontal lines in Figure 6.4 (A, B). Two ranges between the extremes -20° and +100°C are shown where known for each phase; the dashed line represents the range in the simplest aqueous system whereas the solid line shows it in the presence of additional ions. Such lines give indications of the temperature limits in nature.

Metastability and other kinetic influences on crystallization are not considered here because these are problems which are difficult to quantify. However most phases in Figure 6.4 are quite soluble and therefore metastability is not likely to influence the temperature ranges in natural (non-laboratory) brines to a great extent. Salts whose phases are known to exhibit considerable metastability, that is form outside their equilibrium temperature ranges (5.3.1, 6.4.1, 6.4.2), are excluded(that is,calcium and magnesium carbonates (apart from monohydrocalite) and calcium sulphate).

Some other antarctic phases are omitted from the treatment and certain unreported phases are considered. Phases omitted are: the iodate salt(s) (uncertain composition(s)); northupite (lack of data); siderite, dolomite (hydrothermal phases) and volcanogenic salts from Erebus. Calcium phosphate is not shown in Figure 6.4 but forms over a wide range of temperatures (Weast 1971). Figure 6.4B, C shows certain phases that have not been reported, such as additional hydrates of known phases, some of which are possible in Antarctica on the basis of their temperature ranges and composition. A wide variety of phases that contain potassium fall into this latter category (Palache et al. 1951) but have not been considered here because potassium phases are not common in the McMurdo region.

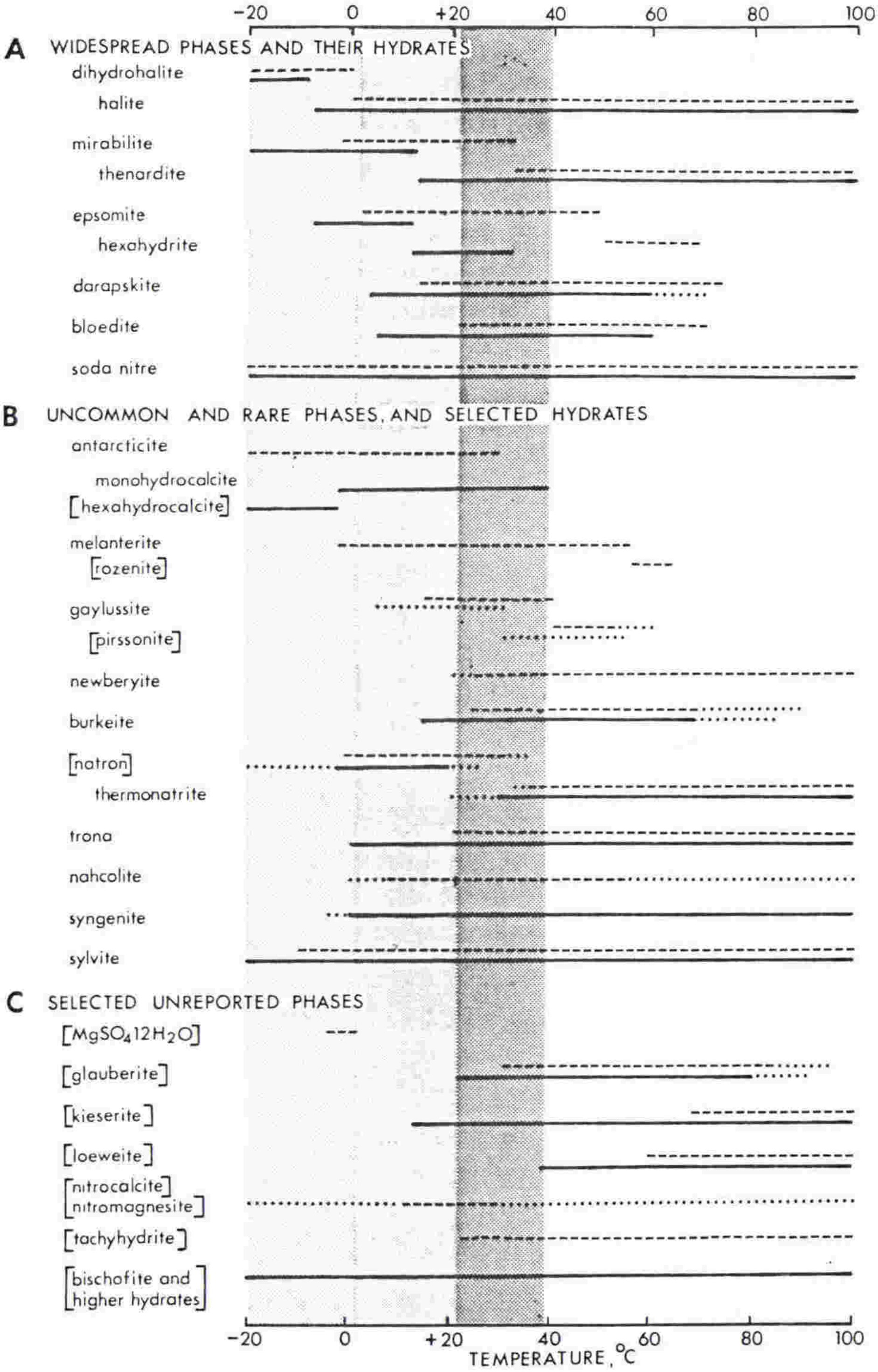


Figure 6.4

Temperature ranges of formation of salt phases under equilibrium conditions between -20 and +100°C. Dashed lines represent range in simplest aqueous systems; solid lines in presence of additional ions usually involving NaCl; dotted lines show uncertainties in the literature mainly due to gaps of knowledge. Dark vertical band between +22 and +39°C represents maximum surface temperature (+30 ± 10°C) in McMurdo oasis; lighter band between +2 and +22 represents maximum temperature at 0.1 m depth in soil (+12 ± 10°C, from Table 2.5). Phases in parentheses have not been reported from the McMurdo region. Data from Hill and Wills (1938), Glasstone (1940), Phillips (1947), Pel'sh (1949), Palache et al. (1951), Deer et al. (1962), Weeks (1962), Stewart (1963), Eugster and Smith (1965), Young (1967), Block et al. (1968), Lippmann (1973), Skinner et al. (1977) and Table 4.7.

All the antarctic phases considered can form in present antarctic temperatures. Dark and lighter vertical bands on Figure 6.4 show the maximum surface and 0.1 m soil temperatures in McMurdo oasis (Table 2.5). The warmer range represents the maximum temperature of formation of phases in surface deposits whereas the cooler range represents an approximate maximum for phases forming beneath surface cobbles (see also 4.4.4). All antarctic phases can form in surface deposits within the temperature constraints defined on Figure 6.4. Thermonatrite forms probably near its lower limit beneath surface cobbles; both it and hexahydrite crystallize probably often in the presence of foreign ions or by dehydration of higher hydrates in subsurface deposits. This is consistent with epsomite being associated with all hexahydrite occurrences noted in Appendix 1.

The complex bicarbonate-carbonate-sulphate assemblage, present at locality 299, on Stadium Cone Mt. Discovery area (samples 24814-5, Appendix 1, p.29) can be rationalized from known phase relations. The activity of species (including carbon dioxide and water)as well as temperature dictate phase relations in aqueous carbonate-bicarbonate systems. Several possibilities exist for the formation of the former deposit (24814). Trona, burkeite, mirabilite and natron could have formed in near-equilibrium conditions in the presence of NaCl, at a temperature of between +14 and 24°C (Eugster and Smith 1965, Fig.6.4). Thermonatrite and thenardite would have formed by subsequent dehydration; at the time of sampling a small amount of a translucent phase probably mirabilite and/or natron was present. Other deposition sequences that are possible involve progressive cooling and/or evaporation, precipitating thermonatrite, burkeite, trona, mirabilite and halite in series (Eugster and Smith 1965). The adjacent deposit (24815) containing trona and thenardite is consistent with a similar brine having a higher salinity and activity of carbon dioxide and/or temperature than the former (Eugster and Smith 1965). The deposits are consistent with a low salinity brine having a low activity of carbon dioxide, in equilibrium with atmospheric CO_2, moving slowly downslope and deaquating.

There is no evidence that any salt phases in the region were formed at temperatures warmer than present day. Relic salts from former warmer, possibly interglacial times, would have the highest chance of being preserved 'intact' in western areas at high elevation, which have been subject to very little water action. There are large amounts of soluble salts present in 2A and 4 type deposits there (6.5.2), the predominant ions being sulphates, calcium, sodium, and magnesium (Figs.5.2, 5.4, 5.9). Therefore 'relic' salts should contain these ions. Three such phases that are possible on compositional grounds alone are glauberite ($Na_2Ca(SO_4)_2$), kieserite ($MgSO_4.H_2O$) and loeweite ($Na_4Mg_2(SO_4)_4.5H_2O$) (from the listing of sulphate phases in Palache et al. 1951). A fourth, vanthoffite, is only found in oceanic evaporite deposits and is not considered here. Kieserite and to a lesser extent loeweite alter to epsomite in moist air (Palache et al. 1951); possibly these phases would not survive more than four million years of antarctic conditions with occasional moistening from summer snowfalls. However if temperatures had been significantly warmer than present day when the salts were formed, then a limited distribution of glauberite at least and possibly loeweite might be expected (Fig.6.4C). In dry conditions such salts can exist metastably for an indefinite period (Palache et al. 1951). Absence of such phases is further evidence for salt formation under present antarctic conditions.

Phases not yet reported probably exist in the antarctic salt system (Figs.6.4B, C). Hexahydrocalcite, natron and $MgSO_4.12H_2O$ are most likely. The carbonates are possibly present in eastern Taylor Valley at least, whereas the magnesium sulphate phase probably exists towards the west such as in the Labyrinth area. Precautions against sample warming and dehydration will need to be taken by workers sampling for these phases. Nitrate and chloride phases of calcium and magnesium are possibly present in some dry soils. Certainly there are no temperature constraints affecting their crystallization.

CHAPTER 7 THE SALTS IN THE SUMMIT AREA OF EREBUS VOLCANO

7.1 Introduction

7.1.1 Outline:

This chapter examines the accumulation patterns, composition and formation of salts on Erebus Volcano. Several patterns of accumulation are evident in the summit area, and are explained in terms of age of the locality and supply of volcanic emanations to the locality. The explanation requires a knowledge of the recent volcanic history of the volcano and the wind regime in the summit area. In particular the determination of recent volcanic history allows the assessment of rates of salt accumulation in the area.

7.1.2 Description of the summit area:

Mt Erebus (3794 m) is an active, alkaline volcano. It is a composite volcanic edifice, composed mainly of anorthoclase phonolite (kenyte) (a rock containing characteristic, lozenge-shaped anorthoclase feldspar phenocrysts). The summit area, composed entirely of anorthoclase phonolite, is defined by a four kilometre wide infilled caldera with a mostly even rim at about 3200 m (Fig. 7.1). Above this rim the gently sloping summit plateau rises towards the base of the active cone at about 3500 m. The active cone contains Main*, Inner* and Side* Craters (Fig. 7.2) and is built up of flows with minor interbedded pyroclastics (Kyle 1976). Present day volcanic activity is focused inside Inner Crater.

Main Crater is slightly elliptical; its maximum diameter is about 600 m and its minimum about 500 m. Its rim is relatively even, varying between about 3730 and 3794 m. The floor of Main Crater lies about 150 m below the summit and has been interpreted as the surface of a frozen lava lake (Beck 1965). A semicircular fault scarp, up to 8 m high, dissects part of the floor (Fig. 7.3) and is possibly due both to withdrawal of the magma column feeding the lake (Beck 1965) and to volume change on crystallization.

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*Names approved by N.Z. Geographic Board

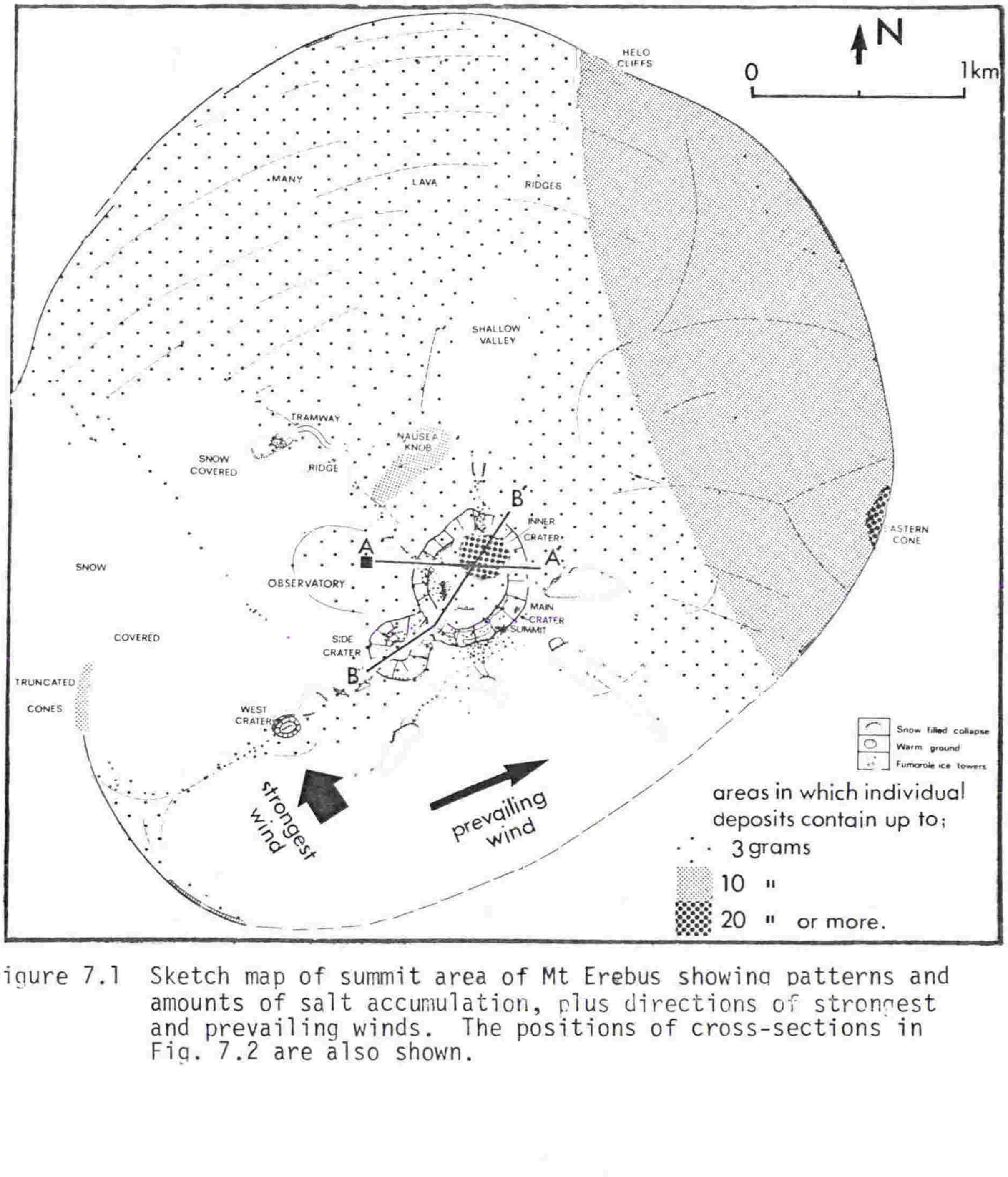

Figure 7.1 Sketch map of summit area of Mt Erebus showing patterns and amounts of salt accumulation, plus directions of strongest and prevailing winds. The positions of cross-sections in Fig. 7.2 are also shown.

Further collapse has led to the formation of cylindrical Inner Crater 200 m wide and 100 m deep in the northeastern sector of Main Crater. This crater is presently divided into two distinct parts by an east-west trending ridge partially covered with spatter. The northern half contains a convecting magma (lava) lake (Plate 7.1) currently roughly elliptical, about 3500±500 m^2 in area. The southern half contains several high pressure and temperature fumaroles some surrounded by volcanogenic sublimates, and a roughly circular vent 20-30 m in diameter, known as 'active vent'. Explosive strombolian eruptions from this vent occasionally eject molten lava to

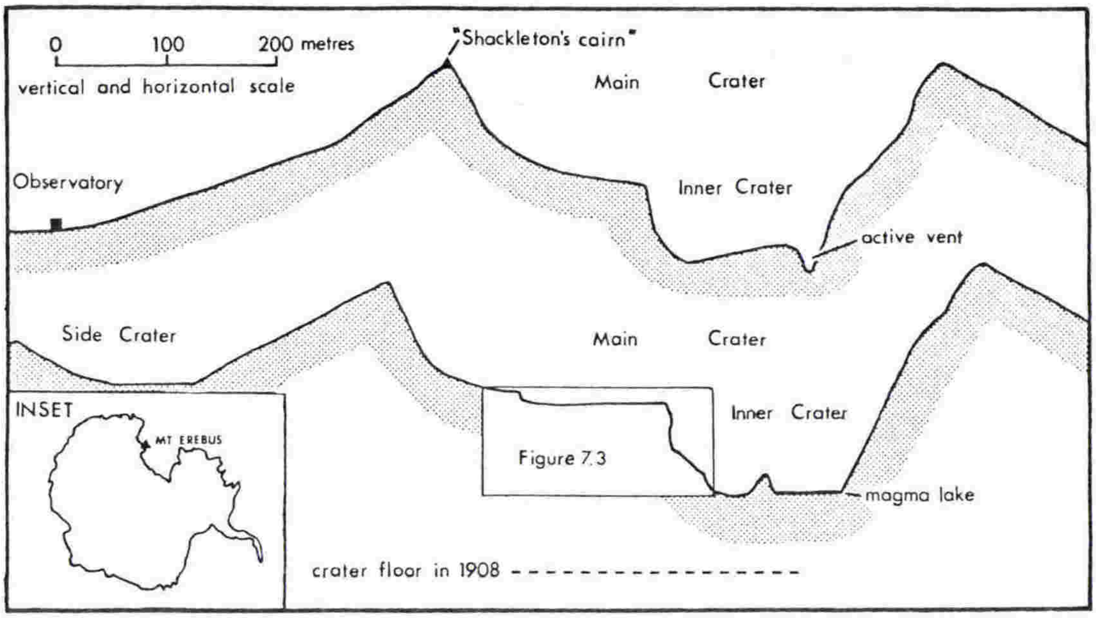

Figure 7.2 Cross-sections of Main Crater between Observatory and active vent, and between Side Crater and magma lake (drawn from preliminary NZ Lands and Survey map).

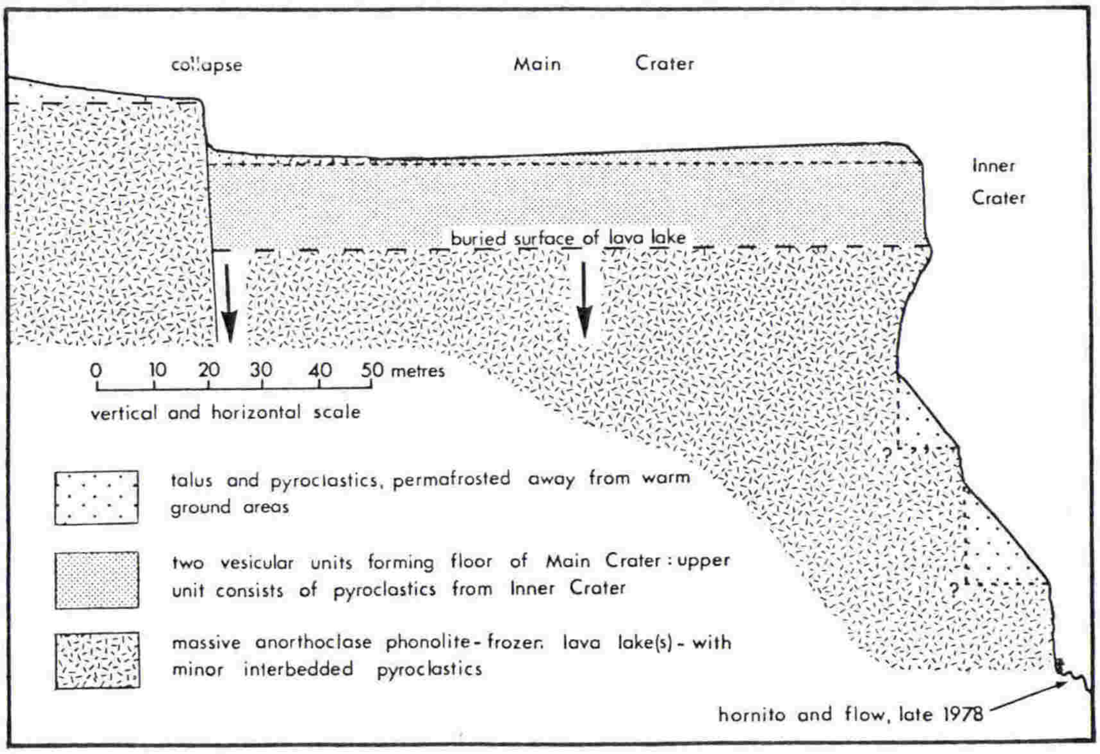

Figure 7.3 Stratigraphy of Inner Crater wall.

heights of 300 m and more. The floor of Main Crater is covered with a veneer of pyroclastic material, mainly volcanic bombs with intermingled ash and snow.

7.1.3 Sources of volcanic emanations:

The greatest volume of volcanic gas from the volcano is produced at present by the degassing magma lake. Most of the time this degassing is quiet, being a result of slow convection of the lava (Plate 7.1). Periodically the convection is more violent, when puffs of gas are released from discrete bubbles that burst through the lake surface. More violent activity is infrequent. Thus the bulk of the magmatic gas from the volcano is mixed non-violently with air, to produce what can be defined as volcanic gas.

Observations on clear days indicate that the volcanic gas becomes visible as a thin blue fume cloud within about 2-5 m of the lake surface (Plate 7.1). This means that cooling and gas particle growth have proceeded sufficiently for particulates to be large enough (0.1 μ) to scatter blue light (Naughton et al. 1974; Harvey 1976). Further cooling usually leads to the formation of copious white plume clouds within 10-20 m above the lake.

The output of volcanic gas from Erebus can be estimated. The plume cloud rises at a speed of around 2 m s^{-1}; individual puffs of cloud take 100 seconds (Polian and Lambert 1979) to travel from the lake to Main Crater rim, a distance of about 200 m (Fig. 7.2). The total output of volcanic gas can be estimated assuming that (1) all gas comes from the magma lake and (2) this is degassing evenly at 2 m s^{-1} over its entire 3500 m^2 surface. Total output is 7000 m^3 s^{-1} or 2 x 10^{11} m^3 a^{-1}. In fact, the flow rate of visible white plume is much greater than 2 x 10^{11} m^3 a^{-1} as it leaves Main Crater. Normally the plume is at least as wide as Inner Crater (200 m). In these conditions the flow rate is about 6 x 10^4 m^3 s^{-1} or 2 x 10^{12} m^3 a^{-1}. The plume usually acquires a horizontal drift within 300 m or so above the summit. However on windy days the plume does not rise more than 50 m or so above the rim and may remain in contact with the ground for at least a kilometre. In the latter conditions the plume is initially the width of Main Crater (500-600 m) because that is

Plate 7.1 The magma lake (c. 50 m wide) in the northern half of Inner Crater, viewed from 'Shackleton's Cairn' (December 1979). Volcanic fume can be seen rising above the slowly convecting lake. A young (< 1 year old) fumarole with an incandescent interior and ringed by white volcanogenic salt (sublimate) is present a few metres from the lake shore (arrow).

Plate 7.2 Steam fumarole (+80°C) with a 100 gram deposit of volcanogenic salt (centre, sample 24886) at the base of the inside wall of Main Crater (locality 331, 21/12/74)

filled with steam. During southeasterly blizzards at the summit, the wind speed is up to 33 m s^{-1} at the Observatory (Appendix 3, Table 12). Therefore, in such conditions the output of diluted volcanic gas is about 9×10^5 m^3 s^{-1} at Main Crater rim.

The plume is quite different in calm or light winds from the southwesterly quarter with low atmospheric relative humidities. On such days the plume is thin and wispy, and almost invisible or blue-grey in colour. In these conditions the main particulates in the plume are NaCl and KCl (Polian and Lambert 1979); particle size is about 0.1 to 10 μ (Cadle and Frank 1968; McClain et al. 1968; Cadle et al. 1969). The plume rises vertically from the magma lake (often without touching the walls of the craters), and in calm conditions may ascend to an altitude of 5000 m or more. In light winds the plume acquires a horizontal drift and may stretch for more than 100 km. The average environmental lapse rate at around 4000 m is 4 to 5°C per 1000 m (Appendix 3, Table 7, p.20) which is significantly less than the saturated adiabatic lapse rate of about 9°C per 1000 m (Harvey 1976) in antarctic conditions. Therefore, the air at the elevation of Erebus is often absolutely stable and in these conditions little mixing and relatively little dilution of the plume will occur.

Other sources of volcanic emanations are: the high pressure and high temperature gas fumaroles inside the southern half of Inner Crater; strong steam fumaroles around the walls (Plate 7.2) inside Main and Side Craters; and weaker steam fumaroles and warm ground inside and outside Main Crater (Fig. 7.1). These latter two sources, often associated with chimney-like ice towers or pinnacles or low roofs of ice, emit mainly water vapour (temperature less than +65°C), probably derived from local snow melt (Lyon and Giggenbach 1974). The stronger steam fumaroles contain significant amounts of acid gas; that shown in Plate 7.2 contains about 3 percent carbon dioxide indicating a direct contribution from outgassing magma (Lyon and Giggenbach 1974). The temperature (+80°C) of this fumarole, the warmest outside Inner Crater, is a few degrees below the boiling point at this elevation (Table 7.1). The gas fumaroles inside Inner Crater have high but probably variable temperatures. Strong incandescence was visible inside two fumaroles in December 1974, indicating temperatures in excess of 700°C. No incandescence was present

Table 7.1 Temperature of the strongest fumarole in Main Crater and the boiling point of water at this elevation (3680 m).

Fumarole temperature (°C) and date of measurement[1]		Extremes of atmospheric pressure[2] during the period 22/12/78 to 1/1/79		Boiling point of water[3] (°C)
		(mb)	(Pa)	
80.5±0.2	(2/1/72)[4]	606.4	6.06×10^4	86.2
79.6±0.2	(21/12/74)	622.0	6.22×10^4	86.9

[1] measured with mercury thermometer with bulb 0.2 m inside fumarole

[2] measured using a standard barometer, corrected for temperature at the Erebus Observatory, elevation 3600 m

[3] from Weast (1971)

[4] measured by W.F. Giggenbach (Chemistry Division, DSIR)

in these same two fumaroles in December 1978. Temperatures of some of the fumaroles inside Inner Crater are probably similar to that of the lava lake, which is close to 1000°C (Keys 1977); temperatures may be considerably higher than 1000°C at depth. Away from source the temperature of volcanic vapours cools rapidly to ambient temperature, generally colder than -15°C. (The mean annual air temperature in the summit area is about -35°C, Appendix 3, Table 9).

Intermittent observations of the plume and red glows at the summit suggest that the volcano has probably been continuously active since at least 1841. This observation record, mainly from sea level, is detailed in Kyle et al. (in press). Since 1841 at least, the main activity has been confined to inside Main Crater. There is strong evidence (7.3.1) that Inner Crater was formed less than 80 years ago. Therefore, on a longer-term basis than 80 years, the main source of volcanic gas should be considered as being Main Crater, not specifically Inner Crater.

In the present study, it is assumed that the chemistry of magmatic gas from Erebus Volcano has remained unchanged for at least 0.7 Ma. The whole rock compositions of very recent (1972, 1974) ejecta from Inner Crater and recent flows from the active cone, are similar to older (at least 0.7 Ma) anorthoclase phonolite flows exposed at the base of Erebus

(Kyle 1977). This suggests that the overall chemistry of Mt Erebus has remained unchanged for this time.

7.2 The Volcanogenic Salts

7.2.1 Accumulation:

The salts form two distinctive asymmetrical accumulation patterns about Main Crater (Fig. 7.1). One pattern consists of an increase in accumulation away from Main Crater towards the northeasterly quarter, with a maximum on the plateau rim at Eastern Cone. The other pattern consists of a maximum accumulation at Nausea Knob, in all the areas at a radius of about 500 m from Inner Crater.

These patterns have been recognised by semiquantitatively estimating the amount of salt in discrete deposits. Outside Main Crater, soluble salts accumulate in discrete deposits mainly under rocks and blocks of frozen lava (Plate 7.3), as white to yellow encrustations, massive deposits, efflorescences and needles. Salts also accumulate in joints and on rock surfaces and soils that are subject to periodic moisture from melting snow in summer (Plate 7.4). The morphology of these deposits is very similar to those in other parts of the McMurdo region. Most of the deposits are well removed, some by as much as 500 m, from any present day fumarolic activity associated with ice towers or warm ground. No fumaroles outside Main and Side Craters are known to have any salt encrustations around them. However, some insoluble salt phases such as calcite, accumulate at or near the surface in some warm ground areas (Plate 7.5). The mass of salt in a discrete deposit was estimated from the measured and estimated volume of the deposit,multiplied by density. The latter ranged from 0.4 to 0.95 g cm^{-3} for five samples; a density of 1 g cm^{-3} was used to give an estimate of maximum amount. Estimations of volume and subsequently mass , made during numerous traverses over the summit area (Appendix 1, Fig. 5) have established the general patterns of salt accumulation. These patterns are summarised in Fig. 7.1.

Outside Main Crater the greater amounts of salt in discrete deposits are found in places along the outer rim of the summit plateau. The greatest single accumulations found to date are about 20 g or so in the vicinity of Eastern Cone (Fig. 7.1). Elsewhere on the outer rim deposits containing up to 10 g or so have been found at Helo Cliffs and Truncated Cones.

Plate 7.3 Yellow volcanogenic salt (sample 24880) under and around cobbles at the base of large blocks of lava on the southeastern (crater-facing) side of Nausea Knob (locality 342, 28/12/74)

Plate 7.4 Yellow salt (type 2A deposit) between a melting snowdrift and a volcanic bomb (mostly buried) on the north side of the active cone. Ice axe points down slope (locality 353, 28/12/74).

Plate 7.5 Calcite deposit (sample 24877, left and right of geological hammer) near the surface of warm ground (+50°C) in Side Crater (locality 338, 31/12/74)

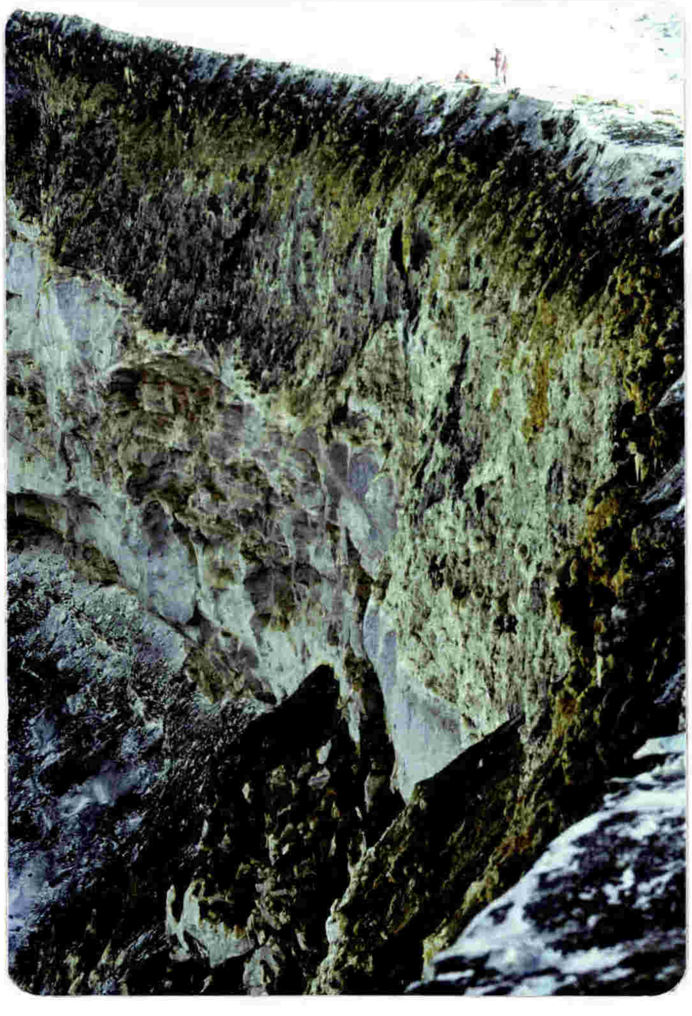

Plate 7.6

The wall of Inner Crater showing bright yellow salt on rock surfaces a few metres below the crater rim. Sample 24885 (locality 330) was taken from this zone of salt accumulation. A yellow surface encrustation can also be seen on flat, boulder-like bombs around the three figures. The thick band of grey rock in the crater wall is massive anorthoclase phonolite (23/12/78).

Outside this rim the deposits decrease in size, until at Fang Peak, 4 km from and 1000 m lower than Main Crater, accumulations are less than a gram. Accumulations generally decrease from the plateau rim towards the active cone. Deposits up to 3 g or so may be found in snow-free terrain on the plateau except to the south and southeast of the active cone. Here, deposits containing less than a gram or so may be found with difficulty. However, deposits up to about 10 g exist around Nausea Knob at a distance of about 500 m northwest of Inner Crater (Fig. 7.1, Plate 7.3). Accumulations are much less in other areas at a 500 m radius from Inner Crater. Very little salt is found at this radius to the south and southeast: snow-free ground is not uncommon there, and therefore this lack of salt is not due solely to the presence of a partial snow cover, as it is in areas to the north (Shallow Valley), west and southwest of the active cone (Fig. 7.1).

Inside Main Crater, a concentric pattern of salt accumulation appears to exist about Inner Crater and the gas sources within it. Strong yellow salt encrustations develop on the surface of bombs on Main Crater floor. This encrustation is thickest (1-5 mm containing up to about 3 g) on average near the rim of Inner Crater. Two to 10 m below that rim on a pyroclastic unit (7.3.1) exposed at the top of Inner Crater wall (Fig. 7.3, Plate 7.6) accumulations of crystalline and massive yellow salt (sample no. 24885) are 20-30 mm thick in places. Deposits contain 100 g or so. Melting snow appears to assist accumulation periodically, and cause local migration of some of this material (7.2.4). On the floor of Inner Crater, sublimates and other salts have accumulated around the orifices of the high temperature fumaroles in both halves of the Crater (Plate 7.1). Some of these deposits probably exceed 1000 g but none have been sampled to date. Strong steam fumaroles near the walls inside Main and Side Craters may also have salt accumulations around them. That fumarole shown in Plate 7.2 has the greatest accumulation known (about 100 g) on any of these steam fumaroles; this unrepresentative deposit is not shown in Fig. 7.1.

7.2.2 Composition:

The salts in Erebus summit area are mixed aluminium, sodium, magnesium, iron, potassium, calcium, chlorides, sulphates and fluorides: silicon is also present and exists in probably both cationic and anionic states (Appendix 1, Tables 7.6, 23-25, pp. 31, 32, 44, 45). This composition and the existence of these salts on an active volcano indicate that the salts are derived from some manifestation of volcanic activity; they can be classed as volcanogenic salts.

The composition of Erebus salts is different from other salts studied in the McMurdo region. There is no evidence for significant amounts of aluminium, silicon or fluorine in pure salt phases elsewhere in the region; iron is known to be present in trace amounts in some macroscopically pure salts from the saline discharge at Taylor Glacier (Chapter 8). Table 7.2 compares Al, Si, Fe and F concentrations in three Erebus salts (samples 24880, 24885, 24886) with those in one salt deposit from Pearse Valley (deaquation deposit, sample 24848). The Erebus salts were free of rock fragments, but sand comprised about 10 percent (by volume) of the sample from the oasis. The trace amounts of Al, Si and Fe in the oasis salt can be attributed to this contamination. Elsewhere in McMurdo oasis, minerals containing Al, Si, Fe and F may be present as trace accessories in some salt deposits (Torii et al. 1966). However, the Erebus salts contain significant proportions of aluminium phases plus phases that may contain silicon, fluorine and minor iron.

Many different crystalline salt phases are present in the salt deposits of the summit area. Table 7.3 lists phases that have been positively or tentatively identified by X-ray diffraction (summarised from Appendix 1, Table 7.6, pp 31,32). Positive identification of most phases by XRD is complicated by peak overlap, deliquescence and dehydration and probably by mutual substitution of ions.

Most of the salt phases that are present or possibly present on Erebus are known to exist in volcanic areas elsewhere in the world. Several of the positively identified phases in Table 7.3 are common in the McMurdo region. However, sylvite is not widespread and alunite is not present away from Erebus (5.3.2). None of the tentatively identified phases in Table 7.3 is present outside Erebus. Two of these phases, chloraluminate and malladrite appear to exist only in volcanic areas (Palache et al. 1951). In fact,all of the phases listed in Table 7.3, with the exception of AlF_3 and $NaAl_4O_4Cl_5$, are known to exist on active volcanoes elsewhere in the world (Palache et al. 1951; Stoiber and Rose 1974). The two exceptions have not previously been described as minerals (Rose, pers. comm.).

Table 7.2 Concentrations (weight percent) of aluminium, iron, fluorine and silicon in Erebus salts and salt from Pearse Valley, McMurdo oasis (analyst W. Zoller, University of Maryland, USA).

	Salt sample			
	Erebus			Pearse Valley
Element	24880	24885	24886	24848
Al	10.4	8.8	12.2	1.9
Si	2.0	10.8	1.7	2.7
Fe	1.9	2.5	0.27	0.56
F	<1	4.8	1.1	<1

Table 7.3 Positively and tentatively identified crystalline salt phases from the summit area of Mt Erebus.

Positively identified	Tentatively identified	
halite	chloraluminate	$AlCl_3.6H_2O$
gypsum	alunogen	$Al_2(SO_4)_3.18H_2O$
alunite	jarosite	$(K,Na)(Fe,Al)(SO_4)_2(OH)_6$
thenardite	malladrite	Na_2SiF_6
sylvite	sulphohalite	$Na_6ClF(SO_4)_2$
mirabilite	aluminium trifluoride	AlF_3
calcite	sodium aluminium oxychloride*	$NaAl_4O_4Cl_5$
	hydromolysite*	$FeCl_3.6H_2O$
	ralstonite*	$NaMgAl(F,OH).H_2O$

*tentatively identified by W. Rose (Michigan Technological University, pers. comm.), who also tentatively identified AlF_3.

The three Erebus salt deposits analysed for major elements (Appendix 1, Table 23) contain mixtures of phases, some of which are unusual. Sample 24880 contains halite and probably a basic chloride or oxychloride; 24885 contains mainly aluminium and silicon halides or oxyhalides; the major component of 24886 is probably a hydrated basic aluminium sulphate similar to aluminate, $Al_2(SO_4)(OH)_4 7H_2O$.

Several volcanogenic salts macroscopically similar to those on Erebus were sampled on White Island and Ngauruhoe Volcanoes in New Zealand during 1978, in a largely unsuccessful attempt to further characterize the Erebus salts. Minerals characterized included halotrichite, $FeAl_2(SO_4)_2.22H_2O$ (apparently absent on Erebus), alunite, gypsum, jarosite, alunogen and sulphur. The apparent lack of halide salts on these temperate volcanoes is a significant difference from the Erebus case. Very little elemental sulphur is present in the Erebus deposits despite their often bright yellow colour (Plates 7.3, 7.4, 7.6). This colouration is due to salts of iron, aluminium and other metals, and is a striking difference from other salts in the McMurdo region.

Elemental and ionic ratios of Erebus salts were evaluated for two reasons. Firstly they were used to determine whether similarities exist between the ratios for the different salts. If similarities exist then the different salts may have formed by similar processes. Rare-earth elements are best for this type of comparison; their chemical properties are so similar that significant fractionation between them may be achieved only during markedly different types of chemical reaction. Secondly, the ratios for Erebus salts were compared with similar literature data for condensates, sublimates, fume and plume from other volcanoes, and for local anorthoclase phonolite rock samples from Erebus itself; this type of comparison may allow elucidation of specific processes of salt formation, of which a number are possible (7.2.3). Both sets of comparisons cannot be taken too far for several reasons: (1) volcanogenic salts normally exhibit highly variable mineralogy (Stoiber and Rose 1974) probably due the different formation processes and fractionation between many different elements and ions prior to, during, and after formation; (2) a limited number of Erebus salts have been fully analysed; (3) Erebus gas, probably a major contributor or source of the Erebus salts is as yet unsampled; and (4) salts, fume and plume at Erebus Volcano may exhibit chemical differences from those at other volcanoes.

Trace and rare-earth element ratios for the four Erebus salts fall into at least two groups (Table 7.4). The two bright yellow salts have

Table 7.4 Trace and Rare-Earth element ratios of volcanogenic salts and rock from Erebus (data from Appendix 1, Tables 24 and 25).

Sample	Rb/Sr	Sr/Y	Y/Zr	Rb/Nb	Sm/Gd	Sm/Yb	Sm/Lu
24880[1]	0.48	6.1	0.040	0.44	1.31	3.34	36.8
24885[2]	0.25	6.4	0.041	0.54	1.39	3.47	8.0
24886[3]	-	-	-	-	1.21	0.061	0.29
24884[4]	0.38	20	0.011	2.1	-	-	-
25725[5]	0.11	10	0.08	0.24	1.40	2.8	-

[1] bright yellow salt from Nausea Knob, locality 342 (Plate 7.3)

[2] bright yellow salt from Inner Crater rim, locality 330 (Plate 7.6)

[3] white salt from around steam fumarole in Main Crater, locality 331 (Plate 7.2)

[4] light yellow salt from Eastern Cone, locality 346

[5] anorthoclase phonolite sample from Erebus summit area (Kyle and Rankin 1976)

similar ratios to each other suggesting that these similar coloured salts at localities zero and 500 m respectively from Inner Crater were formed by similar processes. However, these yellow salts have very different ratios from the white and light yellow salts, suggesting that the latter two salts were formed by different processes.

These differences are consistent with the varying localities of the various salt deposits. The white salt (24886) has accumulated around a steam fumarole (Plate 7.2) which most likely plays an important role in that salt's formation. The light yellow salt (24884) from Eastern Cone is about 2 km from any significant source of volcanic gas. Both of these salts are dissimilar to the bright yellow salts which are adjacent to (24885) or frequently immediately downwind of (24880) the main source of volcanic gas, presently in Inner Crater.

Major element and ion ratios for three of the salts produce groupings that are not always consistent with the ratios discussed above. The two yellow salts have similar Cl/SO_4 ratios but other ratios are dissimilar (Table 7.5). Conversely, two salts which are formed probably in different ways (24885 and 24886) have similar Cl/F and Na/K ratios; the Cl/SO_4 and Ca/Mg ratios of these same two salts are different.

Most ratios for the salts are different from those for local rock. Of the rare-earth elements, only the Sm/Gd ratio for the salt on Inner Crater rim shows a close similarity to that for the rock (Table 7.4). The salt involved (24885) also has the highest Si content (10.8%) of the three analysed (Table 7.2). This possible correlation is not unexpected since rare-earths are generally concentrated in or with phases containing silicon (Krauskopf 1967).

All trace element ratios in the salts are different from in Erebus rock. Rb appears to be consistently enriched relative to Sr and Nb in the three salts, whereas Y is consistently depleted relative to Zr (Table 7.4). Of the major element ratios the Na/K ratio is the only one in which the rock is similar to two of the salts (Table 7.5). Generally there are no consistent similarities between Erebus salt and Erebus rock such as might be expected if the rock played a major role in salt formation.

Anion ratios in the two bright yellow Erebus salts illustrate consistent similarities to condensates and sublimates from volcanoes elsewhere in the world (Table 7.5). Chlorides predominate in such minerals; sulphate is present in minor concentrations despite its predominance in some oxidised plume and fume samples. The chloride predominance in Erebus plume in certain conditions (Polian and Lambert 1979) has been noted earlier (7.1.3). The high concentration of sulphate in the salt around the steam fumarole emphasises the difference between this salt and the two bright yellow salts. The Cl/F ratio in all three Erebus salts is also consistent with the "average condensate" of Stoiber and Rose (1974).

Metal ion ratios are variable in volcanogenic salts, fume and plume (Table 7.5). Na concentrations invariably exceed those of K, and in this the Erebus salts are no different. However, Ca/Mg ratios exhibit a range of values; no pattern is apparent in Table 7.5.

7.2.3 Formation:

The previous subsection verified that Erebus salts are volcanogenic. The two bright yellow salts, appear to have been formed by similar processes: these salts may have formed fairly directly from volcanic gas as they exhibit

Table 7.5 Elemental and ionic ratios of volcanogenic salts and rock from Erebus, and fresh volcanic salts, fume and plume from Hawaiian and Central American volcanoes (data for Erebus salts from Appendix 1, Table 23).

Sample	Cl/SO_4	Cl/F	Na/K	Ca/Mg
24880[1]	6.8	>18	27	0.088
24885[2]	6.3	1.1	1.6	8.0
24886[3]	0.039	1.1	1.6	0.23
whole rock[4]	-	0.60	1.63	2.90
glass[5]	-	-	1.5	3.0
average condensate[6]	4.3-68	⩾1	1.9	2.4
Aloi sublimate[7]	1.7	0.20	18.0	0.13
Mauna Ulu fume[8]	0.002-0.45	0.1-6.8	2.0-4.9	0.33-6.5
Arenal plume[9]	0.21 -0.35	-	2.1-3.1	2.4-2.7

[1] yellow salt from Nausea Knob, locality 342

[2] yellow salt on Inner Crater rim, locality 330

[3] white salt encrusting around strong steam fumarole in Main Crater, locality 331

[4] fresh volcanic bomb from Erebus Volcano (Goldich _et al_. 1975)

[5] volcanic glass from Erebus bombs (Kyle 1976)

[6] mean value of ratios in condensates on Central American volcanoes (Stoiber and Rose 1970, 1974); Cl/SO_4 ratio of condensates on Santiaguito Volcano, Guatemala

[7] sublimate (unoxidized) collected from sealed hole newly drilled through crust in Aloi lava lake, Kilauea Volcano (Naughton _et al_. 1974)

[8] range of ratios of five samples of fume-condensates (oxidized) collected in blue haze region over lava fountain in crater of Mauna Ulu, Kilauea Volcano (Naughton _et al_. 1974)

[9] range of ratios of three samples of plume particulates (oxidized) above Arenal Volcano, Costa Rica (Cadle _et al_. 1969)

similarities to condensate and sublimate minerals on other volcanoes. Other salts on Erebus appear to have been formed by significantly different processes. As yet, there are no strong chemical indications that the local rock plays a major widespread role in salt formation. However, the rock may contribute to deposits around steam fumaroles where acid-rock reactions are likely to be intense.

It is believed that most of the salt deposits in the summit area were formed by sublimation, condensation and precipitation from the volcanic gas and plume that have been emitted from the main source of such gas inside Main Crater. This subsection discusses the probable composition of this Erebus gas. The transformation from magmatic gas to salt deposits are then discussed in a qualitative manner. Finally, examples of acid-rock reactions are examined.

(i) composition of Erebus gas

Gases from most volcanoes are broadly similar in composition and concentration (White and Waring 1963; Giggenbach and Le Guern 1976). Volcanic gas of magmatic origin consists mainly (<70 to 99 percent) of water vapour with lesser amounts (<1 to >10 percent) of carbon dioxide, sulphur dioxide and hydrogen. Small but significant amounts of halogen acids, carbon monoxide, inert gases, metal halides and other constituents are also present (White and Waring 1963; Krauskopf 1967; Naughton et al. 1974; Cadle 1975; Giggenbach and Le Guern 1976).

Erebus gas may be richer in halogens than that from many volcanoes. Gas from some other alkali volcanoes is enriched in halogens (Naboko 1959; Stormer and Carmichael 1971). Halogen concentrations could be higher in rocks from Erebus than from most volcanoes, due to high Cl_2 and F_2 fugacities in Erebus magma (Kyle, Ohio State University, pers. comm.). This belief is supported by the high halogen content (900 ppm Cl, 1500 ppm F) of a fresh bomb from Inner Crater (Goldich et al. 1975).

Erebus plume may also have a high Cl/SO_4 ratio. This ratio is dependent on both the Cl/S and SO_2/SO_4 (or total S/SO_4) ratios as well on magmatic gas composition. When both Cl/S and SO_2/SO_4 are high, Cl/SO_4 will also be high. These ratios are sensitive to the vigour of volcanic activity. During passive degassing phases the Cl/S ratio is generally higher than during explosive activity (Stoiber and Rose 1970, 1974;

Rose 1977; Malinconico 1978). The SO_2/SO_4 ratio is sensitive to the vigour of volcanic activity because this vigour affects the oxidation of magmatic SO_2 gas (Cadle et al. 1971). During passive degassing,normal for the Erebus magma lake (Plate 7.1, 7.1.3), the oxidation is slow (i.e. SO_2/SO_4 is relatively high). Therefore, Cl/S, SO_2/SO_4 and hence Cl/SO_4 ratios should normally be high in Erebus plume, especially if the magmatic gas is itself enriched in halogens.

Polian and Lambert (1979) produced evidence that suggests sulphate particulates are in low concentration in Erebus plume during conditions of low humidity. Under these conditions the main particulates were NaCl and KCl in a single sample collected directly from the plume on Main Crater rim. Furthermore the SO_2/SO_4 ratio was about 20 in this sample. This is entirely consistent with the conclusions of the preceeding paragraphs.

The oxidation of magmatic SO_2 and formation of H_2SO_4 is of additional significance because the oxidation products may further affect the composition of the plume through subsequent reactions. The oxidation may proceed by either of two sets of reactions or reaction intermediates, SO_3 or H_2SO_3. The thermodynamically favoured reaction:

$$SO_{2(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow SO_{3(g)} \qquad \ldots 7.1$$

is slow but may proceed significantly if suitable metal ion catalysts are present, as in volcanic fume. However, the reaction is effectively retarded when the cooling rate is high (Nordlie 1971) as would be expected on Erebus. Therefore,reactions involving SO_2 more likely follow the path:

$$SO_{2(g)} + H_2O_{(v)} \rightarrow [H_2SO_3] \qquad \ldots 7.2A$$

$$[H_2SO_3] + \tfrac{1}{2}O_{2(g)} \rightarrow H_2SO_{4(v)} \qquad \ldots 7.2B$$

Reaction 7.2A is the rate-controlling step since solutions of SO_2 (H_2SO_3) are mild reducing agents, readily oxidised by air (7.2B). 7.2A is relatively slow under conditions in the fume during quiet degassing especially when the condensation of water does not occur (Cadle et al. 1971; Kellogg et al. 1972; Naughton et al. 1974). Hence, many reactions involving SO_2 transformation products such as SO_3, sulphurous acid type intermediates, and H_2SO_4, will probably be retarded in Erebus fume and plume.

The compositions of Erebus salt are consistent with these discussions. Halide phases appear to be most common in the summit area. The possible presence of unusual phases (AlF_3 and $NaAl_4O_4Cl_5$, Table 7.3) may be primarily due to high Cl_2 and F_2 fugacities in Erebus gas. Once formed their continued existence would be made possible by cold, arid conditions that are typical over most of the summit area. The relatively high Cl/SO_4 ratio in two salts studied (Table 7.5) is consistent with a high Cl/SO_4 ratio in Erebus plume.

(ii) transformation of gas to salt

The transformation of magmatic gas, to volcanic gas, fume, plume and thence to salt involves probably a wide variety of physical and chemical processes. These processes include oxidation, sublimation, condensation and reactions between species in the gas, fume and plume. Equilibrium relations between species have been used to model changes in composition on oxidation and cooling within magmatic gas and volcanic fume (Naughton <u>et al</u>. 1974; Stoiber and Rose 1974; Giggenbach and Le Guern 1976). This approach is useful for determining the nature and temperature dependence of many particulate species present. However, the approach does not predict satisfactorily the SO_2/H_2SO_4 ratio (Naughton <u>et al</u>. 1974) due to quenching of the reactions (e.g. 7.1, 7.2) between the sulphur gases (Nordlie 1971).

The Naughton model (Naughton <u>et al</u>. 1974) can be used as a basis for discussing the transformation of magmatic gas. The model is not based on Erebus but on Hawaiian volcanoes in which the initial gas temperature is higher (1200°C) and initial composition is probably slightly different; these differences should be kept in mind during the following discussion. The model suggests that the first reactions within the gas mainly involve oxidation of high temperature oxide species. Crystalline particulates such as Al_2O_3, SiO_2 and $CaSO_4$ are likely products of such reactions. Volatile species such as halides which are probably more abundant in Erebus gas than in Hawaii may also undergo oxidation reactions at this time, such as:

$$2FeCl_{2(g)} + \tfrac{1}{2}O_{2(g)} + 2H_2O_{(g)} \rightarrow Fe_2O_{3(c)} + 4HCl_{(g)} \qquad \ldots 7.3$$

Halides may also react with sulphur gases at an early stage before the latter are cooled. The following may occur:

$$2NaCl_{(g)} + SO_{2(g)} + H_2O_{(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow Na_2SO_{4(c)} + 2HCl_{(g)} \qquad ...7.4$$

Such reactions appear to cause a preponderance of sulphates in condensed phases in Hawaiian fume via intermediates such as SO_3 (Naughton et al. 1974), and may account for some of the metal and sulphate ions in the present study. However, the sulphur content is less than one percent in two of the three samples listed in Table 7.5 (Appendix 1, Table 23) implying that most of these two similar deposits cannot have formed in this way. In Erebus gas the initial temperature is less than at Hawaiian volcanoes as is the rate of oxidation (probably), so that at Erebus these reactions are probably retarded. Therefore, most of the volatile halides probably sublime or condense out, before reacting with sulphur species, as the gas begins to cool and volcanic fume is formed.

By now the cooling fume is visible (7.1.3) and therefore contains many particulates. These provide abundant nucleation centres for water vapour. Condensation of this vapour onto the particulates may promote hydrolysis reactions such as:

$$SiF_{4(g)} + 2H_2O_{(v)} \rightarrow SiO_{2(s)} + 4HF_{(aq)} \text{ (Krauskopf 1967)} \qquad ...7.5$$

which produce further particulates. At this stage white plume cloud is present that normally will fill at least Inner Crater. Within the dense turbulent cloud, water droplets must frequently collide and grow in size.

Several observations inside Main Crater have been made of precipitation, as snow or rime, occurring from the plume cloud. Droplet growth is evidently so rapid that precipitation takes place mostly inside Main Crater. Relatively few precipitable droplets appear to reach Main Crater rim 200 m above the magma lake. Accretion of droplets and ice particles is probably restricted when the temperature of the cooling plume falls below a certain critical temperature. In normal clouds this temperature is about -15°C (Magono and Lee 1966) (Appendix 3, section 5.3) similar to the summer temperature of the plume when it has reached Main Crater rim (-15 to -25°C, Polian and Lambert 1979). Hygroscopic and other species in the plume may affect the critical temperature. During strong winds (especially those from the south to east, Appendix 3, Table 12) and sufficiently humid conditions, precipitation does occur outside the Crater, often as light riming on obstructions such as boulders, guy-ropes and humans.

The amount of this precipitation from the plume is likely to be greatest closest to Inner Crater and diminish away from it. However, the area in which this precipitation falls may be elongated in the direction of Nausea Knob, northwest of Main Crater and shortened to the south and southeast of the Crater. Sublimation of the water content of the precipitation must lead to accumulation of volcanogenic minerals including salt on the ground surface, and to eventual macroscopic accumulations of salt.

It is probable that some 'dry fallout' of crystalline particulates and salt phases occurs, especially in conditions of low relative humidity. Such fallout would also be greater closer to Inner Crater.

The hypothesis is then, that most Erebus salts are formed from the gases being emitted from inside Main Crater. It should follow that the rate of salt accumulation is highest inside the Crater and decreases with increasing distance away from it. The following sections aim to show that accumulation rates vary in this way.

(iii) acid-rock reactions

The presence of acid components such as HCl, HF and H_2SO_4 in Erebus plume must lead to their interaction with minerals in the local rock. The glassy groundmass of anorthoclase phonolite is far more susceptible to such reactions than the anorthoclase feldspar phenocrysts, these being resistant to acid-attack. This, together with intense physical weathering has led to formation of lag deposits of the phenocrysts in the summit area (see Plate 7.4). However, as yet there is little chemical evidence from elemental and ionic ratios to suggest that acid-rock reactions play a widespread role in salt formation in the summit area.

Nevertheless, there are strong indications that acid-rock reactions are significant around steam fumaroles and in warm ground areas. Some salt deposits develop adjacent to, or in, such areas (Plates 7.2, 7.5). Around steam fumaroles some distance from the primary source of volcanic gas, acid-rock reactions appear to be intensified and anorthoclase may be subject to attack here. The main phase in sample 24886 at the +80°C fumarole shown in Plate 7.2 may have formed from a reaction of the type:

$$\underset{\text{albite}}{2\text{Na AlSi}_3\text{O}_8{}_{(s)}} + 2\text{H}^+_{(aq)} + \text{H}_2\text{SO}_4{}_{(aq)} + 19\text{H}_2\text{O} \rightarrow$$

$$\text{Al}_2(\text{SO}_4)(\text{OH})_4.7\text{H}_2\text{O}_{(s)} + 2\text{Na}^+_{(aq)} + 6\text{H}_4\text{SiO}_4{}_{(aq)} \qquad \ldots 7.6$$

About 3 percent (by weight) of sample 24886 consists of Na and K (Appendix 1, Table 23), and these ions are in the same ratio as they are in rock (1.6, Table 7.5) consistent with the acid-rock formation mechanism. However, the rare-earth element ratios are dissimilar (Table 7.4) which is possibly due to some fractionation process between two or more of the magmatic gas, steam source, rock or salt.

A third type of acid-rock reaction probably accounts for the calcite in warm ground (+50°C) inside Side Crater (Plate 7.5). Calcite is not stable in the Ca - O - S - C system at this temperature at the prevailing fugacities of O_2, CO_2 and S_2 in fumarolic vapours (Holland 1959; Stoiber and Rose 1974). Therefore, the presence of calcite in this soil indicates that weathering processes involving aqueous CO_2 are intense at this site. Again, the glassy rock material is most susceptible to weathering so that many phenocrysts remain as loose crystals (see Plate 7.5). Sparingly soluble calcite accumulates near the soil surface whereas other, less mobile reaction products such as iron oxides are distributed throughout the zone of alteration. Gibbsite, $Al(OH)_3$ and clay minerals may also be formed from feldspars in this environment (Ugolini 1967) by reactions that Berner (1971) represented by:

$$\text{H}^+_{(aq)} + \text{NaAlSi}_3\text{O}_8{}_{(s)} + 7\text{H}_2\text{O}_{(1)} \rightarrow \underset{\text{gibbsite}}{\text{Al(OH)}_3{}_{(s)}} + \text{Na}^+_{(aq)} + 3\text{H}_4\text{SiO}_4{}_{(aq)}$$

and

$$2\text{H}^+_{(aq)} + 2\text{NaAlSi}_3\text{O}_8{}_{(s)} + 9\text{H}_2\text{O}_{(1)} \rightarrow \underset{\text{kaolinite}}{\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4{}_{(s)}} + 2\text{Na}^+_{(aq)} + 4\text{H}_4\text{SiO}_4{}_{(aq)}$$

7.2.4 Effect of moisture on Erebus salts:

Once formed the salts are subject to different degrees of water action depending on locality. The calcite locality in steam saturated soil (Plate 7.5) has been strongly leached and no soluble salts have accumulated. The fumarole encrustation is less well leached since it is hotter and exposed to the air (Plate 7.2). Hence, sulphate materials are dominant in this deposit (24886), most of the halide minerals remaining in solution. The yellow salts at Nausea Knob (24880) and Inner Crater rim (24885) are subject to some water action. Snow lying in drifts and on Main Crater floor is partially melted on a few occasions during the height of summer. This causes limited migration of salt into joints and the regolith around Nausea Knob, and down small depressions or gullies in Inner Crater wall. However, the total liquid water available in both of these localities is not large. Therefore, the solutions soon evaporate leaving salts on the surface of the regolith (Plate 7.4), as nodules within the regolith (locality 341), beneath pebbles and cobbles (Plate 7.3) and on Inner Crater wall (Plate 7.6). These salts still contain mainly halides because there has not been enough moisture available to remove them.

A lesser degree of moisture-induced migration is evident at most other salt localities on the summit plateau. At Eastern Cone salts have been redistributed after their formation to accumulate beneath cobbles and blocks of frozen lava or into subsurface soil horizons; the latter deposit (locality 347) indicates the aridity of the area (3.2.3). Fractional crystallization is evident under rocks at some localities. For example, separation occurs between sparingly soluble gypsum, soluble halite and an unidentified suite of volcanogenic salts at locality 345 (Appendix 1, Table 7.6, p. 31).

The summit area appears to be suitable for studying the rates of salt accumulation (6.5.2). At this high elevation (3200 m) the mean annual air temperature is around -35°C (Appendix 3, Table 9), and cold, arid conditions prevail over most of the summit plateau. There is good evidence that salt migration and leaching have been very restricted in most of the summit area, and therefore, little salt can have been leached from the salt deposits during the periods over which they have been accumulating. Net accumulation is probably close to total accumulation. The maximum amounts of salt shown on Figure 7.1 probably represent good estimates of total accumulation.

7.3 Locality Age and Supply of Volcanic Particulates

7.3.1 Recent volcanic history and the age of salt localities:

The recent volcanic history of Erebus has dictated the age of the ground surface in the summit area. The amount of salt in various deposits must be influenced by this age. Therefore, investigation of the recent history of the volcano will assist in the interpretation of salt distribution and rates of salt accumulation.

An attempt at reconstructing the geologic history of Erebus has been made by Kyle (1976). On the basis of some K-Ar dates later published by Armstrong (1978) Kyle suggested that the summit caldera was formed and subsequently filled with lava more than 0.2 Ma ago. Some flows dated at 0.20 Ma were extruded over the caldera rim. Eastern Cone, Truncated Cones and Helo Cliffs were truncated during the formation of the summit caldera, and therefore, are older than 0.2 Ma. The present active cone including Nausea Knob was developed probably within the last 0.1 Ma or so (Kyle 1976).

Details of very recent events inside the active cone may be inferred from US Navy aerial photographs (1956, 1963) and records of early visits (1908, 1912, 1959) to the rim of Main Crater. The visits, however, lasted only an hour or so, and judgement may have been impaired by lack of acclimatisation. Also, steam may have obscured part or all of Main Crater. Some features are easily missed unless a complete traverse of Main Crater is made. In particular estimates of crater widths and depths are unreliable in these conditions.

The first visit to the rim of Main Crater was made on March 10, 1908. The party gained the northwest rim near the high point now known as Shackleton's Cairn. David in Shackleton (1909,p.187) described the scene from this point after a light northerly wind had fanned away the obscuring steam cloud, "...at once the whole crater stood revealed to us in all its vast extent and depth. Mawson's angular measurement made the depth 900 ft (270 m) and the greatest width about half a mile (c. 800 m). There were at least three well-defined openings at the bottom of the cauldron, and it was from these that the steam explosions proceeded."

Apparently the topography of Main Crater has changed since 1908. The apparent depth of 270 m from Shackleton's Cairn is significantly greater than the present day depth of 130 m to the floor of Main Crater. The difference between the greatest width measurement in 1908 and the present distance is only 33 percent. This may be taken as the maximum error in Mawson's measurement, plus that inherent in the preliminary map. (The width of Main Crater is unlikely to have changed significantly in 70 years). The present depth to the floor of Inner Crater is about 210 m and Mawson's measurement of 270 m differs from this by 29 percent (Fig. 7.2). Since this is within the error estimate, it may indicate that the 'base level' of the crater system has not changed appreciably over the last 70 years.

However, the 1908 description does not include a single Inner Crater as exists now, but "at least three well-defined openings...". Furthermore, the greatest part of the "cauldron's" floor is only 130 m below Shackleton's Cairn at the present time. Mawson's measurement differs from this by 115 percent.

This apparent difference can be explained in two ways. Either there has been a major infilling of Main Crater since 1908 or alternatively, in 1908 there was some cloud obscuring all of the floor of Main Crater despite David's statement that "the whole crater stood revealed". In the modern day situation when the floor of Main Crater is obscured then so too is Inner Crater and most of the walls of Main Crater. Thus, the latter alternative is probably not compatible with David's observations of the crater floor and walls.

Excellent aerial photographs of the active cone, virtually steam-free, were taken by the US Navy in December 1956 and November 1963. These show Main Crater much as it is at present, namely with Inner Crater in the northeast sector, and the floor of Main Crater with its semicircular scarp about 130 m below Shackleton's Cairn. It is probable that Inner Crater was formed sometime between 1908 and 1956 after a major influx or influxes and subsequent freezing of lava had occurred in this same period.

Thermal modelling of cooling lava suggests that influx and subsequent freezing of lava is at least physically possible within a 40-50 year period. Order-of-magnitude estimates of cooling times for various thicknesses of lava sheets were obtained using the simplistic formula of Jaegar (1968). These times are given in Table 7.6. The maximum temperature of the

Table 7.6 Order-of-magnitude estimates of cooling times (years) for various depths of lava lake and thicknesses of lava flows (initial lava temperature, 1000°C).

Maximum Temperature of Cooling Lava (°C)	Phase of Lava	Thickness of cooling lava sheet (m)				
		15	25	35	40	100
100	crystalline	7	20	40	50	300
370	crystalline	1.8	4.9	10	13	80
650	crystalline	0.7	2.0	4	5	30
960	near melting point	0.2	0.5	1	1	8

supposedly still cooling lava beneath Main Crater floor may be about 100°C; this is the approximate temperature of the warmest fumarole (Table 7.1) inside Main Crater (but outside Inner Crater). The amount of supposed infilling is 100 to 140 m. The estimates suggest 35-40 m is the maximum thickness of an individual lava lake that could have cooled to 100°C in 40 to 50 years. The inference is that several influxes, involving relatively thin sheets of lava, took place during the supposed infilling. Cooling times could then be longer than shown in Table 7.6. However, a previous lava sheet need not have cooled completely to 100°C before the next was formed above it. Moreover, cooling rates may be relatively fast on Erebus. In fact there are so many uncertainties in these estimates that the only conclusion that can be made is that influxes of lava could have substantially infilled Main Crater between 1908 and about 1956.

The wall of Inner Crater records a sequence of very recent volcanic events. This record assists in the assignment of definite periods of time during which salts inside Main Crater have been accumulating. Figure 7.3 and Plate 7.6 illustrate the Inner Crater wall and the record.

Massive, virtually unfractured anorthoclase phonolite is exposed in most of the wall. This material is interpreted as a frozen lava lake or lakes. Most or all of this rock is younger than probably 1908, but older than 1956. The massive phonolite is overlain by 20 m or so of very vesicular phonolite that is composed of two distinct units of different surface colour and degree of consolidation (Plate 7.6). The lower unit is exposed in a face which is vertical except at the slightly reclining base (Fig. 7.3). The exposed surface of this material is yellowish in colour due to alteration and salt accumulation. The upper unit is c. 3 to 5 m thick and its black face reposes at 50 to 60°. The top surface of this unit comprises the floor of Main Crater.

The upper vesicular unit is composed of pyroclastics erupted from Inner Crater and of minor interbedded snow. Near the rim of Inner Crater current accumulation of these pyroclastics is estimated to occur at an average rate of roughly 0.1 m per year. Few of the bombs presently being deposited onto the floor of Main Crater are thicker than one metre. Therefore, few of such bombs exposed on the floor of Main Crater, near the rim of Inner Crater, are older than about 10 years. The upper unit itself has a minimum age of about 30 years at a pyroclastic accumulation rate of 0.1 m a^{-1} for 3-5 m of thickness.

The immediate-past history of Inner Crater and its sublimate-bearing fumaroles can now be documented more precisely. Apparently Inner Crater itself was formed sometime between 1908 and possibly about 30 years ago (1950). The crater may have been subdivided into two halves (as at present) between the time of Beck's visit in January 1959 and November 1963 (US Navy aerial photograph). In 1959 Beck (1965, p.181) saw "low ash mounds surrounding the vents" in the floor of Inner Crater; this is different from the present topography. A low altitude aerial photograph taken in November 1963 (Kyle 1977) clearly shows the Inner Crater with its two distinct halves like it has at the present time. Several fumaroles, some presently surrounded by sublimates, have persisted for at least 17 years in the southern (non-lava) half of the crater. The evolution of the magma lake in the northern half has been well documented by Kyle et al. (in press). The lake has persisted for eight years now, since its initiation as small pools during 1972. Some fumaroles within a few metres of the lake (Plate 7.1) have lifetimes of less than one year due to small changes in the shoreline and level of the lake, with which these fumaroles are intimately connected.

7.3.2 Supply of volcanogenic particulates and wind regime in the summit area:

The supply of volcanogenic particulates to the ground is likely to be greatest closest to their major source, which for Erebus summit area at present, is the gas being emitted from the magma lake in Inner Crater (7.1.3). Precipitation of snow and rime from the plume cloud from Inner Crater has been observed to diminish away from Main Crater (7.2.3). Therefore, the flux of volcanogenic minerals transported by the plume probably also diminishes away from Inner and Main Craters. Any 'dry fallout' of crystalline material from the present day plume, during conditions of low atmospheric relative humidity must also diminish away from Inner Crater.

The supply of particulates is likely to be affected by wind. Aerial transport of any light material is usually influenced by wind direction; wind increases the distance travelled by such material and will preferentially transport it downwind. Therefore, the fallout zones of the particulates emitted from Erebus Volcano are probably elongated in the directions towards which the strongest and prevailing winds blow at the summit; these fallout zones will be correspondingly shortened in the upwind directions.

The wind regime in the summit area appears to have two main nodes (Appendix 3, section 4.7), shown in Figure 7.1. The prevailing wind direction at this elevation is west-southwest (Schwerdtfeger 1970). However, the pattern of sastrugi height and orientation near the Observatory indicates that the strongest winds are from the southerly quarter. This is supported by observations of wind at the Observatory, which show that the strongest winds are from the southeast to south (Appendix 3, Table 12).

This wind regime appears to have marked seasonal characteristics. Observations show that the southeasterly and southerly winds are the most frequent winds in summer (Appendix 3, Table 12). These winds are often the result of cyclonic disturbances (Appendix 3, section 4.8); they are usually accompanied by snowfall and cloud, indicating high average relative humidities. In contrast, the prevailing west-southwesterly winds may be more common during winter (Appendix 3, section 4.7). These winds are part of the prevailing general circulation of air in the antarctic troposphere (Appendix 3, section 4.8). This air, blowing eastwards and outwards from over the East Antarctic Ice Sheet, is probably colder and drier on the average than the moist, maritime air in cyclonic disturbances (Rusin 1964; and Appendix 3, section 6.1). This is consistent with observations of the plume during light winds from the southwesterly quarter. The plume is often thin and wispy during such winds (7.1.3) indicating a lack of condensation and therefore low atmospheric humidities.

The characteristic wind directions, strengths and humidities must influence the distribution of salt in the summit area. The strongest winds probably transport some of the airborne particulates towards Nausea Knob to the northwest; in light wind conditions these same particulates would most likely be confined inside Main Crater. This is consistent with (1) the similarities which exist between the salts at Nausea Knob (24880) and Inner Crater rim (24885) (Tables 7.4, 7.5), (2) the large amounts of salt around Nausea Knob to the northwest and (3) the small amounts of salt to the southeast (upwind) of Main Crater (Fig. 7.1). The more gentle prevailing winds probably cause a broader fallout zone to be aligned approximately towards Eastern Cone to the east. The particulates falling in this zone may have been affected by their relatively long airborne residence time which could have caused some chemical fractionation. Dry fallout may be more common in this zone elongated by probably drier, colder winds, which could also cause differences in salt chemistry.

7.3.3 Supply of volcanogenic minerals outside the summit area:

Volcanic activity on Erebus has contributed little to salt deposits in the rest of the McMurdo region. This is shown, qualitatively, by the decrease in abundance of volcanogenic salts beyond the rim of the summit plateau (7.2.1). Analyses of radioactive isotopes, sulphur dioxide and hydrogen chloride in the plume sampled at Main Crater rim, allow precise estimates of the influence of Erebus on salts elsewhere (Table 7.7). Based on the estimated output of 2 x 10^{11} m^3 a^{-1} of undiluted gas (7.1.3), the isotope measurements suggest that the annual output of ^{210}Po in Erebus emissions is significant and constitutes about 10 percent of the antarctic budget of ^{210}Po (Polian and Lambert 1979). The percentage output of ^{210}Pb is not significant.

The annual antarctic surface budgets of sulphate and chloride can be obtained from analyses of snow in the East Antarctic Ice Sheet. Delmas and Boutron (1978) found that the mean concentration of sulphate is quite constant at about 7.1 x 10^{-8} kg kg^{-1} in surface snow from Durmont D'Urville Station to Dome C. The assumption is made that this is representative of the whole of Antarctica. Using Bull's (1971) estimate of 150 kg m^{-2} a^{-1} for average snow accumulation in Antarctica, and a continental area (including ice shelves) of 1.41 x 10^7 km^2 (Lebedev 1959), a sulphate budget of 1.5 x 10^8 kg a^{-1} is obtained. Similarly, Boutron et al. (1972) estimated that the annual chloride budget is 2.0 x 10^8 kg a^{-1}. The measured concentration of sulphur dioxide corresponds to about 2.3 x 10^{-6} kg m^{-3} of sulphate assuming complete oxidation or about 4.5 x 10^5 kg a^{-1}. This is small compared to the antarctic surface sulphate budget. Similarly, the chloride output is small compared to the antarctic surface chloride budget (Table 7.7).

These calculations are based on the assumption that samples collected at the edge of the plume are representative of the whole plume, and that this is undiluted volcanic gas. Therefore, the calculations give minimum estimates. A rate of 2 x 10^{12} m^3 a^{-1} for diluted gas flow (7.1.3) gives maximum estimates; at this rate for example, Erebus would contribute about 3 percent to the sulphate budget (Table 7.7). More samples need to be taken to check the validity of the various assumptions. However, the calculations do suggest that volcanic activity has made only a minor contribution to the salts of the rest of the McMurdo region.

Table 7.7 Measured concentrations and estimates of annual outputs of some species in Erebus plume.

Species	Annual budget in Antarctica	Measured[1] concentration in plume (per m^3)	Annual output (kg) at plume emission rate of $2x10^{11}$ m^3 a^{-1}	Percentage of budget (minimum)	Annual output (kg) at plume emission rate of $2x10^{12}$ m^3 a^{-1}	Percentage of budget (maximum)
^{210}Pb	1400 Ci (1)	$8x10^{-12}$ Ci	2	0.1	16	1
^{210}Po	700 Ci (1)	$2.50x10^{-12}$ Ci	50	7	500	70
SO_2	-	$1.5x10^{-6}$ kg	$3x10^5$	-	$3x10^6$	-
$SO_4{}^{2-}$	$1.5x10^8$ kg (2)	-	$4.5x10^5$ (3)	0.3	$4.5x10^6$	3
HCl	-	$8\text{-}31x10^{-7}$ kg	$2\text{-}6x10^5$	-	$2\text{-}6x10^6$	-
Cl^-	$2.0x10^8$ kg (2)	-		0.1-0.3		1-3

(1) Polian and Lambert (1979) and W. Zoller, Chemistry Dept, University of Maryland, USA unpublished manuscript.

(2) subsection 7.3.3.

(3) assuming complete oxidation of SO_2

7.4 Synthesis and Concluding Remarks

7.4.1 Synthesis:

The patterns of salt accumulation (7.2.1, 7.2.2, 7.2.3) can be linked with details of the recent volcanic history (7.3.1) and supply of volcanogenic particulates (7.3.2) to explain salt distribution in the summit area. This synthesis is summarised in tabular form (Table 7.8). Table 7.8 has two parts concerning (A) areas outside Main Crater and (B) areas inside Main Crater, mainly Inner Crater. The Table lists: datable volcanic events (7.3.1) in order of decreasing age; salt locality (locality numbers from Appendix 1, Figure 5); maximum amount of salt in discrete deposits in the locality (Fig. 7.1); and the maximum rate of salt accumulation in the locality.

The area within Main Crater is discussed first (Table 7.8B) because this area is the younger and wind does not appear to affect salt accumulation, asymmetrically at least. High temperature fumaroles inside Inner Crater are point sources of particulates and as such are surrounded by large (10^3 g) deposits of salts (condensates and sublimates). The rate of salt accumulation is probably faster in those fumaroles nearer to the largest source of magmatic gas, that is, the magma column itself, beneath the magma lake. The accumulation rate decreases with increasing distance from the lake. Near the top of Inner Crater wall, about 100-150 m from the lake, salt accumulations up to 20-30 mm thick have developed probably within 30-50 years or so. A slightly slower accumulation rate is evident on recent bomb surfaces on Main Crater floor near Inner Crater rim. This rate further lessens away from that rim; encrustations on bomb surfaces become thinner away from Inner Crater rim.

The area outside Main Crater (Table 7.8A) is more complex because wind appears to create asymmetry in the salt distribution. The fastest rate of salt accumulation ($>1 \times 10^{-4}$ g a^{-1}?) is probably at Nausea Knob. This lies 500 m northwest of Main Crater in the direction towards which volcanogenic salts would be transported by the strongest winds at this elevation. The rate of salt accumulation is perhaps an order of magnitude slower at the same distance upwind (south and southeast) of Main Crater, which is consistent with this hypothesis.

The rate of salt accumulation appears to decrease in a regular fashion away from Main Crater, as it does from Inner Crater. Accumulation seems to be

Table 7.8 Recent volcanic events, salt locality age, maximum amounts and rates of volcanogenic salt accumulation in the summit area of Mt Erebus.

(A) outside Main Crater

Event	Age (years B.P.)	Salt locality	Locality number	Maximum amount of salt in deposit (grams)	Rate of salt accumulation (grams per yr)
formation of summit caldera	>0.2 M	Eastern Cone	346,347	20	<1x10^{-4}
		Helo Cliffs Truncated Cones	362 357	10	<0.5x10^{-4}
formation of summit plateau	0.2 M	plateau ENE of active cone	364	10	0.5x10^{-4}
		plateau NW of active cone	360	3	0.2x10^{-4}
		plateau SE of active cone	350	<1	<0.05x10^{-4}
formation of active cone	<0.1 M?	Nausea Knob	341,342	10	>1x10^{-4}?
		slopes of active cone, south of summit	349	<1	(0.1x10^{-4})?

(B) inside Main Crater

Event	Age (years B.P.)	Salt locality	Locality number	Maximum amount of salt in deposit (grams)	Rate of salt accumulation (grams per yr)
recent eruptions	⩽10	surfaces of largest bombs exposed on floor of Main Crater near Inner Crater rim		3	⩾0.3
formation of Inner Crater	24-72 (30-72)*				
formation of base of top vesicular unit on Inner Crater wall	24-72 (30-50)*	top of wall	330	100	2-3
subdivision of Inner Crater	17-22?	oldest high temperature fumaroles in southern half of Inner Crater		1000	10^{2}
onset of present phase of magma lake activity	8				
minor fluctuations in level and shoreline of lake	⩽1	short lived fumaroles in northern half of Inner Crater		1000	⩾10^{3}

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*more precise estimates of age in parenthesis.

slower at locality 360 on the plateau one kilometre northwest of Nausea Knob, than it is at Nausea Knob itself. This is consistent with the source of the salt being volcanic gas from Main, and more recently Inner Crater.

The generally increasing age of the surface outwards from the active cone is counter to the decreasing trend in accumulation rate. The greater salt deposits are in the older (>0.2 Ma) sections of the rim. The prevailing west-southwest winds appear to have led to the greatest accumulation (20 g) along this rim at Eastern Cone, two kilometres east of Main Crater.

7.4.2 Age of the active cone:

Kyles' (1976) estimated age (<0.1 Ma) of the active cone can be refined to within 10^3 years using a refined estimate of salt accumulation rate at Nausea Knob, of about 0.01 g per year.

The encrusting of newly erupted bombs can be used to indicate rates of salt accumulation. Noticeable colouration of the fresh surface develops within a few weeks inside Main Crater. However, it takes six months to one year, perhaps ten times as long, for this same colouration to develop on Main Crater rim. Therefore, an accumulation rate of around 0.03 g a^{-1} does not seem unreasonable on Main Crater rim. A rate of 0.01 g a^{-1} is probably applicable to Nausea Knob. The maximum of 10 g of salt accumulation at Nausea Knob represents about 10^3 years of accumulation, which gives a maximum age for the active cone.

7.4.3 Conclusion and future work:

This chapter has examined the accumulation, composition and formation of salts in the summit area of Mt Erebus. The salts are volcanogenic in nature, forming mainly from gas emitted from Main and Inner Craters. The rate of salt accumulation decreases outward from the main source of gas but is partly dependent on wind strength and direction. Halide salts predominate, probably due mainly to high fugacities of halogen gases in the magma.

These conclusions need to be strengthened by future work. Elemental analyses of a greater number of salts are required to examine more closely the similarities and trends in the salt deposits, and thus to gain further understanding of their complex formation processes. The Cl/SO_4 ratios would be useful to know in this regard. A more quantitative assessment is required of the amount of salt present in deposits. Measures of total soluble salts or specific conductances in soil-water extracts would be appropriate. This would allow precise mapping of salt accumulation and rates of formation of salt deposits. A better idea of recent volcanic history of the summit region would probably follow.

Sampling of volcanic gas and sublimates on the floor of Inner Crater is a fundamental prerequisite for further study. Analysis of these will fill critical gaps in present knowledge of volcanic activity and salt accumulation on Erebus. Also, systematic sampling of salts from the plateau rim down towards Cape Royds or northeast of Eastern Cone may more precisely delineate the volcano's contribution to salt deposits on the whole mountain.

CHAPTER 8 THE SALINE DISCHARGE AT THE TERMINUS OF TAYLOR GLACIER

8.1 Preamble

8.1.1 Introduction and outline:

This chapter discusses the phenomenon involving discharge of salty water at the terminus of Taylor Glacier. Up to several thousand cubic metres of brine may be discharged from beneath the glacier, during a single discharge event. The ionic composition of the brine is similar to concentrated sea water but the isotopic composition is similar to melted Taylor Glacier ice. At least ten discharge events have occurred since 1956, at intervals of one to five years. Although the onset of discharge has never been observed it can be inferred that the events take place during the winter and spring months. As well as the brine discharge, there are various other features such as salt deposits and orange coloured layers of ice in the terminus area, that are related to and therefore part of the overall phenomenon.

The phenomenon is a unique process of salt migration that has never been completely described. It is difficult to study (and still not completely understood) because of the aperiodic and seasonal timing of the discharges. The discharge events, the brine composition and the various other features of the phenomenon are discussed here. A model for the discharge is proposed in the final section of this case study chapter. An exhaustive investigation into the complex glacio-geochemical system is outside the scope of this thesis.

8.1.2 Taylor Glacier:

Taylor Glacier is almost 100 km long, from its ice divide in the East Antarctic Ice Sheet, to the terminus in Taylor Dry Valley (Figs 1.2, 1.3). The accumulation area is situated on part of a large ice dome and has a maximum elevation of 2400 m asl (Calkin 1974; Drewry et al. 1980). The ablation zone is over 60 km long and terminates in the western end of Lake Bonney, 34 km from the sea (Figs 1.2, 1.3). Along the northern margin of the terminus, the glacier is presently partly overriding an ice-marginal mound (Plates 8.1, 8.2). A stream delta up to 60 m wide has formed between the mound and the older ice-free 'drift' of Taylor Valley. Summer melt

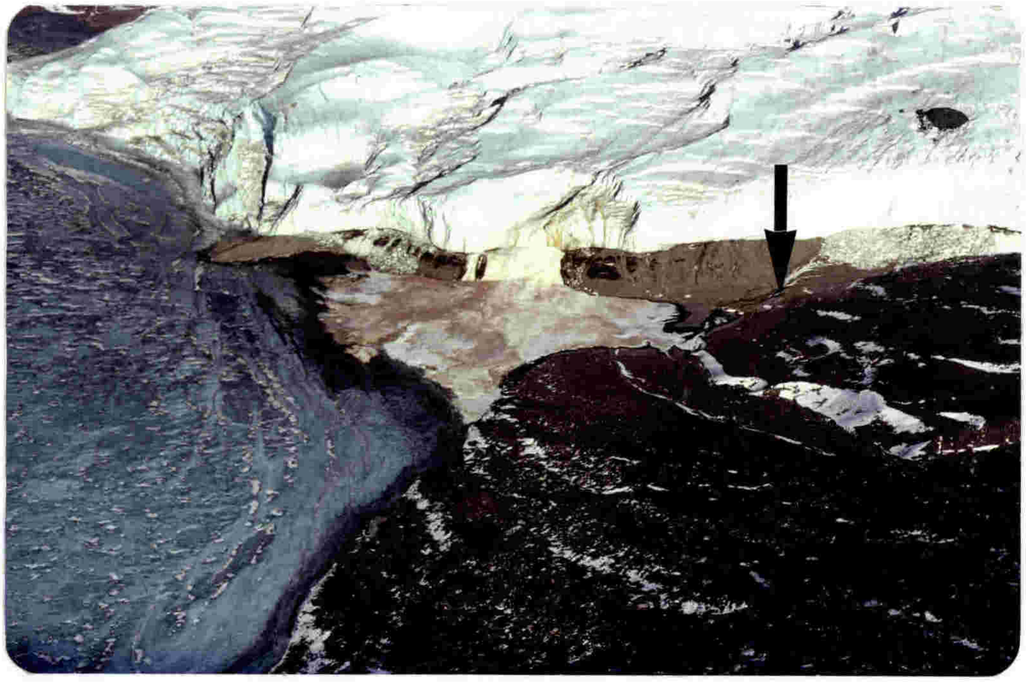

Plate 8.1 Aerial view of Taylor Glacier terminus, from the north, showing an orange coloured saline icing formed during 1978 being enlarged by brine discharging from a crevasse in the glacier in late October 1978. Arrow shows the other site from which saline discharges have occurred.

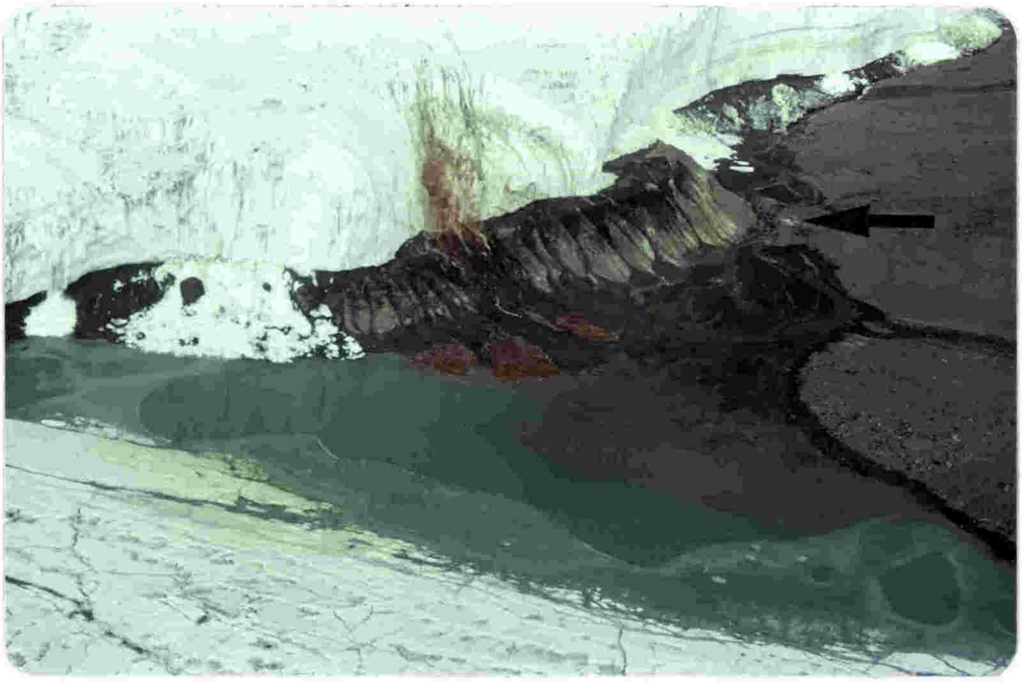

Plate 8.2 Aerial view of the northeastern part of the terminus in mid-January 1979 showing the **dark** orange coloured remnants of the 1978 icing. The lateral discharge site is marked by white salt (arrow), and salt is also prominent on the ice-marginal mound.

water, mainly from Taylor Glacier, forms the braided North Taylor Stream* that flows across this delta (Plate 8.2).

The thermal regime of Taylor Glacier was investigated by Robinson (1979). The glacier is composed largely of 'cold' ice, where englacial temperatures are well below 0°C. However, temperature modelling suggested that large areas of the basal ice are at the pressure melting point (c. 0°C).

Temperatures at the glacier surface rise to 0°C and supraglacial water movement occurs during the short summer melt season (December, January, early February). During this period surface melt water drains into depressions and longitudinal drainage valleys on the glacier surface and flows off the glacier. A very small proportion enters crevasses and freezes. No englacial drainage from the surface to the bed is possible because of the thick intermediate zone of cold 'impermeable' ice (Embelton and King 1975). Subglacial water movement may occur where the basal ice is at pressure melting, that is where it is not frozen to the bed.

8.2 Manifestations and the Record of the Saline Phenomenon at Taylor Glacier

8.2.1 Discharges and icings:

Discharges of salty water are the main manifestation of the phenomenon, and consistently issue from one or both of two localities: (1) a recurring longitudinal crevasse along the northeastern edge of the terminus (Frontispiece, top); and (2) on a small (20 x 10 m) 'peninsula' towards the apex of the stream delta (Plates 8.1, 8.2; Appendix 1, Fig. 3). The crevasse and peninsula localities are hereafter referred to as the glacier discharge site and the lateral discharge site, respectively (localities 1 and 2 in Appendix 1, Fig. 3). The peninsula appears to have been previously connected to the ice-marginal mound but North Taylor Stream has now cut a channel between the mound and the peninsula (Plate 8.2). The two discharge sites were 20±2 m and 2.5-3.0 m respectively, above the surface of the moat ice of Lake Bonney in December 1976.

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[*] Unofficial name.

Brines discharging from the glacier and lateral sites freeze as they flow onto the ice-marginal mound, stream delta and sometimes as far as the moat ice of Lake Bonney. An extensive deposit of salty ice, or saline icing* (Ives 1974; Van Everdingen 1978) is developed during each event (Frontispieces, Plates 8.1, 8.3). The icing has been called an 'ice platform', 'frozen outwash fan', and 'red cone' by Hamilton et al. (1962), Black et al. (1965) and Jones and Faure (1969) but these terms are discarded here in favour of the more widely accepted term 'icing'. The icings are useful because they temporarily preserve the discharge brines in a frozen state.

Individual icings contain up to 7000 m^3 of ice and (3-6) x 10^5 kg of salt. Icings are composed of both hard, dense ice (density 900 kg m^{-3}) and more porous 'snowy' ice (density 400-800 kg m^{-3}, cf Michel and Ramseier 1971); 800 kg m^{-3} seems a reasonable estimate of mean density. Salt content varied from 15 to 40 kg m^{-3} in six melted samples of the 1976 icing (Appendix 1, Tables 14, 17). Parts of the icing are covered by salt crusts containing mainly halite or calcium carbonate and little or no ice, and in places, salts also underlie the icing (Appendix 1, Tables 4, 14, eg localities 3, 7, 24; also Hamilton et al. 1962; Black et al. 1965). The surficial salt crusts develop during ablation whereas the sub-icing salt is probably a remnant of previous icings. Some icings contain partially hollow mounds (domes) of ice (Plate 8.4; Appendix 1, Table 14.1, localities 2, 23, 24). Similar mounds have been observed forming during winter due to hydrostatic uplift of icing layers around perennial springs at Bear Rock, Canadian North West Territories and have been termed icing blisters (Van Everdingen 1978, and written communications 1978).

Icings are coloured orange-brown due to small amounts of hydrated iron oxide (Plates 8.1-8.4). Some wet residues of icings are bright brown (7.5 YR 5/8) and contain about 98-99 percent calcium carbonate plus one to two percent hydrated iron oxide (Hamilton et al. 1962; Stephens and Siegel 1969). Other wet residues, that contain gypsum, are dark reddish brown (2.5 YR 3/6). When dry, these residues are orange (7.5 YR 6/8) and bright brown respectively. The colour is due to finely divided (ie X-ray amorphous) goethite $HFeO_2$ (Black et al. 1965; J.H. Johnston, Chemistry Department,

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*Icings are also termed aufeis (German) or naled (Russian).

Plate 8.3 A & B

Two views from about 60 m up-glacier from the discharge site, looking northeast and down on the (A) 1972 and (B) 1976 saline icings and ice-covered Lake Bonney. Salty, orange coloured englacial layers in the foreground have locally increased the ablation of the glacier forming a small 'ablation valley'. This valley has enlarged significantly over the four year period suggesting that the interaction between salt, glacier and climate is not in a steady state (A 28/11/72; B 23/11/76).

Plate 8.4 The largest icing blister (1.5 m high) on the 1976 icing, near the lateral discharge site. Mounds similar to these occur in cold climates where upwelling ground water (or brine) reaches the surface under pressure (Tricart 1970; Van Everdingen 1978). The mound shown here has a composite structure and was built during more than one cycle of hydrostatic uplift and subsequent rupture (24/10/76).

Plate 8.5 A strongly flowing part (subspring) of the cold saline spring that discharged brine at the lateral discharge site during November and December 1976. The froth and bubbles show that the subspring brine is actively degassing (24/11/76).

VUW, pers. comm.). When the icings are fresh the colouration is not apparent (Frontispiece, top) but develops over a period of more than four hours presumably as oxidation and ablation proceed. The two distinctive colours shown in Plates 8.1 and 8.2 are typical of icings existing in late October-November, and late December-January respectively. The striking colour is an effective tracer linking various manifestations of the phenomenon and helps to distinguish icings of different ages.

Reports and photographs of different icings and the glacier terminus have been used to compile a record of many recent discharge events (Table 8.1). The record may be incomplete prior to 1971 and is inadequate prior to 1962 because icings of less than 1000 m^3 may have completely ablated before being noticed. Earliest photographic evidence of activity at the site is that of Taylor (1922, Plates 69, 70, 73). Taylor mentioned silt and salt, but not orange coloured ice, at the site.

Despite inadequacies, the record is useful for delineating possible causes of the discharges. The record bears no relation to differences in air temperatures from season to season or year to year at Scott Base or from November to January at Vanda Station (Appendix 3, Fig. 2 p.13; no discharges occurred during the three winters Vanda Station was manned). Similarly, the discharge record bears no apparent relation to annual or seasonal changes in the level of Lake Bonney documented by Chinn (1979, unpublished). From January 1972 to January 1979 the mean annual volume change of the lake was one million cubic metres which is three orders of magnitude greater than the average annual volume of brine discharged (Table 8.1). Therefore, it seems unlikely that the two are related.

The discharge events are aperiodic (no regular time between events, Table 8.1) similar to some aperiodic jökulhlaups (Liestöl 1956; Whalley 1971; Mathews 1973). Jökulhlaups are sudden outbursts or floods of up to 10^{10} m^3 of water from subglacial, englacial or ice-marginal ice-dammed lakes draining beneath temperate glaciers* (Thorarinsson 1953; Embleton and King 1975). However, saline or cold-glacier jökulhlaups have not been reported.

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*Temperate glaciers are composed of 'warm' ice, where englacial and basal temperatures are at the pressure melting point, except for a thin surface layer in winter.

Table 8.1 Known record of discharge events at the terminus of Taylor Glacier (discharge from G, glacier discharge site or L, lateral discharge site; P, photographic record; ? uncertainty in record).

Year of discharge event	Occurred between dates as shown (1)	Years since previous event	Volume of saline icing (2) (m^3)	Discharges occurring in successive years, ie pairs of discharges	Point of discharge	Source of discharge information
1910?	before 4/2/11	?	?		G	P in Taylor (1922)
1957?	6/12/56 Dec 57	?	?	┐?	G?	Black (1969)
1958	1/1/58,P 15/12/58	1?	>1000	┘	probably L	Hamilton et al. (1962)
1961?	4/12/59,P 22/11/61	3?	(<1962)	┐?	G and/or L?	Black et al. (1965) Black and Berg (1965)
1962	Jan 62 1/11/62	1? or 4	3000-6000	┘	G	Black et al. (1965)
1967	12/12/66,P Oct/Nov 67,P	5	2000-7000	┐	G and/or L	P by R.L. Armstrong
1968	Oct/Nov 67,P 22/1/69	1	3000-6000	┘	G	Black (1969)
1971	21/12/70,P 9/12/71,P	3	2000-5000	┐	G, and L?	Ps by Y. Yusa
1972	9/12/71,P 29/11/72	1	3000-6000	┘	G	personal observations
1975	22/12/74,P 26/11/75,P	3	2000-5000	┐	L	Ps by P.H. Robinson J. Collen
1976	19/12/75,P 22/10/76+	1	5000-7000	┘	L and G	personal observations
1977	3/1/77,P 1/12/77,P	1	100-500	┐	G	Ps by P.H. Robinson N.E. Logan
1978	12/1/78 22/10/78*	1	3000-4000	┘	G	personal observations

\+ a spring was active at the lateral site after this date.

* discharge event still in progress.

(1) Dates of photographs by US Navy, J.D. McCraw, Black (1969), R.L. Armstrong, Y. Yusa, T. Torii, P.H. Robinson, J. Collen, J.D. Palmer, N.E. Logan; additional photographs on other dates supplied by G.G.C. Claridge, R.F. Black, K.B. Popplewell, T. Torii, J.H. Johnston, R.W. Plume, P.H. Robinson, P. Kyle.

(2) Estimated (with supplementary measurements of area and depth); ablation before visit or photograph neglected; average volume from January 1969 to January 1979 is 2000 ± 700 $m^3 a^{-1}$, equivalent to a brine volume of 1500 ± 500 $m^3 a^{-1}$ (1.5 M $l\ a^{-1}$), and a salt output of about 1.5×10^5 kg a^{-1}; maximum volume of brine discharged during a single event is probably about 5000 m^3.

A complex relationship may exist between discharge volume and time before the previous event. Discharges have a tendency to occur during successive years, as 'pairs' of events, with the second of the pair producing the greater volume of icing. The combined volume of each pair may bear some direct relation to the length of time preceding it (Table 8.1) similar to aperiodic jökulhlaups from Mjölkedalsvatn, Norway (Liestöl 1956). However, the useful Taylor record is only three pairs long and the large errors in estimating volume obscure the possible volume-time relationship at Taylor Glacier.

8.2.2 Discharge brines observed in situ:

The 1978 discharge was observed in the process of forming an icing. In late October 1978 brine was flowing at about 0.5 litres per second beneath a layer of white, slushy ice from the glacier discharge site (Frontispieces, Plate 8.1). Table 8.2 lists discharge and temperature relationships together with environmental details for this crevasse brine. The air temperatures at the time were sufficiently cold to freeze the brine within minutes of sampling but not cold enough to freeze the icing solid on the marginal mound and stream delta; nevertheless, the icing was growing not diminishing.

The brine contained about eight percent dissolved salt (by weight) which allowed a 5.5°C depression* from the freezing point of pure water. This freezing point depression was equal, within the precision of measurement, to the in situ brine temperature (Table 8.2). Therefore, the brine was in thermodynamic equilibrium with the ice, which is consistent with slow flow of brine through a conduit in cold ice, rock or frozen sediment. The composition of the brine was similar to concentrated sea water (Appendix 1, Table 15, p.39; Figs 5.12, 6.2; Table 6.2) and is further discussed in section 8.3.

A saline spring was active at the lateral discharge site (Appendix 1, Fig. 3) in November and December 1976. Brine issued from several distinct subsprings (Plate 8.5) over an area of 16 m², total discharge varying between

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*Salt dissolved in water lowers the vapour pressure of that water, hence lowering the temperature at which ice and water coexist at equilibrium, that is the melting point.

Table 8.2 Discharge and temperature relationships, and environmental details for two discharge brines.

	spring brine	crevasse brine
sample number(s)	76/53B, 76/72	78/01
discharge site	lateral	glacier
year	1976	1978
closely monitored period	22 November-1 December	24 October (4 hours in pm)
estimated mean discharge*[1] (litres per second)	0.5±0.3 l s^{-1}	0.5±0.5 l s^{-1}
discharge trend during monitored period	slowly decreased with diurnal fluctuations similar to fluctuations in air temperature	no apparent change
freezing point of brine (±0.2)	c. -5.5°C	-5.5°C
mean *in situ* temperature of brine (±0.3)	-5.2°C	-5.5°C
in situ temperature trend over monitored period	warmed very slightly*[2] (by no more than 0.2°)	no apparent change (over 21 hours)
salinity (per mille)	92	c. 85
presence of gas bubbles	actively degassed (Plate 8.5)	slight froth
air temperature during monitored period	-8 to +4°C	-14 to -17°C
mean air temperature trend during monitored period	warmed (Fig. 8.1)	cooled
medium that brine is in contact with	sediment; ice-cemented table at 0.2 to 0.5 m depth	icing and glacier ice
temperature range in medium at locality*[3] remote from discharge site	+3.4 to -10.1°C	c. -10°C to colder than -17°C
horizontal distance from site	5 m	25 m

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*[1] estimated by measuring flow rate in known cross-section and by filling known volume (0.5 l s^{-1} = 5 x 10^{-4} m^3 s^{-1}).

*[2] warming less than precision of measurement.

*[3] localities were a dry sediment (0.01-0.8 m depth) and a crevasse (0-4.2 m, locality 96 in Appendix 1, Fig. 3); temperatures for the latter are only approximate because of possible air circulation (P. H. Robinson, pers. comm.).

0 and 1 litres per second. The brine-soaked sediment encompassing the spring site was underlain by ice-cemented material below a depth of about 0.5 m and two 'gaps' up to 0.6 m wide were located in this material. Earlier (late October) the site was covered by the 1976 icing and no liquid discharge was observed. Flow had stopped completely by early January (T. Stern, pers. comm.).

Physically and chemically the spring brine was similar to the crevasse brine (Table 8.2; Appendix 1, Table 15). However, the in situ temperature of the spring brine was slightly warmer than its freezing point depression (Table 8.2) indicating that the brine was slightly out of equilibrium with ice. Slight transfer of heat from solar heated sediment in contact with the brine probably accounted for this minor disequilibrium, as well as the very small warming that may have occurred in the brine over the monitored period (Table 8.2). The air temperature at the time was too warm for significant amounts of freezing to occur, and therefore flow from the spring caused the surrounding icing to melt. The similarity between the crevasse and spring brines indicates that the spring flow represented late-stage discharge from the same source as the glacier discharge somewhere beneath Taylor Glacier.

One sample of the spring brine (76/53A) was taken from a subspring that had just commenced discharge. The in situ temperature of this subspring rose from -7.5°C during sampling (Appendix 1, Table 16) to -5.3°C within 21 hours, typical of such newly active subsprings (see example in Fig. 8.1). Such behaviour possibly represented the release of brine that had been temporarily impounded in an area where the temperature was colder or equal to -7.5°C. In such a situation the brine would partially freeze with a simultaneous drop in temperature and an increase in salinity from steady state discharge values, represented by samples 76/53B (sampled at the same time but from a different subspring) and 76/72 (sampled one week later; Appendix 1, Tables 14.2, 15, 16). Opposite behaviour (ie temporary blocking of flow) would account for a six hour cessation of discharge on November 26; subspring temperatures cooled slightly as discharge ceased but warmed back up to -5.2°C shortly after flow resumed (Fig. 8.1). There was no apparent meteorological reason for this cessation.

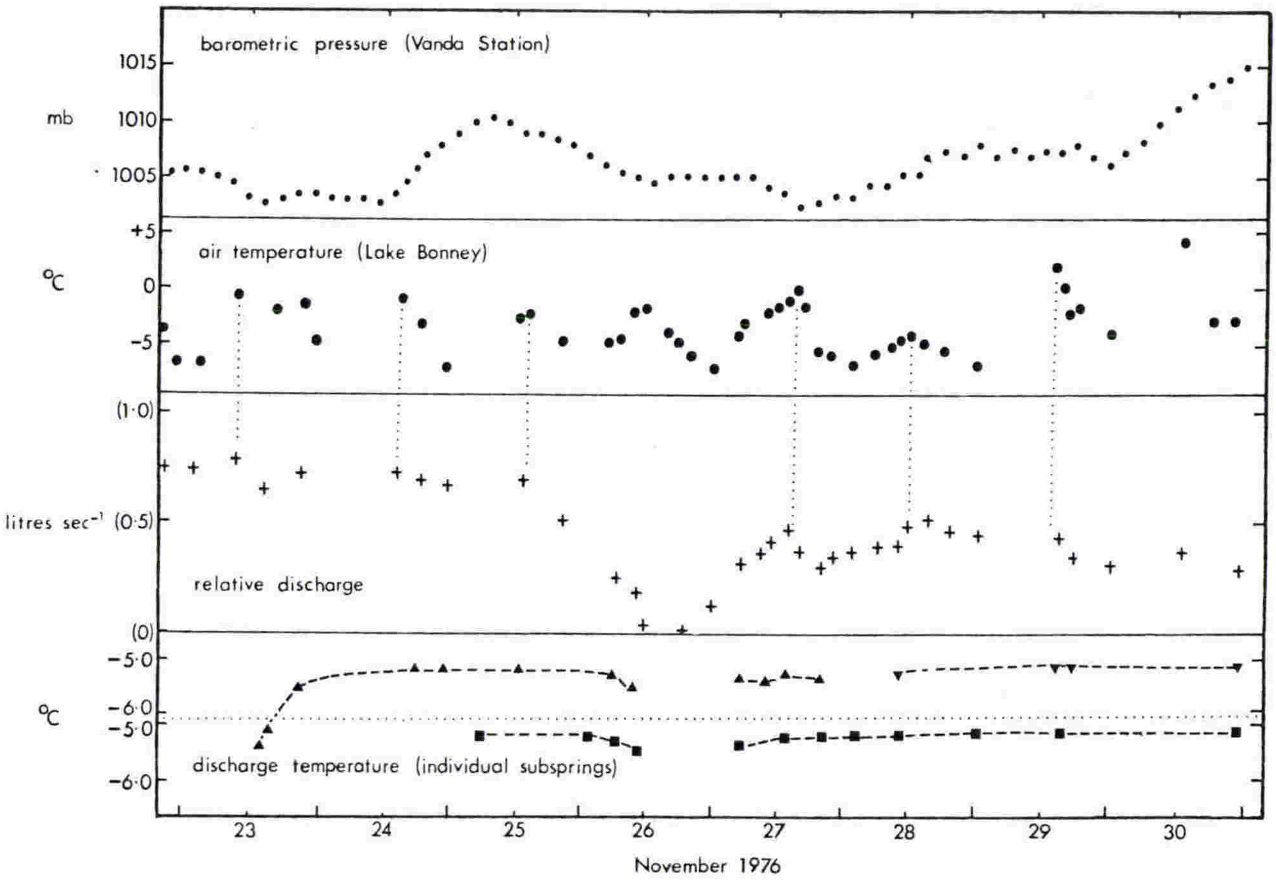

Figure 8.1 Relative discharge and temperature of the saline spring compared to air temperature and pressure. Estimated values of absolute discharge are shown on vertical axis.

Diurnal flow variation of up to about 0.2 ± 0.2 l s^{-1} (up to 40 percent of total flow) was recorded in the spring discharge (Fig. 8.1). The times of maximum and minimum discharge differed from times of daily maximum and minimum air temperatures by about 0-5 hours. Possibly, some relationship existed between discharge and the daily production of melt water on Taylor Glacier although this relationship could not be a direct surface-to-subsurface one (8.1.2). An indirect relationship is not inconceivable because Iken (1972) correlated melt water and ice velocity over short periods on White Glacier (Axel Heiberg Island, Canadian Arctic), a glacier that is composed mostly of cold ice (Muller 1976). The diurnal variation of the spring did not coincide with (1) earth tides since discharge peaks did not occur consistently later each day, nor with (2) barometric pressure at Vanda Station (Fig. 8.1).

8.2.3 Timing of the discharge events:

The timing of the initiation of discharge events may enable delineation of causes of the discharges, and can be inferred from discharge characteristics and observations at the terminus. The concentration of the discharge brines and air temperatures place constraints on the time of the year during which saline icings develop, and by inference, when the discharge events occur. Since the mean monthly air temperatures in the oasis are colder than -5.5°C from February to November (Appendix 3, Table 2, p.8), the discharges that produced icings must have occurred between mid-February to mid-November (ie autumn to spring, Appendix 3, Table 1). This is significantly different from jökulhlaups because these occur mainly during summer and only occasionally as late as early winter (Liestöl 1956; Marcus 1960; Whalley 1971; Mathews 1973). The periodic jökulhlaup from Grimsvötn, Iceland, occurs sometimes during spring (Nye 1976).

Discharge initiation and duration are estimated from estimations of icing volumes and brine flow rate. Total discharge volume is estimated from icing volume times mean density of the icing (800 kg m^{-3}) all divided by brine density (1080 kg m^{-3}, Appendix 1, Table 16). The brine flow rate measured in November 1976 and October 1978 is assumed to be the mean flow rate for the entire duration of both discharge events. This may be a gross simplification considering the variation in flow rate of jökulhlaups which tends to increase to a maximum then abruptly stop (Whalley 1971; Nye 1976). However, the similarity between brine flow rates in 1976 and 1978 (Table 8.2) and the slow decrease in flow of the spring over nine days (Fig. 8.1) mean that the simplification is justified. Volumes and flow rates (listed in Tables 8.1 and 8.2) give estimates of 50-180 days and 20-130 days for the durations of the 1976 and 1978 events respectively. Hence, these events may have commenced sometime between late May to early October (1976) and early July to early October (1978).

Corroborative evidence for this timing comes from a relationship between the saline icings and a system of recurring annual cracks in the annually-formed moat ice of Lake Bonney, adjacent to the discharge sites (Fig. 8.2). The 1972 icing terminated at the cracks indicating that the icing was younger than the cracks. However, the 1976 icing was fractured by cracks indicating that these were younger than the icing. This suggests that the icing and cracks are formed about the same time.

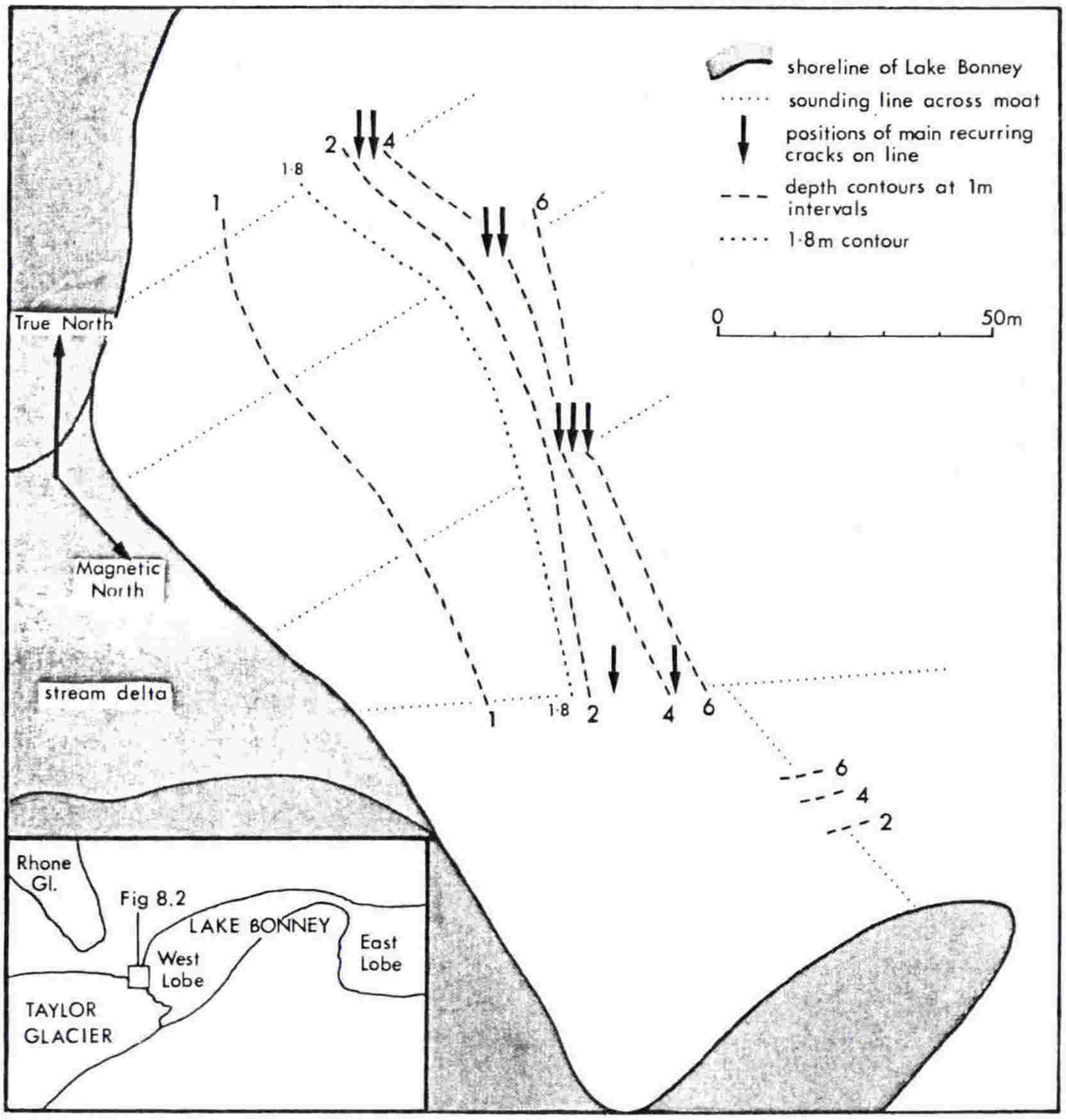

Figure 8.2 Lake depths in the moat of Lake Bonney adjacent to the saline discharge site. Depths measured 18/1/79 using a sounding line from dinghy and annual ice.

The cracks are formed probably between June and October. Figure 8.2 shows that water depth beneath most of these cracks is about 2 to 4 m. Freezing rates of the moat ice of Lake Vanda (Cutfield 1974) suggest that the Lake Bonney moat ice may thicken to 2 to 4 m between June and October. The recurring cracks are believed to develop between these months when tensile and compressive forces accumulate in the ice in this bay (Fig. 8.2, Plate 8.1) and exceed the strength of the ice after this has thickened and frozen to the lake bed. The level of Lake Bonney rose 2.3 m between December 1972 and January 1979 (Chinn 1979, unpublished), but the position of the cracks did not change markedly during that time. This is consistent with the position of a prominent change in slope of the lake bottom at a depth of about two metres (Fig. 8.2). Because of the rapid deepening of the moat at this point the horizontal positions of the 2-4 m depth contours would not have changed by more than a few metres during the measured lake rise. In conclusion, then, the saline discharges probably commence during the period from late May to early October, that is mid-winter to early spring, in contrast to most jökulhlaups.

8.2.4 Orange coloured ice layers, and salt deposits:

Orange coloured ice in basal, englacial and subglacial positions remains in the terminus area after the saline icings have ablated (Plates 8.6, 8.7, 8.8). The basal layers have most significance to the present study.

The basal zone (>2 m thick) of the glacier contains abundant debris (Plate 8.6) that has been entrained, along with occasional orange coloured

Plate 8.6 Salt encrusted debris layers and orange coloured ice in the basal zone of Taylor Glacier, on the south side (locality 35, sample numbers 24827, 76/03I; 23/10/76).

ice, in the glacier by freezing-on (regelation) processes at the bed (Robinson 1979). These processes took place where the temperature, pressure and salt content were such that the ice was at melting point, probably less than one kilometre in from the margin (Robinson ibid); subsequent transport outwards has exposed the debris and the orange coloured layers at the margin. The coloured ice layers occur on both sides of the glacier up to 600 m from Lake Bonney along the north side and 800 m along the south.

Englacial and subglacial orange coloured layers are present at and adjacent to the glacier discharge site. Many of the englacial layers resemble crevasses that have been infilled with brine,direct evidence for such a process being seen in 1976 (Appendix 1, p.38, locality 25). On the glacier surface the layers are near vertical and run sub-parallel to both ice flow and the recurring crevasses at the discharge site (Frontispiece, top, Plates 8.3 A,B). A median septum of bubbles within some layers (Plate 8.7) is a characteristic of frozen crevasse-infillings (Anderton 1967). In several of the layers euhedral crystals of gypsum are present (Sample 76/09B, Appendix 1, Table 4), indicating that the salt crystallized in place (Stephens and Siegel 1969). However, some of the englacial layers may be shear planes or steeply inclined joints that have entrained salts and hydrated iron oxide (Black et al. 1965).

The subglacial layers are exposed as laterally persistent horizontal bands several metres long in the ice-marginal mound (Plate 8.8) and form part of a thick sequence of stagnant ice and basal debris (Frontispiece, bottom) that dips up-glacier beneath the glacier discharge site (Robinson, pers. comm.). From this it is inferred there has been a long record of activity involving salt minerals under Taylor Glacier.

Salt deposits associated with Taylor Glacier are abundant in the terminus area within a distance of 800 m from Lake Bonney (Appendix 1, Fig. 3, Tables 4, 14). Deposits occur most noticeably around the discharge sites. However, salt encrusts all types of orange coloured ice layers early in the season, although the layers themselves have variable salinity, much lower than that of the discharge brines (Appendix 1, Tables 18, 21). Analyses of basal ice from 13.5 to 50 km up-glacier from the terminus (Appendix 1, Table 20) indicate that significant amounts of salt are found in such ice only near the terminus.

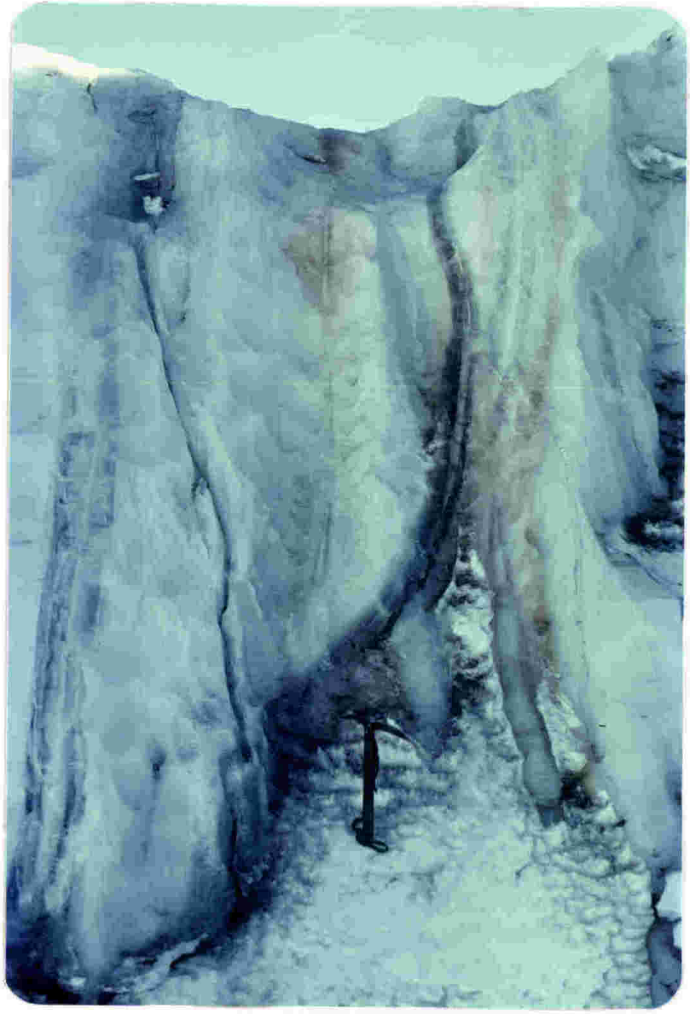

Plate 8.7

Crevasse infillings about 50 m up-glacier from the glacier discharge site. A median septum of bubbles is prominent in each infilling (ice axe for scale, 24/10/76).

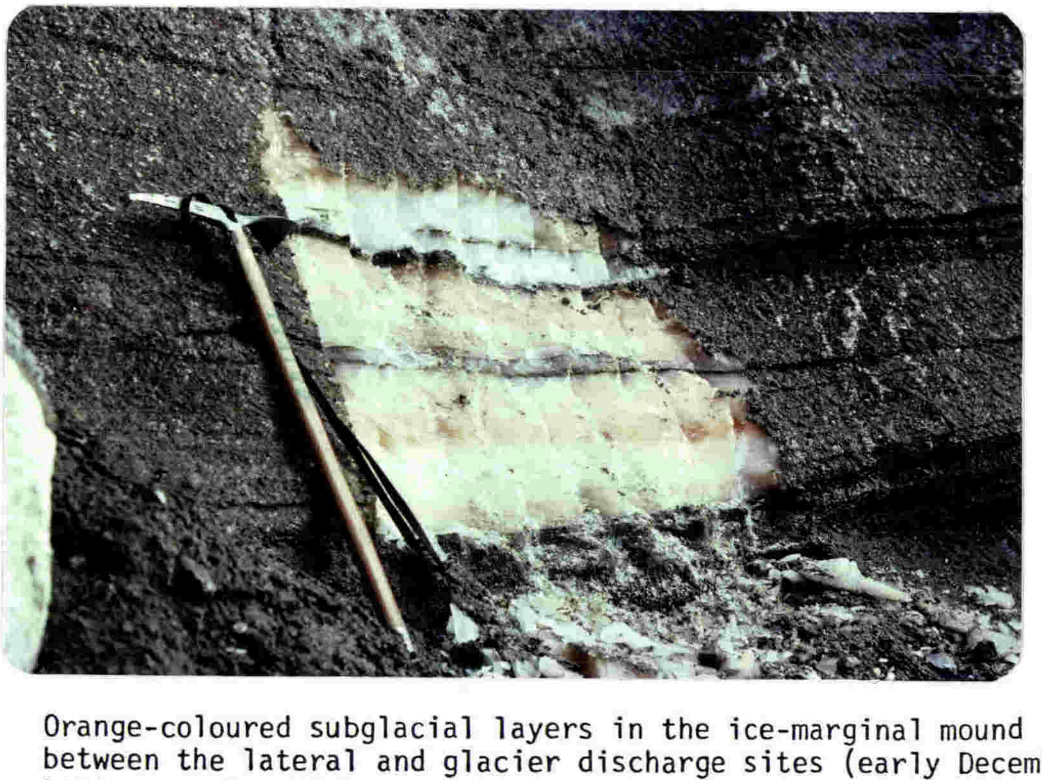

Plate 8.8 Orange-coloured subglacial layers in the ice-marginal mound between the lateral and glacier discharge sites (early December 1976; samples 76/17S and I were taken from locality 19 near here).

The salt composition is similar to that of salt dissolved in the discharge brines. Crystalline phases that have been identified by XRD include halite, gypsum, mirabilite, thenardite, calcite and aragonite. Hamilton et al. (1962) and Black et al. (1965) listed major ion analyses of salts from the 1958 and 1962 icings. These analyses along with reconnaissance analyses of orange coloured salty ice from the terminus area (Appendix 1, Tables 14, 17, 18) show that the salt composition is similar spatially and temporally to that in the discharge brines of 1976 and 1978.

Fractional crystallization and dissolution of phases occurs from brines and salt deposits (Chapter 4, sections 4.4, 4.2); therefore these salts and their analyses are of restricted value for interpreting the original brine or salt deposit that produced them. The discharge brines of 1976 and 1978 provide the most acceptable basis for the interpretation, which is discussed in the following section.

8.3 Composition of Discharge Brines

8.3.1 Composition relative to sea water:

(i) major ions

The ionic composition of brines discharged at Taylor Glacier is similar to that of concentrated sea water. The concentrations of the major ions in the spring and crevasse brines are listed in Appendix 1, Table 15. (Analytical techniques are discussed in Appendix 1, p.4). The ratios of the major cations in the brines, plus Na/Cl and Mg/Cl were very similar to those of sea water (Figs 5.12, 6.2, Table 6.2). Thus, most of the dissolved salt content of the discharge brines is derived from sea water, in some manner.

The precise degree of similarity can be gauged by determining ion enrichment relative to sea water. Enrichment of a particular ion is calculated on a chloride basis here, because Cl^- is the major ion and is usually conserved in migrating brines (4.3.4; Eugster and Jones 1979). Table 8.3 shows that Na^+ and Mg^{2+} are neither enriched nor depleted in the general discharge brine. However, concentrations of other ions are quite different from what they would have been if sea water had been merely concentrated to the observed chlorinity. Ca^{2+} and HCO_3^- have been enriched and K^+ and SO_4^{2-} depleted by some process(es). Fe^{2+} or Fe^{3+} ions appear enriched as well

Table 8.3 Enrichments of ions in discharge brines, relative to concentrated sea water calculated on the basis of chloride concentrations. Enrichment of ion X in sample s is calculated by $\frac{[X_s]}{[X_{sea}]} \times \frac{[Cl_{sea}]}{[Cl_s]}$ from data in Appendix 1, Table 15.

Sea water concentration factor	Sample 76/53A	76/53B	76/72	78/01
(Cl_s/Cl_{sea})	3.04	2.65	2.56	2.32
Na^+	0.97	0.98	0.99	1.03
K^+	0.62	0.59	0.60	0.82
Mg^{2+}	1.1	1.0	1.1	0.99
Ca^{2+}	1.9	1.9	2.0	2.3
Cl^-	1.0	1.0	1.0	1.0
SO_4^{2-}	-	-	0.72	0.71
HCO_3^-	8.0	7.6	8.8	-

(8.2.1). The enrichments calculated for each ion tend to vary slightly from sample to sample, but this variation is probably within analytical error (Appendix 1, Table 15) for all ions except potassium.

The depletion of K^+ has been discussed and attributed to fixation of this ion by clay minerals (4.3.4 ii). The different amounts of depletion, 40 percent in the spring samples but only 20 percent in the crevasse brine are consistent with this. Brine emerging at the spring site was in contact with sediments and clays for a longer period than was the crevasse brine, and therefore, significantly more potassium was removed from the spring brine.

It is likely that processes of dissolution and precipitation affect the concentrations of Ca^{2+}, HCO_3^-, SO_4^{2-} and $Fe^{2+} + Fe^{3+}$ in the brines before they are discharged at the glacier terminus. Ca^{2+} and HCO_3^- are likely to have been enriched after dissolution of subglacial carbonate-bearing rocks. This is an important process under temperate glaciers that override carbonate bedrock (Hallet 1976). Taylor Glacier is presently overriding a marble-rich metasediment belt 150 m wide about three kilometres up-glacier from the terminus (Fig. 1.2). "Limonite-stained calcite" is abundant in the belt comprising up to 30 percent of thin section area in calc-silicate hornfel layers that surround marble cores (Haskell et al. 1965, p.172). An increase in Ca^{2+} (and Fe^{2+} + Fe^{3+}) concentrations by dissolution of such material, may lead to precipitation of gypsum with an associated depletion of SO_4^{2-}.

Reduction of SO_4^{2-} is a mechanism that could possibly account for depletion of this ion. Sulphide species are usually products of such reduction (eg Berner 1971). The major form of dissolved sulphide is hydrogen sulphide at a pH of 6 (Krauskopf 1967) which is the pH of the discharge brines (Appendix 1, Table 16). The characteristic gas was not smelt at the spring, nor were other sulphide species detected in the brines. Therefore, reduction of sulphate has probably not caused the observed depletion of this ion. Note however, a reduction – reoxidation cycle may have occurred in this salt system at some earlier time, as shown by stable isotope analyses of ^{34}S and ^{18}O (SO_4) (6.2.2 ii).

(ii) stable isotopes of the water substance

Stable isotope analyses have shown that the water substance in the discharge brines is derived from melted Taylor Glacier ice not sea water (6.2.4 ii). δD and $\delta^{18}O$ values for spring brines plot between values for (1) Taylor Glacier ice at the terminus (Drewry et al. 1980) and (2) melt water sample 76/54 (δD -291 per mille, $\delta^{18}O$ -37.0 per mille, G.L. Lyon, Institute of Nuclear Sciences, DSIR, written communication 1977; in situ temperature of this water was -0.2°C) from Taylor Glacier below the glacier discharge site (Fig. 6.3). The brine values plot very near the meteoric water trend line; the slight offset from this line is possibly related to fractionation between brine and ice (Lyon, pers. comm.). Therefore, the water is from Taylor Glacier ice.

The isotope analyses indicate that most if not all of the water substance in the original sea water brine was lost before the salt came into contact with Taylor Glacier. The influx of sea water into Taylor Valley has been discussed earlier (6.2.4). Such influx led to trapping of sea water in the drainage basin of Lake Bonney, and in a depression that is now beneath Taylor Glacier. Evaporation from the standing body of trapped sea water would account for the loss of the original water substance.

8.3.2 Gas and iron contents:

Bubbles of gas were evident in the spring brine as it discharged (Plate 8.5). It was not possible to analyse this gas, but the pH (6) of the discharging brine, and the rise in pH after sampling (Appendix 1, Table 16; sample 76/72 had a pH of 7.4 after equilibration with the atmosphere), indicate that considerable carbon dioxide (CO_2) was present. The source of the gas or specifically of this CO_2 is not immediately apparent.

The gas may have come from bubbles in the glacier ice that melted to form the brine. Air trapped in snow falling in the accumulation zone of a glacier ends up as abundant bubbles ($\leqslant$5 mm long) in glacier ice. CO_2 is enriched with respect to atmospheric nitrogen in these bubbles, probably due to chemisorption or physical adsorption of atmospheric CO_2 on the snow (Weiss et al. 1972). These sorption processes act independently of melting, and therefore bubbles in both polar and temperate glaciers contain relatively high concentrations of CO_2. The average CO_2/N_2 ratios in melted ice from 3500 m elevation on Aletsch Glacier, European Alps, were about 50 times as great as in the atmosphere (Weiss et al. 1972). Similar enrichment at Taylor Glacier could account for the CO_2 in the discharge brines.

The degassing of the spring resulted from the change in pressure exerted on the brine as it flowed from beneath the glacier to the surface. Pressure at the base of a glacier is largely dependent on ice thickness (Appendix 5, section A5.1). Interpretation of a gravity survey of Taylor Glacier suggests that the maximum ice thickness within a kilometre of the terminus is about 140-300 m (Stern 1978), which leads to an estimate of $(1.2-2.8) \times 10^6$ pascals (12-28 bars) as the maximum basal pressure in the terminus area (Appendix 5). CO_2, enriched by 50 times in air released from bubbles, would exert a maximum partial pressure of about $(2 \text{ to } 5) \times 10^4$ pascals compared with only 33 pascals in the atmosphere. Such a difference would have accounted for degassing of CO_2 from the spring brine even after most of the brine had been discharged. Active degassing from the crevasse brine was not noticed (Table 8.2) probably because most of the gas pressure had been released inside the crevasse before the brine reached an accessible point.

The presence of goethite in the terminus area (8.2.1, 8.2.4) indicates that the environment under Taylor Glacier favours the mobilization of iron from iron minerals. The mobilization could be due to dissolution of the minerals in the aqueous environment or to reduction of Fe^{III} minerals or to both. The orange colouration due to Fe^{III} in the saline icing takes at least four hours to develop (8.2.1; Frontispieces) which suggests that oxidation of Fe^{2+} by atmospheric oxygen is occurring during this time. Therefore, reduction of Fe^{III} is probably an important subglacial reaction.

A variety of reaction mechanisms involving different iron species may operate but the following is likely to be significant:

$$\underset{\text{goethite}}{2HFe^{III}O_2} \overset{nH_2O}{\rightleftharpoons} \underset{\text{ferric hydroxide}}{Fe_2^{III}O_3.nH_2O} \qquad \ldots 8.1A$$

and for $n \geqslant 3$

$$Fe_2^{III}O_3.nH_2O_{(s)} + 4CO_{2(g)} \underset{\text{oxidizing environment}}{\overset{\text{reducing environment}}{\rightleftharpoons}} 2Fe^{2+}_{(aq)} + 4HCO^-_{3(aq)} + (n-2)H_2O + \tfrac{1}{2}O_{2(g)}$$

$$\ldots 8.1B$$

(Krauskopf 1967; Brown et al. 1970). The metasediment belt three kilometres up from the terminus (Fig. 1.2) contains 'limonite'-stained calcite (8.3.1 i, that is, fine-grained goethite (Krauskopf 1967). Goethite is likely to be released from the calcite (cf Reaction 8.1A) as that dissolves under the high partial pressures of CO_2 beneath the glacier (Reaction 6.8). Furthermore, conditions there favour the production of Fe^{2+} (Reaction 8.1B) because (1) pH is low (<6) due to high P_{CO_2} (Berner 1971; Reaction A5.13), and (2) P_{O_2} cannot be high under a glacier, no enrichment of O_2 being found in bubbles in glacier ice (Weiss et al. 1972). The scheme 8.1 proceeding left to right would represent the mobilization of Fe^{III} beneath Taylor Glacier, whereas the reverse reaction would indicate how colour is developed in the discharge icings. The existence of iron-stained carbonate rocks up-glacier from the terminus, associated with (1) the marked enrichment of Ca^{2+} and HCO_3^- in the discharge brines, the presence of (2) considerable CO_2 in the brines and (3) goethite in the terminus area, together with (4) the slow development of colour due to Fe^{III}, strongly suggests that all are linked through a common subglacial dissolution-redox process such as 8.1.

The only other reports of iron-rich residues in the region are from Miers Valley. X-ray amorphous "iron hydroxides" including limonite occur on the flank of the valley, on the bottom sediment of Lake Miers and on moraine near the lake outlet (Torii et al. 1966, pp. 9, 10). These residues are significant because they occur in an area that has outcrops of marble very similar in appearance to that at Taylor Glacier (Blank et al. 1963; Haskell et al. 1965), further suggesting a link between the residues and the marble.

8.3.3 Solubility relations in the spring brine:

(i) activity coefficients

Precipitation of gypsum and dissolution of marble may have changed the ionic composition of the discharge brines from that of concentrated sea water. This can only be proven quantitatively by determining activity coefficients and hence solubility relations between species in the brines. Activity coefficients can be obtained by calculation, or by analysis using specific ion electrodes. Calculation is used here as it avoids the analytical difficulties associated with concentrated brines (Berner 1971).

There are several methods of calculating activity coefficients in multicomponent aqueous systems. Nesbitt (1980) has reviewed these for sea water brines; the Garrels and Thompson (1962) approach is the best for brines whose ionic strength I is greater than one. This is the method that is used here as it adequately describes ion-ion interaction (complexing) in concentrated brines (e.g. I as large as 6, Polzer and Roberson 1967). The approach calculates a distribution of major dissolved species as the free uncomplexed ions, and those bound up in ion-ion interactions (Appendix 5, section A5.2, Table A5.2). Activity coefficients of the ions can then be obtained, and are shown in Table 8.4.

(ii) gypsum solubility

For a reaction of the type:

$$A_pB_q.nH_2O_{(s)} \rightleftharpoons pA^{q+}_{(aq)} + qB^{p-}_{(aq)} + nH_2O \qquad ...8.2$$

Table 8.4 Total molalities and calculated total activity coefficients for the major species in the spring brine (sample 76/72). Molalities are from Appendix 1, Table 15; activity coefficients from procedure in Appendix 5, section A5.2 and Equation A5.6.

Species	Total molality (m_T)	Total activity coefficient (γ_T) +25°C	-5°C
Na^+	1.11	0.75	0.68
K^+	0.0141	0.57	0.54
Mg^{2+}	0.14	0.28	-
Ca^{2+}	0.050	0.24	0.24
Cl^-	1.30	0.58	0.55
$SO_4{}^{2-}$	0.048	0.033	0.03(3)
$HCO_3{}^-$	0.050	0.31	0.31
H_2CO_3* $CO_{2(g)}$	not determined	1.5	1.(5)
H_2O#	- see below#	-	-

* undifferentiated between $H_2CO_{3(aq)}$ and $CO_{2(aq)}$ (Appendix 5, section A5.3).

( ) indicate uncertainty in coefficient (Appendix 5, section A5.2).

\# The activity of water in a concentrated sea water brine of ionic strength 1.7 is 0.95, and is independent of temperature at this degree of precision (Millero and Leung 1976).

the equilibrium constant K is given by:

$$K = \frac{a_A{}^p . a_B{}^q . a_{H_2O}{}^n}{A_pB_q.nH_2O} \qquad ...8.3$$

where a_i is the activity of species i. If $A_pB_q.nH_2O$ is a pure solid salt phase its activity is approximately unity and is independent of ionic strength. Equation 8.3 reduces to:

$$K_s = a_A{}^p . a_B{}^q . a_{H_2O}{}^n \qquad ...8.4$$

where K_s is the ion-activity solubility product for the phase.

The actual product of ion activities in a brine may not equal K_s. This ion-activity product IAP for the salt phase is given by:

$$IAP = m^p_{TA} \cdot \gamma^p_{TA} \cdot m^q_{TB} \cdot \gamma^q_{TB} \cdot a_{H_2O}{}^n \qquad ...8.5$$

where m_{Ti} is the total (analytical) molality of species i
γ_{Ti} is the total (calculated or analytical) activity coefficient of species i.

The following relationships show the state of saturation of a brine with the particular salt phase:

$IAP > K_s$, the brine is supersaturated with the phase
$IAP = K_s$, the brine is saturated with the phase
$IAP < K_s$, the brine is undersaturated with the phase

Ion activity products for salt phases in the spring brine are obtained by Equation 8.5 from values in Table 8.4. These IAPs are compared with solubility products of the phases at the standard thermodynamic temperature in Table 8.5, which shows that the spring brine was undersaturated with the sodium and potassium phases by one to five orders of magnitude. Depletion of potassium by precipitation of one of its phases did not occur.

The in situ spring brine was saturated or close to saturation with gypsum. Just how close can be gauged by considering data at -5°C. At this temperature the value of the ion-molal solubility product $m_{TCa^{2+}} \times m_{TSO_4{}^{2-}}$ in 1.7 molal NaCl solution is 2.1×10^{-3} (Marshall and Slusher 1966). This solution is a good representation of the spring brine since that brine was mostly composed of Na^+ and Cl^-. The ion molal product (analogous to IAP) of gypsum in the spring brine was 2.4×10^{-3} (from Table 8.4). The closeness of these two values suggests that the in situ spring brine was saturated with gypsum. Therefore, it is concluded that gypsum was precipitated from the salt-brine system under Taylor Glacier and that this precipitation was the cause of the depletion of SO_4^{2-} from that expected for concentrated sea water (Table 8.3).

(iii) calcium carbonate solubility

The solubility of calcium carbonate at Taylor Glacier may be governed by the equilibrium:

$$CaCO_{3(s)} + CO_{2(g)} + H_2O \rightleftharpoons Ca^{2+}_{(aq)} + 2HCO^-_{3(aq)} \qquad ...8.6$$

(Reaction 6.8). The equilibrium constant K_c is given by:

$$K_c = \frac{a_{Ca^{2+}} \cdot (a_{HCO_3^-})^2}{a_{CO_2} \cdot a_{H_2O}} \qquad ...8.7$$

assuming as before that $CaCO_3$ has unit activity. Reaction 8.6 and K_c are temperature, pressure and solute dependent, although only the temperature dependence is considered here as a first approximation. K_c is evaluated for in situ conditions in Appendix 5, section A5.3 and found to have a value of 5.4×10^{-6} at -5°C (cf 1.5×10^{-6} at +25°C, from Berner 1971). Rearranging and expanding Equation 8.7 gives:

$$m'_{THCO_3^-} = \frac{1}{\gamma_{THCO_3^-}} \cdot \left[\frac{K_c \cdot \gamma_{CO_2} \cdot P_{CO_2} \cdot a_{H_2O}}{\gamma_{TCa^{2+}} \cdot m_{TCa^{2+}}}\right]^{\frac{1}{2}} \qquad ...8.8$$

where $m'_{THCO_3^-}$ is the expected analytical molality of HCO_3^- at equilibrium under the conditions experienced by the spring brine; and P_{CO_2} is the partial pressure of CO_2 in equilibrium with the brine and has been estimated (8.3.2) to be in the range (2 to 5) x 10^4 pascals (0.2-0.5 bars) beneath Taylor Glacier. Evaluation of Equation 8.8 from known quantities (Table 8.4) and at different pressures gives various equilibrium concentrations of bicarbonate ion (Table 8.6).

Table 8.5 Solubility relations at +25°C for some salt phases in the spring brine.

Phase	Ion activity product in the brine	Solubility product* K_s
NaCl	6.28×10^{-1}	3.64×10^{1}
$Na_2SO_4.10H_2O$	6.57×10^{-4}	2.99×10^{-2}
$NaHCO_3$	1.3×10^{-2}	3.07×10^{-1}
KCl	6.06×10^{-3}	8.98
K_2SO_4	1.02×10^{-7}	2.0×10^{-2}
$CaSO_4.2H_2O$	1.7×10^{-5}	2.4×10^{-5}

---

*calculated from standard free energies in Berner (1971) and Weast (1971).

Table 8.6 Equilibrium concentrations of bicarbonate $m'_{THCO_3^-}$ calculated for various partial pressures of carbon dioxide at -5°C, using Expression 8.8 (cf. analytical molality 0.050).

Maximum ice thickness (m)	Total pressure (pascals)	Total pressure (bars)	Partial pressure of CO_2 (bars)	Equilibrium concentration of HCO_3^- (moles kg^{-1})
300	2.8×10^6	28	0.5	0.05(8)
140	1.2×10^6	12	0.2	0.03(7)
-	1×10^5 (atmospheric pressure)	1	0.00033	0.001(5)

Dissolution of carbonate-bearing rock material and gaseous CO_2 beneath Taylor Glacier were the cause of the marked enrichment of bicarbonate and calcium ions in the spring brine (Table 8.3) over that expected in concentrated sea water. The analytical molality of HCO_3^- in the brine (0.050) is similar to that expected at high partial pressures of CO_2 in equilibrium with a brine in contact with solid $CaCO_3$ (Table 8.6). Therefore, Reaction 8.6 is probably a good description of the way in which HCO_3^- and Ca^{2+} are enriched in the discharge brines. Since $CaCO_3$ is only sparingly soluble (Table 4.1) the reaction would take some weeks to approach equilibrium; thus, the brine and carbonate rock are probably in close contact for at least some weeks before the brine is discharged at the surface.

Calcium carbonate is precipitated from the discharge brines and collects in and on the saline icing (Appendix 1, Table 4). Table 8.6 shows why this is so. High concentrations of HCO_3^- cannot exist at equilibrium with atmospheric CO_2 and therefore, the brines are supersaturated with $CaCO_3$ when they reach the surface; accordingly, $CaCO_3$ then precipitates. The polymorph favoured, calcite or aragonite, depends on ambient conditions including the concentrations of Mg^{2+}, Na^+ and Sr^{2+} as well as the rates of CO_2 loss and salt precipitation (6.4.1). Post-deposition conditions such as flushing with melt water may transform the metastable aragonite to calcite.

8.4 A Model for the Discharge

8.4.1 The model and previous hypotheses:

A four-step model is proposed here that accounts for the phenomenon involving salts, in particular the discharge of salty water, at the terminus of Taylor Glacier.

(1) Sea water entered the Lake Bonney drainage basin including a depression that is now beneath Taylor Glacier.

(2) The sea water subsequently evaporated to dryness or near dryness during a period(s) of aridity at a time when Taylor Glacier terminated several kilometres further west than it does now. A salt deposit dominated by sodium chloride was formed in the depression.

(3) Taylor Glacier then advanced across the salt deposit which is now causing the basal ice in contact with it to melt.

(4) The resulting brine is impounded in the depression until some instability in the brine-ice system causes release of the brine through

subglacial or sub-bed conduits, and through crevasse conduits in the case of discharges from the glacier discharge site.

Other ways of creating a subglacial salt deposit can be conceived but do not explain the composition of the discharge brines. Sea water could have partially floated Taylor Glacier allowing the water access to a subglacial depression. This water could then have been concentrated by freezing at the base of the glacier. However, the $\delta^{18}O$ isotope content of the brine would then be similar to sea water or at least much less negative than its measured value of -39 per mille (Fig. 6.3). Alternatively, the salt could have been deposited by freeze-concentration not evaporation. However, this would have produced large amounts of sodium sulphate for which there is no evidence in the discharge brines.

Models involving melt waters, cryostatic recycling of lake water, and flushing of salts from a subglacial sedimentary basin by melt water have been proposed for the discharges and icings. However, neither individually nor collectively have these models been able to fully explain the character of the saline discharges.

Hamilton et al. (1962) supposed that melt water mainly from Rhone Glacier produced the 1958 icing seen in December of that year. In order to explain the restricted location of the icing, the flow would necessarily have been mainly subterranean, similar to melt water that supplied a fresh water spring 150 m west of the lateral discharge site in January 1978 (Robinson, pers. comm.; Appendix 1, locality 30, Fig. 3 and p.41, bottom). However, the $\delta^{18}O$ content of melt water from Rhone Glacier (-34 per mille, Hendy et al. 1977) is different from that of the discharge brines (-39 per mille). Furthermore, there is insufficient salt in englacial, basal and subglacial layers of Taylor Glacier and in melt water from Rhone and Taylor Glaciers to account for the high salinity of the saline icing (Appendix 1, Tables 18, 19).

A model of cryostatic recycling of water from Lake Bonney was proposed by Black et al. (1965). They suggested that cryostatic pressure, analogous to that involved in pingo formation, is developed during the refreezing of the annual moat around the perennial ice of the lake. However, it is difficult to envisage how water pressure in Lake Bonney could be sufficient to raise an average of 1500 m^3 a^{-1} (1.5 x 10^6 litres a^{-1}) of brine to a height of 20 m and not produce leaking through cracks in the moat ice or crevasses adjacent to the moat. Moreover, the composition of the lake water is different from that of the discharge brines (Fig. 6.2, Table 6.2).

Flushing of soluble salts from an ancient sedimentary basin by basal melt water was proposed by McGinnis (1968). The salts were believed to be derived from sedimentary rocks beneath the glacier. Although Beacon sediments probably occur beneath Taylor Glacier to the west of Kennar Valley (Calkin 1974; Robinson 1979), they do not contain sodium chloride (Fig. 5.10) or significant amounts of other salts (6.3.3). Therefore, the salts in the discharge brines cannot have come from such a source. Glacial sediment exists beneath the glacier and is probably entrained at the bed from bedrock (Robinson 1979), and so it too is unlikely to contain chloride salts. Similar glacial sediment cored by Dry Valley Drilling Project in eastern Taylor Valley does not contain large amounts of salt (Harris and Mudrey 1974; Chapman-Smith 1975; McKelvey 1975): the maximum salt content in 1:5 extracts of core samples from DVDP 8-10 is about one percent by weight (Ugolini et al. 1979), an order of magnitude less than that of the discharge brines. Probably insufficient quantities of salt exist within sediments beneath Taylor Glacier to verify McGinnis' hypothesis.

Stable isotopes indicate that water in the discharge brines has come directly from Taylor Glacier ice. There is no evidence for an oxygen shift by isotopic exchange with subsurface minerals such as might be expected for connate or other ground waters (White 1957). The isotope content of the brine distinguishes its source from that of ground water discharging into Don Juan Pond; that ground water has a $\delta^{18}O$ value of -16 per mille (Kato et al. 1979).

8.4.2 Location and extent of the salt deposit:

The location of the salt deposit inferred beneath Taylor Glacier can be defined reasonably well. The northern and southern extensions of the deposit can be roughly delineated by tracing the ice flow lines up-glacier from the western-most known exposures of orange coloured ice and salt in the basal layers along the ice margin (8.2.4; Fig. 8.3A). The direction of ice flow has been determined by pole movement surveys on the surface of the glacier, by pebble orientations in the basal ice (Robinson 1979) and from vertical aerial photographs (US Navy). The northern extension of the subglacial salt is probably closer to the ice margin than indicated by

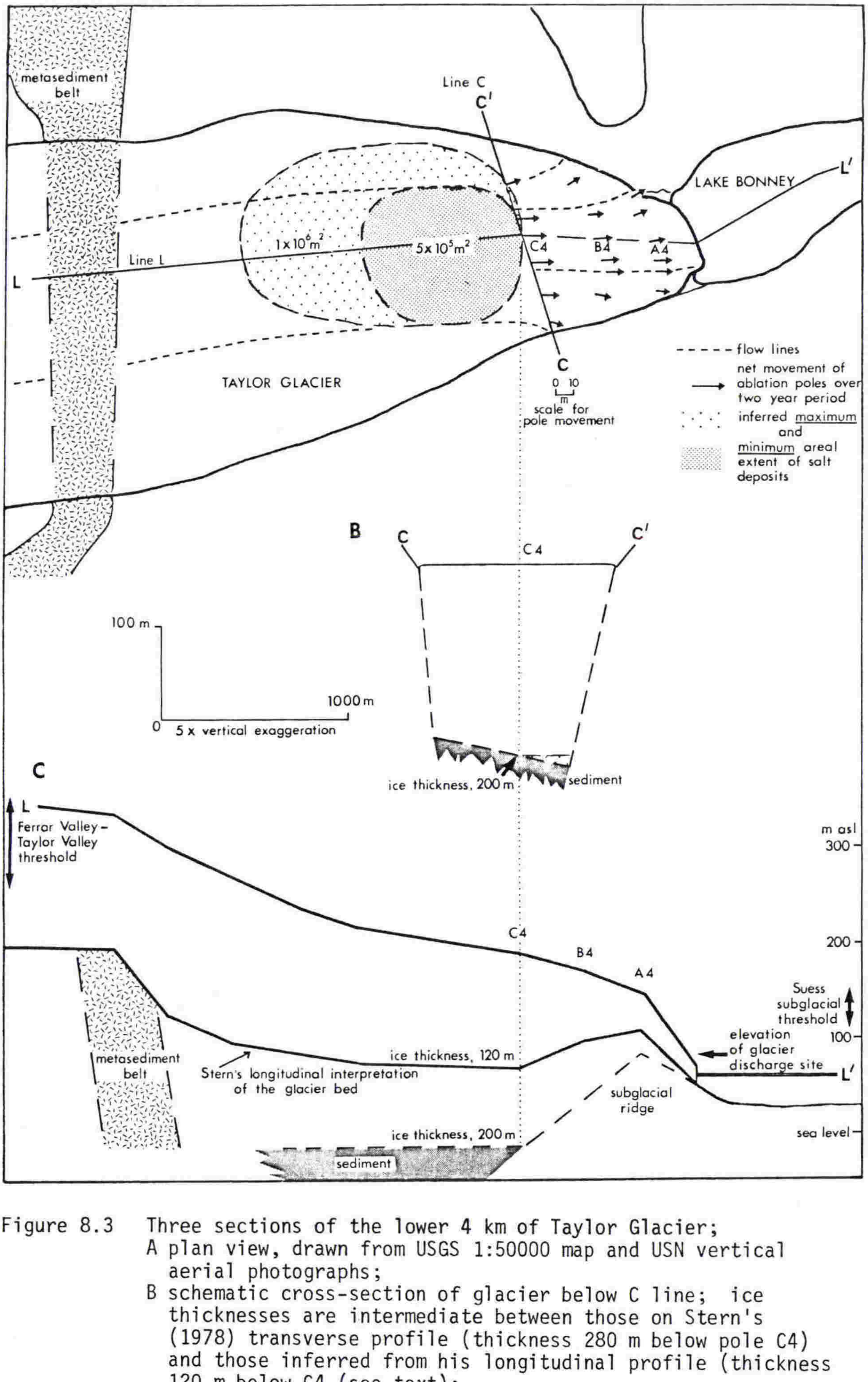

Figure 8.3 Three sections of the lower 4 km of Taylor Glacier;
A plan view, drawn from USGS 1:50000 map and USN vertical aerial photographs;
B schematic cross-section of glacier below C line; ice thicknesses are intermediate between those on Stern's (1978) transverse profile (thickness 280 m below pole C4) and those inferred from his longitudinal profile (thickness 120 m below C4 (see text);
C longitudinal section, drawn from USGS 1:50000 map, Stern's longitudinal profile, and Hendy *et al*. (1977).

the western-most exposure of coloured ice because of the asymmetry of the valley (Fig. 8.3B); relatively little debris-laden basal ice is exposed along the northern margin (Robinson 1979) suggesting that basal orange coloured layers there are mostly obscured.

The maximum up- and down-glacier limits of the deposit are defined by Stern's (1978) longitudinal interpretation of a gravity survey of Taylor Glacier which shows a distinct subglacial depression within three kilometres of the snout (Fig. 8.3C). The discharge brines have been in contact with iron-stained carbonate rocks for probably some weeks before being discharged (8.3.2, 8.3.3 iii). These rocks occur in situ in the metasediment belt (Figs 8.3A, C), and in glacial drift to the east of that belt; no exposures of these rocks are known to the west of the belt. Therefore, the subglacial brine source is down-glacier of the belt.

An estimate of the areal extent of the deposit can be made from the maximum and minimum limits defined above. A small area (5×10^5 m^2) may be defined by the known exposures of coloured ice and the deepest part of the longitudinal profile (Fig. 8.3A). A large area (1×10^6 m^2) is defined by a longer section of the longitudinal profile and the transverse profile (line C), with a small but arbitrary area to the east of line C (Fig. 8.3B) to allow for valley asymmetry.

Accurate delineation of subglacial topography is not possible owing to the lack of data. Stern's (1978) interpretation of the sub-ice profiles beneath lines L and C (Fig. 8.3A) assumed (1) a one (ice-) layer model that extended infinitely in a direction perpendicular to the profiles, and (2) no regional gradient of gravity. The finite distance (less than 1.3 km) to the glacier margin and a large east-west regional gradient of gravity (Stern 1978) affect the longitudinal interpretation most significantly. Therefore, the thickness of the ice below pole (and gravity station) C4 is probably closer to 280 m than 120 m, these being the thicknesses determined for profiles C-C' and L-L' respectively.

However, even 280 m is unreliable because a layer of sediment probably underlies the ice in the depression (Fig. 8.3B,C). Stern (1978) required a thickness of up to 600 m of sediment beneath Taylor Glacier to the south and west of Kukri Hills to account for the difference between his gravity anomaly and Calkin's (1974) ice depth obtained by radio echo sounding. Furthermore, there is more than 320 m of sediment in eastern Taylor Valley

(McKelvey 1975). Stern's interpretation of gravity near the snout of the glacier could not incorporate a layer of sediment because there is no ice depth control near the snout. The probable density of this assumed layer is between that of ice and bedrock and means that ice thickness is less than 280 m below C4. A compromise thickness of 200 m is shown on Fig. 8.3C; Fig. 8.3B is Stern's transverse profile recalculated to 200 m below C4.

The existence, position and height of the subglacial ridge (or high) beneath the glacier at poles A4 and B4 are significant because the ridge represents the down-glacier end of the subglacial depression. This ridge is probably composed of bedrock more resistant to glacial erosion similar to Bonney Riegel nearby (Fig. 8.4). The ridge probably trapped sea water in the depression during a sea water influx(es) and presumably now permits brine to be impounded beneath the glacier. The actual height of the ridge is uncertain due to the lack of good ice bathymetry but the elevation of a low point (or col) in it may be the control on the elevation (80 m asl) of the glacier discharge site. This elevation, Stern's interpretation of the elevation below pole A4, and the elevation of the Suess subglacial threshold (6.2.4 ii) are all shown on Fig. 8.3C. There is no indication that the lowest point of the subglacial ridge is higher than the Suess threshold.

8.4.3 Formation of the deposit:

The salt deposit inferred beneath Taylor Glacier was formed after a sequence of events and climatic conditions. Sea water entered the Lake Bonney drainage basin less than 0.1 Ma BP (Fig. 8.4A). This influx probably occurred as Ross Ice Shelf thickened and advanced into eastern Taylor Valley, possibly between 21000 ^{14}C years and 50000 years ago (6.2.4 iii). The water subsequently evaporated to a concentration where sodium chloride was precipitated during a time(s) of aridity when Taylor Glacier was at least 2-7 km shorter than now. Salt deposits were formed in both the present subglacial depression up to two kilometres west of the present terminus, and East Lobe of Lake Bonney (Fig. 8.4B). Little or no melt water from Taylor Glacier can have been entering the Bonney basin at this time, since arid conditions prevailed in the basin, suggesting that the glacier was then west of the western threshold to the basin, that is, at least about seven kilometres west of the present terminus (from Stern 1978). There is no salt deposit in West Lobe (Hendy et al. 1977) which implies that a connection

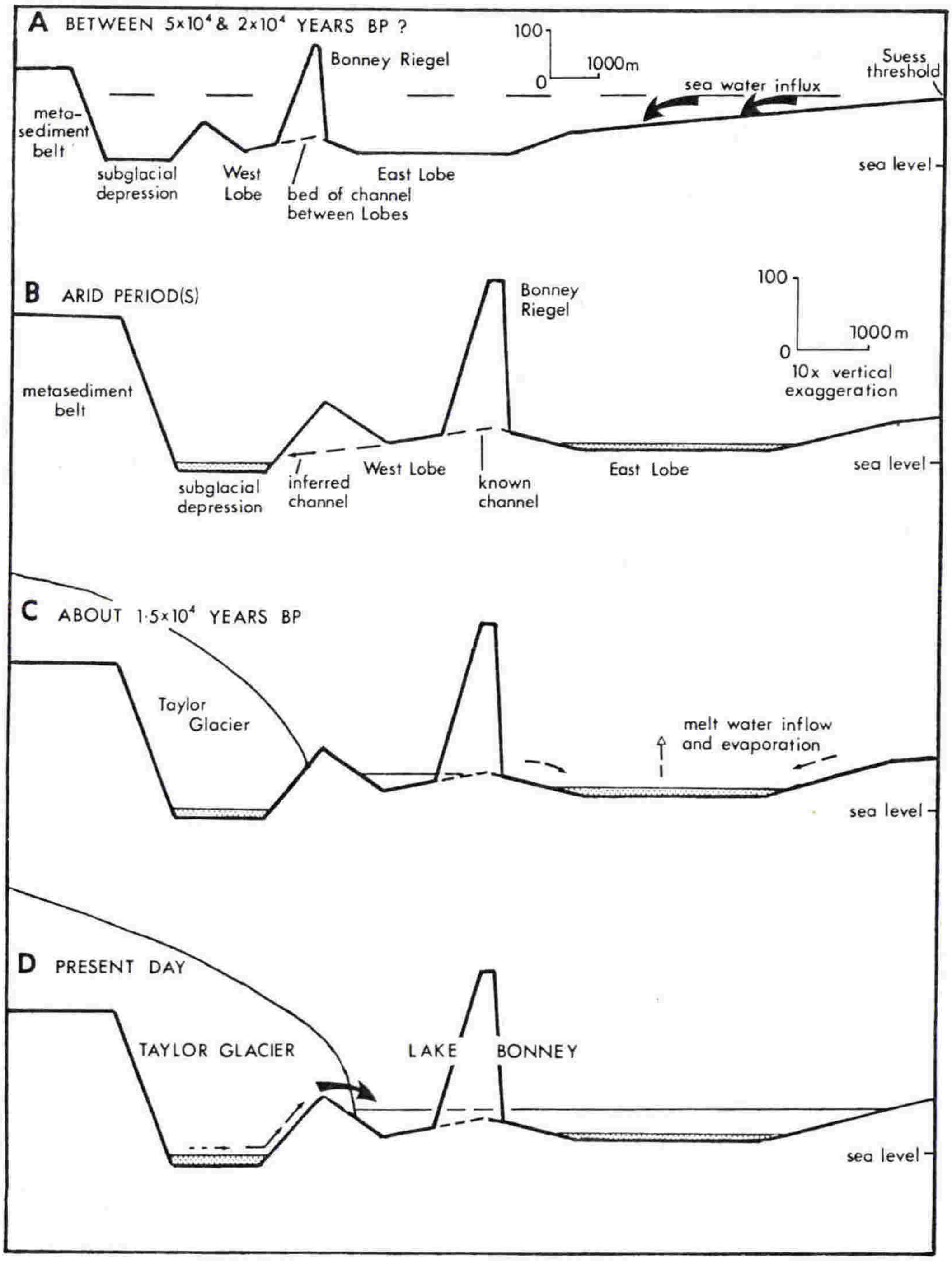

Figure 8.4 Longitudinal section through drainage basin of Lake Bonney:

A Sea water influx(es);
B Evaporation to dryness or near dryness;
C Advance of Taylor Glacier and development of a lake in West Lobe;
D Present day situation with saline discharges.

existed between West Lobe and what is now a subglacial depression, and allowed the salt water to drain out of West Lobe (G. Claridge, pers. comm.). The subglacial depression, therefore, is an ancient lobe of Lake Bonney and may contain a similar amount of salt as does the East Lobe of the lake, that is about (1-2) x 10^{10} kg (from Hendy et al. 1977).

The arid conditions associated with the precipitation of sodium chloride may have occurred both before and after the culmination of Ross Glaciation I (and the full-bodied stage of Glacial Lake Washburn, 17000-21000 ^{14}C years BP, 6.2.4 iii). Hendy et al. (1979) found no evidence for large lakes in Bonney basin existing between about 20000 and 70000 years BP, and little evidence for lakes during the periods 0.13 to 0.18 Ma BP and 0.22 to 0.3 Ma BP. These lake-free periods match global cool periods (Shackleton and Opdyke 1973) quite closely (Hendy et al. 1979). The most recent global cool period extended from about 30000 to 13000 years BP (Shackleton and Opdyke 1973), and thus, the period 30000 to 20000 years BP was probably effectively lake-free in Bonney basin. Presumably, such arid conditions would have led to precipitation of sodium chloride from injected sea water brine.

After the culmination of Ross I, the level of ice-dammed Lake Washburn tended to drop from a high of 308 m asl. The level had dropped to 205 m asl by about 18000 ^{14}C years BP, and to 116 m asl in Bonney basin by about 16500 ^{14}C years ago (Kellogg et al. 1980); by now Suess threshold was exposed, isolating the lake in Bonney basin. West Lobe was apparently dry or nearly dry before a further 1000 ^{14}C years had elapsed (Hendy et al. 1977). Therefore, sodium chloride was probably precipitating in the ancient lobe and East Lobe, sometime between about 16000 and 15000 years ago.

Aspects of the more recent history of both the subglacial salt deposit and Taylor Glacier can also be inferred. Melt water from Taylor Glacier flowed into a dry or near-dry West Lobe about 15000 years ago (Hendy et al. 1977) (6.2.4 iii). By this time the glacier had probably advanced sufficiently to dam this water (Fig. 8.4C). If it had not then the present subglacial lobe would also have been filled with water which would have been pushed out of the lobe as the glacier advanced across it. This expelled water would have probably destroyed the 15000 year old diffusion cell in West Lobe, which did not happen. Therefore, Taylor Glacier must have advanced across the subglacial salt deposit by about 15000 years BP, and has advanced up to a further kilometre or so since then. During this time East Lobe has experienced inflow of melt water, overflow from West Lobe and probably intermediate dry or near-dry stages (Hendy et al. 1977).

8.4.4 Salt and heat balance - feasibility of the model:

Saline discharge events may have been occurring for 15000 years or so. This represents a total output of 2 x 10^9 kg of salt at the average rate of 1 x 10^5 kg a^{-1} (calculated for discharges over the last 10 years, Table 8.1). Clearly, such an extrapolation can be no more than a guide to show that there is sufficient salt beneath the glacier for the discharge process to be feasible even after 15000 years. Certainly, the amount is small compared to (2-3) x 10^{10} kg of salt, which is the amount calculated by Hendy et al. (1977) to be in a volume of sea water equal to that hypothetically impounded behind the Suess threshold (3.6 x 10^{10} kg) less the 1-2 x 10^{10} kg known to be in East Lobe. In fact, the subglacial salt may account for the difference between Hendy et al's two estimates.

It is more difficult to determine whether the discharge process is thermally feasible. The average discharge of brine over the last ten years is about 1500 m^3 a^{-1} (Table 8.1) representing 1.5 x 10^6 kg of melted ice. This requires 3.33 x 10^5 Joules kg^{-1} (Smithsonian Inst. 1954) or 5.0 x 10^{11} Ja^{-1} to melt. The heat of solution of the salt can be neglected here because it is small (less than 7 x 10^4 J kg^{-1} of sodium chloride, Weast 1971, or less than 1 x 10^{10} Ja^{-1}). For the discharge process to be thermally feasible there must be a positive heat balance equivalent to this requirement at the base of the glacier in the subglacial depression.

The heat balance at the base of a glacier depends on geothermal heat flow, ice thickness, surface temperature, ice velocity, presence and amount of melting or freezing of the ice, subglacial water movement, and the amount of heat produced by sliding friction and internal deformation. The balance at a point on the bed below line C is given by:

$$Q_g + Q_d = Q_b + Q_m \qquad \ldots 8.9$$

(Appendix 5, Fig. A5.1) where

Q_g is the geothermal heat flow in McMurdo oasis*, 8.8×10^{-2} Jm^{-2} a^{-1} (Decker and Bucher 1977)

Q_d is the heat produced by internal deformation $\doteqdot 7.3 \times 10^{-3}$ Jm^{-2} s^{-1} below line C (Robinson 1979)

Q_b is the heat flow into the glacier base

Q_m is the heat available for melting ice

assuming that; (1) frictional heating at the base and sides of the glacier, and (2) the horizontal component of ice velocity (5 m a^{-1} at the surface) have negligible effects (Robinson 1979).

The basal temperature and basal temperature gradient must be known before Q_b can be obtained. Robinson derived a modification of Robin's (1955) equation (see Appendix 5, section A5.5) to calculate the basal and englacial temperature regime; basal temperatures were assumed to be at the pressure melting point of salt-free ice (c. 0°C), or colder in which case no basal melting was possible. However, the presence of salt in the subglacial depression means that basal ice can be melting at colder than 0°C. The coldest temperature at which brine can exist in the subglacial salt system is similar to the eutectic temperature of sea water, -54°C (Thompson and Nelson 1956). This is much colder than the mean annual air and surface temperatures in the area, which are around -20°C (Appendix 3, Tables 8, 9).

The in situ temperature of the discharge brines (-5.5°C) provides an estimate of basal temperatures in the subglacial depression. The temperature of the spring brine did not change significantly over 10 days and the freezing point of this brine was the same as the in situ temperature of the crevasse brine (Table 8.2). The crevasse brine was in equilibrium with ice (8.2.2), suggesting that the brines had reached equilibrium with their sub-ice conduits and reflected basal temperatures. If they had not reached equilibrium then they would have cooled with time, because the glacier ice and frozen sediments were colder than -5°C at the surface (Table 8.2). Such cooling was not noted, suggesting that the discharge brines reflected basal temperature at their point of origin, namely the subglacial depression below line C.

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*Decker and Bucher measured the geothermal gradient in DVDP 6, Lake Vida, through granitic rock. Such rock also underlies Taylor Glacier suggesting that the heat flow beneath it is similar to that at Vida, especially since Decker and Bucher explained the high heat flow by a regional-convective model (Robinson 1979).

Heat flow below line C can now be estimated. The temperature difference, between the mean annual surface temperature (-17°C, Appendix 3, Table 8, p.22) and the basal temperature, is assumed to be 11.5°C. The basal temperature gradient representing the basal heat flow Q_b required to produce this temperature difference at line C is calculated from Robinson's equation (Appendix 5, Equation A5.17) and is given in Table 8.7 for two ice thicknesses. Subtracting Q_b from(Q_g plus Q_d)(Equation 8.9) gives the amount of heat Q_m available for melting ice per square metre of contact between the glacier base and the salt at its bed. The heat available is positive, and the total area of salt-ice contact required to balance the heat flow by Equation 8.9 quite reasonable (Table 8.7); furthermore, these areas are similar to those shown on Figure 8.3A. Therefore, the saline discharge process appears to be thermally feasible, assuming that no other subterranean water or brine flows out of the subglacial depression. Melting and refreezing of other water or brine may occur but must be confined to the subglacial depression.

8.4.5 Subsurface brine movement , drainage and release mechanism of the discharge:

Water movement at the bed of a glacier has been discussed by Weertman (1972), Robin and Weertman (1973) and Nye (1976) (and others), who showed how water at the bed of glaciers could move up hill towards areas of lower hydrostatic pressure. The slope of a glacier surface is roughly 10 times more effective than the bed slope in directing the flow of water (Nye 1976). The surface slope between poles A4 and C4 on Taylor Glacier is about 5° (USGS 1:50,000 map) whereas the bed slope is about 8° in the opposite direction (Fig. 8.3C). Because of glacier thinning, the hydrostatic pressure gradient at the bed below C4 is greater than that below A4. This pressure gradient could force the brine, formed by melting in the bottom of the subglacial depression, to flow up the western side of the subglacial ridge (Fig. 8.4D). Such movement could occur so long as basal ice remained at the melting point and sufficient pressure existed to force the brine upwards.

The depth of brine impounded and the average cross-section area of the drainage path cannot be great. The average annual volume of brine discharged ($1500\ m^3\ a^{-1}$) divided by the estimated area of subglacial salt ($0.5 - 1x10^6\ m^2$) suggest that the impounded brine may form a layer as thin as 1-3 mm in a subglacial 'reservoir' between ice and salt. Local deepening could occur

Table 8.7 Heat flow at the base of Taylor Glacier below line C, and the area of salt-ice contact required for basal melting to balance it.

Ice thickness H (m)	Temperature gradient in basal ice(1) (°C m^{-1})	Heat flow into basal ice(2) Q_b (J m^{-2} s^{-1})	Heat Q_m available for melting ice(3) (per unit area of salt-ice contact) (J m^{-2} s^{-1})	(J m^{-2} a^{-1})	Area required to melt ice for saline discharge(4) (m^2)
200	3.7×10^{-2}	8.4×10^{-2}	$+1.2 \times 10^{-2}$	$+3.7 \times 10^{5}$	1.4×10^{6}
300	2.2×10^{-2}	4.9×10^{-2}	$+4.6 \times 10^{-2}$	$+1.5 \times 10^{6}$	3.4×10^{5}

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(1) from Appendix 5, Equation A5.17.

(2) temperature gradient in basal ice times thermal conductivity of ice (thermal conductivity equals 2.26 J m^{-1} s^{-1} °C^{-1} at -5.5°C, Cameron and Bull 1962).

(3) $Q_m = Q_g + Q_d - Q_b$ from Equation 8.9.

(4) Area = average annual mass of ice that is melted to form the saline discharge (1.5×10^6 kg) times latent heat of ice (3.33×10^5 J kg^{-1}), all divided by Q_m, assuming that no other movement of subglacial water/brine takes place into or out of the subglacial depression.

but such a generally thin layer of brine cannot be discharged rapidly, consistent with the estimates of event duration made earlier (1-6 months, 8.2.3). Estimated discharge at the discharge sites was about 0.5 l s^{-1} (5×10^{-4} m^3 s^{-1}) and flow velocity less than 0.1-0.2 m s^{-1} consistent with slow release of brine at least during the latter stages, and probably during most of an event.

Discharge always occurs from one or both of two places (crevasse or lateral site) on the north side of the terminus. This implies that the brine flows in a permanent channel or narrow bedrock defile, such as might exist along the northern side of the subglacial ridge due to valley asymmetry (Fig. 8.3B). The same channel may once have allowed water from the West Lobe of Lake Bonney to drain westwards (Fig. 8.4B) but is now cut off, presumably with glacier ice frozen to the channel sides and bottom. The lower part of the brine drainage course is divergent. Part extends through some kind of permeable sub-ice material to emerge beside the glacier. High electrical resistivity measured around the snout of the glacier by McGinnis and Jensen (1971) has been interpreted as indicating the presence of permeable permafrost. Crevasses in the snout provide conduits for brine flow through the cold 'impermeable' ice at the glacier margin.

Glacier ice and the sides of the subglacial depression impound the brine beneath the glacier preventing a continual slow discharge. Recurrent discharge sites and aperiodic discharge suggest that the point of damming is beneath the glacier and is not due to the annual freeze-up of the active layer at the surface during autumn and early winter. Impounding can occur for more than one reason. Freezing of the glacier to its bed towards the margins establishes an impermeable seal preventing further subglacial drainage, and overburden pressure may exceed hydrostatic pressure thus blocking subglacial and englacial channels.

It is difficult to determine the underlying mechanism leading to release of the impounded brine in the form of aperiodic saline discharges. Similarly, the cause of drainage of ice-dammed lakes in general is not always readily defined. Aperiodic release may be caused by: changing ice velocity, stress patterns, mass balance, thickness and shape; limnological changes including water temperature, salinity, volume and hydrostatic head; and to changes related to climate such as precipitation (Liestöl 1956; Whalley 1971; Mathews 1973). Records of most of these are lacking at Taylor Glacier.

Climate has little direct effect at Taylor Glacier because the ice is too thick even for extreme seasonal events to penetrate to the bed. There is no evidence for explosive release, such as might leave ice blocks incorporated in the saline icing. Mechanisms relying on flotation, or merely build-up to a critical hydrostatic pressure, are not likely as they would produce a marked periodicity, as they do elsewhere (Thorarinsson 1953; Marcus 1960).

The most likely release mechanism may be a melting process that is influenced by glaciological variations including changing stress patterns. Similar processes have been discussed by Liestöl (1956), Whalley (1971) and Mathews (1973) for aperiodic jökulhlaups. Saline brines, much warmer than impounding ice may melt through an ice barrier. An initial leak need only be a thin space or narrow fracture; melting could soon enlarge such a passage giving access to a permanent subglacial channel such as a narrow boulder-filled defile or crack. A narrow drainage channel cleared of ice during one event, should start to be filled by glacier flow in the following year. However, the occurrence of paired events (Table 8.1) suggests that this infilling is not completed before the second of the pair is released. After that event, the subglacial reservoir may be substantially depleted allowing time for more complete establishment of an ice barrier. Such behaviour could account for the discharge record of the last nine years.

The broadly seasonal regularity that is apparent in discharges may be related to glacier movement and associated release of stress. Discharges occur in winter and spring (8.2.3), during which time a system of ice-push (pressure) ridges or arcuate folds are formed most years (or every year) in the moat ice of Lake Bonney (Plate 8.9). The ridges occur in front of the steepest, most crevassed part of the snout as the glacier advances or slumps forward a few metres (Black and Bowser 1968, Figs 9, 11). Fractures (crevasses) in the ridges are deeper than two metres in places (Plate 8.9) indicating that the ridges are formed probably in the second half of the year like the recurring cracks in the moat ice (8.2.3). This timing is consistent with similar ridges formed during late winter elsewhere (Worsley 1974; Birnie 1977). Such minor annual advances have been attributed to a reduced ablation rate during winter (Worsley 1974; Birnie 1977), but could also be influenced by small amounts of lake water drawn beneath the glacier due to the steep gradient of the glacier surface in this area (Robin and Weertman 1973). Glacier movement at this time may produce incipient or larger fractures in the ice that dams the impounded subglacial brine. Leaking and melting could then be initiated at these fractures if the level of, or pressure in the brine is sufficient.

Plate 8.9 Two ice-push ridges in the moat ice of Lake Bonney in front of Taylor Glacier (direction of flow from left to right). Person on left for scale (24/10/78).

8.5 Conclusion

The saline discharges at Taylor Glacier are a result of complex interactions between subglacial salt and glacier ice. Discharges are believed to occur as a result of the glacier riding over a salt deposit that covers at least 5 x 10^5 m^2 situated 1-2 km up-glacier from the glacier terminus. The salt causes a thin layer of ice to melt, and the brine so-formed is aperiodically discharged from and beside the ice margin at the terminus. The brine release mechanism is not known but may be associated with the melting of an ice dam after this has been cracked by glacier movement.

The discharges bear some resemblance to aperiodic jökulhlaups but are not identical to them. In particular, the discharges are of relatively small volume and low flow rate, involving saline not fresh water released from a cold not temperate glacier during mid-winter to early summer, not during summer to early winter.

The salt deposit was formed apparently from evaporated sea water. Deviations from the sea water composition in the discharge brines are due to precipitation of gypsum, dissolution of local marble bedrock and gaseous carbon dioxide, and fixation of potassium by clays. A significant gas, content may be derived from bubbles contained in the melting glacier ice.

The phenomenon gives an indication of the recent history of Taylor Valley and Glacier. Sea water brine was injected into the drainage basin of Lake Bonney perhaps between about 50000 and 20000 years ago. The glacier was probably at least two to seven kilometres shorter than now during a period or periods of aridity during which the trapped sea water evaporated, perhaps about 30000-20000 and/or 16000-15000 years BP. After this last period of aridity, Taylor Glacier advanced to within a kilometre or so of its present position which it reached about 15000 years BP allowing a new lake (West Lobe, Lake Bonney) to form.

CONCLUSIONS

This study of salts and their distribution in the McMurdo region has been of necessity an extensive one. Salt distribution, a small part of salt geochemistry, is a broad topic and quite complex since salt accumulation is not regular. It is a result of different sources of salts, a variety of agents and modes of migration of these salts, their various physico-chemical properties and also environmental conditions. Extensive data are required to examine the topic.

At least 30 salt phases have been recognized. Ten of these, comprising eight different salts, are sufficiently widespread for their distribution to be studied in detail. Classification of salt deposits into five different types has proved to be a useful way of summarizing salt accumulation.

The amount of moisture available in a locality and physico-chemical properties of salts are the two fundamental influences on local distribution of the salts. These salts have accumulated in the region because of its aridity. Despite this aridity a small amount of moisture is present, and results in the movement of salts both within the regolith and towards the lower parts of drainage basins. The more mobile salts tend to occur towards the bottom of the basins. A general relationship appears to exist between salt mobility and eutectic temperature in the binary aqueous salt system; mobility increases with decreasing eutectic temperature.

Slope aspect modifies local distribution in three ways: (1) calcite and gypsum prefer north-facing slopes, (2) surface efflorescences of more soluble phases also prefer north-facing slopes whereas (3) subsurface deposits of the most soluble phases, nitrates, prefer south-facing slopes. Such tendencies are the result of (1) increased production of Ca^{2+} by chemical weathering on north-facing slopes, (2) increased movement of soil brines to the soil surface on north-facing slopes and (3) decreased leaching of nitrates on south-facing slopes. These in turn are caused by a higher availability of moisture on north-facing slopes compared to south-facing slopes.

Salt migration is currently active in the region. Water and wind are the main agents causing this migration. Water transports salts in solution via thin liquid films, capillary water, channelled suprapermafrost flows and streams. Such brine movement is affected by moisture source and structure of the regolith. In McMurdo oasis such transport is probably faster towards the east than the west, and on north-facing slopes, because more moisture is available in these places.

Wind-induced migration is more difficult to study. However, evidence of deflation and shaping of deposits by wind can be seen on individual deposits. On a larger scale, wind has produced asymmetric salt accumulation in the summit area of Erebus Volcano. Although the latter is a special case, it illustrates the important role of wind in transporting salts. Such transport evidently takes place near the ground, as well as in the boundary layer and higher parts of the atmosphere.

Separation of salts occurs during the initial and final stages of the migration of salt solutions. That is, fractional dissolution and crystallization are probably the most important processes producing salt separation. Soil water or brines coming into contact with a salt deposit selectively dissolve those salts having the lower eutectic temperatures and greater solubilities. Such salts may then migrate in solution away from the deposit. During deaquation of the brine the opposite occurs, with salts crystallizing from the brine as their solubility products are exceeded, the first salts crystallizing being those with the smaller solubility products. The separation of specific salt phases depends on chemical equilibria in solution which in turn are dependent on ambient temperature and salt composition. However, there is good evidence from (1) observed relative mobilities of salts, (2) salt properties in binary and multicomponent aqueous systems and (3) migrating saline flows and brines, that calcium chloride is the most evolved product of the separation sequence in McMurdo oasis.

There is a little evidence for effective separation while salts are in solution; ion exchange is a separation process that appears to operate to a limited extent then. The process removes potassium ion from some brines at Taylor Glacier and probably elsewhere, but can have little regional significance.

Ambient humidity and dissociation pressures influence hydrate phase distribution and separation. The relative humidity and temperature of the surrounds determine whether or not the dissociation pressure of a hydrate is exceeded. If it is not, then part or all of the water of crystallization of the hydrate is lost, as is usually the case for mirabilite in surface efflorescences in McMurdo oasis. The hygroscopicity of a salt does not appear to be a significant influence on salt distribution in the region.

Considerable amounts of salt must have migrated from place to place within the oasis during its lifetime of at least four million years. Separation of different salts must have been quite effective during this time and therefore should be noticeable today in places other than where it was studied in this thesis. A significant proportion of the salt in long-exposed drainage basins, such as that of Lake Vanda, is likely to have migrated in dissolved form to the lowest part of the basin. This is consistent with the high concentrations of calcium and chloride ions in the present Lake Vanda and Don Juan Pond, and is one reason why sodium is not the predominant cation in these lakes. However, younger basins such as those presently occupied by Lake Bonney and Fryxell have not had time for a significant enrichment of calcium ions to develop.

This thesis has considered the sources of salts in the McMurdo region. Salt distribution on a regional scale was examined for this purpose. The distribution has been characterized by a set of gradients describing the relative frequency at which salt phases are encountered. Chloride and sodium phases decrease in frequency away from the coast, whereas magnesium phases increase as do the ratios of sulphates-to-chloride and nitrates-to-chloride. Calcium and carbonate show little change except in Taylor Valley where a marked decrease is apparent. Because of these different gradients, this study recognizes that a variety of salt sources exists, and has contributed to the salt system as a whole in the region. Different sources are important in different areas and no single source can account for all the salts. Similarly, different pathways exist for different sources.

Salts of marine origin are regionally and quantitatively most important. This is indicated by (1) the abundance in salt deposits of chloride, sulphate and sodium salts, all of which are derived mainly from the sea, (2) the dominance of gradients involving these ions over those of other ions, (3) the alkaline pH of most soils in the region, (4) the widespread distribution of sulphates whose sulphur isotope composition is related to that of sea water sulphate, and (5) the predominance of chloride in saline lakes. Pathways that are followed by salts of marine origin into the region involve atmospheric aerosols, snowfall, sea water influx, sea spray and dry fallout including salts blown off the sea ice. Subsequent fractionation processes during dissolution, migration and deaquation of brines are mainly responsible for obscuring the marine origin of the salts.

Sea water has been injected, comparatively recently, into Taylor Valley to as far west as at least 37 km from the present coast. The injection took place probably during an expansion of Ross Ice Shelf, possibly as recently as about 20000-50000 years ago. During a subsequent period(s) of aridity, Taylor Glacier terminated at least two to seven kilometres further west than now. Subsequent advance of the glacier to its present position has caused an unusual interaction between salt and ice. This interaction produces aperiodic discharges of salty water, similar in salt composition to concentrated sea water, from beneath the glacier.

Chemical weathering is the main process contributing magnesium, calcium and carbonate ions into the salt system. Weathering reactions can be described in terms of normal chemical decay of the most easily weathered rock and soil minerals. The availability of moisture affects the rate of these reactions. Therefore, these are faster in moister areas, for example north-facing slopes. Although chemical weathering is very slow in Antarctica, it operates over a period in excess of four million years in places and thus the products of such weathering are widespread.

Other sources of salts are locally important. Biological activity seems to have a significance that, generally, has been underestimated in the past. Such activity was responsible for isotopic modification of sulphates, and probably for the production of considerable amounts of carbonate plus bicarbonate phases in eastern Taylor Valley. Hydrothermal fluids contribute to carbonates and sulphates mainly in subsurface volcanic rocks. Volcanic activity has produced extensive and distinctive salt deposits in the summit area of Erebus Volcano but this activity is not of regional or continental significance to salt accumulation.

The salts of the McMurdo region have accumulated during the last four million years at least. They have formed in conditions similar to those of the present day and are still accumulating. There is no evidence that they formed in the earlier, warmer or moister times pre-dating the present ice sheet, that is before 20-25 Ma BP. Three independent lines of evidence exist that illustrate this: (1) the amount of salt on and in comparable soils increases with time, for surfaces up to more than four million years old; (2) over this time surface temperature and moisture conditions do not appear to have changed by a large amount, especially at high elevations where large amounts of salt occur; (3) all salt phases that have been studied from the region can form in present surface and near surface conditions. There are no phases or salts present that can be regarded as 'relic' phases, apart from very small amounts of gypsum and calcium carbonate.

APPENDIX 1

DISTRIBUTION OF SALTS IN THE McMURDO REGION, WITH ANALYSES FROM THE SALINE DISCHARGE AREA AT THE TERMINUS OF TAYLOR GLACIER

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INTRODUCTION

Victoria University of Wellington Antarctic Expeditions have had a long association with the salt accumulations and saline lakes of the McMurdo region (Fig. 1). This publication records the crystalline salt phases that have been characterised in the region to date. X-ray diffraction analyses of over 300 salt accumulations are listed with emphasis on locations in Taylor Valley. Also included are analyses of saline spring and glacier discharge brines and melted samples from the area of the saline discharge (Keys 1979) at the terminus of Taylor Glacier, and from other localities on and around the glacier. Major, trace and rare earth element analyses are given for some volcanogenic salts from Erebus Volcano.

These data are from a Ph.D. study of salt distribution and origin in the McMurdo region, and the Taylor Glacier saline discharge phenomena. The information is important because of the extensive interest in salt accumulation in this part of Antarctica and because of the relationship of the salts, Taylor Glacier and the saline lakes to the glacial history of the region.

ANALYTICAL TECHNIQUES

The salt accumulations were analysed using a Philips PW 1010 x-ray generator and PW 4210 x-ray powder diffractometer (XRD) to determine the crystalline phases. Sample preparation consisted of purification by manually removing rock impurities, grinding in a mortar and pestle and placing in on aluminium sample holder or on a glass slide. Diffraction patterns were interpreted using the indices of the American Society for Testing and Materials.

The major cations in the brines (except sample 78/01), meltwaters and melted ice samples were analysed using atomic absorption (AA) spectrophotometry. With this technique the most accurate results are obtained when the standards consist of all the elements being analysed with these elements in the ratios that they are in the sample. Thus reconnaissance analyses were performed first, based on single element standards, with La^{3+} added to suppress interference. Excess Na^+ was added to the K^+ standard to mask Na^+ interference. The results of these analyses enabled preparation of suitable standards for more precise analyses.

The major cations in an acidified, diluted sample of the 1978 discharge brine (sample 78/01) were analysed independently by N.H. Holden (Chemical Service Laboratories Ltd., Wellington). Na^+ and K^+ were analysed using flame photometry with the working samples doped with excess Li^+ to mask inteference. Mg^{2+} and Ca^{2+} were determined by standard EDTA titrations.

Major anions were determined using standard wet techniques (Vogel 1951; Metson 1956; Brown <u>et al.</u>, 1970). Cl^- was determined as total halides using silver nitrate, with the titrations viewed through yellow lens goggles to improve the end point determination. $SO_4{}^{2-}$ was determined gravimetrically with barium chloride. Analysis of HCO_3^- was not performed at the sampling site because of logistic difficulties. After sampling however, a precipitate of calcium carbonate formed in the spring brine samples. A reasonable estimate of HCO_3^- concentration could be obtained therefore, by analysing the HCO_3^- in the solution above the precipitate (using hydrochloric acid) and by determining the Ca^{2+} (by A.A. spectrophotometry) in the precipitate. It was assumed that the HCO_3^- lost, and the Ca^{2+} determined, are stoichiometrically related as in the equation for the reaction

$$Ca^{2+}_{(aq)} + 2HCO^-_{3(aq)} \longrightarrow CaCO_{3(s)} + CO_{2(g)} + H_2O$$

This reaction also involves, and compensates for, the degassing of carbon dioxide.

The specific conductance of the liquid samples was determined using a standard conductivity bridge and water bath thermostated to +25°C. Freezing point depressions were measured by mercury thermometer, using salt-ice freezing mixtures in an apparatus similar to that illustrated by Glasstone (1940).

Major elements in volcanogenic salts from Erebus Volcano were determined by neutron activation at the University of Maryland, U.S.A., by W. Zoller (see Zoller and Gordon 1970). Selected trace and rare earth elements were analysed in pressed powder discs by x-ray fluorescence, using cellulose-based standards, by P. Kennedy, Victoria University of Wellington.

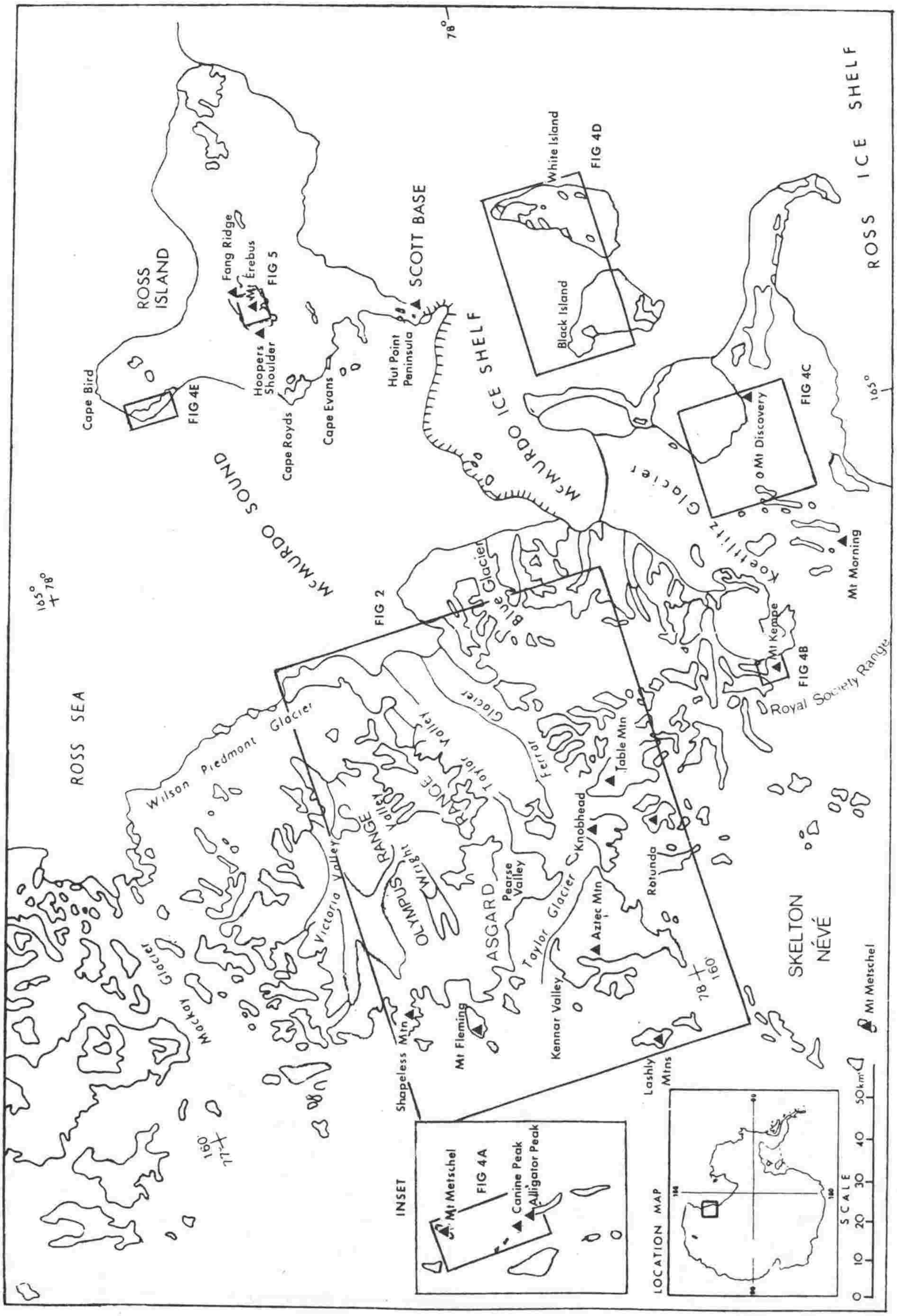

FIGURE 1 The McMurdo region

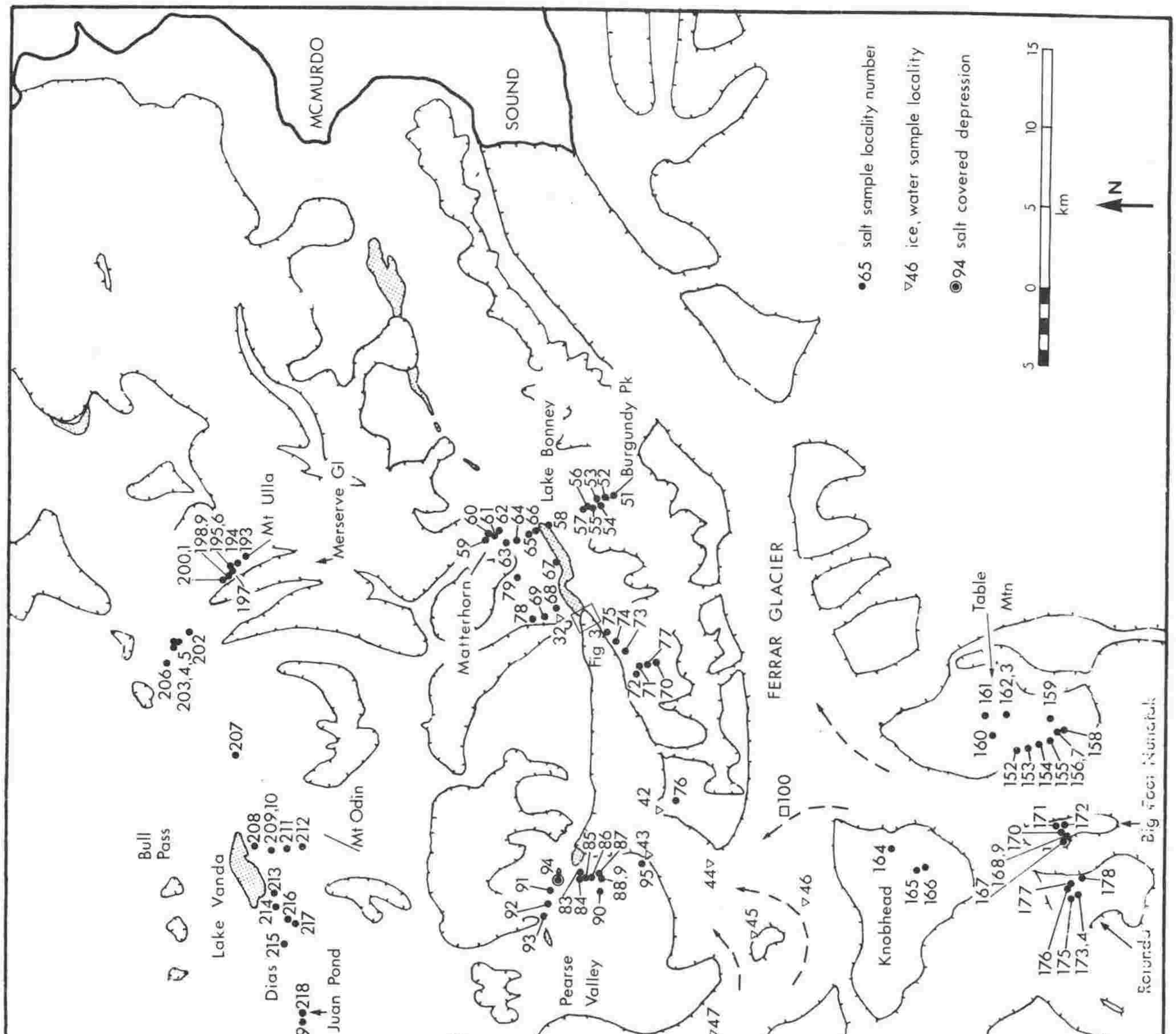

FIGURE 2 Wright, Taylor and Ferrar Valleys

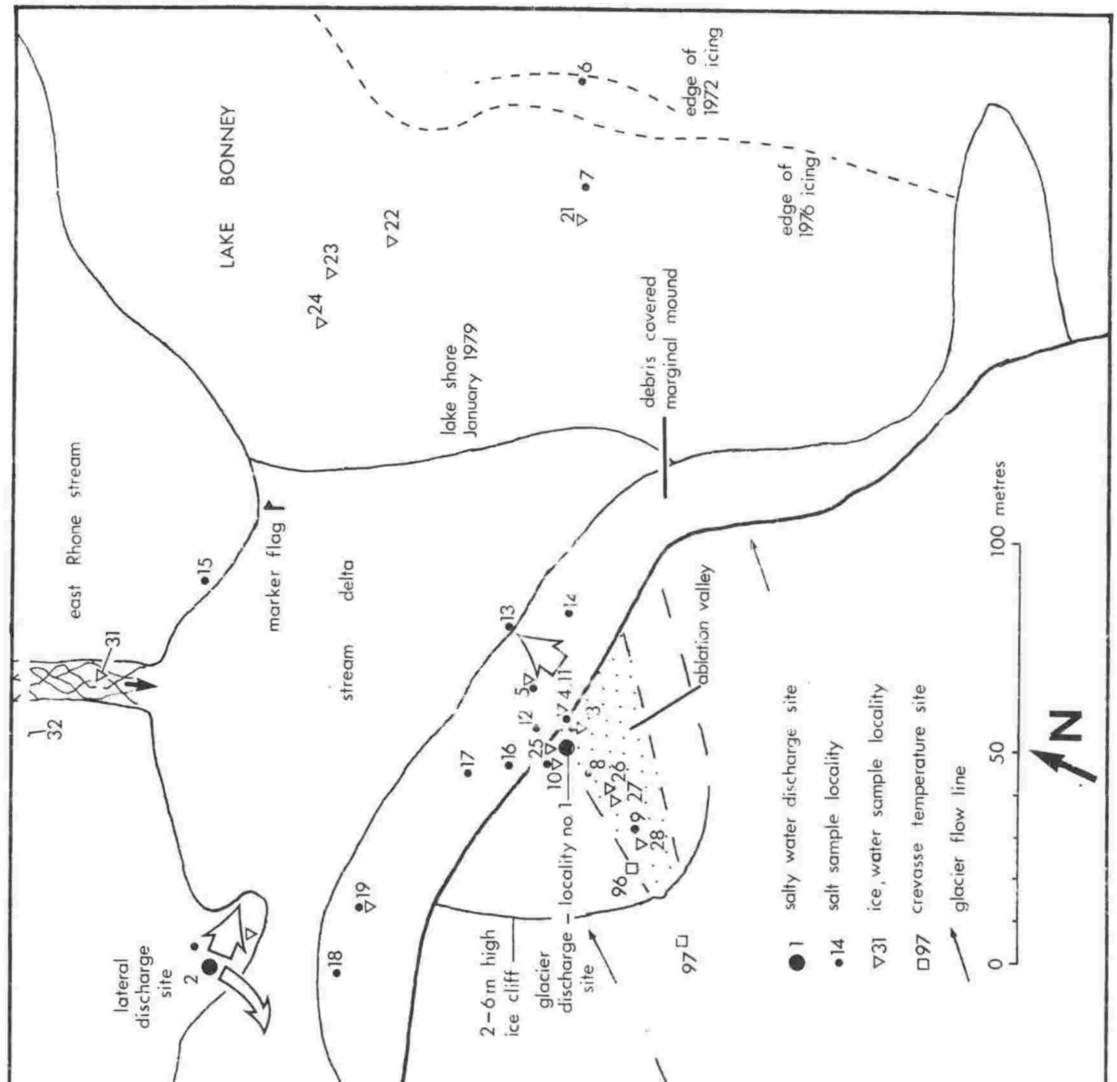

FIGURE 3 Saline discharge area and terminus of Taylor Glacier

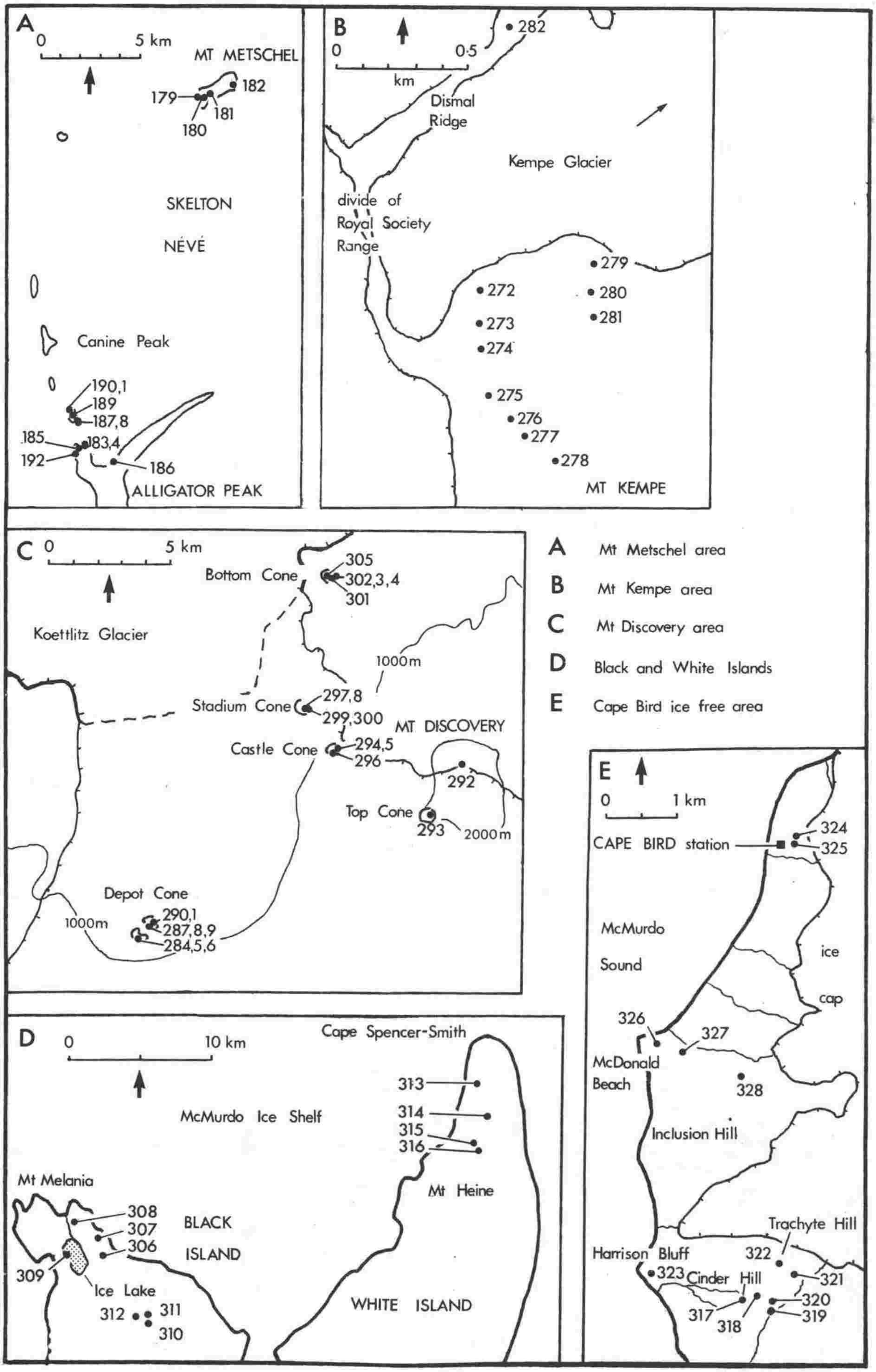

FIGURE 4 Mts Metschel, Alligator, Kempe and Discovery, Black Island, White Island and Cape Bird ice-free area

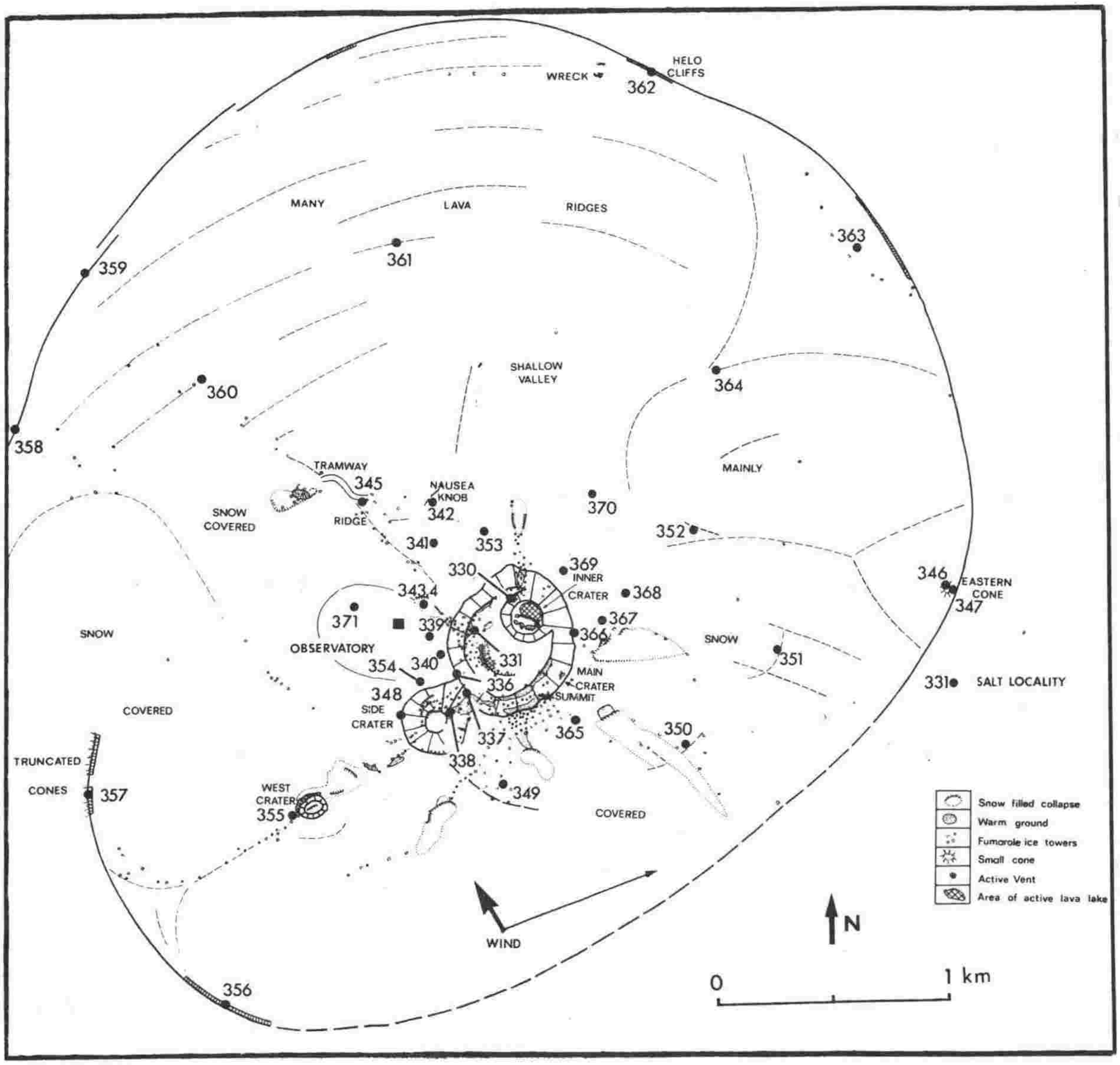

FIGURE 5   Sketch map of summit region of Mt Erebus

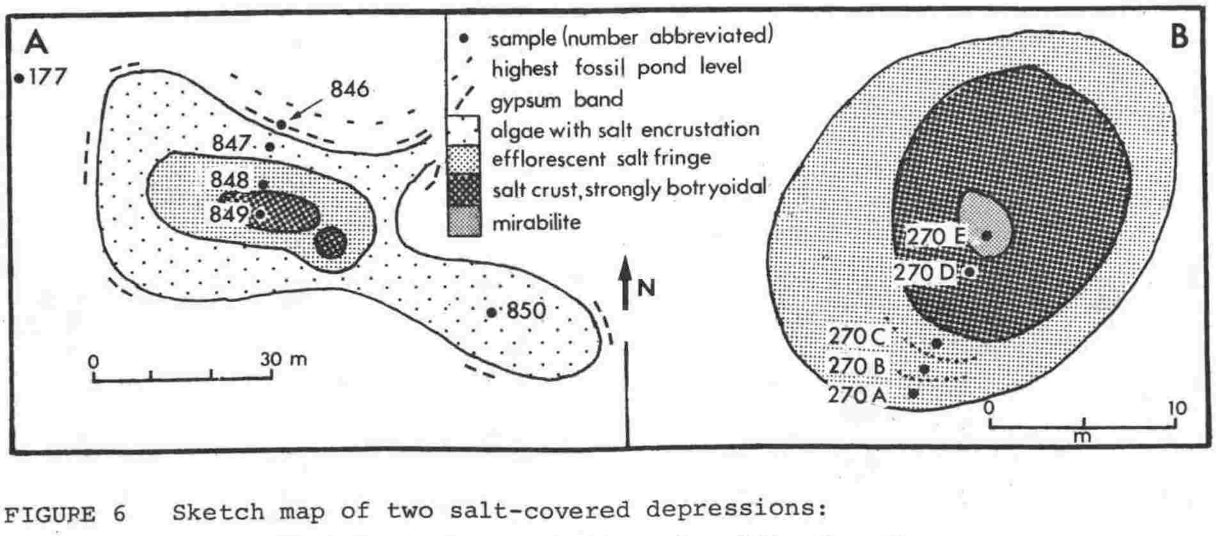

FIGURE 6   Sketch map of two salt-covered depressions:
A. Mae West Pond, Pearse Valley, locality No. 94;
B. Labyrinth area, locality No. 230

NOTES ON SELECTED TABLES

TABLE 1 Crystalline salt phases

More than 30 phases have been reported to date by workers in the region. Here these phases are grouped into three sub-tables on the basis of distribution and frequency of reports in antarctic literature.

The iodate-containing phase present in trace amounts is probably lautarite, rather than sodium iodate as reported by Johannesson and Gibson (1962) and Gibson (1962).

TABLES 3, 5, 6, 7 Distribution of Salt phases in Taylor Valley, upper Ferrar Valley, Wright Valley and McMurdo Sound Area

The tables list: locality number (shown on Figures 2, 4, 5); sample number (either a Victoria University of Wellington, Geology Department five figure catalogue number or a two-part field number); the salt phases (in order of importance in the sample); the deposit type (from Table 2); site aspect (northwest NW etc, flat F, small hollow where aspect is of lesser importance, H); rock types associated with the deposit (determined in the field and using Haskell et al., 1965; Barrett 1971; Barrett and Webb 1973; McKelvey and Webb 1962; and Cole and Ewart 1968); and site elevation (based on barometer readings; and U.S. Geological Survey maps, 1:50,000 topographic series and 1:250,000 reconnaissance series).

TABLE 4 Distribution of crystalline salt phases around the terminus of Taylor Glacier

These salts are related to the saline discharge phenomena. Localities are given in Fig. 3.

TABLES 8-11 Crystalline salt phases in salt-covered depressions

These show the succession of salts after capillary transfer, evaporation and freezing out from solution in saline depressions. Fig. 6 shows the sample locations at the two largest depressions studied.

TABLE 12 Identification of melanterite

The salt deposit consisted of about 0.3 grams of small green crystals, 1 to 2 mm long of melanterite ($FeSO_4.7H_2O$), encrusting part of the magnetite (Fe_3O_4) bed. A small amount of yellow-orange and white encrustation and associated rock detritus was taken with the 0.1g sample. The non-assigned peaks in the diffraction pattern represent the associated material; the yellow-orange and white encrustation consists mostly of iron III and iron II sulphates. More definate identification by XRD is not possible owing to peak interference and to the small sample size.

TABLE 13 Identification of burkeite

The interpretation of this pattern is difficult due to peak overlap. The three annotated, unassigned peaks in the table include the main halite peak at 2.82 Å. The second, third and fourth halite peaks (at 1.994Å, 1.628Å and 3.26Å respectively) are obscured because halite is present in low concentration.

Both of the other annotated, unassigned peaks did not disappear after oven drying at 105°C and can therefore be attributed to an anhydrous species. They probably represent additional or modified planes of ions in the burkeite $Na_6(CO_3)(SO_4)_2$ crystal lattice, caused by mutual substitution of sulphate and carbonate. These anions can mutually substitute over a wide range in the artificially-produced salt (Palache et al., 1951).

The other unassigned peaks all disappeared on oven drying: therefore most of these peaks can be attributed to trona. Thermonatrite which is present in relatively low concentration has little effect on the pattern in this region.

Reference to relative peak intensities assisted the interpretation. The strong peak at 4.89Å disappeared on oven drying and can be assigned to trona although there is a significant discrepancy between the experimental and literature peak positions. Relative peak intensities bear reasonable resemblance to the literature values. As is normally the case, distortions are due to particle size effects.

TABLE 14 Reconnaissance analyses of major cations

Listed here are analyses by AA using single element standards. These results allow semiquantitative comparisons between samples of specific cations. Locality numbers are shown on Figures 2 and 3.

TABLE 15 Composition of saline spring and glacier discharge brines

The concentrations of major cations and anions in these brines and in seawater are given, together with oxygen and deuterium isotope data. In saline spring sample 76/72, the sum of each cation concentration (in moles per kilogram) times its cationic charge, and the corresponding anionic sum, agree within four percent which is within analytical error. Such agreement indicates a satisfactory analysis.

TABLES 17-21 Specific conductance, chloride concentration and freezing point depressions

These five tables present selected analyses to show generic relationships between samples, involving saline icing, englacial and subglacial iron-stained ice. Dirt layer and meltwater samples are included. Sample locations are shown on Figures 2 and 3.

TABLES 23-25 Major trace, and rare earth element analyses of volcanogenic salts from Mt Erebus

X-ray diffraction of these volcanogenic salts, and simple wet tests, indicate that a complex mixture of alums and other volcanogenic phases are present. Unstable hydration states and the possible existence of rare or unknown salt minerals further means that identification of most phases by XRD is difficult. Major element analysis by neutron activation gives the elemental composition of three volcanogenic salts. Analytical totals are within ten percent after equating with oxygen, although normal stoichiometric relationships cannot all be relied upon in these salts. Electroneutrality is difficult to show because of unknown amounts of OH^-, Al^{3+} and other ions. Trace and rare earth elements can be used to determine enrichments of specific species.

TABLE 26 Accumulation of salts

Measurement of the total amount of salt at a site of known absolute or relative age, enables assumptions of the rate of salt accumulation to be tested. Locality numbers are given in Fig. 2.

TABLES 27-36 Frequency data

The data from Tables 1, 3, 4, 5, 6, 7 have been reduced to summary form for construction of histograms and other diagrams. Salt phases are counted in each deposit they occur, subject to constraints depending on the subject of the specific summary table. In several instances insufficient data have been accumulated for statistical purposes.

In each deposit the most common hydrate (or polymorph) is considered in most cases (as indicated). For Tables 27, 28, 29, 31, samples are excluded that are listed as having both surface and subsurface deposit type Deposits in hollows and flats are not considered in Tables 28, 31. To generate sufficient data for Tables 29-31, the eight compass points listed in the parent tables are condensed to quarters by combining NW, NE with N, NE, SE with S etc. The significance of these two-dimensional orientation distributions is tested against randomness using a rearranged equation of Curray (1956), relating the vector magnitude, L (percent), at the significance level, p, to the total number, N, of data, where

$$L = 100 \sqrt{\frac{-\ln P}{N}}$$

If the magnitude of the aspect class is greater than L for significance levels 0.01 and 0.05, then the distribution is not uniform. For Table 32 only those sites were considered where a particular rock type could be qualitatively assessed as being dominant. Only localities on the continent were considered for Table 34 (elevation). In this table salt occurrences in the 4 largest salty depressions were not included. Table 35 (distance from coast) includes data derived from the maps of Nishiyama (1977) for parts of Taylor and Wright Valleys (aragonite occurrences are excluded). Data from Table 7 are not considered here because of difficulties or ambiguities in determining distance. Neglect of those occurrences with unambiguous distances (Table 7.5), has an insignificant effect on Table 35. Gypsum and calcite occurrences are not included in Table 36. No calcite accumulations were recorded at Cape Bird although they are possible having been found nearby in similar situations at Capes Royds, Barne and Evans, and Hut Point Peninsula (Keys 1972). Because of this uncertainty and their generally low frequency of reported occurrences here, these salts are not included.

It is possible that systematic sampling errors have affected the recorded relative frequency of gypsum and calcite deposits. In areas where salt deposits are sparse and small, it is easiest to obtain workable or identifiable samples of gypsum and calcite than the more soluble salts. Therefore some results may portray a stronger trend than really exists. For this reason the more soluble salts have often been considered by themselves here. This makes the trends for such salts clearer but stronger than in reality. Rounding off insignificant figures results in all totals not being exactly 100 per cent.

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TABLE 1 CRYSTALLINE SALT PHASES OCCURRING IN THE McMURDO REGION.
GROUP A (FREQUENTLY NOTED IN ANTARCTIC LITERATURE)

Chemical Name	Mineral Name	Formula
sodium chloride	halite	$NaCl$
sodium sulphate decahydrate	mirabilite	$Na_2SO_4.10H_2O$
sodium sulphate	thenardite	Na_2SO_4
calcium sulphate dihydrate	gypsum	$CaSO_4.2H_2O$
Calcium carbonate	calcite	$CaCO_3$

GROUP B (LESS WIDESPREAD THAN GROUP A)

Chemical Name	Mineral Name	Formula	Early reference
magnesium sulphate heptahydrate	epsomite	$MgSO_4.7H_2O$	Gibson (1962) and others
magnesium sulphate hexahydrate	hexahydrite	$MgSO_4.6H_2O$	Claridge & Campbell (1968 a,b,c), Tasch & Angino (1968)
sodium nitrate	soda nitre	$NaNO_3$	Gibson (1962) & others
sodium-magnesium sulphate quadrahydrate	bloedite (astrakhanite)	$Na_2Mg(SO_4)_2.4H_2O$	Claridge & Campbell (1968 a,b,c)
sodium sulphate-nitrate hydrate	darapskite	$Na_3(NO_3)(SO_4)H_2O$	Claridge & Campbell (1968 a,b,c)
potassium chloride	sylvite	KCl	Nishiyama & Kurasawa (1975), Kumi *et al.* (1976)
calcium chloride hexahydrate	antarcticite	$CaCl_2.6H_2O$	Torii & Ossaka (1965)
calcium carbonate	aragonite	$CaCO_3$	Angino *et al.* (1964 & others)
sodium carbonate hydrate	thermonatrite	$Na_2CO_3.H_2O$	Browne (1973); Nishiyama & Kurasawa (1975)
sodium bicarbonate-carbonate hydrate	trona	$NaH\ CO_3.Na_2CO_3.H_2O$	Nishiyama & Kurasawa (1975)
mineral containing iodate ion	lautarite? (see text)	$Ca(IO_3)_2$	Johannesson & Gibson (1962), Gibson (1962)

TABLE 1 Cont. GROUP C (OCCURRING IN LOCALISED AREAS, AND SELDOM OR NOT PREVIOUSLY REPORTED)

Chemical Name	Mineral Name	Formula	Early reference
sodium bicarbonate	nahcolite	$NaHCO_3$	Keys (1972)
sodium sulphate - carbonate	burkeite	$Na_6(CO_3)(SO_4)_2$	this work (Tables 7.2,13)
calcium-sodium carbonate pentahydrate	gaylussite	$CaCO_3.Na_2CO_3.5H_2O$	Browne (1973)
magnesium carbonate-sodium carbonate-chloride	northupite	$MgCO_3.Na_2CO_3.NaCl$	Browne (1973)
magnesium carbonate	magnesite	$MgCO_3$	Dow & Neall (1974), Watanuki & Morikawa (1974)
magnesium carbonate trihydrate	nesquehonite	$MgCO_3.3H_2O$	Morikawa et al., (1977)
calcium-magnesium carbonate	dolomite	$CaMg(CO_3)_2$	Morikawa et al., (1975)
calcium carbonate	vaterite	$CaCO_3$	Browne (1973)
calcium carbonate hydrate	monohydrocalcite	$CaCO_3.H_2O$	Nishiyama & Kurasawa (1975)
iron (II) carbonate	siderite	$FeCO_3$	Browne (1974)
iron (II) sulphate heptahydrate	melanterite	$FeSO_4.7H_2O$	this work (Tables 5.6,12)
calcium sulphate^{+}	anhydrite	$CaSO_4$	Grindley et al., (1964), Tasch & Angino (1968)
potassium-calcium sulphate hydrate	syngenite	$K_2SO_4.CaSO_4.H_2O$	Lindholm et al., (1969)
sodium chloride dihydrate	dihydrohalite	$NaCl.2H_2O$	Craig et al., (1974), Hoehn et al., (1974)
magnesium chloride phase	bischofite? tachyhydrite? carnallite?	$MgCl_2.6H_2O$ $CaMg_2Cl_6.12H_2O$ $KCl.MgCl_2.6H_2O$	Kumai et al., (1976)
calcium phosphate	whitlockite?	$Ca_3(PO_4)_2$	Campbell & Claridge (1966)
magnesium hydrogen* phosphate trihydrate	newberyite	$MgHPO_4.3H_2O$	Campbell-Smith in Stewart (1964)
volcanogenic salt minerals e.g.		various	this work (Table 7.6)
potassium aluminium basic hydrated sulphate	alunite	$KAl_3(SO_4)_2(OH)_6$	this work (Table 7.6)

\+ reported from the Queen Maud Mountains, Transantarctic Mountains

* reported from Cape Adare, northern Victoria Land

\+ Addendum These reports were based on misidentification of prehnite which has similar optical properties to anhydrite (Barrett 1969). Anhydrite has subsequently been reported in sediments from DVDP 4 (Lake Vanda) by Cartwright et al., 1974b); the phase may have formed during drilling, since it does not appear to be thermodynamically stable under ambient conditions and has not been reported elsewhere from similar samples in this or other lakes.

TABLE 2 MAIN TYPES OF SALT DEPOSIT (EXTENDED FROM NISHIYAMA AND KURASAWA 1975; NISHIYAMA 1977)

Type of deposit	Type Number	Typical salt phase
encrustation on surface of bedrock, boulder or cobble	1A	calcite
accumulation or encrustation in joint crack or behind flake of bedrock, boulder or cobble	1B	calcite, soluble salts
accumulation in cavity in bedrock or boulder	1C	soluble salts
efflorescence or encrustation on surface of regolith	2A	soluble salts
deaquation deposit in enclosed basin	2B	soluble salts
veneer and encrustation on underside of boulder, cobble or pebble	3	calcite, gypsum
accumulation beneath boulder, cobble or pebble	4	soluble salts
strong salt horizon or nodule in regolith	5	soluble salts

TABLE 3 DISTRIBUTION OF SALT PHASES IN TAYLOR VALLEY

Locality No.	Sample No.	Phases present	Deposit type	Aspect	Rock types associated with deposit	Elevation (m)
1. LAKE BONNEY AND LOWER TAYLOR GLACIER AREA - Traverse from Burgundy Peak*, Kukri Hills, to L. Bonney						
51	24789	calcite	1A,3	NW	granodiorite dolerite	1800
52	24788	calcite	1A	N	"	1600
53	24790	calcite	1A	NW	"	1400
53	24801	thenardite, gypsum	2A	NW	"	"
54	24791	gypsum	2A	NW	basalt	1300
55	24792	halite, sylvite	2A,4	NW	"	1100
56	24793	gypsum	2A	NE	"	900
57	24794	thenardite, halite sylvite, gypsum	2A	NW	"	700
58	72/209	halite, thenardite	2A	NW	mixed[1]	57
traverse from base of The Matterhorn, Asgard Range, to L. Bonney						
59	24796	gypsum	1B	SE	granite	1400
59	24802	thenardite	1B	SE	"	"
60	24795	thenardite, mirabilite halite	4	SE	granite, dolerite	1200

TABLE 3 Cont.

61	24797	thenardite, mirabilite	4	SE	granite, dolerite	1100
62	24798	halite, thenardite	4	SE	"	1000
63	24799	halite, minor darapskite	2A,4	SE	granodiorite, dolerite	900
64	24800	thenardite, halite, minor gypsum	2A,1A	SE	mixed[1]	700
65	72/109A	halite, gypsum	2A	S	"	200
65	72/109B	aragonite, minor calcite	broken biscuit	SE	"	"
66	72/106A	halite, thenardite, gypsum	2A	SE	"	70
66	72/106B	aragonite, calcite	broken biscuit	S	"	"
67	72/210	halite	2A	S	"	57
	above Taylor Glacier					
68	72/114	halite, minor thenardite	4	SE	mixed[1]	500
69	72/115	gypsum	2A	SE	basalt	1000
70	76/48A	gypsum	1A,2A	N	"	1100
70	76/48B	calcite	3,1A	N	"	"
71	76/46	thenardite, halite, minor gypsum	2A,1A	NE	"	700
72	24831	darapskite, halite, thenardite, gypsum	1C	NW	"	600
73	76/49	gypsum	1A,2A	NE	granite gneiss	500
74	76/45	calcite	1B	N	metasediments	400
75	76/44	gypsum	4	N	mixed[1]	300
76	72/208	calcite	3	N	granite	600
	terminus of Taylor Glacier					
1-39	(various) see Table 4)	halite, gypsum, calcite, aragonite, thenardite, mirabilite	see Table		mixed[1]	57-120

Footnote

* name approved by N.Z. Geographic Board

[1] mixed i.e. several rock types present including dolerite, granite, metasediments, basalt and sandstone

2. PEARSE VALLEY

Traverse from Lake Joyce up side of Friis Hills

83	24832	thenardite, halite, darapskite, bloedite, minor gypsum	5	N	mixed[2]	450
83	72/154B	thenardite, halite, epsomite, darapskite, minor bloedite	5	N	"	"
84	72/157	thenardite, minor gypsum, halite	4,5	N	"	550
85	72/158	gypsum, calcite	3,4	N	"	"
86	72/165A	halite	1B,1C	N	granite	700
87	72/166	halite, minor gypsum	4	NE	"	800
88	72/170	halite, minor soda nitre	4,5	SE	dolerite	900
89	24833	mirabilite, thenardite, gypsum	2A,(2B?)	H, NW	sandstone[3] dolerite	950
89	72/171B	thenardite, gypsum	2A	NW	"	"
90	72/174	thenardite, halite, minor gypsum darapskite	2A,5	NE	dolerite	1000

Floor of Valley

91	72/189	halite	2A,5 (old 2B?)	F	mixed[2]	400
92	72/194	gypsum	4	NW	"	450
93	72/196	thenardite, gypsum, minor halite, epsomite	2A,5	E	"	400
94	various (see Table 8)	halite, gypsum, thenardite, calcite, darapskite, (epsomite[I])	mainly 2B	H	"	450

Bluff at east end of Friis Hills

95	24834	halite, minor gypsum	1B,4	E	granite	700
"	76/24B	gypsum	1A,1B,4	E	"	"

Footnotes

[2] mixed i.e. several rock types present including dolerite, granite and sandstone

[3] from lower Taylor Group of Beacon Supergroup

[I] crystallised from wet sand at VUW

3. AZTEC MOUNTAIN AREA

Traverse from floor of alpine valley south of Aztec Mountain to summit of Aztec Mountain

101	24835	mirabilite, thenardite, minor gypsum, epsomite	4	F	dolerite, sandstone[4]	1640
102	73/62	gypsum	1A	S	sandstone[4] dolerite	1650
103	23836	darapskite	4	S	"	1680
103	73/66	gypsum	1B	S	"	"
104	73/68	gypsum	1B	SW	"	1700
105	73/69	darapskite, minor thenardite	4	S	"	1720
106	73/70	soda nitre, gypsum	4	SW	"	1750
107	23837	soda nitre	⊛	SW	"	1770
108	73/74	soda nitre, minor gypsum	4	S	"	1780
109	73/79	darapskite, bloedite, thenardite	4	S	dolerite, sandstone[4,5]	1800
110	73/80	thenardite, gypsum	2A	NE	sandstone[5]	1850
111	73/83	gypsum	1A, 1B	NE	"	1900
112	73/84	thenardite, minor gypsum	2A	NE	"	"
113	23838	epsomite, bloedite, thenardite, minor gypsum	4	NE	dolerite	2000

traverse from floor of alpine valley to summit of Inca's Leap*

114	not sampled	calcite	3, 1A	NE	dolerite, sandstone[4,5]	1700
115	73/97A	thenardite, minor gypsum	2A	NE	"	1800
116	73/99A	gypsum	3, 4	N	dolerite	1850
116	73/99B	calcite	3	N	"	"
117	73/101	gypsum	3, 4	NE	dolerite, sandstone[5]	1950
118	73/104	calcite	1A, 1B	E	dolerite	2100
119	73/103	epsomite, bloedite, thenardite, minor gypsum	4, 5	F	"	2200

divide ridge east of Turnabout Valley

120	73/106	gypsum	3, 4	F	dolerite	1800
121	73/PN	calcite	1A, 1B	N	"	1850
121	73/PS	minor calcite	1B	S	"	"

Traverse from floor of alpine valley eastwards, down into Beacon Valley

122	73/113A	soda nitre, gypsum	4	F	dolerite, sandstone	1600
123	73/116	soda nitre, gypsum	2A,4	SE	"	1550
124	73/118	thenardite, epsomite, gypsum, mirabilite	4	SE	"	1500
125	73/121	gypsum	4	E	mixed[7]	1460
126	24839	soda nitre, gypsum	2A,4	SE	"	1400

Traverse from Beacon Valley up into alpine valley east of Aztec Mountains

128	73/126	gypsum	5	NW	mixed[7]	1300
128	73/127	gypsum	1A,2A	NE	"	"
129	24840	gypsum, thenardite	2A	SE	"	1400
130	73/MC	calcite	1A	E	dolerite	1600
131	73/133	gypsum	3,4	NE	mixed[7]	1650

Footnotes

4 Beacon Heights Orthoquartzite, and Aztec Siltstone, formations of the upper Taylor Group

5 mainly Weller Coal Measures, of the Victoria Group, Beacon Supergoup

6 various: upper Taylor Group and Victoria Group

7 mixed: i.e. dolerite, sandstone and some granite

(*) 10-20mm inside bedrock of Beacon Heights Orthoquartzite

4. KENNAR VALLEY

Traverse from lobe of Taylor Glacier up east fork and down west fork

132	76/32	thenardite, gypsum minor darapskite	2A	F	dolerite, sandstone[6]	1500
133	76/KV1	gypsum	4	N	"	1600
134	24841	thenardite, minor darapskite, bloedite gypsum	2A,4	NW	"	1650
135	not sampled	calcite	3	NW	dolerite	1800-2000
136	76/KV2	calcite+	1B	NW	"	2000
137	76/34	thenardite, minor gypsum	2A	W	"	2000
138	various (Table 9)	darapskite, mirabilite, gypsum, bloedite, soda nitre, epsomite, halite	2B,4	H	dolerite, sandstone[6]	1600

6 various: upper Taylor Group and Victoria Group

\+ hydrothermal calcite

5. LASHLY MOUNTAINS

Traverse south along main ridge

139	73/29	gypsum, minor calcite	4	F	sandstone[5]	2400
140	73/36	gypsum, calcite	1B,4	E	"	"
141	73/30	gypsum, calcite	1B	E	"	"

Section L1

142	73/40A	thenardite, gypsum	1B	SW	sandstone[5]	2250
143	73/33	gypsum	1B,4	SE	siltstone[7]	2130
144	24842	gypsum[8]	1B	SE	siltstone[8]	2118
145	73/41	gypsum	4	SE	siltstone[9]	2116

Section L2

146	73/49A	thenardite, minor gypsum	4	NE	sandstone[5] dolerite	2300
147	73/49B	gypsum	3	N	"	"
148	73/52	epsomite	4	SE	dolerite sandstone[5]	2350
149	24843	epsomite, hexahydrite, bloedite, minor gypsum	4	SE	"	2400

Summit plateau of Mt Crean

150	24844	thenardite, minor gypsum	2A	F	dolerite sandstone[10]	2540
150	73/56B	mirabilite, thenardite, minor gypsum	4	F	"	"
151	24845	epsomite, gypsum	4	F	"	"

Footnotes

5 mainly Weller Coal Measures

7 Aztec Siltstone, Unit 10; gypsiferous claystone (Barrett 1971)

8 Aztec Siltstone, Unit 8; in situ Devonian lacustrine gypsum veins, 1 to 3 mm thick, parallel and subparallel to bedding (Barrett 1971)

9 Aztec Siltstone, Unit 7 (Barrett 1971). Elevations of 7,8 and 9 are those measured by Askin and Barrett in Barrett (1971)

10 Victoria Group, probably Feather Conglomerate

TABLE 4. DISTRIBUTION OF CRYSTALLINE SALT PHASES AROUND THE TERMINUS OF TAYLOR GLACIER

Location or description of salt deposit	Locality No.	Sample No.	Phases present
flood "tide mark" of salt on wall of crevasse from which issued the 1972 discharge event	1	24820	gypsum, mirabilite, thenardite, minor halite, calcite
wall of crevasse below tide mark	1	24821	mirabilite, thenardite
surface of 1972 icing, 6m from crevasse	3	24822	aragonite, calcite$^{\circ}$
surface of 1972 icing, 1m above lateral mound	4	72/223	calcite, aragonite$^{\circ}$
surface of 1972 icing, 10m from glacier	5	72/212	halite, calcite
surface of 1972 icing, 110m from glacier, at furthest edge of icing: light orange coloured material	6	24823	calcite$^{\circ}$
darker orange coloured material	6	72/211B	calcite$^{\circ}$
salt in botryoidal surface layer 1-3 cm thick, 4m from edge of 1976 icing: underlain by 5cm icing, over lake moat ice	7	24824	halite, gypsum, minor calcite
surface of englacial orange layer in ablation valley	8	72/219	mirabilite, thenardite, gypsum, halite
salt on cobble in ablation valley	9	72/220	thenardite
salt on surface of englacial orange layer, exposed after calving of ice block	10	76/09A	mirabilite, thenardite, halite
euhedral crystals of salt in ice blocks just calved from glacier	10	76/09B	gypsum$^{\circ}$
1973 surface of orange coloured ice in basal layer of glacier, immediately below 1972 discharge site, 3m above top of ice-marginal mound	11	73/250	calcite, aragonite halite$^{\circ}$
top of marginal mound, 8m NW from locality 11	12	73/252	halite, calcite, gypsum, minor aragonite
foot of marginal mound, beneath glacier discharge site	13	24825	calcite, aragonite, gypsum, minor halite$^{\circ}$
flank of marginal mound, 10m SE of locality 13	14	73/254	halite, gypsum, calcite, aragonite$^{\circ}$
salt occurring in white bands 0.2 to 0.4m above stream delta opposite glacier discharge site	15	73/255	halite, gypsum
surface salt around lateral discharge site	2	78/02	halite, gypsum
top of marginal mound, 5m NW (up glacier) from edge of 1972 icing	16	72/224	halite, thenardite, calcite
flank of marginal mound, 15m NW from edge of 1972 icing	17	72/229	halite, gypsum, minor thenardite
flank of marginal mound, opposite lateral discharge site	18	24826	thenardite, halite

TABLE 4 Cont.

salt on surface of orange coloured ice, within marginal mound, 60m from glacier discharge site	19	76/17S	gypsum
salt on melt-out till at base of glacier on north side 150m up glacier from glacier discharge site	20	76/14	halite, gypsum, minor thenardite
salt encrusting dirt in basal dirt layers on south (true right) side of glacier, 500m from L. Bonney	34	76/02B	halite, gypsum, minor thenardite
salt on surface of orange coloured ice in basal dirt layers on south side of glacier, 180m from lake	35	24827	halite, gypsum
crystalline salt 'nodules' in southern ice cored moraine ridge at terminus of glacier	36	24828	mirabilite, thenardite
salt on surface of this moraine ridge, 10m from glacier	37	76/67A	thenardite, halite
salt on surface of this moraine ridge, 5m from glacier	38	76/67D	gypsum
salt encrusting pebble at base of ridge, 10m from glacier	39	76/67E	mirabilite, thenardite

o stained by hydrated iron oxides

TABLE 5 DISTRIBUTION OF SALT PHASES IN UPPER FERRAR VALLEY AND SKELTON NÉVÉ

Locality No.	Sample No.	Phases present	Deposit Type	Aspect	Rock types associated with deposit	Eleva- (m)
1.	Table Mountain ice free area					
	Traverse along dolerite ridge on westside, towards the south					
152	not sampled	calcite	3	NE	dolerite	1700
153	74/17	gypsum, bloedite, minor halite, epsomite, thenardite	2A	N	"	1800
154	not sampled	calcite	3	N	"	"
155	"	gypsum	4	N	"	1900
156	74/18B	mirabilite	4	S	"	2000
156	74/18A	thenardite	4	S	"	"
157	not sampled	calcite	3	W	"	2050
158	24868	thenardite	2A	NW	sandstone[1], dolerite	2000
158	24869	mirabilite, minor gypsum	4	NW	"	"

TABLE 5 Cont.

158	24870	thenardite, minor gypsum	4	NW	sandstone[1], dolerite	2000
159	not sampled	calcite	3	N	"	1950

Traverse across northern and eastern parts of the ice free area

160	74/22	thenardite, minor gypsum, bloedite, darapskite, mirabilite	4	NW	dolerite, sandstone[2]	1500
161	not sampled	calcite	3	E	"	1600
162	24871	gypsum	1B	S	siltstone[3]	1700
163	74/23B	gypsum	3,4	S	dolerite, sandstone[2]	"

Footnotes

1 mainly New Mountain Sandstone, Taylor Group

2 Taylor Group

3 Terra Cotta Siltstone, lower Taylor Group. Apparently in situ lacustrine gypsum veins, 1-2mm thick, parallel bedding in slatey unit.

2. Knobhead

cirque east of summit

164	74/24A	thenardite, minor darapskite, mirabilite	4	SE	dolerite, sandstone[2]	1700
164	74/24B	mirabilite, thenardite, minor gypsum, darapskite	4	SE	sandstone[2], dolerite	"

on slope to southeast below summit

165	24872	darapskite, thenardite	5	S	dolerite	1700
165	not sampled	calcite	3	S	"	"
166	74/26	darapskite, thenardite	5	S	dolerite, sandstone[2]	1600
166	not sampled	calcite	3	S	"	"

Footnotes

2 Taylor Group

3. Big Foot Nunatak*

Traverse up west side to summit ridge

167	73/230	mirabilite, thenardite	4	SW	sandstone[2], dolerite	1400
167	73/233	gypsum	1A	SW	"	"
167	73/232	gypsum	3	SW	"	"
167	73/231	gypsum	4	SW	"	"
167	not sampled	gypsum	5	SW	"	"
167	73/235	mirabilite, thenardite, minor gypsym	4	SW	"	"
167	73/236	thenardite, gypsum	3,4	SW	"	"

TABLE 5 Cont.

Locality No.	Sample No.	Phases present	Deposit Type	Aspect	Rock types associated with deposit	Elevation (m)
168	73/240	thenardite	2A	W	sandstone[2], dolerite	1400
169	73/241	gypsum	3,4	S	dolerite, sandstone[2]	"
170	73/243	thenardite, minor mirabilite, gypsum	4	W	sandstone[2]	1600
171	73/244	gypsum	3,4	W	sandstone[2], dolerite	1600 to 1900
172	73/245	mirabilite, thenardite, bloedite	4	W	dolerite, sandstone[2]	1800

Footnotes

* Name approved by N.Z. Geographic Board

2 Taylor Group

4. Rotunda*

Traverse from summit of butte capping northend, to Rotunda Glacier* to the east

173	73/206	mirabilite, thenardite, minor gypsum	4	F	sandstone[4]	2250
174	73/207	gypsum	4	F	"	"
174	73/211	gypsum	1B	NW	"	"
175	73/223	calcite	1A	NW	"	2100
176	24873	thenardite, halite, bloedite, darapskite, minor gypsum	4	E	dolerite, sandstone[2]	1700
177	DB/01	calcite	3	E	"	1600
178	73/228	calcite, gypsum	1B	NE	dolerite	1400

Footnotes

2 Taylor Group

4 Arena Sandstone, Taylor Group

5. Mt Metschel

Traverse from west end up southwest ridge to summit

179	73/144	calcite	1B	NW	dolerite	1700
180	73/149A	gypsum	4	W	"	1750
181	24874	soda nitre, minor gypsum epsomite	4	W	"	1830

On east ridge

182	73/159	gypsum	3,4	NE	dolerite, siltstone[5]	1750

Footnotes

5 mainly Aztec Siltstone, but some Victoria Group present

TABLE 5 Cont.

Locality No.	Sample No.	Phases present	Deposit Type	Aspect	Rock types associated with deposit	Elevation
6.	Alligator Peak area					
	Section A1 area, northwest of Alligator Peak					
183	73/165	calcite	1A,1B	NW-S	siltstone[5]	1850
184	73/167	gypsum	4	NE	"	1860
185	73/170	calcite	1A	N	sandstone[6]	1900
	foot of Alligator Ridge					
186	73/178	gypsum, calcite	1A	N	dolerite	1800
186	73/180	gypsum, thenardite epsomite	1A	N	"	"
	Canine Peak*: traverse up southeast ridge to summit, down north ridge and northwest face					
187	73/186	gypsum	1B,4	F	sandstone[6], dolerite	1900
188	24875	epsomite, soda nitre, minor gypsum, darapskite	4	S	dolerite	1950
189	73/192	calcite	1B	SW	"	2000
190	73/195	gypsum	4	N	"	1900
191	73/203	bloedite, epsomite	4	W	"	"
	magnetite bed near section A_3: illustrated by Barrett (1972)					
192	24876	melanterite	1A	W	magnetite	1850

Footnotes

5 mainly Aztec Siltstone, but some Victoria Group present

6 mainly Weller Coal Measures

TABLE 6 DISTRIBUTION OF SALT PHASES IN WRIGHT VALLEY

1.	Wright Lower Valley					
	traverse from summit of Mt Ulla towards valley floor					
193	24803	gypsum	4	NE	dolerite	1550
194	24804	thenardite, gypsum	2A	N	metasediments and other[1]	1350
195	24805	gypsum, thenardite	4	N	"	1200
196	24806	calcite	1A	N	"	1180
197	24807	gypsum	2A	W	"	1100
198	24808	thenardite	4	NW	"	1050
199	24809	thenardite	4	NW	dolerite and other[2]	1000
200	24810	thenardite, gypsum	4	NW	mixed[3]	900
201	24811	halite, thenardite, darapskite, bloedite	4	NW	mixed[3]	850
	traverse up slopes of Olympus Range opposite Merserve Glacier					
202	72/311	halite, minor thenardite	2A	SE	mixed[3]	300
203	72/314	gypsum	4	SE	metasediments and other[1]	800
204	72/315	halite, soda nitre, gypsum	4	SE	"	850

TABLE 6 Cont.

Locality No.	Sample No.	Phases present	Deposit Type	Aspect	Rock types associated with deposit	Elevation
205	72/316	halite, minor gypsum	4	SE	metasediments and other[1]	900
206	72/317	soda nitre, halite, minor gypsum	4	S	mixed[3]	1100
	valley floor beneath Bull Pass					
207	72/318	halite, minor gypsum	2A	S	mixed[4]	150

Footnotes

1 "other" includes dolerite and some lamprophyre and porphyry

2 "other" includes metasediments, and some lamprophyre and porphyry

3 mixed - metasediments, dolerite, granite

4 mixed - dolerite, granite, sandstone and dyke rocks

2. Mt Odin

traverse from Lake Vanda up slopes of Mt Odin

208	72/297A	halite, thenardite	2A,4	NE	mixed[4]	130
208	72/297B	gypsum	4	NE	"	130
209	72/319	thenardite, minor mirabilite	4	N	dolerite and others[5]	500
210	72/320	gypsum	2A	N	"	"
211	72/321A	halite, soda nitre, minor darapskite	2A	N	mainly dolerite	700
211	72/321B	gypsum	2A	N	"	"
212	72/322	thenardite, gypsum	2A	N	"	1000

Footnotes

4 dolerite, granite, sandstone and dyke rocks

5 "other" includes granite, sandstone and dyke rocks

3. Dias and South Fork

east of Dias and east end of Dias

213	72/296	halite, minor gypsum	2A	N	mixed[4]	150
214	not sampled	calcite	3	NW	"	"
215	72/298	halite, thenardite	4	F	dolerite	700
	traverse through Don Juan Pond basin from east to west					
216	72/295	gypsum	4	SW	mixed[4]	200
217	not sampled	calcite	3	SW	"	180
218	72/294A	halite	1C	E	granite	119
218	72/294B	halite, gypsum	2B	H	mixed[4]	118
218	72/292	antarcticite	2B	H	"	"
218	72/291	antarcticite	2B	H	"	"
219	72/293B	halite	2A	E	"	130
220	72/288	gypsum	4	E	mixed[6]	400

TABLE 6 Cont.

Footnotes

5 dolerite, granite, sandstone and dyke rocks

6 granite, dolerite, sandstone

Locality No.	Sample No.	Phases present	Deposit Type	Aspect	Rock types associated with deposit	Elevation
4.		Labyrinth and Wright Upper Glacier area				
		traverse through western and northwest parts of Labyrinth				
221	72/252	gypsum	1B	N	dolerite	900
222	72/249	thenardite, gypsum	4	F	"	"
223	see Table 10	epsomite, halite, gypsum, minor soda nitre, darapskite, thenardite	mainly 2B	H	"	860
224	72/255	thenardite, halite, darapskite	4	H	mixed[6]	850
225	72/256	gypsum, trace halite	2B	H	"	"
226	72/257	gypsum	2A	N	dolerite	870
227	72/258	calcite	1A	E	sandstone[7]	"
228	72/262	gypsum	4	H	dolerite, sandstone[7]	850
229	not sampled	calcite	3	NE	dolerite	"
230	see Table 11	halite, soda nitre, mirabilite, darapskite, bloedite, thenardite, gypsum	mainly 2B	H	dolerite, sandstone[7]	"
		traverse through southern portion of Labyrinth				
231	72/279	gypsum	4	W	dolerite	850
232	72/278	halite, soda nitre, minor gypsum	2A	H	dolerite, sandstone[7]	800
233	not sampled	calcite	3	E	dolerite	850
234	72/286	halite, bloedite, soda nitre, gypsum	2B	H	"	800
235	not sampled	calcite	3	E	"	850
236	72/287A	thenardite, halite	2A	NW	dolerite, sandstone[7]	"
236	72/287B	mirabilite, thenardite	4	NW	"	"
		traverse up and into Tyrol Valley				
237	72/275	gypsum	4	N	dolerite, sandstone[7]	1100
238	72/273A	soda nitre, darapskite, bloedite, minor gypsum	4	N	"	1200
238	72/273B	mirabilite, thenardite	4	N	"	"
239	72/274	soda nitre, darapskite	4	N	sandstone[7], dolerite	1300

TABLE 6 Cont.

Locality No.	Sample No.	Phases present	Deposit Type	Aspect	Rock types associated with deposit	Elevation
		slope of Olympus Range, north of terminus of Wright Upper Glacier				
240	72/284	thenardite	4	S	dolerite, sandstone[7]	1000
241	72/283	soda nitre, epsomite, bloedite, darapskite, minor gypsum	4	S	sandstone[7], dolerite	1100
242	72/280	soda nitre, halite, gypsum	4	S	dolerite, sandstone[7]	1200
243	not sampled	calcite, gypsum	3,4	S	"	1250

Footnotes:

6 granite, dolerite, sandstone

7 Taylor and Victoria Groups

5. Mt Fleming

traverse from cirque basin northeast of summit, to main ridge and southwest towards summit

244	73/15	epsomite, minor gypsum, bloedite	4	NE	dolerite, sandstone[8]	1850
245	73/16	mirabilite, thenardite, bloedite, minor gypsum	4	SE	"	"
246	73/17	gypsum	4	N	sandstone[8]	1950
246	not sampled	calcite	3	N	"[8], dolerite	"
247	73/18A	soda nitre, minor gypsum	4	N	dolerite, sandstone[8]	2000
247	73/18B	mirabilite, thenardite, darapskite	4	N	sandstone[8], dolerite	"
248	73/19A	gypsum	4	N	sandstone[8]	2050
249	73/20	darapskite, mirabilite, thenardite, bloedite, minor gypsum	4	SE	dolerite	2100
250	73/21	mirabilite, thenardite, minor gypsum	4	N	sandstone[9]	"
251	73/22	gypsum	1B	S	coal beds[9]	"

Footnotes

8 mainly Aztec Siltstone, but some Victoria Group

9 Weller Coal Measures

6. Shapeless Mountain

traverse over ridge of dolerite north of summit and down section S9

252	KB/11	epsomite, minor gypsum thenardite	4	NW	dolerite	2400
253	73/04	mirabilite, thenardite, minor gypsum	4	W	"	2500
254	73/05	mirabilite, thenardite	4	W	"	2550
255	73/07	gypsum	4	E	sandstone[10]	2500
256	73/09	thenardite, gypsum	4	NE	sandstone[11]	2300
257	not sampled	calcite	3	NE	sandstone[11], dolerite	"

TABLE 6 Cont.

Locality No.	Sample No.	Phases present	Deposit Type	Aspect	Rock types associated with deposit	Elevation
258	73/10A	epsomite, bloedite	4	NE	sandstone[11], dolerite	2200
258	73/10B	gypsum	4	NE	"	"
259	73/11	gypsum, epsomite	4,2A	S	"	"
260	73/12	bloedite, hexahydrite, minor epsomite	4	SE	dolerite, sandstone[11]	2150
ridge system west of summit						
261	73/24	minor epsomite, hexahydrite	4,1B	N	sandstone[12], dolerite	2500
262	73/25	gypsum	4	SW	sandstone[12]	2600
263	KB/17A	epsomite, gypsum	4	NW	Mawson[13], dolerite	2700
263	KB/17B	gypsum, calcite	4,3	NW	"	"

Footnotes

10 Feather Conglomerate

11 Victoria Group, mainly Weller Coal Measures

12 Lashly Formation, upper Victoria Group

13 Mawson Formation, Ferrar Group

TABLE 7 DISTRIBUTION OF SALT PHASES IN McMURDO SOUND AREA, AND INCLUDING MT KEMPE, ROYAL SOCIETY RANGE

1. Mt Kempe

traverse up northface, and northwest ridge to summit of Mt Kempe

272	74/01	gypsum	4	N	mixed[1]	2500
273	74/02	thenardite	4	N	"	2550
274	74/03	gypsum	1B,1A	N	metasediments	2600
275	74/15A	epsomite, bloedite, minor gypsum	4	N	mixed[1]	2700
276	not sampled	gypsum	1B	NW	siltstone[2]	2800
277	not sampled	gypsum	1B	NW	dolerite	2850
278	74/MK	calcite[+]	1B	SW	"	2900
southside of Kempe Glacier adjacent to marble bluff						
279	74/12	calcite	1A,3	N	mixed[3]	2500
280	not sampled	gypsum	1A,1B	N	marble	2550
281	not sampled	calcite	1A,3	N	metasediments	2600
Dismal Ridge						
282	74/06	gypsum, minor calcite	1B,1A	N	metasediments	2500

Footnotes

1 metasediments (Skelton Group), dolerite, sandstone (lower Taylor Group)

2 Terra Cotta Siltstone

TABLE 7 Cont.

Footnotes

3 metasediments, dolerite, sandstone, alkali basalt cinders

\+ hydrothermal calcite

Locality No.	Sample No.	Phases present	Deposit Type	Aspect	Rock types associated with deposit	Elevation
2.	Mts Discovery and Morning area					
	summit of Mt Morning					
283	24812	thenardite, minor gypsum	4	W	basalt	2720
	Depot Cone**					
284	76/74	gypsum	2A	S	basalt	1000
285	24813	epsomite, minor gypsum, hexahydrite, bloedite	2A	S	"	"
286	not sampled	gypsum	2A	W	"	"
287	76/76	gypsum	2A	F	"	"
288	not sampled	gypsum	2A	NE	"	"
289	76/77	gypsum	1A	NE	"	"
290	76/78	thenardite	2A	E	"	980
291	not sampled	gypsum	2A	SE	"	1000
	summit of Mt Discovery					
292	76/MD	calcite	1A	N	basalt	2670
	summit of Top Cone**					
293	76/80A	gypsum, thenardite, minor halite	4	F	basalt	2000
	Castle Cone**					
294	not sampled	gypsum	2A	S	basalt	1000
295	not sampled	calcite	3	N	"	"
296	76/81	thenardite	4	E	"	"
	Stadium Cone**, southeast portion of crater rim					
297	not sampled	gypsum	2A	NE	basalt	750
298	not sampled	gypsum	4	NE	"	"
299	24814	trona, burkeite, thenardite thermonatrite, trace halite	4	W	"	"
299	24815	thenardite, trona, possibly trace nahcolite	4	W	"	"
300	76/SC	gypsum	4	W	"	"
	Bottom Cone**					
301	not sampled	gypsum	4	S	basalt	180
302	76/83	thenardite, bloedite, minor hexahydrite, epsomite	4	F	"	180
303	not sampled	calcite	3	F	"	180

TABLE 7 Cont.

Locality No.	Sample No.	Phases present	Deposit Type	Aspect	Rock types associated with deposit	Elevation
304	not sampled	gypsum	4	E	basalt	170
305	76/84	mirabilite, thenardite	4,5	NW	"	180

Footnotes

** unofficial name

3. Black Island

traverse from Ice Lake over Mt Melania

Locality No.	Sample No.	Phases present	Deposit Type	Aspect	Rock types associated with deposit	Elevation
306	74/30	mirabilite, thenardite	2A,4	SW	olivine-augite basalt[4]	250
307	74/VUW	mirabilite, thenardite, halite	4[6]	F	mixed alkali basalt[5]	150
308	74/31	halite	2A[7]	W	"	"
309	74/32	mirabilite, thenardite	2A[8]	360°	"	100
Centre of Island						
310	74/33A	mirabilite, minor thenardite	4	SE	trachyte	600
311	74/33B	thenardite, minor mirabilite	2A	N	"	"
312	not sampled	calcite	3	NW	"	550

Footnotes

[4] after Cole and Ewart (1968)

[5] glacial drift

[6] under boulders used for anchoring tent of VUWAE9 Oct-Nov 1964

[7] surface of recent mudflow

[8] ice cored mound of glacial drift, on western shore of Ice Lake

4. White Island

traverse from Cape Spencer-Smith to summit of Mt Heine

Locality No.	Sample No.	Phases present	Deposit Type	Aspect	Rock types associated with deposit	Elevation
313	78/05	thenardite	2A	NW	basalt	400
314	78/06	mirabilite, thenardite	4	SE	"	550
315	not sampled	calcite	3	NW	"	650
316	not sampled	gypsum	2A	NW	"	760

5. Cape Bird, Ross Island

Cinder Hill area

Locality No.	Sample No.	Phases present	Deposit Type	Aspect	Rock types associated with deposit	Elevation
317	72/324A	mirabilite, thenardite	2A	F	olivine, basalt[5]	305
318	72/324B	thenardite, halite	2A	NE	"	"
319	72/328A	halite, minor gypsum	2A	SW	"	280
320	72/328B	halite, thenardite, bloedite	2A	SW	"	"

TABLE 7 Cont.

Locality No.	Sample No.	Phases present	Deposit Type	Aspect	Rock types associated with deposit	Elevation
		traverse over Trachyte Hill to top of Harrison Bluff				
321	72/329	thenardite, halite	2A	SE	hornblende trachyte[9]	430
322	72/330	halite, thenardite	2A	W	"	460
323	24816	halite, thenardite, bloedite, gypsum	2A	F	"	30
		moraines above Cape Bird Station				
324	72/336	mirabilite, thenardite	2A	E	mixed alkali basalt[10]	60
325	72/346	halite, thenardite	2A	NE	"	100
		traverse from McDonald Beach towards Inclusion Hill				
326	72/344	halite	2A	F	mixed alkali basalt[10]	2
327	72/343	halite, minor mirabilite, thenardite	4	W	"	30
328	72/342	halite	2A	N	hornblende-pyroxene trachyte[9]	300

Footnotes

9 after Cole and Ewart (1968)

10 glacial drift or beach deposits

6. Mt Erebus, Ross Island

Locality No.	Sample No.	Phases present	Deposit Type	Aspect	Rock types associated with deposit	Elevation
		Main Crater rim, Side Crater and slopes of active cone				
336	72E/15	halite	4	NW	anothoclase phonolite	3740
337	72E/07	calcite[+]	1B	SE	"	"
338	24877	calcite	5	W	"	3660
339	72E/02	halite	2A	W	"	3670
340	24878	halite, gypsum, sylvite	4	W	"	3680
341	24879	complex mixture including halite, minor gypsum	2A	NW	"	3700
342	24880[I]	halite plus unidentified phases	1B,4	SE	"	"
		inside camp cave				
343	74E/04	mirabilite	1A[x]	-	anorthoclase phonolite	3620
344	74E/10	gypsum	1A[x]	-	"	"
		summit plateau				
345	24881	gypsum, minor other	4	NW	anorthoclase phonolite	3450
345	24882	halite, minor other	4	NW	"	"
345	24883	complex mixture	4	NW	"	"
346 347-371	24884[I] not all sampled	complex mixtures including some alunite, also halite gypsum, thenardite	4,2A	NW and other	"	3200 to 3500

TABLE 7 Cont.

Locality No.	Sample No.	Phases present	Deposit Type	Aspect	Rock types associated with deposit	Elevation
	outer slopes of volcano opposite Fang Peak and on Fang Ridge					
375	74E/01	mirabilite, thenardite	4,2A	NE	anorthoclase phonolite	2800
376	74E/02	complex mixture	4	NE	"	"
377	74E/03	" "	4	N	trachyte	"
	Hoopers Shoulder					
378	24888	mirabilite, thenardite	4	W	anorthoclase phonolite	1800

Footnotes

+ hydrothermal calcite

I see tables 23-25 for further analyses of these samples

x rock face in cave

Tentatively identified phases in the mixtures include chloraluminate, alunogen, jarosite, malladrite, sulphohalite, and aluminium trifluoride.

TABLE 8 CRYSTALLINE SALT PHASES IN MAE WEST POND** AREA, PEARSE VALLEY (LOCALITY NO. 94)

Location or description of salt deposit	Sample No.	Phases present
salt beneath cobble above highest discernable fossil water level	72/177	halite
highest salt level: laterally persistent horizontal band ca 0.1m wide and 5mm thick	24846	gypsum
salt encrusting dried algae	24847	gypsum, minor halite
intense white band of salt bordering central salt area	24848	halite, thenardite, minor gypsum, calcite, darapskite
surface of central salt area: blocks of salt 20mm thick with botryoidal surface, and sand and gravel included	24849	halite, minor calcite, gypsum
beneath central salt area: salt crystallised from sand taken from below saline water table	72/198A	halite, minor epsomite
salt in bottom of higher arm of depression, 30m SE of central salt area	24850	gypsum, minor halite

** unofficial name

TABLE 9 CRYSTALLINE SALT PHASES IN SALT COVERED DEPRESSION IN WEST FORK OF MAIN KENNAR VALLEY SYSTEM (LOCALITY NO.138)

Location or description of salt deposit	Sample No.	Phases present
surface of depression: white salt in layer up to 20mm thick, with botryoidal surface	76/35A	darapskite, bloedite, soda nitre, epsomite, halite, trace gypsum
translucent salt in layer up to 8mm thick underlying sample 76/35A and overlying damp coarse sand	76/35B	mirabilite, trace halite, gypsum, bloedite, epsomite
twinned crystals up to 5mm long beneath surface boulders and cobbles in the depression	76/35C	gypsum

TABLE 10 CRYSTALLINE SALT PHASES IN A 4 METRE WIDE SALT COVERED DEPRESSION CA 100M FROM TERMINUS OF WRIGHT UPPER GLACIER; LOCALITY NO.223

narrow salt fringe around main deposit	72/254B	gypsum, minor darapskite, halite, thenardite
central salt area, botryoidal surface	72/254A	epsomite, halite, minor gypsum, soda nitre

TABLE 11 CRYSTALLINE SALT PHASES IN A 15M WIDE SALT COVERED DEPRESSION ON NORTH SIDE OF LABYRINTH, CA 1.5KM FROM TERMINUS OF WRIGHT UPPER GLACIER; LOCALITY NO. 230

fringe of efflorescent salt around central salt area; 3 distinct zones		
(1) outer zone	72/270A	gypsum, halite, darapskite, bloedite, thenardite
(2) middle zone	72/270B	halite, darapskite, bloedite, thenardite
(3) inner zone	72/270C	halite, bloedite, gypsum, soda nitre
central salt area; 2 distinct zones		
(1) outer zone, 2-4m wide with strongly botryoidal surface	72/270D	halite, soda nitre, bloedite, gypsum
(2) inner zone, 2m wide, of translucent salt	72/270E	mirabilite

TABLE 12 IDENTIFICATION OF MELANTERITE BY INTERPRETATION OF X-RAY DIFFRACTION PATTERN (n.a. = REFLECTION PEAK NOT ASSIGNED)

VUW Sample No.24876		Melanterite; ASTM Card No.1-255	
d spacing (Å)	relative peak intensity	d spacing (Å)	relative peak intensity
-	-	8.0	2
6.7	5	6.8	5
-	-	6.0	2
5.47	15	5.5	13
4.88	100	4.90	100
4.54	12	4.55	8
4.01	14	4.02	8
3.75	47	3.78	64
3.24	40	3.23	20
3.20	15 n.a.	-	-
3.11	14	3.09	6
3.05	5 n.a.	-	-
3.00	9 n.a.	-	-
2.92	8	2.92	3
2.79	14 n.a.	-	-
2.75	12	2.75	11
2.72	18 n.a.	-	-
2.64	18	2.63	16
2.62	15 n.a.	-	-
2.48	10	2.50	3
2.43	9	2.42	2
2.309	11	2.31	10
2.176	7	2.17	2
2.117	2	2.11	2
2.076	11	2.07	5
2.059	5 n.a.	-	-
2.010	15	2.01	8
1.960	22	1.96	8
1.922	5	1.92	2
1.880	10	1.87	8
1.861	17		
1.812	5	1.81	2
1.754	10	1.75	5
1.701	5	1.70	5
1.689	8		
1.627	7	1.63	5
1.600	5 n.a.	-	-
1.555	13	1.56	3
1.530	7	1.53	3
1.526	8		
1.502	4	1.50	3
1.497	4		
1.467	1	1.47	2

TABLE 13 IDENTIFICATION OF BURKEITE BY INTERPRETATION OF X-RAY DIFFRACTION PATTERN (sh, SHOULDER ON PEAK; br, BROAD PEAK; na, UNASSIGNED PEAK WHICH DOES NOT DISAPPEAR AFTER OVEN DRYING; * HALITE PEAK POSITION)

burkeite; ASTM card no. 2-840		thenardite; ASTM card no. 5-631		VUW sample no. 24814		trona; ASTM card no. 11-643		thermonatrite; ASTM card no. 8-448	
d	I/I_1	d	I/I_1	d spacing (Å)	relative peak intensity I/I_1 (percent)	d	I'/I_1	d	I'/I_1
-	-	-	-	9.7	31	9.88	60	-	-
-	-	-	-	5.34	4	-	-	5.35	20
-	-	-	-	5.23	6	-	-	5.24	22
				4.93)	7				
-	-	-	-	4.89)	30	4.92	40	-	-
-	-	-	-	4.71 sh	1	-	-	4.72	2
-	-	4.66	73	4.65	14	-	-	-	-
-	-	-	-	4.50 na	7	-	-	-	-
-	-	-	-	4.14 br	4	4.12	5	4.12	9
-	-	-	-	3.98	8	4.00	20	-	-
3.88	70	3.84	18	3.85 br	15	-	-	-	-
3.78	80	-	-	3.79	32	-	-	-	-
3.51	70	-	-	3.52	28	-	-	-	-
-	-	-	-	3.44	11	3.43	20	-	-
-	-	-	-	3.26 br *	4	-	-	3.24	3
-	-	-	-	3.20	13	3.21	60	-	-
-	-	3.18	51	3.17	5	-	-	-	-
-	-	3.08	47	3.07	67	3.08	80	-	-
-	-	-	-	2.82 sh,na,*	3	-	-	-	-
-	-	-	-	2.794 sh	6	2.79	5	-	-
-	-	2.783	100	2.788	33	-	-	-	-
				2.782)	36				
2.78	100	-	-	2.776)	31	-	-	-	-
-	-	-	-	2.76(6) br	37	2.76	30	2.768	100
-	-	-	-	2.754 sh	14	-	-	2.753	61
2.64 br	100	2.659	100	2.64	70	2.646	48	2.684 2.678 2.667 2.622	50 53 8 8
2.577	50	2.587	20	2.58	80	-	-	-	-
obscured	-	-	-	-	-	-	-	2.550	2
2.510	9	2.510	30	-	-	-	-	-	-
2.475	7	2.485	5	-	-	-	-	2.475	30
2.442	19	2.447	60	-	-	-	-	2.448	22
2.418	8	2.426	20	-	-	-	-	-	-
2.380 sh	2	-	-	-	-	-	-	2.386	10
2.371	13	-	-	-	-	-	-	2.372	62
obscured	-	-	-	-	-	-	-	2.356	<1

TABLE 13 Cont.

burkeite; ASTM card no. 2-840		thenardite; ASTM card no.		VUW sample no. 24814 5-631		trona; ASTM card no. 11-643		thermonatrite; ASTM card no. 8-448	
d	I/I_1	d	I/I_1	d spacing (A)	relative peak intensity I/I_1 (percent)	d	I/I_1	d	I/I_1
2.326	4	-	-	-	-	2.329	21	-	-
2.301 na	7	-	-	-	-	-	-	-	-
2.253	28	2.259	40	-	-	-	-	-	-
2.243 sh	8	-	-	-	-	-	-	2.238	20
2.206	2	-	-	-	-	2.211	5	-	-
2.182	4	2.186	5	-	-	-	-	2.181	15
2.140 br	9	2.149	20	2.13	30	-	-	-	-
		2.119	20						
2.101	3	-	-	2.10	30	-	-	2.114	<1
2.053	8	2.060	20	-	-	-	-	2.065	17
2.037	14	2.040	40	-	-	-	-	2.036	1
2.027	19	2.032	40	-	-	-	-	-	-
2.008	6	-	-	-	-	-	-	2.010	26
2.004 sh	3	-	-	-	-	-	-	2.004	20
1.992 *	7	1.996	30	-	-	-	-	1.985	4
1.973	6	-	-	1.97	10	-	-	-	-
1.960 br	6	1.965	30	-	-	-	-	1.961	3
1.925 br	12	-	-	1.93	40	1.919	4	1.920	7
1.895 br	12	-	-	1.89	40	1.891	4	1.905	3
								1.898	4
1.884	7	1.886	20	-	-	-	-	-	-
obscured	-	(plus 30 peaks not listed)	-	-	-	-	-	1.875	3
1.863 br	3			-	-	1.864	31	1.869	2
1.846	1			-	-	1.841	6	-	-
1.799	1			-	-	1.798	4	-	-
1.778	7	trona peak?		-	-	-	-	1.787	7
1.773 sh	2			-	-	-	-	1.770	5
1.759 br	3			1.75	30	-	-	1.750	4
1.740	7	trona peak?		-	-	-	-	1.741	7
1.736	7	trona peak?		-	-	-	-	-	-
1.716 br	4	trona peak?		-	-	-	-	1.726	2
								1.722	1
obscured	-			-	-	-	-	1.693	3
1.678	5			-	-	1.680	12	1.680	6

TABLE 13 Cont.

burkeite; ASTM card no. 2-840		thenardite; ASTM card no.		VUW sample no. 24814 5-631		trona; ASTM card no. 11-643		thermonatrite; ASTM card no. 8-448	
d	I/I_1	d	I/I_1	d spacing (A)	relative peak intensity I/I_1 (percent)	d	I/I_1	d	I/I_1
1.659	10	trona peak?		-	-	1.662	8	(plus 5 peaks to 1.608, not listed)	
1.619	1			1.62	5	-	-		
1.610	3			-	-	1.605	5		
1.594	12	trona peak?		-	-	-	-		
1.585 sh	3			-	-	1.589	3		
1.552	4			-	-	1.553	10		
1.544	1	trona peak?		-	-	-	-		
1.535	1			-	-	1.537	<1		
1.517	1			-	-	1.512	2		
1.500 br	1			1.50	10	1.497	5		
1.465	4			1.46	10	1.465	<1		

TABLE 14 RECONNAISSANCE ANALYSES OF MAJOR CATIONS IN SAMPLES FROM (1) ICING PRODUCED BY 1976 SALINE DISCHARGE FROM TAYLOR GLACIER DISCHARGE SITES, (2) SALINE SPRING OF NOVEMBER, 1976 (3) IRON-STAINED ENGLACIAL AND SUBGLACIAL LAYERS AND CLEAN GLACIAL ICE FROM TAYLOR GLACIER, (4) MELTWATER FROM TAYLOR AND RHONE GLACIERS (5) SALINE GROUND WATER FROM BENEATH SALT CRUST IN MAE WEST POND, PEARSE VALLEY. CONCENTRATIONS IN g.m^{-3}(mg.l^{-1}) OF MELTED SAMPLE

Sample description	Locality No.	Sample No.	Na^+	K^+	Mg^{2+}	Ca^{2+}
1. 1976 icing						
light orange coloured "snowy" ice from 0-7cm	21	76/05A	7700	130	1100	1300
orange coloured hard ice from 7-14cm underlain by moat ice of L. Bonney	21	76/05B	8500	150	1200	2500
surface "snowy" ice, lighter coloured than sample 76/05A	22	76/07	6500	90	860	390
vertical to subvertical plate crystals of salty ice occupying void of breached, low profile, icing blister	23	76/06	5600	210	1500	790
2cm thick layer of white salt and ice in channel 13-15cm wide, in stream delta, overlain by lake moat ice and multi-layered icing blister	24	76/08	83000	740	8800	2900
orange coloured "snowy" ice on surface of icing blister at lateral discharge site	2	76/10	7100	220	1600	1200
orange coloured ice of 1976 discharge event infilling crevasse on glacier, then exposed after calving of ice block	25	76/12	5200	90	900	620
2. saline spring (liquid samples)						
salty water upwelling from 8 main "subsprings" in 6 x 1m area at lateral discharge site, 22/11/76: subspring 8	2	76/53A	34000	780	9400	2900
subspring 5	2	76/53B	30000	620	8100	2600
Sample from spring taken one week later on 29/11/76; subspring 15	2	76/72	30000	630	8400	2700
3. englacial and subglacial samples						
dark orange coloured englacial layer containing gypsum crystals; sampled just after calving from glacier	10	76/11	140	1.3	8.8	600
13cm thick orange coloured layer from basal dirt layer on south side of glacier, 180m from lake	35	76/03I	2000	20	560	520
orange coloured subglacial ice within marginal mound, 60m from glacier discharge site	19	76/17I	80	2.9	6.4	790

TABLE 14 Cont.

Sample description	Locality No.	Sample No.	Na^+	K^+	Mg^{2+}	Ca^{2+}
clean glacial ice from opposite southern ice cored moraine ridge at glacier terminus	33	76/66	3	0.04	0.6	3
clean glacial ice from 15m below surface of Taylor Glacier at drill hole no.3, opposite Pandora Spire, 40km up from snout	47	76/30	10	0.3	1.0	18
tephra-debris layer in ice from Ferrar Glacier, west of Kukri Hills	44	76/42	30	2.1	6.9	11
4. melt waters (liquid samples)						
dripping icicle on glacier below glacier discharge site, November 1976	4	76/54	1600	16	590	410
water in main crevasse at glacier discharge site, November 1972	1	72/214A	80	3.0	3.5	1
water flowing off glacier, 6m from main crevasse, November, 1972	3	72/214B	220	5.0	7.3	20
melt stream from east side of Rhone Glacier, November, 1976	32	76/62	20	1.2	8.4	12
5. saline ground water, Mae West Pond						
saline ground water from beneath salt crust in centre of salt covered depression. Water table 6cm below surface	94	72/200	60000	2400	5500	840

TABLE 15 COMPOSITION OF SALINE DISCHARGE BRINES FROM SALINE SPRING (LOCALITY NO.2) AND GLACIER DISCHARGE SITE (LOCALITY NO.1), AT TERMINUS OF TAYLOR GLACIER. Concentrations in kg m^{-3} (g l^{-1}) or moles kg^{-1} (*). (nd = not determined).

Ion	Analytical precision (approx %)	Sample					
		76/53A[1]	76/53B[1]	76/72	76/72*	78/01[2]	sea water[3]
Na^+	5	32.1	28.0	27.5	1.11	25.8	10.825
K^+	5	0.730	0.605	0.595	0.0141	0.74	0.390
Mg^{2+}	5	4.2	3.5	3.8	0.14	3.0	1.304
Ca^{2+}	10	2.4	2.1	2.2	0.050	2.2	0.410
Cl^-	1	59.2	51.5	49.8	1.30	45.1	19.455
SO_4^{2-}	5	nd	nd	4.98	0.0480	4.44	2.714
HCO_3^-	10	3.5	2.9	3.3	0.050	nd	0.144
δD (4)	0.6	-311ppt	-308ppt	nd	-	nd	0
$\delta^{18}O$ (4)	0.5	-39.2ppt	-38.7ppt	nd	-	nd	0

* Cations and anions agree within 4% (ie within analytical error) in electroneutrality equation; total ionic strength = 1.72 ± 0.08

1 Nitrate in stream from spring, was 0.25 g.l^{-1} as determined using specific ion electrode

2 Cation concentrations based on analyses by N.H. Holden (Chemical Services Laboratories Ltd, Wellington)

3 Calculated from Sverdrup <u>et al</u>., (1942)

4 Stable isotope analyses by G.L. Lyon (Institute of Nuclear Sciences, DSIR); $\delta^{18}O$ analysis corrected for Mg^{2+}, Ca^{2+} and K^+ content by method of Sofer and Gat (1972)

TABLE 16 BULK PROPERTIES OF SALINE SPRING AND GLACIER DISCHARGE BRINES (parentheses indicate that precipitation had occurred)

Property	Sample				
	76/53A[1]	76/53B[1]	76/72[1]	78/01[2]	sea water[3]
In situ temperature (± 0.3°C)	-7.5	-5.3	-5.1	-5.5	-
Freezing point depression (± 0.2°C)	(-7.9)	(-5.6)	nd	-5.5	-1.9
Specific conductance at 25°C (mmhos.cm^{-1}, ± 1%)	127	115	112	99	53
Density at 20°C (Mg m^{-3}, kg l^{-1})	(1.1)	(1.078)	(1.08)	(1.069)	1.025

1 *In situ* pH 6 measured using Whatman BDH pH papers

2 pH 6.2 ± 0.2 measured using Beckman Zeromatic II pH meter at +23°C, 24 hours after sampling

3 Sverdrup *et al.*, (1942)

TABLE 17 SPECIFIC CONDUCTANCE CHLORIDE CONCENTRATION AND FREEZING POINT DEPRESSION OF MELTED SAMPLES FROM 1976 ICING FROM SALINE DISCHARGE (nd NOT DETERMINED)

Locality No.	Sample No.	Specific conductance[1] at 25°C (m.mho.cm^{-1})	Chloride concentration[1] (kg.m^{-3})	Freezing Point depression[2] (°C)
21	76/05A	53.9	16.0	-2.5
21	76/05B	57.9	17.7	-2.7
22	76/07	36.4	7.39	-1.5
23	76/06	nd	14.5	nd
24	76/08	(38.2)[3]	145	nd
2	76/10	54.4	16.7	nd
25	76/12	31.6	6.82	nd

1 analytical precision ± 1%

2 These values are up to 0.2°C too high owing to precipitation before measurement; analytical precision ± 0.2°C

3 Specific conductance for sample 76/08 diluted 10 times.

TABLE 18 SPECIFIC CONDUCTANCE, CHLORIDE CONCENTRATION AND FREEZING POINT DEPRESSION OF MELTED SAMPLES OF IRON-STAINED AND CLEAN GLACIAL ICE FROM TAYLOR GLACIER (nd = NOT DETERMINED) (UD = UNDETECTABLE)

Locality No.	Sample No.	Specific conductance (m.mho.cm^{-1})	Chloride concentration (kg.m^{-3})	Freezing Point depression (°C)
orange coloured englacial layers in ablation valley near glacier discharge site				
10	76/11	1.85	0.053	0.0
26	76/13	1.47	0.076	nd
27	77/02C	4.81	0.071	nd
27	77/02D	3.48	0.264	ca-0.1
28	77/03D	1.36	0.128	nd
orange coloured layer from basal dirt layers on south side of glacier				
35	76/03I	15.6	1.76	-0.5
orange coloured subglacial ice within marginal mound, 60m from glacier discharge site				
19	76/17I	1.77	0.010	0.0
clean glacial ice				
33	76/66	0.0127	UD	0.00
47	76/30	0.0208	UD	0.00

TABLE 19 SPECIFIC CONDUCTANCE AND CHLORIDE CONCENTRATION OF MELTWATER FROM TAYLOR AND RHONE GLACIERS, LAKE BONNEY WATER AND SALINE GROUND WATER FROM MAE WEST POND

Location and description	Locality	Sample	Specific conductance (m.mho.cm^{-1})	Chloride concentration (kg.m^{-3})
meltwater from vicinity of glacier discharge site				
from melt stream on marginal mound below glacier discharge site, sampled 22/12/73	5	73/256	8.62	2.15
dripping icicle on glacier below glacier discharge site, 22/11/76	4	76/54	nd	1.72
runnoff from ablation valley, sampled below glacier discharge site 30/11/77	3	77/04	2.62	0.146
runnoff from glacier, 6m from main crevasse 28/11/72	3	72/214B	nd	0.136
meltwater in main crevasse at glacier discharge site 28/11/72	1	72/214A	nd	0.047
melt flowing over ice at glacier discharge site, 30/11/77	1	77/05	1.64	0.097
meltwater from Taylor and Rhone Glaciers, dammed by ice block fall and supplying fresh water spring which was issuing 150m west (up glacier) from lateral discharge site				
sampled by P.H. Robinson 2/1/78	30	77/01	0.758	<0.002

TABLE 19 Cont.

Location and description	Locality	Sample	Specific conductance (m.mho.cm^{-1})	Chloride concentration (kg.m^{-3})
meltwater from Rhone Glacier				
melt stream from east side of Rhone Glacier sampled 10m above stream delta adjacent to Taylor Glacier discharge site, 22/12/73	31	73/257	0.195	$<$0.002
same melt stream sampled beside Rhone Glacier, 25/11/76	32	76/62	0.179	0.028
water from west lobe of Lake Bonney				
lake water welling up through a hole in the moat ice below a pressure ridge in front of Taylor Glacier, sampled 22/11/76	29	76/52	2.36	0.596
saline ground water, Mae West Pond				
saline ground water from beneath salt crust in centre of salt covered depression	94	72/200	167	91.7

TABLE 20 SPECIFIC CONDUCTANCE AND CHLORIDE CONCENTRATION OF MELTED SAMPLES OF BASAL AND ENGLACIAL DIRT LAYERS FROM TAYLOR GLACIER UP GLACIER FROM TERMINUS. CLEAN ICE SAMPLE INCLUDED FOR COMPARISON (UD = UNDETECTABLE)

debris rich ice in englacial layer 10m from south side of glacier, 13.5 km from snout	42	76/23	0.429	$<$0.002
northernside of glacier, below eastern end of Friis Hills: two samples (1) lowest debris layer	43	76/25	0.240	$<$0.002
2m from moat ice, (2) englacial debris layer, 8 m east of (1)	43	76/26	0.251	$<$0.002
tephra-debris (englacial) layer in ice from Ferrar Glacier, 1km west of Kukri Hills	44	76/42	0.163	0.012
basal debris layer, northeast side of Cavendish Rocks	45	76/90	0.859	$<$0.002
series of diffuse, low concentration englacial debris layers, 3km SSE of Cavendish Rocks; 2	46	76/29A	0.759	UD
samples from different layers	46	76/29B	0.776	UD
basal debris layer, in Beacon Valley lobe of glacier	48	76/40	0.294	UD
upper part of basal debris layer in Kennar Valley lobe	49	76/36	0.0597	UD
clean ice 1m above previous sample	49	76/37	0.0695	UD
clean glacial ice from 15m below surface, drill hole 3, opposite Pandora Spire	47	76/30	0.0208	UD

TABLE 21 SPECIFIC CONDUCTANCE THROUGH IRON-STAINED LAYERS IN ABLATION VALLEY, ABOVE GLACIER DISCHARGE SITE

Locality No.	Sample No.	Location	Distance from clean ice on southside of layer (m)	Specific conductance (mmho .cm^{-1})
27	77/02A	clean ice	0	0.181
"	77/02B	"	0.4	0.257
"	77/02C	inside layer	0.8	4.81
"	77/02D	"	1.1	3.48
"	77/02E	clean ice	1.4	0.256
"	77/02F	"	1.7	0.221
28	77/03A	clean ice	0	0.106
"	77/03B	clean ice	0.4	0.179
"	77/03C	just inside layer	0.6	0.765
"	77/03D	centre of layer	0.8	1.36

TABLE 22 TRACE ELEMENT ANALYSIS (ppm) OF CARBONATE PRECIPITATE SAMPLE NO. 24822 FROM 1972 SALINE ICING (ANALYSIS BY P. KENNEDY, VUW, USING X-RAY FLUORESCENCE: ANALYTICAL UNCERTAINTY IN LAST FIGURE)

Rb	16
Sr	1110
Y	9
Zr	9
Nb	<2
V	<2
Cr	<2
Ni	5
Cu	<2
Zn	13
Ba	<5
Pb	19
Th	<1

TABLE 23 MAJOR ELEMENT ANALYSES (% BY WT.) OF VOLCANOGENIC SALTS FROM MT. EREBUS. (ANALYSIS BY W. ZOLLER, UNIVERSITY OF MARYLAND, USING NEUTRON ACTIVATION: ANALYTICAL UNCERTAINTY IN LAST FIGURE)

Element	Sample No. 24880[1]	24885[2]	24886[3]
Na	8.2	3.9	1.8
Mg	2.4	0.2	4.0
K	0.30	2.5	1.1
Ca	0.21	1.6	0.9
Si	2.0	10.8	1.7
Al	10.4	8.8	12.2
Fe	1.9	2.5	0.27
Mn	0.17	0.11	0.17
Ti	0.080	0.30	0.04
H	3.9	3.0	3.6
F	<1	4.8	1.1
Cl	17.6	5.3	1.2
S	0.87	0.28	10
S as SO_4^{2-}	2.6	0.84	31

1 Yellow salt in joints and under cobbles on crater-facing side of Nausea Knob; locality no. 342

2 Yellow salt in massive deposit on wall of Inner Crater near Main Crater floor; locality no. 330

3 White salt on surface of rock around steam fumerole in Main Crater; locality no. 331.

TABLE 24 TRACE ELEMENT ANALYSES (ppm) OF VOLCANOGENIC SALTS FROM MT. EREBUS (ANALYSIS BY P. KENNEDY, V.U.W., USING X-RAY FLUORESCENCE)

Element	Sample No. 24880	24884[1]	24885
Rb	76	15	22
Sr	158	39	89
Y	26	2	14
Zr	642	182	340
Nb	171	7	41
V	<2	<2	5
Cu	8	<2	12
Zn	112	134	200
Ba	266	17	40
Pb	87	4	154
Th	11	5	3

1 Light yellow sample from beneath cobbles and lava blocks on Eastern Cone.

TABLE 25 RARE EARTH ELEMENT ANALYSES (PPM) OF VOLCANIC SALTS FROM MT EREBUS (ANALYSIS BY W. ZOLLER, UNIVERSITY OF MARYLAND, USING NEUTRON ACTIVATION)

Element	Sample No. 24880	24885	24886
Sm	7.4	10.4	11.6
Gd	5.6	7.5	9.6
Yb	2.2	3.0	40
Lu	0.2	1.3	190

TABLE 26 ACCUMULATIONS OF SALT WITH TIME IN TAYLOR AND BEACON VALLEYS

1. TAYLOR VALLEY: GREATEST ACCUMULATIONS OF SALT BENEATH COBBLES ON FLAT TERRAIN OF THREE BASALTIC CINDER CONES, DATED BY ARMSTRONG (1978)

(1) 1.53 ± 0.06 million year old cone between Born and Calkin Glaciers, locality no.77

Sample No.	Total salt in sample (g)	Percent salt in sample	Total halides (g)	Percent halides in sample	Percent halides in salt
76/47A	88.3	17.8	33.8	6.8	38.3
76/47B	157.8	26.6	58.2	9.8	36.9
(2) 2.00 ± 0.18 million year old cone beside Rhone Glacier, locality no. 78					
76/63A	14.8	1.1	1.05	0.08	7.1
76/63B	8.6	0.5	0.32	0.02	3.7
76/63C	8.8	0.8	-	-	-
(3) 3.33 ± 0.14 million year old cinder beside Matterhorn Glacier, locality no. 79					
76/64A	178.0	7.9	80.0	3.5	44.9
76/64B	164.1	15.2	85.1	5.2	51.9
76/64C	262.9	16.6	113.6	7.2	43.2

2. BEACON VALLEY, LOCALITY NUMBER 80: REPRESENTATIVE SAMPLES OF SOIL (SURFACE TO FROZEN LEVEL) FROM CENTRE OF FROST POLYGONS ON EITHER SIDE OF YOUNGEST MORAINE OF LOBE OF TAYLOR GLACIER. THIS IS ONE OF BLACK'S (1973) SAND WEDGE GROWTH SITES

Northside of moraine (i.e. younger surface)

Sample No.	Specific conductance of 1:5 soil-water extract (mmho . cm^{-1})
76/38A	2.30
76/38B	1.17
76/38C	1.04

average 1.50, standard deviation 0.69

TABLE 26 Cont.

Southside of moraine (i.e. older surface)

Sample No.	Specific conductance of 1:5 soil-water extract (mmho . cm^{-1})
76/39A	2.78
76/39B	1.28
76/39C	2.66

average 2.24, standard deviation 0.83

TABLE 27 PREFERRED TYPES OF DEPOSIT OF SALT PHASES

(a) Per cent occurrences of various salts in specific deposit types

(1) Soluble salts in Taylor, Wright, Ferrar Valleys, Skelton Névé, Mt Kempe

Salt Phase	Deposit Type		
	surface efflorescence or encrustation (type (2A)	deaquation deposit (type 2B)	accumulation beneath cobble or in soil (4,5)
soda nitre	4	16	8.6
darapskite	4	16	11.7
epsomite	4	8	11.0
hexahydrite	0	0	1.2
bloedite	2	12	11.7
halite	26	28	11.0
thenardite	49	12	30.1
mirabilite	0'	8'	14.7
number of occurrences	45	25	163

' ambiguous locality 89 (Pearse Valley) not included

(2) Soluble salts on Mt's Discovery and Morning, Black and White Islands, Cape Bird, Hoopers Shoulder

Salt Phase	surface efflorescence or encrustation (type (2A)	deaquation deposit (type 2B)	accumulation beneath cobble or in soil (4,5)
soda nitre	0	-	0
darapskite	0	-	0
epsomite	3	-	4
hexahydrite	3	-	4
bloedite	10	-	4
halite	32	-	16
thenardite	39	-	48
mirabilite	13	-	24
number of occurrences	31	0	25

TABLE 27 Cont.

(3) calcite, gypsum and soluble salts as in (1)

Salt	Deposit Type Surface encrustation (1A, 1B, 1C)	Surface efflorescence and encrustation (2A)	Deaquation deposit (2B)	Subsurface accumulation (3, 4, 5)
calcite	44.0	no data	3	13.4
gypsum	48.0	(50.5)	19	34.5
solubles	8.0	(49.5)	78	52.1
no.	75	(91)	32	313

(4) Frequently occurring soluble phases in Aztec, Kennar and Labyrinth areas only (70-80 km from coast)

Salt	Deposit Type surface efflorescence (2A)	subsurface accumulation (4,5)	deaquation deposit (2B)	2A+4+5	Ratios* $\frac{2B}{4+5}$	$\frac{2B}{2A+4+5}$
soda nitre	10	19	21	17	1.1	1.2
darapskite	10	19	16	17	0.8	0.9
epsomite	0	14	10	11	0.8	1.0
bloedite	0	14	16	11	1.2	1.5
halite	20	5	21	8	3.9	2.5
thenardite	60	30	16	36	0.53	0.44
no.	10	37	19	47		

* ratios of percent of occurrences in types as indicated

(b) Percent occurrences of various deposit types of specific salts

(1) as in (a) (1)

Deposit type	Salt soda nitre	darapskite	epsomite	bloedite	halite	thenardite
2A	10	8	9	4	39	29.7
2B	20	16	9	13	17	4.1
4,5	70	76	82	83	44	66.2
number of occurrences	20	25	22	23	41	74
ratio* $\frac{2B}{4+5}$	0.29	0.21	0.11	0.16	0.39	0.061
$\frac{2B}{2A+4+5}$	0.25	0.19	0.10	0.13	0.21	0.042

* ratio of number of occurrences in types as indicated

TABLE 27 Cont.

(2) as in (a) (3)

Deposit Type	Salt		
	calcite	gypsum	solubles
1A, 1B, 1C	44.3	18.4	2.5
2A	no data	23.5	18.8
2B	1.3	3.1	10.5
3, 4, 5	55.3	55.1	68.2
no.	76	196	239
ratio* $\frac{2B}{3+4+5}$	0.024	0.056	0.153
$\frac{2B}{2A+4+5}$	-	0.039	0.120

* ratio of number of occurrences in types as indicated

(3) as in (a) (4) (Number of occurrences, not per cent occurrences)

Deposit Type	Salt					
	soda nitre	darapskite	epsomite	bloedite	halite	thenardite
2A	1	1	0	0	2	6
2B	4	3	2	3	4	3
4,5	7	7	5	5	2	11
2A+4+5	8	8	5	5	4	17
ratios $\frac{2B}{4+5}$	0.6	0.4	0.4	0.6	2	0.27
$\frac{2B}{2A+4+5}$	0.5	0.4	0.4	0.6	1	0.18

TABLE 28 PREFERRED ASPECT OF SOLUBLE SALT ACCUMULATIONS (UNITS: PERCENT IN QUARTERS). DATA FOR TAYLOR, WRIGHT, FERRAR VALLEYS, SKELTON NÉVÉ AND MT KEMPE (p, significance level)

a) aspect bias of surface efflorescences (deposit type 2A)

Aspect (quarter)	Salt phase		
	thenardite[1]	halite, soda nitre, darapskite, bloedite, epsomite[1]	all soluble salts
north	42	47	44
east	19	16	18
south	10	26	16
west	29	11	22
total no. of aspect data	31	19	50
p = 0.05	31	40	25
p = 0.01	39	49	30

1. Mirabilite or hexahydrite counted as thenardite or epsomite but only one phase of each salt counted per sample; eg deposit with mirabilite, epsomite, hexahydrite counted as containing thenardite once and epsomite once.

TABLE 28 Cont.

b) subsurface deposits (types 4 and 5)

(i) aspect bias

Aspect (quarter)	Salt							
	soda nitre	darapskite	both nitrates	epsomite	bloedite	halite	thenardite	all six phases
north	20	32	27	29	33	23	31	29.2
east	15	14	14	29	30	36	21	24.0
south	50	45	48	25	22	36	28	32.2
west	15	9	11	17	15	5	20	14.6
number of aspect data	15	22	37	24	27	22	61	171
p = 0.05	45	37	29	35	33	37	22	13.2
p = 0.01	55	46	35	44	41	46	28	16.4

(2) Salt Separation

Salt	Aspect			
	north	east	south	west
soda nitre	6	5	14	8
darapskite	14	7	18	8
epsomite	14	17	11	16
bloedite	18	20	11	16
halite	10	20	15	4
thenardite	38	32	31	48
number of occurrences	50	41	55	25

TABLE 29 PREFERRED ASPECT OF GYPSUM ACCUMULATIONS (UNITS : PERCENT IN QUARTERS) DATA FROM TAYLOR WRIGHT, FERRAR VALLEYS, SKELTON NÉVÉ AND MT KEMPE (p, significance level)

Aspect (quarter)	Deposit Type		
	surface encrustation on rock (1A,1B)	surface encrustation on regolith (2A)	subsurface accumulation (4,5)
north	36	46	35.2
east	16	21	23.1
south	29	15	22.2
west	19	18	19.4
number of aspect data	31	33	108
p = 0.05	31	30	16.7
p = 0.01	39	37	20.6

TABLE 30 PREFERRED ASPECT OF CALCITE ACCUMULATION (UNITS : PERCENT IN QUARTERS) (p, significance)

Aspect (quarter)	Deposit Type	
	surface encrustation (1A,1B)	veneer (3)
north	49	52
east	18	19
south	12	10
west	21	19
number of aspect data	33	42
p = 0.05	31	27
p = 0.01	37	33

TABLE 31 ASPECT COMPARISONS BETWEEN ACCUMULATIONS OF SOLUBLE, SPARINGLY SOLUBLE, AND INSOLUBLE SALTS (UNITS : PER CENT IN QUARTERS)

Salt	Aspect			
	north	east	south	west
(1) surface encrustation (2A)				
soluble salts[1]	59	55	60	65
gypsum	41	45	40	35
number of occurrence data	37	16	13	17
(2) subsurface encrustations (3,4,5)				
soluble salts[1]	45.5	55.4	66.2	46.3
gypsum	34.5	33.8	28.9	38.9
calcite	20.0	10.8	4.8	14.8
number	110	74	83	54

[1] includes soda nitre, darapskite, epsomite, bloedite, halite, thenardite as on Table 28.

TABLE 32 SALT DISTRIBUTION AS A FUNCTION OF ROCK TYPE (PERCENT OCCURRENCE) (SALTS ON MT EREBUS EXCLUDED)

Salt	Dominant Rock Type						
	volcanics	Dolerite	plutonics	Beacon Supergroup			metasediments
				all	Taylor Group	Victoria Group	
soda nitre	0	5.2	0	6.3	8	0	5
darapskite	1.2	8.5	5	7.9	11	0	0
epsomite[1]	2.4	10.5	0	0	0	0	0
bloedite	4.9	9.8	0	0	0	0	0
halite	22.0	5.2	32	0	0	0	15
thenardite[1]	31.7	19.6	23	20.6	19	26	20
gypsum	30.5	29.4	23	49.2	49	57	45
calcite	7.3	11.8	18	15.9	14	17	15
number	82	153	22	63	37	23	14

[1] hexahydrite and mirabilite included as epsomite or thenardite but only one per sample (see footnote to Table 28a).

TABLE 33 SALT DISTRIBUTION IN WRIGHT, TAYLOR, AND FERRAR VALLEYS - SKELTON NÉVÉ, WHERE DOLERITE IS DOMINANT OR ONLY ROCK TYPE PRESENT (PERCENT). SOLUBLE SALTS ONLY

Salt	Wright Valley	Taylor Valley	Ferrar Valley and Skelton Névé
soda nitre	14	4	7
darapskite	11	14	19
epsomite	11	25	19
bloedite	14	18	19
halite	11	7	7
thenardite	37	32	30
number	35	27	28

TABLE 34 SALT DISTRIBUTION AS A FUNCTION OF ELEVATION (PERCENT OF OCCURRENCES INDICATED ELEVATION RANGE). ROSS, BLACK AND WHITE ISLAND LOCALITIES NOT INCLUDED

Salt	Elevation (m)						
	0-399	400-799	800-1199	1200-1599	1600-1999	2000-2399	≥2400
(a) frequently occurring salts							
soda nitre	0	1.8	6.7	11.8	5.8	1.7	0
darapskite	0	7.3	5.6	7.8	8.7	3.4	0
epsomite[1]	3	3.6	2.2	2.0	6.8	10.3	14
bloedite	3	3.6	4.4	3.9	6.8	8.6	5
halite	32	27.3	17.8	3.9	1.9	1.7	0
thenardite[1]	16	23.6	18.9	25.5	15.5	27.6	16
gypsum	29	30.9	36.7	41.2	36.9	36.2	47
calcite	16	1.8	7.8	3.9	17.5	10.3	19
total no. of occurrences	31	55	90	51	103	58	43

[1] hexahydrite and mirabilite included as epsomite or thenardite but only one per sample

Salt	0-399	400-799	800-1199	1200-1599	1600-1999	2000-2399	≥2400
(b) frequently occurring soluble phases only							
soda nitre	0	3	12	21	13	3	0
darapskite	0	11	10	14	19	7	0
epsomite	6	5	4	4	15	19	40
bloedite	6	5	8	7	15	16	13
halite	59	41	31	7	4	3	0
thenardite	29	35	35	46	34	52	47
number	17	37	50	28	47	31	15
(c) anions							
nitrates (soda nitre (darapskite	0	14	22	36	32	10	0
chlorides (halite)	59	41	32	7	4	3	0
sulphates (epsomite (bloedite thenardite	41	45	46	57	64	87	100
(d) frequently occurring soluble phases in Taylor, Pearse, Wright Valleys below 1600m and within 70 ± 5 km of the coast							
soda nitre	0	3	13	25	-	-	-
darapskite	0	12	11	15	-	-	-
epsomite	0	6	2	0	-	-	-
bloedite	0	6	7	5	-	-	-
halite	70	41	33	15	-	-	-
thenardite	30	32	33	40	-	-	-
number	14	34	45	15	-	-	-

TABLE 34 Cont.

(e) frequently occurring soluble phases in Aztec, Kennar, Lashly, Ferrar, Skelton, Fleming and Shapeless areas, above 1600 metres elevation

Salt	Elevation (m)						
	0-399	400-799	800-1199	1200-1599	1600-1999	2000-2399	≥2400
soda nitre	-	-	-	-	13	3	0
darapskite	-	-	-	-	19	7	0
epsomite	-	-	-	-	15	21	45
bloedite	-	-	-	-	15	17	10
halite	-	-	-	-	4	0	0
thenardite	-	-	-	-	34	52	45
number	-	-	-	-	47	29	11

(f) frequently occurring soluble phases in Aztec, Kennar, Labyrinth Fleming, Shapeless areas (70-80 km from coast)

Salt	Elevation		
	800-1399	1400-1999	≥2000
soda nitre	23	21	4
darapskite	15	14	8
epsomite	4	10	32
bloedite	12	17	16
halite	23	0	0
thenardite	23	38	40
number	26	29	25

TABLE 35 SALT DISTRIBUTION AS A FUNCTION OF MAP DISTANCE INLAND FROM COAST (PERCENT OF OCCURRENCES IN INDICATED DISTANCE RANGE) DATA FROM TABLE 7 (McMURDO SOUND) EXCLUDED. DATA DERIVED FROM NISHIYAMA (1977) INCLUDED (VIZ TAYLOR VALLEY, 0-35KM INLAND; AND WRIGHT VALLEY, 45-60 KM INLAND)

Salt	Map distance inland up valleys (km) (see footnotes)									
	0-5	5-15	15-25[3]	25-35	35-45[4]	45-55	55-65	65-75[5]	75-85	≥100
a) Taylor Valley										
soda nitre	0	0	0	0	0	2	-	9.7	9.8	0
darapskite	0	0	0	0.9	1.6	10	-	8.3	9.8	0
epsommite[1]	0	0	0	0	0	5	-	6.9	6.6	13
bloedite	0	0	0	0	0	5	-	6.9	8.2	4
halite	15.5	32.1	21.5	39.4	36.9	27	-	1.4	1.6	0
thenardite[1]	12.4	25.5	6.2	26.6	25.4	20	-	19.4	19.7	17
trona,[2] thermonatrite	17.5	8.5	0	0	0	0	-	0	0	0
gypsum	2.1	0	9.2	13.8	16.4	27	-	38.9	36.1	52
calcite	52.6	34.0	63.1	19.3	19.7	5	-	8.3	8.2	13

TABLE 35 Cont.

Salt	Map distance inland up valleys (km) (see footnotes)									
	0-5	5-15	15-25[3]	25-35	35-45[4]	45-55	55-65	65-75[5]	75-85	≥100
total no.	97	106	65	109	122	41	no data	72	61	23
b) frequently occurring soluble phases (Taylor, Wright, Ferrar Valleys and Skelton Névé										
soda nitre	0	0	0	0	2.1	4.3	7	23	21.1	12
darapskite	0	0	0	2.4	3.2	9.4	9	15	14.0	6
epsomite[1]	0	0	0	0	0	2.6	0	7	10.5	41
bloedite	0	0	0	1.2	1.1	5.1	9	10	17.5	12
halite	56	55.7	60.8	53.7	53.7	43.6	43	20	1.8	0
thenardite[1]	44	44.3	39.2	42.7	40.0	35.0	33	25	35.1	29
number	27	61	79	82	95	117	44	40	57	17
c) gypsum and calcite, percent of total occurrences in Taylor, Wright Ferrar Valleys and Skelton Névé										
gypsum	1.7	0	9.2	16.1	39	28.8	34.9	32.4	35.9	45.6
calcite	44.0	34.0	63.1	17.7	12	9.9	12.0	8.8	8.7	17.4
number	116	106	65	124	26	191	83	68	103	46

1 hexahydrite and mirabilite included as epsomite or thenardite but only one occurrence per sample

2 occurrences of trona and thermonatrite (Nishiyama 1977) added together but only one per sample

3 percent occurrences in 5-25 km distance range calculated for soluble phases (b) because of insufficient numbers in 15-25 km range

4 percent occurrences in 25-45 km range calculated for Taylor Valley (a) and soluble phases (b) because of insufficient numbers in 35-45 km range

5 percent occurrences in 65-85 km range calculated for Taylor Valley (a) because of insufficient numbers in 65-75 km range

TABLE 36 SALT DISTRIBUTION ALONG A NORTH-SOUTH SECTION FROM CAPE BIRD (NORTH) TO MT DISCOVERY (SOUTH) (PERCENT OCCURRENCE). DATA FROM KEYS (1972) INCLUDED (VIZ CAPES ROYDS, BARNE AND EVANS, AND HUT POINT (PENINSULA). SOLUBLE SALTS ONLY INCLUDED

Salt	Cape Bird	Capes Royds, Barne & Evans	Hut Point Peninsula	Black and White Is.	Mt Discovery area (up to 1000m a.s.l.)
nitrate phases	0	0	0	0	0
epsomite	0	0	10	0	18
bloedite	9	0	0	0	18
halite	48	51	20	20	9
thenardite	43	49	70	80	55
no. of occurrences of soluble phases	21	37	14	9	11
gypsum	9	0	21	8	50
calcite	0	3	21	17	8
total no. of occurrences	23	38	24	12	26
median distance south from Cape Bird, projected onto 166° meridian	0	35	63	90	123

APPENDIX 2 SOURCES OF ERROR IN, AND STATISTICAL TREATMENT OF, SALT DISTRIBUTION DATA

APPENDIX 2 SALT DISTRIBUTION DATA: SOURCES OF ERROR AND STATISTICAL TREATMENT

A2.1 Sources of Error

Salt accumulation is not regular; salts are sporadically distributed and normally cover only a small part of the surface in any area. This makes it difficult to obtain a representative sample from an area, that is, to achieve a high sampling efficiency. During the field work for this study, salt samples were taken from typical deposits that were encountered during many traverses over different parts of the McMurdo region (see Appendix 1, Figs.2, 4, 5). Systematic errors may then have developed due to (1) different sampling efficiencies and (2) variable frequency of sampling. Use of literature data may also introduce error (3).

A2.1.1 Different sampling efficiencies for (i) different salts (ii) different types of deposits:

(i) different salts

In some areas it is easier to obtain workable or identifiable samples of gypsum and calcite than the more soluble salts. Gypsum and calcite often form characteristic encrustations whereas the soluble salts may be dispersed within or on the surface of the regolith. This is most clearly seen at high elevations and in far inland regions where salt deposits are often sparse and small, and also in Taylor Dry Valley where there is an abundance of calcite veneers. Thus some sets of data possibly exaggerate the proportions of gypsum and calcite in salt deposits. Therefore, the proportions and trends for these salts should be separated in some way from those of the more soluble salts. However, any apparent trends for gypsum and calcite must still be compared with those for the soluble salts. Therefore two sets of comparisons are made in this thesis a) between all common salts including gypsum and calcite and b) between the more soluble salts only. The latter salts all have very similar appearances and cannot usually be differentiated in the field.

(ii) different deposit types

It is easiest to obtain workable samples from types 2, 3 and 4 deposits. Types 1 and 5 are often small or contaminated with rock or soil. Therefore, the data may underestimate the importance of these deposits. This is not a serious problem for the thesis, where deposit morphology is of secondary interest only.

A2.1.2 Variable frequency of sampling for (i) salts on slopes of different aspect (ii) salts on different substrates, at different elevations and distances from coast:

(i) salts on slopes of different aspect

Aspect may influence salt distribution in two ways by causing a) preferential movement of salt (Chapter 4) and b) preferential accumulation of salt (Chapters 3 and 6). The aspect variable is examined in this thesis by using rose diagrams. To generate sufficient data and to simplify these diagrams, the eight compass points listed for samples in Appendix 1 are condensed to quarters by combining NW, NE with N, NE, SE with E and so on. Salt data for these quarters (i.e. percent of all occurrences over 360°) are then portrayed as sectors on rose diagrams. A positive mode on such a diagram is caused by either a) a real difference in salt accumulation or b) an increased frequency of sampling over slopes of that particular aspect, i.e. biased sampling. In the present project, deliberate emphasis was placed on north- and south-facing slopes to accentuate the aspect variable. Therefore, data for east- or west-facing slopes are relatively poorly represented in some areas.

An increased frequency of sampling of particular slopes is not a primary cause of positive modes on rose diagrams presented in the thesis. Approximately fifty productive and non-productive sampling traverses were made during the field work in McMurdo oasis (Appendix 1, Figs.2, 4A, B); 29 percent of these traverses were over terrain with a pronounced northerly aspect, 26 percent had a southerly aspect, 19 percent an easterly aspect, 14 percent a westerly aspect and 12 percent were over flat or rolling terrain. Thus, there is no significant difference between north- and south-facing slopes in the numbers of sampling traverses. In any particular area an endeavour was made to examine and sample north- and south-facing slopes to the same extent.

Environmental constraints may also influence aspect data. These constraints include valley orientation, snow and ice accumulations and inaccessibility. Lack of exposure in this way may lead to slight bias in rose diagrams. Nevertheless any difference in salt accumulation on either north- or south-facing slopes is believed to be caused by a real difference in accumulation.

(ii) salts on different substrates, at different elevations and distances from the coast

Environmental constraints such as lack of exposure may also affect the study of the influence of specific variables on regional distribution of salts. However, different numbers of samples obtained, at say different elevations, does not cause bias here because the data are normalized by determining proportions. Therefore, environmental constraints merely limit ability to sample.

A2.1.3 Literature data:

Some XRD data from other workers have been used here though it was recognized that errors might arise if all phases were not identified or were wrongly identified due to poor sample quality, gross peak interference, or inexperience. This source of error can be minimized by careful screening of such data. Nishiyama's (1977, 1979) data are used in some distribution tables in the thesis because he observed the same major phases as those discussed in this thesis; however, the possibility of differing sampling efficiencies (for calcite, for example) as in A2.1.1i above must be kept in mind.

A2.2 Statistical Treatment

A2.2.1 Scope:

The two main subjects for description in the present study, regional salt distribution and relative salt mobility (local distribution) have different sampling requirements. Some variations between salts, especially the more mobile phases, are not large. Therefore, a large amount of data must be collected before statistical significance can be satisfactorily assessed. This can be achieved by (1) sampling a large number of salt deposits in a small area, or (2) a small number of samples taken from many places over a wide area. Since the study of regional distribution of salt was the main aim of this project, initially at least, the latter approach (2) was used. This enabled the statistical significance of regional trends to be examined and shown, but not local trends in general, e.g. not difference in the mobility between the various salts.

A2.2.2 Illustration and testing of the data:

The reliability of a numerical estimate can be gauged from a statistical formula or treatment. The treatments required differ with the way in which the data are presented or illustrated. Here, data are presented as:

(i) histograms
(ii) bivariate plots (scatter diagrams)
(iii) rose diagrams
(iv) miscellaneous, e.g. means

(i) histograms

Frequency (percent) distribution of salt phases are plotted as histograms in this thesis. A colour code is used to differentiate between specific phases, ions or groups of phases or ions (Table A2.1).

Two types of frequency distribution are derived but only one type is used extensively in the thesis. This type is derived by counting a specific phase, one count for each time it is present in a deposit in a particular area, rock type or other property of interest (from the raw data in Appendix 1, Tables 3, 4-7). The relative distribution (proportion) of that phase is then obtained as a percentage of the total number of counts N for all such phases. The relative distribution of ions or groups of ions or phases is obtained from this relative distribution of phases. Determining the proportions in this way maximizes the value of N. Furthermore, sufficiently large or wide class sizes (e.g. elevation ranges) are chosen to ensure sufficient N. Therefore, the effects of random errors on the frequency distribution are minimized. Random errors are caused by omissions of specific phases due to random sampling omissions. It is difficult to obtain a meaningful estimate of this error for these proportions since a complex cumulative multinomial distribution function is involved (R. Renner, VUW statistician, pers.comm.). However an estimate of the statistical significance of the data can be obtained by subsequent treatment as outlined below.

A second type of frequency distribution can be obtained by a similar method. Each phase or ion is counted in each deposit as before. However the relative occurrence of that ion or phase is obtained as a percentage of the total number of deposits N_D examined. N_D is usually less than N since many deposits are composed of more than one phase (Appendix 1). Therefore, the effects of random sampling omissions are more serious with this approach since it involves smaller total numbers of data. Its advantage is that a proportion for a

Table A2.1 Colour code for histogram illustration of distribution of phases, groups of phases and ions

Eight common salt phases (and other hydrates)

Name	Formula	Colour code
halite	$NaCl$	▨
soda nitre	$NaNO_3$	▨
darapskite	$Na_3(NO_3)(SO_4).H_2O$	▨
thenardite	Na_2SO_4	▨
bloedite	$Na_2Mg(SO_4)_2.4H_2O$	▨
epsomite	$MgSO_4.7H_2O$	▨
gypsum	$CaSO_4.2H_2O$	▨
calcite	$CaCO_3$	▨

Two hydrate phases

Name	Formula	Colour code
mirabilite	$Na_2SO_4.10H_2O$	▨
hexahydrite	$MgSO_4.6H_2O$	▨

Specific ions or groups of phases

Group name	Phases in group	Colour code
chloride (Cl^-)	halite	▨
nitrates (NO_3^-)	soda nitre, darapskite*	▨
soluble sulphates (SO_4^{2-})	thenardite, bloedite, epsomite	▨
major sulphates (SO_4^{2-})	gypsum, thenardite, bloedite, epsomite	▨
carbonate (CO_3^{2-})	calcite	▨
major sodiums (Na^+)	halite, soda nitre, darapskite, thenardite	▨
major magnesiums (Mg^{2+})	epsomite, bloedite*	▨
major calciums (Ca^{2+})	gypsum, calcite	▨
six major soluble phases	halite, soda nitre, darapskite, thenardite, bloedite, epsomite	▨
six majors plus 2 hydrates	as above, plus mirabilite, hexahydrite	▨

*In order for there to be no special emphasis placed on double salts, darapskite is considered as a nitrate (not a sulphate) and bloedite is considered as a magnesium phase (not a sodium phase).

specific phase is not directly dependent on the proportions of other phases that are present and the proportions do not sum to 100 as in the former approach. This is an important consideration when the influence of rock type on the ion proportions is being examined in 5.2.3. However, N_D is dependent on more than one phase, and therefore a cumulative binomial distribution is only an approximation of the real case. Furthermore, most values of N_D are too small for such a function to be useful for obtaining meaningful estimates of random errors for all proportions.

(ii) bivariate plots

Plots of variable y_i (e.g. frequency distribution or percent occurrence) versus variable x_i (e.g. distance from sea) are used for examining trends between such variables. Linear regression analysis (least squares fit) was performed on these plots in places in this thesis. A calculator was used to determine the best fit line which is given by:

$$y = A + Bx \qquad \ldots 1$$

One or more of three numerical measures are discussed: a) the slope B of the line; b) the t statistic for the slope; and c) the correlation coefficient r for the line.

a) slope (B): This is obtained by standard calculation methods and may be positive, negative or equal to zero. A positive slope indicates an increasing trend, a negative slope a decreasing trend, and zero slope no trend.

b) t statistic (t): The derivation of this allows assessment of the statistical significance of the value of B, at a given probability or level of confidence. From Freund et al. (1960):

$$t = \frac{B}{\sqrt{\dfrac{S^2}{\sum_{i=1}^{n} (x_i - \bar{x})^2}}} \qquad \ldots 2$$

where S^2 is the residual variance and is given by:

$$S^2 = \sum_{i=1}^{n} \frac{[(y_i - \bar{y}) - B(x_i - \bar{x})]^2}{n - 2} \qquad \ldots 3$$

where n is the number of (x, y) data points and $\bar{x}$ and $\bar{y}$ are the mean values of x and y. n must be greater or equal to three. (The necessity to maximize N as discussed above results in small numbers of n but these are allowed for in this approach) Equation 3 is considered to give the best estimate of the variance (i.e. the standard deviation of y, squared) for a small number of data fitted to a line (Steinhart and Meyer 1961). For a particular level of confidence c, having a numerical value $t_{c/2}$ of 'Students' t distribution for n - 2 degrees of freedom, a relationship such that:

$$t < -t_{c/2} \qquad \text{or} \qquad t > t_{c/2} \qquad \text{(two tail test)}$$

implies that B is significant at that level of confidence (Freund <u>et al.</u> 1960). The confidence level so determined is a maximum since x_i and y_i are assumed to be free of error. While this is usually a good assumption for x_i, it may not be so for y_i especially if y_i is a frequency distribution based on a small number of data, N or N_D. If :

$$-t_{c/2} \leqslant t \leqslant t_{c/2} \qquad \text{for } 80\% \leqslant c \leqslant 90\%$$

then there is some significant relationship between x and y. If :

$$-t_{c/2} \leqslant t \leqslant t_{c/2} \qquad \text{for } c < 80\%$$

there is no linear correlation between x and y. This condition of statistical uniformity may be caused by either constant values of, or irregular variation in, y_i.

c) correlation coefficient (r): The value of r is obtained by standard methods, and varies between -1 and +1. For $|r| \geqslant 0.7$, the values y_i are closely correlated to x_i and the data 'closely fit' the linear regression line, i.e. there is a significant variation that is 'explained' by this ordering of the data. For $|r| < 0.7$ there is a large component of 'unexplained variation'; this component increases as r tends to zero.

(iii) rose diagrams

This treatment is used for showing circular data (e.g. favoured aspect). An equation rearranged from Curray (1956) for two dimensional orientations relates the vector magnitude L (percent) at the significance level p to the total number N as follows:

$$L = 100\sqrt{\frac{-\ln p}{N}} \qquad \ldots 4$$

For example, if the magnitude of the aspect class (north, south, east or west) is greater than L for p = 0.05, then the distribution differs significantly (95% confidence level) from a uniform distribution. If the magnitude is less than L, then any trend that is apparent is not statistically significant at this level.

(iv) means

Mean values are obtained and compared in places in the thesis. The comparison between two means $\bar{x}_1$, $\bar{x}_2$ is made by deriving a t statistic t (Freund et al. 1960) where:

$$t = \frac{\bar{x}_2 - \bar{x}_1}{\sqrt{(n_1 - 1)S_1^2 + (n_2 - 1)S_2^2}}\sqrt{\frac{n_1.n_2(n_1.n_2 - 2)}{n_1 + n_2}} \qquad \ldots 5$$

where n_i and S_i are the number of data and standard deviation respectively. For a particular level of confidence c, having a numerical value $t_{c/2}$ of 'students' t distribution for $n_1 + n_2 - 2$ degrees of freedom, a relationship such that:

$$t < -t_{c/2} \qquad \text{or} \qquad t > t_{c/2} \qquad \text{(two tail test)}$$

implies that the difference between the two means is significant at that level of confidence. The difference is insignificant when:

$$-t_{c/2} \leqslant t \leqslant t_{c/2}$$

APPENDIX 3

AIR TEMPERATURE, WIND, PRECIPITATION AND ATMOSPHERIC HUMIDITY IN THE McMURDO REGION

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AIR TEMPERATURE, WIND, PRECIPITATION AND ATMOSPHERIC HUMIDITY IN THE McMURDO REGION

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AIR TEMPERATURE, WIND, PRECIPITATION AND ATMOSPHERIC HUMIDITY IN THE McMURDO REGION, ANTARCTICA.

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ABSTRACT

The mean annual air temperature near sea level in the McMurdo region is close to $-20^{\circ}C$. This temperature decreases inland. The annual mean amplitude of air temperature is $20^{\circ}C$ at Vanda Station and $13^{\circ}C$ at Scott Base. Stations in the area have recorded air temperatures as warm as $+15^{\circ}C$ and as cold as $-57^{\circ}C$. The yearly warm peak tends to occur early in January at Vanda Station. The cold peak may occur in any month from June through September but has occurred in July in each of the three winters that measurements have been made. Mean daily air temperatures in winter at Vanda Station do not closely correlate with those at Scott Base. The topographic lapse rate in the region is $4.0 \pm 0.5^{\circ}C$ per 1000m. This is at least two orders of magnitude larger than horizontal temperature gradients.

The wind regime in McMurdo oasis is dominated by easterly and westerly winds. The former are more common near the coast whereas the latter predominate in the west. Winds from the southwesterly quarter predominate along the fringe of the continental ice sheet. At Scott Base and for most of Ross Island, winds from the easterly quarter are more common but winds from the southerly quarter are stronger. The predominant winds in the summit area of Mt Erebus are west-southwesterlies.

Precipitation is low in the region and most occurs as snowfall or wind blown snow. Sea spray is not uncommon around the coast when open sea water is present. Mean annual precipitation is probably less than 10mm water equivalent at Vanda but is higher near the coast and at higher elevations. Rain is not unknown but is uncommon.

Atmospheric relative humidities are variable, varying from less than 10 percent to greater than 100 percent (with respect to ice). On the average, relative humidities are less in McMurdo oasis than in McMurdo Sound. Topographic gradients of relative humidity are variable; on the average positive gradients probably exist from low elevations in the central parts of McMurdo oasis towards higher elevations and towards both the west and east. Absolute humidities are around 10^{-3} $kg.m^{-3}$.

1. INTRODUCTION

1.1 Outline

The McMurdo region, comprising Ross Island, McMurdo Sound and McMurdo oasis (Figure 1) is one of the most intensely studied areas in the whole of Antarctica. In particular the oasis, consisting of 3000 - 4000 km^2 of mainly snow-and ice-free ground centred around Taylor, Wright and Victoria Valleys in southern Victoria Land, has been the focus of much earth science research. The climate of the area is fundamental to many studies.

Published data and information on the climate of McMurdo region in general and McMurdo oasis in particular is scattered and incomplete. This publication summarises much of what is known of specific aspects of the climate of the McMurdo region with the emphasis on the oasis. Present patterns of surface weather are detailed, including aspects of air temperature, air temperature gradients, wind, precipitation and atmospheric humidity. Temperature and humidity gradients and circulation in the lower atmosphere are also discussed. New data are presented in some sections.

This review is part of a PhD study of salt distribution and origin in the McMurdo region, and the Taylor Glacier saline discharge phenomena (Keys 1979). The contents of the present review are hence directed particularly towards the requirements of that study, but for completeness other information is presented also.

1.2 The antarctic situation and the surface inversion

Antarctica is cold and arid. The low temperatures are primarily caused by the large angle that the earth's rotation axis makes with the plane of the orbit around the sun. The average angle of incidence of solar radiation is low at high latitudes; at the Antarctic Circle it is $23\frac{2}{3}$ degrees, while at South Pole it is 0 degrees. Thus, unit horizontal areas of the earth's surface receive an annual amount of solar energy that decreases with increasing latitude to reach a minimum at the geographic poles. This effect is accentuated by the properties of the predominant surface cover in these regions. Snow reflects most of the incident (solar, shortwave) radiation and also radiates more energy than it absorbs (as terrestrial, long wave radiation). Descriptions of the heat flux and radiation balance in the region are outside the scope of this paper, and interested readers should refer to Rusin (1964), Solopov (1967), Schwerdtfeger (1970) and Thompson *et al.*, (1961, 1971a). The high mean elevation of Antarctica causes additional cooling. Because of the low temperatures, antarctic air can hold little moisture and the water substance is predominantly in the solid form. Therefore the continent is arid.

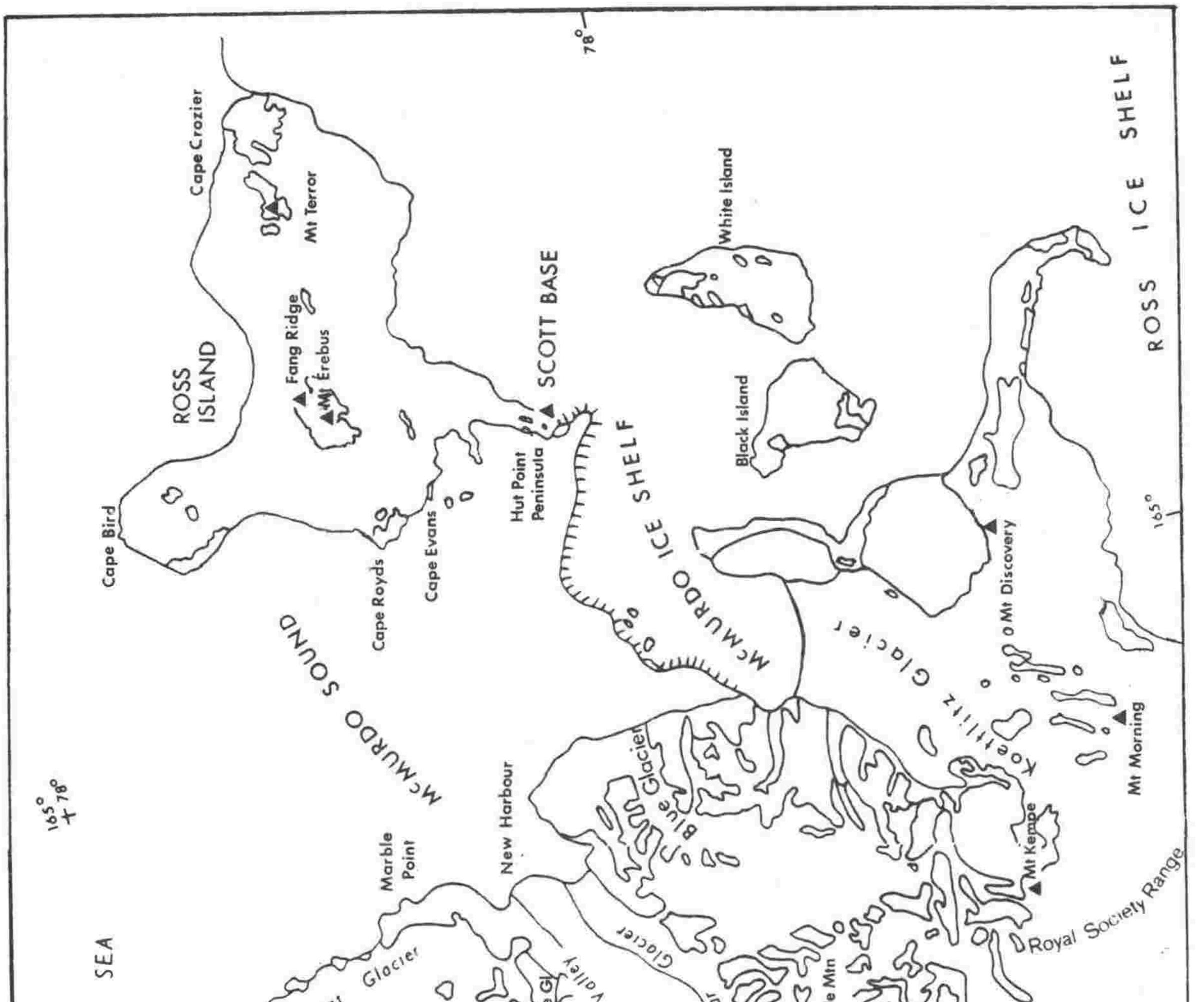


FIGURE 1 The McMurdo region

It is necessary to briefly discuss the phenomenon of the surface inversion, or the temperature increase with height in the lower to 1 to 1.5 km of the troposphere. Inversions are frequent over the McMurdo region, including the oasis, except during summer (Simpson 1919; Thompson and MacDonald 1961; Schwerdtfeger 1970). They are formed in relatively calm conditions when the surface air is cooled by nett radiation loss from the underlying snow surface. Inversion strengths exceeding 30°C in the lower kilometre of the troposphere have been measured in the interior of Antarctica (Weyant 1967; Schwerdtfeger 1970). Air temperatures near the surface are colder during an inversion, but rise when the inversion is destroyed by wind or cloud. Information on the surface inversion phenomena is contained in many articles, including those by Simpson (1919), Thompson and MacDonald (1961), Rusin (1964), Solopov (1967) and Schwerdtfeger (1970).

1.3 Seasons and time

The seasons in Antarctica occur primarily as a result of variations in insolation over the yearly period. Changes between air masses also effect seasonal changes (Hidore 1972). In this publication the seasons are defined as in Table 1, following Rusin (1964).

TABLE 1 Duration of the four seasons in Antarctica (after Rusin 1964) and temperate regions

Season	Duration		
	Antarctica	Temperate	
		(southern hemisphere)	(northern hemisphere)
Summer	December, January	December-February	June - August
Autumn	February, March	March - May	September - November
Winter	April - September	June - August	December - February
Spring	October , November	September - November	March - May

Tables 2 and 3 show that these seasons have characteristic mean air temperatures. Summer is characterised by relatively warm and stable temperatures, while winter is distinguished by the coldest temperatures and relatively little month to month variation. The three sunless months May, June and July are occasionally referred to as the three mid-winter months. As will be seen, however (Fig. 2), the extreme cold temperatures do not always occur in this mid-winter period. In the transitional seasons the temperatures rise rapidly (spring) and fall rapidly (autumn). In the interior of the continent there is some justification for considering winter as the period March through October (Rusin 1964), but this is not done here.

TABLE 2 Mean monthly air temperatures and mean daily range $^{\circ}$C, at Vanda Station, calculated from New Zealand Meteorological Service data. Also included are standard deviations of mean monthly temperatures, monthly temperature extremes and year in which these extremes occurred.

	JAN.	FEB	MARCH	APRIL	MAY	JUNE	JULY	AUG.	SEPT	OCT.	NOV.	DEC.
No. of years of records	6	3	3	3	3	3	3	3	3	3	10	11
Mean monthly air temperature (MMAT)	+1.4	-5.9	-20.4	-29.7	-29.2	-30.2	-38.0	-32.3	-31.2	-15.8	-6.7	+0.2
Standard deviation	1.1	0.8	2.4	2.6	4.7	5.3	1.0	7.3	3.1	2.8	1.2	1.0
Mean daily range	6.7	7.6	9.5	9.6	11.3	10.0	9.2	11.6	11.0	11.5	9.2	6.6
Extreme maximum air temperature	+15.0	+4.4	-0.1	-6.0	-1.2	-0.9	-7.6	-3.2	+2.6	+0.7	+9.5	+14.3
Year of occurrence	1974	1970	1970	1974	1974	1970	1970	1970	1970	1969	1971	1978
Extreme minimum air temperature	-11.4	-21.8	-41.4	-46.7	-48.8	-49.4	-56.9	-55.2	-50.7	-36.7	-24.0	-9.5
Year of occurrence	1972	1969	1974	1969	1969	1969	1969	1970	1970	1974	1976	1968

TABLE 3 Mean monthly air temperatures and mean daily range $^{\circ}$C, and extremes (with years of occurrence) at Scott Base, calculated from New Zealand Meteorological Service records from March 1957 to December 1977. Also included are the MMATs at McMurdo Station after Schwerdtfeger (1970) for the period March 1956 to February 1968.

	JAN.	FEB.	MARCH	APRIL	MAY	JUNE	JULY	AUG.	SEPT.	OCT.	NOV.	DEC.
Scott Base: Mean monthly air temperature (MMAT)	-4.8	-10.8	-20.5	-24.4	-27.4	-26.3	-29.2	-30.3	-28.1	-22.6	-11.9	-5.4
Mean daily range	6.9	7.4	9.1	10.5	12.6	12.2	12.5	13.2	12.3	11.4	8.7	6.9
Extreme maximum air temperature	+6.8	+5.0	-2.0	-4.6	+0.2	-4.8	-4.2	-2.7	-3.3	-0.2	+1.3	+5.0
Year of occurrence	1970	1958	1970	1968	1971	1972	1959	1972	1960	1977	1961	1957
Scott Base: Extreme minimum air temperature	-19.7	-30.2	-44.6	-50.4	-53.2	-52.2	-54.2	-56.1	-57.0	-52.0	-37.2	-22.8
Year of occurrence	1960	1962	1965	1960	1965	1976	1961	1975	1968	1976	1966	1961
McMurdo Station: mean monthly air temperature	-3.4	-8.3	-18.9	-21.2	-23.9	-23.4	-25.5	-27.8	-24.1	-19.9	-8.3	-3.8

The time standard used in the McMurdo region and referred to in this study is New Zealand Standard Time (NZST) and the 24-hour clock is used. Occasionally, literature pertaining to the McMurdo region uses Greenwich Mean Time, 12 hours behind NZST. The local noon in the McMurdo region occurs at about 1300 hours NZST. Where more precision is required the relation

$$\frac{180 - \text{longitude}}{15}$$

gives the time, in hours, that local noon occurs after 1200 NZST.

2. AIR TEMPERATURE

2.1 Mean annual temperatures

The mean annual air temperature (MAAT) at sea level in the McMurdo region is close to -20°C. In South Victoria Land, MAAT decrease inland towards the west as the elevation of the surface increases. Quantitative data for most areas of the oasis are limited: some are derived in this publication in section 3 based on the summary of this present section. Published MAAT at the three stations in the area are: Vanda Station, -20.0°C (for 1969, 1970; Thompson *et al.*, 1971a); Scott Base -20.0°C (Thompson and MacDonald 1961; Thompson 1969); McMurdo Station -17.7°C (1957 - 1963, Nichols and Ball 1964; Anon 1969) and -17.4°C (1956 - 1968, Schwerdtfeger 1970). Some first estimates of the MAAT in McMurdo oasis appear slightly warm (e.g. -18°C, Ragotzkie and Likens 1964; -16°C, Bull and Carnein 1968).

There is a significant difference between the MAAT at Scott and McMurdo, only 2.5 km apart. It is believed that this difference is due to Hut Point Peninsula acting as a dividing ridge, thereby directing air from generally warmer sources onto McMurdo (Thompson and MacDonald 1961). The surface inversion (1.2) may also contribute to the difference, since the recording thermometers at the two stations are located at different heights above the ground (M. Sinclair, NZ Meteorological Service, personal communication) and because McMurdo has a significantly higher mean wind speed than Scott (section 4.5).

In order to update the value of the MAAT at Vanda, data recorded in 1974 by New Zealand Meteorological Service (NZ Met. S.) personnel were added to those of 1969 and 1970. Mean air temperatures for a particular year are obtained by averaging the twelve individual months' mean air temperatures which are in fact the mean daily air temperatures during each one of those twelve months. Mean daily air temperatures for a particular month are determined by averaging that month's mean maximum and mean minimum air temperatures, which themselves are the averaged daily maximum and minimum air temperatures over that month. Mean air temperatures obtained in this way do not differ significantly from those calculated on a day-to-day basis

(Bromley, NZ Met. S., personal communication). The updated MAAT at Vanda was calculated to be -19.6°C. This does not differ significantly from the MAAT at Scott since the average of the mean temperatures for the same three years (1969, 1970, 1974 data from NZ Met. S. records) there, is -19.5°C.

Short time series such as these cannot give accurate representations of MAAT; the standard deviation of the updated MAAT at Vanda is 1.9. A better indication of MAAT at Scott is obtained by averaging the individual yearly mean temperatures from 1958 to 1977 (NZ Met. S. records): the value obtained is -20.2°C with standard deviation of 1.1. Since this cannot be done for Vanda, the individual monthly mean temperatures available (from December 1968 to December 1978, NZ Met. S. records) have been averaged. The resulting mean monthly air temperatures (MMAT) are included in Table 2, along with standard deviations of individual monthly mean temperatures from these MMAT. Table 2 also includes the mean daily temperature range over each month (M. Sinclair, pers. comm.), and monthly temperature extremes, with the year in which the extreme occurred. The MMAT plus mean daily range and extreme maximum and minimum data at Scott (calculated from NZ Met. S. records) and MMAT at McMurdo (Schwerdtfeger 1970) are given in Table 3. From these tables best estimates of MAAT have been calculated for Vanda and Scott and are given in Table 4, along with standard deviations and maximum recorded deviations, plus similar data for January, the warmest month of the year.

TABLE 4 Best estimates of mean annual air temperatures and mean January temperature (warmest month) at Vanda Station and Scott Base.

Parameter	Vanda Station	Scott Base
MAAT (°C)	-19.8	-20.2
standard deviation	1.9	1.1
maximum deviation	-2.0	-2.2
mean January air temperature	+1.4	-4.8
standard deviation	1.1	1.7
maximum deviation	-1.4	-4.0

These best estimates may change by a few tenths of a degree when extra years data are added, because of the short observation series involved.

The difference between the MAAT at Vanda and Scott is not significant even though these sites are some 140 km apart and have significant meteorological differences. However, the MMAT at the two sites are significantly different.

2.2 Mean monthly temperatures, annual amplitudes and annual peaks of air temperatures

The differences between summer and winter MMAT at Vanda and Scott have been discussed previously (Thompson *et al* 1971a; Riordin 1973). It can be seen from Tables 2 and 3 that MMAT at Vanda are about 6 degrees warmer in summer and up to 9 degrees cooler in winter than those at Scott. This reflects the more continental climate of Vanda. The warmer summer temperatures at Vanda are due to higher absorption of solar radiation by the ice-free surface, while the cooler winter temperatures there are caused by increased upward radiation from the surface together with relatively infrequent advection of warmer air into Wright Valley in winter (Thompson *et al* 1971a).

The annual mean amplitudes of the air temperature (half the difference between the warmest MMAT and the coldest MMAT) are 19.7 degrees at Vanda, 12.8 degrees at Scott and 12.2 degrees at McMurdo. These amplitudes may be compared with those calculated from data for twenty-five antarctic stations (including Antarctic Peninsula, South Shetland and South Orkney Island stations), listed in Schwerdtfeger (1970). It may be stated that the annual mean amplitude at Vanda is one of the largest, if not the largest of all antarctic stations. The absolute validity of such comparisons is not certain because of the differing lengths of observation series at some of these stations (Schwerdtfeger 1970).

The extreme range of temperatures is 71.9 degrees at Vanda and 63.8 degrees at Scott. Here too, Vanda's range is greater than that of all twenty-five stations in Schwerdtfeger (1970).

It is unfortunate that extreme minimum temperatures at Vanda have not been obtained for most winters since 1970. Measurement of these has been prevented due to shaking down of the pins in the minimum thermometers, caused by wind-induced vibration of the meteorological screens (Bromley NZ Met. S., personal communication). Other than those in 1969, 1970 and 1974 only two winter extreme temperatures are known for McMurdo oasis. These are -62°C in 1960 at Lake Vida (350m elevation) (Bull 1966) and -47.5°C in 1973 at Screen A (95m elevation) Vanda Station (NZ Met. S. Records).

The extreme maximum temperature measured at Vanda + 15.0°C (January 1974) is warmer than that at any of the twenty-five stations listed by Schwerdtfeger (1970). Extreme maximums of this magnitude have occurred twice in the last decade (NZ Met. S. records) and caused much more melting than occurs in "average" years. (Hoehn *et al*; 1974; Anderton and Fenwick 1976; Chinn 1979). Angino *et al* (1962) measured a maximum air temperature of +23.9°C at Lake Bonney in December 1961, but this was not under standard conditions.

The antarctic "coreless" winter typically lacks a well-defined trough; any of the months from June to September can be the coldest of the year (Rusin 1964). Figure 2 presents daily mean air temperatures averaged over the particular months (i.e. mean daily air temperatures MDAT) at Vanda and Scott, over a number of years since March 1967. Of the eleven winters at Scott recorded in this Figure, the mean cold peak occurs in June once, July three times, August three times and September four times. However, all three winters at Vanda had coldest MDAT in July.

Despite the absence of a well-defined winter cold peak, the McMurdo region does experience a defined summer warm peak. January has the warmest MMAT at both Vanda and Scott. However the mean daily warm peak does not always occur in January (Figure 2). Table 5 presents some data for Vanda indicating this variability.

TABLE 5 Occurrence of extreme maximum summer air temperature and approximate timing of peak on smoothed temperature curve for Vanda Station. Data from sources indicated (nd = not determined)

Summer	Month or date of extreme maximum summer air temperature	Approximate timing of peak on smoothed temperature curve	Reference
1968/69	December	nd	NZ Met.S. records
1969/70	January	early in second week of January	NZ Met.S. records
1970/71	January 3	first week of January	Yoshida *et al* (1971)
1971/72	November 24	last week of December	Torii *et al* (1972)
1972/73	December	nd	NZ Met.S. records
1973/74	January	first week of January	NZ Met.S. records
1974/75	December?	nd	NZ Met.S. records
1975/76	January	nd	NZ Met.S. records
1976/77	January 21	second week of January	NZ Met.S. records
1978/79	December 29	last week of December	NZ Met.S. records

A generalised air temperature curve at Vanda would tend to peak in the first week of January.

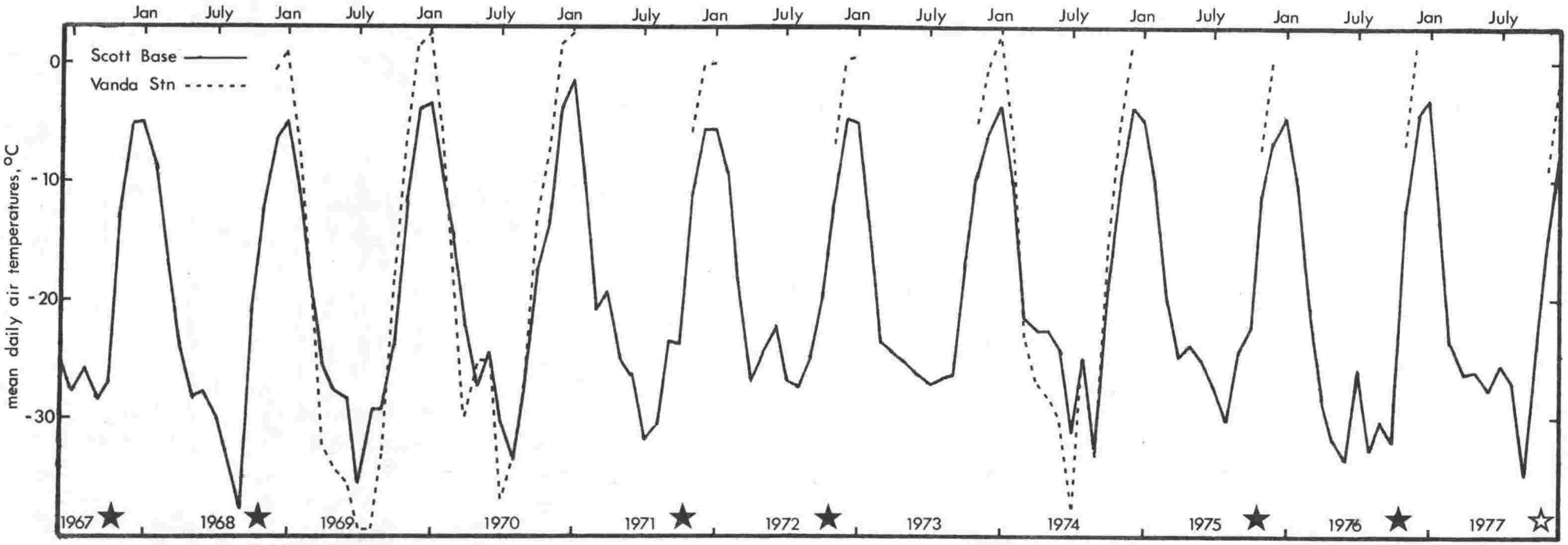


FIGURE 2 Mean daily air temperatures at Vanda Station (dashed line) and Scott Base (solid line) for the months June 1967 to December 1977 inclusive (data from NZ Met. Service records). Stars show years in which saline discharges occurred at Taylor Glacier (Keys 1979).

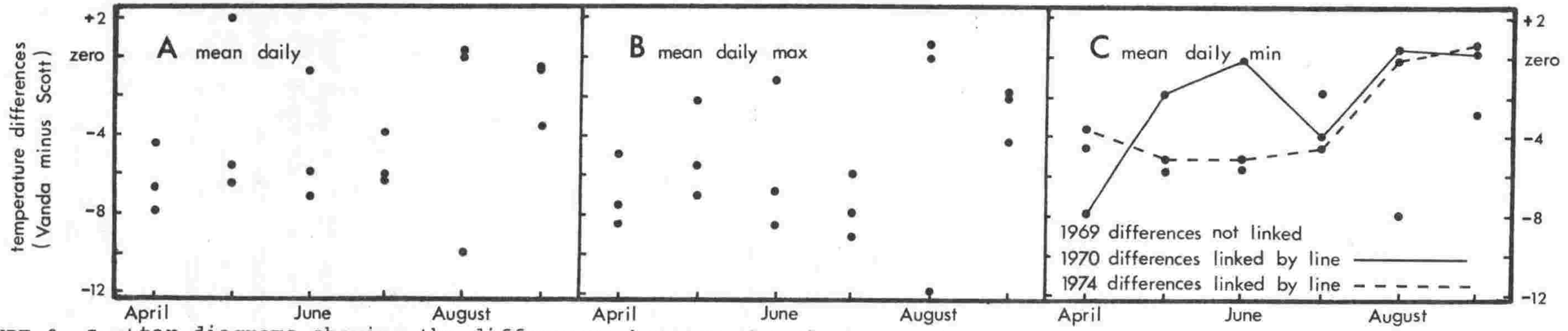


FIGURE 3 Scatter diagrams showing the differences between the air temperatures at Vanda Station and those at Scott Base during the six winter months; A, mean daily temperature differences; B, mean daily maximum temperature differences; C, mean daily minimum temperature difference (differences for individual years are indicated).

2.3 Mean daily air temperatures and phase lags of temperature peaks

The year-to-year variations in MDAT at Vanda and Scott are illustrated in Figure 2. The Figure shows that irregular differences exist between MDAT of corresponding winter months at each site. A close correlation of MDAT does not exist (correlation coefficient for linear regression line is 0.34, see scatter diagram Fig. 3a). Thus winter MDAT for a particular year at Scott should not be used to estimate MDAT values for Vanda. Similarly, little correlation exists between mean daily maximums or minimums over the same period at these two sites (Figures 3 b,c). The differences between the two sets of records are due mainly to the different geographic environments at Vanda and Scott.

Specific examples of the diurnal temperature variation have been published for Vanda (Yoshida *et al* 1971; Torii *et al*, 1972; Riordin 1973) and Scott (Thompson and MacDonald 1961). In addition, Bull (1966) contains similar data for various places in McMurdo oasis. The diurnal range in midsummer seldom exceeds 10 degrees at Vanda, whereas in winter the range may exceed 35 degrees (Riordin 1973; NZ Met. S. records). Large temperature changes may be almost instantaneous in winter (Thompson and MacDonald 1961). Riordin (1973) illustrates an example of a change of greater than 25 degrees (at 0.15m above the ground) in about 6 hours at Vanda in late July 1969.

The mean diurnal temperature ranges for each month at Vanda and Scott are given in Tables 2 and 3. The mean diurnal range is the difference between the mean monthly maximum and the mean monthly minimum.

There is little published data on the phase lag and peaks of the diurnal temperature cycle. Investigation of NZ Met. S. and personal meteorological records indicates that in summer in the oasis, the warm peak generally occurs between about 1300 and 1630 hours, while the cold peak occurs at about 0200 to 0500 hours. This is consistent with the limited data of Thompson *et al* (1971 b) and Colacino and Stocchino (1975) for the oasis, and of Thompson and MacDonald (1961) for Scott Base. In places where extensive shading occurs, these peaks may be offset from these times. At the saline discharge site (Keys 1979) which tends to be shaded around midday by Asgard Range, the warm peak occurs later, generally between 1400 and 1800 hours. Bull (1966) produced data from the 1958/59 summer at Vanda showing that the diurnal warm peak occurred at about 1330 hours when easterly winds were blowing, whereas with westerlies it was about 1630 hours. In winter the warm and cold diurnal peaks are not regular (Thompson *et al*, 1961, 1971 b) since air temperatures then are controlled by meteorological rather than solar influences.

The lags of the diurnal and annual warm peaks from the local noon and from the summer solstice (December 21 - 22) in summer, are due to diurnal and seasonal imbalances between incoming and outgoing radiation (Harvey 1976). These imbalances lead to storing of heat at the surface and in the atmosphere on a diurnal and seasonal basis. Antarctic air possesses a significant heat storage capacity, although it is relatively dry (section 6.1). The annual lag is up to about 15 to 20 days (Table 5), while the diurnal lag is about 1 to 3 hours.

2.4 Air temperature and wind

Air temperature varies markedly with wind as well as with solar radiation (Bull 1966; Thompson *et al* 1971 a; Thompson 1972; Yoshida and Moriwaki 1972; Riordin 1973; Colacino and Stocchino 1975). The wind regime in the McMurdo region is discussed in section 4 below, but some comments are pertinent here.

The relationship between temperature and wind at Vanda is well portrayed by Yoshida and Moriwaki (1972) in their figure 8. Westerly winds in Wright and Taylor Valleys are generally warmer than the easterlies. Westerly winds are generally foehn winds (4.8) where the air is adiabatically warmed as it descends into the valleys: furthermore these winds tend to break up or at least penetrate the surface inversion in the valleys during winter (Thompson 1972; Riordin 1973).

In other areas in the region, temperature and wind are also linked. At McMurdo Station, southerly winds tend to produce warmer temperatures whereas northerlies and easterlies produce cooler temperatures (Weyant 1967).

2.5 Variations over the last 20 to 80 years

Short term temperature changes in the McMurdo region and in Antarctica in general have important consequences for many studies. Nichols and Ball (1964), found that the mean annual sea level air temperature in the McMurdo Sound area has been close to -20°C for some time. This conclusion was drawn from drill hole data and from comparison of air temperatures recorded on the Scott and Shackleton expeditions (-17.4°C) with those recorded more recently at McMurdo Station (-17.7°C). Schwerdtfeger (1970) points out that Wexler's (1959) "warming trend at Little America" can be explained by the latitude difference between the stations (Framheim, 78° 38'S; Little America V, 78° 11' S) involved. Schwerdtfeger also concludes that the only station in southern regions (Orcadas, 60° 44' S, 44° 44' W) with an adequate observational record (1904 - 1967) does not give convincing evidence of "a warming trend in the first half of the century nor of a reversal in the more recent years".

Nevertheless, it is instructive to analyse the Scott Base record of twenty years (Figure 4, Table 5).

Mean air temperatures at Scott Base for the years 1958 through 1977 are shown on Figure 4. Linear regression analysis has been applied to data for selected periods. The single gradient curve for 1958-1977 shows a

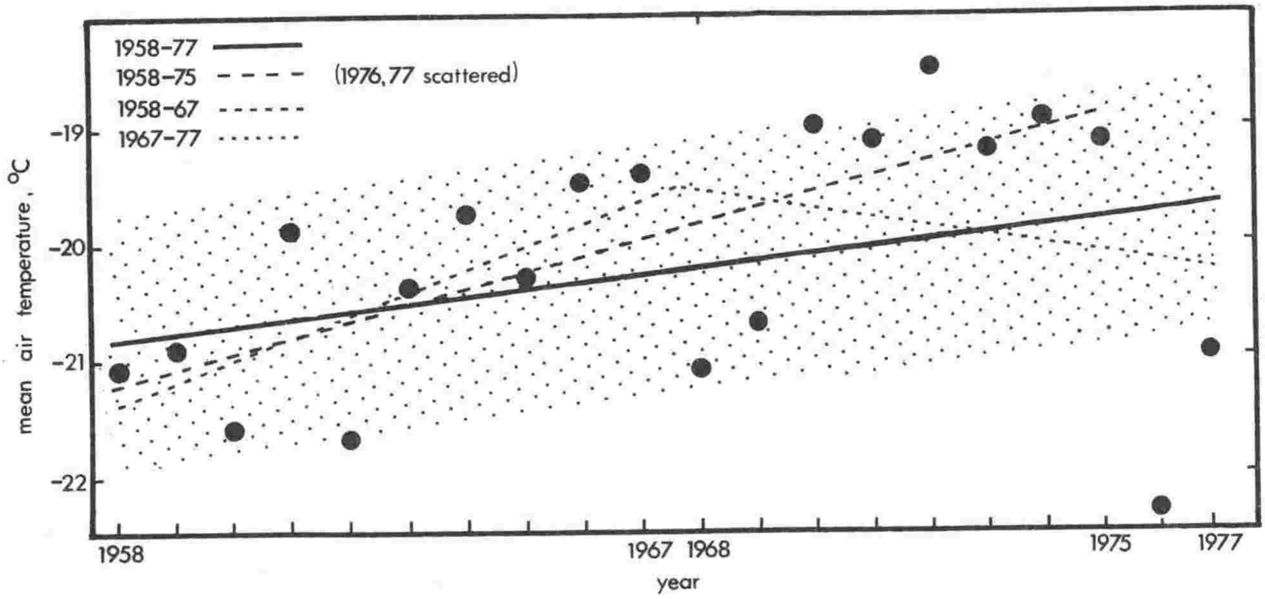


FIGURE 4 Mean air temperature at Scott Base for the years 1958 to 1977 inclusive (data from NZ Met. Service records) with linear regression curves constructed for selected periods. Shading indicates the area lying within one standard error of the 1958-1977 curve.

positive correlation but the curve does not fit the data well (correlation coefficient r=0.32). An improvement in the fit is obtained when the 20 year period is split into two decades, with the period 1958 - 1967 showing a close fit warming trend (r=0.73). However, the 1968-1977 decade cooling trend is poorly fitted (r=0.14). For temperatures up to 1975, a best fit warming trend is again evident (r=0.74). Data are scattered after 1975. The gradients of the regression curves tend to be positive and up to 0.2°C per year indicating up to this amount of warming tendency. The t statistic for a small number of data (Freund *et al* 1960) for the 1958-1977 period is 1.44 (Table 6), whereas the numerical value $t_{c/2}$ of 'students' t distribution for 20 minus 2 degrees of freedom at significance level c, is 1.73 at the 90% confidence level. Since

$$-t_{c/2} \leq t \leq t_{c/2} \qquad \text{(Freund } et\ al \text{ 1960)}$$

the warming trend during 1958 to 1977 is not significant at the 90% confidence level. However the trend for the 1958-1975 period (t=4.37) is significant at the 99% confidence level ($t_{c/2}$ = 2.92 for 16 degrees of freedom) indicating a definite warming between 1958 and 1975. The actual amount of warming is small because of the short time period. Table 6 gives the averages of the multi-annual mean air temperature over the two successive decades, and the t statistic (Freund *et al* 1960) for the difference between the averages. This difference is not statistically significant because t is small.

TABLE 6 Trends of mean air temperature (°C) at Scott Base from 1958 to 1977 from linear regression

Period	Average temperature	Temperature trend (i.e. slope of regression line $(^{\circ}C.a^{-1})$)	Correlation coefficient	Standard deviation (and standard error)	t statistic (see text)
1958-1977	-20.2	0.06	0.32	1.1 (1.0)	1.44
1958-1975(1)	-20.0	0.14	0.74	1.0	4.37
1958-1967	-20.4	0.22	0.73	0.9	0.21
1968-1977	-19.9	-0.06	0.14	1.3	

(1) 1976, 1977 data are scattered well below the regression line by more than one standard error

3. AIR TEMPERATURE GRADIENTS

3.1 Introduction

It has been seen (2.1) that there is a significant difference between the MAAT at Scott Base and McMurdo Station, only 2.5 km apart. Therefore, Vanda's MAAT may not be representative of other places in McMurdo oasis and of Lake Bonney in particular. It is necessary to obtain estimates for horizontal and vertical* temperature gradients, so that the known MAAT may be extrapolated to find those in other areas. Such gradients vary in space and time depending on several inter-related variables including; locality, topography, elevation, season, natures of the ground surface and atmospheric boundary layer and strength of the surface inversion. However a detailed examination of the variation of lapse rates with the nature of the boundary layer and surface inversion is beyond the scope of this work. General atmospheric lapse rates are not of prime concern here since the object of this section is to provide a basis for extrapolating mean screen (i.e. near surface) temperatures.

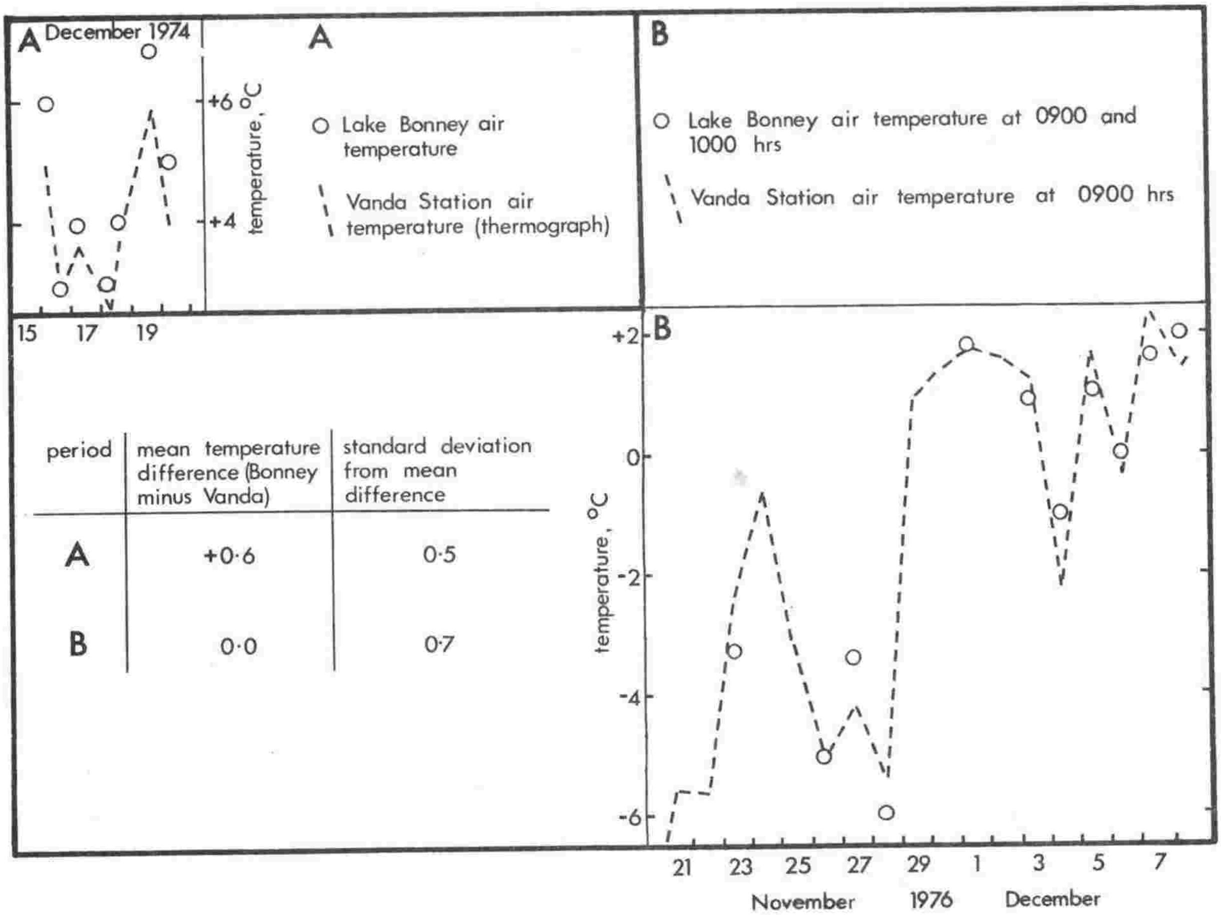
3.2 Horizontal gradients

Horizontal temperature gradients are usually small. The mean meridional temperature gradient in summer for all antarctic stations at sea level is 0 to 0.3 degrees celsius per degree of latitude (Rusin 1964). Schwerdtfeger (1970) indicates that the gradient between Hallett and McMurdo Stations (average longitude 168°E) is about 0.2 to

*the vertical temperature gradient is the lapse rate, which is the decrease of temperature with height. Here it is expressed in °C per 1000m. The meridional gradient is the north-south horizontal gradient.

0.4 degrees celsius per degree of latitude. Therefore the summer temperature difference due to the latitude difference between Vanda Station and the Lake Bonney area should be less than 0.1°C, topography and surface factors being very similar.

The MAAT at Lake Bonney is probably very similar to that of Vanda Station. Figure 5 compares air temperatures measured in Screen A, Vanda Station (77° 31.6'S, 161° 40.1'E, 95m elevation; data from NZ Met.S. records) with some measured at the same or nearly the same time at the western end of Lake Bonney (77° 43.6'S, 162° 17.1'E, 57m elevation). The latter measurements were made using standard whirling psychrometers where the temperature is read off the dry bulb. The temperatures at these two sites are compared in two different ways. In Figure 5a, temperatures measured at various times at Bonney are compared with those at Vanda, using data taken from the thermograph record for the same times. In Figure 5b, the 0900 hours dry bulb temperatures at Vanda are compared with those taken between 0900 and 1000 hours at Bonney. Since there are two distinct sets of data, the temperature difference of each set are treated separately. The differences between the Bonney and Vanda temperatures are very small, (Figure 5) and are not significant considering the magnitude of error associated with the MAAT value at Vanda.



period	mean temperature difference (Bonney minus Vanda)	standard deviation from mean difference
A	+0·6	0·5
B	0·0	0·7

FIGURE 5 Comparison between air temperatures at Lake Bonney and Vanda Station during two short summer periods (data from VUW Antarctic Expeditions and NZ Meteorological Service Records).

Similar temperatures were expected since the terrain at each site is similar and both sites are located in east-west trending valleys. Any small temperature differences due to the lower elevation of Bonney are probably offset by the greater amount of shading due to the Asgard Range and the proximity of Taylor and Rhone Glaciers which are cooling influences. In any case, such differences tend to be evened out by turbulent mixing of air moving through the valleys.

The general climate of these adjacent valleys and at these two sites only 27 km apart, is probably very similar. Therefore the difference between the MAAT at Vanda and Bonney must be small. Hence, -20°C can be considered to be the MAAT at Lake Bonney. Some unsubstantiated previous estimates (e.g. -17°C, Shpaiker 1973) differ from this slightly.

Bull (1966) showed the existence of east-west (zonal) temperature gradients in the valleys of McMurdo oasis, at least in summer. He states (p.182) that "in (the) 1958-1959 (summer) the western end of Wright Valley was 2°C warmer than Marble Point". Although such differences are probably smaller than the variations in mean temperatures from year to year at these sites, it is necessary to examine the east-west gradient.

The summer temperature difference noted by Bull (1966) is due probably to a stronger marine (cooling) influence and decreased solar heating at the coastal site. As will be seen in section 4 below, the occurrence of cooler easterly winds decreases inland to the west throughout the whole year. In winter however, strong radiational cooling at inland sites lowers the temperature well below that of coastal sites. Over the whole year average temperatures at Marble Point and New Harbour will be closer to those at McMurdo Station and Capes Evans and Royds, than to the MAAT at Vanda. The MAAT is probably within a degree of -18°C for the Marble Point - New Harbour area.

The east - west temperature gradient, averaging up to -0.06°C per km in Taylor Valley, would probably not be noticed when windy conditions prevail throughout the entire valley. Under such strong mixing conditions, Colacino and Stocchino (1975) found that air temperature was constant throughout Taylor Valley from New Harbour to Lake Bonney.

3.3 Lapse rates

Elevation is the most important factor controlling MAAT in Antarctica, especially on the continent (Weyant 1967). In antarctic literature it has occasionally (but erroneously) been assumed that average environmental and topographic lapse rates* are equal and have a value

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*the environmental lapse rate (ELR) is the rate of decrease of air temperature with height in free air, whereas the topographic lapse rate (TLR) is the decrease in temperature with elevation up a slope on the earth's surface (Harvey 1976).

equivalent to the dry adiabatic lapse rate of 9.8°C per 1000m (Hughes 1971; Drewry 1977). This assumption is made because the rate of condensation of water vapour is very slow at low temperatures, and hence little latent heat of vaporisation is liberated upon raising (cooling) a parcel of antarctic air. However, because of radiation (surface inversion) and turbulence effects (Simpson 1919) it appears that these average lapse rates are generally even less than the saturated adiabatic lapse rate which is 8.6°C per 1000m at -20°C and 1000 mb (Harvey 1976).

Some environmental and topographic lapse rates for the McMurdo region are given in Table 7. These have been calculated using published data (Weyant 1966a; Ugolini 1967; Schwerdtfeger 1970; Hughes 1971; Holdsworth 1974), and unpublished data. The latter includes air temperatures measured using whirling psychrometer dry bulb thermometers (VUWAE meteorological observations) which were compared with measurements made at the same time by thermograph and/or dry bulb at Screen A, Vanda Station, and at Scott Base (NZ Met. S. records). Lapse rates obtained from balloon ascents in the lower troposphere are environmental lapse rates (ELRs). The englacial temperatures correspond to mean annual surface temperatures (MAST) not MAAT; hence lapse rates obtained using them are topographic lapse rates (TLRs) as are those obtained by surface air temperature comparisons. The lapse rates obtained using unpublished data include the horizontal temperature gradients; the correction for these is neglected here since it amounts to probably no more than 0.2°C.

There is a strong seasonal effect on environmental lapse rates (Table 7). These are lowest in winter when temperature inversions in the boundary layer are strongest and most frequent. Generally the lapse rates are closest to the saturated adiabatic lapse rate in summer, when significant inversions are very infrequent and weak. The range of ELRs indicated is 2 to 7°C per 1000m. Since the lower rates prevail for most of the year, the mean annual ELR in the lower troposphere is about 4 to 5°C per 1000m. This is very similar to the mean ELR above the temperature inversion obtained by Simpson (1919). However, Simpson's data were obtained in relatively low wind conditions such that little vertical mixing of air would have been occurring in the boundary layer. Thus it is possible that the value given above for the mean annual ELR is also biased towards calmer conditions. According to Simpson (1919) and Harvey (1976), the average ELR in the troposphere is about 6.5°C per 1000m, but it is not known by the writer whether this value is applicable to antarctic conditions.

Topographic lapse rates in summer may be slightly greater than the summer ELRs (Table 7). However the validity of the comparison is questionable considering the magnitude of the errors involved in the TLRs. Furthermore, Table 7 contains inhomogenous data on which it is difficult to obtain average values.

TABLE 7 Environmental and topographic lapse rates in McMurdo region for selected months, calculated from published and unpublished data. References; (1) Weyant 1966a, 1967; (2) Ugolini 1967; (3) Schwerdtfeger 1970. (kilometres and geopotential kilometres are assumed to be equal).

Month	Lapse rate (°C per 1000m) † uncorrected for horizontal temperature gradients	Method of data collection (Altitudes in km or geopotential km*)	Source of original temperature and altitude data
January (1958-62)	5.6	MMAT at McMurdo(Table 2.2) and weather balloon (0-1)	2, 3
(1958-62)	6.2	Weather balloon (1-5)	2
February (1959-62)	5.5	MMAT at McMurdo and weather balloon (0-1)	2,3
(1959-62)	4.9	Weather balloon (1-5	2
(1962)	8.0	Air temperature measurements during ascent of Erebus	2
March (1958-62)	3.5	MMAT at McMurdo and weather balloon (0-1)	2,3
(1958-62)	4.2	Weather balloon (1-5)	2
(1956-65)	2.7	Weather balloon (0-2.6*)	1,3
(1908)	mean 4.0†	Air temperature measurements during ascent of Erebus	2 quoting David in Shackleton (1909)
June (1956-65)	2.7	Weather balloon (0-2.6*)	1,3
	5.2	Weather balloon (2.6*-4.9*)	1,3
September (1956-1965)	2.4	Weather balloon (0-2.5*)	1,3
	5.0	Weather balloon (2.5*-4.9*)	1,3
November (1958-61)	6.9	MMAT at McMurdo and weather balloon (0-1)	2,3
(1958-61)	5.8	Weather balloon (1-5)	2
November 18-25, 1974	8.6 ±2.7†	Air temperature measurements made at Table Mtn and compared with Vanda thermograph	Keys; NZ Met.S records; USGS 1:250,000 map.
November 26 - December 4,1974	7.8 ± 2.0†	Air temperature measurements made at Knobhead and compared with Vanda thermograph	Keys; NZ Met.S records; USGS 1:250,000 map
December (1959-61)	8.0	MMAT at McMurdo and weather balloon (0-1)	2,3
(1959-61)	6.3	Weather balloon (1-5)	2
(1956-65)	6.7	(0-2.7*)	1,3
December 5-15,1974	8.3 ±3.0†	Air temperature measurements made at New Mt and compared with Vanda thermographs	Plume; NZ Met. S records; USGS 1:250,000 map
December (1972-1979)	mean 5.2† std.dev 1.4	Air temperature measurements made at Erebus summit camp and compared with Scott Base drybulb measurements (29 comparisons)	Keys; NZ Met S. records
All year	4 to 8	Englacial temperature profiles, Meserve Glacier	Hughes 1971; Holdsworth 1974

A better comparison involves the TLR obtained from englacial temperature profiles in Taylor Glacier. Such profiles enable mean annual surface temperatures (MAST) to be measured. This is normally considered to be the temperature measured at the depth of penetration of seasonal changes of air temperature. For snow substrates the depth taken is 10 metres but this cannot be applied to ice because it has different thermal properties (Müller 1976). A depth of 17 metres was used for the ablation zone of Taylor Glacier. This depth was found by measurement (Robinson 1979), and by calculation using a Fourier equation solution that describes periodic heat flow in one direction through a semi-infinite homogenous solid (for example see Cameron and Bull 1962). In the ablation zone of glaciers at least, MAST are usually a few degrees warmer than MAAT and certainly the two are not equal (Müller 1976). However, MAST differences can be used to obtain TLR's which are assumed herein to be applicable to ice-free areas also.

Englacial temperatures were measured (1976-1977; 1977-1978) by Robinson (1979) using thermistor probes in drill holes and crevasses up to 20m deep. Table 8 shows the derivation of the TLR.

TABLE 8 Topographic lapse rate from mean annual surface temperatures, Taylor Glacier. Elevations (m) from (a) USGS Reconnaissance series maps (b) Stern's (1978) relative altitudes and (c) a combination of (a) and (b).

	Line C (MAST^1 -17.0 ±0.2 °C) to Line F (MAST^2 -20.1± 0.1°C)			
	Elevation Line C	Elevation Line F	Elevation difference	Lapse rate °C per 1000m
(a)	180	950	770	4.0
(b)	140^3	930^4	790	3.9
(c)	180^3	990^4	810	3.8
	Line F (MAST^2 -20.1 ± 0.1 °C) to Line G (MAST^2 -21.5 ±0.1°C)			
	Elevation Line F	Elevation Line G	Elevation difference	Lapse rate °C per 1000m
(a)	950	1250	300	4.7
(b)	930^4	1330^5	400	3.5
(c)	990^4	1330^5	340	4.1
	Central value of lapse rate 4.0 ±0.5 °C per 1000m			

1 From crevasse temperatures near terminus measured by P.H. Robinson
2 From englacial temperatures measured by P.H. Robinson
3 Based on elevation at pole C6 , C line (Figure 8.3A in Chapter 8)
4 Based on elevation at pole F6 , locality 100 (Figure 2 in Appendix 1)
5 Based on elevation at pole G5 , locality 47 (Figure 2 in Appendix 1)

The value, 4.0°C per 1000m is not affected by seasonal changes or wind conditions and is the value used in this study. It appears that the average TLR and average ELR are similar in the McMurdo region. However, they are slightly lower than the TLR in the eastern European Alps (5.3°C per 1000m calculated from the data of Geiger 1965).

Estimates of MAAT at various localities in the McMurdo region can now be made (Table 9). The MAAT at Scott (-20.2 ± 1.1°C) was used for the MAAT determination at Mounts Erebus, Morning and Discovery. Vanda's MAAT (-19.8 ± 1.9°C) was used for the other localities in Table 9.

TABLE 9 Mean annual air temperature estimated at selected localities in the McMurdo region, using a mean lapse rate of 4.0 ± 0.5°C per km and MAAT at Vanda of -19.8 ± 1.9°C and at Scott of -20.2 ± 1.1°C. (Elevation of Vanda, 95m; Scott 16m)

Locality	Elevation (m) (from USGS 1:250,000 map)	Estimated MAAT (°C)	Maximum Error Limits (± °C)
Mt Erebus	3794	-35.3	3.0
Mt Morning	2723	-31.0	2.5
Mt Discovery	2681	-30.9	2.4
main valley at Table Mountain	1600	-25.8	2.7
valley between Knobhead and Mt Handsley	1500	-25.4	2.7
Beacon Valley	1400	-25.0	2.6
Kennar Valley	1600	-25.8	2.7
west end of Labyrinth	900	-23.0	2.4
Lake Vida	350	-20.8	2.1

4. WIND AND CIRCULATION

4.1 Introduction

Distribution of salts is intimately involved with both wind and circulation. In this section the wind regime at Vanda, then the rest of McMurdo oasis, is discussed before the regime at Scott, McMurdo and Ross Island. Finally air circulation over the rest of East Antarctica is discussed.

4.2 Vanda Station

The wind direction at Vanda and in the oasis generally is almost completely controlled by valley orientation. The topography channels the wind into east and west directions (Bull 1966; Nichols 1966; Thompson 1972; Yoshida and Moriwaki 1972). Complete sets of wind roses and histograms for Vanda data from the years 1969 and 1970 have been published by Yoshida *et al* (1972) using NZ Met. S. records. The following wind characteristics at Vanda have been taken from Thompson *et al* (1971a), Thompson (1972), Yoshida and Moriwaki (1972) and Riordin (1973).

Easterly winds are most frequent, especially in summer. The prevailing direction on a yearly basis is around 090° True, while the second most pronounced direction is around 260° True. The easterly winds are relatively light: wind velocities greater than 17-18 m.s^{-1} are restricted to those from the west and southwest. In both 1969 and 1970 the maximum gusts (40, 41 m.s^{-1} or ca. 80 kts) were both from the west and both occurred in August. Winter winds are more intense but less frequent than during the summer. This is shown by Tables 10 and 11. Table 10 gives the mean monthly wind speeds at Vanda averaged from data for 1969, 1970 and 1974 and maximum gusts during 1969. Maximum gusts are defined in different ways, based on different time periods; for this reason they are approximate only. Table 11 gives the wind rose data for Vanda Station for the period January 1972 to January 1978. The data in Table 11 have been normalised so that frequencies per thousand observations are tabulated: the table is based on 176 observations in 'spring', 291 in 'summer', 92 in 'autumn' and 92 in 'winter' where these seasons are defined as in temperate regions (Table 1). Thus, the summer wind regime is better represented although the Table is not weighted towards the summer months.

The well-known diurnal-based wind regime which operates in the valleys of the oasis during the sunlit months is well developed at Vanda. Steady easterlies of 8-10 m.s^{-1} blow during the afternoon and evening when ground temperatures are warmest. Calm periods or westerlies of 0-10 m.s^{-1} develop during the early morning, when the influx of solar radiation is at a minimum (Thompson *et al* 1971a; Thompson 1972, Yoshida and Moriwaki 1972; Riordin 1973). Thompson (1972) has this sequence well illustrated for November 1971. These winds are of limited thickness reaching up the valley sides no further than about 800 to 1200m (Bull 1966; Thompson 1972).

TABLE 10 Mean monthly wind speeds and maximum gusts at Vanda and McMurdo Stations. Vanda mean speed data calculated from New Zealand Meteorological Service records for the years 1969, 1970, 1974; gust data from Riordin (1973) for 1969 only. McMurdo data after Schwerdtfeger (1970). Units are metres sec^{-1} (ng not given)

		JAN	FEB	MARCH	APRIL	MAY	JUNE	JULY	AUG	SEPT	OCT	NOV	DEC	YEAR
VANDA	Mean wind speed	6.6	5.6	3.6	2.2	4.3	3.0	2.8	4.9	4.5	7.2	6.6	7.0	4.9
	Standard deviation	0.2	1.0	0.3	1.1	2.8	1.8	1.6	2.6	1.1	2.1	0.6	0.4	0.6
	Maximum gust 1969	ng	25	28	37	27	26	37	40	34	32	30	ng	41 (1970)
MCMURDO														
	Mean wind speed	5.3	7.0	7.3	6.1	6.9	7.2	6.5	6.4	6.9	6.2	5.4	6.5	6.5
	Maximum gust	24	29	27	28	43	43	36	38	41	37	35	24	43

TABLE 11 Wind rose data for Vanda Station and Scott Base based on daily observations at 0900 NZST. Frequencies are given per thousand observations. 0 indicates occurrences less than 0.5; a blank indicates no occurrences. (After NZ Met.S. computerised records). Conversion from Beaufort Force to wind speeds in m.s^{-1} after Amiran and Schick (1961).

VANDA STATION Total observations used: 651

Beaufort Force:	1	2-3	4	5	6	7+	Total
Direction/ Speed at 2m (m.s^{-1})	0-1.6	1.6-4.8	4.8-8.0	8.0-10.8	10.8-13.8	13.8+	
N	8	1					9
NE	25	22	13	0	1	0	61
E	40	101	82	24	10	1	258
SE	3	2	3	1			9
S	5	3	1	1	2	1	13
SW	2	8	6	17	19	28	80
W	18	21	22	23	24	46	154
NW	9	2	0	1			12
						Calm	402

SCOTT BASE Total observations used: 2221

Beaufort Force	1	2-3	4	5	6	7+	Total
Direction/ Speed (m.s^{-1})	0-1.6	1.6-4.8	4.8-8.0	8.0-10.8	10.8-13.8	13.8+	
N	24	99	81	34	16	1	255
NE	21	151	155	62	16	1	406
E	4	24	16	7	1		52
SE	2	15	12	12	7	3	51
S	5	6	8	7	9	12	47
SW	5	8	3	1	1	3	21
W	6	8	3	0	1		18
NW	3	11	15	13	11	2	55
						Calm	93

4.3 Elsewhere in McMurdo oasis

Elsewhere in Wright Valley the wind regime is slightly different from that at Vanda. In the eastern half of the valley, westerly winds are less common (Bull 1966) especially in the spring and summer. At the hut adjacent to Meserve Glacier, maximum and mean wind speeds are less than at the valley floor (Everett 1971) in the summer at least. During summer in the Wright Upper Glacier area the influence of the easterly winds is reduced from that at Vanda whereas the westerly influence is increased.

Personal meteorological recordings during five periods totalling eight weeks show that the wind patterns are similar in Taylor Valley. Up valley easterly winds are most common in the east and their influence decreases westward towards the ice sheet*. At Lake Bonney a diurnal wind regime, similar to that at Vanda, operates during the spring, summer and probably autumn months. Easterly winds are relatively uncommon as far west as Kennar Valley. Nevertheless, easterly conditions do occasionally occur even further west in Skelton Neve and plateau areas. Strong southwesterly and southerly winds are common along the western fringe of the oasis and in areas within the oasis exposed to the south. These winds are associated with the general surface wind regime of the East Antarctic Ice Sheet and cyclonic storms, and are further discussed in sections 4.8 and 4.9 below. During the winter strong west to southwest winds are important in Taylor Valley, even at the coastal end. This can be seen from geomorphic evidence including wind blown sand and gravel on the sea ice up to 10 km east of Cape Bernacchi. Presumably the wind regime in winter is similar to that in Wright Valley.

Similar wind patterns are followed in the Victoria Valley system. East of Lake Vida, easterly winds are the most predominant, strongest and most constant, at least in the sunlit months; in November 1961 to January 1962 Calkin (1964) found that the wind blew almost constantly from the east, averaging some 4 $m.s^{-1}$. However, northerlies and southwesterlies are known in this area (Bull 1966); gusty, southwesterly winds of at least 23 $m.s^{-1}$ have been recorded (Calkin 1964). Further west, winds off the ice sheet, blowing from the west to southwest are common and are stronger than the easterlies (Calkin 1964; Bull 1966). It is evident from studies of the field of transverse sand dunes in Lower Victoria Valley, that the wind direction there is dominantly from the west in winter, while in the summer, easterlies dominate (Morris *et al* 1972; Selby *et al* 1974). From a study of ventifact distribution in eastern Victoria Valley, Selby *et al* (1973) concluded that the wind regime that exists there at present has probably been similar for much of the Quaternary.

The wind regime at Marble Point is significantly different to that of the valleys of the oasis. South and southeasterly winds predominate, although northerlies, easterlies and local westerlies also occur (Bull

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*the polar plateau

1966; Nichols 1966). A diurnal cycle of north to east winds alternating with westerlies in the summer months appears to be less developed than at Vanda (Bull 1966).

4.4 Winds with vertical development

There are many examples of wind with vertical development. Dust devils and snow and dust whirls occur frequently in Wright Valley (Bromley, N.Z. Met S. personal communication; Riordin 1973) and have been observed in other places as well (personal observations; Mawson 1915; Rusin 1964). Most of the thermally induced dust devils have vortices up to 20m high with diameters up to 5m wide, although vortices up to 400m high and diameters as wide as 100m have been known (NZ Met. S unpublished manuscript'a'). Snow and dust whirls up to 200m high and occasionally tornadoes up to 1000m high occur in the winter during severe westerly gales (Bromley NZ Met. S, personal communication). Velocities in these vortices are sufficient to move and carry large objects such as packing cases, and to damage buildings and stores at Vanda Station (NZ Met. S, unpublished manuscript 'a'). Rusin (1964) noted very sudden velocity increases from zero up to 35m.s^{-1} followed by rapid velocity drop-offs during the passage of such vortices at Mirny Station.

Other examples of vertical winds or updrafts also exist in the McMurdo region. Cumulus clouds indicating upward convection are not uncommon in summer over ice-free areas. Orographic effects and clouds have been noted on Mounts Erebus and Discovery. Much of the kinetic energy of the surface winds, particularly the westerlies, is converted to turbulent energy during their passage over the uneven topography of the oasis (Solopov 1967).

Warmer air from dry valley regions overriding maritime air has also been noted in the region and elsewhere (Mawson 1915; Thompson and MacDonald 1961; Bull 1966). Synoptic scale effects such as convergent wind systems (cyclones) are discussed below in sections 4.8 and 4.9.

4.5 Scott Base and McMurdo Station

The wind regime on Ross Island is significantly different from that in McMurdo oasis. Histograms and wind roses for Scott Base and McMurdo Station have been published in Thompson and MacDonald (1961) and Weyant (1967). The following discussion is based on these works and also on Table 11, which includes wind rose data from Scott Base for the period January 1972 to January 1978 (from NZ Met. S. records). At McMurdo, easterly winds are most frequent during all seasons, although northeasterlies, southeasterlies and southerlies are also common. Southerlies have the highest wind speeds. Northeasterlies are relatively more frequent in the autumn and early winter months, while southeasterlies and southerlies are relatively more common in the winter and spring. Winds from the north to southwest also occur. The pattern is similar at Scott, with northeasterlies predominating, and with southerlies being the strongest. In summer, half the observations record north-easterly winds. Table 10 gives the mean windspeed and maximum gust data at McMurdo (Schwerdtfeger 1970). The mean windspeed at McMurdo is significantly stronger than at both Vanda and Scott which have similar mean speeds. As in the oasis, the strongest winds occur in the winter; however the mean windspeed tends to be highest during the winter at the Ross Island stations, which is not the case at Vanda.

4.6 Ross Island, excluding the summit area of Mt Erebus

Elsewhere on the coast of Ross Island, the annual wind regime is affected by topography. Mt Erebus causes considerable deflection of surface flow. Snow drifts, windscoops and lee effects (e.g. removal of snow cover from the sea ice to the northwest of and north of Dellbridge Islands) indicate that winds from the southeasterly quarter have the dominant effect along the western coast of Ross Island. Also meteorological observations there show that easterly to southeasterly winds predominate, although winds from the north and north-northwest are also common; winds from the western quarter are less common (David and Adams in Shackleton 1909; Simpson 1919). There is apparently some tendency for the wind conditions to become calmer in this area, once the sound has become firmly frozen over (David and Adams in Shackleton 1909). At Cape Crozier the dominant flow is southwesterly (Simpson 1919).

4.7 Summit region of Mt Erebus

The summit of Mt Erebus (3794m) experiences a different wind regime from that at sea level nearby. Observations of the plume of Mt Erebus led to the first statistical study of the prevailing wind direction in the middle troposphere (Schwerdtfeger 1970, quoting Meinardus 1938). This prevailing wind direction is west-southwest (Weyant 1966a; Logvinov 1968; Schwerdtfeger 1970).

However, winds from the west and southwest do not feature strongly on Table 12. This Table summarises wind observations made at the summit Observatory and camp site mainly during summer over a total of 64 days in October to January 1972 to 1979. At this site the topography may put an easterly bias on winds from the south. Wind speeds were measured with hand held anemometers two metres above the ground. The anemometers most commonly used (Sims, Model k/k) gave low readings in temperatures below about -20°C; temperatures are usually colder than this (as cold as -35°C, even in January). Therefore wind speeds were often estimated using the Table in Met 812 (1974), and maximum gusts given in Table 12 are approximations. The Table indicates that southeasterly and southerly winds predominate during the summer months at least - the time people are usually at the summit. Winds from the southwest and west total only about eleven percent of 95 observations. However, when observations made at the acclimatisation camps at Fang Glacier (77° 30'S, 167° 14'E, 2800m elevation) are included, west to southwest winds add up to fifteen percent of the observations.

TABLE 12 Summary of wind observations made at Mt Erebus summit camp/ Observatory site (77° 32'S, 167° 08'E, 3600m asl) over 64 days in October, November, December, January 1972-1979.

Direction	N	NE	E	SE	S	SW	W	NW	Calm
Frequency of occurrence (percent)	4	2	2	35	21	7	4	10	15
Approximate maximum gust at 2m ($m.s^{-1}$)	5	5	20	33	25	5	10	10	-

On the summit plateau and near the Observatory, the sastrugi patterns are dominated by winds from the southerly quarter. Along the northern border of the collapsing snow basin adjacent to the Observatory, the tallest (ca. 0.5m) sastrugi are dominated by south-easterly to southerly winds indicating that these winds are strongest on an annual basis. On the first ascent of the volcano in March 1908 David (in Shackleton 1909) found that the sastrugi were aligned SW-NE on the summit plateau northwest of what is now called Nausea Knob. These sastrugi had "a sharp edge directed towards the west".

According to the studies on sastrugi by Lister (1959) at South Ice, some of the tallest (oldest) sastrugi are aligned parallel to the direction of the strongest winds; the angle at the head of these sastrugi is more acute, they generally have the hardest surfaces and are more undercut. However, the more closely set sastrugi are aligned with the most frequent wind direction, where this is of generally lower velocity (Lister 1959). This is consistent with the sastrugi pattern on Erebus. The more frequent westsouthwest winds tend to steepen the western sides of the more southerly oriented sastrugi. Very occasionally heavy snowfalls (e.g. from the north) could obliterate the existing sastrugi pattern and subsequent winds re-establish a differently oriented pattern. However the dominant wind regime would eventually reassert itself on the modified snow cover. It is of interest here that a snow condition known as windslab, which typically occurs on lee slopes, has been noted (December 1972) on the east-facing inner slope of Side Crater.

A comprehensive set of upper air data from McMurdo Station was not obtained for this study. However rocket soundings from McMurdo (Logvinov 1968) have shown that near the elevation of the summit there is a marked seasonal trend in both wind direction and altitudes where various winds are predominant. Westerly winds dominate the easterlies in the zonal component except in spring and summer while southerlies dominate the meridional component and are strongest in the spring, at an altitude of 4000m. At about 5-6000m however, northerlies dominate the latter component except in the spring. Presumably then, westerlies are more common in winter at the summit of Erebus, although southerlies are stronger.

Evidently wind directions in the troposphere are complex. David and Priestley(in Shackleton 1909) noted this by observing the motions of an eruption cloud from Erebus in June 1908 and other clouds. Up to an altitude of about 2000m asl the wind was northerly; above this a southerly was blowing up to an altitude of about 4600m. From this level to at least 7000m the wind was again northerly. Table 13 illustrates the effect of altitude on wind direction from 10 November to 20 December 1966. The raw wind data was obtained (Bromley, NZ Met.S. personal communication) from upper air maps for midday (NZST) at McMurdo. The altitudes of the 500 mb and 700 mb surfaces are the December values given by Weyant (1966a). A data summary for the Erebus summit campsite gives a comparison; this summary does not include data from observations made in October and January. Although the two observation series are of different lengths and over different years, the following conclusions can be made.

TABLE 13 Frequency (%) of wind directions at various altitudes above McMurdo Station (10 November 1966 to 20 December 1966) and at the summit campsite, Mt Erebus (November, December 1972 - 1979, broken observation series).

Wind Direction (quadrant)	Altitude and Elevation (m) 1000 mb (surface)	700 mb (2700)	Erebus Camp (3600)	500 mb (5100)
North	26	27	7	41
East	27	11	32	4
South	31	35	50	15
West	16	27	11	40

A topographic bias apparently increases the frequency of south to south-east winds at the summit camp over what would be expected at a free atmospheric position of the same altitude. At the campsite, the prevailing winds are probably aligned parallel to the average slope contours, which are approximately north - south. The cold antarctic air tends to flow around topographic obstacles rather than rising over them (M. Sinclair, N.Z. Met. S. personal communication). The prevailing surface flow in the summit area is probably west-southwest, that being the prevailing wind direction in the middle troposphere (Schwerdtfeger 1970). However the strongest winds near the summit cone are south-easterlies to southerlies.

4.8 The cause of winds in the McMurdo region

A detailed account of the relationship between atmospheric pressure and synoptic situations with the surface wind regime is not necessary here. However, some comment on this relationship is desirable.

The local regime at Vanda is a complex interaction between the prevailing synoptic situation and topographical and local circulation effects. The diurnal regime of the sunlit months is due to local insolation and drainage effects along the mountain and valley sides and floor (NZ Met. S., unpublished manuscript 'b'; Thompson *et al* 1971a; Riordin 1973).

The larger scale flow patterns due to synoptic scale systems also affect wind regime in the oasis. Such flow occurs throughout the year when winds from synoptic disturbances aloft are channelled into the valleys becoming easterlies, westerlies (Thompson 1972; Yoshida and Moriwaki 1972; Riordin 1973), and/or northerlies or southerlies in exposed places. The westerly winds are of the foehn type (warmer than the air they displace), rather than true katabatics (gravity flow of cold air, colder than the air they displace), (Schwerdtfeger 1970; Thompson 1972; Yoshida and Moriwaki 1972). Nevertheless, Thompson (1972) acknowledges that gravity may play an important secondary role. In fact the prevailing anticyclonic flow aloft over the oasis, which is southerly (Mather and Miller 1967), has a westerly component along the edge of the plateau adjacent to the oasis. In this region the plateau rises to the west. Apparently then the prevailing flow, often influenced by synoptic disturbances, is deflected down towards the east into the valleys, becoming adiabatically heated during the descent. In the valleys these westerly winds are usually associated with low barometric pressure (Riordin 1973) or large pressure drops (Yoshida and Moriwaki 1972).

Near Scott and McMurdo the prevailing anticyclonic flow is given an easterly component by the bulk of Mt Erebus (Simpson 1919; Mather and Miller 1967). This deflection westwards by Mt Erebus and eastwards by Mt Terror, gives rise to an area of flow divergence with generally lighter winds in the area known as Windless Bight.

Cyclonic storms in the region give rise to strong winds from the south-east and south in the McMurdo Sound area, and also in areas of the oasis exposed to the south. According to Rusin (1964) cyclonic activity has marked seasonal trends; cyclonic winds prevail around the coast in summer but are less common in winter. Although cyclones are common in coastal areas (Rusin 1964), their influence is markedly reduced inland since they only occasionally penetrate deeply into the interior (Lamb and Britton 1955; Astapenko 1964; Rusin 1964; Weyant 1967). Further than about 100 km from the coast of South Victoria Land, frontal passage and cyclone activity are infrequent.

4.9 Surface winds in East Antarctica and general atmospheric circulation

In East Antarctica the predominant surface flow is broadly outwards towards the coast (Mather and Miller 1967). On the plateau surface the prevailing direction is at a constant angle (about 45°) to the true left of the fall line. With increasing height through the lowest few hundred metres of the atmosphere, this prevailing "inversion" wind tends to turn to blow parallel to the contours (Schwerdtfeger 1970). At South Pole the mean annual wind speed is $4.8 m.s^{-1}$ while at Vostok it is $5.1 m.s^{-1}$ (Schwerdtfeger 1970).

Such winds are different from those produced by gravitational attraction for cooled air of greater density lying above steeply inclined snow and ice surfaces. The latter type of wind is a true katabatic (Schwerdtfeger 1970) and is common around the coast of East Antarctica in places where the continental ice sheet drops sharply towards the sea (Cape Denison, Mawson and Mirny Stations). However, winds from the easterly quarter generally prevail in the coastal zone of East Antarctica, outside the regions where katabatic flow occurs (Rusin 1964; Mather and Miller 1967; Weyant 1967; Schwerdtfeger 1970).

Both the inversion and katabatic winds are affected by synoptic disturbances (Rusin 1964; Mather and Miller 1966; Schwerdtfeger 1970), such as cyclones. A simplified current view of the antarctic circulation pattern in the troposphere depicts what is effectively a recurring blocking anticyclone centred over central East Antarctica, surrounded by low pressure areas centred north of the continent (Astapenko 1964; Solopov 1967; Schwerdtfeger 1970, quoting Taljaard 1969). Effectively, the anticyclone allows the prevailing outward surface flow with cyclones orbiting this high, and occasionally penetrating inland.

Astapenko (1964) distinguishes two types of cyclones: relatively shallow cyclones which are formed mainly on Antarctic and intra-Antarctic fronts and move latitudinally from west to east around the continent; and deep, high cyclones which are formed mainly on Polar fronts and move with a meridional component (Solopov 1967). The Antarctic fronts occur at about 60 - 70° S, whereas the Polar fronts occur at about 45 - 50°S (Lamb 1970). Weyant (1967) illustrates the tracks of cyclones with a series of maps depicting mean monthly conditions. These show that some storms completely cross West Antarctica from Ross to Weddell Seas and some cross (eastern) Wilkes Land and northern Victoria Land. Penetration into the East Antarctic interior is infrequent; when this occurs it is usually south from Ross Sea or Marie Byrd Land and only occasionally from the South Atlantic and Indian Oceans. Pressure gradients developed during the passage of these cyclones may strongly affect surface winds (Mather and Miller

1966). The normal surface flow may be intensified or reduced to the extent where winds may become contrary to the prevailing direction.

For example, one low pressure disturbance was observed during its passage into the interior, at Alligator Peak (78^{o} 27'S, 158^{o} 45'E, 1550m elevation) in December 1973. This site is some 75 km from Hillary Coast and 150 km inland from McMurdo Sound. High cloud began arriving at 1400 hours on the 15th and the prevailing strong southwest wind dropped soon after. At 1700 hours on the 16th, a northeast wind of 4.6 $m.s^{-1}$ was blowing. At 2130 hours on the 17th, snow was falling lightly and intermittently, and the wind was again calm. Atmospheric pressure was rising at this time. By 0830 hours on the 18th a light southwest wind was blowing and snow was still falling very intermittently. The prevailing strong southwesterly was blowing by 1330 hours on the 19th.

Upon reaching the high elevation surface of the East Antarctic Ice Sheet, the lower portion of cyclones are deformed and slowed down: hence it is mainly the upper sections which penetrate the interior in the form of currents of relatively warm and humid sea air (Rusin 1964). It is this meridional inflow of tropospheric air that mainly replenishes the heat lost by radiation from Antarctica (Weyant 1966b) and leads to the nourishment (5.1) of the continental ice sheet. The inflow involves mainly Marine Antarctic and Marine Temperate Air masses, but occasionally Marine Tropical Air (Solopov 1967). There are preferred areas of inflow (and outflow) in the atmosphere above Antarctica, although "large deviations of the meridional wind components from their average values exist in space or time" (Lettau 1969 p.332). Modelling the distribution of the nett annual mass flux around the periphery of the continent from the surface up to 50 mb, Lettau (1969) suggested that maximum values of mass inflow occurred at Byrd, Davis and Mirny Stations, while maximum outflow occurred at Hallett, Dumont d'Urville and Ellsworth Stations. Weyant (1966b) suggested that two-thirds of the inflow into the East Antarctic interior occurs in the 140^{o} sector between longitudes 80^{o}E and 140^{o}W. Ohtake (1976) using air trajectory analysis, showed that air arriving at Pole Station normally enters the continent in the 80^{o} sector between 90^{o} W and 170^{o}W.

Meridional circulation also occurs in the antarctic stratosphere (Logvinov 1968; Lettau 1969; Lamb 1970). Logvinov (1968) illustrates the meridional component of wind velocity in the atmosphere, particularly the stratosphere above McMurdo. Southerly flow dominates the meridional component from the surface to about 5 km, while northerly winds (up to about 25 $m.s^{-1}$) dominate this component in the rest of the troposphere and in the entire stratosphere (see also Table 13).

Generally then, the 'average' meridional circulation pattern in the troposphere and stratosphere above East Antarctica, is one of radial inflow followed by subsidence (Logvinov 1968; Lamb 1970; Schwerdtfeger

1970; Lysakov 1978) and outward surface flow. This pattern is superimposed on the dominant strong westerly circulation (the circumpolar vortex) in the upper troposphere and lower stratosphere (Weyant 1966a; Solopov 1967; Logvinov 1968; Schwerdtfeger 1970).

5. PRECIPITATION

5.1 General

Precipitation is an important hydrometeorological element in Antarctica, playing fundamental roles in the water and heat budgets of the continent. The discussion here is mainly based on forms of water, both in the atmosphere and on the ground, as they apply to vertical and horizontal transport of saline material. Some general aspects of precipitation are outlined first, followed by discussions on the precipitation regime in McMurdo oasis and on the various types of precipitation.

The original source of nearly all the atmospheric water vapour precipitated over Antarctica is the open water of the southern hemisphere oceans (Weyant 1966b). This moisture is transported mainly in the troposphere in the regions of preferred inflow as outlined in section 4.9. Most of the moisture is carried by the warmest air (Lettau 1969). However the saturation vapour pressure of water (see section 6.1) is very low at the mean temperatures (see Figure 6) of the antarctic troposphere. Hence there is very little 'precipitable water' in antarctic air and Antarctica experiences an arid or semi arid environment. However there is a large amount of moisture not readily available in the continental ice sheet, glaciers and frozen ground.

In Antarctica, precipitation is almost always in the solid form. Consequently its direct measurement is difficult, mainly due to the influence of wind which under different conditions may cause snow to be blown from, or deposited in snow gauges (Bull 1971). Instead, nett precipitation or accumulation which includes a large contribution from blowing and drifting snow, is often measured. Ablation of surface snow is very small on the plateau west of McMurdo oasis (section 6.2). Therefore there, accumulation is a good measure of total precipitation (including blown snow). The mean annual accumulation over the antarctic continent and ice shelves is around 150 $kg.m^{-2}$ (Bull 1971). This is equivalent to 430mm of snow of density 350 $kg.m^{-3}$ (Bull 1971) or 150mm of water.

In specific localities the accumulation may vary by a large amount from the average of 150 $kg.m^{-2}$ (Table 14). At a snow pit site in the McMurdo Ice Shelf 5 km east of Scott Base, the average accumulation was 176 $mm.a^{-1}$ water equivalent (density 390 $kg.m^{-3}$) for the period 1914 - 1958 (Stuart and Bull 1963). A reliable estimate of precipitation at Scott Base itself is not known, but snow falls there on about 90 days in a year (Thompson 1972). Each typical snowfall amounts to a few millimetres only, but occasionally a fall of a few centimetres occurs. Further north on the coast of McMurdo Sound, snow falls on more days (Rusin 1964). Early expeditions obtained estimates of precipitation of around 200mm water equivalent at Cape Royds (David and Priestley in Shackleton 1909) and 500mm water equivalent at Cape Adare (Wright and Priestly 1922). Annual precipitation is much less at Vanda Station.

TABLE 14 Annual snow accumulation and precipitation in Ross Dependency (Standard deviations in parentheses)

Locality	Accumulation	Precipitation	Reference or source of data
	(water equivalent in millimetres)		
Vanda Station	nil	5 (6)	Thompson *et al* (1971a); NZ Met. S. unpublished manuscript 'c' Section 5.2
whole of McMurdo oasis	0 - 100	100	
Ross Ice Shelf drainage system	100±20	-	Giovinetto (1964)
Skelton Neve (Station 72)	130	-	Crary (1966)
whole of Antarctica (including ice shelves)	150	-	Bull (1971)
5 km east of Scott Base	180 (50)	-	Stuart and Bull (1963).
Cape Royds	Nil	200	David and Priestley in Shackleton (1909)
Cape Adare	Nil	500	Wright and Priestley (1922)

Reasonable estimates of the snowfall at Vanda are 82mm (1969), 7mm (1970) and 115 mm (1974) (Thompson *et al* 1971a; NZ Met. S. unpublished manuscript 'c'); the mean is 68mm.a^{-1} with a standard deviation of 78mm.a^{-1}. Bromley (NZ Met. S. personal communication) determined the snow density of two typical falls to be close to 80 Kg.m^{-3}. This low value is close to that of snow composed of delicate stellar crystals and deposited in little wind (60 Kg.m^{-3}) (La Chapelle 1969). Thus the mean annual precipitation at Vanda is equivalent to around 5 mm of water (standard deviation, 6mm); however the three year observation series is too short for this figure to be reliable. For comparison, at Station 72 on the plateau west of Skelton Neve, the mean annual accumulation is equivalent to about 360 mm of snow (Crary 1966) or about

130mm of water. For the whole Ross Ice Shelf drainage system Giovinetto (1964) calculated that the mean annual accumulation was equivalent to about 300 ± 60mm of snow or about 100 ± 20mm of water. Most of the original precipitation contributing to this accumulation is snow that falls during the passage of cyclones (Rusin 1964).

The general pattern in Antarctica is one of relatively high precipitation on the coast. Precipitation tends to decrease inland away from the sea. The contribution of blowing snow may affect these generalisations. Generally, precipitation is erratic in arid areas; relatively large amounts of precipitation can be expected on a long return basis.

5.2 Snow and precipitation in McMurdo oasis

The precipitation regime at Vanda Station has been discussed by NZ Met. S., unpublished manuscript 'C' entitled "Precipitation in the dry valleys of southern Victoria Land". Some of the following discussion is based on parts of this manuscript.

Snow falls account for virtually all the precipitation in the oasis. Other forms of precipitation occurring in the McMurdo region are discussed below in sections 5.4 and 5.5 The snowfalls at Vanda are very variable; falling snow at the station itself, was reported on 59 days in 1969; but only on 11 days in 1970 (Thompson 1972). In the general vicinity of the station however, snowfalls are not infrequent, occurring on an average of about 100 days per year (standard deviation ca. 60 days, calculated from NZ Met. S., unpublished manuscript 'C'). Although snow may fall at any time during the year, snow falls on more days during the sunlit months. There is no marked increase in precipitation at Vanda during the summer, although there appears to be some tendency for greater amounts of snowfall in the autumn or early winter: in 1970 the heaviest single fall of the year (5mm) occurred in April, while March 1974 had the largest monthly total (89mm) since records began in 1969 (NZ Met. S., unpublished manuscript 'C'). Significantly, March has the most days with snowfall at Hallett Station (Schwerdtfeger 1970) on the coast of northern Victoria Land. February and March also feature in such records at Scott Base (Thompson and MacDonald 1961). This correlates with the greater amount of cloud during autumn at Scott, McMurdo and Hallett (Thompson and MacDonald 1961; Schwerdtfeger 1970) and during December - February at Vanda (Thompson *et al* 1971a).

Snowfalls occur commonly as showers from convective clouds in McMurdo oasis during the sunlight months, although the winter pattern is also followed: in winter lengthier falls occur from low status and strato-cumulus clouds drifting into the valleys from the east and west (Riordin 1973; NZ Met. S., unpublished manuscript 'C'). On these occasions, the snowfalls are associated with major depressions passing over or north of the area. Such depressions give rise to moist east or northeast air streams which have travelled across open sea before passing over the region (NZ Met. S. unpublished manuscript 'C').

There are marked precipitation gradients in the valleys of the oasis. More snow falls in the eastern and far western ends of Wright Valley than at Vanda; generally the eastern parts of the valleys receive the most snowfall (Calkin 1964 ; Bull 1966; Everett 1971; Riordin 1973; NZ Met S., unpublished manuscript 'C'). The snowline is lowest in the east and rises towards the west (Bull 1966; Wilson 1967). Snow drifts left from winter are common in spring along the coastal areas bordering McMurdo Sound, but become less common inland in central parts of the oasis.

Precipitation is higher in Taylor Valley than in Wright Valley. The former is open to the east, whereas Wright Lower and Wilson Piedmont Glaciers form a barrier 300 - 400 metres high, against westward - moving clouds and moist air. Wright Valley is significantly drier than Taylor Valley as indicated by the more common presence of suprapermafrost groundwater in Taylor Valley (Cartwright *et al* 1975), and a greater abundance of small lakes. Snowfall is more prevalent and heavier at higher elevations than on the valley floor. Falls exceeding 100mm may occur above 600m (Riordin 1973 ; NZ Met. S. unpublished manuscript 'C'). Anderton and Fenwick (1976) suggest (in a preliminary report) that in the hanging valleys of Asgard, Olympus and St Johns Ranges (i.e. above about 1000m elevation) the bulk of the annual precipitation usually occurs in summer. On five glaciers in the oasis (Sykes, Alberich, Heimdall, Meserve and Packard) stake networks have shown that the nett annual accumulation is less than 100mm water equivalent at most locations (Anderton and Fenwick 1976). Maximum recorded annual ablation above 1000m elevation on these glaciers is about 100mm water equivalent (Chinn unpublished). Therefore, 200mm water equivalent is probably a rough estimate of maximum annual precipitation above 1000m elevation in McMurdo oasis. Both accumulation and ablation on these glaciers are affected by topography (Chinn unpublished), and therefore the estimate is probably high.

100mm water equivalent (100 kg.m^{-2}or 1000mm of snow of density 100 kg.m^{-3}) is probably a reasonable estimate of average annual precipitation in McMurdo oasis.

The fallen snow does not lie for long periods on the valley floors and lower portions of the valley sides. In winter the snowfall will lie until the arrival of strong to gale foehn westerly winds. These winds which are associated with low relative humidities (6.1) quickly clear most of the snowfall in winter, but often isolated snow drifts are left in sheltered places (Riordin 1973; NZ Met. S., unpublished manuscript 'C'). In summer the foehn winds, high solar radiation and relatively warm ground surfaces quickly clear any snowfall. It is well known that most snow is cleared by sublimation and that little melting occurs on a regional basis. Locally however, melting may occur in summer, especially on sunny days, around the fringes of snowdrifts, snow patches and dark rocks in subzero air temperatures. This occurs from sea level to at least 3800m elevation, (personal observations in December 1974 of the surface of permafrosted ground on Mt Erebus), especially on north-facing slopes. When air temperatures are above zero, melting may be intense.

5.3 Structure and growth of the snow crystals

The typical snow particles falling in McMurdo oasis and near the coast around McMurdo Sound are stellar crystals (dendrites), usually about 1-3mm in diameter (Mawson in Shackleton 1909; NZ Met. S. unpublished manuscript 'C'; personal observations). Individual stellar crystals larger than 5mm have been seen throughout the region in summer, as have large snow flakes (assemblages of individual crystals). Such crystals are probably formed in the saturated environment of stratiform clouds when there is little wind to break up the delicate structures. Such wind conditions during snowfalls are typical of the oasis, especially in winter (NZ Met. S., unpublished manuscript 'C'). Low, detached nimbostratus clouds and probably low level convective clouds, also produce such frail tabular crystalline snow forms and some plates (Wright and Priestley 1922; and quoting Bentley 1901; Shumskii 1964). These crystals may become broken in the slightly stronger winds and turbulence associated with such clouds. The crystals will be broken into many fragments by the strong winds which are typical in blizzards.

Fine granular snow, usually less than 1mm in diameter is also common at Vanda (NZ Met. S., unpublished manuscript 'C'). This snow may be a small form of 'graupel', consisting of fragments of snow crystals completely enveloped in rime due to passage through a supercooled cloud (La Chapelle 1969). Fine granular snow, often less than 0.5mm in diameter and consisting of minute columns and plates, is also typical of snow falling in polar regions (La Chapelle 1969).

More solid crystals are produced in clouds at higher levels. Intermediate-level clouds (altostratus and altocumulus) deposit crystals which have solid hexagonal centres with some dendritic extensions (Wright and Priestley 1922; and quoting Bentley 1901; Shumskii 1964) in relatively warm conditions. Combined ice crystals, up to 1mm diameter, in the form of sideplanes (sectors), bullets and columns are created in such clouds in colder conditions as at South Pole in summer (Ohtake 1978). Cirrus and cirrostratus clouds form compact columnar type crystal assemblages, 1mm or larger, composed of combinations of bullets and some small plates (Shumskii 1964; Ohtake 1978). In general cyclonic disturbances contain different types of clouds at different levels. Large scale vertical mixing of air in these storms will lead to a variety of crystal shapes, many of which will be fragmented.

Evidently then, in Antarctica the growth of snow crystals is predominantly by diffusion controlled processes. In cold, dry air growth of a newly nucleated ice particle is slow and tends to be parallel to the crystallographic c-axis of the ice crystal. The precipitated crystals are small, compact and columnar forms are apparent. Where relatively large amounts of water vapour are present, growth is relatively fast and parallel to the a-axis. Thus the precipitated crystals are larger, and stellar and plate forms are evident. In warm and saturated or supersaturated environments ice and snow crystals may grow by riming as water droplets collide with and freeze to the crystals. This accretional growth occurs in cloud droplet regions when temperatures are between 0 and -15^{o}C (Magono and Lee 1966). At antarctic stations near the coast a significantly high proportion of precipitated crystals have been found to have grown by accretion (Warburton and Linkletter 1978).

5.4 Blowing snow

When wind blows over a snow surface, horizontal stresses are developed in that surface. At a certain wind speed these stresses are strong enough to shear snow particles loose from the surface. These particles are raised to a height determined by the wind speed and turbulence, and travel with the flow of air. Although the technical details of wind transported snow are not discussed here, certain aspects of blowing snow are necessary to the discussion of salt transport.

Under normal antarctic conditions, horizontal snow transport commences near the surface when the wind speed at 5m reaches about 6.5 to 10 $m.s^{-1}$ (Rusin 1964; Oura and Kobayashi 1968) or at 10m exceeds 8 $m.s^{-1}$ (Schwerdtfeger 1970; Maki 1971). The exact speed is dependent on the state and temperature of the snow surface. With higher wind speeds the snow is carried higher into the air. At 18 $m.s^{-1}$ the snow reaches higher than 3m, while in the most violent winds snow may be carried by turbulent suspension to heights of hundreds of metres. Most snow however is transported within about half a metre of the surface, and mainly by saltation processes.

Blowing* and drifting* snow are important sources of snow accumulation in Antarctica. However, in McMurdo oasis their influence is small except in local areas near alpine glacier neves and exposed eastern but more especially western ends of the major valleys. Occasionally vast clouds of blowing snow are swept off the plateau by violent westerly gales. These clouds extend up to 3000m in height and completely fill Wright Valley to the west; however only a little snow settles behind the larger boulders (NZ Met. S., unpublished manuscript 'C').

*Blowing snow consists of snow (and ice) particles raised by the wind to more than a metre above the ground; whereas with drifting snow, the particles are raised to heights of a metre or so, so that visibility at eye level is not noticeably diminished (Armstrong *et al* 1973).

Blowing snow is common in the McMurdo Sound area. Table 11 indicates that winds from all eight major directions are sometimes strong enough to blow snow at localities along the coast. Sticky snow impregnated with salt that is common on the surface of the sea ice of McMurdo Sound (Wellman and Wilson 1963), will be blown free from the surface but at higher velocities than normal macroscopically salt-free snow. Along the coastal areas, blowing snow is responsible for large drifts and permanent ice accumulations. Strong winds from the south and southeast create large drifts in areas where the wind speed locally decreases, such as in the lee of hills and smaller obstacles on the land surface at Cape Evans, Barne and Royds. David and Adams (in Shackleton 1909) noticed that during the earlier part of blizzards, snowdrifts were formed mainly of old snow. Towards the end of the blizzard however, fresh snow would be deposited, probably produced from moisture carried by the upper air currents in the storm.

Blowing snow is of major importance in areas along the western side of McMurdo oasis such as Kennar Valley, Shapeless Mountain (etc) that border the plateau . Snow blowing off the plateau may settle as a thin veneer, or in drifts and may create permanent ice accumulations. Favoured areas for these types of snow accumulations are those where the wind speed locally decreases such as gullies, depressions and north through eastern sides of boulders, hills, bluffs and ridges. From observations in those western ice-free areas such as Kennar Valley it appears that they more commonly experience precipitation from blowing snow than do adjacent areas to the east such as Beacon Valley.

Obviously such accumulation is not restricted to areas west of McMurdo Sound. Blowing snow affects ice-free areas and nunataks along the entire Transantarctic Mountains. At Roberts Massif at the head of Shackleton Glacier, Claridge and Campbell (1968) noted that much of the snow was derived from snow blown off the plateau. They also suspected that most of such snow was removed by sublimation rather than melting.

On the plateau itself, blowing and drifting snow are responsible for transporting vast amounts of snow. This transport is generally outwards from the interior in the direction towards which the prevailing surface wind is blowing (see 4.9). It has been estimated that a flux of around 3×10^6 Kg and 6×10^7 Kg respectively of snow is transported per metre of surface each year at Byrd Station and Cape Denison (Schwerdtfeger 1970). Transport at Pole Station is similar to that at Byrd. The number of days with blowing snow at various antarctic stations is listed in Weyant (1967) and Schwerdtfeger (1970). Byrd, Ellsworth, Little America V, McMurdo, Pole and Wilkes Station areas experience some winter months with 10 to 15 days or more of blowing snow. At most antarctic stations the frequency of blowing snow is less in November through February, mainly because of lower mean wind speeds in those months, but also because of warmer surface conditions.

5.5 Other forms of precipitation

Although snowfall and blowing snow account for most precipitation and accumulation in Antarctica, other forms of precipitation do occur. These other types of precipitation may have some relevance to the question of salt origin.

One of the biggest fallacies popularly held about the antarctic climate is that rain is unknown. Rain, an efficient remover of soluble material from the atmosphere (Gorham 1961) is very uncommon, but does occur occasionally in the coastal regions of Antarctica. Known occurrences of rain or near-rain in and near Ross Dependency are listed in Table 15; each produced very small amounts of precipitation.

TABLE 15 Known occurrences of rain and near-rain in or near Ross Dependency

Precipitation form	Locality	Date	Reference
Drizzle and rain	Ross Sea	February 1842	Ross (1847)
Rainbow	Cape Royds	22.12.08	Murray in Shackleton (1909)
Rain	Ross Sea	1910 - 13 expedition	Wright and Priestley (1922)
Rain	Cape Adare	1910 - 13 expedition	Wright and Priestley (1922)
Rainbow	NNE Cape Evans	14.2.11	Simpson (1919)
Drizzle	Little America V Station	10.5.57	Vickers (1966)
Slushy snow	Little America V Station	11.5.57	Vickers (1966)
Sleet	Little America V Station	31 March and 1 April 1958	Vickers (1966)
Rain	McMurdo Sound	30.11.58	Quartermain (1958)
Rain	Lake Vanda	January 1959	Bull (personal comm.)
Rain and slushy snow	Little Rockford Station 79°S 151°W	early February 1961	Quartermain (1961)
Light drizzle	Hallett Station	18.1.62	Anon (1962)
Light rain shower	Vanda Station and west end of Lake	late December 1968	Bromley, NZ Met.S. personal communication
Rain	Vanda Station	January 1970	NZ Met.S. 'C'
Rain showers	Vanda Station	19.5.74	Bromley NZ Met. S. written communication
Wet snow falls	McMurdo oasis and coast of McMurdo Sound	occasional	Bromley NZ Met.S. personal communication; Keys, personal observations.

Clouds containing super-cooled water droplets are a normal occurrence in Antarctica, especially in summer. Such clouds exist up to at least 3000m. Pilots reported freezing rain on some occasions when flying missions over Antarctica in early Operation Deepfreeze years (Dufek 1957). Fogs, mist, frost smoke+,hoarfrost, ice flowers* and rime accumulations are not uncommon in the McMurdo Sound area. A special case of rime accumulation occurs around the summits of Mounts Discovery and Morning. Snow and ice features up to 20m high are largely covered with the characteristic (La Chapelle 1969) rough, channelled and feathered deposit of rime and rime-cemented snow. Orographic type clouds involving rapid lifting of air in strong winds from the south have been seen (December 1974) blanketing the upper part of Mt Discovery. Such conditions probably lead to the formation of these rime accumulations which indicate the presence of super-cooled water droplets at temperatures as cold as about -20°C. Fogs containing such droplets have been observed at temperatures as low as -34°C in the vicinity of Little America Station (Rusin 1964). In the interior of the continent fogs consist of ice crystals in winter but probably mixtures of ice crystals and super-cooled droplets in summer (Rusin 1964) if the ambient air temperature is warmer than about -40°C.

At Vanda Station a wet formation with "the appearance of a quite heavy dew" is not uncommon: this "dew" forms on rocks, particularly the darker ones around the station (e.g. 11, 12 February 1970; Bromley NZ Met.S., personal communication). Frosts have also been noted (NZ Met. S. records).

Ice crystals falling from a clear sky ('no cloud precipitation') is a common form of precipitation in the interior and also in the McMurdo region (Rusin 1964; Schwerdtfeger 1970;Riordin 1973; Ohtake 1978). At South Pole in summer, this form of precipitation is created in the lowest 1000m above the surface and consists of thin hexagonal plates and columns smaller than 0.2mm (Ohtake 1978). The thin plate crystals are formed at temperatures colder than -22°C (Ohtake 1978) whereas their generally accepted range of formation temperatures is between -10 and -18°C (Magono and Lee 1966). To explain their formation in humidities less than the water or ice saturation values, Ohtake (1978) proposes a mechanism of "deposition nucleation" - water deposition directly onto nuclei under sub-water or -ice saturation conditions.

+ frost smoke is thin fog-like cloud formed by contact of cold air with relatively warm water.

* Ice flowers are fern-like ice formations up to ca.30mm long formed by freezing of frost smoke, fog or water vapour under some conditions: the term, as used here, includes "fog crystals" and some types of "frost crystals" (Wright and Priestley 1922) but not Tyndall figures (forms caused by internal melting of ice (Shumskii 1964, quoting Tyndall 1858). Ice flowers have been seen by the present author on the sea ice of McMurdo Sound and the lake ice of Lake Bonney.

Spray blown from the sea is a major form of precipitation within 200-300m of the coast of McMurdo Sound (Wright and Priestley 1922). For this form of precipitation to be important, there must be open water relatively close to the windward side of land and the wind must be strong enough to blow the tops off waves. Spray is blown from the sea when the wind is stronger than about 10 $m.s^{-1}$; spindrift occurs when the windspeed is 14-17 $m.s^{-1}$ or stronger (Harvey 1976). Winds of this strength are common from the southerly quarter in the coastal areas of the Sound (4.5, 4.7, Table 11). Winds from the northerly quarter are also strong enough on occasions. Open water may exist in late summer, autumn and early winter to the north and south of Cape Armitage, Hut Point, Capes Evans, Barne, Royds, Cape Bird ice-free area and Cape Bernacchi-Marble Point area. In the autumn sea spray may form the well-known 'storm ice foot' along the coast line itself (Wright and Priestley 1922). Early expeditions report instances of heavy deposition of frozen sea spray and the formation of 'spray ridges'. Spray was blown ca.400m inland at Cape Royds during a five-day southeasterly blizzard in February 1908 when Backdoor Bay was only partly clear of ice; accumulations of frozen spray up to ca.2m thick were formed (Shackleton 1909). Clearly, over many years, wind-blown sea spray is an important form of precipitation in coastal areas of McMurdo Sound, despite the presence of sea ice for twelve months of a particular year at some localities.

5.6 Variations in precipitation over the last 80 years

At stations in the McMurdo region the observation series are too short to show any significant recent changes in the precipitation regime. Precipitation parameters from Orcadas Station suggest a slight decline in precipitation activity since 1935; this may be interpreted as a slight lessening in intensity of cyclonic activity in the area (Schwerdtfeger 1970). Some studies have pointed to an increase in snow accumulation in the interior and there is evidence for a decrease of ice in some coastal areas near the Antarctic Circle (Schwerdtfeger 1970). No significant trends are evident in the snow pit data of Stuart and Bull (1963) for 45 years of accumulation between 1913 and 1958 revealed at a site on McMurdo Ice Shelf 5 km east of Scott Base.

6. ATMOSPHERIC HUMIDITY

6.1 General

Humidity affects the hydration state of some salts in the region. Also Wilson (1979) proposed that migration and separation of salts occurs down slopes under the influence of fluctuating humidities and humidity gradients in the McMurdo region. For the separation process to be viable in the field, positive humidity gradients must at times exist up slopes. In this section, atmospheric humidities and humidity gradients are discussed.

Several quantities and characteristics of atmospheric humidity or moisture content may be defined and measured. Here the emphasis is placed on relative humidity, but absolute humidity, water vapour pressure, saturation vapour pressure, dew point and mixing ratio are also mentioned. These terms are defined in Table 16.

TABLE 16 Definitions, symbols and units of terms relating to humidity used in this study (definitions after Wexler 1970; and Weast 1975).

Term or Quantity	Symbol	Unit	Definition and Characteristics
Water vapour pressure	e	millibars*	partial pressure exerted by the water vapour present in the atmosphere.
saturation vapour pressure	E_w E_i	mb	the pressure of water vapour (unmixed with a foreign gas) in equilibrium with a plane surface of pure, liquid, water (Ew), or pure, solid, ice (E_i). Decreases with decreasing temperature (Figure 6).
'saturated'	-	-	a moist gas is said to be saturated with respect to liquid water or solid ice when it can co-exist with pure liquid water or pure solid ice at a given temperature and pressure.
absolute humidity	a	$Kg.m^{-3}$ or mb	mass of water vapour present in a unit volume of the atmosphere. It may also be defined in terms of the water vapour pressure, e
relative humidity	f	percent	the ratio of the quantity (or pressure) of water vapour present in the atmosphere to the quantity which would saturate (or the saturation vapour pressure) at the existing temperature. When the temperature is less than 0^oC at NZ stations in Antarctica, the saturation is defined with respect to ice (Tomlinson, NZ Met.S. personal communication).
dew point (frost point)	T_d T_i	^oC	the temperature at which condensation of atmospheric water vapour takes place: the temperature at which the air is saturated with respect to water (T_d) or ice (T_i).
mixing ratio	r	$g.kg^{-1}$	the mass of water vapour associated with a unit mass of dry air.

*the millibar is not an SI unit: however its use is retained here to be consistent with units of atmospheric pressure previously mentioned and also with NZ Met.S. usage. Note that 1 mb = 100 pascals ($N.m^{-2}$).

The problems of measuring humidity at low temperatures are well known (Thompson and MacDonald 1961; Rusin 1964; Schwerdtfeger 1970; Wexler 1970). These problems are due to the difficulty of measuring the small amounts of water vapour present; the concentration may be less than 0.75 ppm (Wexler 1970). Even some modern hygrometers have reduced sensitivity and accuracy at low temperatures (Wexler 1970). Computational methods based on the temperature-saturation vapour pressure relationship and ambient temperature may be more reliable in such conditions (Schwerdtfeger 1970; Artem'ev 1973). For these reasons many values of humidity given in the antarctic literature must be treated with reserve. Strictly speaking, 'mean relative humidity' or 'mean dew point' cannot be used to deduce the mean moisture content at a locality because of the non-linear relationship between temperature and saturation vapour pressure (Figure 6) (Schwerdtfeger 1970). Often qualitative estimates may be useful.

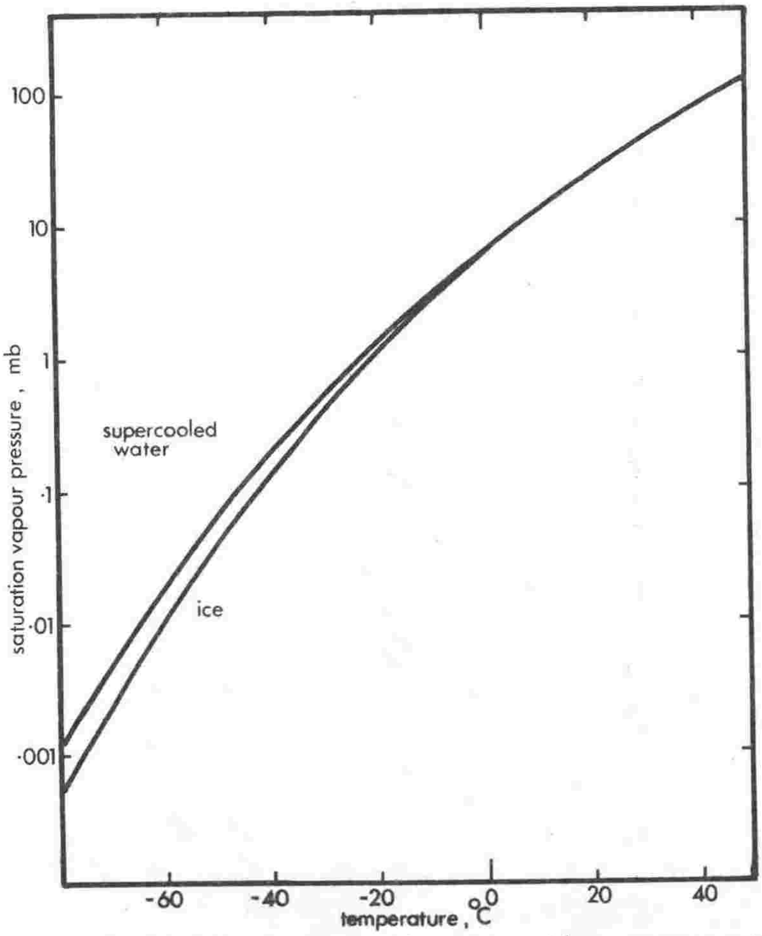

FIGURE 6 Relationship between the saturation vapour pressure and temperature of the pure water substance (after Wexler 1970).

The published monthly averages of relative humidity values at Vanda (Thompson *et al.*, 1971a; Thompson 1972) show consistently lower values in summer. The relative humidities average 30 - 50 percent in summer (minimum less than 10) and probably 50 - 80 percent in winter; during 1969 and 1970 the average RH was 54 percent (Thompson 1972; NZ Met.S. records). At Scott Base, average monthly relative humidities are seldom less than 60 percent and range to more than 80 percent with relatively little difference between winter and summer; during 1958 the average RH was 71 percent (Thompson and MacDonald 1961; NZ Met.S. records). It has been estimated (Schwerdtfeger 1970) and calculated (Artem'ev 1973) that considerable supersaturation with respect to ice may occur in the air at interior stations, especially in winter. It is suggested that this supersaturation, of up to 20 percent probably occurs on occasion in the McMurdo region also, as evidenced by fog, rime and ice crystals (5.5).

The relative humidities at Vanda (and elsewhere) may be converted to absolute humidities using Figure 6 and Equation 3 below. The mean summer temperature at Vanda is about +0.8°C and the mean winter temperature is about -32°C (Table 2); saturation vapour pressures at these temperatures are 6.473 and 0.309 mb respectively (Weast 1975). The absolute humidity a, in $kg.m^{-3}$ is related to the water vapour pressure e, in millibars and to absolute temperature T, by the following approximate formula (Petterssen 1941):

$$a = \frac{0.217e}{T} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; 1$$

For meteorological purposes moist air can be assumed to be an ideal gas; relative humidity f, then is given by:

$$f = \frac{e}{E} \times 100 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; 2$$

where E is the saturation vapour pressure at the ambient temperature, T. By substitution we have:

$$a = \frac{f.E}{T} \times 2.17 \times 10^{-3} \quad . \; . \; . \; . \; . \; . \; . \; . \; 3$$

Using Equation 3 and the mean values of T and E given above, the average values of absolute humidities at Vanda were calculated to be about $(1.5 \text{ to } 2.6) \times 10^{-3}$ $kg.m^{-3}$ in summer, and about $(0.14 \text{ to } 0.22) \times 10^{-3}$ $kg.m^{-3}$ in winter. On a purely scientific basis these results are slightly high due to the non-ideality of moist air; however in practical meteorological terms such precision is not necessary.

The central regions of East Antarctica contain the "Pole of lowest absolute humidity" (Rusin 1964). Generally, it can be stated that the air moving down off the polar plateau has low absolute humidity; that maritime air is relatively moist; and that the relative humidity of both these types of air "masses" will increase when they move over cold water, pack ice, shelf ice or snow-covered ground (Schwerdtfeger 1970).

The relationship between wind and humidity in McMurdo oasis is well known. Westerly winds are adiabatically heated upon entering the oasis (4.8) although the absolute humidity does not usually rise appreciably (Bull 1966). Thus relative humidities and dew points are very low during westerly winds (Bull 1966; Thompson *et al* 1971a; Yoshida and Moriwaki 1972) The minimum humidities are about five percent

(Bull 1966; NZ Met.S. records) indicating a high potential for evaporation in summer. Easterly winds however, have higher humidities and dew points (Bull 1966; Yoshida and Moriwaki 1972) and saturated air is common in the east, especially at higher altitudes.

6.2 Horizontal gradients

It has already been intimated that horizontal gradients of atmospheric humidity may exist in McMurdo oasis. The predominance of cool, moist easterly winds (2.4, 4.3) and higher precipitation (5.2,5.5) in the east of the dry valleys, result in higher average absolute and relative humidities near the coast than in the central parts of the oasis. On the average, a negative gradient of absolute humidity probably exists inland towards the west.

Relative humidity gradients are more complex. Saturated air is common in the east despite the slightly warmer mean annual air temperatures there (3.2). Apparently saturated air is also common in the west on the plateau and along its fringe, despite the low absolute humidities. At Shapeless Mountain an igloo and tracks from four stroke tobaggans made by VUWAE members in November 1971 (Barrett pers.comm. VUW) were virtually unchanged in November 1973. This indicates that ablation was minimal during this two year period, due to the ambient vapour pressure being close to saturation in the cold air temperatures. Furthermore Annexstad (1980) found that ablation is only 0.05 $m.a^{-1}$ on blue-ice at 2000m elevation west of Allan Hills. Snow in the area is likely to ablate even slower than that because of the higher albedo of snow than ice. This is consistent with high average atmospheric humidities (greater than 70 percent) at stations in the interior of East Antarctica (Rusin 1964). Thus on the average, negative gradients of relative humidity probably exist from the western and eastern margins in towards the central parts of the oasis.

6.3 Vertical gradients

Two vertical gradients of atmospheric humidity may be defined, analogous to vertical gradients of air temperature (3.3). The environmental gradient describes the gradient in free air, while the topographic gradient describes the case up an incline on the earth's surface.

Environmental humidity gradients are determined from humidity or dew point measurements during balloon ascents. Reservations may be held about the absolute quantitative worth of the antarctic data for the reasons outlined earlier. Solopov (1967) has studied the environmental gradients above oases and snow and ice covered surfaces along the coast of East Antarctica. He found that the nett environmental relative humidity gradient was predominantly negative upwards over the snow-covered surfaces all year round and over the oases in winter. Over the oases in summer the nett gradient is predominantly positive upwards due to upward transfer of water vapour by turbulent moisture exchange from the ground into the atmosphere. However in summer these gradients are often very small. Average relative humidity gradients in the troposphere are usually negative above most antarctic stations (Weyant 1966a) A negative gradient of mean mixing ratio exists above McMurdo Station in January (Schwerdtfeger 1970).

Although the nett environmental gradients are mostly negative, considerable variation may occur on any particular balloon sounding, due to the presence of cloud and humid layers. Figure 7 illustrates the variation of relative humidity with pressure altitude on three typical soundings in January 1975 from McMurdo Station. The relative humidities in this Figure were obtained (U.S. Naval Support Force, Antarctica) from measurements of dew point by a modern type of dew point hygrometer, and temperature measurements; these relative humidities are probably accurate to within a few percent. The levels of cloud and humid layers are evident on Figure 7.

The presence of cloud against hill and valley sides in the region will create locally positive topographic gradients of relative humidity. The mean cloud cover is significantly greater in summer than in winter at Vanda (Thompson *et al* 1971a) and McMurdo oasis, but only slightly

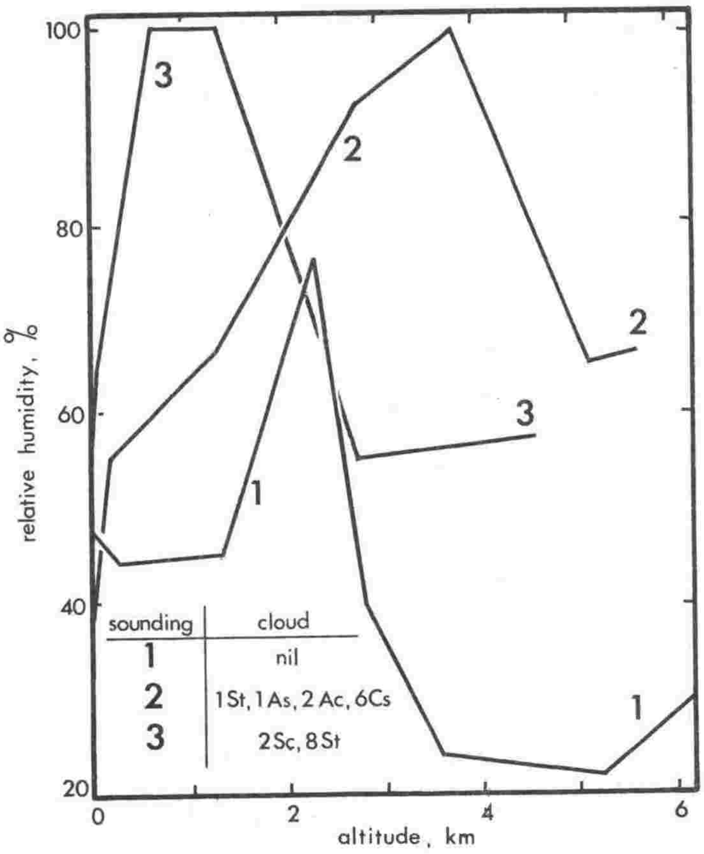

FIGURE 7 Three balloon soundings showing environmental relative humidity gradients above McMurdo Station in January 1975 on the 16th, 20th and 23rd respectively: balloon release time 1130 hours. Independent parameter, altitude, is plotted on the horizontal axis (data from Meteorology Section, Mac Centre, NSFA, McMurdo).

greater in summer at Scott and McMurdo (Thompson and MacDonald 1961; Schwerdtfeger 1970). Furthermore, precipitation increases with elevation in the oasis, especially in summer (5.2). Thus, topographic relative humidity gradients are probably often positive upwards in McMurdo oasis. However Schofield's (1971) observations of lichen growth above 600m only, in Miers Valley, do not provide irrefutable evidence for permanently positive gradients. Moisture is available from other sources such as blown snow and snowfall beside atmospheric water vapour, and the latter moisture supply may be intermittent.

Topographic gradients of humidity were measured at one locality in the region (Figure 8). Relative humidities were measured (13 November 1974) up and down the northern side of Mt Kempe (Royal Society Range), using a Vaisala HM11 Humicap humidity meter and probe; the probe has a film capacitive sensor. The meter had been calibrated with phosphorus pentoxide (zero percent) and saturated water vapour (100 percent) in New Zealand and this calibration was rechecked at Scott Base. The atmospheric relative humidity was measured at 0.3 to 0.5m above the ground surface; the humidity data are probably accurate to within a few percent. The elevations were measured by an altimeter calibrated against the USGS 1:250,000 map, while the air temperatures were measured using a whirling psychrometer. Weather conditions at the time were clear skies with a southwest wind of 0-3.6 $m.s^{-1}$.

In Figure 8 each plot shows a range of relative humidities due to fluctuations of this parameter at each station. The Figure illustrates that topographic relative humidity gradients may be positive or negative. Figure 9 examines the variation of relative humidity with temperatures to determine whether the relative humidity changes in Figure 8 were due to changes in the water vapour content of the air or to temperature changes. If the latter were the case, relative humidity would decrease with increasing temperature. Figure 9 shows that the relative humidities are not inversely dependent on temperature. In fact there is a very weak trend (correlation coefficient +0.43) for relative humidity to increase with temperature. Thus the changes in relative humidity reflect temporal and spatial changes in the water vapour content of the air. Using Equation 3, it can be shown that the air involved here has absolute humidities ranging from 0.14×10^{-3} to 0.29×10^{-3} $kg.m^{-3}$.

Obviously there are a great range of topographic relative humidity gradients that are possible. These reflect fluctuations in atmospheric humidities near the ground. Such humidities vary between 100 percent and less than 10 percent and tend to be higher in winter (Thompson 1972). Fluctuations of at least 10 percent RH may occur within minutes (Figure 8) and of at least 50 percent RH within hours (Yoshida and Moriwaki 1972).

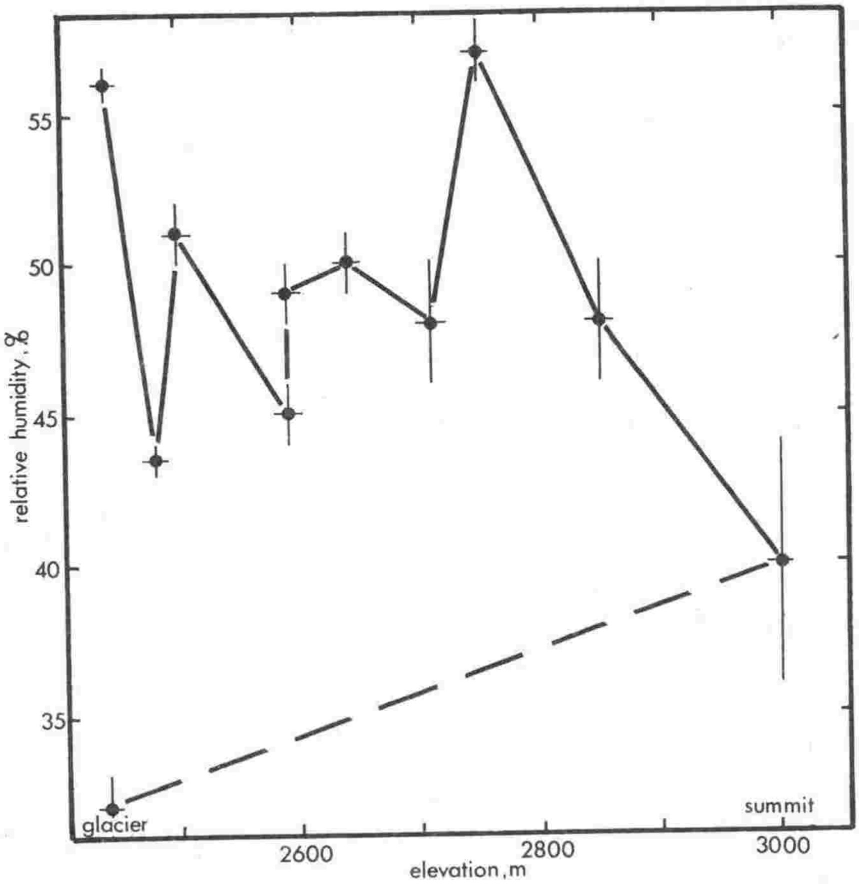

FIGURE 8 Topographic relative humidity gradients between Kempe Glacier and the summit of Mt Kempe (independent parameter, elevation, plotted on the horizontal axis).

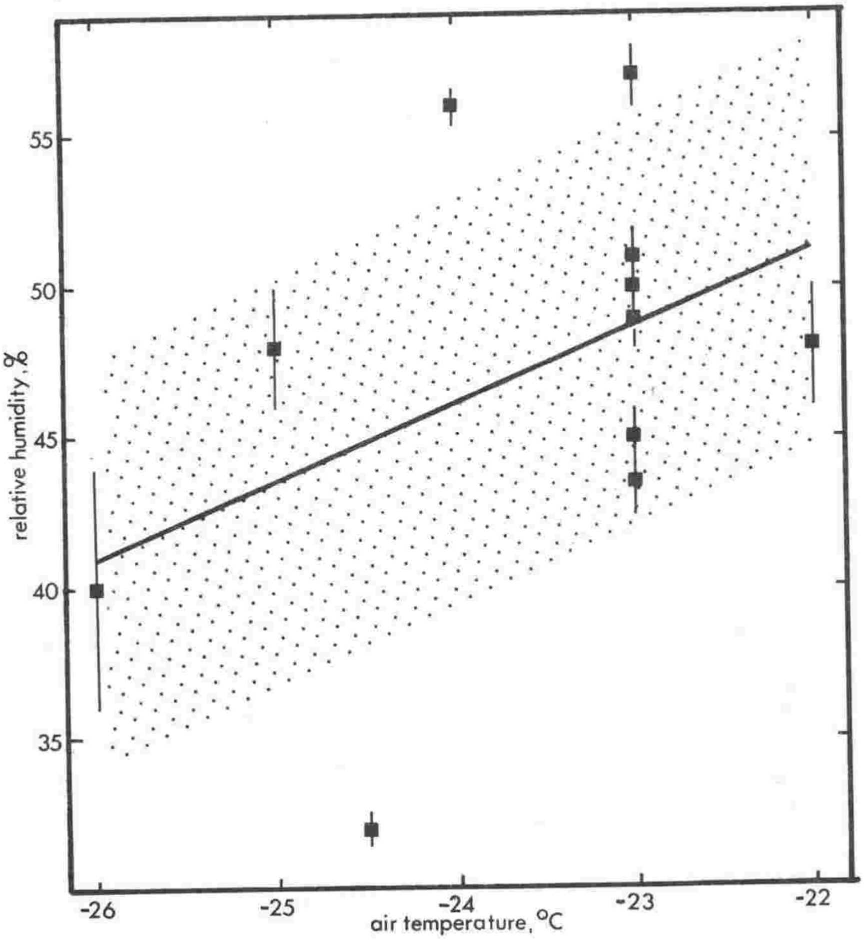

FIGURE 9 Relative humidity versus air temperature on Mt Kempe. Shading indicates the area lying within one standard error of the

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APPENDIX 4 DEPTH TO ICE-CEMENTED TABLE AT SELECTED SITES

Table A4.1 Depot Cone* (78°26'S, 164°28'E, elevation 1000 m); breached volcanic cone in saddle between Mts. Discovery and Morning. Soil sites in areas composed of coarse sand, gravel, pebbles and some cobbles, often situated between low ridges and blocks of lava. Surface colour 5R 4/2 - 10R 5/4, slope angle 0 to 25°. Where range of depths is given, the surface of the ice-cemented table is irregular; all other depths are ±0.003 m. Measurements made 4-7/12/76.

*Unofficial name

Aspect	Depth (m)	Aspect	Depth	Aspect	Depth
SW	0.047	NE	0.038	NW	0.052
SW	0.055	ENE	0.047	WNW	0.04 to 0.05
SW	0.056	ENE	0.020 to 0.025	NW	0.035 to 0.04
SW	0.063	ENE	0.032	NNW	0.035 to 0.04
SW	0.060	ENE	0.038	NNW	0.04 to 0.045
SW	0.085	ENE	0.033	NW	0.034
W	0.072	NE	0.035	WNW	0.04 to 0.05
W	0.048	NE	0.025 to 0.03	NW	0.04
W	0.067	NE	0.02 to 0.025	NW	0.048
W	0.072	NE	0.03 to 0.05	ENE	0.037
W	0.065	E	0.035	ENE	0.055
W	0.066	E	0.034	E	0.048
W	0.057	NE	0.035	ENE	0.045
W	0.095	NE	0.032	E	0.03 to 0.04
W	0.073	NE	0.038	SE	0.059
W	0.064	NNE	0.047	SE	0.053
W	0.060	NNE	0.033	SE	0.065
ESE	0.060	NNE	0.031	ESE	0.054
E	0.055	N	0.016	SW	0.062
ESE	0.065	N	0.019	SW	0.068
ESE	0.066	N	0.020	SW	0.069
ESE	0.068	N	0.005 to 0.010	SW	0.065
ESE	0.070	N	0.010 to 0.015	WSW	0.070
NE	0.047	NNW	0.010 to 0.015	WSW	0.057
ENE	0.055 to 0.065	W	0.038	SE	0.060
NE	0.032	W	0.039	W	0.080
E	0.045	W	0.03 to 0.04	W	0.052
ENE	0.060	W	0.045 to 0.055		

Table A4.2 Top Cone* (78°23'S, 164°55'E, elevation 2000 m). Isolated flat-lying scoria cone on southwest ridge of Mt. Discovery. Soil sites are in areas composed of sand and gravel with some larger scoria fragments. Soil colour approx. 10R 4/4, slope angle 0 to 25°. Depths are ±0.005 m. Measurements made 10/12/76.

*Unofficial name

Aspect	Depth	Aspect	Depth
N	0.015	E	0.055
N	0.015	SSW	0.045
N	0.02	SW	0.03
N	0.02	WSW	0.02
N	0.015	WSW	0.03
NNE	0.02	W	0.02
N	0.03	W	0.02
NW	0.035	W	0.025
NNE	0.04	W	0.03
NE	0.02	SW	0.035 to 0.05
ENE	0.025	SSE	0.03
ENE	0.03	S	0.04
NE	0.045	SW	0.035
NE	0.03 to 0.05	S	0.04
NE	0.04	S	0.03
N	0.035	S	0.03
N	0.03	S	0.045
NE	0.035	S	0.035
ENE	0.03	SSE	0.035
ENE	0.035	S	0.05
N	0.02	S	0.05
N	0.035	SSE	0.06
NNW	0.03	SSE	0.05
ESE	0.045	SSE	0.045
SE	0.04	SE	0.04

Table A4.3 Castle Cone* (78°22'S, 164°47'E, elevation 1000 m). Volcanic cone on northwest flank of Mt. Discovery. Soil sites are sand and gravel areas between loose rocks and boulders. Surface colour mainly 10YR 3/2, slope angle 1 to 20°. Depths are ±0.005 m. Measurements made 13/12/76.

Aspect	Depth	Aspect	Depth
E	0.09	NW	0.08
E	0.095	WNW	0.085
ESE	0.095	W	0.065
ESE	0.09	W	0.07 to 0.09
ESE	0.065	E	0.08 to 0.095
SE	0.095	E	0.095

A4.3 (contd.)

Aspect	Depth	Aspect	Depth
SE	0.08	NE	0.095
SE	0.07	NE	0.09
SSE	0.075	NNE	0.08
SSE	0.07	N	0.07
E	0.075	NW	0.075
E	0.075		
S	0.065 to 0.08		
SE	0.075		
SSE	0.085		
E	0.08		
SSE	0.07		
NNW	0.075		
S	0.09 to 0.11		
NW	0.06 to 0.08		
NNW	0.07		
W	0.07		
W	0.075 to 0.09		
WNW	0.075		
NNW	0.08 to 0.095		

Table A4.4 Stadium Cone* (78°21'S, 164°44'E, elevation 750 m). Volcanic cone on northwest flank of Mt. Discovery. Terrain similar to Depot and Castle Cones. Surface colour 10R 4/4, slope angle 1 to 20°. Depths are ±0.005 m. Measurements made 13/12/76.

Aspect	Depth (m)	Aspect	Depth (m)
NNE	0.115	ENE	0.13
ENE	0.125	NE	0.10 to 0.115
NE	0.125	NE	0.11
NE	0.11 to 0.125	NE	0.105
WSW	0.10 to 0.115	N	0.12
W	0.135	NW	0.11
WSW	0.093	NNW	0.10
W	0.095	NW	0.097
W	0.06 to 0.075	SSW	0.115
WNW	0.068	SW	0.105
NW	0.068	SW	0.105
NW	0.062	NE	0.087
NW	0.095 to 0.11	S	0.155
NW	0.10	SSE	0.12 to 0.135
W	0.09	SSE	0.135
WNW	0.08	S	0.125
WNW	0.087	SW	0.11
NNE	0.09	W	0.093
N	0.098	W	0.135
NNE	0.095 to 0.11	N	0.102
NE	0.075	N	0.105

Table A4.5 Bottom Cone* (78°18'S, 164°47'E, elevation 180 m). Volcanic cone on lower northwestern slope of Mt. Discovery, near Koettlitz Glacier and 7 km southwest of Hahn Island. Even slopes largely covered with fairly massive basaltic cobbles: soil similar to that at other cones. Surface colour mainly 5YR 2/1, slope angle 11 to 21°. Depths are ±0.005 m. Measurements made 13/12/76.

Aspect	Depth	Aspect	Depth
S	0.175	W	0.14 to 0.16
SSW	0.165	W	0.16 to 0.18
SSW	0.165	W	0.145
S	0.175	NNW	0.10 to 0.12
E	0.155	NW	0.105
E	0.115	N	0.115
W	0.10 to 0.16		

Table A4.6 Table Mountain (77°59'E, 161°56'E, elevation 1600 to 2000 m). Various terrain including slopes, terraces, screes with variable extent of soil development on sandstones, siltstone and dolerite bedrock. Surface lightness 4 to 8, various chroma and hue. Slope angle 0 to 40°. Depths are ±0.01 m. [ ] indicates bedrock encountered before ice-cemented table and not included in regression analysis. Measurements made 19-25/11/74.

Aspect	Average depth	Aspect	Average depth	Aspect	Average depth
NW	0.05	NW	0.13	W	0.11
WNW	0.07	N	0.10	SW	0.12
N	0.19	NE	0.09	[W	0.10]
N	0.10	SW	0.30	[W	0.18]
N	0.12	SW	0.26	SW	0.11
N	0.16	SW	0.21	[SW	0.18]
NW	0.08	WSW	0.13	[NE	0.17]
NW	0.09	SSW	0.14	N	0.16
NW	0.10	N	0.17	[N	0.02]
NW	0.11	W	0.09	[NNE	0.05]
NW	0.11	[SW	0.11]	[NE	0.02]
NW	0.08	WSW	0.06	NE	0.08
NW	0.07	WSW	0.10	NNE	0.03
NW	0.08	WNW	0.13	S	0.19
NW	0.08	WNW	0.16	E	0.11
NW	0.09	[NE	0.10]	E	0.07
N	0.14	N	0.05	NE	0.12
SW	0.08	N	0.06	NE	0.08
NW	0.07	NW	0.08	NE	0.08
NNW	0.18	SE	0.12	NE	0.08

APPENDIX 5 GLACIOLOGICAL AND GEOCHEMICAL CALCULATIONS FOR THE SALINE DISCHARGE, AND THE pH OF WATER IN EQUILIBRIUM WITH ATMOSPHERIC CARBON DIOXIDE

APPENDIX 5 GLACIOLOGICAL AND GEOCHEMICAL CALCULATIONS FOR THE SALINE DISCHARGE, AND THE pH OF WATER IN EQUILIBRIUM WITH ATMOSPHERIC CARBON DIOXIDE

A5.1 Basal pressures beneath Taylor Glacier

The total pressure P at the base of the glacier is a sum of the ice over-burden pressure P_{ov} and the basal sheer stress τ_b. The situation is shown in Figure A5.1.

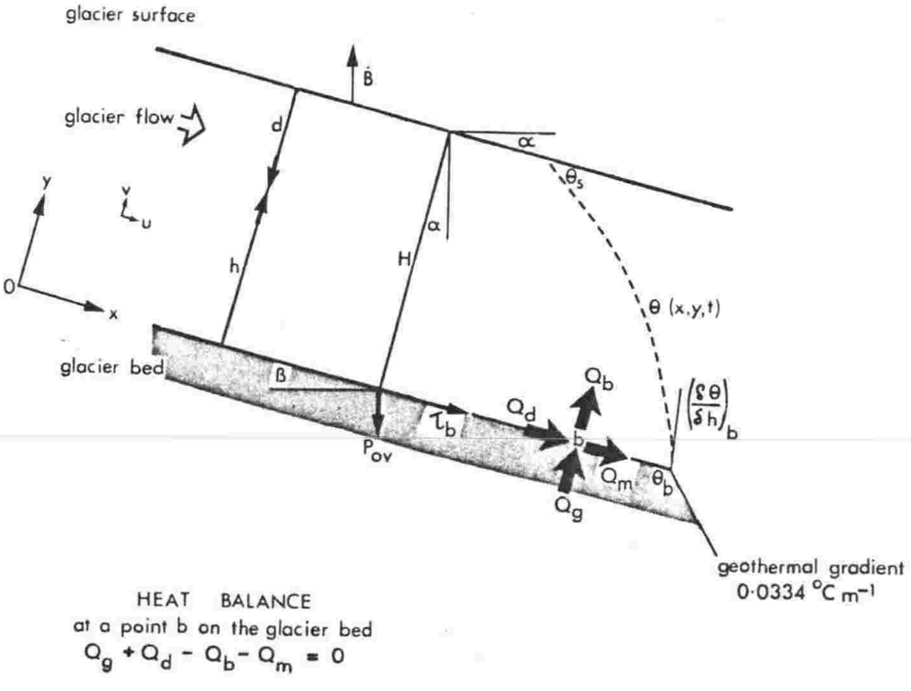

Figure A5.1 Laminar glacier flow down an inclined plane slope; idealised longitudinal section through part of Taylor Glacier showing quantities defined and used in the discussions in Appendix 5.1 and 5.5.

The overburden pressure is dependent on the weight of a column of ice H metres thick acting over a unit area of the glacier bed. For a unit cross-section area, the overburden pressure is:

$$P_{ov} = \frac{\rho.g.H}{\text{Cos}\alpha} \qquad \text{...A5.1}$$

where
ρ = ice density 9.0×10^2 kg m^{-3}
g = standard acceleration of gravity, 9.8 m s^{-2}
H = ice thickness perpendicular to bed
α = slope angle

One kilometre up-glacier from the terminal (at C line, Fig. 8.3A) H has a maximum value of 140-300 m (Stern 1978) and α is 3.8° (measured from USGS 1:50,000 map).
Inserting 300 m and 3.8° into Expression A5.1, we obtain:

$$P_{ov} = 2.7 \times 10^6 \text{ pascals (27 bars)}$$

It can be shown (eg. Andrews 1975) that the average shear stress, τ_b at the glacier bed, across a transverse section is given, to a useful approximation, by:

$$\tau_b = \rho g \frac{A}{P} \sin\alpha \doteqdot \rho g H \sin\alpha \qquad \text{...A5.2}$$

where
A = cross-section area of glacier, 2.3×10^5 m^2
(from Stern 1978)
P = ice contact perimeter, 1.3×10^3 m^2
(from Stern 1978)

A/P is the hydraulic radius and takes into account the average cross-sectional shape and frictional effects along the valley sides. Also, the hydraulic radius is approximately equal to the average ice thickness H which often appears in similar expressions for τ_b.
Using Expression A5.2 we obtain:

$$\tau_b = 1.0 \times 10^5 \text{ pascals}$$

Thus, the total maximum basal pressure beneath Taylor Glacier at C line is about 2.8×10^6 Pa. The range of maximum total pressures for H between 140-300 m is $(1.2\text{-}2.8) \times 10^6$ Pa.

A5.2 Distribution and activity coefficients of dissolved species in the spring brine, by the Garrels and Thompson method of calculation

The activities of dissolved species in concentrated aqueous solutions affect chemical reactions such as dissolution-precipitation equilibria. The activity of a particular species is a function of its concentration and its activity coefficient. Activity coefficients of species in the spring brine are obtained here by a method that calculates a distribution of the major ions in both the free and complexed forms (that is, bound up by ion-ion interactions) at +25°C and one atmosphere total pressure (Garrels and Thompson 1962; Polzer and Roberson 1967; Berner 1971; Nesbitt 1980).

Ion pairs are the only complexes that need to be considered but several can be neglected. No pairs involving OH^- or $CO_3{}^{2-}$ are likely at the pH (6) of the present system and $NO_3{}^-$ and H^+ are present in low concentration. Cl^-, $H_2CO_{3(aq)}$ and $CO_{2(aq)}$ are assumed to be uncomplexed. Thus, the pairs that need to be considered are those between Na^+, K^+, Mg^{2+}, Ca^{2+} and $SO_4{}^{2-}$, $HCO_3{}^-$; however, the association between K^+ and $HCO_3{}^-$ is weak and can be neglected (Garrels and Thompson 1962). The dissociation constants for these ion pairs are given by Garrels and Thompson.

The method of calculation uses analytical molalities, activity coefficients of individual ions, dissociation constants of ion pairs and mass balance relations. The total ionic strength I of the brine (sample 76/72) is 1.7 (Appendix 1, Table 15). Activity coefficients of individual ions in solutions of this ionic strength are determined from the literature as shown in Table A5.1.

Six mass balance equations and seven ion association equilibria can be written. The general ion pair dissociation equilibrium for the ion pair AB^{x-y} involving cation A^{x+} and B^{y-} is:

$$AB^{x-y}_{(aq)} \rightleftharpoons A^{x+}_{(aq)} + B^{y-}_{(aq)} \qquad \text{...A5.1}$$

The general form of the mass balance equations (eg. for B^{y-}) is:

$$m_{TB^{y-}} = m_{B^{y-}} + \Sigma m_{AB^{x-y}} \qquad \ldots A5.2$$

where $m_{TB^{y-}}$ is the total(analytical) molality of anion B (or cation A) given in Appendix 1, Table 15;

$m_{B^{y-}}$ is the molality of the free anion (or cation);

$\Sigma m_{AB^{x-y}}$ is the sum of the molalities of the ion pairs involving the anion (or cation)

Similarly, the general expression for the dissociation constant $K_{AB^{x-y}}$ of the ion pair is:

$$K_{AB^{x-y}} = \frac{\gamma_{A^{x+}} \cdot m_{A^{x+}} \cdot \gamma_{B^{y-}} \cdot m_{B^{y-}}}{\gamma_{AB^{x-y}} \cdot m_{AB^{x-y}}} \qquad \ldots A5.3$$

which, on rearranging gives:

$$m_{AB^{x-y}} = \frac{\gamma_{A^{x+}} \cdot m_{A^{x+}} \cdot \gamma_{B^{y-}} \cdot m_{B^{y-}}}{\gamma_{AB^{x-y}} . K_{AB^{x-y}}} \qquad \ldots A5.4$$

where $\gamma_{A^{x+}}$, $\gamma_{B^{y-}}$ are the individual activity coefficients of the free cation and anion (Table A5.1);

$\gamma_{AB^{x-y}}$ is the individual activity coefficient of the ion pair (Table A5.1).

The rigorous solution of the thirteen equations is tedious but may be simplified by approximation. The solution procedure is to (1) assume that the four major cations are uncomplexed (which is reasonable since they are mostly balanced with Cl^- which does not form ion pairs) and thus, (2) insert the analytical cation molalities into Equation A5.4 along with (3) values of γ from Table A5.1 and $K_{AB^{x-y}}$ from Garrels and Thomson (1962); (4) substitute into Equation A5.2 which then has only one unknown, $m_{B^{y-}}$; (5) insert the solution for $m_{B^{y-}}$ into Equation A5.4 to obtain $m_{A^{x+}}$; and (6) iterate (twice) to obtain constant results. The only significant corrections to the original assumption are for Mg^{2+} and Ca^{2+} which are modified by the presence of SO_4^{2-} and HCO_3^-.

Table A5.1 Species assumed to be present in the spring brine (sample 76/72), and the individual ion and ion pair activity coefficients for solutions of total ionic strength 1.7 at +25°C and -5°C.

Species	Individual activity coefficients (γ)		Method of determination and source of data	
	+25°C	-5°C		
Na^+	0.76	0.69	*, $\gamma^2_{\pm\,NaCl} / \gamma_{\pm\,KCl}$	mean activity coefficients $\gamma_\pm$ from data in Harned and Owen (1958); $\gamma_{Ca^{2+}}$ temperature dependence from Berner (1965)
K^+	0.58	0.55	*, $\gamma_{\pm\,KCl}$	
Mg^{2+}	0.34	-	*, $\gamma^3_{\pm\,MgCl_2} / \gamma^2_{\pm\,KCl}$	
Ca^{2+}	0.29	0.29	*, $\gamma^3_{\pm\,CaCl_2} / \gamma^2_{\pm\,KCl}$	
Cl^-	0.58	0.55	*, $\gamma_{\pm\,KCl}$	
SO_4^{2-}	0.065	-	interpolation of the values of $\gamma_{SO_4^{2-}}$ in Garrels and Thompson (1962) and Polzer and Roberson (1967)	
HCO_3^-	0.63	0.62	γ of free HCO_3^- in an aqueous K/Cl/HCO_3/CO_3 solution at I=1.7, interpolated from Walker et al (1927); temperature dependence from Berner (1965)	
$NaSO_4^-$	0.63	-	from HCO_3^-, as assumed by Garrels and Thompson	
KSO_4^-	0.63	-	" " " " " " "	
$MgHCO_3^+$	0.63	-	" " " " " " "	
$CaHCO_3^+$	0.63	-	" " " " " " "	
H_2CO_3, CO_2	1.5	-	γ of CO_2 and H_2CO_3 dissolved in 1.7 m NaCl solution; interpolated from Walker et al. and Helgeson (1969)	
$NaHCO_3$	1.5	-	from H_2CO_3, as assumed by Garrels and Thompson	
$CaSO_4$	1.5	-	" " " " " " "	
$MgSO_4$	1.5	-	" " " " " " "	

---

* Garrels and Thompson (1962): determined from mean activity coefficients $\gamma_\pm$ for the pure chloride solutions at an ionic strength I of 1.7; equalities are determined by the assumptions of the mean salt method and the equation for $\gamma_\pm$ for a salt A_nB_m that completely dissociates into n cations and m anions

$$\text{ie} \quad \gamma_\pm = \left[\gamma_+^n \cdot \gamma_-^m\right]^{1/n+m} \quad ; \quad \text{eg} \quad \gamma_+ = \left[\gamma_\pm^{n+m} / \gamma_-^m\right]^{1/n}$$

The distribution of species in the spring brine is shown in Table A5.2. This model for the brine is similar to that of Garrels and Thompson (1962) for sea water. However, the percentage of free HCO_3^- is considerably less in the spring brine due mainly to the relatively high concentrations of Ca^{2+} and Mg^{2+} in that brine, with different individual activity coefficients having less effect. The model is likely to be a useful representation of species in the spring brine, because the same approach was successfully used for a more concentrated brine in which the total ionic strength was 6 (Polzer and Roberson 1967). The effective removal of some charged species as a result of complexing means that the effective ionic strength is close to 1.6 compared with the value of 1.7 used. This small difference, just outside analytical error,

Table A5.2 Chemical model of spring brine showing distribution of major dissolved species in sample 76/72 at +25°C at 1 atmosphere total pressure.

Ion A	Total molality m_T	Molality of free ion m		Percent free ion		Percent ASO_4 pair	Percent $AHCO_3$ pair	Total % A complexed
Na^+	1.11	1.09		98.6		1.0	0.4	1.4
K^+	0.0141	0.0139		98.7		1.3	-	1.3
Mg^{2+}	0.14	0.12		83.2		6.8	10.0	16.8
Ca^{2+}	0.050	0.042		84.0		5.2	10.8	16.0
Ion B	m_T	m	Percent free ion	Percent NaB pair	Percent KB pair	Percent MgB pair	Percent CaB pair	Total % B complexed
SO_4^{2-}	0.0480	0.0243	50.5	23.1	0.4	20.5	5.5	49.5
HCO_3^-	0.050	0.025	49.8	9.9	-	29.3	11.0	50.2
Cl^-	1.30	1.30	100	-	-	-	-	-

results in an insignificant difference of one percent in the activity coefficient of Mg^{2+} (the most seriously affected ion).

The total activity coefficients are calculated from the distribution of species as the free ion. The activity a of a species i is given by:

$$a_i = \gamma_i m_i = \gamma_{Ti} . m_{Ti} \qquad \text{...A5.5}$$

or:

$$\gamma_{Ti} = \frac{\gamma_i m_i}{m_{Ti}} \qquad \text{...A5.6}$$

where γ_{Ti} is the total (analytical) activity coefficient of species i. γ_T are tabulated in Table 8.4, using (1) Equation A5.6, (2) γ in Table A5.1, (3) m in Table A5.2 and (4) m_T in Appendix 1, Table 15.

It is difficult to precisely apply the procedure to subzero temperatures. Insufficient data are available to precisely determine all the individual activity coefficients or dissociation constants of the ion pairs at temperatures of -5 to -6°C. Here, the values at +25°C are used, except for some individual ion activities (Table A5.1). In fact, activity coefficients vary little with temperature over the +25 to -6°C range and this variation produces only small changes in the m values calculated. Therefore, the activity coefficient of SO_4^{2-} in particular, given in Table A5.1, can be applied satisfactorily at both +25°C and the in situ temperature. All the individual activity coefficients at -5°C are applied to Equation A5.6 above, to produce total activity coefficients given in Table 8.4.

A5.3 Equilibrium constants for $CaCO_3$ dissolution

The calcite dissolution equilibrium is:

$$CaCO_{3(s)} + CO_{2(g)} + H_2O \rightleftharpoons Ca^{2+}_{(aq)} + 2HCO_3{}^-_{(aq)} \qquad \text{...8.6(6.8)}$$

which is composed of four more simple equilibria:

$CO_{2(g)} + H_2O \rightleftharpoons H_2CO_3^*$ equilibrium constant K_1 ...A5.7

$H_2CO_3^* \rightleftharpoons H^+_{(aq)} + HCO_3^-{}_{(aq)}$ " " K_2 ...A5.8

$H^+_{(aq)} + CO_3^{2-}{}_{(aq)} \rightleftharpoons HCO_3^-{}_{(aq)}$ " " K_3 ...A5.9

$CaCO_{3(s)} \rightleftharpoons Ca^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)}$ " " K_4 ...A5.10

The equilibrium constant K_c for Reaction 8.6 is given by:

$$K_c = K_1.K_2.K_3.K_4 \qquad ...A5.11$$

and is temperature dependent since Equilibria A5.7-10 are also temperature dependent. The slight pressure and solute dependence of K_c are neglected here as a first approximation.

The values of K_i in aqueous solutions at -5°C are determined from the literature. K_1 is calculated (Table A5.3) from the solubility of CO_2 in water using the expression for K_1 from Equilibrium A5.7:

$$K_1 = \frac{a_{H_2CO_3^*}}{a_{CO_2}.a_{H_2O}}$$

which simplifies to:

$$K_1 = \frac{m_{TH_2CO_3^*}}{P_{CO_2}} \quad (a_{H_2O} \doteqdot 1) \qquad ...A5.12$$

(where P_{CO_2} is the partial pressure of CO_2 in equilibrium with the solution) because the activity coefficients of neutral species $H_2CO_3^*$ and CO_2 are assumed to be equal (Garrels and Thompson 1962). Values of log K_i are illustrated on Figure A5.2 except for K_3 which is given as log $1/K_3$, for convenience.

The value for K_c at -5°C is obtained from K_i at -5°C on Fig. A5.2 and Equation A5.11, and is equal to 5.4×10^{-6}.

---

*undifferentiated between $CO_{2(aq)}$ and $H_2CO_{3(aq)}$, that is the equilibrium $CO_{2(aq)} + H_2O \rightleftharpoons H_2CO_{3(aq)}$ can be disregarded as long as $H_2CO_3^*$ is considered consistently (Krauskopf 1967).

Table A5.3 Calculation of the equilibrium constant K_1 for the equilibrium $CO_{2(g)} + H_2O \rightleftharpoons H_2CO_3^*$ at 1.013 bars (one atmosphere) total pressure by Equation A5.12.

Temperature	Solubility of CO_2 (1) (g kg^{-1})	Moles of $H_2CO_3^*$ in solution (m_T)	Vapour pressure (2) of 'water' (bars)	Partial pressure of CO_2 (bars)	K_1
+25	1.5	0.034	0.032	0.98	0.035
0	3.4	0.077	0.0061	1.01	0.076
-5	4.1	0.093	0.0042	1.01	0.092

---

* undifferentiated

(1) Aylward and Findlay (1967); value at -5°C obtained by extrapolation

(2) Weast (1971)

A5.4 pH of water in equilibrium with atmospheric carbon dioxide

The pH of dilute solutions in equilibrium with aqueous carbon dioxide is governed by:

$$CO_{2(g)} + H_2O \rightleftharpoons H^+_{(aq)} + HCO^-_{3(aq)} \qquad \text{...A5.13}$$

and the equilibrium constant K is given by:

$$K = K_1.K_2 = \frac{m_{H^+} \cdot m_{HCO_3^-}}{P_{CO_2}} \qquad \text{...A5.14}$$

(cf Equilibria A5.7, A5.8) since $\gamma_i = a_{H_2O} = 1$ for dilute solutions.

For a weak acid such as H_2CO_3:

$$m_{H^+} \doteqdot m_{HCO_3^-} \qquad \text{(Krauskopf 1967)}$$

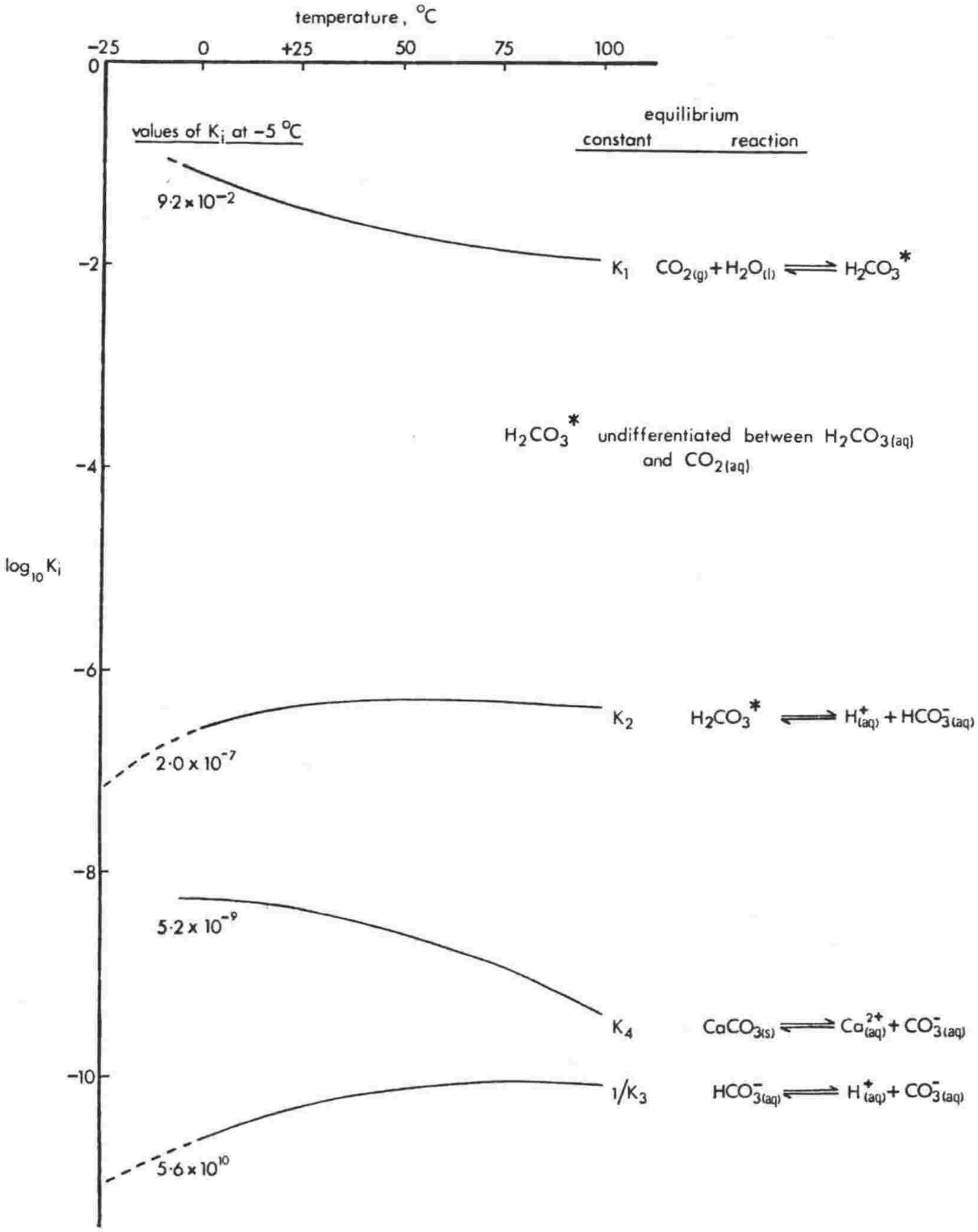

Figure A5.2 Logarithms of constants K_i for subequilibria of calcite dissolution equilibrium, from -25°C to +100°C (dashed lines represent extrapolations). Values from +25 to +100°C from Helgeson (1969) and below +25°C from: Table A5.3 for K_1; Weast (1971), K_2; Harned and Owen (1958), K_3; and Berner (1965), K_4.

and A5.14 becomes

$$m_{H^+} = (K_1.K_2.P_{CO_2})^{\frac{1}{2}} \text{ or } pH = -0.5 \log (K_1.K_2.P_{CO_2}) \qquad \ldots A5.15$$

Table A5.4 lists K_1, K_2 and solutions of Equation A5.15 for dilute solutions in equilibrium with the atmosphere at +25 and 0°C.

Table A5.4 Solutions of Equation A5.15, being the pH of dilute solutions in equilibrium with atmospheric carbon dioxide (P_{CO_2} = 3.3 x 10^{-4} bars). K_i data from Table A5.3 and Fig. A5.2.

Temperature °C	K_1	K_2	pH
+25	$3.5\text{x}10^{-2}$	$4.4(7)\text{x}10^{-7}$	5.6(4)
0	$7.6\text{x}10^{-2}$	$2.0(0)\text{x}10^{-7}$	5.6(5)

A5.5 Calculation of basal temperature gradients in Taylor Glacier

The general equation describing heat transfer in a moving medium is:

$$\frac{\delta\theta}{\delta t} = k_i \frac{\delta^2\theta}{\delta y^2} - u\frac{\delta\theta}{\delta x} - v\frac{\delta\theta}{\delta y} + Q_d \qquad \ldots A5.16$$

where θ = temperature

t = time

u = horizontal velocity in the x direction (positive down-glacier)

v = vertical velocity in the y direction (positive upwards)

k_i = thermal diffusivity of ice (41.6 m^2 a^{-1} at Taylor Glacier, Robinson 1979)

Q_d = heat generated by internal deformation assuming frictional heating at the bed and sides of the glacier is negligible.

The situation is shown in Figure A5.1. Simplifications can be made and Equation A5.16 reduces to (Robinson 1979):

$$\theta_s - \theta_h = \left(\frac{\delta\theta}{\delta h}\right)_b \cdot \sqrt{\frac{2k_i H}{\dot{B}}} \cdot \left[F\left(\sqrt{\frac{\dot{B}H}{2k_i}}\right) . e^{\dot{B}H/2k_i} - F\left(h \sqrt{\frac{\dot{B}}{2k_i H}}\right) . \; e^{\dot{B}h^2/2k_i H} \right] \qquad \text{...A5.17}$$

where θ_s = surface temperature (-17°C, Appendix 3, Table 8)
θ_b = basal temperature (-5.5°C, 8.4.3)
$\dot{B}$ = ablation rate which is the approximate vertical velocity of the ice (0.39 m a^{-1} at C line, Robinson 1979).
$F(x)$ = Dawson's integral

The last term in Equation A5.17 vanishes at the base (h=0). The basal temperature gradient $(\frac{\delta\theta}{\delta h})_b$ is determined from the Equation and solutions are given in Table 8.7.

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