Antarctic Science 18 (4), 515–524 (2006) © Antarctic Science Ltd Printed in the UK DOI: 10.1017/S0954102006000563

PChemistry and stratification of Antarctic meltwater ponds I: Coastal ponds near Bratina Island, McMurdo Ice Shelf

B.R. WAIT[1], J.G. WEBSTER-BROWN[2]*, K.L. BROWN[3], M. HEALY[3] and I. HAWES[4]

[1]*Gateway Antarctica, University of Canterbury, Private Bag 4800, Christchurch, New Zealand*
[2]*SGES, University of Auckland, Private Bag 92019, Auckland, New Zealand*
[3]*Department of Geology, University of Auckland, Private Bag 92019, Auckland, New Zealand*
[4]*National Institute of Water and Atmospheric Research, PO Box 8602, Christchurch, New Zealand*
** Corresponding author: j.webster@auckland.ac.nz*

Abstract: The geochemistry and vertical stratification of shallow meltwater ponds at 78°S near Bratina Island (McMurdo Ice Shelf) have been determined for late winter (October) and summer (January) conditions as part of the Latitudinal Gradient Project. Of the five frozen ponds investigated in October, all were stratified with respect to conductivity, and three had highly saline basal brines beneath the ice at temperatures of -16 to -20°C. In the ice column, inclusions of saline fluid were observed in channels between ice crystals; the abundance increasing with depth and decreasing ice crystal size. In January, seven of the ten ponds investigated (including ponds sampled in October) retained conductivity stratification, whereas significant thermal stratification was observed in only three ponds (maximum $\Delta T = 5.5°C$). Basal brines, ice and meltwaters were Na-Cl or Na-SO_4 dominated. FREZCHEM52 modelling, supported by changes in ion ratios, indicated that the precipitation of mirabilite ($Na_2SO_4.10H_2O$) and gypsum ($CaSO_4.2H_2O$) during progressive freezing is an important determinant in chemical evolution of the basal brine. High pH (8.8–11.2) and over-saturation with respect to dissolved oxygen (> 20 mg L^{-1}) in summer, and the presence of sulphide ions in basal brines in winter, occurred in those ponds which experienced high biological productivity during the summer months.

Received 14 December 2005, accepted 12 June 2006

Key words: freeze concentration, FREZCHEM52, geochemistry, ice, Latitudinal Gradient Project, salt exclusion

Introduction

The area near Bratina Island on the McMurdo Ice Shelf is described as a polar desert, characterized by low temperatures, little precipitation and humidity close to zero. It has also been referred to as Antarctica's largest wetland because the area of the ice shelf around Bratina Island melts out for a few months each summer to form a dynamic network of ponds and streams dominated by cyanobacterial mat communities (Hawes *et al*. 1997). The undulating surface of the ice-cored moraine has allowed numerous small meltwater ponds with depths of < 1 m to 4 m to form with a range of salinities and ionic compositions (de Mora *et al*. 1994), making this an ideal site for the study of chemical and biological processes in Antarctic meltwater systems.

The major source of dissolved salts in Antarctica's coastal regions is marine-derived aerosols (Campbell & Claridge 1987). Ionic ratios in coastal snowfall resemble those of seawater; evidence of the presence of marine aerosols. This, together with aeolian transport, provides a pathway for marine-derived salts to reach coastal meltwater systems (Whitehead 1989). In meltwaters, major ion concentrations can further increase as a result of freeze concentration, ice ablation and/or summer evaporation and, where ponds are located on the ice shelf, the intrusion of seawater through tide cracks or from seawater trapped in the ice shelf (de Mora *et al.* 1994). Freeze concentration involves the exclusion of dissolved ions from ice into the residual water phase, progressively forming a more concentrated brine with a depressed freezing point. Even minor variation in the initial chemistry of pond water can result in major differences in the composition of brines formed by evaporation and freezing (e.g. Green *et al.* 1988).

It is not uncommon for meltwater ponds to be stratified into a fresh upper layer and a more saline lower layer, or to demonstrate a degree of thermal stratification (e.g. Schmidt *et al*. 1991, Webster *et al*. 1994, Hawes *et al*. 1997). It is postulated that stratification arises as a result of dense, saline residual brines, formed during winter freezing, remaining at the base of the pond during the thaw. Ponds are recharged in summer when the pond ice and snow that has accumulated within the pond catchment over winter, melts out. This recharge is more dilute (less dense) than the residual brine and floats on top of the brine unless the ponds are subjected to physical mixing.

Although such stratified ponds have occasionally been reported from the McMurdo Ice Shelf and Dry Valley region, there is little known of the geochemistry of these ponds. Meltwater pond samples are generally collected from the surface or edge of the water bodies (e.g. Whitehead 1989, Webster *et al.* 1994, Timperley 1997) and do not represent whole pond or basal brine conditions. Consequently the chemical conditions experienced by the cyanobacterial mat communities growing at the base of these ponds and, in particular, the chemical extremes they must tolerate during winter in the residual brine at the base of the ponds, remain almost completely unknown. Brine chemistry is difficult to predict because the unusual water chemistry and thermal gradients displayed in many Antarctic ponds are difficult to reconcile with the results of freezing experiments undertaken using more temperate freshwaters or seawater environments (e.g. Thompson & Nelson 1956, Marion *et al.* 1999).

The purpose of this study was therefore to determine the winter and summer geochemistry of Bratina Island ponds, to quantify the degree of vertical stratification and to identify the major processes controlling the chemical composition. The test hypothesis was that pond stratification and basal brine chemistry are principally due to freeze concentration of the pond water over winter. The research has been undertaken as part of the Latitudinal Gradient Project (LGP), and constitutes a definition of pond geochemical processes in mid-latitude (77–78°) coastal regions. Results are compared with those from ponds in inland regions at the same latitude in Healy *et al.* (2006) and will ultimately also be compared with those from higher and lower latitudes in Victoria Land (Howard-Williams *et al.* 2006).

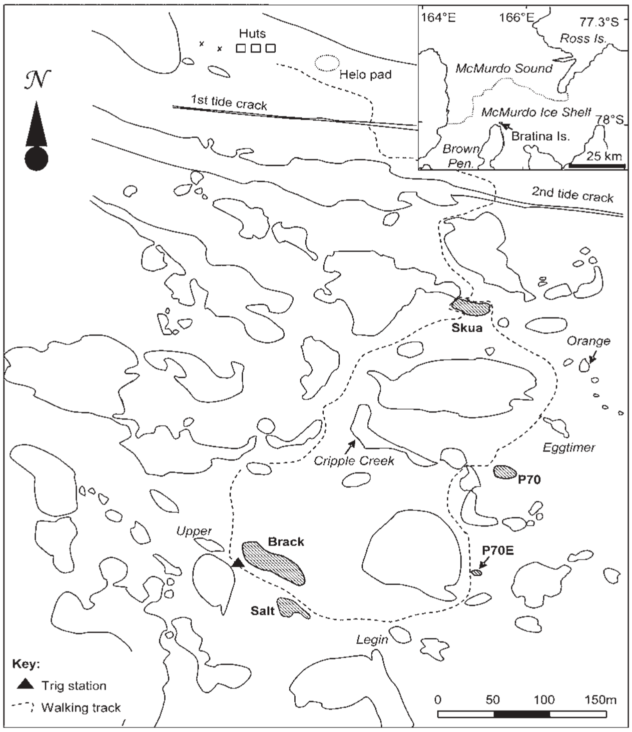

Fig. 1. Locality map for Bratina Island (inset) and the five meltwater ponds used in this study (shaded). In summer, additional conductivity and temperature profiles were measured on a further five ponds identified by name, but not shaded.

Sampling techniques and analytical methods

Field sampling

Field sampling was undertaken in the 2001/2002 field season, in late October (late winter) when the ponds were predominantly frozen and in January (mid summer) when the meltwater ponds were fully melted. It was not feasible to visit the site earlier than October in order to sample more typical winter conditions. The location of Bratina Island and the ten ponds sampled in this study are shown in Fig. 1. In October, five ponds were sampled. After locating the pond under the snow cover, the centre of each frozen pond was drilled with a "Covax" drill to estimate pond depth and then a SIPRE ice auger was used to retrieve an ice core. The core was sectioned at 10 cm or 20 cm depth intervals and then melted into 500 ml HDPE bottles. Basal brines were found in three of the five ponds; Skua, P70E and Brack Pond. These brines were sampled using a hand vacuum pump and plastic tubing. The pH and conductivity of the basal brines and melted ice were measured using portable meters as soon as practicable. Dissolved oxygen was not measured, as it would be meaningless on the melted ice samples, and the probe would not function reliably at the low temperatures of the basal brines. An additional core was collected from Skua Pond and kept frozen for thick and thin ice section analysis. Salt precipitates from the base of Brack and Salt ponds, from the salt dome adjacent to Salt Pond, and from the margin of Salt Pond were collected and sealed in airtight plastic sediment containers for mineral identification. Those collected from the ice in Brack and Salt ponds were dried in an oven at 105°C before analysis.

In January, samples were collected from the same suite of five ponds (now fully melted). Water samples (500 ml) were taken at 10 cm depth intervals, beginning at the surface to avoid excessive mixing of the water column, using a hand vacuum pump, plastic hosing and a 'fishing pole' designed to reach the deepest part of each pond. Dissolved oxygen, pH, temperature, and conductivity were measured *in situ* using portable meters. Additional 50 ml water samples were taken at the top, middle and bottom of each pond for HCO_3 analysis. Conductivity and temperature profiles were measured in a further five ponds using a TPS TC90 temperature/conductivity meter.

Laboratory analysis

Major ion concentrations (Na, K, Mg, Ca, SO_4 and Cl) in the melted ice and meltwater samples were measured using

High Pressure Ion Chromatography (HPIC), with a Dionex IonPac CS12 (10–32) 4 mm chromatography column and a 20 mM methanesulphonic acid eluent for cations, and an AS11 4 mm chromatography column and 10 mM NaOH eluent for anions. Bicarbonate ion concentrations were determined by titration against standardized HCl, with a back titration against NaOH (stored under N_2) to eliminate interference by other ions that may contribute to alkalinity. Bicarbonate concentrations were not determined on melted ice samples, as re-equilibration with atmospheric CO_2 would have altered the initial concentration.

The degree of dilution required for analysis ranged from no dilution (for surface ice melt from Skua Pond for example) to 1:2200 (for Skua Pond basal brine). High dilution can introduce a significant error, and as a quality control measure selected samples with high Cl concentrations (> 100 000 mg kg^{-1}) were also analysed for Cl using a Mohr titration (titration of an undiluted sample against a standardized $AgNO_3$ solution). Good agreement was observed, which is consistent with the previous observation that dilutions of up to 1:6000 have yielded reliable HPIC analytical results (standard deviations < 1%) for meltwater samples taken from the McMurdo Dry Valleys (Welch *et al*. 1996). In those samples for which complete analyses (i.e. including HCO_3) could be obtained, the ion balances were consistently < 10%. The limits for detection were Na: 0.16 mg kg^{-1}, K: 0.21 mg kg^{-1}, Mg: 0.17 mg kg^{-1}, Ca: 0.14 mg kg^{-1}, Cl: 0.32 mg kg^{-1}, HCO_3: 1mg kg^{-1} and SO_4: 0.18 mg kg^{-1}. Concentrations were analysed as mg kg^{-1} (instead of the more usual mg L^{-1}) to allow for comparison of fluids of different density. For all except the winter basal brines, however, this is approximately equal to mg L^{-1}. Precipitates were analysed by X-Ray Diffraction (XRD).

Ice sections

Ice section preparation from the Skua Pond ice core was undertaken in a freezer at -20°C. Thick sections of > 5 mm were cut using a band saw and were planed on one side with 40 grit abrasive paper. The planar side of the thick section was then applied to a heated glass side, and frozen to the slide with a rim of water applied to the edge of the thick section with a pipette. Photographs of the thick sections were taken to identify large scale features in the ice, then the thick sections were then placed in a Leica Sectioning Microtome, levelled, and shaved to a thickness of 2 mm in increments of 40 µm, and then to 1 mm in increments of 10 µm. The resulting "thin section" was photographed under crossed polarizers on a universal stage to identify individual ice crystals and brine inclusions.

Geochemical modelling

The equilibrium chemical thermodynamic model FREZCHEM52 (Marion & Grant 1994), based on the Spencer-Møller-Weare chemical-thermodynamic model for aqueous solutions at subzero temperatures (Spencer *et al*. 1990), was used to model progressive freezing, chemical fractionation, and equilibrium precipitation of salts in Bratina Island meltwaters. FREZCHEM52 models aqueous solutions with high ionic strengths (i.e. up to 20M) using

Table I. Water chemistry at the top and base of the ice or water column for five ponds near Bratina Island, in October (bold italics) and in January. Concentrations are in mg kg^{-1} unless otherwise noted. - indicates that the measurement was not made and < dl indicates values below the limits of detection.

Pond	Depth (cm)	Temp (°C)	pH	Cond	dO_2 (mS cm^{-1})	Na (mg L^{-1})	K	Mg	Ca	Cl	SO_4	HCO_3
Skua	***0–10***	***ice***	***5.26***	***0.004***	***-***	***1.26***	***<dl***	***<dl***	***<dl***	***1.48***	***0.3***	***-***
	150	***-18***	***7.47***	***111***	___-*___	***72500***	***3810***	***1850***	***3.19***	***112000***	***1310***	***9570***
	10	3.9	9.22	1.27	13.1	224	11.2	9.1	12.9	143	224	85.3
	105	4.3	9.59	1.28	12.8	226	8.1	9.5	13.5	134	241	63
P70E	***0–10***	***ice***	***5.69***	***0.061***	***-***	***2.51***	***<dl***	***<dl***	***<dl***	***17.0***	***4.32***	***-***
	80	***-20***	***6.11***	***112***	***-***	***55900***	***1680***	***7890***	***7520***	***135000***	***1880***	***488***
	10	6.5	8.8	7.36	13.5	1050	39.6	237	168	2340	161	130
	100	8.5	9.13	22.6	>20	4250	118	997	892	11500	738	37.3
Brack	***0–10***	***ice***	***6.58***	***9***	***-***	***2400***	***41***	***104***	***91.2***	***798***	***4350***	***-***
	70	***-16***	***6.85***	***101***	___-*___	***54100***	***5550***	***7730***	***3840***	***110000***	***3640***	***899***
	10	0.9	9.65	18	15.91	5080	96	202	173	1930	9120	147
	80	2.5	9.79	17.6	16.3	5080	95	209	177	1850	9060	219
P70	***0–10***	***ice***	***6.83***	***0.326***	***-***	***47.8***	***1.24***	***3.52***	***1.12***	***81.2***	***12.9***	***-***
	60–70	***ice***	***6.82***	***15.6***	***-***	***4100***	***128***	***562***	***42.5***	***6440***	***1370***	***-***
	10	3.3	9.6	5.59	17.3	807	33.1	114	34.5	1530	256	167
	100	4.4	9.85	11.42	>20	2160	75.1	341	110	3660	686	177
Salt	***0–10***	***ice***	***6.95***	***41.3***	***-***	***13900***	***207***	***484***	***51.7***	***6730***	***20800***	***-***
	20–30	***ice***	***6.65***	***49.4***	___-*___	***14300***	***520***	***1030***	***111***	***16800***	***12000***	***-***
	10	5.9	10.9	52.2	>20	17100	273	354	248	4480	29500	207
	50	7	11.2	56.0	>20	18700	267	283	210	5210	33900	203

*H_2S detected in sample.

Pitzer equations to calculate activity coefficients and the activity of the water, and can be used over a temperature range of 25°C to -60°C making it particularly useful in polar geochemistry. The database has 50 solid phases including ice and naturally occurring major ion salts, and the input data required includes Na, K, Ca, Mg, Cl and SO_4 concentrations for the initial fluid, as well as pH, carbonate alkalinity (in this study input as HCO_3) and atmospheric CO_2 (0.00035 mg kg^{-1}, Longinelli *et al.* 2001). In this study the composition of an initial mixed pond chemistry was determined for summer stratified ponds by recalculating a "bulk" pond chemistry using the major ion concentrations and volumes of specific layers in the pond. The initial and final temperature, and required temperature decrement in Kelvin units must also be selected.

Results

Physiochemical parameters and major ion analyses, for the surface water/ice and deepest samples taken from each of the study ponds are shown in Table I. More detailed information for individual parameters and ion concentrations in selected ponds are shown in Figs 2, 4 & 5.

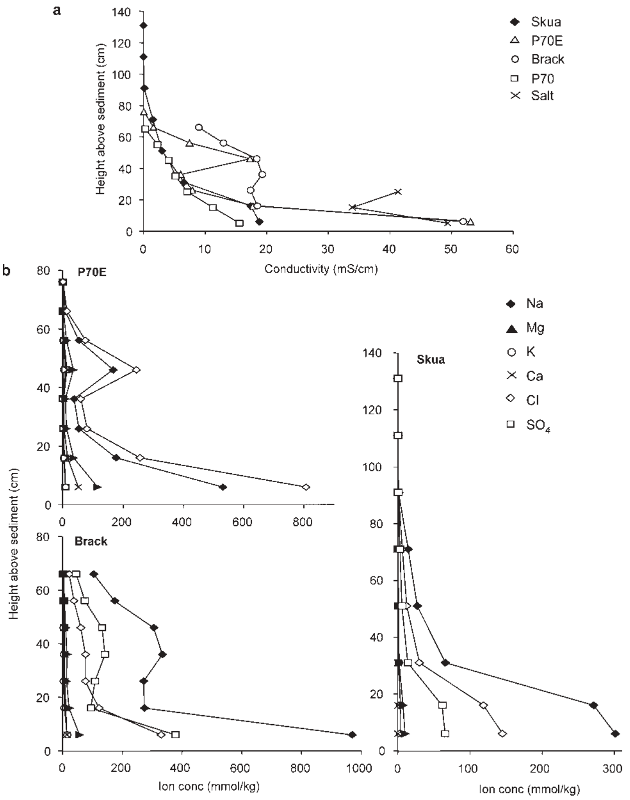

Fig. 2. October (late winter) results; **a.** Conductivity as a function of depth in the five frozen ponds, and **b.** major ion concentrations in the ice columns of P70E, Brack and Skua Pond. Depth is plotted as height above the base of the pond to normalize the trends in ponds of different depths.

The full dataset from this study includes conductivity and temperature profiles for all ten ponds featured in Fig. 1, and major ion profiles for all five study ponds in winter and summer, and can be made available on request. Note that, in all cases, nitrate (NO_3) concentrations were below detectable levels by HPIC (< 0.1 mg kg^{-1}). Previous analyses of NO_3 in Bratina Island ponds have reported concentrations in the surface waters of < 0.01 mg L^{-1} (e.g. Howard-Williams *et al.* 1989).

Late winter ice geochemistry

Chemical stratification was evident in the frozen water column of all five ponds in October, with ice conductivities ranging from 0.004 mS cm^{-1} to 49.4 mS cm^{-1}, and increasing with depth in each pond (Table I, Fig. 2a). This indicates that brine is incorporated into the ice while it is

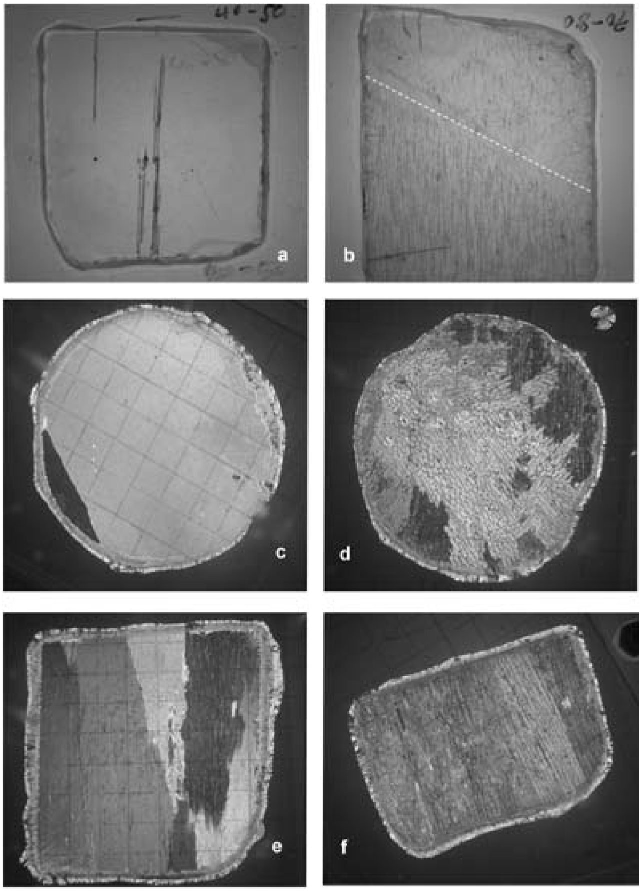

Fig. 3. Micrographs of Skua Pond ice core; **a.** longitudinal thick section from 30–40 cm depth, **b.** longitudinal thick section from 70–80 cm depth (showing transition between discontinuous and continuous brine phases), **c.** cross-sectional thin section from 70 cm depth, **d.** cross-sectional thin section from 150 cm depth, **e.** longitudinal thin section from 120–130 cm depth, and **f.** longitudinal thin section from 140–150 cm depth. Micrographs a and b are shown under transmitted light and the rest under crossed polarized light.

forming, rather than salts being completely excluded as might be expected. High brine content corresponded to a yellowing of the ice, clearly visible in the ice core, and in contrast to the near-surface ice which was glass-like and colourless. The pH ranged from 5.26 to 8.42 in the melted ice core, and major ion concentrations generally reflected the conductivity profile, particularly for the most abundant ions; Cl, Na and SO_4 (Table I, Fig. 2b). The ice columns in Brack and Salt Pond were Na-SO_4 dominated, while Skua, P70, P70E were Na-Cl dominated, although SO_4 remained high in Skua Pond ice (Fig. 2b). In Skua and Brack ponds, basal brine SO_4 concentrations were less than those of the overlying ice, suggesting that SO_4 had been removed either by precipitation of SO_4-bearing salt (discussed below) or by reduction of SO_4 to H_2S (which was noted to be present in both of these ponds). The concentrations of Ca, Mg and K were consistently lower than that of Na.

When longitudinal and cross-sectional thick sections of Skua Pond ice core were observed under transmitted and polarized light, the ice became structurally more complex with increasing depth. In the upper ice layers brine features were sparse (Fig. 3a), whereas below 70 cm depth distinct brine features, in the form of well distributed, horizontally discontinuous linear vertical channels, were present (Fig. 3b). The ice became a horizontally discontinuous phase and the brine features became a continuous phase, as the latter coalesced from a network of fine individual channels into clustered thicker features.

Individual ice crystals could be distinguished in the thin sections when viewed under crossed polarized light, and showed decreasing crystal size with increasing depth in the ice core (contrast Fig. 3c & d). At the base of Skua Pond (140–150 cm), the ice had a honeycomb texture when viewed in cross-section, with < 1 to 5 mm semi-hexagonal and discrete ice crystals separated by opaque or poorly translucent brine features (Fig. 3d). The brine features had a uniform orientation within individual ice crystals, but varied between crystals. In longitudinal section, crystals were columnar with clearly defined, linear edges in the top 130 cm of ice core (Fig. 3e). At > 130 cm depth, the columnar crystals disappeared and boundaries became irregular as the high density of brine inclusions obscured the crystals boundaries, although domains with the same crystal orientation were still readily identified under crossed polarized light (Fig. 3f). As it remained unclear whether such domains are single crystals with internal networked brine inclusions, or groups of aligned ice crystals with brine pockets between them, it is uncertain whether brine features are intracrystalline or intercrystalline in nature.

Late winter fluid geochemistry

Fluid basal brines with conductivities of 101–112 mS cm^{-1} were found beneath the ice column in three of the five ponds sampled; Skua, P70E and Brack Pond. The brines had temperatures between -16°C and -20°C, similar to the air temperature at the time of sampling. The pH ranged 6.11 to 7.47 and in Skua Pond the brine was highly viscous, a dark yellow colour and smelled strongly of H_2S indicating highly reducing redox conditions. The volume of basal brine present in Brack Pond was less, but also smelled of H_2S and was slightly discoloured, and contained suspended salt crystals at the time of sampling. The brine in P70E Pond was colourless, and did not smell of H_2S. Although no basal brine was present in Salt Pond, the ice again smelled of H_2S and was unusually textured with coarse salt crystals, as might be formed in the final stage of salt precipitation from a supersaturated brine entrained in the ice The brines sampled were predominantly of Na-Cl composition (Table I). After Na and Cl, the next most abundant cation or anion varied between the three brines, with Ca and HCO_3 concentrations showing the greatest degree of variability.

Summer fluid geochemistry

Conductivities in the five meltwater ponds during summer were lower than those measured in the ice in winter, but the summer pH values were considerably higher. Conductivity ranged from 1.27 mS cm^{-1} (surface water) to 56.0 mS cm^{-1} (basal water) and pH ranged from 8.8 to 11.2 (Table I). Two of the five study ponds showed conductivity stratification with depth (Fig. 4a); P70 and P70E. An additional five ponds sampled in summer (Cripple Creek, Orange, Eggtimer, Upper and Legin Ponds) also showed

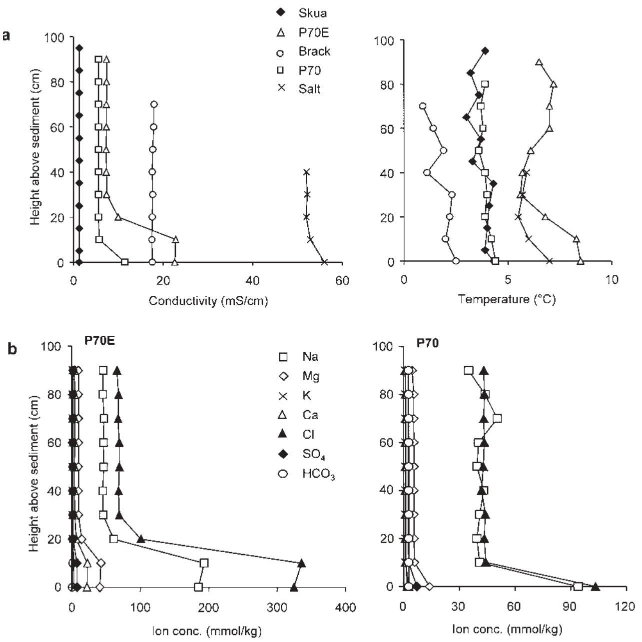

Fig. 4. January (summer) results for fully melted ponds; **a.** Conductivity as a function of depth in the five study ponds, and **b.** major ion concentrations in the stratified ponds; P70 and P70E.

stratification with respect to conductivity, but these ponds were pre-selected as likely to show stratification on the basis of visual characteristics, such as colour change in the cyanobacterial mat or water column with depth. Notably, all of the stratified ponds were increasingly green coloured at their deepest point, which may be due to the high concentrations of major ions affecting the refraction of light (e.g. Pridmore *et al.* 1995). In all stratified ponds, conductivity remained constant in the upper part of the water column, but increases significantly in the deepest 5–20 cm of the pond. The maximum conductivity increase (4.6x) was observed in Upper Pond, where 10 mS cm^{-1} in the upper water column increased to 46.5 mS cm^{-1} 10 cm above the base of the pond.

In the stratified study ponds the concentration of all ions except HCO_3 increased in the lowest 10 cm or 20 cm of the water column (Fig. 4b, Table I). As for the winter ice for these ponds, Brack and Salt Pond meltwaters were Na-SO_4 dominated while those from P70 and P70E were Na-Cl dominated and Skua Pond has a Na-Cl-SO_4 composition (Table I, Fig. 4b).

Significant thermal stratification (> 1°C) occurred in only three out of the ten ponds measured; P70E, Salt and Upper Pond, the latter showing the largest temperature change with $\Delta T = 5.5°C$ (Fig. 4a). Dissolved oxygen concentrations varied between the meltwater ponds, but consistently indicated oxygenated conditions and usually increased with depth. The concentration of dissolved oxygen exceeded the instrument limit of 20 mg L^{-1} at the base of P70 and P70E, and over the entire water column for Salt Pond.

Table II. FREZCHEM52 predicted salt precipitation and the temperature at which this commences, under a decreasing temperature regime emulating progressive freezing of summer pond water, and ion loss during freezing predicted from ternary ion relationships.

Pond	FREZCHEM salt prediction	Temperature (°C)	Quantity precipitated (mmoles L^{-1})	Ion loss (Fig. 6)	Observed salt
Skua	Mirabilite	-2	4	SO_4	
	Gypsum	-1	0.6	Ca	
P70	Mirabilite	-4	4	(minor Ca)	
	Gypsum	-1	1		
P70E	Dolomite	0	8	SO_4	Carbonate
	Mirabilite	-10	2	(minor Mg)	
	Gypsum	-4	1.2		
Brack	Mirabilite	-1	110	SO_4	Mirabilite
	Gypsum	0	10	Na	
	$MgSO_4.12H_2O$	-5	19	(minor Ca)	
Salt	Mirabilite	+2	375	Na	Mirabilite
	Gypsum	-1	10	(minor Ca)	
	$MgSO_4.12H_2O$	-5	25		

Salt identification and modelling results

The salt precipitate found at the margin of Salt Pond was positively identified as thenardite (Na_2SO_4), and the salt dome adjacent to this pond was comprised of coarse crystals of mirabilite ($Na_2SO_4.10H_2O$), and finer crystals of both thenardite and mirabilite. Mirabilite was also identified in the ice column at the base of Salt Pond and Brack Pond. The presence of thernadite and minor amounts of halite (NaCl) in these samples may be due to dehydration either *in situ* or during the drying procedure which was required to remove water from the sample.

The results of FREZCHEM52 modelling of the salt precipitation expected during progressive freezing of a pond water are shown in Table II. In all five ponds, mirabilite is predicted to precipitate early during freezing, and is the dominant phase expected from all ponds except P70E. Gypsum is a secondary salt phase predicted to form in all ponds, while dolomite is predicted to precipitate only in P70E, and $MgSO_4.12H_2O$ only in Brack and Salt Pond.

Discussion

Determinants of pond geochemistry

To get an overview of pond chemistry, all major ion concentrations for the summer meltwaters, winter ice and winter basal brines are plotted as a function of conductivity in Fig. 5. For Na, K, Mg, Cl and SO_4, there are no consistent differences between summer meltwaters and winter ice or brine, as all show a broadly similar trend with conductivity. The ions showing the most consistent relationship with conductivity are Na, Mg, K and Cl, indicating that these ions are not being removed from solution as conductivity increases, or that they are being removed to the same degree in all ponds. Calcium, SO_4 and HCO_3 concentrations, on the other hand, do not always increase with salinity and Ca is consistently higher in summer meltwaters than in winter ice, evidence for the removal of these ions from solution at some stage of the seasonal cycle in the pond.

Ternary relationships between the ions can be used to more definitively identify chemical differences between the meltwater, ice and basal brine from the same pond, and therefore indicate which ions are being removed during progressive freezing. Ternary relationships for cations and anions are shown in Fig. 6 (unfortunately, because HCO_3 concentrations could not be measured in the ice, anions cannot be shown for the ice samples). The ion dominance previously referred to is immediately evident. All ponds are Na-dominated (note the axis for Na has been divided by 10 to spread the data), while P70E & P70 are Cl- dominated, Brack and Salt are SO_4-dominated and Skua Pond has similar concentration of both SO_4 and Cl.

A comparison of summer meltwaters and winter basal brine anion proportions for P70E, Skua and Brack ponds (for which Cl respectively makes up 99%, 95% and 98% of

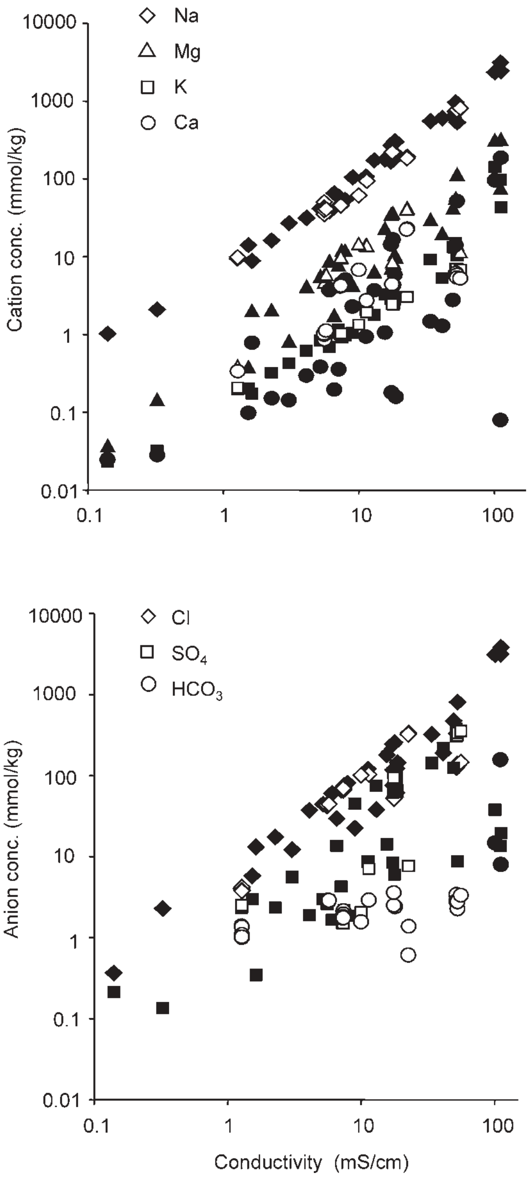

Fig. 5. Cation and anion concentrations (mmol kg^{-1}), plotted as a function of conductivity to identify dominant ions in all pond waters and brines. Late winter ice and basal brines are shown as black symbols.The basal brines are shown at conductivities of ~ 100 mS cm^{-1}. Note that a similar number of data points for winter and summer are plotted, but mixing and homogenization of some pond profiles in summer leads to less points being visible for summer conditions.

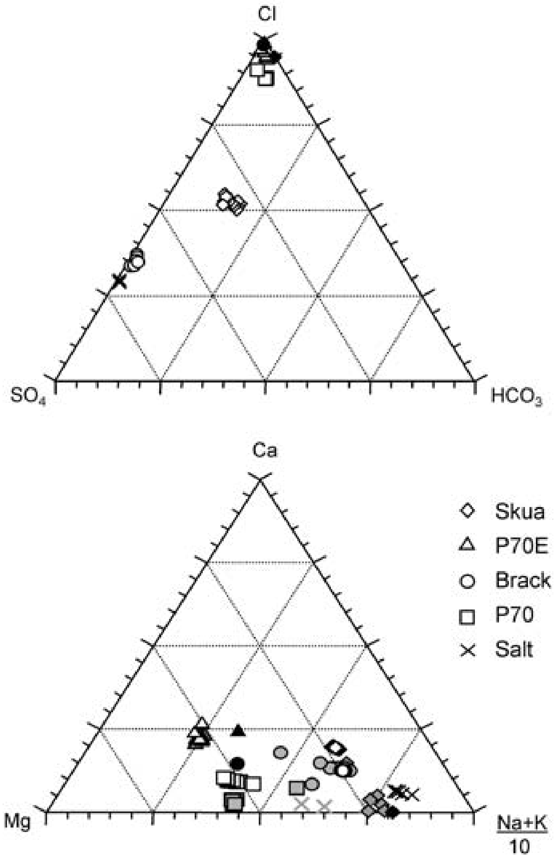

Fig. 6. Ternary diagrams for basal brine (black symbols), ice (grey symbols) and summer meltwaters (open symbols). Note that ice anions cannot be displayed as HCO_3 concentrations could not be reliably determined on melted ice samples.

the total anion concentration) confirms that SO_4 has been removed during freezing. On the cation ternary diagram, a comparison of summer meltwaters, and winter ice and basal brines, reveals divergent trends. Skua Pond and P70 cations indicate a loss of Ca with progressive freezing. Brack and Salt Pond cation ratios show a loss of Na and minor Ca, with the ice and basal brine becoming enriched in Mg relative to the summer meltwaters. Finally, P70E Pond shows little change in cation ratios with progressive freezing, other than minor Mg depletion in the basal brine.

These results are shown in Table II together with FREZCHEM52 predicted salt precipitation and, where available, observed salt mineralogy. Ion ratios support the predicted mirabilite and gypsum precipitation and, in P70E, dolomite precipitation during freezing. However, there appears to be little supporting evidence for the occurrence of the $MgSO_4.12H_2O$ salt predicted by FREZCHEM52.

The highly variable Ca and SO_4 concentrations observed in the ponds (Fig. 5) therefore reflect different degrees of precipitation of Ca (and Ca–Mg) salts. The relationship between Ca (and Mg) and HCO_3 is likely to play a key role in determining the final concentration of both Ca and SO_4 (Hardie & Eugster 1970). If HCO_3 is readily available then Ca and Mg ions will be more readily precipitated as calcite and dolomite, and removed from solution. If not, they will be precipitated as SO_4 minerals such as gypsum, leading to a greater degree of SO_4 removal. In these ponds HCO_3 concentrations in summer meltwaters were consistently low (Fig. 5), and a carbonate mineral (dolomite) was predicted to precipitate during freezing in only one pond (P70E).

Bicarbonate concentrations, together with DO and pH, were significantly influenced by the high biological productivity in summer. Dissolved oxygen concentrations and pH are raised by photosynthesis in the cyanobacterial mats. In the case of DO, supersaturated concentrations occur in lower layers, confined by density stratification in the stratified ponds. High pH values (up to 11.2) are not uncommon in environments hosting high primary productivity such as wetlands, when HCO_3 is the predominant dissolved form of inorganic carbon. Conversion of HCO_3 to CO_2 for use in photosynthesis releases hydroxyl ions, thereby raising pH and simultaneously reducing HCO_3 concentrations. The formation of H_2S by bacterially mediated reduction of SO_4, and the presence of other reduced sulphur compounds (e.g. De Mora *et al.* 1996), testifies to the reducing conditions present in the basal brines of some (but not all) ponds over winter. However, no relict of these reducing conditions is evident in the summer meltwater pond profiles.

Salt exclusion and basal brine formation

The theory of salt exclusion during freezing is that brine is rejected as ice is forming, and removed at the interface between the ice and the remaining liquid by diffusion and convection (Medjani 1996, Molemaker & Dijkstra 1995). The three-phase freezing system comprises a liquid phase (brine), a solid phase (ice) and a mixed solid-liquid phase. The temperature of freezing is dependent on the salinity of the liquid and, as ice is formed, the residual brine increases in salinity and the temperature of ice formation decreases until the eutectic salinity and temperature conditions are reached (i.e. the salinity & temperatures at which all remaining liquid will freeze). For the NaCl–H_2O system, for example, the eutectic is at a temperature of -21°C and a salinity of 230‰ (Medjani 1996). It is unlikely that eutectic conditions were approached, at least on a macro scale, in the ponds of this study as the maximum salinity measured (as estimated from conductivity) was ~80‰.

The presence of highly saline ice cores in this study suggests that the salt exclusion process is not as effective as is often assumed. This is likely to be a consequence of the nature of the mixed "solid-liquid" phase, which is reported to consist of a dendritic structure of ice crystals in residual fluid (Medjani 1996). This residual fluid can be excluded downward towards the ice-water interface, or incorporated into the solid-liquid phase depending on the density relative to the remaining "bulk" pond water. Progressive incorporation of this residual fluid can give rise to a concentration gradient within a body of ice, as well as encouraging density stratification in the remaining water. Drainage channels (tubes) that extend upward into the ice from the irregular ice-water interface also contribute to the formation of brine pockets within sea ice (Medjani 1996), a process which may also occur during meltwater pond freezing.

The closed nature of the meltwater pond environment means that progressive freezing incorporates residual brines of increasing salinity, resulting in a distinct salinity profile in the ice (Fig. 2a), whereas sea ice formation takes place in an open system where the salinity of the remaining fluid is approximately constant (Eicken 2003). Consequently distinct vertical profiles of conductivity were evident in the pond ice in this study. Profiles range from a relatively linear increase in conductivity with depth (e.g. P70 Pond) to the more exponential conductivity increase at the base of the ice as seen in Skua, Salt and Brack pond ice. A more irregular, though broadly exponential, profile was seen in P70E where it appears a quantity of more concentrated brine had become entrained in the ice when the freezing front was 40–50cm above the base of the pond.

The presence of meltwater pond basal brines formed by freezing have been previously reported only once in Antarctica; from two ponds at Cape Evans on Ross Island in which temperature and conductivity at the base of the ponds were monitored over a full year (Schmidt *et al*. 1991). A residual Na-Cl rich liquid was present at the base of the Ross Island ponds from late December until June, with minimum temperatures of -13°C and maximum Na and Cl concentrations of 52 000 mg L^{-1} and 110 000 mg L^{-1} respectively. These brines were less concentrated than those at Bratina Island, which had minimum temperatures of -20°C, and maximum Na and Cl concentrations of 72 000 mg kg^{-1} and 135 000 mg kg^{-1} respectively (measured in separate ponds; Table I).

Maintenance of stratification over summer

As the pond ice thaws during spring and summer, it forms a more dilute fluid than the brine beneath and fresh melt "floats" on the residual basal brine. In the ponds in which this chemical stratification is preserved, this gives rise to the relatively thin (10–20 cm thick) layer of more saline fluid at the base of the pond (e.g. P70E and P70; Fig. 4b) in summer. The depth of this basal layer corresponded to the depth of basal brine or highly saline basal ice evident in the ponds in later winter. Such step-wise increases in conductivity and major ion concentration have often been noted in the much larger inland Antarctic lakes (e.g. Webster *et al.* 1996, Gibson & Andersen 2002), as have the effects of solar radiation in increasing the temperature at the base of the water column. While temperature increases in the order of 10–20°C in the deepest lake waters have been attributed to solar heat adsorption (e.g. Hoare 1968), in the ponds the maximum temperature increase was 5.5°C.

Whether or not chemical stratification is preserved over summer will depend on whether the pond water column circulates after the thaw. Susceptibility to mixing by wind can be assessed using "relative depth"; a ratio of maximum water depth and pond width (Castro & Moore 2000). Typically, natural lakes with a relative depth of < 2% experience mixing when there is no thermocline in autumn and/or spring. At higher relative depths mixing is less likely, although this is also dependent on climate conditions such as wind speed and degree of exposure and, in this study, the stabilizing influence of the salinity gradient. The two most significantly stratified ponds, P70 and P70E, do have high relative depths (9% and 18% respectively, compared to values of 2.6% to 5% for the other ponds) suggesting that wind may be a factor in pond mixing. The presence of an ice cap during the seasonal high winds (in spring) and the presence of a salinity gradient, will also inhibit mixing. The Richardson Number (Ri, Tritton 1988) can be used to assess the effect of a salinity gradient on mixing potential. P70 and P70E ponds showed a significant density difference between the surface and basal water layers (i.e. a positive Ri value). Calculations using different wind speeds indicated that the density differential would prevent mixing up to wind speeds of ~10 m s^{-1}. Salt Pond had a low, positive Ri value, and Skua and Brack ponds had $Ri \leq 0$, consistent with the lack of significant stratification in these ponds.

Finally, alternating periods of positive (precipitation > evaporation) and negative (evaporation > precipitation) water balance may also affect whether a pond remains stratified, as has been noted in the formation and destruction of stratification in saline lakes with no outflow (Ferris *et al.* 1991). The study ponds which maintained stratification during summer were also observed to have a significant snow cover during the October sampling. Those that lacked stratification also lacked snow cover during October, suggesting that a positive water balance during winter may also help to maintain stratification during summer.

Conclusions

The hypothesis of this study was that pond stratification and basal brine chemistry are principally due to freeze concentration of the pond water over winter. The range in salinity and major ion chemistry observed in the ice and fluids of the study ponds near Bratina Island was indeed consistent with that expected to result from progressive freeze concentration of summer meltwaters into residual basal brines, and the consequent removal of Na, Ca and SO_4 through mirabilite and gypsum precipitation. This finding lays the foundation for reliable prediction of winter basal brine chemistry from summer pond water conditions at Bratina Island, using geochemical thermodynamics-based models such as FREZCHEM52. However, the process of salt exclusion from the ice during freezing is not as effective as had been assumed, with inclusions of residual brine encapsulated into the ice at the freezing front. Predictive models need to take account of this. Freeze concentration, and the subsequent formation of strong density gradient during pond thaw, is also likely to be the single most important factor determining whether a pond remains chemically stratified over summer. However, high relative depth, partial or full ice cover during high wind events and a positive water balance are other contributing factors. Freeze concentration was not a major controlling factor determining dissolved oxygen and HCO_3 concentrations, pH or redox conditions, which were instead primarily influenced by the degree of biological productivity in the ponds over summer.

This research increases our understanding of the influence of seasonal change on ecosystem processes in Bratina meltwater pond environments. Longer-term predictions of the chemical evolution of a particular pond at this site are possible, if reliable predictions of future seasonal water balances are available. A comparative study undertaken in the ice-free Dry Valleys at the same latitude, where meltwater ponds occur in salt-bearing soils rather than ice, has shown that similar processes control the seasonal changes in pond chemistry. However, the pond chemistry itself is innately different, due to the reduced contribution of marine aerosols, lower levels of biological activity in the ponds and the effects of soil salt dissolution (see Healy *et al.* 2006).

Acknowledgements

The authors would like to acknowledge the support and help of Antarctica New Zealand, the Aquatic Ecosystems research group (K081) at the NIWA in Christchurch, the University of Auckland's SGES and Geology department staff, and Dr Stephen de Mora for his comments as a reviewer. This study was partly funded by an Antarctica New Zealand Postgraduate Research Scholarship, supported by Antarctica New Zealand and Kelly Tarlton's Underwater World. Ice sectioning was undertaken in the facilities at the Department of Physics at the University of Otago, and the help and advice of staff and students in this department is also gratefully acknowledged. We thank the referees for their useful comments on this paper.

References

Campbell, I.B. & Claridge, G.G.C. 1987. *Antarctica: soils, weathering processes and environment*. Amsterdam: Elsevier, 368 pp.

Castro, J.M. & Moore, J.N. 2000. Pit lakes: their characteristics and the potential for their remediation. *Environmental Geology*, **39**, 1254–1260.

de Mora, S.J., Whitehead, R.F. & Gregory, M. 1994. The chemical composition of glacial meltwater ponds and streams on the McMurdo Ice Shelf, Antarctica. *Antarctic Science*, **6**, 17–27.

de Mora, S.J., Lee, P., Grout, A., Schall, C. & Heumann, K.G. 1996. Aspects of the biogeochemistry of sulphur compounds in glacial melt water ponds on the McMurdo Ice Shelf, Antarctica. *Antarctic Science*, **8**, 15–22.

Eicken, H. 2003. From the microscopic, to the macroscopic, to the regional scale: growth, microstructure and properties of sea ice. *In* Thomas, D.N. & Diekmann, G.S., *eds. Sea ice: an introduction to its physics, chemistry, biology and geology.* Malden, MA: Blackwell, 22–81.

Ferris, J.M., Gibson, J.A.E. & Burton, H.R. 1991. Evidence of density currents with the potential to promote meromixis in ice-covered saline lakes. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **84**, 99–107.

Gibson, J.A.E. & Andersen, D.T. 2002. Physical structure of epishelf lakes of the southern Bunger Hills, East Antarctica. *Antarctic Science*, **14**, 253–261.

Green, W.J., Angle, M.P. & Chave, K.E. 1988. The geochemistry of Antarctic streams and their role in the evolution of four lakes of the McMurdo Dry Valleys. *Geochimica et Cosmochimina Acta*, **53**, 1265–1274.

Hardie, L.A. & Eugster, H.P. 1970. The evolution of closed-basin brines. *Mineralogical Society of Amererica Special Paper*, **3**, 273–290.

Hawes, I., Howard-Williams, C., Schwarz, A.-M.J. & Downes, M.T. 1997. Environment and microbial communities in a tidal lagoon at Bratina Island, McMurdo Ice Shelf, Antarctica. *In* Battaglia, B., Valencia, J. & Walton, D.W.H., *eds. Antarctic communities: species, structure and survival*. Cambridge: Cambridge University Press, 170–177.

Healy, M., Brown K.L., Webster-Brown, J.G. & Lane, V. 2006. Chemistry and stratification of Antarctic meltwater ponds II: Inland ponds in the McMurdo Dry Valleys (Lat 77°S), Victoria Land. *Antarctic Science*, **18**, 525–533.

Hoare, R.A. 1968. Thermohaline convection in Lake Vanda, Antarctica. *Journal of Geophysical Research*, **73**, 607–612.

Howard-Williams, C., Pridmore, R., Downes, M.T. & Vincent, W.F. 1989. Microbial biomass, photosynthesis and chlorophyll a related pigments in the ponds of the McMurdo Ice Shelf, Antarctica. *Antarctic Science*, **1**, 125–131.

Howard-Williams, C., Peterson, D., Lyons, W.B., Cattaneo-Vietti, R. & Gordon, S. 2006. Measuring ecosystem response in a rapidly changing environment: the Latitudinal Gradient Project. *Antarctic Science*, **18**, 465–471.

Longinelli, A., Colombo, T., Giovanelli, G., Lenaz, R., Ori, C. & Selmo, E. 2001. Atmospheric CO_2 concentrations and $\delta^{13}C$ measurements along a hemisphereic course (1998/99, Italy to Antarctica). *Earth and Planetary Science Letters*, **191**, 167–172.

Marion, G.M. & Grant, S.A. 1994. FREZCHEM: a chemical-thermodynamic model for aqueous solutions at subzero temperatures. *Cold Regions Research and Engineering Laboratory*, *Special Report 94-18*, 37 pp.

Marion, G.M., Farren, R.E. & Komrowski, A.J. 1999. Alternative pathways for seawater freezing. *Cold Regions Science & Technology*, **29**, 259–266.

Medjani, K. 1996. Numerical simulation of the formation of brine pockets during the freezing of the NaCl–H_2O compound from above. *International Communications of Heat Mass Transfer*, **23**, 917–928.

Molemaker, M.J. & Dijkstra, H.A. 1995. Layer formation in a salt stratified liquid cooled from above. *Geophysical Monograph*, No. 94, 97–104.

Pridmore, R.D., Vant, W.N. & Cummings, V.J. 1995. Factors affecting the water clarity of ponds on the McMurdo Ice Shelf, Antarctica. *Antarctic Science*, **7**, 145–148.

Schmidt, S., Moskal, W., de Mora, S.J., Howard-Williams, C. & Vincent, W.F. 1991. Limnological properties of Antarctic ponds during winter freezing. *Antarctic Science*, **3**, 379–388.

Spencer, R.J., Møller, N. & Weare, J.H. 1990. The prediction of mineral solubilities in natural waters: a chemical equilibrium model for the Na-Ca-Mg-Cl-SO_4-H_2O system at temperatures below 25°C. *Geochimica et Cosmochimica Acta*, **54**, 575–590.

Thompson, T.G. & Nelson, K.H. 1956. Concentration of Brines and Deposition of Salts from seawater under frigid conditions. *American Journal of Science*, **254**, 227–238.

Timperley, M. 1997. A simple temperature-based model for the chemistry of melt-water ponds in the Darwin Glacier area, 80°S. *In* Lyons, W.B., Howard-Williams, C. & Hawes, I., *eds*. *Ecosystem processes in Antarctic ice free landscapes*. Rotterdam, Netherlands: A.A. Balkema, 197–206.

Tritton, D.J. 1988. *Physical fluid dynamics*. 2nd ed. Oxford: Clarendon Press, 519 pp.

Webster, J.G., Brown, K.L. & Vincent, W.F. 1994. Geochemical processes affecting meltwater chemistry and the formation of saline ponds in the Victoria Valley and Bull Pass region, Antarctica. *Hydrobiologia*, **281**, 171–186.

Webster, J., Hawes, I., Downes, M., Timperley, M. & Howard-Williams, C. 1996. Evidence for regional climate change in the recent evolution of a high latitude pro-glacial lake. *Antarctic Science*, **8**, 49–59.

Welch, K.A., Lyons, W.B., Graham, E., Neumann, K., Thomas, J.M. & Mikesell, D. 1996. Determination of major element chemistry in terrestrial waters from Antarctica by ion chromatography. *Journal of Chromatography*, **A739**, 257–263.

Wetzel, R.G. 1983. *Limnology*. 2nd ed. Philadelphia, PA: Saunders, 858 pp.

Whitehead, R.F. 1989. *Aqueous geochemistry of meltwater on the McMurdo Ice Shelf and the Alph River, Antarctica*. MSc thesis, University of Auckland, 132 pp. [Unpublished].