

# Geochemistry of ice-covered, meromictic Lake A in the Canadian High Arctic

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Abstract. The geochemical processes occurring within meromictic Lake A (max depth 120 m) on northern Ellesmere Island, Canada, were investigated to determine the history of the lake and to provide a baseline for future studies. The lake contained seawater diluted by freshwater input that had been mixed prior to the lake's isolation from tidal action. Input of freshwater after isolation of the lake created vertical stratification resulting in the creation of distinct oxic, suboxic and anoxic zones. Dissolved oxygen was present to 13 m, and sulphide beneath 32 m. Manganese and iron cycling dominated the redox chemistry between these depths. Total manganese concentrations reached 176  $\mu$ M, higher than in most other natural stratified lake or marine environments.

Key words: arctic, biogeochemistry, meromictic, perennial ice, redox, manganese, iron

# 1. Introduction

Meromictic lakes covered by thick, perennial ice-cover are well known from several coastal regions around Antarctica and have proved to be valuable model systems for understanding biogeochemical processes (e.g., Vincent et al., 1981; Canfield and Green, 1985; Lyons et al., 1998). It is less well known that permanently stratified lakes covered by multi-year ice are also to be found in the north polar region (Hattersley-Smith et al., 1970; Ludlam, 1996). Several of these lakes are located along the northern coastline of Ellesmere Island, where their extreme high latitude (83°N) combined with a shaded location in deep, north-facing valleys appears to allow ice to persist on the lakes throughout the annual cycle. Their chemical characteristics, however, have received little attention.

In the present study we undertook a sampling expedition to Lake A, the largest of the northern Ellesmere meromictic lakes. This lake has previously been sampled for some physical and geochemical variables (Jeffries et al., 1984; Jeffries and Krouse, 1985; Ludlam, 1996), but more complete knowledge of the limnological

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*Figure 1.* Maps of showing the location of Ellesmere Island in the Canadian Arctic; the sites of Lake A and other places named in the text in northern Ellesmere Island; and the drainage basin of Lake A. The sampling site is marked by the triangle.

properties of the lake is required to allow an improved understanding of biogeochemical processes and evolution of this north polar lake, and provide a data set for comparison with analogous ecosystems elsewhere in the Arctic and also in the south polar region.

# 2. Setting

Lake A is located near the northern coast of Ellesmere Island approximately 30 km to the west of Cape Columbia, the most northerly point of Canada (Figure 1). It is the northernmost lake on Ellesmere Island, though a smaller lake occurs on Ward Hunt Island 10 kilometres distant to the northeast (Villeneuve et al., 2001). Lake A, which lies in a deep, steep-sided glacially-gouged basin, has an area of 4.9 km<sup>2</sup> (Van Hove et al., 2001) and a maximum recorded depth of 120 m (M. Retelle, personal communication, 1999). It receives input from a rugged but glacier-free drainage basin 37 km<sup>2</sup> in area. The surface level of the lake is 3 m above sea level, and a short outlet stream flows from the northeastern arm of the lake to an epishelf lake dammed by the Ward Hunt Ice Shelf. The development of Lake A has not been studied in any detail, but the general uplift history of the area suggests that it was isolated from the ocean approximately 3000 years BP (Jeffries et al., 1984).

# 3. Methods

Lake A was visited in early June, 1999. At this time, the lake was covered by a 2.0 m layer of ice and 37–58 cm of snow (Belzile et al., 2001). Holes were drilled through the ice to access the water column with a Strike-Master electric-powered ice drill. The water depth at the sampling site was 115 m, close to the maximum recorded depth for the lake. Zero metres for all profiles was taken to be the piezometric water level in the ice hole. Profiling and sampling were undertaken through holes approximately 15 metres apart.

Temperature profiles were recorded to 100 m with a PUV 500 profiler (Biospherical Instruments). Electrical conductivity, pH, and the concentration of dissolved oxygen (DO) were measured to 47.5 m using a Hydrolab Surveyor 3 profiler (Hydrolab Corporation), which was lowered into the water column at intervals of 0.5 m-1 m. The salinity profile to 47.5 m was calculated from conductivity and temperature data using the equations of state for seawater (Fofonoff and Millard, 1983). Salinity beneath 47.5 m was estimated by summation of the concentrations of the major ions. Water samples were collected from 37 depths with an all-plastic Kemmerer bottle, and were placed into polyethylene or glass bottles that were kept at 4 °C or below until analysis was performed.

Samples for the determination of the concentrations of dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), nutrients (NO<sub>3</sub><sup>-</sup>, NH<sub>3</sub>, soluble reactive phosphate (SRP), and reactive Si), and major ions (Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup> and  $SO_4^{2-}$ ) were collected and stored according to the protocols developed by the National Laboratory for Environmental Testing (Burlington, Ontario, Canada), where the samples were analysed (Environment Canada, 1994). A list of the methods used is given in Table I. The total concentrations of trace metals (i.e., including dissolved, colloidal and particulate phases) were measured by ICP-MS after acidification, also at the National Laboratory for Environmental Testing. No attempt was made to measure the concentrations of the various phases separately. The concentrations of the following metals were determined (with detection limits in brackets): Al (370 nM); Ba (3.6 nM); Be (22 nM); Cd (8.9 nM); Co (17 nM); Cr (19 nM); Cu (16 nM); Fe (18 nM); Li (140 nM); Mn (9.1 nM); Ni (34 nM); Pb (24 nM); Sr (5.7 nM); V (20 nM); and Zn (15 nM). The concentration of sulphide in samples fixed in the field with zinc acetate was determined using the methylene blue method of Parsons et al. (1984).

#### 4. Results

# 4.1. TEMPERATURE AND SALINITY

Water temperature rose from near freezing directly under the ice to a maximum of 8.51 °C at 17 m, before dropping to 4.04 °C at 100 m (Figure 2). Salinity was close to zero immediately under the ice, but increased with depth to approximately 90% of that of seawater by 47.5 m. The concentrations of the major ions did not

Analysis	Method description
DOC/DIC	Automated UV digestion and infrared detection
$NO_3^-/NO_2^-$	Automated colorimetric - cadmium reduction/diazotization
NO <sub>2</sub>	Automated colorimetric - diazotization
NH <sub>3</sub>	Automated colorimetric - indophenol blue
SRP	Automated colorimetric - stannous chloride
Reactive Si	Automated colorimetric - heteropolymolybdenum blue
Na <sup>+</sup>	Atomic absorption spectroscopy
$K^+$	Atomic absorption spectroscopy
$Mg^{2+}$	Atomic absorption spectroscopy
Ca <sup>2+</sup>	Atomic absorption spectroscopy
Cl <sup>-</sup>	Automated colorimetric - ferric thiocyanate
$SO_{4}^{2-}$	Automated colorimetric - methylthymol blue

Table I. Methods used for chemical analyses.

change markedly between 50 and 115 m, suggesting that salinity was near constant beneath 47.5 m.

# 4.2. DISSOLVED OXYGEN

DO was present at measurable levels from underneath the ice to 13 m (Figure 2). The maximum concentration, 539  $\mu$ M (equivalent to a saturation of 120%), occurred immediately under the ice. The concentration of DO dropped steadily between 7 and 13 m, where DO was barely detectable. The relatively coarse precision of the Hydrolab profiler made it impossible to measure accurately the low concentrations of DO possibly present in the suboxic region between 13 and 32 m.

# 4.3. рн

pH was between 7.01 and 7.84 over the upper 47.5 m of the water column (Figure 2). Maximum pH occurred in the top few metres, before dropping to a minimum at 13 m. Beneath this depth pH rose steadily again to a secondary maximum near 30 m, but then decreased slightly.

# 4.4. MAJOR IONS

Profiles of Cl<sup>-</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup> are shown in Figure 3a–e. The insets in Figures 3b–e show the enrichment factors (which give an indication of the source of the ion (Duce et al., 1972)), defined as follows:

$$E_{M} = ([M]_{meas}/[Cl]_{meas})/([M]_{sw}/[Cl]_{sw}),$$
(1)



*Figure 2.* Physical and chemical parameters of Lake A: (a) temperature and salinity. The solid salinity line was calculated from electrical conductivity data, and the squares from summation of the concentrations of the major ions; (b) concentration of dissolved oxygen (closed squares), sulphide (open squares) and pH (triangles). The inset shows detail of the oxygen concentration and pH in the surface waters.

where  $E_M$  is the enrichment factor for the ion M, the square brackets indicate concentration (moles  $L^{-1}$ ), and the subscripts 'meas' and 'sw' indicate measured and seawater respectively. Cl<sup>-</sup> was chosen as the base for calculations of the enrichment factors as this ion is typically present at low concentrations in terrestrially-derived waters, and is therefore largely derived from marine sources (de Mora et al., 1994). The enrichment factor would be 1 if all of a particular ion was derived from the dilution of seawater and no subsequent differential diffusion, input of ions from terrestrial sources or biologically-driven redistribution of the ions had occurred. If this were the case, the expected profiles of the ions can be calculated from the concentration of Cl<sup>-</sup> as follows:

$$[\mathbf{M}]_{\text{calc}} = [\mathbf{M}]_{\text{sw}} x ([\mathbf{Cl}]_{\text{meas}} / [\mathbf{Cl}]_{\text{sw}}).$$
<sup>(2)</sup>

These profiles are shown in the main figures by the unbroken curve.

All the major ions showed similar profiles, with the concentrations being lowest directly under the ice, rising slightly in the surface ten metres and then more rapidly between 11 and 27 m. Between 28 and 32 m the concentrations of some of the ions (notably Na<sup>+</sup> and Cl<sup>-</sup>) were near constant, but increased again from 35 to 50 m. The concentrations of all the major ions in the bottom 65 m of the water column were nearly constant. Apparent decreases in the concentrations of



*Figure 3.* Concentrations of major ions in Lake A: (a)  $Cl^-$ ; (b)  $Na^+$ ; (c)  $K^+$ ; (d)  $Mg^{2+}$ ; (e)  $Ca^{2+}$ ; and (f)  $SO_4^{2-}$ . The squares are actual analytical data, the solid curve the expected concentration calculated from  $Cl^-$  using Equation (2), and the inset the enrichment factor with respect to  $Cl^-$  calculated using Equation (1).

the ions at some depths beneath 30 m were likely due to analytical error associated with measuring the high concentrations rather than true variations. Details of the agreement between  $[M]_{calc}$  and  $[M]_{meas}$  differ for each ion, as shown by the plots of the enrichment factors. The profiles of Na<sup>+</sup> and K<sup>+</sup> closely matched those expected from the concentrations of Cl<sup>-</sup>, whereas those of Mg<sup>2+</sup> and Ca<sup>2+</sup> showed that the lake water was relatively enriched in these ions, especially near the surface and in the zone between 20 and 40 m. Ca<sup>2+</sup> was depleted at the base of the water column.

#### 4.5. SULPHATE AND SULPHIDE

The concentration of sulphate increased from under the ice to a maximum of 23 mM at 24 m, before dropping slightly (Figure 3f). The ion was enriched compared to chloride above 8 m, but was slightly depleted between 8 and 12 m. Slight enrichment then occurred between 13 and 25 m, beneath which the ion was present at a lower concentration than expected from Cl<sup>-</sup>. Sulphide was not detected either in the field by smell or by analysis in samples above 32 m (Figure 2). The concentration below this depth increased to a maximum of 48  $\mu$ M at 100 m, which was much lower than the concentration of sulphate. Total inorganic sulphur (the sum of sulphate and sulphide) was below that expected from the dilution of seawater beneath 32 m.

#### 4.6. TRACE METALS

# 4.6.1. Barium

The profile of  $Ba^{2+}$  in Lake A was one of the more complex recorded (Figure 4). The concentration paralleled the profiles of the major ions to 12 m, beneath which it was constant over an interval of six metres. The concentration then increased again from 18 m to a maximum at 32 m, before dropping back sharply to near that at 18 m, a concentration that was maintained between 50 m and the base of the water column.  $Ba^{2+}$  was significantly enriched ( $E_{Ba} = 1780$ ) in the surface water. The enrichment factor decreased before a secondary maximum (circa 20) at 32 m, but then dropped to near 10 for most of the water column.

#### 4.6.2. Lithium and Strontium

The profiles of Li<sup>+</sup> and Sr2<sup>+</sup> generally paralleled those of the major ions (Figure 4).  $E_{Li}$  was near 1 at 10 m (Li<sup>+</sup> concentrations were too low for accurate measurement above this depth), but increased to greater than two by 14 m.  $E_{Li}$  reached a broad maximum between 20 m and 35 m, beneath which it was near constant at about 2.5. Sr<sup>2+</sup> was enriched relative to Cl<sup>-</sup> in the top few metres of the lake, but slightly diluted near 10 m.  $E_{Sr}$  was between 1 and 1.3 from 12 m to the base of the water column, with a slight and broad maximum between 15 m and 30 m.



*Figure 4.* Concentrations of other alkali and alkaline earth metals in Lake A: (a)  $Li^+$ ; (b)  $Sr^{2+}$ ; and (c)  $Ba^{2+}$ . The data points and insets are explained in the caption of Figure 3.

# 4.7. TRANSITION MEALS

The only transition metals present at measurable concentrations over most of the water column were Fe and Mn, which showed markedly different depth profiles to the major ions and to each other. Total Fe (i.e., the sum of dissolved, particulate and colloidal fractions: Fe<sub>T</sub>) was present at concentrations up to 30  $\mu$ M, with a broad peak between 28 m and 35 m (Figure 5). There was a sharp boundary in the Fe<sub>T</sub> distribution between 27 m (where the concentration was below the detection limit of the analytical method: 18 nM) and 28 m (23  $\mu$ M). The concentration tailed off

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*Figure 5.* Concentration of (a) Fe<sub>T</sub> and (b)  $Mn_T$  in Lake A. The insets show detail from the profiles between 10 and 50 m, as well as the concentration of DOC (dotted line). See Figure 6 for complete DOC profiles.

to relatively low but measurable concentrations (90–200 nM) at 50 m and below. The concentrations at all depths below 28 m were far higher than expected from the dilution of seawater, in which Fe is present at a concentration of approximately 1 nM (Broecker and Peng, 1982).

The concentration of total Mn (Mn<sub>T</sub>) was also low in the surface oxygenated water to 11 m (below the detection limit of 9.1 nM to 40 nM), but increased from 12 m in a broad band that peaked at 175  $\mu$ M at 24 m, and then decreased to less than 20  $\mu$ M at 50 m (Figure 5). A marked shoulder occurred in the profile at 28–30 m. The concentration of Mn<sub>T</sub> was near constant beneath 50 m at 18  $\mu$ M. These concentrations were again far above those expected from the dilution of seawater, in which the average concentration of Mn is 5–20 nM (Broecker and Peng, 1982).

The concentrations of the other trace metals measured by ICP-MS were rarely above the detection limit. The maximum concentrations recorded were: Co, 17 nM; Cr, 19 nM; Cu, 94 nM (with a possible trend to higher concentrations in the anoxic water); Mo, 10 nM; V, 20 nM; and Zn, 15 nM. The concentrations of the other metals measured – Be, Cd, Ni and Pb – were beneath the detection limits in all cases.

#### 4.8. NUTRIENTS

Nitrate was below the detection limit (0.7  $\mu$ M) throughout the water column. In contrast, the concentration of NH<sub>3</sub> was low in the oxygenated water above 12 m (maximum 0.8  $\mu$ M at 5 m), but increased rapidly beneath that depth, reaching

650  $\mu$ M at the base of the water column (Figure 6). The concentration of SRP was close to the detection limit in the surface waters, but increased slightly below 12 m, and more rapidly beneath 30 m. The concentration of reactive Si increased from under the ice to a broad maximum near 31 m before decreasing slightly towards the sediment. The profile was very similar to that of Ba<sup>2+</sup>, with a near linear relationship between E<sub>Ba</sub> and E<sub>Si</sub>.

#### 4.9. INORGANIC AND ORGANIC CARBON

Dissolved inorganic carbon was present in the fresh surface waters at a concentration above 1 mM, increasing steadily to 2 mM by 12 m and 9.6 mM at 32 m (Figure 6). Beneath this depth, DIC generally continued to increase, reaching a maximum near the base of the water column.  $E_{DIC}$  was high in the surface water, dropping to 5–6 between 30 and 115 m. DOC was present at much lower concentrations, ranging from 60–100  $\mu$ M above 10 m, and increasing to 300  $\mu$ M throughout most of the water column (Figure 6).

#### 5. Discussion

#### 5.1. ICE COVER

The ice cover on Lake A in 1999 was similar to that recorded previously, in that it was about 2 m thick and was clearly multi-year ice (Hattersley-Smith et al., 1970; Ludlam, 1996). The ice thickness is comparable to that of other permanently ice-covered lakes on Ellesmere Island, but appears to be at the lower end of the range for similar lakes worldwide. For example, the ice cover often reaches 4 to 5 m on lakes of the McMurdo Dry Valleys in Antarctica (Chinn, 1993; Spigel and Priscu, 1998). Relatively thin permanent ice (1.8 m to 2.8 m) has also been reported for other lakes on Ellesmere Island (Hattersley-Smith et al., 1970), and more recently for White Smoke Lake in the Bunger Hills, Antarctica (Doran et al., 2000), while seasonal ice up to 1.7 m thick occurs on lakes elsewhere on Ellesmere Island (Hattersley-Smith et al., 1970). The stability of the ice on Lake A stems in part from the thick layer of snow that appears regularly to cover the surface of the ice. The snow reduces heat loss from the lake during winter and therefore ice production, and, during summer, solar heating of the water column and associated basal melting, as well as surface ablation.

The lake was completely covered by ice when visited in June 1999, but observations made from the air in August 1998 and again in July and August 2001 indicated that a moat maybe 20 m wide forms around the edge of the lake in summer. Similar moats form around the margins of the permanently ice-covered lakes of the McMurdo Dry Valleys (Spigel and Priscu, 1998). The relatively narrow moat around Lake A probably reflects the steeply sloping sides of the lake basin.



Figure 6. Concentrations of (a) DOC, (b) DIC, (c)  $NH_3$ , (d) SRP and (e) reactive Si in Lake A.

# 5.2. SALINITY AND TEMPERATURE

The physical structure of the lake determined in the present study was nearly identical to those reported previously, with the minor differences most likely due to the methods of determining the salinity (Hattersley-Smith et al., 1970; Jeffries et al., 1984; Jeffries and Krouse, 1985; Ludlam, 1996). The major features of the salinity profile are a freshwater layer (salinity  $< 1 \text{ g L}^{-1}$ : 2–10 m), a transition zone (10–50 m) and a deep, near isohaline zone (beneath 50 m). Toth and Lerman (1975) modelled the salinity structure of Lake A, and concluded that the distribution of salt in the lake was the result of diffusion from a saline bottom layer into a freshwater layer on the surface. The surface layer will have a relatively low residence time, as it will be flushed by freshwater flow into the lake from its drainage basin, and out of the lake at its northern end to the Arctic Ocean. This will result in the freshwater end member of the diffusional gradient being regularly renewed. Further discussion of these processes are included in the section on the major ions below.

The mesothermic temperature profile in Lake A was very similar to profiles recorded previously for the lake, as well as in similar saline meromictic lakes in the Arctic (Hattersley-Smith et al., 1970; Ludlam 1996) and the Antarctic (Spigel and Priscu 1998; Gibson 1999). The maximum water temperature recorded in Lake A rose from 7.5 °C to 8.9 °C between 1969 and 1993 (Ludlam 1996), but had dropped by 0.15 °C by 1999. The mid-water temperature maximum reflects the balance of heat loss from the lake during winter and input from solar radiation in summer, and is likely to be sensitive to changes in variables including the extent and timing of the snow cover, which will reduce heat loss from the lake as well solar radiation entering the lake. The maximum temperature in ice covered meromictic lakes decreases during winter (Gibson et al., 1989), and thus the maximum temperature will vary within a year, being coldest in spring, and warmest in late summer. The position of the temperature maximum also changes, becoming deeper in the water column as winter heat loss progresses. Therefore, comparison of maximum temperatures from year to year can be misleading if intra-annual changes have not been taken into account.

The temperature and salinity profiles indicate that there is no vertical mixing within the water column beneath the top few metres. If mixing were to occur, zones of isothermal and isohaline water would be expected, as have been observed in meromictic lakes in Antarctica (Spigel and Priscu, 1998; Gibson, 1999).

# 5.3. CHEMICAL LIMNOLOGY

# 5.3.1. Major Ions

The general trends in the concentrations of the major ions  $(Na^+, K^+, Mg^{2+}, Ca^{2+}$  and  $Cl^-)$  were similar to those reported previously to a depth of 68 m by Jeffries et al. (1984), though the concentrations of all ions were found to be slightly higher in the present study. This difference is most likely the result of the use of different

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analytical techniques rather than actual changes within the lake over the intervening period. Three processes appear to have controlled, or to be controlling, the gross distributions of these ions in the water column of Lake A: the initial isolation of the lake from the ocean, which resulted in the determination of the basic chemistry of the lake; the flow of freshwater into the lake from the drainage basin and out of the lake via the outlet at the northern end, which has resulted in the formation of a low-salinity layer at the surface of the lake with different chemistry to the bulk of the lake; and the diffusion of salts from the more concentrated bottom waters to the more dilute surface waters.

#### 5.4. INITIAL ISOLATION OF THE LAKE

From isotopic data and ionic concentrations, Jeffries et al. (1984) showed that the saline water at 68 m in Lake A was originally seawater that had been diluted by about 12% with freshwater. These authors concluded that the lake water had undergone some process which involved freshening and subsequent mixing of the water column at some time in the past. It is now known that the lake is substantially deeper (circa 120 m), and that the salinity at the base of the water column is not significantly greater than at 68 m, indicating that diffusional processes between full seawater at the bottom of the water column and freshwater at the surface were not responsible for the salinity at 68 m. The data presented here support the suggestion that the entire water column was mixed and freshened at some time. No simple conclusion about the timing or nature of this process can be drawn from the profiles of salinity or the major ions, though the profiles of Li<sup>+</sup> and, in particular, Ba<sup>2+</sup> provide more insight into this process.

If the dilution of the water column with freshwater and mixing occurred prior to isolation of the lake from the ocean, it would be expected that the lake water beneath 50 m (i.e., with little or no influence from shorter-term freshwater input) would have an ionic make up similar to that of the surface waters of the Arctic Ocean. This is the case for the major ions, but, in contrast, the concentrations of  $Ba^{2+}$  (when normalised to the concentration of  $Cl^-$ ) are significantly enriched beneath 50 m with respect to average seawater. Furthermore, the concentration of  $Ba^{2+}$  in the surface waters of the Arctic Ocean is currently much lower (40–70 nM: Falkner et al., 1994; Guay and Falkner, 1997) than at any depth in Lake A, suggesting that surface waters of the open ocean could not have been the sole source of the water deep in the lake.

 $Ba^{2+}$  is present at higher concentrations in rivers and streams (mean 440 nM) than in the ocean (40–100 nM; Broecker and Peng, 1982). The  $Ba^{2+}$  profile in Lake A therefore suggests a significant terrestrially-derived input, not only in the surface freshwater, but also throughout the water column. The question is: how did this  $Ba^{2+}$  become distributed throughout the water column, notably at near constant concentrations in the bottom 50 m of the lake? Two possible mechanisms exist: (i)

precipitation as barite (BaSO<sub>4</sub>) and redissolution deeper in the water column, or (ii) redistribution through mixing.

The precipitation of barite in the surface ocean occurs even though the mineral is not saturated at these depths (Dehairs et al., 1987). Barite redissolves deeper in the water column, leading to a mid-water  $Ba^{2+}$  maximum (Dehairs et al., 1987; Falkner et al., 1993). The  $Ba^{2+}$  profile in Lake A can in part be interpreted in these terms.  $Ba^{2+}$  which enters the lake in freshwater input is partially precipitated as barite. The barite redissolves in a band centred near 32 m, leading to an increase in the concentration of  $Ba^{2+}$  in this zone. This mechanism, however, does not explain the high and near constant  $Ba^{2+}$  concentration beneath 50 m. Diffusion of  $Ba^{2+}$  away from the depth of the peak concentration will occur, but this is unlikely to lead to the observed profile. We suggest that considerable accumulation of  $Ba^{2+}$  occurred in the lake basin by barite precipitation from freshwater inflow and subsequent redissolution at depth prior to a mixing event which then distributed this  $Ba^{2+}$ evenly throughout the water column.

Further evidence for significant terrestrial input prior to mixing comes from the profile of  $\text{Li}^+$ . This ion is highly mobile in aquatic systems, and behaves conservatively.  $\text{E}_{\text{Li}}$  is greater than 2 throughout most of the water column, though apparently lower in the surface water. As  $\text{Li}^+$  could not have become enriched in the surface ocean through biological processes, terrestrial input and water column mixing is again implied.

The requirement for a significant direct terrestrial input into the lake suggests that the mixing of the marine and freshwater occurred after isolation of the lake from the ocean. If this were not the case, it is likely that the mixed, less dense,  $Ba^{2+}$ -rich water would have been replaced by denser,  $Ba^{2+}$ -poor seawater from the open ocean during tidal mixing. However, it is difficult to envisage a process which would have so effectively mixed such a deep water column without the input of tidal energy. Turbulent mixing from the freshwater inflow would presumably have penetrated the top ten metres or so (as is clear from the current salinity profile), while mixing from freeze out of salt during ice formation typically increases salinity of, rather than diluting, the bottom water (Gibson and Burton, 1996; Gibson, 1999).

How did the mixing occur? It is likely that tidal forcing was involved, with terrestrially-derived freshwater input mixed into the saline water without advection of  $Ba^{2+}$ -poor water into the lake basin. An explanation for these apparently contradictory processes might come from the current geography of the area immediately offshore from Lake A. This area is covered by the Ward Hunt Ice Shelf, an extensive area of ice up to 70 m thick and over 4500 years old (Evans and England, 1992) (compared to the estimated 3000 years for Lake A). Along the ice-land margin of the shelf there is a large epishelf lake (Figure 1), which contains freshwater resulting from terrestrial input and from melting of the ice shelf. This lake is, however, still tidal, as there is an hydraulic connection with open ocean. The  $Ba^{2+}$  concentration in this lake is likely to be high (as the water is largely derived from

terrestrial input), as is suggested by the  $Ba^{2+}$  profile in Disraeli Fiord (Figure 1), an extensive epishelf lake in which terrestrially-derived freshwater directly overlies marine water (Van Hove et al., 2001; Vincent et al., 2001). In the water column of Disraeli Fiord,  $Ba^{2+}$  is significantly more concentrated in the freshwater layer (205 nM) than in the underlying marine layer (70 nM). It appears that when the relative sea level in the area was higher and the basin now occupied by Lake A was still connected to the epishelf lake and therefore the ocean, tidal activity mixed seawater trapped in the basin with  $Ba^{2+}$ -rich fresh waters, resulting in the high  $Ba^{2+}$  concentrations observed throughout the water column and the near consistent concentrations in the lower 50 m of the lake.

# 5.5. SURFACE WATER

The surface water of the lake is clearly derived from freshwater input from the drainage basin that flows across the denser, more saline water beneath on its way to the outflow. One major stream enters the lake on its eastern side, as well as a series of other short streams from the surrounding hills (Figure 1). One of these streams is the outflow of Lake B, another marine-derived meromictic lake (Hattersley-Smith et al., 1970). There are no glaciers in the drainage basin of Lake A, so all input will be from melting snow during summer, with no sub-glacial flow. No surface inflow into the lake was apparent during the current visit, but observations made during August 1998 indicated that considerable melt occurs over summer, and that much of the land around the lakes was saturated.

The chemical composition of the terrestrial inflow can be inferred from the composition of the water directly beneath the ice. Some alteration of the composition of this water, however, will occur through freeze out of ions during ice formation in winter, and the concentrations measured in the under ice water might have been higher than in the meltwater input. The chemistry of the input is quite different to that of the bulk of the lake water, highlighted by the relative proportions of the major ions at 2 and 50 m (Table II), which show a markedly higher proportion of  $Ca^{2+}$ , and to a lesser extent  $Mg^{2+}$ , in the surface water, and a relatively lower proportion of  $Na^+$ . In the anions, DIC makes up a much higher proportion directly under the ice than at 50 m, where  $Cl^-$  is dominant.

The source of the ions in the meltwater input is either from interactions with the rock of the drainage basin (terrestrial sources) or from marine-derived aerosols deposited in the drainage basin with precipitation. The terrestrial sources are generally dominated by  $Ca^{2+}$ ,  $Mg^{2+}$  and DIC, whereas marine-derived aerosols are dominated by  $Na^+$  and  $Cl^-$ . It is evident that terrestrial sources play an important role in determining the chemistry of the inflowing water, though marine sources are also significant. Simple mass balance calculations suggest that the terrestrially-derived component was relatively rich in  $Ca^{2+}$  (circa 450  $\mu$ M) and  $Mg^{2+}$  (circa 150  $\mu$ M). Along with the high concentration of DIC in the lake, these concentrations are indicative of the dissolution of carbonate rock (e.g., dolomite) known to

Ion	2 m	50 m
Cations:		
Na <sup>+</sup>	56.1	86.5
K <sup>+</sup>	1.7	2.0
$Mg^{2+}$	14.8	9.8
Ca <sup>2+</sup>	27.4	1.8
Anions:		
Cl <sup>-</sup>	44.9	94.0
$SO_{4}^{2-}$	5.6	3.9
$CO_3^{2-} + HCO_3^{-}$	49.5	2.1

*Table II.* Mole percent concentrations of major cations and anions at 2 m and 50 m.

occur in the area (Trettin, 1981), possibly enhanced by the acidity of precipitation falling in the area (Vincent et al., 2000).

# 5.6. DIFFUSION

The third process that has influenced the distribution of the major ions within the lake is diffusion from the relatively concentrated deeper water to the less concentrated surface waters. The concentrations of the major ions increased with depth, indicating that there would be diffusion towards the surface in all cases. The prime evidence for diffusion playing a major role comes from the concentrations of Mg<sup>2+</sup> and  $Ca^{2+}$  at depths between 20 and 40 m, where the enrichment factors for these ions was greater than for Na<sup>+</sup> and K<sup>+</sup>. The in-mixing of freshwater (even with the relatively high Ca<sup>2+</sup> and Mg<sup>2+</sup> recorded in the surface waters) could not lead to these profiles. As the surface water of the lake has a short half life, any ions diffusing into the surface layer will be rapidly lost from the lake. Singly charged cations diffuse at a faster rate than the dications (Li and Gregory, 1974), and thus greater amounts of Na<sup>+</sup> and K<sup>+</sup> than of Ca<sup>2+</sup> and Mg<sup>2+</sup> will have diffused into the surface water and subsequently flushed from the lake. In contrast, the slowerdiffusing dications remain at higher relative concentrations in the water column, especially in the region between 20 and 40 m in which the greatest diffusional gradient occurs.

An alternative explanation for the presence of relatively high concentrations of  $Mg^{2+}$  and  $Ca^{2+}$  at mid-water depths in Lake A is the sedimentation of insoluble particles (including carbonates) contained in the inflowing water, or which form when this water is mixed into the surface water of the lake. These particles may

become trapped in the density gradient, eventually dissolving and adding to the  $Mg^{2+}$  and  $Ca^{2+}$  inventories.

#### 5.7. THE REDOX STRUCTURE OF LAKE A

The other major determinant of the chemistry of Lake A is the suite of reductionoxidation (redox) reactions occurring in the lake. In stratified lakes, redox reactions, which are often mediated by bacteria and heterotrophic organisms, occur in vertically separated zones of the water column, with the locations of the boundaries between the zones controlled thermodynamically (Davison, 1985). These biogeochemical processes are clearly occurring in Lake A, as shown by the distribution of the redox-active elements. The lake can be divided into three zones depending on which processes occur: the oxic zone, where DO and organic carbon production by photosynthesis and removal by respiration dominate; the sub-oxic zone, in which nitrate, Mn and Fe reduction occurs; and the anoxic zone, where sulphate reduction to sulphide takes place. In the following sections, the processes taking place in each of these zones are discussed.

# 5.8. OXIC ZONE

The production of organic matter by non-bacterial photosynthesis and its subsequent oxidation by oxygen occurs in the lake to a depth of 14 m. No measurement of the rate of photosynthesis was made in the present study, though from the low concentrations of Chlorophyll *a* present (Van Hove et al., 2001) it is likely to be limited. Supersaturation of oxygen occurs in the top 6 metres of the water column, similar to the situation in many Antarctic meromictic lakes (Wharton et al., 1986; Andersen et al., 1998; Rankin et al., 1999). This supersaturation is the result of high DO concentrations in the streams entering the lake, the inability of DO to equilibrate with the atmosphere due to the ice cover, and the decoupling of DO production by photosynthesis and removal by respiration as a result of the redistribution of organic carbon by sedimentation. Ludlam (1996) reported a far higher supersaturation in the surface waters of Lake A (216%) in May 1993 than recorded in the presence study, indicating that the balance between DO production and import, and removal, is a dynamic system. The base of the oxic zone is clearly associated with the maximum penetration of significant amounts of freshwater into the lake. The presumably turbulent mixing involved with this process carried DO to these depths, and since then photosynthesis has maintained the oxygenated conditions.

# 5.9. SUBOXIC ZONE

When oxygen concentration decreases, the efficiency of aerobic oxidation of organic matter will be reduced, and the next process in the redox series, nitrate reduction, will become dominant. Nitrate concentrations were very low (beneath the detection limit) throughout the lake, and so it is likely that this zone was not extensive, and contributed little to organic matter oxidation. This is in contrast to many meromictic lakes (e.g., Lake Vanda, McMurdo Dry Valleys, Antarctica: Vincent et al., 1981; Canfield and Green, 1985), in which a distinct zone is present near the base of the oxic zone where the concentrations of nitrate and other oxidised nitrogen compounds, including  $N_2O$ , reach a maximum as a result of the interplay between nitrifying bacteria, nitrate reduction and incorporation into organic material in photosynthesis.

The next process in the thermodynamic cascade is oxidation of organic matter by Mn(IV) oxides and hydroxides. The particulate Mn(IV) compounds are formed by oxidation of Mn<sup>2+</sup> at the base of the oxic zone. These particles sediment slowly to the top of the anoxic zone below, where they undergo reductive dissolution to reform Mn<sup>2+</sup>, which then diffuses both back towards the surface to complete the cycle, and towards the base of the water column, removing it from the active Mn cycle. It is also possible that MnCO<sub>3</sub> precipitates in the water column, and that sedimentation of this material beneath the top of the anoxic zone provides another mechanism by which Mn is removed from the sub-oxic waters. The particulate Mn(IV) compounds are also able to oxidise organic matter, a process that effectively releases Mn<sup>2+</sup> above the depth at which reductive dissolution occurs. Mn-reducing bacteria facilitate the oxidation of organic matter (Burdige and Nealson, 1985; Nealson and Myers, 1992), though this process can also occur abiotically. The redox cycle often results in twin peaks in the total concentration of Mn: one associated with the precipitation of  $MnO_2$  at the base of the oxic zone, and another at the depth at which reduction occurs at the top of the anoxic zone (Spencer and Brewer, 1971; Davison, 1985). The clearest example of this is in the Black Sea, where the peaks in  $MnO_2$  production and dissolution are separated by circa 40 m (Lewis and Landing, 1991).

The concentrations of  $Mn_T$  in Lake A, up to 176  $\mu$ M, were significantly higher than in many other meromictic lakes and stratified marine systems (Table III). The reason for the high concentration in Lake A is probably related to the chemistry of the freshwater input to the lake. Any dissolved or particulate Mn in the input will precipitate rapidly to the depth of MnO<sub>2</sub> dissolution, where it will enter the Mn cycle of the lake. The shallow depth of MnO<sub>2</sub> precipitation and the steep sides of the lake basin (i.e., less Mn will be lost to oxygenated sediments) will assist in maintaining the high concentration of Mn in the water column.

The profile of  $Mn_T$  in Lake A clearly indicates that active cycling is occurring. Even though the concentrations of the particulate and dissolved Mn were not determined, it is likely that the main peak was largely attributable to particulate Mn, while the shoulder at 30 m indicated the depth of reductive dissolution of  $MnO_2$ . The depth at which  $MnO_2$  is precipitating is likely to be 12–14 m, as it is in this depth interval that  $Mn_T$  first reaches appreciable levels. Support for this conclusion comes from the pH minimum at 13 m, which can be attributed to the

Lake or anoxic Marine basin	Location	Mn <sub>T</sub>	Fe <sub>T</sub>	Reference
А	Ellesmere Island, Canadian	176	30	This study
	Artic			
Vanda	McMurdo Dry Valleys,	62	19	Green et al., 1989
	Antarctica			
Sammamish <sup>1</sup>	Washington, USA	48	25.5	Balistrieri et al., 1992
Sombre <sup>1</sup>	Signy Island, Antarctic	33	330	Gallagher, 1986
	Peninsula			
Mariager Fjord	Denmark	25	3.5	Zopfi et al., 2001
Framvaren	Norway	18	29	Yao and Millero, 1995
Garrow	Little Cornwallis Island,	13	6	Dickman and Ouellet,
	Canadian Arctic			1987
Black Sea		8.4	0.3	Lewis and Landing, 1991
Shield	Vestfold Hills, Antarctica	4.8	2.7	Masuda et al., 1988
Heywood <sup>1</sup>	Signy Island, Antarctic	4.4	52	Gallagher, 1986
	Peninsula			
Fryxell	McMurdo Dry Valleys,	4.0	2.6	Harnish et al., 1993
	Antarctica			
Gotland Deep	Baltic Sea	3.0	0.2	Brügmann et al., 1997
Nurume	Syowa Oasis, Antarctica	2.4	3.8	Sano et al., 1977
Ace	Vestfold Hills, Antarctica	1.5	2.6	Masuda et al., 1988
Cariaco Trench	Caribbean Sea	0.6	0.6	Taylor et al., 2001
Burton	Vestfold Hills, Antarctica	0.3	4.1	Masuda et al., 1988
Jellyfish	Palau, Pacific Ocean	0.032	0.022	Landing et al., 1991

*Table III.* Maximum concentrations ( $\mu$ M) of Mn<sub>T</sub> and Fe<sub>T</sub> in the water columns of selected stratified lakes and marine systems in order of descending Mn concentration.

<sup>1</sup> Seasonally anoxic.

<sup>2</sup> Dissolved fraction only.

protons produced in the following reaction (or similar reactions to form hydroxide species):

$$2Mn^{2+} + 2H_2O \rightarrow 2MnO_2 + 4H^+.$$
 (3)

The  $Mn_T$  maximum lower in the water column indicates reduction of  $MnO_2$  to  $Mn^{2+}$  during oxidation of organic matter at this depth. Supporting evidence for this conclusion comes from the local minimum in the concentration of DOC at this depth, and beam attenuation profiles, which revealed the presence of absorbing and scattering particles, possibly bacteria (Belzile et al., 2001).

The depth difference between the locations of abiotic Mn oxidation and reduction is difficult to determine precisely from the profile presented here, but is probably 15–20 m. In contrast, in meromictic Lake Fryxell in the McMurdo Dry Valleys, Antarctica, the peaks are separated by less than a metre (Harnish et al., 1993), and in Lake Vanda, by approximately 5 m (Green et al., 1989). The reason for the large separation in the peaks in Lake A is presumably related to the high concentration of Mn in the lake, and the relatively low flux of organic material available for oxidation, as evidenced by the low concentrations of DOC compared to other polar meromictic lakes (e.g., 500–960  $\mu$ M in Ace Lake (Rankin et al., 1999) and 5.3 mM in Lake Vanda (Torii and Yamagata, 1981)). A complete understanding of Mn cycling in Lake A requires a further study in which the concentrations of the various Mn fractions are determined.

The profile of Fe<sub>T</sub> was similar to that of  $Mn_T$ , with the exception that the depth range of high Fe<sub>T</sub> was more limited. Fe<sub>T</sub> was below the limit of detection to 28 m, indicating that the concentration of DO at these depths was above the boundary for the stability of Fe<sup>2+</sup>. The maximum Fe<sub>T</sub> concentration, 30  $\mu$ M, which occurred at 30 m, was also high compared to other stratified systems (Table III), and some evidence of a two-peak system, similar to that for Mn, is apparent in the Fe<sub>T</sub> profile. It is clear that Fe cycling in Lake A occurred in a narrower band than for Mn, but, as for Mn, further studies are required to elucidate completely the processes occurring.

# 5.10. ANOXIC ZONE

Sulphate reduction and sulphide accumulation, indicators of anoxic water, occur from 32 m to the base of the water column. Some evidence for the occurrence of sulphide in the suboxic zone comes from the presence of green photosynthetic sulphur bacteria towards the base of this zone (Belzile et al., 2001). It is possible that these bacteria strip most of the sulphide from this section of the water column during anoxygenic photosynthesis. The concentrations of sulphide in Lake A beneath 32 m are comparable to those of the anoxic strata of Antarctic meromictic lakes (Torii and Yamagata, 1981; Burke and Burton, 1988; Franzmann et al., 1988). The total sulphur concentration in Lake A is well below that expected from the dilution of seawater, indicating that a significant amount has been lost by precipitation of metal sulphides. Sulphate is present at the base of the water column, and it is therefore unlikely that significant methane production occurs in the lake.

#### 5.11. NUTRIENT CYCLING

The concentrations of nitrogen (both in the form of nitrate and  $NH_3$ ) were low in the oxic zone, indicating rapid uptake of any nutrient released during respiration or other processes. The concentration of  $NH_3$  began to increase at 20 m, near the depth of the peak in  $Mn_T$  and presumed maximum remineralisation by Mn-oxidising bacteria. In contrast, the concentration of SRP did not begin to rise markedly until 31 m, close to the interface between the suboxic and anoxic zones. It appears that the action of the Mn-oxidising bacteria did not release SRP from organic material, or that any SRP released was immediately taken up by the biota of the zone. The molar ratio between  $NH_3$  and SRP beneath 50 m, 17–18, was close to the Redfield Ratio between these elements in marine organic material (16), indicating firstly that the organic material produced by photosynthesis in Lake A has a similar composition to that in marine systems, and secondly that quantitative release of the nutrients is occurring in the anoxic water of the lake.

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