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# Boron isotopic geochemistry of the McMurdo Dry Valley lakes, Antarctica

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## ABSTRACT

The geochemistry of boron was investigated in the ice-covered lakes and glacier meltwater streams within Taylor and Wright Valley of the McMurdo Dry Valleys (MCM), Antarctica, in order to achieve a greater understanding of the source of boron to these aquatic systems and how in-lake processes control boron concentration. Selected lake depths (surface and bottom water) and streams were analyzed for boron geochemistry. Boron stable isotope values in these waters span the range of +12.3‰ to +51.4‰, which corresponds to the variations from glacier meltwater streams to the hypolimnion of a highly evaporated hypersaline lake. The data demonstrate that the major sources of B to the aquatic system are via terrestrial chemical weathering of aluminosilicates within the stream channels, and a marine source, either currently being introduced by marine-derived aerosols or in the form of ancient seawater. Lakes Fryxell, Hoare, and upper waters of Lake Joyce, which experience more terrestrial influence of aluminosilicate chemical weathering via glacial meltwater streams, display a mixture of these two major sources, while the source of B in the bottom waters of Lake Joyce appears to be primarily of marine origin. Lakes Bonney and Vanda and the Blood Falls brine have a marine-like source whose  $\delta^{11}\text{B}$  values have become more positive by mineral precipitation and/or adsorption. Don Juan Pond displays a terrestrial aluminosilicate influence of a marine-

like source. These hypersaline lake waters from Antarctica are similar in  $\delta^{11}\text{B}$  to other hyper-saline lake waters globally, suggesting that similar processes control their B geochemistry.

## Introduction

The aquatic geochemistry of the McMurdo Dry Valleys (MCM), Antarctica, has been studied for more than four decades. This aquatic system ranges from very low ionic strength glacier melt to orders of magnitude higher ionic strength, closed-basin, ice-covered lake waters that terminate the system (Lyons et al., 1998a). Various isotopic techniques ( $^{86}\text{Sr}/^{87}\text{Sr}$ ,  $^{36}\text{Cl}$ ,  $\delta^{37}\text{Cl}$ ,  $\delta^{13}\text{C}$ ,  $\delta\text{D}$ ,  $\delta^{18}\text{O}$ ,  $^{234}\text{U}/^{238}\text{U}$ , and  $\delta^7\text{Li}$ ) have been used through the years to investigate both the origin of solutes to the closed-basin lakes and in-lake processes (Jones and Faure, 1978; Matsubaya et al., 1979; Carlson et al., 1990; Neumann et al., 1998; Henderson et al., 2006; Witherow et al., 2010).

Dissolved salts have been suggested to originate from chemical weathering of aluminosilicate and carbonate minerals in stream channels, the input of marine aerosols via glacier melt, dissolution of salts on the valley floor, relict seawater, and groundwater discharge (Lyons et al., 2005). Various authors have suggested that each of the numerous lakes in MCM may have different sources of solutes or different mechanisms of salt concentrations based on their past histories (Lyons et al., 1998a). Authors also have speculated that the salt in the hypolimnia of the most saline lakes could originate from a range of processes such as hydrothermal input, capture of relict seawater, and/or evapoconcentration of glacier meltwater during a different climatic regime than the present (Angino et al., 1962; Angino and Armitage, 1963; Lyons et al., 2000, 2005). In general, these previous studies have helped to distinguish the processes that have affected the chemistries among the lakes and the source of individual solutes. However, there is still a need to investigate further the source of specific elements and their in-lake behavior in order to provide a synthetic view of the geochemistry of these unusual systems.

The analysis of B and its isotopes provides an additional geochemical tool to determine solute source and in-lake processes. In natural waters, B inputs may be sourced

from both anthropogenic processes/activities (e.g., pollution from sewage effluents, fertilizers, and landfill leachates) and natural sources (i.e., water–rock interactions, seawater intrusion, exogenous crustal brines, or hydrothermal fluids) (Vengosh et al., 1994, 1999; Weinthal et al., 2005); however, there are no expected anthropogenic sources of B to the MCM. Boron occurs in low concentrations within all rock types of the Earth's crust. Universally, rivers and low salinity groundwater have low B concentrations of  $< 9 \mu\text{M}$  (Neal et al., 1998; Wyness et al., 2003), whereas because of its high solubility, saline water can have much higher B concentrations ( $B_{\text{seawater}} = 440 \mu\text{M}$ ) (Weinthal et al., 2005). In arid and semi-arid climates, B in lake waters can also be elevated (e.g. 29 mM of B in Mono Lake, Great Basin, USA; Steiman et al., 2004).

The MCM lakes are unusual in that over a relatively small geographic area, the geochemistry of the lakes varies dramatically and the lakes have very different histories (Lyons et al., 1998a; Poreda et al., 2004). Initial work demonstrated that the B concentrations varied within the Taylor Valley lakes (Lyons et al., 2005), but more specific B analysis, along with  $\delta^{11}\text{B}$  data, should further elucidate the geochemical dynamics of these systems. Here we analyze the B geochemistry as a tracer for geochemical variations within the MCM lakes and to investigate the source of solutes to these lakes. In addition, the B geochemistry from these Antarctic lakes is compared to saline lakes from other locations, in order to generally assess B behavior in saline lacustrine systems globally.

### ***Study area description***

The McMurdo Dry Valleys, which cover  $\sim 4500 \text{ km}^2$  and are located at  $77^{\circ}30'\text{S}$ ,  $163^{\circ}00'\text{E}$ , constitute the largest relatively ice-free region on the Antarctic continent (Fig. 1). The MCM have been a location for scientific investigations since the 1960s, and in 1993, the McMurdo Dry Valleys Long-Term Ecological Research (MCM-LTER) site was established to monitor environmental change (Fountain et al., 1999). MCM is a polar desert, and has a mean annual temperature of  $\sim -20^{\circ}\text{C}$  (Fountain et al., 1999). Recently Fountain et al. (2010) have suggested that net precipitation may be as low as 2 cm (water equivalent) per year.

Taylor Valley (Fig. 1) is approximately 34 km long and 12 km wide and contains three closed-basin, perennially ice-covered lakes, Lakes Bonney, Hoare, and Fryxell, fed

by 24 ephemeral streams from 15 glaciers (Lyons et al., 1998a). Glaciers, which cover roughly 40% of Taylor Valley, are the primary source of meltwater in the valleys. Glacier meltwater streams flow for ~ 6–10 weeks during the austral summer from November to January; flow is highly variable both daily and seasonally (Conovitz et al., 1998). The perennial lake ice covers (3–6 m) have a profound effect on the chemical, biological, and physical processes in the lakes. The primary loss of water from the lakes occurs by sublimation of the ice cover, which is replenished by the freezing of surface lake water on the bottom of the ice cover (Clow et al., 1988), while there is a lesser loss via evaporation of the moat (i.e. melted region of ice cover at lake edge) water during summer months.

In addition to the Taylor Valley lakes, other waters in the MCM region were included in this study. Blood Falls is a hypersaline discharge from under the Taylor Glacier that flows into the west lobe of Lake Bonney (Mikucki and Priscu, 2007) (Fig. 1), and is thought to be a remnant of Tertiary age seawater previously trapped in Taylor Valley when it was a fjord (Lyons et al., 2005). Lake Joyce, an ice-dammed, proglacial closed-basin lake is situated against a marginal lobe of the Taylor Glacier, located in Pearse Valley (Fig. 1). In Wright Valley northwest of Taylor Valley, the Onyx River is the largest of the meltwater streams in MCM (Fig. 1). It supplies water to Lake Vanda, another closed-basin lake (Fig. 1). Don Juan Pond is a hypersaline pond that is located in the south fork of Wright Valley about 9 km west of Lake Vanda (Fig. 1). It has been interpreted as a groundwater discharge zone (Harris and Cartwright, 1981), but recent work suggests that surface inflow from higher elevations is the major source of water to Don Juan Pond (Dickson et al., 2013). Specific characteristics (lake depth, history, age) of these features are noted in Table 1. In addition, freshwater ponds were sampled above the Nussbaum Riegel at elevation in Taylor Valley. These ponds have been termed the “Upland Ponds” and consist of the Parera Pond and Kaki Pond complexes (Fig. 1) (Lyons et al., 2012).

In order to help provide context to our Antarctic lake samples, saline lake samples from some  $\text{SO}_4^{2-}$ -rich Canadian salt lakes in Saskatchewan (Waldsea Lake, Deadmoose Lake, and Little Manitou) and  $\text{HCO}_3^-$ -rich Great Basin, USA, salt lakes (Abert Lake and Goose Lake) were analyzed for B and  $\delta^{11}\text{B}$  (see Witherow and Lyons, 2011, for the details on lake locations and their chemical compositions).

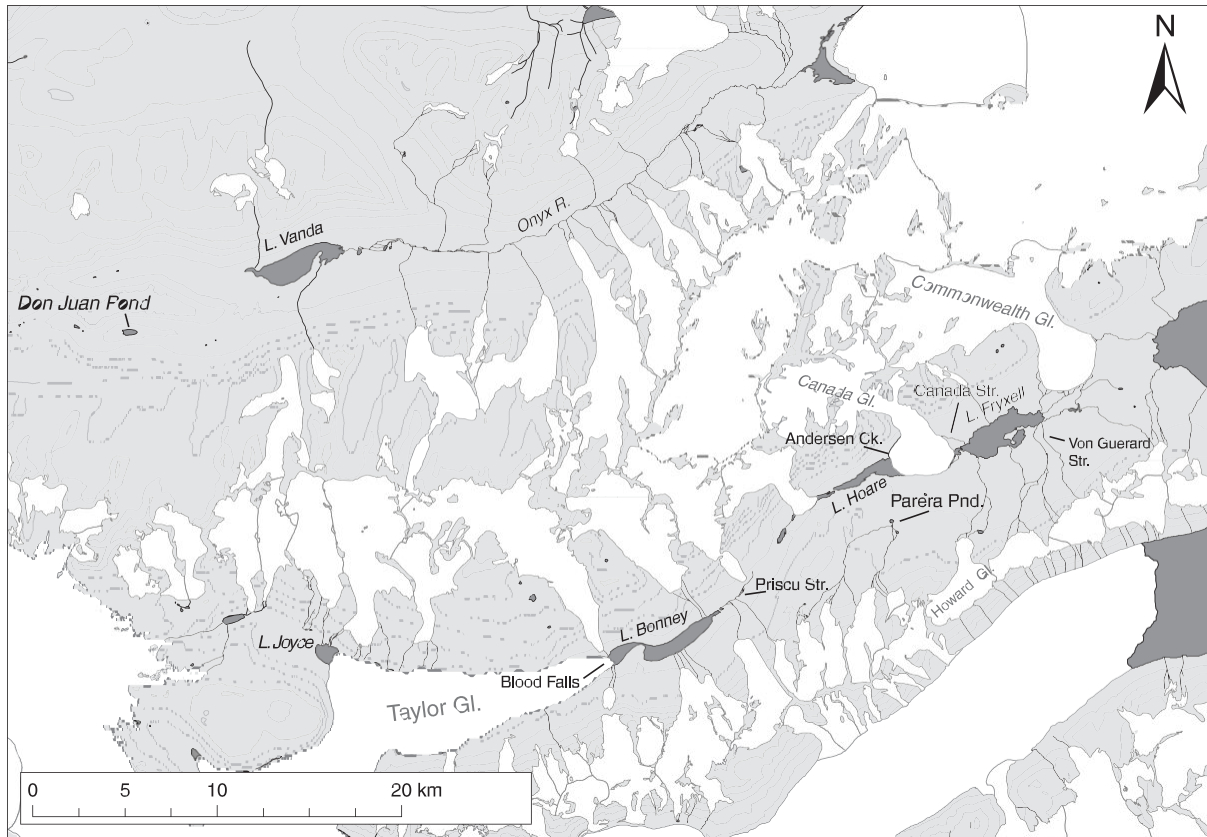


Fig. 1. Map of McMurdo Dry Valleys indicating sampled locations for  $\delta^{11}\text{B}$  within this study in Taylor and Wright Valleys. Light gray areas are ice-free, and dark gray areas are ice-covered water. Lakes within Taylor Valley are Lake Fryxell, Lake Hoare, Lake Bonney, and Lake Joyce, trending east to west in-valley. Glacier meltwater streams include Canada Stream and Von Guerard Stream in Fryxell Basin; Andersen Creek in Hoare Basin; and Blood Falls and Priscu Stream in Bonney Basin. Parera Pond is part of the Upland Ponds complex in Taylor Valley. Taylor Valley glaciers include Canada, Commonwealth, Howard, and Taylor. To the northeast in Wright Valley, the Onyx River flows east–west into Lake Vanda. Don Juan Pond is further west in Wright Valley.

## Materials and methods

### *Sample collection*

In December 2008, as part of the MCM-LTER program, samples were collected at different depths from Lakes Bonney (East and West lobes), Hoare, and Fryxell. A snow sample from the Howard Glacier and an ice sample from Taylor Glacier, were also collected in January 2009 (Fig. 1). Water profiles of Lakes Vanda (collected in December 2007) and Joyce (collected in December 2003) and a Don Juan Pond sample (collected in January 2006) were obtained from samples archived at Byrd Polar Research Center (BPRC), The

Ohio State University, Columbus, Ohio.

Lake profile samples were collected with 5-L Niskin bottles using standard oceanographic/limnetic techniques (procedure found at <http://mcmlter.org>). Samples were filtered through 0.4  $\mu\text{m}$  Whatman™ Nuclepore™ filters into acid washed polyethylene bottles, using a pre-cleaned plastic filtering apparatus and technique outlined in Welch et al. (2010). In January 2009, stream samples were collected at each stream gage site (<http://mcmlter.org>) and filtered in the field directly into pre-cleaned 60 ml polyethylene bottles through a plastic syringe using an attached 0.45  $\mu\text{m}$  Whatman filter cap. Pond water from the Up-land Ponds (Parera Pond, Parera South Pond, Parera West Pond, Khaki Pond) in Taylor Valley and Don Juan Pond in Wright Valley was sampled as far from shore as feasible without stepping directly into the water and re-suspending bottom sediment (usually about 0.5 m inward and at water depths from 5 to 25 cm). Blood Falls brine (collected in January 2008), an archived BPRC sample, was also analyzed. In the BPRC archive, samples are stored dark, but not chilled. The 2008–2009 filtered samples were stored chilled, in the dark, and transported back to McMurdo Station. Samples collected in 2008–2009 were transported back to Ohio State, and upon arrival in the USA, samples were kept stored under refrigeration.

### ***Leaching experiments***

It is now recognized that the solubilization of salts from aeolian transported dust can be a major source of dissolved material to glacier surfaces in MCM (Fortner et al., 2005; Bagshaw et al., 2007). In order to determine the influence of salt dissolution from aeolian debris to the contribution of B in MCM streams, we carried out a simple experiment. Materials from various aeolian landforms and sampling platforms within the MCM were leached with DI water using the method of Deuerling et al. (2014). These simple experiments were undertaken to examine the quantitative effect that liquid water (e.g., snow/ice melt) would have on the production of solutes. Samples from aeolian sediment traps, glacier surfaces, and lake ice cover surfaces that had accumulated aeolian materials from across Taylor Valley were used in our experiments. The aeolian traps used to collect materials were bundt pans mounted 30 cm above the ground, and were part of a long-term MCM-LTER experiment (Šabacká et al., 2012; Deuerling et al.,



2014). These experiments took place at Ohio State on samples that had been stored in the dark in plastic containers at room temperature. Each experiment consisted of two “leachings” with water. In the first leach (“Leach 1”), 50 ml of DI water was added to 25 g of sample sediment and then agitated for 5 min. The leachate was collected by filtering the water through a plastic filter tower containing 0.4  $\mu\text{m}$  Whatman™ Nuclepore™ membrane filter into a pre-cleaned Nalgene low density polyethylene (LDPE) bottle. Another 50 ml of DI water was added to the previously leached sample and then the container was capped and placed in a  $-20\text{ }^{\circ}\text{C}$  freezer for  $\sim 72$  h. After this time, the containers were removed and placed in a laminar flow hood to thaw. Once completely melted, the leachate (“Leach 2”) was filtered in a similar manner as Leach 1 into clean Nalgene LDPE bottles. These samples were stored at  $4\text{ }^{\circ}\text{C}$  until the time of analysis. These experiments were meant to examine the potential of water contact and freeze–thaw action of the release of B into glacier melt, not to quantify the B flux from these materials.

### ***Ion chromatography***

Major cations and anions (i.e.,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ) from surface water samples and experimental leachates were analyzed using ion chromatography (IC) by the techniques described by Welch et al. (2010). Surface water samples were analyzed within the year collected in Crary Laboratory, McMurdo Station, Antarctica; leachates were analyzed within a month of the experiment at Ohio State University. The precision of all the  $\text{Na}^+$  and  $\text{Cl}^-$  measurements is  $\pm 0.7\%$  using relative standard deviation. The accuracy of the measurements based on analysis of check standards is  $\pm 5.1\%$  and  $1.5\%$ , respectively.

### ***Inductively coupled plasma mass spectrometry***

Dissolved B concentrations for all stream, lake water, and leachate samples were measured at Trace Element Research Laboratory (TERL) at Ohio State University using a Perkin Elmer ELAN 6000 quadrupole based inductively coupled plasma mass spectrometer (ICP-MS) with a detection limit of  $0.05\text{ }\mu\text{M}$  of B. Standards and blanks were run repeatedly during the analysis to allow for correction of instrumental drift and sample

washout. The precision of the B measurements was 4–6%. The accuracy, based on the analysis of check standards and calculated using relative standard error, was  $\leq 10\%$ . A 2%  $\text{HNO}_3^-$  rinse was performed to eliminate B residue within the instrument to lower the background signal intensity.

**Table 1**

Descriptions and characteristics of McMurdo Dry Valley lakes (Lakes Fryxell, Hoare, Bonney- East and West, Joyce, Vanda), Don Juan Pond, and Blood Falls brine (Wilson, 1964; Hendy et al., 1979; Matsubaya et al., 1979; Lyons et al., 1998b; Poreda et al., 2004).

Feature	Lake depth profile (m)	Characteristics	History	Relative age
<i>Taylor Valley</i>				
Lake Fryxell	5–18	Brackish hypolimnion	Evaporated to a playa	At least 1000 years old
Lake Hoare	4–29	Fresh	Current glacier melt derived	~1000 years old
Lake Bonney, East	4–37	Hypersaline hypolimnion	Lost ice cover; cryoconcentrated	Possibly 100,000s of years
Lake Bonney, West	4–38	Hypersaline hypolimnion	Cryoconcentrated seawater ?	Possibly 100,000s of years
Blood Falls	Surface	Saline discharge to Lake Bonney from beneath Taylor Glacier	Cryoconcentrated snowpack / subsurface ice	~Tertiary age?
Lake Joyce	6–33	Chemocline, salinity gradient	?	?
<i>Wright Valley</i>				
Lake Vanda*	4–73.5	Hypersaline deep waters	Lost ice cover; cryoconcentrated	?
Don Juan Pond*	Surface	Hypersaline evaporitic pond	Frozen marine fjord	?

\* $\text{CaCl}_2$  composition, while others are NaCl solution.

### ***Boron isotope ratio measurements***

Boron isotopic compositions, of selected MCM streams and MCM, Saskatchewan, and Great Basin lakes, were measured by negative ion thermal ionization mass spectrometry (TIMS) on a Thermo Fisher TRITON thermal ionization mass spectrometer at Duke University, Durham, NC. One milliliter of sample was oxidized for a minimum of 24 h with 25  $\mu\text{l}$  of ultra-pure trace grade hydrogen peroxide to remove organics. In an attempt to load a minimum of 1 ng of B, the volume of sample loaded varied between 1 and 12  $\mu\text{l}$ , based on each sample B concentration. Ideally between 3 and 5 ng of sample was loaded to approximate the amount of NIST 951 standard (5 ng) that was measured. Samples were directly loaded onto Re filaments along with 2  $\mu\text{l}$  of artificial seawater load solution prepared from single element solutions of ICP-MS grade Na, Mg, Ca, and K with final concentrations of roughly 8000 ppm, 1300 ppm, 500 ppm, and 400 ppm, respectively. The certified B blank of this load-solution was 30 ppt (pg/g). The artificial seawater solution allows for a more consistent pre-heat and ionization sequence (Foster et al., 2013). The combined load solution and sample were dried at 0.5A and then heated briefly

(~ 10 s) to 0.8 A. Samples and standards typically ionized at between 890 °C and 950 °C, with in-run mass dependent fractionation less than 0.2‰ over 30–60 min.

Boron isotope ratios of samples were normalized to the long-term average  $^{11}\text{B}/^{10}\text{B}$  of the NIST SRM 951 ( $4.0067 \pm 0.001$ ,  $1\sigma$ ,  $n = 238$ ) that were prepared and measured with similar methods and reported as  $\delta^{11}\text{B}$ , where  $(^{11}\text{B}/^{10}\text{B}_{\text{sample}}/^{11}\text{B}/^{10}\text{B}_{\text{NBS951}}) - 1] \times 1000$ . The long-term precision of NIST SRM was  $\pm 0.25\text{‰}$ , whereas replicate analysis of our samples was higher with an estimated sample precision of 1–2‰. Interlaboratory comparison between the NTIMS procedures analyzed at Duke University, as described here, are consistent with multiple laboratories using MC-ICPMS and NTIMS as reported by Foster et al. (2013).

## Results

### *Major ion and B concentrations*

Depth profiles of Cl and Na (supplemental data) display the chemical stratification within each lake as observed previously in the MCM-LTER program (Lyons et al., 1998a, 2005). Chloride and sodium concentrations increase with depth in all the lakes. Chloride concentrations range from 0.3 mM in the surface water of Lake Hoare to  $7.9 \times 10^3$  mM in Don Juan Pond (supplemental data). The hypolimnia of Lakes Bonney and Vanda, Don Juan Pond, and Blood Falls brine are highly concentrated in Cl relative to seawater. Sodium concentrations range from 0.26 mM in surface waters of Lake Hoare to  $2.2 \times 10^3$  mM in the bottom waters of East Lake Bonney (supplemental data). The hypolimnia of Lake Bonney (East and West) and Blood Falls brine are enriched in Na concentrations compared to seawater.

The Na profiles have a similar shape to the Cl profiles, but each lake has a characteristic transition depth to higher salinity. Lake Hoare has the “freshest” lake waters with the lowest Cl and Na of any of the lakes, and the transition to higher concentrations occurs at 4–12 m. The Upland Ponds Cl and Na range over two orders of magnitude, demonstrating the significance of evapoconcentration via freezing and sublimation and salt dissolution (Lyons et al., 2012). Parera West has higher concentrations reflecting more brackish waters, while the other Upland Ponds have values similar to lake surface waters. Lake Joyce's chemocline occurs at 12–20 m, with a

distinct separation between fresher upper waters and brackish bottom waters. Lake Fryxell is brackish at all depths, and Cl and Na increase linearly with depth.

Lake Bonney surface waters have Cl and Na that are similar to those in Lake Fryxell. The chemocline occurs at ~ 13–30 m and ~ 14–20 m, respectively in the east and west lobes of Lake Bonney; Cl and Na increase sharply at the transition to the hypolimnia. Lake Vanda concentrations are slowly increasing and fresh to 50 m, with an abrupt concentration increase at 55–60 m. The hypolimnia of Lake Vanda and Don Juan Pond in Wright Valley are considered Ca–Cl waters with much higher Ca/Na and ~ 10× lower Na/Cl than the Taylor Valley lakes. The Taylor Valley lakes typically have equimolar Cl and Na, consistent with other North American Na–Cl lakes (Witherow and Lyons, 2011).

Boron concentrations increase with depth in all lakes, and concentrations vary over three orders of magnitude from ~1.5  $\mu\text{M}$  in the surface of Lakes Hoare and Vanda to ~ 4.3 mM at depth in the east lobe of Lake Bonney (Fig. 2; supplemental data). The hypersaline waters in Lake Bonney and the Blood Falls brine have the highest B concentrations, which are greater than levels in seawater. The B/Cl ratios in all of the Taylor Valley Lakes (Fig. 3) are 1× to 4× greater than in seawater, as previously noted by Lyons et al. (2005). The B/Cl ratio in the hypolimnetic waters of Lake Bonney is very similar to that of seawater, while the Ca–Cl waters of Lake Vanda and Don Juan Pond have lower B/Cl ratios than seawater. The B/Cl ratios of the Upland Ponds are lower than seawater, but similar to the surface waters of Lake Vanda (Fig. 3).

Boron concentrations in the freshest waters from streams, ponds, and glacier ice ranged from 0.093  $\mu\text{M}$  to 33  $\mu\text{M}$  (supplemental data). In general, B concentrations in the streams varied inversely with stream discharge (<http://mcmlter.org>), with higher concentrations at low discharges and low concentrations at higher discharges. There was no spatial pattern observed in stream B concentrations. In the Upland Ponds of Taylor Valley, B concentrations were higher compared to the streams, and B concentrations in Taylor Glacier ice and Howard Glacier snow were below our detection of ~0.046  $\mu\text{M}$  (supplemental data).

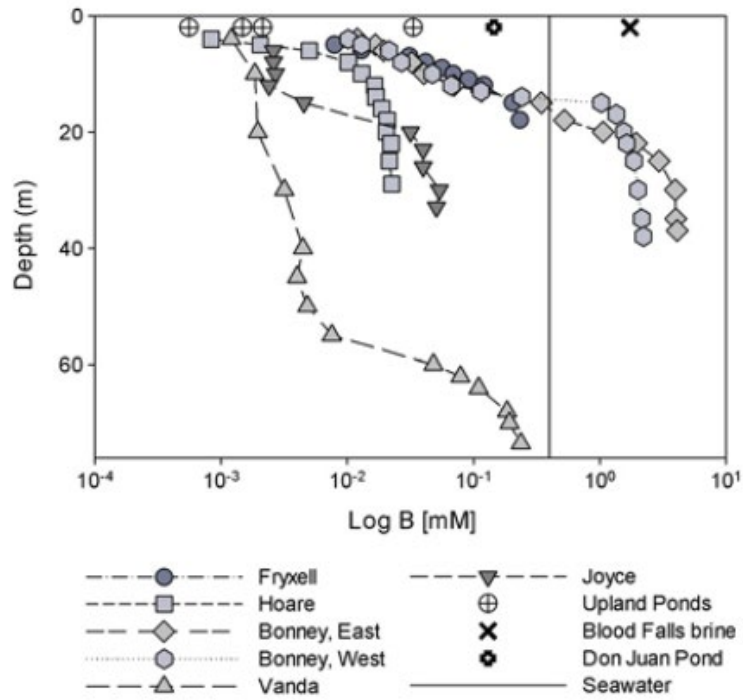


Fig. 2. Depth profiles of boron concentrations in MCM lakes, with Upland Ponds, Blood Falls brine, and Don Juan Pond. This is shown as a log plot.

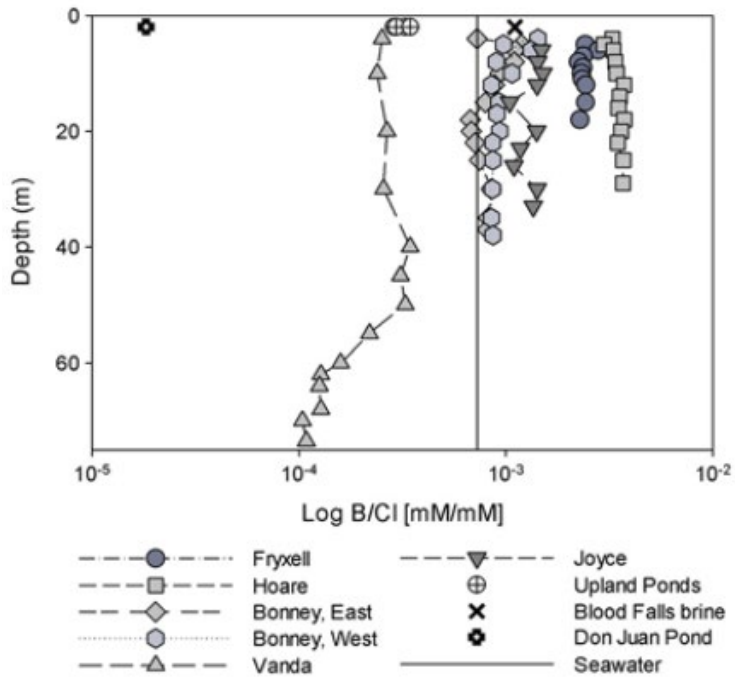


Fig. 3. B/Cl molar ratios for each MCM lake depth profile, with Upland Ponds, Blood Falls brine, and Don Juan Pond. This is shown as a log plot.

Concentrations of water soluble B in the aeolian samples ranged from 0.6 pmol/g to 13 pmol/g (supplemental data). Leach 1 yielded higher B concentrations than the freeze–thaw aliquot of Leach 2, suggesting that the majority of B present is readily soluble. The aeolian trap leachates contained the highest B concentrations, compared to leachate solutions derived from the lakes and glacier surfaces, perhaps indicating a loss of B from the materials initially deposited on these sometimes melted surfaces (supplemental data). The aeolian trap leachate B concentrations decreased progressively from east to west into Taylor Valley, with Lake Fryxell having the highest concentrations, followed by Lake Hoare, and then Lake Bonney.

Boron concentrations from the other saline lake samples from Saskatchewan, Canada, and Great Basin, USA, ranged from 0.31 mM in Deadmoose Lake of Saskatchewan to 9.7 mM in Abert Lake of the Great Basin (supplemental data). The Great Basin lakes (Abert Lake and Goose Lake) had the highest B concentration compared to all the lakes studied. The Saskatchewan lakes (Waldsea Lake, Deadmoose Lake, and Little Manitou) had similar B concentrations to East Lake Bonney.

### ***Boron isotopic data***

Water samples from MCM had  $\delta^{11}\text{B}$  values that ranged from +12.3‰ (Canada Stream) to + 51.4‰ (bottom water of East Lake Bonney) (Table 2). The  $\delta^{11}\text{B}$  concentrations from the other saline lake samples from Saskatchewan, Canada, and Great Basin, USA, were +39.4‰ for Little Manitou Lake of Saskatchewan, +14.6‰ for Goose Lake, and + 11.6‰ for Abert Lake, both of the Great Basin, USA (Table 2). The MCM stream water  $\delta^{11}\text{B}$  ratios varied between +12.3‰ and + 28.5‰. A group of stream waters (Onyx River, Priscu Stream, and Canada Stream) had the lowest B concentrations and lower  $\delta^{11}\text{B}$  values. Waters from Von Guerard Stream and Parera Pond are isotopically heavier than the other streams, but also have slightly higher B concentrations. Andersen Creek and Blood Falls samples exhibit the highest stream concentrations, and have the most positive isotopic values of all the streams. Lake Hoare surface and bottom waters have similar  $\delta^{11}\text{B}$  values, with a small increase in the bottom water (surface = + 23.1‰;

bottom = + 25.6‰). Lake Fryxell also displays similar  $\delta^{11}\text{B}$  isotopic values for the surface (+ 28.9‰) and bottom (+28.8‰) water. Lake Joyce  $\delta^{11}\text{B}$  was 14‰ more positive in the bottom water (+38.0‰) than the surface water (+23.6‰). The  $\delta^{11}\text{B}$  of surface water of Lake Bonney (ELB = East Lake Bonney; WLB = West Lake Bonney) is isotopically similar in both lobes (ELB = +43.4‰; WLB = +42.7‰), while the bottom water  $\delta^{11}\text{B}$  values were ~6‰ more positive (ELB = +51.4‰; WLB = +48.5‰) than the surface waters. The Blood Falls brine, with a  $\delta^{11}\text{B}$  value of +46.9‰, was isotopically more positive by ~ 18‰, compared to the Blood Falls stream sample (+ 28.5‰) suggesting a mixing of the more positive brine with lighter glacier melt. Lake Vanda  $\delta^{11}\text{B}$  was ~ 9‰ more positive in the bottom water (+44.9‰) than the surface lake water (+ 35.9‰), while the lake's source water, the Onyx River, was only + 17.7‰. Don Juan Pond had an intermediate  $\delta^{11}\text{B}$  value of +32.5‰.

**Table 2**

$\delta^{11}\text{B}$  and B concentrations of MCM waters (lake surface and bottom depths, streams, and ponds) and North American saline lakes in Saskatchewan, Canada, and Great Basin, United States.

Global location	Water sample location	$\delta^{11}\text{B}$ (‰)	B (mM)
McMurdo Dry Valleys	<i>Streams</i>		
	Von Guerard Stream	23.6	0.002
	Canada Stream	12.3	0.001
	Priscu Stream	18.6	0.001
	Onyx River	17.7	0.000
	<i>Saline inputs</i>		
	Andersen Creek	28.8	0.013
	Blood Falls Stream	28.5	0.019
	Blood Falls brine	46.9	1.74
	<i>Ponds</i>		
	Don Juan Pond	32.5	0.146
	Parera Pond	28.4	0.002
	<i>Lake and sample depth</i>		
	Lake Fryxell 6 m	28.9	0.019
	Lake Fryxell 18 m	28.8	0.233
	Lake Hoare 5 m	23.1	0.003
	Lake Hoare 22 m	25.6	0.022
	Lake Bonney, East 6 m	43.4	0.019
	Lake Bonney, East 35 m	51.4	4.01
	Lake Bonney, West 5 m	42.7	0.013
	Lake Bonney, West 35 m	48.5	2.15
	Lake Joyce 8 m	23.6	0.003
	Lake Joyce 33 m	38.0	0.051
Lake Vanda 10 m	35.9	0.003	
Lake Vanda 73.5 m	44.9	0.236	
North America	Little Manitou Lake, Saskatchewan, Canada	39.4	2.29
	Goose Lake, Great Basin, United States	14.6	1.04
	Abert Lake, Great Basin, United States	11.6	9.7

## Discussion

### *Terrestrial B inputs and dynamics*

Boron concentrations in the upper continental crust vary greatly from 17 and 47  $\mu\text{g/g}$ , respectively, according to Wedepohl (1995) and Hu and Gao (2008). Sedimentary rocks, especially shale ( $B = 9.3 \mu\text{M/g}$  from Taylor and McLennan, 1985), have higher B concentrations than most crystalline rocks (Li, 2000). Due to the relatively small ionic radius and high charge of B, it does not substitute well into major aluminosilicate minerals, and is considered an incompatible lithophile element. However, B-rich aluminosilicates do occur. The tourmaline group minerals, especially schorlite,  $\text{NaFe}_3\text{B}_3\text{Al}_3(\text{OH})_4(\text{Al}_3\text{Si}_6\text{O}_{27})$  and elbaite,  $\text{Na}_2\text{Li}_3\text{B}_6\text{Al}_9(\text{OH})_8(\text{Al}_3\text{Si}_6\text{O}_{27})_2$  occur in granitic pegmatites (Kerr, 1959).

Granulite facies rocks in Larsemann Hills, East Antarctica, have recently been found to have B concentrations in the range of 680–19,700  $\mu\text{g/g}$  (Grew et al., 2013). This B enrichment has been attributed to premetamorphic hydrothermal alteration. The  $\delta^{11}\text{B}$  of these B rich lithologies are isotopically typically light, ranging from  $-17.8\text{‰}$  to  $-2.8\text{‰}$  (MacGregor et al., 2013). Tourmaline has also been observed as an accessory mineral in pelitic shists and gneisses in Northern Victoria Land, Antarctica (Grew and Sandiford, 1984). Although there are other locations with similar lithologies in East Antarctica (Grew et al., 2013), none of these lithologies have been identified in the MCM region.

We assume that the terrestrial, i.e. continental crust, source of B to the aquatic system is the chemical weathering of aluminosilicate minerals. Although granitoid rocks are abundant in Taylor and Wright Valleys, we were unable to find any B data from these rocks, and there is no mention of tourmaline existence in these rocks (Smillie, 1992; Allibone et al., 1993). Hence, the specific terrestrial aluminosilicate source of  $^{10}\text{B}$ -rich lithogenic rock to the MCM aquatic systems remains unknown. Other potential terrestrial sources include the dissolution of B-salts produced by cryoconcentration/evaporation in wetted soils and aeolian debris, and from marine aerosol deposits on the glaciers and in stream channels, and relict seawater.

Vengosh et al. (1991b) have utilized Na/Cl and B/Cl molar ratios to distinguish among sources of dissolved solids to salt lakes. B/Cl and Na/Cl ratios display large variability within MCM (Fig. 4). Boron concentrations in snow from the Howard Glacier and



ice from Taylor Glacier were below our detection limit. If we assume that the B concentration in snow and ice is at our detection limit of  $0.046 \mu\text{M}$ , the B/Cl ratio of snow and ice would be  $\leq 0.007$  and an order of magnitude greater than seawater ( $\text{B/Cl}_{\text{seawater}} = 0.0007$ ). The Na/Cl ratio of snow ( $\text{Na/Cl} = 0.64$ ) is less than seawater ( $\text{Na/Cl} = 0.86$ ), and the Na/Cl ratio of Taylor Glacier ice ( $\text{Na/Cl} = 0.98$ ) is higher than seawater.

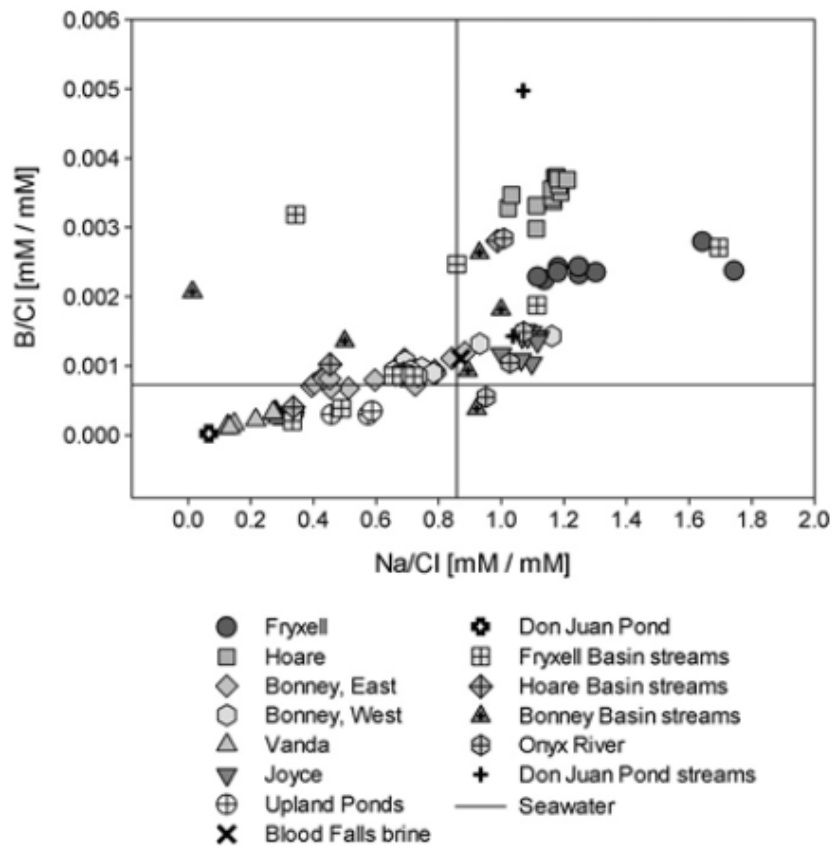


Fig. 4. Na/Cl and B/Cl molar ratios across each MCM lake depth profile, Upland Ponds, Blood Falls brine, and Don Juan Pond with a comparison to streams grouped by lake basin.

Na/Cl and B/Cl molar ratios of the leached aeolian materials ( $\text{Na/Cl} = 0.4\text{--}7.8$ ;  $\text{B/Cl} = 9.4 \times 10^{-7}\text{--}8.5 \times 10^{-5}$ ; supplemental data) also indicate additions and depletions of Na relative to Cl but only depletions of B relative to Cl compared to seawater. These values could also suggest the input of halite with little addition of B. Na/Cl ratios of 0.6 to  $\sim 0.8$  indicate the importance of marine aerosol input, while Na/Cl ratios of 0.8 to

1.1 are consistent with a halite signal (Vengosh et al., 1991b). High Na/Cl values may also indicate an influence of NaSO<sub>4</sub> salts, which are abundant in the MCM valleys. The majority of leachate samples fall along a mixing line between marine salts (Na/Cl = 0.86; B/Cl =  $7 \times 10^{-4}$ ) and halite (Na/Cl = 1, B/Cl = 0), with leachates being depleted in B compared to seawater by ~ 1 to 3 orders of magnitude. The samples with Na/Cl ratios N 1.2 were from aeolian landforms in Taylor Valley, while the aeolian trap data yielded lower ratios. The aeolian trap leachates had Na/Cl ratios from 0.72 to 1.83 and B/Cl ratios of  $9.4 \times 10^{-7}$  to  $8.8 \times 10^{-6}$ . The aeolian trap samples from the Fryxell and Hoare basins have higher B/Cl ratios than the Bonney basin. Because B concentrations in atmospheric aerosols can be enriched by a factor of 2–3 orders of magnitude compared to both the seawater and continental crust (Fogg and Duce, 1985), we hypothesize that these elevated B concentrations likely reflects its proximity to the Ross Sea. This would suggest that modern day marine aerosols are an important source of B to the MCM.

Lakes Hoare, Fryxell, and Joyce are enriched in Na and B compared to Cl at all depths, relative to seawater. Lemarchand et al. (2000) determined that inputs from chemical weathering dominate the global B flux to the ocean. Previous works suggests that the Taylor Valley lakes (Lakes Fryxell and Hoare) must derive significant stream inputs from chemical weathering like the dissolution of silica (Welch et al., 2010). While much less is known about the hydrology and history of Lake Joyce, Green et al. (1988) reported that five inflowing streams contributed ~  $2 \times 10^6$  L of water annually to Lake Joyce, and Shacat et al. (2004) suggested that extensive chemical weathering occurs in Lake Joyce streams because of the high dissolved Al that were observed in the lake surface waters. Dissolved Si concentrations, which range between 80  $\mu$ M and 486  $\mu$ M and increase with depth through the Lake Joyce water column (Si data on <http://mcm.lter.org>), are similar to dissolved Si profiles in Lake Fryxell's 5–12 m depth range (Pugh et al., 2003). These high dissolved Si concentrations reinforce the importance of chemical weathering of aluminosilicates, while strong, statistically significant correlations between dissolved Si and B in these three lakes suggest that B is also derived from aluminosilicate weathering ( $r^2 = 0.63$ ,  $P < 0.05$  (95% CI [0.11, 0.97]) in Lake Joyce;  $r^2 = 0.89$ ,  $P < 0.01$  (95% CI [0.80, 0.99]) in Lake Hoare; and  $r^2 = 0.91$ ,  $P < 0.01$  (95% CI [0.82, 0.99]) in Lake Fryxell). The correlations between dissolved Si and B in

Lake Bonney are weaker, which was previously interpreted to indicate that B in Lake Bonney is predominantly of marine origin (further discussed below) ( $r^2 = 0.55$ ,  $P < 0.01$  (95% CI [0.38, 0.90]) in West Lake Bonney;  $r^2 = 0.06$ ,  $P < 0.1$  (95% CI [-0.30, 0.68]) in East Lake Bonney).

The majority of the stream Na/Cl and B/Cl molar ratios are similar to the lakes that receive input from many glacier meltwater streams. Therefore, we surmise that solutes are controlled by chemical weathering of aluminosilicate minerals within the stream channels (Fig. 4). The outliers are two Lake Fryxell basin streams, the Don Juan Pond inflow, and Blood Falls stream. Both Blood Falls stream and Von Guerard Stream in the Fryxell basin display B enrichment relative to Cl, and Aiken Creek and Don Juan Pond inflow have Na and B enrichments relative to Cl. Why these streams deviate from the majority of the others is not known, but could reflect small-scale differences in mineral distribution within the streams channels or the presence of other soluble sources of B such as B/Cl enriched marine aerosol.

### ***Marine influences***

Unlike the Taylor Valley lakes, the B/Cl and Na/Cl relationships indicate that Lake Bonney, Lake Vanda, and Don Juan Pond have a marine-like end member, with lower B and Na relative to Cl (Fig. 4). However, the lower B/Cl ratio within Lakes Bonney and Vanda and Don Juan Pond could also be due to its loss from solution as the original water has become concentrated. Previous work by our group has clearly demonstrated that Lake Bonney is closely related to marine waters that have been evapoconcentrated and then slightly modified by freshwater input (Lyons et al., 2005). The geochemistry of the hypolimnion of Lake Fryxell also has a seawater-like influence (Lyons et al., 1999). Don Juan Pond and the bottom of Lake Vanda have much more complex evolutionary histories. We have used the Vengosh (2003) evaporation model to better understand the  $\delta^{11}\text{B}$  concentrations in these saline/ hypersaline MCM waters. The model is based on the evaporation of seawater at specific, controlled conditions, and it provides results only true when conditions are identical to those of Vengosh (2003). We realize that much more complex environmental conditions generated the waters in our study. We use this model to approximate of how  $\delta^{11}\text{B}$  might vary through evapoconcentration.

During the progressive evaporation of seawater, Na/Cl ratios decrease while B/Cl ratios and  $\delta^{11}\text{B}$  increase (Vengosh et al., 1992). Fig. 5 shows measured and simulated values of Na/Cl and  $\delta^{11}\text{B}$  ratios as the degree of seawater evaporation increases from 0% to 80% (Vengosh, 2003). Na/Cl ratios of the bottom waters of Lakes Bonney (East and West), Vanda, and Don Juan Pond correspond to a specific degree of evaporation, which was then used to predict a  $\delta^{11}\text{B}$  value. The seawater Na/Cl ratios follow a decreasing trend (0.87–0.07). The individual hypolimnia of the MCM lakes have Na/Cl ratios corresponding to increasing degrees of evaporation: West Lake Bonney 15% N East Lake Bonney 28% N Lake Vanda 54% N Don Juan Pond 74% (Fig. 5). The decreasing Na/Cl ratios are consistent with increasing evaporation (Fig. 4). However, if only evaporation was responsible, then the B/Cl ratios should increase as the Na/Cl ratios decrease, in contrast to the observed values. These data suggest that B may not be behaving conservatively relative to Cl in these systems, as one would expect higher B/Cl ratios (up to 0.005) than observed. Also the Na/Cl and B/Cl ratios of the Blood Falls brine and the surface waters of West Lake Bonney are similar to seawater. This supports previous work arguing that Blood Falls and Lake Bonney are geochemically closely related, and that both are derived from ancient seawater deposits frozen under the Taylor Glacier (Lyons et al., 2005).

In part, B isotope ( $^{11}\text{B}/^{10}\text{B}$ ) fractionation is due to differences in interatomic boron/oxygen vibrational energy and the symmetry between the trigonal B species (undissociated boric acid  $\text{B}(\text{OH})_3$ ) and the tetrahedral anion ( $\text{B}(\text{OH})^-$ ). A number of experiments have examined the isotopic fractionation of B, particularly during the adsorption of B from seawater onto marine clays (Shergina and Kamiskaya, 1967; Schwarcz et al., 1969; Palmer et al., 1987; Spivack and Edmond, 1987). This work found that the isotopic fractionation is dependent on the distribution of the two B species, temperature, pH, and clay mineralogy. During adsorption,  $^{10}\text{B}$  is preferentially incorporated onto the solid phase, likely as the tetrahedral form. As clays have a stronger affinity for  $\text{B}(\text{OH})^-$ , the conditions that are favored for the dominance of  $\text{B}(\text{OH})_3$  species (e.g. low pH 5–8) would cause a lower amount of B adsorption, but higher degree of isotopic fractionation (Vengosh et al., 1991a). Thus, the isotopic fractionation of B during the adsorption process is dependent on the distribution of the B species. During adsorption

onto clay minerals, the maximum boron isotopic transfer between water and mineral was 32‰, reported by Palmer et al. (1987). Therefore, this adsorption depletes  $^{10}\text{B}$  and total B in the water, and the water becomes enriched in  $^{11}\text{B}$  (Vengosh et al., 1991a).

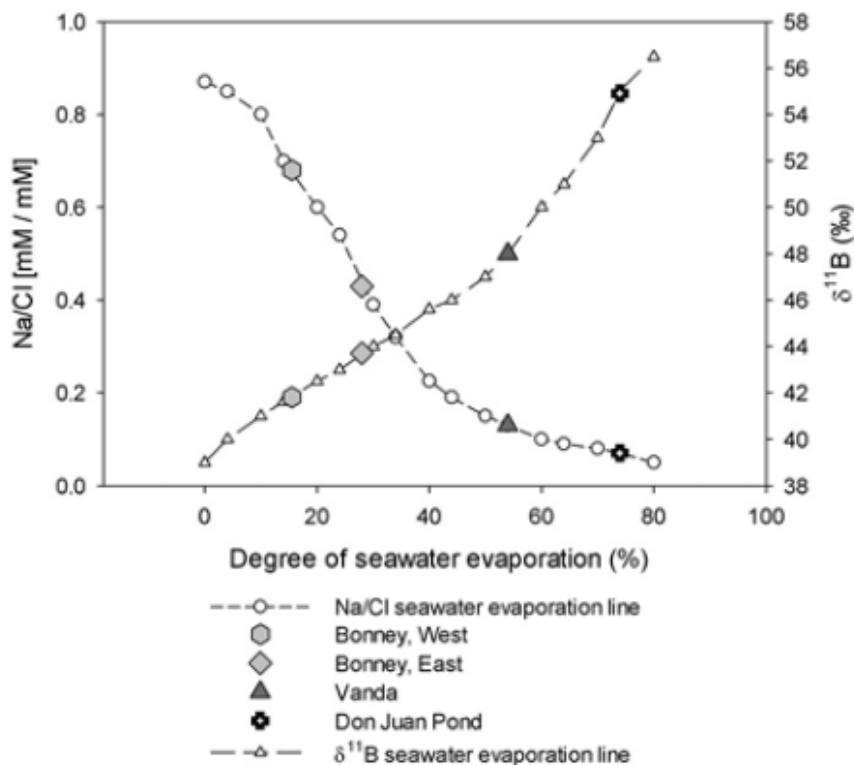


Fig. 5. Variations of Na/Cl molar ratios and  $\delta^{11}\text{B}$  (‰) during the evaporation of seawater (0% to 80%) with plots of the bottom waters of Lake Bonney—East and West, Lake Vanda, and Don Juan Pond along each progression (adapted from Vengosh, 2003). Na/Cl ratios were used to determine the degree of evaporation, which corresponds to the predicted value of  $\delta^{11}\text{B}$  displayed along each line.

The Antarctic stream and surface lake waters have circum-neutral to alkaline pHs ranging at 6.8–9.7, while deeper lake waters exhibit acidic to circum-neutral pHs at 5.3–7.4. The dissociation constant of the  $\text{B}(\text{OH})_3 + \text{H}_2\text{O} \rightleftharpoons \text{B}(\text{OH})_4^- + \text{H}^+$  is 8.6 at 25 °C (Dickson, 1990). Thus, at pH  $\geq$  8.6 borate ions dominate, while at pH  $<$  8.6 boric acid becomes dominant. The majority of MCM waters should have B in the boric acid form. Boron speciation observations from seawater suggest MCM waters with pHs  $<$  8.6 will have a corresponding  $\delta^{11}\text{B}$  ranging +20‰ to +50‰ (Kakihana et al., 1977). These values are similar to our  $\delta^{11}\text{B}$  measurements. So both the isotopic composition of the

source and the variation of pH in these lakes may help control the  $\delta^{11}\text{B}$  of the water.

The  $\delta^{11}\text{B}$  data along with the B/Cl and Na/Cl ratios provide even more geochemical information about these MCM waters. When the Na/Cl ratio is low (b 1; similar to seawater or lower if evaporation occurred) and  $\delta^{11}\text{B}$  is high, the source of dissolved solids to these lakes is dominated by salts derived from seawater or marine-derived aerosol, rather than from the chemical weathering of aluminosilicate minerals in the watershed (Vengosh et al., 1991b). Low B/Cl ratios and high  $\delta^{11}\text{B}$  values (N 39‰) have been interpreted as the interaction of brines with sediments within the lake system with loss of B due to adsorption onto solid surfaces (Vengosh et al., 1991b). MCM waters with lower  $\delta^{11}\text{B}$  (+10‰ to +30‰) values suggest mixing of solutes of marine origin, from which B has been partly removed by adsorption, with waters of terrestrial aluminosilicate weathering origin having low  $\delta^{11}\text{B}$  values (Vengosh et al., 1991b).

Using the degree of evaporation derived from Na/Cl ratios of Lakes Bonney, Vanda, and Don Juan Pond, we can estimate the  $\delta^{11}\text{B}$  for these MCM waters (Fig. 5) (McCaffrey et al., 1987; Raab and Spiro, 1991; Vengosh et al., 1992; Vengosh, 2003). The degree of evaporation is 15% for West Lake Bonney and 74% for Don Juan Pond, with East Lake Bonney and Lake Vanda in between (Fig. 5). The evaporation simulation predicts  $\delta^{11}\text{B}$  values of ~+42‰ for West Lake Bonney bottom water, ~+44‰ for East Lake Bonney bottom water, ~+48‰ for Lake Vanda bottom water, and ~+ 55‰ for Don Juan Pond. The actual measured  $\delta^{11}\text{B}$  values are ~+ 48.5‰ for West Lake Bonney bottom, ~+ 51.4‰ for East Lake Bonney bottom, ~+ 44.9‰ for Lake Vanda bottom, and ~+ 32.5‰ for Don Juan Pond (Table 2). The bottom waters of both lobes of Lake Bonney are slightly more positive than the model estimate (~7‰), Lake Vanda is very close to the estimated value, and Don Juan Pond has a much lighter  $\delta^{11}\text{B}$  value (by ~ 23‰). This exercise demonstrates that these MCM hypersaline, hypolimnetic lake waters represent an evaporitic environment whose brine chemistries are similar to that of evaporated seawater, except for Don Juan Pond.

### ***$\delta^{11}\text{B}$ in closed-basin lakes***

#### ***Taylor Valley lakes***

As noted above, isotopic controls on the  $\delta^{11}\text{B}$  signature of these MCM lake waters

can be related to the source of B (a terrestrial aluminosilicate weathering component versus a marine component) and to the physiochemical processes of adsorption or mineral precipitation occurring within the lakes. The terrestrial component of aluminosilicate mineral weathering is represented by the glacier meltwater end-member (an average of Onyx River, Priscu Stream, and Canada Stream) with  $\delta^{11}\text{B}$  of  $+16\text{‰} \pm 3.4$ . This value is comparable to  $\delta^{11}\text{B}$  found in other rivers, as multiple studies have reported riverine  $\delta^{11}\text{B}$  measurements of  $-6\text{‰}$  to  $+42.8\text{‰}$  (e.g., Spivack, 1986; Lemarchand et al., 2000; Rose et al., 2000). Modern seawater has a  $\delta^{11}\text{B}$  of  $\sim +39\text{‰}$ , and after adsorption or mineral precipitation of a marine-like source, the  $\delta^{11}\text{B}$  evaporated/cryoconcentrated marine component is expected to be  $+39\text{‰}$ . The lighter isotope will be preferentially removed via adsorption or mineral precipitation to increase  $^{11}\text{B}$  within the residual water. The lighter  $\delta^{11}\text{B}$  values in the MCM streamwaters have the lowest B concentrations. Although a portion of this  $^{10}\text{B}$  could come from the desorption of clay minerals in the stream channels, we believe that this contribution is small due to the low concentration of clay minerals in these streams.

When all the MCM waters are plotted on a  $\delta^{11}\text{B}$  versus  $1/\text{B}$  plot, a linear trend is produced with the end-members of glacier meltwater and evaporated hypersaline lake water (Fig. 6). Stream waters (Canada Stream, Onyx River, Priscu Stream, and Von Guerard Stream) and surface waters from Lakes Hoare and Joyce are the freshest waters in the study. These waters are clearly dominated by a crustal input of B with lighter  $\delta^{11}\text{B}$  values and lower B concentrations indicative of silicate mineral weathering. This strongly supports the idea that terrestrial aluminosilicate weathering is a major source of B to the surface waters of Lakes Hoare and Joyce. The major water input to Lake Hoare is from Andersen Creek and direct inflow off of the Canada Glacier. Andersen Creek, Blood Falls, and Parera Pond are grouped due to their similar chemistries and heavier  $\delta^{11}\text{B}$  values compared to the other stream waters. Their  $\delta^{11}\text{B}$  signatures closely resemble the surface waters of Lake Fryxell and bottom waters of Lake Hoare (Figs. 6 and 7). Therefore, the data from Andersen Creek, Blood Falls, and Parera Pond waters indicate that they are a mixture of B from terrestrial aluminosilicate weathering and marine salts, either ancient relict seawater or more recent marine-derived aerosols. As stated earlier, the saline discharge of Blood Falls is from a marine-derived brine trapped beneath Taylor Glacier

that mixes with glacier melt (Lyons et al., 2005). Previous strontium isotope analysis of Blood Falls brine indicated a terrestrial weathering component associated with this brine (Lyons et al., 2002). The sources of the “excess” salt to Andersen Creek are currently unknown, but may be related to hypersaline subsurface flow close to the streams described by Harris et al. (2007) and more recently by Levy et al. (2012).

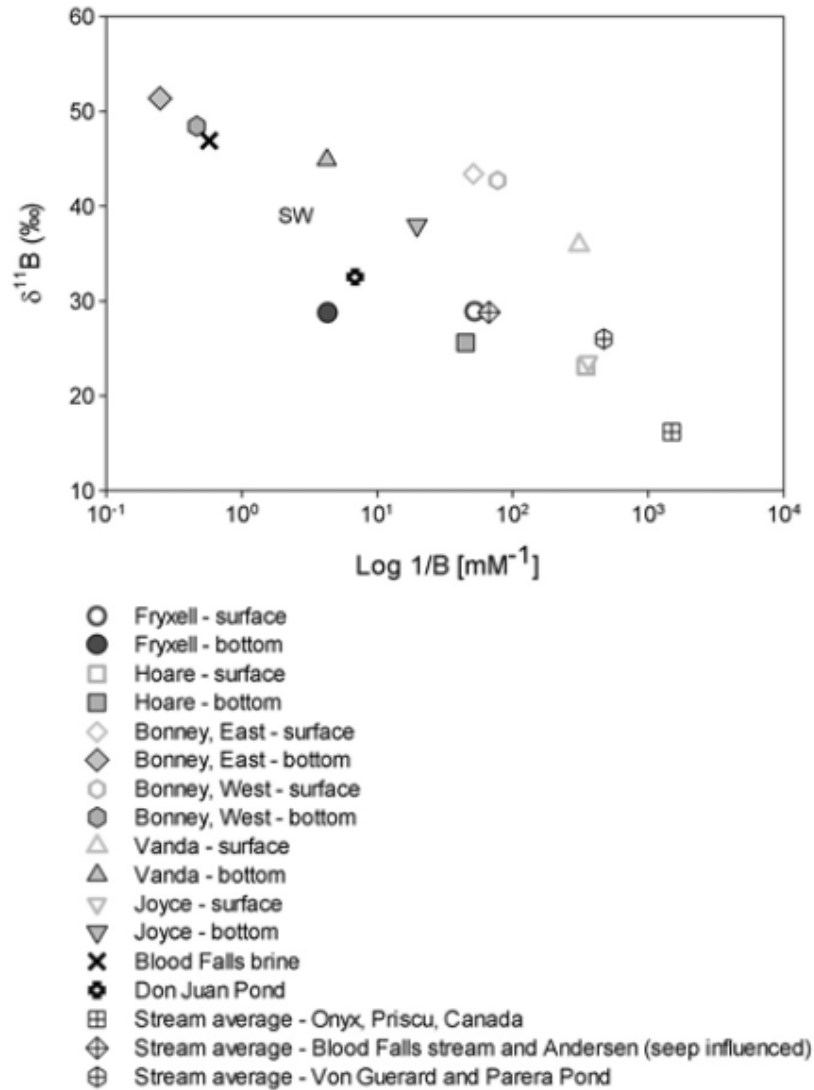


Fig. 6. Log 1/B [mM<sup>-1</sup>] and δ<sup>11</sup>B (‰) of MCM lake surface (open symbols) and bottom (filled symbols) waters, Blood Falls brine, Don Juan Pond, and stream averages grouped according to similar chemistries in comparison to seawater (SW).



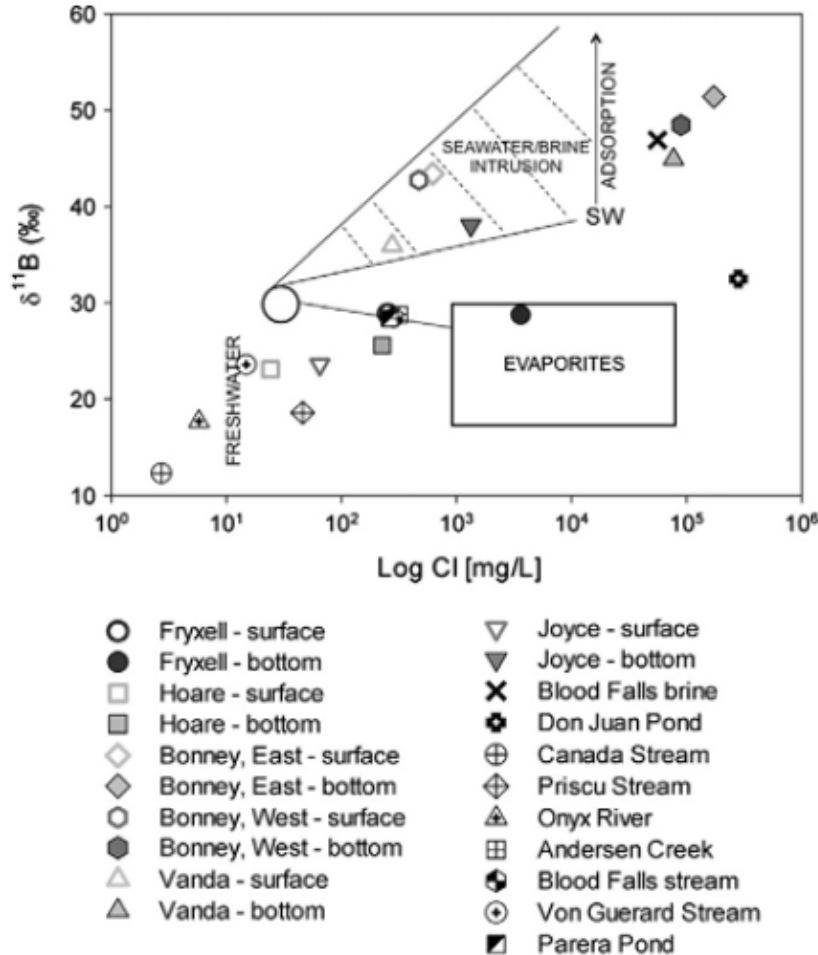


Fig. 7. Log Cl [mg/L] and  $\delta^{11}\text{B}$  (‰) of MCM waters in a schematic illustration of expected boron isotopic variation upon salinization by seawater intrusion, mixing with brines, and dissolution of marine evaporites (adapted from Vengosh, 2003). SW represents sea- water, open symbols are surface waters, and filled symbols are bottom waters.

The B concentrations in the surface waters of Lake Fryxell and the bottom waters of Lake Hoare are influenced by terrestrial aluminosilicate weathering sources (Figs. 6 and 7). Twelve meltwater streams flow into Lake Fryxell leading to a relatively light  $\delta^{11}\text{B}$  value, +28.9‰. Lake Hoare bottom waters have a  $\delta^{11}\text{B}$  of +25.9‰. These lighter  $\delta^{11}\text{B}$  values represent a larger terrestrial influence compared to the other Taylor Valley lakes. Lake Hoare is the youngest and freshest lake with the least chemical stratification (Lyons et al., 1999). Its chemical and iso- topic relationship to stream water is clearly demonstrated by its only slightly more positive  $\delta^{11}\text{B}$  than the Onyx River and Priscu Stream.

Lake Fryxell bottom waters are characterized by the flux of marine derived salt from

the sediments into the lake (McKnight et al., 1991; Aiken et al., 1996) (Fig. 6). Lyons et al. (1998a) suggested that this salt is derived in part from diffusion of a halite-saturated brine from the pore waters of a playa that began to fill with glacier meltwaters ~ 750–1000 years ago. The Na/Cl ratio of  $\geq 1$  for these bottom waters displays control by halite dissolution (Mehta et al., 2000a,b), while the  $\delta^{11}\text{B}$  of +28.8‰ suggests a mixture of terrestrial and marine sources. Within the  $\delta^{11}\text{B}$  and Cl concentration schema discussed above, the chemistry of these waters is predicted to be the result of the dissolution of marine evaporites (Fig. 7). There is no isotopic fractionation between the surface and bottom waters (Fryxell surface water  $\delta^{11}\text{B} = +28.9\text{‰}$ ) and the B/Cl and Na/Cl ratios are relatively constant throughout the water column. These constant ratios indicate that the B is derived from the combination of an isotopically constant freshwater input over the past ~ 1000 years that mixes with the diffusing brine from depth.

The surface waters of Lake Bonney (East and West) and bottom waters of Lake Joyce all have  $\delta^{11}\text{B}$  signatures resembling seawater (Figs. 6 and 7). While not much is known about the evolutionary history of Lake Joyce's hypolimnion ( $\delta^{11}\text{B} = +38\text{‰}$ ), this work suggests a marine source for B and perhaps for other solutes in the bottom waters. Because of its location in direct contact with the Taylor Glacier, a subglacial source of ancient seawater may have influenced Lake Joyce similarly to its influence of Lake Bonney via Blood Falls (Lyons et al., 2005). Surface waters of Lake Bonney (East and West) have very similar B values—both isotopically and elementally (Figs. 6 and 7). Lake Bonney surface waters have a higher  $\delta^{11}\text{B}$  signature (~+43‰) compared to seawater, which suggests some removal of the lighter  $^{10}\text{B}$  isotope has occurred either in the lake itself or prior to the B introduction into the lake.

The higher  $\delta^{11}\text{B}$  signature in Lake Bonney bottom waters and Blood Falls brine indicates loss of the lighter isotope as well. Blood Falls brine with a Na/Cl ratio of 0.87 clearly resembles seawater (Na/Cl = 0.86) as noted by Lyons et al. (2005). With a  $\delta^{11}\text{B}$  of +46.9‰, this brine has been greatly modified by  $^{10}\text{B}$  loss by adsorption or mineral precipitation that has increased its original marine signal. As noted above, this brine is a major source of B and other solutes to the upper waters of Lake Bonney. Blood Falls brine is more similar to the bottom waters of Lake Bonney than to the surface (Figs. 6 and 7). Lake Bonney bottom waters are the heaviest  $^{11}\text{B}$  waters in Taylor Valley (Lake Bonney,

East = + 51.4‰; Lake Bonney, West = +48.5‰) (Figs. 6 and 7). The East Lake Bonney values are comparable to the Dead Sea ( $\delta^{11}\text{B} = \sim +57\text{‰}$ ), both isotopically and in concentration (Vengosh et al., 1991a). West Lake Bonney bottom waters behave more like the predicted evaporation of seawater with B/Cl ratio increasing as the Na/Cl ratio decreases (Fig. 4). The B/Cl ratios of the bottom waters of East Lake Bonney, with a higher degree of evaporation, remain consistently seawater-like in the hypersaline hypolimnion, while the Na/Cl ratios decrease with depth. Numerous authors have argued that the east lobe of Lake Bonney lost its ice cover in the past and underwent extensive evaporative loss, while the west lobe of Lake Bonney did not (Hendy et al., 1979; Matsubaya et al., 1979; Poreda et al., 2004). This contention is also supported by the surface sediments in the east lobe having a NaCl thickness of 2.1 m (Wagner et al., 2010). The B concentration (and total salinity) is nearly twice as high in the bottom waters of East Lake Bonney compared to West Lake Bonney, and this is due to evaporation leading to loss of B that increases  $\delta^{11}\text{B}$ . Hence, the B and  $\delta^{11}\text{B}$  data support past interpretations of the environmental history of the two lobes of Lake Bonney.

### ***Wright Valley waters***

The  $\delta^{11}\text{B}$  of surface waters in Lake Vanda (+ 35.9‰) indicate an influence of marine salts. However, the  $\delta^{11}\text{B}$  of primary inflow to the Onyx River is much lower, demonstrating a terrestrial aluminosilicate weathering source ( $\delta^{11}\text{B} = +17.7\text{‰}$ ) (Figs. 6 and 7). Lake Vanda bottom water  $\delta^{11}\text{B}$  signature of +44.9‰ is much like the hypolimnetic waters of Lake Bonney—a marine source modified through  $^{10}\text{B}$  loss (Figs. 6 and 7). This can be explained by the fact that in Wright Valley a Tertiary marine fjord once existed, and Lake Vanda bottom waters are a remnant of this fjord. These waters have since undergone a complex mixing and cryoconcentration (Smith and Friedman, 1993) yet follow the predicted  $\delta^{11}\text{B}$  ratio based on the degree of evaporation based upon Na/Cl ratio. However, the B concentration in these waters is low, and more comparable in concentration to the bottom waters of Lake Fryxell, rather than to Lake Bonney. In Lake Vanda, B apparently has not accumulated as the lake evolved, but has been removed from the lake.

Don Juan Pond has an estimated degree of evaporation of 74% and a low B/Cl

ratio. However as noted above, this does not follow the modeled  $\delta^{11}\text{B}$  prediction from the Na/Cl ratios ( $\delta^{11}\text{B}$  modeled of +55‰;  $\delta^{11}\text{B}$  measured of +32.5‰). The loss of  $^{11}\text{B}$  through adsorption and/or mineral precipitation is expected to produce a  $\delta^{11}\text{B}$  signature of a more positive value similar to the modeled prediction, but the measured  $\delta^{11}\text{B}$  signature reflects a terrestrial aluminosilicate weathering source of lower  $\delta^{11}\text{B}$  (Fig. 6). The Don Juan Pond Ca–Cl hypersaline brine was previously thought to be fed by groundwater with little surface water input (Harris and Cartwright, 1981). Because of its groundwater source, the higher rock/water ratio should enhance B removal through adsorption. However recent work suggests that the major water source to the pond is from shallow water moving downslope that evaporates as it moves and not deep groundwater input as previously thought (Dickson et al., 2013). Evaporation from this shallow pond is pronounced, 1–3 mm/day (Harris and Cartwright, 1981). Due to the very high salinities in the pond, an ice cover never forms. It appears that B is readily removed, either along its inflow path or in the pond itself, and does not accumulate in the brine (0.15 mM). This geochemical behavior is similar to the hypersaline Ca–Cl brines within the Canadian Shield where marine  $\delta^{11}\text{B}$  values have been lowered and B was removed by mineral fixation in clay minerals (Bottemley and Clark, 2004).

We have compared our  $\delta^{11}\text{B}$  results with the  $\delta^7\text{Li}$  data from Witherow et al. (2010) previously published on similar samples (Fig. 8). Both elements are highly soluble, conservative elements that are concentrated in saline and hypersaline systems; hence B and Li should have similar behavior in the MCM waters. The  $\delta^7\text{Li}$  are from the same lakes and streams as  $\delta^{11}\text{B}$  values with the exception of Canada Stream and Von Guerard Stream. However, samples were not collected during the same field seasons (i.e. 2006–2007 for Li and 2008–2009 for B). The  $\delta^{11}\text{B}$  data from Canada Stream and Von Guerard Stream are compared to  $\delta^7\text{Li}$  from Andersen Creek and McKnight Stream, respectively. Andersen Creek and Canada Stream both originate from Canada Glacier, while McKnight Stream and Von Guerard Stream have a similar landscape position in Fryxell basin (Fig. 1).

There is a general relationship between the isotopic pairs as the freshest waters display a mix between crustal derived and seawater- derived end-members (Fig. 8). This relationship suggests that the MCM waters contain both marine and terrestrial derived Li

and B. This is the consequence of both the chemical weathering of the landscape and the input of marine derived aerosol with the streams having the most lithogenic component. It is clear from the plot that even the freshest waters have significant inputs of “marine” Li and B. The streams, Lake Fryxell surface waters, and Lake Hoare waters represent this group. The lake waters, especially the hypolimnia of the hypersaline lakes, have demonstrated that much of their accumulated salt is derived from marine sources (Lyons et al., 2005). Lake Bonney samples are lighter in  $\delta^7\text{Li}$  but slightly more positive in  $\delta^{11}\text{B}$  with respect to seawater, which both this work and Witherow et al. (2010) have interpreted as in-lake loss of  $^{10}\text{B}$  and  $^6\text{Li}$ , respectively. The deep water of Lake Vanda is notably more positive than seawater for both isotopes. Witherow et al. (2010) argued that the lighter  $\delta^7\text{Li}$  compared to seawater of the Don Juan Pond brine was due to  $^6\text{Li}$  solubilization from fractured dolerite bedrock from groundwater flows. Both isotopic measurements suggest that the Don Juan Pond brine is more influenced by a crustal lithological source than the saline lakes. In general, the arguments for the sources of Li and B and their in-lake behaviors are very compatible.

### ***Global perspective***

In other brackish and saline lake environments, B geochemistry has been used to explain the geochemical evolution of the lake waters and the role of *in-situ* lake processes. Globally, saline lakes (Australia, Dead Sea, Great Basin-United States, and Saskatchewan) demonstrate a very large variation in B concentrations and Na/Cl and B/Cl ratios (Fig. 9). All Great Basin lakes have high B concentrations, and show the greatest enrichment in both B and Na relative to Cl (Fig. 9). This may suggest little to no B removal and concentrations that vary depending on lithologies and hydrological settings of the drainage basins (Johannesson et al., 2000). Boron is added to Pyramid Lake and Walker Lake via B-rich hydrothermal waters, or by B-rich groundwaters (Johannesson et al., 2000). Mono Lake displays a marine-like evaporitic signature, with Na/Cl ratio of 0.82 and B/Cl ratio of 0.11 (Steiman et al., 2004). Goose Lake, Oregon, has a B/Cl ratio of 0.06, Na/Cl ratio of 1.2, and pH of 9.7, reflecting a hydrothermal influence (Na/Cl = N 1; B/Cl = N 0.005; Vengosh, 2003). Abert Lake has the highest B concentration at 9.7 mM, a Na/Cl ratio of 2.6, and a pH of 9.9. Abert Lake waters have Na/Cl ratio of N 1 and B/Cl ratio of N

0.0008. Based on the chemical criteria of major saline sources, these waters could also have been influenced by agricultural return flow (Vengosh, 2003).

Saskatchewan lakes (Waldsea Lake, Deadmoose Lake, and Little Manitou Lake) have Na/Cl ratios of  $\leq 0.4$  and B/Cl ratios of  $\leq 0.004$  (Fig. 9). The Na/Cl ratios indicate a modified marine-like source, but the B/Cl ratios may also suggest an influence from agricultural return flow. These Canadian lakes are similar in B and Cl concentrations to the hypersaline bottom waters of East Lake Bonney, and their Na/Cl ratios predict a degree of evaporation of  $\sim 30\text{--}35\%$ . Deadmoose Lake and Waldsea Lake, Saskatchewan, display depletion in B relative to Cl, similar to East Lake Bonney. This may suggest the possible removal of B within the lake. Little Manitou Lake differs from the other Saskatchewan lakes with a higher B/Cl ratio of 0.0038 and a lower Na/Cl ratio of 0.32. During evaporation the B/Cl ratio increases as the Na/Cl ratio decreases so these data indicate the evaporation of a marine-like initial source for these ions.

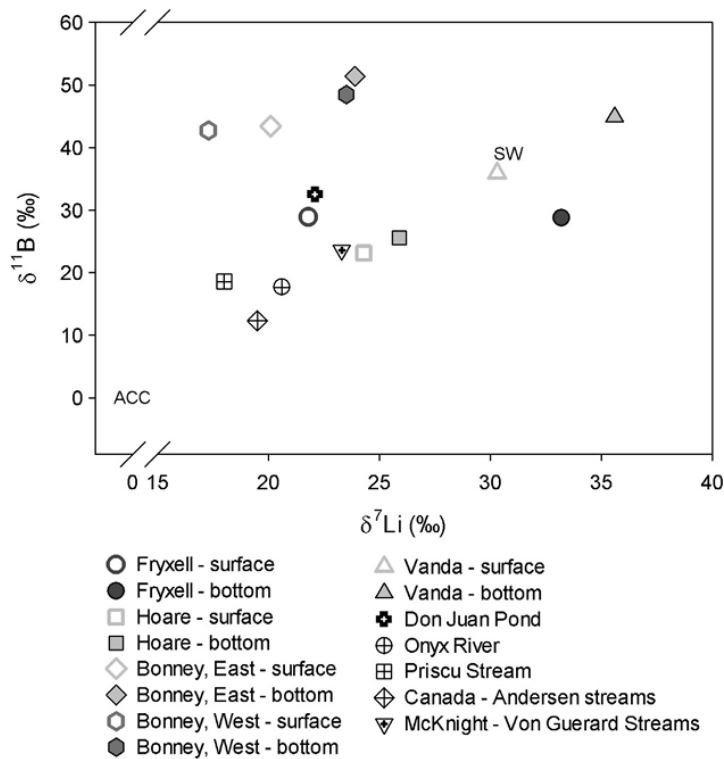


Fig. 8.  $\delta^7\text{Li}$  (‰) from Witherow et al. (2010) and  $\delta^{11}\text{B}$  (‰) of corresponding MCM waters relative to average continental crustal (ACC) value (Vengosh et al., 1994; Teng et al., 2004) and seawater (SW) (Spivack, 1986; Rosner et al., 2007). Open symbols are surface waters, and filled symbols are bottom waters.

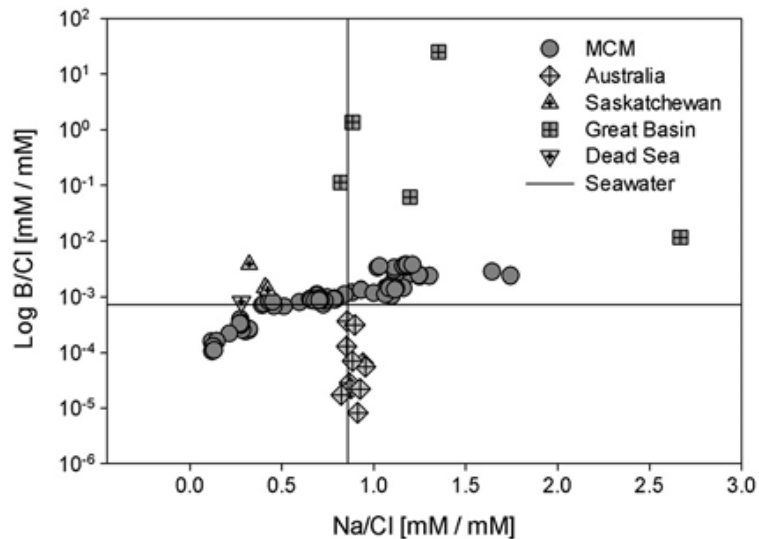


Fig. 9. Na/Cl and log B/Cl molar ratios relative to seawater in saline waters from the McMurdo Dry Valleys, Australia, Great Basin (USA), Saskatchewan (Canada), and the Dead Sea (Israel) (Vengosh et al., 1991a; Vengosh et al., 1991b; Johannesson et al., 2000; Steiman et al., 2004).

Australian salt lakes have Na/Cl ratios of 0.85–0.95 and low B/Cl ratios of  $3.6 \times 10^{-4}$  to  $8.2 \times 10^{-6}$  (Vengosh et al., 1991b). Na/Cl ratios are attributed to a marine salt origin with the low B/Cl ratios relative to seawater indicating B has been removed (Vengosh et al., 1991b). These Australian lakes have B/Cl ratios that are similar to the MCM leachate from aeolian material and B/Cl ratios in the bottom waters of Lake Vanda. The Dead Sea with a Na/Cl ratio of 0.28 and a B/Cl ratio of  $8.2 \times 10^{-3}$  displays a marine B/Cl ratio with an evaporated marine Na/Cl ratio (Vengosh et al., 1991a). It is similar to the MCM lakes but with a higher degree of evaporation, where B has been removed from this system (Vengosh et al., 1991a).

Boron stable isotopes from other salt lakes in North America, Australia, China, and Israel are compared to our saline lake data (i.e., Antarctica, Great Basin, and Saskatchewan lakes; Table 2) (Fig. 10). The  $\delta^{11}\text{B}$  values range +0.50‰ to +57.3‰ in these other saline systems (Vengosh et al., 1991a,b, 1994, 1995; Xiao et al., 1992; Min et al., 2007). Generally, there are two trends in these data as B concentrations increase. In the majority of these systems,  $\delta^{11}\text{B}$  increases as B increases due to the loss of  $^{10}\text{B}$  (Antarctica, Dead Sea, Australia). The second trend involves little to no change in  $\delta^{11}\text{B}$ , as B increases (China and the Great Basin), suggesting that B is not being removed from these waters.

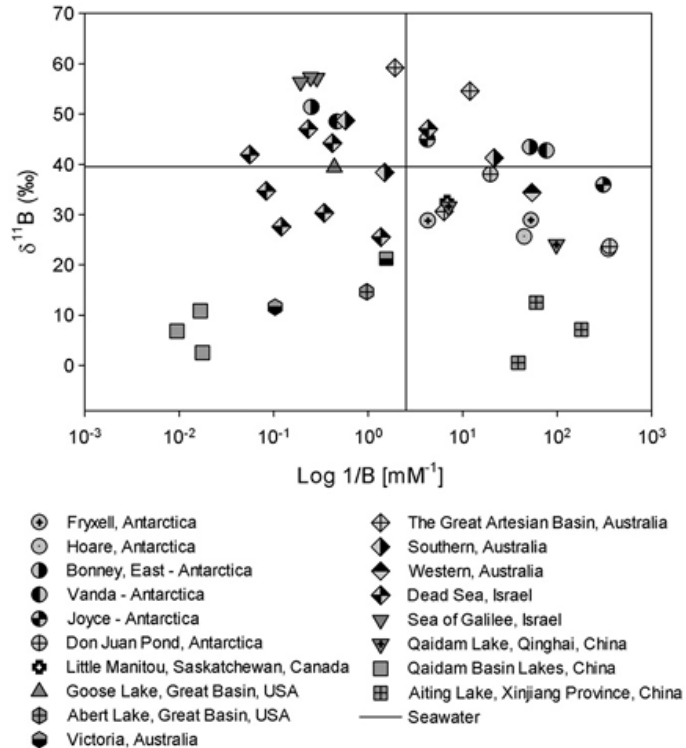


Fig. 10. Log 1/B [mM<sup>-1</sup>] and δ<sup>11</sup>B (‰) relative to seawater comparing boron geochemistry of brine waters in McMurdo Dry Valleys, Australia, China, and Israel (Vengosh et al., 1991a, b, 1994, 1995; Xiao et al., 1992; Min et al., 2007).

As noted above, the Great Basin and Saskatchewan lakes have B concentrations higher than seawater. Little Manitou (δ<sup>11</sup>B= +39.4‰) isotopically also resembles seawater supporting the process of evaporation of a marine-like source as previously suggested. The Great Basin lakes, Goose and Abert, both have a more terrestrial aluminosilicate weathering influenced δ<sup>11</sup>B source—Goose Lake δ<sup>11</sup>B +14.6‰ and Abert Lake δ<sup>11</sup>B +11.6‰. Undoubtedly, the influence of aquifer rock type also plays some role in these differences. The Qaidam basin, China, waters vary greatly in B concentrations (0.006 mM–106 mM), with surface and vents brines of Qaidam Lake having the highest B concentrations. These data suggest a non-marine origin with lighter δ<sup>11</sup>B values, ranging from +0.5‰ to +12.5‰, and a source of B associated with granitic rocks (Fig. 10) (Xiao et al., 1992; Vengosh et al., 1995). The surface brine of Aiting Lake, Xinjiang Province, China, is isotopically similar to the more terrestrial aluminosilicate weathering influenced MCM streams, but has a much higher B concentration (Min et al., 2007) (Fig. 10). Australian salt lakes in Victoria, Southern, Western, and the Great Artesian Basin of Australia range in δ<sup>11</sup>B



from +25‰ to +59‰, similar to the range of the MCM waters (Fig. 10) (Vengosh et al., 1991b). Volcanic-crater lakes of southeastern Australia have  $\delta^{11}\text{B}$  values of +54‰ to +59‰, which have been interpreted to have a marine salt origin and  $^{10}\text{B}$  adsorption at low water/sediment ratios in a closed system (Vengosh et al., 1991b). Southern and Western Australian salt lakes are characterized by  $\delta^{11}\text{B}$  values between +25‰ and +48‰. These values overlap with other surface and brackish waters in Australia (+28‰ to +35‰) and seawater (+39‰) (Vengosh et al., 1991b). Southern and Western Australian salt lakes are similar to Antarctic streams with the highest solute concentrations (Andersen Creek and Blood Falls), ponds, and waters from Lakes Fryxell, Joyce, and Vanda.

Brines from the Dead Sea exhibit a high  $\delta^{11}\text{B}$  value of  $\sim +57\text{‰}$ , which has been interpreted as seawater origin ( $\delta^{11}\text{B} = +39\text{‰}$ ) modified through evaporation, precipitation of salts, and interaction of clay minerals, i.e., adsorption (Vengosh et al., 1991a). Sea of Galilee waters are derived from local rock weathering, with a significant  $\delta^{11}\text{B}$  fractionation between the source springs (+31‰) and the lake (+24‰) (Vengosh et al., 1994). These waters are similar to the more terrestrial aluminosilicate weathering influenced MCM waters. Isotopically, MCM waters are similar in B chemistry to surface brines from South and Western Australia and Israel (Dead Sea and Sea of Galilee waters) (Fig. 10) (Vengosh et al., 1991b, 1994). The  $\delta^{11}\text{B}$  values of Dead Sea brines and of some Australian salt lakes are the highest  $^{11}\text{B}$ -enriched waters observed to date, with Lake Bonney bottom waters being the Antarctic waters most similar to them (Vengosh et al., 1991a,b).

Globally, boron stable isotopes within saline lake systems span a wide range of values, +0.50‰ to +57.3‰; more positive values relate to more concentrated waters. Inputs of marine aerosol to an exposed continental surface can result in the chemical composition of the terrestrial brines being similar to that of evaporated seawater (Herczeg and Lyons, 1991). Through the continual removal of  $^{10}\text{B}$ , a marine-like  $\delta^{11}\text{B}$  can also be produced. Overall, these  $\delta^{11}\text{B}$  values can reflect sources largely from marine aerosols, internal (adsorption) processes within basins, and mixing of chemistry of terrestrial waters controlled by surficial weathering (Vengosh et al., 1991b).

## **Conclusions**

By analyzing the boron isotope geochemistry of these MCM waters, we have further identified the source of solutes in these unusual aquatic environments and have compared the B geochemistry to other saline systems globally. This study demonstrates that the major sources of B to the aquatic system of MCM are likely via terrestrial chemical weathering of aluminosilicates within the stream channels and on glacier surfaces, and a marine source, either currently introduced marine-derived aerosols or ancient seawater. However, in-lake processes can greatly influence the  $\delta^{11}\text{B}$  value by adsorption and/or mineral precipitation, with the removal of B. Waters from the MCM streams, Lakes Fryxell, Hoare, and upper waters of Lake Joyce display a mixing of these two major sources, while we interpret bottom waters of Lake Joyce to be primarily of marine origin. Lakes Bonney and Vanda and the Blood Falls brine are interpreted to be of a marine signature whose  $\delta^{11}\text{B}$  values have become more positive through adsorption and/or mineral precipitation. Don Juan Pond displays a terrestrial aluminosilicate weathering influence of a marine-like source. Our  $\delta^{11}\text{B}$  from these lakes in Antarctica when compared to saline waters globally indicate a wide range of values reflecting variations in B source and B dynamics within MCM watersheds and lakes, with similar processes controlling B geochemistry.

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## **Appendix A. Supplementary data**

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.chemgeo.2014.08.016>.

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