Spatial variations in the geochemistry of glacial meltwater streams in the Taylor Valley, Antarctica

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Abstract: Streams in the McMurdo Dry Valleys, Antarctica, flow during the summer melt season (4–12 weeks) when air temperatures are close to the freezing point of water. Because of the low precipitation rates, streams originate from glacial meltwater and flow to closed-basin lakes on the valley floor. Water samples have been collected from the streams in the Dry Valleys since the start of the McMurdo Dry Valleys Long-Term Ecological Research project in 1993 and these have been analysed for ions and nutrient chemistry. Controls such as landscape position, morphology of the channels, and biotic and abiotic processes are thought to influence the stream chemistry. Sea-salt derived ions tend to be higher in streams that are closer to the ocean and those streams that drain the Taylor Glacier in western Taylor Valley. Chemical weathering is an important process influencing stream chemistry throughout the Dry Valleys. Nutrient availability is dependent on landscape age and varies with distance from the coast. The streams in Taylor Valley span a wide range in composition and total dissolved solids and are surprisingly similar to a wide range of much larger temperate and tropical river systems.

Introduction

Streams in the McMurdo Dry Valleys, Antarctica have been investigated since the IGY in 1957–58. The Onyx River in Wright Valley has the longest flow record of any Antarctic stream (Chinn 1993, McKnight *et al.* 1999), but up until the beginning of the McMurdo Dry Valleys Long-Term Ecological Research program (MCM-LTER) in 1993, biogeochemical and geochemical data had only been collected from the Dry Valley streams on an irregular basis. Although many significant observations were obtained on the geochemistry of these streams prior to the establishment of the MCM-LTER (e.g. Howard-Williams *et al.* 1986, 1989, Vincent & Howard-Williams 1986, Green *et al.* 1988), there were not sufficient data to evaluate long-term differences in stream chemistries related to geographic and biological differences in the streams themselves. This is particularly true in Taylor Valley where a large number of streams exist that vary in slope, landscape position, substrate type, amount of biomass present and other attributes (McKnight *et al.* 1999).

In general, solute concentrations increase downstream due to salt dissolution, evaporation, cryoconcentration and chemical weathering (Lyons *et al.* 1998, Gooseff *et al.* 2002). Chemical weathering of both carbonates and silicate minerals occurs primarily in the hyporheic zones of stream channels and the rates can be quite high (Nezat *et al.* 2001, Gooseff *et al.* 2002, Maurice *et al.* 2002, Green *et al.* 2005).

Biogeochemical processes primarily occurring in microbial mats and in the hyporheic zone can be extremely important in regulating nutrients and trace metals within these streams (Howard-Williams & Vincent 1989, Howard-Williams *et al.* 1986, 1989, Vincent & Howard-Williams 1986, 1989, McKnight *et al.* 2008, Fortner 2008). Ion exchange reactions within the hyporheic zone can also be an important geochemical process in these streams (Gooseff *et al.* 2004).

Because of the MCM-LTER, we now have longer geochemical records of the streams in Taylor Valley. In this paper we will examine these records, especially the spatial variability, in order to assess better the role that landscape position plays in controlling the geochemistry of these streams. The MCM-LTER has routinely measured a suite of inorganic constituents (major element ions: Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^- and SO_4^{2-}; nutrients NO_3^- and PO_4^{3-}; as well as H_4SiO_4 and titration alkalinity (Alk)). All of the solutes have potentially variable sources (i.e. Na^+ could be derived from snowmelt, from dissolution of previously precipitated salts such as NaCl or Na_2SO_4, or from the weathering of Na-rich alumino-silicate minerals such as plagioclase). Our goal in this manuscript is not to ultimately quantify the source of each solute, but rather to examine differences in stream geochemistry among the streams in Taylor Valley and to evaluate the importance of landscape position on stream water geochemistry. This will be done using 16 years (1993–2009) of MCM-LTER data.

Fig. 1. Map of Taylor Valley showing location of streams and lakes discussed in the text.

There is also a relatively high degree of temporal variability, both at seasonal and inter-annual time scales in each stream (http://mcmlter.org). This variability is thought to be primarily related to hydrologic variability such as changes in stream discharge, hyporheic zone exchange and freeze-thaw events. In addition, some of the temporal variability observed may be related to changes in solute sources such as changes in dust flux. Examination of the temporal variability at each stream is beyond the scope of this paper and will not be addressed in detail. Although this work does not address any of the Latitudinal Gradient Project (LGP) key questions directly it does address the issue of local variability at one particular latitude, which has been an acknowledged complication to the LGP concept (Howard-Williams *et al*. 2006).

Site description

The McMurdo Dry Valleys (76°30'–78°00'S, 160°00'–165°00'E) comprise the largest ice-free area of Antarctica (4800 km^2). Taylor Valley has been the primary site of on-going investigation since its establishment as a Long-Term Ecological Research (LTER) site in 1993 (Fig. 1).

Physical processes dominate ecosystem function in this polar desert environment. The mean annual temperature at various sites on the valley floors ranges from -15°C to -30°C with precipitation of less than 3 cm yr^{-1} water equivalent (Doran *et al*. 2002, Fountain *et al*. 2009). Liquid water is very limited on the landscape surface for most of the year due to the cold winter temperatures. However, during the summer air temperatures reach and exceed 0°C, resulting in meltwater generation from glaciers and snow packs. The availability of liquid water on the landscape is one of the most important limitations for life (Kennedy 1993), and hence the routine monitoring of the hydrology and chemistry of streams has been undertaken as part of the on-going ecological studies. Prior to the establishment of the MCM-LTER, limited studies of the Dry Valley streams established the variability of the stream hydrology and chemistry over time and illustrated the sensitivity of the hydrologic system to climate variability (Chinn 1993).

There are subtle spatial differences in the current climate of the Dry Valleys as well as in the climate-related evolution of the lakes (Lyons *et al*. 2000). The climate of the Lake Bonney basin tends to be influenced more by continental air masses and therefore it is warmer, sunnier, and drier than the Lake Fryxell and Hoare basins, which are located closer to the ocean (Fig. 1). The eastern Taylor

Valley is subjected to marine air masses coming from the coast, particularly in the summer months when the streams are flowing (Lyons et al. 2000). Precipitation generally sublimates rather than melting and running off or recharging, resulting in salt accumulation in the soils. The distribution of salts in the soils varies with location in relation to airmass trajectory, landscape position and surface age (Keys & Williams 1981).

Stream descriptions

Streams in the McMurdo Dry Valleys are an important link transferring water and solutes from alpine glaciers to the closed-basin lakes on the valley floors. The stream water is derived from glacial melt during the summer months and in Taylor Valley is the primary source of water to the lakes. Glacial meltwater flows through stream channels with unconsolidated alluvium composed primarily of sand-sized particles (Conovitz et al. 1998). The variations in stream hydrology are related to weather and climate on a daily, seasonal and inter-annual time scale (Conovitz et al. 1998, Ebnet et al. 2005). This hydrological variability has major implications for water and solute input into closed-basin lakes on the valley floor. The response of the Dry Valley ecosystem to this variability is an ongoing theme of the MCM-LTER research.

Most of the stream and lake names referred to in the text have been approved by the US Board on Geographic Names. However, there are a few names that are commonly used in the text that are not official approved names including, Santa Fe, Mariah and Blood Falls.

Lake Fryxell (Fig. 1) is the easternmost lake in Taylor Valley. The gauged streams in the Lake Fryxell basin range in gradient from $0.02\,\mathrm{m\,m^{-1}}$ on the valley floor up to $0.55\,\mathrm{m\,m^{-1}}$ in the steep upper reaches. The streams vary in length from 1.0 km to 11.2 km (Conovitz et al. 1998) with streams on the north and south side of the basin being longer than those on the east and west. The streams in the southern part of the Lake Fryxell basin are among the longest in the Taylor Valley and drain glaciers in the Kukri Hills (Fig. 1).

Andersen Creek (Fig. 1) is the only stream that flows directly into Lake Hoare. Andersen Creek is a proglacial stream that flows along the margin of Canada Glacier into the north-east end of the lake. The Lake Hoare basin has three short streams, Wharton, House and McKay, each c. 0.5 km in length, that flow from the Suess Glacier into Lake Chad, a shallow lake to the west of Lake Hoare (Fig. 1). At times, Lake Chad spills over to Lake Hoare and provides another source of water and solutes to the lake.

Lake Bonney is divided into two lobes and each lobe has several streams flowing into it (Fig. 1). The streams in the Lake Bonney basin tend to be steep, rocky and transport more sediment than those of the Fryxell and Hoare basins and consequently algal mats tend to be sparse

(Alger et al. 1997). Priscu Stream in the east Lake Bonney basin is one of the few second order streams in Taylor Valley. Other streams drain the alpine glaciers on the steep slopes on the south side of the east Lake Bonney basin. The streams flowing from the Taylor Glacier, Santa Fe and Lyons, flow into the west lobe of Lake Bonney and are relatively saline compared to the other glacial melt streams in the Taylor Valley. There are thought to be relict salt deposits under the terminus of the Taylor Glacier (Lyons et al. 2005). The area on the terminus of the Taylor Glacier is known as Blood Falls due to the iron-rich saline water that discharges from below the glacier and creates a distinctive rusty red colour on the glacier surface when the iron is oxidized (Mikucki et al. 2004). The proglacial streams on the north and south of the Taylor Glacier are also relatively saline. However, their ion ratios differ from that of Blood Falls and may reflect an input of salt at a different stage of brine evolution (Lyons et al. 2005). (All stream data collected by the MCM-LTER can be found on the website at www.mcmlter.org).

Methods

Sampling

The sampling of the streams has been conducted by the MCM-LTER field teams from 1993 to present. Most streams are sampled on a weekly basis during the flow season starting at the end of November until the end of January. However, ungauged streams are sampled less frequently. Stream flow can be variable and intermittent, so streams are not always sampled on a regular schedule. Samples are collected just upstream of the stream gauge, or close to the mouth of the stream if the streams are not gauged. Stream water samples are filtered at the field camps within hours of collection using Nuclepore$^{\mathrm{TM}}$ polycarbonate membrane filters with 0.4 μm pore size. Anion and H_4SiO_4 samples are filtered into HDPE bottles that have been rinsed five times with ultra-pure water. Nutrient and cations samples are filtered into HDPE bottles that have been rinsed with 1% or 10% HCl solution and then rinsed five times with ultra pure water. Cation samples are preserved with acid to a pH of approximately 2–3 by addition of 0.1% Ultrex nitric acid. Major ion and reactive Si samples are stored chilled at approximately 4°C until analysis. Nutrient samples are stored frozen until shortly before analysis.

Chemical analysis

Samples were analysed for major anions and cations by ion chromatography. From the years 2000 to present a Dionex DX-120 (Sunnyvale, CA) was used for the major ion analyses. This instrument uses a single piston isocratic pump with constant flow rate set at 1.2 ml per minute and an electrical conductivity detector. For the cation analyses, a Dionex IonPac CS12A analytical column (4 x 250 mm)

Table I. Precision of the major ion and nutrient analytical data is calculated as the average percent difference between duplicate samples. The reporting limit is the lowest concentration that is quantified using our standard methods for each analyte.

	% difference	reporting limit (mg l⁻¹)
Major ions		
Alkalinity (HCO_3^-)	< 10	3
Cl^-	< 1	0.2
SO_4^{2-}	< 2	0.2
Na^+	< 1	0.2
K^+	< 1	0.04
Mg^{2+}	< 1	0.1
Ca^{2+}	< 1	0.1
Nutrients		
N as NO_3^-	< 2	0.003
P as PO_4^{3-}	< 3	0.003

and a CG12A guard column (4 x 50 mm) was used. The eluent is 0.13% methanesulphonic acid solution. A CSRS Ultra Cation Self-Regenerating Suppressor was used. For the anions, a Dionex IonPac AS14 analytical column (4 x 250 m) and an AG14 guard column (4 x 50 mm) was used. The eluent is a 1.0 mM $NaHCO_3$ and 3.5 mM Na_2CO_3 solution. An ASRS Ultra Anion Self-Regenerating Suppressor was used. A measurement of precision and reporting limits for the ions are shown in Table I.

Prior to the year 2000, a DX-300 was used for the anion and cation analysis. The details of analysis have been described elsewhere (Welch *et al*. 1996; Limno Methods Manual, http://www.mcmlter.org/queries/lakes/lakes_home.jsp).
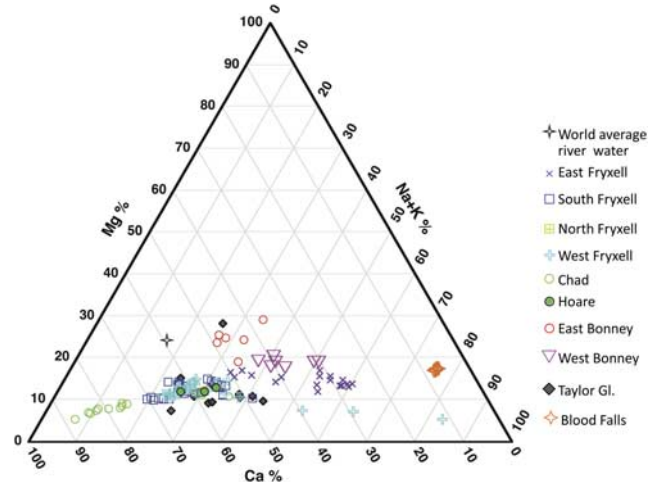

Fig. 2. Cation Piper diagram. Ca^{2+}, Mg^{2+} and $Na^+ + K^+$ are shown as % by equivalents. Streams are grouped by location. East Fryxell includes Lost Seal, McKnight and Aiken. South Fryxell includes VonGuerard, Harnish, Crescent and Delta. North Fryxell is Huey. West Fryxell includes Canada, Mariah and Green. Chad includes Wharton, House and McKay. Hoare is Andersen Creek. East Bonney is Priscu Stream. West Bonney is Lawson Creek. Taylor Glacier represents Santa Fe and Lyons Creek. Blood Falls is plotted separately. World average river data are from Hu *et al*. (1982).

Nutrient analyses were done using a Lachat QuikChem AE analyser prior to 1998 and then a Lachat QuikChem 8000 FIA instrument with Omnion 3.0 software (Loveland, CO) after 1998. The instrument is set up to run four channels
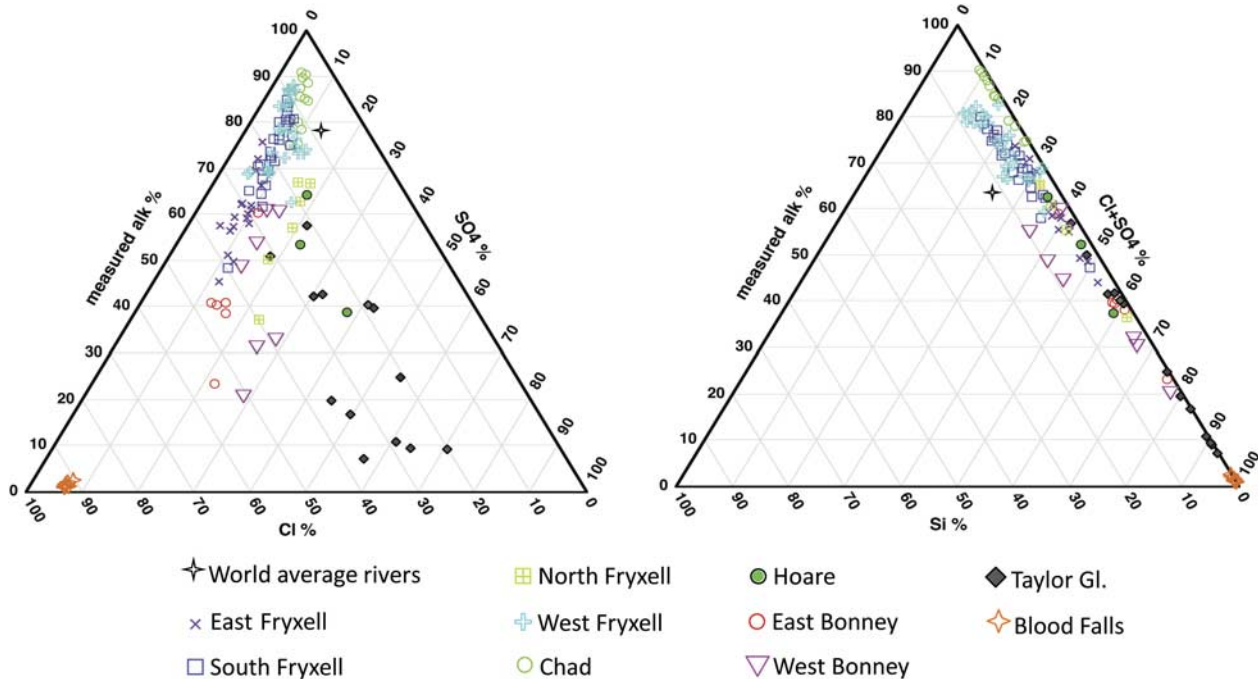

Fig. 3. Two versions of the anion Piper diagram. The first plot shows Cl^-, SO_4^{2-} and Alkalinity in % by equivalents. The second plot shows H_4SiO_4, Alk and $Cl^- + SO_4^{2-}$ as % equivalents. Symbols and locations are the same as Fig. 2.
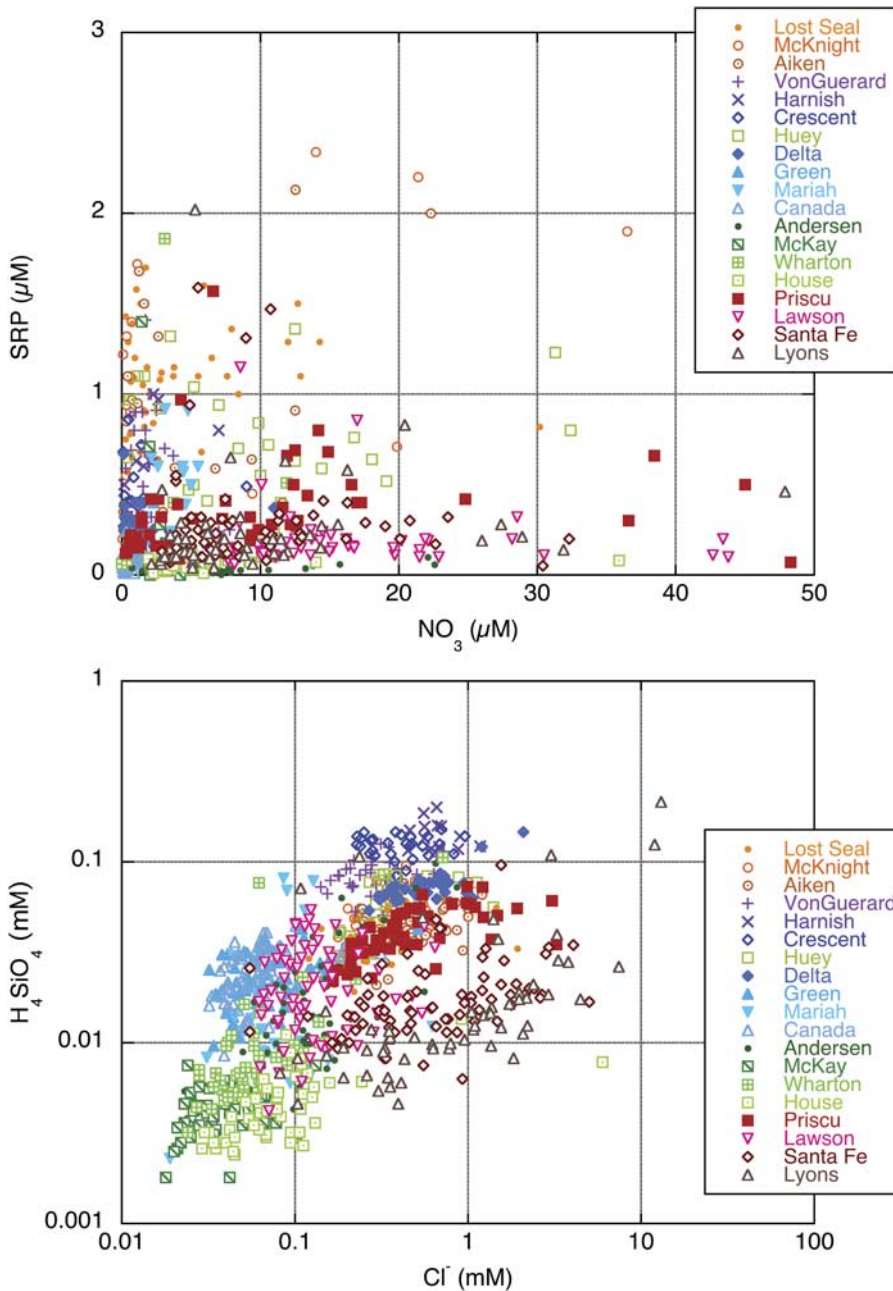
Fig. 4. Plots of soluble reactive phosphorus (SRP) versus nitrate (NO_3^-) in μM concentrations and log scale plot of H_4SiO_4 versus Cl^- in mM concentrations for selected Taylor Valley streams.

simultaneously and methods are optimized for low concentration samples. A measurement of precision and reporting limits for nitrate and soluble reactive phosphorus are shown in Table I.

H_4SiO_4 was determined using a manual colorimetric method based on the method of Mullin & Riley (1955). Details of this method are also described by Pugh et al. (2003).

Samples for titration alkalinity were collected in 20 ml plastic scintillation vials with poly-cone caps. Samples were returned to the Ohio State University for analysis. Alkalinity was determined by titration with 0.1 N standard HCl to a pH of 4.5. At the pHs and low dissolved organic carbon concentrations of these streams, titration alkalinities

are assumed to be primarily bicarbonate. Charge balance errors were calculated by taking the difference between the total anion equivalents, including alkalinity, and total cations and dividing by the sum of anion and cation concentrations in equivalents. The average percent difference was 5%, with a range from 0.1–20%.

Results

Major ions

One of the traditional ways to graphically present water quality data is by use of Piper diagrams. Figure 2 shows the

percentage of Ca^{2+}, Mg^{2+} and $Na^+ + K^+$ (in equivalents) in Taylor Valley streams. In the majority of the streams, Mg^{2+} is less than 20% of the total cation concentration. Only in Priscu Stream samples and one sample draining Santa Fe/Lyons is $Mg^{2+} > 20\%$. The most apparent trend shown in this figure is the variation between Ca^{2+} and $Na^+ + K^+$. The streams flowing into Lake Chad and Andersen Creek in the Lake Hoare basin, the majority of streams in the southern, northern and western portion of the Lake Fryxell basin, and most of the Santa Fe and Lyons samples all have $> 50\%$ Ca^{2+}. Blood Falls and some of the streams in the eastern and western Lake Fryxell basin have $> 50\%$ $Na^+ + K^+$ (Fig. 2). The other streams such as Lawson and Priscu and some of the eastern Fryxell basin streams have cation compositions that are 10–30% Mg^{2+} and the remainder is divided between Ca^{2+} and $Na^+ + K^+$.

One can also plot the anion data using a Piper scheme and the traditional method, the percentage of Cl^-, SO_4^{2-} and Alk (or HCO_3^-) (in equivalents), is shown in Fig. 3. There is a much more diffuse pattern than the cation data, because although the majority of samples are dominated by high percentages of alkalinity, there are a few samples with Cl^- or SO_4^{2-} as the most abundant anion. The Blood Falls samples clearly plot separately as Cl^- enriched, while many of the Santa Fe and Lyons samples are rich in SO_4^{2-}. The chemistry of these streams is clearly dominated by evaporite mineral input, especially NaCl and $CaSO_4 \cdot 2H_2O$. Again the Priscu Stream in the east Lake Bonney basin, Andersen Creek at Lake Hoare and Lawson Creek in the east Lake Bonney basin plot along different trajectories. The Huey Creek in the north Fryxell basin samples plot differently as well with slightly higher SO_4^{2-} than the main trend of samples. The majority of the Lake Chad streams, west Fryxell basin, south Fryxell basin and east Fryxell basin samples plot along a 95% to 45% Alk line with SO_4^{2-} percentages of $< 20\%$, and most $< 10\%$. In general there is a decrease in alkalinity and an increase in Cl^- going from the Lake Chad streams to the west Fryxell basin, to south Fryxell basin to the east Fryxell basin reflecting an increase in Cl^- percentages approaching McMurdo Sound.

A different method of Piper plot using percentage of alkalinity, $Cl^- + SO_4^{2-}$, and Si (i.e. H_4SiO_4), at the apexes was first used by Hu et al. (1982). This plot clearly shows the anionic continuum between Alk and $Cl^- + SO_4^{2-}$ (Fig. 3). In no case is H_4SiO_4 larger than ~10% of the total with the highest H_4SiO_4 percentages in Lawson Creek in the west Lake Bonney basin and some of the west and south Fryxell basin streams. These higher H_4SiO_4 concentrations reflect enhanced weathering in these streams.

Another way to summarize the data is to calculate the mean percentages in equivalents for all the samples. As the Piper diagrams have already demonstrated, Ca^{2+} and Alk are the major constituents of the Taylor Valley streams with Ca^{2+} (55%) $> Na^+$ (28%) $> Mg^{2+}$ (13%) $> K^+$ (4%) and Alk (65%) $> Cl^-$ (22%) $> SO_4^{2-}$ (12%). Because of its
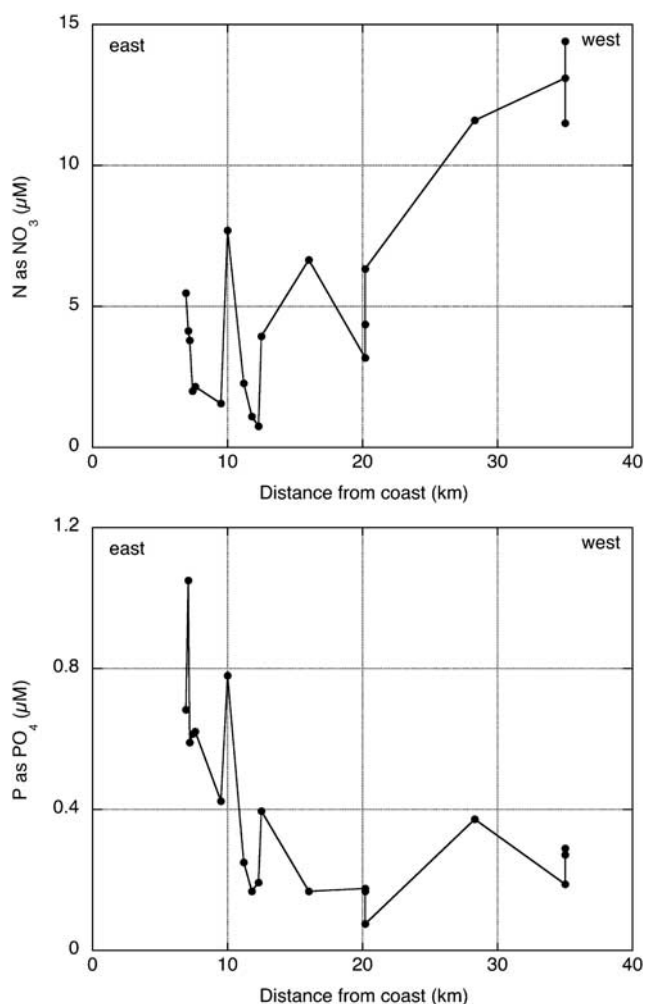

Fig. 5. SRP and NO_3 variation shown as distance from the coast in kilometers. Concentrations are calculated averages from the available data.

relatively low concentration in seawater, and hence aerosols derived from seawater, the HCO_3^- (Alk) in the streams is derived from the chemical weathering of carbonate and silicate minerals. Using the seawater ratios and assuming that all the Na^+ (for the cations) is derived from a marine aerosol, the non-seasalt derived fractions of the other major ions are Ca^{2+} - 98%, K^+ - 83%, and Mg^{2+} - 57%. Of course, not all of the Na^+ is derived from precipitation, so these numbers are the minima contributions for mineral weathering.

Nutrients and H₄SiO₄

Figure 4 shows the soluble reactive phosphate (SRP) data plotted against the NO_3^- data. In general the Bonney basin streams are enriched in NO_3^- and depleted in SRP, while many of the Fryxell basin streams, especially the eastern Fryxell basin, show the opposite trend. This is more readily demonstrated when the data are plotted in a spatial context (Fig. 5).

A plot of H_4SiO_4 versus Cl^- is shown in Fig. 4. The pattern from our dataset is that the streams draining the south Fryxell basin have the highest H_4SiO_4 concentrations (Fig. 4). In general Priscu Stream, the west Fryxell basin streams and some of the east Fryxell basin streams also have relatively high H_4SiO_4. As noted above, these relatively high H_4SiO_4 concentrations reflect enhanced chemical weathering, especially in the hyporheic zones of the lower gradient streams such as those in the Lake Fryxell basin. The Lake Chad streams and Andersen Creek in the Lake Hoare basin as well as some of the west Fryxell basin streams and the west Bonney basin streams have some of the lowest H_4SiO_4 concentrations.

Discussion

Landscape position as a geochemical discriminator

Numerous studies have demonstrated east–west geochemical and biogeochemical trends in the soils, surface waters of the lakes, and glaciers of the McMurdo Dry Valleys (e.g. Keys & Williams 1981, Lyons *et al.* 1998, 2000, 2003, Burkins *et al.* 2000, Witherow *et al.* 2006, Barrett *et al.* 2007). The long-term stream data also indicate variations in major ion and nutrient concentrations that reflect landscape position within Taylor Valley. These geochemical gradients within Taylor Valley have been argued to be due to a number of attributes including distance from the ocean, elevation, age of landscape surface, lithology of the tills and soils, and past climate history. For example Keys & Williams (1981) observed more Cl^- salts in the soils closer to the ocean and attributed this to the input of marine aerosols. Barrett *et al.* (2007) acknowledge the differences in N and P distribution on the Taylor Valley landscape and attributed this in part to the differences in till types as well as age of the tills in each lake basin. The pattern observed in Fig. 5 has led to different nutrient limitations in the lakes within Taylor Valley. For example, Priscu (1995) has demonstrated that Lake Fryxell is N-deficient in regards to nutrient availability for phytoplankton, while Lake Bonney is P-deficient. This is clearly related to the difference in total fluxes and stoichiometry of these inorganic nutrients entering the lakes (Barrett *et al.* 2007), which is observed in the stream data presented in Figs 4 & 5. The impact of such effects as surface age is not subtle in that it has great consequence for the superimposed aquatic ecosystems. This so-called "legacy effect" has been discussed in much detail, primarily for Taylor Valley, and suggests that past events continue to imprint the current ecosystem (Priscu 1995, Moorhead *et al.* 1999, Lyons *et al.* 2000, 2001).

Lyons *et al.* (2003) and Witherow *et al.* (2006) have shown that the surficial geochemistry of glaciers in Taylor Valley varies with landscape position and elevation. Therefore, glacier melt chemistry can also differ between glaciers and this melt can be further modified by the

Table II. Average total dissolved solids (TDS) calculated for selected streams in Taylor Valley.

Stream name	TDS (mg l^{-1})
Lake Fryxell basin	
Lost Seal	69.5
McKnight	99.1
Aiken	109
VonGuerard	120
Harnish	182
Crescent	149
Huey	122
Delta	142
Green	29.1
Mariah	30.8
Canada	19.1
Lake Hoare/Lake Chad basin	
Andersen	47
McKay	37.8
Wharton	53.0
House	44.5
Lake Bonney basin	
Priscu	118
Lawson	23.4
Santa Fe	235
Lyons	452
Blood Falls	34 400

presence or absence of cryoconites on the glacier surface (Lyons *et al.* 2003, Fortner *et al.* 2005, Bagshaw *et al.* 2007). Glaciers with elevated dust burdens can contribute higher solute fluxes to the streams and hence the closed-basin lakes. The abundance of cryoconites can lead to variations in nutrient chemistry of water exiting the glacier surface as well (Bagshaw *et al.* 2007). The weathering and dissolution of aeolian materials on the glacier surfaces and in cryoconites vary in time and space, and therefore, add to the variability of stream geochemistry.

In general, riverine geochemistry can be classified based on the total dissolved solids (TDS) concentration and this, in turn, can be related to watershed bedrock types (Stallard & Edmond 1983, Berner & Berner 1996). Rivers and streams in areas with intensively weathered silicate-rich rocks can have TDS of < 20 mg l^{-1}. Silicate-rich igneous rocks and metamorphic rocks and shales normally have rivers and streams with 20–40 mg l^{-1} TDS, while sedimentary rocks with abundant carbonates have rivers and streams with 40–250 mg l^{-1} TDS. Rivers and streams draining evaporitic rocks can have TDS > 250 mg l^{-1}. TDS for the Taylor Valley streams range from ~ 6 to ~ 4000 mg l^{-1}, but again demonstrate discrete geographic patterns. The highest values of TDS are from Santa Fe and Lyons streams, which are greatly influenced by the saline discharge, Blood Falls (e.g. Lyons *et al.* 2005). Interestingly, Lyons Creek can have very low TDS values as well depending on the year sampled. This undoubtedly reflects the periodic discharge influence of Blood Falls. Streams with the lowest TDS are ones such as Mariah, Canada and Green in the western
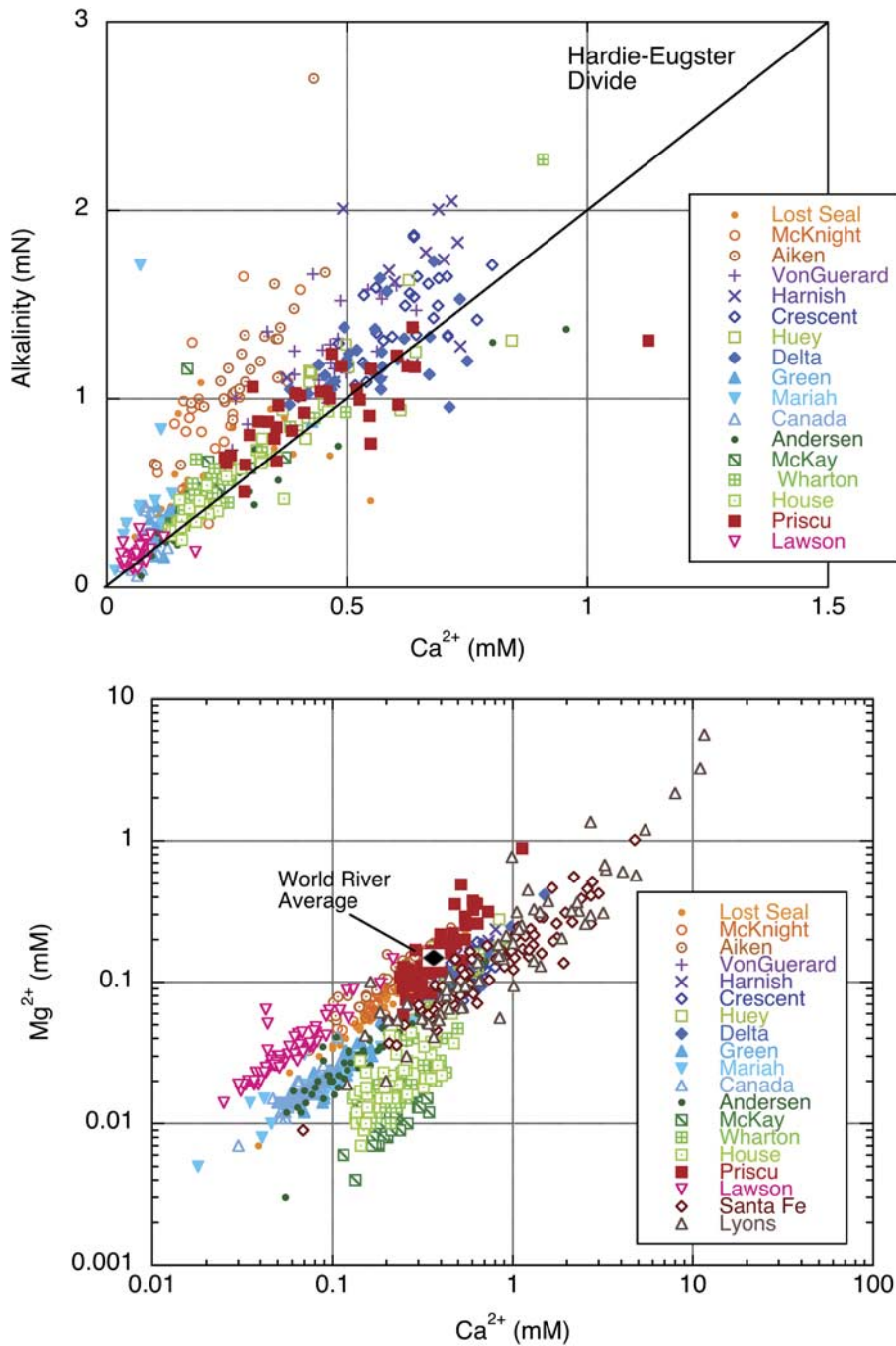
Fig. 6. Plot of alkalinity versus Ca^{2+} for selected Taylor Valley streams. The solid line represents the Hardie-Eugster divide as described in the text. Plot of Mg^{2+} versus Ca^{2+} for selected Taylor Valley streams. The world average river water composition is shown for reference.

Fryxell basin, Lawson in the west Bonney basin, and Andersen in the Lake Hoare basin, and the streams flowing into Lake Chad - House, McKay and Wharton. With the exception of Wharton, all these latter streams have mean TDS of < 50 mg l^{-1}. Only Canada has a mean TDS as low as < 20 mg l^{-1} (Table II). The south and east Fryxell basin streams such as Delta, Crescent, Harnish, VonGuerard, Aiken, and McKnight, as well as Priscu in the east Bonney basin have relatively high TDS (TDS ≥ 100 mg l^{-1}). Thus the west Bonney basin streams with the strong influence of

Blood Falls resemble global streams and rivers draining evaporitic environments or those found in extremely arid regions. The streams with the lowest TDS in Taylor Valley behave like a mixture of crystalline silicate rock-dominated and sedimentary rock watersheds, while streams with intermediate TDS more closely resemble solely sedimentary rock-dominated watersheds. The south and east Fryxell basin streams can have extensive hyporheic zone dynamics (Gooseff *et al.* 2002) and the increased TDS are due in part to extensive chemical weathering within the hyporheic zones

(Gooseff *et al.* 2002, Maurice *et al.* 2002) and they are closer to the ocean as noted above.

Taylor Valley streams in a global geochemical context

Surprisingly, the stream geochemistries of the Taylor Valley encompass the compositions of a wide range of much larger temperate and tropical river systems. For example, most major rivers of the world have > 50% Alk and between 10–30% $Cl^- + SO_4^{2-}$ (Berner & Berner 1996). The world average river water plots just to the H_4SiO_4 rich side of the Fryxell basin stream samples (Fig. 3). In fact, when considering the world's largest rivers, the Taylor Valley streams plot either close to rivers that drain large areas of sedimentary rocks (e.g. Yangtze, Yukon, Danube, Rhine, Mississippi, Huang He and Ohio) or large rivers in arid climates (e.g. Rio Grande, Colorado, Pecos). The former have higher Alk percentages while the latter have higher $Cl^- + SO_4^{2-}$ percentages (Berner & Berner 1996). The only global rivers that are not well represented by the Taylor Valley streams are those that are more enriched in H_4SiO_4 that drain either old crystalline craton (e.g. Niger, Amazon, Orinoco, Guyana, and Congo) or those draining tectonically active volcanic terranes.

Interestingly, a small number of the Taylor Valley streams would be considered "non-pristine" based on their NO_3^- and/or SRP concentrations. When looking at large global rivers, concentrations > 25 µM for NO_3^- and > 1 µM SRP have been determined "non-pristine" (Berner & Berner 1996). As noted above, the NO_3^--rich streams occur in the Bonney basin (Fig. 4). The Bonney basin tills are older and more NO_3^- has accumulated there (Barrett *et al.* 2007). The Fryxell basin streams have the highest SRP, which reflect the

youngest tills in the valley (Barrett *et al.* 2007). Stream nutrient data from Antarctic locations, especially ones that are wetter than the McMurdo Dry Valleys such as Signy Island, are generally equal to or lower than what we report here with the mean values for NO_3^- ranging from 7.8–9.5 µM and SRP being 0.24 and 2.6 µM (Hodson 2006).

Ca-Mg-Alk dynamics and water evolution

Green *et al.* (1988) and Lyons *et al.* (1998) argued that, based on the stream water chemistry entering lakes Hoare and Fryxell and using the evaporitic model of Hardie & Eugster (1970), these two Taylor Valley lakes (Fig. 1) should evolve to $HCO_3^- Na^+$ rich waters and become depleted in Ca over time due to $CaCO_3$ precipitation. Over 16 years of data support the same conclusion (Fig. 6). The Fryxell basin streams are particularly enriched in HCO_3^- relative to Ca^{2+}, which according to the model leads to a HCO_3^- enriched, Ca^{2+} depleted, water over time.

In general, the Ca^{2+} concentrations in these streams are enriched relative to Mg^{2+} when compared to rivers and streams globally (Fig. 6). The average global riverine Mg/Ca ratio is 0.42, which reflects the overall importance of sedimentary rock dissolution (Berner & Berner 1996). The east Fryxell basin streams along with Lawson Creek fall closest to this 0.42 mean, but all of the other streams are substantially lower than this value implying abundant sources of Ca^{2+} relative to Mg^{2+} throughout the rest of Taylor Valley. The streams with the lowest Mg/Ca ratios are the stream flowing into Lake Chad - Wharton, House and McKay. They also have Ca:Alk molar ratios close to 1:2 suggesting that $CaCO_3$ is the primary source of Ca^{2+} into these streams (Fig. 6). $CaCO_3$ is formed as salt crusts
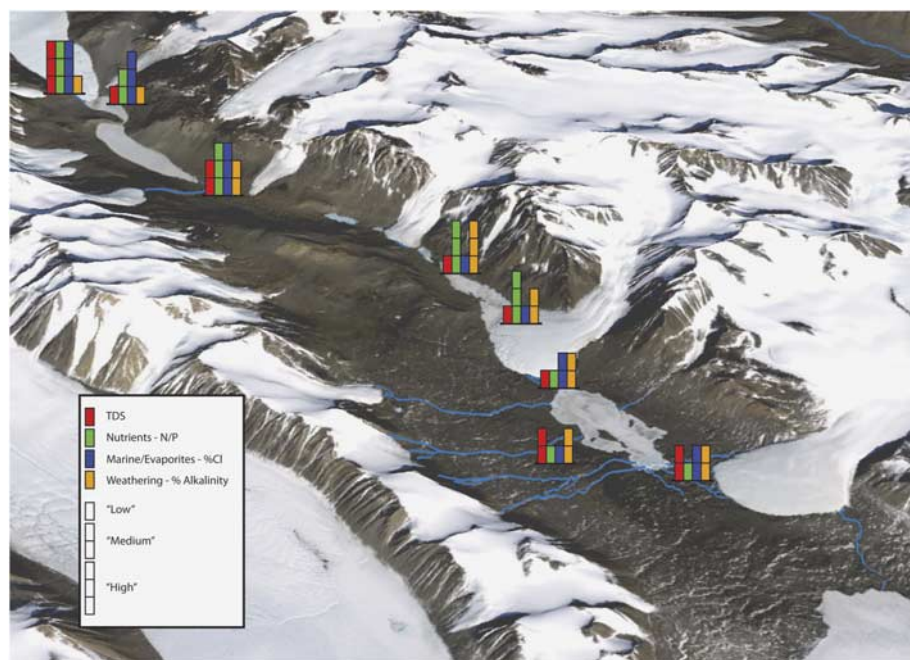

Fig. 7. Map view summarizing the spatial variation in stream chemistry observed in Taylor Valley.

and coatings throughout Taylor Valley (Keys & Williams 1981, Foley et al. 2006). Although some of this $CaCO_3$ is formed in place (i.e. pedogenic), much of it was deposited as lacustrine $CaCO_3$ during higher lake stands (Doran et al. 1994). Wetting and sublimation may add additional $CaCO_3$ around the stream margins, which later can be dissolved and transported. The significance of wetting and drying on stream geochemistry has not been investigated in Taylor Valley, but in warm desert regions it can ultimately lead to differential solubilization of ions to stream waters (Smith & Drever 1976).

Stream chemistry and hydrology under future climate change scenarios

Future climate scenarios suggest that Antarctic regions including the McMurdo Dry Valleys will gradually warm (Chapman & Walsh 2007). This warming will lead to increased glacier melt, more stream flow and hence higher lake levels. The development of warmer, wetter conditions will have important consequences for the aquatic ecology and geochemistry of these systems, some of which has already been discussed (Lyons et al. 2006). Increased stream flow has been shown to lead to increased stream bed scouring and loss of benthic algal materials (McKnight et al. 1999). Increased volume of stream flow will increase the hyporheic zone and perhaps lead to enhanced chemical weathering and mobilization of salts. These changes, in turn, will affect the geochemistry of the stream water. Increased connectivity between the terrestrial and aquatic portions of the landscape will occur (Harris et al. 2007). Hence we predict that solute mobility will increase in a warmer, wetter Taylor Valley with higher fluxes of soluble constituents occurring in these streams. As lake levels rise, stream lengths will decrease and in some cases, some shorter streams could disappear completely so that meltwater would flow directly from the glaciers to the lakes. In this case, direct connection to the terrestrial landscape and its source of solutes would cease, probably decreasing solute fluxes. Therefore, one might envision an increase in TDS then after a time of lake level rise, a decrease in the TDS of the streams and lake surface waters.

Conclusions

The major differences in the stream geochemistry with landscape position in Taylor Valley are depicted in Fig. 7. A number of general conclusions can also be drawn from our analysis. Although there is not a strong relationship between stream length and TDS, solute concentrations tend to be higher in the longer streams such as those draining the south side of the Lake Fryxell basin and sea-salt derived ions tend to be higher in streams that are closer to the ocean as well as those that drain the Taylor Glacier in western Taylor Valley. Chemical weathering is an important process influencing stream chemistry throughout the Dry Valleys, as evidenced by the presence of H_4SiO_4, but

appears to be particularly important in the lower elevation of the Fryxell basin streams. In these streams, intensive hyporheic dynamics aid in chemical weathering. The dominant cation in the Dry Valley streams is calcium and bicarbonate is the dominant anion on an equivalent basis, although landscape position plays an important role in solute variation. Nutrient availability in streams is dependent on landscape age and varies from the coast/inland with higher N/P ratios in the streams further inland.

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References

ALGER, A.S., MCKNIGHT, D.M., SPAULDING, S.A., TATE, C.M., SHUPE, G.H., WELCH, K.A., EDWARDS, R., ANDREWS, E.D. & HOUSE, H.R. 1997. Ecological processes in a cold desert ecosystem: the abundance and species distribution of algal mats in glacial meltwater streams in Taylor Valley. *INSTAAR Occasional Paper*, No. 51, 108 pp.

BAGSHAW, E., TRANTER, M., FOUNTAIN, A., WELCH, K., BASAGIC, H. & LYONS, B. 2007. The biogeochemical evolution of cryoconite holes on glaciers in Taylor Valley, Antarctica. *Journal of Geophysical Research*, **113**, 10.1029/2007JG000442.

BARRETT, J.E., VIRGINIA, R.A., LYONS, W.B., MCKNIGHT, D.M., PRISCU, J.C., DORAN, P.T., FOUNTAIN, A.G., WALL, D.H. & MOORHEAD, D.L. 2007. Biogeochemical stoichiometry of Antarctic Dry Valley ecosystems. *Journal of Geophysical Research*, **112**, 10.1029/2005JG000141.

BERNER, E.K. & BERNER, R.A. 1996. *Global environment: water, air, and geochemical cycles*. London: Prentice Hall, 376 pp.

BURKINS, M.B., VIRGINIA, R.A., CHAMBERLAIN, C.P. & WALL, D.H. 2000. The origin of soil organic matter in Taylor Valley, Antarctica: a legacy of climate change. *Ecology*, **81**, 2377–2391.

CHAPMAN, W.L. & WALSH, J.E. 2007. A synthesis of Antarctic temperatures. *Journal of Climate*, **20**, 4096–4117.

CHINN, T.J. 1993. Physical hydrology of the dry valley lakes. *Antarctic Research Series*, **59**, 1–51.

CONOVITZ, P.A., MCKNIGHT, D.M., MACDONALD, L.H., FOUNTAIN, A.G. & HOUSE, H.R. 1998. Hydrologic processes influencing streamflow variation in Fryxell basin, Antarctica. *Antarctic Research Series*, **72**, 93–108.

DORAN, P.T., WHARTON, JR R.A. & LYONS, W.B. 1994. Paleolimnology of the McMurdo Dry Valleys, Antarctica. *Journal of Paleolimnology*, **10**, 85–114.

DORAN, P.T., MCKAY, C.P., CLOW, G.D., DANA, G.L., FOUNTAIN, A.G., NYLEN, T. & LYONS, W.B. 2002. Valley floor climate observations from the McMurdo Dry Valleys, Antarctica, 1986–2000. *Journal of Geophysical Research*, **107**, 10.1029/2001JD002045

EBNET, A.F., FOUNTAIN, A.G. & NYLEN, T.H. 2005. An index model of stream flow at below freezing-temperatures in Taylor Valley, Antarctica. *Annals of Glaciology*, **40**, 76–82.

FOLEY, K.K., LYONS, W.B., BARRETT, J.E. & VIRGINIA, R.A. 2006. Pedogenic carbonate distribution within glacial till in Taylor Valley, Southern Victoria Land, Antarctica. *Geological Society of America Special Paper*, **416**, 89–103.

FORTNER, S.K. 2008. *The geochemistry of glacier snow and melt: the Oregon Cascades and Taylor Valley, Antarctica.* PhD thesis, The Ohio State University. [Unpublished].

FORTNER, S.K., TRANTER, M., FOUNTAIN, A., LYONS, W.B. & WELCH, K.A. 2005. The geochemistry of supraglacial streams of Canada Glacier, Taylor Valley (Antarctica) and their evolution into proglacial waters. *Aquatic Geochemistry*, **11**, 391–412.

FOUNTAIN, A.G., NYLEN, T.H., MONAGHAN, A., BASAGIC, H.J. & BROMWICH, D. 2009. Snow in the McMurdo Dry Valleys, Antarctica. *International Journal of Climatology*, 10.1002/joc.1933.

GOOSEFF, M.N., McKNIGHT, D.M. & RUNKEL, R.L. 2004. Reach-scale cation exchange controls on major ion chemistry of an Antarctic glacial meltwater stream. *Aquatic Geochemistry*, **10**, 221–238.

GOOSEFF, M.N., McKNIGHT, D.M., LYONS, W.B. & BLUM, A.E. 2002. Weathering reactions and hyporheic exchange controls on stream water chemistry in a glacial meltwater stream in the McMurdo Dry Valleys. *Water Resources Research*, **38**, 10.1029/2001WR000834.

GREEN, W.J., ANGLE, M.P. & CHAVE, K.E. 1988. The geochemistry of Antarctic streams and their role in the evolution of four lakes of the McMurdo Dry Valleys. *Geochimica Cosmochimica Acta*, **52**, 1265–1274.

GREEN, W.J., STAGE, B.R., PRESTON, A., WAGERS, S., SHACAT, J. & NEWELL, S. 2005. Geochemical processes in the Onyx River, Wright Valley, Antarctica: major ions, nutrients, trace metals. *Geochimica Cosmochimica Acta*, **69**, 839–850.

HARDIE, L.A. & EUGSTER, H.P. 1970. The evolution of closed-basin brines. *Mineralogical Society of America Special Publication*, **3**, 273–290.

HARRIS, K., CAREY, A.E., WELCH, K.A., LYONS, W.B. & FOUNTAIN, A.G. 2007. Solute and isotope geochemistry of near-surface ice melt flows in Taylor Valley, Antarctica. *Geological Society of America Bulletin*, **119**, 548–555.

HODSON, A. 2006. Biogeochemistry of snowmelt in an Antarctic glacial ecosystem. *Water Resources Research*, **42**, 10.1029/2005WR004311.

HOWARD-WILLIAMS, C. & VINCENT, W.F. 1989. Microbial communities in Southern Victoria Land streams (Antarctica) I: photosynthesis. *Hydrobiologia*, **172**, 27–38.

HOWARD-WILLIAMS, C., PRISCU, J.C. & VINCENT, W.F. 1989. Nitrogen dynamics in two Antarctic streams. *Hydrobiologia*, **172**, 51–61.

HOWARD-WILLIAMS, C., VINCENT, C.L., BROADY, P.A. & VINCENT, W.F. 1986. Antarctic stream ecosystems: variability in environmental properties and algal community structure. *Internationale Revue der gesamten Hydrobiologie*, **71**, 511–544.

HOWARD-WILLIAMS, C., PETERSON, D., LYONS, W.B., CATTANEO-VIETTI, R. & GORDON, S. 2006. Measuring ecosystem response in a rapidly changing environment: the Latitudinal Gradient Project. *Antarctic Science*, **18**, 465–471.

HU, M.-H., STALLARD, R.F. & EDMOND, J.M. 1982. Major ion chemistry of some large Chinese rivers. *Nature*, **298**, 550–553.

KENNEDY, A.D. 1993. Water as a limiting factor in the Antarctic terrestrial environment: a biogeographical synthesis. *Arctic and Alpine Research*, **25**, 308–315.

KEYS, J.R. & WILLIAMS, K. 1981. Origin of crystalline cold desert salts in the McMurdo region, Antarctica. *Geochimica et Cosmochimica Acta*, **45**, 2299–2309.

LYONS, W.B., LAYBOURN-PARRY, J., WELCH, K.A. & PRISCU, J.C. 2006. Antarctic lake systems and climate change. *In* BERGSTROM, D.M., CONVEY, P. & HUISKES, A.H.L., *eds. Trends in Antarctic terrestrial and limnetic ecosystems: Antarctica as a global indicator.* Dordrecht: Springer, 273–295.

LYONS, W.B., FOUNTAIN, A.G., DORAN, P.T., PRISCU, J.C., NEUMANN, K. & WELCH, K.A. 2000. The importance of landscape position and legacy: the evolution of the lakes Taylor Valley, Antarctica. *Freshwater Biology*, **43**, 355–367.

LYONS, W.B., WELCH, K.A., FOUNTAIN, A.G., DANA, G.L., VAUGHN, B.H. & McKNIGHT, D.M. 2003. Surface glaciochemistry of Taylor Valley, southern Victoria Land, Antarctica and its relationship to stream chemistry. *Hydrological Processes*, **17**, 115–130.

LYONS, W.B., WELCH, K.A., SNYDER, G., OLESIK, J., GRAHAM, E.Y., MARION, G.M. & POREDA, R.J. 2005. Halogen geochemistry of the McMurdo Dry Valleys Lakes, Antarctica: clues to the origin of solutes and lake evolution. *Geochimica et Cosmochimica Acta*, **69**, 305–323.

LYONS, W.B., WELCH, K.A., NEUMANN, K., TOXEY, J.K., McARTHUR, R., WILLIAMS, C., McKNIGHT, D.M. & MOORHEAD, D. 1998. Geochemical linkages among glaciers, streams, and lakes within the Taylor Valley, Antarctica. *Antarctic Research Series*, **72**, 77–92.

LYONS, W.B., WELCH, K.A., PRISCU, J.C., LABOURN-PARRY, J., MOORHEAD, D., McKNIGHT, D.M., DORAN, P.T. & TRANTER, M. 2001. The McMurdo Dry Valleys Long-Term Ecological Research Program: new understanding of the biogeochemistry of the Dry Valley lakes: a review. *Polar Geography*, **25**, 202–217.

MAURICE, P.A., McKNIGHT, D.M., LEFF, L., FULGHUM, J.E. & GOOSEFF, M.N. 2002. Direct observation of aluminosilicate weathering in the hyporheic zone of an Antarctic Dry Valley stream. *Geochimica et Cosmochimica Acta*, **66**, 1335–1347.

McKNIGHT, D.M., GOOSEFF, M.N., VINCENT, W.F. & PETERSON, B.J. 2008. High latitude rivers and streams. *In* VINCENT, W.F. & LAYBOURN-PARRY, J., *eds. Polar lakes and rivers: limnology of Arctic and Antarctic aquatic ecosystems.* Oxford: Oxford University Press, 83–102.

McKNIGHT, D.M., NIYOGI, D.K., ALGER, A.S., BOMBLIES, A., CONOVITZ, P.A. & TATE, C.M. 1999. Dry Valley streams in Antarctica: ecosystems waiting for water. *Bioscience*, **49**, 985–995.

MIKUCKI, J.A., FOREMAN, C.M., SATTLER, B., LYONS, W.B. & PRISCU, J.C. 2004. Geomicrobiology of Blood Falls: an iron-rich saline discharge at the terminus of the Taylor Glacier, Antarctica. *Aquatic Geochemistry*, **10**, 199–200.

MOORHEAD, D.L., DORAN, P., FOUNTAIN, A.G., LYONS, W.B., McKNIGHT, D.M., PRISCU, J.C., VIRGINIA, R.A. & WALL, D.H. 1999. Ecological legacies: impacts on ecosystems of the McMurdo Dry Valleys. *Bioscience*, **49**, 1009–1019.

MULLIN, J.B. & RILEY, J.P. 1955. The colorimetric determination of silicate with special reference to sea and natural waters. *Analytica Chimica Acta*, **12**, 162–176.

NEZAT, C.A., LYONS, W.B. & WELCH, K.A. 2001. Chemical weathering in streams of a polar desert (Taylor Valley, Antarctica). *Geological Society of America Bulletin*, **113**, 1401–1408.

PRISCU, J.C. 1995. Phytoplankton nutrient deficiency in lakes of the McMurdo Dry Valleys, Antarctica. *Freshwater Biology*, **34**, 215–227.

PUGH, H.E., WELCH, K.A., LYONS, W.B., PRISCU, J.C. & McKNIGHT, D.M. 2003. Biochemistry of Si in the McMurdo Dry Valley lakes, Antarctica. *International Journal of Astrobiology*, **1**, 737–749.

SMITH, C.L. & DREVER, J.I. 1976. Controls on the chemistry of springs at Teels Marsh, Mineral County, Nevada. *Geochimica et Cosmochimica Acta*, **40**, 1081–1093.

STALLARD, R.F. & EDMOND, J.M. 1983. Geochemistry of the Amazon. 2. The influence of geology and weathering environment on the dissolved load. *Journal of Geophysical Research*, **88**, 9671–9688.

VINCENT, W.F. & HOWARD-WILLIAMS, C. 1986. Antarctic stream ecosystems: physiological ecology of a blue-green algal epilithon. *Freshwater Biology*, **16**, 219–233.

VINCENT, W.F. & HOWARD-WILLIAMS, C. 1989. Microbial communities in southern Victoria Land streams (Antarctica). II. The effects of low temperature. *Hydrobiologia*, **172**, 39–49.

WELCH, K.A., LYONS, W.B., GRAHAM, E., NEUMANN, K., THOMAS, J.M. & MIKESELL, D. 1996. Determination of major element chemistry in terrestrial waters from Antarctica by ion chromatography. *Journal of Chromatography A*, **739**, 257–263.

WITHEROW, R.A., BERTLER, N.A.N., WELCH, K.A., LYONS, W.B., MAYEWSKI, P.A., SNEED, S.B., NYLEN, T., HANDLEY, M.J. & FOUNTAIN, A. 2006. The aeolian flux of calcium, chloride and nitrate to the McMurdo Dry Valleys landscape: evidence from snow pit analysis. *Antarctic Science*, **18**, 497–505.