Determination of major element chemistry in terrestrial waters from Antarctica by ion chromatography

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Abstract

As part of the new Long Term Ecological Research (LTER) project in the McMurdo Dry Valleys of Antarctica, a systematic aqueous geochemical sampling program has been undertaken. A series of terrestrial water samples have been collected and analyzed for major ion chemistry by ion chromatography. The concentrations of ions cover a wide range of total dissolved solids (TDS) from relatively pristine glacier ice to hypersaline lake waters. Some of the challenges which are encountered while trying to collect and analyze samples covering a wide range of concentrations in such a hostile environment are discussed.

Keywords: Water analysis; Inorganic anions; Inorganic cations

1. Introduction

The McMurdo Dry Valleys (MDV) of southern Victoria Land, Antarctica, are located in the western coast of the Ross Sea at 77°S. These valleys are among the most extreme deserts in the world, having a mean average temperature of ca. −17°C and a precipitation rate of ca. 10 cm per year [1,2]. However, an aquatic system exists in these valleys resulting from short-term glacier melt during the austral summer. These aquatic systems include very dilute snow/ice, ephemeral streams and fresh to brackish to hypersaline lakes. The lakes are perennially ice-covered.

Since the International Geophysical Year

(IGY) of 1958, many investigations have studied the chemistry and ecology of the aquatic systems of the MDV. Major ion chemistry has previously been used as a tool to investigate geochemical processes which are occurring in this region today, and also to investigate the geochemical evolution of this region [3–5]. Previous work has evaluated either individual lake chemistry and/ or determined the geochemical fluxes of certain elements from stream(s) into lake(s). A Long Term Ecological Research (LTER) site has recently been established in the Dry Valleys. Systematic environmental data collection is an extremely important component of the LTER. As part of this environmental monitoring program, samples from glaciers, meltwater streams and lakes are collected for chemical analysis. As part

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of this LTER, our work has dealt with the continuum of terrestrial waters in the MDVs, from the very dilute glacier ice (Cl^- as low as $1.7 \cdot 10^{-5}$ g/l) to the hypolimnion on Lake Bonney (Cl^- concentrations as high as $1.8 \cdot 10^2$ g/l).

In addition, in most of the previous work, ion chromatographic techniques were not utilized. Cations were determined spectrophotometrically and anions by wet chemical techniques [4,5]. Only in the most recent work by our group and that of Italian investigators working in coastal areas north of the MDVs has ion chromatography been the method of choice for both cations and anions [6]. The utilization of ion chromatographic techniques to determine the major element chemistry over such a very wide range of total dissolved solids (TDS) is unique to this study.

1.1. Geochemistry program

Samples collected from the glaciers are used to investigate spatial variability in precipitation chemistry as a function of distance from the ocean and elevation. In addition, the glacier samples can be used to determine the chemistry of the source of water to melt streams. The stream samples are used to determine flux of water, ions and nutrients into the lakes. In addition, the spatial and temporal variability of stream chemistry is studied as a function of source of melt water, stream discharge, weathering rates, stream length and soil and rock type. Water samples collected from the lakes provide major ion data for ecological studies. The data also provide a basis for comparison between the lakes. Samples collected from the lakes are also used to investigate temporal (seasonal and interannual) variability. The major ion chemistry of each of these components is studied and then used to investigate the fluxes of materials (i.e., water, nutrients, ions) within the system.

The range of total dissolved solids (TDS) in the samples varies greatly within this region. For example, concentrations range from a few μg/l in the case of the glacier ice to hypersaline conditions in the deep waters of some of the lakes. In this paper we describe sampling meth-

ods, sample processing and chemical analysis by ion chromatography. In particular, some of the challenges of trying to process and analyze a wide range of samples are discussed.

2. Experimental

2.1. Sample collection

Snow and ice samples were collected from the glaciers by personnel wearing polyethylene gloves to minimize possible contamination. Snow samples were collected by scooping the sample with clean polypropylene straight-sided jars. Glacier ice was sampled by chipping with an ice axe and placing the ice pieces into a precleaned zip-lock bag or a straight-sided polypropylene jar. Before melting the samples, the ice pieces were held with stainless-steel forceps and rinsed with 18-MΩ water to remove any surface contamination [7], then placed in a clean container.

Stream samples were collected in precleaned wide-mouthed polyethylene bottles. The bottles were rinsed three times with stream water and the sample was collected at a point just upstream of the gaging station. Aliquots of the sample were collected for alkalinity titration and for pH. Clean polyethylene gloves were worn during sampling to minimize possible contamination.

The lake sampling was carried out by lowering a Niskin bottle through a hole in the ice cover of the lake to specified depths. Samples were then collected in precleaned plastic bottles. Separate aliquots were collected in serum vials for pH and dissolved inorganic carbon (DIC) measurements. Samples were returned to field laboratories for processing and for time-sensitive analyses such as pH.

Dedicated sampling equipment for each lake and for the streams has been important for maintaining the integrity of the samples. For example, the range of Cl^- concentration in the investigated lakes varies by more than three orders of magnitude. This carryover between samples becomes a potential problem. Carryover can also be a potential problem during analysis

and, therefore analytical blanks are run to monitor this.

For the lake and stream samples, the initial sample processing was carried out in field laboratories. A 100-ml sample aliquot was filtered for each anion and cation sample. All lake and stream samples were filtered through 0.4-μm Nucleopore filters, usually within 12 h of collection. In addition to the dedicated filtration equipment used at each lake, separate filtration equipment was also dedicated to filtering stream samples. The cation samples were filtered into acid-washed polyethylene bottles which had been rinsed with DI water, while the anion samples were filtered into DI-washed bottles. The cation samples were acidified by adding 0.5% (v/v) of concentrated HCl. Quality control was maintained by carefully rinsing all filtration apparatus with DI between samples and by processing filtration blanks which were later run as samples.

The majority of water chemistry samples were returned to the Crary Laboratory, McMurdo Station, Antarctica, for analysis. Some of the samples were returned to our laboratory at the University of Alabama for analysis owing to time constraints during the field season.

2.2. Ion chromatography

A DX-300 ion chromatographic system (Dionex, Sunnyvale, CA, USA) was used for the major ion analyses. The system included a gradient pump module, high-pressure injection valve with a 25-μl sample loop, a Dionex conductivity detector (CDM-3), advanced computer interface and automated sampler. The timed events and data collection were controlled by the Dionex AI-450 chromatography software for Windows. The same ion chromatographic system was used but was switched back and forth between anion and cation configurations.

For the anions, a Dionex Ionpac AS4A-SC analytical column (250 × 4 mm I.D.) and AG4A-SC guard column (50 × 4 mm I.D.) were used along with an Anion Self-Regenerating Suppressor-1. The eluent was 1.8 mM Na$_2$CO$_3$–1.7 mM NaHCO$_3$. The gradient pump flow-rate

was 2 ml/min and the background conductivity was ca. 16 μS.

For the cations, the Dionex Ionpac CS12 analytical column (250 × 4 mm I.D.) and CG12 guard column (50 × 4 mm I.D.) were used with a Cation Self-Regenerating Suppressor-1. The eluent was 0.020 M methanesulfonic acid. The eluent flow-rate was 1.0 ml/min and the background conductivity was ca. 200–250 nS.

The stock standard solutions used for a typical batch of samples from the streams and lakes are specified in Table 1. Appropriate dilutions of the stock standards were used to prepare a range of standards for calibration. Owing to the high salt concentrations in many of the samples, dilutions were made before the samples were run. Many of the stream samples could be run without dilution. However, for the lakes, dilutions ranged from 1:2 for Lake Hoare surface water up to 1:6000 for the Lake Bonney deep water. The samples were diluted by serial dilution, using disposable plastic microbreakers and adjustable pipettors.

Replicate and duplicate samples were run daily. Usually, each sample was injected twice and samples from each batch were run in duplicate to check the precision of the dilutions. In almost every case, the relative standard deviation of the duplicates was less than 1%, even with dilutions of 1:6000. In addition, analytical blanks and filtration blanks were analyzed to check the quality control.

Lake water samples were analyzed in the field

Table 1
Concentrations of ions in the stock standard solutions for cations and anions

Cation	Concentration (mg/l)	Anion	Concentration (mg/l)
Na$^+$	10	Cl$^-$	100
K$^+$	20	SO$_4^{2-}$	100
Mg^{2+}	50		
Ca^{2+}	50		

The relative concentrations were based on the expected ratios of ions in the samples. Working standard solutions used for calibration were prepared by appropriate dilution of the stock standard solutions.

Table 2
Difference between total anions and total cations (%), with
standard deviations in parentheses

All streams	3.4 (2.5)
Lake Hoare	2.1 (2.1)
Lake Fryxell	3.0 (2.0)
East Lake Bonney	1.8 (1.4)
West Lake Bonney	1.4 (1.0)

The ionic balance is determined as a check on the analytical
results.

laboratories for DIC with an infrared gas ana-
lyzer. The alkalinity of the stream samples was
determined by titration with strong acid. The
alkalinity and DIC data were used with the other
major ion data to calculate ionic balances as a
further check on the data quality. Results of the
ionic balance calculations are summarized in
Table 2.

3. Results and discussion

3.1. Acidified samples

During the first field season, problems were
found with many of the cation chromatograms

for the stream samples that had been acidified.
Two cation chromatograms of a sample collected
from a meltwater stream in the Taylor Valley
show differences between acidified and un-
acidified samples (Fig. 1). The upper chromato-
gram shows the sample that had ben acidified by
the addition of 0.5 ml of concentrated HCl to 100
ml of sample, while the lower sample was not
acidified. The acidified sample had poor peak
resolution and an irregular baseline; the peaks
could not be adequately quantified. Most of the
stream samples showed similar peak broadening
after acidification with cation analysis by IC. The
samples had to be re-analyzed for cations using
an unacidified aliquot. Similar chromatographic
interference was observed with water from
Alabama which had been acidified with nitric
acid. This phenomenon seems to be neither
dependent on the type of acid nor specific to
Antarctic waters.

Acidification was necessary for the Antarctic
lake samples, however. Depth profiles of
acidified and unacidified calcium samples in Lake
Hoare, one of the lakes in the study area (Fig. 2),
show that calcium concentrations in the un-
acidified sample were significantly lower, sug-
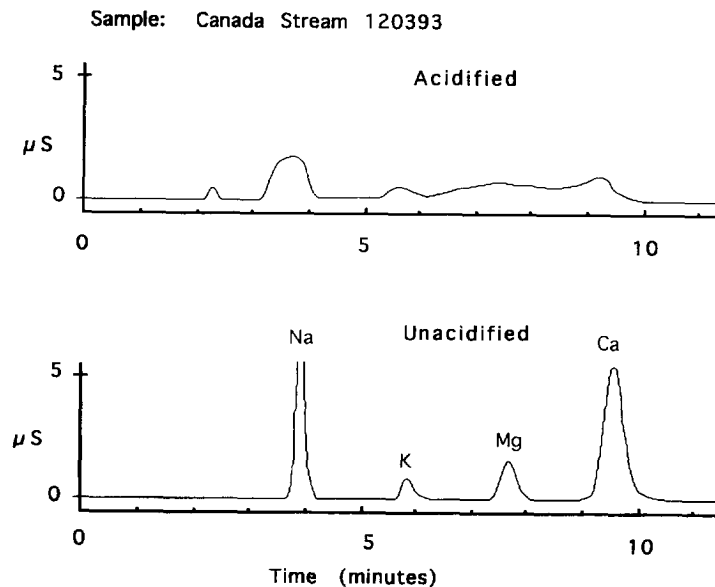gesting that Ca^{2+} was lost from the sample

Fig. 1. Two cation chromatograms for a stream sample demonstrating the difference between acidified and unacidified samples.
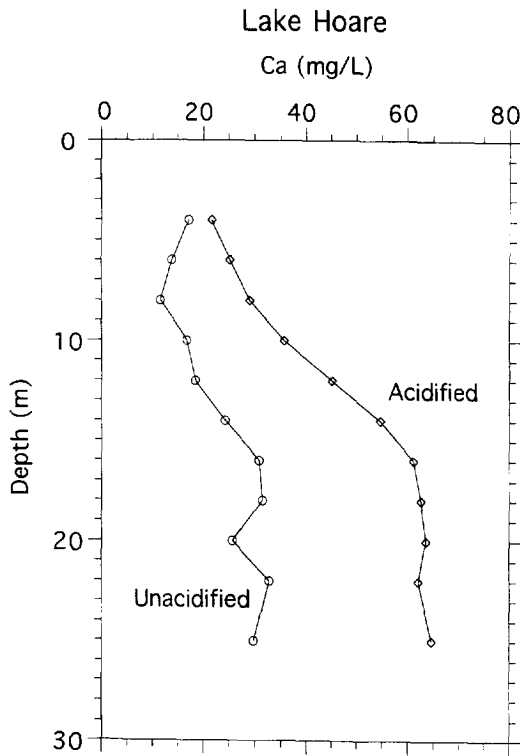
Lake Hoare

Ca (mg/L)

Fig. 2. Depth profiles of Ca^{2+} in Lake Hoare for acidified vs. unacidified samples.

during storage. Our unpublished work and the work of Green et al. [4] indicate that many of the lake samples should be supersaturated with respect to $CaCO_3$ and therefore $CaCO_3$ is predicted to precipitate. Acidification is therefore necessary to keep the calcium in solution. Owing to concern that the addition of acid might interfere with the cation analysis, all of the lake samples were diluted with DI water before analysis, which reduced amount of acid injected on to the column compared with the stream samples. The chromatograms for the lake samples were checked; the baselines looked normal and there was good peak resolution. There was no significant difference between the analyses for the other cations including Na^+, K^+, and Mg^{2+} in the acidified vs. unacidified lake samples. This suggested that this amount of acid does not interfere with the analysis, and that addition of acid is required to keep calcium in solution between the time of collection and analysis.

3.2. Range of samples

Another example of the analytical results shows a log–log plot illustrating the wide range of salt concentrations in the Taylor Valley samples (Fig. 3). For example, Cl^- concentrations within this valley vary by seven orders of magnitude. Although the other major elemental variations are not so extreme, they are still fairly large (Table 3). There is a strong relationship between Cl^- and Na^+ in the various waters from this region and the Cl^- to Na^+ ratio in these samples is close to the seawater ratio (1.8, w/w). This is probably a reflection that a major source of ions in this region is sea salt aerosols in precipitation.

Within the lakes in this valley there is a wide range of salinity. A plot of the Cl^- depth profiles in the lakes shows that the lakes are highly stratified chemically and are different from each other (Fig. 4). Lake Hoare is a freshwater lake, Lake Fryxell becomes brackish at depth and Lake Bonney is hypersaline. The east and west lobes of Lake Bonney are separated by a sill which divides them at 11 m. The strong chemical stratification in the lakes prevents vertical mixing and allows these two lobes of the lake to remain distinct both chemically and biologically. As mentioned above, these systems have been investigated since IGY. However, even after nearly 30 years, little consensus exists on the reasons and the geochemical and biogeochemical mecha-
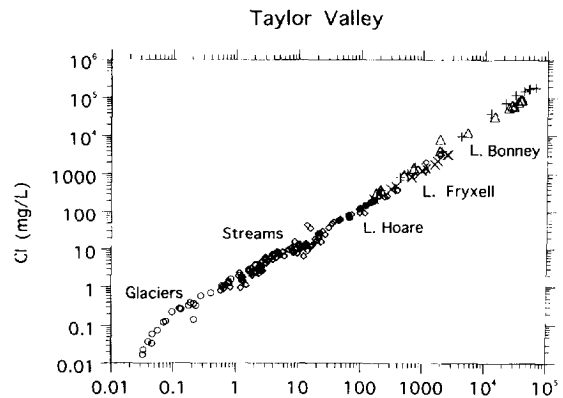
Taylor Valley

Fig. 3. Log–log plot of Cl^- vs. Na^+ in a range of samples collected from the Taylor Valley.

Table 3
Range of major element concentrations (mg/l) in terrestrial waters, Taylor Valley, Antarctica

Location	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	SO_4^{2-}
Lake Bonney	34.1–2558	21.4–36 272	131–68 852	7.4–2986	244–191 044	83.3–5151
Lake Hoare	23.0–9.18	11.6–37.7	54.5–184	9.7–30.7	75.1–239	39.9–109
Lake Fryxell	22.3–147	10.0–371	76.6–2695	9.2–196	108–3733	19.7–206
Streams	1.67–93.4	0.28–272	0.56–1871	0.32–62.9	0.81–94.9	0.73–380
Glaciers	0.023–5.28	0.002–0.48	0.033–2.08	0.004–0.49	0.017–4.00	0.025–3.08

All data from 1994–95 field season.

nisms for this large variation in the chemistry of the lakes. Even the origin of the solutes in the lakes is in dispute. Recent work has suggested that seawater, precipitation (glacier melt) and chemical weathering of the watershed could all contribute solutes to the lakes [8]. Our research on the isotopic variation in the lakes indicates that past climatic changes have been extremely imp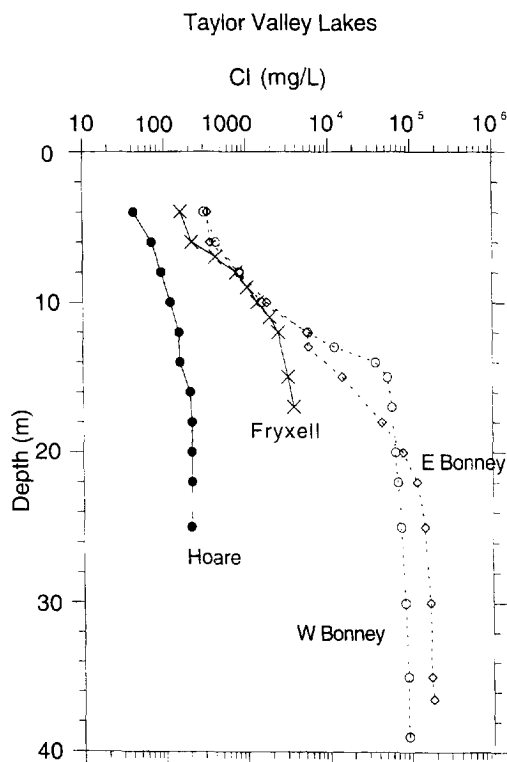ortant in the chemical evolution of the lakes [9]. In any case, the very large chemical variations in solute concentrations and the elemental ratios from lake to lake remain a mystery and merit further investigation.

From an analytical perspective, these lakes also pose a few problems. Cl^- concentrations in the deep waters of the east lobe of Lake Bonney are ca. 180 000 mg/l (Fig. 4). That is approximately ten times the Cl^- concentration of seawater. All of the sampling equipment and filtration equipment must be rinsed thoroughly to prevent carryover of salts from one sample to the next. In addition, these samples require extensive dilution before analysis.

A plot of SO_4^{2-} vs. Na^+ concentrations in the Taylor Valley samples shows that SO_4^{2-} generally increases as Na^+ increases (Fig. 5). However, the relationship is not so strong as that between Cl^- and Na^+. This suggests that Na^+ and SO_4^{2-} are

Fig. 4. Cl^- depth profiles for the major lakes in the Taylor Valley.
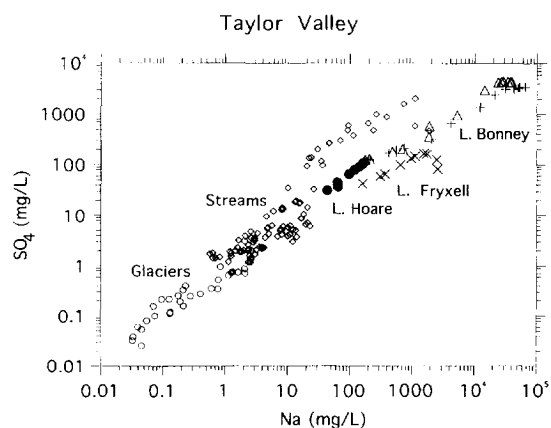

Fig. 5. Log–log plot of SO_4^{2-} vs. Na^+ for samples in the Taylor Valley.

derived from different sources, or that they behave differently in the system. The ratio of SO_4^{2-} to Na^+ in most of the samples is higher than the seawater ratio of 0.25 (w/w). One notable exception is Lake Fryxell, which becomes anoxic at depth and the presence of H_2S has been observed in the samples. Sulfate reduction is occurring in these waters and SO_4^{2-} is removed from the water column [3]. SO_4^{2-} concentrations in Lake Fryxell are low relative to Na^+, compared with the other sites. This reflects a difference in biogeochemical processes going on in the different lakes.

4. Conclusions

The results of our work indicate that with careful sample collection, processing and analysis, accurate and precise measurements of major ion chemistry can be made on a continuum of terrestrial water samples having an extremely wide range of TDS. The use of ion chromatography as the sole analytical tool in this work has greatly enhanced the precision of the measurements and the efficiency of analyzing many samples per field season. This latter point is extremely important in that it is preferable to analyze as many samples as possible in Antarctica rather than to ship them back to the USA for analysis at a much later date.

The data generated from our systematic sample collection and careful sample processing and analysis will help to resolve some of the outstanding questions regarding chemical evolution of the system, the source of solutes to the lakes and biogeochemical cycling in this ecosystem.

Acknowledgements

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