

# The biogeochemistry of Si in the McMurdo Dry Valley lakes, Antarctica

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**Abstract:** The biogeochemical dynamics of Si in temperate lakes is well documented and the role of biological uptake and recycling is well known. In this paper we examine the Si dynamics of a series of ice-covered, closed-basin lakes in the McMurdo Dry Valley region ( $\sim 78^\circ$  S) of Antarctica. Our data and calculations indicate that biological uptake of Si is not a major process in these lakes. Mass balance considerations in Lake Hoare, the youngest and the freshest lake, suggest that annual stream input during relatively low-flow years is minor and that Si dynamics is greatly influenced by hydrological variation and hence climatic changes affecting stream flow and lake level. The data imply that the Si input during high-flow years must dominate the system. Subtle changes in climate have a major control on Si input into the lake, and Si dynamics are not controlled by biogeochemical processes as in temperate systems.

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## Introduction

The McMurdo Dry Valleys (MCM) region of Antarctica has often been described as a terrestrial analogue of Mars. The ice-covered lakes in MCM have been proposed as analogues of the paleolakes that might have existed on Mars during its early history (Wharton *et al.* 1989, 1995; Doran *et al.* 1998). Doran *et al.* (2003) have reviewed the exopaleolimnology and have argued that the variations of the aquatic environments that presently exist in the MCM region may provide important clues as to what features to look for in a search of signs of former life on Mars. Therefore, the investigation of biogeochemical processes in the dry valley lakes could potentially provide insight into the functioning of ancient lake systems on Mars. In addition, the MCM lakes provide extreme environmental end members, the biogeochemistries of which should be compared with more temperate lake systems that have more complicated dynamics (i.e. organic matter input from the landscape).

Although the MCM lakes have been investigated since the International Geophysical Year (1957–1958), there have been few attempts to understand and quantify nutrient dynamics in these lakes (Canfield & Green 1985; Green *et al.* 1989; Priscu 1995; Priscu *et al.* 1999), and these works have primarily dealt with carbon, nitrogen and phosphorus dynamics.

The first quantitative evaluation of silicon biogeochemistry in the Taylor Valley lakes, Southern Victoria Land, was conducted as part of the McMurdo Dry Valleys, Long-Term Ecological Research (MCM-LTER) programme and is presented in this paper. Silicon is a very important element in that it is the major building block of aluminosilicate minerals, the primary mineral of the Earth's (and Martian) crust. It is also a major plant nutrient, especially for diatoms, as they use it for the building of frustules. Because diatoms are ubiquitous in Earth's aquatic environments, the biogeochemistry of silicon is of biological importance.

## Study location

Taylor Valley (Fig. 1),  $77^\circ 40' S$ ,  $163^\circ 00' E$ , is part of the McMurdo Dry Valleys in Southern Victoria Land, Antarctica. The valley is 33 km long and 12 km wide (Fig. 1). Taylor Valley is a polar desert with a mean annual temperature of approximately  $-20^\circ C$  (Clow *et al.* 1988) and a total annual precipitation of less than 10 cm (Keys 1980).

The geomorphology of Taylor Valley has been modified by the movement of glaciers, the inflow of ocean waters and the rising and falling of lake levels over the past few million years (Porter & Beget 1981). Because of the movements of glaciers, the valley floor contains a mosaic of tills of differing age and composition (Péwé 1960; Stuvier *et al.* 1981; Burkins *et al.* 1999). The ages of the morainal materials in the region date to 2.5 Myr (Brown *et al.* 1991). The soils and tills are derived from a number of rock types within the Victoria Land region.

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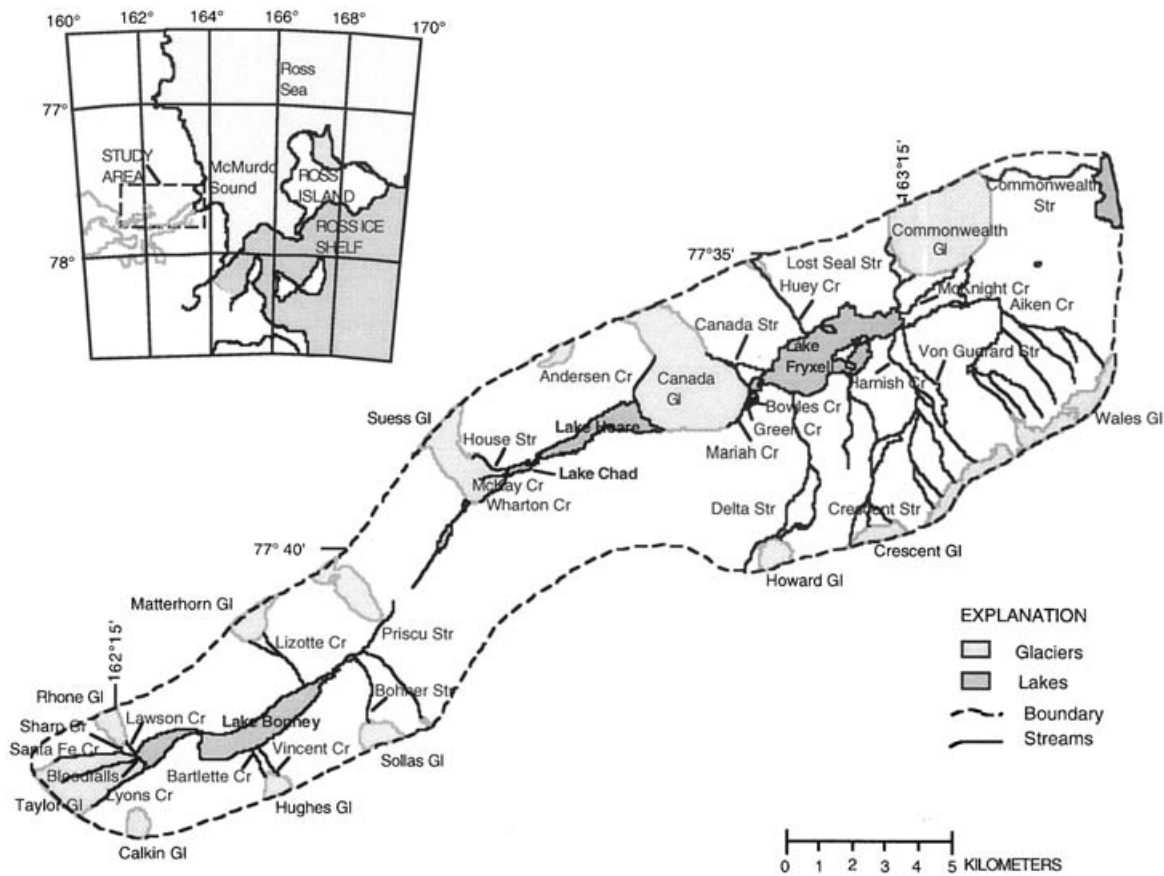


Fig. 1. Map of Taylor Valley.

These include the Precambrian metamorphic basement rocks (Ross Supergroup), early Paleozoic intrusives (Granite Harbor formation), a series of sedimentary rocks of Devonian to Jurassic age (Beacon Supergroup) and the Jurassic age Ferrar Dolerite sills. In addition, more recent McMurdo Volcanic rocks are present. Taylor Valley soils are composed of unconsolidated material ranging from primarily sand to boulder size. Relatively flat areas are often covered by desert pavement, a thin layer of coarse stones or gravel that overlie sandy material (Claridge & Campbell 1977). Permafrost begins about 0.5 m below the ground surface (Conovitz *et al.* 1998).

Taylor Valley contains three major closed-basin lakes: Lake Bonney, Lake Hoare and Lake Fryxell (Fig. 1). These lakes are of the order of 20–60 million m<sup>3</sup> in volume and vary in temperature from  $-4.5$  to  $7$  °C (Table 1). The lakes are covered with perennial ice that is currently 3–6 m thick. During most summers, a moat of water forms at the edges of the lakes, as the ice near the shore melts completely (Fountain *et al.* 1999). From the 1970s until about 1990, there was a net gain in water to the lakes and lake levels had been generally rising (Chinn 1993). From 1990 to 2000, lake levels decreased (Doran *et al.* 2002).

The lakes have abundant planktonic and benthic microbial populations (Vincent 1988). The plankton of these lakes are dominated by unicellular algae and bacteria, although protozoans and rotifers also occur (Priscu *et al.* 1999.) Algal populations are dominated by cryptophytes, crysophytes,

chlorophytes and cyanobacteria (Lizotte & Priscu 1998). No higher forms of life, such as pelagic crustacea, mollusc, insects or fish, have been observed (Doran *et al.* 1994). Microbial mats are primarily composed of cyanobacteria, pennate diatoms and eubacteria (Wharton *et al.* 1983).

Lake Hoare is essentially a freshwater lake with a relatively uniform temperature profile, but an increase in TDS with depth. Lake Fryxell is brackish at depth with a chemocline and an oxycline at  $\sim 9$  m. Lake Bonney consists of two basins that are separated by a sill below  $\sim 13$  m. Both the eastern and western lobes of Lake Bonney are highly stratified with TDS values in the bottom waters of  $\sim 240$  and  $\sim 150$  g l<sup>-1</sup>, respectively (Spigel & Priscu 1998). All three lakes have been described as stable with diffusion being the primary physical/chemical process occurring (Spigel & Priscu 1998). The ice covers essentially eliminate the advective distribution of solutes in these lakes, making them very different from temperate lake systems in that there is no spring or autumn turnover.

Ephemeral streams transport glacial meltwater to terminal lakes that lose water only through sublimation and evaporation (Fountain *et al.* 1999). The only source of water to the streams is glacial melt during the austral summer (Conovitz *et al.* 1998). There is no evidence of significant groundwater flow into these lakes. For 6–10 weeks per year (late November to early February), streams flow from their glacial source to the lakes. Stream flow is intermittent with highly variable

Table 1. *Characteristics of the Taylor Valley Lakes (Lyons et al. 2000)*

Characteristic	Lake Fryxell	Lake Hoare	Lake Bonney
Surface area ( $1 \times 10^6$ m <sup>2</sup> )	7.1	1.91	4.81
Volume ( $1 \times 10^6$ m <sup>3</sup> )	25.2	17.5	64.8
Maximum depth (m)	21	34	40
Water temperature (°C)	0–2.6	0–0.5	–4.5 to 7.0

discharge, both daily and seasonally, owing to temperature and radiation fluctuations (Conovitz *et al.* 1998; McKnight *et al.* 1999).

### *Silica biogeochemistry*

Because Si is one of the most abundant elements in the crust of the Earth, compounds of silicon occur in all natural waters. They may be present either as suspended solids or in solution. Biomineralization of silicon in the form of opal or amorphous hydrated silicon oxide (biogenic silica,  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ ) is performed by a number of aquatic organisms, of which diatoms are the most widely abundant. In the dissolved form, silicon is primarily present as silicic acid,  $\text{H}_4\text{SiO}_4$ , the undissociated monomeric form, which dominates in natural waters at pH below 9 (Aston 1983; Stumm & Morgan 1996). Silicic acid is derived either from weathering reactions of aluminosilicate minerals or from dissolution of the biogenic silica following death of the organism.

It is well known that silicon cycling in temperate lakes is an annual event controlled by diatom production (Hoffmann *et al.* 2002). Diatoms in the epilimnion take up silicic acid. As the frustules settle and the lake stratifies, the planktonic diatom production often becomes limited by silicic acid bio-availability. In stratified lakes, diatom production can be limited by allochthonous silicic acid input as upward diffusion of silicic acid from redissolved diatom debris in sediments is a slow process (Hoffmann *et al.* 2002).

The amorphous silica contained in diatoms dissolves five orders of magnitude faster than mineral silicates, at about  $2 \times 10^{-9}$  mol cm<sup>-2</sup> s<sup>-1</sup> (Hurd 1983). Most of the information available about diatom wall dissolution has been derived in the laboratory for marine species. Oceans are strongly undersaturated with respect to amorphous silica and the silica incorporated into diatom cells is quickly recycled after their death (Nelson *et al.* 1995). Most freshwater systems are also strongly undersaturated. The rate of dissolution of the diatom skeletons is known to be affected by many factors including, the presence of protective organic skins (Bidle & Azam 1999), temperature (dissolution slows in low-temperature waters (Lewin 1961; Werner 1977; Lawson *et al.* 1978)) and the presence of salt (which enhances the dissolution rates of diatoms (Kato & Kitano 1968; Kamatani 1971; Hurd & Birdwhistell 1983; Barker *et al.* 1994)). Silica dissolution has not been as extensively studied in lake water. Some authors have shown that the majority of Si sequestered annually in the form of frustules dissolves before being buried in the permanent sediment of the lake (Parker *et al.* 1977), yet in

other lakes biogenic Si can accumulate in sediments (Callender & Granina 1997).

## Methods

### *Collection*

Members of the MCM-LTER team collected water samples from several Taylor Valley streams throughout the austral summer over a period of three field seasons, 1999–2002. Lake samples are collected two to four times per year in each lake at approximately the same location from year to year. Within 12 h of collection, samples were filtered through 0.4 µm polycarbonate membrane filters into water-washed high-density polyethylene (HDPE) bottles. HDPE bottles were rinsed three times with distilled, deionized 18 MΩ (DI) water and then filled with DI water to soak overnight. Prior to use, the bottles were emptied and left in a class 100 laminar flow hood to dry.

### *Analysis*

Reactive silicate was measured colorimetrically using a method based on Mullin & Riley (1955) in some cases modified for the saline waters in the lakes (Toxey *et al.* 1997). An estimate of the precision of the measurements determined from the percentage relative standard deviation of the standards is <2%. The average percentage error for check standards was also determined to be <2%. Blank values for DI water processed as a sample and stored in our clean bottles were always less than the detection limit of the method.

## Results

Stream concentrations during both field seasons range from 4 to 242 µM (Table 2). The mean values for 1999–2000 were very similar in 2000–2001 for each of the basins except for West Bonney, where the Bloodfalls concentration was much lower in 2000–2001. (Bloodfalls is a frozen saline body beneath the snout of Taylor Glacier. It may be a remnant of a former marine incursion into the valley or a portion of Lake Bonney that has been overridden by the Taylor Glacier.) The Bonney basin streams have the highest average concentration in 1999–2000. However, in 2000–2001, the highest stream average is in the Fryxell basin. In 1999–2000, the Si concentration of Bloodfalls was much higher than any of the other Taylor Valley streams. This stream flows off the snout of the Taylor Glacier over ice with very high concentrations of Cl<sup>-</sup> and other major ions solubilized from frozen salt water pushing up from underneath the glacier. The increased average Si concentration in the Bonney basin for 1999–2000 reflects the high Si concentrations from Bloodfalls samples collected during that season. In both field campaigns, the Lake Hoare basin streams have the lowest average concentration.

Fig. 3 shows plots of the Si profiles for the Taylor Valley lakes. The early summer samples in 1999–2000 are shown for Lake Fryxell and the eastern and western lobes of Lake Bonney. The early and late summer samples for the

Table 2. Taylor Valley stream lengths and Si average concentrations

	1999–2000 Average stream Si concentration $\mu\text{M}$	2000–2001 Average stream Si concentration $\mu\text{M}$
<b>Fryxell Basin</b>	<b>52</b>	<b>61</b>
Aiken Creek	1.3	43
Andrews Creek	1.5	13
Bowles Creek	0.9	82
Canada Stream	1.5	27
Crescent Stream	5.6	–
Delta Stream	11.2	81
Green Creek	1.2	32
Harnish Creek	5.1	–
Huey Creek	2.1	82
Lost Seal Stream	2.2	36
Mariah Creek	0.9	8
McKnight Creek	2.0	50
VonGuerard Stream	4.9	118
<b>Hoare Basin</b>	<b>6.5</b>	<b>7.5</b>
Andersen Creek	1.4	10
House Stream	2.0	4
McKay Creek	0.5	4
Wharton Creek	1.0	8
<b>Bonney Basin</b>		
<i>East</i>	<b>58</b>	<b>57</b>
Bartlette Creek	1.0	55
Bohner Stream	1.2	69
Priscu Stream	3.8	39
Vincent Creek	1.0	71
<i>West</i>	<b>73</b>	<b>28</b>
Lawson Creek	0.3	19
Lyons Creek	0.5	23
Red River (Bloodfalls)	0.1	242
Santa Fe Creek	0.5	19
Sharp Creek	–	63

1999–2000, 2000–2001 and 2001–2002 seasons are displayed for Lake Hoare. The ‘early’ sampling date represents the time before significant stream flow occurred. The Si concentration in Lake Hoare increases with depth. There is a decrease in Si in the upper part of the water column of Lake Hoare over the summer. The dilution of surface waters over the summer is caused by the introduction of less concentrated stream water and ice cover melt (Welch *et al.* 2000). The same effect occurs in the surface waters of Lake Hoare for all three seasons. Over the three summers, bottom water Si concentrations have remained relatively constant in Lake Hoare (Fig. 3).

Both the eastern and western lobes of Lake Bonney have a mid-depth Si maximum. The chemocline in the eastern lobe of Lake Bonney is about 2 m higher than in the western lobe. These Si maxima may be caused by the inflow of Bloodfalls water at this depth. As noted above, the bottom waters of Lake Bonney are hypersaline. It is also possible that Si-rich biological debris may be unable to settle below the very strong pycnocline, and subsequently it is solubilized there, producing these mid-depth Si maxima. Thermodynamic calculations indicate that amorphous  $\text{SiO}_2$  is supersaturated

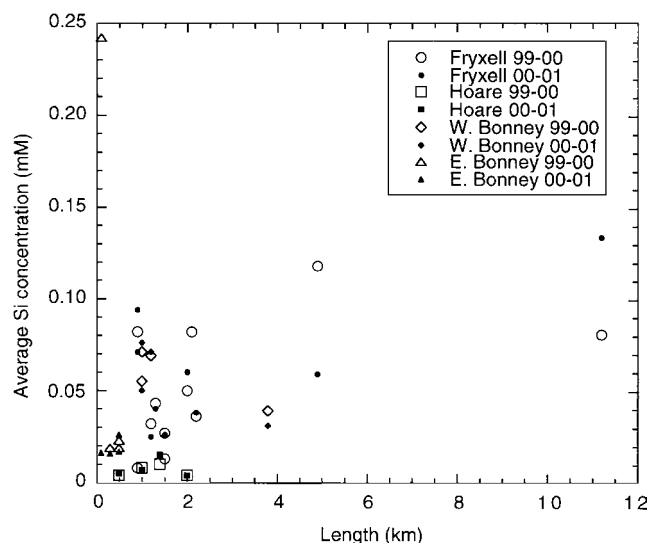


Fig. 2. Si concentrations in Taylor Valley streams versus stream length 1999–2001.

below 20 m in the eastern lobe of Lake Bonney (Lyons *et al.* 1998a); however, there is no evidence of formation of Si minerals at these depths.

## Discussion

### Streams

Dissolved Si present in stream water depends both on the original Si concentration of the glacier meltwater as well as the release of Si via chemical weathering. Differences in stream chemistry reflect the differences in the source water flowing from the glaciers, the chemistry of the rocks and soils, and also the length of time the water is in contact with the regolith (Lyons *et al.* 1998a). More recent work describing chemical weathering in these streams suggests that weathering rates of aluminosilicates can be high (Nezat *et al.* 2001; Maurice *et al.* 2002). Because of the low levels of reactive Si in the meltwaters from the glaciers, it is certain that concentrations of the  $\text{H}_4\text{SiO}_4$  above  $10 \mu\text{M}$  must originate from silicate mineral weathering within the stream reaches (Lyons *et al.* 1998a). Although paleodiatoms are present in perched deltas and lacustrine sediments in Taylor Valley (Kellogg *et al.* 1980), dissolution of diatom debris is minimal in VonGuerard Stream and has not been found to contribute reactive Si to other Taylor Valley streams (Blum *et al.* 1997). In addition, it is hypothesized that present-day diatoms, owing to their low concentrations (< 1% of biomass in most Taylor Valley streams), have little impact on reactive Si concentrations in the stream waters (McKnight *et al.* 1998).

Fig. 2 is a plot of stream length versus average Si concentration for both field seasons. Lake Hoare has relatively short streams and low Si concentrations. Lake Fryxell has the longest streams and relatively high concentrations of Si. However, when all Taylor Valley streams are compared, streams with similar lengths have large ranges of Si concentration. In addition, from year to year, Si concentrations vary within a

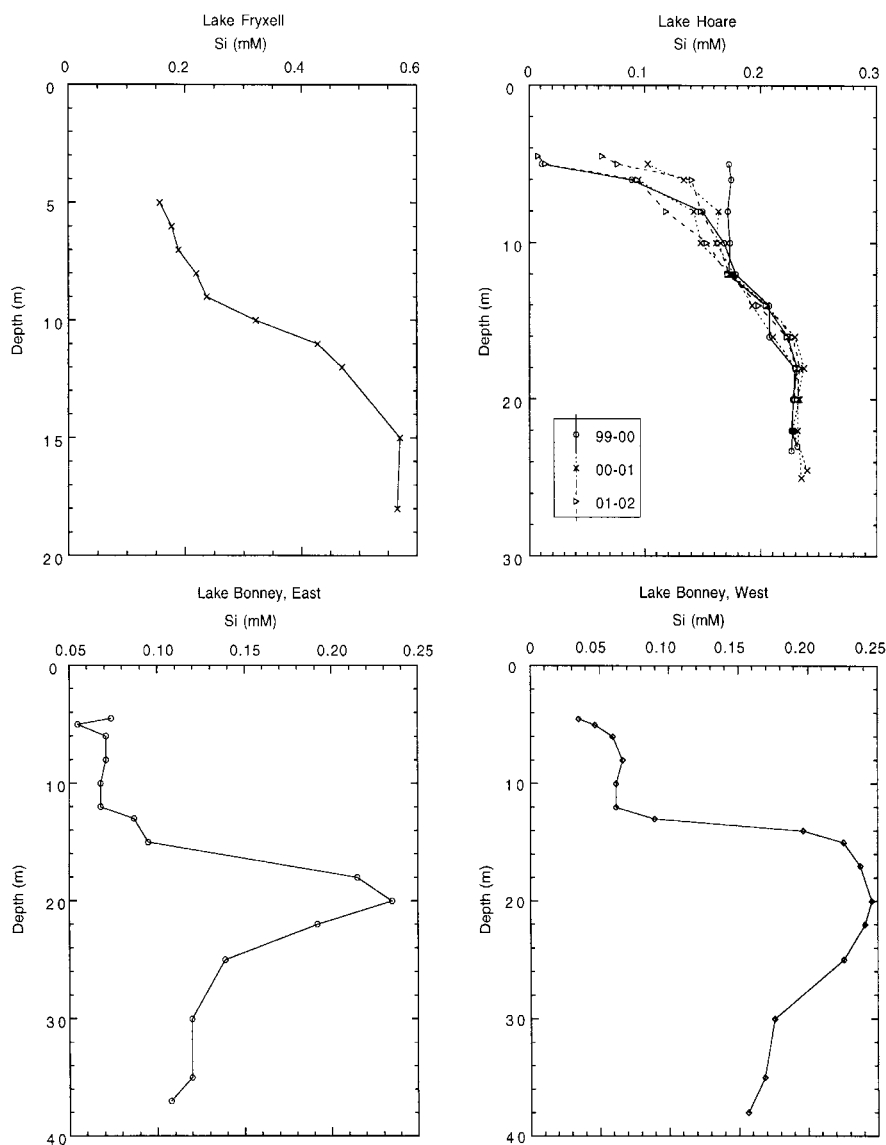


Fig. 3. Si profiles for Taylor Valley lakes.

stream. The longest of all Taylor Valley streams, the Delta Stream (11.2 km) had a higher average Si concentration in 2000–2001 than the previous year, while in the same basin, the VonGuerrard Stream (4.9 km) showed the opposite trend. Therefore, dissolved Si is produced via chemical weathering in this environment, but the rate of production varies both spatially and temporally. Weathering rates are controlled by reactions within the hyporheic zones of the stream channels (Maurice *et al.* 2002) that, in turn, vary as the stream flow varies. Hence the production of dissolved Si and its introduction into the lakes is controlled by climate variability as it is manifested in glacier melt and stream flow conditions.

#### Flux of Si to the lakes

An estimation of the amount of Si entering the lake with the meltwater inflow requires the monitoring of water discharge into the lake as well as regular measurement of the concentrations of dissolved Si contained in the in-flowing water. Si concentrations were averaged for each stream for the

1999–2000 season. For the streams with significant measurable flow for that year, the Si flux ( $\text{kmol yr}^{-1}$ ) was calculated (Table 3). The total flux for each basin was determined by summing the individual stream values. The Lake Bonney basin had the highest Si flux, ( $33.3 \text{ kmol yr}^{-1}$ ), followed by Lake Fryxell ( $7.5 \text{ kmol yr}^{-1}$ ) and Lake Hoare ( $0.85 \text{ kmol yr}^{-1}$ ). These values are conservative because not all of the streams are gauged, therefore the Si flux to the lakes may be greater than reported here.

#### Lakes

In the Taylor Valley aquatic systems,  $\text{Cl}^-$  is conservative and is not removed from the water column except by precipitation of NaCl in the deepest few metres of the eastern lobe of Lake Bonney (Lyons *et al.* 2000). Si/Cl profiles for each lake in the Taylor Valley are shown in Fig. 4. With the exception of Bloodfalls, the ratio of Si/Cl is lower in the lakes than in the streams that flow into them. The average molar ratio of Si/Cl in the streams is 0.2, while the average Si/Cl ratio in

Table 3. *Si flux in Taylor Valley Lake Basins*

	Average Si (mM)	Annual Flow 10 <sup>3</sup> (m <sup>3</sup> /yr)	Si flux mol/year	Sum of Basin Si Flux (mol/yr)	Lake Area (m <sup>2</sup> )	Flux normalized to lake area (mmol Si/m <sup>2</sup> yr)	Si mass for Lake (kmol)	Residence time (yr)
<b>Fryxell Basin</b>				7520	7 291 700	1.03	7970	1060
Aiken Creek	0.043	19.6	836					
Andrews Creek	0.014	–						
Bowles Creek	0.082	–						
Canada Stream	0.027	85.3	2305					
Crescent Stream	–	0.2						
Delta Stream	0.081	0.8	65					
Green Creek	0.032	48.3	1533					
Harnish Creek	–	0.0						
Huey Creek	0.082	1.7	139					
Lost Seal Stream	0.036	73.0	2642					
Mariah Creek	0.008	–						
McKnight Creek	0.050	–						
VonGuerard Stream	0.118	0.0						
<b>Hoare Basin</b>				849	1 941 700	0.44	2790	3280
Andersen Creek	0.010	73.0	716					
House Stream	0.004	31.7	133					
McKay Creek	0.004	–						
Wharton Creek	0.008	–						
<b>Bonney Basin</b>				33 300	4 415 100	7.55	8700	260
<i>East</i>					3 399 580			
Bartlette Creek	0.055	–						
Bohner Stream	0.069	–						
Priscu Stream	0.039	46.3	1820					
Vincent Creek	0.071	–						
<i>West</i>					1 015 520			
Lawson Creek	0.019	119.1	2271					
Lyons Creek	0.023	73.3	1682					
Red River (Bloodfalls)	0.242	–						
Santa Fe Creek	0.019	1458	27541					
Sharp Creek	0.063	–						

Bloodfalls is 0.001. This suggests that the current Si input is greater than in the past. Our past work has also indicated an increased flux of calcium to the lakes over the past 30 years (Lyons *et al.* 1998a), and we have interpreted this as being caused by increased weathering associated with increased stream flow over this time period. The relatively straight Si/Cl profiles in Lake Hoare suggest that physical processes such as evaporative concentration rather than biological processes dominate the concentrations of both Si and Cl. The Si/Cl ratios are highest in Lake Hoare even though Si concentrations are lowest in the Lake Hoare streams. This may indicate that biogenic uptake of Si in Lake Hoare is the lowest of all the lakes. This is supported by primary production rate differences among the lakes as well because Lake Hoare has the lowest primary production rates of the lakes, e.g. <http://huey.colorado.edu>. The lower Si/Cl ratios in the bottom of Lake Bonney and Lake Fryxell reflect in part the high concentrations of Cl<sup>-</sup> at depth. Lake Bonney is thought to be the oldest of the Taylor Valley lakes and the Si/Cl profile reflects the long accumulation of salts within the lake (Lyons *et al.* 1998b). Hendy *et al.* (1977), Matsubaya *et al.* (1979) and Lyons *et al.* (1998b) have demonstrated that Lakes Bonney and Fryxell proceeded through a large-scale lake lowering or drawdown over the past few thousand years. During this time

the input of Si into the lakes via stream flow probably ceased (Lyons *et al.* 1998b). The lower Si:Cl ratios in the hypolimnia of these lakes indicate Si removal relative to Cl<sup>-</sup> as the lakes became evapoconcentrated. It is not clear whether this Si loss was biological or chemical in origin. Priscu *et al.* (1999) and Lyons *et al.* (2000) have argued that these lakes may be more productive at lower lake levels than at present levels, hence increasing the biological uptake of Si during low stands. What is clear is that during the last low stand, the Si:Cl ratio decreased substantially (>10 × in Lake Bonney and >2 × in Lake Fryxell), compared with present inputs.

The total pool of Si in each lake was calculated for the 1999–2000 season (Table 4). Each lake was divided into layers based on midpoints between sample depths. The volume of each layer was multiplied by the Si concentration at the corresponding depth. The layers were then summed to calculate the total amount of Si in each lake. This was done for both the early and late season samples. Lake Fryxell has the largest pool of Si followed by East Bonney, Hoare and West Bonney (Table 4). Both the eastern and western lobes of Lake Bonney and Lake Fryxell show an increase in the total Si pool from early in the austral summer to mid-summer. Lake Hoare does not show the same increase. In the 1999–2000, 2000–2001 and 2001–2002 seasons, there is a significant decrease in the

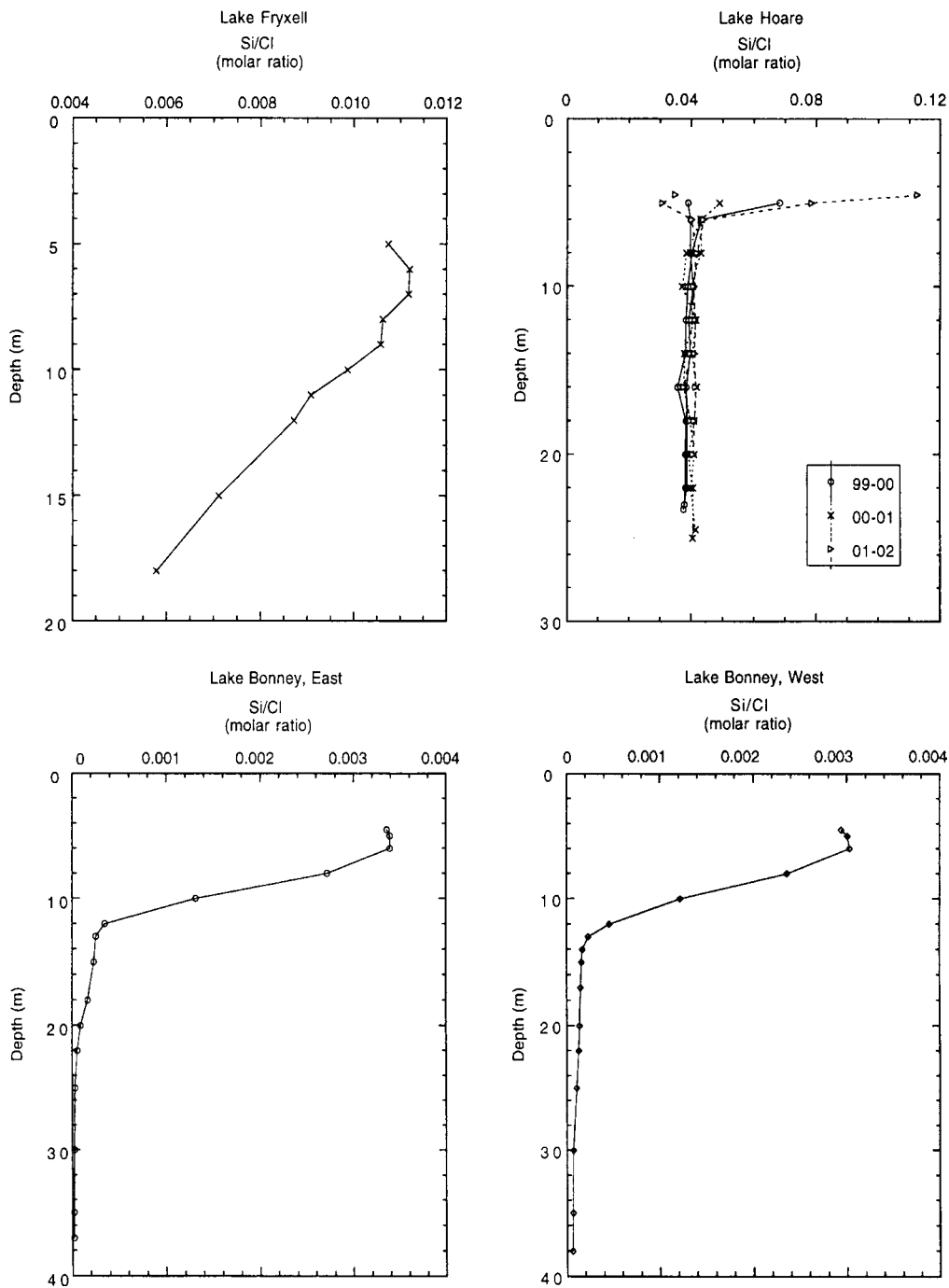


Fig. 4. Si/Cl profiles for Taylor Valley lakes (1999–2000).

amount of Si from early to late summer. This decrease is greater than the precision of the Si measurement, and we consider it to be a true decrease in Si in the water column over this time period. The decrease is probably a result of the dilution of surface water by input of less concentrated ice cover melt and stream water, and possible uptake of Si by diatoms. The very low ionic strength of Lake Hoare compared with the surface waters of the other lakes allows this dilution effect to be clearly observed.

During the winters of 2000 and 2001, an increase in Si concentration occurred in the surface waters of Lake Hoare.

Every winter approximately 35–100 cm of ice is frozen to the bottom of the ice cover (Wharton *et al.* 1993a). Therefore, Si and other solutes are forced into a smaller volume of water, increasing the concentrations in the lake. In the early season sample of the 3 years discussed here, the pool of Si in Lake Hoare has ‘recovered’ to almost the same value. The calculations show that the lake has been increasing in Si each season. This is also observed for major ions (Welch *et al.* 2000) indicating the cryoconcentration of solutes in the surface waters. In this way, climate variations control the surface water concentrations of solutes in these lakes.

Table 4. Pool size of Si determined for Taylor Valley Lakes

Lake	Sampling time	Pool of Si (kmoles)
Lake Fryxell	Early 1999–2000	7968
	Late 1999–2000	8087
Lake Bonney, East	Early 1999–2000	6921
	Late 1999–2000	6926
Lake Bonney, West	Early 1999–2000	1782
	Late 1999–2000	1816
Lake Hoare	Early 1999–2000	2789
	Late 1999–2000	2484
	Early 2000–2001	2820
	Late 2000–2001	2583
	Early 2001–2002	3016
	Late 2001–2002	2530

The residence time for Si was calculated for the three lakes (Table 3). The total amount of Si in each lake was divided by the Si flux to determine the residence time or  $\tau$  for each lake. The residence time for Si was calculated to be just over 1000 years in Lake Fryxell. This value corresponds to the time that Lake Fryxell was thought to begin to refill from a very shallow playa stage at the last draw down event (Lyons *et al.* 1998b). Lake Bonney has the shortest calculated residence time, 260 years. This time is similar to the time when the eastern lobe of Lake Bonney was last free of an ice cover (Poreda *et al.*, in review). Lake Hoare was found to have the longest residence time, over 3200 years. Because the age of Lake Hoare is thought to be only  $\sim 1000$  years (Lyons *et al.* 1998b), this residence time suggests that the current flux of Si to the lake is  $\sim 33\%$  lower than the average over the history of the lake. These calculations are based on flow data from only 1999–2000 and there is variation from year to year. Higher amounts of discharge would increase the Si flux, therefore resulting in shorter residence times. Chinn (1993) has shown that inputs into these lakes were greater in the 1980s than presently. Given this, it is curious that two of the three calculations result in  $\tau$  values that represent important events in past lake development, including a reasonable assessment of the age of Lake Fryxell. This suggests that there has been little accumulation of biogenic Si within Lake Fryxell and the Si inventory as established here represents conservative behaviour of Si within the lake.

#### Output of Si from the lakes

The amount of primary productivity (PPR) in the lakes of Taylor Valley varies between lakes and within the water column (Figs 5a and b). The western lobe of Lake Bonney is the most productive lake with its maximum PPR at 13 m ( $0.601 \mu\text{mol C l}^{-1} \text{day}^{-1}$ ). The highest production in the eastern lobe of Lake Bonney is at 12 m ( $0.092 \mu\text{mol C l}^{-1} \text{day}^{-1}$ ), but it is not nearly as productive as the western lobe. The highest PPR in Lake Fryxell is at 9 m ( $0.173 \mu\text{mol C l}^{-1} \text{day}^{-1}$ ) and the max is at 5 m ( $0.056 \mu\text{mol C l}^{-1} \text{day}^{-1}$ ) in Lake Hoare.

The percentage of Si taken up by diatoms was calculated in each lake based on the sampled depths (Figs 5a and b). A Si/C molar ratio of 0.13 was used to calculate the Si taken

up by diatoms. The PPR averages for each layer are from measurements taken from 1993–1997. A 180 day productivity cycle was used for these calculations. Phytoplankton counts in the lakes indicate that no more than 10% of PPR can be attributed to diatoms in the water column (S. Spaulding, personal communication). The calculated percentage of Si taken up by diatoms is shown in Fig. 5.

Primary production in the Lake Hoare benthos is approximately equal to the primary production in the water column (Hawes & Schwartz 1999). In Lake Hoare, only 10% of PPR can be attributed to diatoms in the benthic mats (S. Spaulding, personal communication). Unfortunately, there are no PPR data for the benthic mats in Lake Fryxell and Bonney. The lower Si/Cl ratios in the lakes compared with the streams suggest, however, that benthic Si uptake could be a more important process than previously thought. Adsorption of Si on to particles (Swedlund & Webster 1999) and authigenic formation of new silicate minerals was not considered as a major removal mechanism in the Taylor Valley lakes, although as mentioned above, thermodynamic calculations suggest  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$  removal at depth in the eastern lobe of Lake Bonney. At this time, we have no evidence of Si removal via inorganic processes in any of these lakes.

Previous work on larger lakes such as the North American Great Lakes, Lake Baikal and Lake Lugano, provides two extremes of Si biogeochemistry. In Lakes Lugano and Baikal essentially the entire input of Si is taken up biologically on an annual basis (Callender & Granina 1997; Hoffmann *et al.* 2002). In Lake Michigan  $\sim 70\%$  of the input is taken up by diatoms (Schelske 1985). However, in Lake Superior only 8–10% of the yearly input of Si is removed biologically (Johnson & Eisenreich 1979; Schelske 1985). Johnson & Eisenreich (1979) argue that the majority of the dissolved Si input into Lake Superior is removed via authigenic silicate mineral formation (i.e. smectite and/or amorphous ferroaluminum silicates). Clearly, the Taylor Valley lakes represent another, heretofore, undescribed case where Si is relatively conserved within the lake system with little to no biological uptake or inorganic uptake. Climatic variations control the input of Si into the lakes and it behaves conservatively within the lakes.

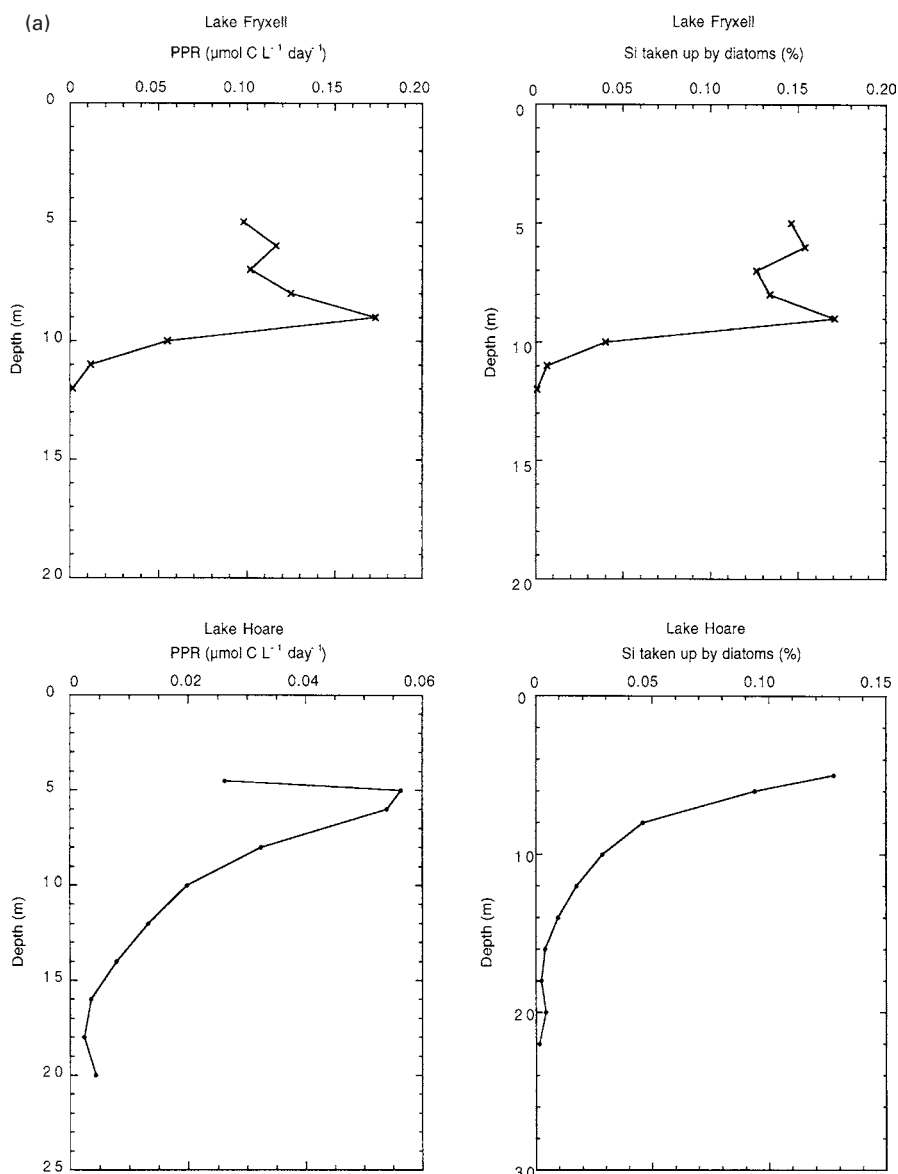
#### Mass balance for Lake Hoare

Numerous authors over the past two decades have used a mass balance approach in order to establish the processes controlling Si distribution in lakes. Most recently Hoffmann *et al.* (2002) have used a similar approach to quantify Si dynamics in Lake Lugano, Switzerland/Italy. They developed the following approach:

$$A + I + P + S = D + R + \Delta M \quad (1)$$

where  $A$  is the atmospheric input of Si to the lake,  $I$  is the tributary input of Si to the lake,  $P$  is the internal lake processes contributing Si to the lake,  $S$  is the Si input from sediment release,  $D$  is the tributary outflow of Si,  $R$  is the removal of Si through internal lake processes such as biological uptake and  $\Delta M$  is the changing concentration of Si through time.





**Fig. 5.** (a) Primary productivity profiles and percentage of Si uptake by diatoms in Lake Fryxell (1999–2000) and in Lake Hoare (2000–2001). (b) Primary productivity profiles and percentage of Si uptake by diatoms, east and west Lake Bonney (1999–2000).

In Lake Hoare,  $A$  and  $D$  are zero. We have determined the yearly values of  $I$  and  $R$  (through biological uptake of diatoms) above, 850 and 8480 mole  $\text{yr}^{-1}$ , respectively. In addition we have scrutinized the long-term Si data from Lake Hoare obtained between 1993–1994 and 2001–2002 (<http://huey.colorado.edu>) and determined the  $\Delta M$  is  $\sim 4 \mu\text{mol l}^{-1} \text{ yr}^{-1}$ . This value is only a ‘best’ approximation and should be taken as an estimate only. Although the accuracy of our reactive Si is better than  $\pm 1 \mu\text{mol l}^{-1}$ , variations in sample depths from year to year (we measure from the water surface) and the  $\text{Cl}^-$  measurements (which are used to ‘normalize’ to depth), lead to some uncertainty when comparing the annual time series. An increase of this magnitude would be a yearly whole-lake addition of  $9.7 \times 10^4$  mole Si  $\text{yr}^{-1}$ , which is very close to the average increase from early 1999 to early 2001 of  $11.3 \times 10^4$  mole Si  $\text{yr}^{-1}$  (Table 4). Therefore

equation (1) reduces to the following expression:

$$P + S = 10.5 \times 10^4 \text{ mole yr}^{-1}. \quad (2)$$

This calculation indicates that internal processes such as the *in situ* dissolution of diatom shells and possible diffusion of Si from the lake sediments could dominate Si cycling. Although other considerations (see below) suggest that there is little addition of Si relative to C, at depth in Lake Hoare. Therefore, we reject the idea that biogenic Si dissolution is the source of this Si. As stated above, there is no evidence of input from biogenic debris within these lakes. This increase in Si over time must originate from processes other than biological ones.

This lack of biogeochemical processes on Si dynamics in the Taylor Valley can be documented in another manner. The molar ratio of dissolved inorganic carbon (DIC) to Si in

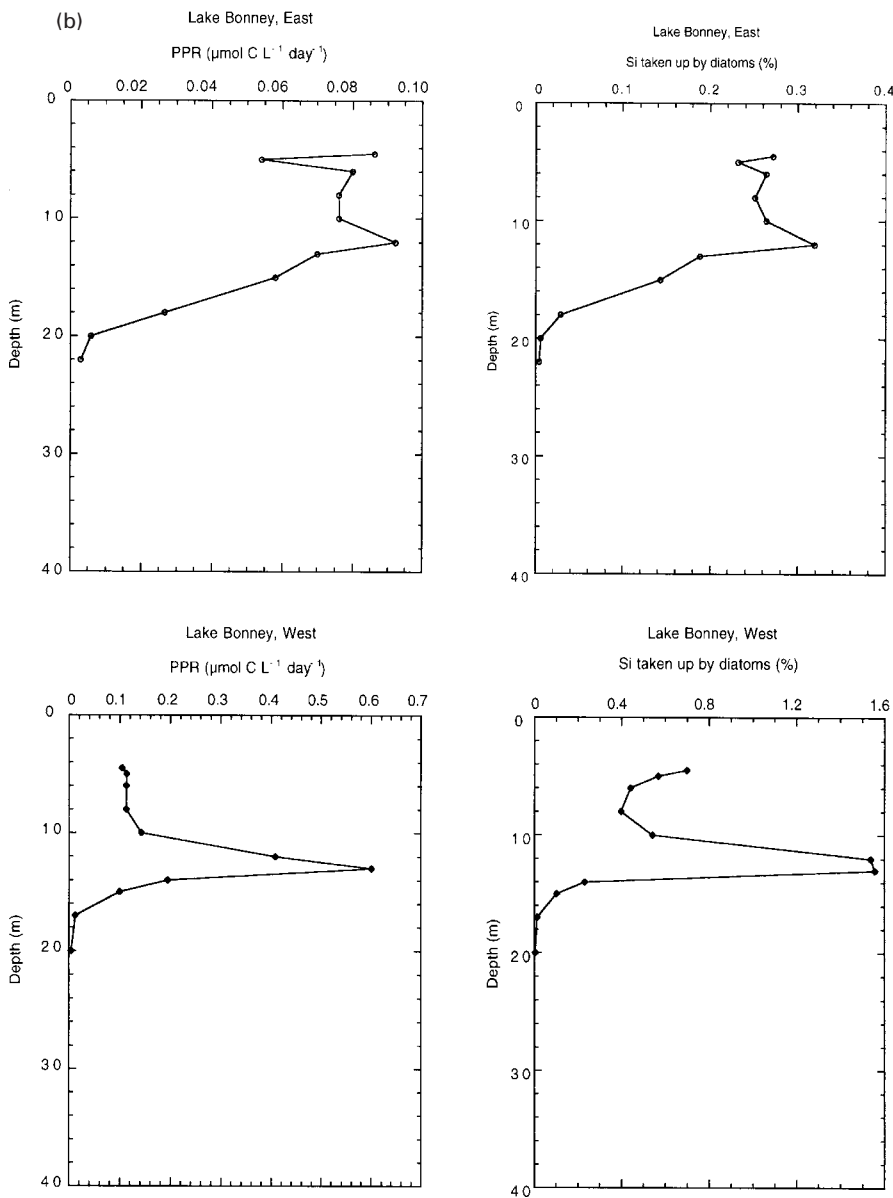


Fig. 5 (cont.)

ocean waters below the thermocline is 14–16:1 (Broecker & Peng 1982). The Si cycle in the oceans is greatly affected by biological uptake of Si at the surface, the rain of diatom debris to the deeper waters and its subsequent dissolution there. The surface and intermediate waters in Lake Hoare have average DIC:Si ratios of 22:1, while the deepest waters of the lake have ratios of 25:1. The Lake Hoare data suggest that there is little biological influence in the cycling of Si within the lake. The C:Si molar ratio in diatoms is 7.7:1 (Nelson *et al.* 1995) and the DIC:Si ratio of Andersen Creek, the primary stream adding Si to Lake Hoare is 22.4 (over a four-season period). These data suggest that the lake water C:Si is little modified from input water from the stream. The C:Si ratio is slightly increased in the lakes, compared with the stream, suggesting the addition of C through organic matter remineralization (Wharton *et al.* 1993b), but little to no input

of Si at depth. This conclusion suggests that there is little Si being introduced through diatom mineralization, unless the C:Si ratio of the mineralization is very non-stoichiometric.

Because these lakes have permanent ice covers, the traditional mass balance approaches, such as the one above, that have been utilized in temperate lakes cannot be adequately applied. The calculated gain of Si of  $\sim 1 \times 10^5 \text{ mole yr}^{-1}$  cannot solely be accounted for by biological recycling as in temperate lakes. The increase in Si is accompanied by an increase in  $\text{Cl}^-$  as well, with an increase of as much as 1.9 mM in the top 14 m of the water column of Lake Hoare from 1999 to 2001 (<http://huey.colorado.edu>). Because of the low-flow years from the early 1990s to 2000, there was a net water loss in Lake Hoare over this time period (Doran *et al.* 2002) and solutes were concentrated in the water column (Welch *et al.* 2000). This process increases the  $\text{Cl}^-$  as well as the silicic acid

concentrations by evapoconcentration, not by the addition of Si through internal recycling such as diatom frustule dissolution as in temperate lakes. Therefore, physical processes driven by variations in the lake's hydrological cycle, not biological processes, drive the Si mass balances in these Antarctic lakes. Variations in Si input from year to year and subsequent evapoconcentration or dilution of the lake waters ultimately control the Si concentrations in these lakes. This is clearly observed when our calculated residence times of Si (Table 3) are compared with lake ages. The calculated residence time of Si for Lakes Hoare and Fryxell are ~3300 and 1000 years, respectively, essentially equal to or greater than the age of the lake itself (i.e. the age of the water). Unlike temperate lakes where biological processes remove Si and therefore decrease the residence time of Si relative to the water, this has not occurred in the Taylor Valley lakes. As mentioned above, the higher Si residence times in Lake Hoare demonstrates that the current input of Si is lower than the average input over the last 1000 years. The shorter residence time of Si in Lake Bonney (Table 3) we interpret to mean that current inputs of Si are higher than in the past as demonstrated by both the Si and Si:Cl depth profiles in these lakes. The higher Si input via Bloodfalls is probably the major source of Si to Lake Bonney and it is known that this source has varied over time in the recent past.

## Conclusion

Si dynamics in Taylor Valley lakes are dominated by processes that are not usually important factors in temperate lakes. The primary productivity is limited by the short growing season when sunlight is available. A 3–6 m ice cover on the lake surface also limits transmission of light during the summer. The average amount of Si uptake by diatoms in the water column is low (<1%) for the lakes as a whole. On average, the glacial meltwater transported to the lakes has Si concentrations that are much lower than the lake Si concentrations. The water balance in the lakes varies greatly from year to year and the evapoconcentration of solutes including Si greatly influences Si concentrations. The amount of Si entering the lakes, based on flux calculations from the 1999–2000 season, is small compared with the total pool of Si in each lake. Our preliminary mass balance assessment for Lake Hoare, the youngest of the lakes in Taylor Valley, indicates that high-flow years dominate the input of Si. All indicators suggest that biological processes play only a minor role in the Si dynamics in the lake, although the role of benthic diatom uptake in Lake Bonney and Fryxell has not been evaluated. Residence time calculations from low-flow years strongly suggest that changes in water inflow to these closed-basin lakes must greatly impact the long-term Si fluxes, as well as present-day concentrations. High-flow years must exert a significant influence on Si input, even though these hydrologic events are relatively rare. As with many other physical and biogeochemical parameters within these lakes, subtle climate changes and their influence on meltwater input may play a major role in controlling Si dynamics.

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