



## CO<sub>2</sub> concentrations in perennially ice-covered lakes of Taylor Valley, Antarctica

KLAUS NEUMANN<sup>1,3</sup>, W. BERRY LYONS<sup>1,4</sup>, JOHN C. PRISCU<sup>2</sup> & RONA J. DONAHOE<sup>1</sup>

<sup>1</sup>Department of Geology, University of Alabama, Tuscaloosa, AL 35487 U.S.A. (e-mail: kneumann@bsu.edu; lyons.142@osu.edu; rdonahoe@wgs.geo.ua.edu);

<sup>2</sup>Department of Land Resources and Environmental Sciences, Montana State University, Bozeman, MT 59717 U.S.A. (e-mail: ubijp@gemini.oscs.montana.edu); <sup>3</sup>Present Address: Department of Geology, Ball State University, Muncie, IN 47306 U.S.A.; <sup>4</sup>Present Address: Byrd Polar Research Center, Ohio State University, Columbus, OH 43210-1002 U.S.A.

**Key words:** calcification, carbon dioxide, diffusion

**Abstract.** Lakes in Taylor Valley, southern Victoria Land, Antarctica, are unusual in that they are perennially covered by a 3–5 m thick ice layer. Previous work on gas concentrations in these lakes has shown that the surface waters are supersaturated with respect to O<sub>2</sub>, N<sub>2</sub>O, as well as the noble gases. Our data show that the dissolved CO<sub>2</sub> (CO<sub>2(aq)</sub>) concentrations, calculated from pH and ΣCO<sub>2</sub>, can be highly undersaturated at shallow depths of the lakes. CO<sub>2</sub> partial pressure values (pCO<sub>2</sub>) are as low as 10<sup>−4.3</sup> atm and 10<sup>−4.2</sup> atm in the east and west lobes of Lake Bonney, respectively, and 10<sup>−3.8</sup> atm in Lake Hoare. CO<sub>2(aq)</sub> depletion occurred only in the uppermost part of the water column, in association with elevated primary productivity (PPR). The upward diffusion of CO<sub>2(aq)</sub> from the aphotic zone, and the annual input of CO<sub>2</sub> via glacial meltwater can not replenish the amount of CO<sub>2(aq)</sub> annually lost to primary productivity in the uppermost meters of the water column. Calcification is a limited source of CO<sub>2(aq)</sub>, since the lakes are undersaturated with respect to calcite through portions of the austral summer. Preliminary respiration rates have been used to obtain an annual inorganic carbon balance. Further down in the water column, at the sites of the deep-water maximum in primary production (PPR<sub>max</sub>), which in Lakes Bonney and Fryxell is associated with nutrient gradients, CO<sub>2(aq)</sub> is not undersaturated. A large upward flux from CO<sub>2</sub>-supersaturated aphotic waters provides a surplus of CO<sub>2(aq)</sub> at the PPR<sub>max</sub>. Lake Fryxell, unlike the other lakes, is supersaturated with CO<sub>2(aq)</sub> throughout the entire water column.

### Introduction

CO<sub>2</sub> is an essential requirement for primary production. Although inorganic carbon is the most abundant nutrient in most aquatic systems (Quay et al. 1986), low dissolved CO<sub>2</sub> (CO<sub>2(aq)</sub>) concentrations can be a limiting factor for primary production in certain situations (Riebesell et al. 1993; Schidlowski

et al. 1994; Gleitz et al. 1995). Previous work has demonstrated that the majority of lakes on Earth, particularly those in the northern polar regions (Kling et al. 1992), are a sink for terrestrially fixed  $\text{CO}_2$ , resulting in  $\text{CO}_{2(\text{aq})}$  supersaturation with respect to the atmosphere. Consequently, these lakes are thought to be a source of  $\text{CO}_2$  to the atmosphere (Cole et al. 1994). Even during times of rapid  $\text{CO}_2$  uptake via photosynthesis, and the removal of carbon into biomass/sediments, diffusional  $\text{CO}_2$  input from the atmosphere can replenish the supply of  $\text{CO}_{2(\text{aq})}$  in most lacustrine environments, thereby minimizing the role of  $\text{CO}_{2(\text{aq})}$  as a limiting nutrient (Schindler et al. 1997).

The lakes of the McMurdo Dry Valleys in southern Victoria Land, Antarctica ( $76^\circ 30' - 78^\circ 30' \text{ S}$ ,  $160 - 164^\circ \text{ E}$ , Figure 1) are unique on this planet in that they maintain a thick (3 to 6 m), permanent ice cover overlying a liquid water column (McKay et al. 1985). The ecology of these permanently ice-covered Antarctic lakes is greatly influenced by the presence of their ice covers, which restrict or eliminate completely the exchange of gases such as  $\text{CO}_2$  between the lake waters and the atmosphere (Wharton et al. 1993; Priscu 1997). In addition, the lakes are fed by glacier melt water streams in landscapes where little or no terrestrial organic matter enters the lake ecosystem. Although much research has been done in the past decade to discern the role of ice-cover on gas dynamics in these lakes, little attention has been paid to  $\text{CO}_{2(\text{aq})}$ . For example, the restriction of atmosphere-lake exchange results in an increase in dissolved  $\text{O}_2$ ,  $\text{N}_2\text{O}$  and Ar above saturated conditions (Wharton et al. 1987; Craig et al. 1992; Priscu et al. 1996; Priscu 1997; Hood et al. 1998). Conversely, dissolved He and Ne are greatly undersaturated with respect to the atmosphere (Hood et al. 1998). The ice cover could lead to elevated  $\text{CO}_{2(\text{aq})}$  levels by preventing  $\text{CO}_2$  produced via respiration of organic matter from evading into the atmosphere, or it could cause undersaturation of  $\text{CO}_{2(\text{aq})}$  if the biological uptake is greater than its replenishment.

These lakes have been studied since the International Geophysical Year (1957–1958), but it has only been recently that carbon dynamics within the lakes have been well enough understood so that budgets can be constructed (Priscu et al. 1999). To describe the biogeochemistry of the lakes, an understanding of the  $\text{CO}_{2(\text{aq})}$  balance in these systems is essential. Photosynthesis and respiration, advective fluxes from streams, diffusion of  $\text{CO}_{2(\text{aq})}$  from deeper waters, and calcification can all alter the  $\text{CO}_{2(\text{aq})}$  balance in these lakes. Because the uptake of  $\text{CO}_{2(\text{aq})}$  is the main source of carbon for primary producers, this paper focuses on the distribution of  $\text{CO}_{2(\text{aq})}$  in the trophic zone of these lakes, and quantifies the processes that control its distribution. Concentrations of  $\text{CO}_{2(\text{aq})}$  will be given as the partial pressure of  $\text{CO}_2$  in water ( $p\text{CO}_2$ ), a common practice that is best suited to describe the wide range in concentrations encountered in these lakes.



*Site description*

The McMurdo Dry Valleys region is the largest ice-free area in Antarctica. Taylor Valley is one of the valleys in the McMurdo region of southern Victoria-land ( $\sim 78^\circ$  S latitude). Taylor Valley has an average temperature of  $-20^\circ\text{C}$  and a mean precipitation rate of  $< 10\text{ cm yr}^{-1}$  (Clow et al. 1988). The lakes in Taylor Valley vary in size from 1 to  $7\text{ km}^2$ , and occupy hydrologically closed basins. The water balance is maintained by inflow of glacial meltwater over a 6–12 week period during the austral summer, and the ablation of  $\sim 0.4\text{ m}$  of ice per year. Evaporation of water and uninhibited gas exchange with the atmosphere can only occur through the moats that can form at the shore of the lakes during about ten weeks of the summer. These moats cover only about 3% of the lake area (Wharton et al. 1986). The role of the moats in gas exchange with the atmosphere is difficult to estimate since the relationship of moat water chemistry and the chemistry of the lake water is not established (Priscu et al. 1996). In general, the Taylor Valley lakes share common features such as chemical stratification and, hence, a high water column stability (Matsubaya et al. 1979; Green et al. 1988; Spigel & Priscu 1996, 1998), and biological communities consisting solely of microorganisms (Vincent 1988; Priscu et al. 1999).

The three largest lakes in Taylor Valley are Lake Fryxell, Lake Hoare and Lake Bonney (Figure 1). Lake Bonney has two lobes separated by a 12 m deep sill that allows exchange of the surface waters, but separates the more dense, saline deep waters (Lawrence & Hendy 1989; Spigel & Priscu 1998). The geochemistry of these lakes is very different, ranging from the hypersaline deep waters of Lake Bonney, to the entirely fresh water of Lake Hoare, and the brackish waters of Lake Fryxell (Green et al. 1988; Lyons et al. 1998a). Many of the chemical differences between the lakes, and especially the existence and composition of the monimolimnions of Lakes Bonney and Fryxell, were caused by past climatic variations that greatly affected the hydrologic balances of the lakes (Matsubaya et al. 1979; Lyons et al. 1998b). Since 1993 the McMurdo Dry Valleys region in general, and Taylor Valley, in particular, has been designated a Long Term Ecological Research (LTER) site, and the lakes have been monitored on a routine basis. More information on the MCM-LTER can be found at <http://huey.colorado.edu/LTER>.

**Materials and methods**

Water samples were collected three to four times during the austral summer (November through January) with 5-L Niskin bottles that were lowered through holes in the ice cover at the locations of greatest lake depth. pH

was measured with a Beckman portable pH-meter with silver/silver chloride glass electrodes in sub-samples immediately after sampling (accuracy =  $\pm 0.05$  pH units). Temperature was measured with a Sea-Bird CTD probe lowered down the same holes in the ice. Samples were stabilized with chloroform, and dissolved inorganic carbon (DIC) measured in the field with a MSA Lira infrared carbon analyzer (standard deviation of measurements =  $\pm 3\%$ ). Major cations and anions were determined on filtered aliquots at McMurdo Station, Antarctica, by ion chromatography, using a Dionex DX-300 chromatographic system. The ionic balance of this data set, using all the major element data including  $\text{HCO}_3^-$  calculated from the DIC, and expressed as difference between total cations and total anions, had an error between 1.4% and 3.0%. A detailed description of the chromatography techniques can be found in Welch et al. (1996). A detailed description of the pH and DIC methods can be found at the McMurdo LTER website <http://huey.colorado.edu/LTER/lakedata.html>.

Chemical, pH and temperature data from the 1994-1995 austral summer were used to calculate the  $\text{CO}_{2(\text{aq})}$  and  $\text{CaCO}_3$  saturation indices under the ambient conditions with the chemical equilibrium models PHREEQE and PHRQPITZ (Parkhurst et al. 1980; Plummer et al. 1988). These models calculate  $\text{pCO}_2$  at *in-situ* temperatures and pH values. The accuracy of the models is mainly controlled by the errors in the pH and DIC measurements. Changes of 0.05 pH units cause an average error of  $\pm 3.3\%$  in  $\text{pCO}_2$ , and a 3% error in the DIC measurements produces a  $\pm 1.3\%$  error in  $\text{pCO}_2$ . The total error depends on pH and DIC in a non-linear manner, and decreases with increasing pH and increases with increasing DIC concentration. Using data from this study, the errors in  $\text{pCO}_2$  are larger than 5% only in the low-pH, high-DIC deep waters of Lake Bonney (maximum error has been calculated to be 10% at 20 m in the west lobe and 8% at 22 m in the east lobe). In the waters above 9 m, high pH and low DIC concentrations reduce the average  $\text{pCO}_2$  errors caused by pH and DIC measurements to  $\pm 1.4$  and 0.5%, respectively.

To verify the model and calculated  $\text{CO}_{2(\text{aq})}$  concentrations, several water samples were taken during the 1996/1997 austral summer to measure the  $\text{CO}_{2(\text{aq})}$  concentration directly via headspace analysis (Kling et al. 1992; Cole et al. 1994). Samples were taken in 250 mL flint glass bottles, with 5 mL of headspace, and stabilized with 0.2 mL concentrated  $\text{HgCl}_2$  solution. Following several days of equilibration, a sample from the headspace was extracted through a Teflon septum, and the  $\text{CO}_{2(\text{aq})}$  concentration was measured with a HP 5890 Series II gas chromatograph. The average error of the  $\text{CO}_{2(\text{aq})}$  measurements was 8.4%. The amount of atmospheric  $\text{CO}_2$  trapped in the headspace during sampling was subtracted in our calculations,

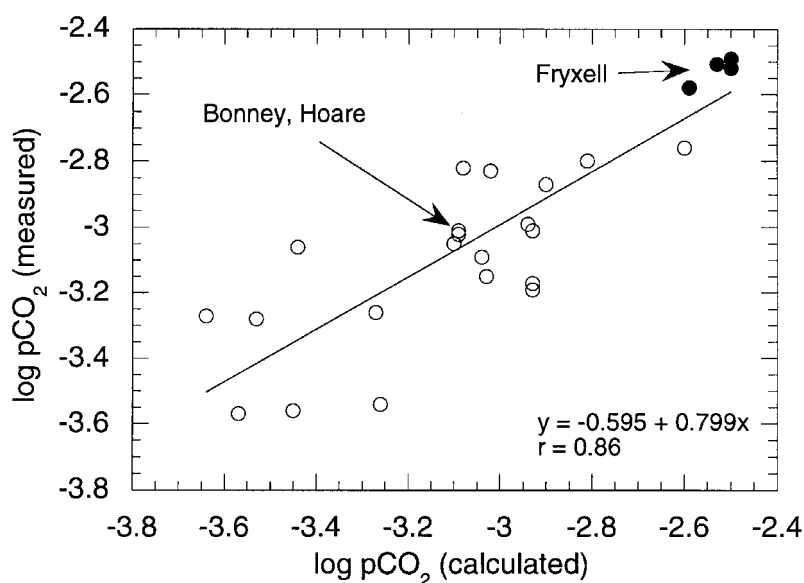


Figure 2. 1996 pCO<sub>2</sub> values modeled with PHREEQE, compared to pCO<sub>2</sub> values obtained from gas-chromatographic headspace measurement (only exponents shown). Open symbols are corrected for calcite precipitation before CO<sub>2</sub> measurement, solid symbols mark the uncorrected Lake Fryxell measurements. See text for further explanation of the calculations. The line represents a least square fit through the data.

assuming a pCO<sub>2</sub> of  $10^{-3.47}$  atm (340 ppmv) in the air (the calculations of pCO<sub>2</sub> from the CO<sub>2(aq)</sub> measurements using Henry's law followed Hope et al. 1995). Due to logistical problems (i.e. the transport of the samples from Taylor Valley to McMurdo Station, ~80 km away), the samples warmed to 21 °C before the CO<sub>2</sub> concentration in the equilibrated headspace could be measured. A white precipitate, assumed to be CaCO<sub>3</sub>, was observed in a number of the bottles containing water from Lake Bonney. The precipitation was presumably caused by the temperature increase. For these samples, the pCO<sub>2</sub> of the water was calculated to be in equilibrium with calcite at 21 °C. In Lake Fryxell, the calcite precipitation is probably inhibited by high DOC and PO<sub>4</sub><sup>3-</sup> concentrations (Neumann et al. 1998b), and it was not initiated by increasing temperatures. Calculations in Lake Fryxell, based on non-equilibrium with CaCO<sub>3</sub>, coincide with values calculated from pH and DIC. All these data show that the calculated values are close to the direct measurements of CO<sub>2(aq)</sub> in our study lakes (Figure 2). Studies on other lakes also show that calculated pCO<sub>2</sub> values using equilibrium thermodynamic calculations generally are in good agreement with measured values (Quay et al. 1986; Berman-Frank et al. 1994; Cole et al. 1994).

## Results

Table 1 shows the pH and DIC values that were used to calculate the partial pressures of dissolved CO<sub>2</sub>. The high concentrations of DIC in some of the monimolimnions are caused by lake level variations over time, and have nothing to do with modern processes (Lyons et al.1998b). In brief, Lake Hoare is proposed to be less than 1200 yrs old (Lyons et al.1998b). Lakes Bonney and Fryxell have undergone a series of evaporitic drawdowns and refillings as the climate has changed during the Holocene (Matsubaya et al. 1979; Lyons et al. 1998b). These drawdowns have helped concentrate DIC in the bottoms of these lakes. The last fresh water influx, over the past ~ 1200 yrs, placed a low-salinity water column on top of the saline brine. The saline and the fresh layers of the water column are separated by sharp gradients. Constituents with elevated concentrations in the monimolimnions such as nutrients, DIC, and the major elements move upward via diffusion (Priscu 1995; Lyons et al. 1998a, b).

Both lobes of Lake Bonney and Lake Hoare had pCO<sub>2</sub> values below atmospheric equilibrium values at various times during the 1994–1995 austral summer (Figure 3). In the west lobe of Lake Bonney, the water just below the ice cover had a pCO<sub>2</sub> as low as 10<sup>-4.2</sup> atm early in the summer, which, in the next three months, increased by one order of magnitude (10<sup>-3.2</sup> atm). This increase was most predominant in the water just below the ice cover, but could be observed to a depth of 10 m (10<sup>-3.3</sup> to 10<sup>-2.7</sup> atm). Below the chemocline at 13 m, values were well above atmospheric values, and increased rapidly to 10<sup>0.1</sup> atm at 20 m, below which PHRQPITZ is not capable of computing carbon dioxide pressures (due to high total dissolved solids, > 100 g L<sup>-1</sup>). The water in the east lobe of Lake Bonney had similar temporal shifts in the uppermost 13 m (10<sup>-4.3</sup> to 10<sup>-3.4</sup> atm). Below this depth, however, pCO<sub>2</sub> increased, reaching 10<sup>-0.3</sup> atm at 22 m, and then decreased to 10<sup>-1.8</sup> atm at the bottom of the lake. In contrast to the fluctuations in Lake Bonney, pCO<sub>2</sub> in Lake Hoare was relatively stable over the season, varying from 10<sup>-3.8</sup> atm to 10<sup>-3.6</sup> atm in the water just below the ice cover. Values increased to 10<sup>-2.1</sup> atm between 8 m and 16 m depth, and changed little below that depth.

Lake Fryxell is the only lake in Taylor Valley having pCO<sub>2</sub> values above atmospheric pressure throughout the entire water column through the entire austral summer. Water just below the ice cover had a pCO<sub>2</sub> of 10<sup>-2.4</sup> atm at the beginning of the austral summer, and later increased to 10<sup>-2.0</sup> atm. The pCO<sub>2</sub> was constant throughout the top 4 m, and increased below the chemocline (9 m).

*Table 1.* pH and DIC values in three Taylor Valley lakes at the beginning and the end of the 1994/1995 Austral summer

[illegible]



Table 1. Continued

	Depth m	Bonney-West				Bonney-East				Hoare				Fryxell			
		pH	DIC mg C/l	pCO <sub>2</sub>	Depth m	pH	DIC mg C/l	pCO <sub>2</sub>	Depth m	pH	DIC mg C/l	pCO <sub>2</sub>	Depth m	pH	DIC mg C/l	pCO <sub>2</sub>	Depth m
Jan. 1995	5	7.7	10.8	-3.16	5	7.9	8.7	-3.46	5	8.5	21.2	-3.57	5	7.0	31.3	-2.05	
	6	8.1	13.7	-3.47	6	8.5	10.1	-4.00	6	8.6	24.0	-3.65	6	7.3	54.8	-2.05	
	8	8.1	20.8	-3.28	8	8.5	15.0	-3.84	8	8.6	26.8	-3.61	7	7.4	72.1	-2.07	
	10	7.8	34.1	-2.74	10	8.4	19.7	-3.61	10	8.4	34.0	-3.34	8	7.5	84.7	-2.09	
	12	7.3	62.5	-2.06	12	7.3	44.2	-2.18	12	8.0	44.9	-2.83	9	7.6	151.7	-1.89	
	13	6.5	203.6	-0.97	13	6.7	93.7	-1.44	14	7.5	59.5	-2.23	10	7.5	229.5	-1.61	
	14	6.0	800.3	-0.08	15	6.6	126.0	-1.23	16	7.3	64.2	-1.98	11	7.3	306.0	-1.38	
	15	5.9	829.9	-0.03	18	6.5	162.2	-1.02	18	7.2	71.5	-1.90	12	7.4	381.2	-1.32	
	17	5.9	871.2	0.01	20	6.2	225.7	-0.58	20	7.1	72.4	-1.82	15	7.3	652.0	-1.04	
	20	5.8	948.3	0.08	22	6.0	240.3	-0.32	22	7.1	72.1	-1.78	18	7.2	739.9	-0.93	
	22	5.7	1193.6		25	6.1	141.6	-0.61	25	7.1	74.0	-1.77					
	25	5.6	1365.2		30	6.6	62.7	-1.39	29	7.0	89.8	-1.64					
	30	5.5	1333.5		35	6.7	55.4	-1.51									
	35	5.5	1419.8		37	6.6	41.3	-1.68									
	38	5.5	1513.6														

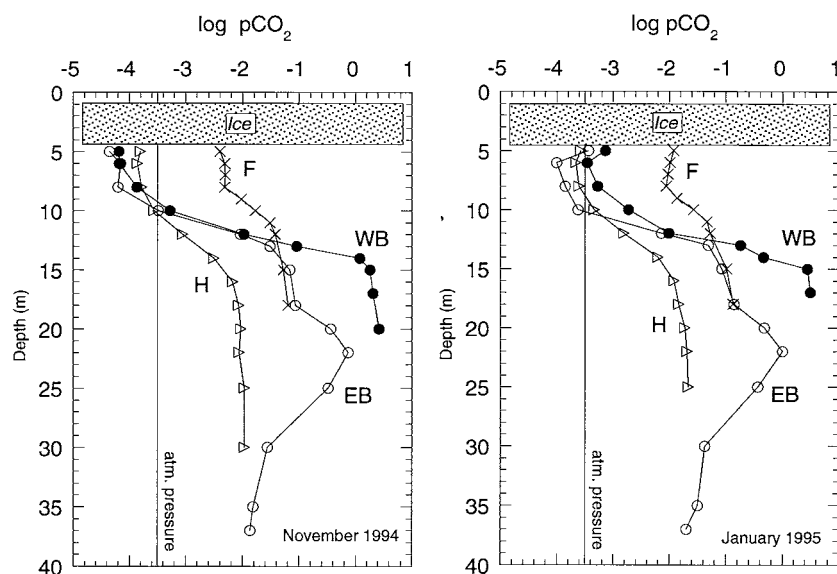


Figure 3.  $p\text{CO}_2$  versus depth for the three lakes at the beginning and end of the Antarctic summer season (November and January). Only exponents are shown. WB = Lake Bonney, west lobe; EB = Lake Bonney, east lobe; H = Lake Hoare and F = Lake Fryxell. The atmospheric pressure of  $\text{CO}_2$  ( $10^{-3.5}$  atm) is marked with a vertical line. Except for Lake Hoare, water below the chemoclines is highly supersaturated with  $\text{CO}_2$ , and shows no seasonal change.

## Discussion

The low concentrations of  $\text{CO}_{2(\text{aq})}$  in the upper waters of Lakes Bonney and Hoare are in stark contrast to dissolved  $\text{O}_2$ ,  $\text{N}_2$ , Ar and  $\text{N}_2\text{O}$  concentrations which are highly supersaturated as a result of exsolution during the freezing of water onto the bottom of the ice cover (Wharton et al. 1987; Priscu et al. 1996, 1997; Hood et al. 1998).  $\text{CO}_{2(\text{aq})}$  will also exsolve when the water freezes, and should therefore be supersaturated in the uppermost part of the water column too. However, the observed undersaturation of  $\text{CO}_{2(\text{aq})}$  is caused by the same perennial ice layer that has led to the supersaturation of other gases.  $\text{CO}_{2(\text{aq})}$  is lost from the upper water via incorporation through primary biologic production and subsequent sedimentation of particulate organic carbon (Neumann 1999; Priscu et al. 1999). Unlike in temperate lakes, and just opposite to its behaviour with respect to  $\text{O}_2$ ,  $\text{N}_2$ , Ar and  $\text{N}_2\text{O}$  where it prevents the escape to the atmosphere, the ice cover also acts as a barrier to  $\text{CO}_2$  infusion from the atmosphere.

The various processes that are involved in the  $\text{CO}_2$  production and consumption within the lakes are depicted in Figure 4. The undersaturation

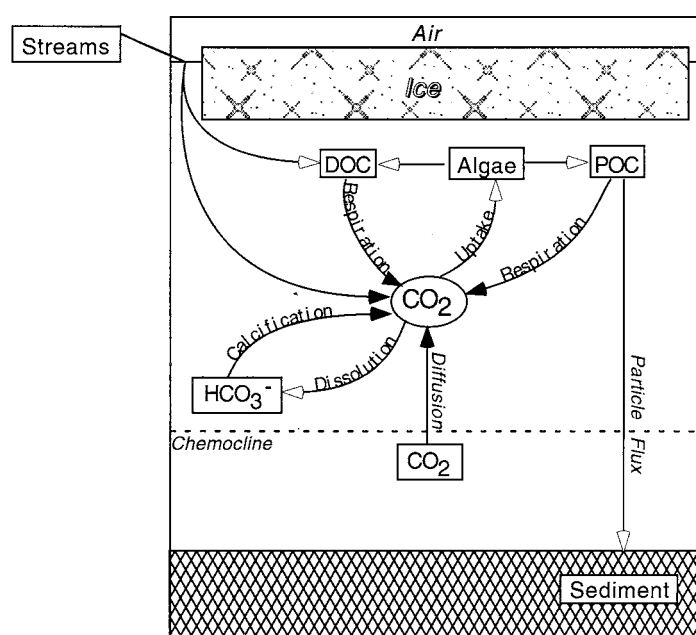


Figure 4. Conceptual model of processes involved in the carbon cycles in the dry valley lakes with chemoclines. Solid arrows denote  $\text{CO}_2$  sources. Diffusion across the chemocline is driven by high  $\text{CO}_2$  concentrations in the monimolimnion that are not the result of ongoing respiration, but remnants of previous lake level lowstands. The unbalanced 'calcification' and 'dissolution' stand for the reaction  $\text{Ca}^{2+} + 2 \text{HCO}_3^- \leftrightarrow \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$ . Note the lack of  $\text{CO}_2$  recharge from the atmosphere.

of  $\text{CO}_{2(\text{aq})}$  observed in the Taylor Valley lakes occurs in other perennially ice-covered Antarctic lakes. For example, Anderson et al. (1998) have also observed  $\text{CO}_{2(\text{aq})}$  undersaturated water in Lake Joyce (in Pearse Valley,  $77^\circ 43' \text{ S}$ ,  $161^\circ 37' \text{ E}$ ) and Lake Miers (in Miers Valley,  $78^\circ 06' \text{ S}$ ,  $164^\circ \text{ E}$ ). Doran et al. (in press) have reported that White Smoke Lake, Bunker Hills, East Antarctica, demonstrates a similar situation.

A comparison of the amount of dissolved  $\text{CO}_2$  in the water with the annual demands for biological  $\text{CO}_2$  uptake is shown in Figure 5. In the uppermost waters of the east and west lobe of Lake Bonney the uptake of  $\text{CO}_2$ , over the duration of a year, is more than 250% and 180% of the dissolved  $\text{CO}_2$ , respectively. In Lake Hoare biological uptake utilizes between 70 and 90% of the  $\text{CO}_{2(\text{aq})}$ , while in Lake Fryxell the uptake consumes only up to 12% of the  $\text{CO}_2$  in the lake water. This corresponds to lower  $\text{pCO}_2$  in the east and west lobe of Lake Bonney, followed by higher values in Lake Hoare (Figure 3). This high utilization rate could be especially important to primary production in these lakes if the  $\text{CO}_{2(\text{aq})}$  removal and potential replenishment

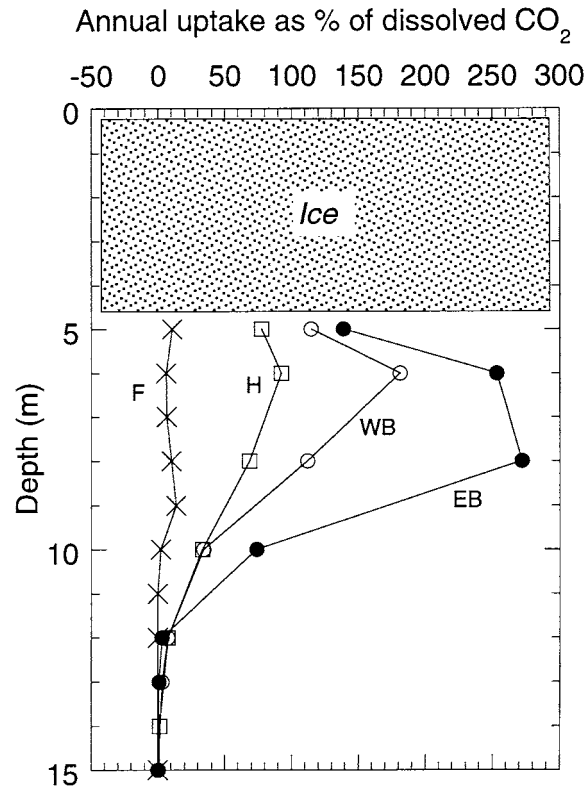


Figure 5. Annual uptake of  $\text{CO}_2$  expressed as percent of  $\text{CO}_2$  dissolved in water ( $\text{CO}_{2\text{aq}}$ ). Values of 250% in the west lobe of Lake Bonney mean that, statistically, every  $\text{CO}_2$  molecule is recycled two and a half times each year, while the 10% in Lake Fryxell suggest that every molecule is used for primary production only every tenth year. Symbols as in Figure 3.

occur at different times and rates. For example, respiration could gradually recharge the water over the whole year, while PPR is limited to the summer (i.e., no sunlight in winter).  $\text{CO}_{2\text{(aq)}}$  produced *in situ* during the winter can become a source for PPR in the summer. Some  $\text{CO}_{2\text{(aq)}}$  must be replenished in the winter, since the  $\text{pCO}_2$  values at the beginning of the growth season have been similar in several years of measurement (on average, the  $\text{pCO}_2$  values varied by  $\pm 0.06$  log units; Neumann 1999). In these lakes,  $\text{CO}_2$  can be replenished from four potential sources (Figure 4): (1) from  $\text{CO}_{2\text{(aq)}}$ -rich meltwater streams that flow for only a few weeks in the austral summer season and advect water just under the ice cover; (2) from the respiration of organic matter in the aerobic zone; (3) from diffusive input from the lower,  $\text{CO}_{2\text{(aq)}}$ -rich zones of the lakes; and (4) from calcification ( $\text{Ca}^{2+} + 2 \text{HCO}_3^- \leftrightarrow \text{CaCO}_3 + \text{CO}_{2\text{(aq)}} + \text{H}_2\text{O}$ ; Note that this process simultaneously leads to an increase

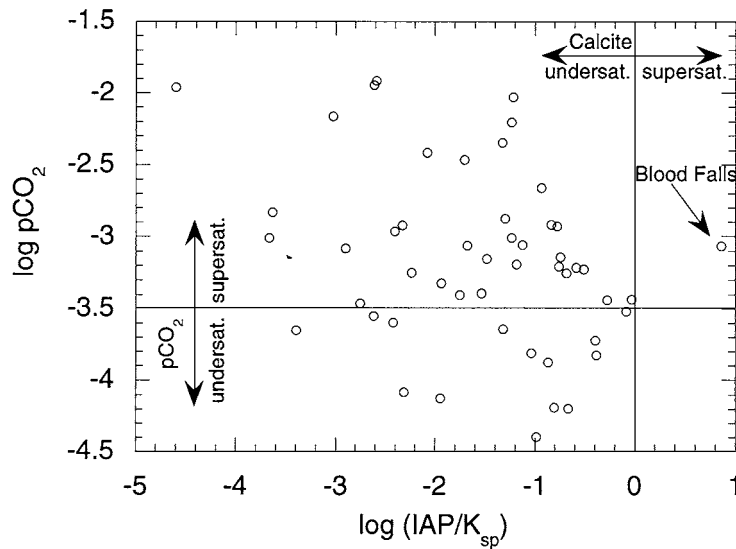


Figure 6. Calcite saturation indices for stream water are plotted against the partial pressure of  $\text{CO}_2$ . With only one exception (Blood Falls, a highly saline glacier discharge at the west lobe of Lake Bonney), all streams are undersaturated with respect to calcite. Also, most of the streams are supersaturated with respect to  $\text{CO}_2$ , some of them by more than an order of magnitude.

of biologically available  $\text{CO}_{2(\text{aq})}$  and to a decrease in DIC). Another potential source of  $\text{CO}_2$  is exsolution when water freezes to the bottom of the ice cover, the main source for the supersaturations of  $\text{O}_2$ ,  $\text{N}_2$ , Ar and  $\text{N}_2\text{O}$ .

#### *Glacial meltwater*

Glacial meltwater provides  $\text{CO}_{2(\text{aq})}$  to the surface waters of all the lakes, as a majority of the streams recharging the lakes are  $\text{CO}_{2(\text{aq})}$ -supersaturated with respect to the atmosphere (Figure 6). Because of its lower density, stream water flowing into the lake is confined to the ice-liquid water interface (McKnight & Andrews 1993; Spiegel & Priscu 1998). We have assumed that the stream input mixes with the uppermost meter of lake water. This input of  $\text{CO}_{2(\text{aq})}$  occurs in the late austral summer, as low-DIC water from streams can be observed in the  $\text{CO}_{2(\text{aq})}$  versus depth profiles for all the lakes (Figure 3). We calculated the annual influx of  $\text{CO}_{2(\text{aq})}$  to the lakes from stream alkalinity and pH data, using the computer code PHREEQE and the steam discharges (McKnight et al. 1998, Table 2). The amount of  $\text{CO}_{2(\text{aq})}$  that entered the uppermost meter of the lakes during the 1994/1995 austral summer was  $1 \text{ mmol m}^{-2} \text{ CO}_{2(\text{aq})}$  in Lake Hoare,  $3 \text{ mmol m}^{-2} \text{ CO}_{2(\text{aq})}$  in Lake Fryxell, and 34 and  $5 \text{ mmol m}^{-2} \text{ CO}_{2(\text{aq})}$  in the west and east lobe of Lake Bonney,

respectively. Only in the west lobe of Lake Bonney does the annual influx of  $\text{CO}_{2(\text{aq})}$  from streams support the primary production in the uppermost meter of water (Neumann 1999). This supply of  $\text{CO}_{2(\text{aq})}$ -rich water comes during the later part of the growing season, while phytoplankton production starts much earlier, in October/November (Vincent & Vincent 1981; Sharp & Priscu 1992). This temporal gap between demand and supply helps account for the undersaturated conditions at the beginning of the growing season as light levels increase.

### *Respiration*

Preliminary bacterial respiration rates were obtained by using estimates of electron transport system (ETS) activity converted to respiration assuming that 0.61 moles of  $\text{O}_2$  are consumed per unit of ETS activity (Priscu et al. 1999). Oxygen consumption was converted to  $\text{CO}_2$  production assuming a 1:1 ratio. The estimated amount of  $\text{CO}_2$  released by respiration is shown in Table 2.  $\text{CO}_2$  respiration by phytoplankton and bacteria exceeds the uptake of  $\text{CO}_2$  in most cases (Priscu et al. 1999, Lyons et al. 2000), yet, as will be shown later, contributes little to the overall  $\text{CO}_2$  balance.

*In-situ* remineralization of particulate organic carbon (POC) partially explains rising  $\text{CO}_{2(\text{aq})}$  levels through the summer. Yet, there is evidence that a large portion of the phytoplankton biomass produced in the surface waters is lost from this region as it sinks toward deeper parts of the lakes before it gets remineralized (Wharton et al. 1989).

No respiration rates or POC decomposition rates have been measured during the austral fall and winter (between February and October), nor has the organic flux to the sediment been accurately quantified in the lakes (Priscu et al. 1999). Although these missing data leave uncertainties in the assessment of the role of respiration on the carbon budget in these lakes, we show below that these data may not be needed in order to constrain the  $\text{CO}_{2(\text{aq})}$  budgets of these lakes.

### *Diffusion*

Because of their density-induced stabilities, and permanent ice covers that eliminate wind-driven mixing, vertical transport in the lakes is dominated by molecular diffusion (Spigel & Priscu 1996, 1998). Recent work also indicates that density-driven mixing can occur, at least sporadically, in Lakes Fryxell and Hoare (Miller & Aiken 1996, Hood et al. 1998, Tyler et al. 1998). This density-driven circulation takes place as the edges of the lake ice, when they thaw in the summer and form 'moats' up to 10 m wide. When the moat begins to freeze at the end of the austral summer, salts are excluded from the ice and

Table 2. CO<sub>2</sub> concentrations, sources, and sinks. WB = west lobe of Lake Bonney, EB = east lobe of Lake Bonney, H = Lake Hoare, F = Lake Fryxell. All rates are given for one year, and for a vertical profile segment of 1 m length. The diffusion is given through a plane of 1 m<sup>2</sup> yr<sup>-1</sup>. Negative values indicate downward diffusion. The input via streams is described as input into the uppermost meter of water. Balance is CO<sub>2</sub> sources (diffusion, stream, respiration) minus sinks (uptake)

	Depth m	Area m <sup>2</sup>	PPR mol m <sup>-2</sup>	CO <sub>2aq</sub> mol m <sup>-2</sup>	Diffusion mol m <sup>-2</sup>	Stream mol m <sup>-2</sup>	Resp. mol m <sup>-2</sup>	Balance mol m <sup>-2</sup>	PPR/ Resp	Uptake as % of CO <sub>2aq</sub>
WB	5	1,004,976	0.027	0.024	-0.0001	0.034	0.032	0.039	0.8	115.0
	6	1,004,976	0.024	0.013	0.005					182.0
	8	897,409	0.026	0.024	0.051					112.0
	10	790,946	0.027	0.079	0.593		0.037	0.603	0.7	34.0
	13	610,887	0.160	4.929	7.359		0.071	7.270	2.2	3.0
EB	15	561,552	0.050	37.010	1.478		0.033	1.461	1.5	0.1
	5	3,037,673	0.023	0.017	-0.0014	0.005	0.022	0.003	1.0	139.0
	6	3,037,673	0.021	0.008	-0.00013					253.0
	8	2,875,404	0.021	0.008	0.002					272.0
	10	2,717,680	0.016	0.022	0.089		0.025	0.096	0.6	74.0
	13	2,447,838	0.018	1.696	0.255		0.029	0.266	0.6	1.0
	15	2,332,853	0.019	3.188	0.079		0.018	0.077	1.1	0.6

Table 2. Continued

	Depth m	Area m <sup>2</sup>	PPR mol m <sup>-2</sup>	CO <sub>2aq</sub> mol m <sup>-2</sup>	Diffusion mol m <sup>-2</sup>	Stream mol m <sup>-2</sup>	Resp. mol m <sup>-2</sup>	Balance mol m <sup>-2</sup>	PPR/ Resp	Uptake as % of CO <sub>2aq</sub>
H	5	1,471,798	0.013	0.016	-0.00066	0.001	0.027	0.015	0.5	78.0
	6	1,471,798	0.011	0.012	0.00002					93.0
	8	1,339,927	0.011	0.017	0.00237		0.028	0.019	0.4	69.0
	12	1,070,634	0.007	0.084	0.03871		0.024	0.056	0.3	8.0
	16	807,719	0.004	0.618	0.02266		0.014	0.033	0.3	0.6
	20	555,119	0.002	0.904	-0.00575		0.012	0.005	0.1	0.2
F	5	2,930,082	0.056	0.518	0.017	0.003	0.053	0.017	1.1	11.0
	6	2,930,082	0.039	0.615	0.002		0.081	0.044	0.5	6.0
	7	2,410,044	0.042	0.620	0.004					7.0
	8	2,104,570	0.072	0.689	0.101		0.080	0.108	0.9	10.0
	9	1,831,355	0.150	1.081	0.317		0.100	0.268	1.5	14.0
	10	1,587,426	0.044	2.152	0.520		0.163	0.638	0.3	2.0
	11	1,369,842	0.006	3.671	0.177		0.193	0.364	0.3	0.2



increase the density of the water. Miller and Aiken (1996) suggest that in Lake Fryxell this process could add  $\sim 1\%$  of the present volume to a depth of 18 m annually. However, they did not see any evidence for recharge into the depths between 5 and 18 m, and, according to Hood et al. (1998), density-driven circulation is weak compared to diffusive processes within the lake column. Hence, we have assumed that this density driven caballing does not greatly affect the  $\text{CO}_{2(\text{aq})}$  budgets of the lakes.

Because the waters below the chemoclines of Lakes Bonney and Fryxell have a large  $\text{CO}_{2(\text{aq})}$  pool, with  $\text{pCO}_2$  values well above equilibrium with the atmosphere (Figure 3), they are potential sources of  $\text{CO}_{2(\text{aq})}$  to the photic zones. We have computed the upward flux of  $\text{CO}_{2(\text{aq})}$  across the chemocline using the Fickian equation  $F = D (\partial C / \partial z)$ , where  $F$  = flux ( $\text{mol cm}^{-2} \text{ s}^{-1}$ ),  $D$  = temperature-dependent diffusion coefficient for  $\text{CO}_{2(\text{aq})}$  ( $1.085 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ ),  $C$  = concentration of  $\text{CO}_{2(\text{aq})}$  ( $\text{mol cm}^{-3}$ ), and  $z$  = distance between two points of known  $\text{CO}_{2(\text{aq})}$  concentration (cm).

The results of the diffusion calculations show that at the top of the chemoclines (sites of  $\text{PPR}_{\text{max}}$ ), upward diffusion of  $\text{CO}_{2(\text{aq})}$  from deeper waters is the most important source of  $\text{CO}_{2(\text{aq})}$  to the euphotic zone (Table 2). For example, the upward diffusion is  $7.36 \text{ mol m}^{-2} \text{ yr}^{-1} \text{ CO}_{2(\text{aq})}$  across the 13 m plane in the west lobe of Lake Bonney, compared to an uptake from primary production of  $0.16 \text{ mol m}^{-2} \text{ yr}^{-1}$  for the 12 to 13 m depth interval. In the east lobe, between 11 and 12 m, the diffusion across the 12 m plane provides  $0.4 \text{ mol m}^{-2} \text{ yr}^{-1} \text{ CO}_{2(\text{aq})}$ , while the uptake from primary production is only  $0.06 \text{ mol m}^{-2} \text{ yr}^{-1} \text{ CO}_{2(\text{aq})}$ . In Lake Fryxell, between 8 and 9 m, the annual upward diffusion of  $0.32 \text{ mol m}^{-2} \text{ yr}^{-1} \text{ CO}_{2(\text{aq})}$  at the chemocline (9 m) exceeds the uptake of  $0.15 \text{ mol m}^{-2} \text{ yr}^{-1} \text{ CO}_{2(\text{aq})}$ . In Lake Hoare, both the  $\text{CO}_{2(\text{aq})}$  concentrations and the  $\text{PPR}_{\text{max}}$  are relatively low compared to the other lakes. However, below 12 m depth, the diffusive flux ( $0.02\text{--}0.04 \text{ mol m}^{-2} \text{ yr}^{-1}$ ) is larger than the uptake rate ( $0.003\text{--}0.007 \text{ mol m}^{-2} \text{ yr}^{-1}$  at various 1 m-depth intervals). In Lake Bonney and Lake Fryxell, large quantities of  $\text{CO}_2$  diffuse upward into the region of  $\text{PPR}_{\text{max}}$ , and photosynthetic uptake does not utilize all of this  $\text{CO}_2$ . Our calculations imply that the  $\text{CO}_{2(\text{aq})}$  concentration could be increasing above the chemocline, and that the chemocline is moving upward over time, an observation that agrees with other work (Matsubaya et al. 1979; Lawrence & Hendy 1985). The work of Doran et al. (1999) using  $^{14}\text{C}$  measurements demonstrated that much of the DIC in these lakes is not recent. Although the antiquity of the DIC may be due, in part, to direct input of glacier melt without reequilibration with the atmosphere, this process of carbon recycling brought about by the diffusive flux from the depth, and lack of atmospheric change due to the permanent ice covers, also adds to the ‘older’ ages of the DIC in these lakes.

Unlike at the chemoclines (9–13 m depth), diffusion from below is contributing little  $\text{CO}_{2(\text{aq})}$  to the surface waters of the lakes (4–6 m depth, directly below the ice cover). In these uppermost layers of the west and east lobes of Lake Bonney and of Lake Hoare, the net diffusive flux of  $\text{CO}_2$  is downward ( $-0.1$ ,  $-1$  and  $-1 \text{ mmol m}^{-2} \text{ yr}^{-1} \text{ CO}_{2(\text{aq})}$ , respectively). The flux from the streams exceeds the upward  $\text{CO}_{2(\text{aq})}$  diffusion into the surface water in Lake Bonney and in Lake Hoare, but is smaller than the diffusive flux in Lake Fryxell. In the west lobe of Lake Bonney, the  $\text{CO}_{2(\text{aq})}$  flux from streams also exceeds the photosynthetic carbon uptake, while in the other lakes the uptake is as much as 15 times higher than the stream influx of  $\text{CO}_{2(\text{aq})}$ . This large  $\text{CO}_{2(\text{aq})}$  stream flux into the west lobe of Lake Bonney probably reflects the high input from streams draining Blood Falls, a hypersaline discharge at the snout of Taylor Glacier (Figure 1; Nezat 1998).

### *Calcification*

The precipitation of  $\text{CaCO}_3$  (calcification) in the water column also can produce  $\text{CO}_{2(\text{aq})}$  (McConnaughey et al. 1994). The potential impact of calcification on  $\text{pCO}_2$  variation can be evaluated by determining calcite saturation indices ( $\text{SI} = \log (\text{IAP}/\text{K}_{\text{sp}})$ ;  $\text{IAP}$  = ion activity product,  $\text{K}_{\text{sp}}$  = solubility product) for the lakes. Saturation indices for these lakes have recently been presented by Lyons et al. (1998b) and Neumann (1999). In Lake Bonney, at the beginning of the austral summer, calcification is a potential source of  $\text{CO}_{2(\text{aq})}$  to the surface waters, while, towards the end of the austral summer, this source becomes unlikely as the SI values decrease and the waters become undersaturated with respect to  $\text{CaCO}_3$ . In Lake Hoare, calcification can contribute  $\text{CO}_{2(\text{aq})}$  during the entire growing season. Conversely, Lake Fryxell was undersaturated with respect to calcite at 5 m (just below the ice) at the beginning of the summer, and became undersaturated to a depth of 8 m by the end of the season. Calcite undersaturation in the photosynthetically active zone eliminates calcification as a source of  $\text{CO}_{2(\text{aq})}$ . Because no massive precipitation events such as lake whittings have been reported for any of the lakes, we have assumed that calcification plays only a small role as a  $\text{CO}_{2(\text{aq})}$  source to these waters. However, calcification is occurring in the benthic algal mats of these lakes, in which abundant calcite crystals have been recorded (Wharton et al. 1983). Whether this process is a contributor to benthic mat primary production via increased  $\text{CO}_{2(\text{aq})}$  availability is not known.

### *$\text{CO}_{2(\text{aq})}$ mass balance*

To understand better  $\text{CO}_2$  dynamics in these lakes, a  $\text{CO}_{2(\text{aq})}$  mass balance for the mixolimnions of the three lakes have been calculated (Figure 7).

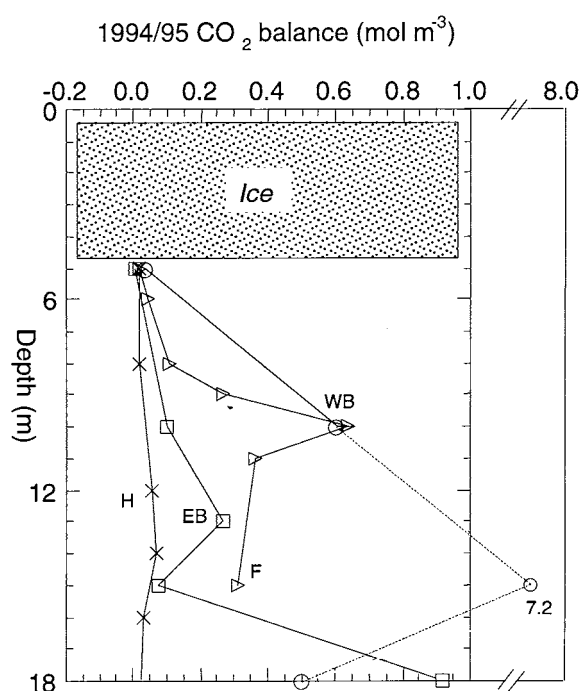


Figure 7. Annual balance for  $\text{CO}_2$  in the three Taylor Valley lakes. The  $\text{CO}_2$  concentration in the water underlying the ice remains basically unchanged, while just above the chemoclines the  $\text{CO}_2$  concentrations should increase over time.

This is achieved by comparing the  $\text{CO}_{2(\text{aq})}$  sinks (primary productivity) with the sources (respiration, stream input, and diffusion), all normalized for a one-year interval. For this calculation, we assume that photosynthesis is active half a year (the austral summer), while respiration and diffusion occur continuously. The stream input is used as described above.

In the upper parts of all the lakes, this annual  $\text{CO}_{2(\text{aq})}$  balance is very close to zero. In the uppermost meter of the east lobe of Lake Bonney and of Lake Fryxell, the balance is slightly negative ( $-0.008$  and  $-0.01 \text{ mol m}^{-2} \text{ yr}^{-1}$ ), while in Lake Hoare the balance is  $+0.01 \text{ mol m}^{-2} \text{ yr}^{-1}$ , and in the west lobe of Lake Bonney it is  $+0.023 \text{ mol m}^{-2} \text{ yr}^{-1}$ . Given the uncertainties of the data used in these calculations, we conclude that the upper depths of the lakes are essentially in balance with respect to  $\text{CO}_{2(\text{aq})}$  production and consumption over an annual period. This is the case, regardless of the varying absolute amounts of DIC,  $\text{CO}_{2(\text{aq})}$ , or PPR, in these lakes. However, as shown above, the  $\text{CO}_{2(\text{aq})}$  concentration is not static. Times of low  $\text{pCO}_2$  will be especially significant, when the ratio between PPR uptake and the pool of available  $\text{CO}_{2(\text{aq})}$  is large, as for Lake Bonney. In this case, the  $\text{CO}_{2(\text{aq})}$  can not 'buffer'

an increased demand from PPR, resulting in  $p\text{CO}_2$  values below atmospheric equilibrium. Only the input via stream water later in the summer, and a rather constant recharge by diffusion and respiration balances the  $\text{CO}_{2(\text{aq})}$  budget through the year. At the chemoclines, the sources of  $\text{CO}_{2(\text{aq})}$  are clearly higher than the sinks in Lakes Bonney and Fryxell, and, to a lesser degree, in Lake Hoare. The  $\text{CO}_{2(\text{aq})}$  surplus is caused by the high rate of diffusion from the lower, supersaturated water column.

An important aspect of our results is the potential for  $\text{CO}_{2(\text{aq})}$  to limit primary productivity. In these Antarctic lakes, it has been shown that light and nutrients, especially inorganic P, can limit phytoplankton growth (Lizotte & Priscu 1992; Priscu 1995). No experiments have yet addressed whether or not  $\text{CO}_{2(\text{aq})}$  could also limit primary production, especially in the upper portions of Lake Bonney and Lake Hoare. Even if the  $\text{CO}_{2(\text{aq})}$  concentrations are not low enough to limit growth, they may decrease the fractionation of  $^{12}\text{C}/^{13}\text{C}$  during  $\text{CO}_2$  uptake by phytoplankton (Fogel et al. 1992). This is of special concern because the  $\text{CO}_{2(\text{aq})}$  undersaturation changes seasonally in some of the lakes, possibly causing changes in the isotopic signature of both organic matter and  $\text{CaCO}_3$  produced in the photic zone (Doran et al. 1998, 2000; Neumann 1999; Neumann et al. 1998a). These effects of  $\text{CO}_2$  limitation have been described in White Smoke Lake, Bunger Hills, Antarctica (Doran et al. 2000), and Bird et al. (1991) used them to explain the  $\delta^{13}\text{C}$  values for the sedimentary organic matter in both Highway and Organic Lakes in the Vestfold Hills, Antarctica. This transient fractionation also adds an additional variable to the interpretation of the sedimentary  $\delta^{13}\text{C}$  record, which is already complicated due to very different  $\delta^{13}\text{C}$  signatures at different depths of the lakes (Neumann et al. 1995).

## Conclusion

The fluxes of  $\text{CO}_{2(\text{aq})}$  in the Taylor Valley lakes can be summarized as follows:  $\text{CO}_{2(\text{aq})}$  from deep, highly supersaturated water diffuses upward across the chemocline into the mixolimnion, providing  $\text{CO}_{2(\text{aq})}$  that is necessary to support planktonic photosynthesis at the deep photosynthetic maximum. The diffusive contribution of deep-water  $\text{CO}_{2(\text{aq})}$  to planktonic photosynthesis immediately beneath the ice is negligible. The advective input of  $\text{CO}_{2(\text{aq})}$  via streams is significant, but, except for the west lobe of Lake Bonney, does not provide adequate  $\text{CO}_{2(\text{aq})}$  to support the measured primary production rates observed there.  $\text{CO}_{2(\text{aq})}$  production via respiration in the lakes is less than the uptake of  $\text{CO}_2$  via primary production, except for Lake Hoare. In the surface waters of Lake Bonney,  $\text{CO}_{2(\text{aq})}$  supply via calcification could be significant in the beginning of the photosynthetic season, and, in Lake Hoare,

it can provide additional  $\text{CO}_{2(\text{aq})}$  throughout the entire season. When these processes are combined, the  $\text{CO}_2$  dynamics (uptake vs. input) are balanced in the surface waters of these lakes.

## Acknowledgements

This research has been supported by NSF grant OPP-921173.

We thank a number of our McMurdo Dry Valley LTER colleagues who helped in the collection and the analyses of these samples. We especially appreciate the help of K. Welch and R. Edwards. We appreciate discussion with P. Doran concerning his work.

## References

- Andersen DT, McKay CP & Wharton RA (1998) Dissolved gases in perennially ice-covered Antarctic lakes of the McMurdo Dry Valleys. *Antarctic Sci.* 10: 124–133
- Berman-Frank I, Zohary T, Erez J & Dubinsky Z (1994)  $\text{CO}_2$  availability, carbonic anhydrase, and the annual dinoflagellate bloom in Lake Kinneret. *Limnol. Oceanogr.* 39: 1822–1834
- Bird MI, Chivas AR, Radnell CR & Burton HR (1991) Sedimentological and stable-isotope evolution of lakes in the Vestfold Hills, Antarctica. *Palaeogeogr., Palaeoclimatol., Palaeoecol.* 84: 109–130
- Clow GD, McKay CP, Simmons GM & Wharton Jr RA (1988) Climatological observations and predicted sublimation rates at Lake Hoare, Antarctica. *J. Climatol.* 1: 715–728
- Cole JJ, Caraco NF, Kling GW & Kratz TK (1994) Carbon dioxide supersaturation in the surface waters of lakes. *Science* 265: 1568–1570
- Craig H, Wharton RA & McKay CP (1992) Oxygen supersaturation in ice-covered Antarctica lakes: Biological vs. physical contributions. *Science* 255: 318–320
- Doran PT, Wharton RA, Lyons WB, Des Marais DJ & Anderson DT (2000) Sedimentology and isotope geochemistry of a perennially ice-covered epishelf lake in Bunge Hills Oasis, East Antarctica. *Antarctic Sci.* 12: 131–140
- Doran PT, Berger G, Wharton Jr RA, Lyons WB, Davisson L, Southon J & Dobb J (1999) Dating Quaternary lacustrine sediments in the McMurdo Dry Valleys Antarctica. *Palaeogeogr., Palaeoclimatol., Palaeoecol.* 147: 223–239
- Doran PT, Wharton RA, Des Marais DJ & McKay CP (1998) Antarctic paleolake sediments and the search for extinct life on Mars. *J. Geophys. Res.* 103: 28481–28493
- Fogel ML, Cifuentes LA, Velinsky DJ & Sharp JH (1992) Relationship of carbon availability in estuarine phytoplankton to isotopic composition. *Marine Ecol. Progr. Ser.* 82: 291–300
- Gleitz M, Loeff MRvd, Thomas DN, Dieckmann GS & Millero FJ (1995) Comparison of summer and winter inorganic carbon, oxygen and nutrient concentrations in Antarctic sea ice brine. *Marine Chem.* 51: 81–91
- Green WL, Angle MP & Chave KE (1988) The geochemistry of Antarctic streams and their role in the evolution of four lakes in the McMurdo Dry Valleys. *Geochim. Cosmochim. Acta* 52: 1265–1274
- Hood M, Howes BL & Jenkins WJ (1998) Dissolved gas dynamics in perennially ice-covered Lake Fryxell, Antarctica. *Limnol. Oceanogr.* 43: 265–272

- Hope D, Dawson JJC, Cresser MS & Billet MF (1995) A method for measuring free CO<sub>2</sub> in upland streamwater using headspace analysis. *J. Hydrol.* 166: 1–14
- Kling GW, Kipphut GW & Miller MC (1992) The flux of CO<sub>2</sub> and CH<sub>4</sub> from lakes and rivers in arctic Alaska. *Hydrobiol.* 240: 23–36
- Lawrence MJF & Hendy CH (1989) Carbonate deposition and Ross Sea ice advance, Fryxell Basin, Taylor Valley, Antarctica. *New Zealand J. Geol. Geophys.* 32: 267–277
- Lawrence MJF & Hendy CH (1985) Water column and sediment characteristics of Lake Fryxell, Taylor Valley, Antarctica. *New Zealand J. Geol. Geophys.* 28: 543–552
- Lizotte MP & Prisco JC (1992) Photosynthesis-irradiance relationships in phytoplankton from the physically stable water column of a perennially ice-covered lake (Lake Bonney, Antarctica). *J. Phycol.* 28: 179–185
- Lyons WB, Fountain A, Doran P, Prisco JC, Neumann K & Welch KA (2000) The importance of landscape position and legacy: the evolution of the Taylor Valley lake district, Antarctica. *Freshwater Biol.* 43: 355–367
- Lyons WB, Tyler SW, Wharton Jr RA, McKnight DM & Vaughn BH (1998a) A late Holocene desiccation of Lake Hoare and Lake Fryxell, McMurdo Dry Valleys, Antarctica. *Antarctic Sci.* 10: 247–256
- Lyons WB, Welch KA, Neumann K, Toxey JK, McArthur R, Williams C, McKnight DM & Moorhead D (1998b) Geochemical linkages among glaciers, streams, and lakes within the Taylor Valley, Antarctica. In: Prisco JC (Ed.) *Ecosystem Dynamics in a Polar Desert: the McMurdo Dry Valleys, Antarctica* (pp 77–92). AGU Antarctic Res. Ser., Washington D.C.
- Matsubaya O, Sakai H, Torii T, Burton H & Kerry K (1979) Antarctic saline lakes-stable isotopic ratios, chemical compositions and evolution. *Geochim. Cosmochim. Acta* 43: 7–25
- McConnaughey TA, LaBaugh JW, Rosenberry DO, Striegl RG, Reddy MM, Schuster PF & Carter V (1994) Carbon budget for a groundwater-fed lake: calcification supports summer photosynthesis. *Limnol. and Oceanogr.* 39: 1329–1332
- McKay CP, Wharton RA & Squires SW (1985) Thickness of ice on perennially frozen lakes. *Nature* 313: 561–562
- McKnight DM, Alger A, Tate CM, Shupe G & Spaulding S (1998) Longitudinal patterns in algal abundance and species distribution in meltwater streams in Taylor Valley, Antarctica. In: Prisco JC (Ed.) *Ecosystem Dynamics in a Polar Desert: the McMurdo Dry Valleys, Antarctica* (pp 109–127). AGU Antarctic Res. Ser., Washington D.C.
- McKnight DM & Andrews ED (1993) Hydrological and geochemical processes at the stream-lake interface in a permanently ice-covered lake in the McMurdo Dry Valleys, Antarctica. *Verh. Intern. Ver. Limnol.* 93: 957–959
- Miller LG & Aiken GR (1996) Effects of glacial meltwater inflows and moat freezing on mixing in an ice-covered Antarctic lake as interpreted from stable isotope and tritium distributions. *Limnol. and Oceanogr.* 41: 966–976
- Neumann K (1999) Carbon dynamics in lakes and streams of Taylor Valley, Antarctica. Ph.D. dissertation, University of Alabama, 176 pp
- Neumann K, Lyons WB & Des Marais DJ (1998a) Inorganic carbon isotope distribution and budget in the Lake Hoare and Lake Fryxell basins, Taylor Valley, Antarctica. *Ann. Glaciol.* 27: 685–690
- Neumann K, Lyons WB, Welch KA & Prisco JC (1998b) Calcite precipitation and dissolution dynamics in ice-covered Antarctic lakes: modeling and experimental results. *EOS* 79(1): OS181. Abstract

- Neumann K, Lyons WB, Des Marais DJ, Priscu JC & Edwards RL (1995)  $^{13}\text{C}$  and  $\text{pCO}_2$  Distribution in Antarctic lakes: Ice cover and biota leave their imprint. *EOS* 76(46): F215. Abstract
- Nezat CA (1998) Chemical weathering in Taylor Valley, Antarctica: Quantity and quality. Masters Thesis. University of Alabama
- Parkhurst DL, Thorstenson DC & Plummer LN (1980) PHREEQE – A computer program for geochemical calculations. U.S. Geol. Surv. Water Res. Invest. Rep. 80–96
- Plummer LN, Parkhurst DL, Fleming GW & Dunkle SA (1988) A computer program incorporating Pitzer's equations for calculation of geochemical reactions in brines. U.S. Geol. Surv. Water Res. Invest. Rep. 88–4135
- Priscu JC (1997) The biogeochemistry of nitrous oxide in permanently ice-covered lakes of the McMurdo dry valley, Antarctica. *Global Change Biol.* 3: 301–315
- Priscu JC (1995) Phytoplankton nutrient deficiency in lakes of the McMurdo dry valleys, Antarctica. *Freshwater Biol.* 34: 215–227
- Priscu JC, Downes MT & McKay CP (1996) Extreme supersaturation of nitrous oxide in a poorly ventilated Antarctic Lake. *Limnol. Oceanogr.* 41: 1544–1551
- Priscu JP, Wolf CF, Takacs CD, Fritsen CH, Laybourn-Parry J, Roberts EC, Stattler B & Lyons WB (1999) Carbon transformations in a perennially ice-covered Antarctic lake. *BioSci.* 49: 997–1008
- Quay PD, Emerson SR, Quay BM & Devol AH (1986) The carbon cycle for Lake Washington – A stable isotope study. *Limnol. Oceanogr.* 31: 596–611
- Riebesell U, Wolf-Gladrow DA & Smetacek V (1993) Carbon dioxide limitation of marine phytoplankton growth rates. *Nature* 361: 249–251
- Schidlowski M, Gorzawski H & Dor I (1994) Carbon isotope variations in a solar pond microbial mat: Role of environmental gradients as steering variables. *Geochim. Cosmochim. Acta* 58: 2289–2298
- Schindler DE, Carpenter SR, Cole JJ, Kitchell KF & Pace ML (1997) Influence of food web structure on carbon exchange between lakes and the atmosphere. *Science* 277: 248–251
- Sharp TJ & Priscu JC (1992) Temporal variation of specific growth rates for phytoplankton in Lake Bonney, Antarctica. *Antarctic J. U.S.* 1992: 257–258
- Spigel RH & Priscu JC (1998) Physical limnology of the McMurdo Dry Valley Lakes. In: Priscu JC (Ed.) *Ecosystem Dynamics in a Polar Desert: the McMurdo Dry Valleys, Antarctica* (pp 153–187). AGU Antarctic Res. Ser., Washington D.C.
- Spigel RH & Priscu JC (1996) Evolution of temperature and salt structure in Lake Bonney, a chemically stratified Antarctic lake. *Hydrobiol.* 321: 177–190
- Tyler SW, Cook PG, Butt AZ, Thomas JM, Doran PT & Lyons WB (1998) Evidence of deep circulation in two perennially ice-covered Antarctic lakes. *Limnol. Oceanogr.* 43: 625–635
- Vincent WF (1988) *Microbial ecosystems of Antarctica*. Cambridge University Press
- Vincent WF & Vincent CL (1981) Factors controlling phytoplankton production in Lake Vanda (77° S). *Canadian J. Fish. Aquatic Sci.* 39: 1602–1609
- Welch KA, Lyons WB, Graham E, Neumann K, Thomas JE & Mikesell D (1996) The determination of major element chemistry in terrestrial waters from Antarctica using ion chromatography. *J. Chromatogr. A* 739: 257–263
- Wharton Jr RA, McKay CP, Clow GD & Anderson DT (1993) Perennial ice covers and their influence on Antarctic lake ecosystems. In: Green W (Ed.) *Physical and Geochemical Processes in Antarctic Lakes* (pp 53–70). AGU Antarctic Res. Ser.
- Wharton Jr RA, McKay CP & Simmons Jr GM (1989) Perennially ice-covered Lake Hoare, Antarctica: physical environment, biology and sedimentation. *Hydrobiol.* 172: 306–320

- Wharton Jr RA, McKay CP, Mancinelli RL & Simmons Jr GM (1987) Perennial N<sub>2</sub> supersaturation in an Antarctic lake. *Nature* 325: 343–345
- Wharton Jr RA, Simmons GM & Parker BC (1986) Oxygen budget of a perennially ice-covered Antarctic lake. *Limnol. Oceanogr.* 31: 437–443
- Wharton Jr RA, Parker BC & Simmons Jr GM (1983) Distribution, species composition and morphology of algal mats in Antarctic dry valley lakes. *Phycol.* 22: 355–365