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The geochemistry of methane in Lake Fryxell, an amictic, permanently ice-covered, antarctic lake

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Abstract. The abundance and distribution of dissolved CH_4 were determined from 1987–1990 in Lake Fryxell, Antarctica, an amictic, permanently ice-covered lake in which solute movement is controlled by diffusion. CH_4 concentrations were < 1 μM in the upper oxic waters, but increased below the oxycline to 936 μM at 18 m. Sediment CH_4 was 1100 μmol (l sed)$^{-1}$ in the 0–5 cm zone. Upward flux from the sediment was the source of the CH_4, NH_4^+, and DOC in the water column; CH_4 was 27% of the DOC + CH_4 carbon at 18 m. Incubations with surficial sediments indicated that $H^{14}CO_3^-$ reduction was 0.4 μmol (l sed)$^{-1}$ day^{-1} or 4x the rate of acetate fermentation to CH_4. There was no measurable CH_4 production in the water column. However, depth profiles of CH_4, NH_4^+, and DIC normalized to bottom water concentrations demonstrated that a significant CH_4 sink was evident in the anoxic, sulfate-containing zone of the water column (10–18 m). The $\delta^{13}CH_4$ in this zone decreased from −72 ‰ at 18 m to −76 ‰ at 12 m, indicating that the consumption mechanism did not result in an isotopic enrichment of $^{13}CH_4$. In contrast, $\delta^{13}CH_4$ increased to −55 ‰ at 9 m due to aerobic oxidation, though this was a minor aspect of the CH_4 cycle. The water column CH_4 profile was modeled by coupling diffusive flux with a first order consumption term; the best-fit rate constant for anaerobic CH_4 consumption was 0.012 yr^{-1}. On a total carbon basis, CH_4 consumption in the anoxic water column exerted a major effect on the flux of carbonaceous material from the underlying sediments and serves to exemplify the importance of CH_4 to carbon cycling in Lake Fryxell.

Introduction

Methane is a key component of the carbon cycle in many aquatic ecosystems. Consequently, methane geochemistry has been studied in a variety of environments, including freshwater lakes and wetlands (King 1990; Kuivila et al. 1988; Molongoski & Klug 1980; Rudd & Hamilton 1978), marine and estuarine sediments and closed basins (Claypool &

Kvenvolden 1983; Martens & Berner 1977; Martens et al. 1986; Reeburgh et al. 1991; Wiesenburg et al. 1985), and meromictic saline lakes (Javor 1989; Oremland & DesMarais 1983; Oremland et al. 1987). Methane production predominantly occurs in sediments, but is ultimately controlled by accretion of organic material that originates from the watershed and the water column of a given habitat (Claypool & Kaplan 1974). Flux of methane from the sediments to the water column, and in some situations to the atmosphere, represents a reverse exchange of carbon and fixed energy and the extent to which it occurs can provide important clues regarding carbon processing within that environment. However, for most aquatic habitats, because of physical mixing processes and the diversity of sources of degradable organic material, it is usually difficult to demonstrate the significance of the methane cycle to the total carbon cycle within the ecosystem.

Lakes in the Antarctic Dry Valleys are uniquely suited to serve as model environments in which to study the interaction of the physical and biogeochemical processes that affect the carbon cycle. Thick, permanent ice sheets cover these lakes and several contain a salinity gradient that extends throughout the entire water column. Together these features can result in true amixis, such that solute movement within some of these lakes is solely controlled by diffusion (Burton 1981; Green et al. 1989; Lawrence & Hendy 1985; Matsubaya et al. 1979; Torii et al. 1975; Wilson 1964). These lakes are situated in an arid, harsh environment which is devoid of higher plants and animals. Dissolved organic material within the lakes is derived autochthonously (Aiken et al. 1991; McKnight et al. 1991; Matsumoto 1989; Matsumoto et al. 1989). As a result of this physical environment, these lakes most closely approximate closed aquatic ecosystems, or systems that are controlled nearly entirely by internal processes.

Little is known about methane within such internally driven ecosystems. There have been a few studies on methane geochemistry in maritime, freshwater, antarctic lakes (Ellis-Evans 1984; Yarrington & Wynn-Williams 1985) and a detailed study in Ace Lake, a meromictic, coastal lake in Antarctica that seasonally looses its ice cover (Burton 1981; Franzmann et al. 1991), but there are only very scattered reports of methane in the saline Dry Valley lakes (Torii & Yamagata 1981; Waguri 1976). This study describes the production and the geochemistry of methane within the context of the total carbon cycle in one of the amictic Dry Valley lakes, Lake Fryxell. We found significant concentrations of methane in Lake Fryxell and that methane is an important aspect of the diffusive flux of carbonaceous material between the sediments and the overlying waters. However, unlike the bulk DOC, which is primarily recalcitrant, methane is being utilized in the water column by anaerobic microbial processes, to the extent that very little methane actually reaches oxygenated water, and none escapes from the lake.

Materials and methods

Study site

Lake Fryxell (77°37′S 163°8′E) is located in the McMurdo Dry Valleys of Antarctica in the vicinity of the Ross Ice Shelf. It is 5.3 km long and 1.9 km wide, with a maximum depth of 19 m and is permanently covered with about 4.5 m of ice. The lake lies in the center of a 230 km^2 closed drainage basin (Lawrence & Hendy 1985), at a surface elevation of 15 m above sea level. In this arid region, the primary source of recharge to the lake is meltwater from the Canada and Commonwealth glaciers during a 2—3 month period in the austral summer. The watersheds of the Dry Valley lakes are noted for their moonscape appearance and an almost complete absence of plants and animals. Fryxell Stream, one of the larger of 10 small ephemeral streams discharging into Lake Fryxell, is colonized by cyanobacterial mats (Howard-Williams & Vincent 1989) and slow-growing, cold-tolerant mosses (*Bryum* sp) (Green 1985), but in general, nutrient and DOC concentrations of streamwater flowing into Lake Fryxell are very low (Aiken 1991; Downes et al. 1986; Green et al. 1989; Howard-Williams & Vincent 1989; McKnight et al. 1991). Stream discharge results in the formation of a shallow, ice-free moat around the lake; the depth of the moat does not exceed the thickness of the ice in the center of the lake.

The ice cover and a density gradient due to chemical stratification have resulted in an extremely stable, amictic water column in Lake Fryxell, which is anoxic below about 9.25 m (Lawrence & Hendy 1985; Torii et al. 1975). The ice cover on the Dry Valley lakes restricts exchange of gases with the atmosphere resulting in unusually high concentrations of N_2, O_2, and CO_2 in the water column (Craig et al. 1992; Lawrence & Hendy 1985; Wharton et al. 1986; Wharton et al. 1987) and it significantly attenuates the flux of photosynthetically active radiation (PAR) into the lake. Consequently, photosynthetic activity in Lake Fryxell is limited by, but adapted to, low light and low nutrient conditions (Priscu et al. 1987; Priscu et al. 1988; Vincent 1981). In 1987 a chlorophyll maximum was located at 8.5 m immediately above the oxycline (Aiken et al. 1991).

Sampling methodology

Water and sediment samples were collected from Lake Fryxell at a station located over the deepest part of the lake basin (see Lawrence & Hendy 1985 for a bathymetric map of the lake). All depths given are relative to the piezometric water level. Water samples were collected through Tygon tubing using a peristaltic pump. A volume of water 3—5x the volume of the tubing was pumped from each depth prior to collecting samples. Bulk samples for chloride were collected in 1 l plastic bottles, returned to shore and filtered through GFF Whatman glass fiber filters. For sulfate determination, 60 ml of water were placed in a bottle containing 10 ml of 100 mM $CdCl_2$ to preserve the sample and to prevent sulfide oxidation. Samples for methane and dissolved inorganic carbon (DIC) analysis were collected by syringe and injected into stoppered serum bottles, while samples for ammonium determination were filtered through 0.45 μm membrane filters and analyzed within 24 hours. Samples for dissolved organic carbon (DOC) and acetate determinations were filtered through 0.45 μm Selas silver membrane filters using a Gelman stainless steel filtration unit and collected in precombusted glass bottles. The samples for acetate analysis were then frozen. Samples for $\delta^{13}CH_4$ (30 ml) were collected in 60 ml syringes, to which was added 30 ml of He. The syringes were vigorously shaken for 2 minutes, then the gas phase was transferred into 120 ml water-filled serum bottles by displacement.

Sediment samples were collected by Eckman dredge and subsampled with cutoff syringes. For methane determination 3 ml of sediment was transferred into 30 ml serum bottles containing 20 ml of water. Bubble ebullition traps (42 cm internal diam.) were deployed through 0.6 m diameter melt holes in the ice and anchored with the funnel opening located at 18 m depth. The traps were checked weekly for a period of 40 days.

Activity assays for methane production

A water sample from 18 m was placed in a glass bottle and sparged with O_2-free N_2 for 35 min., which lowered the ambient methane concentration to <0.1 μM. Twenty ml aliquots were transferred to 15 30 ml serum bottles which were being sparged with O_2-free N_2. The bottles were stoppered, crimped, and flushed an additional 5 min. with N_2. The bottles were then divided into 5 different treatments (in triplicate) and amended to final concentrations of: a) control; b) 40 mM 2-bromoethane sulfonic acid (BES), an inhibitor of methane production (Gunsalus et al. 1978); c) 0.5 mM sodium acetate; d) 0.5 mM glucose; and e) H_2 headspace. The bottles were incubated at 4 °C and the concentration of methane in the headspace determined over a three day period.

Methane production was also assayed in water column and sediment samples using ^{14}C substrates. Water samples (40 ml) from 10, 14, and 18 m were transferred by syringe into 60 ml stoppered serum bottles containing O_2-free Ar and either 0.1 ml of $^{14}C\text{-}NaHCO_3$ (10 μCi/ml; 50 Ci/mol; New England Nuclear Corp.) or 0.25 ml of 2-^{14}C-sodium acetate (25 μCi/ml; 2 Ci/mol; New England Nuclear Corp.) solution. Triplicate serum bottles for each treatment were placed in black bags and incubated in the lake at 11 m for 3 days. At the end of the incubation, the headspace gas in each bottle, which contained any $^{14}CH_4$ that was produced, was transferred to a second 120 ml water-filled serum bottle by displacement. For methane production in sediments, the 0—5 cm depth interval was collected by Eckman dredge. In 1987 each 1 cm vertical interval was subsampled directly from the Eckman grab by cutoff 10 ml glass syringes. In 1989 the 0—5 cm interval was pooled and homogenized in a portable glovebag which contained a He atmosphere. The mixed sediment was then used to fill the cutoff glass syringes. All syringes were stoppered with recessed butyl rubber stoppers and injected at several points along the longitudinal axis with a solution of either ^{14}C-bicarbonate or ^{14}C-acetate (see above for activities). The samples were incubated at 5—10 °C for up to 8 days; activity was stopped by freezing. Radioactive methane was determined using a stripping and oxidation technique described by Whalen et al. (1986). The technique was modified slightly by supplementing the sample with additional $^{12}CH_4$ (1 ml, 100%) to insure consistent recovery. ^{14}C was trapped after oxidation as CO_2 in an ethanolamine/methanol mixture (4 ml/8 ml) and quantified using liquid scintillation counting.

Analytical techniques

Oxygen and temperature were measured with an Orbisphere dissolved oxygen meter (model 27141, Orbisphere Labs, Houston, TX) equipped with a sulfide-insensitive probe. Chloride was determined by titration with a Buchler-Cutlov chloridometer (Buchler Instruments). Ammonium was analyzed colorimetrically using the indophenol technique (Scheiner 1976) and sulfate turbidimetrically (Tabatabai 1974). Acetate was analyzed by HPLC with a UV detector as described by Culbertson et al. (1981) modified by the addition of a 15 cm Hamilton PRP-X300 column and a 2.5 cm guard column of the same material. The detection limit for acetate was 3 μM. DOC was assayed by persulfate oxidation as described by Aiken (1991). This procedure includes acetate in the DOC result (G. Aiken, personal communication). DIC was assayed as carbon dioxide after the addition of 0.5 ml of 2 N H_2SO_4 to the water sample. Methane and carbon dioxide were determined at the lake site with a Carle Analytical gas chromatograph (model AGC-311, Hach Chem. Co., Loveland, CO) equipped with thermal conductivity and flame ionization detectors connected in series using 2 0.3 cm outside diameter columns, 2.4 m of 80% Porapak N + 20% Porapak Q and 1.8 m of Molecular Sieve 5A, configured in a series-bipass arrangement. Carrier gas was He at 30 ml/min; analysis temperature was 90 °C.

The $^{13}C/^{12}C$ content of methane was determined as described by Oremland et al. (1987). Results are expressed on a per mil (‰) basis as:

$$\delta^{13}CH_4 = (((^{13}C/^{12}C)_{sample}/(^{13}C/^{12}C)_{standard}) - 1) \times 1000. \tag{1}$$

The reference standard was Pee Dee Belemnite (PDB).

Results

Lake Fryxell was sampled on an annual basis during the austral summer from 1987—1990. During this period the water column of the lake was extremely stable, as evidenced by a uniform salinity gradient, which did not change during the course of this study. The gradient extended through the entire water column, with chloride concentrations ranging from 10—110 mM (Fig. 1A). Just above the sediment-water interface (18 m) the salinity was 13 ‰, or about 37% that of seawater. The temperature of the lake was also seasonally consistent, increasing with depth from 0.4 °C below the ice to a maximum value of 3.4 °C for the 9—10.5 m depth interval. The temperature decreased somewhat with depth below 10.5 m (Fig. 1B). The upper portion of the water column (5—8.5 m) contained high concentrations of dissolved oxygen, up to 1.13 mM (Fig. 1A), but oxygen decreased markedly with depth in an oxycline between 8.5—9.25 m. The water column was anoxic below 9.25 m. The bottom waters contained high concentrations of reduced compounds, such as NH_4^+ (Fig. 1A) and sulfide (up to 1.1 mM, data not shown), all of which increased with depth below the oxycline. Sulfate was also present in the lake water, with a mid-depth maximum evident between 10—12 m at 1.8 mM (Fig. 1B). Below this depth interval, sulfate concentrations decreased and were only 0.1 mM at 18 m.

Methane concentrations in Lake Fryxell were < 1 μM above 9.25 m in the aerobic region of the water column, but increased exponentially with depth below the oxycline to nearly 1000 μM at 18 m (Fig. 2, Table 1). Methane concentrations in the underlying sediments were 1100 μmoles (1

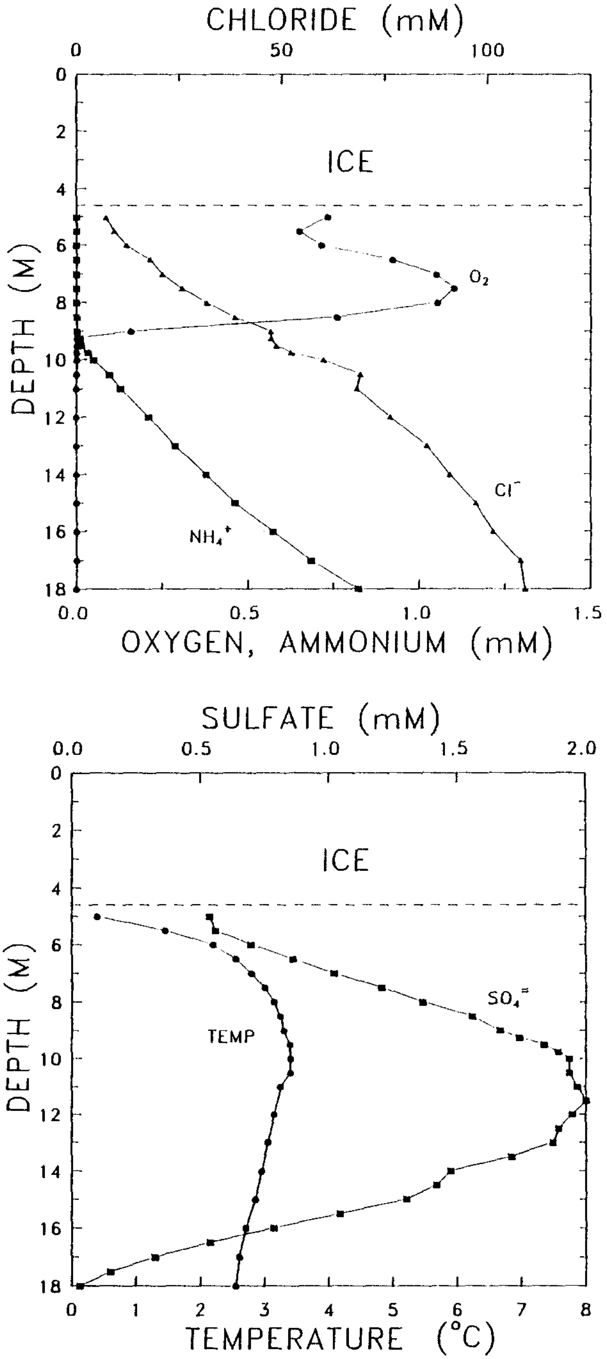

Fig. 1. Depth profile of a) oxygen, chloride, and ammonium and b) temperature and sulfate in Lake Fryxell in November 1989.

Table 1. Distribution of dissolved carbon in the bottom waters of Lake Fryxell.

Depth (m)	Concentration as mmoles/l			$CH_4/DOC + CH_4$ (%)
	DIC	DOC	CH_4	
10	31.4	1.0	0.004	0.4
12	38.3	1.4	0.020	1.4
14	47.1	1.8	0.088	4.7
16	52.5	2.1	0.327	13.5
18	51.6	2.5	0.936	27.2

DIC and CH_4 water samples were collected November, 1989, DOC samples were from December, 1990.

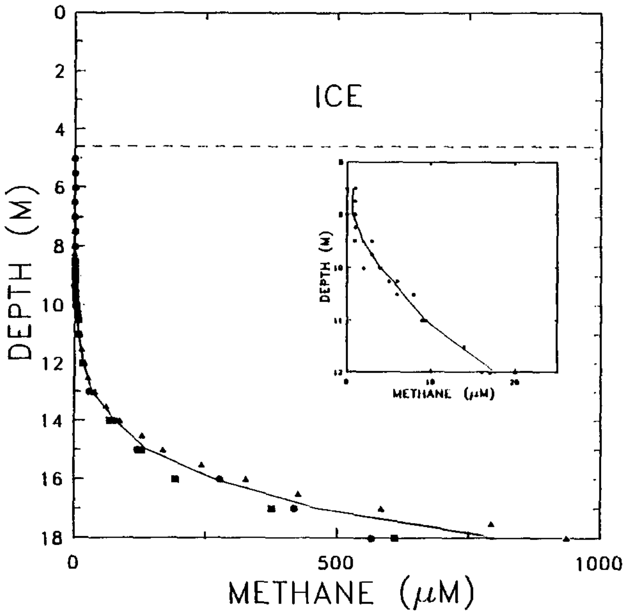

Fig. 2. Depth profile of dissolved methane in Lake Fryxell in December 1987 (●), December 1988 (■), and November 1989 (▲). Insert is an expanded view of the 8.5—12 m interval.

sed)$^{-1}$ in the 0—5 cm interval in 1987 (Table 2); there was no annual variation in the bottom water methane concentration during this study. There was also no evidence of methane flux due to bubble ebullition. Bubble traps situated at 18 m for 40 days did not collect any bubbles, and methane concentrations within and immediately beneath the ice cover

Table 2. Methane concentration and rate of production in Lake Fryxell surface sediments (0—5 cm) in December 1987.

CH_4 concentration μmol (l sed)$^{-1}$	1100
Methane production rate[a] μmol (l sed)$^{-1}$ day^{-1}	
2-^{14}C-acetate	0.1
$H^{14}CO_3$	0.4

[a] Calculated using acetate and DIC concentrations for 18 m water samples.

showed no evidence of elevated methane from dissolution of gas bubbles trapped under the ice. $\delta^{13}CH_4$ values in the water column were at a minimum of −76 ‰ at 12 m, increasing slightly with depth to −72 ‰ at 18 m and increasing markedly above 10 m to −55 ‰ in the aerobic water at 9 m (Fig. 3).

Dissolved inorganic carbon was the largest reservoir of carbon in the water column of Lake Fryxell (Table 1). Below the photic zone, DIC

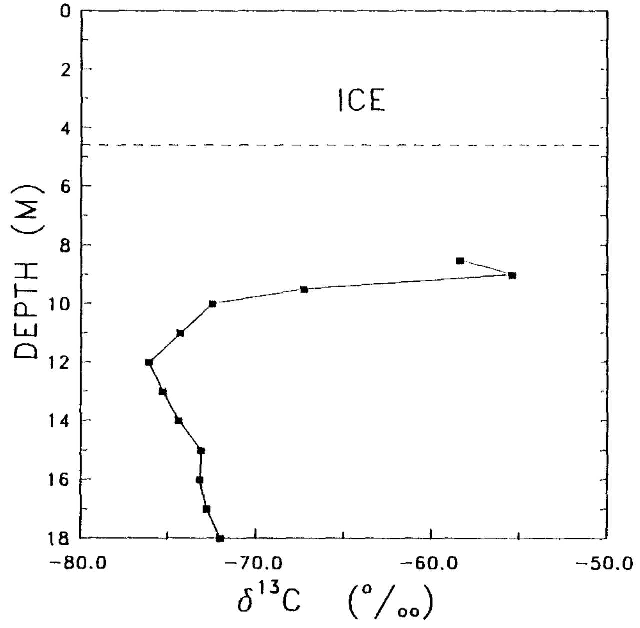

Fig. 3. Depth profile of $\delta^{13}C$ of methane in Lake Fryxell in December 1987.

concentrations increased uniformly with depth (2.7 mM/m) and were greater than 50 mM near the bottom. Depth profiles of DOC were similarly shaped such that below 10 m the DIC/DOC ratio was constant at approximately 25. On the other hand, CH_4/DOC ratios increased significantly with depth, to the extent that at 18 m, methane concentrations were as high as 27% of the DOC + CH_4 pool of carbon (Table 1). At that depth, acetate concentrations were 250 μM, accounting for 20% of the total DOC.

Methane production was assessed in water column and sediment samples during incubations with 2-^{14}C-acetate and $H^{14}CO_3^-$. Production of $^{14}CH_4$ in sediments was linear for both substrates over a 7 day period (Fig. 4). The rate of methane production from CO_2 reduction was 4-fold greater than that from acetate fermentation. The rates were 0.4 and 0.1 μmol (l sed)$^{-1}$ day^{-1}, respectively, for sediments from the 0—5 cm interval (Table 2). In both cases, the amount of substrate added was small relative to *in situ* concentrations. There was no measurable $^{14}CH_4$ production in water column samples from 10, 14, or 18 m with either ^{14}C-acetate or ^{14}C-bicarbonate as substrates. Nor was there any production of $^{12}CH_4$ in 18 m samples when amended with H_2, acetate, or glucose, even when the *in situ* methane concentration was lowered by 6000-fold to improve

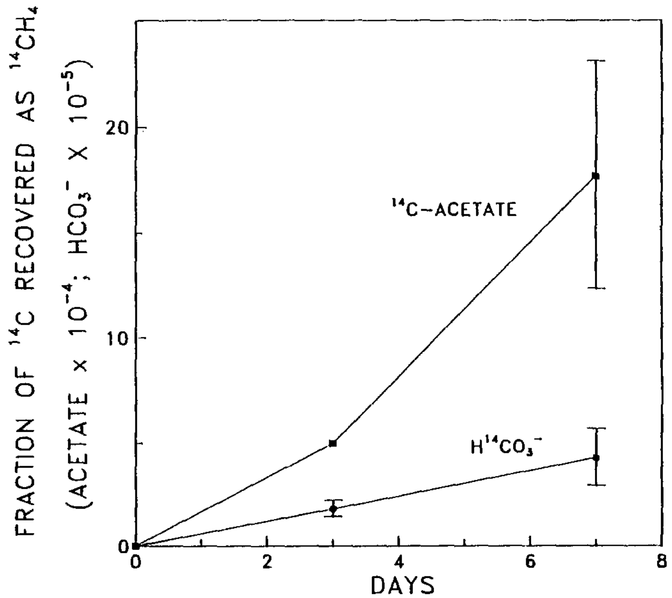

Fig. 4. Time course of $^{14}CH_4$ production by Lake Fryxell sediments collected in December 1989 when amended with either ^{14}C-sodium bicarbonate or 2-^{14}C-sodium acetate. Samples were incubated at 5—10 °C, error bars represent ± one standard error of the mean.

sensitivity. Based on DIC and acetate concentrations of 52 and 0.25 mM, respectively, the lowest detectable rate of $^{14}CH_4$ production at 18 m is estimated to be 15 nmol l^{-1} day^{-1} from HCO_3^- and 0.1 nmol l^{-1} day^{-1} from acetate.

Discussion

The physical environment of the Antarctic continent effectively isolates the closed basin lakes found in the McMurdo Dry Valleys and therefore has a profound effect upon the biogeochemistry of the carbon cycle within these lakes. The consequence of the extreme paucity of plants and animals in the watershed, the low DOC in the glacial meltwater (see Aiken 1991), and the short duration of the annual streamflow into the lakes (6—8 weeks) is that nearly all of the organic matter present within the lakes is the result of autochthonous productivity. In addition, the permanent ice cover restricts exchange of gases with the atmosphere, such as CO_2 and CH_4, so that with respect to the carbon cycle, the lakes can be viewed as closed ecosystems driven by the limited light that penetrates the ice. The composition of the organic matter (low aromatic content and high C/N ratios) within these lakes reflects its microbial origin and the absence of terrestrial or allochthonous inputs (McKnight et al. 1991).

The salinity gradient within the water column of Lake Fryxell (Fig. 1A) superimposes amixis as an additional factor, which differentiates the lake into several distinct, stable zones on a vertical axis. These zones include a photic zone with high oxygen concentrations, an oxycline with a sharp oxygen gradient, a mid-depth sulfate-enriched zone, and deeper waters containing reduced species such as sulfide and ammonium. Between and within these zones, molecular diffusion is the major mechanism for exchange of dissolved constituents. By treating the water column as a simple diffusion cell, Lawrence & Hendy (1985) were able to calculate a diffusion cell age (600—1200 years) and Aiken et al. (1991) determined from the density gradient that the vertical eddy diffusion coefficient was very low, approaching values for molecular diffusion. This approach assumes that lateral mixing is not an important factor in the lake. Certainly, lateral molecular diffusion would be insignificant due to scale differences (meters vertically vs kilometers horizontally) and there is no evidence to indicate that lateral advection is significant either. Depth profiles of oxygen, chloride, methane and DOC did not vary along a 10-station horizontal transect across the lake (RL Smith, unpublished data).

High concentrations of methane, up to 1000 μM, were present in the deepest, anoxic waters of Lake Fryxell (18 m). High concentrations of methane are more typically found within sedimentary habitats (both freshwater and marine) than in the water column of a lake. Lake Fryxell values exceed methane concentrations found in many saline and hypersaline, meromictic bodies of water, which usually contain high concentrations of sulfate (Javor 1989), but are less than the 4 mM methane found in a freshwater meromictic lake (Winfrey & Zeikus 1979) and a hypereutrophic freshwater lake (Molongoski & Klug 1980). Even higher methane concentrations (5 mM) were found in Ace Lake, a seasonally ice-covered, meromictic lake located in the Vestfold Hills of Antarctica (Burton 1980; Franzmann et al. 1991). In both Ace Lake and Lake Fryxell, methane concentrations decreased significantly with distance upward away from the sediment-water interface, which suggested that the sediments were the predominant source of the water column methane (Fig. 2; Franzmann et al. 1991). However, in Ace Lake, measurable rates of methane production, 2.5 μmol kg^{-1} day^{-1}, were found in the water column at 20 m, whereas we found no evidence of methane production in the waters of Lake Fryxell, even when water samples were amended with common methanogenic substrates. Since sulfate concentrations were low in 18-m water from Lake Fryxell (Fig. 1b), while acetate concentrations were relatively high, it appears that at least in the deeper portion of the water column, methane production was not prevented by a limitation in substrate availability. Methane production from formate and the non-competitive precursors of methane, such as dimethyl sulfide and trimethylamine, were not examined in this study.

Surface sediments obtained from Lake Fryxell did display methanogenic activity when amended with ^{14}C-acetate or ^{14}C-bicarbonate and incubated at *in situ* temperature. The combined rate of methane production from these 2 substrates was estimated to be 0.5 μmol (l sed)$^{-1}$ day^{-1} for the 0—5 cm interval (Table 2). The sediments within the lake are calcareous, containing 1—2 cm thick layers of aragonite and calcite (Lawrence & Hendy 1985). A sufficient volume of porewater from the surficial sediments was unavailable for analysis, hence concentrations of acetate and DIC at 18 m were used to calculate rates of methane production in the surface sediments. However, because the lake is a diffusion-dominated system, those samples taken near the sediment-water interface should give reasonable first approximations of sediment pool sizes.

Sulfate reduction also was evident in the surficial sediments of Lake Fryxell. Rates determined with ^{35}S were 0.3 μmol $SO_4^=$ (l sed)$^{-1}$ day^{-1} in the 0—2 cm interval, but decreased to undetectable activity below 8 cm (Howes & Smith 1990). As a comparison, methane production and sulfate reduction rates in surface sediments of temperate, freshwater lakes (i.e. low sulfate environments) were 580 μmol CH_4 (l sed)$^{-1}$ day^{-1} (Smith &

Klug 1987) and 100 μmol $SO_4^=$ (l sed)$^{-1}$ day^{-1} (Smith & Klug 1981) in hypereutrophic Wintergreen Lake (10 °C) and 10 μmol CH_4 (l sed)$^{-1}$ day^{-1} (Winfrey et al. 1977) and 100—500 μmol $SO_4^=$ (l sed)$^{-1}$ day^{-1} (Ingvorsen et al. 1981) in eutrophic Lake Mendota (3—12 °C). Obviously, the rates of these two processes are considerably lower in Lake Fryxell sediments. Franzmann et al. (1991) speculate that because there are no known psychrophilic methanogenic bacteria, temperature may be the most significant factor limiting methane production in cold environments. While this may be true, we note that in general the total heterotrophic activity in the deeper waters of Lake Fryxell (below 12 m) was very low and the adenylate energy charge of the whole microbial population was indicative of a physiologically stressed community (Smith & Howes 1990).

The shape of the methane depth profile in Lake Fryxell suggests that methane was being consumed in the anoxic bottom waters (Fig. 2). The profile has a distinct 'concave up' appearance, especially when compared to normalized concentration gradients of ammonium and DIC (Fig. 5) or

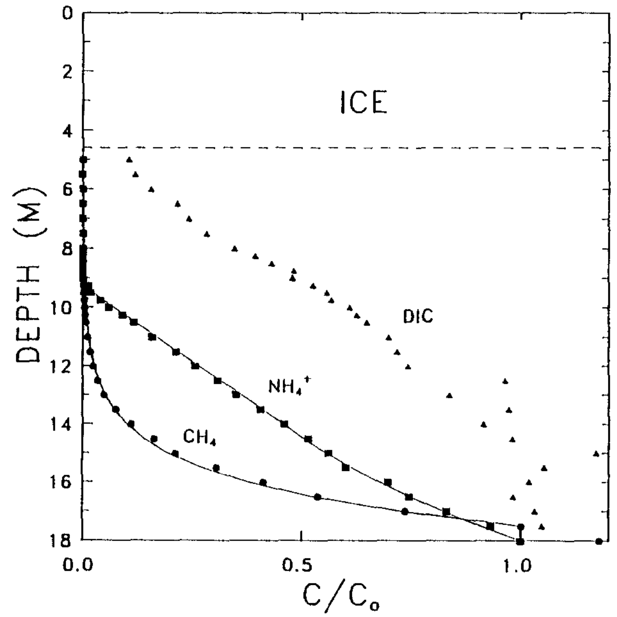

Fig. 5. Depth profiles in Lake Fryxell of methane, ammonium, and DIC concentrations in November 1989 normalized to their values (C_0) at 18 m for ammonium and DIC or 17.5 m for methane. Solid lines are model predictions using Fick's second law of diffusion and a first order reaction term. For methane, the model simulated a consumption term for the entire depth profile. For ammonium, the model simulated a first order consumption term for 14—18 m and simple diffusive flux for 9.25—14 m by assuming that $[NH_4^+] = 0$ at 9.25 m.

the nearly linear depth profile of DOC (Aiken et al. 1991). In sediments, where diffusive flux is also the dominant mechanism for solute movement, concave upwards profiles are considered to be indicative of methane consumption or anaerobic oxidation (Berner 1980; Iversen & Jörgensen 1985; Martens & Berner 1977; Reeburgh 1980). Since there is no measurable methane production occurring in the water column of Lake Fryxell, it seems likely that anaerobic methane oxidation was responsible for the shape of the CH_4 depth profile in the water column. The process is not necessarily restricted to sediments, having also been reported in other planktonic settings such as the sulfate-rich waters of Big Soda Lake, Nevada and in the Cariaco Basin (Iversen et al. 1987; Ward et al. 1987).

The anoxic consumption of methane has a significant effect upon the flux of methane in the water column of Lake Fryxell, especially when compared to the flux of other reduced species. Applying Fick's first law of diffusion (Lerman 1979) to the concentration gradients for methane and ammonium reveals that the flux of methane is twice the flux of ammonium just above the sediment-water interface (Table 3). However, 26 times more ammonium is diffusing upward across the oxycline (Table 3). Clearly, a much larger loss of methane relative to ammonium is occurring within the bottom waters. Assuming that the system is at steady state, no more than 1% of the methane leaving the sediments passes through the anoxic zone and is available for aerobic oxidation, while 67% of the ammonium diffusing from the sediments enters the oxycline. While it is possible that ammonium production was occurring within the water column, the nearly linear nature of the ammonium profile (Fig. 1a) and the

Table 3. Flux of methane and ammonium in the water column of Lake Fryxell. Calculated from concentration gradients measured in 1989.

Parameter	CH_4	NH_4^+
$D_{3\,^{\circ}C}$ (10^{-5} cm^2 sec^{-1})	0.88[a]	1.10[b]
Flux (mmol m^{-2} yr^{-1})		
9.75—9.5 m	0.1	2.6
18—17.5 m	8.0	3.9
First order rate constant for consumption or uptake (yr^{-1})		
10—18 m	0.012	—
14—18 m	—	0.001

[a] Lerman 1977.
[b] Li & Gregory 1974.

low rates of heterotrophic activity in the bottom waters (Smith & Howes 1990) would suggest that the sediments are the predominant source of ammonium.

The methane profile in Lake Fryxell could be modelled by applying a first order reaction term for methane consumption to Fick's second law of diffusion. Assuming steady state conditions, then:

$$D(\partial^2 c/\partial z^2) - kc = 0 \tag{2}$$

where D is the molecular diffusion coefficient of the solute, c is the concentration of the solute, z is the distance above the diffusion plane, and k is the first order rate constant for the consumption reaction. For a boundary condition where c_0 is a constant, equation 2 can be solved (Lerman 1979) as:

$$c = c_0 \exp(-z(k/D)^{\frac{1}{2}}). \tag{3}$$

Using the methane concentration at 17.5 m as c_0 and the value listed in Table 3 for D, the shape of the methane profile could be simulated for the 10—17.5 m interval when $k = 0.012\ yr^{-1}$ (Fig. 5). The good agreement between the measured and the calculated values suggests that anoxic methane consumption was occurring throughout the whole depth interval and was not localized to a specific zone. Significantly, this interval was also characterized by a steep gradient in sulfate concentration (Fig. 1b). Sulfate reduction is often considered to be the electron-accepting process responsible for anaerobic methane oxidation (Iversen et al. 1987), although apparently anaerobic methane consumption in Lake Fryxell was unaffected when sulfate concentrations ranged from 0.1—1.8 mM. Unlike methane, the diffusion-consumption model only fit the ammonium profile for the 14—18 m interval (Fig. 5) and only needed a very low rate constant to do so, 0.001 yr^{-1} (Table 3). Above 14 m the ammonium profile was linear, suggesting that ammonium consumption (or removal) in the water column was localized to the deepest portion of the lake and near the oxycline.

Using the above rate constant and the water column methane values, the calculated rates of anaerobic methane consumption in Lake Fryxell range from 9.52 $\mu M\ yr^{-1}$ at 17.5 m to 0.04 $\mu M\ yr^{-1}$ at 10 m. Ignoring the small amount of methane lost to aerobic oxidation, this corresponds to a turnover time of 83 years for the c_0 methane pool. Martens & Berner (1977) successfully applied a diagenetic model with a first order consumption term to predict methane profiles in Long Island Sound sediments. In that case the rate constant for methane consumption was 20-fold greater at 0.24 yr^{-1}. Other studies using ^{14}C have demonstrated that the consumption mechanism is an oxidation to CO_2 and that the process is first order within the range of environmental methane concentrations (Iversen et al. 1987; Ward et al. 1987). In alkaline Big Soda Lake the oxidation rate in the water column of the monimolimnion was 18 μM yr^{-1} with a rate constant of 0.3 yr^{-1} (Iversen et al. 1987), whereas in the anoxic water column of the Black Sea, methane oxidation was 0.6 μM yr^{-1} (Reeburgh et al. 1991) and in the deep, cold, anoxic water of the Cariaco Basin the rate was 0.15 μM yr^{-1} with a rate constant very similar to that of Lake Fryxell, 0.015 yr^{-1} (Ward et al. 1987). The higher rates of consumption in Fryxell are due to the very high methane concentrations.

It seems unusual for an enzymatically-catalyzed process to be first order at substrate concentrations as high as 1000 μM (Fig. 2). In addition, methane oxidation (both aerobic and anaerobic) is usually associated with an enrichment of ^{13}C in the remaining methane pool (Alperin et al. 1988; Coleman et al. 1981; Oremland & DesMarais 1983). While there was an isotopic fractionation ($\sim$15 ‰) associated with aerobic methane oxidation in Lake Fryxell, there was no ^{13}C-enrichment of the methane carbon associated with anaerobic consumption (Fig. 3). The exact mechanism for anaerobic consumption in Lake Fryxell is unknown, but there are several potential hypotheses. First, is the notion that the first reaction step could be a non-enzymatic equilibrium reaction, the product of which is subsequently utilized (enzymatically) by microorganisms. This mechanism would account for the first order nature of the reaction at high methane concentrations and the absence of an isotopic enrichment of ^{13}C methane. Second, physical removal of methane either by stripping during bubble ebullition or sorption onto particles could also produce the same result. However, there was no evidence that either process was occurring and no appearance within some other region of the water column of the large amounts of methane that would have to be removed. Third, there could be unknown mixing processes that were operating on a time scale similar to the methane residence time that were adding very light sediment methane from shallower depths to the water column of the lake, but there is no evidence of these processes in the profiles of other constituents, such as chloride, sulfate, DOC, DIC, $H_2{}^{18}O$ (Figs. 1, 5; Aiken et al. 1991; LG Miller, unpublished data). Direct measurement of methane oxidation rates in the water column and the sediments of Lake Fryxell and stable isotope measurements for sediment methane are needed to help interpret these results.

The $\delta^{13}C$ methane values in the lower water column actually decreased as methane diffused upwards from −72 ‰ at 18 m to −76 ‰ at 12 m (Fig. 3). This trend could result from either the production of lighter methane in the water column or the differential diffusion of $^{12}CH_4$ and

$^{13}CH_4$. The linear shape of the $\delta^{13}CH_4$ profile between 12 and 18 m suggests that diffusion is the more likely fractionation mechanism, though it has not been clearly demonstrated whether diffusion of methane in water results in an isotopic fractionation (Alperin et al. 1988). This phenomenon could be sufficiently important such that inclusion in diagenetic models for methane flux and consumption would be necessary.

In addition to nearly linear depth profiles for ammonium and DIC, the DOC depth profile in Lake Fryxell was essentially linear (Aiken et al. 1991) and the chemical nature of the dissolved fulvic acids (the major constituent of the DOC pool) were very similar for samples collected from several different depths (Aiken et al. 1991; McKnight et al. 1991). Based on these results and considering the stability of the water column, Aiken et al. (1991) concluded that the sediments were the major source of DOC in the lake and that the more refractory DOC components diffused into and through the water column. While DOC values in the bottom waters of Lake Fryxell are high when compared to most temperate bodies of water, on the same basis, methane concentrations are very high. The net result is that methane carbon is a significant fraction of the total DOC + CH_4 carbon at 18 m (Table 1). [Note: DOC here is an operationally defined parameter; methane and other volatile organics are not included in the DOC determination.] Thus, on a total mass basis, methane is an important aspect of the flux of dissolved organic material from the sediments into the water column. Also, considering that most of the DOC is refractory (Aiken 1991) while all of the methane entering the water column is consumed, methane is an important link between microbial metabolism in the sediments and microbial metabolism in the anoxic portion of the water column.

Summary and conclusions

As a result of its physical environment, Lake Fryxell represents a closed aquatic ecosystem, or a system in which the major biogeochemical cycles are predominantly controlled by internal processes, and a system in which organic material is microbial in origin. In addition, the salinity gradient in the water column, and the resulting amixis, differentiates the lake into several distinct, stable zones on a vertical axis. Significant concentrations of methane were found in the bottom waters of the lake and it appears that methane is an important aspect of the diffusional flux of dissolved organic material between the sediments and the overlying waters. However, unlike the bulk DOC, which is recalcitrant, methane is utilized in the water column by anaerobic microbial processes, to the extent that very little methane actually reaches oxygenated water, and none escapes from the lake. The consumption of methane in the anaerobic zone can be modeled with a first order reaction term; a turnover time of 83 years was calculated for the methane pool at 17.5 m. Interestingly, the process responsible for the anoxic methane consumption does not result in an isotopic fractionation of the methane carbon, although fractionation did occur for the small amount of methane that was oxidized aerobically.

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