

Seasonal water-column dynamics of dissolved inorganic carbon stable isotopic compositions ($\delta^{13}\text{C}_{\text{DIC}}$) in small hardwater lakes in Minnesota and Montana

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Abstract

The carbon stable isotopic value of dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{DIC}}$) was measured over several years at different depths in the water column in six carbonate-precipitating temperate lakes. $\delta^{13}\text{C}_{\text{DIC}}$ behavior in three of these lakes departed from the conventional model wherein epilimnetic waters are seasonally enriched relative to all hypolimnetic waters, and in general $\delta^{13}\text{C}_{\text{DIC}}$ values in the water column were not readily correlated to parameters such as lake stratification, algal productivity, hydraulic residence time, or water chemistry. Additionally, the processes implicated in generating the $\delta^{13}\text{C}_{\text{DIC}}$ values of individual lakes differ between lakes with similar $\delta^{13}\text{C}_{\text{DIC}}$ compositions. Each lake thus initially appears idiosyncratic, but when the effects of carbonate mineral equilibria, microbial activity, and lake residence time are viewed in terms of the magnitude of distinct DIC pools and fluxes in stratified lakes, generalizations can be made that allow lakes to be grouped by $\delta^{13}\text{C}_{\text{DIC}}$ behavior. We recognize three modes in the relationship between $\delta^{13}\text{C}_{\text{DIC}}$ values and DIC concentration ([DIC]) of individual lakes: (A) $\delta^{13}\text{C}_{\text{DIC}}$ values decreasing with increasing [DIC]; (B) $\delta^{13}\text{C}_{\text{DIC}}$ values increasing with increasing [DIC]; (C) $\delta^{13}\text{C}_{\text{DIC}}$ values decreasing with increasing [DIC] but increasing again at the highest [DIC]. This approach is useful both in understanding $\delta^{13}\text{C}_{\text{DIC}}$ dynamics in modern hardwater lakes and in reconstructing the environmental changes recorded by sedimentary $\delta^{13}\text{C}$ components in the lacustrine paleorecord.

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1. Introduction

Stable isotopic values of carbon ($\delta^{13}\text{C}$) in carbonate minerals and sedimentary organic matter have long been used as proxies for paleoproductivity and carbon sequestration in the marine realm. In lakes carbon isotopes track the same processes (Oana and Deevey, 1960; McKenzie, 1985; Quay et al., 1986; Ito, 2001; Meyers and Teranes, 2001), but the interpretation of $\delta^{13}\text{C}$ data from lacustrine paleorecords is complicated by temporal and spatial variability in ionic chemistry and stratification of the water column, disequilibrium between dissolved gases and the atmosphere, and heterogeneous watershed inputs. There remains an incomplete understanding of how these com-

plex lake–landscape interactions generate the $\delta^{13}\text{C}_{\text{DIC}}$ compositions of individual lakes, and consequently the $\delta^{13}\text{C}$ of lacustrine organic matter and carbonate minerals. Both paleorecord interpretation and inter-lake comparison are thus problematic.

Dissolved inorganic carbon in lakes ($\text{DIC} \equiv \text{H}_2\text{CO}_3^\circ + \text{HCO}_3^- + \text{CO}_3^{2-}$) is derived from various sources, including atmospheric CO_2 , the oxidized derivatives of carbon compounds from microbial mineralization of autochthonous and allochthonous organic matter, and geologically derived carbon from the watershed delivered by runoff and groundwater inflow (Striegl et al., 2001; see Bade et al., 2004 for a thorough review). Carbon cycling through each of these linkages involves equilibrium and kinetic fractionation of carbon isotopes (Romanek et al., 1992; Zhang et al., 1995). Preferential photosynthetic uptake of ^{12}C increases epilimnetic stable isotopic values of DIC ($\delta^{13}\text{C}_{\text{DIC}}$), and decomposition of sinking organic

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matter decreases hypolimnetic $\delta^{13}\text{C}_{\text{DIC}}$ values; these processes are recognized as major controls on water-column $\delta^{13}\text{C}_{\text{DIC}}$. However, the sensitivity of $\delta^{13}\text{C}_{\text{DIC}}$ values to environmental change, the directions of trends, and the relationship of $\delta^{13}\text{C}$ to other paleoenvironmental records depend on lake and watershed dynamics that vary greatly across the hydroscape.

We suggest that the factors dominating $\delta^{13}\text{C}_{\text{DIC}}$ values in hardwater lakes are the size of the DIC pool relative to lake carbon fluxes, lake P_{CO_2} relative to the atmosphere, and lake stratification and circulation. In contrast to the recent surveys of lake $\delta^{13}\text{C}_{\text{DIC}}$ by Striegl et al. (2001) and Bade et al. (2004), this paper focuses on lake types that produce authigenic carbonate sedimentary records (Kelts and Hsü, 1978). We expected that, due to carbonate mineral–DIC interactions (dissolution of carbonates from the catchment and precipitation/dissolution of carbonates in the water column), $\delta^{13}\text{C}_{\text{DIC}}$ values in our lakes would be generally enriched relative to those in softwater lakes, and indeed epilimnetic $\delta^{13}\text{C}_{\text{DIC}}$ values range from -7.3‰ to $+2.4\text{‰}$ over a pH range of 7.0–9.8 (cf. Fig. 4a in Bade et al., 2004). Because in-lake processes are important determinants of $\delta^{13}\text{C}_{\text{DIC}}$ values, we examine water-column structure in $\delta^{13}\text{C}_{\text{DIC}}$ composition under seasonally varying conditions of lake stratification, atmospheric exchange, and carbonate mineral saturation over several years. These results help to define the compositional behavior of DIC in small lakes and highlight the scope and uncertainty of inferences that may be drawn from endogenic $\delta^{13}\text{C}_{\text{CaCO}_3}$ paleorecords. Our goal in presenting these results is to underscore carbon cycling processes and modern $\delta^{13}\text{C}_{\text{DIC}}$ sensitivities across a class of lake types often used for paleolimnologic analysis, providing a refined structure for interpretation of changes in $\delta^{13}\text{C}_{\text{DIC}}$ values over time as recorded in lake sediments.

1.1. Site descriptions

Our analysis is based on six field sites: three lakes in east-central Minnesota and three in western Montana, USA (Fig. 1; see Table 1 for lake basin and geochemical characteristics). These mesotrophic and eutrophic lakes represent much of the salinity range of small hardwater lakes in the mid-latitude continental interior of the United States (cf. Gorham et al., 1983).

1.1.1. Minnesota setting

The group of Minnesota lakes are all moderately alkaline, productive calcium-bicarbonate systems. All three are within the range of 150–300 ppm in surface water TDS. Lake McCarrons is located in a highly urban area, whereas Green Lake and Spectacle Lake are rural or suburban. All three lakes are surrounded by year-round residential dwellings and heavily used for recreational purposes such as swimming, boating, and fishing. Regional precipitation is approximately equal to evaporation (Winter, 1990).

Green Lake and Spectacle Lake lie 1 km from each other in the northwest corner of the Anoka Sandplain of east-central Minnesota. Surficial geology is a mix of glacial outwash sand in contact with mixed carbonate-rich (Des Moines lobe) and carbonate-poor (Superior lobe) tills (Wright, 1972), with abundant wetlands in the vicinity of the lakes (Fig. 1). Spectacle Lake is the smaller, deeper, and less productive of the two, with

a shallow macrophyte-dominated eastern basin that comprises about one third of the lake area. The lake is dimictic and groundwater supported, and has neither a surface inlet nor outlet. Eutrophic Green Lake is phytoplankton dominated, with four small surface inlets and one outlet as well as groundwater in- and outflow. Its large surface area and relatively shallow depth allow mixing to within $\sim 1\text{--}2$ m of the lake bottom by early summer, although a cool and geochemically distinct hypolimnion always persists.

Lake McCarrons is also situated in mixed glacial material, in one of the many till- and outwash-filled pre-Holocene paleochannels of the Mississippi River underlying the Minneapolis–St. Paul area (Wright, 1972, p. 537). It is the smallest and deepest of the three Minnesota lakes, and is phytoplankton dominated, with limited areas of macrophyte beds. The inlet flows through a series of detention ponds built in the mid-1980s to reduce nutrient loading and reverse eutrophication, and there is an intermittent tiled outlet, as well as groundwater in- and outflow. Heavy hypolimnetic solute loading (450 ppm with regionally anomalous high values (cf. Gorham et al., 1983) of Cl^- , Na^+ , and Ca^{2+}) from road salt appears to cause incomplete overturn in some years. Hydrogen sulfide odor in deep water samples indicates that sulfate reduction is occurring in the anoxic hypolimnion.

1.1.2. Montana setting

The three Montana lakes described here are located in the Ovando Valley, within the Blackfoot River basin of west-central Montana (Fig. 1). The Ovando Valley is a structural basin of the Northern Rocky Mountains that was occupied by late Pleistocene alpine valley glaciers draining calcareous bedrock (Dea, 1981). Glacial wasting left a poorly integrated drainage system with abundant topographically closed lakes and wetlands. Mean annual evaporation exceeds precipitation by nearly 2-fold.

Jones Lake, Evans Lake, and Lahrity Lake define a wide local geochemical gradient related primarily to hydrogeologic setting and rates of groundwater outflow, which govern solute export and accumulation (Shapley et al., 2005). Jones Lake experiences abundant groundwater outflow, moderating solute accumulation and isotopic evolution. Lake chemistry is slightly alkaline but dilute (<500 ppm dissolved solids) and only moderately evolved (toward higher Mg:Ca ratio) from the calcium-bicarbonate groundwater source by calcium carbonate precipitation. Jones Lake is mesotrophic and supports locally abundant macrophytes and planktonic algae. Outflow from Evans Lake is much more restricted; the lake is alkaline, brackish (ca 10,000 ppm dissolved solids) and strongly evolved toward higher Mg:Ca from inflow compositions; macrophytes are rare, and phytoplankton dominate lake production. Microbial communities include abundant sulfate-reducing and sulfide-oxidizing bacteria evident in the hypolimnion under stratified conditions. Lahrity Lake is more restricted still in groundwater outflow, and is evolved to a saline sodium sulfate chemistry (ca. 30–40,000 ppm dissolved solids) from dilute calcium-bicarbonate source groundwater. Mat-forming microbial communities believed to consist of sulfur metabolizing species are prominent, along with planktonic sulfate-reducing and sulfide-oxidizing bacteria.

2. Methods

2.1. Field data collection

2.1.1. Lake sampling

Sampling depths were chosen based on structure of thermal profiles in all lakes. Samples were taken every 2–4 weeks during the ice-free season (April–October) in Minnesota and approximately quarterly (with higher frequency in summer) in Montana. Montana lakes were sampled in the epilimnion (at 1 m depth below the air–water interface) and in the hypolimnion (3 m in Lahrity Lake, 7 m in Evans Lake, and 11 m in Jones Lake). Minnesota lakes were sampled in the epilimnion (at 2 m below the air–water interface) and at one or two points in the hypolimnion: in relatively shallow Green Lake, which has a thin hypolimnion, only one hypolimnetic sample was taken, about 1 m from the sediment–water interface; in deeper Spectacle Lake and Lake McCarrons, one sample was

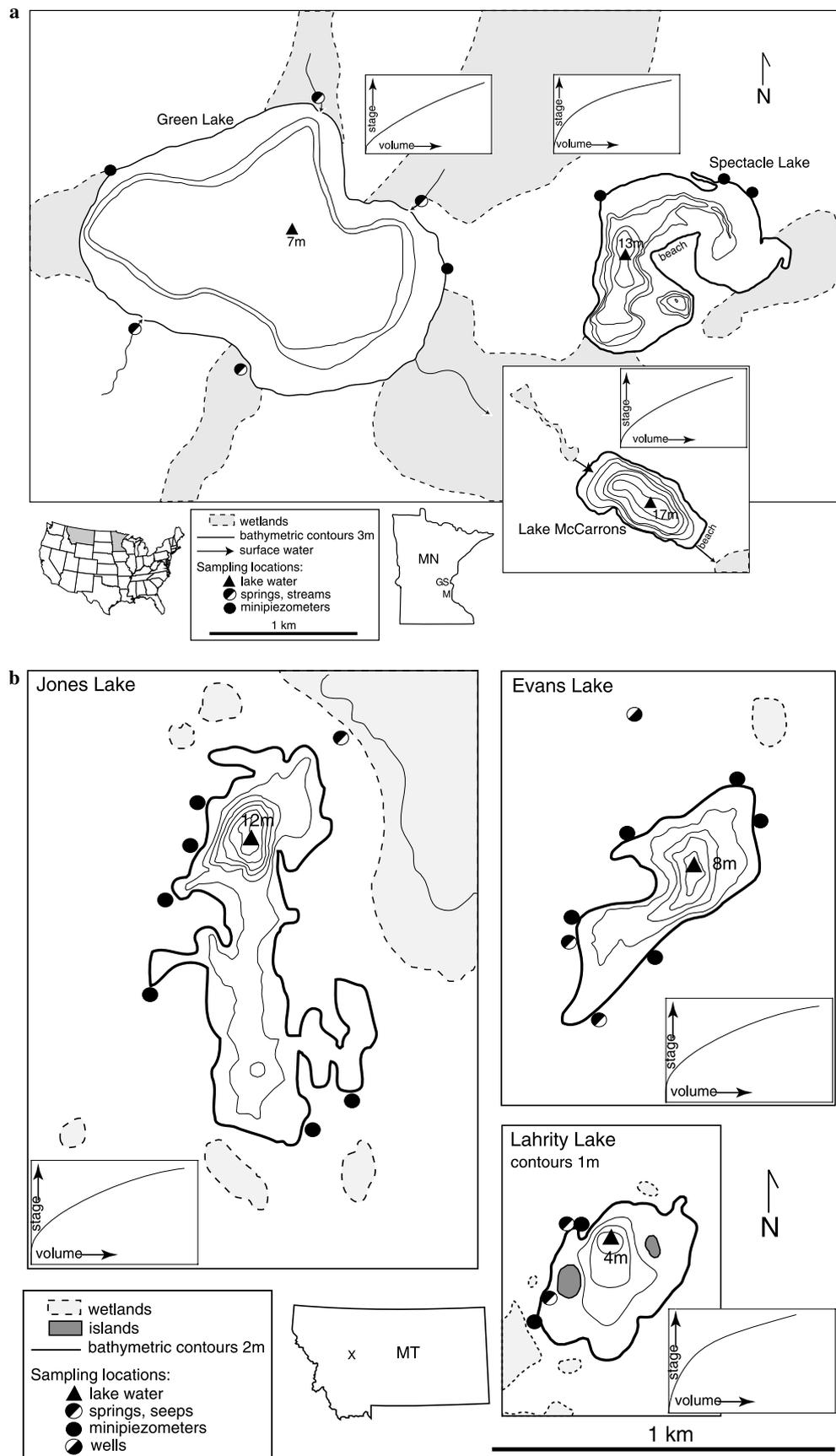


Fig. 1. Location and bathymetric maps of field sites. Hypsometric curve (inset) shows change in lake volume with changing depth for each lake. The origin is 0 in both axes. (a) Minnesota lakes; (b) Montana lakes.

Table 1
Morphometric and limnological characteristics of lakes described in this study

	Minnesota			Montana		
	Spectacle	Green	McCarrons	Jones	Evans	Lahrity
Latitude (°N)	45.57	45.57	45.00	47.04	47.00	47.02
Longitude (°W)	93.41	93.44	93.11	113.14	113.07	113.18
Surface area (ha)	95	325	33	27	26	13
Maximum depth (m)	14	8.5	17.5	13	9	4
Mean depth (m)	3.9	5.2	6.6	2.5	3.0	1.5
Area:maximum depth	7	38	2	2	3	3
Area:mean depth	24	63	5	11	9	9
Water residence time (years)	5	1	2	1	10	No data
Mixing regime	Dimictic	Di/polymictic	Di/oligomictic	Dimictic	Variable; recently dimictic	Irregular
TDS, epilimnetic (ppm)	100–150	200–300	200–300	<500	9500–12,000	24,000–50,000
TDS, hypolimnetic (ppm)	100–200	200–300	400–450	<500	11,000–12,500	40,000–50,000
pH, epilimnetic	7.0–8.8	7.6–9.1	8.6–9.5	7.2–9.1	9.2–9.5	9.2–9.9
pH, hypolimnetic	6.8–8.0	7.1–8.8	7.1–8.0	6.6–7.6	8.8–9.4	7.5–9.5
TOC:TIC burial (recent range)	≥100	3.1	2.5–4.5	11–32	6–13	No data
TOC:TIC burial (prehistorical range)	2.0 to ≥100	0.6	0.9	4	7 to 11	
[DIC]-δ ¹³ C _{DIC} Mode	A	C	C	B	A	A

TOC, total organic carbon; TIC, total inorganic (carbonate) carbon. Burial ratio is calculated using dry mass percentages of these two components in sediment cores. “Recent range” corresponds to the uppermost sedimentary unit, deposited after European settlement (after ~1860 in Minnesota lakes and after ~1890 in Montana lakes). “Prehistorical range” includes the period prior to European settlement and extending back several thousand years in each lake. See Section 4 for explanation of [DIC]-δ¹³C_{DIC} modes.

taken about 1 m from the sediment–water interface and one was taken higher in the hypolimnion, below the base of the thermocline. The purpose of taking two hypolimnetic samples was to evaluate geochemical gradients within the hypolimnion. Profiles of δ¹³C_{DIC} values at 1 m intervals were also collected on one (Minnesota) or two (Montana) dates during the sampling period. In addition to temperature measurements, dissolved oxygen and pH were measured at most sample points throughout the study. Data on pH of Minnesota lakes are missing for a large part of the 4-year sampling period; these samples were therefore not included in the analysis of calculated P_{CO_2} .

Water was collected from the selected depths using a Van Dorn-type sampler or a peristaltic pump. Samples for DIC analysis were transferred to a flushed 60 mL plastic syringe and passed through a 0.45 μm membrane filter into a borosilicate glass serum vial. The sample bottle was flushed and overfilled, and capped with a teflon-coated neoprene seal and an aluminum crimp-cap. Samples were kept refrigerated and in the dark until extraction (within 1–2 weeks of sampling). Samples for major-ion analysis (one each for cations and anions) were filtered into LDPE sample vials.

2.1.1. Groundwater sampling

Groundwater associated with the Montana lakes was sampled using minipiezometer installations in littoral sediments (Winter et al., 1988), at water supply wells, and from springs. Groundwater sampling from minipiezometer installations followed water production by peristaltic pumping to “develop” the screened minipiezometer point and autocontaminate minipiezometer, and pump tubing surfaces. Production wells were sampled at the wellhead or at the most upstream available collection point following discharge of one or more casing volumes of water. Spring waters were directly sampled from the most upgradient point of groundwater discharge. Groundwater was sampled once in two Minnesota lakes by minipiezometer. Conductivity, pH, and redox potential were measured on these samples in the field; other sampling protocols were the same as for lake water samples.

2.2. Laboratory analyses

2.2.1. DIC extraction and δ¹³C analysis

CO₂ gas was generated from sample waters by direct acidification of a 1–4 ml sample with 0.3 ml 105% anhydrous H₃PO₄ (Graber and Aharon,

1991) in an offline extraction. Sample aliquots were injected by gas-tight syringe into evacuated vessels containing the H₃PO₄. Working standards of known δ¹³C value were extracted at least once every 10 samples as quality assurance. Extractions failing leak test protocols were repeated. δ¹³C values of DIC (as CO₂ gas) were measured at the Minnesota Stable Isotope Lab, University of Minnesota, on one of two instruments: a Finnegan-MAT Delta E multi-collector, dual inlet mass spectrometer, or a Finnegan-MAT 252, both with analytical precision of 0.2‰, reported relative to VPDB. Results for several different working standards used over the course of this study yield standard deviations of 0.10‰ or better. Our analysis of duplicate field sample extractions shows a mean difference (absolute value) of 0.12‰ (σ = 0.13‰; n = 28) between duplicate sample pairs, excluding a single Lahrity Lake sample with extremely high P_{CO_2} .

2.2.2. Ionic analyses

Following filtration, samples for cation analyses were stabilized with high purity HNO₃⁻ or HCl (pH < 2) in acid-washed bottles. All major-ion analyses were conducted at the Department of Geology and Geophysics, University of Minnesota. Cation analyses were performed by ICP-MS (Elmer/Sciex Elan 5000 and Thermo Elemental VG instruments) with precision of 2% or better. Anions were analyzed by ion chromatography on a Dionex instrument calibrated daily to five standard solutions per ion.

2.3. Data processing

2.3.1. Calculation and speciation of DIC

Dissolved inorganic carbon concentrations ([DIC]) were determined from CO₂ gas pressures generated during offline DIC extractions, calibrated to pressures from bracketing standards of known inorganic carbon mass. The regression is fitted to CO₂ extraction-line pressure results for aliquots of seven different known DIC masses within the range of our field compositions, with an $R^2 > 0.99$. For duplicated standard aliquots of a given carbon mass, standard deviations are less than 2% of mean values. Concentrations of DIC species (H₂CO₃[°], HCO₃⁻, and CO₃²⁻) were calculated from [DIC], field measurements of water temperature and pH, and temperature dependencies for the equilibrium constants K_{CO_2} , K_1 , and K_2 for the dissolved inorganic carbon system (Plummer and Busenberg, 1982). Values of apparent CO₂ pressure (P_{CO_2}) were calculated according to

$$P_{\text{CO}_2} = [\text{H}_2\text{CO}_3]/K_{\text{CO}_2}$$

with activity coefficients of H_2CO_3 (significantly different from unity only for two of the Montana lakes) calculated according to the 'salting out' coefficient of 0.231 determined by Millero (1983; summarized in Langmuir, 1997, p. 144) and temperature dependence of K_{CO_2} according to data in Langmuir (1997). Values of P_{CO_2} were then normalized to an approximate sea-level atmospheric CO_2 concentration over the period of our investigation of 370 ppm (Keeling and Whorf, 2004); atmospheric P_{CO_2} values at our field sites were adjusted for elevation (ca. 300 m in Minnesota; ca. 1200 m in the Ovando Valley) according to the relationship

$$p(z) \simeq p(0)e^{(-z/H)},$$

where z is the elevation of interest, $p(0)$ is the pressure at sea level, and H is the 'scale height' of the atmosphere, which translates algebraically to the elevation at which pressure drops by a factor of e , approximately 7000 m (Wallace and Hobbs, 1977). Values less than 1 represent undersaturation of water relative to atmospheric equilibrium, whereas values greater than 1 indicate excess dissolved CO_2 relative to atmospheric equilibrium.

2.3.2. Mineral equilibria

Mineral saturation states of lake waters were determined using field measurements of pH and temperature, analytical measurements of common ions, and extended Debye–Hückel equations (Langmuir, 1997). Mineral equilibria were calculated using the PHREEQC for Windows v.2.8 computer code (Parkhurst and Appelo, 1999). The high Mg:Ca ratio in Evans Lake leads to production of aragonite rather than calcite as the dominant authigenic carbonate mineral, so equilibrium results are reported in terms of aragonite saturation. In Lahrity Lake, high ionic strength invalidates the Debye–Hückel assumptions used in our analysis, and mineral equilibria are not presented. Lahrity Lake also produces aragonite as a dominant carbonate phase.

2.3.3. Lake volumes, solute mass, and residence time

Minnesota lake volumes are based on published contour mapping of lake bathymetry (Minnesota Department of Natural Resources). Digitized contours were interpolated using the software package Surfer™ and volumes were calculated from the resulting xyz grid. No depth data were available for the Montana lakes prior to this study; gridded xyz models were therefore interpolated from acoustic profiles of the sediment–water interface collected along numerous lake transects (Shapley et al., 2005). Montana lake volumes, which varied considerably (more than 2-fold in Jones Lake) over the period of study, were monitored by fixed lake-level staff gauges. Estimates of DIC mass were calculated from seasonally varying lake volume, thermocline/chemocline depth and epilimnetic and hypolimnetic DIC concentrations. Residence times for Minnesota lakes were calculated using the aforementioned volume calculations and a combination of calculated (Krabbenhoft et al., 1990), measured, and literature groundwater and surface water inflow values. Residence time calculations for Montana lakes are based on solute mass balance keyed to field measurements of groundwater inflow composition (Shapley, 2005).

3. Results

3.1. Groundwater and surface water sources of DIC

3.1.1. Minnesota lakes

Source water entering Green Lake and Spectacle Lake is consistently lower in $\delta^{13}\text{C}$ than lake water is at any time. (Lake McCarrons source water was not sampled.) Surface inflows to Green Lake range from about -7‰ to -12‰ , and the two groundwater samples are lower (-11.7‰ and -12.4‰). Groundwater values are similar for Spectacle Lake (-12.2‰ and -13.1‰), with the

exception of one sample, which had a value of $+2.3\text{‰}$, considerably more enriched than any other sample from the Minnesota sites. This site also had the highest conductivity and total phosphorus, and the most negative redox potential of any sample, indicating the probable presence of local septic system contamination. Source water [DIC] ranges from about $2\text{--}5\text{ mmol l}^{-1}$, higher than any values measured in the lake water, but calculated P_{CO_2} is within the range of lake water samples, ranging from about $175\text{--}2840\text{ }\mu\text{atm}$, about $5\text{--}80$ times above atmospheric equilibrium.

3.1.2. Montana lakes

Shallow groundwater $\delta^{13}\text{C}$ compositions are similar among Montana sites. Evans Lake minipiezometer samples range in $\delta^{13}\text{C}$ value from -9.7‰ to -13.4‰ and average -11.7‰ ($n = 15$). Samples from shallow groundwater associated with Jones Lake average -13.1‰ (-10.6‰ to -18.6‰ ; $n = 12$). Samples collected around Lahrity Lake average -13.4‰ (-10.7‰ to -15.6‰ ; $n = 4$). Values of a perennial spring fed by shallow groundwater near Lahrity Lake average -12.8‰ (-10.8‰ to -14.4‰ ; $n = 8$). Average minipiezometer DIC concentrations are somewhat higher around Evans Lake (8.0 mmol l^{-1}) and Lahrity Lake (8.4 mmol l^{-1}) than around Jones Lake (5.1 mmol l^{-1}). The Lahrity Lake spring values average 4.3 mmol l^{-1} with little variation observed. Calculated P_{CO_2} of shallow groundwater is typically in the range of 350 to $>3550\text{ }\mu\text{atm}$, or about 10- to more than 100-fold above atmospheric equilibrium.

3.2. Vertical structure and seasonal reallocation of DIC

3.2.1. Minnesota lakes

In all cases, DIC concentration generally increases with depth in the water column, and is higher in the hypolimnion than in the epilimnion in each lake (Fig. 2a). Well-stratified Spectacle and McCarrons lakes build up strong gradients in [DIC] from surface to deep waters, while Green Lake polymixis produces a more uniform water column. Whole-lake, epilimnetic, and hypolimnetic DIC inventories (Fig. 3a, lower plot in each lake) show large seasonal variations and an overall decrease in total mass of DIC in each lake over the course of the summer as photosynthetic carbon uptake outpaces respiration. The smaller Spectacle Lake pool shows this decrease most clearly; the large Green Lake pool shows a less monotonic decrease over the summer due to mixing and ventilation of deep waters. In Lake McCarrons, the size of the DIC pool in the persistent hypolimnion, which is not seasonally homogenized with the epilimnion by overturn, is comparable in size to the epilimnetic pool (unlike all of the other lakes in the study, where hypolimnetic DIC mass is small relative to epilimnetic), so the total lake DIC inventory shows a relatively small response to summer photosynthesis.

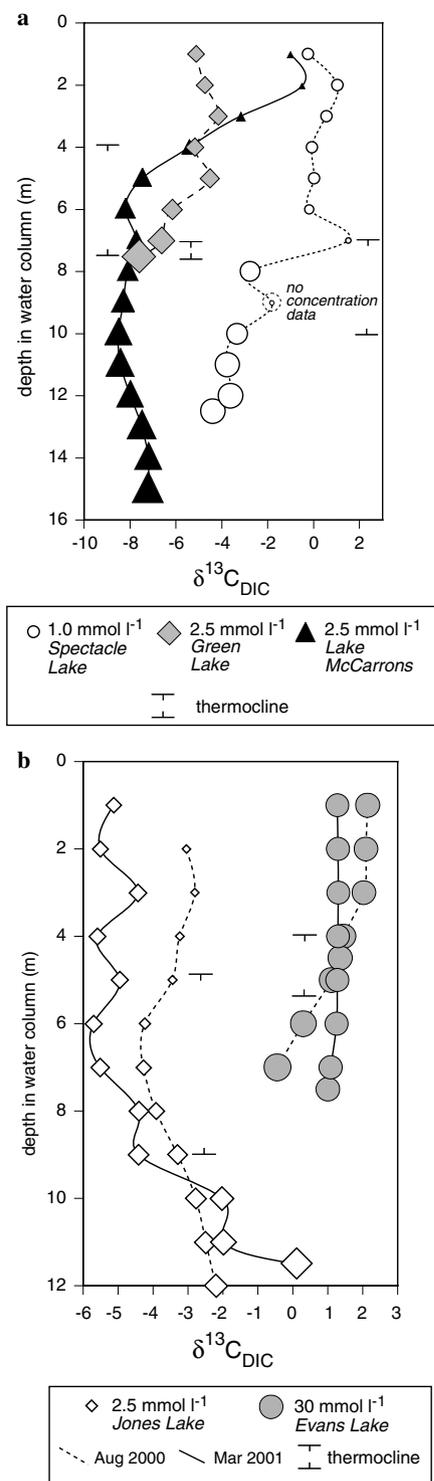


Fig. 2. Depth profiles of $\delta^{13}C_{DIC}$. Symbol sizes are linearly proportional to DIC concentration ([DIC]) for each lake profile. Symbol sizes are not proportional between lakes because of the large differences in [DIC] between lakes. Minnesota lake data are for August 2000 and March 2001. (a) Minnesota data, showing decreasing $\delta^{13}C_{DIC}$ values with depth and with [DIC]. Prominent Spectacle maximum in $\delta^{13}C_{DIC}$ occurs at the base of the mixed layer. (b) Montana data, showing increasing $\delta^{13}C_{DIC}$ values with depth and [DIC] in Jones Lake under stratified conditions. High Evans Lake alkalinity masks the water-column [DIC] gradient and subdues seasonal differences in $\delta^{13}C_{DIC}$. Lahrity Lake profile data not available.

3.2.2. Montana lakes

Stratified conditions lead to accumulation of DIC in hypolimnetic waters of Evans and Jones lakes (Fig. 2b). Average DIC concentrations in Evans Lake and in Lahrity Lake are elevated in the long term by evaporation of lake water and extended hydraulic residence time; groundwater outflow and short residence time prevents similar evaporative concentration in Jones Lake. In Jones Lake, hypolimnetic DIC includes a component derived from dissolution of epilimnetically formed calcite in the low-pH hypolimnion (Shapley et al., 2005). Estimates of seasonal redistribution of Jones Lake carbon mass (Fig. 3b) show whole-lake carbon masses were heavily influenced by irregular lake volume changes (reflecting water management activities surrounding the lake) and therefore reached maxima in the summer months of some years. In Evans Lake, with much higher DIC concentration and total DIC mass, summertime drawdown results in subdued summer minima in whole-lake DIC mass. Lahrity Lake patterns are incompletely defined but appear generally similar to those of Evans Lake, with whole-lake winter DIC maxima and summer minima underlain by a downward trend reflecting a sustained decline in lake volume.

3.3. $\delta^{13}C_{DIC}$ in lake water columns

3.3.1. Minnesota lakes

3.3.1.1. Profiles. All three lakes display a general trend of most enriched values near the lake surface and relatively depleted values in the bottom waters (Fig. 2a), due to photosynthetic export of ^{12}C from the epilimnion and its remineralization in the hypolimnion. However, none of the profiles are monotonic, nor are they identical to one another in their variations. Lake McCarrons shows a slight increase and then a general decline in $\delta^{13}C_{DIC}$ values down through the surface mixed layer and the upper metalimnion, a small reversal in the lower metalimnion, and then relatively constant values in the hypolimnion, with an increase of about 1‰ over the bottom several meters. Green Lake $\delta^{13}C_{DIC}$ values increase from 1 to 3 m, then fluctuate for a few meters before a monotonic decline over the bottom ~2 m. Spectacle Lake $\delta^{13}C_{DIC}$ values increase and are variable across the thermocline, then decline generally to the sediment surface. The sample or two nearest the surface in each lake has a lower $\delta^{13}C$ value than samples lower in the epilimnion, and epilimnetic values overall vary by 1‰ (Spectacle) to 5‰ (McCarrons). It is clear that the surface mixed layer is not isotopically mixed, at least not at the scale of measurement during a day of photosynthetic activity. Excursions in $\delta^{13}C_{DIC}$ such as the datapoint at 7 m in Spectacle Lake (Fig. 2a) may result from the activities of microbial and algal communities in narrow vertical zones in the water column (e.g., Fenchel et al., 1998, pp. 158–162).

3.3.1.2. Time series. There are large differences in patterns, variability, and typical $\delta^{13}C_{DIC}$ values among the three

lakes (Fig. 3a). Spectacle Lake has the most enriched $\delta^{13}\text{C}_{\text{DIC}}$ values in both epilimnetic ($\sim 0\text{‰}$) and hypolimnetic (-4‰) waters; Lake McCarrons values are the most depleted (-6‰ and -10‰ , respectively); Green Lake values are intermediate (-3‰ and -6‰ , respectively), and have higher amplitude variability than those of the other two lakes.

The three Minnesota lakes behave similarly with respect to divergence of epilimnetic from hypolimnetic $\delta^{13}\text{C}_{\text{DIC}}$ values over the course of the growing season (Fig. 3a; cf. the water column profiles above from the late summer). For the years when sampling began early enough to capture mixed conditions, surface- and deep-water values are similar or identical. As the growing sea-

son progresses, epilimnetic values increase while both upper- and lower-hypolimnetic values decrease. In Lake McCarrons, lower-hypolimnetic DIC then becomes progressively more ^{13}C enriched than upper-hypolimnetic DIC; hypolimnetic values in Green Lake $\delta^{13}\text{C}_{\text{DIC}}$ values also become more positive beginning in mid-summer. This trend in both lakes indicates the presence of a flux of ^{13}C -enriched DIC from near the sediment–water interface. At autumn turnover, epilimnetic and hypolimnetic $\delta^{13}\text{C}_{\text{DIC}}$ values reconverge as the lakes return to holomixis. DIC $\delta^{13}\text{C}$ compositions in Lake McCarrons converge only to within 2–4‰, possibly due to incomplete mixing. Samples taken in Lake McCarrons under isothermal ($\sim 4\text{ °C}$) conditions in late November 2003 show

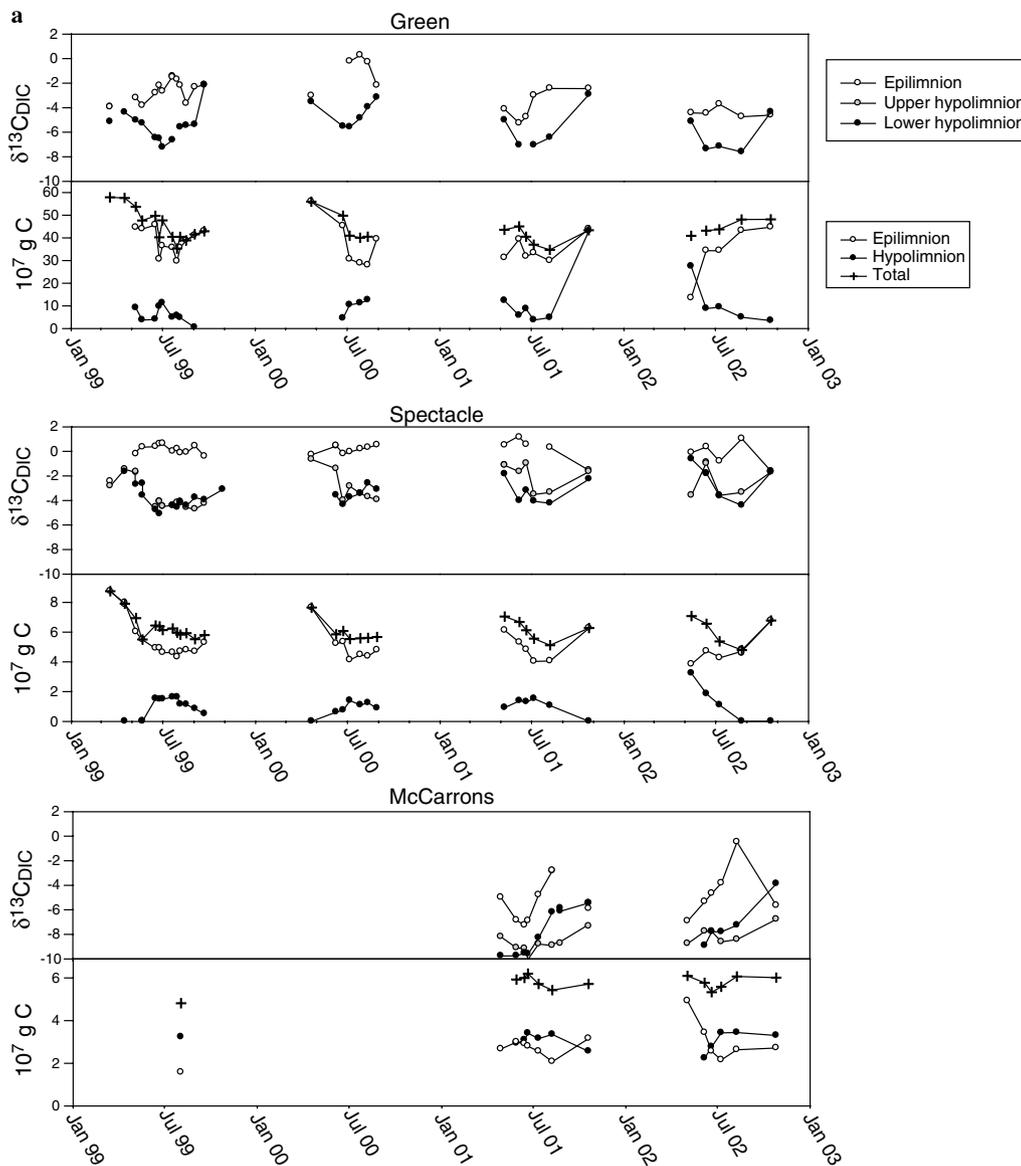


Fig. 3. Time series of $\delta^{13}\text{C}_{\text{DIC}}$ values and estimated seasonal redistribution of lake DIC inventory in grams of carbon. Carbon mass calculations are based on lake morphometric models and routinely measured DIC concentrations (see Section 2). (a) Minnesota data, showing seasonal decrease in epilimnetic carbon mass and increase in $\delta^{13}\text{C}_{\text{DIC}}$ reflecting organic matter export to the hypolimnion. (b) Montana data, showing similar seasonal relations in Evans Lake; Jones Lake trends are strongly influenced by large declines in whole-lake carbon inventory with declining lake volume in 2001.

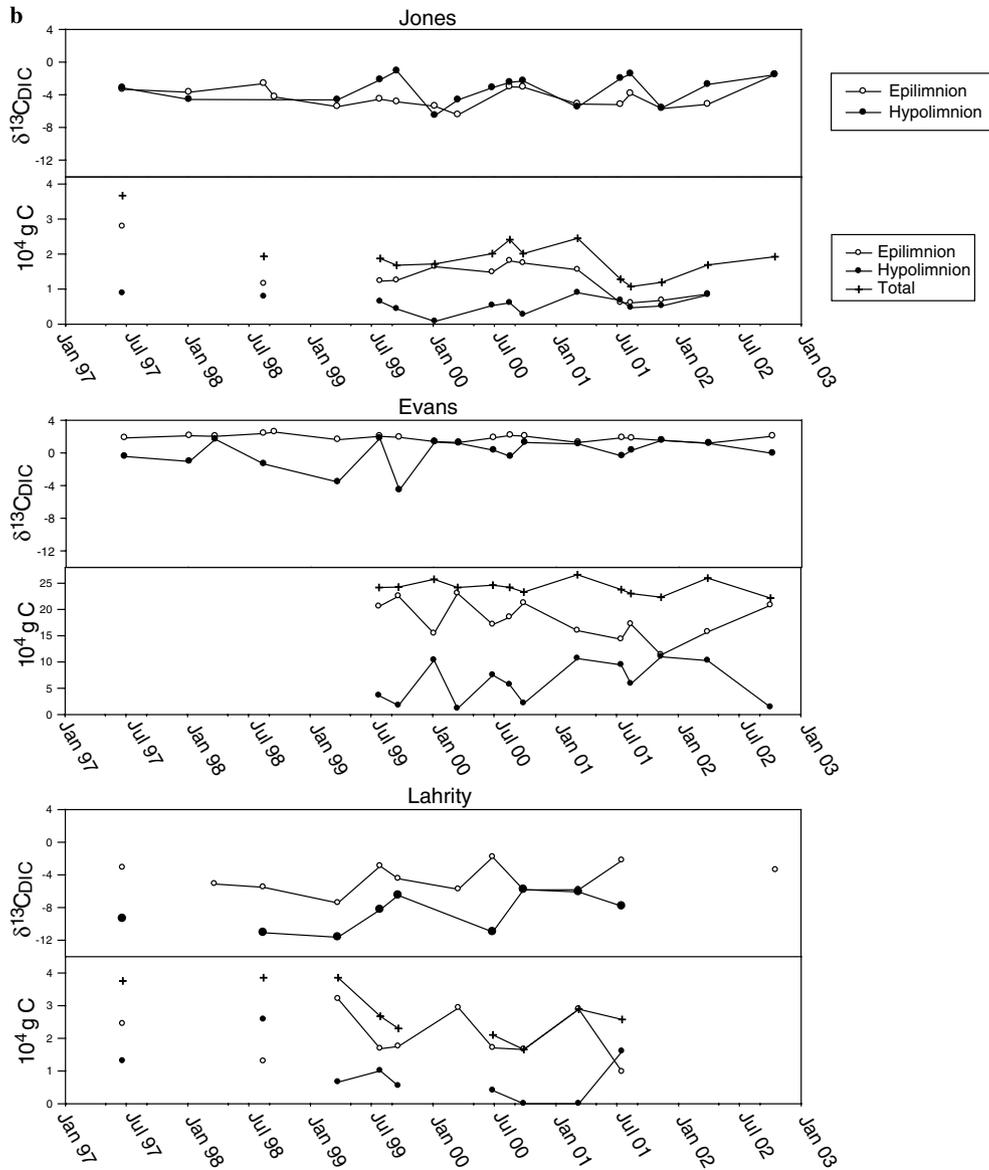


Fig 3. (continued)

variations of 0.7‰ over the water column (data not shown), suggesting that thermal and geochemical mixing are not synchronous, or that a persistent cold hypolimnetic water mass is not being homogenized with the remainder of the water column.

3.3.2. Montana lakes

3.3.2.1. Profiles. Under the summer conditions sampled, Jones Lake $\delta^{13}\text{C}_{\text{DIC}}$ values decline about 1.5‰ with depth through the epilimnion, then increase 2‰ through the hypolimnion to reach a maximum measured value near the sediment–water interface (Fig. 2b). Under winter (ice-covered) conditions, oscillating $\delta^{13}\text{C}_{\text{DIC}}$ values in the upper water column give way to a steeply increasing trend with increasing [DIC] in the lower 5 m of the profile. The inferred net lake-bottom flux of DIC to the water column was enriched in ^{13}C relative to whole-lake compositions

under both sets of seasonal conditions. Under summer conditions, an internal DIC source with a relatively low δ value produces a $\delta^{13}\text{C}_{\text{DIC}}$ minimum near the thermocline.

The Evans Lake DIC profile sampled under summer conditions decreased downward about 3‰ through the hypolimnion; the winter profile observed also decreased slightly near the sediment surface. Net lake-bottom fluxes of DIC to the water column were low in $\delta^{13}\text{C}_{\text{DIC}}$ relative to whole-lake compositions in both cases. The range of vertical variation in $\delta^{13}\text{C}_{\text{DIC}}$ values and [DIC] was subdued relative to Jones Lake and to the Minnesota lakes. Water-column $\delta^{13}\text{C}_{\text{DIC}}$ profiles are not available for Laherty Lake.

3.3.2.2. Time series. Jones Lake shows epilimnetic $\delta^{13}\text{C}_{\text{DIC}}$ values ranging over 4‰ with summer maxima of $-4‰$ to $-2.5‰$. Hypolimnetic $\delta^{13}\text{C}_{\text{DIC}}$ values tend to parallel the

epilimnetic curve (Fig. 3b). Evans Lake shows mean epilimnetic $\delta^{13}\text{C}_{\text{DIC}}$ values around $+1.7\text{‰}$, with seasonal epilimnetic cycling on the order of 1‰ and a summer maximum. The Evans Lake hypolimnion shows an opposing and greater amplitude (around 1.5‰) seasonal cycle. From 1997 to 2000, hypolimnetic $\delta^{13}\text{C}_{\text{DIC}}$ values were apparently becoming progressively lower.

Sparse time series data for Lahrity Lake show epilimnetic compositions ranging approximately 5.5‰ , with summer maxima of -3‰ to -2‰ . Samples taken at 3 m, often collected from a thin hypolimnion, show a range of about 6‰ , mean composition near -9‰ and an irregular seasonal signature. An apparent trend to more negative $\delta^{13}\text{C}_{\text{DIC}}$ values in both shallow and deep samples from 1997 to early 1999 corresponded with a period of relatively persistent meromixis.

3.4. Mineral saturation

3.4.1. Minnesota lakes

Green Lake is above saturation with respect to calcite at all depths, and abundant calcite is preserved in the sediments (Table 2), in spite of high P_{CO_2} derived from remineralization of organic matter. Spectacle Lake and Lake McCarrons are above saturation in the epilimnion and undersaturated in the hypolimnion. In Spectacle Lake, a small amount of calcite forms in the epilimnion but dissolves in hypolimnetic waters. McCarrons deep waters are corrosive to calcite for part of the year but cross the 0 saturation index line by mid-summer, and calcite is preserved in the sediments. Ca^{2+} is enriched in the hypolimnion relative to the epilimnion, suggesting either hypolimnetic calcite dissolution or road salt contamination; a calculation based on the concomitant enrichment in Cl^- and Na^+ suggests that at about 50% of the excess hypolimnetic Ca^{2+} comes from CaCl_2 road salt.

Table 2

Saturation state with respect to the favored carbonate phase (calcite for all but Evans Lake, which precipitates aragonite) for selected water sampling dates

Lake	Epilimnion	Upper hypolimnion	lower-hypolimnion
Spectacle, July	0.22	-0.70	-0.79
Green, July	0.93		0.11
McCarrons, June	0.73	-0.77	-0.77
McCarrons, August	0.80	0.16	0.05
Jones, March	-0.90		-0.89
Jones, June	0.69		-1.15
Evans, March	0.54		0.64
Evans, June	0.74		0.50

Lahrity Lake in Montana is not included because its high salinity precludes use of the extended Debye-Hückel equation; however, the lake actively precipitates large quantities of aragonite. Note that Jones, Spectacle, and McCarrons hypolimnia are at times below carbonate saturation; these waters are corrosive to authigenic carbonates.

3.4.2. Montana lakes

Evans Lake is always near or above saturation with aragonite in both the epilimnion and hypolimnion (Table 2). Strong stratification and high P_{CO_2} drive hypolimnetic pH down but never below 8. Jones Lake epilimnion is above saturation at low (photosynthetically depressed) P_{CO_2} but may drop below saturation under winter conditions (closed-system respiration). The Jones Lake hypolimnion is typically below saturation; nevertheless some calcite is preserved in modern sediments.

3.5. CO_2 partial pressure

3.5.1. Minnesota lakes

Epilimnetic samples from Green and Spectacle lakes are often below equilibrium with atmospheric P_{CO_2} (assumed $350\ \mu\text{atm}$), and Lake McCarrons epilimnetic samples are always below equilibrium (Fig. 4a). Hypolimnetic waters in all three lakes are almost always above atmospheric P_{CO_2} , as are a few epilimnetic samples from Green and Spectacle lakes with relatively low pH. Hypolimnetic and epilimnetic P_{CO_2} ranges in Green Lake overlap due to wind-driven vertical advection.

3.5.2. Montana lakes

Evans Lake (high alkalinity and high pH) is always above equilibrium with atmospheric P_{CO_2} throughout the water column (Fig. 4b). With seasonal stratification and ice cover, epilimnetic P_{CO_2} varies by a factor of 2, from about $495\text{--}1000\ \mu\text{atm}$. With persistent stratification, P_{CO_2} in the hypolimnion may exceed the epilimnion by a factor of 10. Epilimnetic Jones Lake water (moderate alkalinity and pH) crosses atmospheric equilibrium seasonally, with P_{CO_2} ranging from near $670\ \mu\text{atm}$ (>20 times atmospheric P_{CO_2}) under winter (ice-covered) conditions down to $4\ \mu\text{atm}$ during summer peaks in photosynthetic activity. Hypolimnetic water is always well-above atmospheric P_{CO_2} but cycles seasonally over 1 order of magnitude, maximized during summer stratification when epilimnetic P_{CO_2} is minimized. In Lahrity Lake, shallow water also crosses atmospheric equilibrium seasonally, despite relatively high carbonate alkalinity. Near-bottom water varies widely depending on water-column stability, with P_{CO_2} reaching values near $10^5\ \mu\text{atm}$ (>200 -fold atmospheric equilibrium) during some conditions of summertime stratification.

4. Discussion

4.1. Modes of lake water-column $\delta^{13}\text{C}_{\text{DIC}}$ variability

The six lakes fall into three broad categories of $\delta^{13}\text{C}_{\text{DIC}}$ behavior, which are most easily seen in a plot of $\delta^{13}\text{C}_{\text{DIC}}$ values vs. [DIC] (Fig. 5). Spectacle, Evans, and Lahrity lakes have $\delta^{13}\text{C}$ values that are higher in the epilimnion (low [DIC]) than in the hypolimnion (high [DIC]). This is the “textbook” mode of lacustrine water-column DIC behavior (Cohen, 2003, p. 91), which we here call Mode

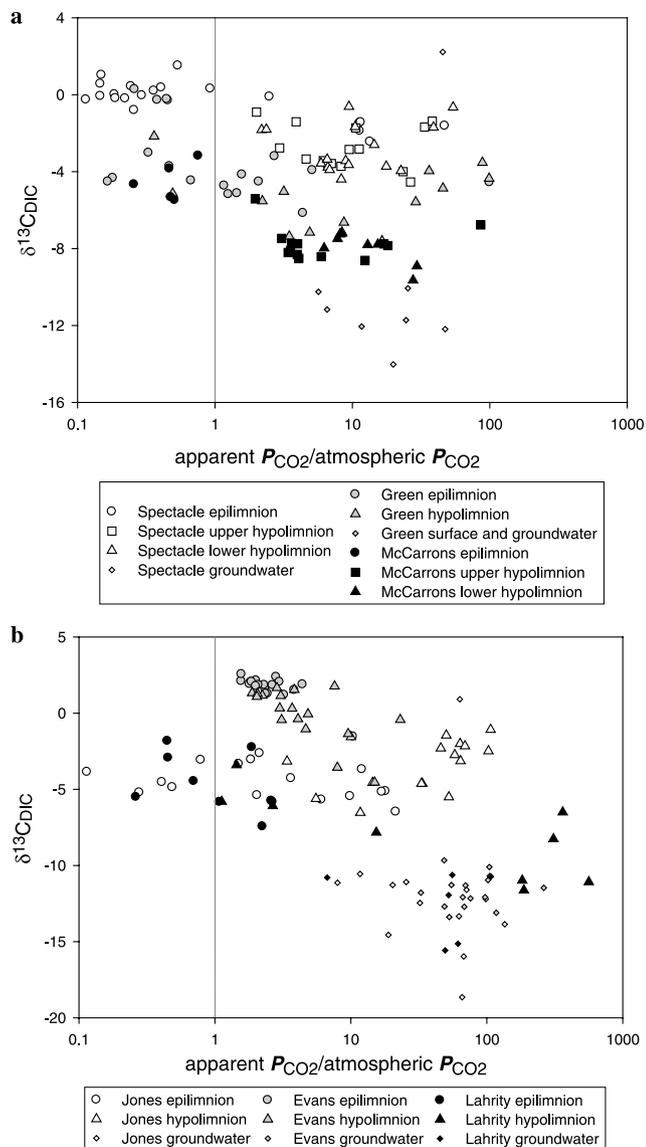


Fig. 4. $\delta^{13}\text{C}_{\text{DIC}}$ composition vs. apparent P_{CO_2} , normalized to atmospheric P_{CO_2} . (a) Minnesota lakes; (b) Montana lakes. Note difference in $\delta^{13}\text{C}_{\text{DIC}}$ scale. Symbols are shaded according to lake TDS from white (lowest) to black (highest). Each lake has a relatively constrained amplitude in $\delta^{13}\text{C}_{\text{DIC}}$ variability even while ranging over one to several orders of magnitude in P_{CO_2} . Note that lake P_{CO_2} routinely evolves to values higher than those of groundwater samples.

A. In contrast, Jones Lake $\delta^{13}\text{C}_{\text{DIC}}$ values are lower in the epilimnion (low [DIC]) than in the hypolimnion (high [DIC]), a condition we will call Mode B. In McCarrons and Green lakes, as [DIC] increases from epilimnion to hypolimnion, $\delta^{13}\text{C}_{\text{DIC}}$ values decrease; however, they increase again at the highest [DIC] values (Mode C). Fig. 5c shows these three modes schematically.

These different modes cannot be simply explained by P_{CO_2} , lake stratification, DIC concentration, mineral saturation, lake size and morphometry, algal productivity, or any individual parameter describing lake state. Jones and Spectacle lakes both vary over the same P_{CO_2} range but exhibit different modes of $\delta^{13}\text{C}_{\text{DIC}}$ behavior (Fig. 4). Green

Lake is polymictic and Lake McCarrons is oligomictic, but both show the same $\delta^{13}\text{C}_{\text{DIC}}$ behavior. Evans and Spectacle lakes show the same $\delta^{13}\text{C}_{\text{DIC}}$ behavior but differ by an order of magnitude in [DIC] (Fig. 5). Hypolimnia of McCarrons, Jones, and Spectacle lakes are all below carbonate saturation (Table 2), but the three lakes fall into three different $\delta^{13}\text{C}_{\text{DIC}}$ modes. Within the relatively narrow size distribution of the lakes in this study (13–325 ha), no apparent relationship exists between $\delta^{13}\text{C}_{\text{DIC}}$ behavior and lake area or $\delta^{13}\text{C}_{\text{DIC}}$ values and area:depth ratio (see Table 1). Spectacle Lake is the least eutrophic of the three Minnesota lakes, but has the highest $\delta^{13}\text{C}_{\text{DIC}}$ values. To attempt to generalize and understand the processes responsible for the $\delta^{13}\text{C}_{\text{DIC}}$ behavior and range of variability in these carbonate-producing lakes, we suggest an approach that considers the relative magnitude of major DIC pools and fluxes.

In Mode A lakes (epilimnetic $\delta^{13}\text{C}_{\text{DIC}}$ values higher than hypolimnetic; Spectacle, Evans, and Lahrity), water-column $\delta^{13}\text{C}_{\text{DIC}}$ distribution appears to be dominated by photosynthesis and decomposition (aerobic or anaerobic), through preferential uptake of ^{12}C from the epilimnion and its release in the hypolimnion (Fig. 3a). Similarly, epilimnetic carbonate mineral precipitation and its hypolimnetic dissolution can preferentially move more ^{13}C -enriched DIC from the surface to deep waters; however, the fractionation between DIC (predominantly HCO_3^- at typical pH ranges for these lakes) and CaCO_3 is lower than that between DIC (CO_2 or HCO_3^-) and organic matter: about +3 for DIC– CaCO_3 vs. -20‰ for DIC–OM (Dean and Stuiver, 1993; Gu et al., 2004). It therefore requires the precipitation of 6–7 mol carbonate to offset the effect on the DIC pool of the generation of 1 mol organic carbon. To achieve Mode A, net carbonate mineral export from the epilimnion to the hypolimnion cannot be large (by a factor of 6–7) relative to net organic carbon export, and net hypolimnetic dissolution of carbonate cannot be large relative to organic matter mineralization.

Mode A can prevail in lakes with a wide range of [DIC]. Spectacle Lake has a small DIC pool and generates a small amount of calcite relative to organic carbon; all of this carbonate dissolves in the lake-bottom waters and within the top few centimeter of the sediment but contributes little to the hypolimnetic DIC pool. Lahrity and Evans lakes have higher [DIC] by factors of 10–20, and preserve all or most of their carbonate mineral production due to saturation of hypolimnetic waters. Organic matter mineralization in these two lakes has a large effect on hypolimnetic $\delta^{13}\text{C}_{\text{DIC}}$ composition, even though [DIC] is large, because their hypolimnetic volumes are small relative to their epilimnia, where algal productivity is taking place. A high ratio of epilimnetic to hypolimnetic volume is likely to characterize most small lakes.

In Mode B (hypolimnetic $\delta^{13}\text{C}_{\text{DIC}}$ values higher than epilimnetic; Jones Lake) much of the large flux of ^{13}C -enriched calcite from the epilimnion is dissolved in the hypolimnion rather than buried in the sediments (e.g., Ramisch

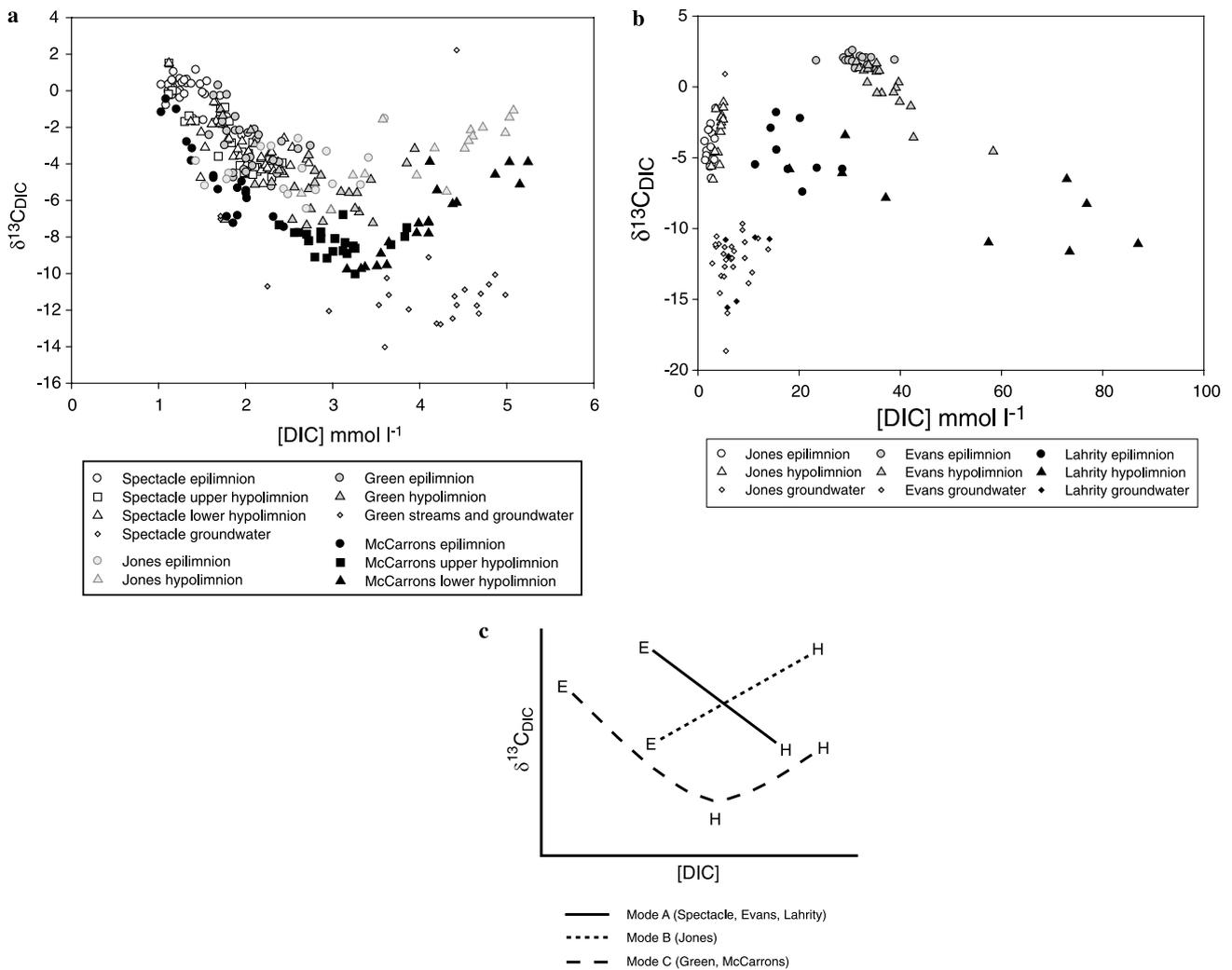


Fig. 5. $\delta^{13}\text{C}_{\text{DIC}}$ composition vs. [DIC]. Note difference in scales. E and H stand for “epilimnetic” and “hypolimnetic,” respectively. Groundwater compositions for all lakes cluster with one another, and appear to be relatively unimportant in contributing to the final isotopic composition of each lake. (a) Minnesota data showing hypolimnetic increase in $\delta^{13}\text{C}_{\text{DIC}}$ at high [DIC] in Lake McCarrons and Green Lake, indicating the action of divergent epilimnetic and hypolimnetic processes. Jones Lake (Montana) data are overlain on this plot because its [DIC] range is similar to those of the Minnesota lakes; note Mode B behavior wherein hypolimnetic (high-[DIC]) $\delta^{13}\text{C}_{\text{DIC}}$ values are higher than epilimnetic. (b) Montana data showing buffering effects of the large Evans Lake DIC pool on epilimnetic $\delta^{13}\text{C}_{\text{DIC}}$: Jones Lake and Laherty Lake are relatively low-[DIC] and low-volume, respectively, and as a result have wider epilimnetic $\delta^{13}\text{C}_{\text{DIC}}$ variations than does the larger, high-DIC Evans Lake. The insensitivity of epilimnetic $\delta^{13}\text{C}_{\text{DIC}}$ values to intra-annual “noise” may make high-DIC lakes such as Evans preferable to lower-[DIC] systems as recorders of long-term environmental change. (c) Schematic of $\delta^{13}\text{C}_{\text{DIC}}$ composition vs. [DIC] modes as discussed in text.

et al., 1999), causing a positive shift in hypolimnetic $\delta^{13}\text{C}_{\text{DIC}}$ values. This hypolimnetic $\delta^{13}\text{C}_{\text{DIC}}$ increase could also be attributed to the addition of ^{13}C -enriched DIC generated as a metabolic byproduct of acetate-fermentation methanogenesis in the deep waters and in the sediments (Hornibrook et al., 2000); we have no measurements of $[\text{CH}_4]$ or of microbial communities that would eliminate this possibility. However, based on carbonate flux calculations (Shapley et al., 2005), mineral equilibria, and sedimentary features (e.g., petrographic observations of corroded carbonate grains), calcite dissolution is occurring in the Jones Lake hypolimnion and is contributing at least part of the observed increase in hypolimnetic relative to epilimnetic $\delta^{13}\text{C}_{\text{DIC}}$ values. Methanogenesis is likely limited in the Mode A lakes above: Spectacle Lake does not

undergo severe hypolimnetic anoxia; in the anoxic hypolimnia of Evans and Laherty lakes, SO_4^{2-} levels are so high that the dissimilatory sulfate reduction pathway is always more favorable than that of acetotrophic methanogenesis.

Mode C (epilimnetic $\delta^{13}\text{C}_{\text{DIC}}$ values typically higher than hypolimnetic, and hypolimnetic $\delta^{13}\text{C}_{\text{DIC}}$ values increasing with increasing [DIC]; McCarrons and Green) has elements of both Mode A and Mode B. Hypolimnetic $\delta^{13}\text{C}_{\text{DIC}}$ values are lower than epilimnetic, but values near the lake bottom become progressively higher as the summer proceeds, indicating a weighted mean flux of ^{13}C -enriched DIC from the sediment–water interface. In these lakes, remineralization of organic matter is evidently accompanied by carbonate dissolution and/or methanogenesis occurring at rates high enough to provide a net

positive $\delta^{13}\text{C}_{\text{DIC}}$ trend with increasing [DIC]. Green Lake and Lake McCarrons are similar geochemically and with respect to production of organic and carbonate carbon, but have very different circulation regimes. Lake McCarrons mixes only occasionally, due to its short fetch and strong salinity and temperature stratification, and so its hypolimnion provides favorable conditions for both methanogenesis and carbonate dissolution. Green Lake, by contrast, is shallow relative to its fetch and the epilimnion extends to within about a meter of the sediment–water interface in the summer. In spite of the resupply of oxygen to deeper waters by ventilation and ample photosynthetic activity (which frequently produces O_2 supersaturation in the epilimnion), the sediments and the minimal hypolimnion are anoxic. Mineral equilibrium calculations indicate that calcite is always supersaturated in the Green Lake hypolimnion, but methanogenesis may occur in the organic-rich sediments and produce ^{13}C -enriched DIC.

4.2. Characteristic lake compositions

The mechanisms responsible for producing characteristic $\delta^{13}\text{C}_{\text{DIC}}$ compositions of individual lakes remain complex in spite of the information on processes gained from the analysis of water-column $\delta^{13}\text{C}_{\text{DIC}}$ behavior. Certainly, there does not appear to be a single controlling variable that sets the mean $\delta^{13}\text{C}_{\text{DIC}}$ value of all (or even many) hardwater lakes. Source water with high DIC (or DOC; [Kritzberg et al., 2004](#); [Pace et al., 2004](#)) may influence lake water composition in some lakes, although source water signatures appear to be readily overprinted by in-lake processes in the lakes described here. Similarly, [Finlay \(2003\)](#) identified scale dependent modification of $\delta^{13}\text{C}_{\text{DIC}}$ source composition in streams and rivers related to residence time and productivity. While the trend of Green and Spectacle water-column values ([Fig. 5a](#)) approximates the slope of a mixing line between source water and atmospheric compositions ($\sim 0\text{‰}$ as DIC, given the fractionation between CO_2 , $\text{CO}_{2(\text{aq})}$, and HCO_3^- ; see [Bade et al., 2004](#)), mixing does not explain these compositions. Inflowing surface- and groundwater likely mixes into lake epilimnia, not hypolimnia, which are intermediate in values between the source water and epilimnetic water. (The hypolimnetic $\delta^{13}\text{C}_{\text{DIC}}$ compositions are similar to source water compositions because the two waters have in common low $\delta^{13}\text{C}_{\text{DIC}}$ values and high [DIC] that are the product of organic matter remineralization.) If source water composition were a significant factor in lake water composition, we would expect the large contrast between compositions of Green and Spectacle lakes ([Fig. 2a](#)) to be reflected in clear differences between the $\delta^{13}\text{C}_{\text{DIC}}$ values of surface- and groundwater entering the two lakes. Instead, the source water compositions ([Figs. 4a and 5a](#)) overlap completely in $\delta^{13}\text{C}_{\text{DIC}}\text{--}P_{\text{CO}_2}\text{--}[\text{DIC}]$ space. Similarly, all the Montana lakes receive groundwater inflow with similar $\delta^{13}\text{C}_{\text{DIC}}$ values, but evolve strongly contrasting compositions and relationships between $\delta^{13}\text{C}_{\text{DIC}}$ values and [DIC] ([Shapley et al., 2005](#)).

Acetotrophic methanogenesis in anoxic deep waters and sediments generates low- $\delta^{13}\text{C}$ CH_4 and high- $\delta^{13}\text{C}$ CO_2 ([Hornibrook et al., 2000](#)) the latter of which can be a significant source of DIC to the water column (e.g., [Ogrinc et al., 1998](#); [Lojen et al., 1999](#)). Although part of this methane may be reoxidized in the water column, generating a relatively depleted $\delta^{13}\text{C}_{\text{DIC}}$ flux, any net effect on $\delta^{13}\text{C}_{\text{DIC}}$ composition resulting from methanogenesis and methane reoxidation should be toward more positive $\delta^{13}\text{C}_{\text{DIC}}$ values ([Gu et al., 2004](#)). Although water-column data from Green, McCarrons, and Jones lakes are consistent with the presence of methanogenesis, these three lakes have ^{13}C -depleted mixed-lake compositions relative to other lakes in this study; therefore, methanogenesis does not appear to be a dominant factor in their mean $\delta^{13}\text{C}_{\text{DIC}}$ values.

Bicarbonate generated by sulfate reduction is relatively low- $\delta^{13}\text{C}$ because the electron donor is low- $\delta^{13}\text{C}$ organic carbon compounds ([Fenchel et al., 1998](#)), and could similarly drive mixed-lake $\delta^{13}\text{C}_{\text{DIC}}$ values downward in those lakes known to have sulfate-reducing microbial communities (McCarrons, Lahrity, and Evans). Sulfate reduction in Lake McCarrons, however, is calculated to contribute only about 1–1.5% of the total DIC to the deep hypolimnion, and so cannot be responsible for the lake's relatively ^{13}C -depleted bulk composition. The process may play a part in the relatively low mixed-lake $\delta^{13}\text{C}_{\text{DIC}}$ values in Lahrity Lake, but sulfate reduction is also important in the low- $\delta^{13}\text{C}_{\text{DIC}}$ hypolimnion of Evans Lake ([Shapley et al., 2005](#)), which has the highest mixed-lake $\delta^{13}\text{C}_{\text{DIC}}$ values of any lake in the study.

Lake-atmosphere disequilibrium with respect to carbon dioxide is common ([Cole et al., 1994](#)). Evasion of CO_2 to the atmosphere has been invoked to explain extreme enrichments in $\delta^{13}\text{C}_{\text{DIC}}$ values ([Schwalb et al., 1999](#); [Vale-ro-Garcés et al., 1999](#)), as fractionation across the air–water interface removes ^{13}C -depleted CO_2 ([Herczeg et al., 2003](#)). In lakes with large external CO_2 influxes (e.g., volcanic or hydrothermal degassing through the lake floor) and long hydraulic residence times this process could produce lake water $\delta^{13}\text{C}_{\text{DIC}}$ values of several per mil above atmospheric equilibrium.

In low-DIC lakes that persistently fall below CO_2 saturation, atmospheric CO_2 invasion may also contribute to the mean epilimnetic $\delta^{13}\text{C}_{\text{DIC}}$ value. Spectacle Lake appears to evolve to and remain near a maximum $\delta^{13}\text{C}_{\text{DIC}}$ value commensurate with an atmospheric CO_2 source; however, the lake's epilimnion is also at times supersaturated with respect to atmospheric P_{CO_2} , so it also loses CO_2 to the atmosphere. The relatively small size of the lake DIC pool allows it to be readily affected by photosynthetic activity and atmospheric exchange. In contrast, the large Evans Lake DIC pool is not subject to atmospheric inputs, although it might at first glance appear that its $\delta^{13}\text{C}_{\text{DIC}}$ composition (most similar to that of Spectacle) is atmospherically derived. The epilimnetic P_{CO_2} of Evans Lake is consistently above atmospheric CO_2 pressure and thus is not subject to atmospheric

CO₂ invasion. In spite of their similar $\delta^{13}\text{C}_{\text{DIC}}$ values, the two lakes also differ in carbon residence time: in Spectacle, for example, the DIC pool is diminished by about 25–30% each year due to photosynthesis (Fig. 3a), i.e., the carbon residence time is no longer than about 4 years. The Evans pool is diminished by only about 10–15% each year, so carbon residence time is close to 10 years. Several processes favor evolution of high $\delta^{13}\text{C}_{\text{DIC}}$ values in Evans Lake: organic matter sequestration exceeding the (low- δ) sediment remineralization flux, possible CO₂ evasion from the lake, the high sulfate activity of lake water (likely preventing acetotrophic methanogenesis), and long solute residence time could all contribute to maintaining high $\delta^{13}\text{C}_{\text{DIC}}$ values over the long term.

4.3. DIC masses and seasonal isotopic change

The sensitivity of an individual lake to short- and long-term environmental change depends in part on the size of the lake DIC pool relative to the magnitude and period of environmental forcing. Lakes with small DIC pools such as Spectacle Lake show high intraannual variability in epilimnetic $\delta^{13}\text{C}_{\text{DIC}}$ values (Fig. 3a), reflecting their strong isotopic response to seasonal productivity cycles. The effects of these cycles on Evans Lake epilimnetic water are damped by its large DIC pool (Fig. 3b) but tend to be prominent in the low-volume Evans Lake hypolimnion, where despite high DIC concentration, DIC mass is low relative to organic carbon delivery. Because of the lake's large epilimnetic:hypolimnetic volume ratio, the epilimnion in turn dominates whole-lake $\delta^{13}\text{C}_{\text{DIC}}$ composition, leading to subdued interannual $\delta^{13}\text{C}_{\text{DIC}}$ variability.

4.4. Application to paleolimnology

The spatial and temporal $\delta^{13}\text{C}_{\text{DIC}}$ patterns described here have several possible implications for the interpretation of isotopic paleorecords from small lakes. From the wide compositional range in lakes with similar $\delta^{13}\text{C}_{\text{DIC}}$ values of groundwater in connected aquifers, lake $\delta^{13}\text{C}_{\text{DIC}}$ values appear to be relatively insensitive to inflow composition. Lakes with similar groundwater source compositions differ in $\delta^{13}\text{C}_{\text{DIC}}$ values by as much as 7–8‰; this is not surprising given the number and importance of in-lake processes resulting in carbon isotope fractionation. Inferences regarding changes in source DIC composition (resulting, for example, from a change in dominance of C3 and C4 plants) would be difficult to support based on carbonate isotopic paleorecords from such lakes.

The presence of Mode B and Mode C lakes in our (small) data set indicates that the simplest (Mode A) model of lake $\delta^{13}\text{C}_{\text{DIC}}$ evolution is commonly inadequate to explain $\delta^{13}\text{C}$ compositional change in small hardwater lakes. Net fluxes of DIC with high $\delta^{13}\text{C}$ values relative to epilim-

netic values are reflected in elevated hypolimnetic compositions in Modes B and C, implying a qualitatively different epilimnetic $\delta^{13}\text{C}_{\text{DIC}}$ balance from Mode A.

$\delta^{13}\text{C}_{\text{DIC}}$ modes tend to bridge different [DIC] conditions and, probably, different mixes of DIC production, highlighting the uncertainty in lake-process interpretations of sediment $\delta^{13}\text{C}$. Mode A itself encompasses lakes with widely differing [DIC], P_{CO_2} conditions and microbial dominance (Fig. 6; e.g., Evans and Spectacle lakes), between which the main distinguishing characteristic in $\delta^{13}\text{C}$ of sediments might be the damped amplitude of variability in alkaline Evans Lake. Here, inferring paleolake $\delta^{13}\text{C}$ influences likely will depend heavily on mineralogical indicators of lake solute concentration and/or on biomarkers of specific microbial processes (Hollander and Smith, 2001).

Less-damped lakes such as Spectacle that record high seasonal isotopic variability in their sedimentary records may provide more complex isotopic records wherein the signal of seasonality is large relative to the record of longer-period paleoenvironmental change. High-resolution sampling of sediment cores from these lakes may inadvertently capture this seasonal variability and so produce records with artificially augmented amplitude of (apparently interannual) variability. Conversely, lakes with damped sensitivity in epilimnetic $\delta^{13}\text{C}_{\text{DIC}}$ values will be relatively insensitive to short-term and small-scale isotopic forcing, but may be better recorders of longer-term environmental change. Minerals formed in authigenic or diagenetic environments near the sediment–water interface (e.g., rhodocrosite (Dean, 1993), high-Mg calcite (Talbot and Kelts, 1986), or siderite (Wittkop, 2004; Crausbay et al., 2006)) may record “noisy” $\delta^{13}\text{C}_{\text{DIC}}$ compositions reflecting the high compositional variability of DIC in low-volume hypolimnia, where fluxes are seasonally large relative to the restricted hypolimnetic DIC pool. Recognition and proper interpretation of such effects requires careful petrographic examination of sediment components and possibly separate isotopic analysis of different sediment mineral phases.

Interlake comparison of $\delta^{13}\text{C}_{\text{DIC}}$ data from these lakes also highlights the lack of a simple relationship between fluid residence time and $\delta^{13}\text{C}_{\text{DIC}}$ evolution. In the Montana lakes, the greatest DIC compositional overlap in mixed-layer water occurs between Jones Lake, with a fluid residence time of a few months, and highly evaporated Lahrity Lake. Evans Lake, also evaporatively concentrated (with residence time near 10 years) has much higher $\delta^{13}\text{C}_{\text{DIC}}$ values, comparable in our data set only to Spectacle Lake, the most dilute lake represented. Carbon isotopic composition relates to DIC residence time and flux balance, which may correlate with fluid residence time, resulting in long-recognized ^{18}O : ^{13}C isotope covariance (Talbot, 1990; Valero-Garcés et al., 1995; Benson et al., 1996; Li and Ku, 1997) but may also be overprinted by fractionating processes generating recycled in-lake DIC sources (carbonate redissolution, methanogenesis, etc.).

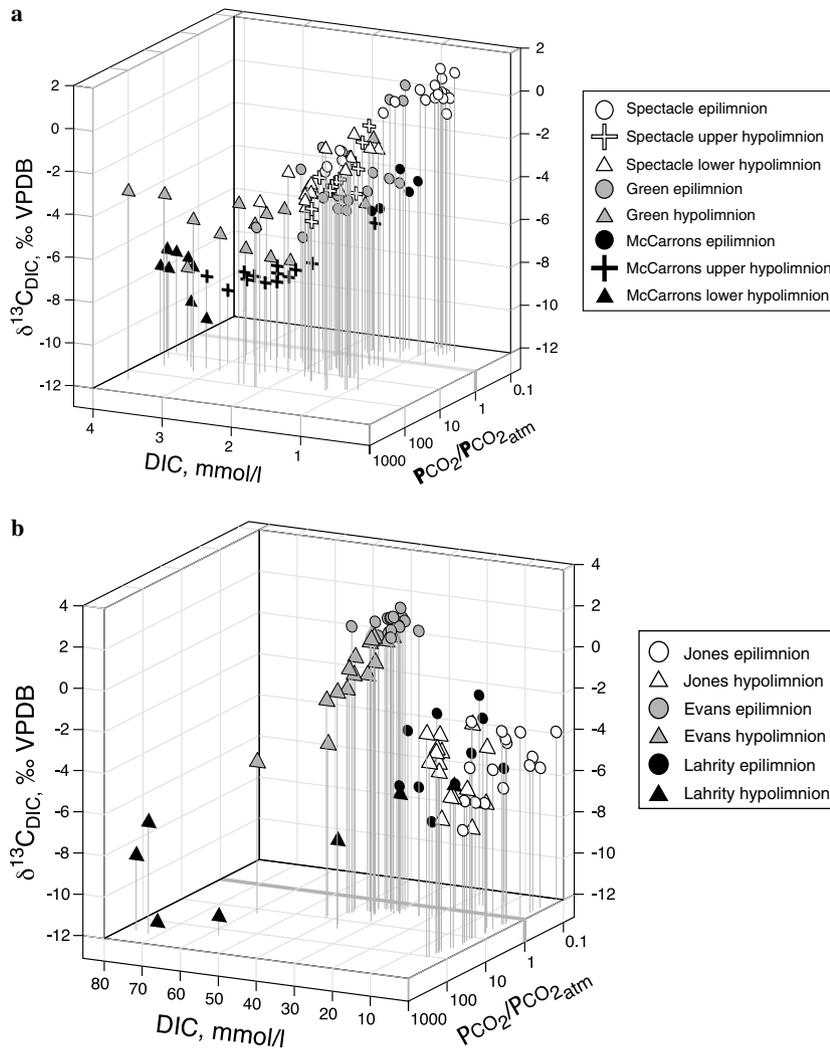


Fig. 6. Three-dimensional plots of relationships between [DIC], normalized P_{CO_2} , and $\delta^{13}C_{DIC}$. Atmospheric CO_2 equilibrium shown by heavy line on $P_{CO_2}/[DIC]$ plane. (a) Pooled Minnesota data, describing inverse correlations between [DIC] and $\delta^{13}C_{DIC}$ and between P_{CO_2} and $\delta^{13}C_{DIC}$ for mixed layers of all lakes, and positive correlations between the same parameters in hypolimnetic waters of Green Lake and Lake McCarrons. (b) Pooled Montana data; Jones Lake data show increasing hypolimnetic $\delta^{13}C_{DIC}$ with P_{CO_2} , while Evans and Laherty show declining $\delta^{13}C_{DIC}$ with increasing [DIC] and P_{CO_2} in low-volume hypolimnia. Note scaling differences between panels (a) and (b).

The decoupling of algal productivity and $\delta^{13}C_{DIC}$ values (e.g., Teranes et al., 1999; Hollander and Smith, 2001; Herczeg et al., 2003; Bade et al., 2004) is evident in the example of the three Minnesota lakes: McCarrons and Green lakes are eutrophic and Spectacle Lake is mesotrophic, but Spectacle Lake has the highest epilimnetic $\delta^{13}C_{DIC}$ values, routinely exceeding 0‰ while the other lakes reach 0‰ only occasionally. Calcite precipitated in equilibrium with this DIC pool in the early summer would, in the standard interpretation, indicate that Spectacle Lake was the most eutrophic of the three. Macrophyte photosynthesis in the shallow part of the lake is responsible in part for the high $\delta^{13}C_{DIC}$, but its contribution is difficult to discern in cores from a deep part of the lake, where pelagic sediments are composed of fine-grained organic material. Understanding the nature of the discrepancy between $\delta^{13}C$ and algal productivity may be especially applicable to historical-scale reconstructions of lake trophic status based on sedimentary

records, where major changes in DIC sources and pool size may lead to changes in $\delta^{13}C_{DIC}$ values that are difficult to explain when viewed only in the context of productivity variations. It is also apparent from this study that the magnitude of $\delta^{13}C_{DIC}$ change effected by summer productivity may or may not be sufficient to greatly alter the composition of the DIC pool. The same productivity variations may thus be recorded with very different sensitivity in two lakes with divergent [DIC], or in the same lake under different epilimnetic DIC pool size, such as might develop under wind regimes that generate different mixed-layer depths from year to year.

5. Conclusion

Lacustrine $\delta^{13}C$ remains an important ecological and paleoenvironmental proxy in spite of the complexity of DIC cycling and the ambiguities inherent in the interpreta-

tion of carbon isotopes in lake sediment records. More agile conceptual models of $\delta^{13}\text{C}_{\text{DIC}}$ evolution and distribution in lake waters are needed to fully exploit sedimentary $\delta^{13}\text{C}$ signals from CaCO_3 -forming lakes, however. Our data emphasize that multiple limnological pathways produce similar whole-lake $\delta^{13}\text{C}_{\text{DIC}}$ values, that gross biological productivity is not necessarily a first-order control over observed $\delta^{13}\text{C}_{\text{DIC}}$ values, and that patterns of lake $\delta^{13}\text{C}_{\text{DIC}}$ with changing [DIC] bridge disparate lake types. Therefore, paleorecord interpretation should entail critical examination of alternate in-lake carbon cycling scenarios that may account for a given stratigraphic result. We suggest that it is most important to evaluate the size of the DIC (paleo-) pool, the presence and isotopic composition of biomarkers of microbial processes, evidence of mineral diagenesis and diagenetic mineral composition, and the relative accumulation rates of organic and carbonate carbon in order to assess the dominance of different processes in the lake water column at the time of sediment deposition. In carbonate-producing lakes, temporal trends in $\delta^{13}\text{C}_{\text{DIC}}$ values are non-unique indicators of changing lake state most usefully viewed in conjunction with other evidence of ecosystem change and physiochemical thresholds.

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