

THE LACUSTRINE CARBON CYCLE AND ITS REPRESENTATION IN LAKE SEDIMENTS

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INTRODUCTION

Carbonate deposition in lakes varies depending on internal lake dynamics, which are ultimately controlled by climate factors such as aridity, windiness, and mean summer temperature (Dean 1993, Locke and Schwab 1997, Hodell et al 1998). Hypolimnetic dissolution of calcite produced in the surface waters is more pronounced in some lakes than in others (Dean 1981, Ramisch et al 1999), and so biases the sedimentary record (i.e., changes the bulk composition of the material that sinks from the epilimnion) differently in different lakes. Similarly, carbon stable isotopic values ($\delta^{13}\text{C}$) of carbonate minerals and organic matter are routine proxies for paleoproductivity (McKenzie 1985, Hollander and McKenzie 1986), but also depend upon factors like lake circulation (wind mixing) and degree of remineralization of autochthonous and allochthonous organic matter. In some cases where the nutrient loading and eutrophication history of a lake are known (e.g., Hollander and Smith in press, for Lake Mendota), behavior of $\delta^{13}\text{C}$ in the sedimentary record is contrary to expectations based on primary productivity control on $\delta^{13}\text{C}$. Such inconsistencies indicate that certain geochemical assumptions developed for $\delta^{13}\text{C}$ studies in the marine realm are inappropriate for studies of lakes, especially lakes that are small or biologically productive.

The approach of this study is to explicitly link modern water-column processes with sedimentary records in three lakes in east-central Minnesota. The research primarily addresses two issues which are important to the interpretation of lacustrine sedimentary records:

1. What is the environmental significance of the presence/absence of authigenic carbonate minerals in lake sediments? How do the biogeochemical and physical controls on carbonate production and preservation lead to threshold behavior observed in some sedimentary records? Does the timing of carbonate loss in lakes in different parts of Minnesota support a common (climatic) cause across the region?

2. In what situations do processes such as wind mixing and organic matter remineralization dominate over primary productivity in the $\delta^{13}\text{C}$ signal?

How do typical $\delta^{13}\text{C}$ response styles in different types of lakes (e.g., deep, shallow, large, meromictic) reflect their carbon cycle dynamics?

STUDY SITES

The lakes in this study are geochemically similar (Table 1), but vary in morphometry from relatively large and shallow to relatively small and deep. Basin morphology is a major control on wind mixing of lake waters, and thus on the chemical differentiation of epilimnion from hypolimnion under summer density stratification.

Lake	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	Cl (mg/L)	SO ₄ (mg/L)	alk (meq/L)	z_{Secchi} (m)	TP (ng/L)	chl-a (ng/L)	trophic state
Green, mixed	40.6	14.6	6.5	8.3	9.7	2.0-3.0	1.6	43	23.7	eutrophic
Spectacle, mixed	29.5	9.3	4.4	4.5	3.5	1.8-2.0	3.6	31	3.7	mesotrophic
McCarrons 2m	22.4	12.9	40.0	73.0	10.8	1.8-3.0	1.5	39	16.4	eutrophic
McCarrons 16.5m	59.5	16.5	55.8	101.0	5.2	2.7-3.0				

Table 1. Water chemistry of lakes in this study. Major ion data, alkalinity, and z_{Secchi} (Secchi depth) from this study; TP (total phosphorous), chl-a (chlorophyll-a), and trophic state from Minnesota Department of Natural Resources average data.

Green Lake and Spectacle Lake, Isanti County, Minnesota, lie 1 km apart in the northwestern corner of the glacial outwash Anoka sandplain. Spectacle Lake is horseshoe-shaped with a surface area of about 100 ha and a maximum depth of 15 m. It is groundwater-fed, with no stream inflows or outflows. Green Lake is round, about three times as large, and half as deep, with several stream inflows and a large outlet. It is eutrophic, and is virtually opaque with algae for much of the summer, while Spectacle is one of the most transparent lakes in the region. Lake McCarrons, Ramsey County, Minnesota, is a eutrophic urban lake with a surface area of only 33 ha, but a maximum depth of 17 m. The lake has a surface inflow through a manmade wetland-detention pond complex, and an intermittent overflow which is above the current average lake level.

All three lakes' Holocene sediments comprise the four typical components of Minnesota lake mud: (1) basin-derived clastic material, e.g., quartz, feldspars, clays, carbonates; (2) authigenic minerals, typically Ca-, Mg-, and Fe-carbonates; (3) siliceous parts of aquatic organisms such as diatoms and sponges; and (4) a combination of autochthonous and allochthonous organic matter. Any one of these four components may dominate in a given lake at a given time.

The sedimentary records of these three lakes are divergent in spite of their comparable aqueous chemistry. Green Lake sediments are homogeneous marl, high in calcium carbonate (up to 80% low-magnesium calcite) throughout the 7.5

m core; in the top 1 m, organic carbon content rises as a relative proportion of the total sediment. Spectacle Lake sediments are calcareous (up to 50% CaCO₃) near the bottom of the core, but carbonate is absent from the upper ~6 m. The intervening lithology comprises a series of light-dark (carbonate-rich – carbonate-poor) bands which will be discussed further below. Lake McCarrons is calcite-rich (up to 80% CaCO₃) and discontinuously varved, especially clearly in the top ~60 cm, which represents about 90 years of sedimentation. Chronologies for the lakes have not yet been obtained (apart from varve counting of the last 90 years in McCarrons and ²¹⁰Pb dating for the last ~140 years in Green Lake), so timing of Holocene events is at present only speculative.

METHODS

I have taken water samples every two to three weeks during the ice-free season, beginning in 1999 in Green and Spectacle and in 2001 in McCarrons. Profiles of temperature and dissolved oxygen at 1 m intervals are concurrently conducted with a submersible YSI probe; in 1999 and 2000 pH and total dissolved solids were measured with benchtop meters only at depths at which water samples were taken; beginning in 2001 a multi-parameter Hydrolab probe enables all four parameters to be measured every meter.

Water samples for stable isotopic analysis of dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{DIC}}$; DIC = H₂CO₃* + HCO₃⁻ + CO₃²⁻) and major dissolved ions are taken in all lakes at 2 m below the water surface and at 1 m above the sediment-water interface, and in Spectacle and McCarrons Lakes also higher in the hypolimnion (approximately 1 m below the bottom of the thermocline). Samples are filtered through 0.45 μm pore size membrane filters into 20 mL crimp-cap amber glass serum vials with teflon-lined rubber seals (for $\delta^{13}\text{C}_{\text{DIC}}$) and 18 mL HDPE scintillation vials (for major ions), both overfilled to eliminate gas headspace. Samples are kept refrigerated and are analyzed within 1-2 weeks following collection. CO₂ is extracted from $\delta^{13}\text{C}_{\text{DIC}}$ samples by on-line direct acidification (Atekwana and Krishnamurthy 1998) and analyzed in the Minnesota Isotope Lab. Samples for anion analysis are left untreated and those for cation analysis are acidified with 0.5 mL ultrapure HNO₃ before measurement by ICP-MS in the Department of Geology and Geophysics, University of Minnesota.

Sediment cores are collected using a Bolivia corer, using a barrel of expendable 70 mm diameter polycarbonate. Core analysis is conducted at the Limnological Research Center, University of Minnesota. Whole cores are analyzed for bulk density and magnetic susceptibility on a Geotek multi-sensor core logger; cores are then split and their sedimentological structures and estimated composition described macroscopically and in smear slides using a petrographic microscope, in accordance with LRC initial core description (ICD) protocols. Subsamples are taken at variable intervals based on lithology, and

typically freeze-dried for all analyses. When possible, all analyses are conducted on splits of the same samples.

Inorganic and organic carbon (IC, OC) are determined by coulometric titration; IC % is converted to calcite abundance by multiplying by 100/12, the fraction of C in CaCO₃, and OC is converted to organic matter by multiplying by 2 (Dean 1974). Carbonate phases and other minerals are identified using powder x-ray diffraction at the Center for Interfacial Engineering, University of Minnesota. Samples for $\delta^{13}\text{C}$ of organic matter ($\delta^{13}\text{C}_{\text{OM}}$) are acidified with 1N HCl to eliminate carbonates, rinsed repeatedly, dried, and ground; those for carbonate isotopic analysis ($\delta^{13}\text{C}_{\text{CC}}$ and $\delta^{18}\text{O}_{\text{CC}}$) are treated with 2.6% NaOCl to eliminate organic matter, rinsed, sieved at 70 μm to remove ostracod shells, dried, and ground. $\delta^{13}\text{C}_{\text{OM}}$ is run at Mountain Mass Spectrometry, Denver, Colorado, and carbonates are run at the Minnesota Isotope Lab.

HYPOTHESES

The morphometric and hydrological differences between Green Lake, Spectacle Lake, and Lake McCarrons will cause each to respond differently to the same history of climate forcing. Clarifying the basis of these differences will allow me to then identify the features in the sedimentary record of each lake best suited to recording different aspects of the same regional climate history.

Green Lake. Because of its long fetch relative to depth, the surface mixed-layer depth in Green Lake presently approaches the sediment-water interface. Intermittent overturn of the water column during summer has two effects: (i) to increase aerobic respiration of sinking organic matter; (ii) to prevent CO₂ from accumulating in the hypolimnion, keeping pH high and the entire water column above carbonate saturation. As the Green Lake basin has filled in with sediment over the Holocene, the total water depth has decreased by more than half. Mixing depth has thus increased as a fraction of total depth, enhancing both effects (i) and (ii).

Green Lake will thus show (i) long-term depletion in $\delta^{13}\text{C}$ due to increased intraannual recycling of organic carbon (remineralization and reuse of CO₂ and nutrients during the same growing season) as the lake bottom aggrades; (ii) long-term increase in the burial rate of CaCO₃ as the bottom waters become progressively less corrosive to carbonate minerals.

Spectacle Lake. Although groundwater inflows to Spectacle Lake are high in Ca²⁺, sediments in the center of the lake are essentially carbonate-free because littoral sediments and calcifying aquatic macrophytes take up Ca²⁺. Open waters are depleted of Ca²⁺ and close to carbonate saturation; what calcite does precipitate dissolves in the undersaturated hypolimnion.

Lake McCarrons. Lake McCarrons is deep, seasonally anoxic, possibly oligomictic, and more productive than Spectacle Lake, but nevertheless preserves a considerable quantity of carbonate in its sediments. Carbonate survives in McCarrons because of the lake's relatively high bottom-water alkalinity, which buffers pH and keeps the hypolimnion above carbonate saturation. As productivity increases in the lake under cultural eutrophication, both organic matter and carbonate accumulation rates will increase.

RESULTS TO DATE

Green Lake. The Green Lake sedimentary record shows a decrease of $\sim 2\%$ in both $\delta^{13}\text{C}_{\text{OM}}$ and $\delta^{13}\text{C}_{\text{CC}}$ over the length of the core (Fig. 1; the section corresponding to human impact, i.e., the top 120 cm, shows a separate trend). These results are consistent with increasing mixing depth:total depth ratio and increasing intraannual recycling of organic carbon. This interpretation of $\delta^{13}\text{C}$ data is supported by $\delta^{18}\text{O}_{\text{CC}}$ data (Fig. 1) which show a concomitant depletion in $\delta^{18}\text{O}$, consistent with a shortening of residence time as lake volume decreases.

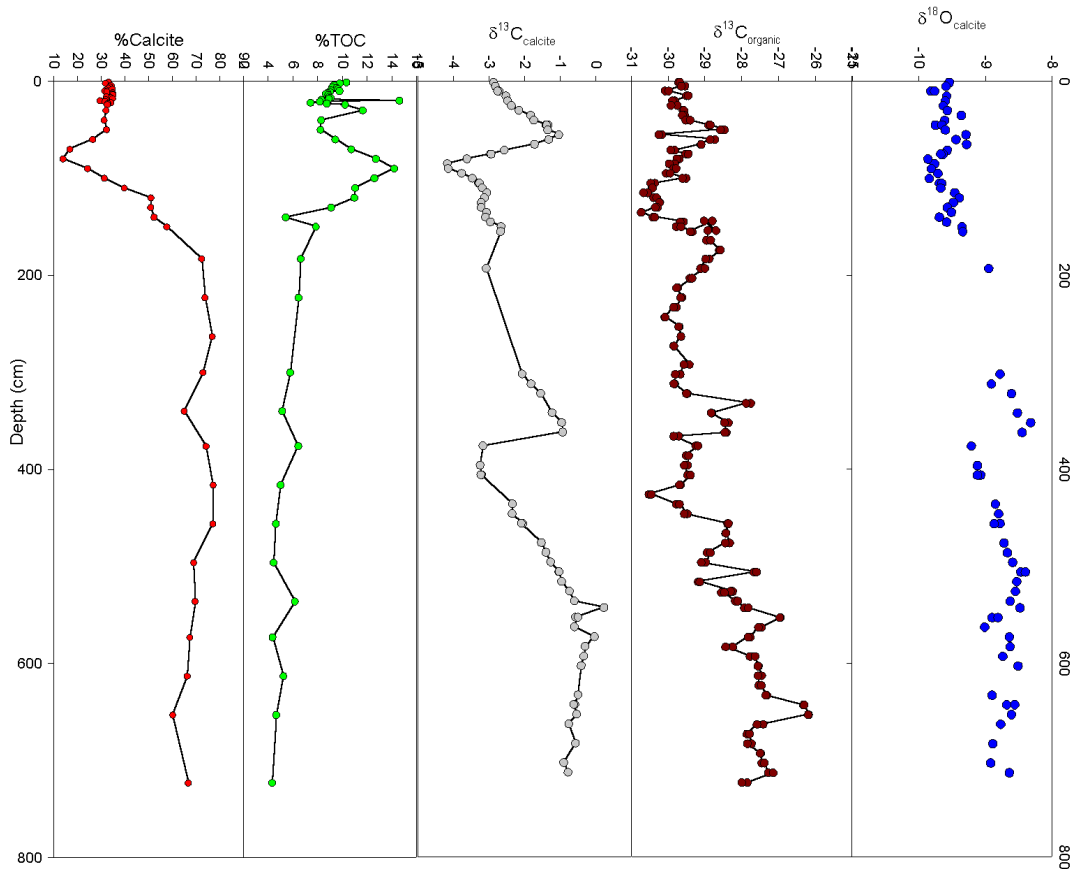


Figure 1. Sediment data from Green Lake core Green-97-1

Water-column $\delta^{13}\text{C}_{\text{DIC}}$ data also suggest that in the summer, while the lake is warm and nearly isothermal, Green Lake has a high incidence of wind-mixing events and consequent remineralization of sinking, ^{13}C -depleted organic matter. Nearby Spectacle Lake (Fig. 2) is more strongly stratified, and shows a seasonal evolution toward stable $\delta^{13}\text{C}_{\text{DIC}}$ values, through partitioning of epilimnetic from hypolimnetic DIC pools. Green Lake water masses are more weakly segregated (Fig. 2), and at two sampling points (late July and early September) there appear to be inversions of the expected $\delta^{13}\text{C}_{\text{DIC}}$ values (i.e., lighter in the epilimnion than in the hypolimnion). Inversions in alkalinity and dissolved oxygen are also commonly observed after storm or high wind events.

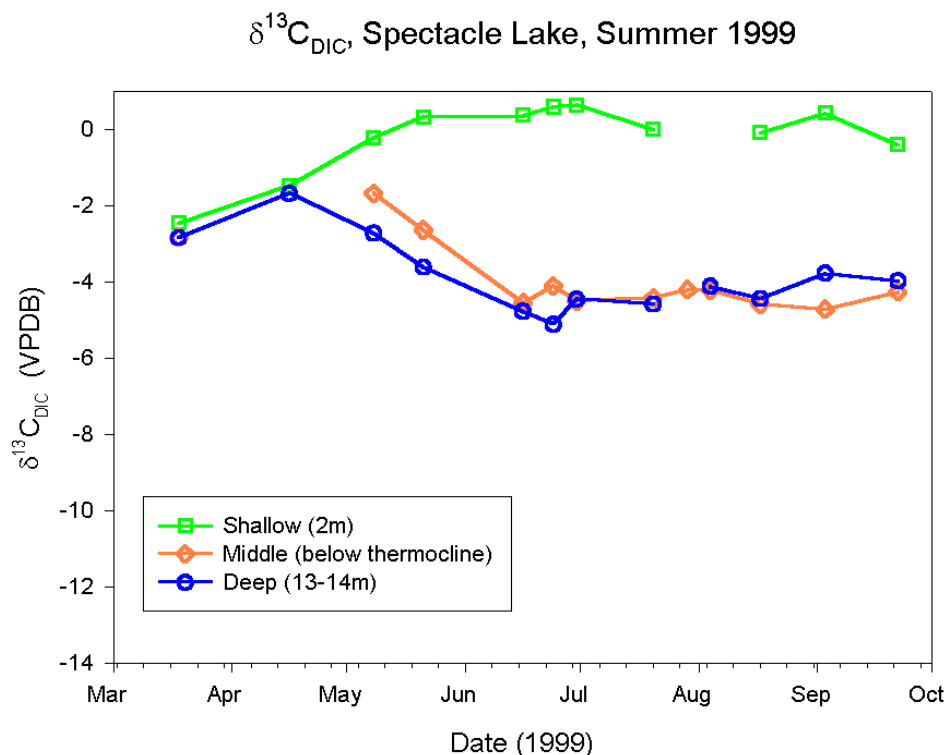


Figure 2. Stable isotopic composition of dissolved inorganic carbon in Spectacle Lake, summer 1999

Spectacle Lake. Dissolved calcium data (Fig. 3) show that by late May in both 1999 and 2000, epilimnetic Ca^{2+} values have dropped below mixed-lake values, while hypolimnetic values are slightly above mixed values. This evidence supports the idea that calcite is indeed precipitating in the lake, but is dissolving in undersaturated deep waters. Compare this with similar profiles from Green Lake (Fig. 4), which show a decrease in epilimnetic Ca^{2+} with similar

timing, but no increase in hypolimnetic values, suggesting that calcite is precipitating in Green but not dissolving in the hypolimnion.

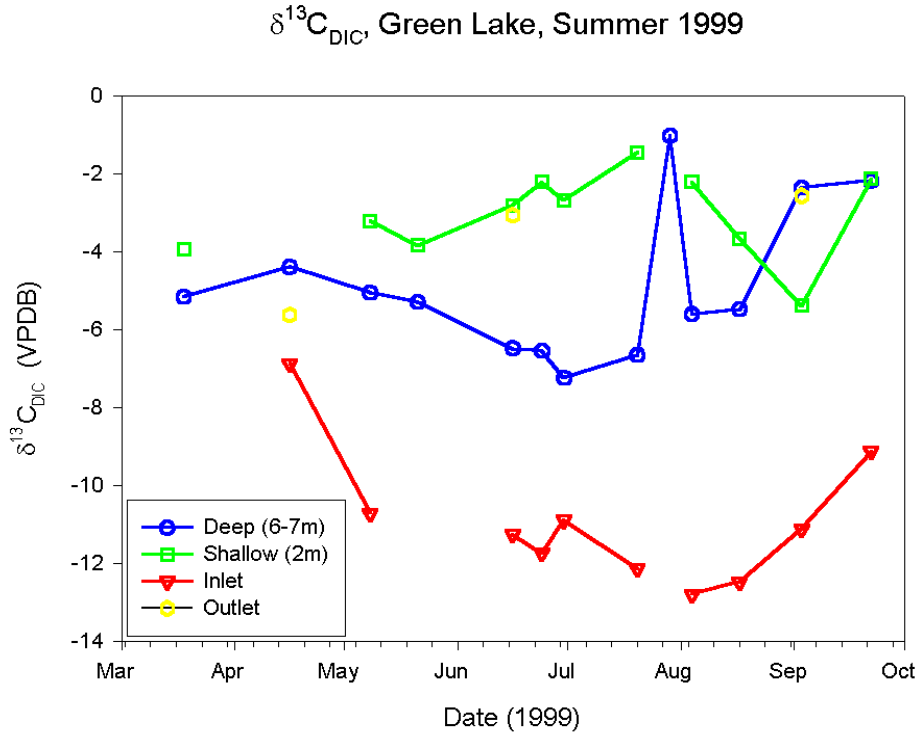


Figure 3. Stable isotopic composition of dissolved inorganic carbon in Green Lake, summer 1999

Lake McCarrons. A considerable body of nutrient, temperature, dissolved oxygen, and biological data on Lake McCarrons has been collected over the past 17 years by the Metropolitan Council as part of a remediation study. I will supplement these data with $\delta^{13}\text{C}_{\text{DIC}}$, major ions, chemical profiles of the water column, and analyses of the historical varved section of lake sediments.

ANTICIPATED RESULTS

Green Lake. Carbonate saturation modeling using field data (pH, temperature, $[\text{Ca}^{2+}]$ and other ions, alkalinity) and the computer program Geochemist's Workbench (GWB) will test whether the water column in Green Lake is consistently above carbonate saturation, and define the fluctuations in saturation index Ω ($\Omega = \text{IAP}/K_{\text{SP}}$, i.e., the ion activity product over the solubility product of the mineral, a measure of how oversaturated a solution is with respect to a given mineral) during the ice-free season. To test whether carbonate accumulation has increased over time, estimates of carbonate mass accumulation rates will be based upon radiocarbon dating of a minimum of 5-10 samples of

aeolian charcoal fragments in the sediment core. Further $\delta^{13}\text{C}_{\text{DIC}}$ and stratification data for the summers of 2000 through 2002 will test the variability of the mixing regime in Green Lake and its control on the behavior of DIC in the water column.

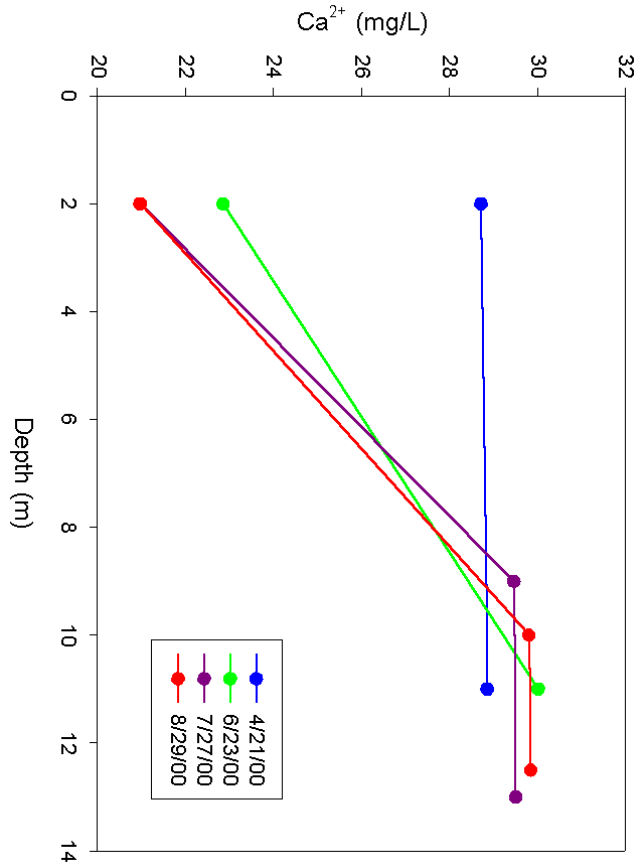


Figure 4. Dissolved calcium in Spectacle Lake, summer 2000

Spectacle Lake. I will use field data (including data from littoral water samples) and GWB to determine carbonate saturation at the surface and in the hypolimnion of Spectacle Lake in order to further support the hypothesis that calcite is precipitating and then dissolving. If littoral areas are sinks for Ca^{2+} as CaCO_3 , a transect of surface samples taken with an Ekman dredge will show CaCO_3 distributed in areas where bottom water is above carbonate saturation – probably in all littoral areas, and on the slopes of the deep basin, to some water depth where pH becomes too low to sustain carbonate preservation. The eastern basin of the lake is much shallower (about 5 m maximum depth) than the western basin where all cores and water samples to date have been taken. The entire water column in the shallow areas may be above carbonate saturation, and so the eastern basin may sequester carbonate where the western does not. A core in the eastern basin dated by ^{210}Pb would provide accumulation rates for

carbonate and organic matter for the past ~140 years, and would serve as a very interesting comparison with the historical section of Green Lake stratigraphy.

Lake McCarrons. Persistence of calcite in anoxic deep waters of Lake McCarrons suggests that geochemical modeling will show the hypolimnion to typically be above carbonate saturation. Carbonate and organic matter accumulation rates will be calculated from analysis of varves representing the past ~90 years of sedimentation, and supported by extant ^{210}Pb dating of a core from the lake. In other Minnesota lakes, the sedimentation rate of authigenic material shows its strongest increase in the 1920s and levels off in the 1970s. Because it is so heavily impacted by human activity, Lake McCarrons is expected to show this trend strongly.

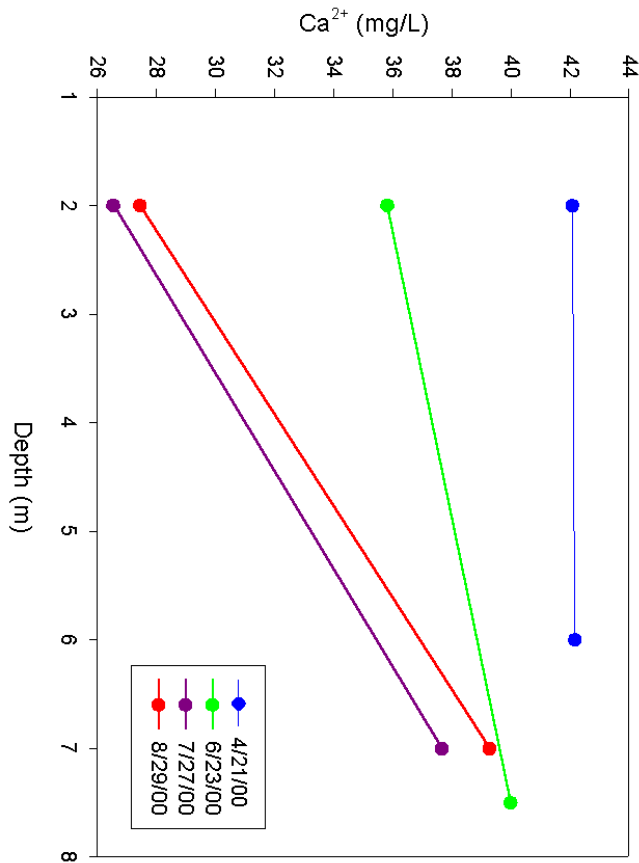


Figure 5. Dissolved calcium in Green Lake, summer 2000

Climate history and core stratigraphy in divergent lake sediments. Ultimately, a chronology for each sediment core from ^{14}C dating of aeolian charcoal and terrestrial macrofossils will enable the comparison of Holocene climate records from the three lakes. Because of the considerable work that has been done on

Minnesota climate records (e.g. Wright 1993, Locke and Schwalb 1997), the parameters of regional climate change are well-defined and this study will focus on the lakes' responses to these changes.

Spectacle Lake and Lake McCarrons are essentially closed basins with respect to surface water outflow, and because of this are expected to be more sensitive than is Green Lake to the changes in moisture balance that are major features of mid-continent Holocene climate. Spectacle and McCarrons may have been open basins in their early history, and lost their surface outlets when lake levels dropped in response to mid-Holocene aridity, as occurred in Williams Lake in the Itasca headwaters region (Locke and Schwalb 1997, Dean and Schwalb, in press). If this was the case, basin closure should appear as a progressive enrichment in $\delta^{18}\text{O}$ during that period. In Green Lake, as discussed earlier, there is a long-term depletion in $\delta^{18}\text{O}$ which is interpreted as a response of lake residence time to gradual infilling of the lake basin.

CONCLUSIONS

Three lakes which have been exposed to the same climate history and which are at present geochemically similar show divergent behavior with respect to their water column processes and sedimentary records. The most significant difference between the lakes is their morphometry, and thus their mixing behavior. This study evaluates the effects of water column circulation on precipitation-dissolution of calcite and on the behavior of stable isotopic values of dissolved inorganic carbon. The internal dynamics of these three lakes are expected to significantly affect how each responds to climate forcing and records signatures of climate change.

REFERENCES

Atekwana E. A. and Krishnamurthy R. V. (1998) Seasonal variations of dissolved inorganic carbon and $\delta^{13}\text{C}$ of surface waters: application of a modified gas evolution technique. *Journal of Hydrology* **205**, 265-278.

Dean W. E. (1981) Carbonate minerals and organic matter in sediments of north temperate hard-water lakes. *SEPM Special Publications* **31**, 213-231.

Dean W. E. (1974) Determination of carbonate and organic matter in calcareous sediments and sedimentary rocks by loss on ignition; comparison with other methods. *Journal of Sedimentary Petrology* **44**, 242-248.

Dean W. E. Physical properties, mineralogy, and geochemistry of Holocene varved sediments from Elk Lake, Minnesota. In Bradbury, J. P. and W. E. Dean eds. *Elk Lake, Minnesota: Evidence for Rapid Climate Change in the North-Central United States*. 135-157. 1993. Boulder, Colorado, Geological Society of America Special Paper 276.

Dean W. E. and Schwalb A. (in prep.) The lacustrine carbon cycle as illuminated by the waters and sediments of two hydrologically distinct hardwater lakes in northwestern Minnesota.

Hodell D. A. et al. (1998) Biologically induced calcite and its isotopic composition in Lake Ontario. *Limnology and Oceanography*.

Hollander D. J. and McKenzie J. A. (1991) CO₂ control on carbon-isotope fractionation during aqueous photosynthesis; a paleo-pCO₂ barometer. *Geology* **19**, 929-932.

Hollander D. J. and Smith M. A. (in press) Microbially mediated carbon cycling as a control on the $\delta^{13}\text{C}$ of sedimentary carbon in eutrophic Lake Mendota (USA): new models for interpreting isotopic excursions in the sedimentary record. *Geochimica et Cosmochimica Acta* **65**.

Locke S. M. and Schwalb A. (1997) In *Hydrological and Biogeochemical Research in the Shingobee River Headwaters Area, North-Central Minnesota* (ed. T. C. Winter). pp. 187-192.

McKenzie J. A. Carbon isotopes and productivity in the lacustrine and marine environment. In Stumm, Werner ed. *Chemical Processes in Lakes*. 99-117. 1985. New York, John Wiley and Sons.

Ramisch F. et al. (1999) Calcite dissolution in two deep, eutrophic lakes. *Geochimica et Cosmochimica Acta* **63**, 3349-3356.

Wright H. E. (1993) In *Elk Lake, Minnesota: Evidence for Rapid Climate Change in the North-Central United States* Vol. Special Paper 276. pp. 7-17. Geological Society of America.