ISOTOPIC ANALYSIS OF SEDIMENTS AS A PROXY FOR ENVIRONMENTAL QUALITY IN TEMPERATE LAKES OF WISCONSIN

JOHN DANNEHL, Washington and Lee University
Research Advisor: Jill Leonard-Pingel

ABSTRACT

There is an increasing need for humans to address anthropogenic changes such as deforestation, eutrophication, and water pollution in our ecosystems. Using a geochemical tool like stable isotopes helps us better understand how humans affect lacustrine environments and determine specifically where we must facilitate management strategies for restoring biodiversity and essential ecosystem services lost due to human activity in the biosphere. Stable isotopes preserved in lacustrine sediments are one such way to reconstruct the environmental history of a region. Here, we use stable isotope analysis from temperate lakes in Wisconsin to highlight paleolimnological changes in response to increasing stress due to human activity. Several changes in the biogeochemical cycle have occurred due to cultural eutrophication in Shadow Lake for example, such as decreased oxygen and increased heavy metal concentrations. We measured $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios of organic and inorganic C (calcite) in the core sediments to infer decadal trends in nutrient loading and primary production at these sites. We hypothesize that the changes in $\delta^{13}C$ values are linked to increased nutrient loading and eutrophication from agricultural and urban development of the area. Changes in $\delta^{18}O$ values point to disruption of thermal stratification in the lakes and suggests a link to sudden climatic changes or water circulation disruptions in the last century. These changes indicate that ecological stresses of anthropogenic origin warrant renewed management strategies that can return lacustrine environments to their natural state.

INTRODUCTION

Humans have become the principal agents of environmental and biotic change on Earth. There is an increasing need to address anthropogenic changes such as deforestation, eutrophication, and water pollution in our ecosystems. By assessing geohistorical records, we can reconstruct the environmental history of a region, identify ecological thresholds that provide evidence of past or approaching ecological collapse in a lacustrine environment, and respond to those changes with appropriate recovery management solutions. The use of paleoecological techniques to assess recent Holocene environmental changes plays an important role in monitoring and preserving human impacted lacustrine habitats because it provides us with a long-term perspective of ecological changes outside the timescale of direct human observation (Froyd & Willis 2008).

Here we focus on isotopic analysis of lacustrine sediments to track anthropogenic influences on temperate lakes in Wisconsin. This method has been used by others to reconstruct disturbances to the biogeochemical cycle in lacustrine environments (Schelske and Hodell 1991). We hope to construct an environmental history of three temperate lakes in Wisconsin, USA, as a means of improving remediation efforts for lacustrine ecosystems. A multi-proxy approach of assessing the quality of lacustrine environments generates useful data for understanding how anthropogenic activity affects Wisconsin lakes (Froyd and Willis 2008). Stable isotope geochemistry is one such proxy that has been

used as a paleoclimate reconstruction tool since Urey et. al (1951) described oxygen isotope compositions as a potential method of paleotemperature reconstruction. Carbon and oxygen isotopes are widely used proxies for reconstructing the environmental history of an ecosystem. Carbon is widely available in both organic and inorganic substances in lakes. This paper focuses on carbon isotope ratios derived from calcite; the distinction between C isotope ratios of organic carbon and inorganic carbon is important because isotope signatures of dissolved organic carbon and calcite vary greatly (Sadurski 2012). Two stable isotopes of carbon exist in nature, ^{12}C and ^{13}C, although ^{12}C makes up most of the carbon on Earth (only 1‰ is ^{13}C). Carbon isotope fractionation in lake systems occurs normally due to thermodynamic processes of the mineral precipitation reaction of calcite. $\partial^{18}O$ variations in calcite are typically attributed to changes in temperature or ratio of precipitation to evaporation in a lake system (Leng and Marshall 2004). Carbon and oxygen isotope analysis of lacustrine carbonates is a readily-employed technique in paleolimnology, and isotopic relationships of paleoenvironmental significance are discussed in this paper.

METHODS

Study Sites

A total of three lakes were cored between 7 and 22 July 2016, representing different gradients of human impact. These three cored lakes were chosen specifically because they represent different "impact statuses": Lake Monona, located in Madison, Wisconsin, represented the most heavily impacted lake in our survey. Shadow Lake in Waupaca, Wisconsin represented an intermediate, remediated lake. Sparkling Lake represented a "pristine" lacustrine environment and is located in Vilas County, Wisconsin.

Core Processing and Description

We performed initial processing and analysis of cores at the LacCore facility at the University of Minnesota. Cores were prepared for analysis using a series of Geotek machines and a medical cast saw to split the cores into two sections. A variety of computer programs were used to measure magnetic

susceptibility and create core descriptions and stratigraphic columns of the lake cores. A standardized method was used for performing loss on ignition tests in our lake cores, as noted in Heiri et al. 2001. We conducted tests on a single deep core from each lake (Table 1).

Lake	Core ID	Water Depth (m)	Core Length (cm)	Sediment Length (cm)	Pb^{210} Dating
Monona	SAEQ-MONA16-1A-1P-1	5.71	115.4	109.4	No
Monona	SAEQ-MONA16-2A-1P-1	7.35	155.6	154.6	No
Monona	SAEQ-MONA16-3A-1P-1	9.37	121.6	114.6	No
Monona	SAEQ-MONA16-4A-1P-1	12.44	123.1	115.1	No
Monona	SAEQ-MONA16-5A-1P-1	16.65	132.8	125.8	No
Monona	SAEQ-MONA16-5B-1P-1	17.28	81	81	Yes
Shadow	SAEQ-SHOW16-1A-1P-1	9.24	136.2	127.2	No
Shadow	SAEQ-SHOW16-2A-1P-1	5.93	132.3	128.3	No
Shadow	SAEQ-SHOW16-3A-1P-1	1.41	110.4	104.4	No
Shadow	SAEQ-SHOW16-1B-1P-1	9.24	67	67	Yes
Sparkling	SAEQ-SPK16-1A-1P-1	17.82	141	132	No
Sparkling	SAEQ-SPK16-1B-1P-1	17.52	70	70	Yes
Sparkling	SAEQ-SPK16-2A-1P-1	10.01	34	29	No

Table 1. Data on lake name, core ID, water depth, core length, sediment length, and cores extracted for Pb^{210} dating. Cores collected between 7 and 22 July, 2016 at Lake Monona, Shadow Lake, and Sparkling Lake in Wisconsin.

Isotopes

The gravity cores from L. Monona, Shadow, and Sparkling were sampled at 1cm intervals for the first 30cm of each core before switching to 5cm increments. Shadow Lake was later sampled in 1cm increments between 50cm and 100cm to verify results obtained from the mass spectrometer. Sparkling Lake did not contain any calcite, so we were unable to collect a record of $\partial^{13}C$ and $\partial^{18}O$ at this site. Sediment samples were measured on a standard isotope ratio mass spectrometer system. The internal reference standard used in this study was NBS 19 limestone. Isotope compositions from the mass spectrometer represent per mil deviations from the Pee Dee Belemnite carbonate standard (Teranes et al. 1999).
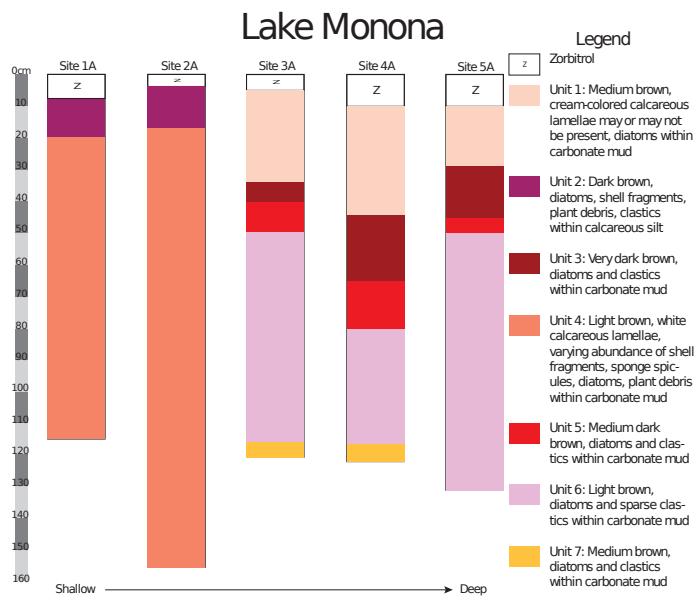
Figure 1. Simplified core description of sites sampled at Lake Monona. Core depth is noted on the left, and a detailed legend of the sedimentary characteristics of each site is presented on the right. Cores are arranged from shallowest to deepest lake depth.

Figure 2. Isotope and LOI data from Lake Monona. Displays core image, carbonate ($CaCO_3$) content, organic C content, $\partial^{13}C$ and $\partial^{18}O$ values, and magnetic susceptibility data.

RESULTS

Lake Monona

From the base of Core 5A upwards, the sedimentology of Lake Monona indicates a homogenous carbonate-rich mud with layers of calcareous silt, clastic, and organic material such as plant debris, shell fragments, and sponge spicules appearing above 40cm in sediment depth (Fig. 1). Calcite composition decreases with time and ranges from 33 to 71%. Organic C composition oscillates between 12 and 24% and experiences no net change overall. Isotopic data from core 5A of Lake Monona indicate a relatively stable trend in $\partial^{13}C$ and $\partial^{18}O$ values compared to Shadow Lake (Fig. 2 and 4).

A complete $\partial^{13}C$ record of calcite is present in Lake Monona starting at the base of the core at 120cm until reaching the sediment water interface at 11cm. C isotopic ratios fluctuate between a maximum of 0.42‰ at 84cm and a minimum of -1.91‰ at 1cm, and generally decrease upcore. Between 104 and 29cm,
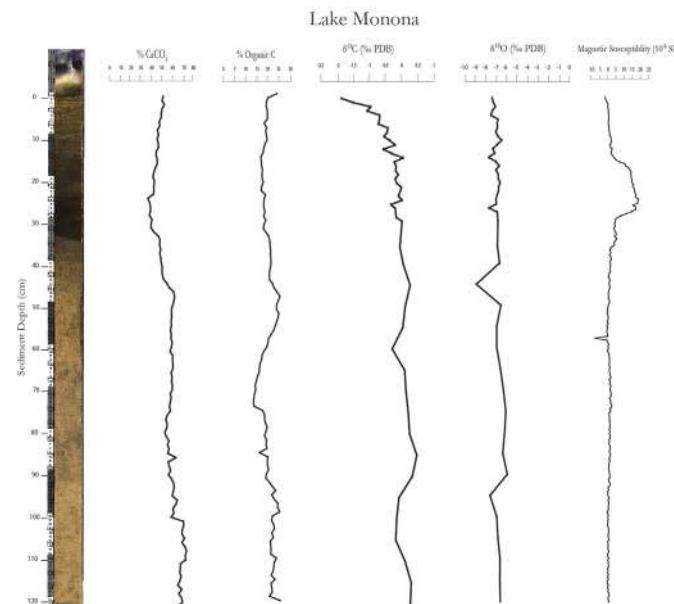
$\partial^{13}C$ values oscillate between -0.34‰ and 0.41‰ in a relatively stable manner. Beginning at 29cm through the top of the core, $\partial^{13}C$ values steadily decrease by nearly 2‰ (from -0.03‰ to -1.91‰). This decrease coincides with increased organic C and calcite content above 29cm. The magnetic susceptibility increases from 5.6 to 18.7 between 30-25cm before steadily decreasing again to -1.6 at the top of the core (0cm) (Fig. 2). We consider the sudden drop in magnetic susceptibility at 58cm to -7.6 to be an outlier.

$\partial^{18}O$ values in calcite range from a maximum of -6.06‰ to a minimum of -8.99‰, although this minimum could be considered an outlier. Several punctuated negative excursions in $\partial^{18}O$ values occur between 95 and 90cm as well as between 50 and 40cm. From 95 to 90cm, $\partial^{18}O$ values increase sharply from -7.71 to -6.06‰. The largest change occurs between 60 and 50cm, where $\partial^{18}O$ sharply decreases from -6.66 to -8.99‰ and increases from -8.99 to -6.79‰ between 45-40cm (Fig. 2).
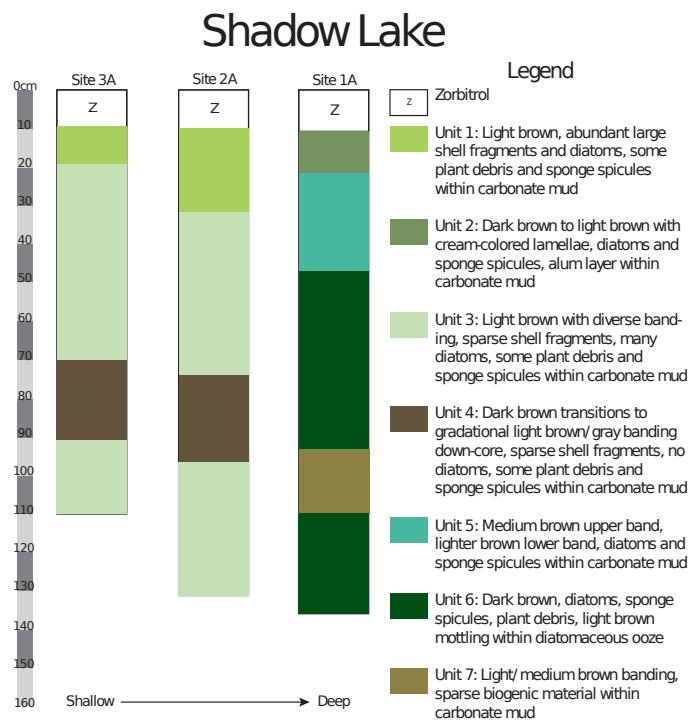
Shadow Lake

Figure 3. Simplified core description of sites sampled at Shadow Lake. Core depth is noted on the left, and a detailed legend of the sedimentary characteristics of each site is presented on the right. Cores are arranged from shallowest to deepest lake depth.

Figure 4. Isotope and LOI data from Shadow Lake. Displays core image, carbonate ($CaCO_3$) content, organic C content, $\partial^{13}C$ and $\partial^{18}O$ values, and magnetic susceptibility data.

Shadow Lake

From the base of core 1A upwards, the sedimentology of Shadow Lake is dominated by a very dark brown, mottled carbonate mud with diatomaceous ooze and sponge spicules. A transition occurs at approximately 40cm where the carbonate mud becomes significantly lighter and dominated by shelly debris and sponge spicules. A layer of alum was noted between 7 and 8cm, followed by a transition to dark brown carbonate mud with cream colored laminae to the top of the core (Fig. 3). Calcite composition fluctuates between a minimum of 1.6% at 70cm and a maximum of 63.3% at 27cm (Fig. 4). Organic C levels tend to decrease upcore, ranging from 8.2% at 8cm to 77.6% at 40cm. The largest decrease in organic C content occurs between 38 and 28cm, where weight composition decreases from 77 to 15%. This sudden change was attributed to sedimentological changes in this section of the core. (Insert Figure 4 after.)

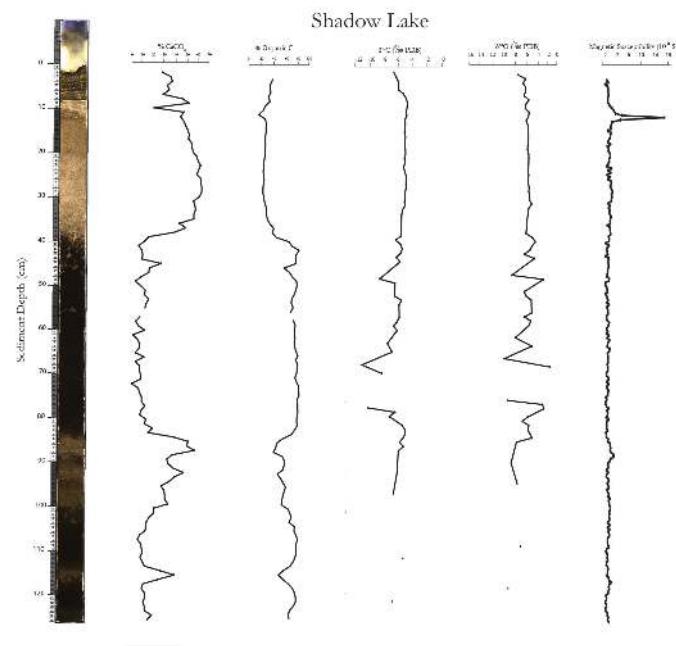Isotopic data from Shadow Lake is partially incomplete because calcite was often too low to measure isotopically throughout two sections of the core (from 48-78cm and 118-123cm). The $\partial^{13}C$ of calcite generally increased upcore, but experienced fluctuations throughout (Fig. 4). C isotope ratios ranged from a minimum of -10.26‰ at 68cm to a maximum of -1.74‰ at 7cm. Between 98 and 83cm, $\partial^{13}C$ values increased from -4.40 to -2.18‰. This trend reverses dramatically between 83 and 68cm, where C isotope values plunge from -2.18 to -9.10‰ at 78cm and then to -10.26‰ at 68cm. C isotope values increase again between 68 and 53 cm and 48 and 7cm, with a punctuated decrease between 53 and 48cm. These values stabilize between 38 and 8cm to about -2‰ before decreasing to -4.3‰ at 0cm (Fig. 4).

Calcite $\partial^{18}O$ from Shadow Lake are highly variable (-13.3 to -1.7‰) and shift between 7 to 11‰ over short (5cm) intervals. $\partial^{18}O$ seem to follow a pattern of cyclical fluctuations between 98 and 31cm. Above 31cm, values stabilize to between -7 and -8‰ and then dip slightly at the top of the sediment layer (-9.8‰). In general, $\partial^{18}O$ values throughout the core were more positive than modern top core values (Fig. 2).

DISCUSSION

Lake Monona and Shadow Lake display very different isotopic results because of significant limnologic variations at each site, which we must consider when reconstructing our environmental history of the lakes. Variations in the carbon isotope ratio of calcite precipitation should be recognizable in the isotopic composition of underlying lacustrine sediments (McKenzie 1985). Increased bulk organic C and fluctuations in $\partial^{13}C$ values from calcite have been interpreted as indicators of eutrophication history and primary productivity in lacustrine systems (Schelske and Hodell 1991; Teranes et al. 1999). A long-term enrichment of $\partial^{13}C$ over time occurs due to preferential removal of the lighter isotope ^{12}C from the euphotic zone late summer months, when calcite is biologically precipitated in the epilimnion (the topmost layer of water in a stratified lake) (Schelske and Hodell 1991). Other lake sediment studies have noted that increased calcite accumulation is linked to increased lake productivity due to eutrophication (McKenzie 1985; Teranes et al. 1999). Because the $\partial^{13}C$ record in Lake Monona follows a generally cyclical pattern, we infer a history of normal seasonal changes related to thermal stratification and primary production until the negative excursion of $\partial^{13}C$ near the top of the core (Figure 2). A decrease in $\partial^{13}C$ reflects decreased primary productivity as biologically induced calcite production slows and isotopically light CO_2 remains in the epilimnion. A steady increase in calcite accumulation followed by a negative $\partial^{13}C$ excursion in Lake Monona near the top of our core suggests that attempts were made to reduce pollution and eutrophication by reducing phosphate levels, which would correspond with a trend towards more negative $\partial^{13}C$ values (McKenzie 1985). $\partial^{18}O$ values in Lake Monona fluctuate very little compared with Shadow Lake, which is much smaller and shallower and thus more sensitive to large calcite $\partial^{18}O$ shifts. In Lake Monona, $\partial^{18}O$ values follow a cyclical pattern that becomes less pronounced above 30cm, which could be related to pressure from humans and a possible ecosystem shift.

The $\partial^{13}C$ and $\partial^{18}O$ record of Shadow Lake is considerably different from that of Lake Monona, and we attribute the larger fluctuations from our results to the smaller size of the lake, which would increase its sensitivity to changes in the carbon and hydrologic cycles (Leng and Marshall 2004). However, records of the environmental history of Shadow Lake already exist and might shed light on the results obtained from our study (Welch and Cooke 1999; Turyk et al. 2004). $\partial^{13}C$ fluctuates from the base of the core to the 40cm mark suggest natural processes in the carbon cycle. The rapid increase in calcite production at this interval, coupled with a termination in the $\partial^{13}C$ rhythm points to a spike in productivity due to eutrophication. This might correspond with events at Shadow Lake in the 1960's and 70's, noted in Turyk et al. 2004, of cultural eutrophication occurring due to runoff from the increasingly urbanized town of Waupaca, WI near the lake system. We attribute a similar disruption to the $\partial^{18}O$ cycle in Shadow Lake as a major restructuring of its hydrologic cycle. Between the 1930's and 1950's an outflow from Shadow Lake was dredged to connect it to the Crystal River, while a wetland inflow was channelized at the same time, diverting stormwater drainage from Waupaca, WI directly into the lake system (Welch and Cooke 1999).

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