Carbonate Paleothermometry in Fayetteville Green Lakes

Micah Wiesner

Abstract

Lacustrine carbonates are important paleoclimate archives, but unkowns in the seasonal timing and depth of precipitation obscure the interpretation of temperatures associated with them. The clumped isotope paleothermometer records the formation temperature $T(\Delta_{47})$ of carbonates. This study examines a set of lacustrine carbonates formed in the water column in addition to core carbonates to better understand the depth and seasonality of carbonate formation in a lacustrine setting. We test that, regardless of season and formation temperature, lacustrine carbonates form in isotopic equilibrium with respect to Δ_{47} and $\delta^{18}O$ fractionation. Further, we account for the effect of our sampling regime, glass-fiber filters mixed with water column calcite, on Δ_{47}, $\delta^{18}O$ and $\delta^{13}C$. Carbonate and water was sampled from Fayetteville Green Lake at depths of 0.5, 2.5, 5, 7.5, 10, and 15 meters below the lake surface. Short core segments, from no deeper than 12 cm depth, were analyzed to compare against water column calcites. Water column carbonate was found throughout the entire season with maximum concentrations of 1.4 mg/l sampled on July 11 at 7.5 meters depth. Average

water column carbonate $\delta^{18}O$ was found to be -9.64 $\pm$ 0.32 $^0/_{00(VPDB)}$. Average core $\delta^{18}O$ values were found to be -9.80 $\pm$ 0.16 $^0/_{00(VPDB)}$, while the average $\delta^{18}O$ from surface water was measured to be -9.10 $\pm$ 0.10 $^0/_{00(VSMOW)}$. $T(\Delta_{47})$ from core carbonate was calculated to be 24 $\pm$ 7 $^\circ C$. Our results suggest that even in lakes prone to whiting events and large temperature and saturation fluctuations carbonates precipitate in isotopic equilibrium with respect to $\delta^{18}O$ and Δ_{47}. $T(\Delta_{47})$ recorded in the sedimentation of Fayeteville Green Lake is indistinguishable from modern summer mean surface water temperatures recorded in June, July, and August. This largely supports the work of Hren and Sheldon in showing that $T(\Delta_{47})$ is a warm season proxy. Our results also suggest that lacustrine carbonates reflect temperatures from the upper 2.5 meters of the water column.

Contents

Discussion   **26**

Conclusions   **33**

References   **34**

List of Figures

Introduction

Geochemical approaches to interrogate the sedimentary archive yield remarkable insight into past environmental conditions across the continents and oceans alike, yet accurate reconstruction of terrestrial temperatures has remained one of the grand challenges to deciphering the paleoclimate record. The lacustrine sedimentary record of marl lakes and other carbonate forming lakes offers great potential in estimating terrestrial temperatures. This carbonate, which forms in the water column and settles into sediment cores, is an abundant sedimentary archive, and records both the formation temperature $T(\Delta_{47})$ in the relative enrichment of the ^{13}C-^{18}O bonds, Δ_{47}, (Eiler 2007) and the formation temperature from the enrichment of $\delta^{18}O$ from H_2O-$CaCO_3$, assuming $\delta^{18}O$ of formation waters is known (McCrea 1950; Kim and O'Neil 1997)).

Although researchers have begun to tease apart how mean surface water temperatur[e (MAWT) relates to mean annual air temperature (MAAT) in lakes (Hren and Sheldon 2012) it is still unclear how recorded carbonate formation temperatures relate to mean annual air temperature. I presume that temperatures $T(\Delta_{47})$ recorded from sediment cores will exceed MAAT as aqueous $CaCO_3$ supersaturation within northern hemisphere lakes reaches its highest values from late May to October (Stabel, 1986; Brunskill, 1969b), a time in which temperatures air in excess of MAAT.

There are no studies of clumped isotopes in modern lake water column carbonates, only a compilation of modern temperature data with clumped isotope records from cores (Hren and Sheldon, 2012) and a few samples ranging from the Pliocene to the Eocene (Huntington,

2010). This study seeks to straddle the unknowns associated with ancient lake settings and idealized laboratory environments by utilizing Fayetteville Green Lake (FGL) (Fig. 1) as a natural laboratory to further probe carbonate paleothermometry. Large amounts of calcite precipitate in Fayetteville Green Lake, making it an ideal natural setting to further test the clumped isotope paleothermometer, in addition to exploring whether oxygen isotope fractionation occurs in equilibrium (McCrea (1950); Kim & O'Neil, 1997). Our objectives are to explore the accuracy of each proxy, the clumped isotope thermometer and the stable isotope thermometer, to determine the seasonal signal recorded in sediment cores, and how seasonal signals for each proxy relate to MAAT in a lake.

Background

Lacustrine Carbonate Formation

Lacustrine carbonates form throughout the year following the basic carbonate reaction,

$$1.\ [Ca^{2+}] + [CO_3^{2-}] <-> CaCO_3(s)$$
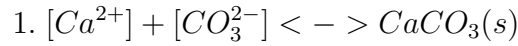
in which $[Ca^{2+}]$ and $[CO_3^{2-}]$ are ionic activies at equilibrium (*Lakes, Chemistry, Geology, Physics*, 1978). The saturation state and amount of calcite precipitated is controlled directly by the $[CO_2]$ dissolved in lake waters in the form of $H_2CO_3^*$ and the pH of the water in the following relation,

$$2.\ \frac{[CO_3^{2-}][H^+]^2}{[H_2CO_3^*]} = K_1 K_2$$

in which $H_2CO_3^*$, $[CO_3^{2-}]$, and $[H^+]$ are the activity of dissolved CO_2, $[CO_3^{2-}]$, and $[H^+]$, while K_1 and K_2 are the dissociation constants of $H_2CO_3^*$ Stumm and Morgan (1970). In a first order sense, Henry's Law (equation 3),

$$3.\ \frac{[H_2CO_3^*]}{p_{CO_2}} = K_H$$

determines the amount of $H_2CO_3^*$ in solution in the water column, though $H_2CO_3^*$ in most lake waters is supersaturated (Cole et al., 1994). Dissolved CO_2 concentrations, $[H_2CO_3^*]$ in lake waters are controlled by changing temperatures (equation 4),

$$4.\ log K_c = 13.870 - 0.04035T - \frac{3059}{T}$$

which over annual lake temperatures of 0-25°C, varies K_c, the solubility constant of calcium carbonate, from -8.35 to -8.42 Plummer and Busenburg (1982), as well as biologic processes, Dissolved Organic Carbon (DOC) concentration (Jonsson et al., 2003), and photosynthesis decreasing available CO_2 (Stumm & Morgan, 1970, p. 429, Talling, 1976; Thompson & Ferris, 1990). Combining all relevant variables from the equations 1-4 leads to the following equation for the saturation state of calcite,

$$5.\ \alpha_{CaCO_3} = \frac{[Ca^{2+}] * pCO_2 * K_1 * K_2 * K_H}{[H+]^2 * K_c}$$

In environments in which $\alpha_{CaCO_3} > 1$ precipitation of $CaCO_3$ is expected, though $CaCO_3$ precipitation often doesn't occur until α_{CaCO_3} far exceeds 1. $CaCO_3$ precipitation can be inhibited by PO_4^{2-} Burton and Walter (1990), Mg/Ca ratio Choudens-Sanchez and Gonzalez (2009), as well as other factors.

Δ_{47} and $\delta^{18}O$ thermometry

Carbonate clumped isotope thermometry is based on the 'clumping' of ^{13}C-^{18}O bonds within $CaCO_3$ Eiler (2007). This 'clumping' (equation 6) is inversely dependent upon temperature Eiler (2007). This technique has the advantage over traditional stable isotope thermometry in that it records temperature independent of the isotopic composition of waters from which carbonates grow Eiler (2011).

$$6.\ Ca^{13}CO_3 + Ca^{12}C^{18}O^{16}O_2 = Ca^{13}C^{18}O^{16}O_2 + Ca^{12}C^{16}O_3 (Eiler, 2011)$$

Recent research has focused on understanding if precipitation rate, water ionic strength, I, and pH affect the clumped isotope temperature calibration Tang et al. (2014) and Watkins et al. (2013). In addition, there is debate as to whether kinetic isotope effects (KIE) can change the Δ_{47} values of carbonates (Tang et al., 2007, Daëron et al. (2019)).

The $\delta^{18}O$ composition of $CaCO_3$ is dependent upon the $\delta^{18}O$ composition and temperature of formation waters Urey (1947) Epstein et al. (1951). $\delta^{18}O$ value of lake water is controlled by the $\delta^{18}O$ composition of meteoric waters and groundwater. The $\delta^{13}C$ composition of $CaCO_3$ is largely controlled by the $\delta^{13}C$ of dissolved inorganic carbon (DIC) (Romanek et al., 1992), of which the largest reservoir at surface water pH is HCO_3^-. The temperature dependent fractionation of $\delta^{18}O$ between the aqueous and solid phase can be defined by equation 7 Kim and O'Neil (1997). Daeron et al. (2019) recently challenged Kim and O'Neil's (1997) equilibrium fractionation curve with a new relationship (eq. 8) defined by data from two very slowly crystalizing isotopic end-member samples that better explain the apparent divergence of some carbonate developed at equilibrium with equation 7.

$$7.\ 1000ln(\alpha) = \frac{18.03 * 10^3}{T} - 32.42 (Kim O'Neil, 1997)$$

$$8.\ 1000ln(\alpha) = \frac{17.57 * 10^3}{T} - 29.13 (Daeron, 2019)$$

Study Area

Fayetteville Green Lake, NY, is interpreted as a bedrock plunge pool formed by differential erosion driven by channelized flow of glacial meltwater from the receding Laurentide ice sheet flowing east into the Mohawk Valley (Miner, 1933; Hilfinger & Mullins, 1997). The channel

and plunge pool likely formed ~13,000 years ago during the recession of the Last Glacial Maximum Hilfinger et al. (2001), and is adjacent to Round Lake, another glacially formed plunge pool. FGL is a meromictic lake. Due to its small surface area, and impressive depth (52 meters) the upper layer of the lake (mixolimnion) does not mix with the lower layer (monimolimnion) Brunskill (1969).

The mean annual air temperature, MAAT, was calculated to be 9°C (Fig. 1) from 1938-2018, while the mean annual (surface) water temperature MAWT at FGL from 1965 to 1967 was 12°C. Surface water temperatures in Fayetteville Green Lake range from 0-25°C by season Brunskill and Ludlam (1969). These temperatures are driven by drastic changes in local air temperature and drive the degassing of CO_2 from the water column.

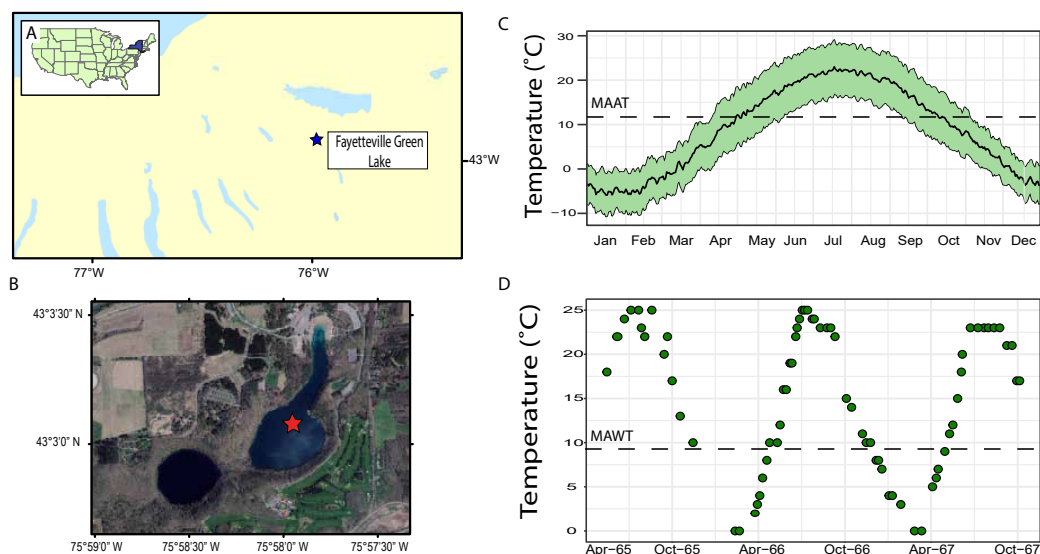Figure 1: Study Area

Figure 1: (A,B) Fayetteville Green Lake is located in upstate New York. (C) Minimum and Maximum air temperature were averaged for each day from 1937 to 2018 from Syracuse Hancock Airport, Site USW00014771 [NOAA], 15 km from FGL. (D) MAAT at FGL is 12 C. Surface water temperatures measured by Brunskill from 1965-1967 show FGL surface water temperatures range from 0-25 C annually.

Sedimentation in FGL is dominated by Summer calcite deposition. Brunskill (1969b) showed calcite to account for 90% of total deposition from June-October. Rates of sedimentation have been calculated to be 0.11 $mm * yr^{-1}$ (Brunskill, 1969b), 0.14 $mm * yr^{-1}$ (Takahashi et al, 1968), and 0.258 $mm * yr^{-1}$ (Ludlam, 1969). Brunskill (1969a) gives a water residence time of 1-1.7 years for the mixolimnion and 2-3 years for the entire lake.

In addition to annual whiting events, periods of massive calcite precipitation during which the lake surface appears white, the lake constantly precipitates calcite throughout the water column. Warming during the summer months reduces solubility of CO_2 accompanied by a rise in pH and an increased saturation of calcite in the water column. Microbial forcing has been posited as an alternative explanation to the formation of calcite within the water column Thompson, Ferris, and Smith (1990), though there is uncertainty to what degree this is the cause. Fayetteville Green Lake also contains thrombolytic tufa deposits (Demott, 2018; Demott et al., 2020). These thrombolites are composed of microcrystalline calcite, likely deposited by Synecchoccus cells living in microbial mats at the edge of the lake Thompson, Ferris, and Smith (1990).

Methods

Field Work

Every two weeks from May 2019 to October 2019 water and calcite from Fayetteville Green Lake was sampled. Calcite laden water was pumped from various depths through a filter apparatus where calcite was captured on 142 mm glass-fiber filters with $> 1\ \mu m$ particle retention while the remaining water was pumped back down to the depth it was sampled. Generally, samples were collected at 0.5, 2.5, 5, 7.5, 10, and 15 meters, but occasional inclement weather, technical difficulties, or time constraints did not permit the full depth sampling on each trip. The total volume of water sampled at each depth was measured using a conventional household water flow meter and ranged from 30 l to 175 l depending on the date and depth sampled. Temperature was measured from post-filter outflow using a hand held digital thermometer with a precision of $\pm$ 0.1 °C. Multiple water samples have been taken at each depth so that water isotopic content and major anions and cations can be measured from each respective sample. A separate filter housing holding a 47 mm diameter 1 micron glass fiber filter was used to filter the organic matter containing the GDGTs. Filters containing GDGTs were freeze dried prior to extraction and analysis.

SEM

The contents of the glass-fiber filters was analyzed using a *JCM-6000Plus* Scanning Electron Microscope. Grain morphology, specifically the size of calcite crystals, was measured for multiple filters and multiple depths. We initially assumed that the majority of calcite

produced in the water column would be between 1 and 50 μm in length. SEM analysis has shown that the majority of calcite crystals captured range from 5 to 20 μm in length, with the median crystal length being 10 μm.

Water Chemistry and Water Isotope Analysis

In concert with calcite sampling water samples were collected from each sampling depth. Samples were collected in 60 mL polyethylene bottles, after being filtered through a 1 μm glass-fiber filter. Bottles were filled to contain no headspace to minimize isotopic fractionation with air and were stored in a refrigerator at ~2°C. Water samples were analyzed for total major anion and cation water chemistry using a Dionex Ion Chromatograph. Using the IC results HCO_3^- was calculated for each depth to satisfy the charge balance of each sample. Field titration data provided by Nick LaRusso and Svetoslava Todorava (Environmental Engineering, Syracuse University) has shown the charge difference calculation method for HCO_3^- to be consistent and accurate within this setting. The ^{18}O and ^2H isotope composition of water for each sample was determined on a *Picarro i2130 CRDS analyzer*.

Carbonate Stable Isotope Analysis

Because the calcite is trapped within the matrix of the glass fiber filter samples were crushed along with the accompanying glass-fiber filter using a ball-mill. The percent carbonate of the aggregate glass fiber filter and sample was measured by calcimetry in which CO_2 evolved from a known mass of synthetic carbonate was correlated to pressure. The stable isotope composition of all carbonates, $\delta^{13}C$ and $\delta^{18}O$, was measured at the University of

Washington's Isolab using a Kiel III Carbonate Device coupled to a Finnigan Delta Plus isotope ratio mass spectrometer (IRMS) for a dual-inlet based $\delta^{13}C$ and $\delta^{18}O$ measurement of carbonate samples. The Kiel III Carbonate Device reacts carbonate samples of ~100 μg with H_3PO_4 for 4.5 minutes. Water vapor from the evolved CO_2 is removed and the CO_2 is analyzed with a mass spectrometer to determine the $\delta^{18}O$ and $\delta^{13}C$ relative to a reference gas.

Clumped-Isotope Analysis

The majority of samples were a mixture of carbonate, and glass-fiber filter material ranging in $CaCO_3$ content from ~2-5%. In addition to these samples, 7 analyses from 2 sections of FGL sediment core, approximately 50% $CaCO_3$ content, were also analyzed. [Number of water column and sediment core samples] were selected for clumped isotope (Δ_{47}) analysis at the University of Washington IsoLab. Sample preparation methods followed Burgener et al. (2016), and data processing methods were modified after Schauer et al. (2016); analytical details, data, and data-processing scripts can be found in the EarthChem data repository. For each analysis, 6-8 mg of $CaCO_3$ powder, and the accompanying glass-fiber filter, was reacted in a common H_3PO_4 bath at 90°C for between 10 and 30 minutes. Resulting CO_2 from the reaction was purified through cooled gas traps of -80°C (ethanol and liquid nitrogen) and a Porapak Q trap (50/80 mesh, 122 cm long, 6.35 cm OD) at -10 to -20°C and sealed in a pyrex tube. Gas within these tubes was then transferred to a 10-port Thermo MAT 253 isotope ratio mass spectrometer with 6 faraday cups (m/z 44-49) for $\delta^{13}C$, $\delta^{18}O$, and Δ_{47} measurement. ^{13}R, ^{18}R, and ^{17}R values were calculated using ^{17}O correction parameters

from Brand et al. (2010). $\delta^{18}O$ carbonate and $\delta^{13}C$ were converted to VPDB scales using internal Isolab laboratory standards. The data were screened based on a series of thresholds for pressure baseline (PBL), number of cycles, bellows pressure, bellows mismatch, $\delta 45$ standard deviation, $\delta 46$ standard deviation, $\delta 47$ standard deviation, and $\delta 48$ standard deviation. Replicate analyses, numbering 2-5 replicates, were completed on all samples. Each day, at minimum one calcium carbonate reference material was run (ETH 1-4 (Bernasconi et al., 2018) or in-house standards including reagent grade calcites C64, C2, 20C_9 and a Porites coral). Δ_{47} values were placed on the carbon dioxide equilibrium scale (CDES) using CO_2 heated to 1000°C and CO_2 equilibrated with water at 60°C and 4°C. Temperature reconstructions (TΔ47) values were calculated from sample mean Δ_{47} values using an acid fractionation factor of 0.088 and the Petersen et al. (2019) calibration, and reported with 95% confidence interval.

The Δ_{47} values were normalized using a suite of carbonate standards over a three-year period of measurement which includes a large proportion of data generated by Kelson et al. (2017), and during which ETH standard values used in interlaboratory comparison (Bernasconi et al., 2018) were generated. This correction is more optimal than ETH standards because of the abundance CDES gas data in comparison to ETH, the much smaller range of Δ_{47} and $\delta 47$ values of ETH carbonates compared to CDES gases, and large variability in Δ_{47} and $\Delta 17O$ of ETH-1 and ETH-2 observed in our laboratory. The magnitude of the correction is 0.01-0.02‰.

Results

Water Temperature, Isotopes, and Chemistry

Water temperatures measured from May to October, 2019 were similar to values measured by Brunskill (1969a). Summer (JJA) surface water temperatures ranged from 20 - 25°C. The Summer surface maximum occurred in mid July and was 25°C.
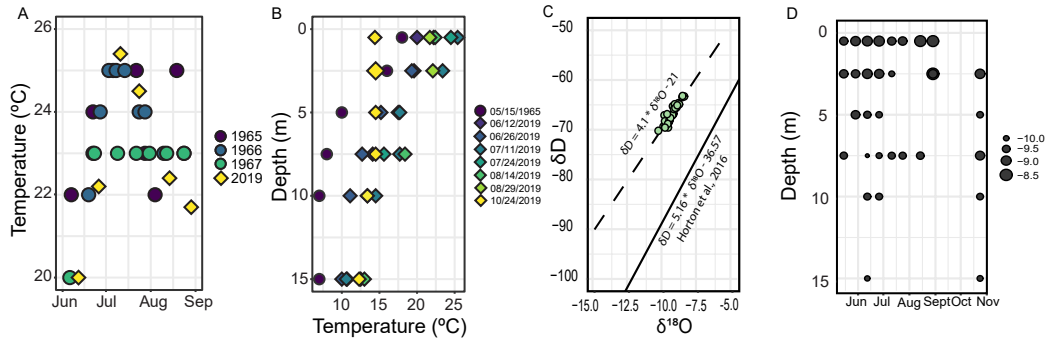

Figure 2: Water Summary

Figure 2: (A, B) Surface temperature and temperature with depth measured in 2019 in FGL. May temperatures from 1965 (Brunskill, 1969a) were used in place of actual data from this period of time in 2019. (C) $\delta^{18}O$ and δD values from FGL averaged around -9.4 and -67 $^0/_{00(VSMOW)}$. (D) Surface water $\delta^{18}O$ in FGL is slightly depleted due to evaporation in comparison to deeper waters.

$\delta^{18}O$ values of FGL waters were measured to range from -10.4 to -8.5 $^0/_{00(VSMOW)}$. Our entire data set yielded an average summer $\delta^{18}O$ value of -9.4 $^0/_{00(VSMOW)}$. The effect of the isotopic enrichment due to evaporation in FGL is largest in surface waters (Fig. 2B). Surface waters, sampled from 0.5 and 2.5 meters depth, yielded an average of -9.13 $^0/_{00(VSMOW)}$. In comparison to our lake water, Ledford & Lautz (2015) reported groundwater $\delta^{18}O$ values ranging from -10.3 to -7.8 $^0/_{00(VSMOW)}$ at a site ~15 km from ours.

17

The meteoric water line of FGL is defined by a smaller slope, 4.1, in comparison to the expected global meteoric water line slope of 8 (Craig, 1961). Global studies of lacustrine systems have confirmed that, similar to FGL, lacustrine water is more isotopically enriched in both δD and $\delta^{18}O$ (Horton et al., 2016) compared to global meteoric waters. The global lacustrine water line can be described by equation 9 (Horton et al., 2016).

$$9. \delta^2 H = 5.16 * \delta^{18}O - 36.57 (Horton, 2016)$$

Water samples from May to August, 2019 were analyzed for total anion and cation content. Concentrations varied seasonally, but were ~10 mM/l and 1 to 2 mM/l for Ca^{2+} and HCO_3^-, respectively. Ca^{2+} concentrations varied throughout the Summer by ~0.5 mM/l. The lowest concentrations of Ca^{2+} was 9.2 mM/l and occurred on the hottest day sampled, July 11 in surface waters.
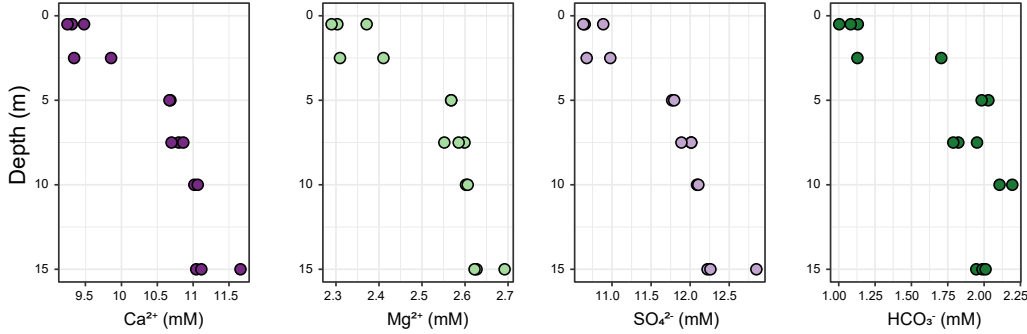

Figure 3: Water Chemistry

Figure 3: Major cation and anion concentrations from the water column of FGL from samples from May, 2019, to September, 2019. Concentrations increase linearly as depth increases towards the chemocline.

From June until July water column concentrations of calcite increased. The highest water

column concentration of calcite occurred on July 11, 2019 at 7.5 meters depth (Fig, 4) and was ~1.4 *mg/l*. This largely agrees with Brunskill (1969b) who found that maximum crystal concentrations general coincided with the thermocline depth. Brunskill and Ludlam (1969b) found a density increase of 0.3 $mg * cm^-3$ to accompany the thermocline. This density barrier explains the increased calcite concentration as calcite crystals slow down prior to passing this layer.
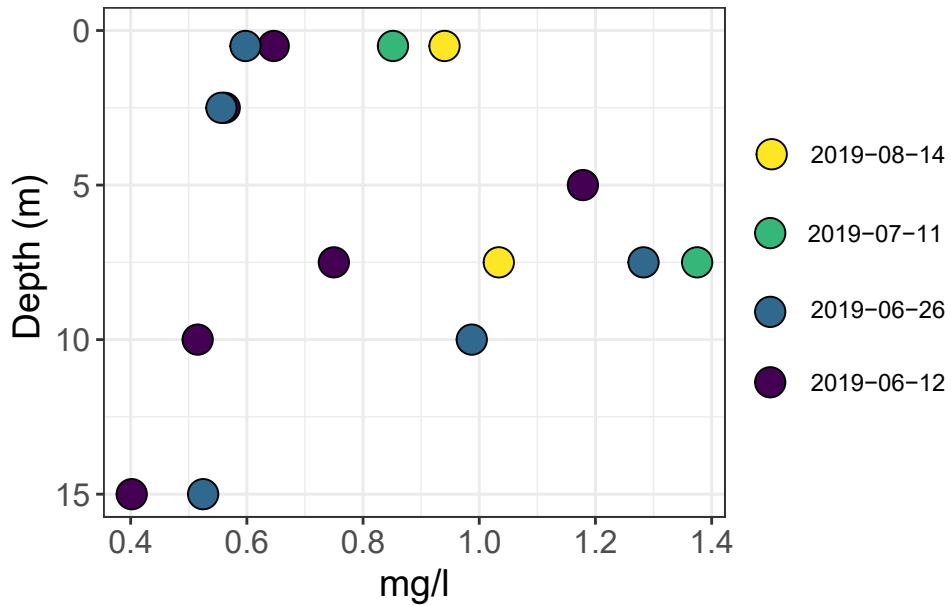
Figure 4: Crystal loads

Figure 4: Crystal loads measured from June to October, 2019 yielded between 0.4 and 1.4 mg/l suspended calcite. The maximal depth of suspended calcite correlates strongly with the thermocline, which moves vertically throughout the summer.

Transfer Functions

Using a global compilation of temperature data empirical transfer functions have been derived to describe MAAT from summer surface average (J,J,A), spring surface average

(A,M,J), and Spring-Summer surface average temperatures (A,M,J,J,A,S,O) (Hren & Sheldon, 2012, eq. 10-12). Water temperature data from this study are limited to the months of May, June, July, August, and October. Using both historically measured temperatures (Brunskill, 1969a) and values measured in this study allows all transfer functions (eq. 7-9) to be utilized.

$$10. \ [JJA] \ MAAT(\circ C) = -0.0055 * Tw^2 + 1.476 * Tw - 18.915$$

$$11. \ [AMJJASO] \ MAAT(\circ C) = -0.00146 * Tw^2 + 1.753 * Tw - 16.079$$

$$12. \ [AMJ] \ MAAT(\circ C) = -0.0097 * Tw^2 + 1.379 * Tw - 8.23$$

Using the summer average transfer function (J,J,A) with data from this study gives a mean annual air temperature of 12°C. Using the summer average transfer function (J,J,A) with data from Brunskill's study also yields 12°C. Applying Brunskill's dataset to Equations 11 and 12 yields mean annual air temperatures of 15°C and 9°C, respectively.

Low % $CaCO_3$ Effect on $\delta^{18}O$, $\delta^{13}C$, and Δ_{47} in Carbonate Samples

Standards analyzed with the same binder free, crushed borosilicate glass-fiber material suggest that these standards exhibited a larger range of variability than UW's long-term standards with respect to Δ_{47}, $\delta^{13}C$, $\delta^{18}O$ (Fig. 3). Further, these standards showed a marked negative offset in $\Delta 47$, and a positive offset in $\delta^{18}O$. It should be noted that the mass ratio of carbonate to borosilicate glass in samples analyzed in the clumped line was ~ 5% (~5-10 mg of CaCO3 to ~100-300 mg filter).

Samples with lower % carbonate showed a larger offset from the Δ_{47} values predicted for the range of measured lake water temperatures. The average Δ_{47} offset from high GFF content is -0.06 $^0/_{00}$, which yields temperatures considerably higher than measured water temperatures. In surface water conditions, temperatures ~8℃-30℃, an offset of -.06 yields a temperature ~20℃ higher than actual water column temperatures. In our analysis a bulk correction of 0.06 $^0/_{00}$, Δ_{47}, and -0.289 $^0/_{00}$, ,$\delta^{18}O$, was applied to all samples.
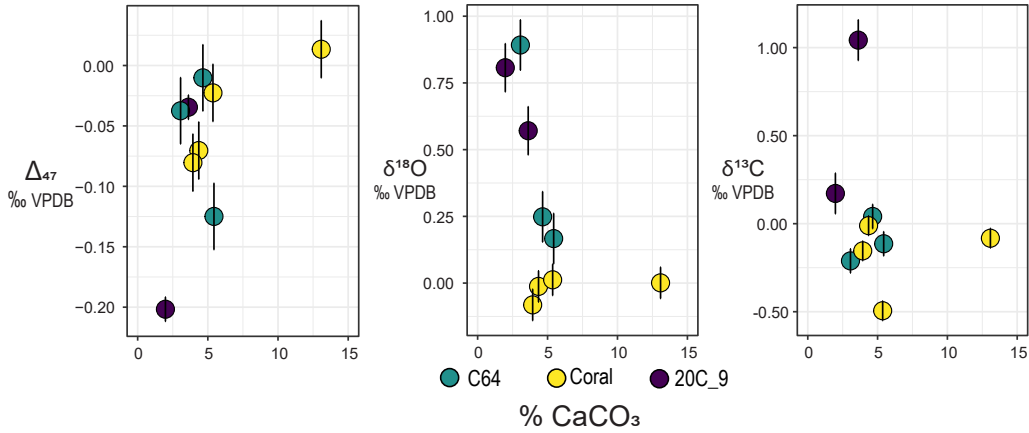
Figure 5: Analytical Corrections

\begin{singlespace} Figure 5: Calcite standards (Coral, C64, and 20C_9) mixed with glass fiber filter material was shown to increase $\delta^{18}O$ by 0.289 $^0/_{00(VPDB)}$ and decrease Δ_{47} by 0.063 $^0/_{00(VPDB)}$ in comparison to the same long-term standard values run at UW Isolab. The offset of $\delta^{13}C$ is negligible, but the variance of this measurement has increased. A standard of ~ 13% calcite shows no clear offset from long term standards. Coral and C64 are long term UW Isolab standards while 20C_9 was created by Kelson (2017). \end{singlespace}

$\delta^{18}O$, $\delta^{13}C$, Δ_{47} results

Water column and core carbonate $\delta^{18}O$, $\delta^{13}C$, Δ_{47} are reported in Table 1. The $\delta^{18}O$ of water column carbonates ranges from -10.00 to -7.12 $^0/_{00(VPDB)}$, and $\delta^{13}C$ ranges from -8.90 to -6.50 $^0/_{00(VPDB)}$ All water column samples analyzed on the MAT253 were corrected for the offset due to low % carbonate. This offset was -0.06 $^0/_{00(VPDB)}$ for Δ_{47}, and 0.289 $^0/_{00(VPDB)}$ for $\delta^{18}O$. $\delta^{13}C$ was not adjusted. Using Pierce's Rejection Criterion (n = 13) sample 190626_5 was found to be an outlier based on its Δ_{47} value.

Two different core sections were analyzed for clumped isotopic content (Δ_{47}), at 11.5-12 cm depth and 2.5-3 cm depth. Assuming a sedimentation rate 0.258 $mm * yr^{-1}$ (Ludlam, 1969) these core sections were deposited 97 and 446 years ago, thus each core is representative of the current climate. $\delta^{18}O$ of core carbonates ranges from -9.90 to -9.67 $^0/_{00(VPDB)}$, and $\delta^{13}C$ (VPDB) ranges from -5.16 to -4.28.

Sample	Δ47	σ Δ47	Δ47*	δ¹⁸O	σ δ¹⁸O	δ¹³C	σ δ¹³C	n	T (Δ47)
190515_0.5	0.63	0.07	0.69	-7.12	0.74	-8.36	0.03	6	23
190515_7.5	0.62	0.04	0.69	-7.49	0.03	-8.48	0.05	2	26
190529_5	0.64	0.04	0.7	-8.47	0.65	-8.9	0.13	7	22
190612_0.5	0.58	0.02	0.64	-9.63	0.03	-6.97	0.09	3	44
190612_5	0.57	0.38	0.63	-9.23	0.01	-6.9	0.02	2	48
190612_7.5	0.59	0.23	0.66	-9.39	0.24	-7.86	0.01	2	37
190711_0.5	0.62	0.02	0.69	-10.00	0.54	-6.5	0.14	2	26
190711_7.5	0.63	NA	0.69	-9.74	NA	-8.66	NA	1	23
190814_0.5	0.65	0.03	0.72	-9.70	0.51	-6.83	0.06	3	16
190814_7.5	0.67	0.03	0.73	-9.96	0.91	-7.18	0.03	3	12
Core_ 11.5	0.69	0.01	NA	-9.90	0.21	-4.28	0.07	4	23
Core_ 2.5	0.69	0.05	NA	-9.67	0.17	-5.16	0.13	3	24

$\Delta_{47}*$ refers to low

The fractionation of oxygen isotope between water-column sampled calcite and water was measured using measured water temperatures for all data except for samples taken on May 15, 2019 and May 29,2019 in which historical water temperature averages were taken from Brunskill (1969a). Uncertainties with these values are estimated to be $\pm 2°C$ which is notably larger than the uncertainty of measured temperatures $\pm 0.1°C$. The oxygen isotope fractionation in Fayetteville Green Lake is defined by equation 12 (Fig. 4B).

$$12.\ 1000 ln(\alpha) = \frac{16.3 * 10^3}{T} - -25.89(R^2 = 0.68)$$
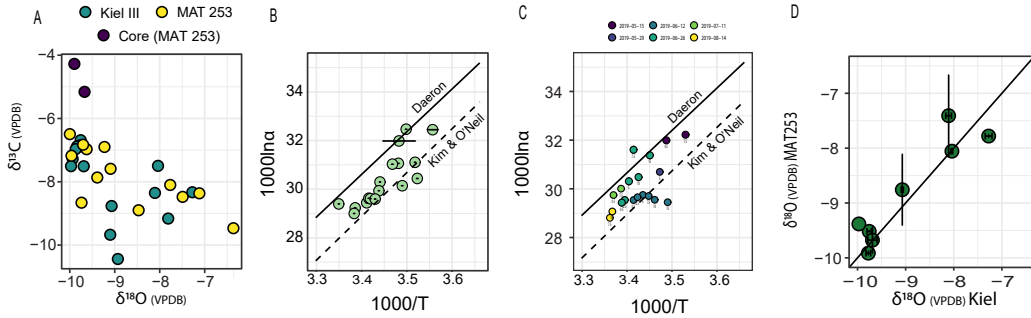
.

Figure 6: Oxygen Fractionation

Figure 6: (A) Core carbonate is considerably more depleted in $\delta^{18}O$ while being more enriched in $\delta^{13}C$ than modern water column carbonate. (B,C) The oxygen isotope fractionation from $H_2O - CaCO_3$ was compared to Daeron and Kim & O'Neil assuming samples were formed at the depth sampled and assuming they were formed at the surface of the water column prior to the date sampled. Carbonate mixed with GFF has shown to increase $\delta^{18}O$ values. $\delta^{18}O$ has been corrected for this GFF Offset. (D) After correcting for the Glass-Fiber Effect on $\delta^{18}O$ *Kiel* stable isotope and *MAT 253* analyses plotted along a one-to-one line.

Crystal Length

Calcite crystal length measured using a *JCM-6000Plus* Scanning Electron Microscope yielded mean crystal lengths of 10-12 microns depending on the sample. We hypothesized that crystal length would be dependent upon depth as calcite precipitated at the surface could precipitate continually throughout its descent. We found that crystal length was on average ~10 μm and the depth at which calcite was sampled did not affect its length (Fig. 5)
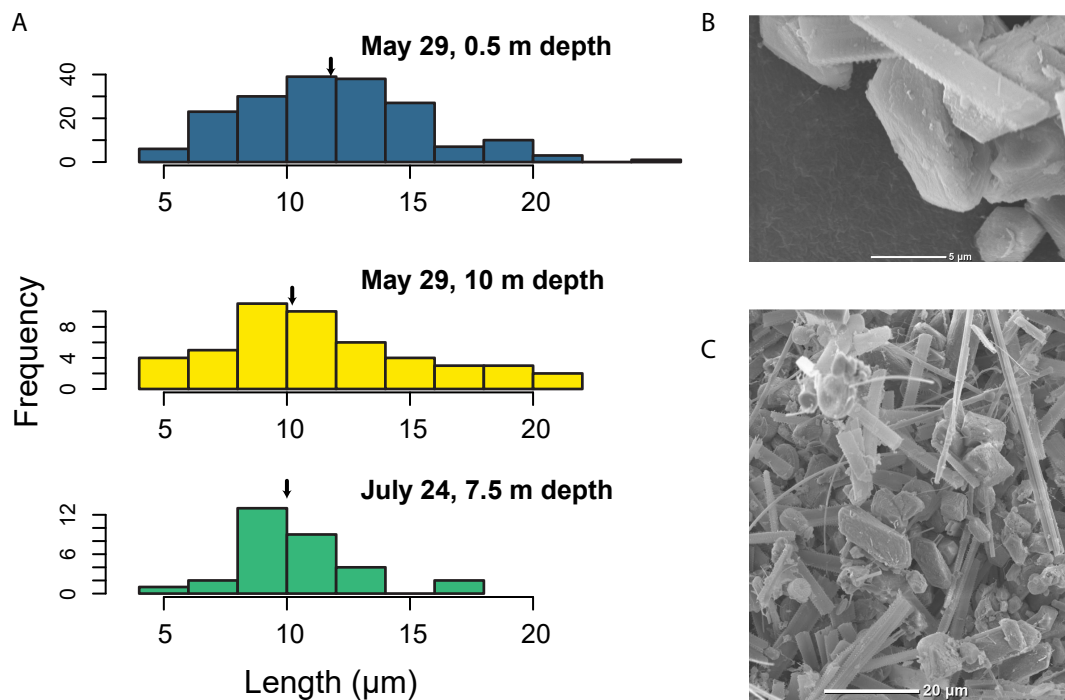
Figure 7: Crystal length

Figure 7: (A) Calcite crystal length was measured using a JCM-6000Plus Scanning Electron Microscope on a suite of three samples, two from May 29 at 0.5 meters and 10 meters depth, and one from July 24. (B,C) Samples were surrounded by a mix of diatoms, spiculues, and within a substrate of glass-fiber filter material.

Discussion

Few studies have utilized the clumped isotope paleothermometer of calcite on lacustrine carbonates while none, to our knowledge, have sampled in situ water column calcite. Huntington (2010, 2015) and Lechler (2013) analyzed Miocene, Pliocene, and Eocene lacustrine carbonates to constrain plateau uplift while Schmid (2011) and Mering (2015) analyzed Holocene lake carbonates. Although our sampling technique resulted in challenging D47 measurements due to low percent carbonate of samples the our results still: 1) Confirms the surficial formation of lacustrine carbonates; 2) assess the applicability of Hren and Sheldon's (2011) transfer function to estimate MAAT, and 3) gives further evidence of a d13C offset between water column and core calcite noted by Havig (2018). Due to its abundant calcite, and seasonally fluctuating temperature Fayetteville Green Lake is an ideal setting to test these questions and provides a sharp contrast in environment to slow precipitating calcite settings thought to represent equilibrium such as Devil's Hole Nevada (Coplen, 2007) the Laghetto Basin (Daeron, 2019).

% Carbonate Effect on $\delta^{18}O$ and Δ_{47}

After correcting for the offset due to low % $CaCO_3$ on the *MAT253* and manual gas extraction line, $\delta^{18}O$ measured on the *Kiel III* and *MAT253* seem to present comparable results. No carbonate standards mixed with GFF were measured on the *Kiel III*, but a suite of replicate analyses measured on both the *Kiel III* and *MAT253* for a given sample plots along a one-to-one line after correcting for the GFF filter offset in samples measured on the *MAT253* (Fig. 6D). The mechanism which is causing an offset of both $\delta^{18}O$ and Δ_{47} is unclear though

it is clear that there may be a threshold of % $CaCO_3$ in which this effect is not noted. In a long-term UW standard mixed with GFF to have ~15% $CaCO_3$ no discernible offset was seen in Δ_{47} and $\delta^{18}O$.

Clumped Isotope Temperatures $T(\Delta_{47})$

Contrary to the $\delta^{18}O$ of calcite, the depth dependence of Δ_{47} was seen to be statistically insignificant. $T(\Delta_{47})$ values from water column samples range from 12°C to 48°C. $T(\Delta_{47})$ values from cores were 23°C and 24°C for the 11.5-12 cm and 1.5-2 cm segment respectively. Average $T(\Delta_{47})$ for Summer 2019 values over the entire water column carbonate dataset was calculated to be $27\,°C \pm 7\,°C$. This agrees with measured Summer mean (JJA) temperature of 23°C. This gives further evidence that the $T(\Delta_{47})$ recorded in lacustrine carbonates is of summer surface water temperatures.

Three samples, 190711_7.5, 190626_15, and 190626_0.5, lack any replicate analyses. The outlier sample, 190626_5 was analyzed with four replicates. This sample yielded both enriched $\delta^{18}O$ and Δ_{47}, and a depleted $\delta^{13}C$ relative to the rest of the samples. Samples affected by kinetic isotope effects, *KIE*, are generally expected to be enriched in $\delta^{18}O$ and depleted in Δ_{47}. This sample contained a similar % carbonate as many other samples and does not seem likely to have experienced a greater analytical error due to low % $CaCO_3$. Core $\delta^{18}O$ values fall within the bounds set by water column samples, but it is unclear why core $\delta^{13}C$ values vary so much between water column and core samples. Havig (2017, 2018) reported water column $\delta^{13}C$ DIC values of -5 to -10 $^0/_{00}$ and core $\delta^{13}C$ -3 to -5 $^0/_{00}$. All cores yielded high D48 values, likely from SO. This is presumed to be due to a high sulfur content, SO_4^{2-}

in the mixolimnion and H_2S in the anoxic zone (Havig et al., 2017).

Evaluation of Transfer Functions

As the highest calcite saturation occurs during summer months in FGL (Brunskill, 1969a) we hypothesized that the summer surface water temperature transfer function (JJA) would be most captured in the carbonate sedimentation of this system. Thus, it was expected that core and water column calcite would yield temperatures far in excess of MAAT and MAWT. Our $T_{(\Delta 47)}$ data from cores demonstrate that the majority of calcite sedimentation likely formed during Summer maximum temperatures as suggested by Hren and Sheldon (2012). Analysis of two segments of core yielded $T_{(\Delta 47)}$ temperatures of 24°C and 23°C, significantly higher than MAAT of 9°C. These core temperatures are indistinguishable from our measured Summer (June, July, August) average temperature. Measured Summer (JJA) ranged from 20-25°C with a mean temperature of 23°C. Applying a JJA transfer function from Hren and Sheldon yields a MAAT at FGL of 12°C which overestimates the true MAAT of 9°C. Further, this agrees with instanteous crystal load data presented by Brunskill, 1969b, which showed the largest calcite precipitation occurred in June, July, and August in 1965, 1966, and 1967.

As noted by Hren and Sheldon (2012) the depth of lacustrine carbonate formation may confound the application of there transfer functions. We presume that calcite was formed between the surface and 2.5 meters depth due to these waters being the most saturated in calcite (Brunskill, 1969a). In JJA 2019 the difference in water temperature between surface waters and waters at 2.5 meters depth never exceeded 3°C (Fig. 2B) and the averaged

difference was 1°C. The difference between surface waters and 7.5 meters depth was much larger and ranged from 4-10°C with an average JJA difference of 6°C. Our last sampled date, October 24, showed an isothermal water column with temperatuers ranging from 12°C to 14°C in the upper 15 meters. Hren and Sheldon note that peak carbonate formation in FGL occurs at ~4 meters depth. This depth of formation seems unlikely as our calculations show $T(\Delta_{47})$ of carbonate sampled from cores to agree with surface waters. Further, we measured the difference between surface waters and 5 meters depth to be 3-8°C. If peak carbonate formation occurred at 4 meters depth $T(\Delta_{47})$ from cores would have yielded temperatures 3-8°C lower than the JJA surface average of 23°C.

Equilibrium

$\delta^{18}O$ fractionation was measured from a suite of data from the *MAT253* as well as the *Kiel IV* device. In samples in which $\delta^{18}O$ was measured from each technique values were averaged as including both points would create unwanted auto correlation. Using a settling rate of $0.5\ m*d^{-1}$ the date of sample formation was calculated to pair samples with an appropriate surface water temperature. As an example, a sample taken from 7.5 m depth was paired with a surface water temperature from 15 days prior. Surface water temperatures from dates not sampled were calculated from a 4th order polynomial fit utilizing Brunskills summer surface water data in addition to our own surface water data.

The settling rate chosen could affect the fractionation as calcite crystals with a slower settling rate come from earlier in the season. It is possible that turbulence in surface waters could delay the settling of crystals. As Brunskill (1969c) settling rate of 2-4 $m*d^{-1}$ does not

specifically account for crystal morphology and researchers have shown rectangular prisms can settle at slower rates than idealized spherical grains (Sheaffer, 1986; Leith, 2007) a slower rate of 0.5 $m*d^{-1}$ was chosen. Further, the change in density of water at the thermocline could cause a slowdown at this boundary and result in a higher crystal load at this point. We present three possible fits for temperature-dependent fractionation $\delta^{18}O$ of calcite in FGL. The first fit (Fig. 6b) assumes temperatures and $\delta^{18}O$ of water from the depth sampled. The second fit utilizes temperatures and $\delta^{18}O$ from surface waters prior to the date sampled (Fig. 6c) and assumes a settling rate of 0.5 $m*d^{-1}$. The third fit uses the same data as the second, but recognizes the well-reported slope of the fractionation and fixes this to a value of 17.57 while solving for the intercept. Standard error in our regression slope and intercept (Fig. 6) are sufficiently large that we cannot exclude either fractionation from Kim & O'Neil(1997) or Daeron (2019). Each of the preceding fits yields (eq. 13 - 15, respectively)

$$13. \ 1000ln(\alpha) = \frac{16.3*10^3}{T} - 25.89$$

$$14. \ 1000ln(\alpha) = \frac{13.47*10^3}{T} - 16.07$$

$$15. \ 1000ln(\alpha) = \frac{17.57*10^3}{T} - 30.13$$

$\delta^{18}O$ fractionation from $H_2O\text{-}CaCO_3$ in FGL does not seem perfectly indicative of reaching equilibrium conditions suggested by Kim & O'Neil(1997). Recently, other locations, Devil's Hole, Nevada, and the Laghetto Basso, Italy, have yielded $H_2O\text{-}CaCO_3$ fractionation suggestive of calcite forming in an equilibrium which differs from Kim & O'Neil (1997) (Daeron et al., 2019, Coplen, 2007, Demeny et al., 2010). Devil's Hole, Nevada and Laghetto Basso,

Italy are be stable in terms of temperature, pH and water chemistry, something which is not true of FGL. FGL experiences large annual temperature swings of 25°C, seasonal changes in $[HCO_3^-]$, and changes in saturation state α. $\delta^{18}O$ fractionation from H_2O-$CaCO_3$ in FGL straddles the equilibrium lines defined by Daeron (2019) and Kim & O'Neil (1997).

We argue that samples are predominantly formed at the surface waters but nonlinear settling rates, and a possible slow down of calcite at the thermocline, adds noise to the calculation of fractionation. Concurrently, core $T_{(\Delta 47)}$ and water column $T_{(\Delta 47)}$ yield temperatures which suggest carbonate forms in the upper surface waters. Average core $\delta^{18}O$ values are -9.78 $^0/_{00(VPDB)}$, while average $\delta^{18}O$ of surface water was calculated to be -9.13 $^0/_{00(VSMOW)}$. Assuming modern $\delta^{18}O$ composition of water is representative of $\delta^{18}O$ during core deposition, this yields a fractionation factor (α) of 1.03015. This α value yields average lake values of $16°C$ and $24°C$, using temperature-fractionation fits from Kim & O'Neil (1997) and Daeron (2019), both of which underestimate Summer average (JJA) measured temperatures to some extent. Further, using the average $\delta^{18}O$ value specifically from surface waters -9.13 $^0/_{00(VSMOW)}$ yields 1.0301321, and 26, 17 for α, and temperatures derived from Kim & O'Neil (1997) and Daeron's (2019) fractionation, respectively. Models of isotopic equilibrium (Devriendt et al., 2017) suggest that the fractionation represented by Kim, & O'Neil (1997) reflects kinetic isotope effects between calcite and CO_3^{2-}. Isotopic equilibrium is thought be achieved in conditions of $\alpha \sim 1$ and low Ionic Strength (I < 0.05 M/l) (Devriendt et al., 2017), neither of which are likely true in FGL during Summer precipitation.

Although Ca^{2+} and HCO_3^- were measured and calculated, saturation states, α, were not calculated as pH was not measured. Havig (2017) measured pH from 7.4 to 8 in the upper 15 meters of the lake with the most alkaline conditions occurring at the surface. Assuming

an average surface water pH of 7.5, and $[Ca^{2+}]$, $[HCO_3^-]$ of 10 and 1 mM respectively yields

a saturation state of α of ~3.

Conclusions

Fayetteville Green Lake in upstate New York provides an ideal environment to study the $\delta^{18}O$, $\delta^{13}C$, and $T(\Delta_{47})$ of modern lacustrine carbonates. Due to agreement between summer surface water temperatures, $T(\Delta_{47})$ from short core segments, and $T(\Delta_{47})$ from water column carbonates lake carbonate samples showed strong likelihood of formation within the upper 2 meters of the water column. Carbonates sampled from cores within the lake show a strong warm-season bias indistinguishable from the summer mean temperature of June, July, and August. An increase in variance in Δ_{47} of our samples due to low % carbonate made seasonal calibration difficult to interpret.

Our work supports that of past research in confirming concentrations of carbonate within the water column from Brunskill (1969b) while utilizing a different methodology. Maximum crystal loads were found at 7.5 meters depth within the water column, though isotope data support the idea that Further, our findings have important implications for the use of lacustrine carbonates as temperature proxies. When applying the clumped-isotope paleothermometer of calcite to lacustrine settings, caution should be taken in interpreting the result as a warm-season proxy and applying the proper latitudinally appropriate transfer function to pair to MAAT. Further, although the majority of our $\delta^{18}O$ fractionation data straddled the bounds set by Kim & O'Neil (1997) and Daeron (2019) it is not clear that a change in the $\delta^{18}O$ of carbonate over some time period in this lacustrine setting is indicative of changing temperatures or changing equilibrium conditions.

References

Brunskill, G. 1969. "Fayetteville Green Lake, New York. II. Precipitation and Sedimentation of Calcite in a Meromictic Lake with Laminated Sediment." *Limnology and Oceanography* 14: 830–47.

Brunskill, G, and S Ludlam. 1969. "Fayetteville Green Lake, New York. I. Physical and Chemical Limnology." *Limnology and Oceanography* 14: 817–29.

Burton, Elizabeth A, and Lynn M Walter. 1990. "The Role of pH in Phosphate Inhibition of Calcite and Aragonite Precipitation Rates in Seawater." *Geochimica et Cosmochimica Acta* 54: 797–808.

Choudens-Sanchez, Vionette De, and Luis A. Gonzalez. 2009. "Calcite and Aragonite Precipitation Under Controlled Instantaneous Supersaturation: Elucidating the Role of Caco3 Saturation State and Mg/ca Ratio on Calcium Carbonate Polymorphism." *Journal of Sedimentary Research* 79: 363–76.

Daëron, M., R.N. Drysdale, M. Peral, D. Huyghe, D. Blamart, T.B. Coplen, F. Lartaud, and G. Zanchetta. 2019. "Calibration of the Calcite-Water Oxygen-Isotope Geothermometer at Devils Hole, Nevada, a Natural Laboratory." *Nature Communications.*

Eiler, John M. 2007. "'Clumped-Isotope' Geochemistry – the Study of Naturally-Occurring, Multiply-Substituted Isotopologues." *Earth and Planetary Science Letters* 262: 309–27.

———. 2011. "Paleoclimate Reconstruction Using Carbonate Clumped Isotope Thermometry." *Earth and Planetary Science Letters* 30: 3575–88.

Epstein, Samuel, Ralph Buchsbaum, Heinz Lowenstam, and Harold Urey. 1951. "Revised

Carbonate-Water Isotopic Temperature Scale." *Geological Society of America Bulletin* 62: 417–26.

Hilfinger, Martin F., Henry T. Mullins, Adam Burnett, and Matthew E. Kirby. 2001. "A 2500 Year Sediment Record from Fayetteville Green Lake, New York: Evidence for Anthropogenic Impacts and Historic Isotope Shift." *Journal of Paleolimnology* 26: 293–305.

Hren, Michael T., and Nathan D. Sheldon. 2012. "Temporal Variations in Lake Water Temperature: Paleoenvironmental Implications of Lake Carbonate d18O and Temperature Records." *Earth and Planetary Science Letters* 61: 77–84.

Kim, and O'Neil. 1997. "Equilibrium and Nonequilibrium Oxygen Isotope Effects in Synthetic Carbonates." *Geochimica et Cosmochimica Acta* 35: 3461–75.

McCrea, J. 1950. "On the Isotopic Chemistry of Carbonates and a Paleotemperature Scale." *The Journal of Chemical Physics* 61: 849–57.

Plummer, L. Niel, and Eurybiades Busenburg. 1982. "The Solubilities of Calcite, Aragonite and Vaterite in Co2-H2o Solutions Between 0 and 90°C, and an Evaluation of the Aqueous Model for the System Caco3-Co2-H2o." *Geochimica et Cosmochimica Acta* 46: 1011–40.

Stumm, Werner, and James Morgan. 1970. *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters.*

Tang, J, M Dietzel, A Fernandez, A.K. Tripati, and B.E. Rosenheim. 2014. "Evaluation of Kinetic Effects on the Clumped Isotope Fractionation During Inorganic Calcite Precipitation." *Geochimica et Cosmochimica Acta* 134: 120–36.

Thompson, Joel, Grant Ferris, and D Smith. 1990. "Geomicrobiology and Sedimentology of

the Mixolimnion and Chemocline in Fayetteville Green Lake." *PALAIOS* 5: 52.

Urey, Harold. 1947. "The Thermodynamic Properties of Isotopic Substances." *Journal of the Chemical Society.*

Watkins, James, Laura Nielsen, Frederick J. Ryerson, and Donald J. Depaolo. 2013. "The Influence of Kinetics on the Oxygen Isotope Composition of Calcium Carbonate." *Earth and Planetary Science Letters* 375: 349–60.