Seasonal variation in stable oxygen and carbon isotope values recovered from modern lacustrine freshwater molluscs: Paleoclimatological implications for sub-weekly temperature records

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Abstract

A fingernail clam (*Sphaerium simile*, Sphaeriidae) from Science Lake, a small watershed located in Allegany State Park, New York, USA and a zebra mussel (*Dreissena polymorpha*, Dreissenidae) from Keuka Lake, New York, the third largest Finger Lake of central New York, were selected to evaluate the applicability of using $\delta^{18}O_{(CaCO_3)}$ and $\delta^{13}C_{(CaCO_3)}$ values for sub-weekly climate records. Seasonal variation in $\delta^{18}O_{(CaCO_3)}$ values was compared with predicted equilibrium values to test the hypothesis that lacustrine molluscs produce shell aragonite according to environmental variables. For the purpose of comparison, aragonite temperature-fractionation equations determined by Grossman & Ku (1986) and Patterson et al. (1993) were used. *Sphaerium simile* appears to produce $\delta^{18}O_{(CaCO_3)}$ values predicted by Patterson et al. (1993), while *Dreissena polymorpha* produces $\delta^{18}O_{(CaCO_3)}$ values in agreement with Grossman & Ku (1986). We attribute the difference to family-specific temperature-fractionation relationships. Because both types of mollusc record climate variables with a high degree of integrity, they should each serve as excellent paleoclimate proxies.

The fingernail clam collected from a small watershed exhibits higher variation about the seasonal pattern than did the zebra mussel collected from a large watershed. This is attributed to the increased sensitivity of the small watershed to storm perturbation. Analysis of fossil molluscs from such watersheds might be useful in discerning paleo-storminess.

Introduction

Stable isotope values of accretionary biogenic carbonate have been used to evaluate paleoenvironmental conditions since the idea was first proposed by Harold Urey over 50 years ago (Urey, 1947). Environmental variables such as temperature and $\delta^{18}O_{(H_2O)}$ values have been derived from $\delta^{18}O_{(CaCO_3)}$ values from a variety of materials including molluscs (e.g., Dettman & Lohmann, 1993; Klein et al., 1996), corals (e.g., Linsley et al., 1994; Leder et al., 1996; Beck et al., 1997), ostracodes (e.g., Xia et al., 1997), and more recently fish otoliths (e.g., Kalish 1991; Patterson et al., 1993; Patterson, 1998). In addition to environmental records, these materials yield information on physiology (e.g., Wefer

& Berger, 1991; Campana, 1999). $\delta^{13}C$ values likely record trophic position and/or metabolic rate, as well as the dissolved inorganic carbon (Tanaka et al., 1986; Schwarcz et al., 1998; Dettman et al., 1999). Recent technological advances permit microsampling of carbonate to obtain records with sub-annual (Dettman & Lohmann, 1995; Wurster et al., 1999) and even daily resolution (this paper). Therefore, micromilling of accretionary biogenic carbonate yields ontogenetic variation in $\delta^{18}O$ and $\delta^{13}C$ values that can be used to characterize the environment and physiology of the $CaCO_3$ secreting organism.

Well-preserved fossil accretionary biogenic carbonates are common in both geological and archaeological settings. These fossils can provide quantitative

information on temperature variability in paleoclimate studies (e.g., Dettman & Lohmann, 1993; Steuber, 1996; Patterson, 1998). However, shell carbonate must be deposited at or near oxygen isotope equilibrium in order to differentiate between environmental and intrinsic organism variation. In this paper 'equilibrium' is defined as a reasonable temperature-fractionation relationship with environmental variables (temperature and $\delta^{18}O_{(H_2O)}$ value) according to well-defined, empirically derived equations.

Disequilibrium precipitation has been reported for many biogenic carbonates, and is usually attributed to kinetic factors related to rapid growth (McConnaughey, 1989a, b; Rahimpour-Bonab et al., 1997). However, marine molluscs generally precipitate under equilibrium conditions (e.g., Wefer & Berger, 1991; Klein et al., 1996). Relatively few studies have focussed on freshwater bivalves (Fastovsky et al., 1993). In the limited number of studies on $\delta^{18}O$ values of modern freshwater bivalves, some researchers have found equilibrium with the environment (Tevesz et al., 1996; Dettman et al., 1999), while other studies conclude disequilibrium precipitation (Fastovsky et al., 1993; von Grafenstein et al., 1999). Some of these studies consider whole shell growth, assume shell growth of the animal through the winter, and/or assume the variation in the $\delta^{18}O_{(H_2O)}$ value of the ambient water. High-resolution sampling provides a means to evaluate these assumptions, because seasonal patterns revealed by the micromilling of modern mollusc shells can be compared to seasonal meteorological records.

Sub-weekly variation in $\delta^{18}O_{(CaCO_3)}$ values are a function of changing $\delta^{18}O_{(H_2O)}$ values and temperature; therefore, variation in $\delta^{18}O_{(H_2O)}$ value related to individual storm events might be recorded in $\delta^{18}O_{(CaCO_3)}$ values if the hydrology of the basin responds to such storms. This provides a technique to evaluate paleostorminess if fossil shells from appropriate basins are analyzed. Storminess is an important component of climate and is often associated with the mean position of the circumpolar vortex (Lamb, 1995). However, only large destructive storms are usually preserved in paleorecords generally in the form of disrupted sediment (e.g., Lamb, 1995; Hass, 1996). Developing a means with which to evaluate the more subtle components of storms (such as temperature and origin of moisture) would be an important breakthrough for paleoclimate studies.

We present high-resolution $\delta^{18}O$ and $\delta^{13}C$ values from two modern lacustrine mollusc shells. These values are compared to predicted $\delta^{18}O_{(CaCO_3)}$ values in order to test whether the carbonate was deposited in equilibrium with the environment. In addition, we examine the hypothesis that shells deposited in relatively small lake basins are more likely to record high-resolution perturbations in $\delta^{18}O_{(H_2O)}$ values (including storminess), while larger lake basins with a relatively constant $\delta^{18}O_{(H_2O)}$ value throughout the year are appropriate for characterizing seasonality of temperature.

Methods

Study area, materials, and $\delta^{18}O_{(H_2O)}$ analysis

Science Lake is a small (1.4 hectares, 10 m deep) man-made lake located within Allegany State Park, New York on the Allegheny Plateau at 565 m elevation (Figure 1). Air temperatures were measured at a nearby weather station (460 m elevation). A 2-week running average is assumed to represent surface water temperature for the purpose of comparing high-resolution data. From March 1998–October 1999, surface water samples were collected approximately once a month from the north edge of the lake in Nalgene™ containers, and sealed until analyzed for $\delta^{18}O_{(H_2O)}$ values. Live fingernail-clams (*Sphaerium* sp., Sphaeriidae) were collected from the upper 6 cm of sediment from Science Lake (at less than 0.5 m water depth) on October 3, 1999. The specimen selected for stable isotope analyses was older than 1 year because 1 seasonal band was located. Younger specimens generally have higher growth rates (Jones et al., 1989), making a higher-resolution study possible.

Keuka Lake, located in central New York at 216 m elevation, is the third largest Finger Lake in surface area (4,700 hectares) and volume (Figure 1). Keuka Lake has a watershed of 45,070 hectares. Water temperature was measured 9 times in 1998 and 8 times in 1999 from April through December (Peter Landre, personal Communication). Surface water samples were collected 9 times during 1998–1999 in high-density Nalgene™ containers, and sealed until analyzed for $\delta^{18}O_{(H_2O)}$ values (Table 1). Living zebra mussels (*Dreissena polymorpha*) aged 1–2 years, were collected on October 31, 1999 from a depth less than 0.5 m on the west central side of Keuka Lake (Figure 1).

$\delta^{18}O_{(H_2O)}$ values were determined using a Finnigan HDO-II water equilibration device directly coupled to a Finnigan MAT 252 gas ratio mass spectrometer. Standard CO_2 gas is equilibrated with water samples for 6 h at 25 °C and then sequentially analyzed. Val-
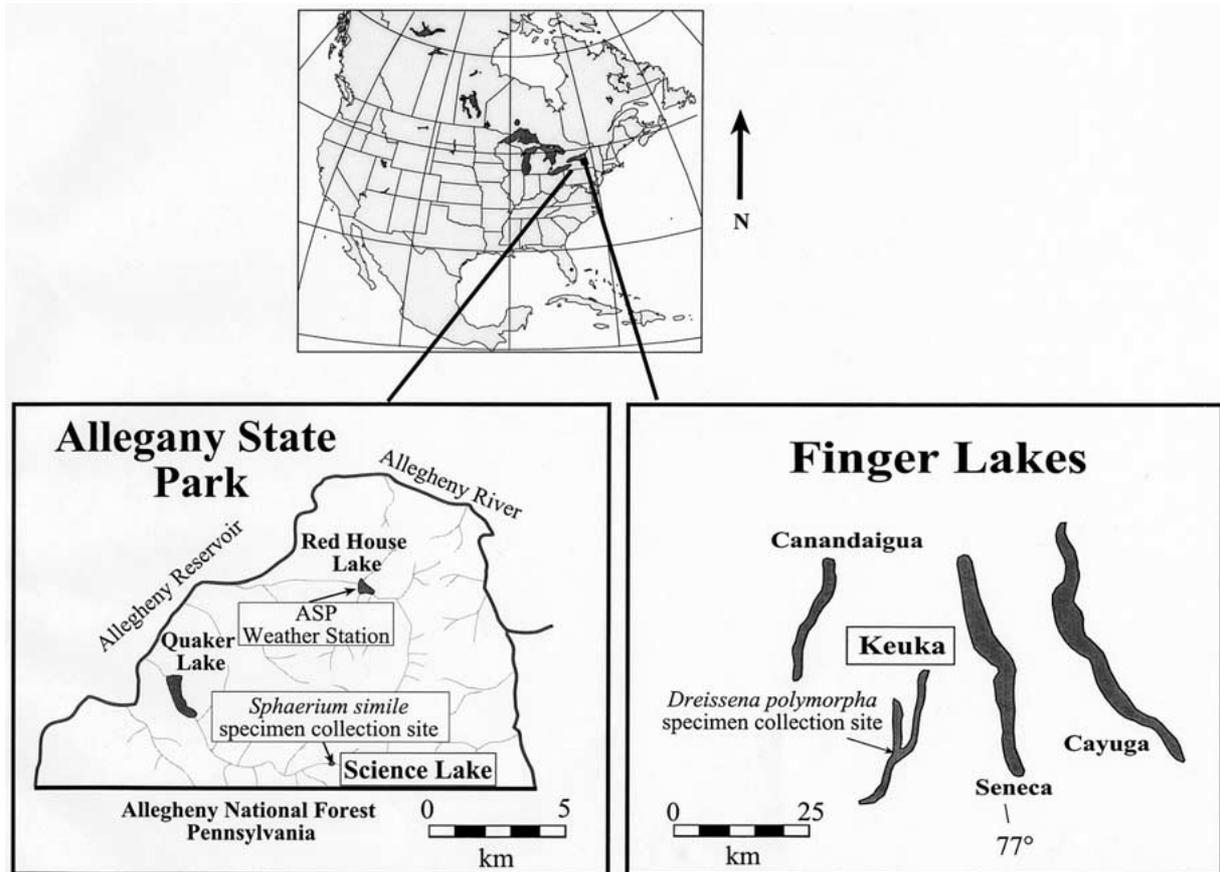
Figure 1. Environments of selected molluscs. The fingernail clam (*Sphaerium simile*) was collected on the north end of Science Lake, a small watershed located in Allegany State Park, New York, USA. The zebra mussel (*Dreissena polymorpha*) was collected on the west-central side of Keuka Lake, New York, USA (the third largest Finger Lake). Note the different scales of each location.

ues are reported to ± 0.1‰. Replicate analyses of water samples were within ± 0.1‰.

High-resolution sampling and stable isotope analysis of carbonate

One valve from each mollusc was mounted to a computer-controlled micromilling stage. Three-dimensional coordinates were digitized in real-time using growth features as a guide. Using x-y-z coordinates it is possible to sample the whole valve without sectioning (Figure 2). A cubic spline best fit through the coordinates provides 'smooth' digitized paths that accurately represent growth features, between which intermediate paths were interpolated. The computer-controlled stage moved along sample paths as a micro burr mills carbonate parallel to growth banding. Typical sample path widths are 20 μm, and typical depths are 40 μm. Care was taken not to mill below the prismatic layer

into the nacreous layer which might represent precipitation at another time. A detailed description of the micromilling apparatus and methodology is presented in Wurster et al. (1999).

Table 1. Keuka Lake $\delta^{18}O_{(H_2O)}$ values

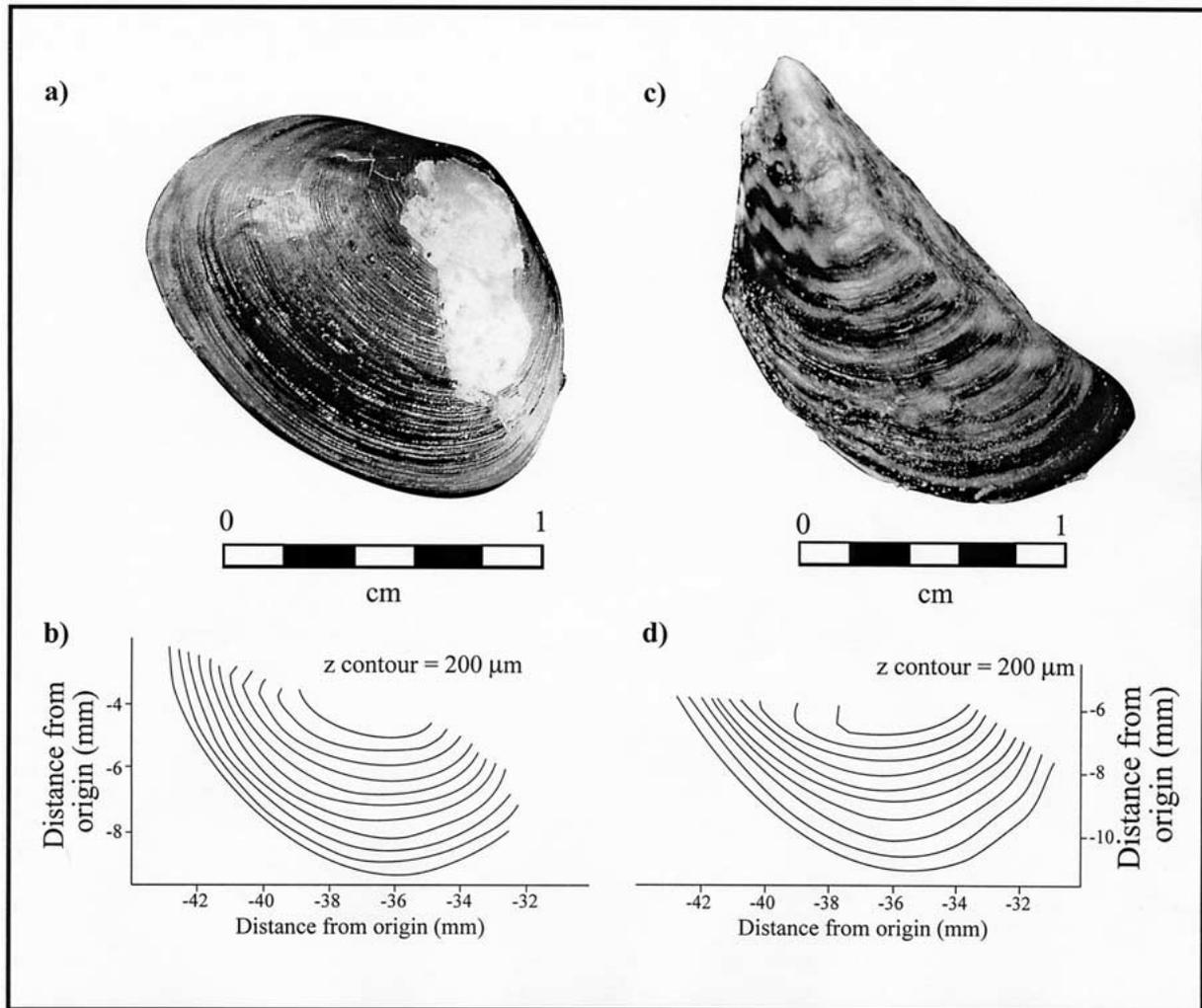| Location of sample	Date of sample	$\delta^{18}O_{(H_2O)}$ value
Outlet	7/1/1998	−8.0
Outlet	7/16/1998	−8.1
Outlet	2/20/1999	−8.1
Outlet	7/27/1999	−7.8
Outlet	8/15/1999	−7.9
Outlet	9/5/1999	−7.5
Mid Lake	7/1/1998	−8.2
South End	7/1/1998	−8.0
South End	10/31/1999	−8.0
Average Value	–	−8.0 ± 0.2

Figure 2. (a) Digital image of the sampled *Sphaerium simile*; (b) illustration of a portion of the morphology of *Sphaerium simile* determined using digital path coordinates; (c) Digital image of *Dreissena polymorpha*; (d) illustration of a portion of the morphology of *Dreissena polymorpha* determined using digital path coordinates.

A fingernail clam (*Sphaerium simile*) from Science Lake was micromilled such that 175 consecutive carbonate samples were isolated over 5 mm of shell growth. $\delta^{18}O$ and $\delta^{13}C$ values were determined for 155 of these carbonate samples. Similarly, a zebra mussel from Keuka Lake was micromilled, yielding 277 individual carbonate samples over 14 mm of shell growth. A subset of 206 samples was analyzed for $\delta^{18}O$ and $\delta^{13}C$ values. Carbonate samples were roasted *in vacuo* for 1 h at 200 °C. Samples were analyzed using an automated carbonate preparation device. Individual samples of carbonate were analyzed with standard precision of ± 0.08‰ (1σ). The minimum estimated sample mass was ~ 20 μg.

Calculation of predicted $\delta^{18}O_{(CaCO_3)}$

In order to calculate predicted $\delta^{18}O_{(CaCO_3)}$, the temperature and $\delta^{18}O_{(H_2O)}$ value must be known. Because water temperature closely tracks air temperature (e.g., McCombie, 1959; Edinger et al., 1968; Dingman, 1972; Webb, 1974; Livingstone & Lotter, 1998; Patterson, 1998), water temperatures for Science Lake were calculated from air temperatures measured at the Allegany State Park (ASP) weather station (Figure 1). Air temperature variation is muted by the thermal inertia of water, therefore water temperature was estimated using a 2-week running average of air temperature.

Predicted equilibrium values were calculated from

two empirical temperature-fractionation relationships published for aragonite. Grossman & Ku (1986) determined the relationship:

$$T(°C) = 20.6 - 4.34(\delta^{18}O_{(CaCO_3)} - \delta^{18}O_{(w)}) \quad (1)$$

where $\delta^{18}O_{(w)}$ is the $\delta^{18}O_{(H_2O)}$ relative to the VSMOW standard subtracted by 0.2‰ in order to relate to the VPDB standard. We use the modified equation derived by Dettman et al. (1999) from the tabulated data in Grossman & Ku (1986) which yields temperature directly from the fractionation factor.

$$10^3\ln(\alpha) = 2.559(10^6T(K)^{-2}) + 0.715 \quad (2)$$

where

$$\alpha = (1000 + \delta^{18}O_{(CaCO_3)} / 1000 + \delta^{18}O_{(H_2O)}) \text{ SMOW} \quad (3)$$

For comparative purposes, we also predict $\delta^{18}O$ values using the temperature-fractionation relationship developed by Patterson et al. (1993), specifically for aragonitic otoliths of freshwater fish.

$$10^3\ln(\alpha) = 18.56(10^3T(K)^{-1}) - 33.49 \quad (4)$$

where α is calculated as in equation (3). Equation (4) predicts values ~ 0.6‰ lower than equation (2) over the range of $\delta^{18}O_{(H_2O)}$ values and temperature discussed herein (for a given $\delta^{18}O_{(H_2O)}$ value, this corresponds to 2.5–3 °C).

Because of the seasonal change in Science Lake $\delta^{18}O_{(H_2O)}$ values, daily $\delta^{18}O_{(H_2O)}$ values were interpolated using a cubic spline best fit to existing data in order to calculate daily $\delta^{18}O_{(CaCO_3)}$ value with which to more easily compare with the $\delta^{18}O_{(mollusc)}$ values. Individual storm events will not be tracked by this assumption, and more variation is expected. For Keuka Lake, $\delta^{18}O_{(H_2O)}$ values were relatively constant (Table 1).

Results

$\delta^{18}O_{(H_2O)}$ values of Science and Keuka Lake

Science Lake $\delta^{18}O_{(H_2O)}$ values range from −9.4 to −12.4‰(VSMOW) with each year (1998 and 1999) displaying a similar amplitude and pattern. In 1999, $\delta^{18}O_{(H_2O)}$ values were 0.2‰ higher than 1998 at both the seasonal minima and maxima (August and March, respectively). The total seasonal variation for this small
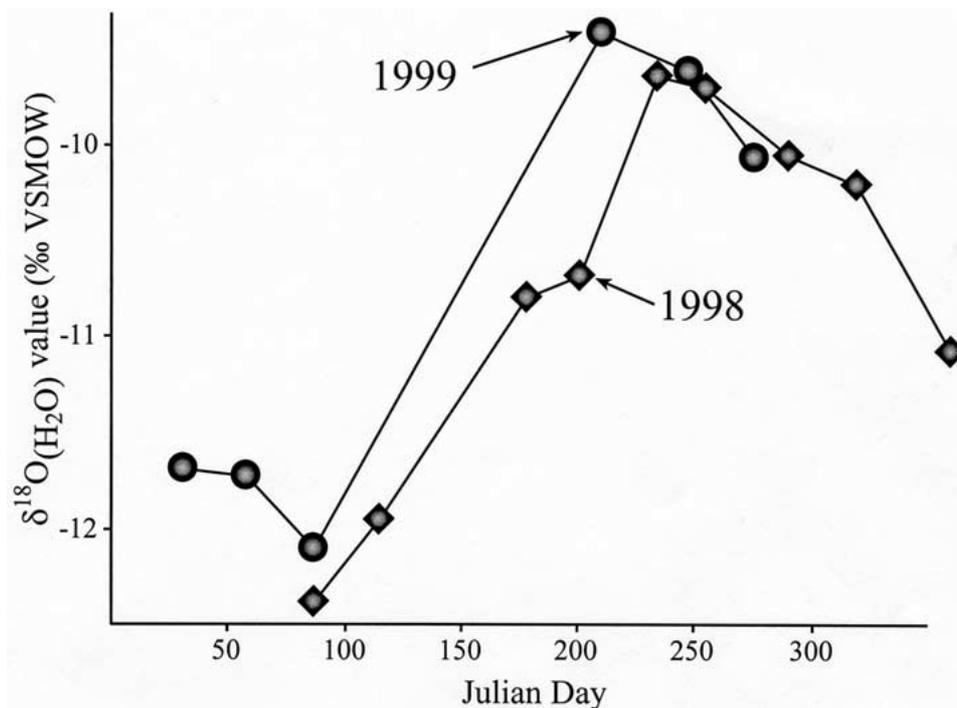

Figure 3. $\delta^{18}O_{(H_2O)}$ values collected from Science Lake. Note that samples were not collected between March and July of 1999.

lake and watershed in both 1998 and 1999 was 2.7‰. The $\delta^{18}O_{(H_2O)}$ value toward the end of March is low, and is suggestive of spring snowmelt.

Keuka Lake $\delta^{18}O_{(H_2O)}$ values are relatively constant at approximately −8.0‰$_{(VSMOW)}$ (Table 1). Approximately 75% of the annual water budget is derived from cool season precipitation with dominant inflow from the south and output through the northeastern branch, and a residence time of about 6 years (Michel & Kraemer, 1995). The isotope value of the lake is principally

determined by variation in the ratio of winter/summer precipitation.

Molluscan $\delta^{18}O$ and $\delta^{13}C$ values

Micromilled carbonate $\delta^{18}O$ and $\delta^{13}C$ values for the fingernail clam from Science Lake exhibits a seasonal pattern (Figure 4). $\delta^{18}O_{(CaCO_3)}$ values range from −11.2 to −8.6‰$_{(VPDB)}$. A plateau with minor variation (0.3‰) from 9.3–10.1 mm averaged −8.9‰$_{(VPDB)}$. $\delta^{13}C$ values

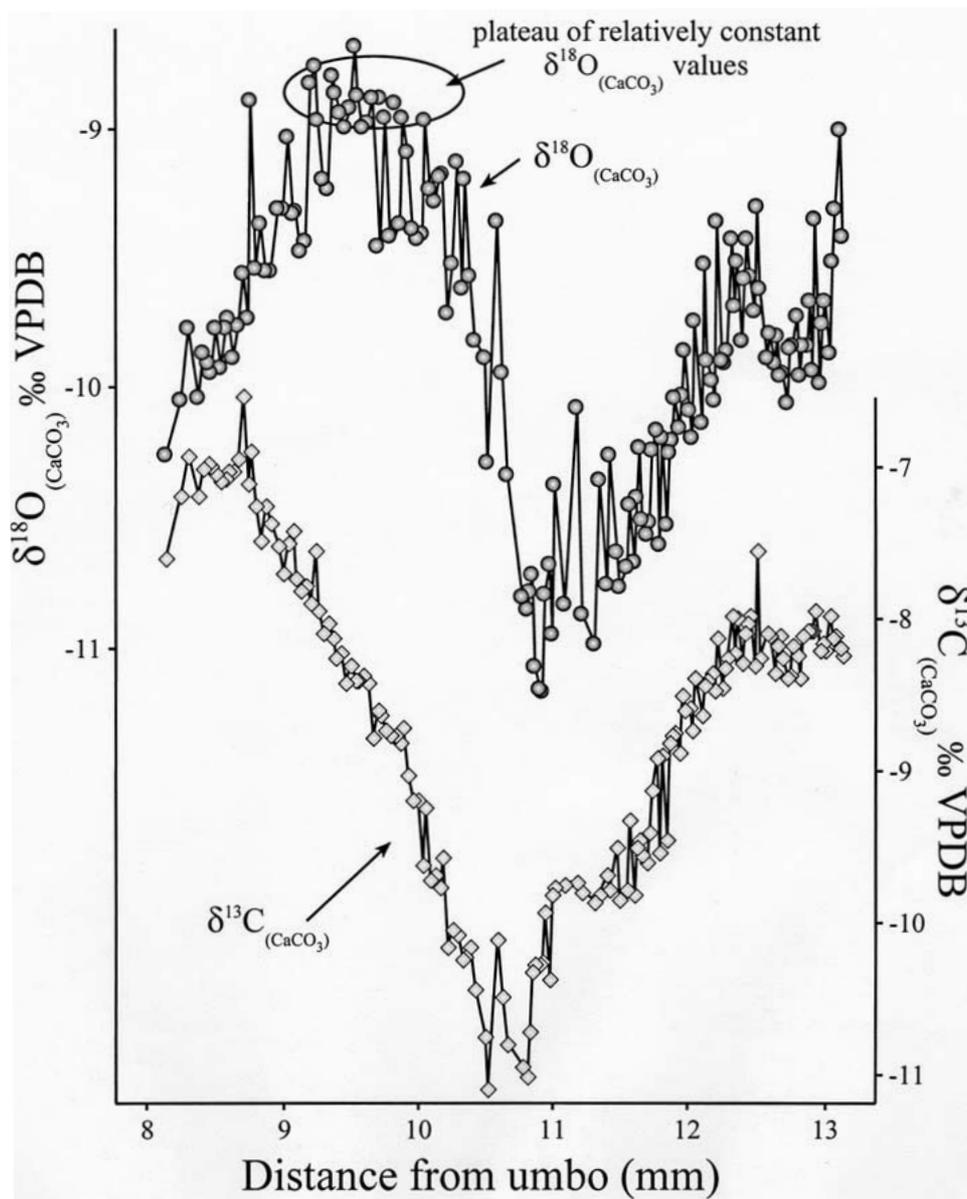*Figure 4.* Intra-molluscan $\delta^{18}O_{(CaCO_3)}$ and $\delta^{13}C_{(CaCO_3)}$ values for a fingernail clam, (*Sphaerium simile*), collected from Science Lake in Allegany State Park, New York, USA.

also show a seasonal pattern with a high degree of variability that ranges from −11.1 to −6.5‰$_{(VPDB)}$. $\delta^{13}C$ values are out of phase with $\delta^{18}O$ values, beginning to decrease at 8.8 mm. $\delta^{18}O$ values increase until 9.2 mm where they plateau, ultimately decreasing at 10 mm.

Although there is less of a degree of variability about a seasonal pattern than found for the fingernail clam, the zebra mussel still shows a seasonal pattern in both $\delta^{18}O_{(CaCO3)}$ and $\delta^{13}C_{(CaCO3)}$ values for less than 2 years of growth (Figure 5). The minimum $\delta^{18}O_{(CaCO3)}$ value is −8.6‰$_{(VPDB)}$, whereas the maximum is −4.1‰$_{(VPDB)}$. $\delta^{13}C_{(CaCO3)}$ values range from −4.0 to −9.1‰$_{(VPDB)}$ and are usually positively co-varied with $\delta^{18}O_{(CaCO3)}$ values ($r^2 = 0.67$); although $\delta^{13}C_{(CaCO3)}$ values near the umbo negatively co-vary with $\delta^{18}O_{(CaCO3)}$.

Discussion

Equilibrium fractionation of $\delta^{18}O_{(CaCO3)}$

Figures 6 and 7 compare predicted and measured $\delta^{18}O_{(CaCO3)}$ values for the fingernail clam and zebra mussel, respectively. Interestingly, there is a close correlation between the Science Lake fingernail clam's $\delta^{18}O_{(CaCO3)}$ values and those predicted using equation (4). In contrast, the $\delta^{18}O_{(CaCO3)}$ values of the zebra mussel from Keuka Lake are best predicted by equation (2). For the fingernail clam, $\delta^{18}O$ values appear to track high-resolution variability that includes the slight warming trend toward the end of 1999. It is also evident that the molluscan $\delta^{18}O_{(CaCO3)}$ values show a much higher
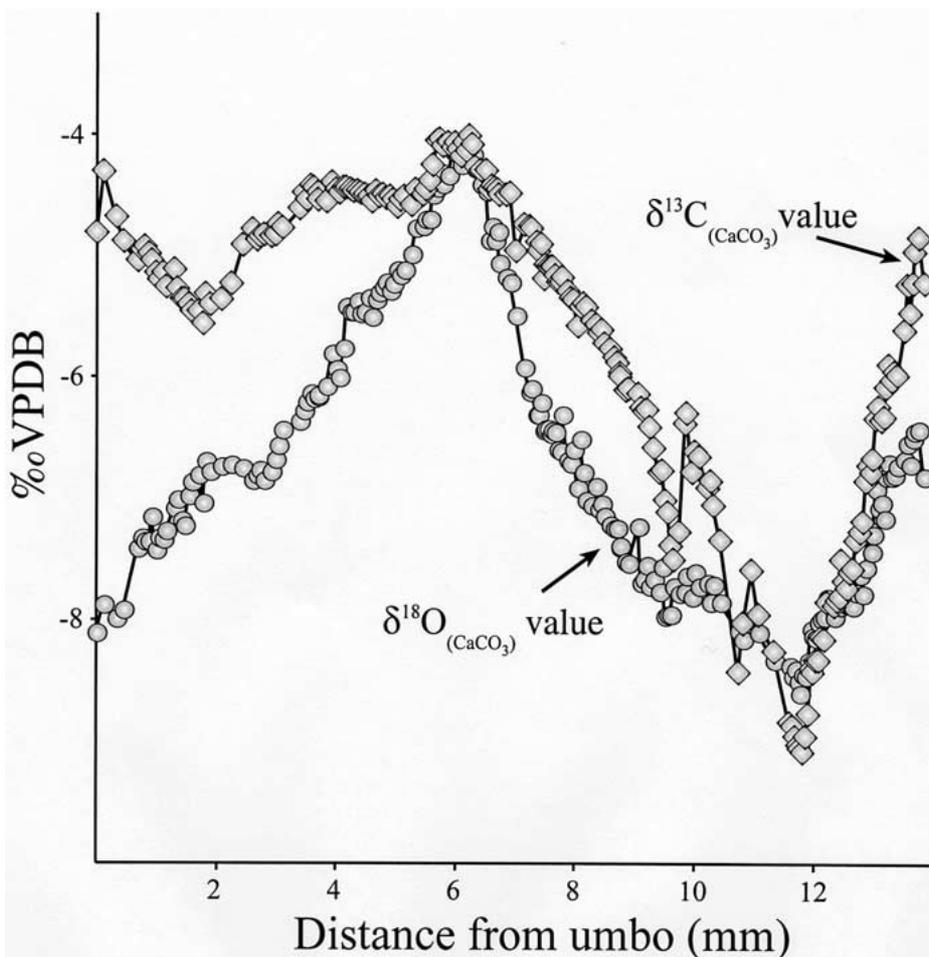

Figure 5. Intra-molluscan $\delta^{18}O_{(CaCO3)}$ and $\delta^{13}C_{(CaCO3)}$ values for a zebra mussel (*Dreissena polymorpha*), collected from Keuka Lake in central New York.

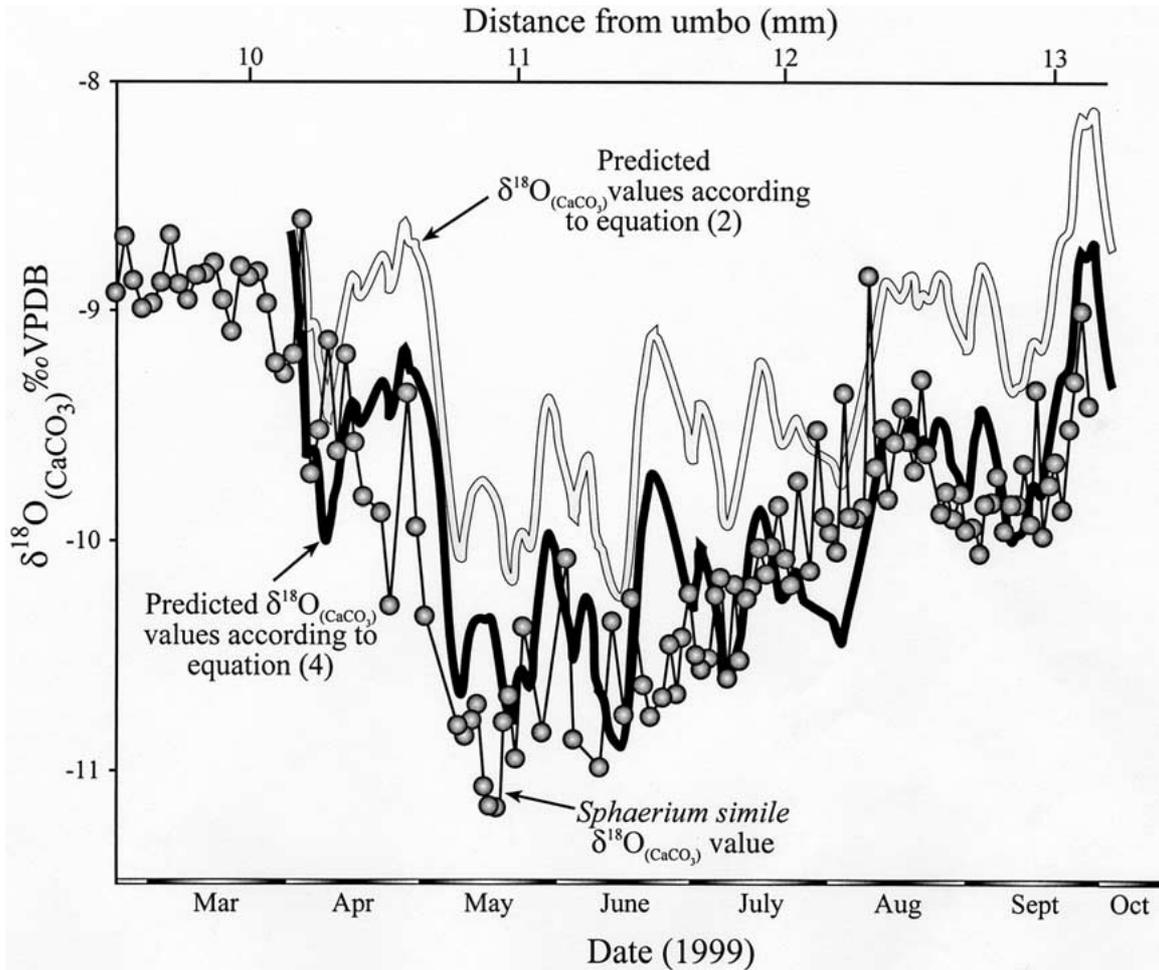*Figure 6.* Comparison between predicted $\delta^{18}O_{(CaCO_3)}$ values and analyzed molluscan $\delta^{18}O_{(CaCO_3)}$ values for *Sphaerium simile*. Molluscan $\delta^{18}O_{(CaCO_3)}$ values were expanded along the x-axis so that the oldest sample from the outer edge matched the date of collection (October 3, 1999), and the minimum $\delta^{18}O_{(CaCO_3)}$ value matched the minimum predicted $\delta^{18}O_{(CaCO_3)}$ value occurring in early April, 1999. No attempt was made to account for seasonal changes in the deposition rate of carbonate.

variation around a similar trend than do the predicted values. This may be due to unmeasured variation in the $\delta^{18}O_{(H_2O)}$ value. However, molluscan $\delta^{18}O_{(CaCO_3)}$ values still appear to be close to 0.25‰ lower than predicted values via equation (4) during the mid-summer. This can perhaps be explained by $\delta^{18}O_{(H_2O)}$ values, which were not measured during April, May, and June of 1999. If the seasonal pattern in $\delta^{18}O_{(H_2O)}$ values in 1999 was similar to that of 1998, a small 'plateau' in $\delta^{18}O_{(H_2O)}$ value occurred during June–July that would not have been interpolated by a cubic spline (Figure 3). This would result in lower predicted $\delta^{18}O_{(CaCO_3)}$ values consistent with those measured in the mollusc.

The zebra mussel from Keuka Lake shows a pattern closely related to equilibrium values predicted using

equation (2). Water temperatures were measured once a month from April to December and predicted $\delta^{18}O_{(CaCO_3)}$ values (using these temperatures) show a good general correlation, but do not display some of the more detailed patterns. In a further test of equilibrium precipitation, we also compare $\delta^{18}O_{(CaCO_3)}$ values predicted from equation (2) using air temperature from Rochester, New York (the nearest WMO weather station to the study site), which displays some of the more detailed variation (Figure 7). Winter $\delta^{18}O_{(CaCO_3)}$ values could not be accurately predicted because water temperatures were not measured during the winter and air temperature goes well below the minimum 0 °C temperature for freshwater. The zebra mussel may produce carbonate throughout the winter because a minimum $\delta^{18}O_{(CaCO_3)}$

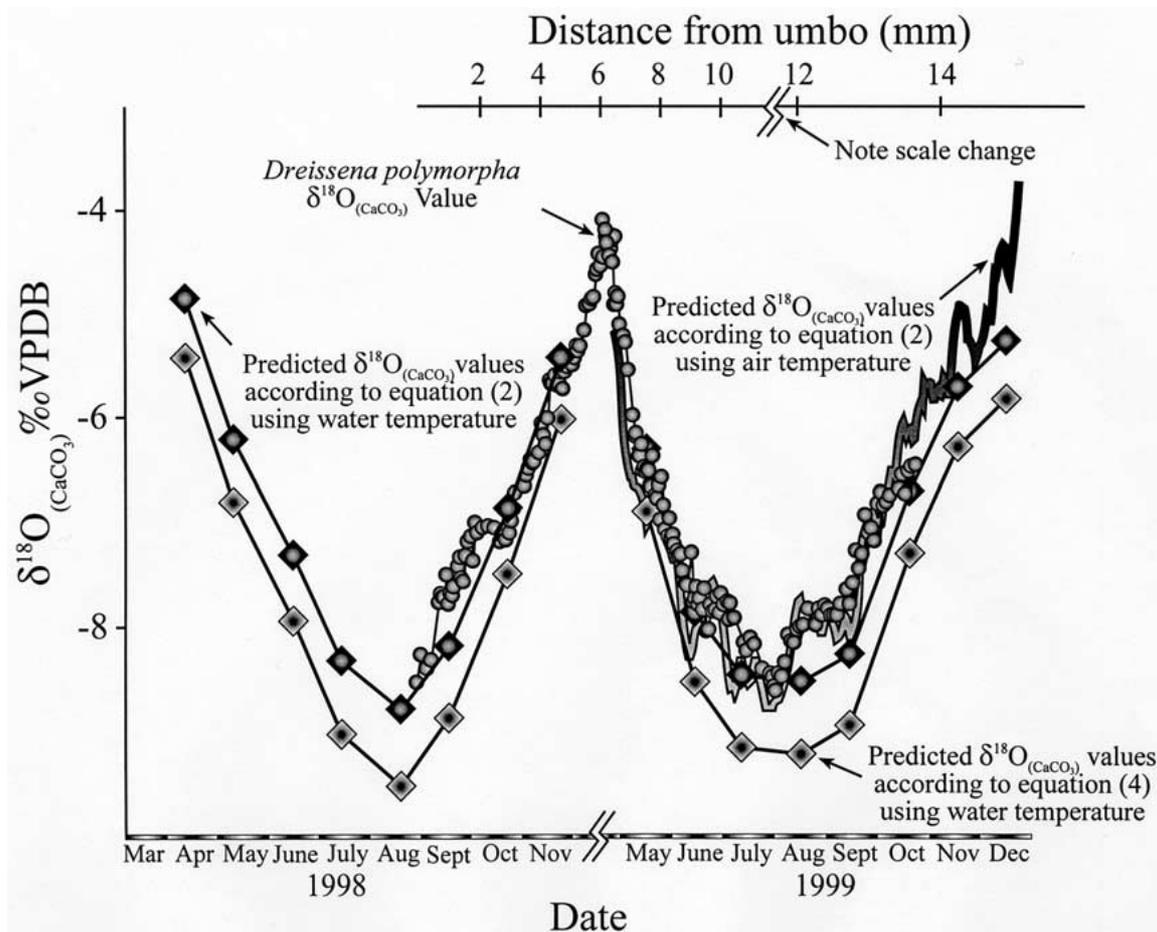*Figure 7*. Comparison between predicted δ18O(CaCO3) values and analyzed molluscan δ18O(CaCO3) values for *Dreissena polymorpha*. In order to satisfactorily compare the data and account for seasonal changes in the deposition of carbonate, different growth scales were used. A different growth scale was used from the umbo to the minimum δ18O(CaCO3) value and from the minimum δ18O(CaCO3) value to last sample. In order to show a more detailed comparison, predicted δ18O(CaCO3) values determined using air temperature from Rochester and equation (2) are also shown. Note that the scale was not changed for the date axis, however November through March are omitted because predicted δ18O(CaCO3) values could not be determined for these months.

value of −4‰(VPDB) corresponds to a temperature of 2 °C using equation (2). This is a reasonable minimum temperature estimate for Keuka Lake because minimum freshwater temperature would lie in the range 0–4 °C.

Equation (2) predicts δ18O(CaCO3) values more positive than those calculated using equation (4). Inorganic aragonite analyzed by Tarutani et al. (1969) was found to have a δ18O(CaCO3) value 0.6‰ more positive than calcite precipitated at 25 °C. If it is assumed that the slope of the fractionation relationship is the same as the inorganic calcite temperature-fractionation relationship of Kim & O'Neil (1997), an estimated fractionation equation for inorganic aragonite can be calculated applying Kim & O'Neil's (1997) revised

acid fractionation factor, enriched by 0.6‰ for calcite-aragonite (Campana, 1999). This estimated inorganic aragonite fractionation relationship is indistinguishable from the Patterson et al. (1993) equation (Campana, 1999), suggesting that equation (4) predicts δ18O(CaCO3) values more in accordance with that predicted by inorganic equilibrium precipitation of aragonite. This compares favorably with several studies of the calcite shells of marine molluscs whose δ18O values appear to be in equilibrium according to inorganic calcite temperature-fractionation relationships (e.g., Wefer & Berger, 1991; Rahimpour-Bonab, 1997).

Several workers have reported δ18O(CaCO3) values for modern freshwater bivalves, although most of these studies have focused on patterns of seasonal variation

or of validating schlerochronological methods and have not directly measured the $\delta^{18}O_{(H2O)}$ value (e.g., Krantz et al., 1987; Jones & Quitmyer, 1996; Veinott & Cornett, 1996). A few studies have attempted to determine whether freshwater bivalve carbonate is deposited in oxygen isotope equilibrium with the environment; however, no consensus was reached. Some recent studies have concluded disequilibrium (Fastovsky et al., 1993; von Grafenstein et al., 1999), while Dettman et al. (1999) using methodology similar to that in this study, concluded that equilibrium precipitation occurs according to the modified Grossman & Ku (1986) temperature-fractionation relationship for aragonite. Our data suggest that *Sphaerium simile* from Science Lake appears to precipitate $\delta^{18}O_{(CaCO3)}$ values according to Patterson et al. (1993), while *Dreissena polymorpha* precipitates $\delta^{18}O_{(CaCO3)}$ values in agreement with Grossman & Ku (1986).

We propose two possible mechanisms for this apparent discrepancy. One possibility is that the environmental variables were not properly estimated. Although possible, this is unlikely because a consistent summer temperature offset of 2.5–3 °C must then have occurred. Furthermore, studies have shown a direct correlation between air temperature and water temperature (e.g., McCombie, 1959; Edinger et al., 1968; Dingman, 1972; Webb, 1974; Livingstone & Lotter, 1998). We also find a close correlation between Rochester air temperature and Keuka Lake temperature (Figure 7). $\delta^{18}O_{(H2O)}$ values for Science Lake display a distinct seasonal component, and water temperature likely responds to atmospheric temperature variation as well. It is possible that because *Sphaerium simile* burrows into the sediment that this species records parameters of a different environment. However, consistently lower temperatures and/or an increase in $\delta^{18}O_{(H2O)}$ values within the sediment (compared to the open water) would have to occur. Furthermore, a consistent offset of ~ 0.6‰ would have to occur for this species to fit the Patterson et al. (1993) aragonite temperature-fractionation relationship. Because fresh, oxygenated water is required for *Sphaerium simile* to respire, it is likely that water exchange between sediment and overlying water column would maintain temperature equality between the two systems.

The second, and more favored hypothesis, is that there is a familial difference in the aragonite temperature-fractionation relationship. We suggest that Unionidae and Dreissenidae may have consistent 'vital effects', while Sphaeriidae may precipitate aragonite more in accord with estimated inorganic aragonite equilibrium. Both bivalve groups can therefore be used to accurately predict temperature and/or $\delta^{18}O_{(H2O)}$ values. There is support for this hypothesis in some recent studies.

A study by von Grafenstein et al. (1999) measured temperature, $\delta^{18}O_{(H2O)}$, and $\delta^{13}C_{(DIC)}$ at different depths throughout the year. Predicted $\delta^{18}O_{(CaCO3)}$ values calculated from the empirically derived calcite temperature-fraction equation of Friedman & O'Neil (1977) were compared to measured $\delta^{18}O_{(CaCO3)}$ values of different species of ostracodes and one bivalve for the purpose of assessing 'vital' effects. *Psidium* (Sphaeriidae) was found to be approximately $0.86 \pm 0.17‰_{(VPDB)}$, more positive than that predicted by the Friedman & O'Neil's (1977) calcite equation, which is similar to Kim and O'Neil (1997) inorganic calcite temperature-fractionation relationship under these conditions. However, *Psidium* sp. precipitates an aragonite shell. If predicted $\delta^{18}O$ values are recalculated using equation (4), it would appear to be much closer to predicted values. The remaining ~ 0.2‰ offset may be related to the moderating effect of whole shell sampling. The only other study that has looked at $\delta^{18}O_{(CaCO3)}$ values from modern *Sphaerium* finds that this genus predicts a mean $\delta^{18}O_{(CaCO3)}$ value 0.6‰ more negative than the mean value for a Unionid shell sampled from the same location and which deposited carbonate during the same time (Tevesz et al., 1996). The authors attributed the contrast to potential winter growth differences and/or 'vital effects'. We find evidence against winter growth and for 'equilibrium' fractionation of $\delta^{18}O_{(CaCO3)}$ values for *Sphaerium*.

Fastovsky et al. (1993) also report disequilibria for freshwater bivalve $\delta^{18}O$ values. They measured $\delta^{18}O_{(CaCO3)}$ values of *Elliptio complanata* 1–3‰ lower than predicted values. An error in the treatment of the $\delta^{18}O_{(H2O)}$ value within Grossman & Ku's (1986) equation resulted in predicted $\delta^{18}O_{(CaCO3)}$ values 0.2‰ more positive (Dettman et al., 1999). If the tabulated $\delta^{18}O_{(CaCO3)}$ value is averaged to represent the growing season and compared to predicted $\delta^{18}O_{(CaCO3)}$ value from equation (4), the average offset is just 0.1‰ for two of three bivalves analyzed. The third bivalve still exhibits a 0.7‰ offset. Dettman et al. (1999) describe how misconceptions of spatial and temporal resolution in shell material might lead to erroneous interpretations for these Unionids. Dettman et al. (1999) used methodology similar to ours, demonstrating that $\delta^{18}O_{(CaCO3)}$ values of several species of Unionids are deposited close to values predicted using equation (2). It is clear that further studies are required to resolve this issue.

Comparison of molluscan seasonal $\delta^{18}O_{(CaCO_3)}$ variation

There is a distinct difference in the degree of variability about the seasonal patterns of $\delta^{18}O_{(CaCO_3)}$ between the fingernail clam and the zebra mussel. We propose that this is a function of the water budget of the different lakes, in particular the residence time and input to volume ratio. The relatively constant seasonal $\delta^{18}O_{(H_2O)}$ value of Keuka Lake is a function of a 6-year residence time and the greater size of the drainage basin that integrates individual precipitation events (Table 1). As a result, the zebra mussel seasonal pattern in $\delta^{18}O_{(CaCO_3)}$ values is predominately a function of temperature (Figure 7).

In contrast, the fingernail clam from Science Lake displays significant variation about the seasonal pattern in $\delta^{18}O_{(CaCO_3)}$ values, that we interpret to be related to untracked variation in the $\delta^{18}O_{(H_2O)}$ value (Figure 6). In small basins such as Science Lake, it may be possible to de-convolve secular trends in storminess and seasonal temperature variation. However, changes in a lake size or residence time may affect the seasonal pattern without, necessarily, a corresponding atmospheric change.

Another distinct difference in seasonal variability between $\delta^{18}O_{(CaCO_3)}$ values of the fingernail clam and the zebra mussel is winter growth. $\delta^{18}O$ values from the fingernail clam from Science Lake suggest that the organism does not accrete $CaCO_3$ during the winter months. A plateau in $\delta^{18}O_{(CaCO_3)}$ values occurs between 9.3–10.1 mm averaging $-8.9‰_{(VPDB)}$, while values peak at $-8.6‰_{(VPDB)}$ (Figure 4). It is not possible to accurately define the growth cessation point because water temperature was not continually monitored; however, a reasonable estimation can be constructed using the 2-week running average of air temperature, which appears to correspond well with the brief warming period toward the end of the fall. The highest value $-8.6‰_{(VPDB)}$ corresponds to a temperature of 10 °C, the same temperature estimated by Krantz et al. (1987) for the marine bivalve *Spisula* and for *Aplodinotus grunniens* fish otoliths (Patterson et al., 1993). If the average 'plateau' value of $-8.9‰_{(VPDB)}$ is taken to correspond to the growth cessation point, then a temperature of ~ 12 °C is estimated, which is in agreement with the results of Dettman et al. (1999) for 3 species of Unionids. The zebra mussel apparently grows well into the winter, recording a maximum $\delta^{18}O_{(CaCO_3)}$ value of $-4.1‰_{(VPDB)}$, which corresponds to a minimum temperature of 2 °C

according to equation (2). Neumann et al. (1993) found virtually no winter shell growth for zebra mussels by applying a negative exponential growth equation in winter months, and tentatively suggested that this might be a function of a growth cessation point and/or inadequate food supply. This study presents evidence that shell material does accrete during the winter months in Keuka Lake via $\delta^{18}O_{(CaCO_3)}$ values taken from a zebra mussel; however, at a much reduced rate when compared to summer growth. Therefore, these results are not necessarily different from those found by Neumann et al. (1993).

Molluscan $\delta^{13}C$ values

Because dissolved inorganic carbon (DIC) isotope values ($\delta^{13}C_{(DIC)}$) were not measured, fractionation of carbon into the $CaCO_3$ shell can only be estimated based on seasonal variation in $\delta^{13}C_{(DIC)}$ in other aquatic systems. $\delta^{13}C_{(CaCO_3)}$ values in both specimens decrease during the summer. However, it is likely that the $\delta^{13}C$ value of the DIC increased with productivity during the summer (e.g., Atekwana & Krishnamurthy, 1998; Dettman et al., 1999; von Grafenstein et al., 1999). $\delta^{13}C_{(CaCO_3)}$ values presented here are on average several per mil more negative and show a greater seasonal range (-7 to $-12‰_{(VPDB)}$ and -4.0 to $-9.1‰_{(VPDB)}$) than is reported for lakes (e.g., von Grafenstein et al., 1999). Additionally, co-variation with $\delta^{18}O_{(CaCO_3)}$ values suggest that there is a non-linear temperature effect on metabolic processes because the temperature influence on inorganic aragonite-HCO_3^- carbon is insignificant (Romaneck et al., 1992).

Geological and archeological implications

The tremendous abundance of fossil molluscs in archaeological and geological records presents exceptional opportunities for deriving geochemical and paleoclimate information from $\delta^{18}O_{(CaCO_3)}$ and $\delta^{13}C_{(CaCO_3)}$ values. $\delta^{13}C_{(CaCO_3)}$ values appear to be related to physiological variables such as metabolic activity, trophic position, and/or reproduction, which may have significant implications for evolutionary and physiological studies, for both extant and extinct species. High-resolution techniques are necessary to uncover seasonal and ontogenetic variation in $\delta^{18}O_{(CaCO_3)}$ values on sub-daily time scales, which are predictably related to the temperature and $\delta^{18}O_{(H_2O)}$ value.

Using the seasonal pattern in $\delta^{18}O_{(CaCO_3)}$ values from fossil shells it may be possible to evaluate changes in

storminess and/or temperature seasonality. Variation about the seasonal pattern in $\delta^{18}O_{(CaCO_3)}$ value in small lake basins is probably a result of individual storm perturbations. We present further evidence of a shut-down temperature in a temperate mollusc (below this temperature, carbonate no longer accretes, whereas above this temperature carbonate accretes). This shut-down temperature (10–12 °C) is in agreement with other findings both on an intraclass (e.g., Krantz et al., 1987; Dettman et al., 1999) and interphylla level (Patterson et al., 1993). A known temperature of skeletal growth cessation would permit a discrete calculation of $\delta^{18}O_{(H_2O)}$ value at that time of year (Patterson, 1993, 1998). If the seasonal variation in $\delta^{18}O_{(H_2O)}$ value can be determined, discrete calculation of temperature for the remainder of the growing season can be defined. While this approach has been used successfully in studies of fish otoliths (Smith & Patterson, 1994; Patterson, 1998), the relative abundance of fossil mollusc material suggests even greater opportunities for studies of paleolimnology, paleoclimatology, and paleoecology.

Because the zebra mussel continued to accrete carbonate during the winter, it provides the opportunity to track the full range of seasonality in high-latitudes. For such a study, $\delta^{18}O_{(H_2O)}$ values would be estimated assuming a minimum temperature of water in a temperate setting (0–4 °C). Lastly, the growth rate of many molluscs, coupled with the technology for high-resolution partitioning of $CaCO_3$, has application toward season-of-capture information, which is important for the establishment of seasonal occupation of archaeological sites (Casteel, 1976).

Conclusions

A high-resolution record was recovered from two species of temperate modern lacustrine molluscs to investigate their suitability for recovering paleoenvironmental records on daily to weekly time scales. *Sphaerium simile* and *Dreissena polymorpha* yield $\delta^{18}O$ values calculated from environmental parameters. Relatively short-term temperature variability, such as a warming trend toward the end of 1999 is faithfully recorded. This finding is in agreement with a recent report of equilibrium oxygen isotope fractionation in several species of temperate freshwater Unionidae molluscs, and in contrast with evidence indicating oxygen isotopic disequilibria in other species of freshwater molluscs. However, we find evidence for familial differences in the temperature-

fractionation equation. The *Sphaerium simile* sampled from Science Lake apparently produced $\delta^{18}O_{(CaCO_3)}$ values more in accord with the temperature-fractionation relationship of Patterson et al. (1993), rather than Grossman & Ku's (1986) equation. Conversely, the zebra mussel from Keuka Lake was found to be in equilibrium with Grossman & Ku's (1986) temperature-fractionation relationship. Further study is needed to better delineate subtle differences and mechanisms in freshwater molluscan fractionation of stable oxygen isotopes. Nonetheless, the seasonal pattern in the $\delta^{18}O_{(CaCO_3)}$ values is a powerful tool for interpreting climates of the past.

We have shown that the seasonal pattern of $\delta^{18}O_{(CaCO_3)}$ value is significantly influenced by the organism's environment. For example, a greater degree of variation about a seasonal trend is found in the mollusc from a small watershed environment. This is probably due to increased sensitivity of the watershed to day-to-day variation in temperature, in addition to $\delta^{18}O_{(H_2O)}$ variability resulting from input of storm water. Selection of an appropriate watershed makes it possible to evaluate secular changes in storminess, an important characteristic of climate. Conversely, interpretation of temperature seasonality is best accomplished using a large watershed that provides a relatively predictable seasonal variation in $\delta^{18}O_{(H_2O)}$ value.

High-resolution $\delta^{18}O_{(CaCO_3)}$ and $\delta^{13}C_{(CaCO_3)}$ values have widespread implications for paleoenvironmental and physiological studies. Climatic and geochemical information can be determined from $\delta^{18}O$ values, while trophic condition, metabolic rate, and/or reproduction systematics may be derived from $\delta^{13}C$ values.

Acknowledgements

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