Oxygen isotope composition of Lampsilis cardium from Boone River and Buffalo Creek in Iowa: implications for seasonal growth

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Oxygen isotope composition of *Lampsilis cardium* from Boone River and Buffalo Creek in Iowa: Implications for seasonal growth

by

Ann Elizabeth Goewert

A thesis submitted to the graduate faculty in partial fulfillment of the requirements for the degree of

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has met the thesis requirements of Iowa State University

Signatures have been redacted for privacy
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Chapter 1: General Introduction

Statement of the Problem

Mollusk shells may preserve both ontogenetic history and local environmental characteristics because of their incremental growth patterns (termed sclerochronology). Growth bands (concentric internal and external features on mollusk shells) have been employed to estimate age and growth rates. Early studies assumed that growth bands were deposited annually (e.g., Isley, 1914; Coker et al., 1921; Chamberlain, 1931; Crowley, 1957; Negus, 1966; Brousseau, 1984). Isley (1914), an early proponent of this aging method, questioned the underlying assumption of annual band deposition and maintained that evidence was lacking to support the absolute age provided by this method. In a later study, Coker et al. (1921) observed shells with growth structures that were clearly not annual, fueling the debate about whether growth bands serve as annual markers. Crowley (1957) compared growth bands in *Anodonta anatine* to methods used in tree ring analysis (dendrochronology), and he reported that growth diminished with age and that accretion of growth bands was influenced by seasonal factors, primarily temperature. Negus (1966) performed a mark and recapture study investigating whether “dark” bands were produced annually. She aged forty-three unionids and found that thirty-seven produced “dark” annual growth bands. Unlike Negus, Hughes and Clausen (1980) studied marine bivalves and found variability in the formation of growth bands. More recent studies estimated theoretical age and growth rate using von Bertalanffy growth equations (McCuaig and Green, 1983; Kesler and Downing 1997; Anthony et al., 2001). McCuaig and Green (1982) used the Ford-Walford plot and von Bertalanffy equations to investigate age and growth and
reported that the annulus-based age technique underestimated age compared to the von Bertalanffy growth equations.

Freshwater bivalves are of great ecological and practical importance. They serve as biomonitors reflecting the health of a system due to their incorporation of organic contaminants and heavy metals (Foster and Bates, 1978; Imlay, 1982; Metcalfe-Smith and Green, 1992). These suspension feeders filter inorganic and organic particles from the water. Their excreted feces are edible for higher trophic levels influencing plankton ecology and trophic dynamics (Winter, 1978; National Native Mollusk Conservation Committee, 1997; Vaughn and Hakenkamp, 2001). They serve as nutrient recyclers (Nalepa et al., 1991; Vaughn and Hakenkamp, 2001). Socio-economically, they contribute to the cultured pearl industry (Thiel and Fritz, 1993; National Native Mollusk Conservation Committee, 1997; Anthony et al., 2001). Historically, the button industry dredged major rivers such as the Mississippi and punched out blanks from the nacre of unionid shells, decimating unionid populations.

Unionids are one of the most threatened groups of animals in North America. Of the nearly 300 species of freshwater bivalves, 70% are listed as endangered, threatened, species of special concern, or extinct (Williams et al., 1993). Anthropogenic factors such as habitat and water quality degradation, river alteration and impoundment, introduction of exotic species from the ballast water of ships, and commercial exploitation have been implicated as causes of unionid decline (Mehlhop and Vaughn, 1994; Neves, 1999; Strayer et al., 2004; Lydeard et al., 2004). Given the decline, age estimates must be more accurate and reliable.
Beamish and MacFarlane (1983) demonstrated that small errors in the determination of growth and age can lead to the devastation of exploited populations and engender disastrous economic consequences. It is therefore important to know whether bivalve aging techniques are reliable. Metcalfe-Smith and Green (1992) found that age estimates of *Elliptio complanata* based on internal bands were more accurate than external bands; however, for *Amblema plicata* age estimates from external bands were more accurate. The accuracy of age estimates based on internal or external growth bands may be species specific. Other studies suggest that age estimates from growth bands may be reliable for younger, faster growing bivalves, but older, slower growing bivalves cannot be aged in this manner (Isley, 1914; Neves and Moyer, 1988; Downing et al., 1992; Downing and Downing, 1993). Downing et al. (1992) concluded that growth bands were decidedly not annual. Given the severity of unionid decline and our lack of reliable aging techniques, it is essential to develop new methods to resolve this issue.

Geochemical analyses sampled parallel to the growth direction may provide an alternative method for aging shells. Oxygen isotope composition of shell carbonate is inversely related to temperature. Therefore, analysis of the oxygen isotope composition could provide information on the seasonality of growth (Tevesz et al., 1996; Dettman et al., 1999; Surge et al., 2001; Wurster and Patterson, 2001; Elliot et al., 2003). This study seeks to test the hypotheses (1) that oxygen isotope composition of the shell ($\delta^{18}O_{\text{shell}}$) of *Lampsilis cardium* (Rafinesque, 1820; plain pocketbook) are in isotopic equilibrium with the ambient environment; and (2) that dark growth bands occur in winter months. To test these hypotheses, bivalves were tagged in BR and BC, Iowa, USA. Water samples were collected
to characterize environmental conditions and provide the data to construct a predictive shell against which to compare the measured variability in isotopic composition of shell carbonate. This approach has been ground-truthed by previous studies (Dettman et al., 1999; Surge et al., 2001; Wurster and Patterson, 2001; Elliot et al., 2003) and is useful for evaluating the season of growth band formation and growth history from one freshwater mollusk species, *Lampsilis cardium*.

**Literature Review**

**Stable Isotope Systematics**

Stable isotopes are naturally occurring elements that have identical numbers of protons, but have different numbers of neutrons and do not decay like radiogenic isotopes. For instance, $^{16}\text{O}$ has 8 protons and 8 neutrons, while $^{18}\text{O}$ has 8 protons and 10 neutrons. This variation in neutrons results in mass differences among isotope species. Heavier atoms have slower vibrational frequency and increased binding energy with greater nuclear stability than lighter atoms.

Isotopic fractionation is the partitioning of heavy and light isotopes between solid, liquid, and gaseous phases due to physical or chemical processes (e.g., between a mineral, such as aragonite, and water). Fractionation can occur via three main processes. Equilibrium isotope effect is when the isotope species arrange themselves in a state of minimum free energy. Kinetic isotope effects refer to differing rates of isotope exchange in chemical or physical reactions. Metabolic isotope effect or vital effect refers to the
preferential enrichment or depletion of an isotope and the fractionation occurring during metabolism.

Fractionation is quantified using the fractionation factor, (α). This is a unitless measure that refers to the magnitude of fractionation (or partitioning) of the heavy relative to the light isotope. It is a temperature-dependent process and is expressed as:

\[ α = \frac{R_A}{R_B} \]  

where \( R \) is the ratio of the heavy isotope to the light isotope, and \( A \) and \( B \) are the two phases (e.g., solid/liquid). Oxygen isotope fractionation under equilibrium conditions is inversely proportional to temperature. Thus, there is less fractionation at higher temperatures and greater fractionation at lower temperatures. Generally, solid phases are enriched in the atoms of the heavy isotope while liquid phases are enriched in the light isotope because of difference in binding energy between the two phases.

When the atoms of heavy and light isotopes fractionate, isotope exchange occurs. For example, when water reacts with carbon dioxide, the water molecule exchanges the oxygen isotope with the carbon dioxide molecule.

\[ \text{H}_2\text{O}^+ + \text{C}^{18}\text{O}^+ \leftrightarrow \text{H}_2^{18}\text{O} + \text{C}^{16}\text{O}_2 \]  

This transfer of isotopes can occur as an equilibrium reaction (e.g., equilibrium isotope effect) or a kinetic reaction (e.g., kinetic isotope effect). Equilibrium reactions adhere to the conservation of mass, where the mass and the number of atoms are preserved before and after the reaction. Non-equilibrium reaction or kinetic reaction occurs because of an incomplete reaction or a one way reaction due to varying rates. Evaporation is an example of a kinetic reaction. During periods of evaporation, the light isotope is preferentially released as a gas vapor while the heavy isotope is preferentially maintained in the liquid
state. In addition to equilibrium and kinetic reactions, there is a biological reaction called "metabolic isotope effect" or "vital effect". This refers to reactions within a biological system which results in measurable fractionation. However, vital effects are more common in stable carbon isotope composition rather than oxygen isotope composition.

Mass spectrometers are generally employed to determine the isotopic composition of a sample. Isotopic composition is expressed in the delta notation in per mil units (‰):

$$\delta = \left[ \frac{R_{SAMPLE}}{R_{STANDARD}} - 1 \right] \times 10^3$$ (3)

Thus, when the sample has a greater isotopic ratio than the standard, the sample is enriched in the heavy isotope relative to the standard. Oxygen isotope composition is measured using an isotope ratio mass spectrometer (IRMS), which is comprised of a source, a flight tube with a magnet, and a detector system. The shell carbonate powder is acidified with $\text{H}_3\text{PO}_4$ and converted to a gaseous form ($\text{CO}_2$) and introduced into the mass spectrometer. The source bombards and ionizes the gas. The ionized gas enters the flight tube where the magnet deflects the light and heavy isotope species into detectors. The detector measures the abundance in ratios of heavy to light isotopes.

**Isotope Paleothermometry**

Stable isotopes were originally employed to examine calcareous organisms in pursuit of paleoclimate and paleoecological data (Urey *et al.*, 1951). Oxygen isotope composition of foraminifera, a form of zooplankton, was analyzed to investigate temperature variation (Wefer and Berger, 1980). In addition to obtaining stable isotope data, some species of foraminifera coil in a known direction with a given temperature range. Therefore, foraminiferal isotope data could be cross-checked by comparing temperature estimated by
coiling to temperature estimated by $\delta^{18}O_{\text{shell}}$. The isotopic composition of skeletal carbonates in aquatic environments is dependent upon water temperature and salinity (the mixing of $\delta^{18}O$ from freshwater and saltwater end members; Epstein et al., 1951; Krantz et al., 1984; Jones et al., 1986; Kirby et al., 1998; Surge et al., 2001; Surge et al., 2003). In other words, $\delta^{18}O_{\text{shell}}$ is a function of the $\delta^{18}O_{\text{water}}$ and the water temperature at the time of accretion.

The application of $\delta^{18}O$ as a paleothermometer in calcite minerals was first developed by Harold Urey (Epstein et al., 1951; Urey et al., 1951; Epstein et al., 1953; Epstein and Lowenstam, 1953; and O’Neil et al., 1969), and later was revised for application to calcite (Epstein et al., 1953; O’Neil et al., 1969) and aragonite (Grossman and Ku, 1986; Dettman et al., 1999). Urey et al. (1951) determined that the oxygen isotope composition of calcite and aragonite from marine belemnites reflected the temperature at which the mineral formed.

Epstein et al. (1953) documented the relation between the $\delta^{18}O$ of skeletal carbonate from marine mollusks and water temperature by notching shells of *Strombus gigas* that were grown in temperature-controlled tanks. The newly accreted aragonite shells were sequentially sampled parallel to the growth direction and analyzed geochemically. By constraining $\delta^{18}O_{\text{water}}$, they determined the fractionation factor for a given temperature. This relationship between calcite and water temperature was later refined by Craig (1965). Tarutani et al. (1969) investigated the oxygen isotope fractionation between aragonite and water at 25°C. This and later studies found that aragonite was enriched by $+0.6\%$ relative to calcite (Tarutani et al., 1969; Aharon and Chappel, 1983; Grossman and Ku, 1986).
Studying isotopic variation in shells from freshwater ecosystems is more complicated than in ocean settings due to mixing of multiple sources of water (e.g., groundwater, surficial runoff, seasonal precipitation, and snow melt) each with a distinct $\delta^{18}O_{\text{water}}$. Dettman et al. (1999) modified the fractionation equation of Grossman and Ku (1986) for freshwater systems by analyzing unionid shells. During the study period, water samples and water temperatures were recorded to construct a predicted shell investigating whether the organism was in isotopic equilibrium with the environment. Such studies allow the application of stable isotope geochemistry to ecological and environmental questions. Incremental growth potentially serves as a record of ambient environmental conditions. Dettman et al. (1999) and others have found that *Lampsilis siliquoidea*, *Alasmisdonata viridis*, *L. radiata*, *Strophitus undulatus*, *Cyclonaias tuberculata*, *Villosa iris*, and *Anondonta grandis* deposit their shells in oxygen isotope equilibrium with ambient environmental conditions (Dettman and Lohmann, 1993; Dettman, 1994; Tevesz et al., 1996; Dettman et al., 1999). By combining stable isotope geochemistry with incremental growth patterns (sclerochronology, discussed below), we can expand our knowledge of molluscan growth rates and population dynamics (Veinott and Cornett, 1996; Jones and Quitmyer, 1996; Kirby et al., 1998; Dettman et al., 1999; Surge et al., 2001; Goodwin et al., 2001; Schöne et al., 2002; Schöne et al., 2003), pollution sources (Schöne et al., 2003), and seasonal data such as temperature, salinity, and productivity (Fritz and Poplawski, 1974; Killingley and Berger, 1979; Arthur et al., 1983; Jones and Allmon, 1995; Bemis and Geary, 1996; Tevesz et al., 1996; Ingram et al., 1996; Kaandrop et al., 2003; Schone et al., 2003).
Unionid Sclerochronology

Sclerochronology is the study of growth banding in accretionary skeletons of corals, mollusks, and otoliths (fish ear bones) (Jones, 1983; Veinott and Cornett, 1996; Jones and Quitmyer, 1996; Kirby et al., 1998; Dettman et al., 1999; Surge et al., 2001; Goodwin et al., 2001; Schöne et al., 2002; Schöne et al., 2003). Accretionary growth features can preserve a chronological record of ontogenetic history which may include information on local environmental conditions. Originally, sclerochronology was applied to coral skeletons to investigate marine environmental conditions (Hudson et al., 1976). Skeletal carbonates such as mollusks, foraminifera, and otoliths have also been employed to study temporal variations in temperature, salinity, and productivity in oceans (Wefer, 1985; Spero and DeNiro, 1987; Spero and Williams, 1988). Mollusks serve as ideal candidates for sclerochronological studies because of their extensive geographic distribution in marine, estuarine, and freshwater habitats.

Bivalve shells are formed by accretion of calcium carbonate by the mantle tissue to the margin of the pallial line (Rhoads and Lutz, 1980). The mineralization process occurs by ion movement from the ambient water to the mollusk’s body epithelium to the mantle epithelium to the shell (Simkiss and Wilbur, 1989). When a bivalve deposits calcium carbonate, isotopic fractionation can occur. However, if disequilibrium fractionation occurs in a predictable manner, information about the ambient environmental conditions can be deciphered from isotopic variation in shell carbonate. This chronological record may serve as an archive of environmental and climate change.

Similar to tree rings, bivalves in temperate regions are thought to grow rapidly in the summer and slowly in the winter, depositing light (opaque) and dark (translucent) bands,
respectively. Chamberlain (1931) observed that at temperatures below 12°C and
disturbances, such as predation, caused bivalves to slow or cease growth in the Mississippi
River at Fairport, Iowa, the White River at Newport, Arizona, and the Rio Grande at
Mercedes, Texas. “Shutting down” or biological stasis refers to the withdrawal of the
mollusk’s tissue from the mantle margin of the shell. This retreat of tissue results in a
matrix relative to the faster growing periods characterized by more calcium carbonate. This
overlap of organic matrix provides an appearance of a translucent band.

Growth bands serve as demarcations of stressors such as aging, predation,
reproduction or an abrupt change in temperature, salinity, or food availability. Jones et al.
(1983) hypothesized that δ¹⁸O and δ¹³C of shell carbonate preserved life history and
environmental conditions and found that shell increments reflected the environmental
conditions. Jones and Quitmyer (1996) compared the timing of band deposition in Neogene
and modern northern and southern Mercenaria spp. and Jurassic Gryphaea arcuata to test
the hypothesis that dark bands formed in the winter due decreased growth rates or lack of
growth. By comparing oxygen isotope composition and temperature to assess the season of
dark band formation, they found that M. mercenaria (northern quahog) formed dark bands in
winter while the M. campechiensis (southern quahog) and G. arcuata deposited dark bands
in summer. This study suggested that the formation of growth bands was not limited to the
winter season.

Dettman et al. (1999) investigated whether two freshwater unionids, Lampsilis ovata
ventricosa (the pocketbook) and Alasmidonta viridis (the slippershell) grew in isotopic
equilibrium and to determine the season of band formation. They calculated the predicted
values based on the water temperature, δ¹⁸O_{WATER} of the Huron River and Fleming Creek in
Michigan, and the fractionation factor for aragonite and water (\( \alpha_{\text{aragonite/water}} \)). They reported that the two species of unionids precipitated their shells in isotopic equilibrium. Barrera and Tevesz (1990) and Tevesz et al. (1996) further documented the usefulness of \( \delta^{18} \text{O} \) values of the shell serving as a tool for ecological and paleoecological investigation of unionids.

The purpose of this thesis research was to investigate the growth history of \( L. \) cardium and the season of growth band formation using geochemical and sclerochronologic methods. This study sought to determine whether unionid shells can be employed as an archive of the ambient environment and ontogenetic growth history.

**Thesis Organization**

The body of this thesis is organized into one manuscript. Chapter 2 of this thesis is written in the format of a manuscript that will be submitted to the journal *Palaeogeography, Palaeoclimatology, Palaeoecology*. It pertains to the use of combining geochemistry and sclerochronology to better understand the ontogenetic history of *Lampsilis cardium*. Chapter 3 is a discussion of the conclusions obtained from this study.

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Chapter 2: OXYGEN ISOTOPE COMPOSITION OF *Lampsilis cardium* FROM BOONE RIVER AND BUFFALO CREEK IN IOWA: IMPLICATIONS FOR SEASONAL GROWTH

A manuscript prepared for submission to *Palaeogeography, Palaeoclimatology, Palaeoecology*.

Ann Goewert, Donna Surge, John Downing, and Scott Carpenter

Abstract

Unionids grow their shells incrementally. Thus, they potentially preserve ontogenetic history and ambient environmental conditions as seasonal variation in oxygen and stable carbon isotope compositions (δ¹⁸O and δ¹³C, respectively). This study combined geochemistry and sclerochronology to investigate whether *Lampsilis cardium* precipitated its shell in isotopic equilibrium with the ambient environment and if growth bands were deposited seasonally. To characterize ambient conditions, we measured temperature, δ¹⁸O[WATER], δ¹³C of dissolved inorganic carbon (DIC), and pH biweekly from September 2002 to July 2004 in two Iowa rivers, Boone River (BR; agricultural watershed with C-4 plants: corn) and Buffalo Creek (BC; urban watershed with C-3 plants: soybeans). These data were used to calculate predicted values of isotopic composition to compare to measured shell values. One hundred fifty-four individuals were marked at the postero-dorsal margin in September 2002 and June 2003. Seven recaptured shells collected in July 2004 were measured isotopically across three growth bands from the growing edge towards the umbo. δ¹⁸O[SHELL] corresponded to predicted values from early spring to early fall. Predicted winter values were not recorded, representing winter growth cessation. Rapid temperature change
appears to control the onset and cessation of growth. The location of seasonal growth bands
corresponded to winter cessation, and non-seasonal disturbance bands were identified. In
BR, $\delta^{13}C_{\text{shell}}$ did not follow predicted values and were offset by +1 to +4% (VPDB). In
BC, three of the four shells tracked predicted values during spring and summer, but not
during fall. This finding suggests that vital effects control $\delta^{13}C$ in some of the shells all of
the time and in all of the shells some of the time. Regardless of the correspondence (or lack
thereof) to predicted values, $\delta^{13}C$ values of shells from BC are more negative than those
from BR. This result is consistent with expected offsets between watersheds having C-4
(BR) versus C-3 vegetation (BC). We conclude that $\delta^{18}O_{\text{shell}}$ can be used to decipher
seasonal variation in shell growth. Although $\delta^{13}C_{\text{shell}}$ may not be useful to reconstruct
seasonal change in sources of DIC, it can be used to reconstruct changes in the dominant
vegetation within a watershed.

1. Introduction

Greater than 70% of the 300 North American species of unionids are extinct,
extirpated, or species of concern (Williams et al., 1993) and little is known about their life
history and growth patterns. Unionids are composed of repeating layers of microstructure
formed by mantle accretion of calcium carbonate (Rhoads and Lutz, 1980). Shell growth
features serve as archives of the individual's growth history and local environmental
conditions (Jones, 1983; Jones et al., 1983; Jones and Quitmyer, 1996; Tevesz et al., 1996;
Veinott and Cornett, 1996; Kirby et al., 1998; Dettman et al., 1999; Goodwin et al., 2001;
Surge et al., 2001; Wurster and Patterson, 2001; Schöne et al., 2002; Schöne et al., 2003;
Elliot et al., 2003). In temperate regions, unionids have been presumed to grow seasonally.
Growth during warm months is characterized by rapid calcium carbonate deposition. In contrast, winter growth is slowed or arrested, producing negligible amounts of calcium carbonate. Arrested growth or biological stasis results in layers of organic matrix (composed of conchiolin) overlapping, providing the appearance of a dark growth band.

Early attempts to estimate age and growth rates used growth bands as a measure of one year (e.g., Isley, 1914; Coker et al., 1921; Chamberlain, 1931; Crowley, 1957; Negus, 1966; Brousseau, 1984). Coker et al. (1921) questioned the validity of this method citing the observation of multiple growth bands deposited in one year, stating that “annual” growth bands were not distinguishable from disturbance bands. Chamberlain (1931) noted that unionids formed two types of bands. Seasonal growth bands form when temperatures dropped below 12°C creating unsuitable growth conditions. In contrast, disturbance bands are triggered by stress, such as predation, turbidity, and non-seasonal spikes in temperature (e.g., release of reservoir water). The formation of both seasonal and disturbance growth bands in one calendar year results in inaccurate estimates of age and growth rates.

Recent methods to determine age use mathematical growth models. von Bertalanffy growth equations have been employed to estimate the theoretical age of unionids (McCuaig and Green, 1982; Kesler and Downing, 1997; Anthony et al., 2001). Anthony et al. (2001) used mark and recapture dates and measurements in conjunction with von Bertalanffy growth equations to compare theoretical age to annulus-based age (growth bands). They reported that the annulus technique underestimated the age of unionids. The reliability of growth bands as age indicators is still controversial.

The combination of geochemistry and sclerochronology (shell growth features) can be employed to elucidate the growth record. Interactions between the local environment and
the physiology of unionids are not well documented. Geochemical variations of shell carbonate have been employed to decipher the influence of environmental factors on bivalve growth, such as the effect of temperature on growth patterns and rates (Jones et al., 1983; Wurster and Patterson, 2001; Elliot et al., 2003; Dettman et al., 2004; Goodwin et al., 2004). Dettman et al. (1999) reported that Lampsilis ovata ventricosa (the pocketbook) and Alasmidonta viridis (the slippershell mussel), in two Michigan rivers, precipitate their shells in isotopic equilibrium with the ambient environment. They concluded that shells reliably record the growth history and environmental variability. In addition, they documented that growth bands occurred in winter months and were triggered by temperatures below 12°C. Thus, shells of other freshwater species may also serve as archives of ontogenetic and environmental history.

L. cardium is an abundant species of freshwater mussel in Iowa rivers and may provide archives of growth history and environmental change associated with historical intensification of agriculture. This study tests the hypotheses that (1) shells of L. cardium are in isotopic equilibrium with the ambient environment; and (2) growth band formation of individuals from temperate regions occurs during winter months when temperature falls below optimal growth conditions.

2. Methods

2.1 Site Description

Intensive agricultural practices have altered the hydrology and the physical structure of rivers, consequently resulting in flashy systems, excessive sediment and nutrient loads, unstable substrates, and decline in the native aquatic fauna (Richter et al., 1997; Wood and
Armitage, 1997). This study focuses on the Boone River (BR), which is situated in Hamilton County in north central Iowa, and Buffalo Creek (BC), located in Linn County in eastern Iowa near Cedar Rapids (Figure 1). BR and BC were selected based on a survey of unionids by Arbuckle (2002), who reported an abundant and diverse molluscan fauna at these sites. Additional site criteria were based on the physical structure of the river serving as suitable molluscan habitat. It was important that the rivers were buffered from the intensive agriculture and that the river beds had a mixture of stable gravel and sand substrate to support a diverse and abundant fauna. A shallow water depth was desirable for collection of the unionids. Overall, the sites were to obtain the greatest number of unionids.

BR begins in Hancock County and empties into the Des Moines River south of Webster City and has a main channel length of 166 km characterized by a riffle-pool structure and a semi-stable gravel and sand substrate. It is buffered from row crops dominated by corn with a surrounding strip of deciduous trees (http://waterdata.usgs.gov/ia/nwis/rt).

BC is a tributary of the Wapsipinicon River starting in Jones County and ending in Fayette County. It also has a riffle-pool structure with a stable gravel and sand substrate. This river is buffered with deciduous trees and soybean crops. Unlike BR, BC runs through an urban environment and is situated primarily among cattle farming (http://waterdata.usgs.gov/ia/nwis/rt).

2.2 Mark and Recapture

*L. cardium* served as an ideal specimen for this study because of its large, thick shell allowing ample shell material for the investigation of seasonal isotopic variation. This
species is also abundant and has a wide distribution in Iowa and other Midwestern rivers. One hundred fifty-four *L. cardium* were collected from BR (*n*=92) and BC (*n*=62). The left valve of each animal was cleaned of organic matter and marked with pointed plastic labels cemented with Zap-it Accelerator and Base®, a type of dental cement (Dental Ventures of America), to the postero-dorsal margin of individual shells (Figure 2). Specimen identification labels identify the locality and the specimen number. The pointed edge of the plastic label was affixed at the postero-dorsal margin of the shell to indicate the beginning of the study (i.e., time zero). At the time of marking, all individuals were measured with vernier calipers (0.1 cm) for length (perpendicular to the hinge at the umbo to the margin), height (along the maximum distance of the postero-anterior axis), and thickness (parallel to the two dorsal shell sides) and then replaced into their original locations. The unionids in BR were marked on September 1, 2002 and recaptured on July 7, 2004, while those in BC were marked June 23, 2003 and recaptured on July 15, 2004. The discrepancy between the marked dates is due to the onset of cooler weather resulting in the bivalves burrowing below the surface of the river bottom. Each recaptured bivalve was measured for length, height, and thickness and then killed on-site. Ten of the ninety-two marked bivalves from BR were recovered, while three of the sixty-two marked animals were found in BC. Three unmarked *L. cardium* were also collected in BC due to the low recapture percent. The high degree of spring showers may have displaced the unionids contributing to the low recapture percent.

2.3 Local environmental conditions

To characterize local environmental conditions, we sampled water (2 meters below the surface) biweekly from September 2002 to July 2004 in BR and from June 2003 to July
2004 in BC. Water temperature and pH were measured using a hand-held YSI multi-parameter probe at a depth of 2 meters below the water surface. Water samples were collected biweekly at each site for isotopic analysis. Fifteen ml of water were stored in plastic Nalgene bottles for $\delta^{18}$O analysis. Thirty ml of water were filtered, poisoned with benzalkonium chloride and stored in glass serum vials sealed with CO$_2$ impermeable septa for $\delta^{13}$C analysis of dissolved inorganic carbon (DIC). Water samples could not be collected from December 2003 to March 2004 in BR because the ice froze to the river bottom. Due to a refrigerator malfunction, 6 of the $\delta^{18}$O$_{\text{WATER}}$ samples and 12 of the $\delta^{13}$C$_{\text{DIC}}$ samples froze and cracked; thus, these samples were discarded.

The $\delta^{18}$O$_{\text{WATER}}$ and $\delta^{13}$C$_{\text{DIC}}$ values were analyzed using a GasBench II auto-preparation system coupled to a Finnigan Delta Plus/XL isotope ratio mass spectrometer (IRMS). Five ml samples of water were equilibrated with CO$_2$. Repeated measurements of an internal water standard normalized the data to within 0.1% standard deviation, and absolute values were normalized to the international standards VSMOW (Vienna Standard Mean Ocean Water) and VSLAP (Vienna Standard Light Antarctic Precipitation). One hundred samples of water were collected from the Skunk River in Ames, Iowa and repeated measurements of individual samples served as the internal standard. $\delta^{18}$O$_{\text{WATER}}$ values are reported in per mil units (‰) with respect to the VSMOW standard. $\delta^{13}$C$_{\text{DIC}}$ values are reported in per mil units relative to VPDB (Vienna Pee Dee Belemnite) standard.
2.4 Shell Samples

To control for varying growth rates associated with size variability, we selected a subset of the recaptured shells for isotopic analysis from roughly the same size class. Three individuals from BR and four from BC were selected for $\delta^{18}$O and $\delta^{13}$C analysis. High-resolution carbonate samples were obtained using a mounted Brasseler dental hand-set fitted with a 0.3 mm burr. Microsamples were drilled from the outer prismatic layer parallel to the growth direction (Table 1). The last three growth bands from the growing edge were crossed. Growth bands were identified and mapped digitally. Approximately 20 $\mu$g of carbonate powder were analyzed isotopically. The carbonate powder produced from the shell was collected and analyzed individually using a Finnigan MAT 252 IRMS with an automated carbonate reaction system (Kiel Device, Finnigan Corporation). Analytical precision for the samples was maintained at less than 0.1%. $\delta^{18}$O$_{\text{SHELL}}$ and $\delta^{13}$C$_{\text{SHELL}}$ are reported in per mil units relative to the VPDB standard.

2.5 Predicted Shell

To evaluate equilibrium precipitation, a predicted shell representing the expected $\delta^{18}$O$_{\text{SHELL}}$ precipitated under isotopic equilibrium was calculated for BR and BC (Figures 3 and 4). The predicted shell is based on water temperature, $\delta^{18}$O$_{\text{WATER}}$, and the temperature-dependent oxygen isotope fractionation between water and aragonite. Using the equilibrium fractionation equation presented by Grossman and Ku (1986) and later modified by Dettman et al. (1999), temperature is indirectly related to the fractionation factor shown by the following equation:
\[ 1000 \ln (\alpha) = 2.559 \left(10^6 T^{-2}\right) + 0.715 \]  

where \( T \) is temperature in Kelvin and \( \alpha \) is the fractionation factor. This modified temperature equation by Dettman et al. (1999) was chosen over the temperature equation of Grossman and Ku (1986) because it avoids uncertainties associated with applying a correction factor to adjust for the measurement scale of water (VSMOW) and oxygen isotope composition of carbonate (VPDB). The oxygen isotope composition of biogenic aragonite was obtained using the following equation:

\[
\alpha_{\text{ARAGONITE/WATER}} = \frac{\left(10^3 + \delta^{18}O_{\text{ARAGONITE/VSMOW}}\right)}{\left(10^3 + \delta^{18}O_{\text{WATER/VSMOW}}\right)}
\]  

The calculated \( \delta^{18}O \) values were converted from VSMOW to VPDB using the equation reported by Gonfiantini et al. (1995):

\[
\delta^{18}O_{\text{SHELL/VPDB}} = \left(\delta^{18}O_{\text{SHELL/VSMOW}} - 30.91\right)/1.0309
\]  

Measured \( \delta^{18}O_{\text{SHELL}} \) values of the marked portion of \( L. \) cardium were compared to the predicted shell for BR and BC (Figures 3 and 4). Measured and predicted \( \delta^{18}O_{\text{SHELL}} \) values were aligned to account for the varying growth rates and periods of stasis. Comparing the measured shell data to the predicted shell required assignments of dates to individual data points. Mark and harvest dates served as anchors for the initial and final increment of growth during the water sampling period. Initial and final growth increments should record the ambient environmental conditions at or near the time of mark and harvest, respectively. The data contained between these anchor points were plotted against the model by stretching the data to account for uniform growth. This method was used successfully by Dettman et al. (1999) and Elliot et al. (2003).
To relate carbon isotope composition ($\delta^{13}C$) of shells to equilibrium precipitation, we calculated predicted $\delta^{13}C$ values. pH influences the relative abundance of aqueous carbon species (CO$_2$, HCO$_3^-$, CO$_3^{2-}$). In BR and BC, greater than 95% of DIC is in the form of HCO$_3^-$ given that our measured pH is between 6.92-8.46 for both rivers (Table 2) (Romanek et al., 1992; Barker et al., 2003). Romanek et al. (1992) report that the following equation can be used to calculate predicted $\delta^{13}C_{\text{shell}}$ values when pH is between 7.5 and 8.0:

$$\delta^{13}C = [(1.0027)(\delta^{13}C_{\text{HCO}_3^-} + 1000)] - 1000$$

(4)

where $\delta^{13}C_{\text{HCO}_3^-}$ represents the carbon isotope composition of bicarbonate. $\delta^{13}C_{\text{HCO}_3^-}$ was calculated using measured $\delta^{13}C_{\text{DIC}}$ and pH following procedures outlined by Romanek et al. (1992).

2.6 von Bertalanffy Growth Equations

von Bertalanffy (1960) growth equations were employed to estimate elapsed time based on mark and recapture data. They were used to validate the utility of this aging method by comparing the estimated elapsed time to the known elapsed time for the marked portion of the shell (Table 3). Anthony et al. (2001) solved von Bertalanffy growth equations for theoretical age of an individual (Equation 5) and the maximum age of an individual at $L_\infty$, theoretical maximum length at infinite age (Equation 6).

$$t = t_0 + \ln\{[1-(L_t/L_\infty)] - K\}$$

(5)

where $t=$theoretical age, $t_0=$age at time zero, $L_t=$length at time $t$, $L_\infty=$theoretical maximum length at infinite age, $K=$growth rate.

$$t_{\text{max}} = (\ln(L_\infty) + (K)(t_0))/K$$

(6)
This study employed the Ford-Walford relation (Equations 7 and 8) to establish the growth rate of *L. cardium* from the two rivers and allow the estimation of the coefficients of the von Bertalanffy growth equations (\(L_\infty=\)theoretical maximum length at infinite age and \(K=\)the rate at which the organism approaches the theoretical maximum length) by regressing \(L\) (length) at \((t + 1)\) as \(y\) and \(L\) (length) at \((t)\) as \(x\) in \(y = bx + a\) (von Bertalanffy, 1960). The spacing of individual data points expresses the geometric growth of juveniles over successive time periods.

A Ford-Walford plot was constructed by comparing the \(L_4\) (growth edge at time of harvest) to \(L_0\) (the growth edge at the time of marking). A linear regression of \(L_4\) to \(L_0\) allowed the estimation of the slope, \(\beta\), and the intercept, \(\alpha\) (Ricker, 1975). The slope and intercept variables were employed to calculate \(L_\infty\), the theoretical maximum length at infinite age (Equation 7).

\[
L_\infty = \frac{\alpha}{1 - \beta}
\]

Equation 8 estimates the growth rate, \(K\), by taking the natural log of the slope (change in size).

\[
K = -\ln \beta
\]

Given the estimated von Bertalanffy growth coefficients, the theoretical time elapsed, \(t\), was calculated using equation 5 while the theoretical maximum age at \(L_\infty\) was calculated using equation 6.
3. Results

3.1 Water Temperature and Chemistry

Water temperature at BR ranged from 0-28°C (Figure 5). The average 2002 to 2004 summer (June to September) temperature was 21.1 ± 5.8°C (n=12) and average winter temperature (December to March) was 1.7 ± 3.1°C (n=12). δ^{18}O_{WATER} varied from -11.32 to -2.49‰ (Figures 3 and 5). The most negative value is an excursion that occurred in late February to early March, 2004. Higher δ^{18}O_{WATER} values occurred during the winter months, and lower δ^{18}O_{WATER} values occurred in the summer. δ^{13}C_{DIC} ranged from -13.8 to -8.96‰ (Figure 6).

BC ranged in water temperature from 0-24°C (Figure 7) with a mean 2003 to 2004 summer temperature of 20.3 ± 4.03°C (n=10) and winter temperature of 20.78 ± 4.31°C (n=5). δ^{18}O_{WATER} values fluctuated seasonally from -9.16 to -3.14‰ (Figures 4 and 7). As in BR, the most negative value is an excursion that occurred during the same time interval. δ^{13}C_{DIC} ranged from -10.59 to -8.81‰ and are more or less similar to values measured in BR (Figures 9 and 10).

3.2 Unionid Shells

Measured δ^{18}O_{SHELL} and δ^{13}C_{SHELL}

Temporal variation in oxygen isotope composition within a shell followed a scalloped-shaped pattern with truncated peaks (Figures 12, 14, 16, 18, 20, 22, and 24). Oxygen isotope composition from shells in BR (specimens BR-22, BR-73, and BR-67) ranged from -8.50 to -4.95‰ (Figures 3 and 8), and those from BC (BC-62, BC-A, BC-B,
and BC-D) ranged from -8.29 and -5.18‰ (Figures 4 and 10). Spatial and temporal variation δ¹⁸O_SHHELL is reported relative to distance from the margin of shell and time, respectively (Figures 12, 14, 16, 18, 20, 22, and 24). δ¹³C_SHHELL ranged from -12.9 to -7.72‰ in BR and -13.7 to -9.68‰ in BC (Figures 6 and 9).

3.3 Predicted Isotopic Compositions

Predicted δ¹⁸O values (Figures 3 and 4) show a seasonal trend similar to a sinusoidal curve, representing the full range of possible values given the local environmental conditions throughout the water monitoring period. In general, lower values corresponded to warmer months and higher values occurred in colder months with the exception of the negative excursion in February and March, 2004. Predicted δ¹⁸O values from BR ranged from -11.32 to -2.49‰ (average summer and winter values are -6.81‰ and -4.38‰) while the predicted shell values from BC ranged from -9.16 to -3.14‰ (average summer and winter values are -7.46‰ and -4.92‰). A snowmelt pulse in late February was captured in the predicted shells from BR and BC as a negative excursion from the expected sinusoidal trend (Figures 3, 4, 5, and 7). This illustrates the influence of δ¹⁸O_WATER on the predicted shell.

Unlike predicted values of δ¹⁸O in BR, predicted δ¹³C values does not follow a seasonal sinusoidal pattern. In contrast, predicted values in BC do follow a seasonal sinusoidal pattern. Both profiles of predicted carbon isotope composition exhibit a peak associated with the snowmelt pulse in February and March, 2004. Predicted values from BR
ranged from -17.7 to -6.62%, and those from BC ranged from -12.9 to -11.1% (Figures 9 and 10).

3.4 von Bertalanffy Growth Equations

The von Bertalanffy growth equations were employed to determine the elapsed time during the mark and recapture study and the theoretical maximum age at \( L_1 \) (Table 3). The calculated linear regression estimated from the Ford-Walford relation was \( y = 0.87(x) + 2.09 \) \((n=10 \ R^2 = 0.79)\). The intercept, \( \alpha=2.09 \), and the slope, \( \beta=0.87 \), were employed to estimate the \( L_\infty \), theoretical maximum length, 16.1. The estimated \( t \), time elapsed, from von Bertalanffy growth equations ranged from 12 to 22 months with a mean of 17 months. The theoretical maximum age at \( L_\infty \) was 19.8 years.

4. Discussion

4.1 Predicted versus Measured \( \delta^{18}O_{\text{shell}} \)

Measured \( \delta^{18}O_{\text{shell}} \) corresponds to predicted values from early spring to early fall (Figure 3 and 4). Least negative predicted values corresponding to the coldest months of the year are not represented by measured shell values. This gap reflects winter growth cessation, which we discuss in detail below. We conclude that shell carbonate of \( L. \text{cardium} \) precipitates in oxygen isotope equilibrium with the ambient water. Although there are slight deviations in the measured \( \delta^{18}O_{\text{shell}} \) from the predicted values, we attribute these small offsets to differential time averaging between sampling methods of shells and water. The microsampled carbonate powder integrates an amount of time (e.g., approximately two
weeks), whereas the water data used to construct the predicted shell was collected at an instant in time. Equilibrium precipitation of \( \delta^{18}O \) in shell carbonate is consistent with the findings of Dettman et al. (1999) who examined two different species of unionids collected from Michigan rivers.

4.2 Timing of Growth Band Formation

To decipher seasonal changes in growth from variation in isotopic composition, Dettman and Lohmann (1993) show schematically the difference in the expected profile of \( \delta^{18}O \) assuming (1) growth throughout the year (sinusoidal curve); and (2) seasonal growth above temperatures of 12°C (scalloped curve with peaks corresponding to winter growth cessation). This scheme provides us with an expected pattern of growth. The seven shells sampled in our study exhibit a scalloped-shaped pattern (Figures 11 to 24). Therefore, \textit{L. cardium} does not grow throughout the entire year and exhibits winter growth cessation.

Temperature has been cited as a stimulus for winter cessation. Chamberlain (1931) and Dettman et al. (1999) report that growth cessation occurred in unionids when temperature drops below 12°C. Moreover, Howard (1921) and Negus (1966) found that the temperature range of growth cessation is species-specific. Others have found that growth is affected by temperature in marine and estuarine bivalves (Goodwin et al., 2001; Surge et al., 2001; Elliot et al., 2003). Our study observed that winter growth cessation and spring growth onset corresponds to rapid changes in temperature (Table 2). Temperatures in BR from September 21, 2002 to October 5, 2002 decreased rapidly from 14.2 to 7.2°C. The last \( \delta^{18}O \) value recorded in shells from both BR and BC occurred in late September, 2002 and early October 2003, respectively. Additionally, temperature in BR for the first measurable
growth in spring 2003 changed rapidly from 9.19 to 15.7°C. These findings are not limited to BR, but are also observed in BC (Table 2).

Another hypothesis of this study was that growth band formation of individuals from temperate regions occurs during winter months when temperature falls below optimal growth conditions. Periods of winter growth cessation consistently correlates to locations of prominent and complete growth bands demonstrating seasonal formation (Figures 11 to 24). Negus (1966) identified disturbance growth bands as incomplete and thin, while a seasonal growth band is complete and thick. Of the individuals sampled in our study, multiple shells (BR-22, BR-67, and BC-62) revealed incompletely formed disturbance growth bands (Figures 12, 20, and 22). These non-seasonal bands have been documented by Downing et al. (1992). Factors attributed to the formation of disturbance bands are non-seasonal temperature change (such as release of reservoir water), predation, and evaporation (Krantz et al., 1987). Our study discriminated disturbance bands from seasonal growth bands by comparing the amplitude of $^{818O}_{\text{shell}}$ values and the completeness of the growth band.

Dettman et al. (1999) reported variations in seasonal amplitude (one peak to one valley) of $\sim$2.5\% in temperate regions. The current study compared the seasonal amplitude variations to those reported by Dettman et al. (1999). We predicted that a seasonal growth band would show an amplitude variation of $\sim$2.5\%. Two amplitudes were observed: $\sim$1\% and $\sim$2.5\%. The growth bands associated with shifts in amplitude of $\sim$2.5\% were thick and complete; therefore, they were identified as seasonal growth bands. As a corollary, these growth bands corresponded to the three major peaks in the profiled of oxygen isotope composition, supporting seasonal growth band formation with one exception (specimen
Of the four growth bands that were recorded, one band had the required shift of 2.5% but the band was thin and incomplete; therefore, using amplitudes alone is insufficient to identify disturbance growth bands. In most cases, disturbance growth bands displayed close to a 1% seasonal shift. This method of distinguishing seasonal growth bands from disturbance growth bands allows for a more accurate estimation of age than visually counting growth bands.

### 4.3 Predicted versus Measured $\delta^{13}C_{\text{shell}}$

Measured $\delta^{13}C_{\text{shell}}$ from BR is offset from predicted values by +1 to +4% (Figure 6). In BC, three of the four measured shells track predicted values during spring and summer, but are offset by -1 to -2% during the winter. Dettman et al. (1999) reported similar findings in unionids from Michigan, except that their measured shell values were more negative than predicted. Our data suggest that metabolic isotope effects (vital effects) control $\delta^{13}C$ in some of the shells all of the time and in all of the shells some of the time.

A metabolic isotope effect refers to reactions within a biological system, which results in measurable fractionation from predicted equilibrium. Such isotope effects can be caused by metabolic controls on or incorporation of various sources of carbon, such as from food or respiration, into shell carbonate. Unionids are filter feeders that ingest fine particulate organic matter (e.g., detritus). Therefore, likely sources of carbon that affect the $\delta^{13}C_{\text{shell}}$ in *L. cardium* are ingested particulate organic matter and the DIC of the water. Corn, a C-4 plant, is the dominant vegetation surrounding the BR watershed. Decomposed corn contributes a distinct carbon isotope composition to the particulate organic matter in river water with an expected average $\delta^{13}C$ of -12% (Schlesinger, 1997). BC is situated in an
urban environment, and soybeans, a C-3 plant, are grown in the watershed. Average $\delta^{13}C$ of C-3 plants is -27‰ (Schlesinger, 1997). Therefore, shells from these two distinct landscapes will potentially record differences in $\delta^{13}C$ values because of ingestion of detritus derived from the local vegetation type.

Some of the factors that influence $\delta^{13}C_{DIC}$ include photosynthesis, decomposition of organic matter, dissolution and precipitation of sedimentary carbonate, pH, and exchange with atmospheric CO$_2$ (Kendall, 1991). The underlying geology in the study area is Paleozoic limestone, and this rock type can act as a buffer in the carbonate system of the river water. Buffering by limestone can dampen the influence of the $\delta^{13}C$ of the local vegetation type on $\delta^{13}C_{DIC}$. The similarity of $\delta^{13}C_{DIC}$ values between BR and BC suggests that these river systems are buffered by the underlying geology. Despite that $\delta^{13}C_{DIC}$ is buffered, $\delta^{13}C_{SHELL}$ reflects the vegetation structure. Measured $\delta^{13}C_{SHELL}$ values from BC are more negative by 1 to 2‰ than those from BR. This result suggests that the local vegetation within the watershed contributes particulate organic matter to the diet of _L. cardium_ and that food carbon heavily influences the $\delta^{13}C$ of shell carbonate. We conclude that although $\delta^{13}C_{SHELL}$ may not accurately reflect seasonal changes in carbon sources affecting $\delta^{13}C_{DIC}$, it may provide a means to reconstruct landscape-scale changes in vegetation type within a watershed. This in turn will contribute to our understanding of the impact of agricultural intensity through time by analyzing isotopically historical collections of unionid shells.
4.4 von Bertalanffy growth equations

In addition to the geochemical method used to identify seasonal growth we compared the theoretical time elapsed obtained from the von Bertalanffy growth equations to the known time elapsed from mark to recapture (Table 3). Others have employed these growth equations to estimate age (McCuaig and Green, 1982; Anthony et al., 2002). von Bertalanffy growth equations validated the time that accrued during the marked period. The duration of the study period for BR was twenty-two months while the estimated theoretical mean was 17 months. Isotopic analysis in conjunction with von Bertalanffy growth equations can provide a method to estimate age and growth rates more accurately. The combination of these two methods, serve as an internal control with each other. The theoretical maximum age estimated using the von Bertalanffy growth equations is 19.85 years old at L∞, the maximum length, which provides a reference of age.

Therefore, geochemical analyses can be used to discriminate disturbance bands from seasonal bands and to obtain more accurate estimations of age. The close correspondence between the theoretical time elapsed and sclerochronologic δ¹⁸OSHELL profiles corroborates seasonal banding and demonstrates the utility of this method to age unionids. This study found that shells record truncated intervals of environmental and ontogenetic archives, which allows the identification of periods of growth and shut-down, the discrimination between seasonal and disturbance growth bands, and the identification of growth and cessation stimuli.
5. Conclusions

*L. cardium* from BR and BC can be used as ontogenetic and environmental archives because they are in oxygen isotope equilibrium with ambient water conditions. This study found that growth bands occur in winter months. Rapid change in temperature is implicated as the trigger for winter growth cessation and spring growth onset. Seasonal and disturbance growth bands were identified by combing geochemistry and sclerochronology. We conclude that oxygen isotope composition can be used to better understand seasonal growth. The implications of this is that we can better assess age and growth rates. Unlike the oxygen isotope composition of shell from BR, $\delta^{13}$C$_{\text{shell}}$ did not follow predicted values and were offset by +1 to +4%. In contrast three of the four shells from BC tracked predicted values during spring and summer, but were offset during the coldest months in the year. This finding suggests that vital effects control $\delta^{13}$C in some of the shells all of the time and in all of the shells some of the time. There was no clear relationship between $\delta^{13}$C$_{\text{shell}}$ and $\delta^{13}$C$_{\text{DIC}}$. It was observed that all shells from BC were more negative than BR. This result is consistent with expected differences between watersheds having C-4 (BR) versus C-3 vegetation (BC). We conclude that $\delta^{13}$C$_{\text{shell}}$ may not be useful to reconstruct seasonal change in sources of DIC, but it can be employed to reconstruct changes in the dominant vegetation within a watershed. Additionally, isotope analysis of historical specimens may better our understanding of the impact agriculture played on unionids.
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Figure 1. Study sites (BR and BC) located in Iowa, USA. The blue lines represent BR and BC and the red starred bullet represents the site locality. Des Moines is represented by the black bullet.
Figure 2. Picture of a marked *Lampsilis cardium* in BR, IA. The label located at the postero-dorsal margin identifies the specific name and number, the black lines added to the image to enhance the seasonal growth bands. The white pits are the locations where the shell was microsampled.
Figure 3. Comparison of predicted $\delta^{18}$O$_{\text{SHELL}}$ (filled black triangle) to measured $\delta^{18}$O$_{\text{SHELL}}$ (BR-67 filled red circles, BR-22 light blue rectangle, and BR-73 dark blue diamond) of *L. cardium* from BR (BR). Submonthly averages are calculated from September 2002 to July 2004. Both the predicted and measured $\delta^{18}$O$_{\text{SHELL}}$ are relative to VPDB ($\%$).
Figure 4. Comparison of predicted $\delta^{18}$O$_{\text{SHELL}}$ (filled black triangle) to measured $\delta^{18}$O$_{\text{SHELL}}$ (BC-D filled red circles, BC-B light blue rectangle, BC-62 dark blue diamond, and BC-A purple triangle) of *L. cardium* from BC (BC). Submonthly averages are calculated from June 2003 to July 2004. Both the predicted and measured $\delta^{18}$O$_{\text{SHELL}}$ are relative to VPDB ($\%$).
Figure 5. Time series of temperature and predicted $\delta^{18}O_{\text{WATER}}$ measured biweekly at BR from September 2002 to July 2004. Filled red circles represent temperature ($^\circ$C) and filled black triangles show predicted $\delta^{18}O_{\text{WATER}}$ relative to VSMOW ($\%$).
Figure 6. Comparison of predicted $\delta^{13}$C_{SHELL} (filled black triangle) to $\delta^{13}$C_{DIC} (open gray circles) to measured $\delta^{13}$C_{SHELL} (BR-67 filled red circles, BR-22 light blue rectangle, and BR-73 dark blue diamond) of L. cardium from BR (BR). Submonthly averages are calculated from September 2002 to July 2004. Both the predicted, $\delta^{13}$C_{DIC}, and measured $\delta^{13}$C_{SHELL} are relative to VPDB (‰).
Figure 7. Time series of temperature and predicted $\delta^{18}O_{\text{WATER}}$ measured biweekly at the BC from June 2003 to July 2004. Filled red circles represent temperature (°C) and filled black triangles show predicted $\delta^{18}O_{\text{WATER}}$ relative to VSMOW (%).
Figure 8. Covariation of $\delta^{18}$O and $\delta^{13}$C values of *L. cardium* from BR. Filled dark blue diamonds=BR-73; filled light blue squares = BR-22; filled red circles= BR-67.
Figure 9. Comparison of predicted $\delta^{13}$C_{SHELL} (filled black triangle) to $\delta^{13}$C_{DIC} (open gray circles) to measured $\delta^{13}$C_{SHELL} (BC-D filled red circles, BC-B light blue rectangle, BC-62 dark blue diamond, and BC-A purple triangle) of *L. cardium* from BC (BC). Submonthly averages are calculated from June 2003 to July 2004. Both the predicted, $\delta^{13}$C_{DIC}, and measured $\delta^{13}$C_{SHELL} are relative to VPDB (‰).
Figure 10. Covariation of $\delta^{18}$O and $\delta^{13}$C values of *L. cardium* from the BC. Filled dark blue diamonds=BC-62; filled light blue squares = BC-B; filled red circles= BC-D; filled purple triangles.
Figure 11. Picture of BC-62 with growth bands numbered and enhanced.
Figure 12. Profiles of $\delta^{18}$O and $\delta^{13}$C values of live-collected specimen BC-62 from the initial sampling location to the growth margin from the BC. Filled circles are $\delta^{18}$O and filled triangles are $\delta^{13}$C. Left y-axis refers to $\delta^{18}$O and right y-axis corresponds to $\delta^{13}$C. Arrows indicate the location of growth bands.
Figure 13. Picture of BC-A with growth bands numbered and enhanced
Figure 14. Profiles of $\delta^{18}$O and $\delta^{13}$C values of live-collected specimen BC-A from the initial sampling location to the growth margin from the BC. Filled circles are $\delta^{18}$O and filled triangles are $\delta^{13}$C. Left y-axis refers to $\delta^{18}$O and right y-axis corresponds to $\delta^{13}$C. Arrows indicate the location of growth bands.
Figure 15. Picture of BC-B with growth bands numbered and enhanced
Figure 16. Profiles of $\delta^{18}$O and $\delta^{13}$C values of live-collected specimen BC-B from the initial sampling location to the growth margin from the BC. Filled circles are $\delta^{18}$O and filled triangles are $\delta^{13}$C. Left y-axis refers to $\delta^{18}$O and right y-axis corresponds to $\delta^{13}$C. Arrows indicate the location of growth bands.
Figure 17. Picture of BC-D with growth bands numbered and enhanced
Figure 18. Profiles of δ^{18}O and δ^{13}C values of live-collected specimen BC-D from the initial sampling location to the growth margin from the BC. Filled circles are δ^{18}O and filled triangles are δ^{13}C. Left y-axis refers to δ^{18}O and right y-axis corresponds to δ^{13}C. Arrows indicate the location of growth bands.
Figure 19. Picture of LC-22 with growth bands numbered and enhanced
Figure 20. Profiles of $\delta^{18}$O and $\delta^{13}$C values of live-collected specimen BR-22 from the initial sampling location to the growth margin from BR. Filled circles are $\delta^{18}$O and filled triangles are $\delta^{13}$C. Left y-axis refers to $\delta^{18}$O and right y-axis corresponds to $\delta^{13}$C. Arrows indicate the location of growth bands.
Figure 21. Picture of LC-67 with growth bands numbered and enhanced
Figure 22. Profiles of $\delta^{18}$O and $\delta^{13}$C values of live-collected specimen BR-67 from the initial sampling location to the growth margin from BR. Filled circles are $\delta^{18}$O and filled triangles are $\delta^{13}$C. Left y-axis refers to $\delta^{18}$O and right y-axis corresponds to $\delta^{13}$C. Arrows indicate the location of growth bands.
Figure 23. Picture of LC-73 with growth bands numbered and enhanced.
**Figure 24.** Profiles of $\delta^{18}$O and $\delta^{13}$C values of live-collected specimen BR-73 from the initial sampling location to the growth margin from BR. Filled circles are $\delta^{18}$O and filled triangles are $\delta^{13}$C. Left y-axis refers to $\delta^{18}$O and right y-axis corresponds to $\delta^{13}$C. Arrows indicate the location of growth bands.
Table 1. Length of shell microsamples (cm) and number of microsamples per shell

<table>
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<th>Specimen ID</th>
<th>Locality</th>
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<th>Number of samples drilled per shell</th>
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Note BC=BC; BR=BR
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K = 0.14, α=2.0, B=.87, L∞=16.1
CHAPTER 3: GENERAL CONCLUSIONS

*L. cardium* from BR and BC can be used as ontogenetic and environmental archives because they are in oxygen isotope equilibrium with ambient water conditions. This study found that growth bands occur in winter months. Rapid change in temperature is implicated as the trigger for winter growth cessation and spring growth onset. Seasonal and disturbance growth bands were identified by combing geochemistry and sclerochronology. We conclude that oxygen isotope composition can be used to better understand seasonal growth. The implications of this is that we can better assess age and growth rates. Unlike the oxygen isotope composition of shell from BR, $\delta^{13}$C$_{\text{shell}}$ did not follow predicted values and were offset by +1 to +4%. In contrast three of the four shells from BC tracked predicted values during spring and summer, but not were offset during the coldest months in the year. This finding suggests that vital effects control $\delta^{13}$C in some of the shells all of the time and in all of the shells some of the time. There was no clear relationship between $\delta^{13}$C$_{\text{shell}}$ and $\delta^{13}$C$_{\text{DIC}}$. It was observed that all shells from BC were more negative than BR. This result is consistent with expected differences between watersheds having C-4 (BR) versus C-3 vegetation (BC). We conclude that $\delta^{13}$C$_{\text{shell}}$ may not be useful to reconstruct seasonal change in sources of DIC, but it can be employed to reconstruct changes in the dominant vegetation within a watershed. Additionally, isotope analysis of historical specimens may better our understanding of the impact agriculture played on unionids.
### APPENDIX A: UNIONID STABLE ISOTOPE DATA

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### BC Calculated Shell Model

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Note: Calculations are based on the Dettman 1999 model for δ¹⁸O(WATER) and a comparison with SHELL (VPDB) for δ¹⁸O(SHELL).