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Controls on magnesium, manganese, strontium, and barium concentrations recorded in freshwater mussel shells from Ohio



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ABSTRACT

Freshwater bivalve shells may record inter-annual fluctuations in water chemistry, which in turn may archive variations in solute load due to pollution or discharge events. Here, using weekly surface water chemistry collected at two locations and shells of *Lampsilis cardium* grown in the surface water we investigate if the Mg/Ca, Mn/Ca, Sr/Ca, and Ba/Ca ratios measured at high resolution in the shells on an intra-annual time scale consistently reflect the chemistry of the surface water. Two relationships appear highly correlated, Sr/Ca_{carb} and Sr/Ca_{water}, and Mn/Ca_{carb} and temperature. Ba/Ca_{carb} correlated strongly with Ba/Ca_{water} in one shell but temperature in another shell yielding inconclusive results. Mn/Ca_{carb} and Mg/Ca_{carb} were not strongly correlated with elemental ratios in the water, but Mn/Ca_{carb} did show variable, weak to moderate correlation with pH. We found consistent partition coefficient (D_{Me}) values between individual shell samples grown in the same water with mean D_{Mg} = 0.0006, D_{Mn} = 17, D_{Ba} = 0.13, and D_{Sr} = 0.176. Sr/Ca_{carb} and Sr/Ca_{water} exhibited the strongest, most consistent correlation with partitioning coefficients that were consistent with published values, suggesting Sr/Ca_{carb} can be used as a proxy for Sr/Ca_{water} in freshwater mussels.

1. Introduction

North America is home to the largest diversity of freshwater mussels in the world, with nearly 300 species, they are found in almost every major lake and river (Ricciardi et al., 1998). Mussels precipitate their shell sequentially as they grow, and derive the building block elements of their shell from their diet and from the surrounding water (see Gibson et al., 2001). This suggests that mussel shells may be a valuable proxy for water quality that may be applicable to many bodies of freshwater in North America. Unfortunately, mussels are also experiencing a higher rate of extinction than any other North American faunal group, due to pollution, loss of habitat, and invasive species (Ricciardi et al., 1998; Ricciardi and Rasmussen, 1999). As much as 12% of North American freshwater mussel species are already extinct, with 60% either threatened or endangered (Ricciardi et al., 1998).

One of the major concerns for freshwater mussels in the United States is increasing concentrations of total dissolved solids (TDS) (Cañedo-Argüelles et al., 2016; Kaushal et al., 2005), including Cl (Kaushal et al., 2005; Metcalfe-Smith et al., 2003; Todd and Kaltenecker, 2012) and degrading water quality. In the majority of regions including the northeastern United States, the salinity of freshwater has consistently increased from year to year (Kaushal et al., 2005; Smith et al., 1987). This is due to a variety of factors including industrial waste, urban runoff, agriculture, and increased construction of low permeability structures such as roads and parking lots (Cunningham et al., 2009; Kaushal et al., 2005; Smith et al., 1987).

Bio-mineralized carbonate skeletal materials such as mussel shells and corals have a long history of producing accurate, high resolution information about past water chemistry (Beck et al., 1992; Dettman et al., 1999; Gillikin et al., 2006a; Goodwin et al., 2013; Schöne et al., 2002). Specifically, metal-calcium and oxygen isotope ratios are useful for reconstructing changes in both water chemistry and temperature in ocean systems (Beck et al., 1992; Lear et al., 2000; Waelbroeck et al., 2002; Walther and Thorrold, 2006). While the body of carbonate proxy studies in paleoceanography is quite large, there is a comparably smaller body of work examining the applicability of carbonate proxies in fresh water (Brown and Severin, 2009; Dettman et al., 1999; Gillikin et al., 2009; Gillikin et al., 2017; Kaandorp et al., 2003; Kelemen et al.,

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2017; O'Neil and Gillikin, 2014; Stuiver, 1970).

Bivalve shells are deposited sequentially in growth bands, growing outward from the soft tissue in distinct layers (Rhoads and Lutz, 1980). The sequential nature of growth allows for the reconstruction of continuous profiles of chemical change throughout the life of the organism, with high enough resolution to detect day and night cycles in some specific cases (Lazareth et al., 2007; Schöne et al., 2002). Because of the broad geographic range and varied life expectancies of freshwater mussels, it may be possible to derive several decades of geochemical data from shell samples, which can be found in a large number of freshwater environments (Goewert et al., 2007; Schöne et al., 2004; Schöne et al., 2010; Versteegh et al., 2010). This would allow for an evaluation of geochemical context of acute events such as spills or discharges to waterways as well as provide baseline measurements against which temporal changes can be compared. Metals may also be used as tracers, allowing a shell to record the time and intensity of anthropogenic or geochemical processes (Åberg, 1995; Markich et al., 2002; Palmer and Edmond, 1992; Stecher et al., 1996).

While marine mussels, corals, foraminifera, and otoliths (all forms of biogenic carbonates) are frequently utilized for their environmental reconstruction capabilities, freshwater mussels have not been similarly examined in as much detail. Our goal is to determine if the chemical composition of freshwater mussel shells correlates strongly and consistently with the chemical composition of the body of water in which the mussels grow. Specifically, do metal-calcium ratio records preserved in the shells of mussels correlate to metal–calcium ratios in the water in which the shell grew with a specific partitioning coefficient? If this partitioning relationship is consistent, it may allow the reconstruction of changes in water chemistry through time, including possible implications for the study of contaminant fate and transport in freshwater systems.

Magnesium, manganese, strontium, and barium are four commonly studied metals in bivalve shells and are frequently utilized as proxies for environmental conditions (Freitas et al., 2005; Immenhauser et al., 2005; Klein et al., 1996a; Poulain et al., 2015; Schöne et al., 2011). Mg/ Ca and Sr/Ca in carbonates are frequently utilized as paleotemperature proxies in seawater, but also may be controlled by vital effects associated with metabolism and growth rate (Freitas et al., 2005; Gillikin et al., 2005b; Purton et al., 1999). Ba/Ca in carbonates has been identified as a good environmental proxy, achieving good correlation with Ba/Ca of the water which varied with salinity (Gillikin et al., 2006a; Poulain et al., 2015). Ba/Ca_{carb} has also been identified as a possible proxy for phytoplankton productivity (Gillikin et al., 2006a; Gillikin et al., 2008; Thébault et al., 2009). Mn/Ca has been suggested as a proxy for several environmental parameters, including temperature (Ullmann et al., 2013), the availability of Mn^{2+} in solution, suggesting influence/control from redox processes (Zhao et al., 2017), changes in primary productivity (Langlet et al., 2007; Vander Putten et al., 2000) as well as phytoplankton activity due to riverine discharge (Lazareth et al., 2003). While interpretations may vary between authors and mechanisms are seldom understood, the temporal and spatial distributions of metals in bivalve shells contain a broad variety of information about environmental conditions and can be accessed through careful analysis of sequentially grown shell material.

2. Material and methods

Specimens for this study grew at the Columbus Zoo and Aquarium Freshwater Mussel Conservation and Research Center, Dublin, OH, located north of Columbus, OH (Fig. 1). A more detailed explanation of the facility and sampling protocol can be found in Goodwin et al. (in this issue). The Research Center is located along the Scioto River in a dammed section that creates the O'Shaughnessy Reservoir. The Scioto River drains to the south and eventually empties into the Ohio River.

Our study uses the same specimens as Goodwin et al. (in this issue) which used the oxygen isotope record to assign dates to the shell



Fig. 1. A Location of Scioto River, and its watershed (shaded region) within Ohio, USA. O'Shaughnessy Reservoir is approximately 25 km northwest of Columbus (rectangle). (B) O'Shaughnessy Reservoir on the Scioto River. The Freshwater Mussel Research Center is on the south-west bank of the reservoir (rectangle). Figure after Goodwin et al. (in this issue).

growth lines. Growth rates can be determined by physical measurement of the shell at known intervals, staining, or notching, but each of these methods introduces handling stress, to which freshwater mussels are sensitive and was not logistically feasible for this study (Haag and Commens-Carson, 2008). Instead, Goodwin et al. measured oxygen isotopes in each shell by micromilling along the outer edge of the shell (see Figs. SI1–3) and aligning this data with predicted oxygen isotopes using a common paleotemperature equation relating temperature, $\delta^{18}O_{water}$ and $\delta^{18}O_{shell}$ (Grossman and Ku, 1986; Dettman et al., 1999). This method has been used extensively to correlate length along the shell with time (Gillikin et al., 2005a; Goewert et al., 2007; Kelemen et al., 2017; Klein et al., 1996a).

Three freshwater mussels of the species *Lampsilis cardium* were selected for analysis. OR3-A1L was grown inside the Center within a sediment-filled raceway supplied with reservoir water and OR4-A1L and OR6-A1L were grown outside in floating sediment cages near the shoreline of the reservoir. The water inside the center was recirculated to maintain approximately 70% "old" recirculated water and 30% new water from the reservoir. Shells were monitored for shell growth between December 2009 and December 2010. *Lampsilis cardium* is found commonly throughout Ohio and ranges from US-Canada border to the Mississippi Basin (Watters et al., 2009). *L. cardium* precipitates a shell of aragonite (Dettman et al., 1999; Goewert et al., 2007; Goodwin et al., in this issue).

Water samples were collected roughly weekly throughout 2010 at both locations; inside (n = 49) and outside (n = 46). Temperature, turbidity, dissolved oxygen (DO), pH, and electrical conductivity were measured at the time of water sample collection using a field meter (YSI, Inc.). Total suspended solids (TSS), were gravimetrically determined using precombusted 47 mm Whatman GF/F filters. Water samples for dissolved element determination were filtered using a $0.2 \,\mu$ m syringe filter (Sartorius Minisart 16532-Q) and were acidified to pH 3 using ultrapure HCl and stored until analysis. Waters were analyzed on a Perkin Elmer Elan 6100 DRC at Union College using a multielement standard matched in concentration. Both SLRS-5 and NIST 1640 standards were analyzed and indicate good accuracy and Collection and sampling information for the Lampsilis cardium specimens.

Specimen	Site	Collected	Sample type	$\delta^{18} O$ samples	Metal/Ca samples	Metal sample length (mm)	Correlation points
OR3-A1L	Inside	22-Sep	Drill point	27	106	17.77	18
OR4-A1L	Outside	22-Sep	Micromill	44	132	20.55	27
OR6-A1L	Outside ^a	10-Dec	Micromill	82	77	12.45	27

^a Transplanted inside 9/22–12/10.

precision (all values were within 8% of recommended values: < 2% for Mg, < 7% for Mn, < 4% for Sr, and 8% for Ba).

Live specimens were harvested on one of two dates, September 22, 2010 (OR3-A1L and OR4-A1L) or December 10, 2010 (OR6-A1L) (Table 1). Following harvesting, flesh was removed and valves of each specimen were sectioned along the dorso-ventral axis. Sections \sim 1.5 mm thick were mounted on glass microscope slides with epoxy.

Shells were analyzed on the Perkin Elmer Elan 6100 DRC ICP-MS at Union College following laser ablation (LA-ICP-MS) with a CETAC LSX-213 frequency quintupled Nd:YAG laser ($\lambda = 213$ nm) following Gillikin and Dehairs (2013). The NIST 612 standard (values from Pearce et al., 1997) was used for calibration and MACS-3 was used as the check standard (all element ratios were within 5% of recommended values and had a relative standard deviation < 5%). The laser was set at 10 Hz and 600 burst counts with a spot size of 50 µm. A pre-ablation period of 15 s was used for gas blank corrections. Helium was used as the carrier gas (600 mL/min) and was mixed with argon after the ablation cell at a rate of 840 mL/min. Shells were analyzed for Mg, Mn, Sr, Ba, and Ca by LA ICP-MS at 150 μ m intervals along the outer edge of the cross section in the stable isotope mill path (oxygen isotopes were used to constrct the age models for the shells (Goodwin et al., in this issue), which allowed precise alignment between δ^{18} O values and elemental ratios), beginning in an area of 2009 shell precipitation and moving towards the most recent growth; Data were reduced using GeoPro software (CETAC).

3. Theory and calculation

Mussels derive the materials used to construct their shell from the aquatic environment in which they live. Precipitation of the shell occurs in the thin layer of fluid between the shell and the mantle of the mussel known as the extrapallial fluid (EPF) (Wheeler, 1992). This fluid is supplied ions by the hemolymph, the main nutrient transporting fluid in a mussel analogous to blood in mammals. The hemolymph is supplied ions by the water passing through the gills, through the digestive tract, and also possibly through direct transport through the periostracum, the organic tissue on the outside of many mussel shells see McConnaughey and Gillikin (2008) for review. While there are several steps in the transport of ions from the surrounding solution into the shell, the relationship between the chemical composition of a body of water and the shells of the mussels living in that body of water is quantified as a non-thermodynamic partitioning coefficient (D_{Me}) as follows:

$$D_{Me} = \frac{\frac{C_{Me,shell}}{C_{Ca,shell}}}{\frac{C_{Me,water}}{C_{Ca,swater}}}$$
(1)

where $\frac{C_{Me,shell}}{C_{Ca,shell}}$ is the metal to calcium ratio in the shell and $\frac{C_{Me,water}}{C_{Ca,water}}$ is the metal to calcium ratio in the water. Metal ratios have been extensively utilized to provide information about temperature, fluxes from rivers or runoff, organism growth rates, and even phytoplankton productivity (Gillikin et al., 2006a; Gillikin et al., 2006b; Lazareth et al., 2003; Schöne et al., 2005; Schöne et al., 2002; Stecher et al., 1996; Zhao et al., 2017).

Using the oxygen isotope envelope method, Goodwin et al. (in this issue) used $\delta^{18}O_{water}$ and $\delta^{18}O_{carb}$ data to date the sequential growth of

each of shell (OR3-A1L, OR4-A1L, and OR6-A1L) to both determine growth rate and to correlate date of growth with a specific distance from the commissure. Because the daily growth rates of each shell were highly variable, only metal ratios collected from sample points adjacent to distances that were age-dated were used in the calculation of correlation coefficients. Using the oxygen isotope dating from Goodwin et al. (in this issue), distances in the shell were assigned a date. These dates were then matched with the closest corresponding laser ablation point to derive a dated shell metal ratio. Likewise, water samples were collected roughly weekly. If the date of water sample collection did not correspond to an exact date of shell growth based on the oxygen isotope method, a weighted linear extrapolation between sample points was used to estimate the metal ratio in the shell. Likewise, where shell sample frequency was limiting a linear extrapolation of water chemistry was used. This was done because the Pearson correlation necessitates 2 matrices of equal size. This reduced the overall dataset for correlation of $\frac{C_{Me,shell}}{C_{Ca,shell}}$ and $\frac{C_{Me,water}}{C_{Ca,water}}$ to n = 18, n = 27, and n = 27 for shells OR3-A1L, OR4-A1L, and OR6-A1L, respectively (Table 1).

For example, water was collected on June 23, but no ablation point in OR6-A1L was age-dated to June 23 so no direct metal ratio data is possible. Instead the metal ratio in the shell from June 20 (Sr/ Ca = 1.242) and June 27 (Sr/Ca = 1.235) were averaged to yield an estimated Sr/Ca value for the shell of 1.238. The change in metal concentration between the two points was assumed to be linear, so if for example a water sample was taken on June 4 and the two closest shell dates were June 1 and June 10, the metal ratio value assigned to June 4 would be calculated as follows:

$$Me/Ca_{shell (6/4)} = 0.4* \frac{Me}{Ca_{shell (6/1)}} + 0.6*Me/Ca_{shell (6/10)}$$
(2)

This results in the closest estimate of shell concentration between the two dates abiding by our assumption of linear change over short time intervals. For OR3-A1L, more water data points than shell data points were available, so the inverse was done: the two closest water data points to a given shell data point were averaged to determine an estimated metal ratio in the water corresponding to the chosen shell date.

4. Results

4.1. Water chemistry

Select field measurements collected at both the inside (n = 49) and outside (n = 46) sample sites are shown in Fig. 2 and the complete data set is provided in the Supplemental Information (Table SI1). Temperature varied seasonally with low temperatures recorded in January–March then warming through July before decreasing until December. Temperatures inside were less extreme than outside, only reaching a minimum of 5 °C and maximum of 25 °C while outside reached a minimum of 0.0 °C and maximum of 32 °C. A water-cooling system limits the upper temperatures observed inside during summer, but no effort is made to control minimum water temperatures. pH inside ranged from a minimum of 6.2 (November) to 8.2 (May) and 6.76 (November) to 9.05 (April) outside. pH was generally higher outside with a maximum difference during the period May–August.

Conductivity, turbidity and total suspended solids (TSS) behaved



Fig. 2. Field measurements for both sample location inside (open circle) and outside (gray circle). A) dissolved oxygen, B) conductivity, C) TSS, D) turbidity, E) pH, and F) temperature.

similarly both inside and outside the facility. Turbidity and TSS varied from January to June, increasing during/following precipitation events, while remaining steady at lower concentrations from July to November when there were few large discharge events in the Scioto River (Fig. 3).



Fig. 3. Discharge of the Scioito River in cubic meters per second (cms). Note the large discharge event on June 10 is the only large discharge event during the growing season (~April–September).

Both TSS and turbidity increase slightly in December. Conductivity ranged from \sim 0.0 to 0.8 mS/cm. While variable through June, a noticeably linear increase in conductivity was recorded July-Dec, with values increasing from 0.5 mS/cm to 0.8 mS/cm.

Dissolved oxygen (DO) concentration measured both inside and outside showed similar patterns for two periods of time, January–April and September–December. From January to April, DO concentrations increased following large precipitation events and in November–December showed a similar slight increase over time. However, from April to October, DO inside the facility decreased steadily from ~10 mg/L to ~6 mg/L while DO outside was variable with a range from 5 to 17 mg/L.

Concentrations of select cations collected at both the inside (n = 49)and outside (n = 46) sample sites are shown in Fig. 4 and the complete data set in the Supplemental Information (Table SI1). Concentrations of cations measured at both sites were very similar with the exception of manganese. In July–October Mn concentrations inside peaked to maximum while samples collected outside were near minimum values. The opposite was true in March, when outside sample concentrations of Mn peaked while inside Mn did not vary.

A second small deviation between concentrations measured inside versus outside was observed in samples collected in February. Here, inside samples contained higher concentrations of Na, Ca, Sr, and Mg relative to outside samples. Barium concentrations were very similar throughout the sampling period. A noticeably linear increase in Na, Ca,



Fig. 4. Major cation concentrations measured in surface water samples collected both inside (open circles) and outside (gray circles).

Sr, and Mg was observed from June–November that was similar to the pattern observed in conductivity (Fig. 2). Na and Sr increased $\sim 5 \times$ from 10 mg/L to 50 mg/L for Na and 0.5 to 3.5 mg/L strontium. During the same time period, calcium and magnesium concentrations more than doubled; Ca increased from 35 to 90 mg/L and Mg from 10 to 30 mg/L. This corresponds to a pronounced period of sustained low stream discharges June 23 through November 19 (Fig. 3).

4.2. Shell records

Sr/Ca, Ba/Ca, Mg/Ca, and Mn/Ca ratios measured in shells OR3-A1L, OR4-A1L, and OR6-A1L are provided in Fig. SI4 and Table SI2. Sr/Ca ratios varied from 1 to 3 mmol/mol in both OR3-A1L and OR6-A1L, while OR4-A1L recorded greater variability in ratios from 1 to 6 mmol/mol (Table SI2). Similar patterns were recorded in Ba/Ca, Mg/Ca and Mn/Ca, with the greatest range in ratios recorded in OR4-A1L, while lower ranges in ratios were recorded in both OR3-A1L and OR6-A1L.

We used the dates obtained by Goodwin et al. (in this issue), to assign dates for each distance where a metal/calcium ratio was measured. Only the ratios obtained near dated sections of the shell were used (n = 18, 27, and 27), for OR3-A1L, OR4-A1L, and OR6-A1L, respectively. Metal/calcium ratios with assigned dates in the shells are displayed relative to the water metal/calcium ratio measured in indoor

(OR3-A1L) and outdoor (OR4-A1L and OR6-A1L) surface water samples during the period of growth (Fig. 5). The complete dataset of metal/ calcium ratios in water (January–December) compared to ratios in shells is proved in Fig. SI5.

5. Discussion

5.1. Pearson correlations

The relationships between our water chemistry data and the chemical data recorded in the shells were investigated through Pearson r coefficients. Pearson correlations are appropriate for determining linear relationships between two continuous variables in which a change in one variable results in a proportional change in another variable. Results for relationships between Me/Ca ratios in water and Me/Ca ratios in shells OR3-A1L, OR4-A1L and OR6-A1L are shown in Table 2. Specimen OR3-A1L, which grew inside consistently displayed lower correlation coefficients relative to both OR4-A1L and OR6-A1L, which grew outside. Some of the lack of correlation could be due to the lower sample resolution (n = 16) for OR3-A1L. Results for relationships between Me/Ca ratios in shells OR4-A1L and OR6-A1L with water temperature and growth rate are shown in Table 2 while relationships with dissolved oxygen and chlorophyll a are provide in Table S4.



Fig. 5. Metal calcium ratios in surface water samples compared to shell samples by date. Sr/Ca, Ba/Ca, Mn/Ca, Mg/Ca. OR3-A1L data (gray squares) are shown on the left panel versus water chemistry results for indoor samples (black circles). On the right panels are the outdoor water chemistry (black circles) data and both OR4-A1L (open circles) and OR6-A1L (gray circles) time series. In all profiles, time passes from left to right. The full water dataset metal/calcium ratios for January–December compared to shell samples by date is proved in Fig. S15.

Relationships were calculated both with and without the data from the large storm event that occurred in June. Correlations reported in the text include the entire data set (no June storm removed) unless otherwise noted.

5.1.1. Magnesium

Magnesium concentrations measured in our carbonates (0.1–1 mmol/mol [100–1000 mg/kg]) were consistent with concentrations reported (0.2–0.6 mmol/mol) in other freshwater bivalves (Izumida et al., 2011) (Table 3). In addition, our D_{Mg} values (0.3 \times 10⁻³ to 0.8 \times 10⁻³) were consistent with published values (0.3 \times 10⁻³ to 0.4 \times 10⁻³) (Izumida et al., 2011).

Fluctuations in Mg/Ca was postulated to reflect temperature changes in marine environments, with correlation coefficients as high as 0.96 (Dodd, 1965; Klein et al., 1996a; Vander Putten et al., 2000), but others reporting poor correlations (Durham et al., 2017; Lorrain et al., 2005; Surge and Lohmann, 2008; Wanamaker Jr et al., 2008). Here, we observe variable degrees of correlation with temperature between 0.21 in OR4-A1L and 0.45 in OR6-A1L, and a correlation between Mg/Ca_{carb} and shell growth rate, between -0.10 in OR4-A1L and 0.69 in OR6-A1L. Mg/Ca also consistently displayed a weak negative correlation between Mg/Ca_{water} and Mg/Ca_{carb} for all shells (Pearson r = -0.32 and -0.45).

A large peak in Mg/Ca_{carb} ratios in OR3-A1L and OR6-A1L

correspond to a large discharge event between 6/10-6/17. A similar increase in Mg/Ca_{carb} is observed in OR4-A1L, but with a more gradual decrease to lower values than observed in OR3-A1L and OR6-A1L. The 6/10-6/17 discharge event did not have a corresponding change in Mg/Cawater ratio, but did see large changes in other water quality parameters. Lower DO, temperature, conductivity and pH were recorded during both the 6/10 and 6/17 surface water sampling events (Fig. 2). Sharp increases were also recorded during this event for TSS and turbidity relative to previous measurements (Fig. 2). Indeed the lowest sodium, calcium, magnesium, strontium, and barium concentrations in surface water samples collected at both sites were recorded on these dates (Fig. 4). Nevertheless, the large discharge event was likely a stressful event for these animals (low DO, temperature, and pH), and stress has been shown to affect Mg incorporation into bivalve shells, (Lorens and Bender, 1980; Poulain et al., 2015) which may explain this large peak in Mg/Ca_{carb} ratios.

Mg/Ca_{water} and Mg/Ca_{carb} did not correlate strongly (i.e., > 0.50), with Pearson r values of between -0.32, and -0.45. This resulted in D_{Mg} values between 0.0003 and 0.0008 (Table 4). Neither temperature nor growth rate correlated well with Mg/Ca in shell OR4-A1L (r = 0.21 and -0.10 respectively), but shell OR6 exhibited much higher correlation coefficients (r = 0.45 and 0.69 respectively). Despite the significant correlation in OR6, D_{Mg} did not correlate well with temperature (r = 0.19) but correlated strongly with growth rate (r = 0.72).

Table 2

Pearson r values for metal ratios recorded in shells OR3-A1L, OR4-A1L and OR6-A1L compared to metal calcium ratios in water, water temperature, growth rate, and pH. A Pearson r > 0.50 suggests a strong correlation (Cohen, 1988) and are shown in bold type.

Relationship	Pearson r			
	Mg	Mn	Sr	Ва
Me/Ca _{carb} vs Me/Ca _{water} OR3-A1L Me/Ca _{carb} vs Me/Ca _{water} OR4-A1L Me/Ca _{carb} vs Me/Ca _{water} OR6-A1L Me/Ca _{carb} vs Me/Ca _{water} OR4 and OR6 Me/Ca _{carb} vs pH OR3-A1L Me/Ca _{carb} vs pH OR3-A1L Me/Ca _{carb} vs pH OR6-A1L Me/Ca _{carb} vs temperature OR3-A1L Me/Ca _{carb} vs temperature OR4-A1L Me/Ca _{carb} vs temperature OR6-A1L Me/Ca _{carb} vs growth rate OR3-A1L Me/Ca _{carb} vs growth rate OR3-A1L Me/Ca _{carb} vs growth rate OR6-A1L Me/Ca _{carb} vs growth rate OR6-A1L	$\begin{array}{r} Mg \\ \hline & -0.39 \\ -0.32 \\ -0.45 \\ -0.36 \\ -0.66 \\ -0.46 \\ 0.00 \\ -0.34 \\ 0.21 \\ 0.45 \\ -0.10 \\ 0.57 \\ -0.36 \\ -0.10 \\ 0.69 \\ 0.11 \\ -0.48 \\ -0.14 \\ -0.24 \end{array}$	Mn 0.15 -0.27 -0.37 -0.34 -0.14 0.48 0.27 -0.17 0.62 0.87 0.87 -0.51 0.48 0.01 0.26 0.07 -0.20 0.37	Sr -0.16 0.79 0.83 0.80 -0.33 0.53 0.40 0.04 -0.33 0.00 0.39 -0.24 0.23 -0.22 0.35 -0.47 0.25	Ba 0.37 0.39 0.56 0.48 -0.48 0.21 -0.10 -0.39 0.40 0.13 0.81 0.74 -0.34 0.26 0.64 0.29 -0.16 -0.41 0.35
D_{Me} OR6-A1L vs temperature D_{Me} OR6-A1L vs growth rate D_{Me} OR4-A1L vs growth rate	0.19 - 0.29 0.04	0.37 -0.31 -0.16	-0.08 -0.29 -0.10	0.13 -0.36 -0.07
D_{Me} OR6A1L vs growth rate D_{Me} OR4-A1L vs D_{Me} OR6-A1L	0.72 0.71	-0.06 0.84	0.49 0.73	0.57 0.79

^a With June storm event removed.

Conversely D_{Mg} for OR4-A1L correlated very poorly with growth rate (r = 0.04). This indicates that Mg/Ca is not a suitable temperature proxy in freshwater mussels, as neither Mg/Ca_{carb} nor D_{Mg} which accounts for relative changes in Mg/Ca_{water}, consistently correlates strongly with temperature. Despite the differences in the shells correlation with temperature and growth rate, correlation between D_{Mg} in shells OR4-A1L and OR6 was very strong (r = 0.71) indicating that while the mechanism may not be understood or easily identified, it is a consistent control other than Mg/Ca_{water}, temperature, or growth rate. Other researchers have noticed a similar trend (Izumida et al., 2011), suggesting that Mg incorporation maybe be controlled by a complex array of factors, including association with organic layers in the shell, or as a mineral complex other than carbonate (Foster et al., 2008) (Schöne et al., 2010).

Thermodynamics predicts a negative correlation between temperature and Mg/Ca in inorganic aragonite (Gaetani and Cohen, 2006), whereas our shells exhibited a small positive correlation. The relative weakness of this correlation, the deviation from expected Chemical Geology 526 (2019) 142-152

Table 4

Mean D_{Me} values for shells grown outside. Values to the bottom are with peaks at the early part of the growing season removed. * indicates calculation with the signal elevated D_{Mn} points for both OR4-A1L and OR6-A1L removed.

Metal/calcium ratio (mmol/mol)	Mg/Ca	Mn/Ca	Mn/Ca*	Sr/Ca	Ba/Ca
OR6-A1L OR4-A1L Combined (OR4-A1L & OR6-A1L) Pearson r	0.0003 0.0008 0.0006 0.7058	31.9 42.8 37.4 0.998	18.9 15.2 17.1 0.832	0.157 0.195 0.176 0.730	0.143 0.117 0.130 0.787
With peak in June 6–10 removed OR6-A1L OR4-A1L Combined (OR4-A1L & OR6-A1L) Pearson r	0.0003 0.0008 0.0005 0.655	34.2 45.9 40.1 0.997	20.1 16.3 18.2 0.812	0.153 0.189 0.171 0.641	0.130 0.108 0.119 0.821

thermodynamic trends, and the inconsistent Mg/Ca-temperature correlation between shells, further cements the notion that Mg/Ca_{carb} in freshwater mussels is not a function of temperature. Despite this, the D_{Mg} was consistent between shells OR4-A1L and OR6-A1L suggesting biological controls on Mg incorporation, likely due in part to aragonite's preferential selection of Sr rather than Mg as a substitute for Ca due its more compatible atomic radius (Dodd, 1965; Dodd, 1967). It is also possible that the deviation from expected behavior of the freshwater samples from marine studies may be due to the extreme differences in salinity between freshwater and saltwater systems, as the small changes in ocean salinity are considered a possible control of Mg/Ca in other biogenic aragonites such as corals (Mitsuguchi et al., 1996).

5.1.2. Manganese

Mn concentrations measured in our carbonates (0.1–0.6 mmol/mol [100–600 mg/kg]) were consistent with concentrations reported in Carroll and Romanek (10–6000 mg/kg) in freshwater bivalves. However, our D_{Mn} was calculated to be 15.2 and 18.9 for OR4-A1L and OR6-A1L, respectively, if the June storm event was included. Average D_{Mn} increased slightly with the storm event removed (20.1 and 16.3 for OR4-A1L and OR6-A1L and OR6-A1L respectively).

Mn/Ca consistently displayed a negative correlation between Mn/Ca_{water} and Mn/Ca_{carb} for shells grown outside (r = -0.27 and -0.37), and a positive, but weak correlation inside (r = 0.15). Fluctuations in Mn/Ca in freshwater bivalves was postulated to reflect phytoplankton productivity (Carroll and Romanek, 2008). Here, we observe no correlation between Mn/Ca_{carb} and Mn/Ca_{water}, which is consistent with the complete data set of shell ratios (n = 4) presented in previous studies (Carroll and Romanek, 2008). When Carroll and Romanek (2008) removed one anomalous sample stream, their correlation improved significantly and was consistent with previous research. Here, only one shell, OR4-A1L, showed a significant correlation between Mn/Ca_{carb} and Mn/Ca_{water}.

Table 3

Comparison of elemental concentrations and partition coefficients in this study with previously published values for freshwater bivalves.

Reference	Sr (mg/kg)	D _{Sr}	Ba (mg/kg)	D _{Ba}	Mg (mg/kg)	$D_{Mg} (\times 10^{-3})$	Mn (mg/kg)	D _{Mn}
Faure et al. (1967)		0.22-0.28						
Nyström et al. (1996)	300-600						10-600	
Mutvei and Westermark (2001)							400-6000	
Markich et al. (2002)							300-1700	0.6
Verdegaal (2002)	120-220			0.1			100-700	0.5
Bailey and Lear (2006)	700-1000	0.28						
Langlet et al. (2007)							100-1000	
Ravera et al. (2007)							200-800	
Carroll and Romanek (2008)	120-2000	0.17, 0.26	60-400	0.05			80-1700	0.2, 0.5
Izumida et al. (2011)					150-500	0.30-0.42		
Zhao et al. (2017)							1130-1380	
This study	820-3343	0.16-0.20	15-270	0.11-0.14	26-1200	0.3–0.8	120-1250	32–42

A large discharge event on 6/10-6/17 resulted in higher Mn/Cawater recorded in water sampled both outside and inside. However, only OR3, grown inside, recorded a similar peak in Mn/Cacarb. Instead, Mn/Cacarb in both OR4-A1L and OR6-A1L strongly correlated with temperature (r = 0.62, 0.87), however, Mn/Ca_{carb} in OR3 did not (r = -0.17). The strong relationship with temperature was explored further by assessing the relationship between Mn/Ca_{carb} and dissolved oxygen (DO), chlorophyll a (Table S4), and pH in the water, all indicators of productivity explored by Goodwin et al. (in this issue). No parameter yielded a strong correlation with Mn/Ca_{carb} (r = 0.39, 0.27, 0.47 respectively for shell OR4-A1L, r = 0.38, 0.34, 0.27 respectively for shell OR6-A1L). While Mn/Cacarb does not correlate with any of these parameters, the obvious seasonal temperature peak and corresponding Mn/Cawater peak during the summer suggests some metric of productivity may still be a viable factor in Mn availability. For example, some sediment microorganisms found in rivers in the eastern United States may oxidize organic matter using Mn(IV) as its primary electron acceptor, which would not change DO, pH, or chlorophyll a levels, but would still be related to increased microbial productivity of that microorganism (Lovley and Phillips, 1988). Another study found seasonal Mn/Ca spikes in a freshwater lake that experiences seasonal upwelling, which drives productivity due to the influx of nutrients and increases the availability of Mn in the sediments, leading to increased Mn uptake in the mussels (Langlet et al., 2007).

It was also observed that the D_{Mn} calculated in this study was higher than in previous studies (Table 3). Despite much higher D-values, our Mn concentration in the shells were consistent with previous literature, further suggesting that Mn_{water} is not a strong control on Mn_{shell} , and that availability of specifically Mn(II) in the sediment-water interface may play the primary role in determining Mn uptake (Barats et al., 2008; Carriker et al., 1980; Jeffree et al., 1995; Zhao et al., 2017).

Mn/Ca in shell OR4-A1L correlated moderately well with growth rate (r = 0.48) while OR6 exhibited no correlation (r = 0.01) suggesting the correlation in OR4-A1L may be coincidental and further suggesting Mn/Ca is not likely metabolically controlled. Previous studies in marine species showed a strong correlation between Mn/Ca_{carb} and Ba/Ca_{carb} (Lazareth et al., 2003; Vander Putten et al., 2000), but our shells did not exhibit any such trend, suggesting different controls on the incorporation of both metals in freshwater systems.

5.1.3. Strontium

Sr concentrations measured in our shells (1–4 mmol/mol [1000–4000 mg/kg]) were consistent with, or slightly higher than concentrations reported in Carroll and Romanek (120–2000 mg/kg) in freshwater bivalves. Our D_{Sr} was calculated to be between a minimum of 0.13 and maximum of 0.31. D_{Sr} of OR4-A1L and OR6-A1L combined were 0.18, slightly lower than but still in good agreement with values reported in previous studies (0.17–0.28; Carroll and Romanek, 2008). The combination of D_{Sr} correlating strongly between the two shells (r = 0.73) and Sr/Ca_{water} and Sr/Ca_{carb} correlating strongly suggests Sr/Ca_{carb} is a reliable proxy for Sr/Ca_{water} in temperate freshwater systems.

Sr/Ca consistently displayed the strongest correlation coefficient between shell and water (Pearson r for Sr/Ca_{water} and Sr/Ca_{carb} in shells OR4-A1L and OR6-A1L was 0.79 and 0.83 respectively). Fluctuations in Sr/Ca in marine bivalves are thought to be strongly regulated by biologic processes (Gillikin et al., 2005b), and similar conclusions have been drawn for freshwater species (Bailey and Lear, 2006; Izumida et al., 2011). One of these studies ruled out carbonate saturation as a control on Sr/Ca, finding that at sites with different degrees of carbonate saturation in the water, partitioning coefficients between the shell and water remained constant at both sites (Bailey and Lear, 2006).

The large discharge event of 6/10-6/17 lowered dissolved Sr concentrations to the lowest concentration recorded and similarly resulted in the lowest Sr/Ca_{water} ratio for both the indoor and outdoor sites. However, while Sr/Ca_{carb} for both outside shells (OR4-A1L and OR6-

A1L) tracked with this trend (i.e., Sr/Ca_{carb} decreased), Sr/Ca_{carb} in the indoor shell (OR3-A1L) instead increased, similar to Mn/Ca_{carb} and Mg/Ca_{carb} in OR3-A1L. The observed changes in the shell grown indoors does not appear consistent with the values observed outdoors and could indicate additional handling stress of the indoor specimen.

A weak correlation between Sr/Ca_{carb} and temperature was observed in OR4-A1L (r = -0.33) and no correlation was observed in OR3-A1L or OR6-A1L (r = 0.04 and 0.00 respectively). This suggests Sr/Ca is not a temperature proxy in freshwater bivalves. Previous studies suggest that Sr/Ca in seawater does not vary considerably unless the salinity is quite low, such as in estuarial waters (Dodd and Crisp, 1982), whereas our Sr/Ca_{water} ratio varied significantly through time, and our proportional salinity variations are much higher throughout the year due to fluctuations in precipitation, discharge, and evaporation.

Variable correlation was observed between Sr/Cacarb and shell growth rate for OR4-A1L and OR6-A1L (r = 0.23 and -0.62 respectively). In marine systems growth rate has been negatively correlated with Sr/Ca ratios (Gillikin et al., 2005b; Izumida et al., 2011; Schöne et al., 2011), but some studies showed a positive correlation (Schöne et al., 2011). The direction of correlation is variable in this study. The shells dispute one another in terms of the strength of correlation and direction. The June storm event also changes the direction of correlation, preventing the drawing of confident conclusions. Other studies suggest that in shells with high mantle metabolic activity, likely an analog of growth rate, Sr/Ca_{carb} varies with Sr/Ca_{water} (Klein et al., 1996b; Vander Putten et al., 2000). This is in agreement with our data, in that during the time period of appreciable shell growth (see Table SI2), Sr/Ca_{carb} very closely tracked Sr/Ca_{water}. This also corroborates with the moderate correlation with growth rate: while a high growth rate may be necessary for the shell to track the water, Sr/Ca_{carb} is more strongly a function of Sr/Cawater during these periods of elevated growth, in our case from May to August.

5.1.4. Barium

Ba concentrations measured in our carbonates (0.1–0.4 mmol/mol [100–400 mg/kg]) were consistent with concentrations reported in Carroll and Romanek (2008) (60–400 mg/kg) and Zhao et al. (2017) (0.08–0.25 mmol/mol) in freshwater bivalves. D_{Ba} of OR4-A1L and OR6-A1L (combined) were between 0.043 and 0.34, covering the range reported in previous studies (Carroll and Romanek, 2008; Gillikin et al., 2006a; Izumida et al., 2011; Zhao et al., 2015).

Fluctuations in Ba/Cacarb were consistent across all shells with typical low ratios punctuated by large brief spikes in elevated ratios, which was consistently observed across multiple studies (Gillikin et al., 2006a; Gillikin et al., 2008; Lazareth et al., 2003; Stecher et al., 1996). Previous work also observed that these peaks corresponded to spring periods when surface water temperatures began to rise. Our spike in Ba/Ca_{shell} is not consistent with that observation. Instead, our peak corresponds to a period of time of rapidly dropping temperatures (6/3 to 6/17) (see Fig. 2 and Table SI1) followed by rising temperatures. The drop in temperature was during the June storm event that resulted in peak Ba/Cawater and Ba/Cacarb but also peaks of Mn/Cawater, Mn/Cacarb, and Mg/Ca_{carb} in some of the shells. Ineed a stronger correlation is observed between Mn/Ca_{shell} and Ba/Ca_{shell} when the anomalous spike is removed (Table SI5). Considering all corresponding data points (including the June peak), Ba/Ca $_{\rm water}$ and Ba/Ca $_{\rm carb}$ consistently displayed a weak correlation for shells OR3-A1L, OR4-A1L, and OR6-A1L (r = 0.37, 0.39, and 0.56 respectively). If the spikes in ratios are removed from the correlation, the remaining Ba/Ca_{carb} ratios are thought to strongly reflect the Ba/Cawater (Gillikin et al., 2006a). Our correlation between Ba/Cawater and Ba/Cacarb with the storm event removed resulted in r-values of 0.16 and 0.42 for shells OR4-A1L and OR6-A1L, markedly lower correlation than when the spike was included.

Strong correlation between water temperature and Ba/Ca_{carb} was observed for both outdoor shells (OR4-A1L and OR6-A1L, r = 0.81 and

0.74 respectively) if the June storm event was removed. Including the June storm event, correlations were much weaker (r = 0.40 and 0.13). During the June storm, Ba/Cacarb spiked strongly, more than doubling within a 7-day period while temperature dropped approximately 9 °C. This suggests that during normal flow conditions and storm events Ba/ Ca_{carb} is not controlled by Ba/Ca_{water}. Determining if temperature influences Ba/Ca_{carb} is still debatable because both temperature and Ba/Cawater has some influence as evidenced by the corresponding spikes in Ba/Ca_{carb} and Ba/Ca_{water}, which increase from mid-June through mid-July and then decrease until harvesting. What remains clear is that Ba/ Ca_{shell} was strongly influenced by the high discharge of the June storm event. A possible explanation for this is that during the storm event. increased sediment flux into the river may have caused a higher rate of Ba-rich particulate matter to be ingested by the mussel. Stecher et al. (1996) predicted this may lead to Ba being ejected to the EPF which then precipitates into the newly grown shell.

Variable correlation was observed between Ba/Ca_{carb} and shell growth rate for all shells, with r-values ranging from 0.26 to 0.64, precluding definitive conclusions about the impact of growth rate on Ba/Ca_{carb}.

5.1.5. Partitioning coefficient correlations

For a description of how D-values are calculated, refer to section 3.0 Theory and Calculation. For all four metals, good agreement was seen between $D_{\rm me}$ in both outdoor shells, OR4-A1L and OR6-A1L (Fig. 6). $D_{\rm Sr}$ and $D_{\rm Ba}$ showed similar behavior in each shell, peaking in early-June during the large discharge event and decreasing through the rest of the year. Scatter plots of metal/calcium ratios in shells compared to metal/calcium ratios in water samples are proved in Fig. SI6 and statistics that describe the variability of D values in each shell (OR3, 4, and 6) are provided in Table S3.

Growth rate is often considered a major factor in Sr incorporation into the shell, although the direction of correlation is not agreed upon and not all species studied reflect this relationship (Gillikin et al., 2005b; Schöne et al., 2011). In these shells, $D_{\rm Sr}$ and $D_{\rm Ba}$ both display increased Sr and Ba incorporation during periods of increased growth rate, although the correlation is not strong. Temperature displayed a similar behavior, peaking during early July and decreasing through the end of the year. While neither $D_{\rm Sr}$.

nor D_{Ba} correlate strongly with temperature,

the consistent decreasing trend suggests a temporal pattern in incorporation. The inclusion of ratios collected during the large discharge event of June 10–17 did not influence the calculations for D_{Sr} , or D_{Ba} , but did change the D_{Mn} significantly (Table 4). Likewise D_{Mn} in both shells OR4-A1L and OR6-A1L contained a large spike in July during one sampling event with the lowest recorded concentration in water, but the highest calculated D_{Mn} . The full D_{Mn} profile is shown in Fig. SI7.

5.1.6. Interpretation of the Shell grown inside

From our results it was clear that the shell that grew inside, OR3-A1L, exhibited markedly different behavior than the two shell samples (OR4-A1L and OR6-A1L) grown outside, both in partitioning coefficients and trends through time. While shells OR4-A1L and OR6-A1L had good agreement, shell OR3-A1L did not. Growing the shell indoors with partially recycled water may have played a major role in the growth and feeding behavior of this shell. The indoor water is circulated through a system that includes large bio-ball towers to remove ammonia. The towers could also alter other water parameters that impact mussel growth. External stressors such as handling, lower pH, lower levels of natural light, DO, and lower levels of food availability due to less algal and plant matter activity as evidenced by the consistently lower chlorophyll levels in the indoor water (see Goodwin et al., in this issue) may all lead to periods of inactivity in which the mussel is not actively feeding. This would lead to non-continuous shell growth and perhaps also cause sporadic and unpredictable correlations with environmental conditions. The shell grown indoors also experienced



Fig. 6. D_{Me} values calculated over time for OR4 and OR6. Values are consistent across both shells with similar seasonal patterns and large perturbations during large discharge events. Note that a single D_{Mn} value calculated for the same date (July 22) was removed for both OR4-A1L and OR6-A1L. The complete D_{Mn} profile is presented in Fig. SI7.

drastically lower turbidity levels, often by an order of magnitude or more, which could indicate lower food availability leading to sporadic feeding and lowering the degree of interaction with the water chemistry. Partitioning coefficients and trace metal incorporation have been shown to be impacted by the level of food availability (Zhao et al., 2015). This suggests that metabolic pathways may be proportionally more important than respiratory pathways for ion incorporation into the mussel shell.

6. Conclusions

Pearson correlations between Me/Ca_{carb} and Me/Ca_{water} were performed on Mg, Mn, Sr, and Ba in freshwater mussel shells. Metal concentrations and partitioning coefficients in our shells for Mg, Sr, and Ba were all consistent with previous literature (Table 3), with only D_{Mn} values varying significantly, likely due to controls other than Mn_{water}. In particular, Sr/Ca_{carb} is strongly a function of Sr/Ca_{water}. Mg, Mn, and Ba did not exhibit similar behavior, with moderate (Ba) to low (Mn, Mg) correlation with Me/Ca_{water} suggesting no degree of certainty about the relationships. The inclusion of ratios collected during large discharge events did not significantly influence the calculations for D_{Sr}, or D_{Ba}, but did change the D_{Mn}. This adds additional confidence to our conclusion that metal concentrations in freshwater shells are reliable, consistent indicators of environmental conditions across a range of concentrations and among species.

Intra-annual shell growth did not consistently correlate strongly with any Me/Ca ratio and also did not correlate strongly with temperature, despite showing a period of elevated growth rates between mid-May and mid-July corresponding with rising water temperatures. Despite metabolic and kinetic control of Sr/Ca in marine mussels, this data suggests that in freshwater bivalve's growth rate does not primarily control Sr incorporation, but may play a role in how well it reflects water chemistry. While growth rate is not directly correlated to temperature, it is likely that many factors influence growth rate such as increased daylight, food abundance, and 'biological clocks' (Schöne et al., 2003).

We can conclude from this data that Sr/Ca_{carb} can be used as a reliable, reproducible proxy of intra-annual fluctuations in Sr/Ca_{water} during the growing season for the shells when Sr/Ca_{water} varies considerably as in our study. However, Sr/Ca_{carb} is only recorded during periods of shell growth, and thus limits the use of shells as a proxy to obtain a full-year picture of water quality as the shells do not grow when water temperatures are too low, while Sr/Ca_{water} may continue to vary during cold periods. By definition the majority of a shell is precipitated during periods of appreciable growth, meaning if age models within the shell are accurate, Sr/Ca_{carb} accurately reflects changes in Sr/Ca_{water} through time. The two shells grown outdoors, shells OR4-A1L and OR6-A1L, displayed excellent agreement, suggesting that while multiple shells may help create more statistical power and more closely predict the true mean of Sr/Ca_{water} , single shell samples of this species may be adequate predictors of water chemistry.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemgeo.2018.01.001.

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