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Controls on strontium and barium incorporation into freshwater bivalve shells (*Corbicula fluminea*)

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ABSTRACT

Trace elements of bivalve shells can potentially serve as proxies of environmental change. However, to reconstruct past environments using the geochemical properties of the shells and determine the degree to which the element levels are biologically influenced, it is essential to experimentally determine the relationship between environmental variables and the element composition of the shells. To disentangle possible controls on the incorporation of strontium and barium into freshwater bivalve shells, we conducted controlled laboratory experiments using the extremely salinity and temperature tolerant Asian clam, *Corbicula fluminea* as a model species. Bivalves were reared for five weeks in two sets of experiments: (1) combinations of different water temperature (10, 16 and 22 °C) and food levels (0.2, 2, 4 and 8 × 10^4 cells/ml) with constant Sr/Ca_{water} (2.45 mmol/mol) and Ba/Ca_{water} (367 μmol/mol) levels; and (2) combinations of different water temperature (10, 16 and 22 °C) and different Sr/Ca_{water} (ca. 4, 8 and 12 mmol/mol) and Ba/Ca_{water} levels (ca. 600, 1150 and 1500 μmol/mol) with constant food level (4 × 10^4 cells/ml). The Sr/Ca_{shell} ratio of *C. fluminea* exhibited a statistically significant negative correlation with temperature and a positive correlation to Sr/Ca_{water}, but was not affected by changing food level or shell growth rate. On the contrary, Ba/Ca_{shell} was influenced by a complexly intertwined set of variables including temperature, food level, Ba/Ca_{water} and shell growth rate. Partition coefficients of $K_D^{Sr/Ca}$ (0.19 to 0.29) and $K_D^{Ba/Ca}$ (0.03 to 0.19) confirmed the control of vital effects over strontium and barium incorporation into the shells. As indicated by the findings, Sr/Ca_{shell} of *C. fluminea* from freshwater environments can serve as a reliable proxy for past water temperature if the spatiotemporal variability of strontium-to-calcium in the water is small, well-known or can be estimated from other proxies. Interpreting Ba/Ca_{shell} values, however, is much more challenging because they are controlled by a large number of environmental and physiological variables. Sr/Ca_{shell} and Ba/Ca_{shell} of *C. fluminea* specimens from estuarine settings in which element-to-calcium ratios are more conservative and stable can potentially function as paleoenvironmental proxies. Findings of this study can be useful to better understand the element incorporation into shells of other bivalves including marine species.

1. Introduction

Trace and minor element signatures of many biogenic carbonates serve as reliable proxies of past environmental variables. Of particular interest are cations that can substitute Ca^{2+} in the crystal lattice because of similar ionic radii and electrochemical properties, specifically Sr^{2+} and Ba^{2+} in aragonite (orthorhombic crystal structure: Bragg, 1924) and Mg^{2+} in calcite (trigonal–rhombohedral crystal structure: Bragg, 1913) (Kastner, 1999). Under ideal circumstances, the incorporation of these ions into the biomineral occurs proportionately to the concentration of the respective dissolved element in the ambient medium and is thermodynamically controlled, but not affected by vital effects. For example, coral Ba/Ca values can document changes in riverine influx (McCulloch et al., 2003; Sinclair and McCulloch, 2004), because freshwater contains much larger amounts of barium than seawater (50 μg/l vs. 6 μg/l Ba^{2+}; Schroeder et al., 1972) and the Ba/Ca ratio of the corals is linearly correlated to that of the water (Sinclair and McCulloch, 2004). The Sr/Ca value of coral aragonite can provide details on ambient temperature during growth (Beck et al., 1992). With increasing water temperature, the Sr/Ca in aragonite decreases because the substitution of calcium by strontium in this polymorph of $CaCO_3$ is an exothermic reaction (Rosenthal and Linsley, 2006). Since the Sr/Ca_{water} ratio is nearly invariant (~8.6–8.8 mmol/mol) in modern seawater above 8 to 10 PSU (Dodd and Crisp, 1982) and corals form their skeletons near equilibrium with the ambient medium with respect to Sr/Ca_{water} (Hanna and Muir, 1990), coral Sr/Ca values can provide reliable temperature estimates over a wide range of different salinities.

Interpreting the trace and minor element content of bivalve shells is a very challenging task, possibly more challenging than in the case of corals and many other organisms. Vital and kinetic effects (Epstein et al., 1951; Urey et al., 1951) dominate the partition of these elements

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