

CONTROLS ON TRACE METAL UPTAKE, DISTRIBUTION, AND ISOTOPE FRACTIONATION IN BIOLOGICALLY PRECIPITATED ARAGONITE: BARIUM, STRONTIUM, AND MANGANESE IN FRESHWATER BIVALVE SHELLS

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Freshwater bivalves are long-lived sedentary animals that continuously precipitate aragonite shells, preserving a multi-decadal record of aquatic geochemistry. However, use of shells as chemical proxies can be complicated by biological and other factors during mineralization. To better understand the controls on metal uptake and distribution, we examined trace metal concentrations and isotopes of barium (Ba) and strontium (Sr) in shells of 7 species of freshwater bivalves from the Ohio River watershed, eastern USA, including native mussels (Order: Unionida) and the invasive zebra mussel (*D. polymorpha*) and Asian clam (*C. fluminea*). River water, sediment porewater, and suspended particulate and organic matter in the water column (seston) were also collected. Extrapallial fluid, from which the inner nacreous layer of the shells are mineralized, was extracted and analyzed to further refine how elements are partitioned and isotopically fractionated between the external riverine environment and the shell. Results demonstrate that Ba isotope fractionation between shell and river water is species dependent, with invasive *C. fluminea* showing little to no offset in $\delta^{138}\text{Ba}$ between shell and river water, while the native *A. plicata* shell is as much as 0.9‰ lower than its corresponding stream water (measurement uncertainty $\leq 0.05\text{‰}$). In contrast, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the shells of all species are indistinguishable from stream water. Preliminary results also indicate: (1) Mn/Ca can be elevated in shells of the order Unionida, but this is not observed universally in freshwater aragonite shells; (2) the inner nacreous layer of Unionida shells has significantly higher concentrations of Ba and Sr relative to the outer nacreous layer, while Ba isotope values do not differ between these layers; and (3) Ba/Ca ratios in shells of *C. fluminea* correlate with respective Ba/Ca values of dissolved river water, but this correlation was not observed in other species. The Ba isotope composition and trace metal concentrations of extrapallial fluid and seston will also be presented. We suggest that species-dependent transport of solutes from water to shell is a major factor in explaining variations in Ba isotope composition and trace element concentration among freshwater aragonite shells, and must be understood to use shells as water quality archives.