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Environmental and vital effects on isotope and trace element ratios in biogenic carbonates: Insights from lithium isotopes across an estuarine salinity gradient

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Isotope and element ratios in the carbonate skeletons of calcifying marine organisms can be used to reconstruct past environments and understand physiological processes that occurred during calcification. To determine whether carbonates are truly faithful geochemical archives of past water, it is crucial to elucidate any environmental or biological factors that could influence carbonate composition and cause deviations from water composition. Lithium isotopes are a novel proxy measurement in biogenic carbonates and are known to record silicate weathering congruency. In this study we measured $\delta^{7}Li$, along with $\delta^{13}C$, $\delta^{18}O$, and metal/Ca ratios, in modern low-Mg calcite shells of the eastern oyster, *Crassostrea virginica*, as well as in the water in which the shells grew. We show that oyster shell $\delta^{7}Li$ tracks water $\delta^{7}Li$ with an offset of $+1.9 \pm 1.5‰$ and is not influenced by salinity in an estuarine environment. This contrasts with inorganic calcite, in which $\delta^{7}Li$ is known to be lighter than seawater values, suggesting a prevalent vital effect in oyster calcite. We ascribe this vital effect to a combination of physiological mechanisms, including preferential active transport of ^{7}Li through calcium channels into the extrapallial fluid (EPF) from which the calcite shell precipitates and a sodium/proton pump that preferentially transports ^{6}Li into the EPF, the latter of which has been proposed by previous studies. We conclude that understanding the mechanism(s) driving the vital effect in biogenic calcite is crucial to establishing $\delta^{7}Li$ as a faithful paleo-archive and a tool for reconstructing past weathering and climate. This study highlights that determining how isotopes are fractionated during biological transport prior to precipitation is imperative to developing robust proxy records from biogenic carbonates.