

Minute co-variations of Sr/Ca ratios and microstructures in the aragonitic shell of *Cerastoderma edule* (Bivalvia) – Are geochemical variations at the ultra-scale masking potential environmental signals?

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Abstract

It remains a challenging task to reconstruct water temperatures from Sr/Ca ratios of bivalve shells. Although in many aragonitic species, Sr/Ca is negatively correlated to temperature – which is expected based on abiogenic precipitation experiments, the incorporation of Sr into the shell of bivalves is strongly controlled by physiological processes and occurs away from the predicted thermodynamic equilibrium. Strontium-to-calcium ratios of aragonitic shells remain far below that of the ambient water. Moreover, Sr concentrations vary considerably among shell portions consisting of different microstructures and/or organic content. Values observed at annual growth lines and within the intervening shell portions (= annual growth increments) deviate much stronger from each other than expected from a change in temperature or Sr/Ca_{water}. As demonstrated here by ultra-high-resolution chemical analysis (EPMA, NanoSIMS) of a *Cerastoderma edule* shell, Sr concentrations are also heterogeneously distributed at approximately micrometer resolution. For example, in the outer portion of the outer shell layer, Sr/Ca ratios were statistically significantly (*t*-, *u*-tests) higher at circatidal growth lines (irregular simple prismatic structure; arithmetic mean ± 1 standard deviation = 2.86 ± 0.38 mmol/mol; *n* = 53) than within circatidal increments (nondenticular prismatic structure; 2.42 ± 0.25 mmol/mol; *n* = 51). S/Ca_{shell}, a representative of the concentration of organics, showed the opposite pattern, i.e., significantly higher values in circatidal increments (2.37 ± 0.29 mmol/mol; *n* = 51) than at circatidal growth lines (2.13 ± 0.47 mmol/mol; *n* = 53). Overall highest values of Sr/Ca_{shell} (3.47 ± 0.65 mmol/mol; *n* = 3) and S/Ca_{shell} (3.98 ± 0.65 mmol/mol; *n* = 3), however, were typically associated with annual growth lines and larger biomineral units. The intimate link between Sr/Ca_{shell}, S/Ca_{shell} and shell architecture may indicate that microstructures or the processes controlling their formation exert a strong control over the incorporation of strontium into shells of *C. edule*. Analytical techniques with lower sampling resolution, e.g., LA-ICP-MS, cannot resolve such fine-scale Sr variations. As a result, the signal-to-noise ratio decreases and the data generated by such techniques may therefore not seem to provide useful paleotemperature data. Future studies should therefore employ a combined analysis of Sr/Ca_{shell} and shell microstructures, and interpret Sr/Ca values of shell portions with different microstructures separately.

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