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Links between shell chemistry and microstructure – A case study using *Arctica islandica*

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Bivalves offer outstanding potential as environmental archives. However, vital effects exert a strong control on the incorporation of many trace and minor elements into the shell so that their use as environmental proxies is currently limited. Furthermore, Sr and Mg show a strong relationship to the micrometer-sized shell architecture (shell microstructure), i.e., near growth lines, which are typically dominated by irregular simple/spherulitic prismatic microstructures, the concentrations of these elements are significantly higher than in portions between growth lines (= growth increments, which are microstructurally more complex). In contrast, Ba is uncoupled from the prevailing shell microstructure. To shed more light on these issues, we conducted a combined element chemical (in-situ analysis by means of LA-ICP-MS) and microstructural analyses (using SEM) of shells of *Arctica islandica* collected alive in NE Iceland.

According to our findings, (1) contemporaneous shell portions in the hinge and ventral margin (both belonging to the outer shell layer) within individual specimens showed nearly identical Sr/Ca and Mg/Ca values, but Ba/Ca was 1.5 – 2.5 times higher in the ventral margin than in the hinge. (2) In agreement with previous studies, Sr and Mg were strongly elevated near annual growth lines. (3) Along an isochronous transect from the inner portion of the outer shell layer near the myostracum toward the outer shell surface (in the ventral margin), Si/Ca values increased, on average, by 75% ± 11%, whereas Na/Ca values decreased by 7% ± 1%. Along this transect, the shell microstructure gradually changed from crossed-acicular to homogeneous suggesting that Si and Na are linked to the prevailing nanometer-sized shell architecture or underlying physicochemical processes controlling their formation. (4) In the hinge, Ba/Ca, Sr/Ca, Mn/Ca and Mg/Ca attained highest values along the axis of maximum growth, but gradually decreased in slower growing (contemporaneous) shell portions away from that axis. (5) In contemporaneous shell portions (in either the hinge or the ventral margin), the concentration of some elements varied significantly among specimens, whereas others showed little variability. For example, in similar and contemporaneous shell portions of different specimens, Na/Ca values exhibited only little variation (17.4 – 23.7 mmol/mol), whereas Sr/Ca and B/Ca differed more severely (0.3 – 1.6

mmol/mol and 0.04 – 0.07 mmol/mol, respectively; both within growth increments). Despite these inter-specimen chemical differences, the shell microstructure remained largely invariant.

Our findings firstly suggest that the extrapallial fluid, if it exists at all, is chemically inhomogeneous. This could result from differences in the efficiency of transmembrane ion transport or to differences in shell formation rate along the growing margin (e.g., faster growth in the outer portion of the outer shell layer than in portions closer to the myostracum). Secondly, chemical differences among specimens may be attributed to physiological differences. Thirdly, some elements such as Ba are uncoupled to microstructural properties, but co-vary strongly among specimens suggesting an environmental control on the uptake and incorporation of this element into the shell.