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Crystallographic texture and microstructure of terebratulide brachiopod shell calcite: An optimized materials design with hierarchical architecture

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Abstract

We analyzed the microstructure, microchemistry, and microhardness variations across the architectural elements of the shells of the brachiopod species *Megerlia truncata* and *Terebratalia transversa* with scanning electron microscopy (SEM), electron backscatter diffraction (EBSD), laser-ablation inductively coupled plasma mass-spectrometry (LA-ICP-MS), and Vickers microhardness indentation (VMHI). The brachiopod valves consist of two principal layers of distinct calcite biomineralization: a thin, nanocrystalline, outer, hard protective layer with VMHI values exceeding 200 HV and a much thicker, inner, secondary layer of a hybrid organic-inorganic fiber composite material. The secondary layer is further structured into two sublayers, an outer part with VMHI values varying between 110 and 140 HV, and a softer inner part ($70 < HV < 110$). Whereas the size of the calcite crystals within the primary layer varies between a few tens of nanometers and 2 μm, calcite crystals within the secondary layer are fibrous, commonly reaching lengths exceeding 150 μm. Cross sections of these fibrous crystals are spade shaped, their dimensions being about 5×20 μm. The fibers are aligned parallel to each other. They are single crystals with their morphological fiber axes pointing almost parallel to the shell vault. The crystallographic orientation of the morphological fiber axes, however, is arbitrary within the **a**-**b** plane of the calcite lattice, whereas the **c**-axis (hexagonal unit-cell setting) is perpendicular to the morphological fiber axes and thus parallel to the radial vector of the valve vault. This morphology strongly indicates that fibrous growth is controlled by confinement within a cell in an organic matrix and not by attachment of biomolecules to specific crystallographic faces. We observe inhomogeneous Sr^{2+} and Mg^{2+} concentrations in the shell calcite within the 0.1–0.9 wt% range. Design of the shell appears to be highly optimized for mechanical performance. Crystal morphology and orientation as well as incorporated organic matter are structured hierarchially at different length levels forming a hybrid organic-inorganic fiber composite architecture.

Keywords: Biomineralization of brachiopod shell calcite, EBSD, texture, microstructure, cathodoluminescence, Vickers microhardness, hybrid biomaterial, fiber composite material