European Mineralogical Conference
Vol. 1, EMC2012-743, 2012
European Mineralogical Conference 2012

Nanoparticle and mesocrystalline domain organization in carbonate biological hard tissues: orientation patterns obtained from 3D-EBSD

E. Griesshaber (1), A. Ziegler (2), and W. Schmahl (1)

(1) Department of Earth and Environment Sciences, LMU Munich, Theresienstr. 41, 80333 Munich, Germany, (2) Central Facility for Electron Microscopy, University of Ulm, Albert-Einsteinstraße 11, 89069 Ulm, Germany

Biological hard tissues are hierarchical composites, where each hierarchical level contributes to the material property and overall function of the end-product. Mineralization starts from an amorphous precursor phase assembled from amorphous nanoparticles. This is followed by an ordered crystallization and growth process producing nanoscale crystals that are assembled to mesocrystalline units. The mesocrystalline units aggregate and form the major functional elements of the biological hard tissue. Electron backscatter diffraction (EBSD) is currently one of the best methods available for a structural characterization of biological hard tissues, since it provides microstructure imaging and crystal orientation information on several hierarchical levels. With EBSD we detect both (Griesshaber et al. 2007), biologic as well as environmental (Hahn et al. 2012) control on skeleton mineralization.

However, an understanding of particle organization across extended length scales requires that EBSD is carried out in three dimensions. This alone yields the necessary comprehension of particle/domain orientation and interlinkeage and thus assessment of biologic skeleton formation. In this contribution we present the first 3D-EBSD analysis on biological hard tissues. This is obtained on a series of microtome cut and microtome polished sections cut from the cuticula of the terrestrial isopods *Tylos europeus*, *Armadilidium vulgare* and *P. scaber*. Isopod cuticules are ideal samples for this purpose, since they are composits of several phases, two organic (protein, chitin) and three mineral phases: Mg-calcite, amorphous calcium carbonate (ACC) and amorphous calcium phosphate (ACP). The comparison of different modes of sectioning (FIB, Ar-laser and microtome sectioning) revealed that for 3D-EBSD on biological hard tissues microtome sectioning is the material adapted way of obtaining thin sample slices. Large and highly smooth sample surfaces are gained, with individual slices being 400 to 500 nm apart. We find significant differences in orientation patterns of calcite and texture sharpness between the studied isopods: In the thick and strong cuticle of *A. vulgare* and *T. europeus* calcite nanocrystalls are assembled into numerous, single crystalline, randomly oriented calcite patches, whereas in the thin and flexible cuticle of *P. scaber* highly coherent narrow zones of calcite dominate. However, despite the strong ordering of calcite within individual patches and zones, the overall degree of calcite orientation within the cuticle of the studied isopods is weak, in particular in the cuticle of *T. europeus*. Copmpared to other carbonate hard tissues (e.g. shells) this is remarkable since calcite is used in both, in the isopod cuticle and in the shells for enforcement of the skeleton and protection of the soft tissue of the animal. This indicates that periodic decomposition and deposition of calcium carbonate during molt renders a disordered conglomeration of calcite. Nevertheless, the low degree of crystal ordering is enhanced and is conditioned by the specific habitat and predation requirements of the animal.

Griesshaber, E., Schmahl, W. W. , Neuser, R. D., Pettke, Th., Blüm, M., Mutterlose, J. & Brand, U. (2007) Crystallographic texture and microstructure of terebratulide brachiopod shell calcite: An optimized materials design with hierarchical architecture. *Amer. Mineral.,* **92**, 722-734.

Hahn, S., Rodolfo-Metalpa, R., Griesshaber, E., Schmahl, W. W., Buhl, D., Hall-Spencer, J. M., Baggini, C., Fehr, K. T. & Immenhauser, A. (2012) Marine bivalve shell geochemistry and shell ultrastructure from modern low pH environments. *Biogeosci. Discussions*, **8**, 10361-10388.