

MECHANICAL FUNCTIONALIZATION OF MINERALS BY ORGANISMS

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Despite the brittleness of Ca-carbonate and –phosphate minerals, these substances are found almost ubiquitously in skeletons or teeth of organisms (LOWENSTAM, 1981). However, unlike inorganic minerals, biominerals are always hybrid composites which include intra- and intercrystalline organic matrix. This matrix controls the structure from the nanofabric to the macroscopic morphology, and the resulting hierarchical composite has dramatically improved mechanical strength, hardness, and, most importantly, fracture toughness (DUNLOP & FRATZL, 2010). With our increasing inventory of detailed investigations by electron backscatter diffraction (EBSD), TEM, AFM, and X-ray microdiffraction, we can now establish systematics of biomineral hierarchical architectures. Bioapatite, the main biomineral in vertebrates, always occurs in the form of nanocrystals embedded in organic matrix. With the possible exception of protozoa, the biocarbonate crystals also consist of primary particles in the 20-80 nm range. However, these particles are crystallographically co-oriented and constitute sub-micro- to-micrometer sized *mesocrystals* (SCHMAHL et al., 2012a, b), which are separated by organic membranes. The bioaragonite of corals (PRZENIOSŁO et al., 2008) and the nacre layers of mollusc shells (GRIESSHABER et al., 2013) consist of such poly-*mesocrystals* with a strong axial crystallographic texture. Biocalcite occurs in this form e.g. in the hard layer of brachiopod shells (GOETZ et al., 2011). More frequently in molluscs and brachiopods the calcite forms long *mesocrystal* fibres, columns, or prisms; and morphologically similar *mesocrystals* are sometimes combined to submillimeter-to-millimeter-sized *hybrid composite crystals*, in which the mesocrystal subunits are separated by organic membranes but are crystallographically co-oriented (KELM et al., 2012, SCHMAHL et al., 2012a, b). If *mesocrystal* subunits of different sizes and shapes are combined and display a “single-crystal”-like 3D crystallographic co-orientation, a *multiplex composite crystal* architecture (SCHMAHL et al., 2012b) is present, e.g. in sea urchin teeth where this architecture is essential for precise and reproducible self-sharpening of the tooth.

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