Hierarchical structure of CaCO3 biominerals – mesocrystals and functionalization

W. Schmahl1, E. Griesshaber1, L. Fernandez-Diaz2, A. Ziegler3, K. Kelm4, B. Maier1, F. Nindiyasari1, G. Jordan1

1 LMU Munich, Department of Earth Sciences, Munich, Germany, 2 Universidad Complutense, Departamento de Cristalografía y Mineralogía, Madrid, Spain, 3 University of Ulm, Center of Electron Microscopy, Ulm, Germany, 4 DLR German Aerospace, Institute of Materials Research, Cologne, Germany

Skeletal parts and teeth of marine organisms, avian eggshells, trilobite and isopod eyes, and many more biomineralized tissues consist of bio-calcite or bio-aragonite crystals. We explore the nano- to micro-scale architectures of these materials by electron backscatter diffraction (EBSD) and complementary techniques. In contrast to their inorganic cousins the biogenic “crystals” are hybrid composites with small amounts of organic matrix controlling morphogenesis and critically improving mechanical performance or other functions. For the biominerals meso-crystal-like structures are ubiquitous, consisting of co-oriented nano-blocks with a mosaic-spread of a few degrees, depending on the organism and on the size of the mesocrystal entity[1, 2, 3]. The nano-mosaic can be attributed to growth by nano-particle accretion from an amorphous or gel-like precursor, where relics of organic matrix cause misorientations between the crystallized nano-blocks. Recently we were able to reproduce this feature in gel-grown calcite [Nindiyasari et al., Crystal Growth and Design, in press]. The mesocrystal-co-orientation spreads on to the micro- and even millimeter-scale, frequently with a fractal nature of co-oriented hierarchical units [Maier et al., Acta Biomaterialia, accepted for publication]. The hierarchically structured morphology of the composite crystal or polycrystal is always directed by organic matrix membranes. Sea urchin teeth show a multiplex composite crystal architecture, where different subunits of engineered shapes, Mg-contents, and small misalignments are essential prerequisites for self-sharpening [1]. The figure shows an EBSD map of dendritic interdigitating calcite crystals in an avian egg shell (color coding for crystal orientation) with an misorientation profile along the grey line.


Keywords: Biomineralization, EBSD, Texture