Biomineral Ultrastructures Revealed by Synchrotron Spectromicroscopy

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The ultrastructure of biominerals is one of the most fascinating aspects of these materials, attracting the attention of materials scientists as well as chemists, physicists and engineers. Typically, the ultrastructure is revealed and analyzed at multiple scales by electron microscopies or x-ray diffraction. Another experimental method, only recently introduced into the study of biominerals, is synchrotron soft-x-ray spectromicroscopy. As this method detects both the organic and mineral components, the bonds at their interface, and crystal orientation at the nano-scale, it revealed several biomineral formation and transformation mechanisms (1-3). Here we discuss recent results on the biomineral ultrastructure, with particular focus on the relative arrangement of crystal orientation in the biomineral tissue of three distinct systems:

(i) Columnar and sheet nacre from a variety of mollusk shells, which are all different from one another. In gastropod columnar nacre we observed gradually ordering tablet crystal orientation with distance from the prismatic-nacre boundary. This was *not* observed either in cephalopod columnar nacre or in bivalve sheet nacre. A theoretical model explains the kinetics of this ordering mechanism with distance in terms of competition for space (4, 5).

(ii) The sea urchin tooth, contrary to conventional wisdom, is not composed of plates, needles and polycrystalline matrix all diffracting as a single crystal. Rather it comprises two distinct and alternating crystal layers A and B, stacked as ABABAB. The angle between A and B crystals is less than 6°. This ultrastructure may explain how the tooth self-sharpens as it grinds limestone, thus far a puzzle in biomineral materials science (6).

(iii) Amorphous calcium carbonate (ACC) is a precursor to the calcite in sea urchin spicules, zebrafish bone, tooth enamel, and possibly mollusk shells. We analyzed the ACC-to-calcite transformation in the sea urchin spicule, and found 2 types of ACC, which slowly convert to crystalline calcite. Crystallinity propagates through the pre-formed amorphous material not by a massive crystal growth front, but via a secondary nucleation mechanism propagating along random walks, akin to fractal network percolation (3).

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