

# TOUGH AS A SHELL: ON THE GROWTH AND ORIENTATION OF A RECORD-PERFORMING BIOLOGICAL NANOSTRUCTURE

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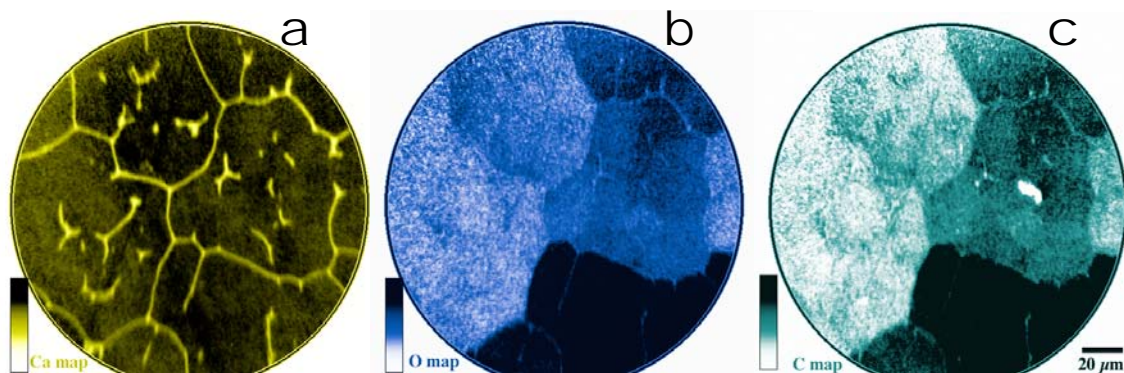
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Like many other biominerals, shell nacre (the inner iridescent layer also known as mother-of-pearl) exhibits spectacular mechanical properties not matched by any man-made material using similar components. Nacre is a composite of aragonite (95% wt) and organics (5% wt), and is 3000 times more fracture resistant than geological aragonite. The origin of such toughness lies in nacre's ordered structure: it is composed of parallel layers of hexagonal aragonite tiles (10-20  $\mu\text{m}$  in diameter, 300-500 nm thick), intercalated by layers of organic matrix, containing, proteins, glycoproteins and polysaccharides. Since nacre is produced by an organism, the organic matrix component must be controlling the growth of the mineral crystals. In particular, it must select the mineral polymorph, the tile habit, size and orientation. The organic matrix may also directly contribute to the mechanical properties as intercrystalline shock absorbers.

Using synchrotron-based X-ray PhotoElectron Emission spectroMicroscopy (XPEEM), we studied some of the shells characteristics at the microscopic level. In particular, Ca L-edge spectra unambiguously show that the organic macromolecules actively direct the growth of aragonite, despite the fact that aragonite is less stable at ambient conditions than its polymorph calcite. Calcite is found in the outer, prismatic layer of the shell. Furthermore, the polarization dependent  $\pi^*$  resonance of the C-O bond reveals the local mis-orientation of the crystals in the prismatic layer (figure 1), in sharp contrast with the well-aligned aragonite crystals of the nacreous layer which give rise to the shell's extreme mechanical resilience.

A full understanding of the nature of the molecular recognition achieved by organic macromolecules in these organisms may lead to the development of new high performance biomimetics materials.



**Figure 1:** Distribution maps of a *pinctada margaritifera* prismatic layer showing the Ca rich mineral crystals that contrast with the Ca poor organic regions (a); and C and O distribution maps based on the intensity of the  $\pi^*$  resonance of the C-O bond revealing the different orientations of the crystals (b and c).

