

Submicron Architecture of Bivalve Shells revealed by Microbeam Techniques

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Bivalve shells are nanocomposite materials, consisting of a wide variety of ultrastructure types of hierarchically structured units of calcium carbonate crystals embedded within an organic scaffold. Although increasingly important as paleoclimate proxy archives, the exact sub-micrometre growth dynamics and the influence of metabolism on bivalve shells are only incompletely understood. Recent years have seen a paradigm shift in our understanding of how biominerals form, away from classical ion-by-ion crystallization to crystallization by colloid attachment and transformation (CAT) [1]. The CAT process applies also to nacreous bivalve shells, where aragonite is observed to mineralize via amorphous calcium carbonate (ACC) and subsequent growth from aggregated nanoparticles to mature, mesocrystalline aragonitic nacre tablets [2]. A number of detailed growth models exist for the nacreprismatic shell structure, but yet leave questions open, such as whether a new aragonite tablet grows by heteroepitaxial growth predefined from the organic scaffold or by homoepitaxial growth through mineral bridges from one generation of crystals to another.

We present here new results on stepwise spatially-downscaled microbeam techniques combined with NanoSIMS elemental mapping on pulsed strontium-labelled shells of (*Mytilus galloprovincialis*, *Pinctada imbricata*, *Kateleysia rhytiphora*, *Anadara trapezia*). Using this approach we are able to show shell architecture at the submicron scale for nacreprism and crossed-lamellar ultrastructures at known growth rates determined in the pulsed strontium aquaculture experiments.

[1] Gower, L.B., Odom, D., (2000). Deposition of calcium carbonate films by a polymer-induced liquid-precursor (PILP) process. *J. Cryst. Growth* 210, 719–734

[2] De Yoreo, et al. (2015). Crystallization by particle attachment in synthetic, biogenic, and geologic environments. *Science*, 349(6247), aaa6760.