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Nanostructure and composition of bivalve shells

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Shells and pearls of unionid mussels (*Hyriopsis cumingii, Margaritifera margaritifera, Diplodon chilensis patagonicus*) were studied by high resolution microbeam methods and μ-computer tomography to gather insight into the nanostructure and chemical composition of nacre and prism layers. Natural and cultured pearls are formed by many mollusc species and their generation is very similar to that of shells resulting in identical prismatic and nacreous structures of shells and pearls. Basic difference is, however that pearl culturing methods induce biomineralisation of $CaCO_3$ around a crystalline bead which results in a reverse structural organisation compared to bivalve shells.

Bivalve shell growth starts from a thick organic matrix (the periostracum; Eyster and Morse, 1984) which is followed towards the inside by two variously thick layers consisting of prismatic $CaCO_3$ aggregations and layers of $CaCO_3$ platelets, respectively. Platelets and prisms are individually covered by a chitinous organic matrix which lends structural support and is thought to exert control over the mineralization process. The minerals within the organic sheaths are highly-aligned poly-twinned crystals with a slightly distorted lattice due to inclusions of organic molecules (Pokroy et al., 2006).

Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Atomic Force Microscopy (AFM) and Raman Microscopy analyses of the shells and pearls show that both structures, prisms and platelets, consist of nanometre-sized organic membrane-coated granules of $CaCO_3$ (Jacob et al., 2008). In the vicinity of the periostracum, the granules consist of amorphous calcium carbonate (ACC), but the crystallinity increases with increasing distance from the periostracum. The transition from disordered (amorphous) to crystalline $CaCO_3$ is gradual within a few micrometers and coincides with a decrease in porosity. Concentrations of sulphur and phosphorus are higher in ACC than in aragonite indicating a higher organic content of ACC.

Bivalve larval shells were shown to consist entirely of ACC before this phase crystallizes to form aragonite (Weiss, et al., 2002). The occurrence of ACC in pearls and adult shells close to the periostracum reported here and by Jacob et al. (2008) is taken as evidence that bivalve shell formation starts from ACC secreted in organic vesicles. Lately, a number of studies reported similar granular nanostructures for many different mollusc species which implies that shell growth by secretion of ACC vesicles could be a widespread phenomenon in biology.

Vaterite could be identified in freshwater cultured pearls as well as in shells of *Hyriopsis cumingii* and *Diplodon chilensis patagonicus*. Aragonite and vaterite were found to coexist and are crosscut by growth lines, implying simultaneous formation. In pearls, it was found that vaterite, like aragonite, forms from ACC (Jacob et al., 2008) and is therefore not the precursor phase of aragonite in this system.

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