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Biomineralisation in Mollusc shells

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The main components of Mollusc shells are carbonate minerals: calcite and aragonite. ACC is present in larval stages. Calcite and aragonite can be secreted simultaneously by the mantle. Despite the small number of varieties, the arrangement of the mineral components is diverse, and dependant upon the taxonomy. They are also associated with organic components much more diverse, the diversity of which reflects the large taxonomic diversity. From TGA analyses, the organic content (water included) is high (>5% in some layers).

The biomineralisation process is not a passive precipitation process, but is strongly controlled by the organism.

The biological-genetic control is shown by the constancy of the arrangement of the layers, the mineralogy and the microstructure in a given species. Microstructural units (i.e. tablets, prisms etc.) have shapes that do not occur in non-biogenic counterparts. Nacreous tablets, for example, are flattened on their crystallographic c axis, which is normally the axis of maximum growth rate for non-biogenic aragonite. Morever, their inner structure is species-specific: the arrangements of nacreous tablets in Gastropoda - Cephalopoda, and in Bivalvia differ, and the inner arrangement of the nacreous tablets is different in ectocochlear and endocochlear Cephalopoda. The organic-mineral ratios also differ in the various layers of a shell. Differences in chemical composition also demonstrates the biological-genetic control: for example, aragonite has a low Sr content unknown in non-biogenic samples; two aragonitic layers in a shell have different Sr and Mg contents, S is higher in calcitic layers.

Decalcification releases soluble (SOM) and insoluble (IOM) organic components. Insoluble components form the main part of the intercrystalline membranes, and contain proteins, polysaccharides and lipids. Soluble phases are present within the crystals and the intercrystalline membranes. These phases are composed of more or less glycosylated proteins and polysaccharides, with a large range of molecular weights. Proteins are rich in acidic aminoacids (aspartic and glutamic acids). Sugars are usually sulphated, and very acidic. Several hundreds of proteins and sugars are present in the SOM. The compositions of IOM and SOM are characteristic for each layer present in a shell.

Topographical relationships of mineral and organic components are visible at different scales of observation. SEM images of etched surfaces display the growth line rhythmicity and concordance between adjacent microstructural units. EPMA maps show similar chemical growth lines in various structures. Whatever the taxa, the average thickness of growth lines is about 2-3 μm, indicating an inner biological rhythm, not dependant on the environmental conditions. Such growth lines are observed in deep sea molluscs at depth where diurnal changes in light and temperature are absent. However, the role of the environment is shown by larger periodicities. Sulphur deserves a special interest, because it is associated with the organic matrices. Electrophoretic data have shown that acidic sulphated sugars are abundant in some layers. XANES analyses confirm these results.

New microscopic techniques allow us to obtain images at a submicrometer scale. AFM images show that all the microstructural units (i.e. tablets, prisms etc.), calcite or aragonite, are composed of small sub-spherical granules with a diameter typically of about 50 nm. These granules are surrounded by a thin cortex (about 8 nm) of organic and/or amorphous material, and are organo-composite material as shown by phase images. They do not have crystalline shapes, despite the fact that the units they build are often monocrystalline.

Molecular biology and genetic studies confirm that the control of the biomineralisation process is exerted at the scale of the whole organism: the expression of genes encoding major shell matrix proteins clearly indicates a regular separation of calcite and aragonite secretory activity.

The main control on the structural and compositional features of mollusc shells is genetic. However, environmental influences do exist. Due to the complex structures and composition of these shells, localized analyses must be preferred. The role of the composition and distribution of the organic matrix in fossilisation processes, and any

potentially induced alterations is not yet known.

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