



Nanostructures of the calcitic and aragonitic crystals of the pearl oyster shells and distribution of their mineralizing organic matrices

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The shell of *Pinctada margaritifera* is composed of a thin outer calcitic prismatic layer, and a thick inner aragonitic nacreous layer. The inner structures and the chemical compositions of these layers clearly differ from those of their non biogenic counterparts.

Within mollusk shells, mineral and organic components are intimately associated. Mineral units are usually surrounded by “insoluble” organic envelopes (IOM), whereas soluble organic components (SOM) can be extracted from within the crystals. Infrared and amino acid analyses have shown that the IOM of the nacreous and prismatic layers are different. In both matrices, sugars and proteins are present, with different ratios. Infrared maps show differences in the organic components of the two layers, as well as differences between the organic envelopes and the intracrystalline matrices. Data from HPLC and electrophoreses demonstrate that the molecular weights and the pI of the nacreous and prismatic SOM differ. However, the main part of the sugars and proteins are acidic in both layers. In situ chemical analyses show that the presence of growth lines in the nacreous and prismatic layers. All of these the growth lines synchronously cross-cut adjacent prisms. XANES maps illustrate that IOM and SOM differ in the nacre and prisms, and that the intra-prismatic organic matrix is heterogeneous and displays fine-scale resolution growth bands. The compositional zonations (as demonstrated by WDS microprobe, NANOSIMS and XANES maps) and the structural growth layers (as shown by SEM) are similar. In both layers, sulfated sugars are dominant over S amino acids, and disulphide bonds are weak or absent. S amino acids are present in the nacreous layer.

Previously, observations of the intracrystalline organic matrix have been a major prob-

lem because the SOM components are too small for SEM resolution, and they are dissolved during the preparative procedures for TEM. However, with an atomic force microscope (AFM), fine-scale structural details of the actual surface of the sample can now be resolved. Additionally, the topographic images obtained are associated with other signals that are sensitive to the composition of the sample. Such images show that the nacreous and the prismatic layers, despite their different mineralogy, structures and biogeochemical compositions, are composed of granules. The average diameter of these granules is approximately 50 nm, and they are surrounded by a thin organic envelope of approximately 7 nm. Detailed AFM images suggest that the granules are organo-mineral composites.

These data support two main hypotheses: (1) growth zonation does not result from a regular series of pure mineral and pure organic layers, but are due to different organic/mineral component ratios within the bands. (2) in both aragonite and calcite, granules are arranged in crystalline units, showing the strong control of the organic matrix on the biomineralisation process. This interplay between the organic and mineral components is a major feature of biominerals. However, the biomineralisation process, and the effects of different IOM and SOM to fossilization processes have not yet been fully investigated.

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