



Biom mineralization process: from supersaturation to nucleation in organic hydrogels

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Biom minerals have morphological, chemical and physical properties that are never shown by the corresponding abiotic crystals. Compositional specificity of organic compounds associated to biom minerals has retained attention as the only possible origin of their peculiar properties, and it has long been postulated that only a large diversity of proteins can explain the nucleation and growth control of so diverse and taxonomy linked mineral sequences. However, as far back as 1961, the dominant role of sulfated mucopolysaccharides was demonstrated.

Aragonite and calcite are the main polymorphs of calcium carbonates. On the other hand, proteins and polysaccharides are the main organic components. Several attempts have been done to unravel the respective influences of sugars and proteins on the mineralogy: is there a simple relationship between the main components of the organic matrix and the mineralogy? In vitro experiments have first shown that the presence of sulfated sugars favours aragonite. However, further experiments and analyses have shown a more complex situation.

The soluble organic matrices of Scleractinia skeletons have high acidic sulfated sugar contents and low protein contents, as shown by electrophoretic data, XANES maps and immunostains. On the opposite, calcitic skeletons of Octocorals have high contents of acidic proteins, with low sugar contents. These features seem in accordance with in vitro results. However, mollusc shells show another pattern. High acidic sulfated sugar contents are known in calcitic prisms, whereas high protein contents are found in aragonitic layers (nacre, crossed lamellar layers...). In addition, both polymorphs are present in a single shell.

In parallel, the role of organic sulfates has been shown in the in vitro nucleation of calcite. Besides, it is well known that the insoluble organic matrix is also involved

in the mineralization process. It has long been postulated that the nucleation process occurs from a saturated solution. Recently, organic fibrous networks have been identified in several mineralizing systems. The structure and composition of these organic networks related to hydrogels influence the mineralogy and the kinetics of crystallization. At last, until recently it was believed that aragonite or calcite directly nucleated, but recent studies have emphasized the fact that the first mineral component is ACC (amorphous calcium carbonate).

Although it is clear that the organic matrices play a major role in biomineralization, there is no simple relationship between the polymorph and the sugar/protein ratio. Only the knowledge of the composition and structure of the hydrogels, and of the macromolecular frameworks will dictate our understanding of the role of the organic components in process of biomineralization, and diagenesis. From an evolutionary point of view, the mineralogical change occurring at the end of the Paleozoic (calcitic to aragonitic corals) could be related to minor changes in the mineralizing organic framework.

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