

Interaction and Association of Calcite with Organic Substances in Biomineralisation and Experimental Approaches

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Calcite (CaCO_3) is a common mineral in biomineralisation, where mineral precipitation generally takes place in association with polyanionic organic molecules and in many cases within gel-like organic network matrices. Both polyanions and network matrices influence crystal growth and eventually become incorporated into biomineral structures. This presentation aims at the significance and effect of mineral-organic interaction in calcite biomineralisation.

For so-called single-crystalline calcitic biominerals with curved morphologies, such as sponge spicules and sea urchin skeletal elements, atomic force microscopy (AFM) revealed an aggregate-like nano-granular construction instead of crystal growth through spreading of monolayers on flat crystal faces as in normal calcite growth. Small amounts of polyanionic proteins have been shown to be intercalated between nano-grain boundaries. Such an aggregate-like crystal growth pattern enables curved morphologies independent of crystal lattice planes. Furthermore, the resulting nano-granular texture increases the mechanical stability of these biocrystals, since crack propagation follows interlocked domain boundaries instead of the calcite cleavage planes.

In corresponding AFM-observed model experiments, calcite growth from solutions was modified by the protein-like polyanionic additive poly(l-aspartate), which inhibited monolayer spreading and formed a gelatinous film on the calcite (10.4) substrate. Subsequently, multiple substrate-conformable nucleation and aggregate-like crystal growth took place inside the gelatinous film, offering the opportunity of incorporating polyanions as in the biocrystals described above.

Other biominerals are polycrystalline structures with the mineral subunits separated by organic network matrices, such as octocoral sclerites, consisting largely of densely packed Mg-calcite fibres. The surfaces of these sclerites, however, show a nano-granular layered structure, from which a transition towards the fibrous bulk structure has been found. This finding suggests that the sclerites grow by initial precipitation of nano-granular layers of Ca-Mg-carbonate in an organic matrix on the sclerite surface. Subsequently, the internal fibrous structure is formed by reorganisation of granular sub-surface layers, including the organic matrix, and alignment of granules to form Mg-calcite fibres. A similar growth pattern has been found for calcite prisms in mollusc shells.

Model experiments of calcite precipitation in polyacrylamide hydrogel have demonstrated that modified crystal growth as clustered growth units via nano-granular surface aggregates can be induced by interaction with an organic network matrix.

These findings from biomineral structures and simplified model systems suggest that gelatinous organic substances in contact with surfaces of growing crystals are a control mechanism of nano-granular aggregate formation, representing a basic design principle in biomineralisation.

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