



Influence of biological processes on the structure of calcium carbonate biominerals: Microscopic approach

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It has been assumed for decades that formation of the mineral components of invertebrate skeletons is analogous to inorganic crystallization of geological or synthetic minerals. In particular, the skeleton of scleractinian corals, which belong to the most prolific biomineralizing organisms on Earth, was considered to be composed of purely inorganic calcium carbonate crystals. Because scleractinian skeletons are among the most frequently used proxies of global climate changes, it is of wide interest to understand the degree of biological and/or inorganic control over their formation.

Research over the last few years has brought strong evidence that it is the coral organism that controls structural and biogeochemical properties of the skeleton via secretion of specific organic macromolecules. Acidic proteins and sulphated polysaccharides have been detected within the skeletal fibers by various spectroscopic techniques and biomimetic experiments have shown affinity of these macromolecules for binding of the mineral ions. Several unique structural properties of biominerals can also be characterized by microscopic techniques. Here, using a spectrum of microscopic and preparative methods, we visualize the distribution of mineral and organic components at various levels of the structural hierarchy of the skeletons of various azooxanthellate and zooxanthellate Recent scleractinians.

Selectively etched (for Scanning Electron Microscopy, SEM) and stained with cationic dyes (for Confocal Laser Scanning Fluorescence Microscopy, CLSM) coral skeleton samples exhibit two basic structural units of the skeleton structure: (1) calcification

centers (highly enriched in organic components) and (2) thickening deposits. Thickening deposits consist of bundles of fibers enveloped by organic sleeves and organized into various microstructural units that may strongly differ between scleractinian taxa. Individual fibers (a few micrometers in length) are subdivided into small (typically ca. 500 nm) units separated by organic-enriched zones. In turn, Field Emission Scanning Electron Microscopy (FESEM) and Atomic Force Microscopy (AFM) observations show that seemingly purely mineral fibrous units are composed of densely packed mineral nanograins (ca. 50-100 nm in diameter). Mineral and organic components of scleractinian biominerals can be also visualized at nano- and atomic levels by High Resolution Transmission Electron Microscopy (HRTEM) techniques.

We believe that the study of the structural complexity of invertebrate biominerals and the underlying mechanisms of their formation will help us to decipher biological information recorded in the skeleton and allow geochemists to use skeletal data rationally in climatic reconstructions.