



Nanostructural and biogeochemical features of the crinoid stereom

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Representatives of all echinoderm clades (e.g., echinoids, holothuroids, ophiuroids, asteroids, and crinoids) form elaborate calcitic (polymorph of calcium carbonate) skeletons composed of numerous plates. Each plate consists of a three-dimensional meshwork of mineral trabeculae (stereom) that results from precisely orchestrated biomineralization processes. Individual skeletal plates behave as single calcite crystals as shown by X-ray diffraction and polarizing microscopy, however, their physico-chemical properties differ significantly from the properties of geologic or synthetic calcites. For example, echinoderm bio-calcite does not show cleavage planes typical of calcite but reveals conchoidal fracture surfaces that reduce the brittleness of the material. The unique properties of echinoderm bio-calcite result from intimate involvement of organic molecules in the biomineralization process and their incorporation into the crystal structure. Remnants of echinoderm skeleton are among the most frequently found fossils in the Mesozoic and Palaeozoic rocks thus, in order to use them as environmental proxies, it is necessary to understand the degree of biological ("vital effect") and inorganic control over their formation. Here, we show first nanoscale structural and biogeochemical properties of the stereom of extant and fossil crinoids. Using FESEM and AFM imaging techniques we show that the skeleton has nanocomposite structure: individual grains have ca. 100 nm in diameter and occasionally form larger aggregates. Fine scale geobiochemical mappings of crinoid plates (NanoSIMS microprobe) show that Mg is distributed heterogeneously in the stereom with higher concentration in the middle part of the trabecular bars. Although organic components constitute only ca. 0.10-0.26 wt% of modern echinoderm bio-calcite, in situ synchrotron sulphur K-edge x-ray absorption near edge structure (XANES) spectra show that the central parts of stereom bars contain higher levels of SO₄ that in various carbonate biominerals are associated with sulphated polysaccharides. These data are consistent with modern models of biomineralization suggesting involvement of magnesium ions and sulphated polysaccharides in early phases of biomineral formation.

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