ACTA PALAEONTOLOGICA POLONICA

Nanostructure of biogenic versus abiogenic calcium carbonate crystals

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Acta Palaeontologica Polonica 50 (4), 2005: 847-865

The mineral phase of the aragonite skeletal fibers of extant scleractinians (*Favia*, *Goniastrea*) examined with Atomic Force Microscope (AFM) consists entirely of grains ca. 50-100 nm in diameter separated from each other by spaces of a few nanometers. A similar pattern of nanograin arrangement was observed in basal calcite skeleton of extant calcareous sponges (*Petrobiona*) and aragonitic extant stylasterid coralla (*Adelopora*). Aragonite fibers of the fossil scleractinians: Neogene Paracyathus (Korytnica, Poland), Cretaceous *Rennensismilia* (Gosau, Austria), *Trochocyathus* (Black Hills, South Dakota, USA), Jurassic *Isastraea* (Ostromice, Poland), and unidentified Triassic tropiastraeid (Alpe di Specie, Italy) are also nanogranular, though boundaries between individual grains occasionally are not well resolved. On the other hand, in diagenetically altered coralla (fibrous skeleton beside aragonite bears distinct calcite signals) of the Triassic corals from Alakir Cay, Turkey (*Pachysolenia*), a typical nanogranular pattern is not recognizable. Also aragonite crystals produced synthetically in sterile environment did not exhibit a nanogranular pattern. Unexpectedly, nanograins were recognized in some crystals of sparry calcite regarded as abiotically precipitated. Our findings support the idea that nanogranular organization of calcium carbonate fibers is not, *per se*, evidence of their biogenic versus abiogenic origin or their aragonitic *versus* calcitic composition but rather, a feature of CaCO3 formed in an aqueous solution in the presence of organic molecules that control nanograin formation. Consistent orientation of crystalographic axes of polycrystalline skeletal fibers in extant or fossil coralla, suggests that nanograins are monocrystalline and crystallographically ordered (at least after deposition). A distinctly granular *versus* an unresolvable pattern of nano-organization of CaCO3 fibers seems to correspond, respectively, to an original *versus* a diagenetically depleted amount of organic matter bounding a mineral phase; this is consistent with qualitative and quantitative analyses of organic matter content in extant and fossil skeletons.

Key words: Scleractinia, Stylasteridae, Calcarea, biominerals, aragonite, calcite, nanostructure, AFM.

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Full text (3,392.8 kB)