



Nanogranules in carbonate skeletons: a universal scheme?

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The main mineral components of calcium carbonate skeletons are calcite and aragonite. It is now well-known these minerals are associated with organic components, the diversity of which reflects the taxonomic diversity. Despite the limited variety of minerals employed, the arrangements of the mineral components are diverse, and dependant upon the taxonomy. For example, the nacreous layer is specific for Molluscs; the arrangement of tablets is specific for Gastropoda and Cephalopoda, and for Bivalvia (Erben 1972, Wise 1972). The inner arrangement of the nacreous tablets is different in ectocochlear and endocochlear Cephalopoda (Mutvei 1970, Dauphin & Keller 1982). Recent high resolution analyses allows us to observe the micro- and ultra- or nanostructures with a continuous range of magnifications on the same sample. Moreover, with atomic force microscopy (AFM), it is now possible to observe the actual surfaces in contrast with transmission and/or scanning electron microscopy. AFM studies have confirmed that the nacreous rods building the sectors of the nacreous layers of the cephalopod *Nautilus* are composed of round granules of 40-50 nm in diameter. These granules are often composite structures, surrounded by thin organic envelopes (Dauphin 2001, 2006). However, these granules do not seem specific for the nacreous layers. Similar granules have been observed in the calcite prismatic layer of *Pinna* and *Pinctada* (Bivalvia)(Dauphin 2003), in the aragonite crossed lamellar layers and in the calcite prismatic layers of *Concholepas* and *Haliotis* (Dauphin et al. 2003), etc. Using a high resolution SEM and etching processes, Addadi et al. have shown 50-70 nm diameter granules in the calcite layers of *Atrina* (Bivalvia) (oral comm.). Moreover, such granules are also present in the aragonite skeletons of *Scleractinia* (Cuif & Dauphin 2005, Dauphin et al. 2006) and in the calcite skeletons of *Octocorallia* (Dauphin 2006).

The thickness of the organic envelopes is about 7 - 10 nm, a size compatible with the known molecular weights of the intracrystalline organic matrices extracted from these shells. Larger granules surrounded by an organic envelope have been observed in Recent brachiopods. Mineral granules with an organic envelope are also present in fish otoliths and crustacean gastroliths, despite differences in the mechanisms of secretion. Until now, no relationship between the shape and size of the granules, and the structure of the layer and/or the taxonomy has been established. Arrangement of the granules in higher order structural units is dependant of the taxonomy of the organisms, but the mechanisms are not yet known. New methods for sample preparations are needed to understand the properties of these organo-mineral assemblages.

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