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Biomineralisation of marine carbonates - ion by ion growth vs. particle accretion

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Ca-Carbonate teeth and skeletons of marine invertebrates show usually show a nanoparticulate morpho-topology in SEM and AFM investigations. Consequently, a paradigm evolved which explains the genesis of biominerals by accretion of carbonate-filled vesicles exocytosed by the mineralizing cells. This model of nanoparticle aggregation was supported by the proposition of "nanoparticles" or pre-nucleation clusters in carbonate solutions suggesting "non-classical" nucleation and growth of carbonates.

Since more than 10 years we studied many Ca-carbonates formed by marine organisms with AFM, SEM/EBSD, TEM and XRD. In addition, we investigated abiotic calcite growing in gels. Today, we feel that the paradigm of nanoparticle accretion as a general model for biomineralization needs to be seen with scrutiny:

i) Protein or polysaccharide gels are fibrous networks with open pores in the ~100 nm range (depending on gel concentration). The mineral forming within the gel incorporates the gel fibres and membranes and thus develops a superficial "nanoparticulate" mesocrystal-like appearance. However, the omnipresent terraces corresponding to regular crystal faces, such as {104} for calcite, indicate ion-by-ion growth of the aggregates.

ii) For most marine biocarbonates the "nanogranule-like" morphologies are in the 50-100 nm size range. The biocarbonate crystals contain incorporated organic networks with structures and size-ranges similar to the gel-grown crystals. Coccoliths are an exception: they do not contain organic matrix and show a classical crystallography. Coccoliths do grow intracellular vesicles.

iii) The "pre-nucleation clusters" in hydrous solution supposed to be responsible for "non-classical crystal growth" are an order of magnitude smaller than the "nanogranules" of biocarbonates, such that there cannot be a direct relationship.

iv) Dense aggregation of any round and similarly-sized particles leaves ~25% open pore space. In contrast, most marine biocarbonates have no such pores.

v) ACC-filled nanovesicles in epithelial cells have so far not been found, despite intensive search.

Thus, the formation of biominerals may well occur by ion-by-ion growth in gel- or PILP-filled extracellular compartments, where the necessary transport of calcium and hydrogencarbonate into the compartment and of protons out of the compartment occurs by the common ion pumps and exchangers in the membranes of the epithelial cells.

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