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Evidence for variable crystallinity in bivalve shells

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Bivalve shells are used as important palaeoclimate proxy archives and monitor regional climate variations. The shells mostly exist of two crystalline polymorphic phases of calcium carbonate calcite (rombohedric) and aragonite (orthorhombic). Calcite is the most stable polymorph at standard conditions, whereas vaterite (hexagonal) is the least stable and only rarely found in these structures.

Shells are characterized by organized structures and several micro architectures of mollusc shell structures have been identified: Nacre shows different types: columnar and bricked forms and consists of composite inorganic-organic at the nano-scale. They are well known to display a "brick and mortar" structure. By AFM and FIB/TEM methods it could be shown, that its nanostructure consists of the structures in the range of 50 – 100 nm [1, 2]. These structures are vesicles, consisting of $CaCO_3$ and are individually coated by a membrane. Most probably, the mantle epithelian cells of the bivalve extrude $CaCO_3$ vesicles.

By Raman spectroscopic investigations the crystalline $CaCO_3$ polymorphs calcite, aragonite and vaterite, as well as ACC were determined. For some species (Diplodon chilensis patagonicus, Hyriopsis cumingii) pure ACC (i.e. not intermingled with a crystalline phase) could be identified. The presence of an amorphous phase is generally deduced from the lack of definite lattice modes, whereas a broad Raman band in this region is to observe.

In most of the cultured pearls (Pinctada maxima and genus Hyriopsis) the ν_1–Raman band of ACC clearly displays an asymmetric shape and splits into two different bands according to a nanocrystalline and an amorphous fraction. The FWHMs of most of the crystalline fractions are too high for well crystallized materials and support the assumption of nanocrystalline calcium carbonate polymorph clusters in ACC. They are primarily composed of amorphous calcium carbonate (ACC) which is later transformed into a crystalline modification [3]. Remnants of ACC can be traced by Raman spectroscopy and allow insight into the processes of biomineralization in bivalves. The crystallinity of solid materials can be quantified Raman spectroscopy by comparison of the FWHM of the ν_1–Raman peak.

We developed a Raman crystallinity index in order to get a measure of the degree of crystallinity [4]. Results presented for shells from several different marine and freshwater bivalve species and compare these with synthetically ACC and stable ACC from Porcellio scaber. The crystalline fraction in the different ACC-areas in shells and pearls supports the hypothesis that ACC acts as a transient precursor to crystalline $CaCO_3$, in which the polymorph is already moulded into nanoclusters. The distribution and the state of crystallization of the calcium carbonate polymorphs in most of the ACC areas are not homogenous and the term ACC includes structurally different material.

[1] Jacob et al., 2008, Geochim. Cosmochim. Acta 72, 229, [2] Jacob et al., 2011; J. Struct. Biol. 173 (2), 241, [3] Addadi et al., Adv. Mater. 2003; (15), 959, [4] Wehrmeister et al., 2011. J. Raman Spectrosc. 42, (5), 926.