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Stability of amorphous calcium carbonates precursors — a novel phase diagram for aqueous $CaCO_3$

Jonathan Avaro, Stefan Wolf, and Denis Gebauer
Konstanz University, Biophysical Chemistry , Physical chemistry , Germany (jonathan.avaro@uni-konstanz.de)

Due to the high availability of calcium and carbonate ions in oceanic system, calcium carbonate is one of the predilection material for many macro- microscopic marine vertebrates and invertebrates for protection, predation, vision, Ca-storage. Generally driven by organic polymer, final mineralised product forms a complex and ordered architecture from the nanoscopic to the macroscopic level. In particular, amorphous calcium carbonate has been in the focus of biomineralisation research as it is assumed to play a key role in the formation mechanism of crystalline biominerals. Detailed investigation into the structure of some biogenic ACCs revealed the existence of distinct short-range order directly related to anhydrous crystalline calcium carbonate polymorphs. Similar short-range order has recently been observed in additives-free ACCs so-called proto-calcite, proto-vaterite and proto-aragonite, introducing the notion of polymorphism in ACCs.
Despite the large variety of ACCs, a detailed understanding of the formation mechanism is still lacking and an exhaustive study of proto-crystalline forms relative stability needs to be established. Here, we investigated the thermodynamic stability of amorphous calcium carbonate precursors over a wide range of temperature and different pH via titration experiments. Such measurement allowed the establishment of a phase diagram for calcium carbonate.