

Towards a Phase Diagram of CaCO_3 Amorphous Polymorphism

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Today, it is generally accepted that amorphous calcium carbonate (ACC) plays a pivotal role during biomineralization processes [1]. The amorphous precursor strategy bears the advantage that the morphologies of particles are not dictated by crystalline lattices, thereby facilitating the generation of complex off-equilibrium shapes, which are typical for biominerals [2]. Moreover, distinct short-range structures in ACC may contribute to the control of crystalline polymorphism, that is, polymorph selection. Such “pre-structuring” of ACC is well known from biomineralization studies, where it is induced by different bio(macro)molecules. Recently, it has been shown that distinct structures in ACC can be controlled by varying pH values, which is evidence that the structure of ACC can depend only on physical-chemical factors during precipitation [3]. Consequently, distinct ACC short-range structures can be discussed from the point of view of amorphous polymorphism (polyamorphism) [4]. Essentially, it can be conjectured that different polyamorphs can become accessible depending on variables of state. Indeed, “aragonitic” short-range structures can be induced at elevated pressures [5].

Here we have assessed the effect of pH and temperature on ACC polyamorphism. Without additives, we find that pH dictates the short-range structure relating to either calcite or vaterite at room temperature. At elevated temperatures, a discrete transition to proto-aragonite ACC occurs, but not at all pH levels. The structural characterization is based on infrared and solid-state nuclear magnetic resonance spectroscopies, along with high resolution transmission electron microscopy. Distinct structures do not result from nanocrystalline features, and the data eventually allows for the construction of a pseudo-phase diagram of calcium carbonate polyamorphism.

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