

The Effect of β -Glycerophosphate on the Crystallization of Amorphous Calcium Carbonate (ACC)

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Calcium carbonate (CaCO_3) minerals are widely distributed in organisms as skeletons and hard tissues. This biomineralization process, which controls the formation of CaCO_3 in nature is a complex, not yet fully understood phenomenon. Indeed, the initial steps of CaCO_3 crystallization most often proceeds via a metastable, amorphous calcium carbonate (ACC) phase. Understanding its formation, and stability is essential for elucidating the crystallization kinetics of biogenic CaCO_3 and for gaining new insights into biomineralization mechanisms in biological systems. While many organic compounds are known to play important roles in ACC formation and crystallization, the role of organic phosphate (OP) compounds remains less understood.

To address this, we investigated the influence of β -Glycerophosphate (β -GP), an organic phosphate compound containing both phosphate and glycerol functional groups, on the nucleation and growth dynamics of ACC and on its crystallization to stable CaCO_3 polymorphs. We combined, fast (2 sec/frame) *in-situ* UV-Vis spectroscopy and *in-situ* dynamic light scattering analyses, with scanning electron microscopy and powder X-ray diffraction (XRD) measurements of the resulting solids and evaluated the ACC formation kinetics and particle size distributions as well as the mineralogy of the CaCO_3 phases forming in the presence (and absence) of β -GP.

Our results revealed that the presence of 10% β -GP affected the life time of ACC by $\sim 12\%$ compared to the pure system. In the absence of β -GP, ACC with two distinct particle size distributions formed (3-10 nm and 200-400 nm), before it transformed to larger vaterite and calcite crystals. In contrary, in the presence of 10% β -GP, ACC only formed the larger particle size group prior to its crystallization, and XRD results indicated a direct transformation from ACC to calcite. Our findings suggests that β -GP may play a key role in both the stability and the sizes of initially formed ACC, additionally suppressing vaterite crystallization, highlighting the relevance of organic compounds in the formation pathways of biogenic calcium carbonate mineral phases.