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AMORPHOUS MATERIALS: PROPERTIES, STRUCTURE, AND DURABILITY†

Acceleration and inhibition effects of phosphate on phase transformation of amorphous calcium carbonate into vaterite

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ABSTRACT

Phase transformation of amorphous calcium carbonate (ACC) into vaterite and its subsequent stability was investigated at a constant pH (~8.2), ionic strength, and temperature that simulated the biological environment. Solutions containing the same concentrations of $CaCl_2$, Na_2CO_3, and tris(hydroxymethyl)aminomethane buffer and various concentrations of PO_4 (0–62.5 μM) were prepared, and precipitates in the solutions were sampled at a constant interval to observe the morphology and type of calcium carbonate polymorphs that appeared. The change in the Ca-ion concentration over time, which served as a guide for phase transformation of ACC into crystalline phases, was measured in relation to the PO_4 concentration. The starting time of phase transformation was at the minimum point when the concentration was ~2–3 μM. Vaterite spherulites consisting of needle-like crystals (0.5–2 μm in length) formed only in this PO_4 range and survived the experimental procedure (~2.5 h). In contrast, the starting time of phase transformation increased exponentially with the PO_4 concentration when it was higher than 5 μM. The vaterite spherulites and calcite crystals co-precipitated, and both polymorphs grew over time. The PO_4 was shown to be an accelerator for phase transformation from ACC into vaterite at low concentrations (Ca/PO_4 molar ratio <3000) and an inhibitor for transformation at high concentrations. We investigated the kinetics of vaterite formation in the presence of PO_4 and derived an advanced concept for cluster-based phase transformation. This investigation showed that the appearance and stability of calcium carbonate polymorphs is easily controlled by adjusting the PO_4 concentration.

Keywords: Vaterite, phase transformation, phosphate, biomineralization, amorphous calcium carbonate