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PO_4 adsorption on the calcite surface modulates calcite formation and crystal size

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Abstract

Calcium carbonate ($CaCO_3$) and particularly its stable phase, calcite, is of great geological significance in the deep carbon cycle since $CaCO_3$ from biomineralized shells and corals form sedimentary rocks. Calcite also attracts attention in medical science and pharmacy as a primary or intermediate component in biomaterials because it possesses excellent biocompatibility along with suitable physicochemical properties. Calcite blocks have already been used during surgical procedures as a bone substitute for reconstructing bone defects formed by diseases and injury. When producing $CaCO_3$ biomaterials and bioceramics, in particular, in vivo control of the size and polymorphic nature of $CaCO_3$ is required. In this study, we investigated the effects of PO_4 on calcite formation during the phase conversion of calcium sulfate anhydrate ($CaSO_4$, CSA), which is sometimes used as a starting material for bone substitutes because of its suitable setting ability. CSA powder was immersed in 2 mol/L Na_2CO_3 solution containing a range of PO_4 concentrations (0–60 mmol/L) at 40 °C for 3 days. The treated samples were investigated by X-ray diffraction, Fourier-transform infrared spectroscopy, X-ray fluorescence spectroscopy, and thermal analysis. In addition, the fine structures of the treated samples were observed by field-emission scanning electron microscopy, and the specific surface area was measured. We found that PO_4, which is universally present in vivo, can modulate the calcite crystal size during calcite formation. A fluorescence study and calcite crystal growth experiments indicated that PO_4 adsorbs tightly onto the surface of calcite, inhibiting crystal growth. In the presence of high PO_4 concentrations, vaterite is formed along with calcite, and the appearance and stability of the $CaCO_3$ polymorphs can be controlled by adjusting the PO_4 concentration. These findings have implications for medical science and pharmacology, along with mineralogy and geochemistry.

Keywords: Calcite, morphology, phosphate, phase transformation, fabrication, calcium carbonate; Biomaterials—Mineralogy Meets Medicine