

PO₄ adsorption on the calcite surface modulates calcite formation and crystal size

YUKI SUGIURA^{1,*}†, KUNIO ISHIKAWA², KAZUO ONUMA³, AND YOJI MAKITA¹

¹Health Environmental Control R.G., National Institute of Advanced Industrial Science and Technology (AIST), 2217-14, Hayashi-cho, Takamatsu, Kagawa 761-0395, Japan

²Department of Biomaterials, Faculty of Dental Science, Kyushu University, 3-1-1, Maidashi, Higashi, Fukuoka 812-8532, Japan

³Biomaterials R.G., National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1, Higashi, Tsukuba, Ibaraki 305-8566, Japan

ABSTRACT

Calcium carbonate (CaCO₃) and particularly its stable phase, calcite, is of great geological significance in the deep carbon cycle since CaCO₃ 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 CaCO₃ biomaterials and bioceramics, in particular, in vivo control of the size and polymorphic nature of CaCO₃ is required. In this study, we investigated the effects of PO₄ on calcite formation during the phase conversion of calcium sulfate anhydrate (CaSO₄, 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 Na₂CO₃ solution containing a range of PO₄ 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 PO₄, 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 PO₄ adsorbs tightly onto the surface of calcite, inhibiting crystal growth. In the presence of high PO₄ concentrations, vaterite is formed along with calcite, and the appearance and stability of the CaCO₃ polymorphs can be controlled by adjusting the PO₄ 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