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

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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 physical-chemical 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 adsors 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

INTRODUCTION

Calcium carbonate (CaCO₃) is of great geochemical significance due to its role in Earth’s carbon cycle (Zeebe et al. 2008; Dasgupta and Hirschmann 2010; Swart 2015). Marine organisms such as corals and mollusks absorb huge amounts of CO₂ from the ocean and atmosphere to form CaCO₃, which is the primary inorganic component in biomaterials because it possesses excellent biocompatibility along with suitable physical-chemical 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 adsors 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.

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Properties are advantageous for drug carriers. In addition, calcite quickly dissolves under acidic conditions. Since the lactic acid in cancer cells causes the surrounding areas to become somewhat acidic (Gillies et al. 2004; Crayton and Tsourkas 2011; Longo et al. 2016), calcite could be used in cancer therapy to achieve selective drug release around cancer cells with minimum side effects. In dentistry and orthopedics, calcite is also an attractive starting or intermediate material of carbonate apatite [CO₃Ap: Ca₁₀₋ₓ(PO₄)₆₋ₙ(CO₃)ₙ(OH)₂₋ₙ], which is the primary inorganic component of bone as well as a new bone substitute. The in vivo properties of CO₃Ap are much better than those of conventional bone substitutes such as hydroxyapatite [HAp: Ca₁₀(PO₄)₆(OH)₂] (Ishikawa 2010; Fujisawa et al. 2018; Hara et al. 2018; Ishikawa et al. 2018; Wang et al. 2018). CO₃Ap cannot be fabricated via sintering because it decomposes at temperatures above 700 °C. Therefore, CO₃Ap, especially CO₃Ap blocks, is fabricated via dissolution/re-precipitation (Rey et al. 1989; Liu et al. 2015; Ishikawa et al. 2018) by immersing calcite in PO₄-containing solution (Sunouchi et al. 2012; Ishikawa et al. 2018). However, for fabricating CO₃Ap blocks using the above method, it is mandatory to achieve a complete reaction. Since