AFM study of the epitaxial growth of brushite (CaHPO₄·2H₂O) on gypsum cleavage surfaces

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ABSTRACT

The epitaxial overgrowth of brushite (CaHPO₄·2H₂O) by the interaction of phosphate-bearing, slightly acidic, aqueous solutions with gypsum (CaSO₄·2H₂O) was investigated in situ using atomic force microscopy (AFM). Brushite growth nuclei were not observed to form on the {010} gypsum cleavage surface, but instead formed in areas of high dissolution, laterally attached to gypsum {010} step edges. During the brushite overgrowth the structural relationships between brushite (Aa) and gypsum (A2/a) result in several phenomena, including the development of induced twofold twinning, habit polarity, and topographic effects due to coalescence of like-oriented crystals. The observed brushite growth is markedly anisotropic, with the growth rate along the main periodic bond chains (PBCs) in the brushite structure increasing in the order {101} > {T01} > {010}, leading to tabular forms elongated on {101}. Such a growth habit may result from the stabilization of the polar {101} direction of brushite due to changes in hydration of calcium ions induced by the presence of sulfate in solution, which is consistent with the stabilization of the gypsum {101} steps during dissolution in the presence of HPO₄²⁻ ions. The coupling between growth and dissolution was found to result in growth rate fluctuations controlled by the changes in the solution composition.

Keywords: Brushite, gypsum, in situ AFM, epitaxy

INTRODUCTION

Calcium phosphate minerals occur in a wide range of environments within the Earth, and the study of these phases is also fundamental to understanding biomineralization within the human body (Boskey 2007; Pasteris et al. 2008). For example, brushite (CaHPO₄·2H₂O) is a major component of kidney and bladder stones (e.g., Wesson and Ward 2007) and has wide use as a coating for bone implants (Arsic et al. 2004). Francis and Webb (1971) showed that, due to the crystallographic similarities between both minerals, brushite may serve as an effective template for the nucleation of hydroxylapatite, Ca₅(PO₄)₃(OH), one of the most important biominerals. More recently, the crystallographic relationships between brushite, pharmacolite (CaHAsO₄·2H₂O), and gypsum (CaSO₄·2H₂O) as well as the development of oriented intergrowths between these minerals have been studied by several authors (Rinaudo et al. 1994; Hina et al. 2001; Rodríguez-Blanco et al. 2007; Pinto et al. 2009). The structural similarity of brushite with gypsum and pharmacolite was first considered in depth by Heijnen and Hartman (1991), who made a comparative study of their theoretical morphologies using an A-setting for the three unit cells. These three dihydrates crystallize in the monoclinic system with nearly identical unit cells, although the space group of brushite and pharmacolite is Aa, while gypsum crystallizes in A2/a. Pinto et al. (2009) described the epitaxial overgrowth of brushite on the gypsum cleavage surface, showing that brushite can grow onto gypsum with two alternative epitaxial relationships related by a twofold rotation axis. To explain such a phenomenon, these authors relied on the existing difference in point symmetry between substrate (2/m) and overgrowth (m). Pinto et al. (2009) discussed these epitaxial relationships in a detailed way, on the basis of microscale observations and a periodical bond chain (PBC) study, but there is still the necessity for an in situ AFM study of the initial stages and mechanisms of the overgrowth process at the nanoscale.

Atomic force microscopy (AFM) studies on gypsum {010} cleavage surfaces have shown that the specific solution chemistry can strongly influence the dissolution and growth micro-topography. Bosbach and Hochella (1996) performed an in situ study of the inhibiting effect of foreign molecules on gypsum growth, by monitoring variations in step configuration and advancement velocity in the presence of phosphonic acid derivatives, Na-citrate, and tartaric acid. These authors successfully correlated the adsorption of foreign molecules into preferential surface sites with the observed changes in surface morphology and growth kinetics. The presence of background electrolytes has also been shown to affect the growth features of gypsum {010} surfaces (Bosbach et al. 1996). Coupled dissolution-crystallization reactions starting with gypsum as the parent solid were observed by Astilleros et al. (2007), who investigated the interaction between gypsum and Pb-bearing aqueous solutions. Combining macroscopic experiments and in situ AFM observations, these authors showed that the dissolution of gypsum is accompanied by the precipitation of anglesite.