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AFM study of the epitaxial growth of brushite ($CaHPO_4 \cdot 2H_2O$) on gypsum cleavage surfaces

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Abstract

The epitaxial overgrowth of brushite ($CaHPO_4 \cdot 2H_2O$) by the interaction of phosphate-bearing, slightly acidic, aqueous solutions with gypsum ($CaSO_4 \cdot 2H_2O$) 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 [101] step edges. During the brushite overgrowth the structural relationships between brushite (*Aa*) and gypsum (*A*2/*a*) result in several phenomena, including the development of induced twofold twining, 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] > [$\bar{1}$01] > [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 HPO_4^{2-} 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