

Uptake of aqueous Pb by Cl⁻, F⁻, and OH⁻ apatites: Mineralogic evidence for nucleation mechanisms

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ABSTRACT

Apatites provide a mechanism for in-situ remediation of Pb-contaminated sites, by supplying phosphate which combines with dissolved Pb to form highly insoluble pyromorphite. This study expanded upon previous research using hydroxylapatite (HAP), to focus on how the surface properties of natural chlorapatite (CAP) and fluorapatite (FAP) affect pyromorphite nucleation and growth, when aqueous Pb²⁺ ([Pb] < 50 mg/L as PbCl₂) is reacted with apatite at pH = 4.2, 22 °C. A combination of atomic force microscopy (AFM), scanning electron microscopy (SEM), optical microscopy, energy dispersive X-ray fluorescence spectroscopy (EDS), infrared spectroscopy (FTIR), and X-ray diffraction (XRD) was used for in-situ and ex-situ examination of the interface and the reaction products.

A variety of experiments were performed, and pyromorphite [PY = Pb₁₀(PO₄)₆Cl₂] was the only identified reaction product. PY nucleated both homogeneously (directly from solution) and heterogeneously on CAP and FAP; relationship between PY and HAP could not be determined definitively. The nucleation mechanism was sensitive to initial experimental conditions, which suggests that care should be taken to consider initial conditions in designing sorption and nucleation experiments. Heterogenous nucleation on FAP and CAP showed strong evidence for epitaxy. Epitaxial crystals of PY on CAP and FAP grew away from the substrate surface, which was the only source of phosphate available for crystal growth. Epitaxial crystals showed distinctly different morphologies from homogeneously nucleated crystals, and appeared to grow by a spiral growth mechanism.