## Aqueous Pb sorption by hydroxylapatite: Applications of atomic force microscopy to dissolution, nucleation, and growth studies

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## ABSTRACT

A combination of atomic force microscopy, scanning election microscopy, transmission electron microscopy, energy dispersive spectroscopy, electron diffraction, and X-ray diffraction were used to study reactions of 0.5–500 mg/L aqueous Pb with Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH, hydroxylapatite (HAP), at pH 6 and 22 °C. Following 2 h reaction time, concentrations of Pb<sub>aq</sub> ([Pb<sub>aq</sub>]) decreased from 500 mg/L to <100 mg/L, and from 0.5–100 mg/L to <15  $\mu$ g/L. This loss of Pb<sub>aq</sub> from solution (i.e., sorption) resulted partially from simultaneous dissolution of HAP and precipitation of Pb<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH, hydroxypyromorphite (HPY), or another solid Pb phase.

The initial saturation state with respect to HPY (defined as the ratio of the ion activity product to equilibrium solubility product) influenced strongly precipitation processes. At a high degree of saturation (initial  $[Pb_{aq}] > 100 \text{ mg/L}$ ), small nuclei or aggregates of poorly crystalline HPY precipitated homogeneously in solution. At intermediate saturation (initial  $[Pb_{aq}] \sim 10-100 \text{ mg/L}$ ), large, euhedral needles of HPY precipitated homogeneously in solution. At a low degree of saturation (initial  $[Pb_{aq}] < 10 \text{ mg/L}$ ), a needle-like Pb-containing phase grew heterogeneously on HAP. These results agree well with concepts derived from nucleation and growth theories and demonstrate that initial saturation state influences strongly the sorption process.