Phosphate-induced Transformation of Calcite to Fluorapatite in the Presence of Fluoride

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Geogenic contamination of fluoride (F) in groundwater is a severe problem affecting livelihoods of millions of people in the developing world. Prevalent F-removal technologies utilize aluminum (Al)-based sorbents that are prone to leach neuro-toxic Al in the treated water. Alternative treatment approaches utilizing calcium-based sorbents are being investigated. The objective of this study was to demonstrate mineralization of fluoride as fluorapatite ($Ca_5(PO_4)_3F$; Fap) in the presence of calcite and phosphate in ultrapure water at room temperature. An year-long batch study was conducted to investigate the long-term dissolution-precipitation processes associated with this system. Dissolved concentrations were analyzed for F, Ca and PO_4. F concentrations decreased below the WHO drinking water limit (1.5 mg/L) within 3 days and the pH of the system remained within the drinking water limits (6.5-8.5) throughout. Thermodynamic calculations consistent with an updated database suggested mild supersaturation of calcium phosphate solids - monetite ($CaHPO_{4(s)}$) for the first three days, octa-calcium phosphate ($Ca_4H(PO_4)_3 \cdot 3H_2O_{(s)}$) for the next four days, and β-tricalcium phosphate ($Ca_3(PO_4)_{2(s)}$) for the remainder of reaction progress. Throughout the experiment, hydroxyapatite ($Ca_5(PO_4)_3OH$; Hap), and Fap were highly supersaturated. The observed molar uptake of PO_4/F was ~3 during the first 30 days of the reaction consistent with Fap stoichiometric ratio. Formation of Fap was confirmed using X-ray diffraction (Fig. 1). SEM-EDS analysis also confirmed presence of fluoride and phosphate in calcite particles This suggests, it may be a gradual transformation of bulk calcite to calcium-phosphate solids. This approach can potentially be extended to treat F-contaminated aquifers with mild phosphate and calcite amendments providing a sustainable solution for F problem.

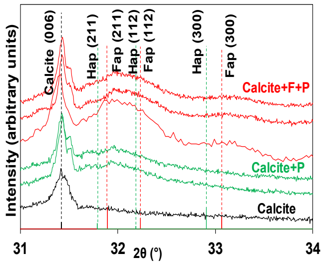

Figure 1. X-ray diffractograms (Cu Kα) of calcite in the presence and absence of phosphate and fluoride. Vertical dotted lines represent peak positions of calcite, fluorapatiteand hydroxyapatite