

Dissolution of poorly soluble uranyl phosphate phases in the Metaautunite Subgroup under uranyl peroxide cage cluster forming conditions

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ABSTRACT

Uranyl phosphate minerals are widespread in uranium deposits and normally exhibit very low solubility in aqueous systems. Uranyl phosphates of the autunite group and metaautunite subgroup impact the mobility of uranium in the environment and have inspired groundwater remediation strategies that emphasize their low solubility. The importance of soluble uranium-bearing macro-anions, including nanoscale uranyl peroxide cage clusters, is largely unexplored relative to solubilization of normally low-solubility uranium minerals. Eight synthetic analogs of metaautunite subgroup minerals have been prepared and placed in various alkaline aqueous solutions containing hydrogen peroxide and tetraethylammonium hydroxide. Each uranyl phosphate studied has a topologically identical anionic sheet of uranyl square bipyramids and phosphate tetrahedra combined with various cations (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Mg^{2+} , Ca^{2+} , Ba^{2+}) and water in the interlayer. Uranyl peroxides formed under many of the experimental conditions examined, including solid studtite $[(\text{UO}_2)(\text{O}_2)(\text{H}_2\text{O})_2](\text{H}_2\text{O})_2$ and soluble uranyl peroxide cage clusters containing as many as 28 uranyl ions. Uranyl phosphate solids in contact with solutions in which uranyl peroxide cage clusters formed dissolved extensively or completely. The greatest dissolution of uranyl phosphates occurred in systems that contained cations with larger hydrated radii, Li^+ and Na^+ . The details of the uranium speciation in solution depended on the pH and counter cations provided from the interlayers of the uranyl phosphate solids.

Keywords: Metaautunite, dissolution, uranium, studtite, uranyl peroxide nanoclusters, peroxide, uranyl phosphate