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 tetrathylammonium 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+, Mg2+, Ca2+, Ba2+) and water in the interlayer. Uranyl peroxides formed under many of the experimental conditions examined, including solid studtite [(UO2)(O2)(H2O)2](H2O); 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

INTRODUCTION

Uranyl phosphates, particularly of the autunite group and metaautunite subgroup, are widespread constituents in oxidized portions of uranium deposits, and are important relative to the environmental transport of uranium and the nuclear fuel cycle due to their low aqueous solubility (Buck et al. 1996; Locock et al. 2004a, 2004b; Suzuki et al. 2005; Wellman et al. 2006a; Astilleros et al. 2013; Dzik et al. 2017a; Gudavalli et al. 2018). In addition to their occurrence in natural uranium deposits (Murakami et al. 1997; Krivovichev and Plášil 2013) and contaminated sites (such as Hanford, Washington) (Singer et al. 2009; Perdrial et al. 2018; Reynolds et al. 2018), formation of uranyl phosphates has been proposed as a remediation strategy for removal of soluble uranium from water (Fuller et al. 2002; Raicevic et al. 2006; Wellman et al. 2006b, 2007a, 2008; Fanizza et al. 2013; Mehta et al. 2014, 2015; Munasinghe et al. 2015; Lammers et al. 2017). Members of the autunite group have composition $A^+$[(UO$_2$)(TO$_3$)](H$_2$O)$_n$, where $A^+$ is a mono-, di-, or trivalent cation, $T$ is P or As, and $n$ is the number of water molecules. The structural unit is [(UO$_2$)(TO$_3$)]$^-$ sheets consisting of uranyl square bipyramids that share equatorial vertices with four different TO$_4$ tetrahedra. Cations and water are in the weakly bonded interstitial complex located between the sheets (Fig. 1) (Burns 2005) and provide linkages between the sheets (Locock et al. 2004a; Locock 2007). The thermodynamic properties (Gorman-Lewis et al. 2009; Dzik et al. 2017a, 2017b), aqueous solubility (VanHaverbeke et al. 1996; Gorman-Lewis et al. 2009), and dissolution behaviors at acidic conditions (Wellman et al. 2007b) of members in the metaautunite subgroup have been studied, although their behavior in alkaline systems containing hydrogen peroxide is unknown.

Studtite, [(UO$_2$)(O$_2$)(H$_2$O)$_2$](H$_2$O)$_3$, is a poorly soluble uranyl peroxide mineral comprised of infinite chains of uranyl hexagonal bipyramids linked together by peroxide bridges (Burns and Hughes 2003). It readily forms as an alteration product when uranium material, ranging from UO$_2$ to uranyl oxide hydrates to uranyl silicates, comes in contact with solutions containing hydrogen peroxide in acidic and neutral environments (Abrefah et al. 1998; Burns and Hughes 2003; Clarens et al. 2005; Hanson et al. 2005; Forbes et al. 2011; Armstrong et al. 2012; Burns et