Dynamic interplay between uranyl phosphate precipitation, sorption, and phase evolution

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ABSTRACT

Natural examples demonstrate uranyl-phosphate minerals can maintain extremely low levels of aqueous uranium in groundwaters due to their low solubility. Therefore, greater understanding of the geochemical factors leading to uranyl phosphate precipitation may lead to successful application of phosphate-based remediation methods. However, the solubility of uranyl phosphate phases varies over >3 orders of magnitude, with the most soluble phases typically observed in lab experiments. To understand the role of common soil/sediment mineral surfaces in the nucleation and transformation of uranyl phosphate minerals under environmentally relevant conditions, batch experiments were carried out with goethite and mica at pH 6 in mixed electrolyte solutions ranging from 1–800 μM U and 1–800 μM P. All experiments ended with uranium concentrations below the USEPA MCL for U, but with 2–3 orders of magnitude difference in uranium concentrations. Despite the presence of many cations that are well known to incorporate into less soluble autunite-group minerals, chernikovite rapidly precipitated in all experiments containing U and P, except for solutions with 1 μM U and 1 μM P that were calculated to be undersaturated. Textures of uranyl phosphates observed by AFM and TEM indicate that nucleation was homogenous and independent of the initial mineral content. Comparison of time-course U and P concentrations from the experiments with thermodynamic modeling of solution equilibria demonstrated that aqueous uranium concentrations in the experimental systems evolved as increasingly sparingly soluble uranyl phosphate phases nucleated over time, with sorption accelerating the transition between phases by influencing solution chemistry. Aqueous uranium concentrations consistent with partially dehydrated (meta-) autunite were achieved only in experiments containing goethite and/or mica. These dynamic nucleation-growth-sorption-nucleation-growth-sorption cycles occur over the time scales of weeks, not hours or days at room temperature. Lab experiments and field-based investigations of uranium phosphate should consider these or longer time scales for the greatest long-term relevance.

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1. Introduction

Uranium enters groundwater through interaction with natural mineral deposits and as a consequence of human activities. Due to its chemical and radiological toxicity, the concentration of uranium in ground- and surface-water used for human consumption is regulated in many countries. Solubilities of many uranium-rich minerals are low enough to suggest that precipitation could be a successful mechanism for remediation (Newsome et al., 2014). However, mineral solubilities and long-term stability in response to changing biogeochemical and hydrologic conditions are complex functions of site-specific details. Research in the fundamental chemistry of uranium mineral precipitation provides insights into which precipitation reactions might be successful under specific conditions (Newsome et al., 2014).

Uranyl (U(VI)) phosphate minerals and U(IV) oxides are the two main potential phases for uranium sequestration in the solid phase. Each has the potential to be stable, however under different geochemical conditions (Fig. 1a). U(IV) oxides such as uraninite (UO_2) are stable over a wide range of pH values (Fig. 1a), but only in reducing conditions where exposure to oxygen is limited (Langmuir, 1978). Uranyl phosphates, such as the autunite group (predominantly $A(UO_2)_2(PO_4)_2 \cdot 10–12H_2O$, where A = a number of possible large monovalent or divalent cations), are most stable at moderately acidic to neutral pH (Fig. 1b). Once formed, they are relatively insensitive to the system redox potential, and are also more resistant to dissolution that other uranium minerals under oxic conditions outside of their stability fields (e.g., Campbell et al., 2011; Sowder et al., 2001; Wellman, 2006; Wellman et al., 2009).
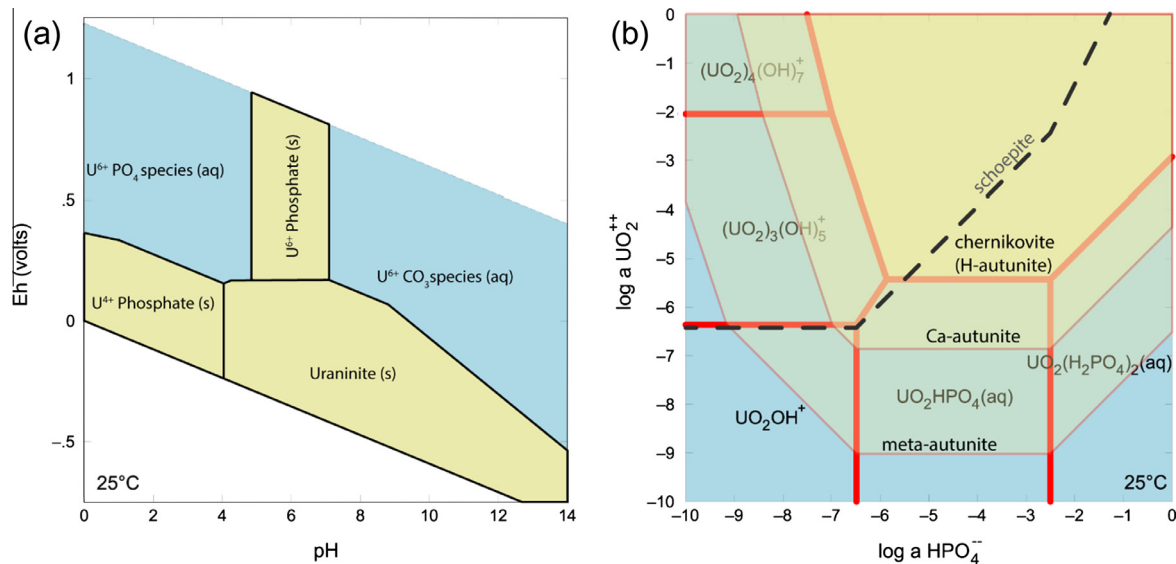
Fig. 1. (A) Generalized Eh–pH diagram illustrating general conditions where various uranium mineral types (solid outlines) versus aqueous species dominate. (B) Stability fields of three autunite-group phases and the oxyhydroxide schoepite on a uranium–phosphorous log–log activity diagram. Additional details about activity diagram calculations in Supplemental Information.

Phosphate-based precipitation of oxidized uranium is a potentially effective groundwater remediation strategy (Shi et al., 2009; Wellman et al., 2011). Many U-contaminated sites are at acidic to neutral pH, including locations at the Oak Ridge Reservation and the Savannah River Site. At acidic pH, uranyl-phosphate complexes will dominate even at low total phosphate concentrations (Langmuir, 1978, 1997; Sandino and Bruno, 1992). Under these favorable pH conditions, the solubility of uranyl phosphate complexes is considerably lower than that of uranyl oxyhydroxides (Felmy et al., 2005; Grenthe and Konings, 1992; Langmuir, 1978; Rai et al., 2005), and depending on the ratio of carbonate to phosphate in the system, uranyl phosphate minerals are expected to precipitate. At low pH conditions, uranyl phosphate complexes exhibit high sorption affinities for mineral surfaces, while uranyl carbonate complexes dominate at neutral or higher pH (Bostick et al., 2002).

Perhaps the greatest challenge limiting the effectiveness of uranyl phosphate precipitation is a mechanism to deliver reactive phosphorous. Experiments with a hydroxyapatite ($Ca_5(PO_4)_3(OH)$) barrier conducted at the Savannah River Site demonstrated that precipitation of uranyl phosphate phases can lower U concentrations from ∼2000 mg/kg to near drinking water standards (Arey et al., 1999). Other experiments focused on methods to disseminate reactive phosphorous through contaminated sediments and soils. For example, previous work demonstrated that microbes native to the Oak Ridge site could metabolize glycerol-3-phosphate, leading to uranyl phosphate precipitation (Beazley et al., 2009, 2011). Wellman et al. pioneered the use of polyphosphate injection (Wellman et al., 2006, 2008, 2011) based on the ability of polyphosphate to remain soluble and gradually hydrolyze into reactive orthophosphate monomers.

Even without active phosphate-based remediation, uranyl phosphate minerals have been observed in a wide range of natural and contaminated environments and appear to play a critical role in limiting uranium mobility within these systems. Autunite, schoepite ($(UO_2)_8O_2(OH)_{12}·12H_2O$), and uranium metaphosphate ($U(PO_3)_4$) have been observed in contaminated sediments at DOE's Fernald, OH former uranium processing facility (Buck et al., 1995; Morris et al., 1996). Recent work suggests that uranium release within sediments from the North and South 300

A Process Ponds at Hanford has been limited due to the low solubility of metatorbernite ($Cu(UO_2PO_4)_2·2.8H_2O$) observed in sediments associated with the site (Catalano et al., 2006; Stubbs et al., 2009). Ca–U–P phases have also been observed in uranium contaminated soils at DOE's K-25 processing facility in Oak Ridge, TN (Roh et al., 2000). In addition, uranium phosphate complexes and phases have been observed in bulk sediment samples (Bostick et al., 2002; Phillips et al., 2006) and in close association with Fe and Mn oxide minerals within the contaminant plume at the Oak Ridge Y-12 site (Stubbs et al., 2006).

Several geologically formed uranium deposits have been studied as analogues for the behavior of uranium in the environment, and in many instances, the formation of uranyl phosphates during weathering of the reduced ore effectively prevents uranium mobility and holds uranium concentrations in groundwater to tens of ppb of U or less for many thousands of years (Denecke et al., 2005; Jensen et al., 2002; Jerden et al., 2003a, 2003b; Jerden and Sinha, 2006; Murakami et al., 1997, 2005). However, these naturally low U solubility conditions have proven difficult to replicate experimentally. The relative contributions of sorption and precipitation remain difficult to distinguish in these experiments. In addition, low phosphate concentrations can even lead to elevated uranium in solution due to aqueous complex formation (Singh et al., 2010). While the predominant uranyl phosphate mineral produced in experiments is chernikovite (($(H_3O)_2(UO_2)_2(PO_4)_2·6(H_2O)$)) (Beazley et al., 2011; Fuller et al., 2002; Mehta et al., 2014; Singh et al., 2010, 2012), the autunite-group mineral with the highest solubility and H^+-interlayers, partially dehydrated "meta-" autunite group minerals are dominant in natural systems or long-term field sites. For example, Mehta et al. (2014) found limited formation of Ca-autunite in precipitation experiments despite significant chernikovite formation. In similar experiments, Kanematsu et al. (2014) observed initial K-bearing autunite-group minerals underwent structural change to a more phosphuranylite-like structure after 30 days, based on EXAFS spectra. Both thermodynamic models and experiments (Gorman-Lewis et al., 2008, 2009; Grenthe and Konings, 1992; Langmuir, 1997) suggest that autunite minerals with different interlayer cations and different hydration states lead to strikingly different equilibrium solubilities (e.g., Fig. 1b). Thus, linking lab and field observations of uranyl phosphate precipitates has