Mobility of uranium during weathering

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ABSTRACT

Mineralogical and geochemical mechanisms of U fixation under oxidizing conditions in the vicinity of the secondary U ore deposit at Koongarra, Australia, were examined using transmission and scanning electron microscopy and thermodynamic calculations. The formation of saléite, Mg(UO₂)(PO₄)₂·10H₂O, is the predominant mechanism for U fixation upstream from the deposit, where saléite replaces sklodowskite and granular apatite. Within the deposit and further downstream, U is fixed in microcrystals (10–50 nm) of saléite and (meta)torbernite scattered within veins of fine-grained (2–50 nm) Fe³⁺ minerals (primarily goethite and hematite). Thermodynamic calculations indicate the groundwater is undersaturated with respect to saléite and metatorbernite and that these minerals should precipitate at higher U or P concentrations than observed. This suggests that the upstream saléite precipitated at the reaction interfaces of dissolving sklodowskite and apatite under local saturation conditions. Observed textural relationships of saléite and (meta)torbernite microcrystals with the Fe minerals, combined with thermodynamic calculations, suggest surface precipitation as the formation mechanism for saléite and (meta)torbernite microcrystals within, and downstream from, the secondary ore deposit. Phosphorous released during the aging of ferrihydrite and U adsorbed onto Fe minerals are probably the sources of the major components of the microcrystals. Downstream, the microcrystals exist where groundwater U concentrations are as low as 10–30 μg/L. Once released from the ore deposit, U is fixed in uranyl phosphates even where measured groundwater is undersaturated with respect to uranyl phosphates. The surface precipitation is an important example of long-term post-adsorption U fixation in a natural system. The fully crystalline and radiation-damaged microstructures of saléite indicate uranyl phosphates have formed continuously (or intermittently) for the last few million years.

INTRODUCTION

The two important oxidation states for U in natural waters are 4⁺ and 6⁺. The U⁴⁺ ion is essentially insoluble in mildly acidic to alkaline groundwaters, whereas U⁶⁺ solubility is commonly controlled by uraninite (see Table 1 for U mineral formulas and information) or coffinite. On the other hand, the U⁶⁺ ion is potentially much more mobile, due in part to the greater solubilities of most U⁶⁺ minerals (e.g., Osmond and Ivanovich 1992). Uranium dissolved in groundwater commonly forms complex ions, depending on geochemical conditions such as pH, Eh, and the presence of other dissolved ions (Langmuir 1978). The mobility of dissolved U in natural waters is affected by processes such as adsorption or desorption of U ions and precipitation or dissolution of U-bearing minerals. More complete information about the mechanisms of fixation and transport of U in groundwaters would enhance our understanding of the surficial U cycle (Gascouyne 1992).

Uranium sorption has been studied extensively, particularly U⁶⁺ sorption by Fe minerals at the Earth’s surface (e.g., Tripathi 1983; Hsi and Langmuir 1985). Despite these studies, the chemical forms of U on solid substrates in natural systems are poorly understood, particularly at low U concentrations. Identifying the chemical forms of U is necessary for understanding the change in relationship between U and solid substrates after adsorption over a geologic time-scale, that is, long-term post-adsorption phenomena directly related to U mobility in natural systems. Waite et al. (1994) examined the chemical forms of U sorbed on ferrihydrite at pH 5 and 5.5 under atmospheric conditions using extended X-ray absorption fine structure (EXAFS) spectroscopy. They showed that mononuclear uranyl complexes on ferrihydrite surfaces share edges with Fe octahedra in ferrihydrite and no polynuclear uranyl complexes are evident as sorbed species, even at relatively high U concentration (approximately 20 mg/L). EXAFS studies of U⁶⁺ sorbed onto smectites led to different conclusions for local structures of UO₂⁻ complexes, similar to those in solution (Dent et al. 1992) and distorted and distinct (Chisholm-Brause et al. 1994). In contrast, a laboratory experiment by Bruno et al. (1995) demonstrated schoepite can precipitate on the surfaces of Fe⁶⁺ oxyhydroxides following U sorption in 0.2–200 mg/L U solu-