Effects of pH, temperature, and aqueous organic material on the dissolution kinetics of meta-autunite minerals, (Na, Ca)$_2_3$[(UO$_2$)(PO$_4$)$_2$]$_2$·3H$_2$O

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ABSTRACT

Autunite-group minerals have been frequently identified in contaminated sediments as the long-term controlling phase of U. Under these conditions, the mobility of U in subsurface pore waters is limited by the rate of dissolution of autunite and meta-autunite group minerals, $X_n^m[\text{UO}_2(\text{PO}_4)_2]_m \cdot x\text{H}_2\text{O}$, where $X = \text{Ca}$ or $\text{Na}$. Single-pass flow-through (SPFT) tests were conducted to quantify the dissolution kinetics of natural Ca meta-autunite, Ca[\text{UO}_2(\text{PO}_4)_2]_2·3\text{H}_2\text{O}, and synthetic Na meta-autunite, Na$_2$[(\text{UO}_2)(\text{PO}_4)]$_2$·3\text{H}_2\text{O}, as a function of pH (7–10) and temperature (5–70 °C) in the presence and absence of aqueous organic material. The data indicate that release of U and P are non-stoichiometric over the range of experimental conditions investigated. In a 0.1 M NH$_4$OH buffer solution, acquisition of valid dissolution rate data was limited by uramphite solubility, NH$_4$[(UO$_2$)(PO$_4$)$_2$]·xH$_2$O. Dissolution rates obtained in a 0.01 M TRIS [tris (hydroxymethyl) aminomethane] buffered solution increased by a factor of ~100× over the pH interval of 7 to 10 ($\eta = 0.90 \pm 0.08$), irrespective of temperature. At constant pH the rate data showed a minor increase with temperature. Data from experiments using a more concentrated 0.05 M TRIS buffer exhibited a ~35-fold increase in rates compared to those in a 0.01 M TRIS buffer at constant temperature and pH. The difference in release rate between interlayer cation (Na$^+$ or Ca$^{2+}$) and U is ~10000 in neutral solutions; however, the difference diminishes to ~10 at higher pH values. The combination of structural dissolution and ion exchange explain these trends in interlayer cation behavior. Data presented here illustrate the significance of pH and dissolved organic material on the dissolution of autunite minerals.

Keywords: Autunite, dissolution, kinetics, uranium, organic material

INTRODUCTION

Uranyl-phosphate phases are advanced secondary U minerals formed during the oxidized weathering of primary UO$_2$ deposits (Garrels and Christ 1965). The general paragenetic sequence of secondary mineral formation has been well-documented (Finch and Murakami 1999); however, uranyl silicates and phosphates are typically the solubility limiting minerals that persist in locales geographically removed from the primary deposit (Murakami et al. 1997). The presence of phosphate in groundwater, even in minor concentrations (10$^{-8}$ M), promotes the formation of autunite-group minerals, $X_n^m[\text{UO}_2(\text{PO}_4)_2]_m \cdot x\text{H}_2\text{O}$, thereby limiting the mobility of the uranyl cation (UO$_2^+$) in subsurface environments.

In addition to natural settings, operations related to nuclear energy and weapons production have resulted in widespread U contamination of geologic media in surface and subsurface environments (Abdelouas et al. 1999). Within the United States, U has been recognized as one of the two most common radionuclides occurring in groundwater, and is the most common one occurring in soils/sediments at Department of Energy (DOE) facilities (Riley et al. 1992). Characterization of sediments from contaminated sites has identified discrete uranyl-phosphate, autunite-group minerals (Bertsch et al. 1994; Buck et al. 1994, 1995, 1996; Morris et al. 1996; Tidwell et al. 1996) for which autunite solubility has been suggested to be the dominant control on U concentration in the underlying aquifer (Elless and Lee 1998).

Previous experimental results have established the low solubility and high stability of many uranyl-phosphate minerals (Chukhlantsev and Stepanov 1956; Karpov 1961; Moskvin et al. 1967; Scheyer and Baes 1954; Vesely et al. 1965). However, knowledge of the stability of the uranyl-phosphate phases is restricted to a narrow range of experimental conditions involving low-pH media with high concentrations of phosphoric acid (Karpov 1961; Scheyer and Baes 1954; Vesely et al. 1965). Furthermore, all known studies related to autunite stability and solubility are based on synthetic, rather than natural, phases (Giammar 2001; Karpov 1961; Pekarek and Vesel 1965; Scheyer and Baes 1954; Sowder et al. 2000; Vesely et al. 1965), and interpretations of dissolution studies have been confounded by impurities present within the starting material (Giammar 2001).

An additional void in the fundamental understanding of meta-