Thermodynamic investigation of uranyl vanadate minerals: Implications for structural stability

TYLER L. SPANO1, EWA A. DZIK1, MELIKA SHARIFIRONIZI1, MEGAN K. DUSTIN1, MADISON TURNER1, AND PETER C. BURNS1,2,*

1Department of Civil and Environmental Engineering and Earth Sciences, University of Notre Dame, Notre Dame, Indiana 46556, U.S.A.
2Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556, U.S.A.

ABSTRACT

Understanding the crystal chemistry, materials properties, and thermodynamics of uranyl minerals and their synthetic analogs is an essential step for predicting and controlling the long-term environmental behavior of uranium. Uranyl vanadate minerals are relatively insoluble and widely disseminated within U ore deposits and mine and mill tailings. Pure uranyl vanadate mineral analogs were synthesized for investigation using high-temperature drop solution calorimetry. Calculated standard-state enthalpies of formation were found to be –4928.52 ± 13.90, –5748.81 ± 13.59, and –6402.88 ± 21.01, kJ/mol for carnotite, curienite, and francévilleite, respectively. Enthalpies of formation from binary oxides for uranyl vanadate minerals exhibit a positive linear correlation as a function of the acidity of oxides. Normalized charge deficiency per anion (NCDA) is presented to relate bonding requirements of the structural units and interstitial complexes. An exponential correlation was observed between NCDA and energetic stability (enthalpy of formation from binary oxides) for the studied minerals. Additionally, NCDA and oxide acidity exhibit an exponential correlation where decreasing oxide acidity results in an exponential decrease in NCDA. The number of occurrences of uranyl vanadate mineral species are found to correlate with both enthalpy of formation from oxides and NCDA.

Keywords: Uranyl vanadate, carnotite, thermodynamics, structure stability

INTRODUCTION

In 1948, the U.S. Atomic Energy Commission guaranteed a minimum price for uranium ore mined in the United States to decrease dependence on foreign sources (Brugge and Goble 2002). The resulting expansion of exploration and mining in the southwestern United States led to identification of over 7000,000 tons of U ore (Brugge and Goble 2002). Carnotite, ideally $K_2(UO_2)_3V_2O_7·3H_2O$, and other uranyl vanadate minerals, is widespread in U deposits of the American Southwest and was thus especially important during this mining “boom.” Uranium and vanadium ore deposits located within the Urraval mineral belt in western Colorado and eastern Utah accounted for nearly 13% of the total U produced by the United States (Chenoweth 1981). In addition to the American Southwest, uranyl vanadate minerals originating from Africa were an important source of U for the development of both nuclear weapons and nuclear energy during and after World War II (Dumett 1985). The solid-solution series between curienite [Pb(UO$_2$)$_3$V$_2$O$_7·5H_2O$] and francévilleite [Ba(UO$_2$)$_3$V$_2$O$_7·5H_2O$] was first observed in samples from the mines of the Belgian Congo (now the Democratic Republic of the Congo), but has since been observed in other localities (Janecek 1999; Mereiter 1986).

In the American Southwest and Africa, uranyl vanadate minerals are most common in areas where reduced uranium and reduced vanadium species are undergoing oxidation (Finch and Murakami 1999). Primary U and V minerals that may alter to form uranyl vanadates include uraninite (UO$_2$·s), montroseite (V$^{3+}$,Fe$^{3+}$,V$^{5+}$)O(OH), and davidite [La(Y,U)Fe$_6$(Ti,Fe,Cr,V)$_8$(O,OH,F)$_3$] (Krivovichev and Plášil 2013; Weeks 1961). Carnotite and other uranyl vanadates occur in Colorado Plateau-type U-V deposits, located on or near fossil carbonaceous matter, and as alteration products in close proximity to uraninite (Dahlkamp 1993; Evans and Garrels 1958).

Over a range of conditions, uranyl vanadate minerals are among the most insoluble alteration products of supergene U oxides, which are also significant ore sources (Barton 1957; Krivovichev and Plášil 2013; Plasil 2014; Weeks 1961). Owing to their insolubility, they retain uranium in natural systems. Between pH-Eh ranges of 4.5–8, and 1.0–0.0 V, respectively, carnotite is stable, and uranyl vanadate minerals precipitate when dilute UO$_2^{2-}$ and VO$_4^{3-}$ are present in aqueous systems (Langmuir 1978; Schindler et al. 2000). The solubility of carnotite in groundwater is very low, having been noted as being approximately 1 ppb U in the pH range of 5.5–7.5 (Barton 1957). Carnotite precipitation from U-contaminated groundwater has been proposed as a potential method for treatment and remediation of groundwater and legacy wastes from mining operations (Tokunaga et al. 2009). A decrease in U concentrations in water below the drinking water standard of 30 ppb U, as outlined by the U.S. Environmental Protection Agency, was observed in batch experiments and calculations in which carnotite was precipitated (Tokunaga et al. 2009).

Over one century of research concerning uranyl vanadate minerals has yielded limited insight into the thermodynamic properties of these materials (Karyakin et al. 2003). Quantitative thermodynamic data are needed to define the relations between

* E-mail: pburns@nd.edu
Special collection papers can be found online at http://www.minsocam.org/MSA/AmMin/special-collections.html.