American Mineralogist, Volume 102, pages 1149–1153, 2017

ACTINIDES IN GEOLOGY, ENERGY, AND THE ENVIRONMENT

Thermodynamic investigation of uranyl vanadate minerals: Implications for structural stability

Tyler L. Spano[1], Ewa A. Dzik[1], Melika Sharifironizi[1], Megan K. Dustin[1], Madison Turner[1], and Peter C. Burns[1,2,*]

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