Thermodynamic characterization of synthetic autunite

EWA A. DZIK1, HAYLIE L. LOBECK1, LEI ZHANG1, 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

Autunite, Ca[(UO3)(PO4)4](H2O)11, is a common uranyl mineral found in oxidized portions of uranium deposits, as well as subsurface environments contaminated by uranium. Enthalpies of formation of autunite were obtained via high-temperature oxide melt calorimetry using a 3Na2O-4MoO3 solvent at 976 K. The synthetic analog of autunite was prepared using slow mixing by diffusion into an aqueous barrier solution at room temperature. Prior to calorimetric measurements, the material was characterized using powder X-ray diffraction (PXRD), inductively coupled plasma optical emission spectrometry (ICP-OES), thermogravimetric analysis (TGA), and Raman spectroscopy, to ensure purity. The calculated enthalpy of formation from binary oxides of autunite is –579.92 ± 21.68 kJ/mol; the enthalpy of formation from the elements is –8311.32 ± 21.79 kJ/mol. The measured drop solution enthalpy allowed calculation of the enthalpy of the reaction of dehydration of autunite to meta-autunite. The results demonstrate that autunite is a metastable phase and explain the observed rapid dehydration to meta-autunite, a lower hydrate, as well as the common occurrence of the latter mineral in nature.

Keywords: Autunite, calorimetry, uranium, enthalpy, thermodynamics, metaphase, Actinides in Geology, Energy, and the Environment.

INTRODUCTION

Autunite, Ca[(UO3)(PO4)4](H2O)11, forms spectacular tabular crystals at famous localities including Spokanie Co. (Washington, U.S.A.) (Leo 1960) and the Viseu District, Portugal (Cook 2005). Large autunite crystals are prized by museums and collectors, although their dehydration is spontaneous in air and can reduce the clarity of the crystals. It is a relatively common mineral in the altered portions of uranium deposits where phosphorous and calcium are present in groundwater (Krivovichev and Plášil 2013). Its role in limiting the migration of uranium away from a uranium deposit was documented at Koongara, Australia (Murakami et al. 1997). Autunite is also recognized as an important uranium-bearing phase in the contaminated subsurface of various sites related to the production of nuclear weapons, including Fernald (Ohio, U.S.A.) (Buck et al. 1996) and Oak Ridge (Tennessee, U.S.A.) (Roh et al. 2000).

Locock and Burns determined the crystal structure of autunite using single-crystal X-ray diffraction (Locock and Burns 2003). Owing to its rapid dehydration in air, the crystallographic data was collected for a single crystal contained in its mother solution (Locock and Burns 2003). Autunite is orthorhombic, space group Pnma, although the crystals are pseudo-tetragonal. The structure of autunite consists of anionic sheets of uranyl square bipyramids and phosphate tetrahedra that are linked to each other by sharing vertices, giving a structural unit with composition [(UO3)8(P04)4]2+ (Burns 2005; Burns et al. 1997); Ca and H2O are located in the interlayer region. About 40 phosphate and arsenate minerals and inorganic compounds contain sheets with the autunite-type typology (Krivovichev and Plášil 2013; Locock 2007).

Most, or perhaps all, natural specimens available are dehydrated forms of autunite, known as meta-autunite. Autunite is unstable in air (Locock and Burns 2003; Sadow et al. 1996; Takano 1961) and will eventually dehydrate to form its lower hydrate. Here we specifically focus on the synthetic analog of autunite, and determination of its thermochemical properties for the first time. Gorman-Lewis performed batch solubility experiments of autunite from under- and supersaturation, and determined its solubility product and the standard Gibbs energy (Gorman-Lewis et al. 2009). Karyakin (Karyakin et al. 1998) reported thermodynamic properties of anhydrous and intermediate hydrates of (meta)autunite obtained using an adiabatic calorimeter in HCl solvent. However, no enthalpy or entropy data have been published for autunite. We have measured drop solution enthalpies using high-temperature oxide melt calorimetry for autunite and calculated its enthalpies of formation from oxides and elements. These values can be used to evaluate the long-term stability of autunite in geochemical models related to uranium ore deposit genesis, the mobility of uranium in a contaminated subsurface, and a geologic repository for nuclear waste.

MATERIALS and METHODS

Synthesis

Natural specimens of autunite typically lack the purity required for thorough determination of their thermodynamic data, as well as the specific hydration state because autunite is susceptible to partial dehydration. The simple apparatus used previously for synthesis of other uranyl mineral analogs (Dzik et al. 2017) and employed in this study provides high-quality and -purity material that is easy to recover, as well as the substantial quantity of sample needed to perform full thermodynamic evaluation, preceded by thorough chemical characterization. Crystals of the synthetic analog of autunite were obtained by the slow mixing of reactants by diffusion into an aqueous barrier solution at room temperature, as described in