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Thermodynamic characterization of synthetic autunite

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Abstract

Autunite, $Ca[(UO_2)(PO_4)]_2(H_2O)_{11}$, 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 $3Na_2O{\cdot}4MoO_3$ 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