



ELSEVIER

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

High-temperature calorimetric measurements of thermodynamic properties of uranyl arsenates of the meta-autunite group

Ewa A. Dzik^a, Haylie L. Lobeck^a, Lei Zhang^a, Peter C. Burns^{a,b,*}^a Department of Civil and Environmental Engineering and Earth Sciences, University of Notre Dame, Notre Dame, IN 46556, United States^b Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556, United States

ARTICLE INFO

Editor: Karen J.

Keywords:

Uranium

Calorimetry

Uranyl arsenates

Autunite

Enthalpy

ABSTRACT

Five uranyl arsenates of the meta-autunite group with mono (Li, K, Cs) and divalent (Sr and Cu) cations were synthesized at room temperature and characterized. Their thermodynamic properties were measured using high-temperature oxide melt calorimetry in a molten $3\text{Na}_2\text{O}\cdot 4\text{MoO}_3$ solvent at 976 K. Measured enthalpies of drop solution of each compound were used to calculate their respective enthalpies of formation from oxides and elements. Calculated standard state enthalpies of formation from the elements are -3301 ± 14 kJ/mol for LiUAs , -3089 ± 14 kJ/mol for KUAs , -5607 ± 15 kJ/mol for CsUAs , -6638 ± 21 kJ/mol for SrUAs , and -6161 ± 24 kJ/mol for CuUAs . These values are evaluated relative to acid-base interactions using oxide acidity expressed on Smith's scale, as well as the normalized charge deficiency per anion (NCDA), which probes relationships between structural units and interstitial complexes. Linear relationships exist between the heats of formation, acidity of binary oxides, and bond requirements within these meta-autunite type structures. The new thermodynamic data combined with published results yield insights into the thermodynamic behavior of uranyl arsenates. Thermodynamic properties presented here are important for understanding the genesis of uranium deposits and uranium mobility in the subsurface.

1. Introduction

Activities related to the nuclear fuel cycle, including mining and milling of uranium, fuel fabrication, electricity generation and waste storage, as well as production of nuclear weapons, have resulted in large quantities of radioactive waste. Arsenic and uranium are commonly associated in uranium deposits, such as in the world's largest uranium mine in Key Lake, Saskatchewan, Canada (Schindler et al., 2013). Both elements are toxic and carcinogenic, and uranium is radioactive. This is reflected by environmental regulations, with the maximum concentration of arsenic and uranium in ground water permitted by the United States Environmental Protection Agency (US EPA) being 10 ppb and 30 ppb (US EPA, 2017), respectively. Uranyl arsenates have low aqueous solubility under environmental conditions, and can immobilize uranium, arsenic and other cations contained in their structures (Finch and Murakami, 1999; Murakami et al., 1997) in groundwater and some contaminated sites. For example, ^{90}Sr and ^{137}Cs are major fission products of uranium, and nuclear waste in Sweden is stored in Cu canisters (Hedman et al., 2002; Rosborg and Werme, 2008). Both elements can be incorporated into U-bearing phases.

The concentration of arsenic in uranium ores can be as high as

2–3 wt% (Cullen and Reimer, 1989), with arsenic released during oxidation of As-bearing sulfide minerals (Finch and Murakami, 1999; Krivovichev and Plášil, 2013). Arsenates are often considered as a subclass of phosphate minerals due to the similarity in size and charge of the arsenate and phosphate anionic units. Uranyl arsenates and their corresponding phosphates are generally isostructural (Locock, 2007; Locock and Burns, 2003b; Locock et al., 2004a). Uranyl arsenates usually adopt the meta-autunite type structure that combines anionic sheets of uranyl square bipyramids and arsenate tetrahedra with interlayer cations and H_2O (Fig. 1, the interstitial complex).

Thermodynamic data for several synthetic analogues of uranyl arsenate minerals have been reported. An adiabatic calorimeter was used to measure heat capacities of Li, Na, K, Rb, Cs, Mg, Ca, Ba and Cu uranyl arsenates (Karyakin et al., 2003; Suleimanov et al., 2002; Suleimanov et al., 2006a; Suleimanov et al., 2006b), and the resulting values were used to calculate their standard enthalpies of formation. Here, we present rapid measurements of the heats of formation of several uranyl arsenates using high-temperature calorimetry. This method is advantageous because the high sensitivity of the instrument allows measurements for small amounts of sample (~5 mg per drop), and most compounds readily dissolve in the high-temperature solvent

* Corresponding author at: 301 Stinson-Remick Hall, Notre Dame, IN 46556, United States.
E-mail address: pburns@nd.edu (P.C. Burns).

<https://doi.org/10.1016/j.chemgeo.2018.06.009>

Received 2 February 2018; Received in revised form 7 June 2018; Accepted 13 June 2018
0009-2541/ © 2018 Published by Elsevier B.V.

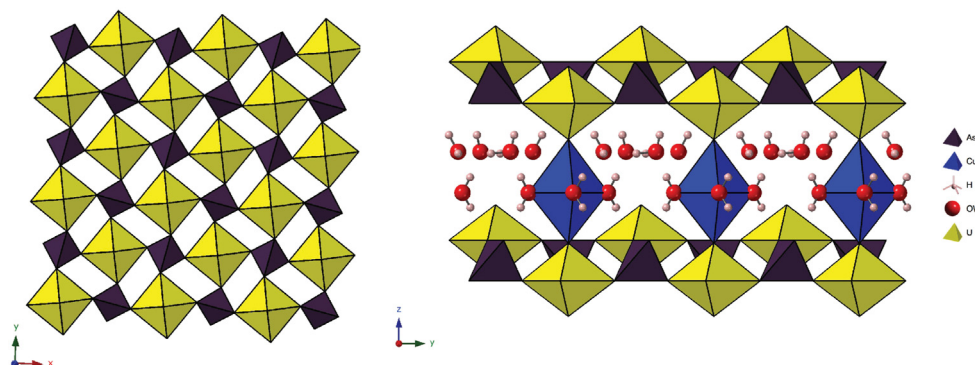


Fig. 1. Illustration of the structure of metazeunerite, showing the uranyl arsenate sheet (left) and interstitial complex (right).

Table 1

Experimental details for the synthesis of uranyl arsenates.

Sample name	Left vial	Right vial	Barrier solution	pH of barrier solution
<i>LiUAs</i>	$\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_{6(\text{aq})}$	As_2O_5	LiNO_3	4.56
<i>KUAs</i>	$\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_{6(\text{aq})}$	As_2O_5	KNO_3	5.66
<i>CsUAs</i>	$\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_{6(\text{aq})}$	As_2O_5	CsNO_3	3.05
<i>SrUAs</i>	$\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_{6(\text{aq})}$	As_2O_5	$\text{Sr}(\text{NO}_3)_2$	2.25
<i>CuUAs</i>	$\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_{6(\text{aq})}$	As_2O_5	$\text{Cu}(\text{NO}_3)_2$	2.55

(Navrotsky, 1977; Navrotsky, 1997; Navrotsky, 2014; Shvareva et al., 2012).

We report heats of formation of five uranyl arsenates of the meta-autunite structure type, and examine the role of the interlayer cation in determining their thermochemical and structural stability. As the structural units, consisting of uranyl arsenate sheets, are identical across this series of compounds, it is possible to ascribe differences in thermodynamic data to interactions between the structural units and interstitial complexes. We study synthetic analogues of two minerals and three phases that have the same structural sheets, but have not yet been reported as minerals. These compounds studied, and their abbreviated designations, are *LiUAs* $\text{Li}[(\text{UO}_2)(\text{AsO}_4)](\text{H}_2\text{O})_4$ (*LiUAs*), *K* $[(\text{UO}_2)(\text{AsO}_4)](\text{H}_2\text{O})_3$ (*KUAs*, abernathyite), *Cs* $(\text{H}_3\text{O})[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_5$ (*CsUAs*), *Sr* $[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_8$ (*SrUAs*), and *Cu* $[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_8$ (*CuUAs*, metazeunerite).

2. Materials and methods

2.1. Synthesis

Natural specimens of uranyl arsenates generally lack the purity needed for rigorous thermodynamic measurements. Synthetic compounds were obtained using a room temperature method involving slow mixing of reactants in a barrier solution. This method previously provided synthetic phosphate members of the autunite family, and is described in detail by Dzik et al. (2017). Saturated aqueous solutions of $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_6$ and As_2O_5 are allowed to slowly diffuse into a cation-containing barrier solution. The pH of the barrier solution was initially adjusted in some of the experiments as described in Table 1. This simple apparatus provides the high quality, high purity, and high yield of material required for calorimetric studies. Once a sufficiently large yield of crystals (usually after about two weeks) had formed, the experiment was terminated, the mother solution was decanted and the crystals were collected by vacuum filtration. All reagents, unless stated otherwise, were analytical grade. LiNO_3 (99.9%, Sigma-Aldrich), KNO_3 (99.9%, Sigma-Aldrich), CsNO_3 (99.9%, Sigma-Aldrich), $\text{Sr}(\text{NO}_3)_2$ (99.9%, Alfa-Aesar), and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (99.9%, Acros Organics) were used to prepare barrier solutions. $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (IBI Labs) and aqueous 0.5 M As_2O_5 (99.9%, Acros Organics) were used to create

saturated solutions that were then placed in small cups (later contained in the barrier solution) in the synthesis apparatus. 15.8 M nitric acid was used to adjust the pH of the barrier solutions.

2.2. Characterization

2.2.1. Powder X-ray diffraction

Powder X-ray diffraction data were collected for samples during the stages of synthesis optimization and to confirm phase purity. A Bruker D8 Advance DaVinci diffractometer with Bragg – Brentano geometry and $\text{CuK}\alpha$ radiation was used. Each sample was gently dry ground in a mortar and pestle, and then was placed onto a zero-background quartz slide. Data were collected over the 2θ range of $5\text{--}55^\circ$ with a step size of 0.01° , and a counting time of 1 s/step. The sample was rotated during data collection to reduce the effect of preferred orientation that results from the platy morphology of the compounds. Diffractograms for each sample were analyzed using the ICCD PDF-4+ software.

2.2.2. Chemical analysis

Chemical analyses for molar concentrations of uranium, arsenic, and the appropriate cation were done using inductively coupled plasma optical emission spectrophotometry (ICP-OES). About 25 mg of each sample was dissolved in 6 M HCl, with subsequent dilutions in 5% HNO_3 . A Perkin Elmer Optima 8000 ICP-OES instrument was used with 1400 W torch power, nebulizer flow rate of 0.6 L/min, sample flow rate of 1.8 mL/min, and a 45 s read delay. Eight standards ranging from 0.5–15 ppm for each element were used to provide external calibration curves for evaluation of measured concentrations. Yttrium was added as an internal standard in samples and blanks at 0.5 ppm. The resulting concentrations of elements of interest were then calculated based on calibration coefficients of 0.99 or higher.

Molar concentrations of Cs in *CsUAs* were obtained using a Nu Instruments Attom inductively coupled plasma mass spectrometer (ICP-MS). Crystals of *CsUAs* were dissolved in concentrated HNO_3 and further diluted to obtain metals in the ppb range in double distilled 5% HNO_3 . The sample was prepared in triplicate and the concentration of ^{133}Cs was analyzed in solution mode in medium resolution by the external calibration method. An internal standard, ^{185}Re , was added to the samples, standards and blank to monitor for matrix effects and instrumental drift.

2.2.3. Thermogravimetric analysis

Compounds of the meta-autunite group, including the uranyl arsenates under study here, can have multiple hydration states. To quantify the quantity of water in each sample, thermogravimetric analyses were performed using a Mettler Toledo TGA/DSC-1 instrument. About 10 mg of each sample was placed in an alumina crucible and was heated from ambient to 800°C , at a rate of $5^\circ\text{C}/\text{min}$, under a constant N_2 flow. The measured weight loss resulting from heating the sample was used to calculate the water content in each sample.

Download English Version:

<https://daneshyari.com/en/article/8910154>

Download Persian Version:

<https://daneshyari.com/article/8910154>

[Daneshyari.com](https://daneshyari.com)