DT # 44635

QA:NA

5/11/05

Revision 1

MOL.20050705.0239

**Thermodynamics of uranyl minerals:
Enthalpies of formation of uranyl oxide hydrates**

**KARRIE-ANN KUBATKO¹, KATHERYN HELEAN², ALEXANDRA NAVROTSKY², PETER C.
BURNS*¹**

¹Department of Civil Engineering and Geological Sciences, University of Notre Dame, 156
Fitzpatrick Hall, Notre Dame, Indiana 46556, U.S.A.

²Thermochemistry Facility and NEAT ORU, University of California at Davis, One Shields
Avenue, Davis, CA 95616, U.S.A.

*E-mail: pburns@nd.edu

ABSTRACT

The enthalpies of formation of seven uranyl oxide hydrate phases and one uranate have been determined using high-temperature oxide melt solution calorimetry: $[(\text{UO}_2)_4\text{O}(\text{OH})_6](\text{H}_2\text{O})_5$, metaschoepite; $\beta\text{-UO}_2(\text{OH})_2$; CaUO_4 ; $\text{Ca}(\text{UO}_2)_6\text{O}_4(\text{OH})_6(\text{H}_2\text{O})_8$, becquerelite; $\text{Ca}(\text{UO}_2)_4\text{O}_3(\text{OH})_4(\text{H}_2\text{O})_2$; $\text{Na}(\text{UO}_2)\text{O}(\text{OH})$, clarkeite; $\text{Na}_2(\text{UO}_2)_6\text{O}_4(\text{OH})_6(\text{H}_2\text{O})_7$, the sodium analogue of compregnacite and $\text{Pb}_3(\text{UO}_2)_8\text{O}_8(\text{OH})_6(\text{H}_2\text{O})_2$, curite. The enthalpy of formation from the binary oxides, $\Delta H_{f\text{-ox}}$, at 298 K was calculated for each compound from the respective drop solution enthalpy, ΔH_{ds} . The standard enthalpies of formation from the elements, ΔH_f° , at 298 K are -1791.0 ± 3.2 , -1536.2 ± 2.8 , -2002.0 ± 3.2 , -11389.2 ± 13.5 , -6653.1 ± 13.8 , -1724.7 ± 5.1 , -10936.4 ± 14.5 and $-13163.2 \pm 34.4 \text{ kJ mol}^{-1}$, respectively. These values are useful in exploring the stability of uranyl oxide hydrates in auxiliary chemical systems, such as those expected in U-contaminated environments.

INTRODUCTION

Uranyl oxide hydrates are an important and structurally diverse group of uranyl minerals. They are common alteration products of uraninite, UO_{2+x} , and are often found in the oxidized portions of U deposits (Fron del 1956, Finch and Ewing 1992). They occur in soils contaminated by actinides (Roh et al. 2000, Yamakawa and Traina 2001), where they impact the mobility of U. In experiments intended to simulate the alteration of spent nuclear fuel under conditions expected in the proposed geological repository at Yucca Mountain, uranyl oxide hydrates were found as early alteration products of unirradiated UO_2 (Wronkiewicz et al. 1992, 1996) and spent nuclear fuel (Finn et al. 1996, Finch et al. 1999). Despite the obvious importance of uranyl oxide hydrates, and uranyl minerals in general, few studies have examined the thermochemistry of these compounds. Knowledge of uranyl minerals lags behind most other major mineral groups, owing to the difficulty of studying these phases that often occur as intimate intergrowths of multiple species. Recently, considerable progress has been made concerning the crystal structures, compositions, and synthesis of uranyl oxide hydrates (Burns 1999, Weller et al. 2000, Li and Burns 2000a, 2001, Burns and Li 2002, Glatz et al. 2002). The structures of most are now known, and it is possible to synthetically prepare substantial quantities of pure material for detailed study. We are conducting a systematic study of the thermochemistry of various uranyl minerals (e.g., Kubatko et al. 2003). Here we report direct calorimetric measurement of the heats of formation of eight uranyl oxide hydrate phases, of which four have been described as minerals.

STRUCTURES OF URANYL OXIDE HYDRATES

The structures of uranyl oxide hydrates are almost invariably dominated by two dimensional sheets of linked uranyl polyhedra, with lower-valence cations and H₂O groups located in interlayer positions (Burns 1999). We have selected a series of uranyl oxide hydrates (and one anhydrous phase) for study that present significant chemical and structural diversity. These are, together with references for their crystal structures, metaschoepite, [(UO₂)₄O(OH)₆](H₂O)₅ {i.e. (UO₃)(H₂O)₂} (Weller et al. 2000); β -UO₂(OH)₂ (Bannister and Taylor 1982); CaUO₄ (Takahashi et al. 1993); becquerelite, Ca[(UO₂)₆O₄(OH)₆](H₂O)₈ (Burns and Li 2002); Ca(UO₂)₄O₃(OH)₄(H₂O)₂ (Glatz et al. 2002); clarkeite, Na(UO₂)O(OH) (Finch and Ewing 1997); Na₂(UO₂)₆O₄(OH)₆(H₂O)₇, the Na analogue of compreignacite (Burns 1998), and curite, Pb₃(UO₂)₈O₈(OH)₆(H₂O)₂ (Li and Burns 2000a).

The structure of metaschoepite contains sheets of uranyl pentagonal bipyramids that are based upon the fourmarierite anion-topology (Fig. 1a), which also occurs in the structures of schoepite (Finch et al. 1996) and fourmarierite (Li and Burns 2000b). In metaschoepite, the sheets of polyhedra are electroneutral, and the interlayer region contains only H₂O groups that link to the sheets by H bonding. In contrast, β -UO₂(OH)₂ contains electroneutral sheets of uranyl square bipyramids derived from the autunite anion-topology (Fig. 1b). The structure does not contain any interlayer constituents; the sheets are linked directly by H bonds.

The most common structural theme in uranyl oxide hydrates is sheets of uranyl pentagonal bipyramids that are based upon the protasite (α -U₃O₈) anion-topology (Fig. 1c)

(Burns 1999). Several minerals, including becquerelite, and the synthetic compound $\text{Na}_2(\text{UO}_2)_6\text{O}_4(\text{OH})_6(\text{H}_2\text{O})_7$ contain this sheet (the latter by analogy with compreignacite, which X-ray powder diffraction shows to be isostructural). Although the topologies of the sheets are constant within this group, there are at least four distinct distributions of OH groups within the sheets that are achieved by substitution of OH at different equatorial positions of the uranyl polyhedra (Burns 1999).

Despite its chemical similarity to becquerelite, the structure of $\text{Ca}(\text{UO}_2)_4\text{O}_3(\text{OH})_4(\text{H}_2\text{O})_2$ contains unusual sheets of distorted uranyl square bipyramids and uranyl pentagonal bipyramids (Fig. 1d). This phase has not been observed in Nature, but is readily synthesized under a variety of hydrothermal conditions (Glatz et al. 2002), and often occurs in the products of these experiments together with becquerelite. The structure of CaUO_4 contains sheets of edge-sharing uranyl hexagonal bipyramids (Fig. 1e), with interlayer Ca providing the linkages between sheets.

Curite is a relatively common mineral in the oxidized portions of geologically old U deposits, due to the buildup of radiogenic Pb. Its structure contains an unusual sheet of highly distorted uranyl square bipyramids and uranyl pentagonal bipyramids (Fig. 1f). Pb^{2+} cations containing stereoactive lone-pairs of electrons occur in the interlayer region. The Sr analogue of curite is isostructural with curite, thus indicating the unusual topology of the sheets is not due to the highly distorted polyhedra about the Pb^{2+} cations (Burns and Hill 2000).

An approximate structure for clarkeite was reported by Finch and Ewing (1997) on the basis of X-ray powder diffractometry. Recently, Catalano and Brown (2004) reported

EXAFS spectra for natural clarkeite inconsistent with the structure proposed earlier, thus it appears additional studies are needed to further elucidate the structure.

URANYL OXIDE HYDRATES AS ALTERATION PHASES OF SPENT NUCLEAR FUEL

Studies of the alteration of spent nuclear fuel (Finch et al. 1999, Finn et al. 1996) and UO_2 (Wronkiewicz et al. 1992, 1996) have been done in the presence of slowly dripping groundwater to simulate conditions in the proposed geological repository at Yucca Mountain, where groundwater could drip onto spent fuel following canister failure. Finch et al. (1999) examined the alteration products that formed after groundwater dripped onto the fuel for six years at 90°C. The experiments used two pressurized-water-reactor fuels, ATM103 and ATM106, with corresponding burn-up histories of ~30 MWd/kg-U and ~45 MWd/kg-U, respectively. The water used was from well J-13 at the Yucca Mountain site that was reacted with crushed Topopah Springs tuff at 90°C for 80 days (designated EJ-13 water). Alteration of the spent fuel in experiments with various drip rates was extensive after six years, and uranyl oxide hydrates were the first phases to form at the onset of alteration. These included metaschoepite, dehydrated schoepite, $\text{UO}_3(\text{H}_2\text{O})_{0.8}$, and tentatively the Na analogue of compregnacite (Finch et al. 1999).

Wronkiewicz et al. (1992, 1996) examined UO_2 that was under dripping EJ-13 water at 90°C for more than 10 years. The extensive accumulation of alteration products present up to 10 years after the onset of the experiment was characterized. Uranyl oxide hydrate phases formed early at the onset of alteration, and persisted throughout the experiments. Uranyl oxide hydrates identified were metaschoepite, dehydrated schoepite,

compreignacite and becquerelite. Wronkiewicz et al. (1996) reported that the paragenetic sequence of uranyl phases that formed throughout the experiments involved initially uranyl oxide hydrates, followed by uranyl silicates. This sequence is similar to those observed in natural analogue studies, such as the Nopal I deposit, Peña Blanca District, Chihuahua, Mexico (Pearcy et al. 1996).

Burns et al. (1997) proposed that incorporation of radionuclides into the uranyl phases that form due to alteration of nuclear waste in a geological repository could retard radionuclide release. Incorporation of fission products such as Sr and Cs can occur in uranyl oxide hydrates (Hill and Burns 1999, Cahill and Burns 2000, Burns and Li 2002). Burns et al. (2004) studied the composition of powders of several uranyl minerals that were synthesized in the presence of small amounts of Np^{5+} , and found up to 400 ppm of Np in the Na analogue of compreignacite, $\text{Na}_2(\text{UO}_2)_6\text{O}_4(\text{OH})_6(\text{H}_2\text{O})_7$. Thus, there is considerable evidence that uranyl oxide hydrate minerals that form due to the alteration of spent nuclear fuel in Yucca Mountain may impact the release rates of a variety of radionuclides, as these phases may persist for millions of years.

PREVIOUS THERMOCHEMICAL STUDIES OF URANYL OXIDE HYDRATES

Enthalpies, entropies and solubility constants are established for the anhydrous uranyl oxide polymorphs α - UO_3 , β - UO_3 , γ - UO_3 , δ - UO_3 , ϵ - UO_3 and amorphous UO_3 (Hemingway 1982, Grenthe et al. 1992). Several uranyl oxide hydrates have been described, ranging in composition from $\text{UO}_3(\text{H}_2\text{O})_{0.4}$ to $\text{UO}_3(\text{H}_2\text{O})_2$, where $\text{UO}_3(\text{H}_2\text{O})_2$ is the composition of metaschoepite (Hoekstra and Siegel 1973, Hemingway 1982, Grenthe et al. 1992), however the

structural and chemical relations amongst many of these phases are unclear. Thermodynamic parameters are available for $\text{UO}_3(\text{H}_2\text{O})_{0.4}$, $\text{UO}_3(\text{H}_2\text{O})_{0.5}$, $\text{UO}_3(\text{H}_2\text{O})_{0.8}$, $\text{UO}_3(\text{H}_2\text{O})_{0.9}$, $\alpha\text{-UO}_2(\text{OH})_2$, $\beta\text{-UO}_2(\text{OH})_2$, $\alpha\text{-UO}_3(\text{H}_2\text{O})_2$, $\beta\text{-UO}_3(\text{H}_2\text{O})_2$ and $\varepsilon\text{-UO}_3(\text{H}_2\text{O})_2$ (Cordfunke 1964, Cordfunke and O'Hare 1978, Hemingway 1982, Hughes Kubatko et al. 2003). The previously reported values of ΔG_f° , ΔH_f° and S° for $\beta\text{-UO}_2(\text{OH})_2$ and $\text{UO}_3(\text{H}_2\text{O})_2$ (metaschoepite) are listed in Table 1. The enthalpy of formation from the elements of $\beta\text{-UO}_2(\text{OH})_2$, $\Delta H_f^\circ = -1533.4 \pm 1.2 \text{ kJ mol}^{-1}$, was calculated by Cordfunke (1964). Hemingway (1982) used this value to obtain ΔG_f° and S° of $\beta\text{-UO}_2(\text{OH})_2$ ($-1397.1 \pm 4.0 \text{ kJ mol}^{-1}$ and $123 \pm 8 \text{ J mol}^{-1}\text{K}^{-1}$, respectively). Grenthe et al. (1992) estimated the ΔH_f° of $\beta\text{-UO}_2(\text{OH})_2$ based on the difference between the enthalpy of solution of $\beta\text{-UO}_2(\text{OH})_2$ and enthalpy of solution of $\gamma\text{-UO}_3$, calculated S° from the phase transition of $\text{UO}_3(\text{H}_2\text{O})_2$ (metaschoepite) to $\beta\text{-UO}_2(\text{OH})_2$, and calculated ΔG_f° from these values.

Thermodynamic parameters exist for several anhydrous uranates, including CaUO_4 (O'Hare et al. 1976, Westrum et al 1980, Hemingway 1982, Grenthe et al. 1992, Guillaumont et al. 2003), see Table 1. Acid solution calorimetry of well-characterized CaUO_4 yielded ΔH_f° values of -2001.7 ± 2.1 (O'Hare et al. 1976) and $-2002.3 \pm 2.3 \text{ kJ mol}^{-1}$ (Grenthe et al. 1992). Measured C_p values (Westrum et al. 1980) of CaUO_4 were used to calculate S° , which enables calculation of ΔG_f° (Hemingway 1982, Grenthe et al. 1992). Thermodynamic parameters for the Ca, Na and Pb uranyl oxide hydrate phases have not been reported; however predicted values are available for Na and Ca-bearing uranyl oxide hydrates based on estimated binary oxide contributions (Chen et al. 1999).

SYNTHESIS OF URANYL OXIDE HYDRATES

Crystals of metaschoepite, β - $\text{UO}_2(\text{OH})_2$, CaUO_4 , becquerelite, $\text{Ca}(\text{UO}_2)_4\text{O}_3(\text{OH})_4(\text{H}_2\text{O})_2$, clarkeite, Na compregnacite and curite were synthesized under mild hydrothermal conditions using Teflon-lined Parr reaction vessels (Table 2). Upon cooling, the products were recovered by filtration and rinsed using H_2O . Synthesis procedures were done multiple times to achieve desired quantities of material.

ANALYTICAL METHODS

X-ray powder diffraction

X-ray powder diffraction patterns were collected for each synthetic uranyl oxide hydrate sample. Aliquots of each sample (~4 mg) were ground to a fine powder and deposited onto the surface of a zero-background oriented silicon wafer. Data were collected using a Rigaku Miniflex diffractometer over the 2θ range 5 to 120° with a step-width of 0.01° and one second spent counting per step. All powder diffraction patterns exhibit sharp profiles and no peaks that are attributable to impurity phases.

Electron microprobe analysis

Syntheses products were examined using a JEOL JXA 8600 Superprobe. An aliquot of each sample (~20 mg) was mounted on a half-inch piece of double-sided carbon-coated tape on a round one-inch glass slide and carbon-coated. Back-scattered electron images were consistent with phase homogeneity of each sample. Energy dispersive spectra were consistent with the expected chemical constituents of each sample.

Thermogravimetric analysis

Thermogravimetric analyses were performed using ~50 mg aliquots of each sample and a Netzsch 449 thermal analysis system. All samples were heated at a rate of 10 K min⁻¹. Metaschoepite and β -UO₂(OH)₂ were heated from 298 K to 823 K, with weight losses of 11.18 (10.85% theoretical) and 6.00% (5.92% theoretical), respectively. CaUO₄, becquerelite, Ca(UO₂)₄O₃(OH)₄(H₂O)₂, clarkeite and curite were heated from 298 K to 873 K, with weight losses of 0.08, 10.01 (10.06% theoretical), 5.58 (5.66% theoretical), 2.78 (2.76% theoretical), and 2.92% (2.96% theoretical), respectively. Sodium compraignacite was heated from 298 K to 1073 K, with a weight loss of 9.18% (9.20% theoretical). The samples do not contain excess water.

CALORIMETRIC MEASUREMENTS

High temperature drop solution calorimetry was done using a custom-built Calvet-type calorimeter, details of which are given elsewhere (Navrotsky 1977, 1997). Drop solution enthalpies were measured by dropping ~5 mg pressed pellets of material from room temperature, 298 K, into the molten sodium molybdate (3Na₂O·4MoO₃) solvent at calorimetric temperature, 976 K. The calorimeter was calibrated using the heat content of ~5 mg pellets of α -Al₂O₃. It was flushed continuously with O₂ throughout the experiments to ensure an oxidizing atmosphere.

Prior to the calorimetric experiments, complete dissolution of each phase in the 3Na₂O·4MoO₃ solvent at 976 K was confirmed by visual inspection in a furnace. The large

and rapidly generated endothermic enthalpy of drop solution for each phase, return of the calorimetric signal to its baseline value, and a solvent color change from almost white to yellow indicates that each phase dissolved fully in the melt. Calorimetry was straightforward and problem free, as is the case with other uranyl phases (Hughes Kubatko et al. 2003, Helean et al. 2003).

Earlier experiments on UO_3 confirm that U^{6+} is the stable oxidation state of U dissolved at low concentrations in $3\text{Na}_2\text{O}\cdot 4\text{MoO}_3$ at 976 K (Helean et al. 2003). Thus the dissolution of the uranyl oxide hydrates, likewise, involve no oxidation-reduction. Samples dissolved readily and quickly. H_2O was evolved into the gas above the solvent and swept out of the calorimeter by the flowing O_2 gas, as demonstrated previously by Navrotsky et al. (1994).

RESULTS AND DISCUSSION

Uranyl oxide hydrates

The enthalpies of formation from the binary oxides, $\Delta H_{f\text{-ox}}$, for metaschoepite and $\beta\text{-UO}_2(\text{OH})_2$ were calculated from their respective drop solution enthalpies and from the heat contents of UO_3 and H_2O , as in the following reactions (Table 4): (xl: crystalline, l: liquid)

$$\Delta H_{f\text{-ox}} = 4.4 \pm 3.1 \text{ kJ mol}^{-1}$$

$$\Delta H_{f\text{-ox}} = -26.6 \pm 2.8 \text{ kJ mol}^{-1}$$

The ΔH_{f-ox} value for $\beta\text{-UO}_2(\text{OH})_2$ is exothermic, thus it is stable in enthalpy with respect to UO_3 and liquid H_2O , whereas metaschoepite is unstable in enthalpy with respect to UO_3 and liquid H_2O . Entropies were not measured, but ΔS_f values are expected to be close to zero or probably slightly negative as liquid water is converted to more tightly bond crystalline H_2O or OH species.

In the $\text{UO}_3 + x\text{H}_2\text{O} = \text{UO}_3(\text{H}_2\text{O})_x$ ($0.4 < x < 2.2$) system, metaschoepite has an endothermic heat of formation relative to the oxides, however the less hydrous phases $\beta\text{-UO}_2(\text{OH})_2$ ($\Delta H_{f-ox} = -26.6 \pm 2.8 \text{ kJ mol}^{-1}$), and $\text{UO}_3(\text{H}_2\text{O})_{0.8}$ ($\Delta H_{f-ox} = -17.5 \pm 2.1 \text{ kJ mol}^{-1}$, Kubatko et al. 2003) have exothermic heats of formation from the oxides. While the ΔH_{f-ox} of schoepite, $\text{UO}_3(\text{H}_2\text{O})_{2.2}$, has not been measured, it may be thermodynamically unstable relative to metaschoepite, as schoepite transforms readily and rapidly in air to form metaschoepite with a loss of 1/6 the H_2O groups, and dehydrated schoepite, $\text{UO}_3(\text{H}_2\text{O})_{0.8}$, with a loss of all interlayer water and a collapse of the c -cell dimension (Finch and Hawthorne 1998). Such a spontaneous dehydration of schoepite to metaschoepite and dehydrated schoepite may be entropy driven, with the more hydrous schoepite being more stable at lower temperature. If this is indeed the case, the dehydration temperature for schoepite may be below ambient temperature for normal humidities. However, the observed positive enthalpy of formation of metaschoepite from the oxides implies a negative enthalpy of dehydration. With ΔH negative and ΔS positive for dehydration, metaschoepite, and probably schoepite, would be metastable under all conditions. Metaschoepite often occurs in nature as a polycrystalline mixture with dehydrated schoepite, $\text{UO}_3(\text{H}_2\text{O})_{0.8}$.

While β - $\text{UO}_2(\text{OH})_2$ is not known to occur naturally, it is synthesized readily and rapidly when UO_3 or $\text{UO}_3(\text{H}_2\text{O})_2$ are in contact with H_2O under acidic conditions.

The calorimetric data enable the calculation of the enthalpy of formation from the elements, ΔH_f° , at 298 K for metaschoepite and β - $\text{UO}_2(\text{OH})_2$, as in the following reaction (Table 4). (g: gas)

$$\Delta H_f^\circ = -1791.0 \pm 3.2 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ = -1536.2 \pm 2.8 \text{ kJ mol}^{-1}$$

While the ΔH_f° value for β - $\text{UO}_2(\text{OH})_2$ is in accord with previously published values of -1533.4 ± 1.2 (Cordfunke 1964) and $-1533.8 \pm 1.3 \text{ kJ mol}^{-1}$ (Grenthe et al. 1992), the ΔH_f° value for metaschoepite differs from the previously published values of $-1826.0 \pm 4.0 \text{ kJ mol}^{-1}$ (Hemingway 1982) and $-1826.1 \pm 1.7 \text{ kJ mol}^{-1}$ (Guillaumont et al. 2003). Santalova et al. (1971) and Tasker et al. (1988) independently measured the enthalpy of hydration of γ - UO_3 to $\text{UO}_3(\text{H}_2\text{O})_2$ based on differences in the enthalpy of solution of the two solids in dilute HF. The value given by Guillaumont et al. (2003) was calculated using the average enthalpy difference between those of Santalova et al. (1971) and Tasker et al. (1988) along with $\Delta H_f^\circ \text{ UO}_3 \text{ (xl, 298 K)}$ and $\Delta H_f^\circ \text{ H}_2\text{O (l, 298 K)}$. Santalova et al. (1971) report that their water content was determined with substantial error. The X-ray diffraction pattern of the sample used in Tasker et al. (1987) reportedly matched that of schoepite,

rather than metaschoepite. The discrepancy between our value and that of Guillaumont et al. (2003) may arise from such a difference in starting material, as the value of Guillaumont et al. (2003) is in agreement with that of schoepite of $-1826.1 \pm 1.7 \text{ kJ mol}^{-1}$ (Grenthe et al. 1992). The value of $\Delta H_f^\circ \alpha\text{-UO}_3(\text{H}_2\text{O})_2$ reported in Hemingway (1982) is reported as that of “paraschoepite”. This value, owing to the lack of experimental details, may have been a calculation for a mixture of schoepite and metaschoepite as the existence of three uranyl oxyhydrates are discussed. Preferred thermodynamic values are given in Table 5.

Calcium uranyl oxide hydrates

The enthalpies of formation from the binary oxides, $\Delta H_{f\text{-ox}}$, at 298 K for CaUO_4 , becquerelite and $\text{Ca}(\text{UO}_2)_4\text{O}_3(\text{OH})_4(\text{H}_2\text{O})_2$ were calculated from the drop solution enthalpies of each compound (Table 3), respectively, and from the heat of drop solution of CaO , UO_3 , and H_2O from the following reactions (Table 4):

$$\Delta H_{f\text{-ox}} = -143.1 \pm 3.0 \text{ kJ mol}^{-1}$$

$$\Delta H_{f\text{-ox}} = -267.5 \pm 13.3 \text{ kJ mol}^{-1}$$

$$\Delta H_{f-ox} = 20.4 \pm 13.8 \text{ kJ mol}^{-1}$$

The resulting ΔH_{f-ox} values enable the calculation of the standard enthalpies of formation from the elements, ΔH_f° , at 298 K, as in the following reactions (Table 4):

$$\Delta H_f^\circ = -2002.0 \pm 3.2 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ = -11389.2 \pm 13.5 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ = -6653.1 \pm 13.8 \text{ kJ mol}^{-1}$$

The ΔH_f° value of CaUO_4 is in accord with previous published values of -2001 ± 2.1 (O'Hare et al 1976) and $-2002.3 \pm 2.3 \text{ kJ mol}^{-1}$ (Grenthe et al. 1992).

Measured ΔH_f° values for becquerelite and $\text{Ca(UO}_2)_4\text{O}_3(\text{OH})_4(\text{H}_2\text{O})_2$ are reported here for the first time. These values permit examination of additional reactions, such as formation of these phases from metaschoepite and CaO , as in the following reactions (calculated using ΔH_f° values from Table 4):

$$\Delta H^\circ_r = \Delta H_f^\circ (\text{CaUO}_4) + 2\Delta H_f^\circ (\text{H}_2\text{O}) - \Delta H_f^\circ (\text{UO}_3(\text{H}_2\text{O})_2) - \Delta H_f^\circ (\text{CaO})$$

$$\Delta H^\circ_r = -147.6 \pm 4.5 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ_r = \Delta H_f^\circ (\text{Ca}(\text{UO}_2)_6\text{O}_4(\text{OH})_6(\text{H}_2\text{O})_8) + \Delta H_f^\circ (\text{H}_2\text{O}) - 6\Delta H_f^\circ$$

$$(\text{UO}_3(\text{H}_2\text{O})_2) - \Delta H_f^\circ (\text{CaO})$$

$$\Delta H^\circ_r = -293.7 \pm 15.6 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ_r = \Delta H_f^\circ (\text{Ca}(\text{UO}_2)_4\text{O}_3(\text{OH})_4(\text{H}_2\text{O})_2) + 4\Delta H_f^\circ (\text{H}_2\text{O}) - 4\Delta H_f^\circ$$

$$(\text{UO}_3(\text{H}_2\text{O})_2) - \Delta H_f^\circ (\text{CaO})$$

$$\Delta H^\circ_r = 2.8 \pm 15.2 \text{ kJ mol}^{-1}$$

Of the three Ca-bearing uranyl oxide hydrates studied, becquerelite is the most stable in enthalpy in the $\text{UO}_3(\text{H}_2\text{O})_2$ -CaO- H_2O system. While CaUO_4 , becquerelite and $\text{Ca}(\text{UO}_2)_4\text{O}_3(\text{OH})_4(\text{H}_2\text{O})_2$ all crystallize rapidly and readily in laboratory experiments, only becquerelite is found in Nature. Laboratory experiments have demonstrated that schoepite and metaschoepite rapidly alter to becquerelite in Ca-bearing solutions (Vochten and Van

Haverbeke 1990, Sowder et al. 1996, 1999). Becquerelite is expected to be the most stable phase in the $\text{UO}_3(\text{H}_2\text{O})_2$ -CaO- H_2O system under normal geochemical conditions.

Our study shows that $\text{Ca}(\text{UO}_2)_4\text{O}_3(\text{OH})_4(\text{H}_2\text{O})_2$ is unstable in enthalpy relative to the oxides and unstable in enthalpy relative to metaschoepite and CaO. Presumably this phase is favored by kinetic effects in some laboratory syntheses, but it is unlikely that this will be an important phase in nature or in a geological repository for nuclear waste.

Sodium uranyl oxide hydrates

The mean drop solution enthalpies of clarkeite and $\text{Na}_2(\text{UO}_2)_6\text{O}_4(\text{OH})_6(\text{H}_2\text{O})_7$ (Table 3) and the heat content of Na_2O , UO_3 , and H_2O were used to calculate the enthalpy of formation of each compound from the binary oxides, $\Delta H_{f-\text{ox}}$, at 298 K, as shown in the following reactions:

The $\Delta H_{f-\text{ox}}$ values permit calculation of standard enthalpy of formation, ΔH_f° , at 298 K for these phases, as in the following reaction (Table 4):

$$\Delta H_f^\circ = -1724.7 \pm 5.1 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ = -10936.4 \pm 14.5 \text{ kJ mol}^{-1}$$

Lead uranyl oxide hydrate

The enthalpy of formation from the binary oxides, $\Delta H_{f\text{-ox}}$, at 298 K for curite was calculated from the mean drop solution enthalpy of curite (Table 3) and from the heat content of PbO, UO₃, and H₂O as shown in reaction 20 (Table 4):

$$\Delta H_{f\text{-ox}} = -1291.9 \pm 34.4 \text{ kJ mol}^{-1}$$

The $\Delta H_{f\text{-ox}}$ value is exothermic, indicating that curite is stable in enthalpy as compared to the oxides at 298 K. While the entropy of this reaction was not determined, $T\Delta S$ at 298 K is expected to be small compared to the large ΔH value.

The calorimetric data enable the calculation of enthalpy of formation, ΔH_f° , at 298 K for curite, as in the following reaction (Table 4):

COMPARISON TO PREDICTED VALUES

The thermodynamic database for uranyl phases is limited. Consequently, empirical models for prediction of Gibbs free energies and enthalpies from the elements have emerged (e.g.: Chen et al. 1999). Predictive models offer approximation of thermodynamic parameters.

Considering the phases of the current study, the predictive model of Chen et al. (1999) provides enthalpies of formation from the elements, ΔH_f° , for each phase that are within 2.7% the current data. However, significant disparities between predicted and measured values emerge when the enthalpies of formation from the binary oxides, $\Delta H_{f-\text{ox}}$, are calculated (Table 6). For example, calculating the formation of metaschoepite from the binary oxides UO_3 and H_2O (Reaction 1) using ΔH_f° (metaschoepite) from Chen et al. (1999), one obtains a $\Delta H_{f-\text{ox}}$ of $-29.51 \text{ kJ mol}^{-1}$, rather than $4.4 \pm 3.1 \text{ kJ mol}^{-1}$ from the current data. This suggests that metaschoepite is more stable in enthalpy with respect to UO_3 and H_2O than dehydrated schoepite, $\text{UO}_3(\text{H}_2\text{O})_{0.8}$ (Kubatko et al. 2003), $\Delta H_{f-\text{ox}}$ of $-17.81 \pm 2.12 \text{ kJ mol}^{-1}$. The enthalpy of formation, $\Delta H_{f-\text{ox}}$, of $\text{Ca}(\text{UO}_2)_4\text{O}_3(\text{OH})_4(\text{H}_2\text{O})_2$ with

respect to CaO, UO₃ and H₂O calculated from the predicted values of Chen et al. (1999) is -159.59 kJ mol⁻¹ (Chen et al. 1999), as opposed to 20.4 ± 14 kJ mol⁻¹ from the current data. Our results indicate that Ca(UO₂)₄O₃(OH)₄(H₂O)₂ is unstable in enthalpy relative to the oxides and unstable in enthalpy relative to metaschoepite and CaO, however a value of -159.59 kJ mol⁻¹ would indicate stability in enthalpy.

Predictive models are useful for estimates of enthalpies from the elements for uranyl phases when measured thermodynamic parameters are absent, which is the case for the majority of uranyl phases. With respect to the enthalpies of formation from the binary oxides calculated using predicted values, caution is warranted as significant disparities sometimes arise.

CONCLUSION

Thermodynamic trends of uranyl oxide hydrate formation from the binary oxides UO₃ and H₂O may be entropy driven; however, the observed positive enthalpy of formation of metaschoepite from the oxides implies a negative enthalpy of dehydration. With ΔH negative and ΔS positive for dehydration, metaschoepite, and probably schoepite, would be metastable under all conditions. Energetic trends of uranyl oxide hydrate formation from the binary oxides UO₃ and H₂O in the presence of Ca, Na, or Pb appear to be dominated by the acid-base character of the binary oxides and additional favorable interactions arising from hydration and/or changes in cation environments. Measurement, by cryogenic adiabatic calorimetry, of the heat capacities of these materials would be highly desirable.

ACKNOWLEDGEMENTS

This research was supported by the Environmental Management Science Program of the Office of Science, U.S. Department of Energy, grants DE-FG07-97ER14820 and DE-FG03-97SF14749 as well as the Office of Civilian Radioactive Waste Management Science and Technology program. This report was prepared by University of Notre Dame pursuant to a cooperative agreement (DE-FC28-04RW12255) funded by the United States Department of Energy (DOE), Office of Civilian Radioactive Waste Management (OCRWM), Office of Science and Technology and International (OST&I), and neither, University of Notre Dame nor any of its contractors or subcontractors nor the DOE/OCRWM/OST&I, nor any person acting on behalf of either: Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately-owned rights; or Assumes any liabilities with respect to the use of, or for damages resulting from the use of, any information, apparatus, method, or process disclosed in this report. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by DOE/OCRWM/OST&I. The views, opinions, findings, and conclusions or recommendations of authors expressed herein do not necessarily state or reflect those of the DOE/OCRWM/OST&I.

REFERENCES

- Bannister, M.J. and Taylor, J.C. (1982) The Crystal Structure and Anisotropic Thermal Expansion of β uranyl dihydroxide, $\text{UO}_2(\text{OH})_2$. *Acta Crystallographica B*, 24, 1968-38.
- Burns, P.C. (1998) The structure of compreignacite, $\text{K}_2[(\text{UO}_2)_3\text{O}_2(\text{OH})_3]_2(\text{H}_2\text{O})_7$. *Canadian Mineralogist*, 36, 1061-1067.
- Burns, P.C. (1999) The crystal chemistry of uranium. *Reviews in Mineralogy*, 38, 23-90.
- Burns, P.C. and Hill, F.C. (2000) Implications of the synthesis and structure of the Sr analogue of curite. *Canadian Mineralogist*, 38, 175-182.
- Burns, P.C. and Li, Y. (2002) The structures of becquerelite and Sr-exchanged becquerelite. *American Mineralogist*, 87, 550-557
- Burns, P.C., Ewing, R.C. and Miller, M.L. (1997) Incorporation mechanisms of actinide elements into the structures of U^{6+} phases formed during the oxidation of spent nuclear fuel. *Journal of Nuclear Materials*, 245, 1-9.
- Burns, P.C., Deely, K.M. and Skanthakumar, S. (2004) Neptunium incorporation into uranyl compounds that form as alteration products of spent nuclear fuel: Implications for geologic repository performance. *Radiochimica Acta*, 92, 151-159.
- Cahill, C.L. and Burns, P.C. (2000) The structure of agrinierite: A Sr-containing uranyl oxide hydrate mineral. *American Mineralogist*, 85, 1294-1297.
- Catalano J.G., Brown G.E. (2004) Analysis of uranyl-bearing phases by EXAFS spectroscopy: Interferences, multiple scattering, accuracy of structural parameters, and spectral differences. *American Mineralogist*, 89, 1004-1021.

- Chen, F., Ewing, R.C., Clark, S.B. (1999) The Gibbs free energies and enthalpies of formation of U^{6+} phases: An empirical method of prediction. *American Mineralogist*, 84, 650-664.
- Cordfunke, E.H.P. (1964) Heats of formation of some hexavalent uranium compounds. *Journal of Physical Chemistry*, 68, 3353-3356.
- Cordfunke, E.H.P. and O'Hare, P.A.G. (1978) The chemical thermodynamics of actinide elements and compounds. Part 3. Miscellaneous actinide compounds: International Atomic Energy Agency, Vienna, Austria, 83pp.
- Finch, R.J. and Ewing, R.C. (1992) The corrosion of uraninite under oxidizing conditions. *Journal of Nuclear Materials*, 190, 133-156.
- Finch, R.J. and Ewing, R.C. (1997) Clarkeite: New chemical and structural data. *American Mineralogist*, 82, 607-619.
- Finch, R.J. and Hawthorne, F.C. (1998) Structural relations among schoepite, meta-schoepite and "dehydrated schoepite". *Canadian Mineralogist*, 36, 831-845.
- Finch, R.J., Cooper, M., Hawthorne, F.C, Ewing, R.C. (1996) The crystal structure of schoepite. *Canadian Mineralogist*, 34, 1071-1088.
- Finch, R.J., Buck E., Finn, P., Bates, J. (1999) Oxidative corrosion of spent UO_2 fuel in vapor and dripping groundwater at 90°C. *Materials Research Society Symposium Proceedings*, 556, 431-438.
- Finn, P., Hoh, J., Wolf, S., Slater, S., Bates, J. (1996) The release of uranium, plutonium, cesium, strontium, technetium and iodine from spent nuclear fuel under unsaturated conditions. *Radiochimica Acta* 65-71.

- Fron del, C. (1956) Systematic Mineralogy of Uranium and Thorium. U.S. Geological Survey Bulletin. 1064, 400 p.
- Glatz, R.E., Li, Yaping, Hughes, K.A., Cahill, C.L. and Burns, P.C. (2002): Synthesis and structure of a new Ca uranyl oxide hydrate, $\text{Ca}[(\text{UO}_2)_4\text{O}_3(\text{OH})_4](\text{H}_2\text{O})_2$, and its relationship to becquerelite. *Canadian Mineralogist* 40, 217-224.
- Grenthe, I., Fuger, J., Konings, R., Lemire, R., Muler, A., Nguyen-Trung, C. and Wanner, H. (1992) Chemical Thermodynamics of Uranium, 715 p., Elsevier, Amsterdam.
- Guillaumont, R., Fanghänel, T., Fuger, J., Grenthe, I., Neck, V., Palmer, D., Rand, M. (2003) Update on the Chemical Thermodynamics of Uranium, Neptunium, and Plutonium, Americium, and Technetium, 919 p., Elsevier, Amsterdam.
- Helean, K.B, Navrotsky, A., Vance, E.R. Carter, M.L. Ebbinghaus, B. Krikorian, O. Lian, J. Wang, L.M. and Catalano, J.G. (2002) Enthalpies of formation of Ce-pyrochlore, $\text{Ca}_{0.93}\text{Ce}_{1.00}\text{Ti}_{2.035}\text{O}_{7.00}$, U-pyrochlore, $\text{Ca}_{1.46}\text{U}^{4+}_{0.23}\text{U}^{6+}_{0.46}\text{Ti}_{1.85}\text{O}_{7.00}$ and Gd-pyrochlore, $\text{Gd}_2\text{Ti}_2\text{O}_7$: three materials relevant to the proposed waste form for excess weapons plutonium. *Journal of Nuclear Materials*, 303, 226-239.
- Hemingway, B.S (1982) Thermodynamic properties of selected uranium compounds at 298.15 K and 1 bar and at higher temperatures--Preliminary models for the origin of coffinite deposits, U.S. Geological Survey Open-File Report 82-619.
- Hill, F.C. and Burns, P.C. (1999) Structure of a synthetic Cs uranyl oxide hydrate and its relationship to compregnacite. *Canadian Mineralogist*, 37, 1283-1288.
- Hoekstra, H.R. and Siegel, S. (1973) The uranium trioxide-water system. *Journal of Inorganic Nuclear Chemistry*, 35, 761-779.

- Kubatko, K-A.H., Helean, K., Navrotsky, A., Burns, P.C. (2003) Stability of peroxide-containing uranyl minerals. *Science*, 302, 1191-1193.
- Kubatko, K-A., Helean, K., Navrotsky, A., Burns, P.C. (2005) Thermodynamics of uranyl minerals: Enthalpies of formation of rutherfordine, UO_2CO_3 , andersonite, $\text{Na}_2\text{CaUO}_2(\text{CO}_3)_3(\text{H}_2\text{O})_5$, and grimselite, $\text{K}_3\text{NaUO}_2(\text{CO}_3)_3\text{H}_2\text{O}$. *American Mineralogist*, (MS 1821)
- Li, Y. and Burns, P.C. (2000a) Investigations of crystal-chemical variation in lead uranyl oxide hydrates. I. Curite. *Canadian Mineralogist* 38, 727-735.
- Li, Y. and Burns, P.C. (2000b) Investigations of crystal-chemical variation in lead uranyl oxide hydrates. II. Fourmarierite. *Canadian Mineralogist* 38, 737-749.
- Li, Y and Burns, P.C. (2001) The structures of two sodium uranyl compounds relevant to nuclear waste disposal. *Journal of Nuclear Materials* 299, 219-226.
- Navrotsky, A. (1977) Recent progress and new directions in high T calorimetry. *Physics and Chemistry of Minerals*, 2, 89-104.
- Navrotsky, A. (1997) Progress and new directions in high T calorimetry revisited. *Physics and Chemistry of Minerals*, 24, 222-241.
- Navrotsky, A., Rapp, R.P., Smelik, E., Burnley, P., Circone, S., Chat, L., Bose, K., Westrich, H.R. (1994) The behavior of H_2O and CO_2 in high temperature lead borate solution calorimetry of volatile-bearing phases. *American Mineralogist*, 79, 1099.
- O'Hare, P.A.G., Boeria, J., and Hoekstra, H.R. (1976) Thermochemistry of uranium compounds VIII. Standard enthalpies of formation at 298.25K of the urيناتes of

- calcium (CaUO_4) and barium (BaUO_4). Thermodynamics of the behavior of barium in nuclear fuel. *Journal of Chemical Thermodynamics*, 8, 845-855.
- Pearcy, E.C., Prikryl, J.D., Murphy, W.M., and Leslie, B.W. (1994) Alteration of uraninite from the Nopal I deposit, Peña Blanca District, Mexico, compared to degradation of spent nuclear fuel in the proposed U.S. high-level nuclear waste repository at Yucca Mountain, Nevada. *Applied Geochemistry*, 9, 713-732.
- Rane, M. V., Navrotsky, A., and Rossetti, G.A. Jr. (2001) Enthalpies of formation of lead zirconate titanate (PZT) solid solutions, *Journal of Solid State Chemistry*, 161, 402-409.
- Roh Y., Lee S.R. and Choi S.K. (2000) Physicochemical and mineralogical characterization of uranium-contaminated soils. *Soil and Sediment Contamination*, 9, 463-486.
- Robie, R.A., Hemingway, B.S., and Fisher, J.R. (1978) Thermodynamic properties of minerals and related substances at 298.15 K and 1 Bar pressure and at higher temperatures. U .S. Geological Survey Bulletin, 1452. 456p.
- Robie, R.A. and Hemingway, B.S. (1995) Thermodynamic properties of minerals and related substances at 298.15 K and 1 Bar pressure and at higher temperatures. U .S. Geological Survey Bulletin, 2131. 461p.
- Santalova, N.A., Vidavskii, L.M., Dunaeva, K.M. and Ippolitova, E.A. (1971) Enthalpy of formation of uranium trioxide dehydrate. *Soviet Radiochemica*, 13, 608-612.
- Sowder, A.G., Clark, S.B., and Fjeld, R.A. (1996) The effect of silica and phosphate on the transformation of schoepite to becquerelite and other uranyl phases. *Radiochimica Acta*, 74, 45-49.

- Sowder, A.G., Clark, S.B., and Fjeld, R.A. (1999) The transformation of uranyl oxide hydrates: the effect of dehydration on synthetic meta-schoepite and its alteration to becquerelite. *Environmental Science and Technology*, 33, 3552-3557.
- Takahashi, K., Fujino, T., Morss, L.R. (1993) Crystal-chemical and thermodynamic study on CaUO_4 . *Journal of Solid state chemistry*, 105, 234-246.
- Tasker, I.R., O'Hare, P.A.G., Lewis, B.M., Johnson, G.K. and Corkfunke, E.P.H. (1988) Thermochemistry of uranium compounds: XVI. Calorimetric determination of the standard molar enthalpy of formation at 298.15 K, low-temperature heat capacity, and high temperature enthalpy increments of $\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$ (schoepite). *Canadian Journal of Chemistry*, 66, 620-625.
- Weller, M.T., Light, M.E., Gelbrich, T. (2000) Structure of uranium(VI) oxide dihydrate, $\text{UO}_3 \cdot 2\text{H}_2\text{O}$; synthetic meta-schoepite $(\text{UO}_2)_4\text{O}(\text{OH})_6 \cdot 5\text{H}_2\text{O}$. *Acta Crystallographica Section B, Structural Science*, 56, 577-583.
- Westrum, E.F., Jr., Zainel, H.A., and Jakes, D. (1980) Alkaline earth urinates: An exploration of their thermophysical stabilities, in: *Thermodynamics nuclear materials 1979*, Proceedings Symposium, Jülich, Federal Republic of Germany, Vienna: International Atomic Energy Agency, 143-154.
- Wronkiewicz, D., Bates, J., Gerding, T., Veleckis, E., Tani, B. (1992) Uranium release and secondary phase formation during unsaturated testing of UO_2 at 90°C. *Journal of Nuclear Materials*, 190, 107-127.
- Wronkiewicz, D., Bates, J., Wolf, S., Buck, E. (1996) Ten-year results from unsaturated drip tests with UO_2 at 90°C: implications for the corrosion of spent nuclear fuel. *Journal of Nuclear Materials*, 238, 78-95.

Vochten, R. and Van Haverbeke, L. (1990) Transformation of schoepite into the uranyl oxide hydrates: becquerelite, billietite and wölsendorfite. *Mineralogy and Petrology*, 43, 65-72.

Yamakawa, I. and Traina, S.J. (2001) Precipitation processes of uranium in highly alkaline solutions: Possible chemical reactions occurring in the Hanford vadose zone. *Abstracts of Papers to the American Chemical Society*, 222, 55, 1.

FIGURE 1. Polyhedral representations of the sheets of uranyl polyhedra in the structures of (a) metaschoepite, (b) β - $\text{UO}_2(\text{OH})_2$, (c) becquerelite and $\text{Na}_2(\text{UO}_2)_6\text{O}_4(\text{OH})_6(\text{H}_2\text{O})_7$, (d) $\text{Ca}(\text{UO}_2)_4\text{O}_3(\text{OH})_4(\text{H}_2\text{O})_2$, (e) CaUO_4 and (f) curite

TABLE 1. Previously reported values of ΔG_f° , ΔH_f° and S° of uranyl oxide hydrates considered in this study.

	ΔG_f° (kJ mol ⁻¹)	ΔH_f° (kJ mol ⁻¹)	ΔS_{298} (J mol ⁻¹ K ⁻¹)
β -UO ₂ (OH) ₂	-1397.1 ± 4.0 ¹	-1533.4 ± 1.2 ²	134 ± 8 ¹
	-1398.7 ± 1.8 ^{3,4}	-1533.8 ± 1.3 ^{3,4}	138 ± 4 ^{3,4}
UO ₃ (H ₂ O) ₂	-1632.0 ± 4.0 ¹	-1826.0 ± 4.0 ¹	174 ± 8 ¹
	-1636.5 ± 1.7 ⁴	-1826.1 ± 1.7 ⁴	188.5 ± 0.4 ⁴
CaUO ₄	-1895.0 ± 3.0 ¹	-2001.7 ± 2.1 ⁴	144.3 ± 8.0 ¹
	-1888.7 ± 2.4 ³	-2002.3 ± 2.3 ³	121.1 ± 2.5 ³

¹Hemingway 1982, ²Cordfunke 1964, ³Grenthe et al. 1992, ⁴Guillaumont et al. 2003

TABLE 2. Hydrothermal synthesis procedures for uranyl oxide hydrates. All experiments were done in Parr reaction vessels. pH adjustments were made where noted.

	reactants	pH	T (K)	t (days)
$\text{UO}_3(\text{H}_2\text{O})_2$	0.14 g UO_3 5 mL H_2O		348	1
$\beta\text{-UO}_2(\text{OH})_2$	0.01 g $\text{UO}_3(\text{H}_2\text{O})_2$ 5 mL H_2O	adjusted to 2 using HCl	373	1
CaUO_4	0.052 g UO_3 0.055 g calcite (3 crystals) 5 mL H_2O	adjusted to 10 using NH_4OH	453	20
$\text{Ca}(\text{UO}_2)_6\text{O}_4(\text{OH})_6(\text{H}_2\text{O})_8$	0.165 g UO_3 0.25 g calcite (5 crystals) 5 mL H_2O	adjusted to 3 using HCl	453	10
$\text{Ca}(\text{UO}_2)_4\text{O}_3(\text{OH})_4(\text{H}_2\text{O})_2$	0.02 g UO_3 0.01 g CaCl 4 mL H_2O		503	4
$\text{Na}(\text{UO}_2)\text{O}(\text{OH})$	10 mL 0.2 M $\text{UO}_2(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_2$ 0.17 g Na_2CO_3		493	14
$\text{Na}_2(\text{UO}_2)_6\text{O}_4(\text{OH})_6(\text{H}_2\text{O})_7$	10 mL 0.2 M $\text{UO}_2(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_2$ 0.17 g Na_2CO_3	adjusted to 6 using NaOH	373	1
$\text{Pb}_3(\text{UO}_2)_8\text{O}_8(\text{OH})_6(\text{H}_2\text{O})_2$	5 mL 0.2 M $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_6$ 5 mL 0.2 M $\text{PbCl}_2(\text{H}_2\text{O})_6$		458	5

TABLE 3. Enthalpies of drop solution, ΔH_{ds} (kJ mol⁻¹), for uranyl oxide hydrates. Data were collected using 3Na₂O·4MoO₃ solvent at 976 K.

Metaschoepite		$UO_3(H_2O)_2$		$UO_2(OH)_2$		$CaUO_4$		Becquerelite	
mass (mg)	ΔH_{ds} (kJ/mol)	mass (mg)	ΔH_{ds} (kJ/mol)	mass (mg)	ΔH_{ds} (kJ/mol)	mass (mg)	ΔH_{ds} (kJ/mol)	mass (mg)	ΔH_{ds} (kJ/mol)
4.81	144.55	5.00	100.16	5.08	62.54	5.34	990.09	5.34	990.09
4.98	146.41	4.26	105.58	5.23	59.94	5.52	996.18	5.52	996.18
4.97	143.83	4.63	106.75	5.42	63.79	4.94	971.18	4.94	971.18
5.52	143.42	5.89	106.63	5.65	62.96	5.20	1009.75	5.20	1009.75
5.49	140.36	5.51	104.54	5.18	61.84	4.85	993.83	4.85	993.83
4.93	140.07	5.37	104.63	4.96	63.94	5.25	987.09	5.25	987.09
4.82	139.62	5.51	106.59	5.56	59.34	5.01	1009.25	5.01	1009.25
5.56	146.27	5.02	105.66			4.60	986.58		
Average	143.07		105.07		62.05		992.99		
Error	2.74		2.16		1.80		12.63		

$Ca(UO_2)_4O_3(OH)_4(H_2O)_2$		Clarkeite		Na compreignacite		Curie	
mass (mg)	ΔH_{ds} (kJ/mol)	mass (mg)	ΔH_{ds} (kJ/mol)	mass (mg)	ΔH_{ds} (kJ/mol)	mass (mg)	ΔH_{ds} (kJ/mol)
5.33	210.13	5.24	88.54	5.43	863.41	5.48	1601.97
5.28	204.19	5.38	81.58	4.84	853.27	5.16	1693.80
4.71	198.77	4.99	89.72	5.24	859.22	5.38	1647.51
4.68	203.62	4.49	81.51	5.15	858.85	5.74	1680.80
4.75	220.96	4.68	86.36	5.01	837.81	5.38	1642.43
4.68	180.87	5.15	86.55	4.56	825.77	5.68	1676.81
		5.83	89.13	4.76	858.65	5.45	1638.90
		5.55	90.42	4.98	858.63	5.08	1604.74
Average	203.09		86.73		851.95		1648.37
Error	13.29		3.50		13.14		34.04

TABLE 4. Thermochemical cycles for nine uranyl oxide hydrate phases in the calculation of the enthalpy of formation from the binary oxides, $\Delta H_{f,ox}$, and the standard enthalpy of formation from the elements, ΔH_f° , at 298 K.

Reaction	ΔH (kJ mol ⁻¹)
(1) ΔH_{ds} (metaschoepite)	143.1 $\pm$ 2.7
(2) ΔH_{ds} ($UO_2(OH)_2$)	105.1 $\pm$ 2.2
(3) ΔH_{ds} ($CaUO_4$)	62.1 $\pm$ 1.8
(4) ΔH_{ds} (bequerelite)	993.0 $\pm$ 12.6
(5) ΔH_{ds} ($Ca(UO_2)_4O_3(OH)_4(H_2O)_2$)	203.1 $\pm$ 13.3
(6) ΔH_{ds} (clarkite)	86.7 $\pm$ 3.5
(7) ΔH_{ds} (Na comprégnacite)	852.0 $\pm$ 13.1
(8) ΔH_{ds} (curite)	1648.4 $\pm$ 34.0
(9) ΔH_{ds} (UO_3)	9.5 $\pm$ 1.5
(10) ΔH_{inc} (H_2O)	69.0
(11) ΔH_{ds} (CaO)	-90.5 $\pm$ 1.8
(12) ΔH_{ds} (Na_2O)	-215.8 $\pm$ 4.4
(13) ΔH_{ds} (PbO)	-21.5 $\pm$ 1.5
(14) ΔH_f° (UO_3)	-1223.8 $\pm$ 0.8
(15) ΔH_f° (H_2O)	-285.8 $\pm$ 0.1
(16) ΔH_f° (CaO)	-635.1 $\pm$ 0.9
(17) ΔH_f° (Na_2O)	-414.8 $\pm$ 0.3
(18) ΔH_f° (PbO)	-217.3 $\pm$ 0.3

Thermodynamic Cycles

ΔH (kJ mol⁻¹)

metaschoepite, $UO_3(H_2O)_2$

$$\Delta H_{f,ox} = -\Delta H1 + \Delta H9 + 2\Delta H10$$

$$UO_3 (xl, 298 K) + 2H_2O (l, 298 K) = UO_3(H_2O)_2 (xl, 298 K)$$

$$\Delta H_f^\circ = -\Delta H1 + \Delta H9 + 2\Delta H10 + \Delta H14 + 2\Delta H15$$

$$U (xl, 298 K) + 2H_2 (g, 298 K) + 5/2O_2 (g, 298 K) = UO_3(H_2O)_2 (xl, 298 K)$$

$UO_2(OH)_2$

$$\Delta H_{f,ox} = -\Delta H2 + \Delta H9 + \Delta H10$$

$$UO_3 (xl, 298 K) + H_2O (l, 298 K) = UO_2(OH)_2 (xl, 298 K)$$

$$\Delta H_f^\circ = -\Delta H2 + \Delta H9 + \Delta H10 + \Delta H14 + \Delta H15$$

$$U (xl, 298 K) + H_2 (g, 298 K) + 2O_2 (g, 298 K) = UO_2(OH)_2 (xl, 298 K)$$

$CaUO_4$

$$\Delta H_{f,ox} = -\Delta H3 + \Delta H11 + \Delta H9$$

-1536.2 $\pm$ 2.8

-26.6 $\pm$ 2.8

-1791.0 $\pm$ 3.2

4.4 $\pm$ 3.1

$\text{CaO (xl, 298 K)} + \text{UO}_3 \text{ (xl, 298 K)} = \text{CaUO}_4 \text{ (xl, 298 K)}$	-143.1 ± 3.0
$\Delta H_f^\circ = -\Delta H_3 + \Delta H_{11} + \Delta H_9 + \Delta H_{16} + \Delta H_{14}$	
$\text{Ca (xl, 298 K)} + \text{U (xl, 298 K)} + 2\text{O}_2 \text{ (g, 298 K)} = \text{CaUO}_4 \text{ (xl, 298 K)}$	-2002.0 ± 3.2
<i>becquerelite</i> , $\text{Ca(UO}_2)_6\text{O}_4(\text{OH})_6(\text{H}_2\text{O})_8$	
$\Delta H_{f,\text{ox}}^\circ = -\Delta H_4 + \Delta H_{11} + 6\Delta H_9 + 11\Delta H_{10}$	
$\text{CaO (xl, 298 K)} + 6\text{UO}_3 \text{ (xl, 298 K)} + 11\text{H}_2\text{O (l, 298 K)} = \text{Ca(UO}_2)_6\text{O}_4(\text{OH})_6(\text{H}_2\text{O})_8 \text{ (xl, 298 K)}$	-267.5 ± 13.3
$\Delta H_f^\circ = -\Delta H_4 + \Delta H_{11} + 6\Delta H_9 + 11\Delta H_{10} + \Delta H_{16} + 6\Delta H_{14} + 11\Delta H_{15}$	
$\text{Ca (xl, 298 K)} + 6\text{U (xl, 298 K)} + 11\text{H}_2 \text{ (g, 298 K)} + 15\text{O}_2 \text{ (g, 298 K)} = \text{Ca(UO}_2)_6\text{O}_4(\text{OH})_6(\text{H}_2\text{O})_8 \text{ (xl, 298 K)}$	-11389.2 ± 13.5
$\text{Ca(UO}_2)_4\text{O}_3(\text{OH})_4(\text{H}_2\text{O})_2$	
$\Delta H_{f,\text{ox}}^\circ = -\Delta H_5 + \Delta H_{11} + 4\Delta H_9 + 4\Delta H_{10}$	
$\text{CaO (xl, 298 K)} + 4\text{UO}_3 \text{ (xl, 298 K)} + 4\text{H}_2\text{O (l, 298 K)} = \text{Ca(UO}_2)_4\text{O}_3(\text{OH})_4(\text{H}_2\text{O})_2 \text{ (xl, 298 K)}$	20.4 ± 13.8
$\Delta H_f^\circ = -\Delta H_5 + \Delta H_{11} + 4\Delta H_9 + 4\Delta H_{10} + \Delta H_{16} + 4\Delta H_{14} + 4\Delta H_{15}$	
$\text{Ca (xl, 298 K)} + 4\text{U (xl, 298 K)} + 4\text{H}_2 \text{ (g, 298 K)} + 17/2\text{O}_2 \text{ (g, 298 K)} = \text{Ca(UO}_2)_4\text{O}_3(\text{OH})_4(\text{H}_2\text{O})_2 \text{ (xl, 298 K)}$	-6653.1 ± 13.8
<i>clarkeite</i> , $\text{Na(UO}_2)_2\text{O(OH)}$	
$\Delta H_{f,\text{ox}}^\circ = -\Delta H_6 + 1/2\Delta H_{12} + \Delta H_9 + 1/2\Delta H_{10}$	
$1/2\text{Na}_2\text{O (xl, 298 K)} + \text{UO}_3 \text{ (xl, 298 K)} + 1/2\text{H}_2\text{O (l, 298 K)} = \text{Na(UO}_2)_2\text{O(OH)} \text{ (xl, 298 K)}$	-150.6 ± 4.9
$\Delta H_f^\circ = -\Delta H_6 + 1/2\Delta H_{12} + \Delta H_9 + 1/2\Delta H_{10} + 1/2\Delta H_{17} + \Delta H_{14} + 1/2\Delta H_{15}$	
$\text{Na (xl, 298 K)} + \text{U (xl, 298 K)} + 1/2\text{H}_2 \text{ (g, 298 K)} + 2\text{O}_2 \text{ (g, 298 K)} = \text{Na(UO}_2)_2\text{O(OH)} \text{ (xl, 298 K)}$	-1724.7 ± 5.1
<i>sodium compeignacite</i> , $\text{Na}_2(\text{UO}_2)_6\text{O}_4(\text{OH})_6(\text{H}_2\text{O})_7$	
$\Delta H_{f,\text{ox}}^\circ = -\Delta H_7 + \Delta H_{12} + 6\Delta H_9 + 10\Delta H_{10}$	
$\text{Na}_2\text{O (xl, 298 K)} + 6\text{UO}_3 \text{ (xl, 298 K)} + 10\text{H}_2\text{O (l, 298 K)} = \text{Na}_2(\text{UO}_2)_6\text{O}_4(\text{OH})_6(\text{H}_2\text{O})_7 \text{ (xl, 298 K)}$	-320.8 ± 14.3
$\Delta H_f^\circ = -\Delta H_7 + \Delta H_{12} + 6\Delta H_9 + 10\Delta H_{10} + \Delta H_{17} + 6\Delta H_{14} + 10\Delta H_{15}$	
$2\text{Na (xl, 298 K)} + 6\text{U (xl, 298 K)} + 10\text{H}_2 \text{ (g, 298 K)} + 29/2\text{O}_2 \text{ (g, 298 K)} = \text{Na}_2(\text{UO}_2)_6\text{O}_4(\text{OH})_6(\text{H}_2\text{O})_7 \text{ (xl, 298 K)}$	-10936.4 ± 14.5
<i>curite</i> , $\text{Pb}_3(\text{UO}_2)_8\text{O}_8(\text{OH})_6(\text{H}_2\text{O})_2$	
$\Delta H_{f,\text{ox}}^\circ = -\Delta H_8 + 3\Delta H_{13} + 8\Delta H_9 + 5\Delta H_{10}$	
$3\text{PbO (xl, 298 K)} + 8\text{UO}_3 \text{ (xl, 298 K)} + 5\text{H}_2\text{O (l, 298 K)} = \text{Pb}_3(\text{UO}_2)_8\text{O}_8(\text{OH})_6(\text{H}_2\text{O})_2 \text{ (xl, 298 K)}$	-1291.9 ± 34.4
$\Delta H_f^\circ = -\Delta H_8 + 3\Delta H_{13} + 8\Delta H_9 + 5\Delta H_{10} + 3\Delta H_{18} + 8\Delta H_{14} + 5\Delta H_{15}$	
$3\text{Pb (xl, 298 K)} + 8\text{U (xl, 298 K)} + 5\text{H}_2 \text{ (g, 298 K)} + 16\text{O}_2 \text{ (g, 298 K)} = \text{Pb}_3(\text{UO}_2)_8\text{O}_8(\text{OH})_6(\text{H}_2\text{O})_2 \text{ (xl, 298 K)}$	-13163.2 ± 34.4

¹Helgeson et al 2003, ²Robie and Hemingway 1995, ³Hughes Kubarko et al. in review, ⁴Rane et al. 2001, ⁵Robie and Hemingway 1978

TABLE 5. Preferred values of ΔG_f° and ΔH_f° for uranyl oxides discussed in this study.

	ΔG_f° (kJ mol ⁻¹)	ΔH_f° (kJ mol ⁻¹)
UO ₃ (H ₂ O) ₂	-1632.0 ± 4.0 ¹	-1791.0 ± 3.2 ²
β-UO ₂ (OH) ₂	-1398.7 ± 1.8 ³	-1536.2 ± 2.8 ²
CaUO ₄	-1888.7 ± 2.4 ³	-2002.0 ± 3.2 ²
Ca(UO ₂) ₆ O ₄ (OH) ₆ (H ₂ O) ₈		-11389.2 ± 13.5 ²
Ca(UO ₂) ₄ O ₃ (OH) ₄ (H ₂ O) ₂		-6653.1 ± 13.8 ²
Na(UO ₂)O(OH)		-1724.7 ± 5.1 ²
Na ₂ (UO ₂) ₆ O ₄ (OH) ₆ (H ₂ O) ₇		-10936.4 ± 14.5 ²
Pb ₃ (UO ₂) ₈ O ₈ (OH) ₆ (H ₂ O) ₂		-13163.2 ± 34.4 ²

¹Hemingway 1982, ²value reported herein, ³Grenthe et al 1992

TABLE 6. Comparison of current data and predicted values of Chen et al. (1999). All values are reported in kJ mol⁻¹

	ΔH_f°	ΔH_f°	ΔH_{f-ox}	ΔH_{f-ox}
	current data	Chen et al. (1999)	current data	calculated from Chen et al. (1999)
UO ₃ (H ₂ O) ₂	-1791.0 ± 3.2	-1824.91	4.4 ± 3.1	-29.51
β-UO ₂ (OH) ₂	-1536.2 ± 2.8	-1529.33	-26.6 ± 2.8	-19.73
CaUO ₄	-2002.0 ± 3.2	-1949.52	-143.1 ± 3.0	-90.62
Ca(UO ₂) ₆ O ₄ (OH) ₆ (H ₂ O) ₈	-11389.2 ± 13.5	-11369.65	-267.5 ± 13.3	-247.95
Ca(UO ₂) ₄ O ₃ (OH) ₄ (H ₂ O) ₂	-6653.1 ± 13.8	-6833.09	20.4 ± 13.8	-159.59
Na(UO ₂)O(OH)	-1724.7 ± 5.1	-1749.69	-150.6 ± 4.9	-175.59
Na ₂ (UO ₂) ₆ O ₄ (OH) ₆ (H ₂ O) ₇	-10936.4 ± 14.5	-11094.6	-320.8 ± 14.3	-479
Pb ₃ (UO ₂) ₈ O ₈ (OH) ₆ (H ₂ O) ₂	-13163.2 ± 34.4	no data available	-1291.9 ± 34.4	---

Note: errors are not given in Chen et al. (1999) and therefore were not propagated through auxiliary calculations