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# Thermodynamics of uranyl minerals: Enthalpies of formation of rutherfordine, $UO_2CO_3$, andersonite, $Na_2CaUO_2(CO_3)_3(H_2O)_5$, and grimselite, $K_3NaUO_2(CO_3)_3H_2O$

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## ABSTRACT

Enthalpies of formation of rutherfordine, $UO_2CO_3$, andersonite, $Na_2CaUO_2(CO_3)_3(H_2O)_5$, and grimselite, $K_3NaUO_2(CO_3)_3(H_2O)$, have been determined using high-temperature oxide melt solution calorimetry. The enthalpy of formation of rutherfordine from the binary oxides, $\Delta H_{\text{r-ox}}$, is –99.1 ± 4.2 kJ/mol for the reaction $UO_3$ (xl, 298 K) + $CO_2$ (g, 298 K) = $UO_2CO_3$ (xl, 298 K). The $\Delta H_{\text{r-ox}}$ for andersonite is –710.4 ± 9.1 kJ/mol for the reaction $Na_2O$ (xl, 298 K) + CaO (xl, 298 K) + $UO_3$ (xl, 298 K) + $3CO_2$ (g, 298 K) + $5H_2O$ (l, 298 K) = $Na_2CaUO_2(CO_3)_3(H_2O)_6$ (xl, 298 K). The $\Delta H_{\text{r-ox}}$ for grimselite is –989.3 ± 14.0 kJ/mol for the reaction 1.5 $K_2O$ (xl, 298 K) + $0.5Na_2O$ (xl, 298 K) + $UO_3$ (xl, 298 K) + $3CO_2$ (g, 298 K) + $H_2O$ (l, 298 K) = $K_3NaUO_2(CO_3)_3H_2O$ (xl, 298 K). The standard enthalpies of formation from the elements, $\Delta H^{\circ}_{f}$, are –1716.4 ± 4.2, –5593.6 ± 9.1, and –4431.6 ± 15.3 kJ/mol for rutherfordine, andersonite, and grimselite, respectively. Energetic trends of uranyl carbonate formation from the binary oxides and ternary carbonates are dominated by the acid-base character of the binary oxides. However, even relative to mixtures of $UO_2CO_3$, $K_2CO_3$, and $Na_2CO_3$ or $CaCO_3$, andersonite and grimselite are energetically stable by 111.7 ± 10.2 and 139.6 ± 16.1 kJ/mol, respectively, suggesting additional favorable interactions arising from hydration and/or changes in cation environments. These enthalpy values are discussed in comparison with earlier estimates.

## INTRODUCTION

Uranyl minerals, which contain $U^{6+}$, are significant for understanding the genesis of U deposits (Frondel and Meyrowitz 1956), as well as the water-rock interactions that occur in U-rich rocks. They impact the mobility of actinides in contaminated soils (e.g., Buck et al. 1996) and in vadose zone sediments polluted with actinides, such as the Hanford and Savannah River sites in the U.S. (e.g., Yamakawa and Traina 2001). Precipitation of uranyl phosphate minerals in the vadose zone of contaminated sites, by the addition of phosphate, has been proposed to mitigate U plumes in groundwater (Fuller et al. 2002). Uranyl minerals can be bio-precipitated (Macaskie and Lloyd 2002), and potentially provide redox-active U to serve as an electron acceptor permitting bacterial anaerobic respiration. Uranyl minerals are important phases of alteration of nuclear waste forms under simulated geological repository conditions, such as those expected in the proposed repository at Yucca Mountain, Nevada (e.g., Finch et al. 1999; Finn et al. 1996; Wronkiewicz et al. 1996).

About 200 uranyl minerals have been described from nature. Uranyl minerals typically occur in the oxidized zones of U deposits, where it is common to find the coexistence of several uranyl mineral species, often in intimate intergrowths. Owing to their structural and chemical complexity, and the experimental difficulties associated with their characterization, the current level of understanding of the thermodynamic properties of uranyl minerals lags far behind that of most major mineral groups. We have undertaken a systematic study of the heats of formation of well-characterized uranyl minerals and their synthetic analogues. An earlier report examined the stability and origin of studtite, $[(UO_2)O_2(H_2O)_2](H_2O)_2$, which is one of two known peroxide minerals (Kubatko et al. 2003). Here, we examine the thermodynamic properties of three uranyl carbonate minerals.

Aqueous uranyl carbonate complexes are important aqueous species of hexavalent uranium under near-neutral to alkaline conditions (Langmuir 1978; Clark et al. 1995). Although many uranyl carbonates are fairly soluble in natural waters, some species, such as rutherfordine, $(UO_2)(CO_3)$, may persist in nature for tens to hundreds of thousands of years (Finch et al. 1999). Uranyl carbonates may impact the mobility of actinides in contaminated soils, the vadose zone, uranium mine and mill tailings, and a geological repository for nuclear waste. Here, we report heats of formation of rutherfordine, $(UO_2)(CO_3)$; andersonite, $Na_2CaUO_2(CO_3)_3(H_2O)_5$; and grimselite, $K_3NaUO_2(CO_3)_3(H_2O)$.

## STRUCTURES OF RUTHERFORDINE, ANDERSONITE, AND GRIMSELITE

Rutherfordine forms under acidic to neutral pH and is the only known phase that contains only uranyl and carbonate. It was discovered by Marckwald (1906) and described as a mineral species by Frondel and Meyrowitz (1956). The structure of rutherfordine was provided by Christ and Clark (1955) and refined by Finch et al. (1999). It contains approximately linear $(UO_2)^{2+}$ uranyl ions that are coordinated by six O atoms arranged at the equatorial vertices of uranyl hexagonal bipyramids. Each uranyl

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polyhedron is linked to two other uranyl polyhedra in a trans arrangement by edge sharing, resulting in chains of polyhedra. Adjacent chains are linked by the sharing of equatorial vertices between uranyl polyhedra, which results in a sheet structure that contains triangular voids. Carbonate triangles occupy one half of the voids, such that they share the equatorial edges of two adjacent uranyl hexagonal bipyramids and single vertices of two additional uranyl polyhedra (Fig. 1). The resulting sheets are electroneutral, and adjacent sheets in rutherfordine are bonded together by Van der Waals forces.

Andersonite and grimselite form under near-neutral to alkaline conditions. Their structures contain topologically identical uranyl tricarbonate clusters that are found in a significant number of compounds (Fig. 2). The cluster contains a uranyl hexagonal bipyramid that shares three of its equatorial edges with carbonate triangles, resulting in a cluster composition of $[(UO_2)(CO_3)_3]^{4-}$. In each structure the tricarbonate clusters are connected only by bonds to lower-valence cations such as Na, K, and Ca, and by hydrogen bonding.

## PREVIOUS THERMOCHEMICAL STUDIES

Extensive literature exists for equilibria in the aqueous $UO_2^{2+}$-$CO_3^{2-}$ system (Langmuir 1978; Ciavatta et al. 1979; Lemire and Tremaine 1980; Ciavatta et al. 1981; Hemingway 1982; Robel 1983). The carbonate ion ($CO_3^{2-}$) is a strong base and the uranyl ion ($UO_2^{2+}$) is a strong acid, thus uranyl carbonate complexes are quite stable. The stoichiometric compositions of the dominant aqueous uranyl carbonate complexes are well established, as are their equilibrium constants (Guillaumont et al. 2003):

$$UO_2^{2+}\,(aq) + CO_3^{2-}\,(aq) = UO_2CO_3^{0}\,(aq)$$
$$\log_{10}K^\circ = 9.94 \pm 0.03 \qquad (1)$$

$$UO_2^{2+}\,(aq) + 2CO_3^{2-}\,(aq) = UO_2(CO_3)_2^{2-}\,(aq)$$
$$\log_{10}K^\circ = 16.61 \pm 0.09 \qquad (2)$$

$$UO_2^{2+}\,(aq) + 3CO_3^{2-}\,(aq) = UO_2(CO_3)_3^{4-}\,(aq)$$
$$\log_{10}K^\circ = 21.84 \pm 0.04 \qquad (3)$$

Only three reliable determinations of the solubility product for the following reaction exist (Sergeyeva et al. 1972; Nikolaeva 1976; Grenthe et al. 1984):

$$UO_2CO_3\,(xl) = UO_2^{2+}\,(aq) + CO_3^{2-}\,(aq)$$
$$K^\circ = [UO_2^{2+}][CO_3^{2-}] \qquad (4)$$

The currently accepted value (Guillaumont et al. 2003) of $\log_{10}K^\circ = 14.76 \pm 0.02$ is the weighted average of these three independent values. This value for the solubility product, combined with values for $\Delta G_f^\circ$ ($UO_2^{2+}$) and $\Delta G_f^\circ$ ($CO_3^{2-}$) were used to calculate the $\Delta G_f^\circ$ of rutherfordine (Guillaumont et al. 2003) (Table 1). Entropy, $S^\circ$, and heat capacity, $C_P^\circ$ of rutherfordine were determined experimentally by Gurevich et al. (1987). The currently accepted standard enthalpy of formation value for rutherfordine, $\Delta H_f^\circ = -1691.3 \pm 1.8$ kJ/mol, was calculated from these previously reported $\Delta G_f^\circ$ (Guillaumont et al. 2003) and S° (Gurevich et al. 1987) values.

Cordfunke and O'Hare (1978) and Langmuir (1978) calculated the $\Delta G_f^\circ$ of rutherfordine based on the reported solubility product of Sergeyeva et al. (1972), obtaining $-1561.9 \pm 3.3$ kJ/mol and $-1563.1 \pm 3.4$ kJ/mol, respectively (Table 1). Both studies estimated the entropy, $S^\circ$, of rutherfordine and calculated the enthalpy, $\Delta H_f^\circ$, based on their calculated $\Delta G_f^\circ$ and $S^\circ$ values. Hemingway (1982) calculated the $\Delta H_f^\circ$ of rutherfordine from enthalpy of solution measurements of rutherfordine in HCl. Using the estimated entropy given by Langmuir (1978), Hemingway (1982) calculated $\Delta G_f^\circ$ of $-1577.0 \pm 2.0$ kJ/mol.

Alwan and Williams (1980) reported Gibbs free energy, $\Delta G_f^\circ$, and enthalpy, $\Delta H_f^\circ$, values for synthetic andersonite based on solubility determinations at five temperatures ranging from 273 to 298 K (Table 1). The authors did not include experimental details or auxiliary calculations for their reported $\Delta G_f^\circ$ and $\Delta H_f^\circ$ values and their resulting solubility product for andersonite differs widely from those of bayleyite, swartzite, and liebigite, the other uranyl tricarbonates in their study. Their results are not consistent with the stability fields for minerals of the liebigite group (andersonite, bayleyite, swartzite, and liebigite) (Grenthe et al. 1992). In addition, the temperature range over which they determined solubility is small.

O'Brien and Williams (1983) calculated the $\Delta G_f^\circ$ for synthetic grimselite (Table 1) based on one solubility measurement at 298.2 K. $\Delta H_f^\circ$ was estimated by calculating the solubility product at a

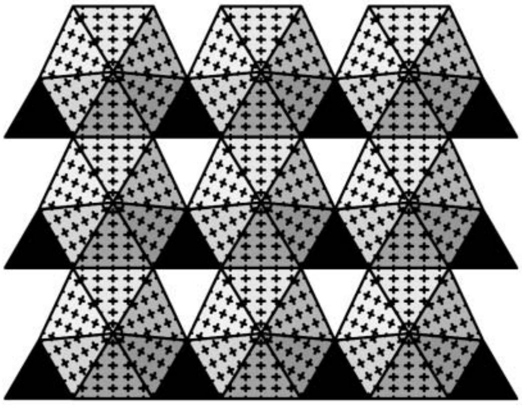

**FIGURE 1.** Polyhedral representation of the crystal structure of rutherfordine. The uranyl hexagonal bipyramids are shown as hatched polyhedra, $CO_3$ as black triangles.

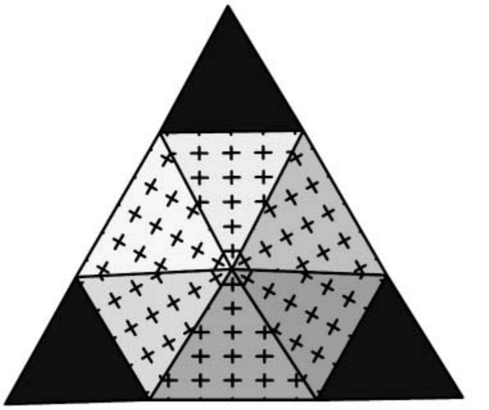

**FIGURE 2.** Polyhedral representation of the uranyl tricarbonate cluster in the structures of andersonite and grimselite.

series of temperatures ranging from 278.8 to 298.2 K. These seven measurements were treated with the Arrhenius equation to obtain $\Delta H^{\circ}_{f}$. Again, only a small range of temperature was studied.

## SYNTHESIS OF URANYL CARBONATES

Rutherfordine was synthesized by placing 0.400 g amorphous $UO_3$ (Strem Chemicals) in 20 mL deionized water; the lack of crystallinity of the $UO_3$ was verified by X-ray powder diffraction. The beaker containing the reactants was placed in a glove box and purged with 70 kPa $CO_2$ for 24 hours. After 24 hours, the microcrystalline precipitate was filtered and dried at room temperature.

Andersonite was obtained following the methods of Meyrowitz and Ross (1961) by the slow addition of 1 mL solution containing 0.354 g $Ca(NO_3)_2(H_2O)_4$ (Alpha Aesar) to 11 mL of solution contain 0.477 g $Na_2CO_3$ (J.T. Baker) and 0.753 g $UO_2(NO_3)_2(H_2O)_6$ (Alpha Aesar). Following 28 days in a sealed vessel, columnar crystals of andersonite up to 2 mm maximum dimension were recovered from the mother solution, rinsed twice with deionized water, and dried in air.

Grimselite was synthesized by the slow addition of 20 mL of solution containing 1.04 g $UO_2(NO_3)_2(H_2O)_6$ (Alpha Aesar) into 80 mL of solution containing 1.06 g $Na_2CO_3$ (J.T. Baker) and 4.14 g $K_2CO_3$ (J.T. Baker). The resulting solution was left to evaporate in air for 28 days at room temperature and pressure. The resulting elongated-columnar crystals, up to 4 mm maximum dimension, were removed from the vessel and rinsed twice with deionized water to remove any impurities.

## ANALYTICAL METHODS

### X-ray diffraction

X-ray powder diffraction patterns were collected for the synthetic analogues of rutherfordine, andersonite, and grimselite using ~4 mg of powder deposited onto the surface of a zero-background oriented silicon wafer. Data were collected using Cu$K\alpha$ radiation and 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. The three powder diffraction patterns exhibit sharp profiles and no peaks attributable to impurity phases.

### Electron microprobe analysis

Synthesis products were examined using a JEOL JXA 8600 Superprobe. A ~40 mg aliquot of each sample was mounted on a half-inch piece of double-sided carbon-coated tape on a round 1 inch glass slide and carbon-coated. Back-scattered electron images established the morphological phase homogeneity of each sample. Energy dispersive spectra were consistent with chemical homogeneity of each sample.

### Thermogravimetry

Thermogravimetric analyses were done for ~25 mg aliquots of synthetic rutherfordine, andersonite, and grimselite using a Netzsch 449 thermal analysis system. Rutherfordine was heated at 10 K/min from 298 K to 923 K. The mass loss for rutherfordine was in agreement with the formula $UO_2CO_3$. Andersonite and grimselite were heated to 1173 K at a rate of 10 K/min, and the total mass lost in each case was in agreement with the ideal chemical formulae $Na_2CaUO_2(CO_3)_3(H_2O)_5$ and $K_3NaUO_2(CO_3)_3H_2O$, respectively. Thus, the samples do not contain excess water.

## CALORIMETRIC MEASUREMENTS

High temperature oxide melt solution calorimetry was used to obtain the drop solution enthalpies, $\Delta H_{ds}$, of rutherfordine, andersonite, and grimselite (Table 2). Measurements were done using a Calvet-type high temperature custom-built calorimeter, details of which are given elsewhere (Navrotsky 1977, 1997). Solution enthalpies for each sample were measured by dropping ~5 mg pressed pellets of material from room temperature, 298 K, into the molten oxide solvent, $3Na_2O$-$4MoO_3$, at calorimetric temperature, 976 K (Table 2). The calorimeter was calibrated using the heat content of $\alpha$-$Al_2O_3$. It was flushed continuously with $O_2$ throughout the experiments to ensure an oxidizing atmosphere.

Prior to the calorimetric experiments, complete dissolution of rutherfordine, grimselite, and andersonite in the solvent at calorimetric conditions was established in a furnace at 976 K. 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 white to yellow indicates that each phase dissolved fully in the melt. Calorimetry was straightforward and problem free, as is the case with other $U^{6+}$ phases (Kubatko et al. 2003; Helean et al. 2002).

Earlier experiments for $UO_3$ confirmed that $U^{6+}$ is the stable oxidation state of U dissolved at low concentrations in $3Na_2O\cdot4MoO_3$ at 976 K (Helean et al. 2002). Thus, the dissolution of rutherfordine, andersonite, and grimselite, likewise, involves no oxidation-reduction. Samples dissolved readily and quickly. $H_2O$ and $CO_2$ were evolved into the gas above the solvent and swept out of the calorimeter by the flowing $O_2$ gas, as demonstrated previously (Navrotsky et al. 1994). The calorimetry, as standard practice, is done using solute concentrations in the dilute (Henry's Law) limit, where the heat of solution does not depend on the concentration of dissolved sample or the presence of other solutes (Navrotsky 1977, 1997).

## RESULTS AND DISCUSSION

The enthalpies of formation of rutherfordine, andersonite, and grimselite from the binary oxides, $\Delta H_{r\text{-}ox}$, at 298 K were calculated from the drop solution enthalpies and from the heat content of the corresponding binary oxides as shown in reactions 5, 6, and 7 (Table 3): (g = gas, l = liquid, xl = crystalline)

$$UO_3\ (xl,\ 298\ K) + CO_2\ (g,\ 298\ K) = UO_2CO_3\ (xl,\ 298\ K) \quad (5)$$
$$\Delta H_{r\text{-}ox} = -99.1 \pm 4.2\ kJ/mol$$

**TABLE 1.** Previously reported values of $\Delta G^{\circ}_{f}$, $\Delta H^{\circ}_{f}$, $S^{\circ}_{298}$, and $C^{\circ}_{p}$ for rutherfordine, andersonite, and grimselite

| | | $\Delta G^{\circ}_{f}$ (kJ/mol) | $\Delta H^{\circ}_{f}$ (kJ/mol) | $S^{\circ}_{m}$ [J/(K·mol)] | $C^{\circ}_{p,m}$ [J/(K·mol)] |
|---|---|---|---|---|---|
| Rutherfordine | $(UO_2)(CO_3)$ | –1564.7 ± 1.8* | –1691.3 ± 1.8† | 144.2 ± 0.3‡ | 120.1 ± 0.1‡ |
| | | –1577.0 ± 2.1§ | –1704.1 ± 2.0§ | 142.7 ± 2.0§ | |
| | | –1561.9 ± 3.3‖ | –1686.1 ± 4.2‖ | 139‖ | |
| | | –1563.1 ± 3.4# | –1689.9 ± 4# | 142.7# | |
| Andersonite | $Na_2Ca(UO_2)(CO_3)_3(H_2O)_5$ | –5651 ± 24** | –5916 ± 36** | | |
| Grimselite | $K_3Na(UO_2)(CO_3)_3(H_2O)$ | –4051.3 ± 1.8†† | –4359.9 ± 1.8†† | | |

* Guillaumont et al. 2003.
† Calculated based on the values of Guillaumont et al. 2003 and Gurevich et al. 1987.
‡ Gurevich et al. 1987.
§ Hemingway 1982.
‖ Cordfunke and O'Hare 1978.
\# Langmuir 1978.
** Alwan and Williams 1980.
†† O'Brien and Williams 1983.

**TABLE 2.** Enthalpies of drop solution, $\Delta H_{ds}$ (kJ/mol), for uranyl carbonates

| | Rutherfordine $(UO_2)(CO_3)$ | | Andersonite $Na_2Ca(UO_2)(CO_3)_3(H_2O)_5$ | | Grimselite $K_3Na(UO_2)(CO_3)_3(H_2O)$ | |
|---|---|---|---|---|---|---|
| | mass (mg) | $\Delta H_{ds}$ (kJ/mol) | mass (mg) | $\Delta H_{ds}$ (kJ/mol) | mass (mg) | $\Delta H_{ds}$ (kJ/mol) |
| | 5.08 | 134.13 | 5.02 | 854.99 | 5.11 | 574.72 |
| | 5.09 | 141.82 | 4.93 | 844.10 | 5.35 | 556.57 |
| | 4.95 | 135.27 | 4.76 | 853.66 | 5.22 | 578.94 |
| | 5.08 | 142.60 | 4.86 | 852.72 | 5.51 | 590.47 |
| | 5.28 | 141.82 | 5.06 | 849.00 | 5.47 | 582.11 |
| | 5.03 | 143.02 | 5.29 | 864.66 | 5.28 | 596.14 |
| | 5.58 | 141.87 | 4.62 | 867.00 | 5.75 | 584.46 |
| | 5.54 | 145.13 | 4.77 | 856.22 | 5.66 | 562.09 |
| | | | | | 5.66 | 559.18 |
| | | | | | 5.54 | 584.86 |
| Average | 140.71 | | | 855.29 | | 576.95 |
| Error | 3.88 | | | 7.56 | | 13.57 |
| Error (%) | 2.75 | | | 0.88 | | 2.35 |

*Notes:* Data were collected using $3Na_2O{\cdot}4MoO_3$ solvent at 976 K. Errors are reported as two standard deviations of the mean.

**TABLE 3.** Thermochemical cycles for rutherfordine, $UO_2CO_3$, andersonite, $Na_2Ca(UO_2)(CO_3)_3(H_2O)_5$, and grimselite, $K_3Na(UO_2)(CO_3)_3(H_2O)$, for the calculation of the enthalpy of formation from the oxides, $\Delta H^{\circ}_{r\text{-}ox}$, enthalpy of formation from the carbonates, $\Delta H^{\circ}_{r\text{-}c}$, and the standard enthalpy of formation, $\Delta H^{\circ}_{f}$, at 298 K

| Reactions | $\Delta H$ (kJ/mol) | | |
|---|---|---|---|
| (1) | $\Delta H_{ds}$ (rutherfordine) | $UO_2CO_3$ (xl, 298 K) = $UO_3$ (soln, 976 K) + $CO_2$ (g, 976 K) | 140.7 ± 3.9 |
| (2) | $\Delta H_{ds}$ (andersonite) | $Na_2Ca(UO_2)(CO_3)_3(H_2O)_5$ (xl, 298 K) = $Na_2O$ (soln, 976 K) + CaO (soln, 976 K) + $UO_3$ (soln, 976 K) + $3CO_2$ (g, 976 K) + $5H_2O$ (g, 976 K) | 855.3 ± 7.6 |
| (3) | $\Delta H_{ds}$ (grimselite) | $K_3Na(UO_2)(CO_3)_3H_2O$ (xl, 298 K) = $11.5K_2O$ (soln, 976 K) + $0.5Na_2O$ (soln, 976 K) + $UO_3$ (soln, 976 K) + $3CO_2$ (g, 976 K) + $H_2O$ (g, 976 K) | 577.0 ± 13.6 |
| (4) | $\Delta H_{ds}$ ($UO_3$) | $UO_3$ (xl, 298 K) = $UO_3$ (soln, 976 K) | 9.5 ± 1.5* |
| (5) | $\Delta H_{ds}$ ($Na_2O$) | $Na_2O$ (xl, 298 K) = $Na_2O$ (soln, 976 K) | –215.8 ± 4.4† |
| (6) | $\Delta H_{ds}$ (CaO) | CaO (xl, 298 K) = CaO (soln, 976 K) | –90.3 ± 1.8† |
| (7) | $\Delta H_{ds}$ ($K_2O$) | $K_2O$ (xl, 298 K) = $K_2O$ (soln, 298 K) | –319.6 ± 4.6‡ |
| (8) | $\Delta H_{hc}$ ($CO_2$) | $CO_2$ (g, 298 K) = $CO_2$ (g, 976 K) | 32.2§ |
| (9) | $\Delta H_{hc}$ ($H_2O$) | $H_2O$ (l, 298 K) = $H_2O$ (g, 976 K) | 69.0§ |
| (10) | $\Delta H^{\circ}_{f}$ ($UO_3$) | U (xl, 298 K) + $1.5O_2$ (g, 298 K) = $UO_3$ (xl, 298 K) | –1223.8 ± 0.8‖ |
| (11) | $\Delta H^{\circ}_{f}$ ($Na_2O$) | 2Na (xl, 298 K) + $0.5O_2$ (g, 298 K) = $Na_2O$ (xl, 298 K) | –414.8 ± 0.3§ |
| (12) | $\Delta H^{\circ}_{f}$ (CaO) | Ca (xl, 298 K) + $0.5O_2$ (g, 298 K) = CaO (xl, 298 K) | –635.1 ± 0.9§ |
| (13) | $\Delta H^{\circ}_{f}$ ($K_2O$) | 2K (xl, 298 K) + $0.5O_2$ (g, 298 K) = $K_2O$ (xl, 298 K) | –363.2 ± 2.1§ |
| (14) | $\Delta H^{\circ}_{f}$ ($CO_2$) | C (g, 298 K) + $O_2$ (g, 298 K) = $CO_2$ (g, 298 K) | –393.5 ± 0.1§ |
| (15) | $\Delta H^{\circ}_{f}$ ($H_2O$) | $H_2$ (g, 298 K) + $0.5O_2$ (g, 298 K) = $H_2O$ (l, 298 K) | –285.8 ± 0.1§ |
| (16) | $\Delta H^{\circ}_{f}$ ($Na_2CO_3$) | 2Na (xl, 298 K) + C (g, 298 K) + $3/2O_2$ (g, 298 K) = $Na_2CO_3$ (xl, 298 K) | –1129 ± 0.3§ |
| (17) | $\Delta H^{\circ}_{f}$ ($CaCO_3$) | Ca (xl, 298 K) + C (g, 298 K) + $3/2O_2$ (g, 298 K) = $CaCO_3$ (xl, 298 K) | –1207 ± 1.3§ |
| (18) | $\Delta H^{\circ}_{f}$ ($K_2CO_3$) | 2K (xl, 298 K) + C (g, 298 K) + $3/2O_2$ (g, 298 K) = $K_2CO_3$ (xl, 298 K) | –1150 ± 2.1# |
| Thermodynamic Cycles | | | |
| **rutherfordine** | | | |
| | $\Delta H_{r\text{-}ox}$ (rutherfordine) = $-\Delta H(1) + \Delta H(4) + \Delta H(8)$ | | |
| | $UO_3$ (xl, 298 K) + $CO_2$ (g, 298 K) = $UO_2CO_3$ (xl, 298 K) | | –99.1 ± 4.2 |
| | $\Delta H_f^{\circ}$ (rutherfordine) = $-\Delta H(1) + \Delta H(4) + \Delta H(8) + H(10) + H(14)$ | | |
| | U (xl, 298 K) + C (g, 298 k) + 2.5 $O_2$ (g, 298 K) = $UO_2CO_3$ (xl, 298 K) | | –1716.4 ± 4.2 |
| **andersonite** | | | |
| | $\Delta H^{\circ}_{r\text{-}c}$ (andersonite) = $\Delta H^{\circ}_{f}$ (andersonite) – $\Delta H^{\circ}_{f}$ (rutherfordine) + $\Delta H(16) + \Delta H(17) + 5\Delta H(15)$ | | |
| | $Na_2CO_3$ (xl, 298 K) + $CaCO_3$ (xl, 298 K) + $UO_2CO_3$ (xl, 298 K) + 5 $H_2O$ (l, 298 K) = $Na_2Ca(UO_2)(CO_3)_3(H_2O)_5$ (xl, 298 K) | | –111.7 ± 0.2 |
| | $\Delta H_{r\text{-}ox} = -\Delta H(2) + \Delta H(5) + \Delta H(6) + \Delta H(4) + 3\Delta H(8) + 5\Delta H(9)$ | | |
| | $Na_2O$ (xl, 298 K) + CaO (xl, 298 K) + $UO_3$ (xl, 298 K) + $3CO_2$ (g, 298 K) + $5H_2O$ (l, 298 K) = $Na_2Ca(UO_2)(CO_3)_3(H_2O)_5$ (xl, 298 K) | | –710.4 ± 9.1 |
| | $\Delta H^{\circ}_{f} = -\Delta H(2) + \Delta H(5) + \Delta H(6) + \Delta H(4) + 3\Delta H(8) + 5\Delta H(9) + \Delta H(11) + \Delta H(12) + \Delta H(10) + 3\Delta H(14) + 5\Delta H(15)$ | | |
| | 2Na (xl, 298 K) + Ca (xl, 298 K) + U (xl, 298 K) + 3C (g, 298 K) + $5H_2$ (g, 298 K) + $8O_2$ (g, 298 K) = $Na_2Ca(UO_2)(CO_3)_3(H_2O)_5$ (xl, 298 K) | | –5593.6 ± 9.1 |
| **grimselite** | | | |
| | $\Delta H^{\circ}_{r\text{-}c}$ (grimselite) = $\Delta H^{\circ}_{f}$ (grimselite) – $\Delta H^{\circ}_{f}$ (rutherfordine) + $0.5\Delta H(16) + 1.5\Delta H(18)$ | | |
| | 1.5 $K_2CO_3$ (xl, 298 K) + 0.5 $Na_2CO_3$ (xl, 298 K) + $UO_2CO_3$ (xl, 298 K) + $H_2O$ (l, 298 K) = $K_3Na(UO_2)(CO_3)_3(H_2O)$ (xl, 298 K) | | –139.6 ± 16.1 |
| | $\Delta H_{r\text{-}ox} = -\Delta H(3) + 0.5\Delta H(5) + 1.5\Delta H(7) + \Delta H(4) + 3\Delta H(8) + \Delta H(9)$ | | |
| | 1.5 $K_2O$ (xl, 298 K) + 0.5 $Na_2O$ (xl, 298 K) + $UO_3$ (xl, 298 K) + $3CO_2$ (g, 298 K) + $H_2O$ (l, 298 K) = $K_3Na(UO_2)(CO_3)_3(H_2O)$ (xl, 298 K) | | –989.3 ± 14.0 |
| | $\Delta H^{\circ}_{f} = -\Delta H(3) + 0.5\Delta H(5) + 1.5\Delta H(7) + \Delta H(4) + 3\Delta H(8) + \Delta H(9) + 0.5\Delta H(11) + 1.5\Delta H(13) + \Delta H(10) + 3\Delta H(14) + \Delta H(15)$ | | |
| | 3K (xl, 298 K) + Na (xl, 298 K) + U (xl, 298 K) + 3C (g, 298 K) + 2H (g, 298 K) + $6O_2$ (g, 298 K) = $K_3Na(UO_2)(CO_3)_3(H_2O)$ (xl, 298 K) | | –4431.6 ± 15.3 |

*Notes:* xl = crystalline, soln = solution, l = liquid, g = gas.

* Helean et al. 2003.

† Table 4.

‡ Molodetsky et al. 2000.

§ Robie and Hemingway 1995.

‖ Robie et al. 1978.

\# Chase 1998.

**TABLE 4.** Thermochemical cycles for the values of $\Delta H_{ds}$ ($K_2O$) and $\Delta H_{ds}$ ($Na_2O$) used in Table 3

| Reactions | $\Delta H$ (kJ/mol) | | |
|---|---|---|---|
| (1) | $\Delta H_{ds}$ ($K_2SO_4$) | $K_2SO_4$ (xl, 298 K) = $K_2O$ (soln, 973 K) + $SO_3$ (soln, 973 K) | 153.4 ± 1.8* |
| (2) | $\Delta H_{ds}$ ($Na_2SO_4$) | $Na_2SO_4$ (xl, 298 K) = $Na_2O$ (soln, 973 K) + $SO_3$ (soln, 973 K) | 155.7 ± 2.3* |
| (3) | $\Delta H_{ds}$ ($SO_3$) | $SO_3$ (g, 298 K) = $SO_3$ (soln, 973 K) | –205.8 ± 3.7† |
| (4) | $\Delta H^\circ_f$ ($K_2SO_4$) | 2K (xl, 298 K) + S (xl, 298 K) + $2O_2$ (g, 298 K) = $K_2SO_4$ (xl, 298 K) | –1437.7 ± 0.5† |
| (5) | $\Delta H^\circ_f$ ($Na_2SO_4$) | 2Na (xl, 298 K) + S (xl, 298 K) + $2O_2$ (g, 298 K) = $Na_2SO_4$ (xl, 298 K) | –1387.8 ± 0.4† |
| (6) | $\Delta H^\circ_f$ ($K_2O$) | 2K (xl, 298 K) + $0.5O_2$ (g, 298 K) = $K_2O$ (xl, 298 K) | –363.2 ± 2.1† |
| (7) | $\Delta H^\circ_f$ ($Na_2O$) | 2Na (xl, 298 K) + $0.5O_2$ (g, 298 K) = $Na_2O$ (xl, 298 K) | –414.8 ± 0.3† |
| (8) | $\Delta H^\circ_f$ ($SO_3$) | S (xl, 298 K) + $1.5O_2$ (g, 298 K) = $SO_3$ (g, 298K) | –395.7 ± 0.7† |
| Thermodynamic Cycles | | | |
| $\Delta H_{ds}$ ($K_2O$) = $\Delta H$(1) – $\Delta H$(3) + $\Delta H$(4) – $\Delta H$(6) – $\Delta H$(8) | | | –319.6 ± 4.7 |
| $K_2O$ (xl, 298 K) = $K_2O$ (soln, 973 K) | | | |
| $\Delta H_{ds}$ ($Na_2O$) = $\Delta H$(2) – $\Delta H$(3) + $\Delta H$(5) – $\Delta H$(7) – $\Delta H$(8) | | | –215.8 ± 4.4 |
| $Na_2O$ (xl, 298 K) = $Na_2O$ (soln, 973 K) | | | |

*Notes:* xl = crystalline, soln = solution, g = gas.
* Drouet and Navrotsky 2003.
† Robie and Hemingway 1995.

$Na_2O$ (xl, 298 K) + CaO (xl, 298 K) + $UO_3$ (xl, 298 K) + $3CO_2$ (g, 298 K) + $5H_2O$
(l, 298 K) = $Na_2CaUO_2(CO_3)_3(H_2O)_5$ (xl, 298 K)
$\Delta H_{r\text{-}ox} = -710.6 \pm 9.1$ kJ/mol (6)

$1.5K_2O$ (xl, 298 K) + $Na_2O$ (xl, 298 K) + $UO_3$ (xl, 298 K) + $3CO_2$ (g, 298 K) + $H_2O$
(l, 298 K) = $K_3NaUO_2(CO_{3\neq})_3H_2O$ (xl, 298 K)
$\Delta H_{r\text{-}ox} = -989.3 \pm 14.0$ kJ/mol (7)

The $\Delta H_{r\text{-}ox}$ values are exothermic, indicating these phases are stable in enthalpy relative to the oxides at 298 K. These values become increasingly exothermic from rutherfordine to andersonite to grimselite.

This trend reflects the Lewis acid-base chemistry of the oxides involved. Considering the primary acid-base reactions that involve oxide ions, from basic to acidic oxides, two primary reactions can be written:

$$UO_3 + CO_2 = UO_2^{2+} + CO_3^{2-} \quad (8)$$

$$M_2O \text{ (or MO)} + CO_2 = 2M^+ \text{ (or } M^{2+}) + CO_3^{2-} \quad (9)$$

Reaction 8 can be identified with reaction 5, the formation of rutherfordine from uranium trioxide and carbon dioxide, with an enthalpy of –99.1 ± 4.2 kJ/mol. This large exothermic value reflects the stability of the uranyl ($UO_2^{2+}$) ion and its electrostatic interaction with the carbonate ion. Assuming these interactions contribute similarly to the energetics of andersonite and grimselite, then their additional energetic stabilization relates, at least in part, to the enthalpy of reaction 8 and the number of moles of $MCO_3$ and $M_2CO_3$ involved, as well as to hydration effects and further interactions among the species in the solid state.

The enthalpy of formation of binary carbonates, reaction 9, becomes more exothermic as the oxide becomes more basic, in the order Ca, Na, K. Thus, it is reasonable that the enthalpy of formation of grimselite (involving 1.5 mols of $K_2CO_3$ and 0.5 mols of $Na_2CO_3$) is more exothermic than that of andersonite (involving 1 mol of $Na_2CO_3$ and 1 mol of $CaCO_3$), as indeed is observed.

To subtract, to a first approximation, the effects of carbonate-forming acid-base reactions, consider the energetics of formation of andersonite and grimselite from the corresponding carbonates plus water:

$Na_2CO_3$ (xl, 298 K) + $CaCO_3$ (xl, 298 K) + 5 $H_2O$ (l, 298 K) + $UO_2CO_3$ (xl, 298 K) = $Na_2CaUO_2(CO_3)_3(H_2O)_{5\neq}$ (xl, 298 K)
$\Delta H^\circ_{r\text{-}carb} = -111.7 \pm 10.2$ kJ/mol (10)

$1.5K_2CO_3$ (xl, 298 K) + $0.5Na_2CO_3$ (xl, 298 K) + $H_2O$ (l, 298 K) + $UO_2CO_3$ (xl, 298 K) = $K_3NaUO_2(CO_3)_3H_2O_{\neq}$ (xl, 298 K)
$\Delta H^\circ_{r\text{-}carb} = -139.6 \pm 16.1$ kJ/mol (11)

These values are still strikingly exothermic. This additional stabilization may arise from several factors, including the role of hydration. On the basis of one mole of $H_2O$, the values are even more disparate, –22.4 ± 2.0 kJ/mol for andersonite and –139.6 ± 16.1 kJ/mol for grimselite. The enthalpies of formation of hydrated carbonates are much less exothermic; thus for the reactions (Robie and Hemingway 1995):

$CaCO_3$ (calcite) + $H_2O$ (l) = $CaCO_3(H_2O)$ (monohydrocalcite)
$\Delta H^\circ$ (298 K) = –5.1 kJ/mol (12)

$CaCO_3$ (calcite) + $6H_2O$ (l) = $CaCO_3(H_2O)_6$ (ikaite)
$\Delta H^\circ$ (298 K) = –29.2 kJ/mol (13)

$Na_2CO_3$ + $H_2O$ (l) = $Na_2CO_3(H_2O)$ (thermonatrite)
$\Delta H^\circ$ (298 K) = –14.7 kJ/mol (14)

For comparison, the hydration of Na, K, and Ca as cations in zeolites, when the cations are located within large cages, is typically exothermic by 30–40 kJ/mol of liquid water. Thus, it appears unlikely that hydration contributes more than a small portion of the additional stabilization observed in uranyl carbonates. Similar conclusions appear to hold for uranyl oxide hydrates (Kubatko et al. 2006).

Double carbonates exist in the $K_2CO_3$-$CaCO_3$ system and their enthalpies of formation have been determined (Navrotsky et al. 1997):

$K_2CO_3$ (xl) + $CaCO_3$ (calcite) = $K_2Ca(CO_3)_2$ (butschlite)
$\Delta H^\circ$ (298 K) = –38.7 ± 3.2 kJ/mol (15)

$K_2CO_3$ (xl) + $CaCO_3$ (calcite) = $K_2Ca(CO_3)_2$ (fairchildite)
$\Delta H^\circ$ (298 K) = –5.1 ± 3.3 kJ/mol (16)

$$K_2CO_3\ (\mathrm{xl}) + 2CaCO_3\ (\mathrm{calcite}) = K_2Ca_2(CO_3)_3\ (\mathrm{xl})$$
$$\Delta H^\circ\ (298\ \mathrm{K}) = -7.2 \pm 5.8\ \mathrm{kJ/mol} \tag{17}$$

These energetics suggest that some additional stabilization associated with changes in cation coordination environments are possible. Whereas in butschlite, fairchildite, and $K_2Ca_2(CO_3)_3$ the $CO_3$ triangle is strongly bonded to K or Ca polyhedra by sharing an edge, in the structures of rutherfordine, andersonite, and grimselite the $CO_3$ triangle is strongly bonded to uranyl polyhedra and only shares vertices with Na and Ca or K polyhedra. We predict more stabilization in edge-sharing of a $CO_3$ group than in corner-sharing, as the $CO_3$ is then more tightly bonded.

The $\Delta H_{\mathrm{r\text{-}ox}}$ (andersonite) is 278.7 kJ/mol less exothermic than $\Delta H_{\mathrm{r\text{-}ox}}$ (grimselite). Since grimselite contains K and Na, increased cation basicity appears to correlate with increased stability in formation from carbonates as well as from oxides.

The calorimetric data permit calculation of the standard enthalpy of formation from the elements, $\Delta H_{\mathrm{f}}^{\mathrm{o}}$, at 298 K for rutherfordine, andersonite, and grimselite in the following reactions (Table 3):

$$U\ (\mathrm{xl, 298\ K}) + C\ (\mathrm{xl, 298\ K}) + 5/2O_2\ (\mathrm{g, 298\ K}) = UO_2CO_3\ (\mathrm{xl, 298\ K})$$
$$\Delta H_{\mathrm{f}}^{\circ} = -1716.4 \pm 4.2\ \mathrm{kJ/mol} \tag{18}$$

$$2Na\ (\mathrm{xl, 298\ K}) + Ca\ (\mathrm{xl, 298\ K}) + U\ (\mathrm{xl, 298\ K}) + 3C\ (\mathrm{xl, 298\ K}) + 5H_2\ (\mathrm{g, 298\ K}) + 8O_2\ (\mathrm{g, 298\ K}) = Na_2CaUO_2(CO_3)_3(H_2O)_5\ (\mathrm{xl, 298\ K})$$
$$\Delta H_{\mathrm{f}}^{\mathrm{o}} = -5593.8 \pm 9.1\ \mathrm{kJ/mol} \tag{19}$$

$$3K\ (\mathrm{xl, 298\ K}) + Na\ (\mathrm{xl, 298\ K}) + U\ (\mathrm{xl, 298\ K}) + 3C\ (\mathrm{xl, 298\ K}) + H_2\ (\mathrm{g, 298\ K}) + 6O_2\ (\mathrm{g, 298\ K}) = Na_2CaUO_2(CO_3)_3(H_2O)_5\ (\mathrm{xl, 298\ K})$$
$$\Delta H_{\mathrm{f}}^{\mathrm{o}} = -4431.6 \pm 15.3\ \mathrm{kJ/mol} \tag{20}$$

These $\Delta H_{\mathrm{f}}^{\mathrm{o}}$ values are useful for calculating enthalpies for other reactions of interest, particularly those involving aqueous species.

The previously reported enthalpy of formation of rutherfordine is –1691.3 ± 1.8 kJ/mol (Guillaumont et al. 2003). Previous values of $\Delta H_{\mathrm{f}}^{\mathrm{o}}$ for andersonite (Alwan and Williams 1980) and grimselite (O'Brien and Williams 1983) were estimated based on solubility measurements at various temperatures. However, because of the assumptions needed for these calculations, and especially the small temperature range of measurement, we consider our new values of enthalpy of formation of rutherfordine, andersonite, and grimselite more direct and more reliable. Although the previous studies provide some free energy data, attempts to obtain entropies of formation, either from the temperature dependence of solubilities or by combining those free energies with our newly measured enthalpies, lead to unacceptably high propagated uncertainties in both the entropy of formation, $\Delta S_{\mathrm{f}}$, and the standard entropy, $S^{\mathrm{o}}$. Therefore we choose not to present "preferred" values of entropies and free energies at this time. Measurement, by cryogenic adiabatic calorimetry, of the heat capacities of these materials would be highly desirable.

Increasingly negative enthalpies of formation from rutherfordine to andersonite to grimselite reflect the dominance of Lewis acid-base chemistry of the oxides involved. This suggests that the thermodynamically stable uranyl phases in uranium-bearing soils may be those with the strongest Lewis acid-base chemical reaction. However, the data presented here suggest that additional favorable reactions, such as hydration or cation environments, also contribute to the stabilization in enthalpy. Further calorimetric data on uranyl minerals, particularly those relevant to storage and remediation of nuclear waste, are necessary.

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## REFERENCES CITED

Alwan, A.K. and Williams, P.A. (1980) The aqueous chemistry of uranium minerals. Part 2. Minerals of the liebigite group. Mineralogical Magazine, 43, 665–667.

Buck, E.C., Brown, N.R., and Dietz, N.L. (1996) Contaminant uranium phases and leaching at the Fernald Site in Ohio. Environmental Science and Technology, 30, 81–88.

Chase, M.W. (1998) NIST-JANAF Thermochemical Tables, Fourth Edition, Monograph No. 9 (Part I and Part II), 1952 p. American Institute of Physics, Melville, New York.

Christ, C.L. and Clark, J.R. (1955) Some observations on rutherfordine. American Mineralogist, 41, 844–850.

Ciavatta, L., Ferri, D., Grimaldi, M., Palombari, R., and Salvatore, F. (1979) Dioxouranium (VI) carbonate complexes in acid solution. Journal of Inorganic and Nuclear Chemistry, 41, 1175–1182.

Ciavatta, L., Ferri, D. Grenthe, I., and Salvatore, F. (1981) The first acidification step of the tris(carbonato)dioxouranate(VI) ion, $UO_2(CO_3)_3^{4-}$. Inorganic Chemistry, 20, 463–467.

Clark, D.L., Hobart, D.E., and Neu., M.P. (1995) Actinide carbonate complexes and their importance in actinide environmental chemistry. Chemical Reviews, 95, 25–48.

Cordfunke, E.P.H. and O'Hare, P.A.G. (1978) The chemical thermodynamics of actinide elements and compounds: Part 3. Miscellaneous actinide compounds. Vienna, 83 p. International Atomic Energy Agency.

Drouet, C. and Navrotsky, A. (2003) Synthesis, characterization and thermochemistry of K-Na-$H_3O$ jarosites. Geochimica et Cosmochimica Acta, 63, 2063–2076.

Finch, R., Cooper, M., and Hawthorne, F. (1999) Refinement of the crystal structure of rutherfordine. Canadian Mineralogist, 37, 929–938.

Finn, P., Hoh, J., Wolf, S., Slater, S., and Bates, J. (1996) The release of uranium, plutonium, cesium, strontium, technetium and iodine from spent nuclear fuel under unsaturated conditions. Radiochimica Acta, 74, 65–71.

Frondel, C. and Meyrowitz, R. (1956) Studies of uranium minerals (XIX): rutherfordine, diderichite, and clarkeite. American Mineralogist, 41, 127–133.

Fuller, C.C., Bargar, J.R., Davis, J.A. and Piana, M.J. (2002) Mechanisms of uranium interactions with hydroxyapatite: implications for ground water remediation. Environmental Science and Technology, 36, 58–65.

Grenthe, I., Ferri, D., Salvatore, F., and Riccio, G. (1984) Studies on metal carbonate equilibria: Part 10. A solubility study of the complex formation in the uranium (VI) water-carbon dioxide system at 25°C. Journal of the Chemical SocietyóDalton Transactions. 2439–2443.

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., and Rand, M. (2003) Update on the Chemical Thermodynamics of Uranium, Neptunium, and Plutonium, Americium, and Technetium, 919 p. Elsevier, Amsterdam.

Gurevich, V.M., Seregeyeva, E.I., Gavrichev, K.S., Gorbunov, V.E., and Khodakovsky, I.L. (1987) Low temperature specific heat of $UO_2CO_3$. Russian Journal of Physical Chemistry, 61, 856–857.

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, $Ca_{0.93}Ce_{1.00}Ti_{2.035}O_{7.00}$, U-pyrochlore, $Ca_{1.46}U^{4+}_{0.23}U^{6+}_{0.46}Ti_{1.85}O_{7.00}$ and Gd-pyrochlore, $Gd_2Ti_2O_7$: 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 temperaturesóPreliminary models for the origin of coffinite deposits.USGS Open-File Report 82–619.

Kubatko, K.A., Helean, K., Navrotsky, A., and Burns, P.C. (2003) Stability of peroxide containing uranyl minerals. Science, 302, 1191–1193.

Kubatko, K.A., Helean, K., Navrotsky A., Burns, P.C. (2006) Thermodynamics of uranyl minerals: Enthalpies of formation of uranyl oxide hydrates. American Mineralogist, in press.

Langmuir, D. (1978) U solution mineral equilibria at low temperatures with applications to sedimentary ore deposits. Geochimica et Cosmochimica Acta, 42, 547–569.

Lemire, R.J. and Tremaine, P.R. (1980): Uranium and plutonium equilibria in aqueous solutions to 200 °C. Journal of Chemical and Engineering Data, 25, 361–370.

Macaskie, L.E. and Lloyd, J.R. (2002) Microbial interactions with radioactive wastes and potential applications. In F.R. Livens and M. Keith-Roach, Eds., Interactions of microorganisms with radionuclides. Elsevier, Oxford.

Marckwald, W. (1906) Über Uranerze aus Deutsh-Ostafrika. Centralblatt Mineralogy, 763.

Meyrowitz, R. and Ross, D. (1961) The synthesis of large crystals of andersonite. U.S. Geological Survey Professional Papers, 424B, 266.

Molodetsky, I., Navrotsky, A., DiSalvo, F., and Lerch, M. (2000) Energetics of oxidation of oxynitrites: Zr-N-O, Y-Zr-N-O, and Mg-Zr-N-O. Journal of Materials Research, 15, 2558–2570.

Navrotsky, A. (1977) Recent progress and new directions in high T calorimetry. Physics and Chemistry of Minerals, 2, 89–104.

———(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., and 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, 1099–1109.

Navrotsky, A., Putnam, R.L., Winbo, C., and Rosen, E. (1997) Thermochemistry of double carbonates in the $K_2CO_3$-$CaCO_3$ system. American Mineralogist, 82, 546–548.

Nikolaeva, N.M. (1976) Solubility product of $UO_2CO_3$ at elevated temperature. Izvestiya Sibirskogo Otdeleniya Akademii Nauk SSSR Seriya Khimicheskikh Nauk, 6, 30–31.

O'Brien, T.J. and Williams, P.A. (1983) The aqueous chemistry of uranium minerals. 4. Schröckingerite, grimselite, and related alkali uranyl carbonates. Mineralogical Magazine, 47, 69–73.

Robel, X. (1983) Chemical thermodynamics, Gmelin handbook of inorganic chemistry, 8th edition, Uranium, vol. A6. Springer-Verlag, Berlin.

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.

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. 456 p.

Sergeyeva, E.I., Nikitin, A.A., Khodakovsky, I.L., and Naumov, G.B. (1972) Experimental investigation of equilibria in the system $UO_3$-$CO_2$-$H_2O$ in 25–200 °C temperature interval. Geochemistry International, 11, 900–910.

Wronkiewicz, D., Bates, J., Wolf, S., and 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

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 American Chemical Society, 222, 55-GEOC Part 1.

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