Thermodynamics of uranyl minerals: Enthalpies of formation of rutherfordine, \( \text{UO}_2\text{CO}_3 \), andersonite, \( \text{Na}_2\text{CaUO}_2\text{(CO}_3\text{)}_3(\text{H}_2\text{O})_5 \), and grimselite, \( \text{K}_3\text{NaUO}_2\text{(CO}_3\text{)}_3\text{(H}_2\text{O})_6 \)

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**ABSTRACT**

Enthalpies of formation of rutherfordine, \( \text{UO}_2\text{CO}_3 \), andersonite, \( \text{Na}_2\text{CaUO}_2\text{(CO}_3\text{)}_3(\text{H}_2\text{O})_5 \), and grimselite, \( \text{K}_3\text{NaUO}_2\text{(CO}_3\text{)}_3(\text{H}_2\text{O})_6 \), have been determined using high-temperature oxide melt solution calorimetry. The enthalpy of formation of rutherfordine from the binary oxides, \( \Delta H_{f,\text{r-ox}} \), is \(-99.1 \pm 4.2 \) kJ/mol for the reaction \( \text{UO}_2 \text{(xI, 298 K)} + \text{CO}_2 \text{(g, 298 K)} = \text{UO}_2\text{CO}_3 \text{(xI, 298 K)} \). The \( \Delta H_{f,\text{r-ox}} \) for andersonite is \(-710.4 \pm 9.1 \) kJ/mol for the reaction \( \text{Na}_2\text{O} \text{(xI, 298 K)} + \text{CaO} \text{(xI, 298 K)} + \text{UO}_3 \text{(xI, 298 K)} + 3\text{CO}_2 \text{(g, 298 K)} + 5\text{H}_2\text{O} \text{(l, 298 K)} = \text{Na}_2\text{CaUO}_2\text{(CO}_3\text{)}_3(\text{H}_2\text{O})_5 \text{(xI, 298 K)} \). The \( \Delta H_{f,\text{r-ox}} \) for grimselite is \(-989.3 \pm 14.0 \) kJ/mol for the reaction 1.5 \( \text{K}_2\text{O} \text{(xI, 298 K)} + 0.5\text{Na}_2\text{O} \text{(xI, 298 K)} + \text{UO}_3 \text{(xI, 298 K)} + 3\text{CO}_2 \text{(g, 298 K)} + \text{H}_2\text{O} \text{(l, 298 K)} = \text{K}_3\text{NaUO}_2\text{(CO}_3\text{)}_3(\text{H}_2\text{O})_6 \text{(xI, 298 K)} \). The standard enthalpies of formation from the elements, \( \Delta H_f \), are \(-1716.4 \pm 4.2 \), \(-5593.6 \pm 9.1 \), and \(-4431.6 \pm 15.3 \) 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 \( \text{UO}_2\text{CO}_3 \), \( \text{K}_2\text{CO}_3 \), and \( \text{Na}_2\text{CO}_3 \) or \( \text{CaCO}_3 \), andersonite and grimselite are energetically stable by 111.7 \pm 10.2 and 139.6 \pm 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 \( \text{U}^{VI} \), 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). 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, \( \text{UO}_2\text{(CO}_3\text{)}_3 \); andersonite, \( \text{Na}_2\text{CaUO}_2\text{(CO}_3\text{)}_3(\text{H}_2\text{O})_5 \); and grimselite, \( \text{K}_3\text{NaUO}_2\text{(CO}_3\text{)}_3(\text{H}_2\text{O})_6 \).

**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 \( \text{UO}_3^{2+} \) uranyl ions that are coordinated by six O atoms arranged at the equatorial vertices of uranyl hexagonal bipyramids. Each uranyl...
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 \([\text{UO}_2\text{(CO}_3\text{)}_3]^{4–}\). In each structure the tricarbonate clusters are connected only 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):

\[
\text{UO}_2^{2+} \text{(aq)} + \text{CO}_3^{2–} \text{(aq)} = \text{UO}_2\text{CO}_3^– \text{(aq)}
\]

\[
\log_{10}K^\text{'} = 9.94 \pm 0.03
\]

\(1\)

\[
\text{UO}_2^{2+} \text{(aq)} + 2\text{CO}_3^{2–} \text{(aq)} = \text{UO}_2\text{(CO}_3\text{)}_2^{2–} \text{(aq)}
\]

\[
\log_{10}K^\text{'} = 16.61 \pm 0.09
\]

\(2\)

\[
\text{UO}_2^{2+} \text{(aq)} + 3\text{CO}_3^{2–} \text{(aq)} = \text{UO}_2\text{(CO}_3\text{)}_3^– \text{(aq)}
\]

\[
\log_{10}K^\text{'} = 21.84 \pm 0.04
\]

\(3\)

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

\[
\text{UO}_2\text{CO}_3 \text{(xl)} = \text{UO}_2^{2+} \text{(aq)} + \text{CO}_3^{2–} \text{(aq)}
\]

\[
K^\text{'} = [\text{UO}_2^{2+}][\text{CO}_3^{2–}]
\]

\(4\)

The currently accepted value (Guillaumont et al. 2003) of \(\log_{10}K^\text{'} = 14.76 \pm 0.02\) is the weighted average of these three independent values. This value for the solubility product, combined with values for \(\Delta G^\text{'}_f\) (UO\(_2^{2+}\)) and \(\Delta G^\text{'}_f\) (CO\(_3^{2–}\)) were used to calculate the \(\Delta G^\text{'}_f\) of rutherfordine (Guillaumont et al. 2003) (Table 1). Entropy, \(S^\text{'}\), and heat capacity, \(C^\text{'}_P\) of rutherfordine were determined experimentally by Gurevich et al. (1987). The currently accepted standard enthalpy of formation value for rutherfordine, \(\Delta H^\text{'}_f = −1691.3 \pm 1.8\ \text{kJ/mol}\), was calculated from these previously reported \(\Delta G^\text{'}_f\) (Guillaumont et al. 2003) and \(S^\text{'}\) (Gurevich et al. 1987) values.

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

Alwan and Williams (1980) reported Gibbs free energy, \(\Delta G^\text{'}_f\), and enthalpy, \(\Delta H^\text{'}_f\), 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 \(\Delta G^\text{'}_f\) and \(\Delta H^\text{'}_f\) 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 \(\Delta G^\text{'}_f\) for synthetic grimselite (Table 1) based on one solubility measurement at 298.2 K. \(\Delta H^\text{'}_f\) was estimated by calculating the solubility product at a

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**FIGURE 1.** Polyhedral representation of the crystal structure of rutherfordine. The uranyl hexagonal bipyramids are shown as hatched polyhedra, CO\(_3^2–\) 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 $\Delta H^\circ$ 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$_2$O)$_4$ (Alpha Aesar) to 11 mL of solution contain 0.477 g Na$_2$CO$_3$ (J.T. Baker) and 0.753 g UO$_2$(NO$_3$)$_2$(H$_2$O)$_4$ (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$_2$O)$_4$ (Alpha Aesar) into 80 mL of solution containing 1.06 g Na$_2$CO$_3$ (J.T. Baker) and 4.14 g K$_2$CO$_3$ (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 CuKα radiation and a Rigaku Miniflex diffractometer over the 20 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 ideal chemical formulae Na$_2$Ca(UO$_2$)(CO$_3$)$_3$(H$_2$O)$_5$ and KNa$_3$UO$_2$(CO$_3$)$_3$(H$_2$O)$_6$, 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).

**RESULTS AND DISCUSSION**

The enthalpies of formation of rutherfordine, andersonite, and grimselite from the binary oxides, $\Delta H_{\text{r-ox}}$, 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)

$$\text{UO}_2(\text{g}, 298 \text{ K}) + \text{CO}_2(\text{g}, 298 \text{ K}) = \text{UO}_2\text{CO}_3(\text{xl}, 298 \text{ K}) \quad (5)$$

$$\Delta H_{\text{r-ox}} = -99.1 \pm 4.2 \text{ kJ/mol}$$

**TABLE 1. Previously reported values of $\Delta G^\circ$, $\Delta H^\circ$, $S^\circ$, and $C^\circ_p$ for rutherfordine, andersonite, and grimselite**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta G^\circ$ (kJ/mol)</th>
<th>$\Delta H^\circ$ (kJ/mol)</th>
<th>$S^\circ$ [J/(K·mol)]</th>
<th>$C^\circ_p$ [J/(K·mol)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rutherfordine</td>
<td>$-1564.7 \pm 1.8^*$</td>
<td>$-1691.3 \pm 1.8^*$</td>
<td>$144.2 \pm 0.3^*$</td>
<td>$120.1 \pm 0.1^*$</td>
</tr>
<tr>
<td>Andersonite</td>
<td>$-1577.0 \pm 2.1^</td>
<td>$</td>
<td>$-1704.1 \pm 2.0^</td>
<td>$</td>
</tr>
<tr>
<td>Grimselite</td>
<td>$-1563.1 \pm 3.4^</td>
<td>$</td>
<td>$-1686.1 \pm 4.2^</td>
<td>$</td>
</tr>
</tbody>
</table>

* 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.
** Alwan and Williams 1980.
†† O’Brien and Williams 1983.
TABLE 2. Enthalpies of drop solution, ∆H_DS (kJ/mol), for uranyl carbonates

<table>
<thead>
<tr>
<th></th>
<th>Rutherfordine</th>
<th>Andersonite</th>
<th>Grimselite</th>
</tr>
</thead>
<tbody>
<tr>
<td>(UO₂)(CO₃)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mass (mg)</td>
<td>5.08</td>
<td>4.95</td>
<td>5.00</td>
</tr>
<tr>
<td>∆H_DS (kJ/mol)</td>
<td>134.13</td>
<td>135.27</td>
<td>141.82</td>
</tr>
<tr>
<td></td>
<td>5.09</td>
<td>4.93</td>
<td>5.06</td>
</tr>
<tr>
<td></td>
<td>5.08</td>
<td>4.76</td>
<td>5.29</td>
</tr>
<tr>
<td></td>
<td>5.03</td>
<td>4.86</td>
<td>5.29</td>
</tr>
<tr>
<td></td>
<td>5.08</td>
<td>5.06</td>
<td>5.29</td>
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<td></td>
<td>5.03</td>
<td>5.06</td>
<td>5.29</td>
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<td></td>
<td>5.08</td>
<td>4.77</td>
<td>5.29</td>
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<td>5.03</td>
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<td>5.29</td>
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<td></td>
<td>5.08</td>
<td>5.06</td>
<td>5.29</td>
</tr>
<tr>
<td></td>
<td>5.03</td>
<td>5.06</td>
<td>5.29</td>
</tr>
<tr>
<td>Average</td>
<td>140.71</td>
<td>855.29</td>
<td>576.95</td>
</tr>
<tr>
<td>Error (%)</td>
<td>2.75</td>
<td>0.88</td>
<td>2.35</td>
</tr>
</tbody>
</table>

Notes: Data were collected using 3Na₂O·4MoO₃ solvent at 976 K. Errors are reported as two standard deviations of the mean.

TABLE 3. Thermochemical cycles for rutherfordine, UO₂CO₃, andersonite, Na₂Ca(UO₂)(CO₃)(H₂O)₅, and grimselite, K₃Na(UO₂)(CO₃)(H₂O), for the calculation of the enthalpy of formation from the oxides, ∆H°_r-ox, enthalpy of formation from the carbonates, ∆H°_c, and the standard enthalpy of formation, ∆H° at 298 K

<table>
<thead>
<tr>
<th></th>
<th>Rutherfordine</th>
<th>Andersonite</th>
<th>Grimselite</th>
</tr>
</thead>
<tbody>
<tr>
<td>(UO₂)(CO₃)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UO₂(g, 298 K)  + C (g, 298 K) + 2.5 O₂ (g, 298 K) = UO₂CO₃ (g, 298 K) –1716.4 ± 4.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₂CO₃ (g, 298 K) + CaCO₃ (g, 298 K) + UO₂CO₃ (g, 298 K) + 5 H₂O (l, 298 K) = Na₂Ca(UO₂)(CO₃)(H₂O)₅ (g, 298 K) –111.7 ± 0.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UO₃ (g, 298 K) + CO₂ (g, 298 K) = UO₂CO₃ (g, 298 K) –99.1 ± 4.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.5 K₂O (g, 298 K) + 0.5 Na₂O (g, 298 K) + UO₃ (g, 298 K) + 3CO₂ (g, 298 K) + H₂O (l, 298 K) = K₃Na(UO₂)(CO₃)(H₂O) (g, 298 K) –139.6 ± 16.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.5 K₂O (g, 298 K) + 0.5 Na₂O (g, 298 K) + UO₃ (g, 298 K) + 3CO₂ (g, 298 K) + H₂O (l, 298 K) = K₃Na(UO₂)(CO₃)(H₂O) (g, 298 K) –989.3 ± 14.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3K (g, 298 K) + Na (g, 298 K) + U (g, 298 K) + 3C (g, 298 K) + 2H (g, 298 K) + 6O₂ (g, 298 K) = K₃Na(UO₂)(CO₃)(H₂O) (g, 298 K) –4431.6 ± 15.3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notes: xl = crystalline, soln = solution, l = liquid, g = gas.
† Table 4.
‡ Molodetsky et al. 2000.
§ Robie and Hemingway 1995.
|| Robie et al. 1978.
†† Chase 1998.
reactions can be written:

\[ \text{Na}_2\text{O} (s) + \text{CaCO}_3 (l) = \text{K}_2\text{Ca} (\text{CO}_3)_2 (l) \]

plus water:

\[ \text{K}_2\text{CO}_3 (l) + \text{CaCO}_3 (l) = \text{K}_2\text{Ca} (\text{CO}_3)_2 (l) \]

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\(_2\)O, 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):

\[ \Delta H_{\text{f, carb}} = -319.6 \pm 4.7 \text{ kJ/mol} \]

\[ \Delta H_{\text{f, carb}} = -215.8 \pm 4.4 \text{ kJ/mol} \]

The \( \Delta H_{\text{f, ex}} \) 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:

\[ \text{UO}_3 + \text{CO}_2 = \text{UO}_2^2+ + \text{CO}_3^2- \]

\[ \text{M}_2\text{O} (\text{or MO}) + \text{CO}_2 = 2\text{M}^+ (\text{or M}^{2+}) + \text{CO}_3^2- \]

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\(_2\)CO\(_3\) 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\(_2\)CO\(_3\) and 0.5 mols of Na\(_2\)CO\(_3\)) is more exothermic than that of andersonite (involving 1 mol of Na\(_2\)CO\(_3\) and 1 mol of Ca\(_2\)CO\(_3\)), 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.
K\(_2\)CO\(_3\)(s) + 2CaCO\(_3\) (calcite) = K\(_2\)Ca\(_2\)(CO\(_3\))\(_3\) (s) \\
\Delta H^\circ (\text{mol}^{-1}) = -7.2 \pm 5.8 \text{ kJ/mol} (17)

These energetics suggest that some additional stabilization associated with changes in cation coordination environments are possible. Whereas in butschlite, fairchildite, and K\(_2\)Ca\(_2\)(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 \(\Delta H^\circ\) (andersonite) is 278.7 kJ/mol less exothermic than \(\Delta H^\circ\) (grimselite). Since grimselite contains K and Na, increased cation basicity appears to correlate with increased stabilization in formation from carbonates as well as from oxides.

The calorimetric data permit calculation of the standard enthalpy of formation from the elements, \(\Delta H^\circ_f\), at 298 K for rutherfordine, andersonite, and grimselite in the following reactions (Table 3):

\[
\text{U (s, 298 K) + C (s, 298 K) + 5/2O}_2 (g, 298 K) = \text{UO}_2\text{CO}_3 (s, 298 K) \\
\Delta H^\circ_f = -1716.4 \pm 4.2 \text{ kJ/mol}
\]

\[
2\text{Na (s, 298 K) + Ca (s, 298 K) + U (s, 298 K) + 3C (s, 298 K) + 5H}_2 (g, 298 K) + 8O}_2 (g, 298 K) = \text{Na}_2\text{CaUO}_2\text{(CO}_3\text{)}_3\text{(H}_2\text{O)}_5 (s, 298 K) \\
\Delta H^\circ_f = -5593.8 \pm 9.1 \text{ kJ/mol}
\]

\[
3\text{K (s, 298 K) + Na (s, 298 K) + U (s, 298 K) + 3C (s, 298 K) + H}_2 (g, 298 K) + 6O}_2 (g, 298 K) = \text{Na}_2\text{CaUO}_2\text{(CO}_3\text{)}_3\text{(H}_2\text{O)}_5 (s, 298 K) \\
\Delta H^\circ_f = -4431.6 \pm 15.3 \text{ kJ/mol}
\]

These \(\Delta H^\circ_f\) 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 \(-1691.3 \pm 1.8 \text{ kJ/mol}\) (Guillaumont et al. 2003). Previous values of \(\Delta H^\circ_f\) 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, \(\Delta S^\circ\), and the standard entropy, \(S^\circ\). 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**


