Thermodynamics of formation of coffinite, USiO$_4$

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Coffinite, USiO$_4$, is an important U(IV) mineral, but its thermodynamic properties are not well-constrained. In this work, two different coffinite samples were synthesized under hydrothermal conditions and purified from a mixture of products. The enthalpy of formation was obtained by high-temperature oxide melt solubility calorimetry. Coffinite is energetically metastable with respect to a mixture of UO$_2$ (uraninite) and SiO$_2$ (quartz) by 25.6 ± 3.9 kJ/mol. Its standard enthalpy of formation from the elements at 25 °C is $-1,970.0 \pm 4.2$ kJ/mol. Decomposition of the two samples was characterized by X-ray diffraction and by thermogravimetry and differential scanning calorimetry coupled with mass spectrometric analysis of evolved gases. Coffinite slowly decomposes to U$_2$O$_3$ and SiO$_2$ starting around 450 °C in air and thus has poor thermal stability in the ambient environment. The energetic metastability explains why coffinite cannot be synthesized directly from uraninite and quartz but can be made by low-temperature precipitation in aqueous and hydrothermal environments. These thermochemical constraints are in accord with observations of the occurrence of coffinite in nature and are relevant to spent nuclear fuel corrosion.

In many countries with nuclear energy programs, spent nuclear fuel (SNF) and/or vitrified high-level radioactive waste will be disposed in an underground geological repository. Demonstrating the long-term (10$^6$–10$^{10}$ y) safety of such a repository system is a major challenge. The potential release of radionuclides into the environment strongly depends on the availability of water and the subsequent corrosion of the waste form as well as the formation of secondary phases, which control the radionuclide solubility. Coffinite (1), USiO$_4$, is expected to be an important alteration product of SNF in contact with silica-enriched groundwater under reducing conditions (2–8). It is also found, accompanied by thorium orthosilicate and uranothorite, in igneous and metamorphic rocks and ore minerals from uranium and thorium sedimentary deposits (2, 4, 5, 8–16). Under reducing conditions in the repository system, the uranium solubility (very low) in aqueous solutions is typically derived from the solubility product of UO$_2$. Stable U(IV) minerals, which could form as secondary phases, would impart lower uranium solubility to such systems. Thus, knowledge of coffinite thermodynamics is needed to constrain the solubility of U(IV) in natural environments and would be useful in repository assessment.

In natural uranium deposits such as Oklo (Gabon) (4, 7, 11, 12, 14, 17, 18) and Cigar Lake (Canada) (5, 13, 15), coffinite has been suggested to coexist with uraninite, based on electron probe microanalysis (EPMA) (4, 5, 7, 11, 13, 17, 19, 20) and transmission electron microscopy (TEM) (8, 15). However, it is not clear whether such apparent replacement of uraninite by a coffinite-like phase is a direct solid-state process or occurs mediated by dissolution and reprecipitation.

The precipitation of USiO$_4$ as a secondary phase should be favored in contact with silica-rich groundwater (21) [silica concentration >10$^{-4}$ mol/L (22, 23)]. Natural coffinite samples are often fine-grained (4, 5, 8, 11, 13, 15, 24), due to the long exposure to alpha-decay event irradiation (4, 6, 25, 26) and are associated with other minerals and organic matter (6, 8, 12, 18, 27, 28). Hence the determination of accurate thermodynamic data from natural samples is not straightforward. However, the synthesis of pure coffinite also has challenges. It appears not to form by reacting the oxides under dry high-temperature conditions (24, 29). Synthesis from aqueous solutions usually produces UO$_2$ and amorphous SiO$_2$ impurities, with coffinite sometimes being only a minor phase (24, 30–35). It is not clear whether these difficulties arise from kinetic factors (slow reaction rates) or reflect intrinsic thermodynamic instability (33). Thus, there are only a few reported estimates of thermodynamic properties of coffinite (22, 36–40) and some of them are inconsistent. To resolve these uncertainties, we directly investigated the energetics of synthetic coffinite by high-temperature oxide melt solution calorimetry to obtain a reliable enthalpy of formation and explored its thermal decomposition.

Results and Discussion

We used two independently prepared coffinite samples. A phase-pure coffinite sample prepared at Institut de Chimie Séparative de Marcoule (ICSM), France is labeled “coffinite-F” and a less pure material prepared at Forschungszentrum Jülich, Germany is labeled “coffinite-E”.

Significance

Coffinite, USiO$_4$, is an important alteration mineral of uraninite. Its somewhat unexpected formation and persistence in a large variety of natural and contaminated low-temperature aqueous settings must be governed by its thermodynamic properties, which, at present, are poorly constrained. We report direct calorimetric measurements of the enthalpy of formation of coffinite. The calorimetric data confirm the thermodynamic metastability of coffinite with respect to uraninite plus quartz but show that it can form from silica-rich aqueous solutions in contact with dissolved uranium species in a reducing environment. These constraints on thermodynamic properties support that coffinitization in uranium deposits and spent nuclear fuel occurs through dissolution of UO$_2$ (often forming hexavalent uranium intermediates) followed by reaction with silica-rich fluids.


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labeled “coffinite-G.” In both cases, considerable purification after initial synthesis was done to separate impurities (SI Appendix). The purpose of measuring and comparing both samples was to test whether consistent thermochemical data could be obtained on materials prepared and purified independently in different laboratories.

Before calorimetric measurements, samples were characterized by TEM, infrared spectroscopy (IR), powder X-ray diffraction (XRD), simultaneous differential scanning calorimetry and thermogravimetric analysis (DSC-TG) coupled with mass spectrometric analysis of evolved gases (MS-EGA), and by EPMA. The details are given in Experimental Methods and in SI Appendix.

The XRD patterns (SI Appendix, Fig. S1) show the reflections expected for a zircon-type structure (space group 141/amd). Lattice parameters are a = b = 6.983(3) Å and c = 6.263(4) Å for coffinite-G, and a = b = 6.990(1) Å and c = 6.261(1) Å for coffinite-F. Crystallite size was estimated from X-ray peak broadening (65 nm for coffinite-G and 85 nm for coffinite-F). This observation is consistent with previous reports (8, 24, 26, 34, 40). Although the particle size may affect the thermodynamic properties, we did not investigate this further. Even though coarse-grained but impure coffinite (>10 μm) has been documented from the Grants uranium region, New Mexico (8, 41), Colorado (8, 10), and hydrothermal deposits in Czech Republic (42), natural coffinite and materials produced in SNF alteration are usually fine-grained, having similar particle size as our synthetic samples. So, the data obtained here are applicable to most “real world” situations.

TG (Fig. 1) indicates a negligible amount of water in sample coffinite-F, not quantifiable from the MS trace. This observation agrees with Raman spectra on the same sample which show no signal associated with water (43). The water content of coffinite-G quantified by MS-EGA is 0.37 mol H2O per mole of USiO4 (slightly less than that estimated from TG analysis: 0.43 mol H2O per mole of USiO4). The water signal from MS suggests that there may be two water bonding sites, one with release near 150 °C and the other around 275 °C. The second peak (Fig. 1C) has a high-temperature tail up to 450 °C, suggesting some water molecules are strongly interacting with the sample.

Above 450 °C, both samples oxidize and slowly decompose in air, as indicated by weight increase on the TG trace due to oxidation of U(IV). This is consistent with previous reports (24, 30). After heating to 1,000 °C in air, as indicated by weight increase on the TG trace due to oxidation of U(IV). This is consistent with previous reports (24, 30). After heating to 1,000 °C in air, no trace of USiO4 is detected in either sample. Coffinite-F decomposes to U3O8 and amorphous SiO2 (SI Appendix, Fig. S2), and coffinite-G decomposes to a mixture of crystalline and amorphous SiO2 phases and a uranium-rich phase (possibly containing some silica and whose XRD pattern resembles that of U3O8). EPMA of coffinite-F (SI Appendix, Table S1) confirms USiO4 stoichiometry. The X-ray map (SI Appendix, Fig. S3) and backscattered electron image show that coffinite-F is pure and homogeneous with no detectable secondary phases. As for coffinite-G, the Si/U ratio of this sample is 4.19 and its chemical composition is USiO4·3.19SiO2·0.37H2O, obtained by combining EPMA result and water content from MS, described in detail in SI Appendix. This bulk composition is used to interpret the calorimetric data.

Through thermochemical cycles (SI Appendix, Tables S2 and S3), the enthalpy of formation (ΔHf,ox) of coffinite-F from binary oxides (uraninite plus quartz) is 24.6 ± 3.1 kJ/mol, obtained from calorimetry in sodium molybdate (3Na2O·4MoO3); and 26.7 ± 4.7 kJ/mol, derived from calorimetry in lead borate (2PbO·B2O3) (Table 1). Using independent measurements in two different solvents confirms consistency and indicates that there were no unanticipated problems in calorimetric procedures. Details of calorimetry are given in SI Appendix.

Due to limited sample amount, calorimetry of coffinite-G was performed only in 3Na2O·4MoO3 solvent. Correction for excess silica and water was required to derive ΔHf,ox of coffinite from this sample. The excess Si is present as amorphous to poorly crystalline silica (SI Appendix, Fig. S4), and was corrected by using the drop solution enthalpy of silica glass. The correction for excess water is less simple. If the water is “free water” and thus weakly bonded to the sample, the corrected ΔHf,ox of coffinite is −5.5 ± 3.5 kJ/mol (SI Appendix, Table S4). However, it is unlikely the H2O is free water, as IR shows water signal for the sample dried at 200 °C for 48 h (SI Appendix, Fig. S6), and MS shows that the water is removed gradually up to 450 °C, which suggests that at least part of the H2O in this sample is strongly bonded. Assuming water in coffinite is adsorbed on the surface with an integral adsorption enthalpy of −80 kJ/mol per mole of...
H₂O, similar to the values observed for water adsorption on alumina and titania (44–46) and, through proper thermochemical cycles (SI Appendix, Table S4), a value of ΔH°ox of coffinite (24.1 ± 3.5 kJ/mol) is obtained, in agreement with the results for coffinite-F (Table 1).

The tightly bound water could originate from metaschoepite (UO₂·2H₂O), which could be formed from partial oxidation of U(IV) (47) that originally was not incorporated in the coffinite structure, but rather was embedded in the gelatinous layer of excess amorphous silica (33). This phase may be hard to detect by XRD, especially if it is fine-grained or poorly crystalline. If all this water is in metaschoepite, the composition of coffinite-G can be written as 0.815(UO₃)·0.185(UO₃)·3.379SiO₂·0.185(UO₃)·2H₂O. Making this correction through an appropriate thermochemical cycle (SI Appendix, Table S5) gives the corrected ΔH°ox of USiO₄ as 23.9 ± 4.0 kJ/mol, again in agreement with the value for coffinite-F.

Thus, our measurements indicate that coffinite is energetically metastable with respect to uraninite plus quartz by about 25 kJ/mol. Coffinite is also energetically metastable with respect to mixture of UO₂ and amorphous SiO₂, as the enthalpy difference between quartz and glass is 9.1 kJ/mol (48). For the Gibbs free energy of coffinite formation from uraninite plus quartz to be negative at 25 °C, the entropy of formation must be strongly positive and probably unreasonably large for a solid-state reaction. Thus, we conclude that coffinite is thermodynamically metastable relative to uraninite plus quartz under ambient conditions. This conclusion is in good agreement with the solubility experiments and calculations of Szenknect et al. (40) using reference entropy data (22, 40) and obtaining ΔH°ox = 10 ± 32 kJ/mol (Table 2). The present values disagree with ΔH°ox = -5.8 kJ/mol estimated by

Table 1. Measured enthalpies of drop solution and enthalpies of formation from oxides

<table>
<thead>
<tr>
<th>Source</th>
<th>ΔH°, kJ/mol</th>
<th>ΔH°ox, kJ/mol*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coffinite-F</td>
<td>-121.43 ± 1.54*</td>
<td>24.6 ± 3.1</td>
</tr>
<tr>
<td>Coffinite-G</td>
<td>44.14 ± 0.94*</td>
<td>24.1 ± 3.5</td>
</tr>
<tr>
<td>Coffinite-G</td>
<td>44.39 ± 0.94*</td>
<td>23.9 ± 4.0*</td>
</tr>
</tbody>
</table>

*Measured in 3Na₂O·4MoO₃ solvent.
†Measured in 2PbO·B₂O₃ solvent.
‡This value obtained from a correction considering metaschoepite as an impurity phase containing all of the water.

Langmuir (22) or ΔH°ox = 4.3 ± 5.6 kJ/mol collected in the book edited by Grenthe (37) and suggest that the estimation by Szenknect et al. (40) is more reliable than those values (Table 2).

The substantially positive ΔH°ox also explains why coffinite cannot be formed directly from UO₂ and SiO₂ and agrees with the observation that coffinite decomposes upon heating to a moderate temperature as seen from DSC-TG experiments.

Coffinite metastability was also inferred by Costin et al. (33) in hydrothermal synthesis. They noted that the dissolution–precipitation process slows toward the coffinite end of the Th₁₋ₓUₓSiO₄ series, forming a correspondingly increasing amount of a Th–U dioxide phase. As a result, the formation of a uranothorite phase with x > 0.26 (coffinite included) is suggested to be thermodynamically unfavorable (40). In addition, a Th–U dioxide phase and amorphous silica were inevitably present in these products (24, 30).

Because coffinite is metastable with respect to uraninite plus quartz, why can it form and persist widely in uranium ore deposits (2, 12, 19)? First, one should realize that coffinite can be stable with respect to aqueous solutions over a wide range of concentrations. Langmuir (22) assumed the average silica concentration to be 10⁻³ M in the solution where the aqueous equilibrium between coffinite and uraninite is established (5): USiO₄(ə) + 2H₂O(l) ⇄ UO₂(ə) + SiOH₄(ə). A calculation based on Gibbs free energy obtained from solubility experiments done by Szenknect et al. (40) and auxiliary data (37) gives the Gibbs free energy of this reaction to be 5.7 ± 5.8 kJ/mol, which is essentially zero. Thus, their analysis suggests that coffinite can form from aqueous U(IV) in contact with silica-rich aqueous solutions, even though it is metastable with respect to crystalline UO₂ plus SiO₂. Our enthalpy data support this general conclusion. Therefore, coffinite can be an alteration product of UO₂ under repository, hydrothermal, metamorphic, or even igneous conditions as long as its formation can proceed through precipitation from aqueous solution.

The presence of water may play an additional significant role in stabilizing the coffinite phase or favoring the coffinitization process (4). Deditzius et al. (8) studied the composition of natural coffinite and found it can crystallize with variable amounts of H₂O apparently incorporated in the material. However, whether this water is truly in the coffinite structure (24, 49), is associated with the excess silica (24, 43), or represents a fine intergrowth of coffinite and some other phase, e.g., metaschoepite, is not clear.

Although it is plausible that coffinite forms as an alteration product from interaction of uraninite with Si-rich fluids, there may also be an alternative explanation for its formation. Consider underground nuclear waste repositories, ore deposits, or natural reactors where the high alpha dose (6, 25, 50) triggers

Table 2. Comparison of thermodynamics of formation of coffinite at 25 °C obtained in different studies

<table>
<thead>
<tr>
<th>Source</th>
<th>ΔH°ox, kJ/mol</th>
<th>ΔG°ox, kJ/mol*</th>
<th>ΔS°ox, J mol⁻¹ K⁻¹</th>
<th>ΔH°, kJ/mol</th>
<th>ΔG°, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir (22)</td>
<td>-5.7¹</td>
<td>5.6</td>
<td>-37.9</td>
<td>-2,001.3</td>
<td>-1,882.4</td>
</tr>
<tr>
<td>Grenthe et al. (37)</td>
<td>4.3 ± 5.6²</td>
<td>4.4 ± 4.2</td>
<td>-0.4 ± 12.8</td>
<td>-1,991.3 ± 5.4</td>
<td>-1,883.6 ± 4.0</td>
</tr>
<tr>
<td>Hemingway (36)</td>
<td>2 ± 6</td>
<td></td>
<td>-19.1 ± 12.8</td>
<td>-2,101 ± 32</td>
<td>-1,872 ± 6</td>
</tr>
<tr>
<td>Szenknect (40)</td>
<td>-105 ± 32³</td>
<td>16 ± 6</td>
<td>-407 ± 56</td>
<td>-2,101 ± 32</td>
<td>-1,872 ± 6</td>
</tr>
<tr>
<td>Fleche (39)</td>
<td>82</td>
<td></td>
<td></td>
<td>-1,913</td>
<td></td>
</tr>
<tr>
<td>Coffinite-F</td>
<td>24.6 ± 3.1</td>
<td>26.7 ± 4.7</td>
<td>-1,971.0 ± 3.4⁴</td>
<td>-1,968.9 ± 4.9⁴</td>
<td></td>
</tr>
<tr>
<td>Coffinite-G</td>
<td>(-5.5 ± 3.5)</td>
<td>24.1 ± 3.5</td>
<td>-1,971.5 ± 3.8⁴</td>
<td>-1,971.7 ± 4.2⁴</td>
<td></td>
</tr>
</tbody>
</table>

¹Calculated with auxiliary data from ref. 48.
²This value was calculated.
³The entropy value was taken from averaging reference data (22, 37), and then was used to calculate the enthalpy of formation.
⁴The entropy was taken from ref. 48.
radiolysis of water to form H2O2 (25, 51–53); the localized oxidizing conditions would help dissolve uraninite into more soluble uranyl (UO22+) species (47). Organic matter in the natural system (6, 8, 12, 18, 28) could then play an important reducing role to precipitate coffinite as summarized by Dediu et al. (8). A sequence of UO2 oxidation by peroxide, transport of U(VI) species in aqueous solution, and reduction by organic matter in the presence of a silica source could produce coffinite at locations distant from the initial UO2 phase. Under such conditions, USiO4 could form if its crystallization were kinetically favored over that of UO2. Thus, the process of coffinitization may involve a sequence of reactions: UO2 dissolution under locally oxidizing conditions, transport of the dissolved U(VI) species into more reducing environments containing dissolved silica, followed by coffinite precipitation.

**Experimental Methods**

Coffinite-F and -G samples were prepared by hydrothermal synthesis routes, described elsewhere (33, 35). Because these syntheses routes inevitably have UO2 and amorphous silica as byproducts, further purification is needed. HNO3 and KOH solution were used to wash the samples as described in the purification protocol proposed by Clavier et al. (54). More synthesis and purification details are shown in SI Appendix.

XRD measurements were performed at room temperature using a Bruker D8 diffractometer with Bragg-Brentano geometry (Cu Kα radiation, 40 kV, and 40 mA), using a step size of 0.016–0.028°. Lattice parameters were refined by a Rietveld method (55). DSC-TG measurements were performed with a Setaram LabSys instrument coupled with a quadrupole mass spectrometer (MKS Ciris2) for evolved gas analysis. Coffinite samples (~10 mg) were placed in Pt crucibles without lids and heated in airflow (40 mL/min) to 1,000 °C at 10 °C/min. For quantitative analysis of evolved gases, MS traces for H2O (m/z = 18) and CO2 (m/z = 44) were calibrated by decomposition of calcium oxalate in the same experimental conditions.

Chemical composition and homogeneity were determined using a Cameca SX-100 electron microscope with wavelength dispersive spectroscopy (15-kV accelerating voltage, 10-nA beam current, and a spot size of 1 μm). Samples were pelletized, polished, and carbon coated before analysis. The determination of Nd in cofinite-G were recovered after DSC-TG and the ratio of Si/U was further analyzed.

High-temperature oxide melt calorimetry was conducted using a custom-built Tian-Calvet twin microlitermometer (52–54). Powdered samples were hand pressed into small pellets (~5 mg) and were dropped from room temperature into either 30 g of molten 2PbO·B2O3 solvent at 802 °C, or 20 g of molten 3Na2O·4MgO·SiO2 solvent presaturated with 100 mg of SiO2 (56) at 703 °C. Each sample hold in Pt crucible was continuously bubbled through the melt at 5 mL/min to ensure an oxidizing environment and facilitate dissolution of samples to prevent local saturation (57). Flushing O2 gas at ~50 mL/min through the calorimeter chamber assisted in maintaining a constant gas environment above the solvent and removing any evolved gases (57). The calorimeter was calibrated using the heat content of ~5 mg α-Al2O3 pellets (58, 59). Upon rapid and complete dissolution of the sample, the enthalpy of drop solution ΔHdrop was obtained. Finally, using appropriate thermochemical cycles, enthalpies of formation from the oxides ΔfHm were calculated.

Previous studies show that silica has a low solubility in 3Na2O·4MgO·SiO2 but silica-containing samples dissolve, precipitating silica as cristobalite (56). A test of this solvent on the dissolution of zircon structure materials was done by dropping 2ZrO2 and HfSiO4 in this setup and yielded consistent results with experiments done in molten lead 2PbO·B2O3 solvent at 802 °C.

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4. Janeczek J, Ewing RC (1991) Coffinitization—A mechanism for the alteration of UO2 and amorphous silica as byproducts, further purification is needed. HNO3 and KOH solution were used to wash the samples as described in the purification protocol proposed by Clavier et al. (54). More synthesis and purification details are shown in SI Appendix.
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Thermodynamics of Formation of Coffinite, USiO<sub>4</sub>

Short Title: Thermodynamics of coffinite

Physical Science: Chemistry

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Supporting Information:
Synthesis and purification of coffinite-F and coffinite-G

Coffinite was prepared from uranium tetrachloride solution prepared by dissolving depleted U metal (U metal chips supplied by CETAMA (Analytical Methods Committee, CEA France) for coffinite-F, and U metal turnings from Prof. Florian Kraus from TU Munich for coffinite-G) in HCl (6M) in application of the protocol developed by Dacheux et al. (1, 2). The concentration of the solution was determined by ICP-AES/MS. The rest of the reagents were obtained from Sigma-Aldrich and were of analytical grade.

The synthesis route of coffinite-F was a modification (3) of the procedure of Fuchs and Hoekstra.(4, 5). The synthesis consists of slowly pouring a solution of UCl₄ (13.35 g, 6.05 mmol) into a solution containing dissolved Na₂SiO₃ (0.81 g, 6.66 mmol). The pH of the mixture was then raised by adding NaOH (8M) drop wise to reach 11.3 ± 0.1, then buffered to 8.7 ± 0.1 by adding NaHCO₃ (powder). The final green gelatinous mixture (46 mL) was transferred into a teflon acid digestion vessel and placed in an oven. In order to avoid oxidation of the U(IV), the mixing was performed in a glove box filled with Ar and free from oxygen (less than 1 ppm). Moreover, the deionized water used in the reactions was also boiled for one hour and cooled under a N₂ stream. The final product was separated by centrifugation twice with deionized water followed by ethanol and dried overnight in air at room temperature. The synthesis of coffinite-G followed a similar protocol, and the differences and synthesis details were described by Labs et al. (6). Instead of using Na₂SiO₃ in ~ 10 % molar excess of silicate, a 6-fold amount of silica solution was mixed with UCl₄ solution.

The analyses of the obtained solid by SEM and PXRD showed the presence of the coffinite mixed with UO₂ and amorphous silica byproducts. Therefore pure coffinite-F was obtained by following the protocol proposed by Clavier et al.(7) It consists of placing 100 mg of the raw powder (as-prepared product) in 50 mL of HNO₃ (10⁻² mol. L⁻¹) for 3 - 5 days, then the solid was washed three times in de-ionized water then the remaining solid was placed in 50 mL of KOH solution (10⁻² mol.L⁻¹) for 3 - 5 days. Finally the solid was recovered by centrifugation using deionized water. The purification cycle was repeated three times leading to pure coffinite-F. The purification of coffinite-G also used similar procedures.
Characterization of coffinite-F and coffinite-G

XRD Analysis
Figure S1. X-ray diffraction patterns of coffinite samples (Cu Kα1,2 radiation). Top: coffinite-F; refinement parameters: Rp = 1.96 %, wRp = 2.92 %, $\chi^2 = 3.27$. Middle: coffinite-G. Positions of the USiO$_4$ (blue) and quartz SiO$_2$ phase (green) are marked; Le Bail fit statistics: Rp = 6.78 %, wRp = 8.84 %. Bottom: comparison of the PXRD patterns of the Coffinite F and G. * corresponds to the principal peaks of the quartz. The Coffinite-F PXRD pattern was slightly shifted for better clarity.

In the diffraction pattern of coffinite-G, an additional broad reflection can be seen in the range $2\theta = 21 - 23$ °, which is attributed to amorphous SiO$_2$, a weak sharp reflection attributable to quartz can be observed at ~27 °. The lattice parameters obtained from Rietveld refinement are in very good agreement with those reported in literature. Other uranium phases were not detected. The diffraction pattern is thus consistent with the presence of coffinite and a mostly amorphous SiO$_2$ phase.
Figure S2. XRD on retrieved decomposed coffinite-F (a) and -G (b) samples after heated in DSC-TG.

Electron Microprobe Analysis

Table S1. Compositions obtained by electron microprobe analysis.

<table>
<thead>
<tr>
<th></th>
<th>Coffinite-F†</th>
<th>Coffinite-G, area 1‡</th>
<th>Coffinite-G, area 2‡</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>$7.43 \pm 0.13(16.65)$</td>
<td>$39.59 \pm 0.36(31.59)$</td>
<td>$8.77 \pm 0.11(15.47)$</td>
</tr>
<tr>
<td>U</td>
<td>$62.89 \pm 1.32(16.68)$</td>
<td>$13.11 \pm 0.46(1.30)$</td>
<td>$64.28 \pm 0.15(13.39)$</td>
</tr>
</tbody>
</table>

* wt. % with at. % in parenthesis; uncertainty is two standard deviations of the mean; two significant digits were presented to avoid roundoff error in calculations; † the Si/U ratio is 1.00; ‡ area 1: Si$_{0.96}$U$_{0.04}$O$_2$; area 2: U$_{13.4}$Si$_{15.5}$O$_{71.0}$.

Decomposed coffinite samples after DSC-TG measurements were examined by XRD (Fig. S2) and EPMA. X-ray map of coffinite-F is shown in Fig. S3, in which the element U was
represented in red and Si was in blue. The magenta color of the whole phase indicates a homogeneous distributions of both U and Si. Fig. S3 also shows the X-ray map of thermally decomposed coffinite-F. The homogeneity suggests that coffinite-F decomposes to crystalline \( \text{U}_3\text{O}_8 \) and amorphous nanograinned \( \text{SiO}_2 \), which is also seen from the broadening in the XRD pattern in Fig. S2.

![X-ray map of coffinite samples](image)

**Figure S3.** X-ray map of coffinite-F sample (a); of decomposed coffinite-F sample (b); of coffinite-G sample (e); of decomposed coffinite sample (f). Si in blue, and U in red.

The high temperature decomposition products of coffinite-G retrieved form DSC-TG were heated at 800 °C for 22 h and then investigated by EPMA. Seen from XRD in Fig. S2, the decomposed phases are complicated because of the nature of the coffinite-G sample (see X-ray map of this sample in Fig. S3). Due to the intimate intergrowth of the Si-rich and the U-rich phases in coffinite-G sample, the determination of the Si/U ratio is challenging. Obtained data were processed with ImageJ by extracting the area of Si-rich (area 1) and U-rich (area 2) (Fig.
S3) and multiplying it with the elemental density. This way, the mass fractions were derived and from this the composition was calculated. This information was used together with their chemical compositions (Table S1) to estimate the Si/U ratio in the overall sample as 4.19. It is likely that the silica rich phase (area 1) contains a small amount of uranium and the uranium rich phase (area 2) contains a small amount of silica, probably present as nanoscale intergrowths. Assuming this to be the case, and combining this compositional information with water content obtained from MS, the chemical composition of coffinite-G was determined to be USiO$_4$·3.19SiO$_2$·0.37H$_2$O.

**TEM**

Investigation with TEM reveals that the lenticulate particles in coffinite-G themselves are composed of even smaller crystallites. The particles appear to be large agglomerates of smaller particles, which are covered in an amorphous silicate layer (yellow arrow in Figure S4; amorphous to poorly crystalline SiO$_2$), as seen in the HRTEM images shown below.
Figure S4. HRTEM micrograph of the coffinite-G sample. FFT below: Distances of the marked planes correspond to d(200) = 0.34 nm (left). View of particles along four-fold axis (right). Lattice planes d(200) = d(020) = 0.34 nm and d(220) = 0.25 nm are visible.
Infrared Spectra

The IR spectrum shows a signal for the ν(OH) and δ(HOH) vibrations. It has to be concluded that water is present in the sample. The sample had been dried at 200 °C for 48 hr, so the remaining water is presumably more strongly bound in the sample than liquid water.

Figure S6. IR spectrum of coffinite-G sample. [Bruker TGA-IR Equinox 55, KBr pellet.]
Calorimetry of coffinite

Table S2. Thermochemical cycles for determination of the enthalpy of formation of coffinite-F from binary oxides (sodium molybdate solvent). *

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \Delta H ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) ( \text{USiO}_4(s, 25 , ^\circ\text{C}) + \frac{1}{2}\text{O}_2(g, 703 , ^\circ\text{C}) \rightarrow \text{UO}_3(\text{sln, 703} , ^\circ\text{C}) + \text{SiO}_2(\text{cristobalite, 703} , ^\circ\text{C}) )</td>
<td>( \Delta H_1 = \Delta H_{ds} = -121.43 \pm 1.54 ) † (4)§</td>
</tr>
<tr>
<td>(2) ( \text{UO}_2(s, 25 , ^\circ\text{C}) + \frac{1}{2}\text{O}_2(g, 703 , ^\circ\text{C}) \rightarrow \text{UO}_3(\text{sln, 703} , ^\circ\text{C}) )</td>
<td>( \Delta H_2 = -140.40 \pm 2.67 ) ‡ (9)</td>
</tr>
<tr>
<td>(3) ( \text{SiO}_2(\text{quartz, s, 25} , ^\circ\text{C}) \rightarrow \text{SiO}_2(\text{cristobalite, 703} , ^\circ\text{C}) )</td>
<td>( \Delta H_3 = 43.54 \pm 0.60 ) (3)</td>
</tr>
<tr>
<td>(4) ( \text{UO}_2(s, 25 , ^\circ\text{C}) + \text{SiO}_2(\text{quartz, 25} , ^\circ\text{C}) \rightarrow \text{USiO}_4(s, 25 , ^\circ\text{C}) )</td>
<td>( \Delta H_4 = \Delta H_{f,ox} )</td>
</tr>
</tbody>
</table>

**Enthalpy of formation of coffinite from UO\(_2\), SiO\(_2\) (quartz):**

\[
\Delta H_{f,ox}(\text{USiO}_4) = - \Delta H_{ds}(\text{USiO}_4) + \Delta H_2 + \Delta H_3
\]

\[
= +24.57 \pm 3.14 \text{ kJ/mol}
\]

* Before calorimetry sample was dried at 200 °C for 10 hours; † Average, two significant digits were presented to avoid roundoff error in calculations; ‡ Two standard deviations of the average value; § Number of measurements.

Table S3. Thermochemical cycles for determination of the enthalpy of formation of coffinite-F from binary oxides (lead borate solvent).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \Delta H ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) ( \text{USiO}_4(s, 25 , ^\circ\text{C}) + \frac{1}{2}\text{O}_2(g, 802 , ^\circ\text{C}) \rightarrow \text{UO}_3(\text{sln, 802} , ^\circ\text{C}) + \text{SiO}_2(\text{sln, 802} , ^\circ\text{C}) )</td>
<td>( \Delta H_1 = \Delta H_{ds} = -102.01 \pm 3.10 ) (4)</td>
</tr>
<tr>
<td>(2) ( \text{UO}_2(s, 25 , ^\circ\text{C}) + \frac{1}{2}\text{O}_2(g, 802 , ^\circ\text{C}) \rightarrow \text{UO}_3(\text{sln, 802} , ^\circ\text{C}) )</td>
<td>( \Delta H_2 = -125.21 \pm 3.41 ) (9)</td>
</tr>
<tr>
<td>(3) ( \text{SiO}_2(\text{quartz, s, 25} , ^\circ\text{C}) \rightarrow \text{SiO}_2(\text{sln, 802} , ^\circ\text{C}) )</td>
<td>( \Delta H_3 = 49.90 \pm 0.80 ) (10)</td>
</tr>
<tr>
<td>(4) ( \text{UO}_2(s, 25 , ^\circ\text{C}) + \text{SiO}_2(\text{quartz, 25} , ^\circ\text{C}) \rightarrow \text{USiO}_4(s, 25 , ^\circ\text{C}) )</td>
<td>( \Delta H_4 = \Delta H_{f,ox} )</td>
</tr>
</tbody>
</table>

**Enthalpy of formation of coffinite from UO\(_2\), SiO\(_2\) (quartz):**

\[
\Delta H_{f,ox}(\text{USiO}_4) = - \Delta H_{ds}(\text{USiO}_4) + \Delta H_2 + \Delta H_3
\]

\[
= +26.70 \pm 4.68 \text{ kJ/mol}
\]
Table S4. Thermochemical cycles for determination of the enthalpy of formation of coffinite-G (sodium molybdate solvent).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) $\text{USiO}_4 \cdot 3.19\text{SiO}_2 \cdot 0.37\text{H}_2\text{O} (s, 25 , ^\circ C) + \frac{1}{2}\text{O}_2 (g, 703 , ^\circ C)$</td>
<td>$\Delta H_1 = \Delta H_{ds} = 44.14 \pm 0.94(4)$</td>
</tr>
<tr>
<td>$\rightarrow \text{UO}_3 (\text{sln}, 703 , ^\circ C) + 4.19\text{SiO}_2 (\text{cristobalite}, 703 , ^\circ C) + 0.37\text{H}_2\text{O} (g, 703 , ^\circ C)$</td>
<td></td>
</tr>
<tr>
<td>(2) $\text{UO}_2 (s, 25 , ^\circ C) + \frac{1}{2}\text{O}_2 (g, 703 , ^\circ C) \rightarrow \text{UO}_3 (\text{sln}, 703 , ^\circ C)$</td>
<td>$\Delta H_2 = -140.40 \pm 2.67(4)$</td>
</tr>
<tr>
<td>(3) $\text{SiO}_2 (\text{quartz}, s, 25 , ^\circ C) \rightarrow \text{SiO}_2 (\text{cristobalite}, 703 , ^\circ C)$</td>
<td>$\Delta H_3 = 43.54 \pm 0.60(3)$</td>
</tr>
<tr>
<td>(4) $\text{SiO}_2 (\text{glass}, s, 25 , ^\circ C) \rightarrow \text{SiO}_2 (\text{quartz}, s, 25 , ^\circ C)$</td>
<td>$\Delta H_4 = -9.1(11)$</td>
</tr>
<tr>
<td>(5) $\text{H}_2\text{O} (l, 25 , ^\circ C) \rightarrow \text{H}_2\text{O} (g, 703 , ^\circ C)$</td>
<td>$\Delta H_5 = 69.0(11)$</td>
</tr>
<tr>
<td>(6) $\text{H}_2\text{O} (l, 25 , ^\circ C) \rightarrow \text{H}_2\text{O} (cr, 25 , ^\circ C)$</td>
<td>$\Delta H_6 = -80.0^*$</td>
</tr>
<tr>
<td>(7) $\text{UO}_2 (s, 25 , ^\circ C) + \text{SiO}_2 (\text{quartz}, 25 , ^\circ C) \rightarrow \text{USiO}_4 (s, 25 , ^\circ C)$</td>
<td>$\Delta H_7 = \Delta H_{f,ox}$</td>
</tr>
</tbody>
</table>

Corrected enthalpy of drop solution value assuming $\text{H}_2\text{O}$ behaves like liquid water, and the enthalpy of formation of coffinite from $\text{UO}_2$, $\text{SiO}_2$ (quartz):

$$\Delta H_{ds}(\text{USiO}_4) = \Delta H_1 - 3.19 \cdot (\Delta H_3 + \Delta H_4) - 0.37 \Delta H_5$$

$$= -91.4 \pm 2.1 \text{ kJ/mol}$$

$$\Delta H_{f,ox}(\text{USiO}_4) = - \Delta H_{ds}(\text{USiO}_4) + \Delta H_2 + \Delta H_3$$

$$= -5.5 \pm 3.5 \text{ kJ/mol}$$

Corrected enthalpy of drop solution value assuming water is strongly bonded but all uranium is in coffinite, and the enthalpy of formation of coffinite from $\text{UO}_2$, $\text{SiO}_2$ (quartz):

$$\Delta H_{ds}(\text{USiO}_4) = \Delta H_1 - (3.19) \cdot (\Delta H_3 + \Delta H_4) - 0.37 \cdot (\Delta H_5 + \Delta H_6)$$

$$= -121.0 \pm 2.1 \text{ kJ/mol}$$

$$\Delta H_{f,ox}(\text{USiO}_4) = - \Delta H_{ds}(\text{USiO}_4) + \Delta H_2 + \Delta H_3$$

$$= +24.1 \pm 3.5 \text{ kJ/mol}$$
Table S5. Thermochemical cycles for determination of the enthalpy of formation of coffinite-G (sodium molybdate solvent, assuming all H₂O is tied up in a metaschoepite phase).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔH (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) 0.815USiO₄·3.379SiO₂·0.185(UO₃·2H₂O)(s, 25 °C) + 0.408O₂(g, 703 °C) → UO₃(sln, 703 °C) + 4.19SiO₂(cristobalite, 703 °C) + 0.37H₂O(g, 703 °C)</td>
<td>ΔH₁ = ΔHₜₘ = 44.39 ± 0.94(4)</td>
</tr>
<tr>
<td>(2) UO₂(s, 25 °C) + 1/2O₂(g, 703 °C) → UO₃(sln, 703 °C)</td>
<td>ΔH₂ = -140.40 ± 2.67(4)</td>
</tr>
<tr>
<td>(3) SiO₂(quartz, s, 25 °C) → SiO₂(cristobalite, 703 °C)</td>
<td>ΔH₃ = 43.54 ± 0.60(3)</td>
</tr>
<tr>
<td>(4) SiO₂(glass, s, 25 °C) → SiO₂(quartz, s, 25 °C)</td>
<td>ΔH₄ = -9.1(11)</td>
</tr>
<tr>
<td>(5) H₂O(l, 25 °C) → H₂O(g, 703 °C)</td>
<td>ΔH₅ = 69.0(11)</td>
</tr>
<tr>
<td>(6) UO₃(s, 25 °C) + 2H₂O(l, 25 °C) → UO₃·2H₂O(s, 25 °C)</td>
<td>ΔH₆ = 4.40 ± 3.10(12)</td>
</tr>
<tr>
<td>(7) UO₃(s, 25 °C) → UO₃(sln, 703 °C)</td>
<td>ΔH₇ = 9.45 ± 1.50(2)(13)</td>
</tr>
<tr>
<td>(8) UO₃·2H₂O(s, 25 °C) → UO₃(sln, 703 °C) + 2H₂O(g, 703 °C)</td>
<td>ΔH₈ = 143.05 ± 3.44</td>
</tr>
<tr>
<td>(9) UO₂(s, 25 °C) + SiO₂(quartz, 25 °C) → USiO₄(s, 25 °C)</td>
<td>ΔH₉ = ΔHₜₘ</td>
</tr>
</tbody>
</table>

Corrected enthalpy of drop solution value:

ΔHₜₘ(USiO₄) = [ΔH₁ - 3.379(ΔH₃ + ΔH₄) - 0.185ΔH₈]/0.815

= -120.8 ± 2.9 kJ/mol

Enthalpy of formation of coffinite from UO₂, SiO₂ (quartz):

ΔHₜₘ(USiO₄) = ΔHₜₘ(USiO₄) + ΔH₂ + ΔH₃

= +23.9 ± 4.0 kJ/mol

Calorimetry of uranium oxides

Calorimetry of UO₂12 and γ-UO₃·0.47H₂O was done in both sodium molybdate (3Na₂O·4MoO₃) and lead borate (2PbO·B₂O₃). The purpose was to obtain consistent values of the enthalpy of drop solution of stoichiometric UO₂ (itself has difficult to obtain and maintain stoichiometric) to use in cycles for the heat of formation of USiO₄. 3Na₂O·4MoO₃ solvent at 703 °C has been previously demonstrated to readily dissolve U compounds and have a well-defined final oxidation state of U(VI) in the melt (13). Here we repeated these experiments with well characterized uranium oxide samples. The stoichiometry of UO₂,₁₂ was measured by TG.
and the oxygen content was determined to be 2.116 ± 0.003. The water content of γ-UO₃·0.47H₂O measured by TG and MS is 0.47 ± 0.03 per mole of γ-UO₃ sample. Because ΔH°ᵣ of uranium oxides has a linear relationship with oxygen content per U, we correct ΔHₐₛ(UO₂,12) for the presence of an additional 0.12 mol of U⁶⁺ per formula unit of U⁴⁺ (reaction 9 in Table S6) to derive ΔHₐₛ(UO₂) = -140.40 ± 2.67 kJ/mol. This large exothermic effect confirms that UO₂ was oxidized during its dissolution in the melt solvent. The interaction enthalpy of water in γ-UO₃·0.47H₂O measured by TG and MS is 0.47 ± 0.03 per mole of γ-UO₃ sample. Because ΔH° of uranium oxides has a linear relationship with oxygen content per U (14), we correct ΔHₐₛ(UO₂,12) for the presence of an additional 0.12 mol of U⁶⁺ per formula unit of U⁴⁺ (reaction 9 in Table S6) to derive ΔHₐₛ(UO₂) = -140.40 ± 2.67 kJ/mol. This large exothermic effect confirms that UO₂ was oxidized during its dissolution in the melt solvent. The interaction enthalpy of water in γ-UO₃·0.47H₂O was obtained from ΔHₐₛ(γ-UO₃·0.47H₂O), ΔHₐₛ(γ-UO₃), and heat enthalpy of water from 25 to 703 °C to be 17.04 ± 2.72 kJ/mol (reaction 8 in Table S6). These new obtained calorimetric data from 3Na₂O·4MoO₃ solvent were verified against the enthalpy of oxidation of UO₂ → γ-UO₃ at room temperature (reaction 10 in Table S6), 138.98 ± 3.08 kJ/mol, with 0.1 % of difference from the value calculated from reference data, -138.8 ± 1.3 kJ/mol(11).

The calorimetry of γ-UO₃ and UO₂ in 2PbO-B₂O₃ solvent at 802 °C was studied for the first time. ΔHₐₛ(γ-UO₃) = 26.67 ± 4.02 kJ/mol was derived by subtracting the energetic contribution of water from ΔHₐₛ(γ-UO₃·0.47H₂O). Corrected ΔHₐₛ(UO₂) is -125.21 ± 3.41 kJ/mol. Similarly, the oxidation enthalpy of UO₂ to γ-UO₃ derived from data obtained from 2PbO-B₂O₃ solvent, -139.19 ± 5.27 kJ/mol, was also verified against that reference data with a 0.3 % difference. This consistency also confirms the final state of U in the 2PbO-B₂O₃ melt to be hexavalent.

**Table S6.** Thermodynamic data for γ-UO₃ and UO₂ in sodium molybdate solvent at 703 °C.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔH (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) γ-UO₃·0.47H₂O(s, 25 °C) → UO₃(sln, 703 °C) + 0.47 H₂O(g, 703 °C)</td>
<td>ΔH₁ = ΔHₐₛ</td>
</tr>
<tr>
<td></td>
<td>= 58.88 ± 2.25(3)</td>
</tr>
<tr>
<td>(2) γ-UO₃(s, 25 °C) → UO₃(sln, 703 °C)</td>
<td>ΔH₂ = 9.49 ± 1.53(13)</td>
</tr>
<tr>
<td>(3) 0.88 UO₂(s, 25 °C) + 0.12 UO₃(s, 25 °C) + 0.44 O₂(g, 703 °C) → UO₃(sln, 703 °C)</td>
<td>ΔH₃ = -123.02 ± 2.36(4)</td>
</tr>
<tr>
<td>(4) H₂O(l, 25 °C) → H₂O(g, 703 °C)</td>
<td>ΔH₄ = 73.2(11)</td>
</tr>
<tr>
<td>(5) O₂(g, 25 °C) → O₂(g, 703 °C)</td>
<td>ΔH₅ = 25.4(15)</td>
</tr>
<tr>
<td>(6) U(s, 25 °C) + O₂(g, 25 °C) → UO₂(s, 25 °C)</td>
<td>ΔH₆ = -1084.9 ± 1.0(11)</td>
</tr>
<tr>
<td>(7) U(s, 25 °C) + 3/2O₂(g, 25 °C) → γ-UO₃(s, 25 °C)</td>
<td>ΔH₇ = -1223.8 ± 0.8(11)</td>
</tr>
</tbody>
</table>
**Thermochemical cycles**

Cycle for calculating $\Delta H_{\text{inter}}$ of bonding water in $\gamma$-UO$_3$·0.47H$_2$O

(1) $\gamma$-UO$_3$·0.47H$_2$O$_{(s, 25 \degree C)}$ → $\gamma$-UO$_3(s, 25 \degree C)$ + 0.47 H$_2$O$_{(l, 25 \degree C)}$

$$\Delta H_8 = \Delta H_1 - \Delta H_2 - 0.47 \Delta H_4$$

$= 17.04 \pm 2.72$

Cycle for calculating $\Delta H_{ds}$ of UO$_2$ correcting for oxidation

(9) UO$_2(s, 25 \degree C)$ + 1/2 O$_2(g, 703 \degree C)$ → UO$_3$(sln, 703 \degree C)

$$\Delta H_9 = \left[\Delta H_3 - 0.12 \Delta H_2\right]/0.88$$

$= -140.40 \pm 2.67$

Cycle for calculating $\Delta H^o$ oxidation of UO$_2$

(10) UO$_2(s, 25 \degree C)$ + 1/2 O$_2(g, 25 \degree C)$ → $\gamma$-UO$_3(s, 25 \degree C)$

Measured $\Delta H_{10} = \Delta H_9 - \Delta H_2 + 1/2 \Delta H_5$

Reference $= -\Delta H_6 + \Delta H_7$

(138.89 ± 1.30) (11)

**Table S7. Thermodynamic data for $\gamma$-UO$_3$ and UO$_2$ in lead borate solvent at 802 °C.**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H$ (kJ/mol)</th>
</tr>
</thead>
</table>
| (1) $\gamma$-UO$_3$·0.47H$_2$O$_{(s, 25 \degree C)}$ → UO$_3(sln, 802 \degree C)$ + 0.47 H$_2$O$_{(g, 802 \degree C)}$ | $\Delta H_1 = \Delta H_{ds}$

$= 78.02 \pm 2.96(3)$ |
| (2) 0.88 UO$_2(s, 25 \degree C)$ + 0.12 UO$_3(s, 25 \degree C)$ + 0.44 O$_2(g,802 \degree C)$ → UO$_3$(sln, 802 \degree C) | $\Delta H_2 = -107.59 \pm 2.98(5)$ |
| (3) H$_2$O$_{(l, 25 \degree C)}$ → H$_2$O$_{(g, 802 \degree C)}$ | $\Delta H_3 = 73.2(11)$ |
| (4) O$_2(g, 25 \degree C)$ → O$_2(g, 802 \degree C)$ | $\Delta H_4 = 25.4(15)$ |
| (5) U$_{(s, 25 \degree C)}$ + O$_2(g, 25 \degree C)$ → UO$_2(s, 25 \degree C)$ | $\Delta H_5 = -1084.9 \pm 1.0(11)$ |
| (6) U$_{(s, 25 \degree C)}$ + 3/2O$_2(g, 25 \degree C)$ → $\gamma$-UO$_3(s, 25 \degree C)$ | $\Delta H_6 = -1223.8 \pm 0.8(11)$ |

**Thermochemical cycles**

Cycle for calculating $\Delta H_{ds}$ of $\gamma$-UO$_3$ correcting for water content

(7) $\gamma$-UO$_3$·0.47H$_2$O$_{(s, 25 \degree C)}$ → UO$_3(sln, 802 \degree C)$ + 0.47 H$_2$O$_{(g, 802 \degree C)}$

$$\Delta H_7 = \Delta H_1 - 0.47 \Delta H_3 - \Delta H_{\text{inter}}$$

$= 26.67 \pm 4.02$

Cycle for calculating $\Delta H_{ds}$ of UO$_2$ correcting for oxidation

(8) UO$_2(s, 25 \degree C)$ + 1/2 O$_2(g, 802 \degree C)$ → UO$_3$(sln, 802 \degree C)

$$\Delta H_8 = [\Delta H_2 - 0.12 \Delta H_7]/0.88$$

$= -125.21 \pm 3.41$
(9) $\text{UO}_2(s, 25 \, ^\circ\!\!\!\!\text{C}) + \frac{1}{2} \text{O}_2(g, 25 \, ^\circ\!\!\!\!\text{C}) \rightarrow \gamma-\text{UO}_3(s, 25 \, ^\circ\!\!\!\!\text{C})$

Measured $\Delta H_9 = \Delta H_8 - \Delta H_7 + \frac{1}{2} \Delta H_4$

Reference $= -\Delta H_5 + \Delta H_6$

$\Delta H_9 = 139.19 \pm 5.27$

$\Delta H_{\text{inter}}$ was taken from $\Delta H_8$ in Table S6.

**Table S8.** Enthalpy of drop solution of uranium oxides.

<table>
<thead>
<tr>
<th>Uranium oxides</th>
<th>$\Delta H_{\text{ds}}(703 , ^\circ!!!!\text{C}, \text{sodium molybdate})$</th>
<th>$\Delta H_{\text{ds}}(802 , ^\circ!!!!\text{C}, \text{lead borate})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$-$\text{UO}_3$</td>
<td>9.49 ± 1.53 (13)</td>
<td>26.67 ± 4.02</td>
</tr>
<tr>
<td>$\text{UO}_2$</td>
<td>-140.40 ± 2.67</td>
<td>-125.21 ± 3.41</td>
</tr>
<tr>
<td>$\text{UO}_2 - \gamma$-$\text{UO}_3$</td>
<td>-138.98 ± 3.08 (0.1%)$^*$</td>
<td>-139.19 ± 5.27 (0.3%)$^*$</td>
</tr>
</tbody>
</table>

$^*$ compared to -138.89 ± 1.13 kJ/mol (11)
References


