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Authors

Guo, Xiaofeng
Szenknect, Stéphanie
Mesbah, Adel
et al.

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Thermodynamics of formation of coffinite, USiO_4

Xiaofeng Guo^{a,b}, Stéphanie Szenknect^c, Adel Mesbah^c, Sabrina Labs^d, Nicolas Clavier^c, Christophe Poinssot^e, Sergey V. Ushakov^a, Hildegard Curtius^d, Dirk Bosbach^d, Rodney C. Ewing^f, Peter C. Burns^g, Nicolas Dacheux^c, and Alexandra Navrotsky^{a,1}

^aPeter A. Rock Thermochemistry Laboratory and Nanomaterials in the Environment, Agriculture, and Technology Organized Research Unit, University of California, Davis, CA 95616; ^bEarth and Environmental Sciences Division, Los Alamos National Laboratory, Los Alamos, NM 87545; ^cInstitut de Chimie Séparative de Marcoule, UMR 5257, CNRS/CEA/Université Montpellier/Ecole Nationale Supérieure de Chimie de Montpellier, Site de Marcoule, 30207 Bagnols sur Cèze, France; ^dInstitute of Energy and Climate Research, Nuclear Waste Management, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany; ^eCEA, Nuclear Energy Division, RadioChemistry & Processes Department, BP 17171, 30207 Bagnols sur Cèze, France; ^fDepartment of Geological and Environmental Sciences, School of Earth Sciences, Stanford University, Stanford, CA 94305; and ^gDepartment of Civil and Environmental Engineering and Earth Sciences, University of Notre Dame, Notre Dame, IN 46556

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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 solution 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_3O_8 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.

uranium | coffinite | USiO_4 | U(IV) minerals | calorimetry

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 – 10^9 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 uranohorite, 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

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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¹To whom correspondence should be addressed. Email: anavrotsky@ucdavis.edu.

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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 I41/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, 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 back-scattered 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 ($\Delta H_{f,ox}$) 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 $\Delta H_{f,ox}$ of coffinite from this sample. The excess Si is present as amorphous to poorly

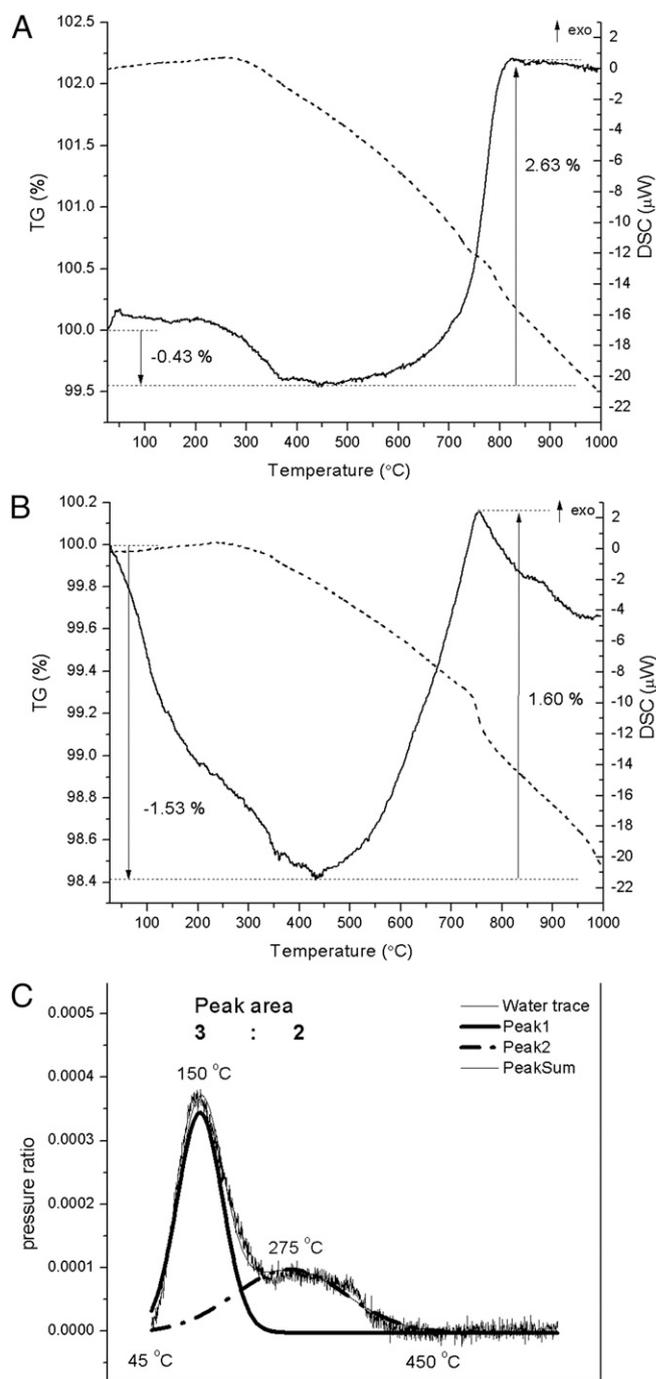


Fig. 1. DSC-TG of coffinite-F [DSC trace in bold solid, and TG trace in bold dash (A)] and coffinite-G (B) with corresponding H₂O⁺ (*m/z* +18) trace from MS-EGA (C).

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 $\Delta H_{f,ox}$ 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

radiolysis of water to form H_2O_2 (25, 51–53); the localized oxidative conditions would help dissolve uraninite into more soluble uranyl (UO_2^{2+}) 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 Deditius et al. (8). A sequence of UO_2 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 UO_2 phase. Under such conditions, USiO_4 could form if its crystallization were kinetically favored over that of UO_2 . Thus, the process of coffinitization may involve a sequence of reactions: UO_2 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 UO_2 and amorphous silica as byproducts, further purification is needed. HNO_3 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 ($\text{Cu K}\alpha$ radiation, 40 kV, and 40 mA), using a step size of 0.016–0.028°. Lattice parameters were refined by the Le Bail method (55).

DSC-TG measurements were performed with a Setaram LabSys instrument coupled with a quadrupole mass spectrometer (MKS Cirrus2) 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 H_2O^+ ($m/z = 18$) and CO_2 ($m/z = 44$) were calibrated by decomposition of calcium oxalate in the same experimental conditions.

Chemical composition and homogeneity were determined using a Cameca SX-100 electron microprobe 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 decomposition products of coffinite-G were recovered after DSC-TG and the ratio of Si/U was further analyzed.

High-temperature oxide melt solution calorimetry was conducted using a custom-built Tian-Calvet twin microcalorimeter (52–54). Powdered samples were hand pressed into small pellets (~5 mg) and were dropped from room temperature into either 30 g of molten $2\text{PbO}\cdot\text{B}_2\text{O}_3$ solvent at 802 °C, or 20 g of molten $3\text{Na}_2\text{O}\cdot 4\text{MoO}_3$ solvent presaturated with 100 mg of SiO_2 (56) at 703 °C, each held in Pt crucibles. O_2 gas 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 O_2 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 $\alpha\text{-Al}_2\text{O}_3$ pellets (58, 59). Upon rapid and complete dissolution of the sample, the enthalpy of drop solution ΔH_{ds} was obtained. Finally, using appropriate thermochemical cycles, enthalpies of formation from the oxides $\Delta H_{\text{f,ox}}$ were calculated.

Previous studies show that silica has a low solubility in $3\text{Na}_2\text{O}\cdot 4\text{MoO}_3$ 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 ZrSiO_4 and HfSiO_4 in this setup and yielded consistent results with experiments done in molten lead $2\text{PbO}\cdot\text{B}_2\text{O}_3$ solvent at 802 °C.

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