Thermodynamic properties of the uranyl carbonate minerals roubaultite, fontanite, widenmannite, grimselite, čejkaite and bayleyite†

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In this paper, the fundamental thermodynamic functions of six important uranyl carbonate minerals, roubaultite, fontanite, widenmannite, grimselite, čejkaite and bayleyite, are computed using first principles solid-state methods based on Periodic Density Functional Theory, from their energy-optimized crystal structures determined in previous works. These properties are obtained within a wide range of temperature (250–800 K) and are employed in order to derive the thermodynamic functions of formation of these minerals in terms of the elements. The resulting temperature-dependent functions of formation are merged with the thermodynamic functions of other prominent uranyl-containing minerals, also determined using theoretical methods, to determine a rich set of thermodynamic functions of reaction for a series of chemical reactions relating these mineral phases. The influence of the presence of hydrogen peroxide in many of these reactions is also investigated. These additional minerals include uranyl oxide hydrates, hydroxides, peroxides, silicates, sulfates and other uranyl carbonate mineral (rutherfordine) and, therefore, a detailed and wide-ranging view of the relative thermodynamic stability of uranyl minerals is afforded. Unexpectedly, the uranyl tr carbonate minerals, grimselite, čejkaite and bayleyite, are shown to be by far the most stable phases within the full range of temperature considered and under the presence and absence of hydrogen peroxide. Furthermore, the analysis of the solubility products of the considered uranyl carbonate minerals, obtained from the Gibbs free energies of the dissolution reactions, reveals that the widespread belief of the great solubility of these minerals is not supported. Except for roubaultite and widenmannite, all these minerals are sparingly soluble. As a consequence, the development of accurate temperature-dependent thermodynamic functions of an even larger number of uranyl carbonate minerals is mandatory for the simulation of the migration of uranium from nuclear waste repositories, uraninite deposits and uranium contaminated sites, as well as for the study of the paragenetic sequence of uranyl minerals arising from the oxidative dissolution processes occurring in uraninite ore deposits and corrosion of spent nuclear fuel.

1 Introduction

The uranyl carbonate^{1–20} minerals are extraordinarily important in actinide environmental chemistry^{1–3,13–15,21–30} because their dissolution/precipitation processes control the aqueous mobility of uranium^{1–10,13–17,19,23–30} in circumneutral to alkaline conditions^{2,8,10} and, therefore, their knowledge is essential in the research of migration of uranium from contaminated sites^{31–39} and nuclear waste repositories (NWR).^{1,8,11,13–15,20,40–45} In recent papers,^{46–48} the energy-optimized crystal structures of a large set of uranyl carbonate minerals were accurately determined using first principles solid-state methods based on Density Functional Theory (DFT) employing plane wave basis

sets and pseudopotential functions.^{49–50} The knowledge of the crystal structures of uranyl-containing minerals is interesting itself for the investigation of the paragenetic sequence of minerals arising from the oxidative dissolution processes of uraninite in uranium ore deposits^{8,10,15,19,51–52} and spent nuclear fuel (SNF) in NWRs,^{8,11,20,40–45} and for the evaluation of the incorporation of fission products and actinides in the corresponding structures.^{53–56} However, the availability of the full crystal structures of uranyl containing minerals is also relevant because opens the possibility of the safe and efficient computation of their vibrational spectra^{47–48,57–68} and physico-chemical properties^{46,48,58–81} employing the first principles solid-state methodology. The knowledge of the optimized structures of the uranyl carbonate minerals rutherfordine, bayleyite, roubaultite, fontanite, widenmannite, grimselite and čejkaite^{46–48} was exploited for the theoretical determination of their mechanical properties.^{46,48,69,73} The thermodynamic properties of rutherfordine were also accurately determined.^{69–72} The main purpose of this work is to extend the previous studies concerning the first principles computation of the thermodynamic properties of uranyl minerals^{59,66–72,75–76} by

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† Electronic Supplementary Information (ESI) available: (a) Plots of the computed heat capacities, entropies, enthalpies and Gibbs free energies of roubaultite, fontanite, widenmannite, grimselite, čejkaite and bayleyite as a function of temperature; (b) Plots of the computed thermodynamic functions of formation; (c) Computed thermodynamic properties of reaction; For ESI, see DOI:10.1039/000000x.

including a representative set of uranyl carbonate minerals. The evaluation of the thermodynamic properties of the uranyl carbonate minerals is crucial because their stabilities and the reaction constants for the chemical reactions in which they are involved, including their solubility products, are functions of their Gibbs free energy, enthalpy, and entropy thermodynamic functions of formation.

The essential importance of the thermodynamic information of materials containing uranium and actinide elements in nuclear technology and environmental sciences for the prediction of the chemical behavior of these materials and for the safety assessment of NWRs, strongly stimulated the research in this area and a significant number of high quality experimental studies reporting the thermodynamic properties of a large set of important materials^{4-7,16-17,82-97} were performed. These efforts have been compiled in large reviews and updates¹³⁻¹⁴ and have driven the generation of several nuclear thermodynamic databases.⁹⁸⁻¹⁰³ Despite these achievements, the thermodynamic information of many uranium-containing materials is unreliable due to the large experimental uncertainties.³ Furthermore, the range of conditions of temperature and pressure for which the thermodynamic parameters are available for most uranium containing materials is rather limited.^{3,70-72} The lack of temperature-dependent thermodynamic information for these phases is due to the great difficulty and expense associated with the thermodynamic measurements for moderately high temperatures. The almost complete absence of temperature-dependent information is a substantial drawback because precludes the possibility of performing reliable thermodynamic modelling studies for the performance assessment of NWRs within the temperature range of interest in a repository, from 295 K to 450 K.¹⁰⁴⁻¹⁰⁵ As a simple illustration, temperature-dependent thermodynamic data have not been published for any of the uranyl carbonate minerals studied in this paper. For grimselite, čejkaite and bayleyite only their enthalpies and Gibbs free energies of formation at 298.15 K have been measured.^{4-7,16} For roubaultite, fontanite and widenmannite there are not experimental data even at room temperature. The values of fundamental thermodynamic functions as the specific heat are completely unknown for all the minerals considered here. The lack of thermodynamic data for the uranyl carbonate minerals and the discrepancies found between some of the measured properties may be related to the difficulties encountered with attempting to control atmospheric compositions.¹⁷ A detailed analysis of the previous theoretical studies,^{59,66-72,75-76} suggests that the first principles methodology is an excellent complement to experimental methodology and provides accurate temperature-dependent thermodynamic functions for uranyl-containing materials. These studies showed that there are significant variations on the relative thermodynamic stabilities (ThS) of uranium minerals as the temperature increases.^{71-72,68} Therefore, the necessity of temperature-dependent data to understand the thermal history of the mineral assemblages is evident. This is particularly important for the performance assessment of NWRs in which significant variations of the temperature are expected over time.

This paper is organized as follows. In Section 2, the first principles solid-state methodology employed in this work to determine the thermodynamic properties of the minerals considered is presented. The main results of this paper are given and discussed in Section 3. In this section, the fundamental thermodynamic functions, the thermodynamic functions of formation and the thermodynamic functions of reaction are reported separately (Subsections 3.1 to 3.3). Then, in Subsection 3.4, the relative thermodynamic stabilities of all these minerals is studied. Subsection 3.5 provides a brief study of the solubility of uranyl carbonates. The conclusions of this work are given in the final Section 4.

2 Computational methods

The energy-optimized crystal structures of the uranyl carbonate materials roubaultite, fontanite, widenmannite, grimselite and čejkaite were determined employing first principles solid-state methods based on Periodic Density Functional Theory employing plane wave basis sets and pseudopotentials to describe the internal atomic electrons⁴⁹ in a recent paper.⁴⁶ The same methods were also used for the computation of the crystal structures of bayleyite⁴⁸ and rutherfordine.⁴⁷ The Perdew-Burke-Ernzerhof (PBE)¹⁰⁶ energy-density functional supplemented with Grimme's empirical dispersion correction¹⁰⁷ was utilized for all the hydrogen-containing minerals (roubaultite, fontanite, widenmannite, grimselite and bayleyite) and the PBEsol functional¹⁰⁸ was employed for čejkaite and rutherfordine. In the present work, the same methods, energy-density functionals, norm-conserving pseudopotentials,¹⁰⁹ plane wave basis sets and *k*-meshes were employed as in the previous papers⁴⁶⁻⁴⁸ to determine the thermodynamic functions of the uranyl carbonate materials. All the calculations were performed using the Cambridge Serial Total Energy Program (CASTEP),⁵⁰ a module of the Materials Studio program suite.¹¹⁰ The specific methods used to determine the fundamental thermodynamic functions (ThF), the thermodynamic functions of formation (ThFOF) and the thermodynamic functions of reaction (ThFOR) are described in the next three subsections, respectively.

2.1 Fundamental thermodynamic properties

The fundamental ThFs were obtained by performing phonon calculations at the energy-optimized crystal structures. The phonon spectra at all the points of the Brillouin zone were calculated using Density Functional Perturbation Theory (DFPT).¹¹¹⁻¹¹² The computed phonon spectra, the phonon dispersion curves and density of states were evaluated and, from them, the fundamental ThFs (Gibbs free energies, *G*, enthalpies, *H*, entropies, *S*, and isobaric specific heats, *C_p*) were obtained.¹¹³ The ThFOFs and ThFORs were then derived from the calculated fundamental ThFs using the methods described in the next two subsections.⁷⁰⁻⁷² All the calculations were performed at zero pressure. The difference with respect to the results at the standard pressure of 1 bar should be very small.

2.2 Thermodynamic properties of formation

For a given reaction of formation of a certain compound, C , in terms of the corresponding elements $[A_1, A_2, \dots]$:

the enthalpies of formation (EnOF) and Gibbs free energies of formation (GiFEOf) of the compound were calculated in terms of the computed enthalpy and entropy functions, $(H_T - H_{298})^{calc}$ and S_T^{calc} using the expressions:^{70,114}

$$\Delta_f H(T) = \Delta_f H^0 + (H_T - H_{298})^{calc} - \sum_i^{elements} n_i (H_T - H_{298})_i^{exp} \quad (2)$$

$$\Delta_f G(T) = \Delta_f H(T) - T \Delta_f S(T) = \Delta_f H(T) - T \left\{ S_T^{calc} - \sum_i^{elements} n_i (S_T)_i^{exp} \right\} \quad (3)$$

where $\Delta_f H^0$ is the enthalpy of formation of the material studied (C) at the standard state (temperature of 295.15 K and pressure of 1 bar), and $(H_T - H_{298})_i^{exp}$ and $(S_T)_i^{exp}$ are the enthalpy and entropy functions of the element A_i forming part of this material with stoichiometric coefficient n_i , respectively. The $\Delta_f H^0$ values used in this work for each mineral are given in Section 3.2. The thermodynamic functions for all the elements except uranium (Na, K, Ca, Cu, Pb, C, O and H) were taken from JANAF (Joint Army-Navy-Air Force) thermochemical tables¹¹⁴. The ThFs for uranium were obtained from Barin.¹¹⁵ The reaction constants of the reactions of formation were evaluated in terms of the corresponding GiFEOfs through the equation:¹¹⁴

$$\Delta G(T) = -R T \ln K \quad (4)$$

2.3 Thermodynamic properties of reaction

For a given chemical reaction,

the enthalpies of reaction (EnOR) and Gibbs free energies of reaction (GiFEOR) as a function of temperature were obtained from the calculated Gibbs free energy and entropy of formation functions, $\Delta_f G(T)^{calc}$ and $\Delta_f S(T)^{calc}$, by means of the equations:^{71,114}

$$\Delta_r G(T) = \sum_i^{products} m_i \Delta_f G^i(T) - \sum_j^{reactants} n_j \Delta_f G^j(T) \quad (6)$$

$$\Delta_r H(T) = \Delta_r G(T) + T \cdot \Delta_r S(T) \quad (7)$$

where,

$$\Delta_r S(T) = \sum_i^{products} m_i \Delta_f S^i(T) - \sum_j^{reactants} n_j \Delta_f S^j(T) \quad (8)$$

In equations (7) and (8), $\Delta_f G^i(T)$ and $\Delta_f S^i(T)$ denote the Gibbs free energy and entropy of formation at temperature T of the compound i . The thermodynamic functions for $Na_2O(cr)$, $K_2O(cr)$, $CaO(cr)$, $CuO(cr)$, $PbO(cr)$, $CO_2(g)$, $O_2(g)$, $H_2O(l)$, and $SiO_2(cr)$ were taken from JANAF thermochemical tables¹¹⁴ and those of $H_2O_2(l)$ from Barin.¹¹⁵ The reaction constants were determined in terms of the corresponding GiFEOfs by using the equation (4).

3. Results and discussion

3.1 Fundamental thermodynamic functions

The computed fundamental ThFs of roubaultite, fontanite, widenmannite, grimselite, čejkaite and bayleyite, in the range of temperature from 250 to 800 K, are given in Table 1. The ThFs are also plotted in Figs. S.1 to S.6 of the ESI.† All the thermodynamic functions given in this paper are given uniformly for a formula of the compound having a single uranium atom. For example, the thermodynamic functions of fontanite correspond to $1/3 Ca[(UO_2)_3(CO_3)_2O_2] \cdot 6 H_2O$. The values of the enthalpies and Gibbs free energies given in Table 1 were divided by the temperature to use the same units for all the ThFs ($J \cdot K^{-1} \cdot mol^{-1}$).

The structural formulae and the calculated isobaric specific heats and entropies at 298.15 K for all the uranyl carbonate minerals are compiled in Table 2. The values of these two important thermodynamic properties have not been reported so far even at room temperature for any of the minerals considered in this paper. The accuracy of the specific heats and entropies at 298.15 K determined using first principles methods was evaluated in a previous paper⁷² from the comparison of the computed and measured values in uranyl-containing materials in which experimental data were available. The accuracy was better than 3-5%. The same accuracy was found for other materials without uranium as natroxalate¹¹⁶ and oxammite¹¹⁷ minerals and for solid squaric acid.¹¹⁸ The same accuracy may be expected for the uranyl carbonate minerals studied in this work since essentially the same methods have been used. The temperature dependence of thermodynamic functions is also expected to be accurate. For example, the computed high-temperature specific heats and entropies of rutherfordine,⁶⁹ γ -uranium trioxide⁵⁹ and metaschoepite⁷⁵ were in very good agreement with their experimental counterparts. The exceptionally large specific heat of bayleyite is clearly a direct consequence of its large water content. The computed values of C_p at the temperature of 1000 K were 268.2, 269.0, 381.8, 501.2, 444.6 and 1402.7 $J \cdot K^{-1} \cdot mol^{-1}$ for roubaultite, fontanite, widenmannite, grimselite, čejkaite and bayleyite, respectively. These values are still 12.8, 14.9, 10.0, 8.7, 6.2 and 20.8% lower than the asymptotic limits imposed by the Dulong-Petit law (307.6, 315.9, 424.0, 548.7, 473.9 and 1770.9 $J \cdot K^{-1} \cdot mol^{-1}$, respectively).

Table 1. Calculated heat capacity, entropy, enthalpy and free-energy functions of roubaultite, fontanite, widenmannite, grimselite, čejkaite and bayleyite (C_p^{calc} , S^{calc} , $(H_T - H_{298})^{calc}$ and $(G_T - H_{298})^{calc}$, respectively). All values are given in units of $J \cdot K^{-1} \cdot mol^{-1}$.

T(K)	Roubaultite				Fontanite			
	C_p^{calc}	S^{calc}	$(H_T - H_{298})^{calc}$	$(G_T - H_{298})^{calc}$	C_p^{calc}	S^{calc}	$(H_T - H_{298})^{calc}$	$(G_T - H_{298})^{calc}$
298.15	188.9248	224.0734	0.0000	-224.0705	190.9762	228.9850	0.0000	-228.9829
250	173.2224	192.1725	-34.9264	-227.0990	175.8175	196.6732	-35.3751	-232.0483
300	189.4673	225.2430	1.1667	-224.0763	191.4982	230.1681	1.1793	-228.9888
350	202.6549	255.4745	29.0408	-226.4337	204.1215	260.6694	29.3007	-231.3687
400	213.4543	283.2637	51.4394	-231.8242	214.4474	288.6223	51.8194	-236.8029
450	222.3865	308.9368	69.9526	-238.9842	223.0219	314.3906	70.3797	-244.0109
500	229.8584	332.7656	85.5803	-247.1853	230.2445	338.2726	86.0150	-252.2576
550	236.1877	354.9782	98.9918	-255.9865	236.4145	360.5139	99.4142	-261.0997
600	241.6207	375.7679	110.6567	-265.1113	241.7598	381.3191	111.0587	-270.2605
650	246.3468	395.2987	120.9166	-274.3821	246.4548	400.8595	121.2969	-279.5626
700	250.5103	413.7104	130.0276	-283.6829	250.6321	419.2795	130.3887	-288.8908
750	254.2201	431.1227	138.1857	-292.9370	254.3918	436.7017	138.5323	-298.1694
800	257.5583	447.6381	145.5439	-302.0942	257.8094	453.2305	145.8820	-307.3486

T(K)	Widenmannite				Grimselite			
	C_p^{calc}	S^{calc}	$(H_T - H_{298})^{calc}$	$(G_T - H_{298})^{calc}$	C_p^{calc}	S^{calc}	$(H_T - H_{298})^{calc}$	$(G_T - H_{298})^{calc}$
298.15	280.0623	375.0464	0.0000	-375.0536	368.2694	494.3524	0.0000	-494.3555
250	259.4614	327.5224	-52.0190	-379.5414	344.1602	431.6035	-68.6679	-500.2714
300	280.7642	376.7760	1.7292	-375.0468	369.0989	496.6196	2.2735	-494.3461
350	298.2538	421.4128	42.8809	-378.5319	390.2356	555.1479	56.2278	-498.9201
400	312.7003	462.2124	75.7338	-386.4787	408.2125	608.4624	99.1325	-509.3299
450	324.6899	499.7571	102.7499	-397.0072	423.5225	657.4508	134.3480	-523.1029
500	334.6923	534.4999	125.4588	-409.0411	436.5832	702.7674	163.9356	-538.8318
550	343.0891	566.8047	144.8726	-421.9321	447.7563	744.9159	189.2427	-555.6733
600	350.1901	596.9702	161.6946	-435.2756	457.3533	784.2977	211.1953	-573.1024
650	356.2448	625.2457	176.4331	-448.8126	465.6382	821.2406	230.4568	-590.7838
700	361.4529	651.8416	189.4674	-462.3742	472.8314	856.0175	247.5183	-608.4992
750	365.9724	676.9370	201.0872	-475.8498	479.1143	888.8585	262.7532	-626.1053
800	369.9284	700.6853	211.5188	-489.1665	484.6354	919.9598	276.4520	-643.5079

T(K)	Čejkaite				Bayleyite			
	C_p^{calc}	S^{calc}	$(H_T - H_{298})^{calc}$	$(G_T - H_{298})^{calc}$	C_p^{calc}	S^{calc}	$(H_T - H_{298})^{calc}$	$(G_T - H_{298})^{calc}$
298.15	327.2191	414.3117	0.0000	-414.3074	861.3010	917.8259	0.0000	-917.8135
250	304.9834	358.6272	-60.9438	-419.5710	770.9813	774.0870	-157.4267	-931.5137
300	328.0015	416.3303	2.0203	-414.3101	864.4715	923.1604	5.3211	-917.8393
350	347.3280	468.3854	50.0085	-418.3769	943.1683	1062.5027	133.8391	-928.6636
400	363.6718	515.8617	88.2232	-427.6385	1009.6285	1192.9060	239.2733	-953.6326
450	377.5253	559.5183	119.6193	-439.8990	1066.2442	1315.1778	328.0948	-987.0830
500	389.2827	599.9199	146.0138	-453.9061	1115.0414	1430.1042	404.4073	-1025.6969
550	399.2772	637.5041	168.5957	-468.9084	1157.6666	1538.4214	470.9893	-1067.4321
600	407.7925	672.6206	188.1833	-484.4373	1195.4236	1640.8017	529.8155	-1110.9861
650	415.0691	705.5563	205.3634	-500.1929	1229.3190	1737.8480	582.3419	-1155.5061
700	421.3095	736.5504	220.5709	-515.9795	1260.1131	1830.0945	629.6709	-1200.4236
750	426.6824	765.8056	234.1370	-531.6686	1288.3691	1918.0101	672.6551	-1245.3550
800	431.3278	793.4949	246.3197	-547.1752	1314.4995	2002.0042	711.9639	-1290.0402

Table 2. Computed isobaric specific heats and entropies at 298.15 K.

Mineral	Structural Formula	$C_p(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$	$S(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$
Roubaultite	$\text{Cu}_2[(\text{UO}_2)_3(\text{CO}_3)_2\text{O}_2(\text{OH})_2] \cdot 4 \text{H}_2\text{O}$	188.92	224.07
Fontanite	$\text{Ca}[(\text{UO}_2)_3(\text{CO}_3)_2\text{O}_2] \cdot 6 \text{H}_2\text{O}$	190.98	228.99
Widenmannite	$\text{Pb}_2[\text{UO}_2(\text{CO}_3)_2(\text{OH})_2]$	280.06	375.05
Grimselite	$\text{K}_3\text{Na}[\text{UO}_2(\text{CO}_3)_3] \cdot \text{H}_2\text{O}$	368.27	494.35
Čejkaite	$\text{Na}_4[\text{UO}_2(\text{CO}_3)_3]$	327.22	414.31
Bayleyite	$\text{Mg}_2[\text{UO}_2(\text{CO}_3)_3] \cdot 18 \text{H}_2\text{O}$	861.30	917.83

Table 3. Standard state enthalpies and Gibbs free energies of formation used in this paper.

Mineral	$\Delta_f H^0 (\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_f G^0 (\text{kJ} \cdot \text{mol}^{-1})$
Roubaultite	-2139.94 ± 10.0^d	-1915.2 ± 10.0^a
Fontanite	-2408.20 ± 10.0^d	-2174.4 ± 10.0^b
Widenmannite	-2871.61 ± 10.0^d	-2581.6 ± 10.0^a
Grimselite	-4431.6 ± 15.3^{16}	-4079.73 ± 15.3^c
Čejkaite	-4032.17 ± 2.3^d	$-3737.8 \pm 2.3^{4,14}$
Bayleyite	-9278.17 ± 8.0^d	-7924.0 ± 8.0^5

^aEstimated in this work.^bEstimated by Finch⁹ and Chen *et al.*¹¹⁹^cDetermined from the experimental¹⁶ value of $\Delta_f H^0$ and the computed value of the entropy (Table 2).^dDetermined from the value of $\Delta_f G^0$ (third column) and the computed value of the entropy (Table 2).**Table 4.** Calculated enthalpies ($\Delta_f H$) and free energies ($\Delta_f G$) of formation and associated reaction constants ($\log K$) of roubaultite, fontanite, widenmannite, grimselite, čejkaite and bayleyite as a function of temperature. The values of $\Delta_f H$ and $\Delta_f G$ are in units of $\text{kJ} \cdot \text{mol}^{-1}$.

T(K)	Roubaultite			Fontanite			Widenmannite		
	$\Delta_f H$	$\Delta_f G$	$\log K$	$\Delta_f H$	$\Delta_f G$	$\log K$	$\Delta_f H$	$\Delta_f G$	$\log K$
298.15	-2139.94	-1915.20	335.53	-2408.20	-2174.40	380.94	-2871.61	-2581.60	452.27
300	-2139.13	-1912.99	333.07	-2407.39	-2172.12	378.19	-2870.39	-2578.58	448.96
350	-2121.14	-1857.23	277.17	-2389.25	-2114.69	315.59	-2843.13	-2503.33	373.59
400	-2108.82	-1807.55	236.04	-2376.89	-2063.43	269.45	-2824.52	-2437.28	318.27
450	-2100.58	-1762.32	204.56	-2368.59	-2016.62	234.08	-2812.12	-2377.90	276.01
500	-2095.42	-1720.47	179.73	-2363.63	-1973.29	206.14	-2804.38	-2323.51	242.73
550	-2092.69	-1681.27	159.67	-2361.05	-1932.58	183.54	-2800.28	-2272.98	215.86
600	-2091.90	-1644.19	143.14	-2360.35	-1893.98	164.88	-2799.15	-2225.70	193.76
650	-2092.71	-1608.86	129.29	-2361.26	-1857.11	149.24	-2807.44	-2180.32	175.21
700	-2094.86	-1575.00	117.52	-2363.59	-1821.71	135.93	-2813.38	-2136.60	159.43
750	-2098.17	-1542.36	107.42	-2367.18	-1787.51	124.49	-2818.76	-2094.78	145.89
800	-2102.48	-1510.80	98.64	-2371.80	-1754.35	114.54	-2824.86	-2054.70	134.15
T(K)	Grimselite			Čejkaite			Bayleyite		
	$\Delta_f H$	$\Delta_f G$	$\log K$	$\Delta_f H$	$\Delta_f G$	$\log K$	$\Delta_f H$	$\Delta_f G$	$\log K$
298.15	-4431.60	-4079.73	714.73	-4032.17	-3737.80	654.83	-9278.17	-7924.00	1388.22
300	-4429.99	-4075.92	709.66	-4030.74	-3734.55	650.23	-9274.77	-7911.86	1377.54
350	-4394.57	-3975.53	593.30	-3999.54	-3654.12	545.33	-9199.10	-7600.80	1134.33
400	-4370.74	-3890.10	507.98	-3978.95	-3584.34	468.06	-9147.25	-7315.54	955.29
450	-4355.20	-3814.82	442.80	-3965.85	-3522.17	408.83	-9112.77	-7049.53	818.27
500	-4345.88	-3746.55	391.39	-3958.28	-3465.67	362.05	-9091.49	-6798.50	710.22
550	-4341.41	-3683.36	349.81	-3954.94	-3413.59	324.19	-9080.67	-6559.54	622.96
600	-4340.77	-3624.11	315.50	-3954.96	-3365.00	292.94	-9078.24	-6330.44	551.10
650	-4343.28	-3568.25	286.74	-3957.72	-3319.24	266.73	-9082.76	-6109.66	490.97
700	-4348.59	-3515.49	262.32	-3962.77	-3275.84	244.44	-9093.12	-5896.04	439.96
750	-4356.73	-3465.74	241.37	-3969.80	-3234.42	225.26	-9108.45	-5688.58	396.18
800	-4368.35	-3419.33	223.25	-3978.56	-3194.72	208.59	-9128.12	-5486.62	358.23

3.2 Thermodynamic functions of formation

3.2.1 Standard state enthalpies and Gibbs free energies of formation

The standard state enthalpies and Gibbs free energies of formation employed in this paper are given in Table 3. The standard state enthalpy of formation of grimselite was taken from Kubatko *et al.*¹⁶ and the corresponding free energy of formation was determined from it and the computed entropy given in Table 2. For bayleyite, the standard state free energy of formation was given by Alwan and Williams⁵ and the enthalpy of formation was obtained from this value of $\Delta_f G^0$ and the calculated entropy (Table 2). The $\Delta_f G^0$ of čejkaite was reported by Guillaumont *et al.*¹⁴ which, in turn, derived it from the solubility value measured by Blake *et al.*⁴ As for bayleyite, the enthalpy of formation was derived from $\Delta_f G^0$ and the calculated entropy. Finally, for roubaultite, fontanite and

widenmannite, the thermodynamic properties of formation have not been measured up to date. For fontanite, the estimate of the standard state Gibbs free energy of formation reported by Finch⁹ and Chen *et al.*¹¹⁹ was used in this paper. Using the same method,^{9,119-121} similar estimates of the Gibbs free energy of formation of roubaultite and widenmannite were obtained.

3.2.2 Computed thermodynamic functions of formation

From the computed fundamental ThFs given in Table 1, the standard state enthalpies of formation given in Table 3 and the experimental ThFs of the corresponding elements,¹¹⁴⁻¹¹⁵ the ThFOFs of the considered uranyl carbonate minerals were derived. The resulting ThFOFs are given in Table 4 and displayed in Fig. S.7 of the ESI.† The expected accuracy of the temperature dependent ThFOFs computed using the same methods as those used in this work was, as for the fundamental ThFs, evaluated in a previous paper.⁷² For rutherfordine, γ uranium trioxide and metaschoepite, the differences of the

calculated and experimental values of the Gibbs free energies of formation were lower than 1% at ambient temperature and remained below 3% at temperatures as high as 800 K.⁷²

According to Eqs. (2) and (3), the contribution of the standard state enthalpy to the EnOF and GiFEOR at a given temperature is strictly additive. Therefore, if the value of $\Delta_f H^0$ of roubaultite, fontanite and widenmannite is measured experimentally in the future, the temperature-dependent thermodynamic functions of formation could be re-evaluated by subtracting the estimated value of $\Delta_f H^0$ from the values reported in Table 4 and adding the experimental value. Similarly, if new improved experimental values of the $\Delta_f H^0$ of grimselite, čejkaite and bayleyite are reported in the future, improved ThFOFs could be generated using the same procedure.

3.3 Thermodynamic functions of reaction

3.3.1 Roubaultite

The calculated ThFOFs of roubaultite were merged with those of γ -uranium trioxide (γ – UO_3), dehydrated schoepite ($\text{UO}_3 \cdot \text{H}_2\text{O}$) rutherfordine (UO_2CO_3) and soddyite ($(\text{UO}_2)_2(\text{SiO}_4) \cdot 2\text{H}_2\text{O}$), derived in a previous work,⁷⁰ in order to derive the ThFORs of the reactions:

The computed EnORs and GiFEORs of reactions (I.A) to (I.D) are reported in Table S.1 of the ESI† and displayed in Fig. 1. Fig. 1.I.A shows that the Gibbs free energy of reaction (I.A) is negative from 298.15 to 371 K. Therefore, the reaction of formation of roubaultite in terms of the corresponding oxides is spontaneous up to 371 K (98 °C). However, from this temperature, roubaultite becomes unstable with respect to the oxides. Similarly, from Fig. 1.I.B, it follows that roubaultite is stable with respect to dehydrated schoepite for temperatures below 345 K (72 °C). As shown in Fig. 1.I.C, the Gibbs free energy of the reaction of transformation of rutherfordine into roubaultite is positive for the full range of temperatures considered (298.15 to 500 K), and therefore roubaultite should transform spontaneously into rutherfordine at all these temperatures. Finally, Fig. 1.I.D shows that in the presence of silicon dioxide, roubaultite will transform into soddyite from 298.15 to 500 K.

3.3.1.1 The presence hydrogen peroxide

The computed ThFOFs of roubaultite were combined with those of schoepite ($[(\text{UO}_2)_8\text{O}_2(\text{OH})_{12}] \cdot 12 \text{H}_2\text{O}(\text{cr})$) and studtite ($(\text{UO}_2)_2\text{O}_2 \cdot 4 \text{H}_2\text{O}$) determined in previous works,^{75,70} to determine ThFORs of the reactions:

The first reaction represents the transformation of roubaultite into schoepite in the presence of equal amounts of water and hydrogen peroxide. Schoepite has been shown to be very stable under the simultaneous presence of H_2O and H_2O_2 .⁷⁵ The second reaction is the conversion of roubaultite into studtite under the presence of hydrogen peroxide and absence of water. The resulting EnORs and GiFEORs are reported in Table S.1 of the ESI† and displayed in Fig. 1. As may be observed in Fig. 1.I.E, roubaultite should transform into schoepite under equal amounts of H_2O and H_2O_2 from 298.15 K and 500 K because the GiFEOR of reaction (I.E) is negative for all temperatures. Likewise, roubaultite should convert into studtite under high concentrations of H_2O_2 from 298.15 K and 500 K since the GiFEOR of reaction (I.F) is negative for all temperatures.

In a deep geological disposal, the contact of the waste with groundwater is expected after a time period of the order of some thousands of years after closure,¹²² when the barriers that protect the waste will be breach.⁴⁵ The reducing conditions in the repository will not be maintained at this time since an oxidative environment in a layer near the fuel surface¹²³ (within 50 μm of the surface) will be produced. These oxidant conditions are consequence of the radiolysis of water due to the strong ionizing radiation associated with the spent fuel^{124–125} leading to the production of oxidants as hydrogen peroxide.¹²⁶ The presence of H_2O_2 and absence of H_2O in reaction (I.E) is a very important condition since it must be met under the effect of intense radiation fields producing the radiolysis of most of the water reaching the surface of the spent nuclear fuel.^{127–130}

3.3.2 Fontanite

As in previous Subsection, the calculated ThFOFs of fontanite were merged with those of γ -uranium trioxide, dehydrated schoepite, rutherfordine and soddyite⁷⁰ to obtain the ThFORs of the corresponding transformation reactions:

Table S.2 of the ESI† contains the computed EnORs and GiFEORs of reactions (II.A) to (II.D). The GiFEORs and the associated reaction constants are plotted in Fig. 2.

Fig. 1. Computed Gibbs free energies of reaction and corresponding reaction constants for the reactions (I.A) to (I.F) as a function of temperature.

Fig. 2. Computed Gibbs free energies of reaction and corresponding reaction constants for the reactions (II.A) to (II.F) as a function of temperature.

Fig. 3. Computed Gibbs free energies of reaction and corresponding reaction constants for the reactions (III.A) to (III.F) as a function of temperature.

Fontanite is stable with respect to the corresponding oxides within the complete range of temperatures considered in this work as shown in Fig. 2.II.A. Furthermore, from Figs. 2.II.B, 2.II.B and 2.II.C, it follows that fontanite is more stable than dehydrated schoepite, rutherfordine and soddyite from 298.15 K to 500 K since the Gibbs free energies of reaction associated with reactions (II.B), (II.C) and (II.D) are negative everywhere. Therefore, fontanite is more stable than the uranyl silicate mineral soddyite that was shown to be very stable under H_2O_2 -free conditions in previous works.^{71-72,75-76,66-68}

3.3.2.1 The presence hydrogen peroxide

The reactions of transformation of fontanite into schoepite in the presence of equal amounts of water and hydrogen peroxide and into studtite in the presence of hydrogen peroxide and absence of water are:

The calculated ThFORs of reactions (II.E) and (II.F) are reported in Table S.2 and displayed in Fig. 2. Since the GiFEOR of reaction (II.E) is positive from 298.15 to 500 K (Fig. 2.II.E), it follows that schoepite will transform into fontanite in the presence of carbon dioxide and equal amounts of water and hydrogen peroxide. However, fontanite will transform into studtite in the presence of high concentration of H_2O_2 because the GiFEOR of reaction (II.F) is negative at all the temperatures.

3.3.3 Widenmannite

The reactions of transformation of γ -uranium trioxide, dehydrated schoepite, rutherfordine and soddyite into widenmannite can be written as:

The ThFORs of these reactions, given in Table S.3 of the ESI† and displayed in Fig 3, were obtained by combining the ThFs of γ -uranium trioxide, dehydrated schoepite, rutherfordine and soddyite⁷⁰ with the ThFs of widenmannite determined in this paper. Fig. 3.III.A, shows that widenmannite becomes unstable

with respect to uranium, lead and carbon oxides and water at 341 K (68 °C). Similarly, from Fig. 3.III.B, it follows that widenmannite is stable with respect to dehydrated schoepite for temperatures below 326 K (53 °C). Widenmannite is unstable with respect to rutherfordine at the full range of temperatures considered (Fig. 3.III.C). Finally, in the presence of silicon dioxide, widenmannite should transform into soddyite from 298.15 to 500 K.

3.3.3.1 The presence hydrogen peroxide

The transformations of widenmannite into schoepite in the presence of equal amounts of water and hydrogen peroxide and into studtite in the presence of hydrogen peroxide and absence of water read:

The corresponding ThFORs are provided in Table S.3 of the ESI† and plotted in Fig. 3. Widenmannite transforms spontaneously into schoepite and studtite according to reactions (III.E) and (III.F), respectively, from 298.15 to 500 K, since the corresponding ThFORs are negative in this complete range of temperature.

3.3.4 Grimselite

The reactions of transformation of grimselite into γ -uranium trioxide, dehydrated schoepite, rutherfordine and soddyite may be written as:

The ThFORs of reactions (IV.A) to (IV.D), are reported in Table S.4 of the ESI† and are shown in Fig 4.

Fig. 4. Computed Gibbs free energies of reaction and corresponding reaction constants for the reactions (IV.A) to (IV.F) as a function of temperature.

Fig. 5. Computed Gibbs free energies of reaction and corresponding reaction constants for the reactions (V.A) to (V.F) as a function of temperature.

Fig. 6. Computed Gibbs free energies of reaction and corresponding reaction constants for the reactions (VI.A) to (VI.F) as a function of temperature.

As shown in Fig. 4, grimselite is stable with respect the corresponding oxides (uranium trioxide dipotassium oxide, disodium oxide, carbon dioxide and water), dehydrated schoepite, rutherfordine and soddyite from 298.15 to 500 K. The GiFEORs of these four reactions are negative and extremely large in absolute value at all temperatures. For example, at room temperature, the calculated GiFEORs of reactions (IV.A), (IV.B), (IV.C) and (IV.E) have the values -841.9 , -828.3 , -803.9 and -791.9 $\text{kJ} \cdot \text{mol}^{-1}$, respectively.

3.3.4.1 The presence hydrogen peroxide

The reactions of transformation of grimselite into schoepite in the presence of equal amounts of H_2O and H_2O_2 and into studtite in the presence of H_2O_2 and absence of H_2O are:

The calculated ThFORs of reactions (IV.E) and (IV.F) are given in Table S.4 and shown in Figs. 4.E and 4.F, respectively. As can be seen in these figures, the ThFORs of these reactions are positive in the full range of temperature studied and, therefore, grimselite is more stable than schoepite and studtite at the corresponding conditions. As in the case of H_2O_2 -free conditions, the GiFEOR of reactions (IV.E) and (IV.F) are extremely large (750.1 and 586.4 $\text{kJ} \cdot \text{mol}^{-1}$ at 298.15 K, respectively).

3.3.5 Čejkaite

The transformations of γ -uranium trioxide, dehydrated schoepite, rutherfordine and soddyite into čejkaite can be expressed as:

Table S.5 contains the calculated ThFORs of these reactions, which are also plotted in Fig 5. As grimselite, čejkaite is stable with respect to the corresponding oxides, dehydrated schoepite, rutherfordine and soddyite from 298.15 to 500 K, and the GiFEORs of the four reactions are negative and their absolute values, although smaller than for grimselite, are also exceptionally large at all temperatures. At 298.15 K, the

GiFEORs of reactions (V.A), (V.B), (V.C) and (V.E) are -651.5 , -637.9 , -828.3 , -613.6 and -601.6 $\text{kJ} \cdot \text{mol}^{-1}$, respectively.

3.3.5.1 The presence hydrogen peroxide

The reaction of conversion of čejkaite into schoepite in the presence of equal amounts of H_2O and H_2O_2 is:

and the transformation of čejkaite into studtite in the presence of H_2O_2 and absence of H_2O :

The calculated ThFORs of these reactions are provided in Table S.5 and displayed Fig. 5. The ThFORs of both reactions are positive and large from 298.15 to 500 K, but smaller than for grimselite, 501.4 and 279.3 $\text{kJ} \cdot \text{mol}^{-1}$ at room temperature, respectively.

3.3.6 Bayleyite

Bayleyite transforms into γ -uranium trioxide, dehydrated schoepite, rutherfordine and soddyite according to the reactions:

The computed ThFORs of reactions (VI.A) to (VI.D) are provided in Table S.6 of the ESI† and represented graphically in Fig. 6. As shown in Figs. 6.I.1 and 6.I.2, bayleyite is stable with respect to the corresponding oxides up to 370 K (97°C) and with respect dehydrated schoepite up to 367 K (94°C). Bayleyite is also stable with respect to rutherfordine and soddyite below 360 K (87°C) and 353 K (80°C), respectively.

3.3.6.1 The presence hydrogen peroxide

The reactions of transformation into bayleyite under equal amounts of H_2O and H_2O_2 and into studtite under the presence of H_2O_2 and absence of water are:

and

The computed ThFORs of these reactions are given in Table S.6 and displayed in Fig. 6. The GiFEORs of reaction (VI.E) and (VI.F) are positive and exceedingly large, 1090.7 and 1919.9 kJ · mol⁻¹ at room temperature, nearly 391 and 1333.5 kJ · mol⁻¹ larger than the corresponding GiFEORs for grimselite, respectively. Therefore, bayleyite is highly stabilized under the presence of high concentrations of hydrogen peroxide.

3.4 Relative thermodynamic stabilities

The relative ThSs of eighteen important secondary phases of SNF were determined from the computed thermodynamic functions of the uranyl carbonate minerals obtained in this work and those reported in previous papers.^{59,66-72,75-76} This set is composed of the seven uranyl carbonate minerals studied here

and studtite, metastudtite, soddyite, dehydrated schoepite, schoepite, metaschoepite, becquerelite, vandenbrandeite, uranosphaerite, uranopilite and γ -UO₃. The stability of these phases was evaluated: (A) under H₂O₂-free conditions; (B) in the simultaneous presence of H₂O and H₂O₂; and (C) under high concentration of H₂O₂. The resulting thermodynamic stabilities are displayed in Figs. 7.A, 7.B and 7.C, respectively, in the temperature range going from 300 to 500 K.

Fig. 7.A, shows that the most stable phase at H₂O₂-free conditions is grimselite, which is more stable than soddyite, the most stable phase found in previous works, by -791.9 kJ · mol⁻¹ at room temperature. The next more stable phases are čejkaite, bayleyite and fontanite, which are also more stable than soddyite. Bayleyite, under these conditions, is strongly destabilized as the temperature increases and becomes less stable than fontanite at 341 K and soddyite at 353 K.

Fig. 7. Relative ThS of the uranyl carbonate minerals: (A) Under the absence of hydrogen peroxide; (B) Under the presence of water and hydrogen peroxide; (C) Under high concentrations of hydrogen peroxide. The labels of the different phases are ordered vertically according to their relative ThS at 300 K.

Table 5. Calculated solubility products of the uranyl carbonate minerals, roubaultite, fontanite, widenmannite, grimselite, čejkaite, and bayleyite.

Mineral	Dissolution Reaction	Log K_S		Dissolution Reaction	Log K_S	
		Calc.	Exp.		Calc.	Exp.
Roubaultite	(VII.1)	-11.4 ± 1.7	-	(VIII.1)	$+5.2 \pm 1.7$	-
Fontanite	(VII.2)	-28.0 ± 1.7	-	(VIII.2)	-11.4 ± 1.7	-
Widenmannite	(VII.3)	-8.8 ± 1.7	-	(VIII.3)	$+7.8 \pm 1.7$	-
Grimselite	(VII.4)	-34.5 ± 2.6	$-29.6 \pm 0.2,^6 -37.1 \pm 0.3^{17}$	(VIII.4)	-12.6 ± 2.6	-
Čejkaite	(VII.5)	-26.9 ± 0.4	-	(VIII.5)	-5.1 ± 0.4	-5.34 ± 0.16^{14}
Bayleyite	(VII.6)	-36.5 ± 1.4	$-40.6 \pm 0.8,^5 -36.6 \pm 1.4^{17}$	(VIII.6)	-14.7 ± 1.3	-

The relative ThS of the uranyl minerals are significantly altered as the concentration of hydrogen peroxide increases. As can be observed in Fig. 7.B, in the presence of equal amounts of water and hydrogen peroxide, bayleyite becomes by far the most stable phase within the full range of temperature. The next three more stable phases are grimselite, čejkaite, and fontanite. These four uranyl carbonate minerals are more stable than the uranyl sulfate mineral uranopilite, the most stable phase found in previous works⁶⁸ under the presence of water and hydrogen peroxide. At 298.15 K, bayleyite is more stable than uranopilite at these conditions by 1090.7 kJ · mol⁻¹.

Finally, under the presence of high concentration of hydrogen peroxide (Fig. 7.C), the three most stable phases are again the three uranyl tricarboxylate minerals bayleyite, grimselite, and čejkaite over the full range of temperatures. The dominance of bayleyite at this condition over the remaining phases is notable, being more stable at 298.15 K than grimselite by 1333.53 kJ · mol⁻¹ and more stable than studtite, the most stable phase encountered in previous works, by 1919.9.7 kJ · mol⁻¹.

The great stability of highly hydrated phases at high concentrations of hydrogen peroxide, noted in the previous works,^{68,70,75} is again observed here because bayleyite containing 18 water molecules per formula unit is the most stable phase. However, grimselite and čejkaite containing only one or no water molecules per formula unit are the second and third most stable minerals and, hence, the larger stability of the higher hydrates only occurs between compounds having the same compositions. For example studtite and schoepite are more stable than the corresponding lower hydrates, metastudtite and metaschoepite, at these conditions.^{71,75}

The results given in this Section must be interpreted considering the availability of the different cations and anions for the formation of the corresponding minerals. For example, at high concentration of hydrogen peroxide, if magnesium is not present, bayleyite cannot be formed and grimselite will be the most stable phase instead. Likewise, if magnesium and potassium are not available, the sodium uranyl tricarboxylate čejkaite will be formed. Finally, in the absence of these cations, or in the presence of them and absence of carbonate, studtite is the dominant phase.

The present results demonstrate the great thermodynamic dominance of the uranyl tricarboxylate minerals. However, their formation in the environment may be limited due to kinetic constraints. Therefore, the interplay of thermodynamics and kinetics should clearly be investigated to complement the results of the present work.

3.5 Solubility products

Let us consider the following dissolution reactions for roubaultite, fontanite, widenmannite, grimselite, čejkaite, and bayleyite, respectively:

From the computed Gibbs free energies of formation of the uranyl carbonate minerals at 298.15 K and the Gibbs free energies of formation of water and the aqueous ions $\text{UO}_2^{2+}(\text{aq})$, $\text{CO}_3^{2-}(\text{aq})$, $\text{Cu}^{2+}(\text{aq})$, $\text{Ca}^{2+}(\text{aq})$, $\text{Pb}^{2+}(\text{aq})$, $\text{K}^+(\text{aq})$, $\text{Na}^+(\text{aq})$ and $\text{Mg}^{2+}(\text{aq})$,^{14,131} we can obtain the corresponding GiFEORs and associated reaction constants (the solubility products, K_S). The values obtained for the logarithm of the solubility product, Log K_S , of roubaultite, fontanite, widenmannite, grimselite, čejkaite and bayleyite are -11.4 ± 1.7 , -28.04 ± 1.7 , -8.84 ± 1.7 , -34.5 ± 2.6 , -26.9 ± 0.4 and -36.5 ± 1.4 , respectively (Table 5). The computed solubility products for grimselite and bayleyite agree well with the experimental values reported by O'Brien and Williams,⁶ -29.6 ± 0.2 , and Alwan and Williams, -40.6 ± 0.8 ,⁵ respectively, and the more recent values given by Gorman-Lewis *et al.*,¹⁷ -37.1 ± 0.3 and -36.6 ± 1.4 , respectively. However, these values were determined from the Gibbs free energies of the hypothetical reactions (VII.4) and (VII.6) and are not true experimental

values. The calculated solubility product of čejkaite, -26.95 ± 0.4 , disagrees with the experimental value of $\log K_S = -5.34 \pm 0.16$.¹⁴ This is because reactions (VII.1) to (VII.6) neglect the possibility of formation of highly stable uranyl carbonate complexes. A set of more realistic dissolution reactions are:

Using the computed Gibbs free energies of formation of the uranyl carbonate minerals and the Gibbs free energies of formation of water and the aqueous ions $[\text{UO}_2(\text{CO}_3^{2-})_2]^{2-}(\text{aq})$, $\text{UO}_2(\text{CO}_3)_3^{4-}(\text{aq})$, $\text{UO}_2^{2+}(\text{aq})$, $\text{Cu}^{2+}(\text{aq})$, $\text{Ca}^{2+}(\text{aq})$, $\text{Pb}^{2+}(\text{aq})$, $\text{K}^+(\text{aq})$, $\text{Na}^+(\text{aq})$ and $\text{Mg}^{2+}(\text{aq})$,^{14,131} the corresponding solubility products were determined and are given in Table 5. The value obtained for $\log K_S$ of čejkaite is -5.1 ± 0.4 , which is in excellent agreement with the experimental value of -5.34 ± 0.16 .¹⁴ The consideration of the proper dissolution reactions including highly stable uranyl carbonate complexes strongly increases the calculated solubility products and brings the solubility product of čejkaite into agreement with experiment. The resulting values of $\log K_S$ for fontanite, grimselite, čejkaite and bayleyite (-11.4 ± 1.7 , -12.6 ± 2.6 , -5.1 ± 0.4 , -14.7 ± 1.3 , respectively) are negative and large. Therefore, these five minerals are sparingly soluble. The same occurs for the uranyl carbonate mineral rutherfordine, which has a solubility product $\log K_S = -14.76 \pm 0.02$.¹⁴ In contrast, roubaultite and widemannite have larger solubilities and the values of $\log K_S$ are positive ($+5.2 \pm 1.7$ and $+7.8 \pm 1.7$).

Other dissolution processes competing with (VIII.1)–(VIII.6) could be considered but, due to the great stability¹⁴ of the complexes $[\text{UO}_2(\text{CO}_3^{2-})_2]^{2-}$ and $[\text{UO}_2(\text{CO}_3)_3]^{4-}$, the values given in Table 5 should be an upper bound of the experimental values. As a reference, the $\log K_S$ values for other well-known uranyl-containing minerals as schoepite, metaschoepite, soddyite and uranophane are 4.6 ± 1.7 , 5.6 ± 0.2 , 6.4 ± 0.4 and 9.4 ± 0.5 , respectively.^{17,75} Therefore, the three uranyl tricarbonate minerals considered (grimselite, čejkaite and bayleyite) and fontanite have small solubilities and the solubilities of roubaultite and widemannite are of the same order as those of other uranyl-containing minerals. Therefore, the widespread belief of the great solubility of uranyl carbonate minerals is not supported by the present work.

4 Conclusions

In this work, the specific heat, entropy, enthalpy, and Gibbs free energy functions of the uranyl carbonate minerals, roubaultite, fontanite, widemannite, grimselite, čejkaite and bayleyite are determined using first principles solid-state methods. These

properties are obtained within the range of temperature from 250 to 800 K and are used to derive the thermodynamic functions of formation of these minerals. Then, these temperature dependent functions of formation are combined with the thermodynamic functions of formation of other prominent uranyl-containing minerals, also determined using theoretical methods in previous papers,^{59,66–72,75–76} to get the thermodynamic functions of reaction for a large series of chemical reactions connecting these mineral phases. A wide-ranging view of the relative thermodynamic stability of eighteen different uranyl minerals, including uranyl oxide hydrates, hydroxides, peroxides, silicates, sulfates and carbonates is provided. The uranyl tricarbonate minerals, grimselite, čejkaite and bayleyite, are shown to be by far the most stable uranyl-containing phases among those studied in this paper, within the full range of temperature considered and under the presence and absence of hydrogen peroxide. Significant changes in the relative stabilities of these minerals as the temperature increases are observed. For example, at H_2O_2 -free conditions, bayleyite being substantially more stable than the uranyl silicate soddyite at room temperature is destabilized as the temperature increases and becomes less stable than soddyite at 325 K. Furthermore, the analysis of the solubility products of the uranyl carbonate minerals studied reveals that they are quite insoluble in contrast to the common conviction that most uranyl carbonates are soluble. From the results, it is concluded that, due to the ubiquitous presence of organic matter and carbon-containing materials, additional efforts, experimental and theoretical, should be made for the development of accurate temperature-dependent thermodynamic functions of an extended set of uranyl carbonate minerals, containing additional chemical elements, for the proper simulation and understanding of the dissolution/precipitation processes involved in the migration of uranium from contaminated sites, uranium ore deposits and nuclear waste repositories.

Conflict of Interest

There are no conflicts of interest to declare.

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