

The aqueous chemistry of uranium minerals. 4. Schröckingerite, grimselite, and related alkali uranyl carbonates

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ABSTRACT. Using solution techniques, $\Delta G_{f(298.2\text{ K})}^{\circ}$ has been calculated for schröckingerite, $\text{NaCa}_3\text{UO}_2(\text{CO}_3)_3\text{SO}_4\text{F}\cdot 10\text{H}_2\text{O}$, and grimselite, $\text{NaK}_3\text{UO}_2(\text{CO}_3)_3\cdot \text{H}_2\text{O}$. The values are -8077.3 ± 8.7 and -4051.3 ± 1.8 kJ mol⁻¹ respectively. $\Delta H_{f(298.2\text{ K})}^{\circ}$ for grimselite is -4359.0 ± 1.8 kJ mol⁻¹. An estimate for ΔG_f° of the synthetic compound $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$, using previously published equilibria has been made, -3720.0 ± 9.7 kJ mol⁻¹. The results have been used to reconstruct the chemical environments in which these and related compounds can form. Grimselite is only stable at relatively high activities of $\text{K}_{(\text{aq})}^+$ and the alkali metal carbonates containing only potassium or sodium ions have not been reported to occur naturally. This is most probably due to their relatively high solubility in water. Schröckingerite can form from solutions which are more than saturated with respect to calcite and fluorite. The close relationship of schröckingerite with gypsum, observed frequently in the field, is evident from synthetic and solution studies.

In previous papers in this series we have reported the stabilities of a variety of secondary uranyl minerals which may play a part in the dispersion of uranium from its orebodies by the action of groundwater. Part 3 (O'Brien and Williams, 1981) dealt with divalent cation zippeites which contain sulphate and previous studies concentrated on minerals which contain the complex ion $\text{UO}_2(\text{CO}_3)_3^{4-}$ (Alwan and Williams, 1980). Species containing this ion are of widespread occurrence but in small quantities. The most common, and perhaps most complex, is the mineral schröckingerite, $\text{NaCa}_3\text{UO}_2(\text{CO}_3)_3\text{SO}_4\text{F}\cdot 10\text{H}_2\text{O}$, originally described by Schrauf (1873). The true formula was established by Jaffe *et al.* (1948), and confirmed by synthesis (Ross, 1955). A list of earlier occurrences has been compiled by Frondel (1958) and more recent finds in the Ambrosia Lake district of New Mexico have been reported by Barczak (1966). Schröckingerite frequently occurs admixed with gypsum and other members of the *tris*-carbonato-dioxouranium (VI) group of minerals.

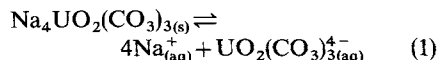
Another sodium-containing species, grimselite, $\text{NaK}_3\text{UO}_2(\text{CO}_3)_3\cdot \text{H}_2\text{O}$, was recently described by Walenta (1972). Found in a cable tunnel in the Aarmassif, Switzerland, it was associated with monohydrocalcite and also schröckingerite. In this paper we report the thermodynamic stabilities of both schröckingerite and grimselite, calculated from solution experiments, and describe the chemical environments in which they may crystallize from aqueous solution. In addition we have attempted to relate these conditions to others in which the related minerals andersonite, $\text{Na}_2\text{CaUO}_2(\text{CO}_3)_3\cdot 6\text{H}_2\text{O}$, and liebigite, $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3\cdot 10\text{H}_2\text{O}$ can be formed. The synthetic alkali metal species $\text{K}_4\text{UO}_2(\text{CO}_3)_3$ and $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$ are also discussed, and an estimate has been made of the magnitude of ΔG_f° of the latter. Neither of the alkali uranyl carbonates has been reported to occur naturally, and a comment can be made on this fact in the light of the compounds' solubility in water.

Schröckingerite was synthesized using the method of Ross (*op. cit.*). We have found that several recrystallizations of the synthetic material from aqueous solution do not entirely remove all the gypsum impurity present in this preparation and have carried out our solution studies with this fact in mind. The solubility of schröckingerite at 298.2 K was determined by uranyl analysis, but sulphate was analysed separately so that the contribution of $\text{Ca}_{(\text{aq})}^{2+}$ and $\text{SO}_{4(\text{aq})}^{2-}$ from gypsum dissolution could also be taken into account. A check on the nature of solids remaining after each experiment, using X-ray powder methods, revealed that schröckingerite dissolves congruently. Furthermore, the presence of gypsum in the solid afforded an evaluation of the validity of computer calculations, using the program COMICS (Perrin and Sayce, 1967), of the species distributions in the aqueous solutions in equilibrium with schröckingerite (*vide infra*). Grimselite was synthesized by

slowly adding an aqueous solution of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}_{(s)}$ to one of $\text{Na}_2\text{CO}_{3(s)}$ and $\text{K}_2\text{CO}_{3(s)}$ in the stoichiometric ratio. Evaporation of the mixture at room temperature yielded crystals up to 1 cm in size of the required compound. This method is essentially the same as that employed by Mazzi and Rinaldi (1960, 1961), except that these workers used somewhat different ratios of starting materials and reported no water of crystallization in their product. Grimselite prepared using our method was analysed for water and corresponds to the formula $\text{NaK}_3\text{CO}_2(\text{CO}_3)_3 \cdot \text{H}_2\text{O}$ [$\text{H}_2\text{O}(\text{calc.}) = 2.96$; $\text{H}_2\text{O}(\text{found}) = 2.7\%$] and corresponds with the reported X-ray powder diffraction data (Walenta, 1972).

Free energies of formation of schröckingerite and grimselite were calculated in the usual way using previously published procedures (Alwan and Williams, 1979). $\Delta H_{f(298.2\text{K})}^\circ$ for grimselite was estimated by calculation of its solubility product

at a series of temperatures and treatment of the usual Arrhenius expression. The solubility of schröckingerite in water at 298.2 K is $0.0083 \pm 0.0003 \text{ mol dm}^{-3}$, and with varying pH from 7.69 to 8.40. The solubility of grimselite from 278.8 K to 298.2 K was constant and equal to $0.0446 \pm 0.0005 \text{ mol dm}^{-3}$ but the pH varied from 9.47 to 10.08 over this temperature range. The negligible variation of solubility of grimselite over the temperature range parallels some properties of the synthetic compound $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$. Blake *et al.* (1956) found that the equilibrium constant for equation (1) was equal to $10^{-2.68}$ with little variation from 299.2 to 303.2 K.



Accordingly, we have extrapolated this value to 298.2 and used it, together with that for the formation of the *tris*-carbonato anion taken from

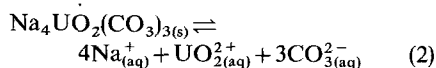
TABLE I. Solubility and computed equilibrium concentrations in mol dm^{-3} together with other solution parameters for the calculations for schröckingerite and grimselite.

Schröckingerite												
T/K	$10^2[\text{UO}_2^{2+}]_{\text{TOT}}$	$10[\text{SO}_4^{2-}]_{\text{TOT}}$	$[\text{UO}_2^{2+}]_e$	$10^2[\text{Ca}^{2+}]_e$	$10^3[\text{Na}^+]_e$	$10^5[\text{CO}_3^{2-}]_e$	$10^3[\text{SO}_4^{2-}]_e$	$10^3[\text{F}^-]_e$	pH			
293.2	0.8303	0.916	1.474×10^{-10}	1.999	8.184	1.977	5.392	7.541	7.69			
298.2	0.8303	1.06	1.331×10^{-11}	2.113	8.181	5.396	6.290	7.549	8.31			
298.2	0.8303	0.993	1.611×10^{-11}	2.058	8.188	4.998	5.945	7.572	8.34			
298.2	0.8303	0.937	9.784×10^{-12}	2.050	8.192	6.086	5.609	7.565	8.40			
	$\gamma_{\text{UO}_2^{2+}}$	$\gamma_{\text{Ca}^{2+}}$	γ_{Na^+}	$\gamma_{\text{CO}_3^{2-}}$	$\gamma_{\text{SO}_4^{2-}}$	γ_{F^-}	I	$10^{39}K_{\text{SP}}^a$				
298.2	0.409	0.399	0.787	0.395	0.382	0.767	0.0924	1.111				
298.2	0.391	0.382	0.778	0.376	0.363	0.755	0.1079	1.890				
298.2	0.395	0.385	0.779	0.380	0.366	0.758	0.1047	1.64 μ				
298.2	0.392	0.383	0.778	0.378	0.353	0.756	0.1067	1.627				
Grimselite												
	$10[\text{UO}_2^{2+}]_{\text{TOT}}$	$10^{14}[\text{UO}_2^{2+}]_e$	$[\text{K}^+]_e$	$10^2[\text{Na}^+]_e$	$10^4[\text{CO}_3^{2-}]_e$	pH	$\gamma_{\text{UO}_2^{2+}}$	γ_{K^+}	γ_{Na^+}	$\gamma_{\text{CO}_3^{2-}}$	I	$10^{30}K_{\text{SP}}^b$
278.8	0.446	7.019	0.134	4.454	5.782	10.00	0.268	0.660	0.719	0.247	0.4387	1.219
283.1	0.446	4.237	0.134	4.451	7.334	10.08	0.266	0.658	0.717	0.246	0.4384	1.446
283.8	0.446	6.359	0.134	4.450	6.468	9.80	0.266	0.658	0.717	0.246	0.4365	1.485
288.0	0.446	8.536	0.134	4.446	6.228	9.50	0.265	0.658	0.716	0.245	0.4324	1.743
288.0	0.446	3.609	0.134	4.446	8.358	9.92	0.264	0.657	0.716	0.244	0.4363	1.755
293.3	0.446	4.882	0.134	4.439	8.164	9.55	0.262	0.655	0.714	0.242	0.4311	2.130
298.2	0.446	4.050	0.134	4.430	9.359	9.47	0.261	0.654	0.712	0.240	0.4277	2.557

^a K_{SP} for reaction $\text{NaCa}_3\text{UO}_2(\text{CO}_3)_3\text{SO}_4 \cdot 10\text{H}_2\text{O}_{(s)} \rightleftharpoons \text{Na}_{(aq)}^+ + 3\text{Ca}_{(aq)}^{2+} + \text{UO}_2^{2+}_{(aq)} + 3\text{CO}_3^{2-}_{(aq)} + \text{SO}_4^{2-}_{(aq)} + \text{F}^-_{(aq)} + 10\text{H}_2\text{O}_{(l)}$.

^b K_{SP} for reaction $\text{K}_3\text{NaUO}_2(\text{CO}_3)_3 \cdot \text{H}_2\text{O}_{(s)} \rightleftharpoons 3\text{K}_{(aq)}^+ + \text{Na}_{(aq)}^+ + \text{UO}_2^{2+}_{(aq)} + 3\text{CO}_3^{2-}_{(aq)} + \text{H}_2\text{O}_{(l)}$.

Langmuir (1978) to estimate ΔG° for the equation (2).



Thus we have been able to estimate in turn ΔG_f° for $\text{Na}_4\text{UO}_2(\text{CO}_3)_3(\text{s})$ at 298.2 K as $-3720.0 \pm 9.7 \text{ kJ mol}^{-1}$.

Concentrations calculated by the program COMICS were for the aqueous species UO_2^{2+} , Ca^{2+} , Na^+ , K^+ , CO_3^{2-} , SO_4^{2-} , and F^- , together with the complex ions UO_2OH^+ , $(\text{UO}_2)_2(\text{OH})_2^{2+}$, $(\text{UO}_2)_3(\text{OH})_5^+$, $(\text{UO}_2)_3(\text{OH})_4^{2+}$, UO_2CO_3 , $\text{UO}_2(\text{CO}_3)_2^{2-}$, $\text{UO}_2(\text{CO}_3)_3^{4-}$, UO_2SO_4 , $\text{UO}_2(\text{SO}_4)_2^{2-}$, UO_2F^+ , UO_2F_2 , UO_2F_3 , UO_2F_4^- , NaHCO_3 , NaCO_3^- , Na_2CO_3 , NaSO_4^- , Na_2SO_4 , CaOH^+ , CaHCO_3^+ , CaCO_3 , CaSO_4 , CaF^+ , HCO_3^- , H_2CO_3 , HSO_4^- , HF° , and HF_2^- . Equilibrium constants for the hydrolysed species were taken from Baes and Mesmer (1976), and those for all other uranyl species from Langmuir (1978). Except for the species CaF^+ , HCO_3^- , H_2CO_3 , HF° , HF_2^- , and NaSO_4^- (Smith and Martell, 1975), all other equilibrium constants are taken from Truesdell and Jones (1974). Corrections for ionic strength to the equilibrium constants and for individual ionic activities were made using data from the above authors and the methods of Reardon and Langmuir (1976), Kielland (1937) and Alwan (1980). Solubility data, computed concentrations of free ionic species, and relevant thermodynamic and equilibrium quantities are shown for schrockingerite and grimselite in Table I. Values of ΔG_f° and ΔH_f° for these compounds, and others of interest taken from Alwan and Williams (1980) are given in Table II. Opportunity is taken here to correct an error for $\Delta G_f^\circ(298.2 \text{ K})$ of andersonite in the last reference. It was given as $-5651.0 \text{ kJ mol}^{-1}$, but should read $-5251 \text{ kJ mol}^{-1}$. Because gypsum was admixed with the schrockingerite used in this study, K_{sp} could be calculated for this mineral and hence ΔG_f° . This quantity at 298.2 K was found to be $-1799.8 \pm 1.9 \text{ kJ mol}^{-1}$ which is in excellent agreement with recent published values of $-1797.2 \pm 4.6 \text{ kJ mol}^{-1}$ (Robie *et al.*, 1978). The correlation indicates that the rather complex calculation involved with

the determination of the solubility product of schrockingerite is valid. The data of Robie *et al.* (1978) for ΔG_f° and ΔH_f° of free ions and $\text{H}_2\text{O}(\text{l})$ was used except for $\text{UO}_2^{2+}(\text{aq})$, values for which were taken from Fuger and Oetting (1976).

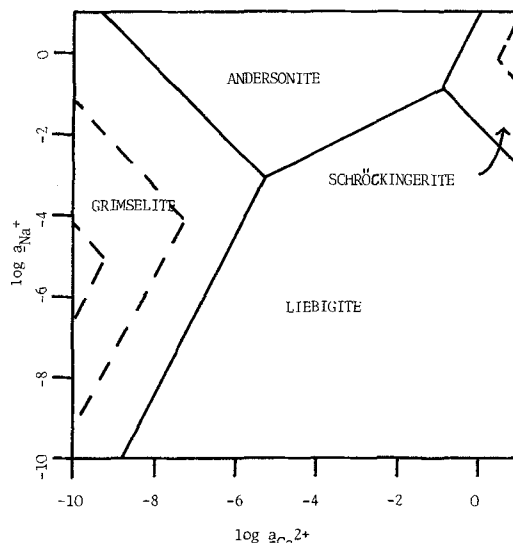
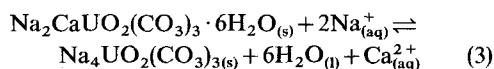


FIG. 1. Stability field diagram for the minerals. The wedge-shaped grimselite field on the left is contoured for the values of a_{K^+} as marked. The schrockingerite field on the right is contoured for (—) $\log a_{\text{SO}_4^{2-}} = \log a_{\text{F}^-} = 0$, and (---) $\log a_{\text{SO}_4^{2-}} = \log a_{\text{F}^-} = -1$.

Fig. 1 shows fields of stability of grimselite, expressed in terms of activity of $\text{Na}_{(\text{aq})}^+$ and $\text{Ca}_{(\text{aq})}^{2+}$, relative to the potassium-free minerals andersonite and liebigite. At very high values of a_{K^+} , the grimselite field impinges significantly on to those of the latter two species. However, it should be remembered that potassium ion in natural aqueous solution is usually of a significantly lower concentration (and activity) than sodium ion. It is therefore expected that grimselite will be of somewhat limited occurrence compared with, say, andersonite or liebigite. This is indeed the case as grimselite has been reported from only one locality.

With this in mind it is worth drawing attention to the fact that neither $\text{Na}_4\text{UO}_2(\text{CO}_3)_3(\text{s})$ nor $\text{K}_4\text{UO}_2(\text{CO}_3)_3$ has been found to occur naturally. Using data from Table II and from Robie *et al.* (1978) the boundary of thermodynamic stability between the sodium member and andersonite (3) can be calculated, giving rise to expression (4).



$$\log a_{\text{Na}^+} = 6.77 + 0.5 \log a_{\text{Ca}^{2+}} \quad (4)$$

TABLE II. Thermodynamic quantities at 298.2 K for the minerals

Mineral	$\Delta G_f^\circ/\text{kJ mol}^{-1}$	$\Delta H_f^\circ/\text{kJ mol}^{-1}$	Reference
schrockingerite	-8077.3 ± 8.7	—	this work
grimselite	-4051.3 ± 1.8	-4359.0 ± 1.8	this work
andersonite	-5251 ± 24	-5916 ± 36	see text
liebigite	-6226 ± 12	-7037 ± 24	see text
$\text{Na}_4\text{UO}_2(\text{CO}_3)_3(\text{s})$	-3720.0 ± 9.7	—	this work

The exceptionally high activities of $\text{Na}_{(\text{aq})}^+$ required in most instances to effect the transformation are unlikely to obtain naturally, especially in view of the associated low activities of calcium ion also required. These thermodynamic expressions are the result of the considerably greater solubility of $\text{Na}_4\text{UO}_2(\text{CO}_3)_{3(\text{s})}$ compared with the other minerals.

Similarly, although thermodynamic data are not available, to our knowledge, for $\text{K}_4\text{UO}_2(\text{CO}_3)_{3(\text{s})}$, the solubility studies of Bachelet *et al.* (1954) indicate that such is also the case for this compound. The absence to date of recognition of the alkali metal end members of the series $M_x^+ M_{(4-x)}^+ \text{UO}_2(\text{CO}_3)_3 \cdot n\text{H}_2\text{O}$ in nature appears to rest on their significantly higher solubility in aqueous solution.

Also plotted in fig. 1 is the field of stability, relative to the same other uranyl carbonates, of schröckingerite, calculated at $\log a_{\text{SO}_4^{2-}} = \log a_{\text{F}^-} = -1$ and 0. These high activities are necessary to express any stability field for the compound and the values can only be achieved in comparatively concentrated solution. Therefore it is necessary to consider the general solution chemistry of schröckingerite in order to explain its widespread occurrence in the oxidation zones of uraniferous orebodies. In particular the calculated activities of free ions in equilibrium with schröckingerite (Table I) deserves some attention. Several ion products for relevant sparingly soluble salts may be calculated from the experimental data. This has already been done when the value for $\Delta G_{\text{f}}^\circ(298.2 \text{ K})$ of gypsum was derived. The frequent association of gypsum with schröckingerite (Fron del, 1958) appears to be readily understandable. The calculated activity product $a_{\text{UO}_3^{2+}} a_{\text{CO}_3^{2-}}$ for the four solutions varies between 1.1×10^{-16} and 8.3×10^{-17} which is lower than that of rutherfordine, $\text{UO}_2\text{CO}_{3(\text{s})}$ at 298.2 K (Robie *et al.*, 1978). Using data taken from the same source, similar products can be found for calcite, $\text{CaCO}_{3(\text{s})}$, and fluorite, $\text{CaF}_{2(\text{s})}$. Reference to the results in Table I shows that the ion products $a_{\text{Ca}^{2+}} a_{\text{CO}_3^{2-}}$ and $a_{\text{Ca}^{2+}} a_{\text{F}^-}^2$ vary between 6.3×10^{-8} and 1.7×10^{-7} , and $2.6\text{--}2.7 \times 10^{-7}$, respectively. Thus the solutions in equilibrium with schröckingerite are slightly supersaturated with respect to calcite and considerably supersaturated with respect to fluorite. Neither of these minerals was detected using X-ray methods in the excess solids remaining at the end of the solution experiments. It must be concluded on this basis that schröckingerite may crystallize metastably from solutions which are supersaturated with respect to the two minerals, and indeed, under conditions which should give rise to either liebigite or andersonite. The inhibition of nucleation of

some inorganic compounds due to the presence of certain ionic species in solution is well known. Perhaps the most classic case concerns the inhibition of calcite nucleation and growth by magnesium ions (Krauskopf, 1979). It is evident that similar processes obtain in solutions that give rise to the crystallization of schröckingerite. In this respect it is worth noting that in the only occurrence of grimselite, the mineral was found associated with schröckingerite, but no other U(VI) carbonate was present. Thermodynamic stability fields for these two species (fig. 1) are widely separated by a range of chemical conditions more probable to occur naturally.

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