The aqueous chemistry of uranium minerals. Part 2. Minerals of the liebigite group

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SYNOPSIS

FREE energies of formation of liebigite, $Ca_2UO_2(CO_3)_3 \cdot 10H_2O$, swartzite, $CaMgUO_2(CO_3)_3 \cdot 12H_2O$, bayleyite, $Mg_2UO_2(CO_3)_3 \cdot 18H_2O$, and andersonite, $Na_2CaUO_2(CO_3)_3 \cdot 6H_2O$ have been determined from solution studies at various temperatures. $\Delta G^0_{f(298.2K)}$ values for the above minerals are -6226 ± 12, -6607 ± 8, -7924 ± 8 and -5651 ± 24 kJ mol^{-1} respectively. $\Delta H^0_{f(298.2K)}$ values respectively are -7037 ± 24, -7535 ± 20, -9192 ± 20, and -5916 ± 36 kJ mol^{-1}. These results have been used to construct the stability diagram for the four minerals shown in fig. 1. Andersonite can only form when the activity of the sodium ion, a_{Na^+}, is relatively high and $a_{Ca^{2+}}$ and $a_{Mg^{2+}}$ are small. The interconversions of the sodium-free species are defined. When $a_{Mg^{2+}}/a_{Ca^{2+}} < 0.32$ liebigite is the stable phase. If $a_{Mg^{2+}}/a_{Ca^{2+}} > 7.94$, bayleyite forms preferentially. One might therefore expect the bayleyite-andersonite association to be more common than liebigite-andersonite, but this is entirely dependent upon the relative concentrations of $Mg^{2+}_{(aq)}$ and $Ca^{2+}_{(aq)}$ in the solutions from which the minerals form.

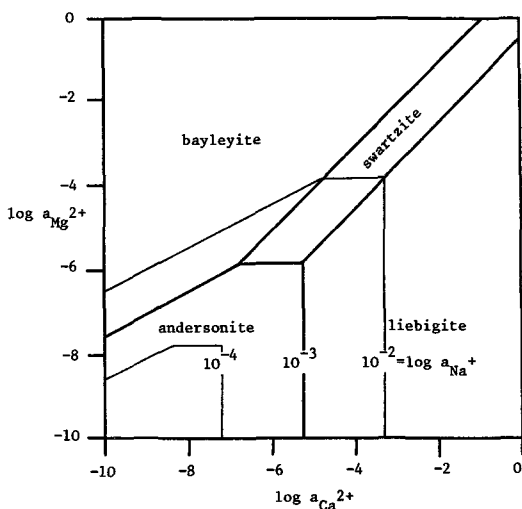FIG. 1. Stability fields for the minerals of the liebigite group at 298.2K in terms of $a_{Mg^{2+}}$ and $a_{Ca^{2+}}$. The firm line defining the andersonite field is calculated for $a_{Na^+} = 10^{-3}$ mol dm^{-3}. The faint lines indicate the same boundary for $a_{Na^+} = 10^{-2}$ and 10^{-4} mol dm^{-3}.

REFERENCE

Haacke (D. F.) and Williams (P. A.), 1979. *Mineral. Mag.* **43**, 539-41.

[Note added in proof. FIG. 1. For log a_{Na^+} read a_{Na^+}.]

THE AQUEOUS CHEMISTRY OF URANIUM MINERALS. PART 2. MINERALS OF THE
LIEBIGITE GROUP.

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The important role of carbonato-complexes of the uranyl ion (UO_2^{2+} $_{(aq)}$) in the transport of uranium in ground waters has long been recognized. In an oxidizing environment, the stability field of the complexes $UO_2CO_{3(aq)}^0$, $UO_2(CO_3)_2^{2-}$ $_{(aq)}$ and $UO_2(CO_3)_3^{4-}$ $_{(aq)}$ impinge significantly on that of $UO_{2(s)}$ and are the most important U(VI) species when $CO_{2(aq)}$ is available for coordination. However, when such anions as VO_4^{3-} $_{(aq)}$, PO_4^{3-} $_{(aq)}$ or AsO_4^{3-} $_{(aq)}$ are present, several suites of more insoluble minerals can form preferentially (Langmuir, 1978 a,b). Although the $UO_2(CO_3)_3^{4-}$ $_{(aq)}$ ion is remarkably stable and soluble in aqueous solution, should it become concentrated enough, several secondary minerals based upon its structure can form depending upon the availability of suitable counterions. These minerals are often, but not always, found as efflorescences on the walls of old mine workings where the rate of evaporation is high. In a sense the minerals are intermediate between oxidized uranium ore deposits and uranium species dissolved in ground waters and as such are of particular interest to the exploration geochemist. Perhaps the most widespread of the minerals based on the tris-(carbonato)-dioxouranium(VI) ion are those containing the alkali earth cations. Liebigite, $Ca_2UO_2(CO_3)_3.10H_2O$, the most common species was recognised as early as 1848 (Smith 1848, 1851). Other earlier occurrences are described by Frondel (1958). More recent occurrences have been noted in Germany, Japan, Canada and Sweden (Matsobara, 1976; Rimsaite, 1977; Walenta, 1977; Watanabe, 1976; Welin, 1958). The other commonly found members of the liebigite group are bayleyite, $Mg_2UO_2(CO_3)_3.18H_2O$, swartzite, $CaMgUO_2(CO_3)_3.12H_2O$, and andersonite, $Na_2CaUO_2(CO_3)_3.6H_2O$, none of which is isomorphous with liebigite (Frondel, 1958), and which were all initially found at the Hillside mine, Yavapai County, Arizona (Axelrod et al., 1951). All of these minerals have since been noted at other localities (Frondel, 1958; Rimsaite, 1977; Welin, 1958; Matsobara, 1976; Wilkins, 1971; Jedlicka, 1959; Barczat, 1966; Davidson and Kerr, 1968; Wilkins, 1971). A rather more enigmatic but possible member of this group is rabbittite, $Ca_2Mg_3(UO_2)_2(CO_3)_6(OH)_4.18H_2O$, but this mineral is only reported from one locality (Thompson, Weeks and Sherwood, 1955) and only one analysis has been made.

The chemical and thermodynamic stabilities of the various members of the liebigite group are not understood. We have therefore undertaken a study of the stabilities of the group comprising liebigite, swartzite, bayleyite and andersonite in order to place the formation and interconversion of the compounds from and in aqueous solution on a firm footing. We present the results of our studies below.

The compounds were synthesised by published methods (Meyrowitz and Lindberg, 1960; Meyrowitz and Ross, 1961; Meyrowitz, 1962; Meyrowitz, Ross and Weeks, 1963) and checked by the thermogravimetric analysis (Stanton Redcroft TG750 balance) and published powder X-ray data (Frondel, 1958). For determination of solubility, an excess of solid phase was admitted to a flask containing a magnetic follower (teflon covered) and filled with boiled-out CO_2-free water. No gaseous phase was left in the flasks (to avoid $CO_{2(g)}$ equilibration) which were then immersed in a thermostatted water bath and maintained at constant temperature ($\pm$ 0.2°). Preliminary experiments showed that equilibrium was achieved after about 48 hours (constant pH and $[UO_2^{2+}]$ readings). After one week, samples of solution were removed from the flasks, filtered through Whatman GF/F fibreglass filter paper (>0.7 µm retention, prewashed), the pH of the filtrate recorded and the filtrate retained for analysis. For analysis, an aliquot of the supernatant was acidified with HNO_3 and $[UO_2^{2+}]_{TOT}$ measured spectrophotometrically at 412 nm using a Beckman DK2A recording spectrophotometer and uranium standards prepared in the same concentration of HNO_3. Total concentration of carbonate and alkali earth and alkali metal cations were then calculated from the stoichiometry of the appropriate mineral phase. Species distributions in solution at each temperature were then calculated using the well-tested programme COMICS (Perrin and Sayce, 1967) and refinement carried out as described previously (Alwan and Williams, 1979). The complex species included in the programme are tabulated in Table I. Stability constants

TABLE I.   Species included for the calculations

HCO_3^- $_{(aq)}$	$CaHCO_3^+$ $_{(aq)}$	$UO_2(CO_3)_2^{2-}$ $_{(aq)}$	$(UO_2)_3(OH)_4^{2+}$ $_{(aq)}$
$H_2CO_{3(aq)}$	$CaCO_3^0$ $_{(aq)}$	$UO_2(CO_3)_3^{4-}$ $_{(aq)}$	$CaOH^+$ $_{(aq)}$
$NaHCO_3^0$ $_{(aq)}$	$MgHCO_3^+$ $_{(aq)}$	UO_2OH^+ $_{(aq)}$	$MgOH^+$ $_{(aq)}$
$NaCO_3^-$ $_{(aq)}$	$MgCO_3^0$ $_{(aq)}$	$(UO_2)_2(OH)_2^{2+}$ $_{(aq)}$	$Mg_4(OH)_4^{4+}$ $_{(aq)}$
$Na_2CO_3^0$ $_{(aq)}$	$UO_2CO_3^0$ $_{(aq)}$	$(UO_2)_3(OH)_5^+$ $_{(aq)}$	

were taken from Baes and Mesmer (1976), Langmuir (1978), Truesdell and Jones (1974), Reardon and Langmuir (1974), Babko and Kodenskaya (1960), Sergeyeva et al., (1972), Cirméide et al., (1975) and Scanion (1977).

Full lists of all concentrations of aqueous species at equilibrium at each temperature are available from the authors on request. For each mineral, at each temperature, the solubility product, K_{SP}, was calculated using the usual procedure (Haacke and Williams, 1979). An Arrhenius plot of log K_{SP} against 1/T for each mineral (Figure 2) yielded a good straight line from which the pertinent thermodynamic quantities for the compounds could be obtained in the usual way. ΔG_f^0 and ΔH_f^0 for the ions concerned and for water were taken from Barner and Scheuerman (1978). For example for the dissociation of liebigite,

$$Ca_2UO_2(CO_3)_2.10H_2O_{(s)} \rightleftharpoons 2Ca^{2+}_{(aq)} + UO_2^{2+}_{(aq)} + 3CO_3^{2-}_{(aq)} + 10H_2O_{(1)},$$

ΔH^0 for the reaction as written is 26.8(3.3)kJ mole^{-1}. Values of the corresponding quantity for swartzite, bayleyite and andersonite are 19.7(1.3), 40.6(0.8) and 109.6(9.2) kJ mole^{-1} respectively. Derived values of ΔG_f^0 and ΔH_f^0 for the four minerals are given in Table II, together with their estimated errors.

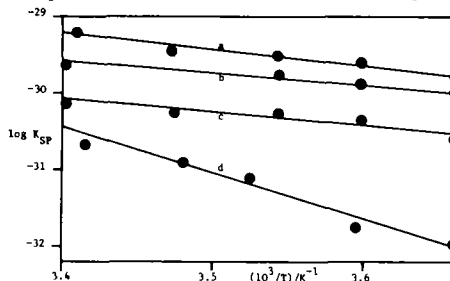Using these values, we have constructed a stability field diagram,

Figure 2. Arrhenius plots of K_{SP} values for a, bayleyite; b, liebigite; c, swartzite; d, andersonite.

for the four minerals, which is shown in Fig. 1. We have chosen to represent the field in terms of $a_{Ca}{}^{2+}$ and $a_{Mg}{}^{2+}$. The full contour for the andersonite stability field is chosen at $a_{Na}{}^+$ = 10^{-3} mol dm^{-3}. Fainter

TABLE II. Thermodynamic quantities at 298.2K for the minerals of the liebigite group.

Mineral	Formula	ΔG_f^0/kJ mol^{-1}	ΔH_f^0/kJ mol^{-1}
liebigite	$Ca_2UO_2(CO_3)_3.10H_2O$	-6226 $\pm$ 12	-7037 $\pm$ 24
swartzite	$CaMgUO_2(CO_3)_3.12H_2O$	-6607 $\pm$ 8	-7535 $\pm$ 20
bayleyite	$Mg_2UO_2(CO_3)_3.18H_2O$	-7924 $\pm$ 8	-9192 $\pm$ 20
andersonite	$Na_2CaUO_2(CO_3)_3.6H_2O$	-5651 $\pm$ 24	-5916 $\pm$ 36

contours are also given for $a_{Na}{}^+$ = 10^{-2} and 10^{-4} mol dm^{-3}. It should first be noted that andersonite is only stable when the activity of sodium is very high and the activities of calcium and magnesium ions very low. Such concentrations of sodium ion in groundwaters are most easily achieved via evaporation and correspond with observations of these carbonates on the surfaces of mine workings. Welin (1958) has suggested that almost complete evaporation of the uranium-bearing solutions is necessary for deposition. This of course is a consequence of the stability of the $UO_2(CO_3)_3^{4-}$ $_{(aq)}$ ion, and its solubility. The relationships between the three Na-free minerals are shown clearly in the same diagram. During the synthesis of the minerals from nitrate-containing solutions, Meyrowitz (1962) noted the apparently small field of stability of swartzite relative to liebigite and bayleyite, an observation we confirm. Under his experimental conditions he reported that if Ca:Mg is 7:8 or greater, liebigite formed from solutions containing Ca^{2+}, Mg^{2+}, NO_3^- and $UO_2(CO_3)_3^{4-}$. If the ratio was 5:8 or less bayleyite formed. The studies reported here allow the interconversions to be rigorously defined. If $a_{Mg}{}^{2+}/a_{Ca}{}^{2+}$ <0.32, liebigite is the stable phase. If $a_{Mg}{}^{2+}/a_{Ca}{}^{2+}$ > 7.94, bayleyite forms preferentially. Swartzite is stable under the intermediate conditions. Finally it should be noted that increasing $a_{Na}{}^+$ impinges far more on the fields of liebigite and swartzite relative to that of bayleyite. One might therefore expect the association of andersonite-bayleyite to be more common than andersonite-liebigite. However, this will of course depend on the relative availabilities of calcium and magnesium ions to the solutions from which the minerals form.

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