SHORT COMMUNICATIONS

Chemistry of formation of lanarkite, Pb_2OSO_4

WE have recently reported (Humphreys *et al.*, 1980; Abdul-Samad *et al.*, 1982) the free energies of formation of a variety of chloride-bearing minerals of Pb(II) and Cu(II) together with carbonate and sulphate species of the same metals including leadhillite, $Pb_4SO_4(CO_3)_2(OH)_2$, caledonite, $Pb_5Cu_2CO_3(SO_4)_3(OH)_6$, and linarite, $(Pb,Cu)_2 SO_4(OH)_2$. By using suitable phase diagrams it has proved possible to reconstruct, in part, the chemical history of the development of some complex secondary mineral assemblages such as those at the Mammoth–St. Anthony mine, Tiger, Arizona, and the halide and carbonate suite of the Mendip Hills, Somerset.

A celebrated locality for the three sulphate-bearing minerals above is the Leadhills–Wanlockhead district of Scotland (Wilson, 1921; Heddle, 1923, 1924) from which the minerals leadhillite and caledonite were first described, and in which several other rare species have been noted including susannite, the hexagonal dimorph of leadhillite, hydrocerussite, $Pb_3(CO_3)_2(OH)_2$ and lanarkite, Pb_2OSO_4. Preliminary attempts to incorporate this last species into our thermodynamic model for secondary mineral formation were frustrated because of the wide variation in the reported values for its free energy of formation. We have therefore redetermined this quantity, and use it to outline possible conditions for the crystallization of lanarkite from aqueous solution.

An early estimate of $\Delta G^0_{f(298.2 \text{ K})}$ (-1083.2 kJ mol^{-1}) was made by Latimer (1952) and more recently a value of -1071.9 kJ mol^{-1} was reported by Wagman *et al.* (1968). However, calculation of the free energy change between anglesite and lanarkite as given in equation (1) and using ΔG^0_f values by Wagman *et al.* (1968) for lanarkite and those listed in Barner and Scheuerman (1978) for the other species in the reaction, leads to a $\Delta G^0_{298.2 \text{ K}}$ value of 46.6 kJ mol^{-1}. This value can be used to derive equation (2) which defines the boundary between the two minerals at equilibrium and at $T = 298$ K.

$$2PbSO_{4(s)} + H_2O_{(l)} \rightleftharpoons$$
$$Pb_2OSO_{4(s)} + 2H^+_{(aq)} + SO^{2-}_{4(aq)} \qquad (1)$$
$$pH = 4.08 + 0.5 \log a_{SO_4^{2-}} \qquad (2)$$
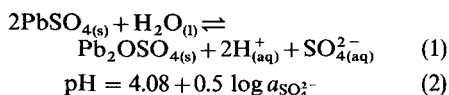
Such a result suggests that lanarkite would be thermodynamically stable, even at the expense of anglesite in many chemical environments, a conclu-

sion which is at odds with the widespread occurrence of the simple sulphate and the extreme rarity of the basic salt, and with aqueous synthetic procedures for the preparation of the compound (Bode and Voss, 1959), which involve reaction of anglesite in basic solution.

Kellog and Basu (1960) also determined ΔG^0_f for $Pb_2OSO_{4(s)}$ at 298.16 K using the method of univariant equilibria in the system Pb–S–O. They obtained a value of -1016.4 kJ mol^{-1} based on literature values for $PbO_{(s)}$, $PbS_{(s)}$, $PbSO_{4(s)}$, and $SO_{2(g)}$ and another of -1019.8 kJ mol^{-1} based on adjusted values for the above compounds. These two results, for which the error was estimated to be about 4.5 kJ mol^{-1}, seem to be considerably more compatible with observed associations than the earlier values.

We have redetermined the free energy of formation of lanarkite at 298.2 K using previously published solution techniques (Alwan and Williams, 1979). The lanarkite, (BM 44522) from the Susanna mine, Leadhills, Scotland was donated by the British Museum (Natural History). The value obtained is -1014.6 ± 0.8 kJ mol^{-1}, which is in excellent agreement with those by Kellog and Basu (1960). The solubility of lanarkite in water at 298.2 K is $7.57(36) \times 10^{-5}$ mol dm^{-3} at pH 7.67 and the computed concentrations (Perrin and Sayce, 1967) of $Pb^{2+}_{(aq)}$ and $SO^{2-}_{4(aq)}$ in equilibrium with solid lanarkite are 7.24(31) and $7.27(36) \times 10^{-5}$ mol dm^{-3} respectively. The value of the equilibrium constant for (3) is:

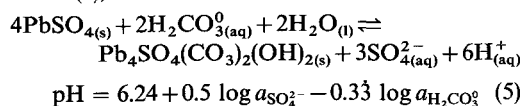$$Pb_2OSO_{4(s)} + 2H^+_{(aq)} \rightleftharpoons$$
$$2Pb^{2+}_{(aq)} + SO^{2-}_{4(aq)} + H_2O_{(l)} \qquad (3)$$
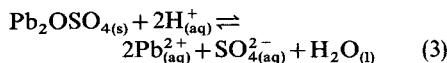
corrected to zero ionic strength and $\Delta G^0_{f(Pb_2OSO_4)}$ calculated in the usual way. Thus the pH value shown in (4) has been calculated as the boundary condition for the reaction given in (1).
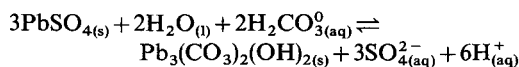
$$pH = 9.10 + 0.5 \log a_{SO_4^{2-}} \qquad (4)$$

This result may be used to explain the known occurrences of lanarkite. Our conclusions are reinforced by calculations involving other minerals formed from carbonate-bearing solutions.

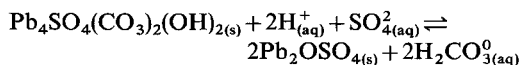The boundaries between anglesite and leadhillite (5),

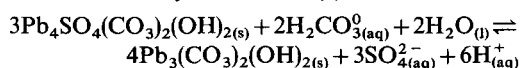$$4PbSO_{4(s)} + 2H_2CO^0_{3(aq)} + 2H_2O_{(l)} \rightleftharpoons$$
$$Pb_4SO_4(CO_3)_2(OH)_{2(s)} + 3SO^{2-}_{4(aq)} + 6H^+_{(aq)}$$

$$pH = 6.24 + 0.5 \log a_{SO_4^{2-}} - 0.3\dot{3} \log a_{H_2CO_3^0} \quad (5)$$

anglesite and hydrocerussite (6),

$$3PbSO_{4(s)} + 2H_2O_{(l)} + 2H_2CO^0_{3(aq)} \rightleftharpoons$$
$$Pb_3(CO_3)_2(OH)_{2(s)} + 3SO^{2-}_{4(aq)} + 6H^+_{(aq)}$$

$$pH = 6.49 + 0.5 \log a_{SO_4^{2-}} - 0.3\dot{3} \log a_{H_2CO_3^0} \quad (6)$$

leadhillite and lanarkite (7),

$$Pb_4SO_4(CO_3)_2(OH)_{2(s)} + 2H^+_{(aq)} + SO^{2-}_{4(aq)} \rightleftharpoons$$
$$2Pb_2OSO_{4(s)} + 2H_2CO^0_{3(aq)}$$

$$pH = 0.51 + 0.5 \log a_{SO_4^{2-}} - \log a_{H_2CO_3^0} \quad (7)$$

leadhillite and hydrocerussite (8),

$$3Pb_4SO_4(CO_3)_2(OH)_{2(s)} + 2H_2CO^0_{3(aq)} + 2H_2O_{(l)} \rightleftharpoons$$
$$4Pb_3(CO_3)_2(OH)_{2(s)} + 3SO^{2-}_{4(aq)} + 6H^+_{(aq)}$$

$$pH = 7.26 + 0.5 \log a_{SO_4^{2-}} - 0.3\dot{3} \log a_{H_2CO_3^0} \quad (8)$$

and lanarkite and hydrocerussite (9),

$$3Pb_2OSO_{4(s)} + 4H_2CO^0_{3(aq)} + H_2O_{(l)} \rightleftharpoons$$
$$2Pb_3(CO_3)_2(OH)_{2(s)} + 3SO^{2-}_{4(aq)} + 6H^+_{(aq)}$$
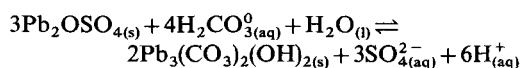
$$pH = 3.88 + 0.5 \log a_{SO_4^{2-}} - 0.66 \log a_{H_2CO_3^0} \quad (9)$$

are all dependent upon $a_{H_2CO_3^0}$ and thus the stability fields of these minerals, and of cerussite, $PbCO_3$, must be limited by this quantity. Inspection of equations (4)–(9) indicates that lanarkite is thermodynamically stable only at very low activities of $H_2CO^0_{3(aq)}$. It is clear from other studies involving secondary copper and lead minerals (Abdul-Samad et al., 1982) that such low activities are achieved only rarely in nature and hence lanarkite should be an uncommon mineral.

In appropriate conditions with $a_{H_2CO_3^0}$ c. $10^{-8.6}$, the thermodynamic model predicts that the associated minerals that might be expected, not taking into account those species containing Cu(II), are anglesite and leadhillite. Field observations on the occurrence of lanarkite bear this out.

Even in the Leadhills district, lanarkite was identified with certainty from only one mine, the Susanna, although Brown (1919) reported its occurrence on dumps from other veins in the district. It was adjudged to be 'the rarest mineral occurring in the district' (Wilson, 1921) and 'much the rarest of the minerals occurring at Leadhills' (Heddle, 1924). The latter author lists lanarkite as being associated with susannite and caledonite, rarely with cerussite, but also notes its association with anglesite, linarite, leadhillite, and pyromorphite. Anglesite was abundant in the Susanna mine, associated with linarite, cerussite, and lanarkite; leadhillite was also found in large quantities in combination with cerussite or with cerussite and lanarkite. A series of pseudomorphs of particular interest here is listed by Heddle (1923) and Wilson (1921), specifically cerussite after lanarkite, anglesite, and leadhillite. These replacements support the

conclusion that $a_{H_2CO_3^0}$ rose during the later development of the Susanna oxidized zone, after the formation of lanarkite, leadhillite, and anglesite.

Two more recent reports have appeared concerning the mineralogy of the Leadhills–Wanlockhead mining field (Temple, 1956; Gillanders, 1981). Some paragenetic sequences of mineral formation pertinent to our work are listed, including the noteworthy observation that cerussite was the first mineral in many sequences. In the 'exclusively lead ores' Temple (1956) notes leadhillite after cerussite, followed by lanarkite, but less commonly than the classic order galena, PbS → anglesite → cerussite. A further observation of hydrocerussite after cerussite firmly establishes that during the formation of the secondary minerals, the $a_{H_2CO_3^0}$ fell and then rose again, parallelling observations concerning the emplacement of the complex oxide zone at Tiger, Arizona (Abdul-Samad et al., 1982). All these observations neatly fit the experimental results on the thermodynamic stability of lanarkite, and thus its rarity.

Finally, a recent report (Crowley, 1980) outlines the first documented occurrence of lanarkite in the USA at the C. and B. mine, Gila county, Arizona. All the specimens were altered, being partially or completely replaced by cerussite, with fewer than a dozen out of some one hundred cerussite specimens, some of which were completely replaced pseudomorphs, still containing any of the basic sulphate. Neither at this deposit nor at the Susanna mine was the expected alteration sequence lanarkite → hydrocerussite → cerussite observed, and further examination of the specimens especially at grain boundaries, may reveal the basic carbonate.

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A pectolite sedimentary xenolith from kimberlite, Sierra Leone

THE Archaean granitoid basement complex of eastern Sierra Leone is cut by numerous dykes and a few small pipes of kimberlite of Cretaceous age. The pipes carry a suite of unmetamorphosed volcanic and sedimentary rock xenoliths which are the only evidence remaining of a cover sequence now removed from the region by erosion. Such xenoliths from the Koidu pipe (11° 6' W., 8° 40' N.) have been briefly described and the possible correlation of the parent sequence with either the Upper Proterozoic Rokel River Series or the Palaeozoic Saionya Scarp Series of western and northern Sierra Leone discussed (Hubbard, 1967).

A white porcellanous rock from the suite of accidental xenoliths in the Koidu kimberlite pipe has an unusual composition and an uncertain origin. The rock is uniformly composed of rounded, monomineralic, polycrystalline grains, 0.2–0.4 mm diameter, in a coarse-grained, poikilotopic, calcite matrix. A few, isolated, sub-rounded grains of microcline and quartz serve only to emphasize the striking compositional homogeneity of the rock. Strong compaction is indicated by the tight packing of the grains with long intergrain contacts, some straight, some concave-convex. Aggregates of compacted grains, rather than isolated grains, are enclosed in the poikilotopic calcite grains of the matrix.

The polycrystalline grains are composed of non-oriented, felted aggregates of mineral fibres and thin plates. The grains are monomineralic and there is no indication that they are the products of secondary replacement. The colourless mineral has a dusty appearance, the interference colours range up to blue of the second order, the fibres are length slow, and the extinction to elongation is near parallel. It was not found possible to obtain satisfactory interference figures.

Optical and routine XRD data suggested that the mineral of the grains was pectolite. Since this is an unusual paragenesis for pectolite a more detailed examination was undertaken to test the identification. Slow scan ($\frac{1}{2}$° 2θ/min) X-ray diffraction runs were made on untreated and HCl-treated powder mounts. The HCl treatment removed the calcite peaks from the diffractograms but also appeared to affect the crystallinity of the pectolite, reducing intensities and causing peak broadening. Reflections in the range 5–50° 2θ were measured and indexed by reference to the data for pectolite in Borg and Smith (1969). The derived cell constants ($a = 7.998$, $b = 7.039$, $c = 7.041$ Å, $\alpha = 90.50°$, $\beta = 95.20°$, $\gamma = 102.40°$) compare rather closely with those published for pectolite by Prewitt (1967).

TEM-ED thin film analyses were made on finely powdered mineral material by the method of Cliff and Lorimer (1975) using element k-values determined from silicate mineral standards (McGill and Hubbard, 1981). A nominal 3 % water content was assumed for normalization and the analyses were recalculated on the basis of 18(O,OH) (Table I). The derived formula closely corresponds with the theoretical formula for pectolite $(Ca,Fe)_4Na_2H_2(SiO_3)_6$ and serves to confirm the identification.

No literature reference to pectolite occurring in the mode described for the xenolith from the Sierra