The chemical stability of mendipite, diaboleïte, chloroxiphite, and cumengéite, and their relationships to other secondary lead(II) minerals

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SUMMARY. The chemical stabilities of mendipite, $Pb_3O_2Cl_2$, diaboleïte, $Pb_2CuCl_2(OH)_4$, chloroxiphite, $Pb_3CuCl_2O_2(OH)_2$, and cumengéite, $Pb_{19}Cu_{24}Cl_{42}(OH)_{44}$, have been determined in aqueous solution at 298.2 K. Values of standard Gibbs free energy of formation, ΔG_f°, for the four minerals are -740, -1160, -1129, and -15163 ± 20 kJ mol^{-1} respectively. These values have been used to construct the stability diagram shown in fig. 1 which illustrates their relationships to each other and to the minerals cotunnite, $PbCl_2$, paralaurionite, PbOHCl, and litharge, PbO. This diagram shows that mendipite occupies a large stability field and should readily form from cold, aqueous, mineralizing solutions containing variable amounts of lead and chloride ions, and over a broad pH range. The formation of para-laurionite and of cotunnite requires a considerable increase in chloride ion concentration, although para-laurionite can crystallize under much less extreme conditions than cotunnite. The encroachment of the copper minerals on to the stability fields of those mineral phases containing lead(II) only is significant even at very low relative activities of cupric ion. Chloroxiphite has a large stability field, and at given concentrations of cupric ion, diaboleïte is stable at relatively high a_{Cl^-}. Cumengéite will only form at high concentrations of chloride ion.

HALIDE salts are generally soluble in water, which explains why halide minerals of the transition elements are usually absent from the vicinity of oxidizing orebodies. In such an environment low pH values also tend to facilitate the solution of most species. Nevertheless, many halide minerals are known and occur in considerable quantities at some localities. Two groups of halide minerals containing Cu(II) and Pb(II) are outstanding in their complexity and rarity. These are the boléite group (Winchell and Rouse, 1974) and the mendipite–paralaurionite–diaboleïte–chloro-

xiphite assemblage. Chloroxiphite, mendipite, and diaboleïte were all originally described from deposits in the Mendip Hills, Somerset, England (Spencer and Mountain, 1923), and from which area paralaurionite has also recently been recorded (Symes and Embrey, 1977). Chloroxiphite is known only from this area.
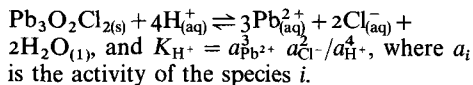
The occurrence of mendipite, paralaurionite, diaboleïte, and the boléite group in settings which could only derive from aqueous solutions (Winchell and Rouse, 1974; Palache et al., 1951) suggests that all of these minerals can have a secondary origin. These observations have prompted us to determine the stability fields of several members of the group at 298 K in equilibrium with aqueous solutions. Here we report the chemical stabilities of mendipite, $Pb_3O_2Cl_2$, diaboleïte, $Pb_2CuCl_2(OH)_4$, chloroxiphite, $Pb_3CuCl_2O_2(OH)_2$, and cumengéite, $Pb_{19}Cu_{24}Cl_{42}(OH)_{44}$, and their relationships to cotunnite, $PbCl_2$, paralaurionite, PbOHCl, and litharge, PbO.

Method. Mendipite and chloroxiphite from the Merehead Quarry, Somerset, England (Symes and Embrey, 1977), diaboleïte from the Mammoth mine, Tiger, Arizona (Anthony et al., 1977), and cumengéite from Santa Rosalia, Baja California, Mexico (Wilson and Rocha, 1955), were used in this study. Individual crystal fragments were hand-picked under the microscope and freed from any contaminating material. The compounds were checked by their X-ray powder patterns. For the determination of thermodynamic stabilities, the compounds were ground finely in an agate mortar and added in excess to boiled-out, CO_2-free water in flasks from which all gas was excluded. The aqueous systems were allowed to come to equili-

brium (constant pH) in a thermostatted water bath (298.2 ± 0.2 K). The solutions were then treated as previously described (Haacke and Williams, 1979), the pH measured (Orion 470-A Ionaliser), and the total concentrations of $Pb^{2+}_{(aq)}$, $Cu^{2+}_{(aq)}$, and $Cl^-_{(aq)}$ in equilibrium with each solid phase determined by atomic absorption spectroscopy (Pb and Cu) using a Varian AA6 instrument fitted with carbon rod attachment, and colorimetry (Cl) using standard techniques (Huang and Johns, 1967). For determination of solubility products, the activity of the free ions involved must be determined and for this purpose ionic species distributions in the aqueous solutions were calculated using a previously described method (Alwan and Williams, 1979) involving the well-tested computer program COMICS (Perrin and Sayce, 1967). The extended Debye–Hückel approximation (Truesdell and Jones, 1974; Kielland, 1937) was used to obtain individual ionic activity coefficients (γ_i). In the species distribution calculation, the ions considered were $CuCl^+_{(aq)}$, $CuCl^0_{2(aq)}$, $CuCl^-_{3(aq)}$, $CuCl^{2-}_{4(aq)}$, $PbCl^+_{(aq)}$, $PbCl^0_{2(aq)}$, $PbCl^-_{3(aq)}$, $PbCl^{2-}_{4(aq)}$, $CuOH^+_{(aq)}$, $Cu(OH)^0_{2(aq)}$, $Cu(OH)^-_{3(aq)}$, $Cu(OH)^{2-}_{4(aq)}$, $Cu_2(OH)^{2+}_{2(aq)}$, $PbOH^+_{(aq)}$, $Pb(OH)^0_{2(aq)}$, $Pb(OH)^-_{3(aq)}$, $Pb_2OH^{3+}_{(aq)}$, $Pb_3(OH)^{2+}_{4(aq)}$, $Pb_4(OH)^{4+}_{4(aq)}$, and $Pb_6(OH)^{4+}_{8(aq)}$.

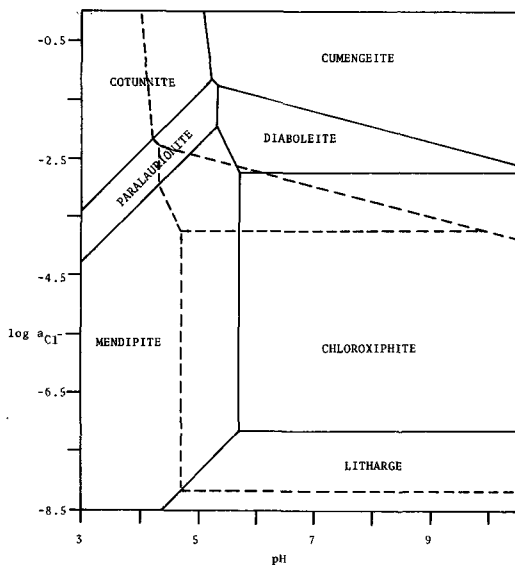Equilibrium constants for the formation of these ions were obtained from Baes and Mesmer (1976),

FIG. I. Stability fields for the copper and lead halide minerals in terms of a_{Cl^-} and pH at 298 K. The bold line delineating the Cu-containing species refers to an $a_{Cu^{2+}}$ of 10^{-8} mol dm^{-3}. The limits for $a_{Cu^{2+}} = 10^{-6}$ mol dm^{-3} are shown with a dashed line.

Vuceta and Morgan (1977), and Zirino and Yamamoto (1972). An example of the calculations used is (for mendipite):

$$Pb_3O_2Cl_{2(s)} + 4H^+_{(aq)} \rightleftharpoons 3Pb^{2+}_{(aq)} + 2Cl^-_{(aq)} +$$
$$2H_2O_{(1)}, \text{ and } K_{H^+} = a^3_{Pb^{2+}}\, a^2_{Cl^-}/a^4_{H^+}, \text{ where } a_i$$
is the activity of the species *i*.

a_{H^+} is available directly from the pH measurement, $a_{Pb^{2+}}$ and a_{Cl^-} are obtained from the free concentrations of the $Pb^{2+}_{(aq)}$ and $Cl^-_{(aq)}$ ions and their calculated activity coefficients. From K_{H^+}, ΔG^0 for the reaction is obtained from the relation $\Delta G^0 = -RT \ln K_{H^+}$ and using ΔG^0_f values for $Pb^{2+}_{(aq)}$, $Cl^-_{(aq)}$, and $H_2O_{(1)}$ (Barner and Scheuerman, 1978), ΔG^0_f for the mineral is calculated. Full lists of ionic species distributions for all of the minerals are available from the authors on request. A series of repeat experiments established the limits of errors in the ΔG^0_f values below as ± 20 kJ mol^{-1}. The ΔG^0_f values calculated in this study are given in Table I, together with those of cotunnite and litharge (Barner and Scheuerman, 1978) and paralaurionite. No distinction is drawn here between paralaurionite and its dimorph, laurionite (Palache *et al.*, 1951) which has not been observed in the Mendip Hills associations. The value of ΔG^0_f for $PbOHCl_{(s)}$ of -408.3 kJ mol given in Wagman *et al.* (1968 and 1969) is clearly too high as evidenced by comparison with values for $PbFCl_{(s)}$ and $Pb(OH)_{2(s)}$, and by calculation of the stability field of $PbOHCl_{(s)}$, relative to that of cotunnite. Fortunately a value for $PbOHCl_{(s)}$ can be derived from the work of Yadava *et al.* (1968) who studied the ionization of $PbOHCl_{(s)}$ in aqueous solution at 308.2 K. The ion product $[PbOH^+]\,[Cl^-]$ at this temperature was found to be 7.6×10^{-7} and from this value $\Delta G^0_{308.2\,K}$ was calculated for the solid phase (see above). The value obtained, -383.7 kJ mol^{-1}, agrees well with calculations of other phases (see below) and although there is a temperature discrepancy between the value chosen for paralaurionite and all other solid phases, this will have a minimal effect on the nature of the stability field of the former mineral (Garrels and Christ, 1965).

Of course, a difference in ΔG^0_f between paralaurionite and laurionite is to be expected. Yadava *et al.* do not report, in their study of PbOHCl, to which dimorph their work refers. However, any difference in ΔG^0_f for the two minerals will be so small as to make no visible changes to the stability field diagrams shown in figs. I and 2.

Discussion. The results obtained above have been used to construct the stability field diagram shown in fig. I. Calculations were made to eliminate $a_{Pb^{2+}}$ as a variable in the system. For the Cu-containing phases, the bold boundaries refer to an

TABLE I. ΔG_f^0 values* derived and used in this study

Mineral	Formula	ΔG_f^0/kJ mol^{-1}	
mendipite	$Pb_3O_2Cl_2$	-740 ± 20	
diaboleite	$Pb_2CuCl_2(OH)_4$	-1160 ± 20	this work
chloroxiphite	$Pb_3CuCl_2O_2(OH)_2$	-1129 ± 20	
cumengeite	$Pb_{19}Cu_{24}Cl_{42}(OH)_{44}$	-15163 ± 20	
cotunnite	$PbCl_2$	-314.2	
litharge	PbO	-189.1	see text
paralaurionite	$PbOHCl$	-383.7	

* Calculated at 298.2 K except for PbOHCl (see text).

equilibrium $a_{Cu^{2+}}$ of 10^{-8} mol dm^{-3}. The boundaries with $a_{Cu^{2+}} = 10^{-6}$ mol dm^{-3} are also shown in faint lines. A diagram showing Cu-free minerals is shown in fig. 2, on which is also contoured $a_{Pb^{2+}}$ in equilibrium with the mineral phases.

Conditions under which the Cu-free minerals can form vary considerably. Cotunnite can only form from acid solutions where both a_{Cl^-} and $a_{Pb^{2+}}$ are high, but post-depositional increase in pH causing complete conversion to paralaurionite and eventually mendipite may account for its absence from certain deposits. Paralaurionite also has an appreciable solubility in aqueous solution

FIG. 2. Stability fields for the Cu-free minerals, contoured with faint lines for equilibrium $a_{Pb^{2+}}$. The cut-off for the solid phases has been arbitrarily chosen as $a_{Pb^{2+}} = 1.0$ mol dm^{-3}.

although it can crystallize under much less extreme conditions than cotunnite. Activities of $Pb_{(aq)}^{2+}$ and $Cl_{(aq)}^-$ of the order of 10^{-2} mol dm^{-3} and a pH of about 5.5 are sufficient for paralaurionite to be stable. It is also worth noting, in view of the possible involvement of mineralizing solutions at greater temperature than those used in the experiments, that $PbCl_{2(s)}$ and $PbOHCl_{(s)}$ are appreciably more soluble in hot water than in cold. Hence their stability fields would be reduced at elevated temperatures.

Mendipite, on the other hand, occupies a much larger stability field than these two former species and will readily form from cold, aqueous mineralizing solutions containing variable $a_{Pb^{2+}}$ and a_{Cl^-}, and over a broad pH range. For example a few ppm of aqueous Pb(II) and chloride ions at a pH of about 8 will lead to the deposition of mendipite. From fig. 1 it is predicted that as the pH rises and a_{Cl^-} falls, litharge should form. However, the rate of the interconversion of mendipite and litharge is not taken into account by the above calculations, and it is undoubtedly affected by the presence of CO_2. It is also possible that the interconversion of these lead oxychlorides one to another as solution conditions vary may be hindered by their envelopment by more stable mineral assemblages, for instance by iron and manganese oxides, which provide a layer impervious to later aqueous solutions (Symes and Embrey, 1977).

The encroachment of the copper species on to the fields of those minerals containing lead only, shown in fig. 1, is significant even at very low activities of cupric ion. At $a_{Cu^{2+}} = 10^{-8}$ mol dm^{-3} copper species occupy the whole field at $a_{Cl^-} > 10^{-7}$ mol dm^{-3} and pH > 5.7. For $a_{Cu^{2+}} = 10^{-6}$ mol dm^{-3} (of the order of 1 ppm), corresponding a_{Cl^-} and pH values are 10^{-8} mol dm^{-3} and 4.7. These values are significant as it is probable that the minerals containing only lead were also deposited within similar concentration limits. As soon as any cupric ion becomes available to the
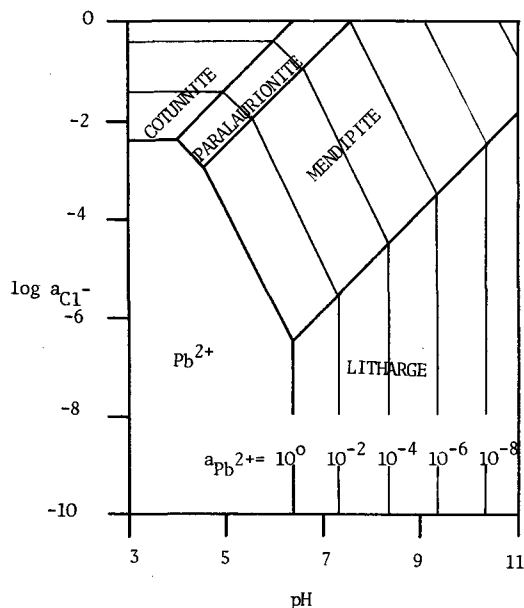
solutions, copper species crystallize until the Cu(II) ions are exhausted, at which time deposition of the lead-only minerals recommences.

From the phase diagram (fig. 1) it is seen that diaboleïte and chloroxiphite have a common boundary and that one or other can form at constant pH by subtle variations of either $a_{Cu^{2+}}$ or a_{Cl^-}. In addition, depending upon chemical conditions at the time, either mineral may coexist with mendipite, and diaboleïte can also form from solutions whose bulk characteristics give rise to the crystallization of paralaurionite. Chloroxiphite in particular has a large stability field and it is at first glance somewhat surprising that it has been reported from only one locality. It is possible, however, that the kinetics of decomposition of chloroxiphite are favourable and thus it may readily react to form other species with changing solution conditions. At the given concentrations of cupric ion, diaboleïte is stable at relatively high a_{Cl^-}.

Cumengéite is only stable at even higher a_{Cl^-} values. Boléite, $Pb_{26}Cu_{24}Cl_{62}(OH)_{47} \cdot H_2O$, pseudoboleïte, $Pb_5Cu_4Cl_{10}(OH)_8 \cdot 2H_2O(?)$, and cumengéite are all structurally related (Winchell and Rouse, 1974; Rouse, 1973). Ignoring the constitutional silver requirement of boléite and perhaps pseudoboléite (Mücke, 1972) these three minerals are thus apparently confined to systems where the availability of chloride ions is very high. Indeed, in those environments in which they have been known to form, this is the case (Winchell and Rouse, 1974; Wilson and Rocha, 1955).

This paper is the first in a series which will include solution chemistry studies on the secondary lead carbonates, and the effect of CO_2 upon the naturally occurring oxychloride mineral assemblages. Finally, a detailed mineralogical description of the paragenesis and alteration of the Mendip Hills oxychloride assemblage will be presented.

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