Studies of secondary mineral formation in the $PbO–H_2O–HCl$ system

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Abstract

New stability constant data are presented for the minerals blixite, mendipite and the compound $Pb_7O_6Cl_2.2H_2O$ at 298.2 K and $P = 10^5$ Pa. Mendipite is in fact a metastable phase at this temperature, being thermodynamically stable under the appropriate conditions at temperatures above about 29 °C. Kinetic influences are of some significance with respect to the sequence of formation of solid phases in the $PbO–HCl–H_2O$ system, and these have been elucidated for some important reactions. Penfieldite and fiedlerite appear to be metastable phases at all temperatures at 10^5 Pa. The results have been used to reassess the conditions of formation of the lead(II) oxy- and hydroxychloride phases that are known to form as minerals and as corrosion products of lead-containing artefacts. The effect of CO_2 on the system is also described.

KEYWORDS: lead minerals, blixite, mendipite, stability, secondary minerals.

Introduction

THE corrosion of lead under saline conditions and the hydrolysis of Pb(II) ions in aqueous chloride media yield a considerable number of species. The associated presence of sulfate and carbonate ions can also lead to the formation of simple and basic double salts under certain circumstances. Such compounds are known as minerals in the usual sense (Palache *et al.*, 1951; Symes and Embrey, 1977; Abdul-Samad *et al.*, 1982; Alabaster, 1989), but are also found as corrosion products of ancient lead artefacts (Lacroix, 1910; Russell, 1920; Goni *et al.*, 1954; Gettens, 1963; Weir, 1973; Borelli, 1975; Gorman, 1976; Kohlberger, 1976; Campbell and Mills, 1977; Robinson, 1980; Tylecote, 1983; Turgoose, 1985; Schnorrer-Köhler, 1986; Schnorrer-Köhler *et al.*, 1988). Aside from these double salts, a considerable number of minerals are associated with the $PbO–H_2O–HCl$ system alone, and these are listed in Table 1. Other basic chlorides and fluorides have been reported as minerals (Palache *et al.*, 1951; Fleischer, 1987; Kampf *et al.*, 1989), but these usually contain further subsidiary anionic groups or other cations in addition to Pb(II).

The formula given for blixite in Table 1 is an idealised one and refers to the corresponding, fully hydrated, synthetic phase. Solids isolated from preparative mixtures are in fact always somewhat dehydrated (*vide infra*). Naturally occurring blixite has been assigned a stoichiometry $Pb_2Cl(O,OH)_{2-x}$, with *x ca.* 0.3 (Gabrielson *et al.*, 1958). Lorettoite (Wells and Larsen, 1916) is a discredited species, White (1979) having shown that available material in collections is artificial in origin. However, Schnorrer-Köhler and co-workers (1986, 1988) have reported a phase of the same composition to be present in the Laurium lead slags, and titration of aqueous $PbCl_2$ solutions with base at high pH gives the hydrated phase $Pb_7O_6Cl_2.2H_2O$ prior to the formation of normal Pb(II) oxide (Kiyama *et al.*, 1976; Aurivillius, 1983). These separate observations lead us to conclude that the compound does occur naturally, but needs redefinition as a mineral species. Other synthetic Pb(II)

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Table 1. Known minerals and related phases in the $PbCl_2$-H_2O system.

Formula	Mineral
$PbCl_2$	Cotunnite
Pb_2Cl_3OH	Penfieldite
$Pb_3Cl_4(OH)_2$	Fiedlerite
$PbCl(OH)$	Laurionite
	Paralaurionite
$Pb_3O_2Cl_2$	Mendipite
$Pb_2Cl(OH)_3$[a]	Blixite
$Pb_7O_6Cl_2$	Lorettoite[b]
$Pb_7O_6Cl_2.2H_2O$[c]	
PbO	Litharge
	Massicot
$3PbO.PbCl_2$	Damaraite[d]

[a] Idealised formula. [b] Discredited as a mineral species; see text. [c] Product from the titration of aqueous $PbCl_2$ with base; see text. [d] IMA approved (A.J. Criddle, pers. comm.).

oxychlorides and related hydrated compounds have been known for some time (Mellor, 1929), but any relationships that they might have with natural systems are as yet unknown. We also note that the thermodynamically stable dimorphs of PbO and PbOHCl at 298.2 K and $P = 10^5$ Pa are litharge and laurionite, respectively. However, for the latter species, this conclusion is made on the basis of synthetic experiments at that temperature.

With respect to naturally occurring compounds, descriptions of deposits in the Mendip Hills, England (Spencer and Mountain, 1923; Symes and Embrey, 1977; Alabaster, 1989), the Tiger Mine, Arizona, USA (Bideaux, 1980; Abdul-Samad *et al.*, 1982), Långban, Sweden (Gabrielson *et al.*, 1958), and at a small number of Chilean localities (Palache *et al.*, 1951) are noteworthy. It is of special interest that many of the Pb(II) oxychlorides have been reported as alteration products of the Laurium slags (Palache *et al.*, 1958; Schnorrer-Köhler, 1986; Schnorrer-Köhler *et al.*, 1988). Indeed, fiedlerite is known only from this locality, and Laurium is the most important locality for penfieldite. The latter species decomposes in water (as does fiedlerite) but has also been reported from a mine in the Sierra Gorda, Chile, and as a corrosion product of lead objects in the marine environment.

Efforts have been made in the past to try to explain the chemistry of formation of these minerals in terms of an equilibrium model (Humphreys *et al.*, 1980; Abdul-Samad *et al.*, 1982), and these have met with some success. We have now completed an extended study of the system which incorporates new species in terms of their thermodynamic stabilities, and which has revealed certain important but previously unappreciated kinetic aspects. The results of this study, incorporating observations on the corrosion of lead in seawater and related naturally occurring solutions, are reported below.

Experimental

Titration experiments. All preparations and titrations were carried out under an atmosphere of dinitrogen to ensure the exclusion of CO_2.

Titration of lead chloride with base. To a stirred, carbonate-free, aqueous solution (100 cm^3) of $PbCl_2$ (0.745 g, 2.71 mmol), thermostatted at 25 °C (or other chosen temperatures), carbonate-free NaOH (0.11 M) was added dropwise. The pH of the mixture was recorded after each addition, and when a constant reading was obtained, using a Radiometer PHM85 pH meter fitted with a Radiometer GK2401C combination electrode. The course of a typical titration is shown in Fig. 1. Other titrations were carried out at various temperatures (from 0 to 65 °C) with varying concentrations of Pb(II) ions and base. The total chloride concentration was varied by addition of appropriate amounts of NaCl, and ranged from 0.5 to 3 M. Three solid phases were observed for each titration. These were collected at the pump, washed with water and acetone, and dried *in vacuo* over silica gel. The solid phases laurionite, blixite and $Pb_7O_6Cl_2.2H_2O$, were identified by thermogravimetric analysis using a Stanton Redcroft TG750 thermobalance, infrared measurements in KBr pellets on a Perkin-Elmer 783 spectrophotometer, and by powder X-ray methods (360 mm circumference Debye-Scherrer camera, Cu-$K\alpha$ radiation), by comparison with data in the JCPDS powder file.

Preparation of lead oxyhydroxide. Lead oxyhydroxide, sometimes known as 'lead hydroxide', was synthesized by the addition of base to a solution of soluble lead salt (Todd and Parry, 1964). NaOH (0.5 M, 50 cm^3) was added slowly to a cold, stirred, aqueous solution (100 cm^3) of $Pb(ClO_4)_2.3H_2O$ (4.688 g, 12.36 mmol). The resulting white precipitate was collected and identified as above, except that the IR was recorded in nujol mull. The composition of this 'lead hydroxide' on analysis, was found to be $5PbO.2H_2O$, in accordance with previous observations (Todd and Parry, 1964; Howie and Moser, 1968).

Titration of 'lead hydroxide' with acid. $5PbO.2H_2O$ (0.370 g, 0.267 mmol) was slurried in degassed water (100 cm^3) at 25 °C. Aqueous HCl (0.123 M) was added dropwise using a microburette. The pH of the mixture was recorded after each addition. The temperature and rate of addition was varied from 0 to 65 °C and from 15 to 90 min between each successive addition of acid, respectively. During the course of the titration at 25 °C, three solid phases were observed, corresponding to those described above. The titrations carried out at 65 °C and with very slow addition of acid produced four solid phases, namely $Pb_7O_6Cl_2.2H_2O$, blixite, mendipite and laurionite. Fig. 2 shows the result of this titration using $5PbO.2H_2O$ (0.2248 g, 0.195 mmol) in water (100 cm^3) with HCl (0.123 M). It was also observed that if the acid was added too quickly in the appropriate pH region, mendipite is not observed due to the faster reaction of blixite to give laurionite.

Synthesis of mendipite. Mendipite can be synthesized by titration (*vide supra*), but is more conveniently prepared by the reaction of 2 mol equivalents of PbO with 1 mol equivalent of $PbCl_2$ in aqueous solution. $PbCl_2$ (0.310 g, 1.114 mmol) was added to a slurry of PbO (0.497 g, 2.228 mmol) in carbonate-free water (100 cm^3). Light was excluded (using aluminium foil) from the reaction mixture, which was set to reflux for 2 days, when the orange colour of lead oxide had disappeared. The creamy white product was collected and identified as above. Thus mendipite was obtained quantitatively. This was also found to be the case for similar reactions when the mixtures of lead chloride and lead oxide were stirred until reaction was complete at

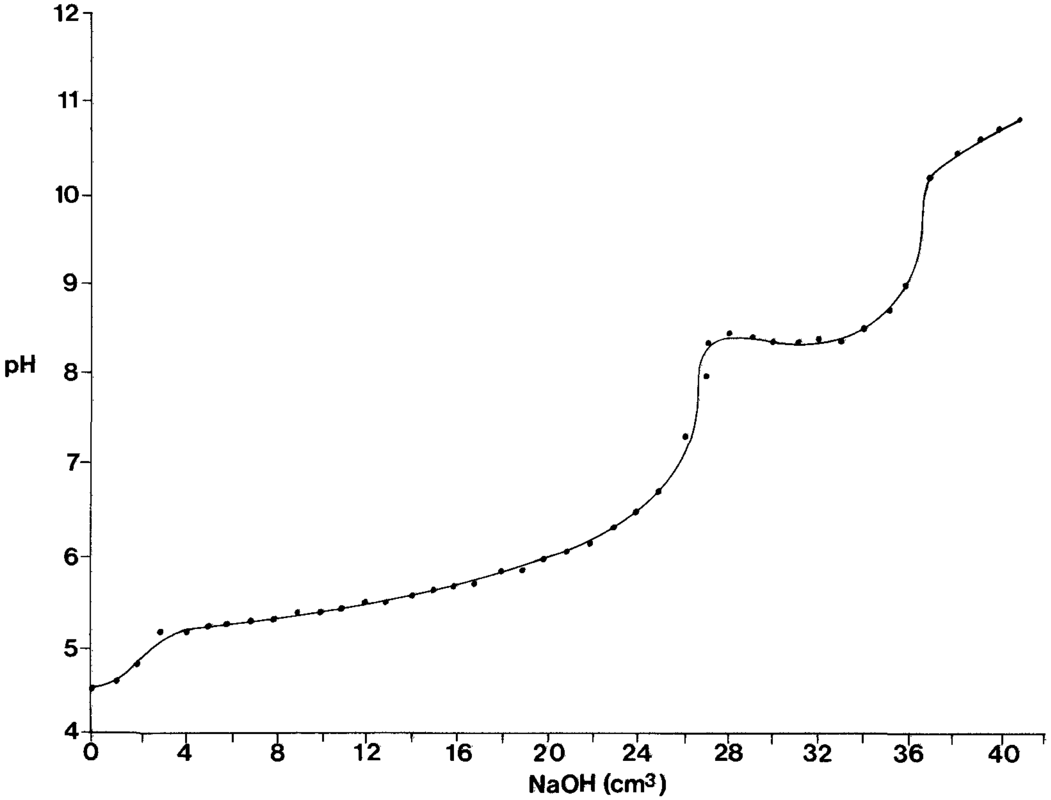

FIG. 1. A typical pH titration of $PbCl_2$ (2.71 mmol) in H_2O (100 cm^3) with aqueous NaOH (0.11 M) under dinitrogen at 25 °C.

temperatures greater than or equal to 29 °C. Products of the reaction below this transition temperature are laurionite and blixite, although mendipite does persist metastably at 25 °C for very long times, and use of this fact is made in determining its stability.

Equilibrium solubility determinations. Mendipite was prepared as outlined above, by refluxing a series of mixtures of PbO (0.2975 g, 1.333 mmol, for example) with $PbCl_2$ (0.1843 g, 0.663 mmol, for example) in degassed deionised water (100 cm^3) for 2 days. The reaction mixture was then cooled slowly to room temperature under dinitrogen and sealed. The sealed flask was placed in a thermostatted water bath at 25 °C for 2 months for the solid phase to equilibrate. A number of preliminary experiments established that equilibrium was achieved well within this length of time. This system in fact represents a metastable equilibrium, but during the course of the experiments, no other solid phases could be detected in the mixtures, as judged by powder X-ray and infrared examination of isolated solids. Thus we have determined a stability constant at 25 °C, in the full knowledge that the transition temperature for the thermodynamic stability of the mineral lies somewhere between 25 and 29 °C.

Prior to filtration of the solid phase, the solution pH was measured. Negligible variation of pH was observed between successive solutions. The solid was collected at the pump on Whatman GF/F fibreglass filter paper, and dried *in vacuo* over silica gel. The product was identified as a single phase by IR and XRD. Total Pb^{2+} ion concentrations in solutions were analysed by atomic absorption spectroscopy using a Varian 275 Series atomic absorption spectrophotometer. From a knowledge of the stoichiometry of mendipite and the total lead concentration, the total Cl^{-1} ion concentration can be calculated. Results are listed in Table 2.

The synthesis of $Pb_7O_6Cl_2.2H_2O$ was carried out following a method similar to that previously described (Kiyama *et al.*, 1976). It was found that for ratios of 2[NaOH]/[$PbCl_2$] of 0.9 and greater, the only phase present was $Pb_7O_6Cl_2.2H_2O$. To a series of stirred aqueous solutions (100 cm^3) containing, typically, $PbCl_2$ (0.7573 g, 1.815 mmol), NaOH (49.50 cm^3, 0.110 M) was added dropwise. The reaction mixtures were sealed and placed in a thermostatted water bath for 2 months at 25 °C. Equilibrium values of pH, and Pb^{2+} and Cl^{-1} ion concentrations were determined as above, and are given in Table 3.

To calculate stability constants for mendipite and $Pb_7O_6Cl_2.2H_2O$ from the values of total lead

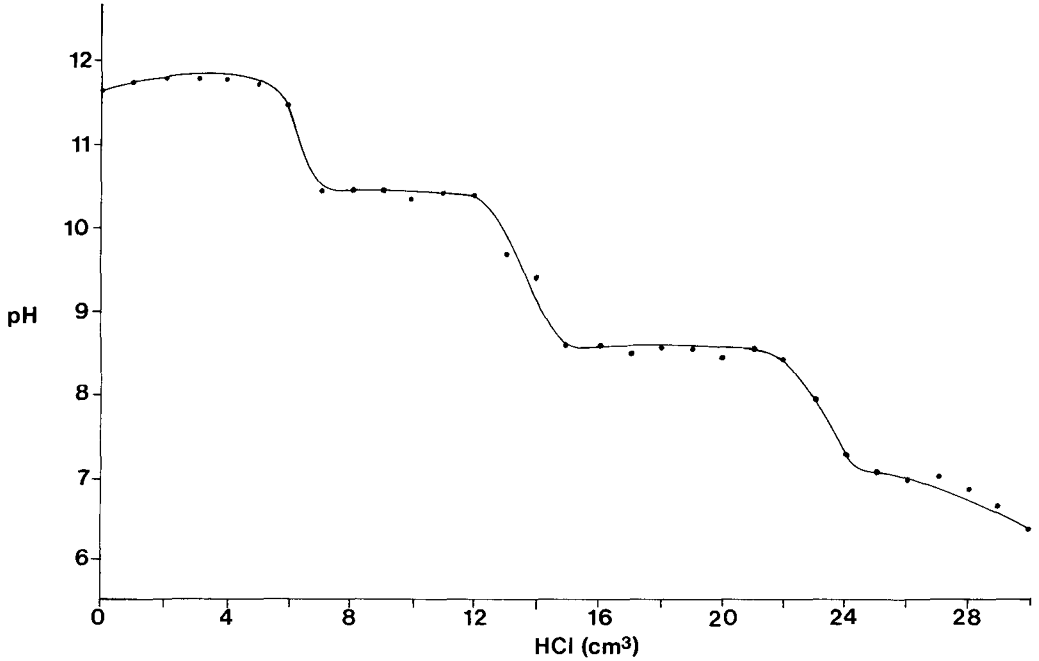

FIG. 2. A typical pH titration of 'lead hydroxide' (0.27 mmol) in H_2O (100 cm^3) with aqueous HCl (0 12.M) under dinitrogen at 65 °C.

and chloride ion concentrations, and the pH of the equilibrated solutions, species distribution calculations using COMICS (Perrin and Sayce, 1967) were carried out in order to derive the concentrations of the free lead(II) and chloride ions. Complex species taken into account were $PbCl^+$, $PbCl_2$, $PbCl_3^-$, $PbCl_4^{2-}$, $Pb(OH)^+$, $Pb(OH)_2$, $Pb(OH)_3^-$, $Pb_2(OH)^{3+}$, $Pb_3(OH)_4^{2+}$, $Pb_4(OH)_4^{4+}$, $Pb_6(OH)_8^{4+}$ and NaOH. Values for their formation constants, corrected for ionic strength by a series of iterative calculations, were taken from the compilation of Smith and Martell (1976).

The concentrations of the free lead and chloride ions (also given in Tables 2 and 3) were corrected for ionic strength using the Davies modification of the Debye-Hückel equation, and thus values for equations (1) and (2) could in turn be derived. Equilibrium constants for these equations are the K_{H^+} terms in the above Tables. Average values of log K_{H^+} for equations (1) and (2) are 9.21(4) and 9.65(1), respectively.

$$Pb_3O_2Cl_2 + 4H^+ \leftrightharpoons 3Pb^{2+} + 2Cl^- + 2H_2O \quad (1)$$

$$\tfrac{1}{6}Pb_7O_6Cl_2.2H_2O + 2H^+ \leftrightharpoons \tfrac{7}{6}Pb^{2+} + \tfrac{1}{3}Cl^- + \tfrac{4}{3}H_2O \quad (2)$$

A somewhat different approach was adopted to obtain a value of the stability constant for blixite, as the reported numerical results of Näsänen and Lindell (1978) proved to be inconsistent with the expressed experimental conditions in relation to other phases necessarily present, and well-established thermodynamic quantities for mendipite and laurionite (*vide infra*).

During the course of transformation of solid laurionite to solid blixite in water by titration of $PbCl_2(aq)$ with NaOH(aq), the relationships (3) and (4) hold. The value $10^{-13.377}$ at 25 °C can be used for the solubility product of laurionite, as derived by Näsänen and Lindell (1976); this is in good agreement with

$$2PbClOH(s) + OH^-(aq) \leftrightharpoons Pb_2Cl(OH)_3(s) + Cl^-(aq) \quad (3)$$

$$\log K_{sp}(blix) = \log a_{OH^-} - \log a_{OH^-} + 2\log K_{sp} \quad (4)$$

that derived by Charreton (1956) at the same temperature, and this value is adopted here.

It is a simple matter to calculate the ionic strength of the solution (NaCl) from a knowledge of starting amounts, titres and concentrations. With reference to equation (4) the only missing quantity is thus γ_{Cl^-}, making the entirely reasonable assumption that lead is essentially precipitated and thus corrections for lead chloride complexes are negligible with respect to the total chloride ion concentration. Values for the activity coefficient were calculated as described above.

Table 2. Experimental and derived data for the stability of mendipite at 298.2K.

$[Pb^{2+}]^a$ $/10^{-4}$	$[Cl^-]^a$ $/10^{-4}$	$[Pb^{2+}]^b$ $/10^{-4}$	$[Cl^-]^b$ $/10^{-4}$	pH	I^b $/10^{-3}$	$\gamma_{2\pm}$	$\gamma_\pm$	log K_{H^+}
7.163	4.775	6.673	4.654	6.43	1.594	0.835	0.956	9.255
6.670	4.447	6.189	4.342	6.46	1.487	0.840	0.957	9.221
6.472	4.317	6.017	4.218	6.46	1.439	0.842	0.958	9.167
6.771	4.514	6.336	4.405	6.45	1.509	0.839	0.957	9.227
6.550	4.367	6.096	4.226	6.45	1.454	0.812	0.958	9.167

[a] Total analytical concentrations at equilibrium. [b] Calculated concentrations at equilibrium using the COMICS program. All concentrations are in units of mol dm^{-1}.

Table 3. Experimental and derived data for the stability of $Pb_7O_6Cl_2.2H_2O$ at 298.2K.

$[Pb^{2+}]^a$ /10^{-5}	$[Cl^-]^a$ /10^{-2}	$[Na^+]^a$ /10^{-2}	pH	I^b /10^{-2}
3.608	2.341	2.792	11.22	2.57
3.924	2.272	2.650	11.24	2.46
3.924	2.205	2.646	11.23	2.43
3.480	2.272	2.646	11.19	2.46
3.825	2.695	2.709	11.25	2.70

$[Pb^{2+}]^b$ /10^{-11}	$[Cl^-]^b$ /10^{-2}	$[Na^+]^b$ /10^{-2}	$\gamma^{2\pm}$	$\gamma\pm$	log K_{H^+}
6.278	2.341	2.789	0.523	0.850	9.636
5.980	2.272	2.647	0.529	0.853	9.657
6.238	2.203	2.643	0.531	0.854	9.648
7.035	2.272	2.643	0.529	0.853	9.646
5.453	2.695	2.706	0.515	0.847	9.643

[a] Total analytical concentrations at equilibrium.
[b] Calculated concentrations at equilibrium using the COMICS program. All concentrations are in units of mol dm^{-1}.

Thus, a series of titrations at 25 °C were carried out using aqueous solutions of $PbCl_2$ to which were added various quantities of NaOH and NaCl, in analogous fashion to the experimental procedure reported by Näsänen and Lindell (1978). Relevant details are given in Table 4, the amounts of base added being such that both blixite and laurionite were present in the solid phases. When a steady reading of pH was obtained, the system was taken to have reached equilibrium, and the solubility product was calculated using the method outlined above. Of course, these measurements are only a check of those already reported, and it is possible to treat the experimental data of Näsänen and Lindell (1978) in exactly the same fashion. From the results of Table 4, log K_{sp} for blixite at 298.2 K is $-31.6(2)$, as compared with a recalculated value from the literature of $-30.5(1)$. This is at variance with the value derived by the previous workers (-33.8). The cause for this discrepancy lies in an apparently erroneous correction for ionic strength. It can simply be demonstrated that use of the latter value in equilibrium calculations leads to the conclusion that laurionite has no thermodynamic stability at 25 °C, a suggestion patently wrong in that laurionite was present during the experiments used to derive the constant. Thus we have adopted our value for further calculations involving relative stabilities.

When values for free energies of formation of the various solid phases have been calculated, corresponding values for component ions and water have been taken from the compilation of

Table 4. Experimental and derived data for the stability of blixite at 98.2K.

$PbCl_2$^{a}	NaCl^a	$[OH^-]^b$ /10^{-3}	pH^c	I^c	γ_{Cl^-}	$-\log K_{sp}$
0.556	-	2.250	7.680	0.025	0.845	31.33
0.278	4.694	1.050	8.625	0.464	0.621	31.56
0.556	4.694	2.250	8.450	0.435	0.627	31.74

[a] Weight (g) of starting material dissolved in 100 cm^3 H_2O.
[b] Number of moles of base added. [c] Data at equilibrium.

Robie *et al.* (1978). The results, in association with other observations concerning temperature dependencies of the stabilities of some of the phases can be used to construct an equilibrium model for the formation of the several basic lead(II) chlorides. It is also possible to take into account a number of related kinetic observations, as discussed below.

Results and discussion

Equilibrium constants derived from COMICS calculations used for the determination of K_{H^+} (equations 1 and 2) and associated data are given in Tables 2 and 3. The average values of log K_{H^+} at 298.2 K for mendipite and $Pb_7O_6Cl_2.2H_2O$ are 9.20(5) and 9.64(6), respectively. These results in turn lead to values of $\Delta fG°$ (mendipite, s, 289.2 K) of -757.06 ± 0.20 kJ mol^{-1} and of $\Delta fG°$ ($Pb_7O_6Cl_2.2H_2O$, s, 298.2 K) of -1999.29 ± 0.29 kJ mol^{-1}. It should be noted that the former value is in good agreement with, though clearly more accurate than, the value reported by Humphreys *et al.* (1980) of -740 ± 20 kJ mol^{-1}. Log K_{sp} for blixite, calculated using equation 3, is $-31.55(1)$, and thus $\Delta fG°$ (blixite, s, 298.2 K) is equal to -832.5 ± 2.2 kJ mol^{-1}.

At all temperatures and under all conditions studied, laurionite is the first phase to crystallise as the pH of an aqueous solution of lead chloride is increased. Paralaurionite, a dimorph of laurionite, has not been observed in any titration. This is of significance as the two minerals occur in association with one another in certain deposits, including the Wesley Mine, near Bristol (Alabaster, 1989) and in the Laurium slags (Palache, 1934). It is not absolutely certain whether laurionite is the thermodynamically stable phase at ambient temperatures; paralaurionite is known, for example, in comparatively large amounts in the Mammoth–St. Anthony Mine, Tiger, Arizona (Bideaux, 1980). No laurionite has been reported from this latter deposit. The two forms of Pb(OH)Cl can be easily distinguished by their X-ray diffraction patterns, laurionite being orthorhombic and paralaurionite monoclinic. Our observations are in agreement with those of Kiyama *et al.* (1976), who also found that laurionite is formed in preference to paralaurionite.

With increasing pH as a typical titration proceeds, the laurionite is replaced by the more basic lead hydroxychloride, blixite. Blixite, first reported from Långban, Sweden, has an empirical formula of $Pb_{16}Cl_8(O,OH)_{16-x}$, where $x \approx 2.6$, idealised to $Pb_2Cl(O,OH)_2$. The synthetic phase identified by TGA and XRD is identical to the mineral species, rather than the fully hydrated form $Pb_2Cl(OH)_3$. However, the latter is the stoichiometry adopted for the purposes of phase relationship calculations; such an approach would have negligible effect on the conclusions reached below.

The most basic lead oxychloride isolated is $Pb_7O_6Cl_2.2H_2O$, a hydrated form of the discredited mineral lorettoite. As mentioned above, lorettoite has now been identified in the Laurium lead slags. The anhydrate is in fact dimorphous, two powder X-ray patterns being deposited in the JCPD powder file. We note that the dihydrate of the same stoichiometry has also been reported as a corrosion product of buried lead cable sheaths (Shrier, 1963). When the synthetic compound is dehydrated at 110 °C, however, the dimorph β-$Pb_7O_6Cl_2$ is obtained, not lorettoite. No information is available concerning the relative stabilities of the dimorphs.

The titration of aqueous lead chloride solutions with aqueous sodium hydroxide at 25 °C in a CO_2-free environment results in the formation of three solid lead oxychlorides, namely laurionite, blixite and $Pb_7O_6Cl_2.2H_2O$. If sufficient time elapses between additions of base, then lead hydroxide, and finally lead oxide (litharge) are also formed at very high pH values. A notable absence from the titrations under these conditions is mendipite. It was found that on very slow addition of acid to a slurry of lead oxyhydroxide at a temperature of 65 °C, mendipite crystallised over a definite pH range. Further studies showed that mendipite can be synthesised in aqueous solution from the stoichiometric amounts of lead chloride and lead oxide, at temperatures of 29 °C and greater. Below this transition temperature, the reaction products at pH values when mendipite is expected to form are a mixture of laurionite and blixite. It is necessary when carrying out this synthesis to protect the product from light, as the surface of the creamy white mendipite precipitate becomes discoloured. Photochemical decomposition leads to the formation of lead oxide, as first noted by Mellor (1929). Alabaster (1989), on examination of specimens of mendipite from the Wesley Mine found that the mineral darkens slowly and irreversibly on exposure to air and sunlight. By continuous monitoring of the reflectance electronic spectrum of a powdered sample, the products of the photochemical reaction were found to be PbO_2, laurionite and paralaurionite.

It should be further noted that mendipite is only observed during the titration of lead oxyhydroxide with dilute hydrochloric acid under the conditions specified above. The phase is not observed, at any temperature or rate of addition of base, during the titration of aqueous lead chloride with aqueous sodium hydroxide. This implies that nucleation of blixite, when solutions in contact with laurionite are made more basic, is faster than mendipite. Thus under some conditions blixite can be formed metastably in relation to mendipite. Consequently we are forced to conclude that the crystallisation of mendipite is most probably effected in nature under conditions when quite alkaline solutions bearing appropriate amounts of lead and chloride ions decrease in pH.

Mendipite does, however, persist metastably below 29 °C. A sample kept in contact with the mother liquor from which it had crystallised was maintained at 25 °C for 2 months, after which time the only solid phase which could be detected by infrared and powder X-ray methods was mendipite.

In order to evaluate the relationships of the lead hydroxychloride minerals to one another, an equilibrium model has been constructed for the formation of these various phases. Thermodynamic data for the minerals cotunnite, laurionite, mendipite, blixite, $Pb_7O_6Cl_2.2H_2O$, and litharge, along with others used in the calculations for the stability field diagrams are given in Table 5. All other thermodynamic data necessary for calculating the relative stabilities of these phases were taken from the compilation of Robie *et al.* (1978).

A stability field diagram for the PbO–HCl–H_2O system at 289.2 K is shown in Fig. 3 This illustrates the interrelationships between the various lead hydroxychloride phases. Under natural saline conditions, seawater for example, where approximate chloride concentrations are 0.5 M, and the pH is about 8, the preferred phase to crystallise would be laurionite or its dimorph paralaurionite (no distinction is made here between the two), and this is reflected by frequency of reports of its occurrence under such conditions (Russell, 1920; Palache, 1934; Palache *et al.*, 1951; Kohlberger, 1976; Campbell and Mills, 1977; Symes and Embrey, 1977; Bideaux, 1980; Schnorrer-Köhler, 1986; Schnorrer-Köhler *et al.*, 1988; Alabaster, 1989). Reduction of salinity or an increase of pH gives rise to conditions when blixite can form. Further increase of pH also provides the possibility for the formation of lorettoite, or the hydrated analogue. Such extremes might be rare, but are locally possible, such as on the surface of the corroding lead, where hydroxide ions may accumulate due to the reduction of oxygen.

Cotunnite, although rare, has also been

Table 5. Standard thermodynamic data for lead minerals and related phases.

Mineral	ΔfG^o (298.2K) /kJ mol^{-1}	Ref.
Blixite	-832.5	this work
Cerussite	-625.3	Bilinski and Schindler (1982)
Cotunnite	-314.0	Robie *et al.* (1978)
Hydrocerussite	-1706.0	Bilinski and Schindler (1982)
Laurionite	-389.1	Näsänen and Lindell (1976)
Litharge	-189.2	Robie *et al.* (1978)
Mendipite	-757.1	this work
Phosgenite	-952.1	Näsänen *et al.* (1962)
$Pb_7O_6Cl_2.2H_2O$	-1999.3	this work

reported as a marine corrosion product of lead (Russell, 1920; Schnorrer-Köhler, 1986; Schnorrer-Köhler *et al.*, 1988). The stabilisation of cotunnite requires a more acidic environment and high chloride activities. These conditions are not impossible to attain, but are only expected to be encountered rarely.

Mendipite does not appear as a stable phase on Fig. 3, but has been included as a *metastable* phase in Fig. 4 Thus, the small temperature increase from 25 to 29 °C, where mendipite is known to be thermodynamically stable, has been ignored in constructing the diagram. Mendipite is an infrequently reported lead oxychloride. A possible explanation for this, based on our experimental evidence, is that mendipite is thermodynamically stable only at temperatures greater than 29 °C. These conditions were clearly met with in the Mendip Hills, where mendipite occurs in a number of deposits (Symes and Embrey, 1977; Alabaster, 1989). It is known (Alabaster, 199, and refs. therein) that the percolating saline ground waters in the region are hydrothermal in origin and the elevated temperatures necessary for the crystallisation of mendipite as a thermodynamically stable phase could easily have obtained. This is certainly true of the mode of occurrence of mendipite in the Auguste Victoria Mines at Hüls, Westphalia, Germany (Rechenberg, 1951), where, due to the action of a hot concentrated NaCl brine on sulfide ores, a host of alteration products has recently resulted. Mendipite, cotunnite and laurionite have been noted from these deposits, crystallising from solutions at temperatures of up to 65 °C.

Mendipite is nearly always found associated with other lead hydroxychlorides. At the Wesley Mine it is invariably intergrown with laurionite

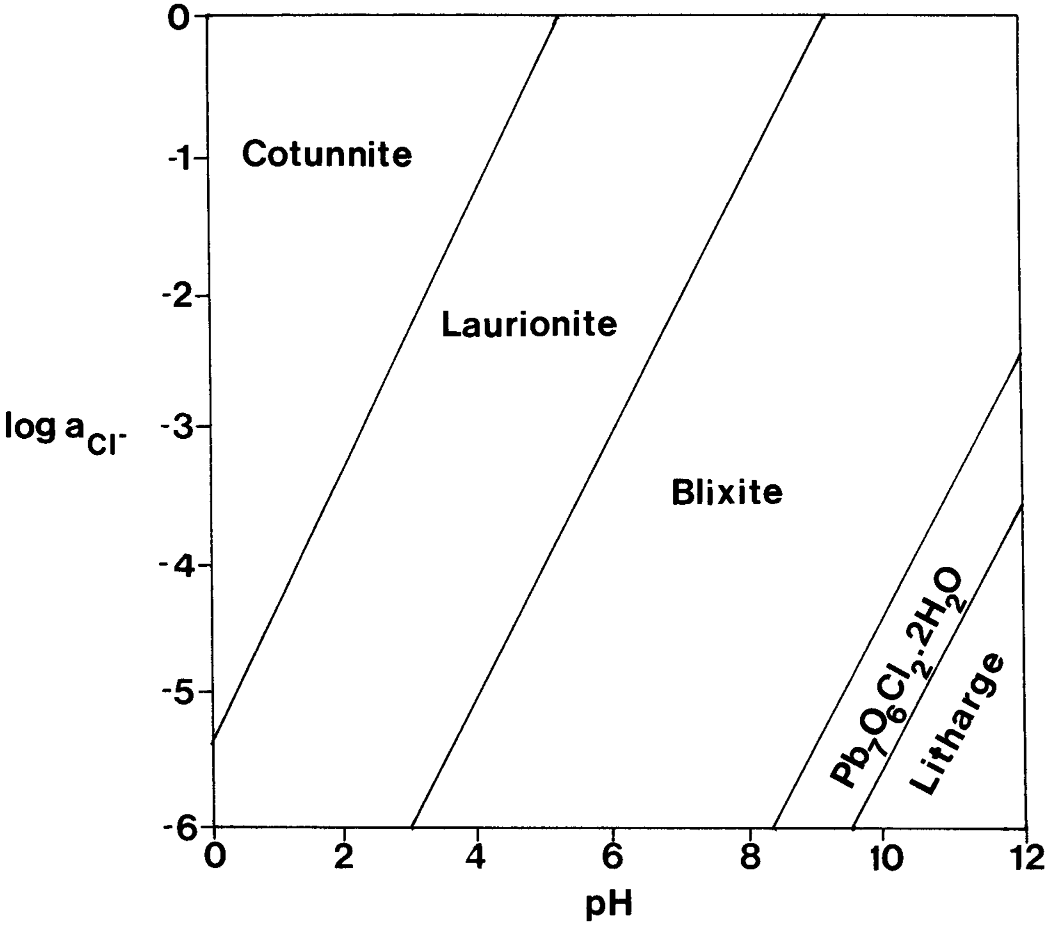

FIG. 3. Stability field diagram for the PbO–HCl–H_2O system at 298.2 K and 10^5 Pa.

and paralaurionite (Alabaster, 1989). This suggests that solution conditions during crystallisation fluctuated about the laurionite–mendipite phase boundary. On the other hand, mendipite from Merehead Quarry, is often found intimately associated with a blixite-like mineral (Symes and Embrey, 1977). Solution conditions would therefore have been slightly different to those encountered at the Wesley Mine; they would indeed have been somewhat more basic, given comparable chloride activities.

When carbon dioxide is present in solution, the chemistry of lead oxychloride formation is dramatically altered. Phases such as cerussite, Hydrocerussite and phosgenite can now be present, and their formation with respect to the basic chlorides can now be assessed. Bilinski and Schindler (1982) and Näsänen *et al.* (1962) have reported solubility products for cerussite, hydrocerussite and phosgenite. From these data, standard Gibbs free energies of formation at 298.2 K can be calculated, and these are listed in Table 5. Figs. 5 and 6 illustrate stabilities in the $PbO–HCl–H_2O–CO_2$ system at 298.2 K with a carbon dioxide partial pressure of $10^{-12.91}$, when laurionite and phosgenite are at equilibrium, and of $10^{-12.22}$, when cerussite and hydrocerussite are at equilibrium, respectively. Equations (5) and (6) are those for which the boundary conditions were calculated.

$$2Pb(OH)Cl(s) + CO_2(g) \rightleftharpoons Pb_2CO_3Cl_2(s) + H_2O \quad (5)$$

$$Pb_3(CO_3)_2(OH)_2(s) + CO_2(g) \rightleftharpoons 3PbCO_3(s) + H_2O \quad (6)$$

The diagrams do show how certain paragenetic sequences can be developed as a result of the reaction of pre-existing lead oxychlorides with

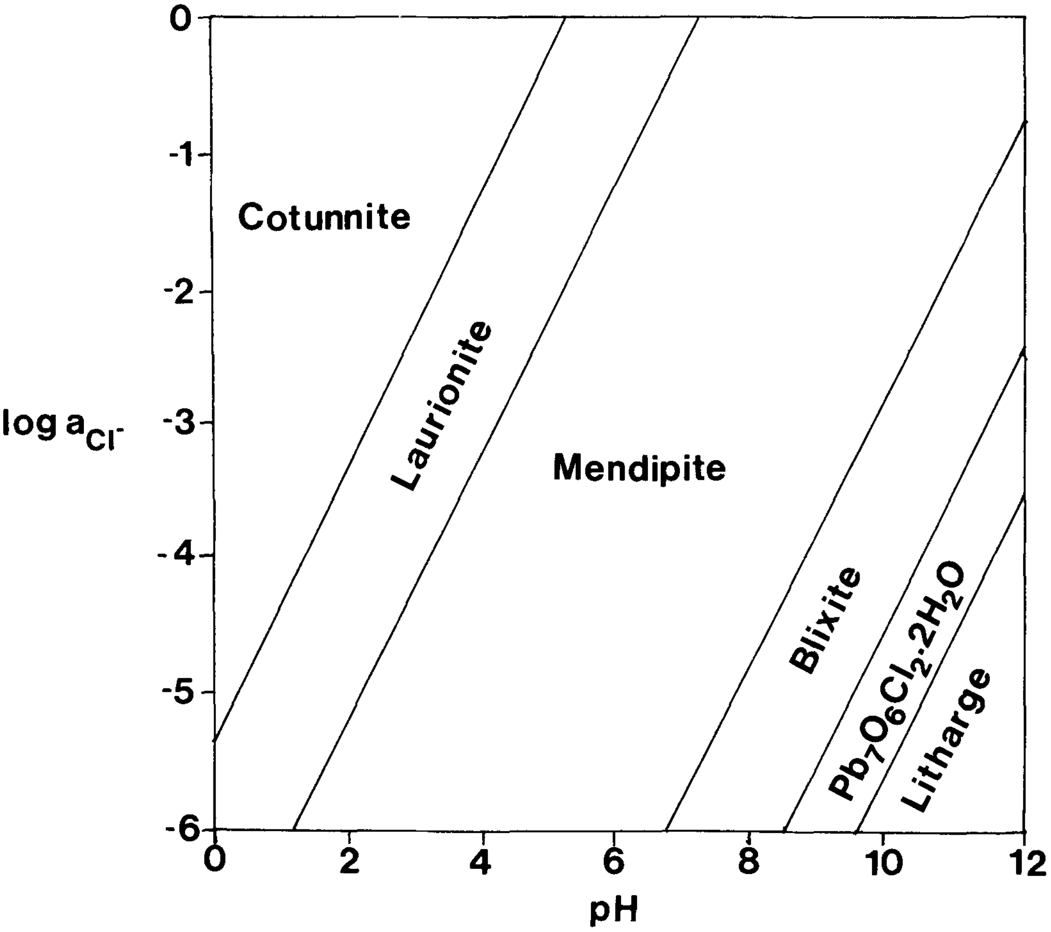

FIG. 4. Stability field diagram for the $PbO–HCl–H_2O$ system at 302.2 K and 10^5 Pa.

CO_2 increasing in the system. These relationships have been explored previously for a number of deposits (Bideaux, 1980). Those conclusions are reinforced here and more accurate phase relationships are provided.

The results of this study can also be used to relate the various corrosion products found on archaeological lead objects to the environments to which they were exposed. Commonly, cerussite, hydrocerussite, phosgenite and laurionite are identified on such artefacts (Campbell and Mills, 1977; Lacroix, 1910; Gorman, 1976). Cotunnite has been observed on several occasions (Russell, 1920; Lacroix, 1910; Gorman, 1976), and, through a knowledge of stability field relationships, interpretation of the conditions of formation of these phases under equilibrium conditions is possible.

Occasionally, quite uncommon compounds have been observed as alteration products. One particular example is that of penfieldite on a Roman anchor recovered from the Mediterranean Sea (Goni *et al.*, 1954). We wish finally to comment on this phase and fiedlerite. Numerous attempts to synthesise these minerals under various conditions (chloride ion concentrations from dilute to 3 M, lead ion concentrations from dilute to saturated, different rates and sense of addition of base, and at temperatures from 0 to 65 °C) have all been unsuccessful. These observations, in the light of given stoichiometries and mineralogical reports (Palache *et al.*, 1951; Kohlberger, 1977), lead us to believe that laurionite is thermodynamically stable with respect to penfieldite and fiedlerite. We cannot comment on possible conditions for their likely formation, but

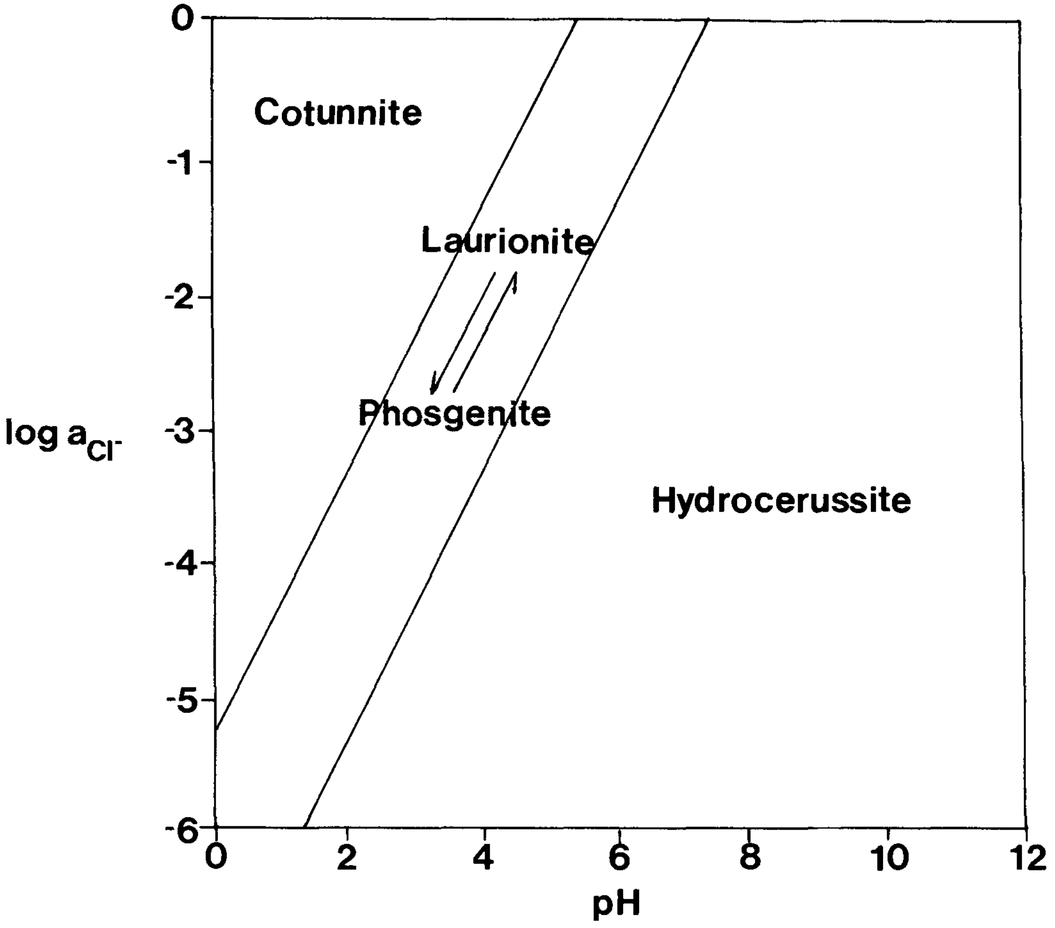

FIG. 5. Stability field diagram for the PbO–HCl–H_2O–CO_2 system at 298.2 K and 10^5 Pa and a partial pressure of $CO_2(g)$ equal to $10^{-12.91}$.

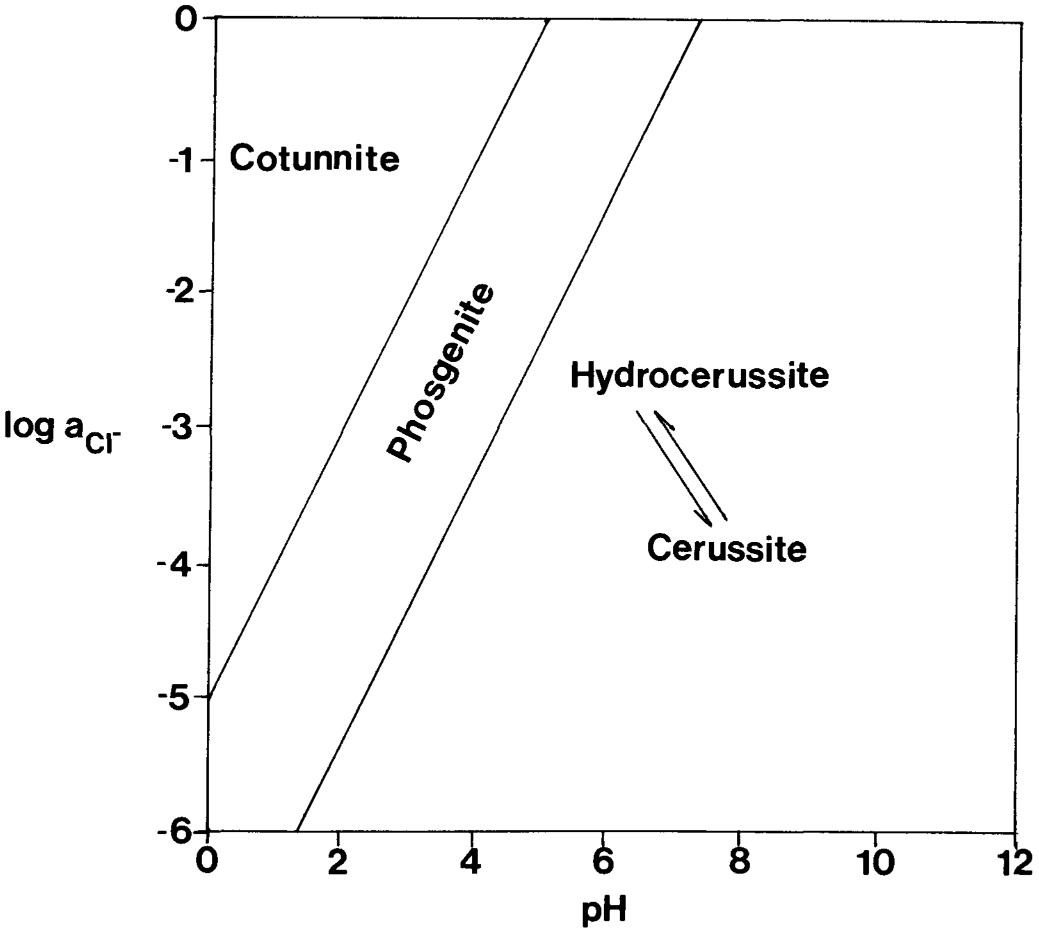

FIG. 6. Stability field diagram for the PbO–HCl–H_2O–CO_2 system at 298.8 K and 10^5 Pa and a partial pressure of $CO_2(g)$ equal to $10^{-12.22}$.

do note that attempts to synthesise the minerals were conditioned by their given formulae. With this in mind, we have undertaken a single-crystal X-ray structure determination of fiedlerite, the results of which will be communicated in the near future.

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