

The chemical stability of mimetite and distribution coefficients for pyromorphite–mimetite solid-solutions

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Abstract

The equilibrium solubility of mimetite has been determined in aqueous solution at 298.2 K. For the reaction $\text{Pb}_5(\text{AsO}_4)_3\text{Cl}(\text{s}, \text{mimetite}) + 6\text{H}^+(\text{aq}) \rightleftharpoons 5\text{Pb}^{2+}(\text{aq}) + 3\text{H}_2\text{AsO}_4^-(\text{aq}) + \text{Cl}^-(\text{aq})$ at this temperature $\log K_{\text{H}^+}$, extrapolated to zero ionic strength, is equal to $-27.9(4)$. This value is equal, within experimental error, to that corresponding to pyromorphite, $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$, derived from the literature, and redetermined here under analogous conditions. Distribution coefficients in terms of both HXO_4^{2-} and $\text{H}_2\text{XO}_4^-(\text{aq})$ ions ($X = \text{P}, \text{As}$) have also been determined for solid phases of the pyromorphite–mimetite solid solution series containing from 5 to 95 mol. % mimetite. Although the two end-members are isostructural without being strictly isomorphous, the solid solution series behaves ideally over the whole compositional range; that is, the composition of the solid phase reflects the ratio of arsenate to phosphate species in aqueous solution at pH values corresponding to naturally-occurring aqueous solutions generally associated with the oxidized zones of base metal orebodies. Some relationships between mimetite and other secondary lead(II) and copper(II) arsenate minerals have been explored.

KEYWORDS: chemical stability, mimetite, distribution coefficients, pyromorphite–mimetite, solid-solutions.

Introduction

MIMETITE is probably the most common secondary lead(II) arsenate mineral to be found in the oxidized zones of base metal orebodies. It is one end-member of a large family of minerals, the apatites, with general formula $M_5(\text{XO}_4)_3\text{Y}$, usually with M being a divalent cation, $X = \text{P}, \text{As}, \text{V}$, and Y being a univalent anion such as OH^- or halide (Palache *et al.*, 1951; Fleischer, 1987). Extensive solid solution is known between many end-members of the group, particularly between mimetite, $\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$, and pyromorphite, $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$. Förtsch (1970) has collected together much analytical data to support this fact as well as other data concerning the vanadate analogue vanadinite and the substitution of Ca(II) ion in the three end-member lattices.

It has become apparent, however, that while pyromorphite and mimetite are isostructural, they are not isomorphous, crystallizing in space groups $P6_3/m$ and $P2_1/b$, respectively (Baker, 1966; Keppler, 1968, 1969; Förtsch, 1970) and this intro-

duces a complication into any classical treatment of solid-solution phenomena involving the two minerals. Nriagu (1973) has reported a reliable value for the solubility product of pyromorphite. Unfortunately no such data are available for mimetite. Furthermore, we are unaware of any published studies concerning distribution coefficients for intermediate members of the series, relating the extent of solid-substitution to species distributions in the aqueous solutions from which they crystallize.

Determinations of these data would be desirable in view of the widespread distribution of minerals of the mimetite–pyromorphite series and their potential importance in limiting the concentrations of Pb(II) and $\text{H}_x\text{XO}_4^{3-x}$ ions of groundwaters in the vicinity of oxide zones.

We have undertaken such a study, the results of which are reported here. The findings are also applied to the crystallization of mimetite in relation to other secondary arsenate minerals of Pb(II), Cu(II), and species which contain both cations.

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TABLE 1. Masses of Compounds Used in Pyromorphite and Mimetite Syntheses.

Experiment No.	Mass ^a of Starting Compound /g	
	PbHPO ₄ (s)	PbHAsO ₄ (s)
SP1	3.5901	
SP2	3.7898	
SP3	3.9834	
SP4	4.1951	
SP5	4.3996	
SP6	4.6002	
SM1		3.5601
SM2		3.8003
SM3		4.0445
SM4		4.2005
SM5		4.4000
SM6		4.6000
SM7		4.8003
SM8		4.9055

^aEach equilibrated in 100 cm³ of 0.1 mol dm⁻³ aqueous NaCl solution.

Experimental

Lead hydrogen phosphate, PbHPO₄(s), was prepared by slowly mixing 0.1 mol dm⁻³ aqueous solutions of lead(II) nitrate and disodium hydrogen phosphate in equal amounts at room temperature. After the mixture had been gently stirred for 24 hours, the solid was collected at the pump, washed exhaustively with cold water and dried at 85 °C.

Schultenite, PbHAsO₄, was prepared in the same way except for the substitution of KH₂AsO₄ for Na₂HPO₄. The identities of the products, and all other solids prepared, were checked by X-ray powder diffraction measurements.

Mimetite and pyromorphite were prepared by adding known amounts (c. 3–5 g) of PbHAsO₄(s) and PbHPO₄(s), respectively, to known volumes (nominally 100 cm³ in calibrated volumetric glassware) of accurate 0.1 mol dm⁻³ aqueous NaCl solutions, following the method of Nriagu (1973). Equilibrium between solid and aqueous phases is quickly established (Nriagu, 1973), but the mixtures were kept in a thermostated bath at 25 ± 0.2 °C for fourteen (mimetite) or sixteen (pyromorphite) weeks, and were stirred occasionally. The pH of the supernatant was then

recorded, and the mixtures were filtered through prewashed Whatman GF/F fibreglass filter papers (0.3 μ). The filtrates were conserved for analysis (*vide infra*) and the solids were washed with water, alcohol, then ether, and air-dried. Lead contents of the supernatants were estimated by AAS methods (Varian Techtron, 1979) using the method of standard additions. Since the lead in all experimental runs is almost quantitatively precipitated, total chloride, arsenate and phosphate concentrations may be accurately calculated using the stoichiometric relationships and a knowledge of the exact amounts of solid PbHXO₄ and the concentration and volume of NaCl(aq) solution used in each case.

In the pyromorphite–mimetite solid solution experiments, known amounts of PbHAsO₄(s) and PbHPO₄(s) were added to 100 cm³ of 0.1 mol dm⁻³ aqueous NaCl solution, and the mixtures left to equilibrate as above for twenty weeks at 25.0 ± 0.2 °C. With respect to quantities required for the calculation of distribution coefficients, the very low concentration of Pb(II) in the final solutions compared to concentration of arsenate, phosphate and proton, renders its determination unnecessary. However, arsenate or phosphate must be determined in one phase or the other. The equilibrated samples were treated as above, with the pH being measured, and the solids saved for later X-ray examination. Phosphate was determined in the filtrate using the method of Liu and Chen (1981). Stoichiometric calculations based on the results and the known weights of PbHAsO₄(s) and PbHPO₄(s) used in the individual experiments afforded in turn the formula of the precipitated solids.

Weights of solids used in the equilibrations and analytical results from them are listed in Tables 1 to 4. Species distributions in the various experimental solutions were calculated using the programme COMICS (Perrin and Sayce, 1967). Species calculated in the end-member pyromorphite and mimetite experiments were HXO₄²⁻, H₂XO₄⁻, H₃XO₄⁰, PbHXO₄⁰, PbH₂XO₄⁺, NaHXO₄⁻, PbCl⁺, PbCl₂⁰, PbCl₃⁻ and PbCl₄²⁻(aq). Equilibrium constant data for all species except for PbHAsO₄⁰, PbH₂AsO₄⁺ and NaHAsO₄⁻(aq) were taken from the critical compilation of Smith and Martell (1976) and corrected to I = 0.1 mol dm⁻³ using the Davies form of the Debye-Huckel expression [$\log \gamma_i = -Az_i^2 I^{\frac{1}{2}} / (I + I^{\frac{1}{2}}) + 0.3I$], where necessary. Minor actual variations in ionic strength yield changes in equilibrium constants well within their estimated error, and so constant ionic strength (I = 0.1 mol dm⁻³) was assumed throughout. Equilibrium constants for the Pb(II) and Na(I) arsenate species mentioned above were

TABLE 2. Masses of Solids Used in the Solid-Solution Experiments.^a

Experiment No.	Masses/g		Amounts ^b /millimol	
	PbHPO ₄ (s)	PbHAsO ₄ (s)	PbHPO ₄ (s)	PbHAsO ₄ (s)
SSS 1	0.1552	3.3202	0.5	9.5
SSS 2	0.3152	3.1257	1.0	9.0
SSS 3	0.4200	2.9602	1.5	8.5
SSS 4	0.6151	2.8201	2.0	8.0
SSS 5	0.7598	2.5951	2.5	7.5
SSS 6	0.9399	2.4299	3.0	7.0
SSS 7	1.2301	2.0828	4.0	6.0
SSS 8	1.5301	1.7353	5.0	5.0
SSS 9	1.8203	1.3952	6.0	4.0
SSS 10	2.1451	1.0448	7.0	3.0
SSS 11	2.2750	0.8653	7.5	2.5
SSS 12	2.4505	0.7051	8.0	2.0
SSS 13	2.5900	0.5351	8.5	1.5
SSS 14	2.7606	0.3471	9.0	1.0
SSS 15	2.9100	0.1810	9.5	0.5

^a Equilibrated in 100 cm³ of 0.1 mol dm⁻³ aqueous NaCl solution.

^b Approximate.

set at the same values as for the phosphate analogues, with appropriate allowance for differences in the acid dissociation constants for arsenic and phosphoric acids (the COMICS programme requires cumulative equilibrium constants to be supplied). This assumption is reasonable in view of the close similarities between arsenate, phosphate and their conjugate acid species. However, a number of check calculations were carried out in which the equilibrium constants for PbHAsO₄⁰, PbH₂AsO₄⁻ and NaHAsO₄⁻(aq) were systematically varied by one order of magnitude. Final values for the equilibrium constants for the minerals obtained under these circumstances were inside the experimental error calculated from the several runs and thus the above assumption is valid; values for analogous phosphate and arsenate complexes with lead and sodium ions would have to be very different indeed for any significant variation in the results to become apparent.

Lead not being analytically determined in the solid-solution experiments, no Pb(II) species were included in the species distribution calculations in this case. This approach too is quite justified in view of the fact that lead concentrations in solution are negligible compared with total arsenic and phosphorus.

Lists of calculated concentrations of pertinent species in solution obtained from the computer calculations are given in Tables 5 and 6, together with values observed in turn for activity coefficients and equilibrium constants, as discussed below.

Measurements of pH were made using a Radiometer PHM 85 pH meter fitted with a combination electrode. AAS measurements were made using a Varian AA-275 instrument. Absorption readings for the colorimetric analyses of phosphate in the presence of arsenate were obtained with a Perkin Elmer 559 or LAMDA 5 spectrophotometer. Powder X-ray photographs were recorded using a Debye-Scherrer camera and Cu-K α radiation. Spacings were measured visually using a Vernier reader accurate to 0.05 mm.

Results and discussion

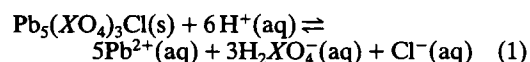
For the sake of internal consistency and in order to make comparison with previously published data, we have redetermined the solubility of pyromorphite during the course of the reported experiments. Values for K_{H^+} , defined in equation (1) for pyromorphite at 298.2 K are listed in

TABLE 3. Analytical Results for the Pyromorphite and Mimetite Equilibrations at 298.2K.

Experiment No.	pH	$10^7[\text{Pb}^{2+}]_{\text{TOT}}/\text{mol dm}^{-3}$	$10^2[\text{P,As}]_{\text{TOT}}^{\text{a}}/\text{mol dm}^{-3}$	$10^2[\text{Cl}^{-}]_{\text{TOT}}^{\text{a}}/\text{mol dm}^{-3}$	$10[\text{Na}^{+}]_{\text{TOT}}^{\text{a}}/\text{mol dm}^{-3}$
SP1	2.16	5.540	4.737	7.511	0.988
SP2	2.16	5.529	5.000	7.380	0.988
SP3	2.25	5.570	5.257	7.252	0.988
SP4	2.26	5.575	5.535	7.113	0.988
SP5	2.28	5.602	5.805	6.978	0.988
SP6	2.36	6.059	6.069	6.845	0.988
SM1	2.32	4.733	4.102	7.999	1.005
SM2	2.34	4.917	4.376	7.860	1.005
SM3	2.35	5.219	4.660	7.720	1.005
SM4	2.35	5.369	4.802	7.650	1.005
SM5	2.37	5.445	5.071	7.515	1.005
SM6	2.37	5.490	5.301	7.400	1.005
SM7	2.38	5.559	5.532	7.290	1.005
SM8	2.38	5.722	5.647	7.227	1.005

^a Calculated from stoichiometric relationships.

Table 5. Our value for $\log K$ (298.2 K) is equal to $-28.3(7)$. This compares



with the reported value of Nriagu (1973) of $-27.4(1)$. In addition, we have recalculated the experimental data of Nriagu (1973) using our method, to yield a value of $-27.4(1)$. Agreement between the sets of values is excellent. Nevertheless, for the purpose of later calculations involving the pyromorphite-mimetite solid solutions it is necessary to pick a particular value and in order to maintain the internal consistency, we have averaged our values together with the recalculated ones from Nriagu's original experimental work. This yields a value for $\log K_{\text{H}^+}$ (298.2 K) for pyromorphite of $-27.8(7)$.

Also listed in Table 5 are values for $\log K_{\text{H}^+}$ (298.2), with respect to equation (1), for mimetite. The average value is equal to $-27.9(4)$, which is experimentally equal to that for pyromorphite. Such a finding suggests that, should the solid solution behave ideally, then the composition of the solid phase would reflect simply the relative concentrations of H_2PO_4^- and H_2AsO_4^- in the solutions from which they crystallize. We do find experimentally that this

is in fact the case although the situation is somewhat complicated by the differing space groups of the two end-members and the effect of varying solution pH (*vide infra*). In all these calculations, values for the acid dissociation constants for arsenic and phosphoric acids are taken from the compilation of Smith and Martell (1976).

The equilibrium constant derived for mimetite may be used to indicate its relative stability with respect to other arsenate-containing secondary minerals. Fig. 1 shows the stability fields for a number of Cu(II) and Pb(II) arsenate minerals taken from the work of Magalhães *et al.* (1986). The diagram is calculated for $a_{\text{Pb}^{2+}} = 10^{-7}$, a reasonable value in the light of the experiments described above, and for $a_{\text{Cl}^-} = 10^{-3}$ (corresponding to a weakly saline groundwater), 10^{-2} and 10^{-1} . It is seen that variations over this range of chloride ion activities have little effect on the positions of the mimetite field boundaries. As an illustration of the use to which this kind of phase diagram might be put in deducing the chemical environment of secondary mineral formation, attention may be focussed on some of the arsenate-suite minerals known to occur at Tsumeb, Namibia. Excellent descriptions of mineral associations in the deposit are available (Keller, 1977; Keller and Bartelke 1982; Pinch and Wilson, 1977).

Of the arsenates in Tsumeb, duftite, PbCu

TABLE 4. Analytical and Calculated Factors for the Solid-Solution Experiments at 298.2K.

Sample No.	pH	$10^2[\text{P}]_{\text{TOT}}/\text{mol dm}^{-3}$	$10^2[\text{As}]_{\text{TOT}}^{\text{a}}/\text{mol dm}^{-3}$	Solid ^a Composition	$n_{\text{mim}}^{\text{b}}$
SSS1	2.353	0.19	3.84	$\text{Pb}_5(\text{PO}_4)_{0.16}(\text{AsO}_4)_{2.84}\text{Cl}$	0.95
SSS2	2.354	0.39	3.62	$\text{Pb}_5(\text{PO}_4)_{0.32}(\text{AsO}_4)_{2.68}\text{Cl}$	0.89
SSS3	2.354	0.60	3.43	$\text{Pb}_5(\text{PO}_4)_{0.47}(\text{AsO}_4)_{2.53}\text{Cl}$	0.84
SSS4	2.355	0.79	3.27	$\text{Pb}_5(\text{PO}_4)_{0.61}(\text{AsO}_4)_{2.39}\text{Cl}$	0.80
SSS5	2.356	0.98	3.01	$\text{Pb}_5(\text{PO}_4)_{0.76}(\text{AsO}_4)_{2.24}\text{Cl}$	0.75
SSS6	2.356	1.22	2.82	$\text{Pb}_5(\text{PO}_4)_{0.93}(\text{AsO}_4)_{2.07}\text{Cl}$	0.69
SSS7	2.358	1.60	2.42	$\text{Pb}_5(\text{PO}_4)_{1.22}(\text{AsO}_4)_{1.78}\text{Cl}$	0.59
SSS8	2.363	1.96	2.06	$\text{Pb}_5(\text{PO}_4)_{1.54}(\text{AsO}_4)_{1.46}\text{Cl}$	0.49
SSS9	2.363	2.32	1.63	$\text{Pb}_5(\text{PO}_4)_{1.81}(\text{AsO}_4)_{1.19}\text{Cl}$	0.40
SSS10	2.364	2.81	1.22	$\text{Pb}_5(\text{PO}_4)_{2.12}(\text{AsO}_4)_{0.88}\text{Cl}$	0.30
SSS11	2.365	2.98	1.00	$\text{Pb}_5(\text{PO}_4)_{2.26}(\text{AsO}_4)_{0.74}\text{Cl}$	0.25
SSS12	2.366	3.21	0.84	$\text{Pb}_5(\text{PO}_4)_{2.41}(\text{AsO}_4)_{0.59}\text{Cl}$	0.20
SSS13	2.366	3.39	0.65	$\text{Pb}_5(\text{PO}_4)_{2.55}(\text{AsO}_4)_{0.45}\text{Cl}$	0.15
SSS14	2.367	3.60	0.44	$\text{Pb}_5(\text{PO}_4)_{2.72}(\text{AsO}_4)_{0.28}\text{Cl}$	0.09
SSS15	2.367	3.81	0.24	$\text{Pb}_5(\text{PO}_4)_{2.86}(\text{AsO}_4)_{0.14}\text{Cl}$	0.05

^aCalculated from stoichiometric relationships. ^bMol fraction of mimetite in solid solution, to two significant figures. More accurate values are used to calculate distribution coefficients (see text).

$\text{AsO}_4(\text{OH})$, is the most common associate of mimetite. This is a significant observation in that it places a limit on chloride ion activities during crystallization. Duftite is usually encountered as crusts and films of small crystals, a habit which would be expected to be rather easily replaced with widely varying solution conditions. Fig. 1 indicates that Duftite would be completely replaced by mimetite (its equilibrium stability field vanishes) at a_{Cl^-} values around 10^{-1} . Since both minerals occur together frequently, it can be safely concluded that the mineralizing solutions involved were weakly saline. A value of about 10^{-3} (~35 ppm chloride ion) would seem appropriate. Next, the associations of Olivenite, $\text{Cu}_2\text{AsO}_4(\text{OH})$, Bayldonite, $\text{Cu}_3\text{Pb}(\text{AsO}_4)_2(\text{OH})_2$, Duftite, and Schultenite, PbHASO_4 , which have been reported are noteworthy. The noted occurrence of Bayldonite with Schultenite also indicates a weakly saline solution condition. Mimetite is very frequently found with these other arsenates and thus further reference to Fig. 1 indicates a reasonable range of $a_{\text{Cu}^{2+}}$ and pH values for the several assemblages. The former would vary

between 10^{-2} and $10^{-3.5}$ and pH from about 3.5 to 5.5. Therefore, the several observed paragenetic relationships between these minerals and their associates (Keller, 1977; Pinch and Wilson, 1977) can be explained by subtle variations in the activities of their component ions in aqueous solution. No gross change in chemistry is required, and the concentrations or activities of lead, copper, chloride and hydrogen ions may be quite closely defined. Keller (1977) has concluded on the basis of mineral associations that the pH of mineralizing solutions was neutral to acidic during the formation of mimetite and of its associates. If Cornubite, Cornwallite or Clinoclase occur at Tsumeb, they do so very rarely (Pinch and Wilson, 1977). This, too, places limits on pH- $a_{\text{Cu}^{2+}}$ variations in the absence of other ions in solution.

Descriptions of solution conditions concerning the relationships between mimetite and other common secondary lead(II) minerals are complicated because of the number of variables that are involved. However, mention should be made in passing of Cerussite, PbCO_3 , because of its common association with mimetite (Palache *et al.*,

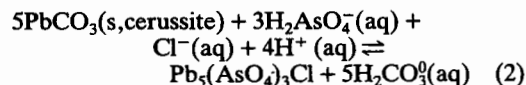
TABLE 5. Calculated Equilibrium Concentrations and Other Parameters^a
in the Pyromorphite and Mimetite Experiments at 298.2K.

Experiment No.	$10^7[\text{Pb}^{2+}]/\text{mol dm}^{-3}$	$10^2[\text{H}_2\text{XO}_4^{-}]/\text{mol dm}^{-3}$	$10^2[\text{Cl}^{-}]/\text{mol dm}^{-3}$	$\log K_{\text{H}^+}^{\text{b}}$
SP1	2.474	2.677	7.512	-29.12
SP2	2.514	2.826	7.380	-29.02
SP3	2.507	3.235	7.252	-28.31
SP4	2.509	3.436	7.113	-28.19
SP5	2.516	3.666	6.978	-27.98
SP6	2.694	4.086	6.845	-27.22
SM1	2.104	2.475	7.999	-28.58
SM2	2.184	2.688	7.861	-28.31
SM3	2.318	2.888	7.720	-28.01
SM4	2.386	2.976	7.649	-27.91
SM5	2.416	3.197	7.515	-27.68
SM6	2.438	3.342	7.400	-27.61
SM7	2.467	3.517	7.290	-27.46
SM8	3.541	3.590	7.227	-27.37

^a For $I = 0.1 \text{ mol dm}^{-3}$, $\gamma_{\pm} = 0.704$, $\gamma_{2\pm} = 0.303$.

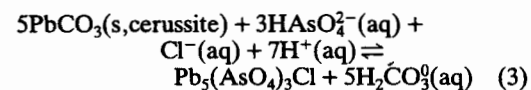
^b See text.

1951) and because some simplifications can be made. We may write the equation (2) to illustrate the transformation of one mineral to the other.



Since $\text{H}_2\text{AsO}_4^{-}(\text{aq})$ ion predominates in aqueous solution from about pH3 to pH7 (Smith and Martell, 1976), the equation would be valid for pH values at the upper limit of this range, since we are dealing with a solid carbonate mineral, should we wish to consider conditions under which both species might form. However, even at the upper end of the above pH range, preliminary calculations indicate that no reasonable values of $a_{\text{H}_2\text{AsO}_4^{-}}$, $a_{\text{H}_2\text{CO}_3^0}$ and $a_{\text{Cl}^{-}}$ in combination are possible. In other words, it is apparent that the cerussite-mimetite assemblage must form under basic conditions, and indeed at rather elevated P_{CO_2} values should both minerals be stable. With this in mind, it is worthwhile to evaluate the equilibrium boundary for (3) for which equation (4) may be derived using data taken from the literature for

the other species (Robie *et al.*, 1978; Smith and Martell, 1976) at 298.2 K.¹



$$\text{pH} = 9.75 - \frac{5}{2} \log a_{\text{H}_2\text{CO}_3^0} + \frac{1}{2} \log a_{\text{Cl}^{-}} + \frac{3}{2} \log a_{\text{HAsO}_4^{2-}} \quad (4)$$

First it is apparent that wide variations in $a_{\text{Cl}^{-}}$ do not much alter the boundary conditions. Variation of this parameter from 10^{-3} (a weakly saline groundwater) to 10^{-1} (a moderately saline groundwater) alter the constant in (4) from 9.32 to 9.61. For the sake of further comparison $a_{\text{Cl}^{-}} = 10^{-2}$ has been chosen. Then, for $a_{\text{HAsO}_4^{2-}} = 10^{-7}$, for $P_{\text{CO}_2} = 10^{-1}, 10^{-2}, 10^{-3}$ and 10^{-4} , the

¹ $\Delta_f G^\circ (\text{AsO}_4^{3-}, \text{aq})$ at 298.2 K is taken from Barner and Scheuerman (1978). A value for $\Delta_f G^\circ (\text{HAsO}_4^{2-})$ may be estimated from these data in conjunction with the acid-base equilibria tabulated by Smith and Martell (1976). It may also be used, together with other thermodynamic data from Robie *et al.*, (1978), to give $\Delta_f G^\circ (\text{mimetite, s})$ at 298.2 K as $-2674.3 \pm 3.0 \text{ kJ mol}^{-1}$. No errors for $\Delta_f G^\circ$ of arsenate species are listed in the above reference, and it is not included in our estimate.

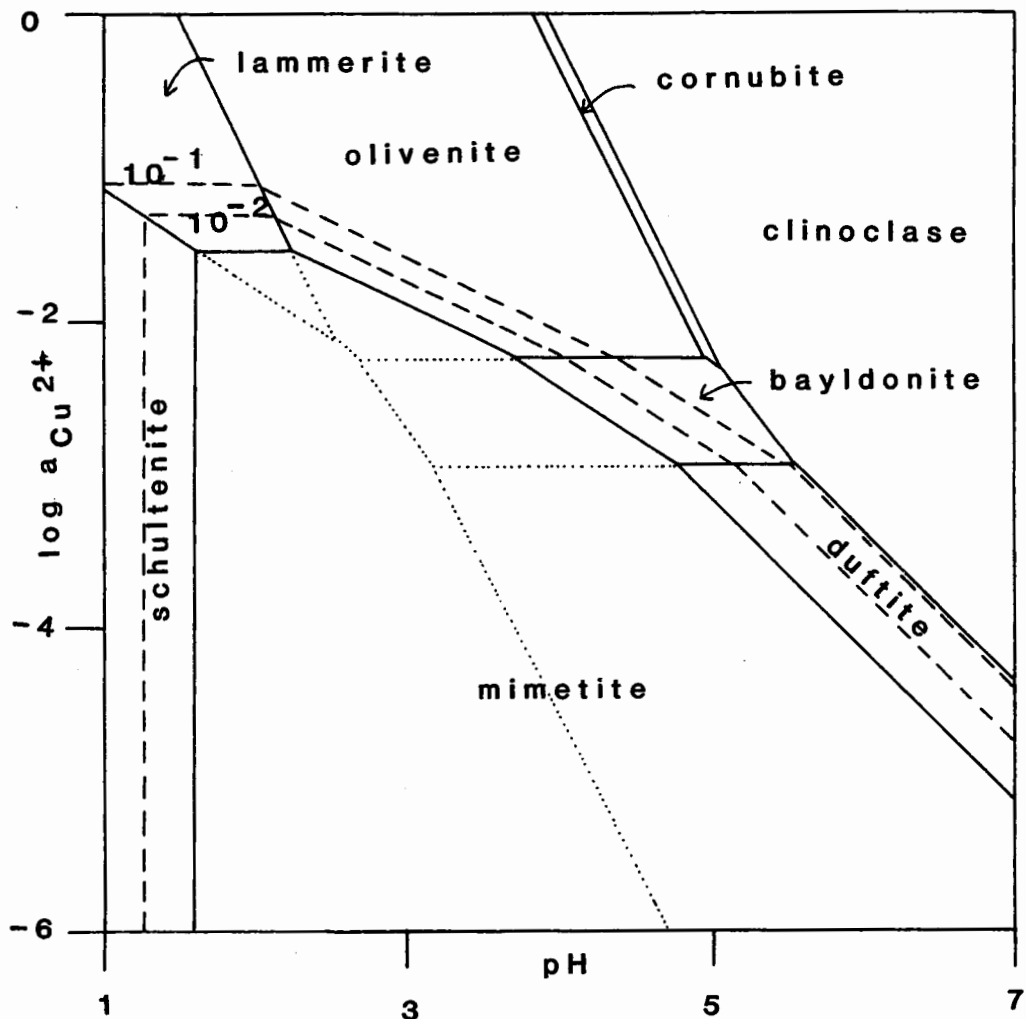


FIG. 1. Stability field diagram for some secondary Cu(II) and Pb(II) arsenate minerals. All boundaries in full lines are drawn for $a_{Pb^{2+}} = 10^{-7}$ and $a_{Cl^-} = 10^{-3}$. Dotted lines indicate other phase boundaries in the absence of chloride ion. The dashed lines indicate the change in the mimetite stability field with increasing chloride ion activity (10^{-2} and 10^{-1} , as indicated on the diagram).

calculated pH for the boundary is 8.22, 8.93, 9.65 and 10.43, respectively. Alteration of $a_{H_2AsO_4^{2-}}$ to 10^{-8} for the same P_{CO_2} values gives corresponding equilibrium pH values of 7.79, 8.50, 9.22 and 10.00, respectively. Since the pH of groundwaters in the natural environment is limited to about 9.5 (Garrels and Christ, 1965; Baas Becking *et al.*, 1960) except in very unusual circumstances unlikely to be encountered in oxidizing sulphide ores (Kharaka *et al.*, 1984; Neal and Stanger, 1984), cerussite and mimetite may only crystallize together, at equilibrium, under conditions of high

pH, rather low activities of dissolved arsenic, and with considerable partial pressures of $CO_2(g)$. Other calculations involving other secondary lead(II) minerals are beyond the scope of this work, and should more profitably be carried out to suit particular suites. In any case, the data are available should the calculation be required.

With the reasonable assumption that $\gamma_{H_2PO_4^-} = \gamma_{H_2AsO_4^{2-}}$ in aqueous solution, the usual distribution coefficient in terms of these ions may be derived from equation (5), for the solid solution series, where the solubility products of the phases

TABLE 6. Calculated Equilibrium Concentrations in the Solid-Solution Experiments at 298.2K.

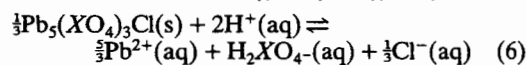
Experiment No.	$10^2[\text{H}_2\text{AsO}_4^-]/\text{mol dm}^{-3}$	$10^2[\text{H}_2\text{PO}_4^-]/\text{mol dm}^{-3}$	$10^7[\text{HAsO}_4^-]/\text{mol dm}^{-3}$	$10^7[\text{HPO}_4^-]/\text{mol dm}^{-3}$	K_D^a	$K_D^{b'}$
SSSS 1	2.381	0.126	13.609	0.414	0.94	0.54
SSSS 2	2.245	0.264	12.830	0.871	0.98	0.57
SSSS 3	2.135	0.400	12.316	1.331	1.01	0.58
SSSS 4	2.035	0.531	11.765	1.769	1.02	0.59
SSSS 5	1.876	0.659	10.867	2.203	1.04	0.60
SSSS 6	1.758	0.817	10.189	2.730	1.03	0.59
SSSS 7	1.513	1.074	8.808	3.607	1.03	0.59
SSSS 8	1.288	1.325	7.587	4.499	0.98	0.56
SSSS 9	1.023	1.605	6.022	5.450	1.03	0.59
SSSS 10	0.768	1.897	4.535	6.457	1.03	0.60
SSSS 11	0.637	2.017	3.769	6.880	1.04	0.60
SSSS 12	0.530	2.166	3.140	7.408	1.00	0.58
SSSS 13	0.407	2.297	2.410	7.856	1.00	0.58
SSSS 14	0.268	2.447	1.592	8.388	0.94	0.54
SSSS 15	0.150	2.579	0.889	8.839	0.84	0.49

^a Distribution coefficient for the H_2XO_4^- species.

^b Distribution coefficient for the HXO_4^{2-} species. For an explanation of both of these terms, refer to text.

$$\frac{K_{\text{SP}}(\text{pyromorphite})}{K_{\text{SP}}(\text{mimetite})} =$$

$$\frac{[\text{H}_2\text{PO}_4^-] N_{\text{mimetite}} \gamma_{\text{mimetite}}}{[\text{H}_2\text{AsO}_4^-] N_{\text{pyromorphite}} \gamma_{\text{pyromorphite}}} \quad (5)$$



are represented by (6). On the basis of the experiments described above, the left hand term of the equation (5) is equal to unity, within experimental error, and the distribution coefficient K_D is that term shown in (7).

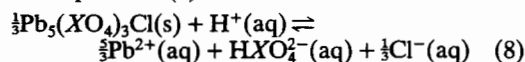
$$K_D = \frac{[\text{H}_2\text{PO}_4^-] N_{\text{mimetite}}}{[\text{H}_2\text{AsO}_4^-] N_{\text{pyromorphite}}} \quad (7)$$

Table 6 gives the experimentally determined values of K_D at 25 °C together with associated equilibrium concentrations of relevant dissolved species. K_D is found to be constant over the full range of mole fractions investigated, $0.05 \leq N_{\text{mimete}}$

≤ 0.95 and to be equal to unity [0.99 (5)]. Thus the solid-solution behaves ideally, irrespective of the fact that although the two end-members are isostructural, they are not isomorphous. From a chemical point of view, the important conclusion to be drawn is that the composition of the solid phase in the pyromorphite–mimetite solid solution reflects exactly the composition of the aqueous solution from which it crystallizes; whatever the amounts of arsenate and phosphate present (here between pH 3 and 7, where the diprotonated anions predominate), they will be incorporated in the lattice. It should be mentioned that X-ray diffraction measurements of the precipitated phases showed that no mixture of pyromorphite and mimetite was formed. Only one solid phase could be detected. Förtsch (1970) has reported that the change from hexagonal (pyromorphite) to monoclinic (mimetite) symmetry occurs at apparently 65 mol % mimetite. We have found the transformation to occur between samples SSS9 and SSS10, but no further refinement of the structural/compositional change was attempted. Irrespective of this fact, no variation

in K_D is evident at 25 °C over this stoichiometric range.

Because of slight differences in dissociation constants for arsenic and phosphoric acids and their conjugate bases, K_D values are pH dependent. From pH 7 to 12, a range which encompasses virtually all natural basicities in aqueous solution, the predominant dissolved species of arsenate and phosphate are the HAsO_4^{2-} and HPO_4^{2-} anions. In this case, K'_{SP} values for mimetite and pyromorphite refer to equation (8), and the expression (9) is derived.



$$\frac{K'_{\text{SP}}(\text{pyromorphite})}{K'_{\text{SP}}(\text{mimetite})} = \frac{[\text{HPO}_4^{2-}]N_{\text{mimetite}}\gamma_{\text{mimetite}}}{[\text{HAsO}_4^{2-}]N_{\text{pyromorphite}}\gamma_{\text{pyromorphite}}} \quad (9)$$

Using our results and acid-base equilibria for $\text{HXO}_4^-/\text{HXO}_4^{2-}$ taken from the references given above, $K'_{\text{SP}}(\text{pyromorphite})/K'_{\text{SP}}(\text{mimetite})$ is calculated to be equal to 0.60 at 25 °C. By similar reasoning to that already outlined, the distribution coefficient K'_D , (10), is derived, values for which are also listed in Table 6. These are no longer equal to unity, although

$$K'_D = \frac{[\text{HPO}_4^{2-}]N_{\text{mimetite}}}{[\text{HAsO}_4^{2-}]N_{\text{pyromorphite}}} \quad (10)$$

they are constant over the whole compositional range at 0.57(3), as shown in Table 6. The variation is of course due to differences in acid/base properties of H_3PO_4 vs. H_3AsO_4 . It should be noted that although the distribution coefficients are pH-dependent, $\gamma_{\text{mimetite}}/\gamma_{\text{pyromorphite}}$ is equal to unity over the whole range of solid solutions, within experimental error, and independent (as expected) of pH. That is, the pyromorphite-mimetite solid solution behaves ideally.

The results of this study may be used in turn to evaluate solution concentration ratios of arsenate and phosphate which obtained when the solid phases crystallized should analytical data for the minerals be available. This is notwithstanding the fact that phosphate/arsenate zoning in the pyromorphite-mimetite solid solution series is known (Förtsch, 1970). Such data, in conjunction with other studies, may be of value in deducing the chemical characteristics of groundwaters

associated with the development of complex oxidized orebodies. With this in mind, we have carried out a study of the composition of pyromorphite specimens from the oxidized zone at Broken Hill, New South Wales, Australia, the results of which will be communicated in the near future.

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