The chemistry of formation of some secondary arsenate minerals of Cu(II), Zn(II) and Pb(II)

M. CLARA F. MAGALHÃES, JULIO D. PEDROSA DE JESUS
Department of Chemistry, University of Aveiro, Aveiro, Portugal

AND

PETER A. WILLIAMS
Department of Chemistry, University College, PO Box 78, Cardiff, Wales, CF1 1XL

Abstract

Solution studies have been carried out on natural and synthetic arsenate minerals, which are often found in the oxide zones of base metal orebodies. Solubility products and free energy of formation data have been derived for the minerals olivenite, cornubite, clinoclase, adamite, legrandite, euchroite, duftite, conichalcite, austinite, bayldonite, and schultenite at 298.2 K (25 °C). The data have been used in turn to construct stability field diagrams illustrating the chemical conditions under which the various species may crystallize from aqueous solution. This equilibrium model is then compared with several natural occurrences of the arsenate suites and it is demonstrated that it can be used to explain a number of observed paragenetic sequences. Descriptions of solution conditions which describe the stabilities of the arsenate minerals with respect to more commonly found secondary minerals of Pb(II), Cu(II), and Zn(II) involve more complex calculations and estimates of the likely levels of various dissolved species, but it is shown how these may be taken into account in the development of a more complex equilibrium model.

KEYWORDS: chemistry, formation, secondary minerals, arsenates, solution studies, stability diagrams.

Introduction

BASE-METAL phosphates and arsenates form two groups of secondary minerals which are exceptionally widespread in the oxidized zones of sulphide orebodies. In these environments arsenate is derived from the common mineral arsenopyrite (FeAsS) or from less common species such as löllingite ($FeAs_2$) and arsenic-containing sulphosalts. Secondary arsenates and phosphates display a wide range of stoichiometries even when the only other anion present in the lattice is hydroxide and only one metallic cation is involved. This compositional elaboration is further accentuated when the presence of other anions and more than one cation in the lattice is taken into account. Scores of arsenates and phosphates are thus known as minerals, many being involved in complex solid-solution series (Palache *et al.*, 1951; Fleischer, 1987).

A few studies have appeared concerning the formation of some of the secondary phosphate minerals (Nriagu and Moore, 1984), and more recently Magalhães *et al.* (1986) have reported experimental results concerning the chemistry of formation of some Cu(II) and Zn(II) phosphate species. Almost no information is recorded in the literature concerning related arsenate species although these do considerably outnumber the known secondary phosphate minerals. Approximate values for the solubility products of lammerite ($Cu_3(AsO_4)_2$) and köttigite ($Zn_3(AsO_4)_2 . 8H_2O$) may be derived from reported solution studies (Chukhlantsev, 1956). Williams (1963) carried out solution experiments on adamite, $Zn_2AsO_4(OH)$, legrandite ($Zn_2AsO_4(OH) . H_2O$) and austinite ($CaZnAsO_4OH$). Unfortunately, the precise stoichiometry of legrandite was not known at that time.

Over the last few years we have been engaged in developing an equilibrium model for the formation of secondary minerals in the oxidized zone of

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base metal orebodies (Magalhães *et al.*, 1986, and references therein). In the course of this work we have considered the chemistry associated with the crystallization of some of the more common secondary arsenates, especially those with comparatively simple stoichiometries. The results of studies on a series of Cu(II), Zn(II), and Pb(II) arsenate minerals are presented here. In particular, efforts have been directed towards the development of a series of chemical models which illustrate the various paragenetic sequences that may be found. Conclusions which may be drawn from the solution experiments have been applied to several deposits in which the minerals are known to occur.

Experimental

Mineral species. The minerals and analogues used in this study were derived from a number of sources. Natural samples of conichalcite (BM 1977, 46) from Tsumeb, Namibia, cornubite (BM 60682) from Cornwall, UK and euchroite (BM 14302) from Libethen, Czechoslovakia, were taken from samples supplied by the British Museum (Natural History). Austinite (NMW 73.11G.M9) from Gold Hill, Utah, USA, olivenite (NMW 24.3G.R2) from Wheal Gorland, Cornwall, UK, and schultenite (NMW 77.16G.M12) from Tsumeb, Namibia, were taken from samples supplied by the National Museum of Wales, Cardiff. Legrandite and adamite from the Ojuela mine, Mapimi, Mexico, and clinoclase from the Majuba Hill mine, Nevada, USA, were hand-picked from specimens acquired from Gregory Bottley and Lloyd, London. The last three specimens are retained in the Department of Chemistry, University College, Cardiff. The nature of each mineral sample was confirmed by X-ray powder diffraction and by SEM X-ray analysis. All of the species conformed closely to the ideal stoichiometry; in particular, for the samples used, negligible ($<0.2\%$) concentrations of phosphate were present.

Initial studies involving bayldonite (BM 1912, 517) and duftite (BM 1981, 306), both from Tsumeb, Namibia, showed that variable substitution patterns for cations, and phosphate for arsenate, were particularly pronounced within small fragments of the one specimen. Therefore, experiments with natural samples of these two species were abandoned.

Synthetic bayldonite was prepared using the method of Guillemin (1956). Equal volumes of 0.01 mol dm^{-3} aqueous $Na_2HAsO_4.7H_2O$ and a solution which was both 5×10^{-3} mol dm^{-3} aqueous $Pb(CH_3COO)_2.3H_2O$ and 0.015 mol dm^{-3} aqueous $Cu(NO_3)_2.3H_2O$ were added together and the resulting mixture was boiled for 10 minutes. The mixture was cooled to room temperature, filtered at the pump, washed with water and air-dried. Powder X-ray diffraction of the resulting solid proved that both bayldonite and schultenite were present. Solution equilibrium experiments were carried out on this mixture (*vide infra*) which gave additional equilibrium constant data for schultenite as well as for bayldonite.

We have attempted, without success, to transform these mixtures containing bayldonite and schultenite to duftite by treatment with acid. Such attempts were prompted by earlier comments concerning the relative stabilities of bayldonite *versus* duftite with changing pH (Guillemin, 1956; Keller, 1977). In all cases we found more dissolution of material and the isolated solids contained the same two starting phases, albeit in different proportions.

Aqueous solutions were prepared, one being 10^{-2} mol dm^{-3} in both Cu(II) and Pb(II), using copper(II) perchlorate hexahydrate and lead(II) acetate trihydrate and the other 10^{-2} mol dm^{-3} in arsenate(V), using disodium hydrogen arsenate(V) heptahydrate. A mixture of 100 cm^3 of each of these solutions was adjusted to pH 3 using 0.1 mol dm^{-3} aqueous $HClO_4$, added in drops. The resulting mixture, in a glass liner, was heated for 48 hours at 180 °C in a bomb; it was cooled to room temperature and the precipitated solids collected at the pump, washed with water and air-dried. X-ray powder diffraction measurements showed that the solid was a mixture of duftite, schultenite, and an as yet unidentified phase. Experiments to determine the solubility product of duftite using this mixture (*vide infra*) also furnished additional data for schultenite as was the case with the bayldonite experiments.

Equilibrium solubility determinations. With the exception of bayldonite and duftite, solubilities of the mineral phases were determined at 25.0 ± 0.1 °C in 8.736×10^{-4} aqueous $HClO_4$ using exactly the same methods as those described previously for related phosphate mineral species (Magalhães *et al.*, 1986). For austinite, the mineral was equilibrated in the solutions which were also 10^{-3} mol dm^{-3} in Ca^{2+}, as $CaCl_2$. Preliminary experiments established in each case the time taken to reach equilibrium; solutions used for analytical determination of pH and dissolved species were equilibrated for up to 20 times, but at least twice as long as appeared necessary to reach equilibrium. The presence of the parent phases was checked by X-ray diffraction of the filtered residues. Prior to filtration, pH was measured using a WTW 521 pH meter fitted with Metrohm EA120 combination electrode. Filtered aliquots (Millipore 0.54μ) were analysed for arsenate using the method of Liu and Chen (1982) and for metal ions by AAS using a Perkin Elmer 400 spectrophotometer. Duplicate analyses from each experimental run were carried out.

It was necessary to adopt a different approach to obtain the required data for bayldonite and duftite. For the former mineral, a series of experimental preparations of the compound, together with admixed schultenite, was carried out (*vide supra*). After each mixture was cooled, its volume was readjusted to 500 cm^3 and solutions and solids sealed in a flask containing a magnetic follower and from which all gaseous phases were excluded. The mixtures were kept at 25.0 ± 0.1 °C using a Grant SB3/74GB thermostatted water bath and magnetic stirrers. Preliminary experiments established that equilibrium was reached within three weeks. Solutions equilibrated for this time and up to five weeks, were used for analysis. Measurements of pH, lead, copper and arsenic concentrations were carried out in the way described above. With the exception of acetate ions, other anion concentrations were simply calculated *via* a knowledge of the stoichiometry of reactants involved, the total volume being known. Acetate, as acetic acid, was determined using gas chromatographic methods (Banfield *et al.*, 1978), employing a Shimadzu GC-9A instrument connected to a Shimadzu C-R1B integrator. A two metre teflon column packed with Tenax GC (60–80 mesh) was used, with detection by the usual flame ionization technique.

Additional experiments were carried out in the usual way using the isolated solids containing bayldonite and schultenite equilibrated in solutions to which was added $HClO_4$ in various amounts, but insufficient to dissolve all solids. Total perchlorate ion concentrations in these solutions varied from 3.9 to 6.5×10^{-3} mol dm^{-3}.

For duftite, one equilibration experiment was carried out using the solids and solution from a synthetic preparation (*vide supra*) and analysis of solution components carried out as for bayldonite. A further series of experiments using the isolated solids from separate syntheses, and containing duftite, schultenite and the unidentified phase, were performed. The solids were equilibrated with 8.736×10^{-4} mol dm^{-3} aqueous $HClO_4$. Equilibration was carried out for more than two months, although preliminary experiments showed that equilibrium is attained in a much shorter time. Analysis of residues by X-ray methods showed that both duftite and schultenite were present at the end of the experimental runs. A few check analyses of perchlorate ion concentrations were carried out using the methods of Iwasaki *et al.* (1963) and Motomizu *et al.* (1981).

It should be noted that additional values for the solubility product of schultenite, obtained in experiments involving bayldonite and duftite, agree very closely with those found in experiments on schultenite alone.

Derivation of solubility products and related thermodynamic properties. Species distributions in aqueous solutions in equilibrium with the various mineral phases were calculated from equilibrium solubility and pH data using the computer program COMICS (Perrin and Sayce, 1967). Equilibrium constants for arsenate, chloride, and acetate species were taken from Smith and Martell (1976) and for hydrolysed species from Baes and Mesmer (1976). No stability constants for dissolved metal arsenate species were included in the calculations. Negligible metal-phosphate complexation is found under analogous conditions (Magalhães *et al.*, 1986) and it is perfectly reasonable to assume that values for metal–arsenate and metal-phosphate stability constants are quite similar for the metals involved here.

Using the results of the COMICS computations, we were able to calculate in turn values for the equilibrium constants as shown in (1).

$$M_p(AsO_4)_q(OH)_r . nH_2O(s) + (2q+r)H^+(aq) \rightleftharpoons pM^{2+}(aq) + qH_2AsO_4^-(aq) + (n+r)H_2O(l) \quad (1)$$

Values for these equilibrium constants were corrected to zero ionic strength. In the case of perchloric acid equilibrations, the limiting Debye–Hückel law was used and in the cases of duftite, austinite, and bayldonite the extended form [$\log \gamma_i = -Az_i^2 I^{\frac{1}{2}}/(1+I^{\frac{1}{2}})$] was employed. Errors for equilibrium constants (1) are quoted as standard deviations derived from multiple measurements.

The equilibrium constant data were used in turn to derive a value of $\Delta fG°$ (298.2 K) for each mineral. Values of $\Delta fG°$ (298.2 K) for component ions, except arsenate species, and for water, were taken from the compilation of Robie *et al.* (1978). A value for $\Delta fG°$ (298.2 K, $H_2AsO_4^-$, aq) was calculated from that for AsO_4^{3-}(aq) (Barner and Scheuerman, 1978) and from the stability constants for the appropriate conjugate acid species of arsenic acid and protonated anions (Smith and Martell, 1976).

Results and Discussion

Solubility and thermodynamic data. Full lists of solubility data for each mineral, species distributions from COMICS calculations, and derived constants have been deposited with the Principal Editor and are available upon request. Table 1 gives values for equilibrium constants for equation (1), as shown in (2), the number of experiments used to derive each value and the calculated free energy of formation of each mineral at 298.2 K.

$$K_{H^+} = (a^p_{M^{2+}} + a^q_{H_2SO_4^-})/a^{(2q+r)}_{H^+} \quad (2)$$

In order to evaluate the potential significance of these data with respect to mineral formation in the oxide zones of base metal orebodies, we have taken data from the literature for $Cu_3(AsO_4)_2(s)$ and $Zn_3(AsO_4)_2(s)$, measured at 20 °C (Chukhlantsev, 1956). K_{sp} values for these species are given as 7.6×10^{-36} and 1.3×10^{-28}, respectively. The former value was taken to represent the mineral lammerite, $Cu_3(AsO_4)_2$, and the latter value was recast to yield a working value for the mineral köttigite, $Zn_3(AsO_4)_2 . 8H_2O$. Using data from the references given above, values for $\Delta fG°$ (293.2 K, lammerite) and for köttigite were calculated at -1300.8 and -3795.2 kJ mol^{-1}, respectively. Similarly, a value of -3061.5 kJ mol^{-1} was derived for $Ca_3(AsO_4)_2$ using solubility data from Chukhlantsev (1956). It should be pointed out here that errors in the values of $\Delta fG°$, derived from uncertainties in those values for constituent ions and water molecules, cancel out in calculations relating conditions under which various mineral pairs are stable. Thus the stability field diagrams show relationships between minerals for which errors are associated only with those derived from experimental measurements of K_{H^+}. The greater uncertainties which attend values for lammerite, köttigite, and $Ca_3(AsO_4)_2$ are not critical as it is clear that these species form under comparatively extreme conditions in solution compared with those responsible for the crystallization of more basic stoichiometries. Nevertheless, it would be desirable for new determinations to be carried out for these three, and indeed other, normal arsenate salts.

TABLE 1. Values for K_{H^+}, (2), and $\Delta fG°$ (298.2K) determined for the arsenate minerals.[a]

Mineral	Formula	n	log K_{H^+}	$\Delta fG°$/kJ mol^{-1}
olivenite	$Cu_2AsO_4(OH)$	8	2.38(23)	-846.4 ± 1.6
cornubite	$Cu_5(AsO_4)_2(OH)_4$	11	12.40(58)	-2057.9 ± 4.1
clinoclase	$Cu_3AsO_4(OH)_3$	8	10.10(38)	-1211.2 ± 2.7
adamite	$Zn_2AsO_4(OH)$	7	5.71(22)	-1252.9 ± 1.8
legrandite	$Zn_2AsO_4(OH).H_2O$	5	5.97(40)	-1488.6 ± 2.9
euchroite	$Cu_2AsO_4(OH).3H_2O$	7	3.28(17)	-1552.7 ± 1.5
duftite	$PbCuAsO_4(OH)$	6	-1.97(5)	-961.1 ± 0.6
conichalcite	$CaCuAsO_4(OH)$	9	1.29(33)	-1471.7 ± 3.3
austinite	$CaZnAsO_4(OH)$	10	6.88(21)	-1652.5 ± 2.7
bayldonite	$PbCu_3(AsO_4)_2(OH)_2$	11	0.03(5)	-1809.8 ± 0.9
schultenite	$PbHAsO_4$	23[b]	-5.41(2)	-809.2 ± 0.2

[a] Error in log K_{H^+} is quoted as SD/$n^{½}$, where n is the number of duplicate experiments carried out. Error in $\Delta fG°$ is given as the error calculated from that of K_{H^+} in energy terms plus the sum of the estimated errors in $\Delta fG°$ of component ions and water molecules as listed by Robie et al., (1978). No error is available for $\Delta fG°(H_2AsO_4^-,aq)$, and this is not included in the summation. [b] Seventeen values are derived from experiments involving bayldonite and duftite (see Experimental Section). The expression for K_{H^+} in this case refers to the equation $PbHAsO_4(s) + H^+(aq) \rightleftharpoons Pb^{2+}(aq) + H_2AsO_4^-(aq)$.

Stability relationships among the various arsenate minerals. A stability field diagram for the copper arsenate minerals is shown in Fig. 1. Data for lammerite are taken from the source previously described. Cornubite is dimorphous with cornwallite, these two crystallizing in space groups *P*1 or *P*$\bar{1}$ and *P*2$_1$/*c*, respectively (Berry, 1951; Claringbull *et al.*, 1959). It is not possible to discern which dimorph is the thermodynamically stable phase at 298.2 K. This ambiguity is not clarified by reference to natural occurrences where both minerals are found. Specimens from Wheal Carpenter, Cornwall, have later cornubite on cornwallite, but the reverse is true for material from Potts Gill mine, Cumberland (Claringbull *et al.*, 1959). Cornwallite after cornubite is known from Shindamona Hill, Zambia, and from the Majuba Hill mine, Utah (Berbeleac, 1975; Jensen, 1985), but the minerals may occur in a spatially unrelated fashion (Rushton, 1972). In our studies we found no evidence for any transformation of cornubite to any other phase during solution experiments. This fact suggests that, although cornubite is extremely rare, it may be the thermodynamically stable phase at room temperature. However, cornwallite itself is a rare mineral. Our findings indicate the reason for this is that it occupies a very narrow field of stability between that of olivenite and clinoclase. Small variations in solution chemistry will cause one of these two latter species to crystallize preferentially. Guillemin's observation that cornwallite is very difficult to synthesize bears out these conclusions (Guillemin, 1956).

When cornubite (or cornwallite) does crystallize, it might be expected to be accompanied by either olivenite or clinoclase, or both, depending upon the sense of small $a_{Cu^{2+}}$ or pH variations in mineralizing solutions. Guillemin (1956) notes a number of African and French localities where olivenite is present together with an association of cornwallite and conichalcite. Other olivenite–cornwallite associations are known (Berry, 1951; Claringbull *et al.*, 1959; Berbeleac, 1945; Walenta, 1969, 1975; Segeler and Molon, 1981). Clinoclase is found with cornwallite at the American Eagle mine, Tintic, Utah (Hillebrand and Washington, 1888), and in the Dome Rock copper deposit, South Australia (Ryall and Segnit, 1976). Probably the best described locality for this copper arsenate suite is the Majuba Hill mine, where the established

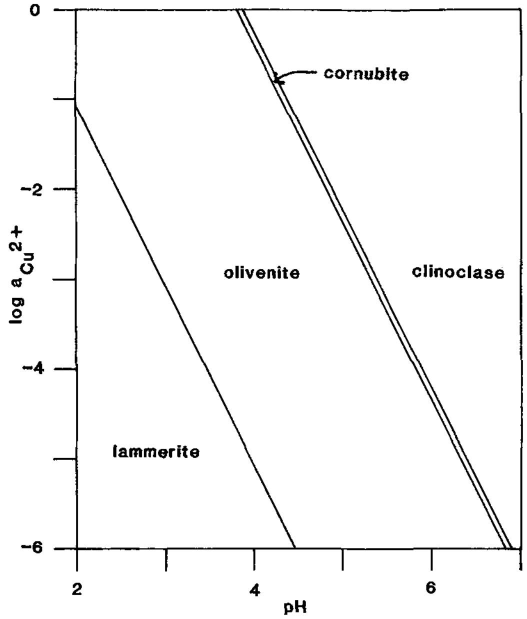

FIG. 1. Stability field diagram for the copper(II) arsenate minerals. Limits of pH have been set to those corresponding to the predominance in aqueous solution of the $H_2AsO_4^-$(aq) ion.

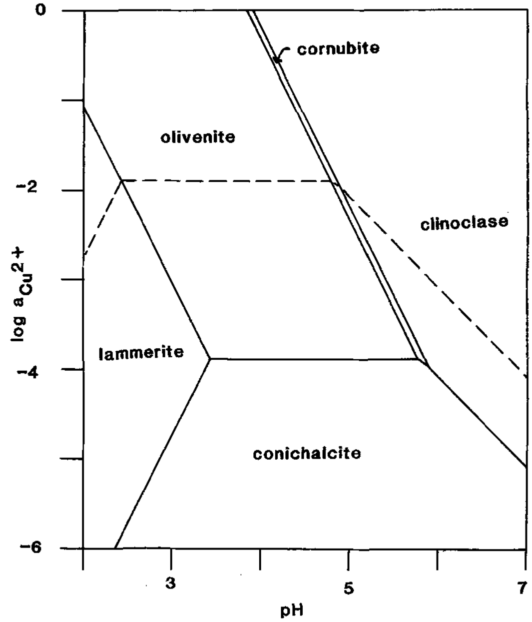

FIG. 2. Influence of Ca^{2+}(aq) on the stability fields of the copper minerals; (——) $a_{Ca^{2+}} = 10^{-5}$; (---) $a_{Ca^{2+}} = 10^{-3}$.

paragenetic sequence in the oxide zone is clinoclase → cornwallite → cornubite → olivenite (Jensen, 1985). These observations suggest that, during the crystallization sequence, the pH and /or copper ion activity decreased slightly in solution. Many of the above references mention instances of olivenite associated with clinoclase. The stability field diagram (Fig. 1) indicates that cornubite or cornwallite should crystallize at some stage during the chemical changes necessary to form the other two phases. However, any cornwallite that forms might be replaced by the next phase, or remain as a thin film or reaction rim between the olivenite and clinoclase. Moreover, if sufficient Ca^{2+}(aq) is present to develop sequences containing conichalcite, as appears to be frequently the case, a different association can be predicted (*vide infra*). In general, we conclude that the rarity of cornubite and cornwallite in nature is a true reflection of the thermodynamic data.

By reference to Fig. 1, the extreme rarity of lammerite may also be explained. This mineral was originally described from Bolivia (Keller *et al.*, 1981) together with olivenite, a natural association in view of the chemical studies. The only other known or reported locality for lammerite is Tsumeb, Namibia (Keller, 1981; Keller and Bartelke, 1982), where it is found often associated with chalcanthite ($CuSO_4.5H_2O$) and leightonite ($K_2Cu_2Cu(SO_4)_4.2H_2O$). The combination of low pH and high copper and arsenate concentrations necessary for the crystallization of lammerite will be rarely encountered in nature. Its above associates reinforce this view. Using data from the literature for chalcanthite and antlerite (Robie *et al.*, 1978; Garrels and Christ, 1965) we calculate the equilibrium boundary for the equation

$$CuSO_4.5H_2O\,(\text{s, chalcanthite}) + 2Cu^{2+}_{(aq)} \rightleftharpoons Cu_3SO_4(OH)_4\ (\text{s, antlerite}) + 4H^+_{(aq)} + H_2O(l)$$

at 298.2 K to be $pH = 2.89–0.5 \log a_{Cu^{2+}}$. Since antlerite has not been reported with lammerite, crystallization conditions will most probably be on the acid side of this boundary for the normal Cu(II) arsenate.

Fig. 2 shows the changes to the stability field diagram produced when the Ca(II) ion is present in solution and conichalcite can crystallize. No other arsenate phases containing calcium are plotted on the field. Such species are of course well-known and include the minerals vladimirite ($Ca_3(AsO_4)_2.4H_2O$), rauenthalite, and phaunouxite, the corresponding deca- and undecahydrates of the same composition, as well as several hydrogenarsenates (Palache *et al.*, 1951; Schnorrer-Köhler, 1984). We have omitted such phases on the basis of calculations concerning the stability of $Ca_3(AsO_4)_2$ (Smith, 1973). Transformations involving calcium arsenate (and by association its hydrates), lammerite, and conichalcite have equilibrium boundary conditions which plot well outside the region of chemical interest in Fig. 2. In other words, the presence of small amounts of Cu^{2+}(aq) in the appropriate mineralizing solutions renders the calcium arsenates thermodynamically unstable with respect to species containing copper.

Conichalcite is a relatively common associate of both olivenite and clinoclase as well as occurring alone. The reason for this is seen in Fig. 2, which shows that the presence of reasonably small amounts of calcium ion in solution give rise to an appreciable encroachment of the thermodynamic stability field of conichalcite upon those of olivenite, cornubite, and clinoclase. In addition, we note that assemblages of clinoclase, conichalcite, and olivenite are capable of being developed without the crystallization of cornwallite or cornubite. For example, in Fig. 2, for $a_{Ca^{2+}} = 10^{-6}$, small variations around pH 6.5 and $a_{Cu^{2+}} = 10^{-5.5}$ would suffice to bring such a paragenesis about. While individual occurrences of conichalcite are too numerous to list here, one locality deserves special mention.

This is the Dome Rock copper mine, South Australia (Ryall and Segnit, 1976; Bayliss *et al.*, 1966; Segnit, 1978), where conichalcite is late in the paragenesis and is observed coating chrysocolla, cornwallite, and clinoclase. Pseudomorphs of conichalcite after olivenite are also known. Some of these contain an olivenite core. We have examined several dozen specimens in the collection of the Australian Museum from the deposit, and in confirming the above observations have noted that cornwallite is later than clinoclase. These observations, taken together, indicate that the assemblages at Dome Rock have developed as a result of the solutions becoming slightly more acidic to form the clinoclase → cornwallite → olivenite sequence (the paragenetic relationship of olivenite is not established unequivocally) and the later conichalcite has formed with increasing $a_{Ca^{2+}}$. It should be noted, however, that a more elegant explanation in terms of the number of variables is possible. If the calcium content of the mineralizing groundwaters were to remain constant, the observed sequence could simply be developed by small decreases in copper ion activity, even at constant pH.

In this section on copper(II) arsenate minerals, we wish to draw attention to euchroite ($Cu_2(AsO_4)(OH).3H_2O$) and its relationship to olivenite, strashimirite ($Cu_2AsO_4(OH).1.25H_2O$) and arhbarite ($Cu_2AsO_4(OH).6H_2O$). For the reaction given below, ΔrG° (298.2 K) is equal to -5.1 kJ mol^{-1}.

$$Cu_2AsO_4(OH).3H_2O \text{ (s, euchroite)} \rightleftharpoons Cu_2AsO_4(OH) \text{ (s, olivenite)} + 3H_2O(l)$$

During our solution studies, detailed above, we found that the slow rate of recrystallization of euchroite, compared with its rapid attainment of a metastable equilibrium with saturated aqueous solutions, permitted the evaluation of its free energy of formation. However, it is metastable with respect to olivenite at 298.2 K and might thus be expected to be a rare species, or stable at lower temperatures. Euchroite is indeed a very rare mineral and has been reported from only three localities. These are the type locality at Libethen in Hungary (Palache *et al.*, 1951), the Zapachitsa deposit in Bulgaria (Mincheva-Stefanova, 1962), and at Laurium, Greece (Kohlberger, 1976). At Libethen, euchroite is associated with olivenite and pseudomorphs of the latter after euchroite with internal residual cores are mentioned by Guillemin (1956). He also notes that natural or artificial euchroite is converted to olivenite in water at steam-bath temperatures over five days, or less in sealed tubes at elevated temperatures. Furthermore, synthesis of euchroite was achieved in cold aqueous solutions over short times. Olivenite formed at length and euchroite's rarity was attributed to the ease of the transformation as well as the unusual synthetic conditions required to crystallize it as a metastable phase. All of these observations are in accord with our deductions made on the basis of our solution studies. Strashimirite and arhbarite also are probably metastable with respect to olivenite. Arhbarite is known only from one locality. Fine crystals of strashimirite are known from Majuba Hill, Nevada, and olivenite is a common associate. Olivenite is also known to be associated with specimens from various deposits in the Black Forest (Schmetzer, 1982). A rather complex paragenetic sequence was noted at the type locality in Bulgaria. The sequence of deposition of copper arsenate minerals in the Zapachitsa deposit is said to be cornwallite – olivenite – tyrolite – strashimirite – conichalcite. Thermodynamic data for tyrolite, $Ca_2Cu_9(AsO_4)_4(OH)_{10}.10H_2O$, are not available, but its stoichiometry suggests that it might occupy a narrow zone of stability between those of olivenite and conichalcite. Tyrolite is a rare mineral and could also be metastable with respect to the latter two species. Although it is possible that the tyrolite → strashimirite reaction might be thermodynamically favourable under some conditions, thus explaining its presence in the above sequence, it should be reiterated that strashimirite is almost certainly metastable with respect to olivenite at room temperature. In addition, there is some doubt as to the true composition of tyrolite, with some analyses indicating the presence of carbonate or sulphate in significant amounts. Should these ions be necessary constituents of the mineral it would not plot on Fig. 2 for the chosen conditions in any case.

A similar relationship to that found for euchroite and olivenite exists between the two minerals adamite and legrandite as shown below.

$$\mathrm{Zn_2AsO_4(OH).H_2O\ (s,\ legrandite)} \rightleftharpoons \mathrm{Zn_2AsO_4(OH)(s) + H_2O(l)}$$

From our thermodynamic data we calculate ΔrG° (298.2 K) for this reaction to be equal to -1.4 kJ $\mathrm{mol^{-1}}$. This represents a small thermodynamic stability in favour of adamite but is within the experimental error of the determinations of ΔfG° (298.2 K) of the two minerals involved. Nevertheless, legrandite is a very much rarer mineral and we suggest that it is in fact metastable with respect to adamite at room temperature, although it may crystallize as the stable phase under appropriate conditions at temperatures between 0 and 25 °C. Thus it is of interest that legrandite has been found at several localities without adamite. These include the type locality at the Flor de Peña mine, Lampazos, Mexico (Drugman and Hey, 1932), where it is associated with siderite ($FeCO_3$) mimetite (?) ($Pb_5(AsO_4)_3Cl$), and pyrite on sphalerite, and a Russian deposit (Moiseeva, 1970) in which the associates are scorodite ($FeAsO_4.2H_2O$), hemimorphite ($Zn_4Si_2O_4(OH)_2.H_2O$), and cerussite ($PbCO_3$).

The most famous locality for legrandite is the Ojuela mine, Durango, Mexico, where it occurs as radiating yellow sprays and crystals up to 18 cm in length (Wilson, 1978). Crystallized in cavities in a dense ferruginous gossan, it is usually associated with single crystals and aggregates of adamite and a member of the conichalcite–austinite group (Desautels and Clarke, 1963). Köttigite, $Zn_3(AsO_4)_2.8H_2O$, and varieties between this Zn(II) end-member and parasymplesite are also known from the Ojuela mine. A recent discovery at the Sterling Hill mine, New Jersey, has a similar assemblage (Parker and Troy, 1982). Legrandite with adamite, köttigite, scorodite, and metalodèrite ($Zn(UO_2)_2(AsO_4)_2.10H_2O$) were found on the 340-foot level in ore containing dark-coloured willemite (Zn_2SiO_4) and franklinite, a zinc manganese iron oxide of the spinel group. Austinite ($CaZn(AsO_4)OH$) is known from elsewhere in this deposit as well as from the Ojuela mine.

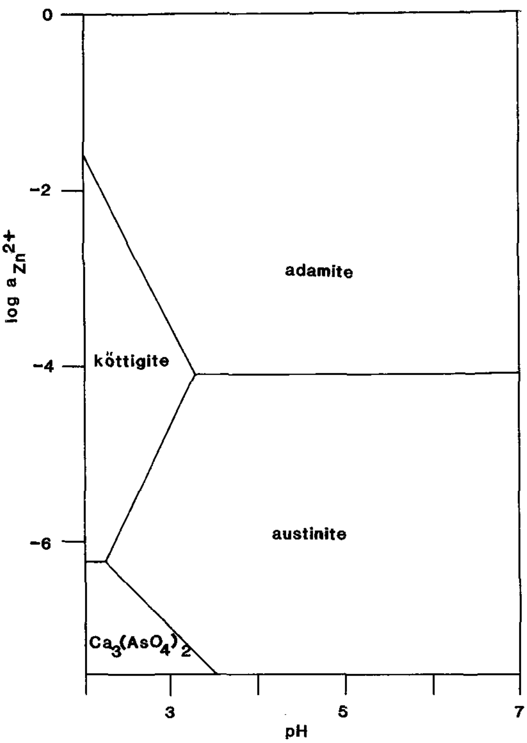

FIG. 3. Stability Fields for some zinc(II) arsenate minerals and $Ca_3(AsO_4)_2(s)$; $a_{Ca^{2+}} = 10^{-3}$.

Because of the smaller number of basic double salts containing Zn(II) as the only metallic cation, the mineralogy of zinc arsenate species is somewhat simpler than is the case with Cu(II), although simple hydrogen arsenates are known, as are more or less hydrated analogues of köttigite, some containing other cations in addition to Zn(II). Fig. 3 shows the basic pattern of stabilities for the common zinc arsenates in the absence of significant concentrations of metal ions other than Zn(II) and Ca(II). The widespread occurrence of adamite in oxide zones containing zinc and arsenate is readily understood from the diagram because of the large range of chemical conditions under which it is the thermodynamically stable phase. Other cations frequently substitute in the adamite lattice and we will comment on these phenomena in a later paper. The dimorph of adamite, paradamite, which crystallizes in the triclinic space group $P1$, is a very rare mineral and has been reported from only a few localities, among these being the Ojuela mine and Tsumeb. In the former case, its associates included adamite and legrandite. We assume that paradamite is metastable with respect to adamite under most conditions.

For our purposes, the stability field for adamite will embrace that of its dimorph and for similar reasons outlined above, of legrandite. Reported

TABLE 2. Simple zinc(II)-containing arsenate minerals from Tsumeb (Keller and Bartelke, 1982; Pinch and Wilson, 1977).

Mineral	Stoichiometry
Koritnigite	$Zn(HAsO_4).H_2O$
O'Danielite	$Na(Zn,Mg)_3H_2(AsO_4)_3$
Warikahnite	$Zn_3(AsO_4)_2.2H_2O$
Prosperite	$CaZn_2(AsO_4)_2.\frac{1}{2}H_2O$
Johillerite	$Na(Mg,Zn)_3Cu(AsO_4)_3$
Helmutwinklerite	$Pb(Zn,Cu)_2(AsO_4)_2.2H_2O$
Gaitite	$Ca_2Zn(AsO_4)_2.2H_2O$
Tsumcorite	$PbZnFe(AsO_4)_2.H_2O$
Keyite	$(Cu,Zn,Cd)_3(AsO_4)_2$
Stranskiite	$Zn_2Cu(AsO_4)_2$
Chudobaite*	$(Mg,Zn)_5H_2(AsO_4)_3.10H_2O(?)$

*There is some controversy as to whether this mineral necessarily contains Na, F, and perhaps Ca (Fleischer, 1977)

localities for adamite are too numerous to list here and reference should be made to the general literature (Palache *et al.*, 1951).

The comparative rarity of köttigite in nature is, as is the case with lammerite, due to the acidic environment required for its stability and consequently the high concentrations, geochemically speaking, of total arsenate and zinc ions necessary for its solubility product to be exceeded. Köttigite is known in small amounts from a number of sites.

At low pH other zinc-containing arsenates can form depending on the availability of other cations in solution. Tsumeb presents a most complex assemblage of species formed in such an environment (Keller and Bartelke, 1982) and a list of the relevant minerals is given in Table 2. All of these have stoichiometries which can be written as simple hydrates, or sometimes anhydrates, of arsenate or hydrogen arsenate, and they somewhat complicate the thermodynamic model which we would like to keep here in as simple a form as possible. Fortunately some clarifications can be easily made. Except perhaps for tsumcorite, all of these species, together with köttigite and lammerite, are found in association with either cuproadamite, conichalcite, or olivenite, and thus will form under conditions somewhat to the left of the köttigite–adamite boundary of Fig. 3. More particularly, Keller and Bartelke (1982), in a careful summary of typical assemblages containing these minerals at Tsumeb, point out that it is quite clear that they occur more or less in the same environment in the mine and that they must have crystallized from very acidic solutions, perhaps with a pH as low as 1. This conclusion is reinforced by a report of the synthesis of lammerite in acidic solution (Keller, 1981) and by the observation of hydrogen arsenates. We conclude, therefore, that subtle variations in various metal ion activities in low pH solution, given the presence of enough arsenate, will suffice to cause all of these minerals to become thermodynamically stable with respect to others from time to time.

From Fig. 3 we may make further simplifications due to the chosen conditions. Consideration of the effects of calcium ions alone on the diagram, a necessity with respect to the incorporation of austinite into the model, eliminates all of the species in Table 2 save koritnigite, warikahnite, prosperite, and gaitite. Unless these minerals possess an anomalous stability, an extremely unlikely possibility in view of their rarity in nature, the diagram is little altered. Konitnigite will crystallize at pH values less than those which can give rise to köttigite, and warikahnite is probably stable only at higher temperatures than we have chosen for our experimental studies. If prosperite and gaitite do have regions of thermodynamic stability, these will plot as narrow zones between köttigite and $Ca_3(AsO_4)_2$ which has been chosen to represent the species vladimirite, rauenthalite, and phaunouxite, as discussed earlier.

With these points in mind, we have included stability fields for austinite and $Ca_3(AsO_4)_2(s)$ in Fig. 3. Austinite is also a comparatively rare mineral and has been found at few localities. Notable among these are Tsumeb (Pinch and Wilson, 1977), Bou-Azzer, Morocco (Pallix, 1978) and Gold Hill, Utah (Staples, 1935; Williams and de Azevedo, 1967). Austinite is frequently accompanied by adamite and occupies a stability field of a similar kind to that of conichalcite. It is frequently cuprian, as expected from its structure, being part of the extensive adelite group (Fleischer, 1987). The reported assemblages are in accord with the results of our thermodynamic study.

Many arsenate materials of Pb(II) are known. Usually other cations are also present and occasionally other anions, as for instance in mimetite, $Pb_5(AsO_4)_3Cl$. Three simple arsenates of Pb(II) with or without necessary copper occur in nature. These are schultenite ($PbHAsO_4$), bayldonite ($PbCu_3(AsO_4)_2(OH)_2$ or $Pb(Cu,Zn)_3(AsO_4)_2(OH)_2$; Ghose and Wan, 1979), and duftite ($PbCuAsO_4OH$), the Ca- and Zn-free end-member of a complex solid-solution series. Of these, the last two are found in small amounts at a number of localities around the world. Schultenite is so far reported only from the oxide zone at Tsumeb, a locality in the Black Forest, Germany, and an American deposit (Keller and Bartelke, 1982; Walenta, 1980, 1981; Falls *et al.*, 1985). We have

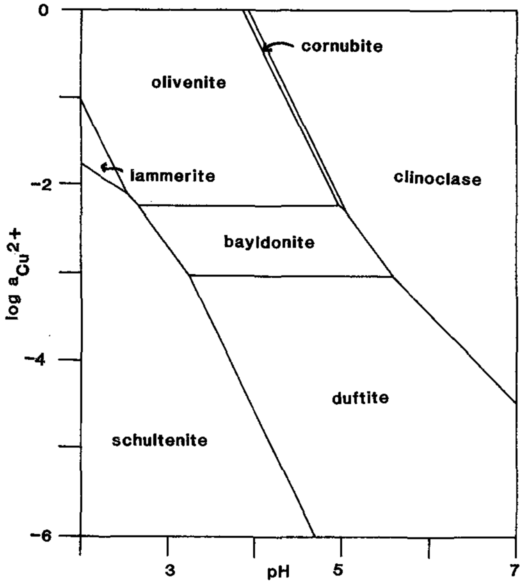

FIG. 4. Equilibrium stability relationships between some copper(II) and lead(II) arsenates, and between mixed species; $a_{Pb^{2+}} = 10^{-7}$.

chosen to determine their stabilities because of their association with some of the previously mentioned arsenates of copper(II), as well as the fact that they constitute the simplest series in a complex assemblage formed when copper, lead and zinc minerals oxidize in the presence of arsenate ions. Calculated stability fields for the minerals, together with those of the basic copper arsenates, are shown in Fig. 4. The choice of a realistic lead ion activity, in this case equal to 10^{-7}, serves to eliminate most conditions which can give rise to the crystallization of lammerite.

Attention should be drawn to the olivenite-bayldonite-duftite sequence. Guillemin (1956) has reported syntheses of duftite and bayldonite and noted that the former was more easily obtained in acid solution using the reactants and conditions chosen. We wish to strongly make the point that all three minerals can form at the same pH, and relative stabilities depend only upon the $a_{Cu^{2+}}/a_{Pb^{2+}}$ ratio. Thus, they might be expected to form under conditions which are otherwise comparable. In other experiments, Guillemin (1956) also noted transformations from one species to another with varying concentrations of either metal ion. Duftite was transformed to olivenite by reacting the former in a concentrated copper(II) sulphate solution. Similarly an excess of copper caused bayldonite to react to yield olivenite. Lead hydrogen arsenate in equimolar proportions with copper(II) nitrate afforded duftite. A large excess of copper led to the crystallization of bayldonite. All of these reactions are readily understood by reference to Fig. 4.

Natural occurrences of the minerals when they are found together are also easily understood in terms of the equilibrium model. Specimens from Cap Garonne, France, consisting of earlier duftite and later bayldonite are known. From Tsumeb Guillemin (1956) also describes bayldonite masses reacting to olivenite, so that the lead mineral remains as a ragged core. Another specimen from this locality consists of schultenite entirely replaced by bayldonite and duftite. Finally a further specimen is described as consisting of masses of mottramite, $PbCu(VO_4)(OH)$, surrounded by duftite. The latter mineral is partly converted to olivenite which has in turn some later malachite superimposed. We point out that the direct duftite → olivenite transformation is not possible and that a reaction rim of bayldonite should be present between the two. Its presence might only be revealed, however, under the microscope. Other Tsumeb occurrences are also strikingly similar in their association (Keller, 1977; Pinch and Wilson, 1977). Early bayldonite collected there was found

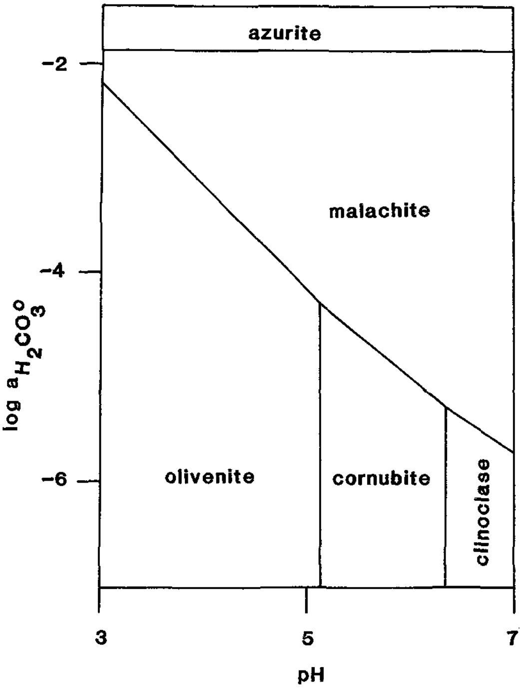

FIG. 5. Boundaries between the copper(II) arsenates and more common secondary carbonate minerals; $a_{H_2AsO_4^-} = 10^{-8}$.

with olivenite and a later find was of large crystals associated with cuproadamite, keyite [$(Cu,Zn,Cd)_3(AsO_4)_2$], and schultenite. Duftite is widely distributed in the oxide zone at Tsumeb in small amounts and in association with many species. However, its most common associates are carbonates such as cerussite, malachite and smithsonite; also mimetite, wulfenite ($PbMoO_4$), and dioptase ($CuSiO_2(OH)_2$). This complexity indicates that it is formed under varying chemical conditions, over an appreciable pH range, and from solutions of complex compositions. Nevertheless, it is also commonly found associated with olivenite. Schultenite, from the lower oxidation zone at Tsumeb, is associated with cuproadamite. The type specimen consists (Spencer, 1926) of anglesite ($PbSO_4$) altered in part to bayldonite which pseudomorphs earlier mimetite and (?) chalcanthite. Schultenite crystals rest on the bayldonite and are somewhat intermixed with this species. On the basis of all these observations, we may conclude that the bayldonite-schultenite and several of the duftite-bayldonite-olivenite assemblages were generated from fairly acidic solutions by fluctuations of the concentration of copper(II) ions present.

It is apparent that the equilibrium model employed here is quite successful in explaining many paragenetic sequences of base metal arsenates from a number of deposits. It should also be applicable to many others. No doubt the model will be refined as further data for some of the rarer species become available and new stoichiometries are discovered which further delineate local solution conditions which applied when certain of these oxide zones were emplaced. The model also indicates phases which might be sought in certain cases but which have not yet been noted in individual deposits; such a search is worthy, but outside the scope of this paper.

It should finally be mentioned that the more common secondary minerals of Cu(II), Zn(II) and Pb(II) may be incorporated into the model via appropriate calculations and choice of solute concentrations. Figs. 5-7 illustrate how basic copper sulphate minerals and common carbonate species containing Zn(II) and Cu(II) relate to arsenate-containing minerals of those ions. Data other than that mentioned previously has been taken from the literature for brochantite, malachite, azurite, smithsonite and hydrozincite (Smith and Martell, 1976; Robie *et al.*, 1978; Alwan and Williams, 1979). However, a detailed evaluation of these diagrams is not warranted here. Reference should be made to individual associations in particular deposits.

Similar calculations may be carried out for the Pb(II) minerals. For example at Tsumeb duftite is commonly associated with cerussite, data for which are available (Robie *et al.*, 1978; Smith and Martell, 1976). The equilibrium boundary for the equation

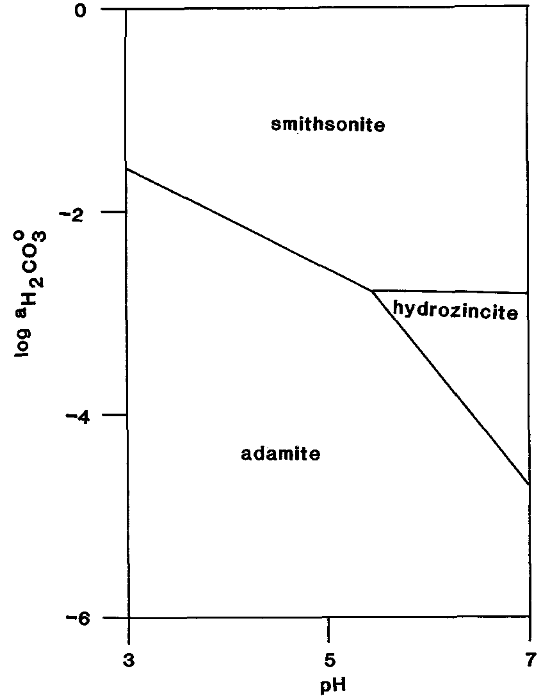

FIG. 6. Relationships between the copper (II) arsenates and some more common secondary sulphate minerals of Cu(II); $a_{H_2AsO_4^-} = 10^{-8}$.

$$\begin{aligned}2PbCuAsO_4(OH)\ (s,\ \text{duftite}) + 3H_2CO_3^\circ\ (aq) &\rightleftharpoons \\ 2PbCO_3\ (s,\ \text{cerussite}) &+ \\ Cu_2CO_3(OH)_2\ (s,\ \text{malachite}) &+ \\ 2H_2AsO_4^-\ (aq) + 2H^+\ (aq)&\end{aligned}$$

is approximately equal to

$$pH = 11 + \log a_{H_2AsO_4^-} - 1.5 \log a_{H_2CO_3^\circ}$$

and is seen to represent a complicated balance of conditions in terms of pH, arsenate, and carbonate activities. However, this is a simplification, since equations describing duftite → cerussite or duftite → malachite transformations involve a further variable, that of one or other of the metal ion activities. For an atmospheric pressure of $CO_{2(g)}$ of $10^{-3.5}$ atm (~ 32 Pa), the equilibrium activity of $H_2CO_3^\circ$ in pure water is equal to 1.09×10^{-5}. Under such conditions the above equation becomes

$$pH \doteqdot 15.5 + \log a_{H_2AsO_4^-}.$$

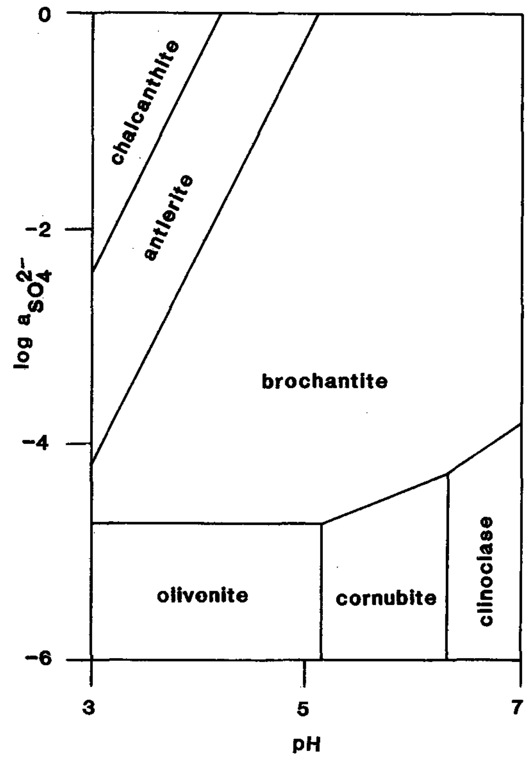

FIG. 7. Stability field diagram showing the relationships between adamite, smithsonite and hydrozincite at $a_{H_2AsO_4^-} = 10^{-8}$.

The implication here is that arsenate activities must drop to around 10^{-8} to 10^{-10} to give a realistic pH for the transformation described (pH 5.6–7.6). In other words, duftite is a relatively stable phase when solutions containing its ionic constituents can crystallize a solid phase. It is emphasized that relationships involving carbonate and sulphate are complex and should we consider the formation of duftite-anglesite or bayldonite-anglesite assemblages for example, it is probably more appropriate to carry out individual calculations based on estimates of solution conditions and knowledge of particular associations than to construct more elaborate stability field diagrams for one set of fixed parameters. Nevertheless, the data are now available for the treatment of these kinds of transformations between some of the lead(II) arsenate species considered here and more commonly occurring phases. We simply point out that the information inherent in Fig. 4 is sufficient to describe many of the paragenetic sequences of Cu(II) and Pb(II) arsenates found in nature.

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References

Alwan, A. K. and Williams, P. A. (1979) *Transition Metal Chem.* **4**, 128–32.
Baes, C. F. and Mesmer, R. E. (1976) *The Hydrolysis of Cations.* John Wiley and Sons, New York.
Banfield, F. S., Meek, D. M., and Lowden, G. F. (1978) *Technical Report TR76.* Water Research Centre, Medmenham Laboratory, Harlow, U.K.
Barbeleac, I. (1975) *Rev. Roum. Géol. Géophys. Géog., Géol. Ser.* **19**, 85–94.
Barner, H. E. and Scheuerman, R. H. (1978) *Handbook of Thermochemical Data for Compounds and Aqueous Species.* John Wiley and Sons, New York.
Bayliss, P., Lawrence, L. J., and Watson, D. (1966) *Austral. J. Sci.* **29**, 145–6.
Berry, L. G. (1951) *Am. Mineral.* **36**, 484–503.
Chukhlantsev, V. G. (1956) *J. Inorg. Chem. USSR*, **1**, 1975–82.
Claringbull, G. F., Hey, M. H., and Davis, R. J. (1959) *Mineral. Mag.* **32**, 1–5.
Desautels, P. E. and Clarke, R. S. (1963) *Am. Mineral.* **48**, 1258–65.
Drugman, J. and Hey, M. H. (1932) *Mineral. Mag.* **23**, 175–8.
Falls, R., Cannon, B., and Mandarino, J. A. (1985) Ibid. **49**, 65–9.
Fleischer, M. (1977) *Am. Mineral.* **62**, 599.
——(1987) *Glossary of Mineral Species.* 5th Ed., Mineralogical Record Inc., Tucson.
Garrels, R. M. and Christ, C. L. (1965) *Solutions, Minerals and Equilibria.* Harper and Row, New York.
Ghose, S. and Wan, C. (1979) *Acta Crystallogr.* **B35**, 819–23.
Guillemin, C. (1956) *Bull. Soc. fr. Minéral. Crystallogr.* **79**, 7–95.
Hillebrand, W. F. and Washington, H. S. (1888) *Am. J. Sci.* **35**, 298–307.
Iwasaki, I., Utsumi, S., and Kang, C. (1963) *Bull. Chem. Soc. Japan*, **36**, 325–31.
Jensen, M. (1985) *Mineral. Rec.* **16**, 57–72.
Keller, P. (1977) Ibid. **8**, 38–47.
——(1981) *Aufschluss*, **32**, 437–41.
——and Bartelke, W. (1982) *Mineral. Rec.* **13**, 137–47.
——Parr, W. H., and Dunn, P. J. (1981) *Tschermaks Mineral. Petr. Mitt.* **28**, 157–64.

Kohlberger, W. (1976) *Mineral. Rec.* **7,** 114-25.

Liu, F. and Chen, D. (1982) *Anal. Abs.* **42**(2), 28130.

Magalhães, M. C. F., Pedrosa de Jesus, J., and Williams, P. A. (1986) *Mineral. Mag.* **50,** 33-9.

Mincheva-Stefanova, I. (1962) *Izv. Geol. Inst. Bulg. Akad. Nauk,* **10,** 23-8 [MA: **16,** 179].

Moiseeva, M. I. (1970) *Mineral. Uzb.* **3,** 20.

Motomizu, S., Fuguwara, S. and Toei, K. (1981) *Anal. Chim. Acta,* **128,** 185-94.

Nriagu, J. O. and Moore, P. B., eds. (1984) *Phosphate Minerals,* Springer-Verlag, Berlin.

Palache, C., Berman, H., and Frondel, C. (1951) *The System of Mineralogy.* **II,** John Wiley and Sons, New York.

Pallix, G. (1978) *Mineral. Rec.* **9,** 69-73.

Parker, F. J. and Troy, J. (1982) Ibid. **13,** 35-8.

Perrin, D. D. and Sayce, I. G. (1967) *Talanta,* **14,** 833-42.

Pinch, W. W. and Wilson, W. E. (1977) *Mineral. Rec.* **8,** 17-37.

Robie, R. A., Hemingway, B. S., and Fisher, J. R. (1978) *Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 Bar (10^5 Pascal) Pressure and at Higher Temperatures.* U.S. Geol. Surv. Bull. 1452.

Rushton, D. R. A. (1972) *Mineral. Mag.* **38,** 626-7.

Ryall, W. R. and Segnit, E. R. (1976) *Austral. Min.* **2,** 5-8.

Schmetzer, K. (1982) *Aufschluss,* **33,** 1-2.

Schnorrer-Köhler, G. (1984) Ibid. **35,** 93-109.

Segeler, C. G. and Molon, J. (1981) *Rocks and Minerals,* **56,** 233-9.

Segnit, E. R. (1978) *Austral. Min.* **15,** 73-4.

Smith, J. D. (1973) In *Comprehensive Inorganic Chemistry* (J. C. Bailar, Jr., A. J. Emeléus, R. S. Nyholm and A. F. Trotman-Dickenson, eds.), **2.** Pergamon Press, Oxford.

Smith, R. M. and Martell, A. E. (1976) *Critical Stability Constants,* **4,** Plenum Press, New York.

Spencer, L. J. (1926) *Mineral. Mag.* **21,** 149-55.

Staples, L. W. (1935) *Am. Mineral.* **20,** 371.

Walenta, K. (1969) *Aufschluss,* **20,** 85-93.

——(1975) Ibid. **26,** 369-411.

——(1980) Ibid. **31,** 141-50.

——(1981) Ibid. **32,** 333-40.

Williams, S. A. (1963) *Econ. Geol.* **58,** 599-601.

——and de Azevedo, J. (1967) *Am. Mineral.* **52,** 1224-6.

Wilson, W. E. (1978) *Mineral. Rec.* **9,** 192-5.

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