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Stability constants and formation of Cu(II) and Zn(II) phosphate minerals in the oxidized zone of base metal orebodies

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ABSTRACT. The free energies of formation of the minerals libethenite, Cu_2PO_4OH, pseudomalachite, $Cu_5(PO_4)_2(OH)_4$, cornetite, $Cu_3PO_4(OH)_3$, tarbuttite, Zn_2PO_4OH, spencerite, $Zn_2PO_4OH \cdot 1.5H_2O$, and scholzite, $CaZn_2(PO_4)_2 \cdot 2H_2O$, have been determined at 298.2 K using solution techniques. The values of $\Delta f G°$ (298.2 K) for the above minerals are, respectively, -1228.8 ± 3.0, -2840.3 ± 4.2, -1600.9 ± 5.9, -1632.1 ± 4.0, -1982.4 ± 3.1, and -3556.7 ± 7.6 kJ mol^{-1}. These results, together with others from the literature concerning hopeite, $Zn_3(PO_4)_2 \cdot 4H_2O$, hydroxyapatite, $Ca_5(PO_4)_3(OH)$, and the synthetic salt $Cu_3(PO_4)_2 \cdot 2H_2O$ have been used to construct a model for the formation of suites of Zn(II) and Cu(II) phosphate minerals found in the oxidation zone of base metal orebodies. The distributions and modes of occurrence of many natural assemblages of these minerals are readily explained by the model. Particular attention has been focused on deposits at Broken Hill, Zambia, and Saginaw Hill, Arizona, USA.

KEYWORDS: stability constants, phosphate minerals, libethenite, pseudomalachite, cornetite, tarbuttite, spencerite, scholzite.

IN the mineral kingdom, species containing the phosphate ion are among the most widespread and, in terms of their stoichiometries, the most elaborate. In a recent comprehensive review, Nriagu and Moore (1984) have highlighted these facts, and collated much of our present knowledge concerning phosphate minerals. It has been pointed out (Nriagu, 1984) that approaches to an understanding of the chemical processes responsible for phosphate mineral formation have been hampered by a lack of pertinent and accurate thermodynamic data.

Phosphate minerals occur both in extensive bedded sedimentary deposits and as primary phases in pegmatites and associated igneous rocks. In addition, a variety of phosphate-containing species are found in the oxidized zones of many base metal orebodies. Cu(II), Zn(II), and Pb(II) minerals from this setting have been shown to have a number of different stoichiometries and these metal ions are incorporated into an analogous but more complex suite of arsenates (Hey, 1955).

We have begun a series of thermochemical studies aimed at developing a model to explain the formation of, and paragenetic sequences observed in, suites of transition and base metal arsenates and phosphates in oxidized ores. On the basis of estimated thermodynamic parameters (Nriagu and Dell, 1974; Nriagu, 1975; Vieillard and Tardy, 1984), Nriagu (1984) has examined a number of such phosphate minerals. Our results, which we present below, concerning the experimentally determined free energies of formation of the minerals libethenite, Cu_2PO_4OH, pseudomalachite, $Cu_5(PO_4)_2(OH)_4$, cornetite, $Cu_3PO_4(OH)_3$, tarbuttite, Zn_2PO_4OH, spencerite, $Zn_2PO_4OH \cdot 1\frac{1}{2}H_2O$, and scholzite, $CaZn_2(PO_4)_2 \cdot 2H_2O$, indicate that previously predicted values are not of sufficient precision to describe known mineralogical and geochemical relationships. We are able to demonstrate that accurate thermodynamic parameters for these minerals lend themselves to incorporation into a model which neatly predicts many classical field observations. Reference is made to a number of deposits, especially those at Broken Hill, Zambia, and Saginaw Hill, Arizona, USA.

Libethenite from the Mindola open pit, Rokana mine, Kitwe, Zambia, pseudomalachite from the West Bogan mine, Collerina Hall, NSW, Australia,

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cornetite from the Mine de L'Etoile, Katanga, Zaïre, tarbuttite from Kopje No. 2, Broken Hill, Zambia, spencerite from the HB Zinc mine, Salmo, British Columbia, Canada, and scholzite from Reaphook Hill, SA, Australia, were used in the study. The latter three species were kindly supplied by the British Museum (Natural History) and their respective specimen numbers are BM1929,1629, BM1916,377, and BM1970,114. The minerals were freed of contaminating material and clean crystal fragments hand-picked under the microscope. The identities of all species were confirmed using X-ray powder methods employing Cu-$K\alpha$ radiation and a Debye–Scherrer camera.

Water was distilled using an FI Streem 4 automatic glass apparatus and then passed through an Elgastat B104 HR resin column. The conductivity of the water was found to be 0.6 μS cm^{-1} as determined using a WTW LF530 conductivity meter. Measurements of pH were performed using a WTW 521 meter fitted with a WTW E56 combination electrode. Electronic spectral and AAS measurements were carried out using a Perkin Elmer Hitachi 200 spectrophotometer and a Perkin Elmer 400 spectrometer, respectively. Phosphate determinations were carried out using published methods (Environmental Protection Agency, 1979). IR spectra were recorded in KBr discs using a Perkin Elmer 257 instrument.

Finely powdered mineral samples were placed in sealed flasks filled with aqueous perchloric acid (8.736×10^{-4} mol dm^{-3}) and to which a teflon-covered magnetic follower had been added. The flasks were thermostatted at 298.2±0.1 K in a Grant SB3/74GB bath and stirring was effected by positioning magnetic stirrers underneath it. A series of preliminary experiments, during which the pH of the reaction mixtures was monitored, established the time necessary for equilibrium to be achieved. The flasks were allowed to remain in the experimental apparatus for at least double this period at which time they were removed and the mixtures filtered through a 0.45 μ millipore ® pad.

The volumes of the equilibrating solutions were 100 cm^3, and the flasks were filled to remove any gaseous phase. A large excess of solid powdered mineral was admitted (*c.*200 mg) in each case. The preliminary experiments showed that equilibrium was achieved in the solutions after two weeks in all cases. Nevertheless, the solutions were equilibrated with the solid phases for at least four weeks, and in the case of cornetite, for up to twelve weeks.

The pH of the reaction solution was measured prior to filtration and total metal ion (by AAS) and total phosphate (colorimetrically) concentrations determined in the filtrates. All minerals dissolved congruently, as evidence by IR spectra of the filtered, washed solids, which were identical to those of the authenic minerals involved. The computer programme COMICS (Perrin and Sayce,

TABLE I Equilibrium constants used as input for COMICS calculations.[a]

Species[b]	log K	Reference
$H_2PO_4^-$	7.20	Smith and Martell (1976)
$H_3PO_4^\circ$	9.35	Smith and Martell (1976)
$CaHPO_4^\circ$	2.74	Smith and Martell (1976)
$CaH_2PO_4^+$	8.60	Smith and Martell (1976)
$CaPO_4^-$	-5.89[c]	Smith and Martell (1976); Truesdell and Jones (1974)
$CuHPO_4^\circ$	2.34	Smith and Martell (1976)
$CuH_2PO_4^+$	8.50[d]	Smith and Martell (1976)
$ZnOH^+$	-8.96	Baes and Mesmer (1976)
Zn_2OH^{3+}	-9.00	Baes and Mesmer (1976)
$ZnHPO_4^\circ$	1.56	Smith and Martell (1976)

[a] At I = 0 and 298.2K except where noted. [b] Early COMICS runs including hydrolysed Cu(II) species gave negligible concentrations for them. They were not included in later calculations. [c] Calculated as for the $[Ca(HPO_4)(OH)]^-$ complex. [d] 310.2K, I = 0.15.

1967) was used to calculate the species distribution in each solution. Equilibrium constants, which were not corrected due to the low ionic strengths involved in the calculations, are given in Table I. Solubilities of the minerals are given in Table II.

TABLE II. Experimentally determined solubilities of the minerals at 298.2K in 8.736×10^{-4}M aqueous $HClO_4$

Mineral	10^4 Solubility/mol dm^{-3}	$pH^{a,b}$
libethenite	2.839	3.98
	2.610	3.90
	2.273	3.88
	2.312	3.95
pseudomalachite	0.939	4.00
	0.869	4.00
	0.856	3.99
	0.811	4.07
cornetite	1.515	4.37
	1.464	4.35
	1.588	4.44
	1.625	4.41
	1.483	4.54
	1.506	4.29
	1.547	4.25
tarbuttite	2.656	5.18
	2.710	5.23
	2.405	5.39
	2.602	5.24
	2.606	5.12
	2.695	5.10
spencerite	2.549	5.46
	2.483	5.49
	3.259	5.52
	2.813	5.50
	2.914	5.53
scholzite	2.089	5.54
	2.125	5.67
	1.901	5.44
	2.167	5.56
	2.151	5.51
	2.047	5.66

[a] At equilibrium.

[b] Equilibrium established prior to transformation to any other phase.

The ionic strength of each solution was calculated from the species distribution data and these values were used in turn to estimate individual ionic activity coefficients via the Debye-Hückel limiting expression. Relevant thermodynamic data used for the calculation of the equilibrium constants for expressions (1) and (2) are given in Table III, together with values for K_{H^+} (2).

$$M_x(PO_4)_y(OH)_z \cdot nH_2O_{(s)} + (2y+z)H^+_{(aq)} \rightleftharpoons xM^{2+}_{(aq)} + yH_2PO^-_{4\,(aq)} + (n+z)H_2O_{(l)} \qquad (1)$$

$$K_{H^+} = a^x_{M^{2+}} a^y_{H_2PO_4^-} / a^{(2y+z)}_{H^+}. \qquad (2)$$

The free energies of formation of the minerals at 298.2 K, ΔfG° (298.2 K), were calculated in the usual way from the results and are listed in Table IV. Errors were determined from those associated with the values of K_{H^+} and estimated errors in the free energies of formation of the products of (2) (Robie *et al.*, 1978). ΔfG° (298.2 K) values for these species are taken from the same source except for that of $H_2PO^-_{4\,(aq)}$, which was calculated on the basis of ΔfG° ($PO^{3-}_{4(aq)}$, 298.2 K) and stability constants for the phosphate conjugate acid anions (Smith and Martell, 1976).

Possibly the most famous deposits of zinc phosphate mineralization in oxidized base metal ores occur at Broken Hill, Zambia. A particularly striking aspect of the occurrence concerns the intimate relationship of hopeite, its dimorph parahopeite, tarbuttite, and scholzite, with deposits of human and animal bones. These fossil remains have been replaced in part by the zinc-containing species (Notebaart and Korowski, 1980; Chubb, 1908; White, 1908). This fact, together with our values for the free energies of formation of the zinc minerals and observed paragenetic sequences in the deposits, permits a reconstruction of the chemical environment which gave rise to their crystallization.

Spencerite has not been found at Broken Hill. ΔrG° (298.2 K) for reaction (3) is calculated to be equal to $+5.4$ kJ mol^{-1}. Given that

$$Zn_2PO_4OH_{(s)} + 1\tfrac{1}{2}H_2O_{(l)} \rightleftharpoons Zn_2PO_4OH \cdot 1\tfrac{1}{2}H_2O_{(s)} \qquad (3)$$

the activity of water in relevant mineralizing solutions is about equal to unity, it is clear that at 298.2 K, spencerite is thermodynamically unstable with respect to tarbuttite, and can only crystallize at this temperature as a metastable phase. Otherwise it forms at somewhat different temperatures. Spencerite has only been observed at two localities. No detailed information is available concerning its occurrence in the Turf Pits mine, Yorkshire, UK (Embrey, 1978), but at the type locality in British Columbia it was found with hopeite and parahopeite as the central core of stalactites, coated with hemimorphite in oxidized zinc ores (Walker, 1916; 1918). This coating probably preserved the spencerite from further reaction or dissolution and the mineral's rarity is in accord with the above thermodynamic data.

In order to understand the environment of zinc mineralization at Broken Hill, we have constructed the diagram shown in fig. 1. The pH limits have been chosen as they not only encompass all of the phase boundaries of interest, but over the range of from 3 to 6.5 all the phosphate in aqueous solution can be essentially treated as the $H_2PO^-_{4\,(aq)}$ ion. The major constraint on the calculations used in the construction of the diagram, bearing in mind that at Broken Hill the hydroxyapatite of the fossil bones is replaced by hopeite, parahopeite, and tarbuttite, is that the aqueous mineralizing solutions

TABLE III Results from COMICS runs used to derive free energy of formation values at 298.2K.

Mineral	10^4[Cu^{2+}], 10^4[Zn^{2+}]/ mol dm^{-3}	10^4[$H_2PO_4^-$]/ mol dm^{-3}	pH	10^3I^a/ mol dm^{-3}	$\gamma_{M^{2+}}$	$\gamma_{H_2PO_4^-}$	$\log K^b_{H+}$	
libethenite	5.647	2.765	3.98	1.759	0.821	0.952	1.69	1.38 ± 0.31
	5.194	2.537	3.90	1.667	0.825	0.953	1.35	
	4.526	2.211	3.88	1.520	0.832	0.955	1.12	
	4.603	2.254	3.95	1.527	0.832	0.955	1.35	
pseudomalachite	4.676	1.833	4.00	1.515	0.834	0.955	7.44	7.33 ± 0.25
	4.329	1.698	4.00	1.438	0.836	0.956	7.21	
	4.268	1.673	3.99	1.426	0.837	0.956	7.09	
	4.043	1.590	4.07	1.368	0.840	0.957	7.58	
cornetite	4.531	1.490	4.37	1.440	0.836	0.957	7.74	7.80 ± 0.76
	4.379	1.440	4.35	1.408	0.838	0.957	7.58	
	4.749	1.562	4.44	1.484	0.834	0.956	8.17	
	4.859	1.598	4.41	1.509	0.833	0.955	8.06	
	4.436	1.461	4.54	1.413	0.838	0.957	8.56	
	4.505	1.480	4.29	1.438	0.836	0.956	7.33	
	4.627	1.519	4.25	1.467	0.835	0.956	7.17	
tarbuttite	5.311	2.628	5.18	1.639	0.826	0.953	5.22	5.29 ± 0.44
	5.418	2.679	5.23	1.663	0.825	0.953	5.40	
	4.808	2.366	5.39	1.526	0.832	0.955	5.73	
	5.203	2.571	5.24	1.615	0.828	0.954	5.38	
	5.212	2.582	5.12	1.616	0.827	0.954	5.02	
	5.389	2.670	5.10	1.656	0.826	0.953	5.00	
spencerite	5.096	2.501	5.46	1.592	0.829	0.954	6.01	6.24 ± 0.25
	4.964	2.434	5.49	1.562	0.830	0.955	6.07	
	6.514	3.189	5.52	1.914	0.814	0.950	6.49	
	5.623	2.756	5.50	1.712	0.823	0.952	6.25	
	5.825	2.851	5.53	1.758	0.821	0.952	6.38	
scholzite^c	4.175	4.055	5.54	1.906	0.814	0.950	4.62	4.70 ± 0.67
	4.246	4.091	5.67	1.935	0.813	0.950	5.17	
	3.800	3.711	5.44	1.773	0.820	0.952	4.03	
	4.331	4.201	5.56	1.961	0.812	0.949	4.77	
	4.299	4.181	5.51	1.949	0.812	0.949	4.56	
	4.090	3.945	5.66	1.880	0.815	0.950	5.05	

[a] Ionic strength. For the experiments, because of the temperatures and concentrations employed the approximation mol dm^{-3} = mol Kg^{-1} is well within experimental error. [b] With respect to eqn(2). [c] The equilibrium concentrations of $Ca^{2+}_{(aq)}$ for these experimental runs were calculated to be 2.058, 2.090, 1.877, 2.113, 2.119 and 2.014×10^{-4} mol dm^{-3}, respectively.

are saturated with respect to $Ca_5(PO_4)_3(OH)_{(s)}$. We have taken the value of $\Delta f G°$ (298 K) for hydroxyapatite from the compilation of Robie *et al.*, 1978. Over the range of the diagram hydroxyapatite is assumed to dissolve congruently as shown in equation (4), and that [$Ca^{2+}_{(aq)}$] is equal to $\frac{5}{3}$[$H_2PO^-_{4(aq)}$],

$$Ca_5(PO_4)_3OH_{(s)} + 7H^+_{(aq)} \rightleftharpoons 5Ca^{2+}_{(aq)} + 3H_2PO^-_{4(aq)} + H_2O_{(l)} \quad (4)$$

activities not being taken into account. A number of check calculations indicate that this assumption makes negligible differences to the boundaries shown in fig. 1. Thus, for example, at pH 3, [Ca^{2+}] = 5.405×10^{-2} mol dm^{-3} and [$H_2PO_4^-$] = 3.243×10^{-2} mol dm^{-3}; at pH 6.5, the corresponding concentrations are 4.687 and 2.812×10^{-5} mol dm^{-3}, respectively.

The question may then be posed as to what activities of $Zn^{2+}_{(aq)}$ must be achieved in order for hopeite, tarbuttite, and scholzite to be precipitated from solution. These pH-dependent activities define the conditions under which the hydroxyapatite of the bone beds at Broken Hill would be replaced by the zinc minerals. Calculations show that scholzite cannot be crystallized under the chosen condi-

TABLE IV. Calculated values of $\Delta fG°(298.2K)$ for the minerals

Mineral	$\Delta fG°(298.2K)/kJmol^{-1}$
libethenite	-1228.8 ± 3.0
pseudomalachite	-2840.3 ± 4.2
cornetite	-1600.9 ± 5.9
tarbuttite	-1632.1 ± 4.0
spencerite	-1982.4 ± 3.1
scholzite	-3556.7 ± 7.6

tions. It is thermodynamically unstable with respect to hopeite and tarbuttite, should the mineralizing solutions also be in equilibrium with hydroxyapatite. Conditions necessary for the crystallization of scholzite are discussed below.

Calculations show that at 298 K, the only stable solid phases under conditions of varying $a_{Zn^{2+}}$ are hopeite (or its dimorph), tarbuttite, and hydroxyapatite. At Broken Hill, tarbuttite is observed to have crystallized after hopeite and parahopeite and thus the changing solution composition giving rise to the reported paragenetic sequences (Notebaart and Korowski, 1980; Spencer, 1980) can be represented by bold arrow shown on fig. 1. Zinc ion activities rose, no doubt as a consequence of the oxidation of sphalerite, until the hopeite boundary conditions were attained. A small basic shift of solution pH leads to conditions such that hydroxyapatite is replaced by tarbuttite. This simple model is sufficient to describe the formation of the three main zinc phosphate species hopeite, parahopeite, and tarbuttite, found in the Broken Hill orebody.

Subsequently, the restriction concerning the presence of hydroxyapatite is lifted. This mineral has been replaced. Locally, calcium ion activities may rise or relative zinc activities may fall to such a level as to permit the crystallization of scholzite. The value of $\Delta rG°$ (298 K) for reaction (5) is +5.2 kJ mol^{-1} and $\log K_{298\,K}$

$$Zn_3(PO_4)_2\cdot 4H_2O_{(s)} + Ca^{2+}_{(aq)} \rightleftharpoons CaZn_2(PO_4)_2\cdot 2H_2O_{(s)} + 2H_2O_{(l)} + Zn^{2+}_{(aq)} \quad (5)$$

$\{K = a_{Zn^{2+}}/a_{Ca^{2+}}\}$ is equal to -0.91. An excellent paragenetic confirmation of these considerations is provided by observations of the mode of occurrence of scholzite at Broken Hill (Notebaart and Korowski, 1980). When scholzite is present with the other zinc phosphates it is found as radiating clusters of needles which coat parahopeite. Scholzite is thus later in the sequence of crystallization.

The above considerations are entirely applicable

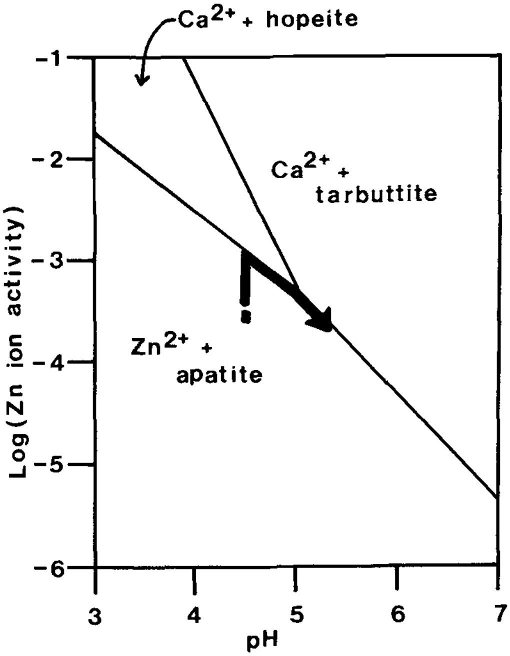

FIG. 1. Stability field diagram for the Zn(II) minerals with the aqueous phase equilibria controlled by the solubility of hydroxyapatite. The bold arrow is the indicated change in chemical conditions which gave rise to the Broken Hill Zambia parageneses.

to one other remarkable deposit of zinc phosphate minerals at Reaphook Hill, SA, Australia (Johnston and Hill, 1978). It has been concluded that the minerals were derived from phosphorites in conjunction with Zn(II) ions scavenged by manganese oxides to produce locally high concentrations of this ion. Parahopeite is found unaltered only rarely, and is most frequently associated with later scholzite. Since a general trend involving decreasing Zn/P ratios is evident as a result of observations of the occurrence of other phosphate minerals in the assemblage (Johnston and Hill, 1978), it may be concluded that the zinc phosphate minerals of the Reaphook Hill deposit were formed as a result of chemical changes similar to those deduced for the sequence at Broken Hill, Zambia.

Three phosphate minerals which contain Cu(II) as the only cation are known from oxidized copper ores. An inspection of the stoichiometries of these minerals, libethenite, Cu_2PO_4OH, pseudomalachite, $Cu_5(PO_4)_2(OH)_4$, and cornetite, $Cu_3PO_4(OH)_3$, indicates that each would form, respectively, from solutions of increasing basicity. Thus a general trend for the crystallization of the phases is established. Using estimated thermodynamic quantities, Nriagu (1984) has derived a phase diagram in which this order is not preserved. The reason for this is the fact that the estimated free energy of formation of pseudomalachite is some 70 kJ mol^{-1} too positive. On the basis of our experimental results, using the data given in Table IV, we have constructed the stability field diagram shown in fig. 2. The anticipated sequence of mineral stabilities with changing pH is readily apparent. Furthermore, this sequence is borne out by numerous field observations (Berry, 1950; Aires-Barros, 1966; Khin, 1970; McColl, 1978; Korowski and Notebaart, 1978; Roe, 1980; Noble, 1980; Henderson, 1981). Pseudomalachite is the commonest of the Cu(II) minerals and the two pairs libethenite-pseudomalachite and pseudomalachite-cornetite are most frequently observed. Only rarely are all three minerals found in the same deposit; a notable occurrence is at Saginaw Hill, Arizona, USA. Libethenite with cornetite alone has never been reported. This is in accordance with predictions inferred by the stability field diagram shown in fig. 2. At Saginaw Hill, pseudomalachite is observed to replace both libethenite and cornetite. The cornetite in this deposit is most frequently found as crystalline clots altering to pseudomalachite (Khin, 1970). The comparative rarity of cornetite may be explained on the basis of fig. 2 in that it is only thermodynamically stable at relatively high pH and high $a_{Cu^{2+}}$ values. In naturally occurring mineralizing groundwaters other anions such as carbonate, sulphate, and the like will be present and as a consequence other basic salts of Cu(II) might be expected to form in preference, unless, of course, cornetite crystallizes as a metastable phase, a possibility indicated by the solution data in the experimental runs. It is also worth noting that the Saginaw Hill deposit was probably developed during several events since a marked range of phosphate activities are indicated by the phosphate suite reported and the replacements indicative of both increasing and decreasing pH which have been reported.

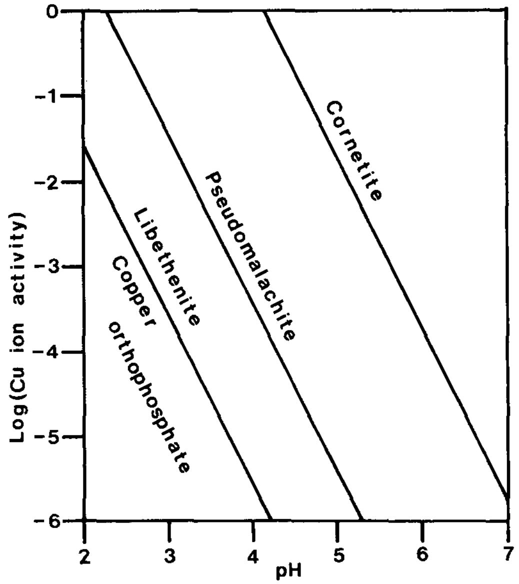

FIG. 2. Stability field diagram for the Cu(II) minerals.

Also shown in fig. 2 is the stability field for the normal Cu(II) phosphate, $Cu_3(PO_4)_2 \cdot 2H_2O$, data for which have been taken from the literature (Volkov, 1979). This substance has not been reported as a naturally occurring mineral phase and evidently the reason for this is that solutions with the high copper, phosphate, and proton activities necessary for its stability are rarely if ever encountered in the natural environment.

Finally, the occurrence of zincian libethenite, $(Cu,Zn)_2PO_4OH$, at Broken Hill, Zambia should be mentioned (Notebaart and Korowski, 1980). It is found as an alteration product of tarbuttite and is of very limited extent in the oxide zone. The equilibrium constant for equation (6) is

$$Zn_2PO_4OH_{(s)} + 2Cu^{2+}_{(aq)} \rightleftharpoons Cu_2PO_4OH_{(s)} + 2Zn^{2+}_{(aq)} \qquad (6)$$

calculated to be 7.98×10^3; the equilibrium $a_{Zn^{2+}}/a_{Cu^{2+}}$ ratio is 89.3. Such a result may be interpreted as meaning that the Zn(II) phosphate minerals in general will only form if comparatively negligible amounts of Cu(II) ion are present in the appropriate mineralizing solutions. Crystallization of zincian libethenite at Broken Hill must have taken place locally as a result of a significant (with respect to Zn) input of Cu ions to solution, most probably by the oxidation of chalcopyrite or its congeners.

We have been able to demonstrate that a simple thermodynamic model can explain observed paragenetic sequences of Cu(II) and Zn(II) phosphate minerals in oxidized base metal orebodies. It should be recalled, however, that pyromorphite, $Pb_5(PO_4)_3Cl$, is a very insoluble salt and is commonly found in such environments. Generally speaking, the Cu and Zn phosphates must be emplaced by solutions of low Pb(II) ion activities. We are extending our experimental studies to include those base and transition metal minerals containing the arsenate anion, which have also been found in a few of the deposits mentioned above, as well as in many others. We will report these results in the near future.

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REFERENCES

Aires-Barros, L. (1966) *Garcia de Orta.* **14,** 103–8.

Baes, C. F., and Mesmer, R. E. (1976) *The Hydrolysis of Cations.* John Wiley and Sons.

Berry, L. G. (1950) *Am. Mineral.* **35,** 365–85.

Chubb, E. C. (1908) *Proc. Rhodesia Scientific Assoc.* **7,** 21–5.

Embrey, P. G. (1978) *Mineral. Mag.* **42,** 169–77.

Environmental Protection Agency (1979) *Methods for Chemical Analysis of Water and Waste.* Choice of Research and Development, US Environmental Protection Agency. Cincinatti, Ohio.

Henderson, B. (1981) *Mineral. Rec.* **12,** 105–11.

Hey, M. H. (1955) *An Index of Mineral Species and Varieties Arranged Chemically.* British Museum (Natural History).

Johnston, C. W., and Hill, R. J. (1978) *Mineral. Rec.* **9,** 20–4.

Khin, B. (1970) Ibid. **1,** 117–18.

Korowski, S. P., and Notebaart, C. W. (1978) Ibid. **9,** 341–6.

McColl, D. H. (1978) Ibid. **9,** 295.

Noble, R. J. (1980) *Quart. Geol. Notes Geol. Surv. S. Aust.* **76,** 2–5.

Notebaart, C. W., and Korowski, S. P. (1980) *Mineral. Rec.* **11,** 339–48.

Nriagu, J. O. (1975) *Can. J. Earth Sci.* **13,** 717–36.

——(1984) in *Phosphate Minerals* (J. O. Nriagu and P. B. Moore, eds.). Springer-Verlag, 318–29.

——and Dell, C. I. (1974) *Am. Mineral.* **59,** 934–46.

——and Moore, P. B., eds. (1984) *Phosphate Minerals.* Springer-Verlag.

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

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 Pascals) Pressure and at Higher Temperatures.* US Geol. Surv. Bull. 1452.

Roe, A. (1980) *Mineral. Rec.* **11,** 261–5.

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

Spencer, L. J. (1908) *Mineral. Mag.* **15,** 1–38.

Truesdell, A. H., and Jones, B. F. (1974) *J. Res. US Geol. Surv.* **2,** 233–48.

Vieillard, P., and Tardy, Y. (1984) in *Phosphate Minerals* (J. O. Nriagu and P. B. Moore, eds.). Springer-Verlag, 171–214.

Volkov, A. I. (1979) *Khim. Khim. Tekhnol. (Minsk),* **14,** 58–64.

Walker, T. L. (1916) *Mineral. Mag.* **18,** 76–81.

——(1918) *Univ. Toronto Stud., Geol. Ser.* **10,** 1–25.

White, F. (1908) *Proc. Rhodesia Scientific Assoc.* **7,** 13–21.

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