Connellite: stability relationships with other secondary copper minerals

A. M. POLLARD, R. G. THOMAS AND P. A. WILLIAMS

School of Chemistry and Applied Chemistry, University of Wales College of Cardiff,
P.O. Box 912, Cardiff CF1 3TB

Abstract

The stability of synthetic connellite has been determined at 298.2K (25 °C) and 10^5 Pa, using solution methods. For the reaction $1/37\{62H^+(aq) + Cu_{37}Cl_8(SO_4)_2(OH)_{62}.8H_2O(s) \rightleftharpoons Cu^{2+}(aq) + 8Cl^-(aq) + 2SO_4^{2-}(aq) + 70H_2O(l)\}$, log K_{H+} is equal to 6.44(2). This result has been used in turn to calculate a value for $\Delta fG^\circ(1/37Cu_{37}Cl_8(SO_4)_2(OH)_{62}.8H_2O$, s, 298.2K) of -423.7 ± 6.6 kJ mol^{-1}. During the synthesis of connellite, claringbullite sometimes forms as a metastable phase. This solid recrystallizes to connellite if kept in contact with the reaction solution. The results have been used to construct an equilibrium model for the formation of connellite in relation to other common secondary copper (II) minerals. Connellite crystallizes from solution over an appreciable range of conditions. This result is consistent with the observed widespread occurrence of connellite, though as a very minor phase, in the oxidized zones of cupriferous sulfide ores.

KEYWORDS: connellite, stability, phase relationships.

Introduction

As part of a study of the basic copper chlorides of stoichiometry $Cu_2Cl(OH)_3$ (Pollard et al., 1989a), a number of titrations of copper(II) chloride with aqueous sodium hydroxide solutions were carried out. It was noted that under some circumstances, towards the end point of the titrations, recrystallization at 25 °C of the initially produced solid phase gave an unexpected blue crystalline material. This blue solid was subsequently identified by powder X-ray methods as connellite (Bannister et al., 1950). The source of the sulfate ion was eventually traced to impurities present in the particular batch of $CuCl_2.2H_2O$ used, and the use of dilute sulfuric acid to rid flasks of residual paratacamite between titrations. It was then found that the synthesis could be reproducibly performed by the deliberate addition of small amounts of sodium sulfate to the copper(II) chloride solutions prior to the addition of base.

Although connellite has been classed as a rare mineral, it has been reported from a surprising number of localities. The adventitious laboratory synthesis provided an opportunity to investigate the mineral in order to elucidate its stability with respect to other secondary copper(II) minerals with which it is associated. The results of this study are presented below.

Experimental

Synthesis of connellite. Laboratory syntheses of connellite were carried out using a method similar to that previously described (Pollard et al., 1989b). To a stirred aqueous solution (100 cm^3) containing $CuCl_2.2H_2O$ (0.725 g, 4.25 mmol), NaCl (1.6055 g, 27.5 mmol) and $Na_2SO_4.10H_2O$ (0.7 g, 2.2 mmol), CO_2-free aqueous NaOH solution (0.05 mol dm^{-3}) was added until the pH of the mixture was 7.2. Fast addition of the hydroxide gave a blue precipitate which recrystallized to connellite within 48 hours if the mixture was kept in a sealed container to exclude CO_2, regulated with a thermostat at 25 °C. X-ray powder diffraction measurements of this transient blue phase showed it to be claringbullite, $Cu_8(OH)_{14}Cl_2.H_2O$, (Fejer et al., 1977), although other amorphous solids may also be present in admixture. The five strongest lines are observed at 5.76, 4.90, 4.60, 2.70 and 2.42Å, as compared with literature values of 5.75, 4.89, 4.59, 2.700 and 2.445Å. Synthetic claringbullite prepared by this method is reasonably fine-grained, as evidenced by the somewhat faint and broad diffraction lines observed. In these conditions, claringbullite is metastable with respect to connel-

lite. If the addition of base was carried out more slowly however, then the first-formed solid phase quickly recrystallized to paratacamite. The paratacamite also recrystallized to connellite under the same conditions as outlined above, but much more slowly (several weeks).

Equilibrium solubility measurements. Four reaction solutions similar to those employed for the synthetic experiments above were titrated with base to a pH of about 7, the mixtures sealed in the flasks exclude CO_2 and placed in a Grant FH15 waterbath with fitted thermostat for a period of 2 months. Preliminary experiments established that paratacamite, if formed, completely recrystallized to connellite within this time, and that the mixtures attained equilibrium.

Prior to filtration of the solid phase, the solution pH was measured using a Radiometer PHM85 meter fitted with a combination electrode. The solid was collected at the pump using a $0.45\,\mu m$ Millipore filter. Total Cu^{2+}(aq) concentrations were measured using a Varian AA-275 atomic absorption spectrophotometer. The identity and purity of the solid phase present was checked using infrared spectroscopy (nujol mull) employing a Perkin Elmer 783 spectrophotometer (Pollard *et al.*, 1989*b*) and by X-ray powder diffraction using a 114.6 mm diameter Debye–Scherrer camera and Cu-$K\alpha$ radiation camera (Bannister *et al.*, 1950). Since precipitation of copper as connellite is essentially complete under the conditions employed in the experiments, it is more accurate to calculate the total concentrations of other solution species from a knowledge of the initial concentrations and the stoichiometry of connellite.

The single crystal X-ray structure of a natural connellite crystal has been reported (McLean and Anthony, 1972). In the particular crystal used for the structure determination some nitrate is present in the sulfate site (cf. buttgenbachite; Palache *et al.*, 1951). Other disorder (Cl^-, OH^-, H_2O) is also apparent, and these facts result in fractional occupancy of one of the Cu^{2+} sites. In addition, it has been recently shown that carbonate ions can substitute in the lattice, again replacing sulfate (Pollard *et al.*, 1989*b*). We have chosen the stoichiometry $Cu_{37}Cl_8(SO_4)_2(OH)_{62}.8H_2O$ to represent the phase in accordance with the crystal structure and other available analytical data (McLean and Anthony, 1972; Palache *et al.*, 1951). Slight variations from this formula as are observed in natural material will have negligible effect on the equilibrium model developed below.

Derivation of stability constants and related quantities. Species distributions in aqueous solutions in equilibrium with connellite were calculated from equilibrium solubility data and pH
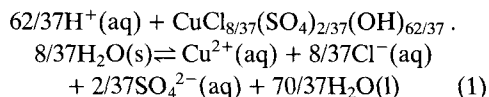
TABLE 1

Equilibrium constants used for COMICS calculations

Species	LogK	Ref.[b]
$CuCl^+$	0.4	1
$CuCl_2{}^0$	-0.71	2
$CuCl_3{}^-$	-2.3	2
$CuCl_4{}^{2-}$	-4.6	2
$CuOH^+$	-7.6	1
$Cu(OH)_2{}^0$	-13.7	2
$Cu(OH)_3{}^-$	-27.0	2
$Cu_2(OH)_2{}^{2-}$	-10.3	1
$CuSO_4{}^0$	2.36	1
$NaOH^0$	-14.3	1
$NaSO_4{}^-$	0.7	1
$HSO_4{}^-$	1.99	1

[a]At I = 0 and 298.2K. [b]1: Smith and Martell (1976) 2: Long and Angino (1977).

measurements using the program COMICS (Perrin and Sayce, 1967). Values for the equilibrium constants used in the computation are given in Table 1, together with their source.

Using the results of the COMICS calculations, the equilibrium constants for the separate experiments were calculated with respect to equation (1).

$$62/37H^+(aq) + CuCl_{8/37}(SO_4)_{2/37}(OH)_{62/37} \cdot$$
$$8/37H_2O(s) \rightleftharpoons Cu^{2+}(aq) + 8/37Cl^-(aq)$$
$$+ 2/37SO_4{}^{2-}(aq) + 70/37H_2O(l) \qquad (1)$$

Values for the equilibrium constants were corrected to zero ionic strength using the extended form of the Debye–Hückel law [log $\gamma_i = -Az_i^2I^{1/2}/(1+I^{1/2})$; values of activity coefficients for uni- and divalent ions are given in Table 2]; stability constants for the complex ions in solution were similarly corrected. The error for the equilibrium constant for (1) is quoted as a standard deviation from multiple measurements. Values for ΔfG°(298.2K) for component ions and water used to calculate the standard free energy of formation of connellite were taken from the compilation of Robie *et al.* (1978).

Results and discussion

Equilibrium concentrations derived from COMICS calculations used for determination of K_H+ (equation (1)) and associated data are given in Table 2. The average value of K_H+ is 6.44(2) at 298.2K. This result in turn leads to a value of ΔfG°(connellite,s) of -423.7 ± 6.6 kJ mol^{-1} at this temperature, based on the formula $1/37\{Cu_{37}Cl_8(SO_4)_2(OH)_{62}.8H_2O\}$, and taking into

TABLE 2

Equilibrium concentrations[a] from COMICS calculations and
other data used in the calculations of stability constants.

$[Cu^{2+}]$ /10^{-6}	$[Cl^-]$ /10^{-2}	$[SO_4^{2-}]$ /10^{-3}	I[b]/ 10^{-2}	pH	$\gamma^{+/-}$	$\gamma^{2+/-}$	log K_{H^+}
2.109	3.424	1.598	3.897	7.730	0.824	0.461	6.436
4.064	3.423	1.597	3.913	7.554	0.824	0.461	6.426
56.73	3.422	1.581	3.907	6.870	0.824	0.461	6.424
73.83	3.422	1.577	3.925	6.832	0.824	0.461	6.460

[a]Mol dm^{-3}. [b]Ionic strength.

TABLE 3

Values of ΔfG°(298.2K) for the minerals
considered in the stability diagram calculations.

Mineral	ΔfG°(298.2)/kJ mol^{-1}	Ref.[a]
chalcanthite	-1879.8	1
antlerite	-1446.6	2
brochantite	-1818.0	1
eriochalcite	-656.1	3
paratacamite	-1341.8	2
malachite	-902.6	4
azurite	-1436.3	1
cuprite	-146.0	1
tenorite	-129.6	1

[a]1: Robie et al. (1976); 2: Woods and Garrels
(1986); 3: Wagman et al. (1969); 4: Symes and
Kester (1984).

account two standard deviations with respect to log K_{H^+}. The error in free energy is that associated with calculated error in the value of K_{H^+} plus the sum of the errors associated with the standard free energy terms for the component ions and water molecules, taken from Robie et al. (1978).

In order to evaluate the significance of these data with respect to connellite formation in the oxidized zones of base metal orebodies, an equilibrium model has been constructed for the formation of connellite in relation to other common secondary minerals of copper. Thermodynamic data for the minerals cuprite, tenorite, chalcanthite, antlerite, brochantite, malachite, azurite, and paratacamite used in the calculations are given in Table 3. Other thermodynamic data for solution species necessary for calculating the relative stability of these minerals were taken from Robie et al. (1978). It should be noted that errors

in the values of ΔfG°, derived from uncertainties in the values for constituent ions and water molecules, cancel out in calculations relating conditions under which various pairs of minerals are stable. Thus the stability field diagrams presented show relationships between minerals for which the errors are associated only with experimental measurements of K_{H^+} (or of ΔfH° and S°, where these may be determined independently).

The results obtained for connellite have in the first instance been used to construct the stability field diagram shown in Fig. 1. For the phases illustrated, the solid boundaries refer to an equilibrium sulfate activity equal to 10^{-3}. Boundaries with respect to a sulfate activity of 10^{-1} are also shown as broken lines. Fig. 1 shows connellite to occupy a significant field of thermodynamic stability between those of the common minerals paratacamite, brochantite and tenorite. Its boundary with paratacamite can be shown not to vary significantly over the range of chloride ion activities commonly encountered in natural groundwaters (ca. 10^{-1} to 10^{-3}). Far greater variation is seen to attend the field of stability of connellite with respect to that of brochantite; high sulfate ion activities shift the stability field of connellite to a region outside the pH range found in most natural environments, including oxidizing sulfide ores apart from unbuffered cases when pyrite is abundant.

Fig. 2 shows alterations to the previous diagram effected by choosing a CO_2(g) partial pressure equal to that of the atmosphere ($10^{-3.5}$), and when malachite is the thermodynamically stable phase with respect to both tenorite and azurite. It can be seen that at this pressure of CO_2(g), the stability field of connellite is essentially undiminished by that of malachite. The effect of increasing carbon dioxide pressure to a value at which azurite is thermodynamically stable ($10^{-1.36}$) is shown in Fig. 3; the stability field for connellite ultimately vanishes at high CO_2(g) par-
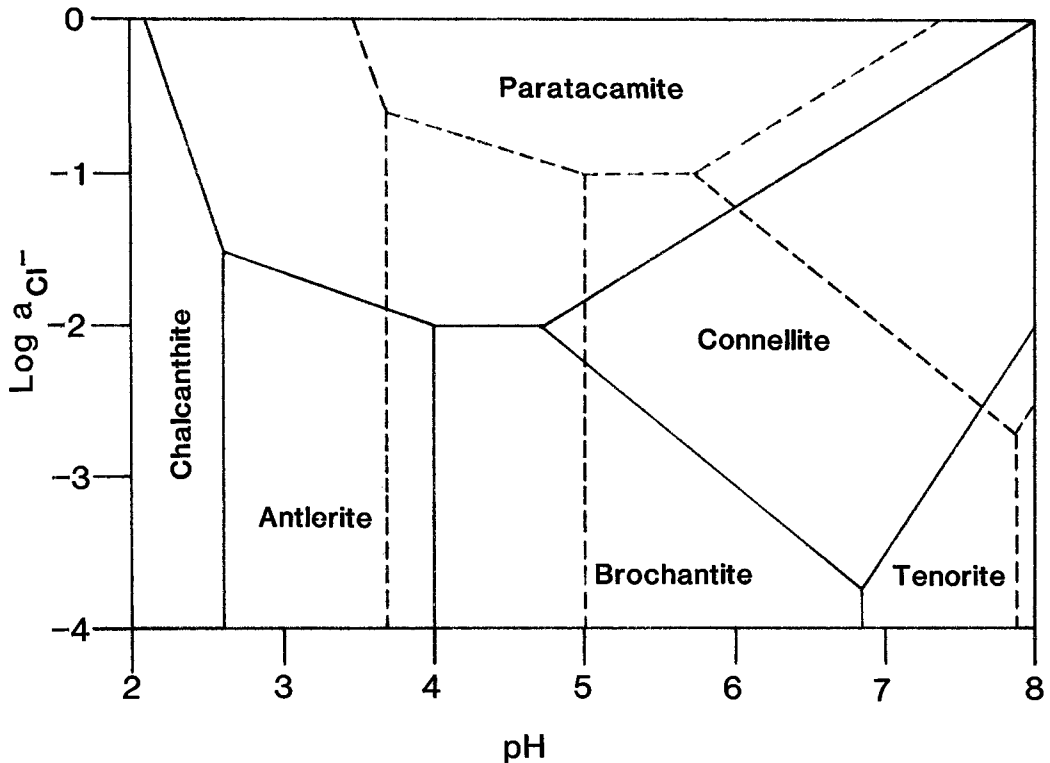
FIG. 1. Stability field diagram for the copper(II) halide minerals in the absence of CO_2. The firm and dashed lines are drawn for sulfate activities of 10^{-3} and 10^{-1}, respectively.

tial pressures. The significant range of conditions which can give rise to connellite is in accord with the fact that the mineral is known to occur at a number of localities, albeit in small quantities. Its observation in oxidized copper ores is being made more frequently, as judged by recent reports in the literature (*vide infra*).

Using the results of this study it is possible to explain many of the mineral associations that appear in the literature with references to connellite. Its occurrence with basic copper chlorides of the stoichiometry $Cu_2Cl(OH)_3$, as noted by Kato *et al.* (1980) and Kirchner (1978), can be seen to be the result of crystallization having taken place in a saline environment. Although the latter author noted that atacamite was present, this is consistent with conversion of this phase to the thermodynamically stable form paratacamite being kinetically very slow under rather saline conditions (Pollard *et al.*, 1989). This association was also noted in a connellite sample from the Perran St. George Mine, Cornwall.

Other occurrences of connellite, such as those at Bisbee, Arizona (Anthony *et al.*, 1977), South

Greenland (Karup-Møller *et al.*, 1978) and the Britannia Mine, North Wales (Pollard *et al.*, 1989*b*) involve the association of both brochantite and malachite. These suites indicate crystallization having taken place from solutions of lower chloride activities than those cases when paratacamite (or atacamite) and connellite are found together. This also applies to the case of botallackite–connellite assemblages (Bannister *et al.*, 1950). Finally, it can be seen by reference to the electrode potential–pH diagram shown in Fig. 4 that with suitable chloride and sulfate activities in conjunction with CO_2 pressures, the commonly observed association of connellite with cuprite (Graeme, 1981; Anthony *et al.*, 1977) can be viewed in terms of oxidation to a thermodynamically stable phase.

Claringbullite has a similar mode of occurrence in vughs of cuprite in oxidized copper ore (Fejer *et al.*, 1977). Our synthetic experiments indicate that it is thermodynamically unstable with respect to connellite, at least under the conditions employed. It may be that claringbullite is always a metastable phase; it is certainly a rare species.
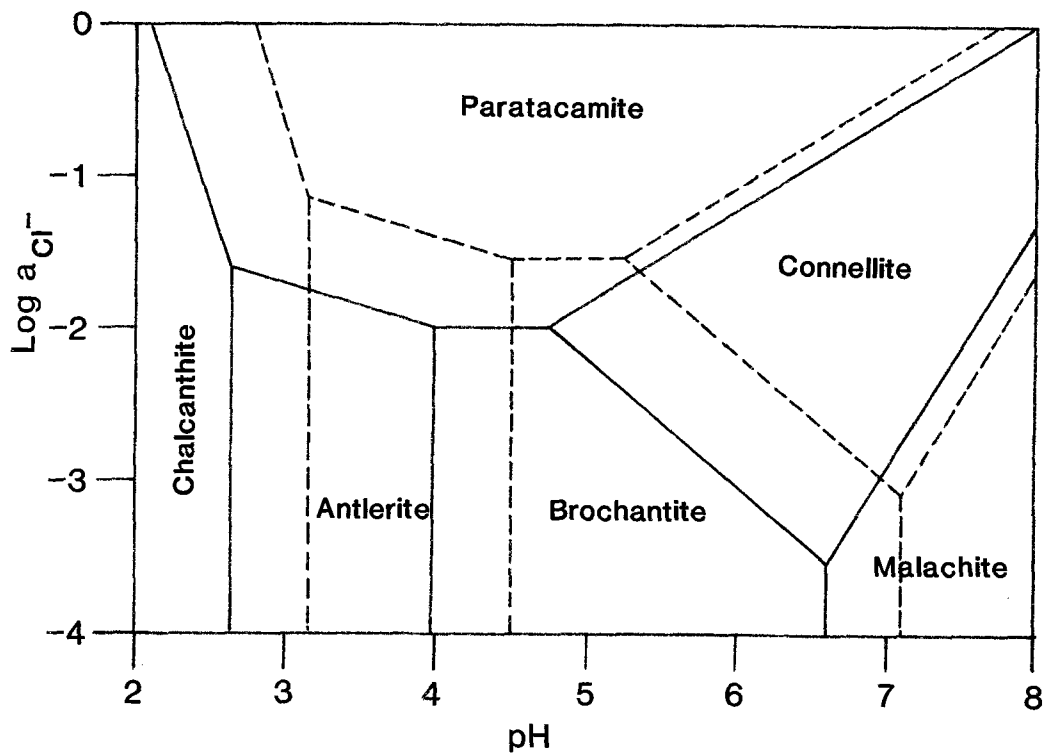
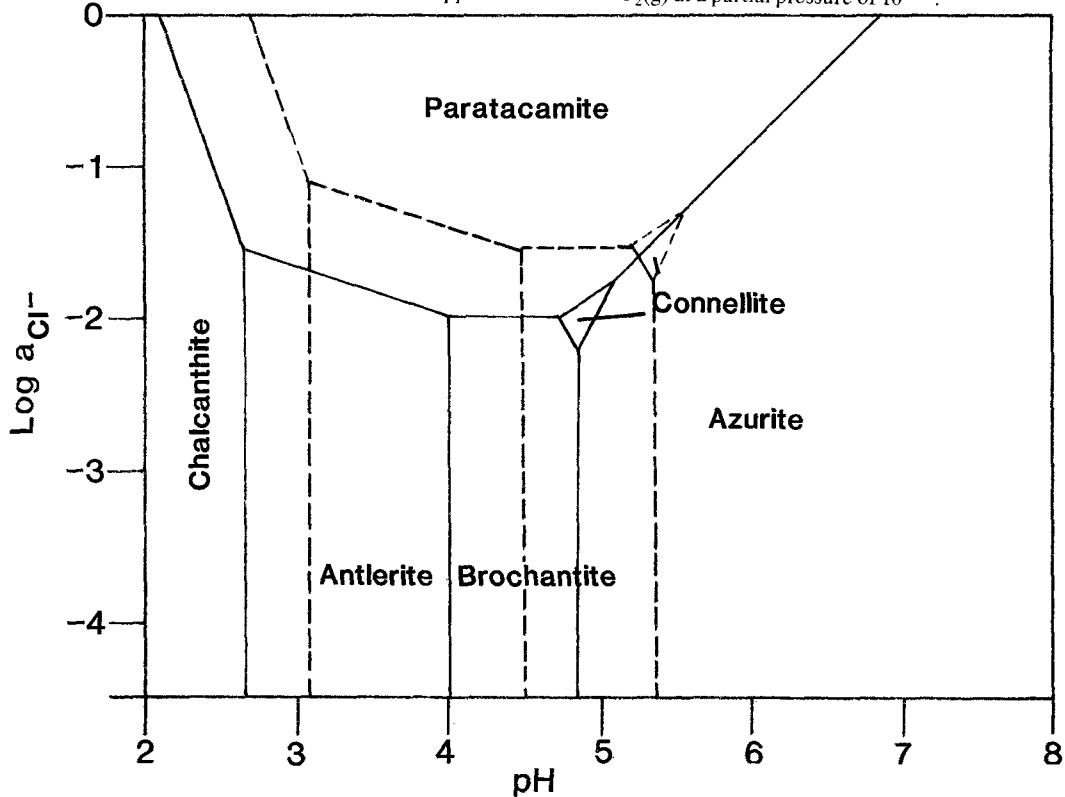FIG. 2. Effect on stabilities of the copper chlorides of $CO_2(g)$ at a partial pressure of $10^{-3.5}$.

FIG. 3. Effect on stabilities as in Fig. 2, but with a partial pressure of $CO_2(g)$ equal to $10^{-1.36}$. Azurite is just stable with respect to malachite.
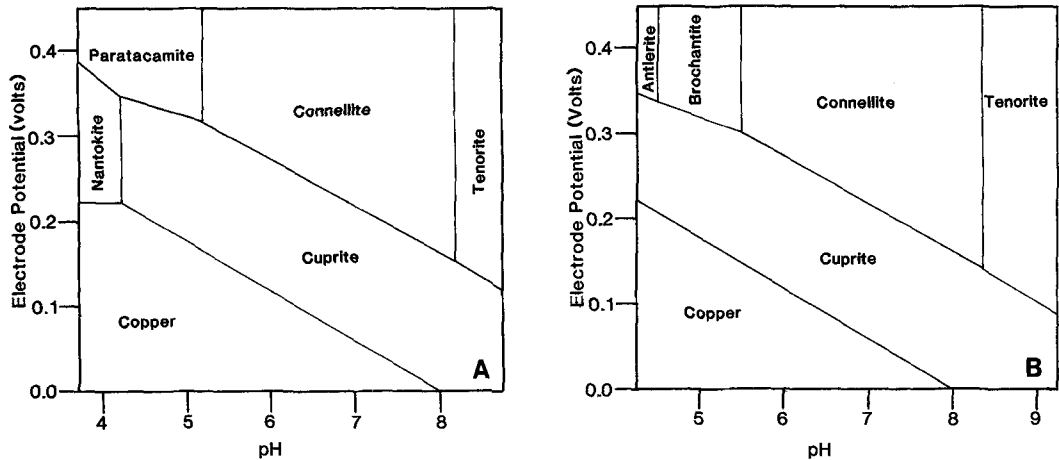
FIG. 4. A: Redox–pH diagram for the copper minerals with activities of SO_4^{2-}(aq) and Cl^-(aq) equal to 10^{-3} and $10^{-1.75}$, respectively; B: as for A, but with a sulfate activity of 10^{-2}.

However, we cannot yet be certain of the conditions necessary for its persistence in the natural environment, even as an intermediate in the formation of connellite from aqueous solution.

Acknowledgements

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