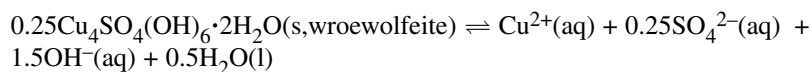


Synthesis and stability of wroewolfeite, $\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot 2\text{H}_2\text{O}^*$

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Abstract: Titration of aqueous copper(II) sulfate solutions with aqueous NaOH at temperatures ranging from 0 to 25 °C results in a complex Ostwald step rule cascade of basic copper sulfate phases. At 25 °C, the thermodynamically stable phase is brochantite $[\text{Cu}_4\text{SO}_4(\text{OH})_6]$, but posnjakite $[\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot \text{H}_2\text{O}]$ is formed first. At lower temperatures, but above 0 °C, wroewolfeite $[\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot 2\text{H}_2\text{O}]$ forms first. If left in contact with the reaction solution, wroewolfeite is converted to posnjakite and brochantite in turn. However, at 0 °C, synthetic wroewolfeite is stable for periods longer than a week, even in contact with the reaction solution, and a stability constant could be determined for its formation. For the reaction below, $\lg K = -16.3(1)$ at 0 °C and $I = 0$, as determined by solution methods.



Stability relations between minerals of stoichiometry $\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot n\text{H}_2\text{O}$ ($n = 0, 1, 2$) are discussed. High concentrations of Mg^{2+} ions (1 M) prevent the isolation of wroewolfeite at any temperature down to 0 °C.

Keywords: wroewolfeite; basic copper sulfates; synthesis; stability; supergene mineralogy.

INTRODUCTION

Several basic copper(II) sulfates occur naturally [1,2]. Those that contain Cu^{2+} as the only cation and sulfate and hydroxide as the only anions are antlerite $[\text{Cu}_3\text{SO}_4(\text{OH})_4]$, brochantite $[\text{Cu}_4\text{SO}_4(\text{OH})_6]$, posnjakite $[\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot \text{H}_2\text{O}]$, langite and wroewolfeite $[\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot 2\text{H}_2\text{O}]$, and redgillite $[\text{Cu}_6\text{SO}_4(\text{OH})_{10} \cdot \text{H}_2\text{O}]$. Some of these phases have in the past been important ore minerals of copper. Current interest in their chemistry stems in part from their environmental significance, including their presence in acid mine drainage trains and their role in the removal of copper from waste waters [3,4]. The chemical conditions that give rise to the formation of redgillite are unknown; it was reported to be commonly associated with langite and rarely brochantite, connellite, cuprite, and malachite. Redgillite is structurally related to wroewolfeite, langite, and posnjakite [2]. Well-established synthetic methods are available in the literature for brochantite and posnjakite [3,5] and a synthesis of langite has been published [6], although it is now apparent that posnjakite was in fact obtained. Wroewolfeite was first described from Loudville, Massachusetts, by P. J. Dunn et al. [7], who listed two other British locali-

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ties. Shortly thereafter, Livingstone et al. [8] noted its occurrence at Blackcraig, Scotland. Braithwaite [9] reported its occurrence from five localities in England and Wales and listed characteristic IR data for the various basic copper(II) sulfate minerals. Since that time, the mineral has been reported from over 50 other localities, principally in Europe (<www.mindat.org/min-4315.html>). In the vast majority of cases, brochantite, posnjakite, and langite are associated with wroewolfeite, and this suggests an intimately related chemical origin [8–12].

It is well known that titrations of aqueous copper(II) sulfate solutions with aqueous NaOH solutions are noncommutative [13,14]. At ambient temperatures, addition of copper(II) sulfate to base initially gives a metastable precipitate of spertiniite [$\text{Cu}(\text{OH})_2$], and addition of base to copper(II) sulfate initially gives a metastable precipitate of posnjakite. It has been suggested [3] that the nature of the precipitate depends on the concentrations of reagents and their rate of addition, although solution experiments have confused posnjakite with langite [3]. To our knowledge, no unambiguous syntheses of the dihydrate dimorphs have been reported, although Braithwaite [9] mentioned in passing that experiments aimed at synthesizing wroewolfeite had in some cases yielded langite; no details were given. However, during the course of a series of experiments aimed at determining the relative stabilities of posnjakite and brochantite, we have found that wroewolfeite can conveniently be prepared by titration of aqueous copper(II) sulfate solutions with aqueous NaOH at 0 °C. It is now clear that the sampling time of the precipitate and the temperature at which the experiment is conducted can account for a number of apparently contradictory observations that have appeared in the literature. A stability constant for wroewolfeite at 0 °C has been determined using solution methods. Results of this study are presented below, together with an appraisal of its relationships with its congeners.

EXPERIMENTAL

Powder X-ray diffraction (XRD) data were recorded using a Philips PW1825-20 powder diffractometer (Cu $K\alpha$ radiation with pure Si as internal standard). A Radiometer PHM 93 meter fitted with a Radiometer IJ44 combination electrode calibrated for measurement at 0 °C was used for pH measurements. Constant temperatures were maintained between 4 and 25 °C using a Grant SS40-D water bath fitted with a Grant refrigeration unit. A stirred ice/water bath was used for experiments conducted at 0 °C. A constant temperature room was used to monitor changes in reaction products at 4 °C. Analytical grade $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and NaOH were used to make up solutions in precalibrated volumetric glassware.

An aqueous solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.100 M, 25 cm³) was used to standardize an aqueous solution of NaOH (0.1022 M) by titration to the 2:3 (Cu:OH) end-point. Aliquots of the NaOH solution corresponding to 50, 60, 70, 80, and 90 % of the end-point volume were thermally equilibrated at 0 °C and then added to separate solutions of the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ solution that had also been thermally equilibrated at 0 °C. The pH of the solution was monitored until metastable equilibrium was attained (in less than 30 min in all cases). Separate checks were made of the nature of the precipitates obtained by filtering off samples, washing them in turn with ice-cold water, then acetone, and air-drying. In all cases, the sole species present was wroewolfeite, as determined by powder XRD measurements. It is emphasized that the temperature must be kept at 0 °C during these procedures. Even at 4 °C, mixtures of wroewolfeite and posnjakite are obtained. However, the transformation of wroewolfeite to posnjakite and ultimately brochantite at 0 °C is very slow; material kept at 0 °C in contact with reaction solutions during one week showed no sign of the presence of any other solid phase.

Total solution concentrations of Cu^{2+} , Na^+ , and SO_4^{2-} were calculated from the known volumes and concentrations of reagents used and the stoichiometry of the precipitation, $\text{Cu}^{2+}(\text{aq}) + 0.25\text{SO}_4^{2-}(\text{aq}) + 1.5\text{OH}^-(\text{aq}) + 0.5\text{H}_2\text{O} \rightleftharpoons 0.25\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot 2\text{H}_2\text{O}(\text{s})$. Values of total solution concentrations and metastable equilibrium pH are listed in Table 1. Species distributions for each experiment were calculated with the program COMICS [15]. Stability constants for CuSO_4° and $\text{Cu}_2(\text{OH})_2^{2+}$

at 0 °C were calculated from the data of Smith and Martell [16]. Those used for HSO_4^- , NaSO_4^- , CuOH^+ , Cu(OH)_2^0 , Cu(OH)_3^- , and Cu(OH)_4^{2-} at 0 °C were taken from van der Lee and Lomenech [17]. The extended Davies equation $\lg \gamma = -0.4883z_i^2[I^{1/2}/(1+I^{1/2}) - 0.3I]$, where the symbols have their usual meaning, was used to correct for ionic strength, together with a value of $\lg K_w$ of -14.94 [18]. Cycles of COMICS calculations were performed with the ionic strength from the calculated species distribution being used to refine the stability constants, until the calculations converged. At this stage, the calculated free ionic concentrations of $\text{Cu}^{2+}(\text{aq})$ and $\text{SO}_4^{2-}(\text{aq})$ and the pH of each solution were used to calculate an equilibrium constant for the equation $\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot 2\text{H}_2\text{O}(\text{s}) + 6\text{H}^+ \rightleftharpoons 4\text{Cu}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) + 8\text{H}_2\text{O}(\text{l})$, with appropriate γ values again being derived from the extended Davies equation.

Table 1 Total solution concentrations (M) and metastable pH values (± 0.005) for titrations of aqueous $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ with aqueous NaOH at 0 °C.

pH	$10^2[\text{Cu}^{2+}]_T$	$10^2[\text{Na}^{2+}]_T$	$10^2[\text{SO}_4^{2-}]_T$
5.832	2.883	4.326	5.046
5.865	2.126	4.786	4.519
5.954	1.479	5.180	4.069
6.087	0.919	5.520	3.679
6.178	0.430	5.817	3.339

RESULTS AND DISCUSSION

Table 2 lists values of the free ionic concentrations of Cu^{2+} and SO_4^{2-} , and pH, I , and γ values for solutions in metastable equilibrium with wroewolfeite at 0 °C. Also listed are values of $\lg K$ for reaction 1. The average value of $\lg K$ is 24.3 ± 0.6 . From this value and that of K_w at 0 °C [18], $\lg K$ with respect to eq. 2 is -16.3 ± 0.2 ; the quoted error does not include that for K_w as the latter is negligible compared with that of the solubility constant and does not change the overall uncertainty to any significant extent. This value may be used to compare the relative stabilities of the minerals of stoichiometry $\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot n\text{H}_2\text{O}$ ($n = 0, 1, 2$).

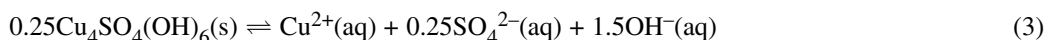
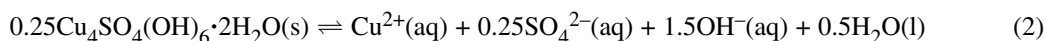
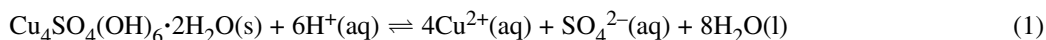


Table 2 Equilibrium solution concentrations (M), pH values (± 0.005) and calculated quantities for solutions in metastable equilibrium with wroewolfeite at 0 °C.

pH	$10^2[\text{Cu}^{2+}]$	$10^2[\text{SO}_4^{2-}]$	I	$\gamma^{2\pm}$	$\lg K^a$
5.832	2.311	4.329	0.158	0.344	24.77
5.865	1.725	3.918	0.143	0.353	24.48
5.954	1.201	3.553	0.122	0.367	24.32
6.087	0.744	3.245	0.109	0.380	24.42
6.178	0.354	2.974	0.097	0.393	23.71

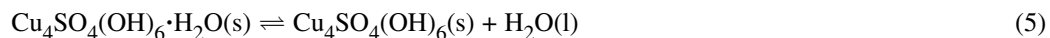
^aEq. 1, $I = 0$. $\gamma^{2\pm}$ is the activity coefficient used for divalent cations and anions.

For brochantite, Smith and Martell [16] give $\lg K = -17.16 \pm 0.04$ (25 °C, $I = 0$) for eq. 3. Original data are from Barton and Bethke [5], who give $\Delta_f G^\circ$ (25 °C, brochantite) = $-1817.1 \text{ kJ mol}^{-1}$ and $\Delta_f H^\circ$

(25 °C, brochantite) = $-2198.3 \text{ kJ mol}^{-1}$. Other data in the literature for brochantite are tightly grouped. The results of Marani et al. [3] give a value for (3) of $\lg K = -17.3$ (25 °C, $I = 0$). This is in good agreement with the data of Smith and Martell [16] and Barton and Bethke [5]. Other data for $\Delta_f G^\circ$ (25 °C, brochantite) are -1817.9 , -1818.0 , -1817.7 and $-1818.4 \text{ kJ mol}^{-1}$ [19,20,21,3, respectively]. The critical compilation by Robie and Hemingway [20] lists an error in $\Delta_f G^\circ$ of $\pm 2.5 \text{ kJ mol}^{-1}$, and is in fact based on the experimental work of Barton and Bethke [5]. This translates to an error in the $\lg K$ value of Smith and Martell [16] of ± 0.1 . Data of Barton and Bethke [5], in conjunction with $\Delta_f H^\circ$ values of Robie and Hemingway [20], give $\lg K = -17.84$ (0 °C, $I = 0$) for eq. 3, assuming $\Delta C_p = 0$. It is difficult to assign an error to this value, despite the high precision quoted by Smith and Martell [16].

The mistaken attribution of the stoichiometries $\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot \text{H}_2\text{O}$ and $\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot 1.3\text{H}_2\text{O}$ to langite that appear in the literature is understandable in the light of a series of structural and other studies. The original single-crystal X-ray structure [22] was based on photographic data of low precision and two-dimensional Fourier syntheses. It mis-attributed an OH^- group to an H_2O site and failed to locate a further OH^- group coordinated to a copper ion. Early analyses of langite [23] indicated approximately 1 molecule of water per formula unit, but later work indicated the composition to be $\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot 2\text{H}_2\text{O}$ [24,25]. The definitive single-crystal structure of Gentsch and Weber [26] confirmed the dihydrate formulation. One water molecule lies between sheets of composition $\infty^2[\text{Cu}_4(\text{OH})_6(\text{H}_2\text{O})\text{O}]$ (the same structural unit as found in posnjakite) and is connected to the lattice solely by hydrogen bonds. If this water is somewhat "zeolitic" in nature, low analytical values for contained water might be expected. Wagman et al. [21] quote $\Delta_f G^\circ$ (25 °C, langite) = $-2044.0 \text{ kJ mol}^{-1}$ and $\Delta_f H^\circ$ (25 °C, langite) = $-2485 \text{ kJ mol}^{-1}$, but give the formula as $\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot \text{H}_2\text{O}$. Assuming that the data refer to langite, these values should be amended to -2281.1 and $-2770.8 \text{ kJ mol}^{-1}$, respectively, for the dihydrate formulation. Using the same approach as above for brochantite, $\lg K(0 \text{ °C}, I = 0)$ equals -17.3 for eq. 2. However, these data are derived from the work of Silman [6]. Marani et al. [3] point out that the material used in the experiments was in fact posnjakite. It is not surprising to discover other thermodynamic data for what is supposed to be langite in the literature with other attributed stoichiometries. Values for $\Delta_f G^\circ$ of -1930.9 and $-2115.0 \text{ kJ mol}^{-1}$ at 25 °C are listed by Naumov et al. [19] and Silman [6], respectively, for $\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot 1.3\text{H}_2\text{O}$. Correction of these values to those of the true formula give -2096.9 and $-2281.0 \text{ kJ mol}^{-1}$, respectively. The latter is equal, within error, to that calculated above for other data listed by Silman [6]; the former value is not consistent with any other calculations and has not been considered further.

Alwan and Williams [27] give $\lg K(25 \text{ °C}) = -17.3(2)$ for langite with respect to eq. 2, for a series of determinations at 14 °C (8 samples) and 30 °C (1 sample) involving natural solutions in contact with authentic langite from the South Crofty and Wheal Pendarves mines, Cornwall, UK. They assumed the monohydrate stoichiometry on the basis of the then-accepted formulation, but powder XRD data established that the mineral is truly langite. Since no dependence of $\lg K$ was noted for the two temperatures, $\lg K$ at 0 °C is estimated to have the same value.



As far as posnjakite is concerned, the data of Marani et al. [3] can be used to derive a value for eq. 4 of $\lg K = -16.7$ (25 °C, $I = 0$). Thus, at 25 °C for eq. 5, $\Delta_f G^\circ = -12.8 \text{ kJ mol}^{-1}$, a value consistent with the observed thermodynamic stability of brochantite with respect to posnjakite at this temperature. Marani et al. [3] noted that Silman [6] gave a value for the dehydration of langite (as a monohydrate) to brochantite of $-11.7 \text{ kJ mol}^{-1}$, but that the material used in the experiments was actually posnjakite. In this light, the data of Marani et al. [3] and Silman [6] are in good agreement. No data exist for posnjakite at 0 °C, but an estimate can be made assuming that $\Delta_f H^\circ$ for eqs. 3 and 4 are the same and $\Delta C_p = 0$. This gives a value of $\lg K = -17.4$ at $I = 0$ and 0 °C for eq. 4, a result that is quite consistent with that

derived from the data of Silman [6] and Wagman et al. [21]. A summary of the relative stabilities of the minerals of stoichiometry $\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot n\text{H}_2\text{O}$ ($n = 0, 1, 2$) is given in Table 3.

Table 3 Stabilities^a of the $\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot n\text{H}_2\text{O}$ minerals at 0 °C, $I = 0$.

Mineral	lg K^a	References
Brochantite	-17.8 ± 0.3^b	[5,16,20]
Posnjakite	-17.3	[6,21]
	-17.4	[3]
Langite	-17.3(2)	[27]
Wroewolfeite	-16.3 ± 0.2	this work

^aFor the equation $0.25\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot n\text{H}_2\text{O}(\text{s}) = \text{Cu}^{2+}(\text{aq}) + 0.25\text{SO}_4^{2-}(\text{aq}) + 1.5\text{OH}^-(\text{aq}) + 0.25n\text{H}_2\text{O}(\text{l})$; errors associated with K_w are not included.

^bThree times the error associated with lg K_{sp} for brochantite at 25 °C.

The data of Table 3 indicate that for compounds of stoichiometry $\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot n\text{H}_2\text{O}$ ($n = 0, 1, 2$), brochantite is the thermodynamically stable phase at 0 °C; other experiments show that this holds true for all temperatures up to ambient. Wroewolfeite is the least stable phase at 0 °C. It is possible to isolate pure wroewolfeite by reaction of aqueous NaOH with aqueous $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ solutions at 0 °C, but at 4 °C and higher mixtures of wroewolfeite and posnjakite are obtained. Between about 10 and 25 °C, no wroewolfeite could be isolated but presumably would have been present transiently in the reaction mixture. At these temperatures, posnjakite is obtained first and then slowly transforms to brochantite if kept in contact with the reaction solution as long as the latter is not too basic. At pH values higher than that of the 3:2 end-point, decomposition to poorly crystalline tenorite (CuO) takes place. These observations are manifestations of the Ostwald step rule [28,29], and the complex Ostwald cascade found is wroewolfeite \rightarrow posnjakite \rightarrow brochantite.

Just what serves to stabilize any particular phase in the natural environment is somewhat of an enigma. Nucleation and growth of the hydrated phases at temperatures less than 25 °C, followed by removal of the aqueous solutions responsible would serve to preserve the metastable phases. Dry solids can be stored indefinitely, and, of course, the minerals are present in significant quantities in many deposits [1]. Alternatively, since natural mineralizing solutions are chemically more complex than those used in the syntheses, certain dissolved species may serve to either selectively promote the nucleation of one phase, or to inhibit the growth of another. Just what species these are and what their role might be remains speculative. However, we have carried out experiments analogous to those outlined above, in which aqueous (0.1 M CuSO_4 + 1.0 M MgSO_4) was titrated with 0.1 M NaOH to the 2:3 end-point. Under these conditions, it is remarkable that no wroewolfeite was detected at any temperature down to 0 °C. Either the $\text{Mg}^{2+}(\text{aq})$ ion promotes the nucleation of posnjakite, or inhibits the nucleation of wroewolfeite. Parallel experiments using added Na_2SO_4 did not show the same effect, ruling out the possibility that higher sulfate concentrations were responsible.

A related possibility, given the fact that stability constants for several of the hydrated basic copper(II) sulfates based on the brochantite stoichiometry and brochantite are of similar magnitude, is that small amounts of foreign ions substituted in the lattice may cause one or other of the hydrates to become thermodynamically stable with respect to others at a given temperature. This is not, however, suggested by an examination of the literature. Analyses of posnjakite and wroewolfeite given in their original descriptions are close to stoichiometric, with no mention of trace or other levels of substituents [7,30]. Anthony et al. [1] give analytical data for posnjakite from another Russian locality; it contained (wt %) Fe_2O_3 , 0.38; CaO, 0.34; MgO, 0.05. Analyses of langite [1,23] correspond reasonably to the sto-

ichiometrically pure composition except for one which lists (wt %) CaO, 0.83; MgO, 0.29. It is unlikely that Ca^{2+} would occupy Jahn–Teller distorted Cu^{2+} sites in the structures, and the above-mentioned Fe_2O_3 value may be due to small amounts of goethite or hematite present in the matrix of the specimen. In any case, negligible substitution in the lattices is evident from published analyses and single-crystal X-ray structure determinations of brochantite [31], posnjakite [32], langite [26], and wroewolfeite [33] give no hint of any irregularity at any crystallographic Cu(II) site.

Langite was not identified in any experiment using the reaction conditions reported above. This must be due to reasons akin to those given above. Finally, in this connection, it is noted that langite can reportedly be made by reaction of aqueous copper sulfate solutions with aqueous potassium hydroxide solutions [23]. This would be feasible if the K^+ ion stabilizes the langite lattice via substitution, promotes the preferential nucleation of langite, or inhibits the nucleation of other hydrates in a way that the Na^+ ion does not. However, we have carried out a series of experiments as outlined above using KOH instead of NaOH and exactly the same sequence of stabilities was obtained. The early report (1862) noted by Palache et al. [23] is perhaps not all too surprising in that at the time the separate identities of posnjakite and wroewolfeite were unknown [7,30].

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