# Chemical studies on the stabilities of boleite and pseudoboleite

FAWZY A. ABDUL-SAMAD, D. ALUN HUMPHRIES, JOHN H. THOMAS, AND PETER A. WILLIAMS

Department of Chemistry, University College, Cardiff, CF1 1XL

## SYNOPSIS

FREE energies of formation of boleite, $Pb_{26}Cu_{24}$ $Ag_9Cl_{62}(OH)_{47} \cdot H_2O$, and pseudoboleite, $Pb_5Cu_4$ $Cl_{10}(OH)_8 \cdot 2H_2O$, have been determined from solution studies at 298.2 K. $\Delta G_f^0$ values for the minerals are $-19097.9 \pm 4.1$ and $-3705.4 \pm 5.5$ kJ mol$^{-1}$ respectively. These values, together with results of earlier studies (Humphreys et al., 1980) have been used to construct the stability field diagram shown in fig. 1. The boundaries for boleite and pseudoboleite are shown separately. If fields
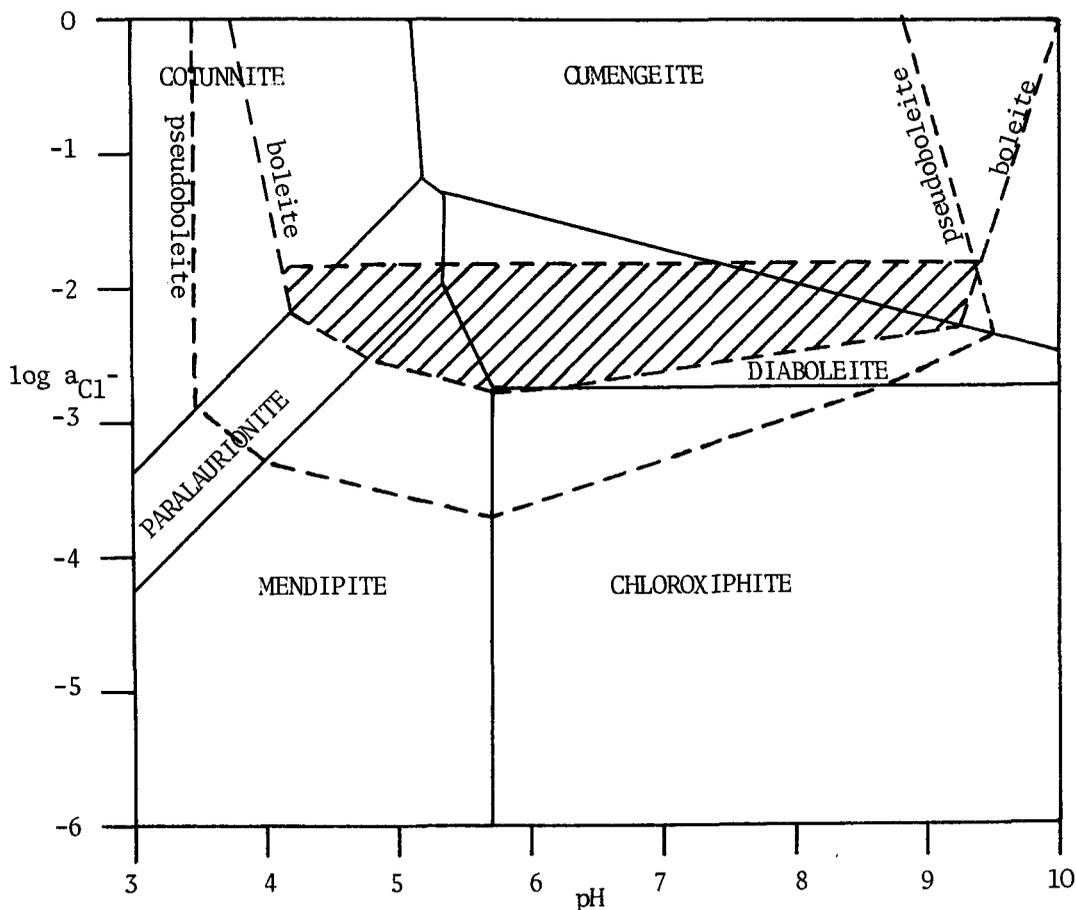


FIG. 1. Stability field diagram for the lead- and copper-chloride minerals. Boundaries are calculated for $a_{Cu^{2+}}$ and $a_{Ag^+}$ equal to $10^{-6}$ and $10^{-8}$ mol dm$^{-3}$ respectively. The boundaries for pseudoboleite and boleite are plotted separately as dashed lines. The hatched area indicates the range of conditions under which boleite may form metastably with respect to pseudoboleite. This field is bounded by the line above which chlorargyrite, AgCl, precipitates.

for the two minerals are plotted together, boleite has no thermodynamic stability at the silver ion activity chosen. At higher activities of $Ag^+_{(aq)}$ the boleite field is negligible in extent.

The results can, however, be rationalized in terms of kinetics of mineral formation, rather than thermodynamic considerations alone. Since pseudoboleite is never found *without* boleite upon which it is observed to grow epitaxially (Winchell, 1963), it is clear that boleite must form metastably prior to any pseudoboleite deposition. Accordingly, boleite has a large range of solution compositions, from which it may precipitate. The hatched area of fig. 1 shows this at the $Cu^{2+}_{(aq)}$ and $Ag^+_{(aq)}$, activities chosen. The field is terminated at high $a_{Cl^-}$ by the AgCl line, above which silver is precipitated as $AgCl_{(s)}$, chlorargyrite.

It is also evident from the chemical studies that the deposition of several assemblages in the lead-copper-chloride group of minerals is simply related to variations of chloride activity. With decreasing $a_{Cl^-}$ the associations cumengeite + boleite + pseudoboleite, diaboleite + boleite + pseudoboleite, and diaboleite + chloroxiphite are expected in turn. This relationship is apparently borne out by field observations of occurrences of the minerals.

## REFERENCES

Humphreys, D. A., Thomas, J. H., Williams, P. A., and Symes, R. F. (1980). *Mineral. Mag.* **43**, 901-4.
Winchell, R. E. (1963). Thesis, Ohio State University.

CHEMICAL STUDIES ON THE STABILITIES OF
BOLEITE AND PSEUDOBOLEITE

Fawzy A. Abdul-Samad, D. Alun Humphreys, John H. Thomas and Peter A. Williams.

Department of Chemistry, University College, Cardiff, CF1 1XL.

We have previously reported on the stabilities of some complex lead (II) and copper (II) halide minerals (Humphreys et al., 1980) and here we present data on boleite, $Pb_{26}Cu_{24}Ag_9Cl_{62}(OH)_{47}.H_2O$, cumengeite, $Pb_{19}Cu_{24}Cl_{42}(OH)_{44}$, and pseudoboleite, $Pb_5Cu_4Cl_{10}(OH)_8.\beta H_2O$. Pseudoboleite occurs only as epitaxial overgrowths on boleite (Winchell, 1963), and for some time it was doubted that these two were distinct species. Cumengeite has only been found in deposits associated with high contents of halite and it appears that this compound only forms from aqueous oxidizing solutions when the activity of chloride ion, $a_{Cl^-}$, is high (Wilson and Rocha, 1955; Winchell and Rouse, 1974). We have been engaged in a programme of studies, the object of which is to elucidate the mode of formation of these and related minerals from aqueous solution, and the kinds of pathways via which they may transform one into another. Here we present results concerning the chemical stabilities of boleite and pseudoboleite, and comment on the apparently simple relationship between chloride ion concentration and associations of particular members of the lead (II)- copper(II)-chloride group which are observed in the field.

Boleite single crystals from the Amelia mine, Boleo, Baja California, were purchased from the Mineralogical Research Co., San Jose, California. The crystals were shaved to remove any surface pseudoboleite, the absence of which was confirmed by X-ray powder studies. Pseudoboleite, admixed with cotunnite, was synthesised according to the evaporation method (Winchell, 1963). Solutions used in the synthesis were slowly evaporated to dryness so that the cotunnite grew in crystals up to 8mm in length. These could easily be removed by hand picking and a sample of pseudoboleite was obtained which was free from cotunnite, and any other phase, as far as could be ascertained by X-ray powder studies.

The procedures used to obtain solubility products and thus values of $\Delta G^o_f$ for the minerals have been described elsewhere (Alwan and Williams, 1979). Full lists of species calculated in equilibrium with the solid phases at 298.2K are available from the authors on request. Values of $\Delta G^o_f$ of -3705.4 ± 5.5 and -19097.9 ± 4.1 kJ mol $^{-1}$ were calculated for pseudoboleite and boleite respectively. The stoichiometric formula $Pb_5Cu_4Cl_{10}(OH)_8.2H_2O$ (Winchell and Rouse, 1974) for pseudoboleite was adopted, though a single crystal study of the compound has not yet been reported. Any minor change in the stoichiometric ratios of the constituent ions in the compound, however, will have little bearing on the free energy value or the conclusions reached in this paper because of the logarithmic relationship between the equilibrium constant for dissolution of the solid and the free energy of this process. The crystal structure of boleite has been reported (Rouse, 1973), and warrants some comment. It is found to crystallise in space group $\underline{Pm3m}$ with $\underline{a}$ = 15.29 $\overset{o}{A}$, $\underline{Z}$ = 1, and with all atoms occupying special positions. In the report of the structure the stoichiometry $Pb_{26}Cu_{24}Ag_9Cl_{62}(OH)_{48}$ was given. With Pb, Cu and Ag in their usual di-, di-,and monovalent oxidation states respectively, this formulation has one excess negative charge per formula unit. Accordingly, we have revised the formula to $Pb_{26}Cu_{24}Ag_9Cl_{62}(OH)_{47}.H_2O$, implying a single proton disordered over the whole unit cell, and base our calculations on this new formula.

Figure 1 shows fields of stability of a series of halide minerals including cotunnite, $PbCl_2$, paralaurionite, $PbOHCl$, mendipite, $Pb_3O_2Cl_2$, diaboleite, $Pb_2CuCl_2(OH)_4$, and chloroxiphite, $Pb_3CuCl_2(OH)_2O_2$, taken from previous workers (Humphreys et al., 1980). Superimposed on this diagram, separately, are those fields occupied by boleite and pseudoboleite. Values chosen for $a_{Cu^{2+}}$ and $Cl_{Ag^+}$ are $10^{-6}$ and $10^{-8}$ mol dm$^{-3}$ respectively. Also shown on the diagram is the boundary above which chlorargyrite, AgCl, will precipitate at this silver activity, calculated on the basis of well-established thermodynamic data (Robie et al., 1978).

The reason for choosing to represent the results in this fashion is that the formation of pseudoboleite and boleite is kinetically controlled. The thermodynamic stability fields of all of the minerals taken together are plotted on Figure 2, for $a_{Ag^+}$ = $10^{-8}$ mol dm$^{-3}$ and a range of $Cu^{2+}_{(aq)}$ activities. At this activity of $Ag^+_{(aq)}$ the stability field of boleite is considerably smaller than that of pseudoboleite, and lies above the chlorargyrite boundary no matter how $a_{Cu^{2+}}$ varies. Thus, thermodynamically, under these conditions boleite can never form.

It is of interest then to calculate how variations of silver ion activity alters the relationship between the boleite stability field and the precipitation boundary of chlorargyrite. This relationship, with reference to the wedge-shaped boleite field and the chlorargyrite line is shown in Figure 3, calculated for $a_{Cu^{2+}}$ = $10^{-6}$ mol dm$^{-3}$. At an $a_{Ag^+}$ = $10^{-6}$ mol dm$^{-3}$, the solution conditions under which boleite is thermodynamically stable are almost vanishingly small. Indeed, with silver activities of the order of 1 mol dm$^{-3}$ the boleite field is still very restricted. Of course such silver concentrations never obtain in natural waters, not even in the rather special circumstance of an oxidizing argentiferous sulphide orebody.
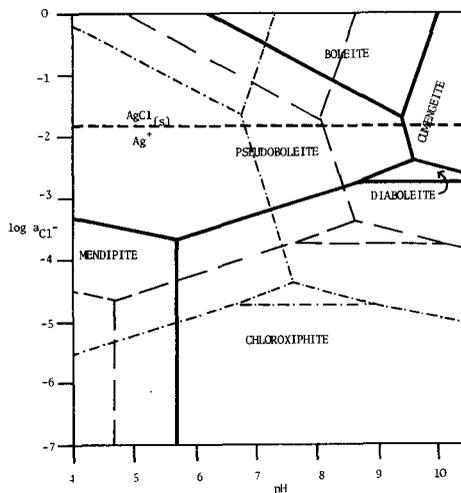


FIG. 2. Thermodynamic stability fields for the minerals. The bold lines indicate the extents of the fields calculated at $a_{Ag^+}$ = $10^{-8}$ mol dm$^{-3}$ and $a_{Cu^{2+}}$ = $10^{-8}$ mol dm$^{-3}$. The Ag$^+$ - AgCl boundary at this $a_{Ag^+}$ is denoted by short, firm dashes. How the fields are changed by increasing $a_{Cu^{2+}}$ is shown for $a_{Cu^{2+}}$ = $10^{-6}$ mol dm$^{-3}$ (— —) and $a_{Cu^{2+}}$ = $10^{-4}$ mol dm$^{-3}$ (— . — . —).

An explanation for this apparent anomaly is to be found in field observations on the occurrence of pseudoboleite. This mineral, as is noted above, is always found growing epitaxially on boleite. It has never yet been observed altering from cotunnite, laurionite, paralaurionite, mendipite, chloroxiphite, diaboleite or cumengeite, although all of these species share a thermodynamic boundary with pseudoboleite. These facts indicate that pseudoboleite will not nucleate from naturally occurring aqueous solutions except on boleite, and that therefore its formation is kinetically controlled in that in the absence of silver all of the minerals above excepting boleite will preferentially crystallise from solutions which themselves are supersaturated with respect to pseudoboleite.

Once this is realised it is a simple matter to demonstrate that at low silver ion activities boleite has a large field of metastability which lies below the chlorargyrite boundary. Ignoring the pseudoboleite field shown in Figure 1, for the solution concentrations of $Cu^{2+}_{(aq)}$ and $Ag^{+}_{(aq)}$, the shaded area shows the range of pH and $a_{Cl^-}$ values which will give rise to the crystallization of boleite. Only after this has occurred can the thermodynamic constraints be satisfied, and pseudoboleite deposit.

These conclusions case some light on the known associations of the lead-copper-chloride suite of minerals, and on the chemistry of the solutions responsible for their formation. At an $a_{Cu^{2+}} \doteq 10^{-6}$ mol dm$^{-3}$ and a normal pH range of from 6 to 8, variation of chloride ion activity can give rise to different groups of associates. For $a_{Cl^-} \doteq 10^{-2}$ mol dm$^{-3}$ diaboleite and chloroxiphite are stable, whereas when $10^{-2.75} < a_{Cl^-} < 10^{-1.25}$ diaboleite alone will form. At higher chloride ion activities diaboleite and cumengeite can be associated. Introduction of silver to the mineralizing solutions in the middle chloride range will give rise to a diaboleite + boleite + pseudoboleite assemblage. If the chloride activity is high, then the cumengeite + boleite + pseudoboleite suite will be formed.

Such assemblages have been reported. Cumengeite, boleite and pseudoboleite are found in the oxidized ores of the copper deposits of the Boleo district, Mexico (Wilson and Rocha, 1955; Winchell and Rouse, 1974). No diaboleite has been reported from this locality. In the Mammoth - St. Anthony mine, Tiger, Arizona, diaboleite, boleite and pseudoboleite are found, but not cumengeite (Anthony et al., 1977; Bideaux, 1980). In the Mendip Hills, Somerset, England, chloroxiphite and diaboleite are found intimately associated (Symes and Embrey, 1977; Spencer and Mountain, 1923), together with paralaurionite and mendipite, but with no other lead- and copper-containing halide minerals. It seems therefore probable that the mineral occurrences reflect the chloride concentrations of the solutions responsible for their deposition in the manner described above.

The authors wish to thank John Anthony and Arthur Roe of the Department of Geosciences, University of Arizona, Richard Bideaux, Tucson, Arizona, Peter Embrey and Bob Symes, Department of Mineralogy, British Museum (Natural History) and Sid Williams, Phelps Dodge Corporation, Douglas, Arizona, for their helpful discussion and encouragement during the course of this work. Thanks are also due to the above, and Bill Panczner of the Arizona-Sonora Desert Museum for permission to examine their respective collections from the Mendips, Boleo and Tiger.
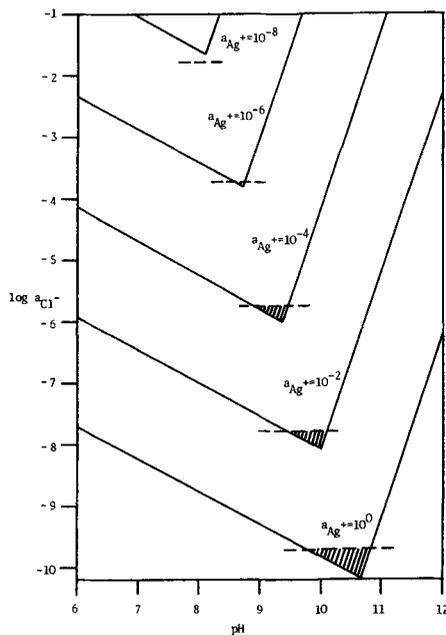


FIG 3. Areas of thermodynamic stability of boleite (**hatched**) at $a_{Cu^{2+}} = 10^{-6}$ mol dm$^{-3}$ and $a_{Ag^+}$ as marked. Fields are bounded by others of pseudoboleite and cumengeite (firm lines), and the AgCl precipitation limit (dashed line).

REFERENCES

Alwan (A. K.) and Williams (P.A.) 1979. Transition Metal Chem. **4**, 128-32
Anthony (J. W.), Williams (S. A.), and Bideaux (R. A.) 1977. Mineralogy of Arizona, University of Arizona.
Bideaux (R. A.) 1980. Mineral. Rec. **11** , 155 - 81.
Humphreys (D. A.), Thomas (J. H.), Williams (P. A.) and Symes (R. F.) 1980. Mineral.Mag. **43**, 901 - 4.
Robie (R. A.), Hemingway (B.S.) and Fisher (J. R.) 1978. U.S.G.S. Bull. 1452.
Rouse (R.C.) 1973. J.Solid State Chem. **6**, 86-92.
Spencer (L.J.) and Mountain (E.D.) 1923. Mineral.Mag., **20**, 67-92.
Symes (R.F.) and Embrey (P.G.) 1977. Mineral.Rec. **8**, 298-303.
Wilson (I.F.) and Rocha (V.S.) 1955. Prof.Paper U.S.G.S. 273.
Winchell (R.E.) 1963. Thesis, Ohio State University
Winchell (R.E.) and Rouse (R.C.) 1974. Mineral.Rec. **5**, 280-7.