The Cu–Bi–S system: results from low-temperature experiments

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Abstract

Low-temperature experiments in the 'dry' ternary Cu–Bi–S system, conducted by using sulphidation methods down to 120°C produced a new metastable solid solution series $Cu_{10}Bi_2S_{13}$–$Cu_5Bi_2S_8$ at 178°C, coexisting with CuS. This transformed slowly at 190–200°C to an assemblage of either CuS–$(Cu,Bi)_8S_9$ or CuS–Bi_2S_3 or both, depending on available sulphur. Sulphidation experiments on Cu_3BiS_3 similarly revealed a solid solution range for the phase $(Cu,Bi)_8S_9$ of up to Cu/Bi = 3/2 at 178–190°C, and a lower stability limit of 138°C. Isothermal sections of the system were constructed at 200 and 300°C, based on the new information collected but excluding the metastable series.

KEYWORDS: Cu–Bi–S system, wittichenite, cuprobismutite, emplectite, hodrushite, low-temperature experiments.

Introduction

THE Cu–Bi–S system, an essential part of several multicomponent sulphosalt systems, contains four mineral species: wittichenite, cuprobismutite, emplectite and hodrushite. Of these, wittichenite and emplectite are known to have stability ranges extending from higher temperatures down to below 200°C, whereas hodrushite probably occurs only at very low temperatures. Their paragenetic relations, despite several detailed experimental studies (Buhlmann, 1965, 1971; Sugaki and Shima, 1971; Sugaki, 1972; Chen and Chang, 1974; Sugaki *et al.*, 1978), remain obscure. Sluggish reaction rates, particularly in runs where no valence changes are involved, commonly result in non-equilibrium assemblages at the run temperatures. Accelerated reaction rates obtained for certain preferred reactant pairs, however, led unexpectedly to equilibrium or near-equilibrium conditions in relatively short periods, even at 200°C. The reactant pair Bi_2S_3–metallic-Cu yielded, for example, useful data for the Cu_2S–Bi_2S_3 join (Wang, 1989). Due to its affinity for sulphur, metallic Cu is readily sulphidized to univalent Cu^+, whereas part of the trivalent Bi^{3+} component is simultaneously reduced to the metallic state, at temperatures near to 200°C. A second simple experimental approach, which proved to be more fruitful, involved the sulphidation of the intermediate, mostly metal-rich products (Wang, 1982, 1984, 1988). A combination of these two processes yielded paragenetic information for the system at temperature ranges otherwise inaccessible through experiments in the dry system.

Sulphidation of the hexagonal Cu_2S series

The high-temperature hexagonal Cu_2S solid solution series on the Cu_2S–Bi_2S_3 join, as investigated by Buhlmann (1965, 1971), Sugaki and Shima (1972) and by Mariolacos (1980), was redetermined to cover a homogeneous Cu/Bi range from 12/1 to about 5/1 at 500°C. The sulphidation products of this series obtained overnight at 178°C consisted of a new metastable series on the CuS–Bi_2S_3 join with compositions ranging from $Cu_{10}Bi_2S_{13}$ to $Cu_5Bi_2S_8$, and intergranular CuS. This new series is pleochroic (light grey-yellow) and strongly anisotropic. No characteristic powder diffraction pattern could be isolated from the intense, partially overlapping CuS reflections. Prolonged sulphidation at 178°C and 190°C of the Bi_2S_3-rich partial range produced, in the metastable product, finely exsolved lamellae or myrmekitic intergrowth, similar to those observed following the sulphidation of bornite (Wang, 1984). Re-equilibration of this material at 178, 190 and 200°C, for periods of up to nine months

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led to a final assemblage of either CuS–Bi_2S_3, or CuS–$(Cu,Bi)_8S_9$ or both, depending on the amount or sulphur available. The sulphidation product of the Cu_2S-rich partial range, however, remained usually free from the exsolution product even at 230°C. At 250°C, the complete transition series broke down to the equilibrium assemblage CuS, $(Cu,Bi)_8S_9$, and sulphur.

The composition and stability range of the $(Cu,Bi)_8S_9$ series

This sulphur-rich ternary phase, with a currently accepted formula $Cu_4Bi_4S_9$, was obtained above 300°C from reaction of $2CuS + Cu_2S + 2Bi_2S_3$ or from sulphidation of presynthesized $CuBiS_2$. It was found to coexist with CuS in the sulphidation product of Cu_3BiS_3 even at 138°C. Reported metal/sulphur ratios include 6/7 (Sugaki and Shima, 1971; Godovikov *et al.*, 1972), 16/19 (Buhlmann, 1965; Sugaki and Shima, 1972) and 8/9 (Tekeuchi and Ozawa, 1975). Detailed synthesis over the temperature range 120–500°C confirmed the temperature dependence of this ratio. At 300°C and lower temperatures, $Cu_4Bi_4S_9$ and other sulphur-rich members were stable. With increasing temperature, this phase became metal-enriched with respect to the stoichiometric 8/9 formula. In the structure work of Tekeuchi and Ozawa (1975), the analysed mean composition of the material used, $Cu_{4.2}Bi_{3.76}S_9$, deviates considerably from the theoretical formula. At least part of the material is expected to be more Cu-rich than the mean composition.

Some selected sulphidation experiments were conducted to determine this Cu-rich range. A mixture of wittichenite and cuprobismutite (initial bulk composition $3Cu_2S{\cdot}2Bi_2S_3$) was sulphidized to $Cu_3Bi_2S_6$ at 190°C which produced, in six months, an assemblage with $(Cu,Bi)_8S_9$, Bi_2S_3 and a trace of CuS. Microprobe analysis of the main product indicated a Cu/Bi ratio of 3/2. A second sulphidation experiment, performed independently on homogeneous Cu_3BiS_3 at 180°C for eight months, yielded for the main product a spectrum of compositions with a Cu/Bi ratio extending even beyond the 3/2 limit. Although still without equilibrium, this result demonstrated the credible existence of a solid solution range for the $(Cu,Bi)_8S_9$ series at least to Cu/Bi = 3/2 at 180–190°C. Further heating of the run product at 300°C led to the disappearance of the coexisting Bi_2S_3, the segregation of liquid sulphur, and the gradual breakdown of the Cu-rich partial range of the series, as reflected by the increasing amount of coexisting CuS. In marked contrast to these runs, similar sulphidation at 145°C gave only compositions close to $Cu_4Bi_4S_9$ and coexisting CuS. This analysed 3/2 ratio corresponds to the fictitious metallic composition of the discredited mineral species 'klaprothite' on the Cu_2S–Bi_2S_3 join (Nuffield, 1947; Springer and Demirsoy,1969; Buhlmann, 1971; Sugaki and Shima, 1971; Bente *et al.*, 1977). The analytical result, however, does not provide a conclusive link between the phase $(Cu,Bi)_8S_9$ and the name klaprothite. The inconsistency in the sulphur/metal ratio and the lack of other convincing data preclude, at the present stage, a correlation of the two. 'Klaprothite' or the slightly more anisotropic 'emplectite' from the 'type locality', Wittichen, must be re-investigated as regards its chemical composition and powder pattern before a correlation can be speculated. The synthetic series $(Cu,Bi)_8S_9$, despite its stability only under relatively high sulphur fugacities (Bente, 1986), has a good chance to occur as a mineral in Cu-bearing Bi deposits. Its stability range extends from 138°C to almost 500°C and its tie line to Bi_2S_3 persists up to 420°C, as confirmed from numerous experimental runs in the present study.

Low-temperature phase relations

The information collected for the central part of the system permits the construction of two isothermal sections at 200 and 300°C (Fig. 1).

At 200°C, two ternary phases are stable on the Cu_2S–Bi_2S_3 join: Cu_3BiS_3 (wittichenite) and $CuBiS_2$ (emplectite). Both of them, as well as Cu_2S or its Bi-bearing members, coexist with metallic bismuth, as confirmed by the respective ternary and binary assemblages (Wang, 1989). The metastable series $Cu_{10}Bi_2S_{13}$–$Cu_5Bi_2S_8$ on the CuS–Bi_2S_3 join, was obtained as a primary sulphidation product at 178°C. However, its Bi-rich partial range was found to break down after extended heating at 200°C, whereas the Cu-rich partial range remained unaltered at this temperature. Consequently, all phase assemblages which involve this series were considered to be metastable and not included in the 200°C isotherm.

A second solid-solution series, intermediate to the two joins, $(Cu,Bi)_8S_9$, coexists stably at 200°C with Cu_3BiS_3, $CuBiS_2$ and Bi_2S_3. However, its expected coexistence with liquid sulphur at this temperature is interrupted by the phase assemblage CuS–Bi_2S_3 repeatedly observed at 190–200°C in the final sulphidation products, on and above CuS–Bi_2S_3 join. This CuS–Bi_2S_3 assemblage appears to conflict with the absence of a corresponding natural paragenesis covellite-bismuthinite and it is uncertain if this final sulphidation product represents an equilibrium assemblage or not, at the temperatures concerned. Because of this uncertainly, the observed CuS–Bi_2S_3 tie line is plotted as a dashed line on the 200°C isotherm.

At 300°C, the phases Cu_3BiS_3 and $CuBiS_2$ persist on the Cu_2S–Bi_2S_3 join. The $(Cu,Bi)_8S_9$ series becomes slightly metal-enriched with compositions approaching $Cu_4Bi_4S_9$. Tie lines radiating from this phase to the following six phases were observed: CuS, Cu_3BiS_3, $CuBiS_2$, $CuBi_3S_5$, Bi_2S_3 and sulphur (Fig. 1). The assemblage $Cu_4Bi_4S_9$–Bi_2S_3 remained stable up to 420°C, where it was replaced by the assemblage $CuBi_3S_5$s.s. and liquid sulphur. The new addition $CuBi_3S_5$ at 300°C was detected in various assemblages only above 275°C. The phases cuprobismutite (Wang, 1989) and $Cu_3Bi_5S_9$ on the Cu_2S–Bi_2S_3 join appeared at higher temperatures and, therefore, are not included in the 300°C isotherm.

The X-ray powder pattern of hodrushite (Kodera *et al.*, 1970) bears a striking resemblance to the pattern of cuprobismutite due to their lattice analogy. In the present experiments, however, neither cuprobismutite, nor other similar patterns with comparable *d*-spacings were observed below 300°C along the Cu_2S–Bi_2S_3 join which implicate the existence of the mineral hodrushite. Additional sulphur- or metal-enriched runs also gave negative results. The stable assemblage $CuBiS_2$ (emplectite) + Bi_2S_3 (or $CuBi_3S_5$) + metallic Bi observed between 200 and 300°C practically rule out the expected existence of a ternary hodrushite in this temperature range. The initial analysis of hodrushite (Kodera *et al.*, 1970) contains a maximum of 0.47 wt.% Pb, along with other impurities like Fe and Ag. In a later, more refined analysis (Makovicky and Maclean, 1972), the Pb content was not admitted into the hodrushite formula, $Cu_8Bi_{10}Me_2S_{22}$, because its amount was below the detecting limit. The impurities, inte-

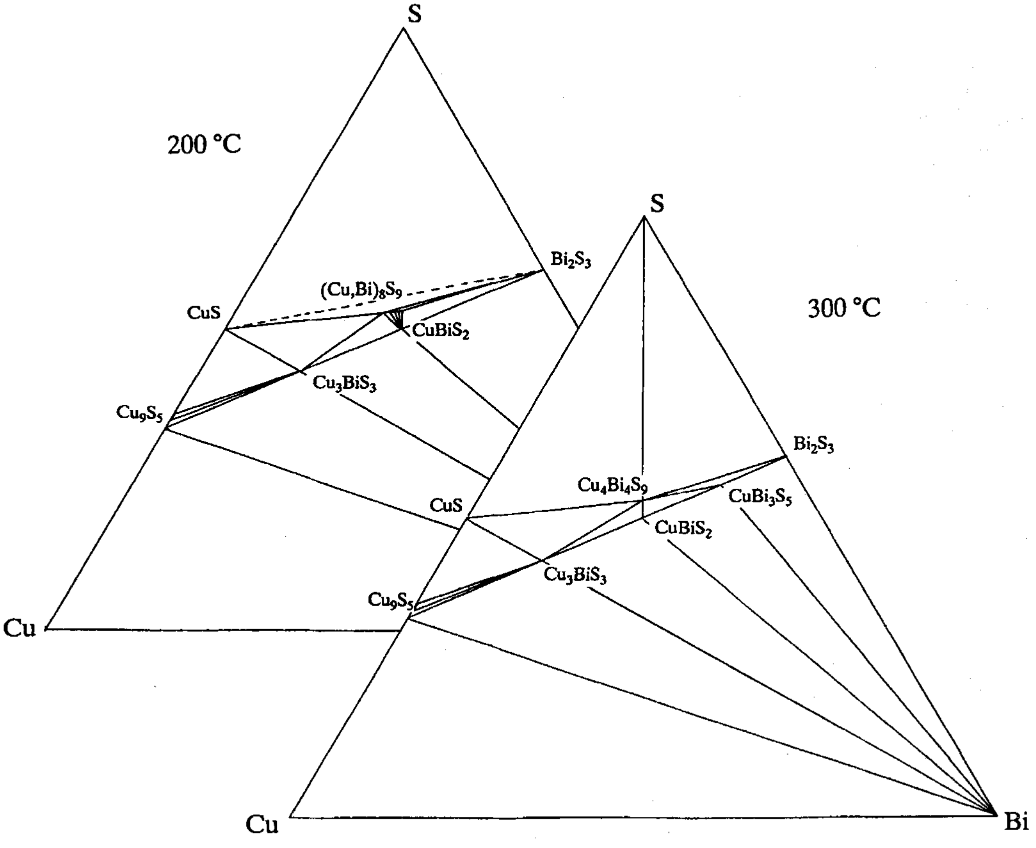

FIG. 1. The ternary isotherms at 200 and 300°C.

grated in the *Me* part of this non-ternary formula, may be conceived as being responsible for the stability of this cuprobismutite-like mineral in the natural environment, and certainly under low temperature conditions.

Pentavalent bismuth

Stable phases or phase assemblages on the Cu_2S–Bi_2S_3 join, like $CuBiS_2$ or $CuBi_3S_5$, are able to take in, at low temperatures (e.g. 145°C), excess amounts of sulphur sufficient to transform their Cu component to a bivalent state, and part of their Bi component to a pentavalent state. Subsequent temperature increases result in the release of the absorbed sulphur under simultaneous reduction of the stable or metastable Bi^{5+} back to the normal trivalent state. X-ray powder diffraction data acquired in association with this valency promotion could not confirm any structure changes from phases containing the normal state Bi^{3+}. In the 200°C isotherm, however, no corresponding solid solution range is plotted which reflects this reversible process. The co-existing pair Bi^{3+}/Bi^{5+}, if properly calibrated against temperature, might conceivably be employed as a measure of sulphur fugacity over low-temperature Bi-bearing assemblages.

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