

ABSTRACT

Phase equilibrium study in the system $\text{Cu}_2\text{S-PbS-Sb}_2\text{S}_3$ has been undertaken by successfully experimenting 99 number of charges in total, at 500, 440 and 300°C. Synthesis of end members and that of sulfosalts, as well as the phase equilibrium experiments were conducted in evacuated silica tubes, aided by halide fluxes when required, in horizontal tube furnaces. Invariance of the run products to melting and then annealing, extra heating, use/nonuse of fluxes proves attainment of equilibrium. The ambient sulfur fugacity of all run products were monitored by the two-pyrrhotite indicator method, which furnished excellent results but with a few exceptions. Phase identification was carried out by optical microscopy and powder X-ray diffraction methods, well supplemented by detailed microprobe analysis.

There are significant modifications in phase relations at 500°C with regard to the position and extent of the Cu_2S and Sb_2S_3 -rich melt fields. Consequently, new tie lines join the Cu_2S -rich melt with bournonite and chalcostibite, and there is effective alteration in the positions of the earlier defined tie lines. The meneghinite field, being narrower and tapering towards its Sb_2S_3 -rich end, leads to important changes in the phase relations in its surrounding region. The phase-Z field, which appears at 440°C, is much smaller and less Cu_2S -rich compared to the same at 400°C of Hoda and Chang (1975). Phase relations at 300°C, although semi-schematic to some extent, provide compelling evidence of instability of meneghinite and phase-Z. In addition, semseyite appears and robinsonite disappears at this temperature. Three new tie lines, i. e., bournonite-boulangerite, bournonite-semseyite and chalcostibite-semseyite are set up. Falkmanite is found to be stable at both 500 and 440°C.

PbS -poor meneghinites do not indicate low crystallinity as previously thought. Solid solubility in meneghinite can be best explained by a substitution scheme of $\text{Pb}^{2+} + \text{Cu}^+ \rightleftharpoons \text{Sb}^{3+}$, as this leads to the least vacancy in Pb-site compared to other schemes. From 500 to 440°C, the meneghinite field becomes narrower by the shift of its Cu_2S -rich boundary towards the Cu_2S -poor boundary, which remains unchanged, and the Sb_2S_3 -rich end moves up towards the PbS -rich end. The Cu_2S -poor boundary moves away from the $\text{PbS-Sb}_2\text{S}_3$ binary with increasing Sb_2S_3 , implying that PbS -poor meneghinites need more and more Cu for their stabilization. While robinsonite has a solid solubility, mainly along the

PbS-Sb₂S₃ binary, zinkenite shows considerable incorporation of Cu at its PbS-rich end. Similar to meneghinite, zinkenite field tapers down towards its Sb₂S₃-rich end. Although famatinite was presumed to be stable at 440° C in one of the earlier runs, its formation being ascribed to the reaction $3\text{CuSbS}_2 + \frac{1}{2}\text{S}_2 = \text{Cu}_3\text{SbS}_4 + \text{Sb}_2\text{S}_3$, later f_{S_2} -imposed experiments confirmed that it cannot be stable in the ambient f_{S_2} condition.

f_{S_2} -monitored experiments show negligible isothermal variation in sulfur fugacity within three-phase fields and decrease in f_{S_2} with decreasing temperature for corresponding assemblages, barring a few exceptions. The minimum f_{S_2} values for some assemblages at 500 and 440° C, according to the formulation of Craig and Barton (1973) compare reasonably well with the corresponding experimentally determined values. Large disagreement between the two is observed in the case of formation of the single sulfosalts, namely, boulangerite, bournonite and skinnerite, for which a simple ideal mechanical mixing model attempted in the present study furnishes reasonably comparable estimates.

Pertinent sulfosalt mineral parageneses from Yellowknife Bay area, Canada; Ilimaussaq, Greenland; Hällefors, Sweden; Pinnacles mine, Broken Hill; Rajpura-Dariba, India and Rujevac, Yugoslavia; represent stable equilibrium assemblages, as implied from the present, as well as the earlier study. However, at Vall de Ribes, Spain, disequilibrium assemblages are prevalent and equilibrium is achieved only in small domains. Compositions of natural meneghinites from a wide variety of ore deposits, exclusively cluster at the PbS-rich boundary of the meneghinite solid solution field. Complete absence of natural Sb₂S₃-rich meneghinites may be explained by nonavailability of a suitably Cu-enriched ore fluid and hence, its incapability to cater for the increasing need for Cu by the same for their stabilization. Compositions of natural robinsonite and zinkenite fall within their respective fields, as determined in the present study. Similarly, compositions of tintinaite coexisting with robinsonite at Tintina, Yukon, coincide with the composition of phase-Z that is stable with robinsonite in the present experimental work. Thus the observation of Moëlo et al. (1984), that tintinaite is the natural analog of phase-Z, is reiterated. The possibility of expansion of the broad PbS-rich end of the meneghinite field at high temperature, and its eventual partial merging with the PbS-Sb₂S₃ binary, provisionally resolve the dispute pertaining to the existence of Cu-free meneghinites.