SOLID SOLUTION IN SYNTHETIC ZINKENITE, ROBINSONITE AND MENEGHINITE IN THE SYSTEM $Cu_2S–PbS–Sb_2S_3$

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ABSTRACT

The extent of solid solution in zinkenite, robinsonite and meneghinite has been determined from electron-microprobe-established compositions of their synthetic analogs in pertinent assemblages in the course of a phase-equilibrium study of the system $Cu_2S–PbS–Sb_2S_3$. All three solid-solution fields are elongate more or less parallel to the $PbS–Sb_2S_3$ binary join, and are relatively broader at their PbS-rich ends. The positions of the PbS-rich ends are practically insensitive to variations in temperature. Robinsonite and meneghinite are not stable at 300°C. Plots of molar proportions of Sb_2S_3 *versus* PbS suggest a common scheme of substitution, $3Pb^{2+} \rightleftharpoons 2Sb^{3+}$. In PbS-rich compositions of the solid solutions, the proportion of Cu is substantial, and Cu must be incorporated on the left-hand side of the substitution scheme. Natural compositions of meneghinite cluster at one point in the $Cu_2S–PbS–Sb_2S_3$ ternary system, but zinkenite and robinsonite have variable compositions. The most appropriate formula for zinkenite appears to be $6PbS•7Sb_2S_3$. Likewise, $4PbS•3Sb_2S_3$ is the preferred formula for robinsonite.

Keywords: solid solution, zinkenite, robinsonite, meneghinite, substitution scheme, phase-equilibrium study.

SOMMAIRE

Nous avons déterminé l'étendue de solution solide pour les minéraux zinkenite, robinsonite et ménéghinite à partir de données obtenues par microsonde électronique sur la composition d'équivalents synthétiques, dans le contexte d'une étude du système $Cu_2S–PbS–Sb_2S_3$. Les trois champs de solution solide sont allongés plus ou moins le long de la série binaire $PbS–Sb_2S_3$, et deviennent plus larges à leur extrémité riche en PbS. La position de ces extrémités est pratiquement insensible aux variations en température. La robinsonite et la ménéghinite ne sont pas stables à 300°C. La relation entre fractions molaires de Sb_2S_3 et de PbS fait penser que le schéma de substitution $3Pb^{2+} \rightleftharpoons 2Sb^{3+}$ s'applique aux trois phases. Dans les compositions proches du pôle PbS, la teneur en Cu est importante, de sorte que le Cu doit participer avec le Pb dans ce schéma de substitution. Les compositions de ménéghinite naturelle sont concentrées à un point dans le système ternaire $Cu_2S–PbS–Sb_2S_3$, mais la zinkenite et la robinsonite ont des compositions variables. La formule $6PbS•7Sb_2S_3$ semble être la plus appropriée pour la zinkenite. De même, nous préconisons la formule $4PbS•3Sb_2S_3$ pour la robinsonite.

(Traduit par la Rédaction)

Mots-clés: solution solide, zinkenite, robinsonite, ménéghinite, schéma de substitution, étude de l'équilibre des phases.

INTRODUCTION

Evidence from nature does not seem to support the generally accepted structural formulae of zinkenite ($PbS•Sb_2S_3$) and robinsonite ($7PbS•6Sb_2S_3$). Both zinkenite and robinsonite contain minor elements, like Cu, Zn and Fe, in addition to Pb and Sb. Our experimental study of the pseudoternary system $Cu_2S–PbS–Sb_2S_3$ proves that these phases show a considerable amount of solid solution.

We here provide results of experimental studies in the system $Cu_2S–PbS–Sb_2S_3$. These results support the formulae $6PbS•7Sb_2S_3$ and $4PbS•3Sb_2S_3$, respectively, for zinkenite and robinsonite. We also attempt to draw a parallelism in the nature of solid solution in zinkenite, robinsonite and meneghinite. Phase relations were determined at 500°, 440° and 300°C (Pruseth *et al.* 1997). Because robinsonite and meneghinite were found to be unstable at 300°C, we restrict our discussion to the 500° and 440°C isotherms only.

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BACKGROUND INFORMATION

Garvin (1973) failed to synthesize homogeneous zinkenite from the starting material $PbS \cdot Sb_2S_3$. Robinsonite was found to form with zinkenite. However, Harris (1965) obtained a homogeneous phase of zinkenite from $6PbS \cdot 7Sb_2S_3$. Lebas & Le Bihan (1976) proposed the formula $Pb_{1+n}Sb_{4-n}S_{27}$ for zinkenite, with $0.50 \leq n \leq 0.67$. Thus the composition can vary from $6PbS \cdot 7Sb_2S_3$ to $PbS \cdot Sb_2S_3$. In contrast, natural compositions of zinkenite do not have a $PbS:Sb_2S_3$ ratio of more than 6 : 7. Jambor & Owens (1982) reported the occurrence of a phase of composition $PbS \cdot Sb_2S_3$ that occurs along with zinkenite ($6PbS \cdot 7Sb_2S_3$) as inclusions in robinsonite at Vall de Ribes, Spain. However, the $PbS \cdot Sb_2S_3$ phase showed an X-ray-diffraction pattern similar to that of zinkenite, but with enlarged unit-cell parameters.

Natural examples of robinsonite also show a range of Pb:Sb ratio. Berry *et al.* (1952) proposed the formula $7PbS \cdot 6Sb_2S_3$ for robinsonite. Jambor & Plant (1975), on the other hand, deduced the formula $4PbS \cdot 3Sb_2S_3$ on the basis of electron-microprobe analyses of both synthetic and natural representatives and of the comparison of their calculated densities with the measured ones. Ayora & Gali (1981) presented further data on robinsonite from two localities at Vall de Ribes, Spain in support of the formula of Jambor & Plant (1975).

EXPERIMENTAL PROCEDURE

Experiments were conducted in silica tubes, evacuated to 10^{-4} atm., in horizontal tube furnaces. Temperature was controlled within $\pm 2°C$ with the use of solid-state temperature controllers. The end-member reactant phases were synthesized from 99.999% Cu, Pb, Sb and S supplied by Aldrich Chemical Company, Inc., Milwaukee, Wisconsin, and were characterized by optical and powder X-ray-diffraction methods prior to their use in the phase-equilibrium study. For the synthesis of Cu_2S, filings of copper, obtained by abrading a copper rod with a steel file, and cleaned with dilute HCl after the removal of the filings of steel with a magnet, were heated with sulfur at 200°C for 48 hours. After the completion of the initial reaction, the charge was annealed at 700°C for 48 hours. The product was ground under acetone and then reacted with a few ingots of copper at 700°C for an additional 48 to 72 hours. Unreacted ingots of copper were picked out from the final product. X-ray-diffraction analysis provided patterns of stoichiometric chalcocite (Roseboom 1966). PbS was synthesized by reacting pieces of lead and powdered sulfur at 700°C for 4 to 5 days. Coatings of Pb oxide on the pieces of lead were removed by scraping with a stainless steel knife. Sb_2S_3 was synthesized from powders of antimony and sulfur. Following the initial reaction at 200°C for 48 hours, the product was melted at 570°C, and then

annealed at 500°C for 6 to 7 days. The boundaries of the solid-solution fields were determined from a phase-equilibrium study of the system $Cu_2S–PbS–Sb_2S_3$ (Pruseth *et al.* 1997). The durations of experiments were: 43–123 days at 500°C, 51–200 days at 440°C, and 473 days at 300°C. The end products of phase-equilibrium experiments were checked by optical microscopy to ensure attainment of textural equilibrium. Consistency in phase assemblages obtained and in electron-microprobe results were assumed to indicate the attainment of chemical equilibrium. Further details of the experimental procedures are dealt with in Pruseth *et al.* (1997) and Mishra & Pruseth (1994).

ELECTRON-MICROPROBE ANALYSES

Most of the run products were analyzed with a four-channel Cameca (CAMEBAX) wavelength-dispersion microprobe analyzer at the Mineralogisch–Petrologishes Institut, Universität Bonn, operating at an accelerating potential of 15 kV and a beam current of 14 nA, with a beam diameter of 1–2 μm. A synthetic tetrahedrite standard was used for $CuK\alpha$, $SbL\alpha$ and $SK\alpha$. Synthetic galena was used for $PbM\alpha$. A ZAF correction was performed with the Cameca software. A few run products at 440° and 500°C were analyzed with a CAMEBAX SX–50 electron-microprobe equipped with four wavelength-dispersion and one energy-dispersion spectrometers at the Zentrale Elektronen-Microsonde, Ruhr Universität, Bochum. The operating conditions were: accelerating voltage 20 kV, beam current 7–8 nA, and a beam diameter slightly less than 1 μm. Synthetic CuS was used as the standard ($CuK\alpha$ and $SK\alpha$). Synthetic PbS and Sb_2S_3 were used as standards ($PbM\alpha$ and $SbM\alpha$, respectively). The ZAF correction was done with the program PAP (Pouchou & Pichoir 1984). Replicate analyses showed no statistical difference. Table 1 presents the average result of analyses of zinkenite, robinsonite and meneghinite along with the extent of charge balance. It also lists the assemblage of run products.

RESULTS

Minor amounts of reactants persisted even after 370 days of heating at 300°C, but were not detected in the run products after 473 days of heating. The absence of robinsonite and meneghinite in any of the run products is indicative of the instability of the two at and below 300°C.

All three solid-solution fields are broader at the PbS-rich ends, where they contain the maximum amount of copper (Fig. 1). The observation of Moëlo (1978) that zinkenite with a high Pb:Sb atomic ratio should be the most enriched in minor elements thus is corroborated. In this study, $6PbS \cdot 7Sb_2S_3$ and $4PbS \cdot 3Sb_2S_3$ have been assumed to be the ideal formulae, respectively, for zinkenite and robinsonite.

TABLE 1. RESULTS OF ELECTRON-MICROPROBE ANALYSES OF SYNTHETIC ZINKENITE, ROBINSONITE AND MENEGHINITE FROM PHASE EQUILIBRIUM STUDY

Run no.	Assemblage	n	Weight%					Formulae				Charge
			Cu	Pb	Sb	S	Total	Cu	Pb	Sb	S	balance (%)
Zinkenite												
500°C												
CPS41	Zkt,Mgt,Melt	2	1.71	34.24	42.08	23.34	101.38	1.00	6.13	12.82	27	−4.24
CPS42	Zkt,Stb,Melt	14	0.40	29.94	45.06	23.54	98.94	0.23	5.32	13.61	27	−4.27
CPS43	Zkt,Melt	4	1.92	30.69	43.34	23.26	99.20	1.12	5.52	13.24	27	−3.91
CPS50	Zkt,Stb,Melt	3	0.72	28.72	46.37	24.66	100.48	0.40	4.87	13.37	27	−6.96
440°C												
CPS17	Zkt,Stb	7	0.00	31.73	45.93	23.08	100.75	0.00	5.75	14.16	27	−0.03
CPS72	Zkt,PhZ	1	1.41	34.07	41.48	23.63	100.59	0.81	6.03	12.48	27	−6.82
CPS75	Zkt,Cst,PhZ	4	1.50	34.01	41.29	23.51	100.31	0.87	6.04	12.49	27	−6.60
CPS76	Zkt,Cst,PhZ	8	1.74	32.90	42.96	23.93	101.53	0.99	5.74	12.77	27	−5.96
CPS77	Zkt,Cst,Stb	2	1.41	30.32	43.58	23.59	98.89	0.81	5.37	13.14	27	−5.62
CPS79	Zkt,Cst,Stb	9	0.94	30.61	45.39	24.08	101.01	0.53	5.31	13.41	27	−4.86
CPS80	Zkt,Cst,Stb	2	0.94	30.96	45.50	23.88	101.28	0.54	5.42	13.55	27	−3.67
CPS83	Zkt,Cst,Stb	4	0.89	31.40	44.63	23.99	100.90	0.50	5.47	13.23	27	−5.31
Robinsonite												
500°C												
CPS20	Rbt,Mgt,PhIV	3	0.37	44.72	35.78	19.95	100.82	0.12	4.51	6.14	13	6.03
440°C												
CPS66	Rbt,Mgt	5	0.33	42.54	35.95	22.07	100.90	0.10	3.88	5.58	13	−5.42
CPS67	Rbt,Mgt,PhZ	6	0.40	42.55	35.53	21.77	100.26	0.12	3.93	5.59	13	−4.81
CPS71	Rbt,PhZ	7	0.23	42.69	35.72	22.24	100.88	0.07	3.86	5.50	13	−6.56
Meneghinite												
500°C												
CPS14/5	Mgt,Bnt	4	2.97	56.65	22.57	17.60	99.78	2.04	11.96	8.11	24	4.78
CPS15/5	Mgt,Gn	9	1.66	61.13	19.26	18.46	100.51	1.10	12.34	6.61	24	−4.97
CPS16/5	Mgt,Fkt,Gn	7	0.68	59.38	21.55	18.96	100.57	0.43	11.64	7.19	24	−5.64
CPS20	Rbt,Mgt,PhIV	1	2.52	43.89	34.28	20.27	100.96	1.50	8.04	10.69	24	3.47
CPS34	Mgt,Bnt,Gn	4	2.52	63.00	16.79	17.71	100.02	1.72	13.21	5.99	24	−3.91
CPS35	Mgt,Bnt,Gn	3	2.89	62.10	17.31	17.50	99.79	2.00	13.18	6.25	24	−1.81
CPS36	Mgt,Bnt,Melt	10	2.87	48.65	27.72	20.16	99.40	1.72	8.96	8.67	24	−4.75
CPS37	Mgt,Bnt,Melt	2	3.78	44.74	30.19	20.73	99.42	2.21	8.02	9.20	24	−4.47
CPS38	Mgt,Bnt,Melt	3	2.78	49.88	28.10	20.34	101.10	1.66	9.11	8.73	24	−4.03
CPS39	Mgt,Bnt,Melt	6	3.33	41.04	34.43	21.59	100.37	1.86	7.06	10.08	24	−3.69
CPS41	Zkt,Mgt,Melt	7	3.37	39.52	35.98	22.00	100.86	1.85	6.67	10.34	24	−3.71
CPS43	Mgt,Melt	2	3.60	38.70	36.74	21.95	100.99	1.98	6.55	10.58	24	−2.44
440°C												
CPS10	Mgt,Bnt,Gn	3	2.00	64.14	17.56	17.05	100.76	1.42	13.99	6.52	24	1.98
CPS14	Mgt,Bnt	8	1.75	61.49	19.27	17.85	100.36	1.19	12.81	6.83	24	−1.46
CPS15	Mgt,Gn	3	1.45	63.12	17.45	17.02	99.04	1.03	13.83	6.47	24	0.24
CPS16	Mgt,Fkt,Gn	5	0.90	61.69	20.77	17.31	100.66	0.63	13.25	7.59	24	3.94
CPS61	Mgt,Bnt	7	1.89	61.10	18.36	18.29	99.64	1.25	12.41	6.35	24	−6.02
CPS62	Mgt,Bnt,PhZ	11	1.69	51.63	27.46	20.23	101.02	1.01	9.48	8.58	24	−4.77
CPS63	Mgt,PhZ	12	1.54	51.58	27.48	20.15	100.75	0.92	9.51	8.62	24	−4.57
CPS64	Mgt,PhZ	10	1.49	51.77	27.59	20.26	101.11	0.89	9.49	8.61	24	−4.77
CPS65	Mgt,Blt	8	0.91	60.16	21.32	18.81	101.21	0.59	11.88	7.17	24	−4.47
CPS66	Rbt,Mgt	7	1.03	51.50	28.13	20.43	101.10	0.61	9.36	8.70	24	−5.32
CPS67	Rbt,Mgt,PhZ	2	1.11	49.94	27.33	20.12	98.50	0.67	9.22	8.59	24	−6.52
CPS68	Mgt,Bnt	9	1.89	52.07	26.94	20.15	101.06	1.14	9.60	8.45	24	−4.84

Number of analyses are indicated by "n". Weight% Cu, Pb, Sb and S are within, respectively, ±0.10, ±0.71, ±0.41 and ±0.23.
Mineral Abbreviations: Blt-boulangerite, Bnt-bournonite, Cst-chalcostibite, Fkt-falkmanite, Gn-galena, Mgt-meneghinite, PhZ-phase-Z, Rbt-robinsonite, Stb-stibnite, Zkt-zinkenite.
Charge Balance $= \frac{\sum n_C Z_C - n_S Z_S}{n_S Z_S} \times 100$, where n_C, n_S, Z_C and Z_S are the formula contents and charge of the metals (+ semimetals) and sulfur, respectively.

All structural formulae, accordingly, have been calculated on the basis of 27 sulfur atoms for zinkenite and 13 sulfur atoms for robinsonite. The absolute charge-balance values for all compositions also are consistently low (Table 1). The only set of analyses of robinsonite from a single run-product at 500°C does not show the general trend of negative charge-balance. The meneghinite solid-solution field at 500°C extends beyond the phase-Z field and partially encloses it. The PbS-rich ends are relatively stable, and the shrinkage at lower temperature occurs from the PbS-poor ends (Fig. 1). Copper tends to be enriched with increasing PbS, and the maximum possible content of copper seems to be unaffected by change of temperature.

DISCUSSION

A compilation of compositions of natural zinkenite, robinsonite and meneghinite from various localities is presented in Table 2. Figure 1 shows the same
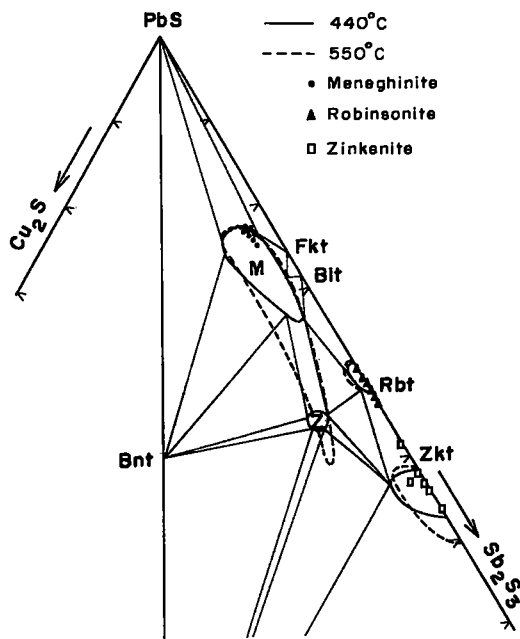
FIG. 1. Compositions of zinkenite, robinsonite and meneghinite from selected sulfide ore deposits plotted on a portion of the system $Cu_2S–PbS–Sb_2S_3$. Mineral abbreviations are same as in Table 1. Symbols: M meneghinite, Z phase Z.

The ternary composition of zinkenite that is stable with any two of the phases chalcostibite, phase Z, and robinsonite has the composition $0.49Cu_2S • 5.74PbS • 6.92Sb_2S_3$. The most PbS-rich Cu-free zinkenite is $5.75PbS • 7.80Sb_2S_3$. Paradoxically, the ratio $PbS:Sb_2S_3$ in the former equals 0.83, whereas in the latter it is 0.74. To attain the ratio $PbS:Sb_2S_3 = 1$, thus still more copper has to enter the structure of zinkenite. Conversely, there seems to be an upper limit to the amount of copper that can be incorporated in the mineral. At 500°C, the maximum Cu_2S content of zinkenite is approximately 4.3 mole % (Pruseth 1996). Therefore, zinkenite of the composition $PbS•Sb_2S_3$ is impossible because such a phase requires a considerable amount of a minor element (e.g., Cu) to maintain the ratio of PbS to Sb_2S_3 close to 1. Garvin (1973) also could not synthesize zinkenite of the composition $PbS•Sb_2S_3$. In nature, ternary compositions of zinkenite should be more abundant than their binary counterparts. Failure to recognize the role of a minor element in stabilizing the crystal structure of ternary zinkenite may have led to the acceptance of the formula $PbS•Sb_2S_3$. Unequivocal support in favor of the formula $6PbS•7Sb_2S_3$ can only be obtained from further work on crystal structure of zinkenite.

information plotted on a portion of the 440°C isotherm, experimentally determined in the $Cu_2S–PbS–Sb_2S_3$ system (Pruseth et al. 1997). It is clear that natural samples of zinkenite and robinsonite tend to have variable compositions, whereas meneghinite has a more or less constant composition despite its relatively larger extent of solid solution, as determined experimentally. One composition that does not fall within the scope of the zinkenite solid-solution field is the $PbS•Sb_2S_3$ phase of Jambor & Owens (1982), referred to in the introduction. The two compositions of meneghinite that plot off the main cluster are from Rajpura–Dariba, India, and contain considerable Tl.

Previous investigators, e.g., Salanci & Moh (1970), Garvin (1973), Craig et al. (1973), Hoda & Chang (1975) and Salanci (1979) reported no solid solution in either zinkenite or robinsonite. On the basis of compositions of natural phases, Moëlo et al. (1984) showed zinkenite to have compositions ranging from approximately 44 mole % PbS on the $PbS–Sb_2S_3$ binary join to a point with nearly 47 mole % PbS, but with approximately 3 mole % Cu_2S. However, they did not indicate the probability of a solid-solution field for zinkenite. Experimental results of Pruseth et al. (1997) show that the zinkenite solid-solution field is the largest at 500°C and gradually shrinks with a decrease of temperature (Fig. 1).

TABLE 2. COMPOSITIONS OF ZINKENITE, ROBINSONITE AND MENEGHINITE FROM VARIOUS POLYMETALLIC SULFIDE ORE DEPOSITS

Locality	n	Cu	Pb	Sb	S	Total	Reference*
Zinkenite							
Vall de Ribes, Spain		0.46	33.78	43.80	22.45	100.49	(1)
		0.00	32.59	44.85	22.53	99.97	(1)
		0.00	30.03	46.31	23.01	99.35	(1)
		0.00	32.70	44.40	23.00	100.10	(2)
		0.00	37.40	41.90	20.60	99.90	(2)
Rujevac, Yugoslavia		0.00	33.60	43.20	23.10	99.90	(3)
Robinsonite							
Vall de Ribes, Spain		0.00	43.17	35.38	20.22	98.77	(1)
		0.00	42.59	36.80	20.93	100.32	(1)
		0.00	41.24	36.73	21.08	99.05	(1)
	3	0.00	41.40	36.90	20.67	98.97	(4)
	10	0.00	43.93	36.37	20.23	100.53	(4)
	9	0.00	42.07	36.41	20.16	98.64	(4)
	3	0.00	42.92	36.35	20.44	99.71	(4)
Rujevac, Yugoslavia	3	0.00	42.20	36.60	21.20	100.00	(3)
Tintina, Yukon	4	0.00	40.44	36.83	21.14	98.41	(5)
Red Bird Mine, Nevada		0.00	45.5	35.4	20.5	101.4	(6)
		0.00	42.6	35.5	20.9	99.0	(7)
Meneghinite							
Hällefors, Sweden	4	1.50	61.90	18.90	17.20	99.50	(8)
Dhurode, Ireland		1.35	61.52	19.34	17.12	99.33	(9)
Vall de Ribes, Spain		1.56	61.08	18.52	17.14	98.30	(1)
Botino, Italy		1.20	61.52	19.53	17.59	99.84	(10)
Anglesea Tp., Ontario		1.46	61.30	19.55	17.88	100.19	(10)
Perry Silver Mine, Ontario		1.49	61.92	18.55	17.69	99.65	(10)
Marmora, Ontario		1.52	62.44	19.47	17.49	100.92	(10)
Pinnacles Mine, Australia	4	1.18	61.49	19.24	16.79	98.70	(11)
Rajpura-Dariba, India		1.35	59.94	20.10	17.99	99.38	(12)
		1.39	58.89	20.32	18.12	98.72	(12)
Borde, Malko Tornoro, Bulgaria	6	1.20	61.09	19.84	17.35	99.48	(13)

Number of analyses are indicated by "n".

*1. Ayora & Phillips (1981), 2. Jambor & Owens (1982), 3. Moëlo et al. (1983), 4. Ayora & Gali (1981), 5. Moëlo et al. (1984), 6. Jambor (1967), 7. Jambor & Plant (1975), 8. Zakrzewski & Nugteren (1984), 9. Wen et al. (1991), 10. Hicks & Nuffield (1978), 11. McQueen (1984), 12. Basu (1981), 13. Bonev & Jordanov (1983)
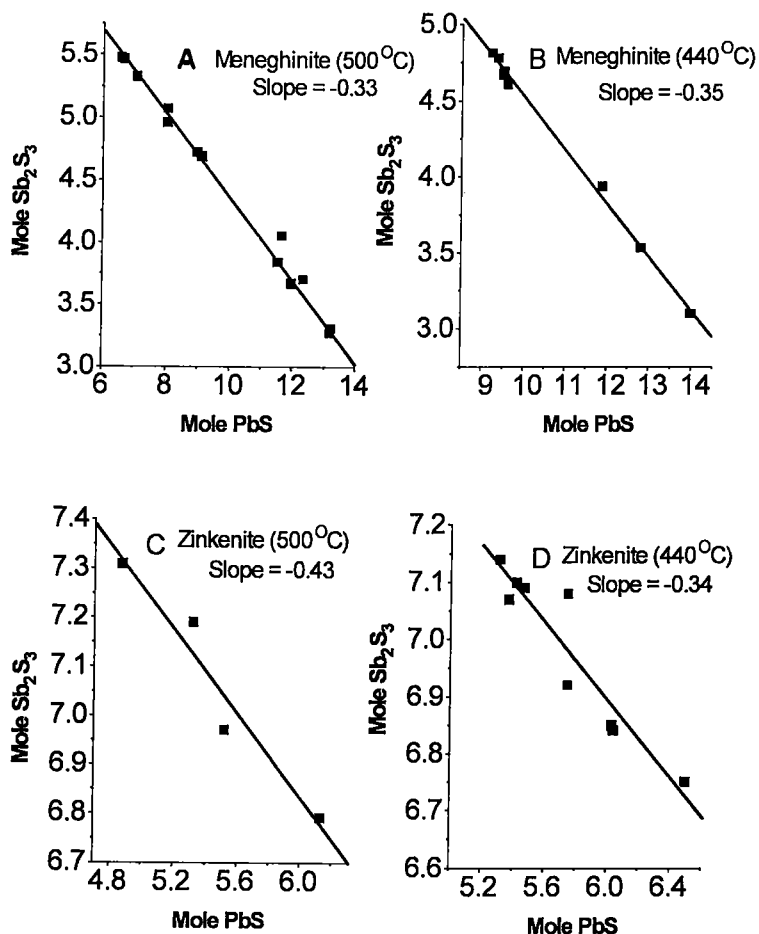
FIG. 2. Plots of molar proportion of Sb_2S_3 *versus* that of PbS in meneghinite and zinkenite from phase-equilibrium experiments at 500° and 440°C. Moles Sb_2S_3 in the formulae have been recalculated as $[S - (Cu/2) - Pb]/3$.

Robinsonite coexisting with either phase Z and zinkenite or phase Z and meneghinite has a composition close to $0.06Cu_2S \cdot 3.93PbS \cdot 3.00Sb_2S_3$, which is almost identical with $4PbS \cdot 3Sb_2S_3$. This formula is the most acceptable as the ideal formula for robinsonite because the individual phases in a three-phase field have unique compositions. At still lower temperatures, robinsonite most likely will match the proposed formula exactly because it would be entirely free of copper.

As shown in Figures 2a and b, the plots of molar proportion of Sb_2S_3 against that of PbS at both 500° and 440°C can be approximated by straight lines. At 500°C, all points, excluding the compositions of CPS15/5 and CPS16/5, describe a near-perfect straight line. Similar straight lines also fit to the data of

zinkenite (Figs. 2c, d). The near-perfect linear relationship between the molar proportions of PbS and Sb_2S_3 in the formulae of these phases shows the strong negative correlation between PbS and Sb_2S_3 content. Ideally, compositions on the Cu-rich and Cu-poor boundaries of the solid-solution fields should plot on different straight lines. The longer the solid-solution field, the closer will be the two straight lines and the less scattered will be the plotted points. For the same reason, the data at lower temperatures will be more scattered than those at higher temperatures. This is evident from Figures 2c and d. The slope for meneghinite is –0.33 at 500°C, and that at 440°C is –0.35. The straight line for zinkenite has a slope of –0.43 at 500°C, and –0.34 at 440°C. The Cu_2S-rich boundary runs through almost the entire length of

the zinkenite solid-solution field (Fig. 1), parallel to the $PbS-Sb_2S_3$ binary join. Thus there is an under-representation from the Cu_2S-poor zinkenite compositions and hence the higher slope. A small amount of Cu_2S is released from the structure as Sb_2S_3 substitutes for PbS. However, the substitution can be approximated with a scheme of $3Pb^{2+} \rightleftharpoons 2Sb^{3+}$, on the basis of observed slopes. Insufficient data exist for robinsonite. Nevertheless, the same substitution scheme, $3Pb^{2+} \rightleftharpoons 2Sb^{3+}$, may explain the nature of solid solution in robinsonite, considering the similarity of the shape of its solid-solution field with those of zinkenite and meneghinite.

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