

GROWTH ZONING IN TETRAHEDRITE-TENNANTITE FROM THE HOCK HOCKING MINE, ALMA, COLORADO

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ABSTRACT

The Hock Hocking is a small Pb-Zn-Ag-Au mine within the Alma district, Park County, Colorado. Ore occurs in fissure-faults that cut a series of pre-Pennsylvanian dolomites, quartzites and shales. Ore minerals consist predominantly of pyrite, chalcopyrite, galena and sphalerite, along with lesser amounts of tetrahedrite-tennantite, jalpaite, polybasite, stromeyerite, electrum and native silver in a gangue of manganoan dolomite and quartz. Microprobe analysis of growth-zoned tetrahedrite-tennantite coexisting with sphalerite of constant composition shows that Fe/Zn is positively correlated with As/(As + Sb) in the semi-metal site. Based on fluid-inclusion temperatures, paragenetic constraints and previous experimental studies (Sack & Loucks 1983, 1985), it appears that the Gibbs energy for the reciprocal reaction $\text{Cu}_{10}\text{Zn}_2\text{Sb}_4\text{S}_{13} + \text{Cu}_{10}\text{Fe}_2\text{As}_4\text{S}_{13} = \text{Cu}_{10}\text{Zn}_2\text{As}_4\text{S}_{13} + \text{Cu}_{10}\text{Fe}_2\text{Sb}_4\text{S}_{13}$ is temperature-independent over the range 200–500°C.

Keywords: tetrahedrite-tennantite, growth zoning, osmotic equilibrium, Zn-Fe exchange, As/(As + Sb), reciprocal reaction, geothermometry, Hock Hocking mine, Colorado.

SOMMAIRE

La mine Hock Hocking exploite un petit gisement de Pb-Zn-Ag-Au dans le district d'Alma, comté de Park au Colorado. Le minerai tapisse les fissures d'un système de failles qui recoupe dolomites, quartzites et shales d'âge pré-Pennsylvanien. On y trouve surtout pyrite, chalcopyrite, galène, sphalérite, et, en quantités moins importantes, tétraédrite-tennantite, jalpaïte, polybasite, stromeyerite, électrum et argent natif dans une gangue de dolomite manganière et de quartz. L'analyse à la microsonde de cristaux de tétraédrite-tennantite zonés en coexistence avec une sphalérite de composition constante montre que le rapport Fe/Zn du sulfosel varie avec le rapport As/(As + Sb) dans le site semi-métallique. Vu les températures dérivées de l'étude des inclusions fluides, les contraintes paragenétiques et les études expérimentales antérieures (Sack & Loucks 1983, 1985), l'énergie libre de Gibbs pour la réaction réciproque $\text{Cu}_{10}\text{Zn}_2\text{Sb}_4\text{S}_{13} + \text{Cu}_{10}\text{Fe}_2\text{As}_4\text{S}_{13} = \text{Cu}_{10}\text{Zn}_2\text{As}_4\text{S}_{13} + \text{Cu}_{10}\text{Fe}_2\text{Sb}_4\text{S}_{13}$ serait indépendante de la température dans l'intervalle de 200 à 500°C.

(Traduit par la Rédaction)

Mots-clés: tétraédrite-tennantite, zonation de croissance, équilibre osmotique, échange Zn-Fe, As/(As + Sb), réaction réciproque, géothermométrie, mine Hock Hocking, Colorado.

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INTRODUCTION

The Hock Hocking mine (e.g., Raabe 1983) is a small Pb-Zn-Ag-Au mine within the Alma district, on the eastern slope of the Mosquito Range of central Colorado (Fig. 1). Ore is localized in northeast-trending fissure-faults within the upper plate of a small reverse fault. Wall rocks include a series of shallowly dipping pre-Pennsylvanian dolomites, quartzites and shales intruded by granodioritic porphyry sills of Laramide age. The fissures are generally barren except in the Ordovician Manitou Dolomite and within dolomitic units of the Cambrian Sawatch Quartzite.

Ore minerals consist predominantly of pyrite, chalcopyrite, galena and sphalerite in a dolomite and quartz gangue. Shoots within the veins contain tetrahedrite-tennantite, jalpaite, polybasite, stromeyerite and electrum $\text{Au}_{0.72}\text{Ag}_{0.28}$. Secondary processes have enriched the ores, producing wire silver, covellite, chalcocite, malachite and cerussite, along with various iron and manganese oxides and hydroxides.

Microprobe data on pyrite, chalcopyrite, galena, sphalerite, jalpaite and stromeyerite indicate that these minerals are homogeneous within the precision of the analytical method (see Table 1). Sphalerite averages 0.26 and 0.40 wt. % Fe and Cd, respectively; Mn and Cu are at the minimum detection-limits of the microprobe.

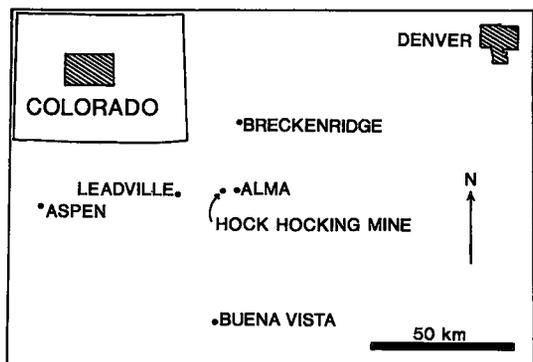


FIG. 1. Map of central Colorado, showing location of the Hock Hocking mine.

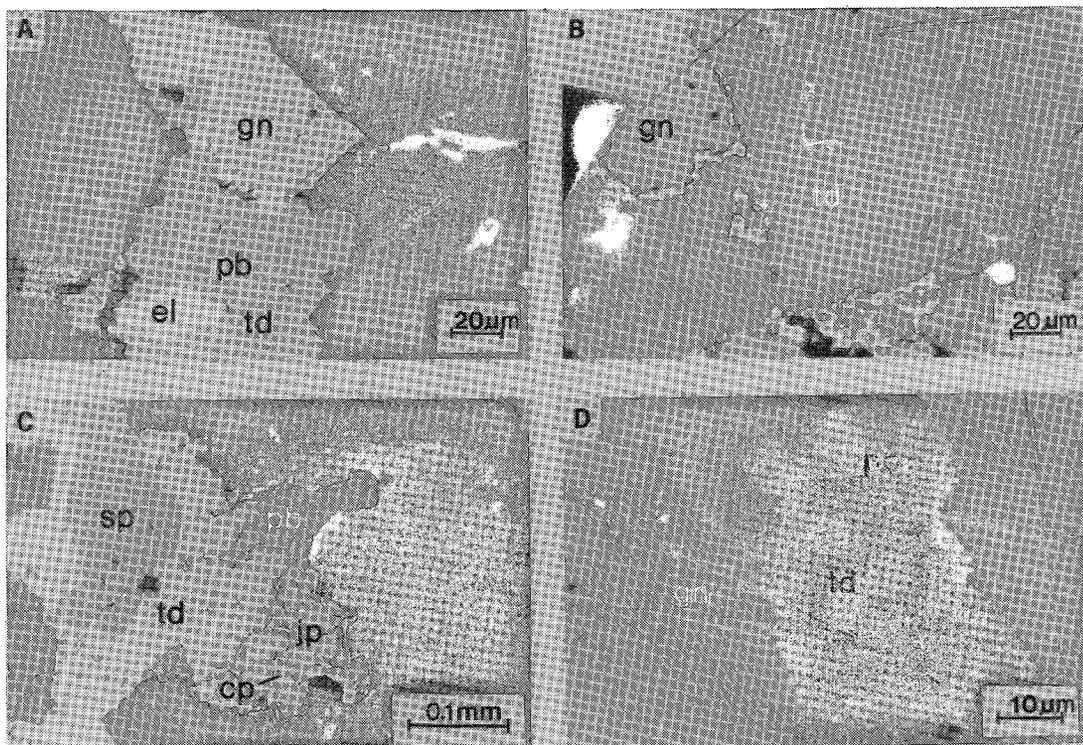


FIG. 2. Reflected light photomicrographs of ore minerals. Letter designations are as follows: sp sphalerite, gn galena, cp chalcopyrite, jp jalpaite, pb polybasite, td tetrahedrite, el electrum, Ag silver. (A) Electrum, galena and tetrahedrite-polybasite intergrowth in dolomite from HH45. (B) Native silver rimming tetrahedrite in galena from HH50. (C) Tetrahedrite replaced by jalpaite, polybasite and chalcopyrite from HH49. (D) Galena replaced by tetrahedrite-polybasite intergrowth from HH45 (crossed nicols).

Dolomite is the main gangue-mineral deposited during ore formation. Compositionally, the dolomite extends from nearly pure $\text{CaMg}(\text{CO}_3)_2$ with a few percent Fe to a composition near $\text{Ca}(\text{Mg}_{0.30}\text{Mn}_{0.45}\text{Fe}_{0.25})(\text{CO}_3)_2$. Fe and Mn show a positive correlation and a near-constant ratio of approximately 1:2.

GENESIS OF THE ORES

The paragenesis of ore mineralization at the Hock Hocking mine is relatively simple. Quartz and minor barite were the first vein-minerals to precipitate, followed closely by pyrite. A period of fracturing ensued, opening the veins to a new pulse of hydrothermal solution that deposited sphalerite, chalcopyrite, tetrahedrite-tennantite, pyrite and galena in a manganoan dolomite gangue (Fig. 2). Electrum was also deposited at this time. Near the end of hypogene mineralization, low-temperature silver minerals were deposited, including jalpaite, stromeyerite and polybasite.

The source of the mineralizing fluid has not been

identified, but it is probably related to the igneous activity that produced the porphyry sills found throughout the district. The ore fluid rose from depth along a reverse fault, and was tapped off by northeast-trending fractures within the upper fault-plate. This fluid had a high sulfidation-oxidation state and a low pH (Figs. 3, 4). Reaction of such a solution with carbonate wall-rocks, such as those of the dolomite-cemented Sawatch Quartzite, would result in a sharp increase in pH and the rapid deposition of Fe-poor sphalerite, pyrite, tetrahedrite, galena and chalcopyrite. Further upward migration of such fluids produced smaller lead-zinc-silver deposits of replacement type, such as those found in the Manitou Dolomite.

Stability relations of coexisting ore-minerals only provide absolute constraints on temperature of deposition between 117 and 360°C (Fig. 4). However, fluid-inclusion studies of sphalerite indicate a temperature of $249 \pm 7^\circ\text{C}$ based on five fluid inclusions in sphalerite from HH54. This estimate does not include a small positive pressure-correction that would be within the standard error of the measure-

ments. In combination with this temperature, an estimate of $f(S_2)$ of 10^{-10} bars can be deduced from the iron content of sphalerite (e.g., Czamanske 1974; Fig. 5).

TETRAHEDRITE-TENNANTITE

Tetrahedrite-tennantite is the most abundant sulfosalt at the mine. It is closely associated with sphalerite and galena. Tetrahedrite-tennantite is often replaced by jalpaite; it commonly is rimmed by native silver (Fig. 2). Symplectitic intergrowths with polybasite are common, especially as replacements of galena (e.g., Ramdohr 1969).

Microprobe analyses demonstrate that the Hock Hocking tetrahedrite is close to the simple stoichiometry $^{TR}(Cu,Ag)_6^{TET}[Cu_4,(Fe,Zn)_2]^{SM}(As,Sb)_4S_{13}$, corresponding to an ideal structure with 208 valence electrons per unit cell and full occupancy of the 6 trigonal-planar (TR), 6 tetrahedral (TET), and 4 semimetal (SM) sites in the formula unit based on 13 sulfur atoms (Wuensch 1964, Johnson & Jeanloz 1983). Results of twenty-five microprobe analyses of Hock Hocking tetrahedrite-tennantite from sample HH54 give average values of 10.04 ± 0.17 , 1.97 ± 0.07 and 4.00 ± 0.22 for the quantities (Cu + Ag), (Fe + Zn) and (Sb + As), on the basis of a 13-sulfur-atom formula unit. Variations in the

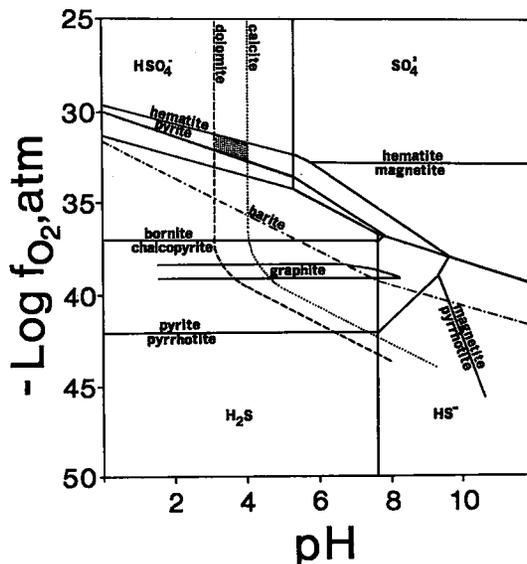


FIG. 3. A $f(O_2)$ -pH mineral-stability diagram calculated at 250°C. Boundaries represent activities of $S = 0.1$, $C = 0.1$, $Ca^{2+} = 0.1$, and $Ba^{2+} = 0.001$ (modified from Crerar & Barnes 1976). Shaded area represents stability field for Hock Hocking ore solution. Boundary positions only approximate due to lack of data on chemistry of the fluid.

TABLE 1. CHEMICAL COMPOSITION OF THE ORE MINERALS

	S	As	Sb	Bi	Fe	Zn	Cu	Ag	Other	Total
Pyrite*	53.55	0.11	na	na	46.61	0.10	0.30	-	0.10 ¹⁾	100.77
Chalcopyrite*	34.93	0.12	na	na	29.92	0.10	34.52	0.20	0.10 ¹⁾	99.89
Galena*	13.40	0.10	-	-	0.10	0.16	0.10	-	86.60 ²⁾	100.46
Sphalerite*	33.12	-	-	-	0.26	65.98	-	-	0.40 ³⁾	99.76
Electrum (HH49)	0.14	na	na	0.54	-	-	-	23.37	75.64 ⁴⁾	99.69
Electrum (HH56)	0.29	na	na	0.44	0.12	0.14	0.14	25.10	72.96 ⁴⁾	99.19
Silver (HH49)	0.22	na	na	0.10	0.10	na	0.26	99.24	-	99.12
Jalpaite (HH49)	14.41	0.28	-	-	0.14	0.30	14.02	71.53	-	100.68
Jalpaite (HH49)	14.57	0.11	-	0.10	0.13	0.18	13.46	75.15	-	99.70
Stromeyerite (HH49)	16.27	-	-	-	-	0.10	28.21	53.31	0.10 ⁴⁾	97.99
Polybasite (HH45)	16.87	1.44	8.52	-	-	-	13.89	60.94	0.12 ⁴⁾	101.78
Polybasite (HH48)	15.99	0.29	9.52	-	-	0.11	9.47	64.43	-	99.81
TD-TN (HH54)	25.71	4.12	20.52	0.14	0.29	7.38	38.56	1.69	-	98.14
"	25.63	2.64	23.95	-	0.16	7.47	37.26	2.34	-	99.46
"	25.83	3.99	23.04	-	0.17	7.61	37.08	2.10	-	99.82
"	25.30	1.55	27.03	-	0.12	7.52	37.13	2.81	-	101.46
"	26.78	5.68	18.32	-	0.27	8.04	40.16	0.67	-	99.91
"	26.72	6.43	16.29	0.10	0.31	8.24	40.19	0.59	-	98.87
"	26.89	6.31	17.64	-	0.24	7.76	40.39	0.74	-	99.97
"	25.39	0.88	27.86	-	0.34	7.44	36.65	2.93	-	101.50
"	25.28	1.57	26.51	0.10	0.17	7.21	36.41	2.98	-	100.23
"	26.50	4.20	20.91	0.10	0.35	7.43	39.80	1.43	-	100.72
"	26.48	3.77	20.44	-	0.35	7.70	39.36	1.21	-	99.32
"	24.85	4.46	22.38	-	0.44	7.25	37.18	1.64	-	99.20
"	24.84	8.14	17.54	-	0.51	7.60	39.08	1.13	-	98.83
"	24.91	8.77	17.70	-	0.15	7.71	38.77	1.13	-	99.14
"	26.86	12.97	11.71	-	0.21	7.80	39.87	1.09	-	100.51
"	25.98	10.13	15.62	-	0.35	7.97	39.43	0.94	-	100.42
"	26.55	12.59	11.42	-	0.28	8.17	40.31	0.71	-	100.43
"	27.86	19.68	0.37	-	0.73	7.93	42.49	0.39	-	99.05
"	28.06	20.04	0.40	0.11	0.60	8.05	43.30	0.26	-	100.82
"	27.76	19.96	0.60	-	0.78	8.05	42.59	0.46	-	100.20
"	27.91	19.93	0.29	0.10	0.82	7.98	42.40	0.47	-	99.79
"	27.99	20.65	0.25	-	0.74	7.76	42.94	0.31	-	100.62
"	27.89	20.35	0.41	0.14	0.71	7.60	42.66	0.22	-	99.99
"	28.08	20.32	0.31	-	0.63	8.09	42.86	0.15	-	100.46
"	27.05	14.63	9.05	-	0.70	8.00	41.00	0.57	-	101.00
"	26.45	12.13	10.00	-	0.59	7.82	41.13	0.76	-	99.01

Analyses (wt. % elements) obtained using the Purdue University automated MAC 500 electron microprobe operating at 15 KV, a beam current of 0.25 μ A and MAGIC IV corrections. Standards used include: Ag, Au, Mn and Zn metals; $CuFeS_2$; $AgBiS_2$; $AgBiSe_2$; CoS_2 ; $Cu_{10}Zn_2Sb_4S_{13}$; $Cu_{10}Fe_2Sb_4S_{13}$; $Cu_{10}Zn_{1.3}Fe_{0.7}As_4S_{13}$; PbS ; Sb_2S_3 . Analytical uncertainty in microprobe data is estimated to be $\pm 2\%$ for major elements (> 3.5 wt.%) and ± 0.10 wt.% for minor elements (< 3.5 wt.%). Notation: \bar{x} , average of all analyses; 1), Co; 2), Pb; 3), Cd; 4), Au; na, not analyzed.

Sb/As and Zn/Fe ratios were detected within single grains of tetrahedrite-tennantite, although zoning patterns occur on too fine a scale to be resolved with the microprobe. The As/Sb and Zn/Fe ratios of tetrahedrite-tennantite exhibit a negative correlation (Fig. 5). This compositional zoning contrasts with the apparent absence of zoning in sphalerite.

The mole fraction X_{FeS} in sphalerite from sample HH54 was determined to be 0.0030 by atomic absorption and 0.0023 by electron-microprobe analysis. Homogeneity with respect to Fe is suggested by the absence of color zoning within grains, a sensitive indicator of Fe homogeneity (Barton *et al.* 1963). Consequently, it is likely that X_{FeS} was nearly constant during the growth of tetrahedrite.

Assuming isothermal precipitation of tetrahedrite-tennantite and local equilibrium with respect to Fe-Zn exchange between aqueous solutions and each successive growth-zone of the sulfosalts (*e.g.*,

Thompson 1959), sphalerite of constant composition requires that the Fe-Zn ratio of a growth zone be governed by the condition of osmotic Fe-Zn exchange-equilibrium:

$$\begin{aligned} & \overset{(a)}{\mu_{\text{Cu}_{10}\text{Fe}_2\text{Sb}_4\text{S}_{13}}} - \overset{(a)}{\mu_{\text{Cu}_{10}\text{Zn}_2\text{Sb}_4\text{S}_{13}}} = \\ & \overset{(b)}{\mu_{\text{Cu}_{10}\text{Fe}_2\text{Sb}_4\text{S}_{13}}} - \overset{(b)}{\mu_{\text{Cu}_{10}\text{Zn}_2\text{Sb}_4\text{S}_{13}}} \end{aligned} \quad (1)$$

where (a) and (b) denote any two points in the tetrahedrite and the μ_i expressions are the chemical potentials of the i components. Assuming sulfosalts to be ideal reciprocal solutions (*e.g.*, Sack 1982, Sack & Loucks 1985), the condition of osmotic Fe-Zn exchange-equilibrium for $\text{Cu}_{10}(\text{Fe,Zn})_2(\text{Sb,As})_4\text{S}_{13}$ sulfosalts may be written as

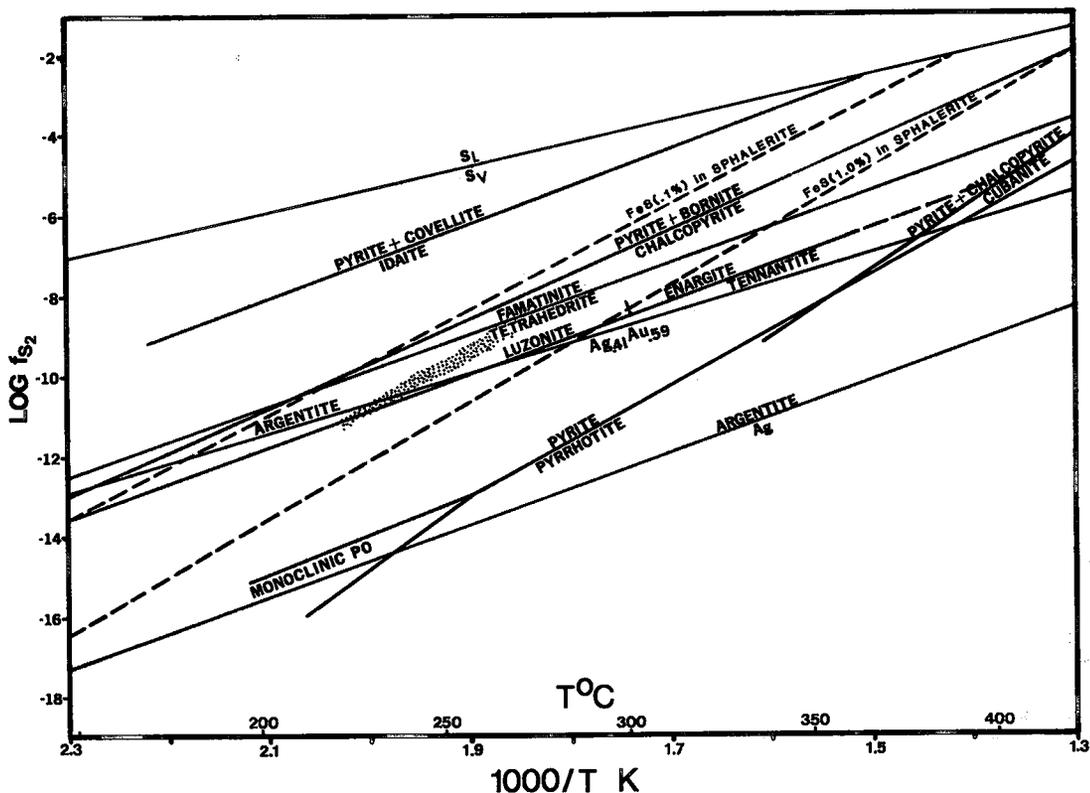


FIG. 4. A $f(\text{S}_2)$ -temperature diagram of sulfidation reactions applicable to Hock Hocking ore minerals. Sphalerite isopleths from Czamanske (1974). Remainder of data from Barton & Skinner (1979). Shaded area represents depositional conditions of Hock Hocking ore solution lying along the $X_{\text{FeS}} = 0.003$ isopleth between 200–300°C. Absolute paragenetic constraints are provided by the presence of jalpaite (formed near the end of mineralization) and the pyrite-chalcopyrite assemblage. These constraints require $117 < T < 360^\circ\text{C}$. The remaining curves on Figure 4 are for comparative purposes only as the requisite assemblage is not present in the Hock Hocking mine or the sulfidation curve corresponds to reactions in the simple system (*e.g.*, tetrahedrite-famatinite and tennantite-enargite).

$$\ln K_D^{\text{OSM}} \equiv \frac{X_{\text{Fe}}^{(\text{a})\text{TET}}}{X_{\text{Zn}}^{(\text{a})\text{TET}}} \frac{X_{\text{Zn}}^{(\text{b})\text{TET}}}{X_{\text{Fe}}^{(\text{b})\text{TET}}} = \frac{\Delta \bar{G}_x^{\circ}}{2RT} [(^{\text{a}})X_{\text{As}}^{\text{SM}} - (^{\text{b}})X_{\text{As}}^{\text{SM}}] \quad (2)$$

where $\Delta \bar{G}_x^{\circ}$ is a quantity that describes the departure of the Gibbs energy of the reciprocal end-members $\text{Cu}_{10}\text{Fe}_2\text{Sb}_4\text{S}_{13}$, $\text{Cu}_{10}\text{Zn}_2\text{Sb}_4\text{S}_{13}$, $\text{Cu}_{10}\text{Fe}_2\text{As}_4\text{S}_{13}$, and $\text{Cu}_{10}\text{Zn}_2\text{As}_4\text{S}_{13}$, from coplanarity; it is defined by the expression

$$\Delta \bar{G}_x^{\circ} = [\bar{G}_{\text{Cu}_{10}\text{Zn}_2\text{As}_4\text{S}_{13}}^{\circ} - \bar{G}_{\text{Cu}_{10}\text{Fe}_2\text{As}_4\text{S}_{13}}^{\circ}] - [\bar{G}_{\text{Cu}_{10}\text{Zn}_2\text{Sb}_4\text{S}_{13}}^{\circ} - \bar{G}_{\text{Cu}_{10}\text{Fe}_2\text{Sb}_4\text{S}_{13}}^{\circ}] \quad (3)$$

The negative correlation between $\ln(\text{Zn}/\text{Fe})$ and X_{As} observed in tetrahedrite-tennantite from Hock Hocking and other epithermal-mesothermal ore deposits (e.g., Bushnell 1983) is consistent with a positive value of $\Delta \bar{G}_x^{\circ}$. Sack & Loucks (1985) have determined that $\Delta \bar{G}_x^{\circ}$ is 2.64 ± 0.12 kcal/gfw at 500°C from Fe-Zn exchange experiments between sphalerite and tetrahedrite-tennantite with X_{As} of 0, 0.65 and 1; their preliminary data suggest that, to a first approximation, $\Delta \bar{G}_x^{\circ}$ is temperature-independent over the temperature range 365 – 500°C . If it is assumed that $\Delta \bar{G}_x^{\circ}$ is temperature-independent and that the addition of a small fraction of Ag to the trigonal planar sites does not alter the relative energies of Fe and Zn on tetrahedral sites, then the slope m defined from a plot of $\ln(X_{\text{Zn}}^{\text{TET}}/X_{\text{Fe}}^{\text{TET}})$ versus $X_{\text{As}}/(X_{\text{As}}^{\text{SM}} + X_{\text{Sb}}^{\text{SM}})$ for the tetrahedrite-tennantite compositions of a given sample should be related to the temperature of formation *via* the expression

$$T(\text{K}) = -(664 \pm 30)/m \quad (4)$$

Because the slope m defined by the tetrahedrite-tennantite compositions from sample HH54 is 1.30 ± 0.10 (see caption to Fig. 5), application of (4) to this sample indicates a temperature of formation of $238 \pm 46^{\circ}\text{C}$. This estimate was obtained after eliminating tetrahedrite-tennantite samples in which there is a large uncertainty in the microprobe determination of Fe ($\text{Fe} \leq 0.10$ wt. %).

Sb-rich tetrahedrite-tennantite samples from the mine commonly contained the most marked concentrations of Ag. Although the effect of Ag in the trigonal site upon Fe-Zn exchange in the neighboring tetrahedral site is unknown, it appears to be minimal within the precision of the data in this study. Data points for Ag-rich samples are randomly distributed around the least-squares-fit line in Figure 5.

CONCLUSIONS

Chemical zoning in tetrahedrite-tennantite from the Hock Hocking mine confirms that the occupancy

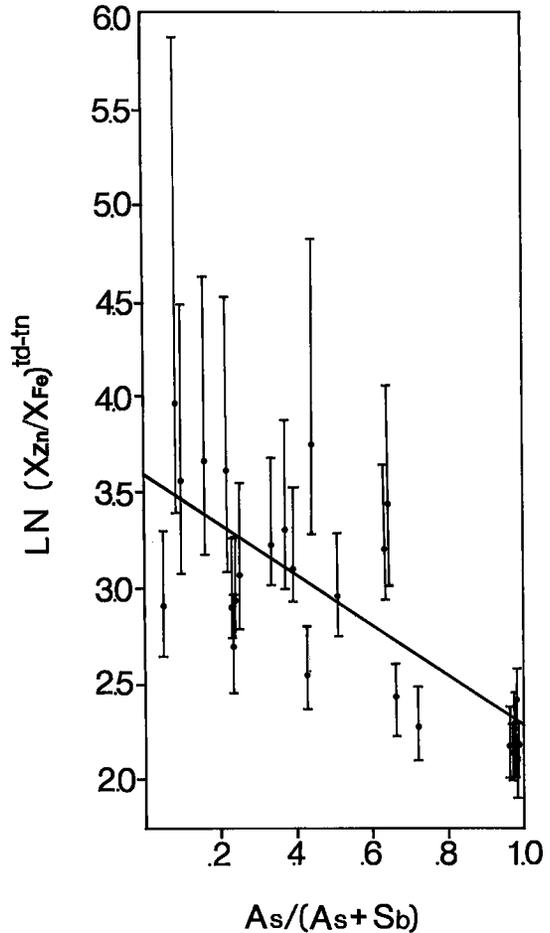


FIG. 5. Plot of $\ln(X_{\text{Zn}}/X_{\text{Fe}})$ versus $\text{As}/(\text{As}+\text{Sb})$ for growth-zoned tetrahedrite-tennantite from sample HH54. Sulfosalts coexist with homogeneous sphalerite ($X_{\text{FeS}} = 0.003$). Each data-point represents a single microprobe determination. Line is a least-squares fit through data with a slope of -1.30 and r of -0.76 . Taking into account that $\ln(X_{\text{Zn}}^{\text{TET}}/X_{\text{Fe}}^{\text{TET}})$ becomes less uncertain with increasing $X_{\text{As}}^{\text{SM}}$, a conservative estimate of the uncertainty in the slope of ± 0.10 was obtained by determining the standard deviation of slopes obtained by linear regression of the data sets defined by the seven tennantite compositions ($X_{\text{As}}^{\text{SM}} > 0.99$) and 12 of 17 remaining tetrahedrite-tennantite compositions selected at random. Error bars in $\ln(X_{\text{Zn}}^{\text{TET}}/X_{\text{Fe}}^{\text{TET}})$ were calculated from the estimates of analytical uncertainty in microprobe data given in the caption to Table 1. Analytical uncertainty in $\text{As}/(\text{As}+\text{Sb})$ is not shown, but is generally negligible by comparison.

of the semimetal site strongly influences the Fe/Zn ratio of tetrahedrite-tennantite at fixed Fe/Zn ratio of coexisting sphalerite, temperature and pressure. Positive correlation of $\ln(\text{Zn}/\text{Fe})$ with $\text{Sb}/(\text{As} + \text{Sb})$ at constant Fe-Zn exchange potential μ_{FeZn} (i.e., constant composition of sphalerite) corresponds to destabilization of Fe relative to Zn due to electronic compression caused by substituting Sb for As in nearest-neighbor semimetal sites (e.g., Sack & Loucks 1985). Within the precision of the data presented here, it appears that the difference in relative energies of Zn and Fe in pure, ideal tetrahedrite and tennantite,

$$[\bar{G}_{\text{Cu}_{10}\text{Zn}_2\text{As}_4\text{S}_{13}}^{\circ} - \bar{G}_{\text{Cu}_{10}\text{Fe}_2\text{As}_4\text{S}_{13}}^{\circ}] - [\bar{G}_{\text{Cu}_{10}\text{Zn}_2\text{Sb}_4\text{S}_{13}}^{\circ} - \bar{G}_{\text{Cu}_{10}\text{Fe}_2\text{Sb}_4\text{S}_{13}}^{\circ}] \quad (5)$$

is temperature-independent over the temperature range 200–500°C, using the value of $+2.64 \pm 0.12$ kcal/gfw as determined by Sack & Loucks (1983). Thus, the analysis of compositional zoning in growth-zoned tetrahedrite-tennantite may have many applications to geothermometry of epithermal-mesothermal bonanza silver deposits; at least, it emphasizes the importance of tetrahedrite-tennantite solid solutions as sliding-scale indicators of the environment of ore deposition (e.g., Barton & Skinner 1979, Wu & Petersen 1977).

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