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TETRAHEDRITE AND TENNANTITE: EVALUATION OF THERMODYNAMIC DATA AND PHASE EQUILIBRIA

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ABSTRACT

Tetrahedrite and tennantite are extremely common in a variety of ore deposits, but the genetic information they record is difficult to decipher because of the limited understanding of their phase relations in multicomponent systems. Most natural compositions can be described by the general formula $(Cu,Ag)_{10}(Fe,Zn,Cu)_2(Sb,As)_4S_{13}$. Consideration of the compositional variations found in natural samples suggests that results of electron-microprobe analyses of tetrahedrite and tennantite are best normalized on the basis of four semimetal atoms (Sb, As, Bi, Te). Expressions for the Gibbs free energy of formation for Fe-tetrahedrite ($Cu_{10}Fe_2Sb_4S_{13}$; FeTd), Zn-tetrahedrite ($Cu_{10}Zn_2Sb_4S_{13}$; ZnTd), Fe-tennantite ($Cu_{10}Fe_2As_4S_{13}$; FeTn) and Zn-tennantite ($Cu_{10}Zn_2As_4S_{13}$; ZnTn) have been derived that best fit the available experimental and natural phase- equilibrium constraints. The provisionally recommended expressions [J/mole; T(K); relative to the elements and ideal S_2 gas] and the temperature ranges for which they are valid are:

ΔG°_{FeTn} = -1,933,305 + 865.7 T (25 - 602°C)
ΔG°_{ZnTn} = -2,119,070 + 908.3 T (25 - 420°C)
ΔG°_{ZnTn} = -2,130,050 + 923.9 T (420 - 602°C)
ΔG°_{FeTd} = -1,871,251 + 860.8 T (25 - 630°C)
ΔG°_{ZnTd} = -2,058,151 + 903.2 T (25 - 420°C)
ΔG°_{ZnTd} = -2,069,130 + 918.9 T (420 - 630°C)

Calculated phase-relations indicate that tetrahedrite and tennantite form under normal hydrothermal conditions in terms of temperature, and sulfur and oxygen fugacities. The stability of the rare sulfosalt skinnerite (Cu_3SbS_3) is limited to Zn- and Fe-deficient environments and is restricted by reactions involving Zn- and Fe-tetrahedrite.

Keywords: tetrahedrite, tennantite, phase equilibria, electron-microprobe analysis, entropy estimates, Gibbs free energy.

SOMMAIRE

Tétraédrite et tennantite sont très répandues dans plusieurs types de gîtes minéraux, mais l'information génétique qu'elles renferment est difficilement déchifrable à cause d'une lacune dans nos connaissances des relations de phase dans les systèmes à plusieurs composantes. La plupart des compositions naturelles de ces minéraux répondent à la formule générale $(Cu,Ag)_{10}(Fe,Zn,Cu)_2(Sb,As)_4S_{13}$. Suite à une étude des variations en composition des échantillons naturels, nous pensons que les résultats des analyses à la microsonde électronique devraient être normalisés sur quatre atomes de semi-métaux (Sb, As, Bi, Te). Les expressions dérivées de l'énergie libre de formation de Gibbs pour les pôles tétraédrite-Fe ($Cu_{10}Fe_2Sb_4S_{13}$; FeTd), tétraédrite-Zn ($Cu_{10}Zn_2Sb_4S_{13}$; ZnTd), tennantite-Fe ($Cu_{10}Fe_2As_4S_{13}$; FeTn) et tennantite-Zn ($Cu_{10}Zn_2As_4S_{13}$; ZnTn) résultent de la meilleure concordance avec les contraintes imposées par les équilibres des phases naturelles et synthétiques. Les expressions recommandées provisoires, relatives aux éléments et un gaz S_2 idéal [J/mole; T(K)], ainsi que les intervalles de température de leur validité, sont:

ΔG°_{FeTn} = -1,933,305 + 865.7 T (25 - 602°C)
ΔG°_{ZnTn} = -2,119,070 + 908.3 T (25 - 420°C)
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ΔG°_{FeTd} = -1,871,251 + 860.8 T (25 - 630°C)
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ΔG°_{ZnTd} = -2,069,130 + 918.9 T (420 - 630°C)

Les relations de phases calculées montrent que tétraédrite et tennantite cristallisent à des conditions hydrothermales jugées normales en termes de température et de fugacités d'oxygène et de soufre. La skinnerite, Cu_3SbS_3, sulfosel rare, est limitée aux milieux pauvres en Zn et Fe, et son champ de stabilité est restreint par des réactions qui impliquent à la fois tétraédrite-Zn et tétraédrite-Fe.

(Traduit par la Rédaction)

Mots-clés: tétraédrite, tennantite, équilibre des phases, données à la microsonde électronique, entropie, énergie libre de formation de Gibbs.

INTRODUCTION

Tetrahedrite and tennantite are common in a variety of ore deposits, but the genetic information they record is difficult to decipher because of their compositional complexity and the general lack of thermodynamic data. Published compilations of tetrahedrite and tennantite compositions (Johnson *et al.* 1986, Charlat & Lévy 1974) indicate that the formula $(Cu,Ag)_{10}(Fe,Zn)_2(Sb,As)_4S_{13}$ accurately represents the composition of most natural examples of tetrahedrite and tennantite. However, detailed chemical studies demonstrate limited substitution of Cu, Hg and Cd for Fe and Zn, Bi and Te for Sb and As, and Se for S (Johnson *et al.* 1986). Thus, many of the earlier experimental studies restricted to the systems Cu–As–S and Cu–Sb–S (Maske & Skinner

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1971, Skinner *et al.* 1972, Luce *et al.* 1977) have limited applicability to natural systems.

The present study has three main goals. This paper provides a critical assessment of the available experimental and thermodynamic data for tetrahedrite–tennantite in more complex Fe- and Zn-bearing systems. Second, we outline recommendations for recasting electron-microprobe data on tetrahedrite and tennantite. Finally, selected occurrences of tetrahedrite–tennantite are used either to place constraints upon the phase relations calculated or, conversely, to illustrate how these relations can be helpful in interpreting conditions of formation of these natural assemblages.

ANALYTICAL METHODS AND DATA

Analytical conditions and standards

Sulfosalt and sulfide samples were quantitatively analyzed using a fully automated Cameca CAMEBAX electron microprobe in the Electron Microanalysis Laboratory at the University of Michigan. Tetrahedrite–tennantite samples were analyzed for Cu, Ag, Fe, Zn, Sb, As, Bi and S using Cu*Kα*, Ag*Lα*, Fe*Kα*, Zn*Kα*, Sb*Lα*, As*Lα*, Bi*Lα* and S*Kα* lines at an accelerating voltage of 20 kV and a sample current of 10 nA. The Se and Te contents of all samples were checked by energy-dispersion analysis and found to be below the detection limits. Sphalerite samples were analyzed for Zn, Fe, Mn, Cd and S using Zn*Kα*, Fe*Kα*, Mn*Kα*, Cd*Lα* and S*Kα* lines, also at an accelerating voltage of 20 kV and a sample current of 10 nA. For the sulfosalts, synthetic tetrahedrite and tennantite compositions were used as Cu, Fe, Zn, Sb, As and S standards, and matildite ($AgBiS_2$) was used for Ag and Bi. For sphalerite, synthetic sphalerite compositions were used as Zn, Fe, Mn and S standards, and reagent-grade CdS was used for Cd. All standards, except for CdS, were provided by Dr. Robert R. Loucks (Purdue University). The quality of the analyses was monitored by analyzing standards before, during and after analytical sessions. The error (1σ) estimated for these analytical data is less than 2% for all elements.

Method of normalization

Despite the abundance of compositional data on tetrahedrite and tennantite in the literature (*cf.* Johnson *et al.* 1986), there is no consensus as to how to recast these data into structural formulae. Various investigators have recalculated analytical data on the basis of twelve metal, four semimetal, thirteen sulfur or 29 total atoms.

Several lines of evidence suggest that normalization to twelve metal atoms may not be universally applicable to these minerals. Experimental studies suggest that there may be some nonstoichiometry of Cu atoms in synthetic tetrahedrite and tennantite (Maske & Skinner 1971, Skinner *et al.* 1972, Luce *et al.* 1977, Makovicky & Skinner 1978). Second, the

TABLE 1. ELECTRON-MICROPROBE DATA FOR TETRAHEDRITE-TENNANTITE AND SPHALERITE

Sample	RAMM6	CLYM1	CLYM3	BARM1	CDA201	CDA202
TETRAHEDRITE-TENNANTITE						
Cu(Wt%)	36.96	31.98	29.75	39.27	33.91	33.91
Ag(Wt%)	3.50	10.88	13.45	1.04	5.67	6.06
Zn(Wt%)	2.22	6.80	7.10	7.02	3.94	3.45
Fe(Wt%)	5.48	0.96	0.61	1.30	3.54	3.63
Sb(Wt%)	24.87	18.77	21.32	21.47	27.47	27.34
As(Wt%)	2.68	6.53	4.51	5.55	0.57	0.59
Bi(Wt%)	0.55	0.00	0.09	0.02	0.47	0.53
S (Wt%)	24.78	24.90	24.12	25.47	24.31	24.04
Total	101.04	100.82	100.95	101.14	99.88	99.55
Normalized to 4 Semimetal Atoms						
Cu	9.59	8.34	7.94	9.87	9.06	9.08
Ag	0.53	1.67	2.12	0.15	0.89	0.96
Zn	0.56	1.72	1.84	1.71	1.02	0.90
Fe	1.62	0.28	0.19	0.37	1.08	1.11
Sb	3.37	2.56	2.97	2.82	3.83	3.82
As	0.59	1.44	1.02	1.18	0.13	0.13
Bi	0.04	0.00	0.01	0.00	0.04	0.04
S	12.74	12.87	12.77	12.68	12.88	12.76
SPHALERITE						
Zn(Wt%)	65.40	65.06	66.34	64.98	63.69	63.31
Fe(Wt%)	0.54	0.72	0.08	0.70	2.55	2.68
Cd(Wt%)	0.06	0.14	0.35	0.22	0.32	0.38
Mn(Wt%)	0.00	0.00	0.01	0.00	0.01	0.02
S (Wt%)	32.89	32.97	33.06	32.40	33.02	32.83
Total	98.89	98.89	99.84	98.30	99.59	99.22
Normalized to 1 Sulfur Atom						
Zn	0.975	0.967	0.984	0.983	0.946	0.945
Fe	0.009	0.013	0.001	0.012	0.044	0.047
Cd	0.001	0.001	0.003	0.002	0.003	0.003
Mn	0.000	0.000	0.000	0.000	0.000	0.000
T(°C)*	-30	495	80	300	195	185
Sample	MRC521	MRC522	MRC523	1528	1534A1	1534A2
TETRAHEDRITE-TENNANTITE						
Cu(Wt%)	42.42	42.85	42.95	37.29	37.13	36.71
Ag(Wt%)	0.36	0.39	0.39	3.22	2.36	2.62
Zn(Wt%)	7.20	6.56	6.65	6.57	7.32	7.46
Fe(Wt%)	1.07	1.19	1.20	0.97	0.54	0.49
Sb(Wt%)	2.83	3.15	2.76	19.65	24.69	24.46
As(Wt%)	18.62	18.49	18.81	6.72	3.03	3.03
Bi(Wt%)	0.00	0.04	0.06	0.03	0.27	0.00
S (Wt%)	27.49	27.23	27.32	25.82	25.44	25.45
Total	99.99	99.90	100.14	100.27	100.78	100.22
Normalized to 4 Semimetal Atoms						
Cu	9.82	9.89	9.86	9.34	9.56	9.57
Ag	0.05	0.05	0.05	0.47	0.36	0.40
Zn	1.62	1.47	1.48	1.60	1.83	1.89
Fe	0.28	0.31	0.31	0.28	0.16	0.14
Sb	0.34	0.38	0.33	2.57	3.32	3.33
As	3.66	3.62	3.66	1.43	0.66	0.67
Bi	0.00	0.00	0.00	0.00	0.02	0.00
S	12.62	12.45	12.44	12.83	12.98	13.16
SPHALERITE						
Zn(Wt%)	63.94	63.13	62.13	64.92	66.72	66.92
Fe(Wt%)	0.09	0.15	0.16	0.38	0.21	0.10
Cd(Wt%)	0.29	0.25	0.32	0.17	0.38	0.52
Mn(Wt%)	2.34	3.25	3.95	1.35	0.01	0.01
S (Wt%)	32.50	32.96	32.82	32.96	33.02	32.80
Total	99.16	99.74	99.38	99.78	100.34	100.35
Normalized to 1 Sulfur Atom						
Zn	0.965	0.939	0.928	0.966	0.991	1.000
Fe	0.002	0.003	0.003	0.007	0.004	0.002
Cd	0.003	0.002	0.003	0.001	0.003	0.004
Mn	0.042	0.058	0.070	0.024	0.000	0.000
T(°C)*	165	190	195	255	230	140

*Temperature determined by tetrahedrite-sphalerite thermometry
RAMM: Ramshorn mine, Bayhorse district, Idaho
CLYM: Clayton Silver mine, Bayhorse district, Idaho
BARM: Barton mine, Bayhorse district, Idaho
CDA: Lucky Friday mine, Coeur d'Alene district, Idaho
MRC: Morococha, Peru
1528: Carmen Vein, Casapalca, Peru
1534A: Arias mine, Huancavelica, Peru

presence in natural solid-solutions of Te substituting as the goldfieldite component ($Cu_{10}Te_4S_{13}$) requires deficiencies in the metal sites from the ideal twelve-metal stoichiometry (Johnson & Jeanloz 1983). Finally, Johnson *et al.* (1986) noted a slight correlation between Cu and S atoms, implying that some coupled atomic deficiencies may be present in tetrahedrite–tennantite.

Ebel (1988) suggested that sulfur deficiency may be an artifact of analytical procedures. Regardless of origin, the possibility of sulfur-deficient compositions indicates that normalization to 13 sulfur atoms also is inappropriate. If any of the components sum to less than stoichiometric values, then normalization to 29 total atoms also will yield incorrect results. Therefore, the most general method for recasting microprobe data into structural formulae is based on normalization to four semimetal atoms. However, because the semimetal atoms only constitute four of the 29 atoms in an ideal tetrahedrite–tennantite, small analytical errors in the amount of semimetals will translate into larger errors in the recast number of sulfur and metal atoms.

Analytical data

Compositions of natural samples of tetrahedrite–tennantite and sphalerite are presented in Table 1. Calculated temperatures derived from "tetrahedrite–sphalerite" thermometry using the formulation of Sack *et al.* (1987) and the data from Ebel & Sack (1989) also are presented in Table 1.

THERMODYNAMIC DATA

Insufficient data are presently available to rigorously calculate values of the Gibbs free energy for tetrahedrite–tennantite end-members. Therefore, to extract meaningful information from natural assemblages, values of free energy must be used that rely to varying degrees on estimations or approximations. The purpose of the present study is to estimate values of the Gibbs free energy for tetrahedrite–tennantite end-members that are both internally consistent and accurate. Tetrahedrite and tennantite will be considered as solid solutions spanning the compositional range defined by four end-members: $Cu_{10}Fe_2Sb_4S_{13}$ (Fe-tetrahedrite), $Cu_{10}Zn_2Sb_4S_{13}$ (Zn-tetrahedrite), $Cu_{10}Fe_2As_4S_{13}$ (Fe-tennantite) and $Cu_{10}Zn_2As_4S_{13}$ (Zn-tennantite). Silver-bearing end-members will not be considered beyond their effect in reducing the activity of these four components.

There are several approaches available to derive values of free energy for end-member compositions. Craig & Barton (1973) developed a method of approximating free energies for complex sulfosalts by summing expressions for the free energy of component sulfides. Alternatively, Bryndzia (pers. comm., 1988) measured enthalpies of formation of end-member compositions that can be used to calculate values of free energy when combined with estimates for entropy. The work of Sack & Loucks (1985) contains insufficient constraints to extract free energies for individual end-members, but it provides an excellent test for internal consistency or, conversely, constraints for one end-member given a value for another. The accuracy of resulting expressions will be assessed by comparing calculated equilibria with natural assemblages. For all calculations, the reference state of ideal gas S_2 was adopted. A list of mineral names, abbreviations and chemical formulae used in this paper is presented in Table 2.

TABLE 2. MINERAL ABBREVIATIONS & END-MEMBER FORMULAE

Mineral	Abbreviation	Formula
Fe-Tetrahedrite	FeTd	$Cu_{10}Fe_2Sb_4S_{13}$
Zn-Tetrahedrite	ZnTd	$Cu_{10}Zn_2Sb_4S_{13}$
Fe-Tennantite	FeTn	$Cu_{10}Fe_2As_4S_{13}$
Zn-Tennantite	ZnTn	$Cu_{10}Zn_2As_4S_{13}$
Pyrite	Py	FeS_2
Pyrrhotite	Po	$Fe_{1-x}S$
Hematite	Hm	Fe_2O_3
Chalcocite	Cc	Cu_2S
Chalcopyrite	Cp	$CuFeS_2$
Bornite	Bn	Cu_5FeS_4
Skinnerite	Sk	Cu_3SbS_3
Sphalerite	Sph	ZnS
Arsenopyrite	Asp	FeAsS
Enargite	En	Cu_3AsS_4
Luzonite	Lz	Cu_3AsS_4
Stibnite	St	Sb_2S_3
Native Antimony	Sb	Sb
Berthierite	Brt	$FeSb_2S_4$
Löllingite	Lo	$FeAs_2$
Siderite	Sd	$FeCO_3$

Craig & Barton approximations

Craig & Barton (1973) presented a method of approximating the values of Gibbs free energy of sulfosalts based on the summation of free energy data for component sulfides. Their approach assumes no enthalpy of mixing, but uses a theoretically derived term for the entropy of mixing. In the present study, we have estimated the free energy of the four end-members using this method, and combined these with the data for component sulfides from Barton & Skinner (1979). The resulting expressions (J/mole; T in K) are:

$$\begin{aligned}\Delta G^\circ{}_{\mathrm{FeTd}} &= -1{,}728{,}628 + 823.5T\\ \Delta G^\circ{}_{\mathrm{ZnTd}} &= -1{,}966{,}109 + 900.0T\\ \Delta G^\circ{}_{\mathrm{FeTn}} &= -1{,}610{,}268 + 819.2T\\ \Delta G^\circ{}_{\mathrm{ZnTn}} &= -1{,}847{,}749 + 895.9T.\end{aligned}$$

The expressions for the Zn-bearing end-members were calculated relative to a Zn liquid standard state to facilitate comparison with the 500°C experimental data of Sack & Loucks (1985).

Estimates based on enthalpies

Values of the Gibbs free energy of formation can be rigorously calculated from $\Delta H^\circ_{f,298}$, S°_{298} and C_p data using standard equations. For end-member tetrahedrite and tennantite, the enthalpy of formation ($\Delta H^\circ_{f,298}$) relative to component sulfides has been measured by L. Taras Bryndzia (pers. comm., 1988). However, S°_{298} and C_p data are not available for these sulfosalts.

Bryndzia (pers. comm., 1988) reported $\Delta H^\circ_{f,298}$ values (kJ/mole), relative to component sulfides (Cu_2S, FeS, ZnS, Sb_2S_3, As_2S_3), obtained by high-temperature direct-synthesis calorimetry, of -280.4 ± 8.4 (1σ) for Fe-tetrahedrite, -158.8 ± 5.7 (1σ) for Zn-tetrahedrite, -338.5 ± 12.5 (1σ) for Fe-tennantite and -308.0 ± 1.9 (1σ) for Zn-tennantite. These values were derived from preliminary experiments with reproducible results, but imperfect yields, owing to the formation of minor quantities of additional phases. Therefore, these values must be regarded with caution, and their accuracy must be rigorously assessed. Values for component sulfides were obtained from Mills (1974), Johnson *et al.* (1981) and Barton (1969).

Several methods for estimating standard molar entropies (S°_{298}) were evaluated. Latimer (1952) and Grønvold & Westrum (1962) outlined methods for estimating entropy by summing entropy values for each atom in a formula unit. Fyfe *et al.* (1958) described a method of estimating entropies for silicates based on a summation of measured entropies for component oxides and a volume correction for structural differences between the phase in question and the component oxides. Because of the bonding differences between sulfides and sulfosalts *versus* silicates, the present study adopts an approach in which entropies for sulfosalts were estimated by summing entropies for component sulfides without adjusting for structural differences. For example, the standard molar entropy of Zn-tennantite and that of Zn-tetrahedrite are estimated using the following formulae:

$$S^\circ_{298,ZnTn} = 5S^\circ_{298,Cu_2S} + 2S^\circ_{298,ZnS} + 2S^\circ_{298,As_2S_3}$$

and

$$S^\circ_{298,ZnTd} = 5S^\circ_{298,Cu_2S} + 2S^\circ_{298,ZnS} + 2S^\circ_{298,Sb_2S_3}.$$

All three methods of estimation were used to calculate the entropies of chalcopyrite ($CuFeS_2$), proustite (Ag_3AsS_3) and smithite ($AgAsS_2$), for which S°_{298} has been measured (Table 3). In all cases, the "sulfide sum" method produced the most accurate results, with the differences between the measured and estimated values representing a maximum of 2.5% of the total entropy of these compounds; therefore, we have adopted the "sulfide sum" method for estimating entropies of sulfosalts. Given a choice of two polymorphs of a sulfide component, the polymorph that is structurally most similar to the sulfosalt is selected. For example, the entropy value of sphalerite is used rather than that for wurtzite in the approximations for Zn-tetrahedrite and Zn-tennantite because of the structural similarities between sphalerite and tetrahedrite (Wuensch 1974). Likewise, chalcopyrite ($CuFeS_2$) is used to model the FeS component in Fe-tetrahedrite and Fe-tennantite through the equations:

TABLE 3. COMPARISON OF MEASURED & ESTIMATED STANDARD MOLAR ENTROPIES (S°_{298}) FOR CHALCOPYRITE, PROUSTITE & SMITHITE

Phase	Measured	Sulfide Sum	Latimer	Grønvold & Westrum
Chalcopyrite $CuFeS_2$	124.9	126.8	130.5	119.2
Proustite Ag_3AsS_3	303.7	296.1	268.8	261.7
Smithite $AgAsS_2$	150.5	153.2	127.3	131.9

All values in J/moleK.
Measured values for chalcopyrite from Robie *et al.* (1985); proustite and smithite from Gurevich *et al.* (1989).

$$S^\circ_{298,FeTd} = S^\circ_{298,Cu_2S} + 2S^\circ_{298,CuFeS_2} - 2S^\circ_{298,CuS} + 2S^\circ_{298,Sb_2S_3}$$

$$S^\circ_{298,FeTn} = S^\circ_{298,Cu_2S} + 2S^\circ_{298,CuFeS_2} - 2S^\circ_{298,CuS} + 2S^\circ_{298,As_2S_3}.$$

This approach was taken because of the structural similarities between tetrahedrite–tennantite and chalcopyrite (Wuensch 1974), and to assure consistency with the method of estimating heat capacities (C_p).

The heat capacities for sulfosalts were estimated by summing the expressions of the component sulfides in the stoichiometric proportions of the sulfosalts. For sulfide components that undergo one or more polymorphic transformations in the temperature range of interest, the expression for the heat capacity of the polymorph that is structurally the most similar to tetrahedrite–tennantite being approximated was assumed valid throughout the temperature range in question. As with the entropy estimates, the FeS component of Fe-tetrahedrite and Fe-tennantite was modeled as one mole of $CuFeS_2$ less one mole of CuS. This scheme is preferred over one that uses expressions for FeS because of the structural similarity between chalcopyrite and tetrahedrite–tennantite, and because it avoids the numerous discontinuities in heat capacity observed in FeS due to polymorphic and magnetic transitions (Mills 1974).

The Gibbs free energies of formation (ΔG°_T) for the tetrahedrite and tennantite end-members have been calculated relative to the elements and ideal gas

S_2. A linear equation is then fitted to the calculated values. The resulting equations (J/mole; T in K) are:

$$\Delta G^\circ_{\mathrm{FeTd}} = -1{,}963{,}427 + 860.7T$$
$$\Delta G^\circ_{\mathrm{ZnTd}} = -2{,}069{,}130 + 918.9T$$
$$\Delta G^\circ_{\mathrm{FeTn}} = -1{,}933{,}305 + 865.7T$$
$$\Delta G^\circ_{\mathrm{ZnTn}} = -2{,}130{,}050 + 923.9T.$$

The thermodynamic data for pure elements and sulfides were taken from the compilations of Mills (1974), Robie *et al.* (1978), Pankratz (1982) and Barton & Skinner (1979) and the recent work of Robie *et al.* (1985) and Johnson *et al.* (1981).

Comparison with experimental work

Sack & Loucks (1985) conducted extensive experiments at 500°C involving exchange reactions between tetrahedrite–tennantite end-members and Fe-bearing sphalerite. The difference in free energy between Fe- and Zn-tennantite and between Fe- and Zn-tetrahedrite at 500°C can be extracted from their data using data from Barton & Skinner (1979) for ZnS and FeS. A comparison of these differences in free energy derived by various methods is presented in Table 4. For both tetrahedrite and tennantite, the Craig & Barton estimates produce larger differences between Zn and Fe end-members than determined by Sack & Loucks (1985). For the estimates based on measured enthalpies, the difference in free energy between Zn- and Fe-tennantite is in excellent agreement with the work of Sack & Loucks (1985), within the error of the $\Delta H^\circ_{f,298}$ values. However, the calculated difference between the tetrahedrite end-members significantly disagrees with the data of Sack & Loucks (1985), and lies beyond the error associated with the $\Delta H^\circ_{f,298}$ values.

Alternatively, the data of Sack & Loucks (1985) may be used to calculate a Gibbs free energy for one tetrahedrite end-member at 500°C, given a value for the other. Thus, for the tetrahedrite end-members, the calculated free energy for Zn-tetrahedrite, the end-member with the ΔH value with the smallest experimental error (± 5.7 kJ/mole), was used to calculate the Gibbs free energy of Fe-tetrahedrite at 500°C using the data of Sack & Loucks (1985). When combined with the entropy estimate from the present study, this value yields the following equation (J/mole; T in K):

$$\Delta G^\circ_{\mathrm{FeTd}} = -1{,}871{,}251 + 860.6T.$$

The accuracy of this expression will be discussed in the next section by comparing calculated phase-equilibria with natural assemblages.

Comparison with natural assemblages

TABLE 4. COMPARISON OF THE GIBBS FREE ENERGY DIFFERENCES BETWEEN Zn & Fe TETRAHEDRITE & TENNANTITE AT 500°C

Source	$\Delta G^\circ_{\mathrm{ZnTd}}-\Delta G^\circ_{\mathrm{FeTd}}$ (kJ/mole)	$\Delta G^\circ_{\mathrm{ZnTn}}-\Delta G^\circ_{\mathrm{FeTn}}$ (kJ/mole)
Sack & Loucks (1985)	-151.9	-141.0
Craig & Barton Estimate	-178.4	-178.2
Difference from Sack & Loucks	-26.5	-37.2
Enthalpy-based Estimate	-60.7	-151.7
Difference from Sack & Loucks	+91.2	-10.7

Harris (1986) reported the assemblage chalcopyrite, stibnite, berthierite, pyrite and tetrahedrite from the Hemlo deposit, Ontario. If this assemblage records equilibrium conditions, it requires that the reactions

$$10CuFeS_2 + 2Sb_2S_3 + 3/2S_2 = Cu_{10}Fe_2Sb_4S_{13} + 8FeS_2 \qquad (1)$$

and

$$Sb_2S_3 + FeS_2 = FeSb_2S_4 + 1/2S_2 \qquad (2)$$

coincide at some point in log$f(S_2)$ – temperature space. Therefore, this assemblage may be used to test the accuracy of the various expressions for the Gibbs free energy of Fe-tetrahedrite. Of the phases in question, only tetrahedrite exhibits solid-solution substitutions of sufficient magnitude to displace Reaction 1 in terms of temperature and $f(S_2)$. In Figure 1, the calculated stability for Reaction 1 for various ΔG values for Fe-tetrahedrite are shown relative to various reactions in the system Cu–Fe–Sb–S for the temperature range 300 to 500°C. The Craig & Barton approximation for pure Fe-tetrahedrite places Reaction 1 above the sulfur condensation curve. Reaction 1 lies above Reaction 2 by 5.8 to 7.6 log$f(S_2)$ units. The coincidence of these two reactions would require that the activity of the Fe-tetrahedrite component be reduced to values ranging from $10^{-8.6}$ to $10^{-11.5}$. Whereas this is not impossible, such low activities for tetrahedrite in these assemblages seems highly unlikely because of the notable scarcity of Ag and the relative abundance of Fe- and Sb-bearing phases (Harris 1986). This suggests that the substitution of Ag for Cu would be minimal. The concentrations of Fe and Sb in the tetrahedrite would be sufficient to preclude such low activities for the Fe-tetrahedrite component. In contrast, the unadjusted enthalpy-derived free energies yield a metastable curve for the end-member reaction that lies 3.5 to 5.3 log$f(S_2)$ units below Reaction 2. The coincidence of this curve with Reaction 1 would require activities of the Fe-tetrahedrite component well in excess of unity or extreme solid-solution effects in stibnite and chalcopyrite that are well beyond documented substitutions. On the other hand, the adjusted expression for free energy results in a stable curve for Reaction 1 that lies 0.25 to 0.63

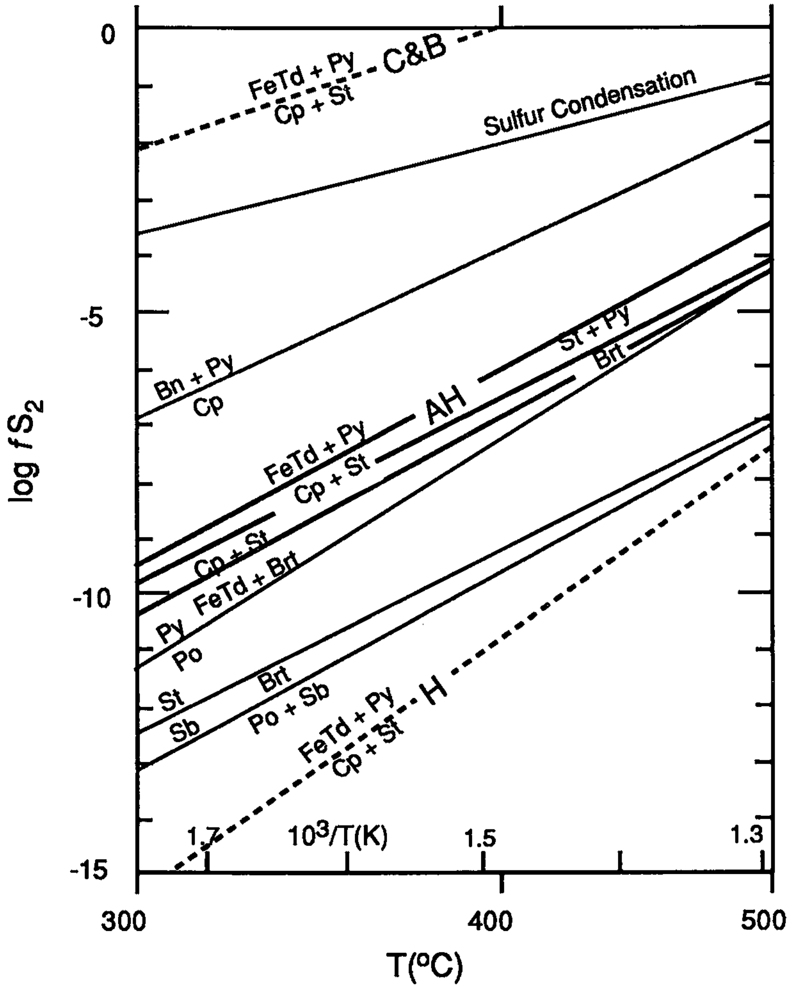

FIG. 1. Phase equilibria in the system Cu–Fe–Sb–S as a function of temperature and sulfur fugacity. The curves labelled C&B, H and AH correspond to stabilities for Reaction 1 calculated using free energies for Fe-tetrahedrite derived from a Craig & Barton approximation, an enthalpy-based estimate and an adjusted enthalpy-based estimate, respectively. Dashed curves represent metastable equilibria. Thermodynamic data for sulfides from Barton & Skinner (1979). Abbreviations are defined in Table 2.

log$f$(S_2) unit above Reaction 2. Geologically reasonable reduced activities for the Fe-tetrahedrite component of 0.11 to 0.42 would produce a stable field for the five-phase assemblage. Therefore, the adjusted estimate based on measured enthalpies appears to be the most accurate.

The most useful test of the accuracy of the free energy values for Fe-tennantite comes from the assemblage tennantite + pyrite + chalcopyrite + arsenopyrite and the FeS component, where FeS occurs as Fe-bearing sphalerite or pyrrhotite. The phases in this low-variance assemblage are related through the reaction:

$$10CuFeS_2 + 4FeAsS + FeS_2 = Cu_{10}Fe_2As_4S_{13} + 13FeS \quad (3)$$

At temperatures below this isobaric invariant point, tennantite and arsenopyrite are related through the reaction:

$$10CuFeS_2 + 4FeAsS + 13/2S_2 = Cu_{10}Fe_2As_4S_{13} + 12FeS_2 \quad (4)$$

At higher temperatures, tennantite and arsenopyrite are related by the reaction:

$$10CuFeS_2 + 4FeAsS + 1/2S_2 = Cu_{10}Fe_2As_4S_{13} + 12FeS \quad (5)$$

McKinstry (1963) reported assemblages in the system Cu–Fe–As–S from a variety of ore deposits that suggest that Reaction 8 occurs stably at temperatures and sulfur fugacities within the normal range of hydrothermal conditions. In addition, Loucks & Petersen (1989) reported the low-variance assemblage tetrahedrite–tennantite + pyrite + chalcopyrite + arsenopyrite + Fe-bearing sphalerite in the epithermal ores of the Topia district, Mexico. Therefore, equilibrium temperatures calculated for the pyrrhotite-bearing isobaric invariant point for Reaction 3 may be used as a test of the appropriateness of various expressions of the free energy of Fe-tennantite. The Craig & Barton estimate results in a geologically and thermodynamically unrealistic temperature of 755 ± 35°C, which is outside of the stability of all phases except pyrrhotite. The estimate based on measured enthalpies results in a calculated temperature of 235 ± 60°C, that is both geologically reasonable and within the stability fields of all of the phases.

The five-phase assemblage reported by Loucks & Petersen (1989) may also be used to calculate a Gibbs free energy for the Fe-tennantite component, which then can be used to calculate an invariant temperature for the end-member five-phase assemblage when combined with the temperature dependency from the present study. Loucks & Petersen (1989) and Loucks (1984) provided data on temperatures of fluid-inclusion homogenization (225 ± 10°C) and electron-microprobe data for tetrahedrite and sphalerite. Activities of the Fe-tennantite component for these compositions are low, ranging from $10^{-6.9}$ to $10^{-13.2}$, as calculated using the formulation of Sack *et al.* (1987) and the data from Ebel & Sack (1989). The activity of FeS in sphalerite was calculated using the model of Fleet (1975). These data result in a $\Delta G°_{225}$ value for Fe-tennantite of −1405.6 ± 12.4 kJ/mole. When combined with the temperature dependency from the present study, this value of free energy results in an invariant temperature of 415 ± 25°C for the pyrrhotite-bearing five-phase assemblage.

Natural assemblages also provide a check on the activity model of Sack *et al.* (1987) through "tetrahedrite–sphalerite" thermometry. Temperatures were calculated from electron-microprobe data for tetrahedrite–sphalerite pairs by iteratively solving the Fe–Zn exchange and Ag-ordering equations of Sack *et al.* (1987), using the thermodynamic data summarized by Ebel & Sack (1989). The calculated temperatures are presented in Table 1. In general, there is good agreement between the tetrahedrite–sphalerite temperatures and independent estimates.

The Bayhorse district, in south-central Idaho, contains several tetrahedrite–tennantite-bearing base- and precious-metal deposits (Hobbs 1985, Seal 1989). In the Barton mine, tetrahedrite coexists with minor sphalerite, pyrite, chalcopyrite and galena. Fluid-inclusion data (Seal 1989) suggest that mineralization occurred at temperatures above 280°C, which is in excellent agreement with the calculated tetrahedrite–sphalerite temperature of 300°C. In the Ramshorn mine, tetrahedrite and minor pyrite are cut by veinlets of chalcopyrite, arsenopyrite and trace sphalerite. Fluid-inclusion and stable isotope data indicate similar temperatures (>300°C) to those inferred for the Barton mine. In contrast, the calculated tetrahedrite–sphalerite temperature is unreasonably low (−30°C), and thus confirms the disequilibrium nature of this paragenesis. In the Clayton Silver mine, tetrahedrite occurs with sphalerite, pyrite, chalcopyrite and galena. Independent estimates of temperature are less certain. Geological similarities between this deposit and the Barton and Ramshorn mines suggest similar temperatures around 300°C, compared to highly variable calculated temperatures of 80 and 495°C. The large difference between these two calculated temperatures may reflect lower-temperature re-equilibration of tetrahedrite and sphalerite.

Additional tetrahedrite–sphalerite pairs examined in this study originate from Morococha, Huancavelica and Casapalca, Peru, and the Lucky Friday mine, Coeur d'Alene district, Idaho. Samples from Morococha and Huancavelica yielded reasonable calculated temperatures ranging from 140 to 230°C. At Casapalca, Rye & Sawkins (1974) concluded that the late sulfide stage formed between 280 and 320°C,

TABLE 5. PROVISIONALLY RECOMMENDED EXPRESSIONS FOR GIBBS FREE ENERGY & MOLAR THERMODYNAMIC DATA FOR TETRAHEDRITES AND TENNANTITES

Phase	$\Delta G°_T$ (J/mole; T(K))[1]	T Range (°C)
Fe-tennantite	-1,933,305 + 865.7 T	25 - 602
Zn-tennantite	-2,119,070 + 908.3 T	25 - 420
	-2,130,050 + 923.9 T	420 - 602
Fe-tetrahedrite	-1,871,251 + 860.8 T	25 - 630
Zn-tetrahedrite	-2,058,151 + 903.2 T	25 - 420
	-2,069,130 + 918.9 T	420 - 630

Phase	$\Delta H°_{298}$ (kJ)[1]	$S°_{298}$ (J/K)	V_{298} (cm³)[2]
Fe-tennantite	-1968.6	1048.9	322.1
Zn-tennantite	-2150.0	1048.9	322.1
Fe-tetrahedrite	-1909.5	1085.7	336.7
Zn-tetrahedrite	-2091.9	1085.7	336.7

	Heat Capacity Coefficients[3]			
Phase	a	$b \times 10^3$	$c \times 10^{-4}$	d
Fe-tennantite	-627.3	792.20	-2944.1	25499.4
Zn-tennantite	734.9	83.43	-97.1	
Fe-tetrahedrite	-634.5	840.40	-2944.1	25499.4
Zn-tetrahedrite	727.3	131.63	-97.1	

[1] Relative to the elements and ideal gas S_2.
[2] Calculated from the cell parameters of Johnson *et al.* (1987).
[3] $C_P(J) = a + bT + cT^{-2} + dT^{-0.5}$; T in K.

compared to a calculated temperature of 255°C. For the Coeur d'Alene district, Leach *et al.* (1988) concluded that ore deposition occurred between 250 and 350°C, which is in fair agreement with the calculated temperatures of 185 and 195°C.

Recommended free energies

From the analysis presented above for the Fe-tetrahedrite and tennantite end-members, it appears that the Craig & Barton method of approximation produces values of Gibbs free energy for these minerals that are less negative than is warranted by natural assemblages and the limited experimental and calorimetric data that are currently available. This conclusion is not surprising considering the significantly non-zero enthalpies of formation from the component sulfides reported by Bryndzia (pers. comm., 1988). However, Bryndzia & Kleppa (1989) noted that the assumption of no enthalpy of mixing is valid for some sulfosalts.

For the Fe and Zn end-member tennantites, the enthalpy-derived values of free energy at 500°C agree well with the experimental work of Sack & Loucks (1985). Therefore, these values are selected as best estimates for the free energies of these end members. Furthermore, calculated phase-equilibria involving Fe-tennantite and other minerals in the Cu–Fe–As–S system appear to be consistent with natural assemblages. The estimate based on measured enthalpies for Fe-tennantite is favored over the calculated value based on the natural assemblage of Loucks & Petersen (1989), because of the uncertainties related to the extremely low activities calculated for the Fe-

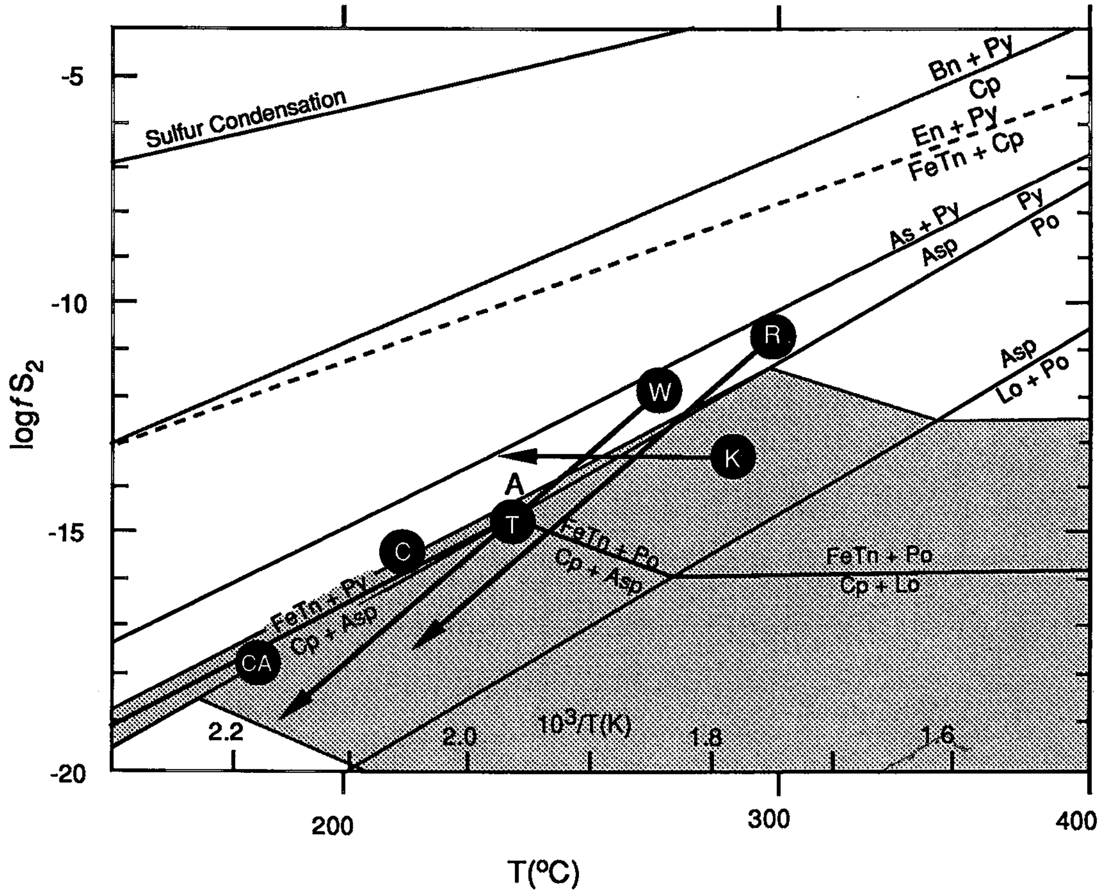

FIG. 2. Phase equilibria in the system Cu–Fe–As–S as a function of temperature and sulfur fugacity. Dashed curve represents schematically depicted equilibria. Symbols: R Ramshorn mine, C Clayton Silver mine, W Woodlawn mine, K Keno Hill, T Topia district, and CA Coeur d'Alene district. Arrows represent general trends recorded by the assemblages from these areas. The shaded area represents the uncertainty in the equilibria relating Fe-tennantite to arsenopyrite or löllingite resulting from the reported precision of the $\Delta H^\circ_{f,298}$ value. Thermodynamic data for sulfides from Barton & Skinner (1979). Abbreviations are defined in Table 2.

tennantite component. For the Sb end-members, the enthalpy-derived values are in distinct disagreement with the work of Sack & Loucks (1985). However, when the Gibbs free energy of Fe-tetrahedrite is recalculated relative to that for Zn-tetrahedrite, constrained by the data of Sack & Loucks (1985), the resultant free energy yields calculated phase equilibria that are in good agreement with natural assemblages. Therefore, this set of expressions is adopted for the tetrahedrite end-members. Table 5 is a compilation of the provisionally recommended free-energy expressions.

TENNANTITE EQUILIBRIA

The Cu–Fe–As–S (Fe-tennantite) system is by far the most interesting tennantite subsystem with respect to the number of stable equilibria that may be calculated between tennantite and associated ore and gangue phases. The uniqueness of the system results from the occurrence of common, multicomponent As phases, such as arsenopyrite, enargite and luzonite, in addition to tennantite.

At low sulfur fugacities in common ore-mineral assemblages, tennantite stability is restricted by reactions involving arsenopyrite. Equilibria dependent upon $f(S_2)$, as discussed above, emanate from the five-phase isobaric invariant point for Reaction 3, which has a calculated temperature of 235 ± 60°C for pure end-member compositions and assemblages including pyrrhotite. This reaction is nearly independent of pressure, as indicated by the calculated slope (dP/dT) of 570 bars/°C, from the cell-edge data of Johnson *et al.* (1987), and the S°_{298} estimate for Fe-tennantite from the present study and published values for the other phases.

At higher $f(S_2)$ values, tennantite stability is restricted by reactions involving enargite (Cu_3AsS_4), or its low-temperature polymorph, luzonite. The assemblages reported by McKinstry (1963) suggest that these phases are related within the chalcopyrite field through the reaction

$$4Cu_3AsS_4 + 4FeS_2 = Cu_{10}Fe_2As_4S_{13} + 2CuFeS_2 + 7/2S_2 \quad (6)$$

At present, insufficient thermodynamic data are available for enargite and luzonite. Therefore, this

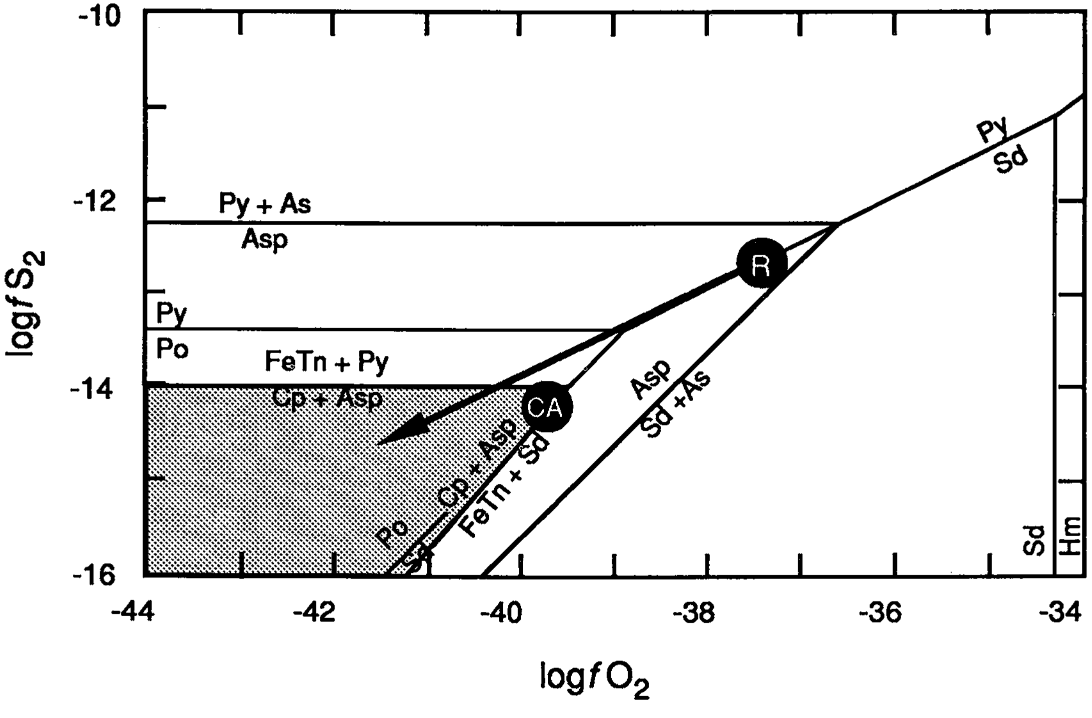

FIG. 3. Phase equilibria in the system Cu–Fe–As–S as a function of sulfur and oxygen fugacity at a temperature of 250°C. The siderite field is drawn to completely overlap the magnetite field at a fixed, but unspecified $f(CO_2)$. Symbols: R Ramshorn mine, Bayhorse district, Idaho, and CA Lucky Friday mine, Coeur d'Alene district, Idaho. Shaded area represents the stability of the assemblage arsenopyrite + chalcopyrite. Thermodynamic data for sulfides and oxides from Barton & Skinner (1979). Abbreviations area defined in Table 2.

reaction is only schematically represented in Figure 2 based on the assemblages presented by McKinstry (1963).

In terms of $f(S_2)$ and $f(O_2)$ at a fixed $f(CO_2)$, the stability of Fe-tennantite may be related to arsenopyrite through the reaction

$$10CuFeS_2 + 4FeAsS + 4CO_2 + 8O_2 = Cu_{10}Fe_2As_4S_{13} + 4FeCO_3 + 11/2S_2 \qquad (7)$$

This equilibrium restricts arsenopyrite + chalcopyrite to a field similar to that for pyrrhotite (Fig. 3).

Assemblages recording the low $f(S_2)$ equilibria are common in a variety of types of hydrothermal ore deposits, including porphyry copper deposits, epithermal and mesothermal veins, and volcanogenic massive sulfides. These ores appear to be typified by one of two trajectories in temperature – $f(S_2)$ space. The first trajectory is characterized by both a decrease in temperature and $f(S_2)$. The Ramshorn mine of the Bayhorse district, Idaho, records this hydrothermal evolution, in which early tetrahedrite-tennantite + pyrite is veined by later chalcopyrite + arsenopyrite. In the Woodlawn deposit, New South Wales, Australia, this transition probably represents either a late hydrothermal alteration or low-grade metamorphism (McKay & Hazeldene 1987, McKay 1989). In contrast, the ores of the Keno Hill district, Yukon, record a trajectory that is dominated by decreasing temperature at constant or slightly increasing $f(S_2)$. This path is represented by pyrrhotite + arsenopyrite giving way to pyrite + arsenopyrite, with tetrahedrite-tennantite persistent throughout (Lynch 1989). The Topia district, Mexico, records the low-variance assemblage tetrahedrite-tennantite + pyrite + chalcopyrite + arsenopyrite + Fe-bearing sphalerite (Loucks & Petersen 1989).

The mesothermal ores of the Bayhorse district and the Coeur d'Alene district (Leach *et al.* 1988) record early tetrahedrite-tennantite coexisting with siderite and pyrite. In the Ramshorn mine, the transition

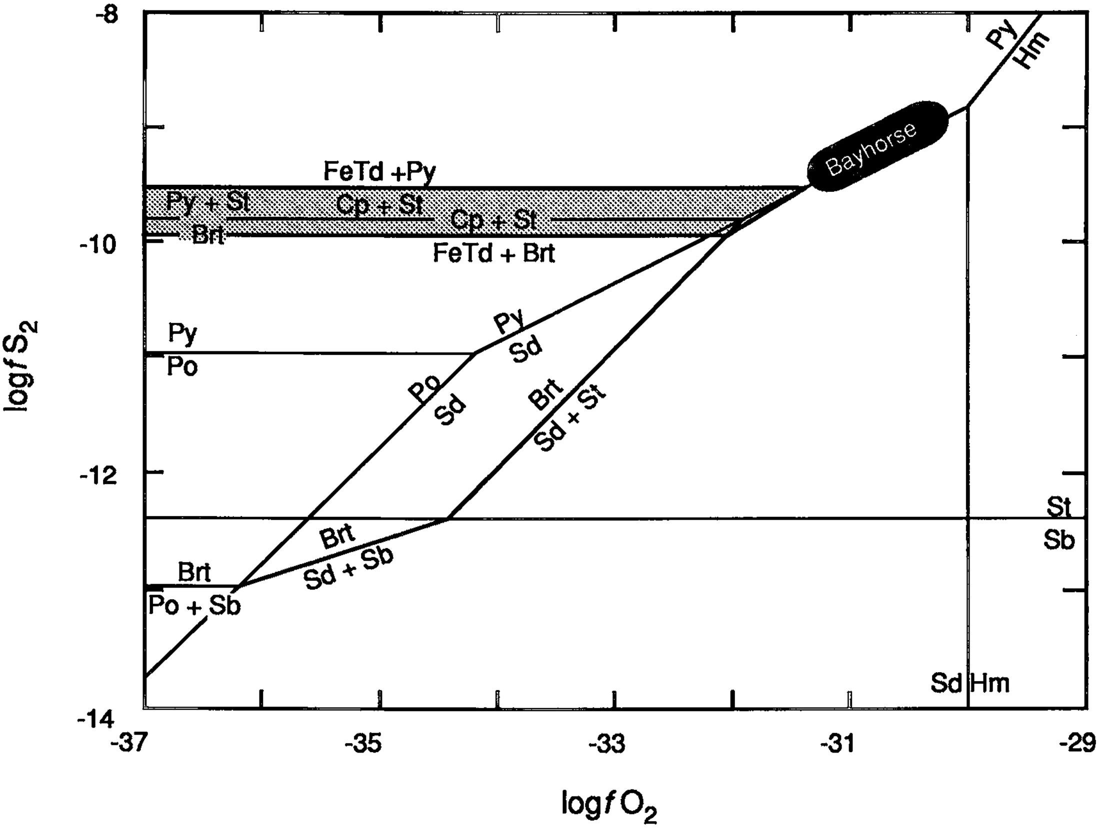

FIG. 4. Phase equilibria in the system Cu–Fe–Sb–S as a function of sulfur and oxygen fugacity at a temperature of 300°C. The siderite field is drawn to completely overlap the magnetite field at a fixed, but unspecified $f(CO_2)$. Bayhorse: stability field recorded by the ores of the Bayhorse district, Idaho. Shaded area represents the stability of the assemblage stibnite + chalcopyrite. Equilibria involving Sb_2O_3 have been omitted for simplicity. Thermodynamic data for sulfides and oxides from Barton & Skinner (1979). Abbreviations area defined in Table 2.

from this assemblage to late arsenopyrite + chalcopyrite requires a decrease in $f(O_2)$ in addition to the decrease in temperature and $f(S_2)$ discussed above (Fig. 3).

TETRAHEDRITE EQUILIBRIA

The Sb end-members appear to be more stable than the As end-members. In addition to Reaction 1, Fe-tetrahedrite stability is also restricted by the reaction

$$Cu_{10}Fe_2Sb_4S_{13} + 2FeSb_2S_4 + 11/2S_2 = 10CuFeS_2 + 4Sb_2S_3 \quad (8)$$

These equilibria greatly restrict the stability of the assemblage chalcopyrite + stibnite. Given that tetrahedrite is the only phase that exhibits appreciable

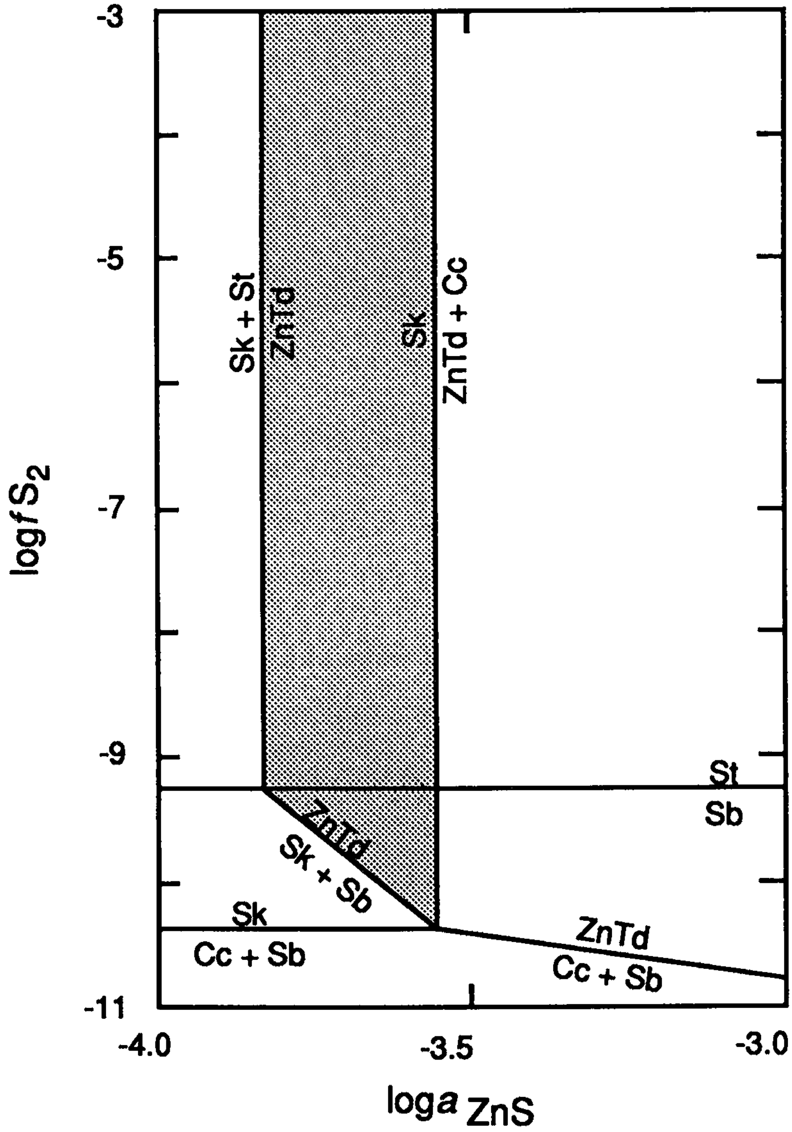

FIG. 5. Phase equilibria involving skinnerite at a temperature of 400°C. The shaded area represents the stability of the assemblage Zn-tetrahedrite + skinnerite (see text). The value of a(ZnS) is calculated relative to sphalerite. Thermodynamic data for sulfides from Barton & Skinner (1979), and for skinnerite, from Craig & Barton (1973). Abbreviations are defined in Table 2.

solid-solution, any solid-solution substitution would shift the location of these reactions so as to eliminate the stability of chalcopyrite + stibnite in most natural settings. This observation is consistent with the rarity of this assemblage (Gumiel & Arribas 1987). Hemlo is one of the few deposits where chalcopyrite + stibnite has been reported with tetrahedrite, pyrite and berthierite (Harris 1986). The overwhelming stability of Fe-tetrahedrite in the system Cu–Fe–Sb–S is consistent with the 500°C experimental work of Tatsuka & Morimoto (1977), who concluded that Fe-tetrahedrite stably exists with all binary and ternary sulfide phases except covellite.

In terms of $f(S_2)$ and $f(O_2)$, the reaction

$$Cu_{10}Fe_2Sb_4S_{13} + 8FeCO_3 + 13/2S_2 = 10CuFeS_2 + 2Sb_2S_3 + 8CO_2 + 4O_2 \qquad (9)$$

serves to limit the stability of chalcopyrite + stibnite in CO_2-bearing environments. Stable equilibria between famatinite (Cu_3SbS_4) and tetrahedrite also may be important, but the lack of thermodynamic data for famatinite precludes a more rigorous evaluation of these equilibria. In the mesothermal veins of the Bayhorse and Coeur d'Alene districts, Idaho, tetrahedrite + pyrite + siderite is a common assemblage that constrains the prevailing $f(S_2)$ and $f(O_2)$ accompanying mineralization at a fixed $f(CO_2)$ (Fig. 4).

The Gibbs free energies for Zn- and Fe-tetrahedrite permit the stability of the rare sulfosalt skinnerite (Cu_3SbS_3) to be evaluated in a more realistic fashion than allowed by phase relations in the simple system Cu–Sb–S (Skinner *et al.* 1972). For example, the new data on free energy in the present study permit the phase relations reported by Karup-Møller (1974) for the Cu–Sb sulfosalts from the Ilímaussaq complex, Greenland, to be reinterpreted.

Phase equilibria as a function of sulfur fugacity and activity of zinc sulfide (relative to sphalerite) between Zn-tetrahedrite and skinnerite (Fig. 5) have been calculated at 400°C, similar to that inferred for the Cu–Sb mineralization of the Ilímaussaq complex (Karup-Møller 1974). In this analysis, only those equilibria which limit the stability of tetrahedrite or skinnerite have been considered. Equilibria involving chalcostibite ($CuSbS_2$) have been omitted for the sake of simplicity because the Gibbs free energy for the reaction

$$CuSbS_2 + Cu_2S = Cu_3SbS_3 \qquad (10)$$

is only –1289 J/mole at 400°C.

In skinnerite-bearing assemblages, the stability of Zn-tetrahedrite is limited by the reactions

$$3Cu_{10}Zn_2Sb_4S_{13} = 10Cu_3SbS_3 + 2Sb + 6ZnS + 3/2S_2 \qquad (11)$$

$$3Cu_{10}Zn_2Sb_4S_{13} = 10Cu_3SbS_3 + Sb_2S_3 + 6ZnS \qquad (12)$$

and

$$Cu_{10}Zn_2Sb_4S_{13} = 5Cu_2S + 4Sb + 2ZnS + 3S_2 \qquad (13)$$

Conversely, the stability of skinnerite is constrained by the reactions

$$2Cu_3SbS_3 = 3Cu_2S + 2Sb + 3/2S_2 \qquad (14)$$

and

$$4Cu_3SbS_3 + 2ZnS = Cu_{10}Zn_2Sb_4S_{13} + Cu_2S \qquad (15)$$

An important feature of the calculated phase-equilibria in this system is that they indicate the incompatibility of skinnerite and sphalerite. Similar calculations in the system Cu–Fe–Sb–S yield identical results, which suggest that this mineral should only be found in low-Fe environments as well.

In the Ilímaussaq intrusive complex, Karup-Møller (1974) described two localities containing tetrahedrite. In the first occurrence, tetrahedrite coexists with skinnerite, but not sphalerite or iron sulfides. At the second locality, tetrahedrite occurs with sphalerite, but not skinnerite. The calculated stabilities of these phases explain these observations. For the first locality, skinnerite occurs in assemblages lacking sphalerite, as predicted in Figure 5; for the second locality, sphalerite-bearing assemblages lack skinnerite, as would be expected for environments with a(ZnS) values sufficiently high to stabilize sphalerite. Bryndzia & Davis (1989) suggested that the quenching properties of skinnerite and subsolidus peritectic breakdown reactions also contribute to its rarity in nature.

CONCLUSIONS

Tetrahedrite and tennantite are compositionally complex phases that cannot be accurately described by the system Cu–Sb–As–S. The formula $(Cu,Ag)_{10}(Fe,Zn)_2(Sb,As)_4S_{13}$ describes well the compositional variations found in most samples of natural tetrahedrite and tennantite. Accordingly, phase-equilibrium calculations with these compositions will have greater applicability to natural settings than the previously proposed simpler formulae. The present study has demonstrated that tetrahedrite and tennantite are extremely stable relative to other sulfosalts and certain other sulfide phases, and it is this stability that accounts for their common occurrence in a variety of mineral deposits. This widespread occurrence, in turn, increases the usefulness of tetrahedrite and tennantite reactions in constraining temperatures and fugacities of volatile components in a given deposit. Whereas this study is intended to enhance our ability to retrieve genetic information from these common sulfosalts, greater precision in defining the stabilities of tetrahedrite and tennantite is required, and must await additional laboratory work.

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