Arsenic–silver incompatibility in fahlore

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Abstract

Silver-bearing zinc–iron tetrahedrite–tennantite and freibergit fahlores approximating the simplified formula $(Ag,Cu)_{10}(Fe,Zn)_2(As,Sb)_4S_{13}$ have been equilibrated with excess electrum (Au_xAg_{1-x}) and chalcopyrite + pyrite + iron-bearing sphalerite ($CuFeS_2 + FeS_2 + Fe_{0.05}Zn_{0.95}S$) in evacuated silica tubes at 300 °C, in reversed silver–copper exchange experiments with less than 0.1 mg NH_4Cl added as a transport medium. A thermodynamic formulation and parameters describing As–Ag incompatibility at 400 °C (Ebel and Sack, 1989), which incorporate large temperature dependencies of standard-state properties and composition-ordering systematics, are shown to apply equally well to these 300 °C results. A generalised graphical model for this mineral assemblage is presented, describing fahlore composition as a function of temperature and the compositions of coexisting electrum and (Fe,Zn)S, which define the $Ag(Cu)_{-1}$ and $Fe(Zn)_{-1}$ exchange properties controlling fahlore compositions.

KEYWORDS: tetrahedrite, thermodynamics, fahlore, silver, sulphosalt, geothermometer, electrum.

Introduction

A wide variety of mineral names and modifiers, rivalling the spinel appelative arcanum, has been applied to what Ramdohr (1969, p. 554) called the *Fahlerzgruppe*, an isomorphous mineral family approximating $M_6^{TRG}M_6^{TET}X_4Y_{13}$, where M = Ag, Cu, Zn, Fe, Cd, Mn, etc. in trigonal-planar and tetrahedral sites; X = As, Sb, Bi; and Y = S, Te (Spiridonov, 1984; see also Note 1). Fahlores approximating the ideal stoichiometry

$$(Ag,Cu)_6^{TRG}[(Ag,Cu)_{2/3}(Fe,Zn)_{1/3}]_6^{TET}(As,Sb)_4S_{13}$$

include the tetrahedrite–tennantite solid-solution series and freibergite, and encompass most compositions found in nature. This sulfosalt is an ideal indicator of intensive parameters (e.g. temperature, and the potentials for chemical exchange of its surroundings) at the time of its crystallisation, because it often preserves its primary depositional chemistry (Yui, 1971; Raabe and Sack, 1984), and is so ubiquitous and variable.

In order to better understand their response to variation of intensive parameters, fahlores of varying As : Sb ratios have been equilibrated with electrums of varying Ag contents. In each experiment, fahlore with a particular fixed As : Sb ratio and some initial known Ag : Cu ratio is swamped with electrum of a fixed Ag content, and all the experiments also contain a large mass of pyrite + chalcopyrite + $Fe_{0.05}Zn_{0.95}S$ (sphalerite). The mass ratios ensure that only the fahlore changes composition, and an equilibrium fahlore composition is approached from two directions by starting with high and low initial Ag : Cu ratios in the fahlore for each electrum. For each fahlore of fixed As : Sb ratio, the final Ag : Cu ratio depends on the Ag content of the electrum with which it has been equilibrated.

The compositions of the mineral products of these experiments at 300 °C are used to test the authors' (1989) interpretation of results of similar experiments at 400 °C. At the lower temperature, a given fahlore incorporates much less Ag when it coexists with a given electrum, so the present results are very different from those of the 400 °C work. Since the model equations are very sensitive to variations in temperature, their extrapolation to 300 °C is a significant test. The new results confirm a very large value for the Gibbs free energy ($\Delta\bar{G}_{34}^{o}$) of the reciprocal reaction

$$Cu_{10}F_2As_4S_{13} + Ag_{10}Fe_2Sb_4S_{13} = Cu_{10}Fe_2Sb_4S_{13} + Ag_{10}Fe_2As_4S_{13}, \quad (1)$$

which expresses the crystal–chemical incompatibility between As and Ag in fahlores.

The model or tetrahedrite–tennantite thermochemistry, proposed by Sack *et al.* (1987) and augmented here, remains a subset of an as yet unrealised model for all the fahlore minerals and associated sulfosalts. However, its demonstrably accurate extension to the upper range of temperatures thought to characterise ore deposits of the fissure-vein type makes it immediately applicable

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to the problems of geothermometry and chemical potential gradients encountered by the sulfide petrologist. We therefore present a graphical description of fahlore behaviour at temperatures representative of those at which ore deposits preserve features of chemical equilibrium.

Thermodynamic formulation

An expression for the molar Gibbs energy of any tetrahedrite–tennantite fahlore mineral, at any temperature, is formulated as the linear combination of (1) a standard expression for the mixing of atoms on sites, describing the configurational energy, and (2) a Taylor expansion of second degree in the linearly independent composition (X_2, X_3, X_4) and ordering (s) variables (see Table 1), describing the nonconfigurational ('vibrational') energy. Coefficients of the Taylor expansion are identified with physical parameters, vibrational energies of end-member components, energies of reciprocal and reciprocal-ordering reactions ($\Delta\bar{G}^{o}_{ij}$ and $\Delta\bar{G}^{*}_{ij}$; see Note 2), and binary regular solution parameters (W^{site}_{AB}) describing non-ideal mixing of atoms on sites (see Note 3).

The order variable (s) describes the average (long-range) distribution of silver and copper between trigonal-planar (TRG) and tetrahedral (TET) metal sites. O'Leary and Sack (1987) and Sack *et al.* (1987) demonstrated that miscibility gap features, and parallels between Zn(Fe)$_{-1}$ exchange potential—X_4 and cell volume—composition systematics in Sb-rich argentian fahlores, could be simply explained if Ag–Cu site ordering, as described by the variable s, changes from positive to negative with increasing Ag in fahlores with intermediate values of X_4 (see Note 4). The value of s is given by solution of the condition of homogeneous (internal) equilibrium (Table 1), which is evaluated by setting the partial derivative of the molar Gibbs energy ($\bar{G}$), with respect to the internal ordering variable (s), equal to zero. The expression for $\bar{G}$ is similarly differentiated (cf. Sack, 1982; Sack *et al.*, 1987; Ghiorso, 1990) to obtain an expression for the difference between the chemical potentials of Ag and Cu end-member fahlore components (i.e. the Ag(Cu)$_{-1}$ exchange potential $\mu_{Ag(Cu)_{-1}}$ in fahlore), as a function of fahlore composition and temperature (Table 1).

Two heterogeneous equilibria are relevant to the present discussion of fahlore thermodynamics. Sphalerite and fahlore will exchange Fe and Zn until they attain Zn(Fe)$_{-1}$ exchange equilibrium. Work on mineral assemblages from the laboratory (Sack and Loucks, 1985) and the field (O'Leary and Sack, 1987) has resulted in tight constraints on the parameters describing this exchange, and its separate effects on Ag(Cu)$_{-1}$ and As(Sb)$_{-1}$ exchanges in fahlore. Algebraic expressions describing the relevant equilibria, and the calibration of the parameters, have been developed in detail elsewhere (see Table 1).

The heterogeneous equilibrium of greatest interest here is the exchange of Ag and Cu between fahlore and a mineral assemblage saturated with pyrite, chalcopyrite, and electrum, as governed by the reaction

$$(1/10)Cu_{10}Fe_2Sb_4S_{13} + Ag^{EL} + FeS_2 = (1/10)Ag_{10}Fe_2Sb_4S_{13} + CuFeS_2, \quad (2)$$

or equivalent Zn, As and Zn–As end-member reactions. The condition for heterogeneous equilibrium governing the Ag–Cu exchange reaction is formulated for the assumption that pyrite and chalcopyrite are unary (of fixed composition). A quantity Q^*_x is then defined (Table 1; see Note 5), which is linear in the variables of interest. The complete thermochemical formulation for silver bearing tetrahedrite–tennantite fahlores can be applied in a variety of ways by algebraic manipulation of expressions derived from chemical reactions, utilising the full set of parameters listed in Table 1.

Method of experimentation

The technique closely follows that of Ebel and Sack (1989). To several mm of a finely ground mixture of $CuFeS_2$ (synthetic), FeS_2 (from Bingham, Utah, U.S.A.), and $Fe_{0.05}Zn_{0.95}S$ (synthetic) in a 2 mm (inner diam.) silica glass tube, a 1 mm layer of electrum filings ($Ag_{0.3}Au_{0.7}$, $Ag_{0.4}Au_{0.6}$, or $Ag_{0.7}Au_{0.3}$) was added, followed by several large (0.1 to 0.5 mm diam.) grains of fahlore. Starting compositions of fahlores are listed in Ebel and Sack (1989). More electrum (1 mm) was then added, followed by several more millimeters of the mixture, with a very small quantity (0.8 ± 0.2 mg) of NH_4Cl. The tubes were then welded shut around a silica glass rod, after (ongoing) evacuation on a diffusion pump apparatus, and placed horizontally in a furnace at 300 °C (±5°). Upon quenching in water, the tubes were cut open, and the fahlore was mounted in epoxy for microprobe analysis, using synthetic fahlore standards as described by Ebel and Sack (1989), on a CAMECA SX-50 at 15 KV, 30 nA, 30 sec each element, with a 1 micrometre beam, using CAMECA's PAP correction scheme.

Table 1. Notation, relevant equations, and parameter values.

$$X^{EL}_{Ag} = \frac{Ag}{(Ag+Au)} \quad \text{in electrum} \quad Ag_X Ag_{1-X}$$

$$X^{SPH}_{FeS} = \frac{Fe}{(Fe+Zn)} \quad \text{in sphalerite} \quad Fe_X Zn_{1-X} S$$

Composition and ordering variables in fahlore:

$$X_2 = \frac{Zn}{(Zn+Fe)} = X^{TET}_{Zn} \qquad X_3 = \frac{As}{(As+Sb)} = X^{SM}_{As}$$

$$X_4 = \frac{Ag}{(Ag+Cu)} = \frac{3}{5} X^{TET}_{Ag} + \frac{3}{5} X^{TRG}_{Ag} \qquad s = X^{TRG}_{Ag} - \frac{3}{2} X^{TET}_{Ag}$$

fahlore: $(Ag,Cu)^{TRiGonal}_6([Ag,Cu]_{2/3}[Fe,Zn]_{1/3})^{TETrahedral}_6(As,Sb)^{SemiMetal}_4 S_{13}$

Condition of homogeneous equilibrium for Ag-bearing fahlores:

$$\left(\frac{\partial \bar{G}}{\partial s}\right)_{T,X_2,X_3,X_4} = \frac{12}{5} RT\ln\left[\left(\frac{X_4 + \frac{2}{5} s}{1 - X_4 - \frac{2}{5} s} \right)\cdot\left(\frac{\frac{2}{3} - \frac{2}{3} X_4 + \frac{2}{5} s}{\frac{2}{3} X_4 - \frac{2}{5} s} \right) \right]$$

$$+ \Delta\bar{G}^*_{2s} X_2 + \Delta\bar{G}^*_{3s} X_3 + \Delta\bar{G}^*_{s} + \frac{2}{25}\left(6\Delta\bar{G}^*_{4s} - 9W^{TET}_{AgCu} - 4W^{TRG}_{AgCu}\right) s$$

$$+ \frac{1}{10}\left(\Delta\bar{G}^*_{4s} + 6W^{TET}_{AgCu} - 4W^{TRG}_{AgCu}\right)(2X_4 - 1) = 0$$

Ag-for-Cu exchange potential in fahlore:

$$\mu^{fahlore}_{Ag(Cu)_{-1}} = \frac{1}{10}\left[\bar{G}^O_{Ag_{10}Fe_2Sb_4S_{13}} - \bar{G}^O_{Cu_{10}Fe_2Sb_4S_{13}} - \Delta\bar{G}^O_{24} X_2 + \Delta\bar{G}^O_{34} X_3 \right.$$

$$\left. + \left(\Delta\bar{G}^*_{4s} + W^{TET}_{AgCu} + W^{TRG}_{AgCu}\right)(1 - 2X_4) + \frac{1}{5}\left(\Delta\bar{G}^*_{4s} + 6W^{TET}_{AgCu} - 4W^{TRG}_{AgCu}\right) s \right]$$

$$+ \frac{1}{10} RT\ln\left[\left(\frac{X_4 + \frac{2}{5} s}{1 - X_4 - \frac{2}{5} s} \right)^6 \cdot \left(\frac{\frac{2}{3} X_4 - \frac{2}{5} s}{\frac{2}{3} - \frac{2}{3} X_4 + \frac{2}{5} s} \right)^4 \right]$$

Condition of heterogeneous equilibrium:

$$\mu^{fahlore}_{Ag(Cu)_{-1}} = \mu^{electrum}_{Ag} + \mu^{pyrite}_{FeS_2} - \mu^{chalcopyrite}_{CuFeS_2} = \mu^{system}_{Ag(Cu)_{-1}}$$

Definition of $\bar{Q}^*_X$:

$$\frac{1}{10} RT\ln\left[\left(\frac{1 - X_4 - \frac{2}{5} s}{X_4 + \frac{2}{5} s} \right)^6 \cdot \left(\frac{\frac{2}{3} - \frac{2}{3} X_4 + \frac{2}{5} s}{\frac{2}{3} X_4 - \frac{2}{5} s} \right)^4 \right] - \frac{1}{10} \Delta\bar{G}^O_{24} X_2$$

$$- \frac{1}{10}\left(\Delta\bar{G}^*_{4s} + W^{TET}_{AgCu} + W^{TRG}_{AgCu}\right)(1 - 2X_4) - \frac{1}{50}\left(\Delta\bar{G}^*_{4s} + 6W^{TET}_{AgCu} - 4W^{TRG}_{AgCu}\right) s$$

$$\equiv \bar{Q}^*_X = \left(\left[\Delta\bar{H}^O_{Ag(Cu)_{-1}} - T\cdot\Delta\bar{S}^O_{Ag(Cu)_{-1}} \right] - RT\ln(a^{electrum}_{Ag}) \right) + \frac{1}{10} \Delta\bar{G}^O_{34} X_3$$

Parameter values†:

$\Delta\bar{G}^O_{23} = 2.59 \pm 0.14^{1,2}$ $\Delta\bar{G}^O_{24} = 2.30^{3,4}$ $\Delta\bar{G}^O_{34} = 12.25 \pm 1.92^5$ $\Delta\bar{G}^*_{s} = -0.40^3$

$\Delta\bar{G}^*_{2s} = 2.60^3$ $\Delta\bar{G}^*_{3s} = 0.0^3$ $\Delta\bar{G}^*_{4s} = -2.60^3$ $W^{TET}_{FeZn} = W^{TRG}_{AgCu} = 0.0^{3,4}$

$W^{TET}_{AgCu} = 6.933^{3,4}$ $W^{SM}_{AsSb} = 4.0^6$ $\Delta\bar{G}^O_{Zn(Fe)_{-1}} = 2.07 \pm 0.07^2$

$\Delta\bar{S}^O_{Ag(Cu)_{-1}} = 10.38^{5,7}$ cal deg^{-1} gfw^{-1} $\Delta\bar{H}^O_{Ag(Cu)_{-1}} = 4.137 \pm 0.12$ kcal/gfw^5

$R = 0.01987$ kcal deg^{-1} mole^{-1} (gas constant) T = temperature (K)

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† Kilocalories per gram–formula–weight, unless noted otherwise. Error is estimated only for values derived directly from data. Subscripts refer to composition variables (X_2, X_3, X_4, s) involved in reciprocal reactions.

References for parameter values:
1 Raabe and Sack (1984)
2 Sack and Loucks (1985)
3 Sack *et al.* (1987)
4 O'Leary and Sack (1987)
5 Ebel and Sack (1989)
6 Sack (1991)
7 Barton and Skinner (1979)
8 Barton (1980)

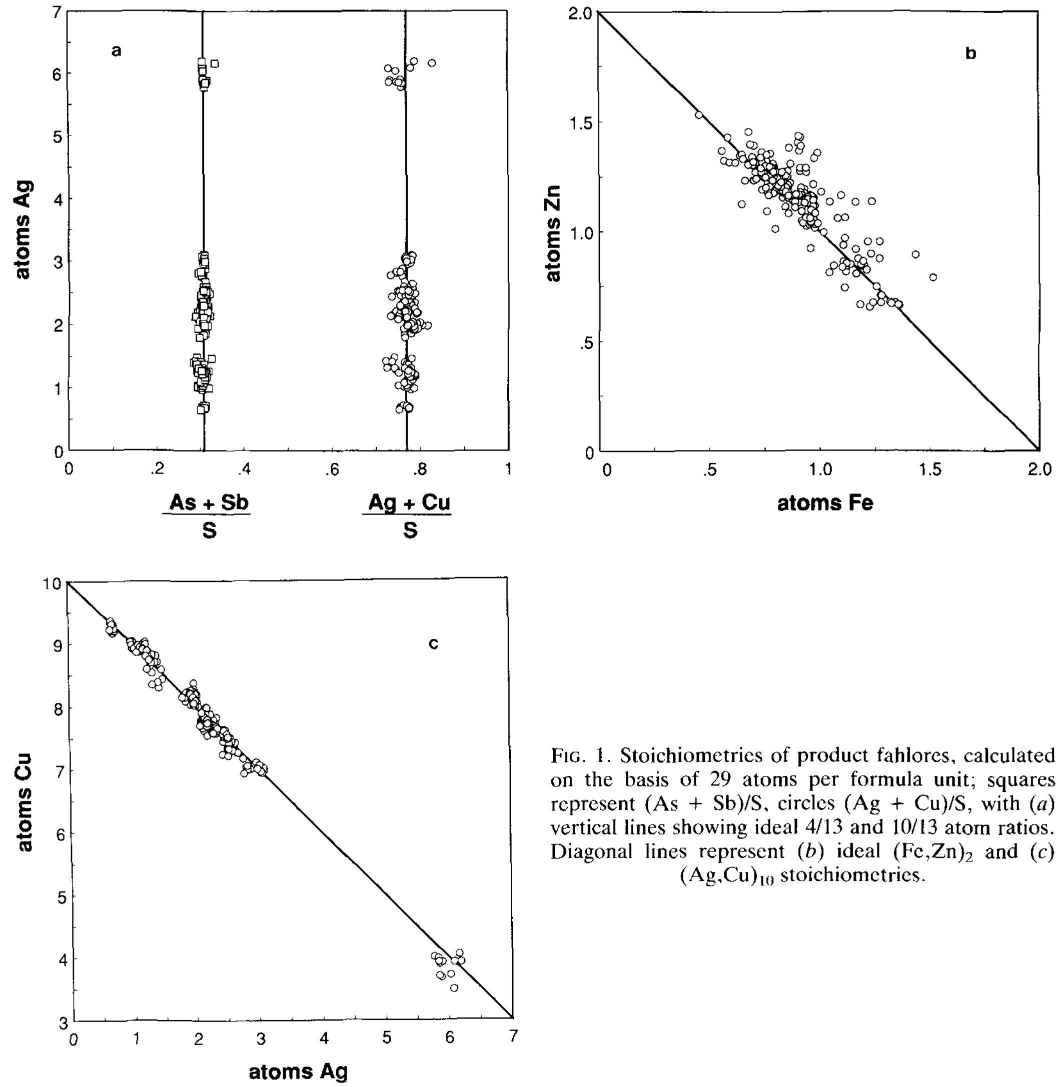

FIG. 1. Stoichiometries of product fahlores, calculated on the basis of 29 atoms per formula unit; squares represent (As + Sb)/S, circles (Ag + Cu)/S, with (*a*) vertical lines showing ideal 4/13 and 10/13 atom ratios. Diagonal lines represent (*b*) ideal $(Fe,Zn)_2$ and (*c*) $(Ag,Cu)_{10}$ stoichiometries.

Results of experiments

Experimental products were found to closely match the ideal fahlore stoichiometry (Fig. 1). Both X_4 [Ag/(Ag + Cu)] and X_2 [Zn/(Fe + Zn)] ratios were found to change in the product fahlore grains (Table 2; see also Note 6) relative to initial compositions. Because the fahlores were initially synthesised with X_2 calculated to be in equilibrium with sphalerite $Fe_{0.05}Zn_{0.95}S$ at 400 °C (Sack and Loucks, 1985; Ebel and Sack, 1989), they re-equilibrated to compositions more appropriate for 300 °C (cf. O'Leary and Sack, 1987). Despite sluggish kinetics at 300 °C, tight constraints on $Ag(Cu)_{-1}$ exchange were obtained for experiments with $X_{Ag}^{EL} \approx 0.3$ and 0.4. Identical combinations of initial fahlore and electrum produced fahlores with Ag contents changed in the same direction in all cases, and for this reason only experiments with the greatest such change are reported in Table 2 and Fig. 2.

Values of the quantity $\bar{Q}_x^*$ are calculated from the results of the experiments (Table 2), using the left side of the definition of $\bar{Q}_x^*$ (Table 1), and plotted in Fig. 2. The lines on Fig. 2 have slope $\Delta\bar{G}_{34}^o$, and are calculated from the right side of the equation defining $\bar{Q}_x^*$.

In several experiments, with an initial fahlore of composition ($X_2 = 0.48$ $X_3 = 0.5$ $X_4 = 0.2$), a new fahlore with lower X_4 resulted, which was

Table 2. Run conditions, final sulfosalt compositions (wt. %), and calculated values for order variable (s). Standard deviations for N analyses are indicated.

label*	date	hours	N	Cu σ	Ag σ	Fe σ	Zn σ	Sb σ	As σ	S σ	sum σ	*s* σ
30 mole % Ag in electrum; 300 °C												
A7-1	4/28/89	6122	10	32.50 (0.63)	8.91 (0.48)	2.45 (0.42)	4.58 (0.49)	21.95 (0.99)	4.19 (0.64)	25.36 (0.44)	99.94 (1.04)	0.086 (0.008)
C7-1	5/1/88	2520	22	35.22 (0.35)	7.08 (0.32)	3.06 (0.21)	5.08 (0.32)	14.34 (0.77)	9.59 (0.46)	25.70 (0.33)	100.02 (0.72)	0.075 (0.003)
H7-2	4/28/89	9266	26	29.88 (0.35)	12.17 (0.25)	2.56 (0.22)	4.77 (0.30)	27.72 (0.24)	0.00 (0.00)	23.71 (0.24)	100.79 (0.84)	0.097 (0.006)
S7-1	2/2/89	5133	11	33.99 (0.60)	8.03 (0.36)	3.62 (0.60)	3.27 (0.71)	18.55 (0.80)	6.84 (0.53)	24.97 (0.17)	99.22 (0.43)	0.097 (0.009)
V7-1	2/2/89	5133	10	37.00 (0.26)	4.65 (0.15)	3.25 (0.09)	4.72 (0.10)	13.14 (0.70)	10.77 (0.40)	26.14 (0.27)	99.54 (0.44)	0.054 (0.002)
40 mole % Ag in electrum; 300 °C												
B8-1	5/1/88	2520	29	28.23 (0.56)	14.07 (0.48)	3.13 (0.57)	3.91 (0.69)	20.99 (0.37)	4.50 (0.30)	23.97 (0.14)	98.79 (0.40)	0.115 (0.019)
D8-2	5/1/88	2520	7	36.68 (0.27)	8.94 (0.24)	3.94 (0.40)	4.53 (0.43)	0.00 (0.00)	19.36 (0.43)	27.43 (0.27)	100.72 (1.00)	0.093 (0.006)
G8-1	5/1/88	2520	6	27.37 (0.32)	15.83 (0.23)	3.13 (0.15)	4.32 (0.08)	19.94 (0.46)	5.38 (0.26)	24.17 (0.36)	99.82 (0.76)	0.104 (0.003)
H8-1	4/28/89	6122	32	27.98 (0.37)	13.22 (0.31)	2.48 (0.19)	4.60 (0.24)	27.64 (0.38)	0.00 (0.00)	23.70 (0.34)	99.89 (0.64)	0.095 (0.006)
K8-1	5/1/88	2520	21	24.74 (0.41)	17.77 (0.50)	2.42 (0.37)	4.50 (0.40)	27.04 (0.38)	0.00 (0.00)	23.15 (0.41)	99.58 (0.91)	0.054 (0.023)
L8-1	2/1/89	5210	13	28.48 (0.75)	14.34 (0.89)	2.83 (0.25)	4.51 (0.28)	20.94 (0.71)	4.42 (0.41)	24.10 (0.21)	99.57 (0.44)	0.101 (0.008)
M8-1	2/1/89	5210	17	26.91 (0.45)	15.44 (0.46)	3.56 (0.42)	3.32 (0.52)	23.91 (0.46)	2.34 (0.17)	23.60 (0.18)	98.99 (0.55)	0.129 (0.018)
S8-1	2/1/89	5210	10	29.94 (0.87)	12.56 (0.81)	3.25 (1.04)	3.99 (0.98)	18.14 (0.50)	6.46 (0.27)	24.53 (0.28)	98.79 (0.63)	0.114 (0.026)
70 mole % Ag in electrum; 300 °C												
K0N2	4/28/89	9266	12	12.82 (0.54)	33.65 (0.65)	3.15 (0.64)	4.09 (0.67)	25.76 (0.50)	0.00 (0.00)	21.65 (0.47)	101.28 (0.62)	-0.295 (0.027)

* First letter corresponds to initial sulfosalt composition (cf. Ebel and Sack, 1989, Table 3).

in reaction relationship with the assemblage $(Ag,Cu)_{16}(As,Sb)_2S_{11}$ (polybasite–pearcite solid-solution) + $CuFeS_2$ + ZnS, as evidenced by their intergrowth texture. This result supports an inference that the surface described by the equation for the molar Gibbs energy of fahlore, $\bar{G} = g(X_2,X_3,X_4,s,T)$, flattens in this composition region, resulting in solid-state immiscibility at slightly lower temperatures (cf. Sack *et al.*, 1987; Sack, 1919), or instability with respect to sulfo-

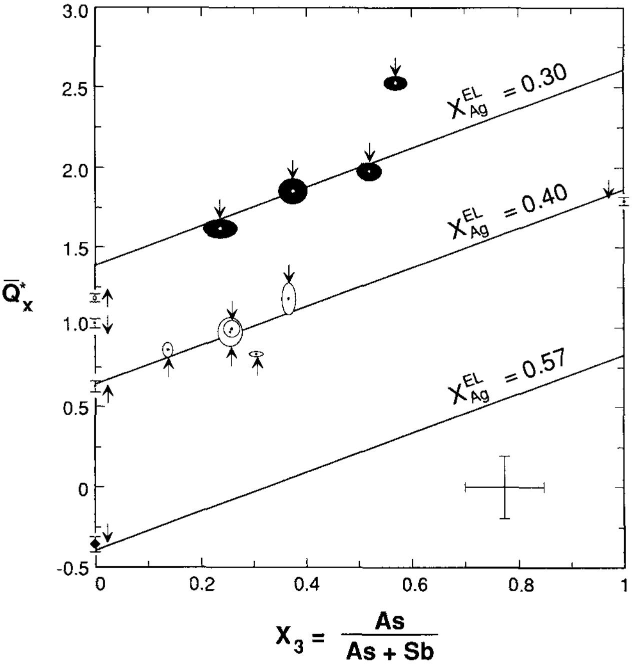

FIG. 2. $\bar{Q}^*_x$ *versus* X_4 for 300 °C experiments. Lines show predicted values for various X^{EL}_{Ag}, all with $X^{SPH}_{FeS} = 0.05$ at 300 °C. Ellipses and error brackets represent standard deviations for experiments with $X^{EL}_{Ag} \simeq 0.3$ (shaded), and 0.4 (open). A diamond represents experiment KON2, with initial $X^{EL}_{Ag} \simeq 0.7$, calculated to re-equilibrate to $X^{EL}_{Ag} = 0.57$ due to formation of Ag_2S (see Fig. 3). Arrows indicate direction of change of $\bar{Q}^*_x$ during experiments. Brackets to lower right illustrate the effect of simultaneously increasing As and Ag by 1.5 wt.% with equivalent decrease in Sb and Cu, and vice versa, for a typical data point.

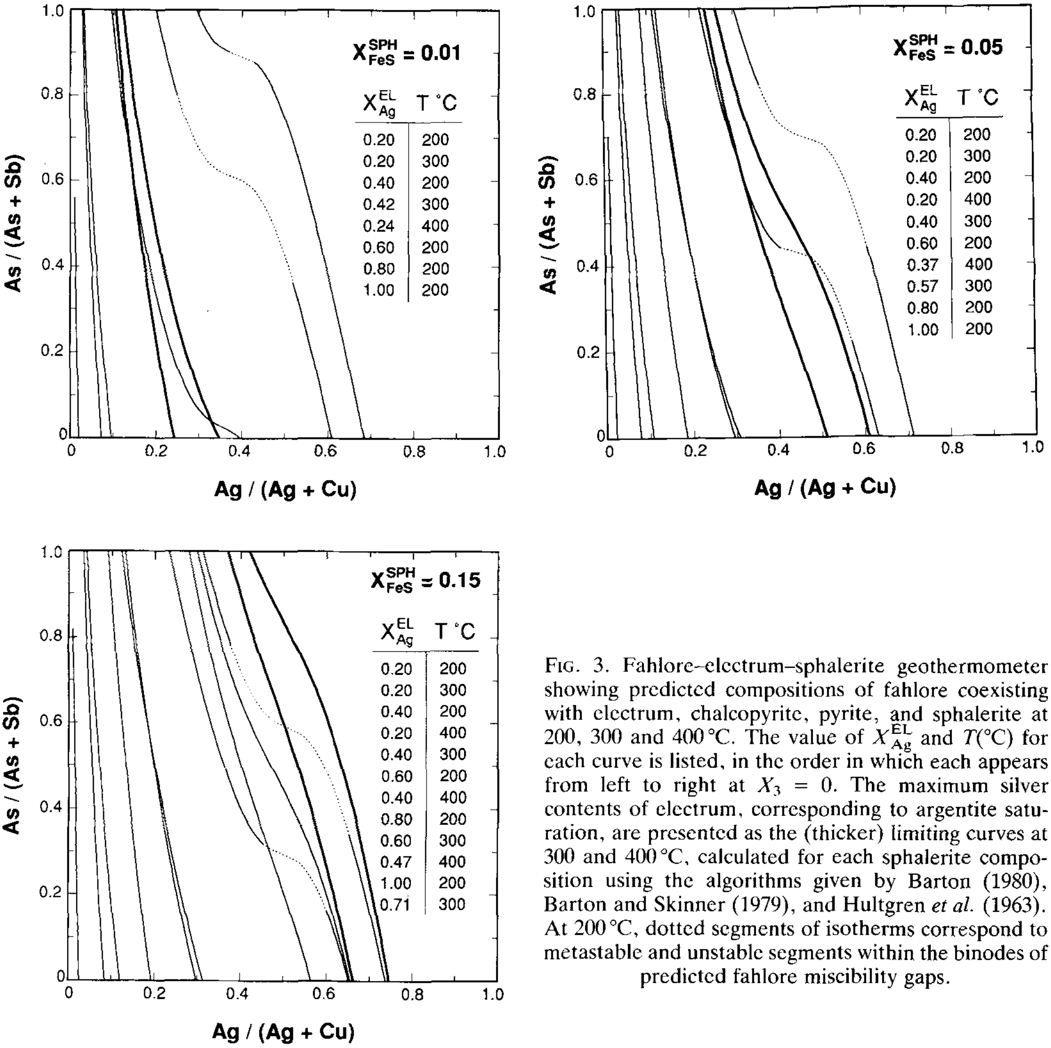

FIG. 3. Fahlore–electrum–sphalerite geothermometer showing predicted compositions of fahlore coexisting with electrum, chalcopyrite, pyrite, and sphalerite at 200, 300 and 400 °C. The value of X_{Ag}^{EL} and T(°C) for each curve is listed, in the order in which each appears from left to right at X_3 = 0. The maximum silver contents of electrum, corresponding to argentite saturation, are presented as the (thicker) limiting curves at 300 and 400 °C, calculated for each sphalerite composition using the algorithms given by Barton (1980), Barton and Skinner (1979), and Hultgren *et al.* (1963). At 200 °C, dotted segments of isotherms correspond to metastable and unstable segments within the binodes of predicted fahlore miscibility gaps.

salts in the argentian sulfosalt tetrahedron (Ag_2S–Cu_2S–$(As,Sb)_2S_3$) at temperatures around 350 °C (cf. Hall, 1967).

Tetrahedrite (X_3 = 0) with $X_4 \simeq 0.61$ was obtained in an experiment with initial $X_{Ag}^{EL} \simeq 0.70$ and $X_{FeS}^{SPH} = 0.05$ at 300 °C. Calculations using data of Barton (1980), Barton and Skinner (1979), and Hultgren *et al.* (1963) show $X_{Ag}^{EL} \simeq 0.57$ to be the limiting stable composition of electrum at 300 °C with respect to argentite (Ag_2S), which was found in abundance in these experiments. This result provides additional confirmation of the model discussed below.

Discussion of results

A strong temperature dependence of the Ag–Cu exchange reaction between electrum and fahlore has been documented in a set of experiments spanning a wide range of As/(As + Sb) ratios in fahlore. This dramatic temperature dependence is successfully accounted for by the documented entropy of the constituent reaction

$$Cu + FeS_2 = CuFeS_2 \qquad (3)$$

($\Delta\bar{S}$ = 10.38 cal deg^{-1} gfw^{-1}; Barton and Skinner, 1979), by the change in activity of Ag in electrum (Barton, 1980), and by the parameterisation for s provided by previous studies. Only the parameterisation for s is dependent upon the model for fahlore thermodynamics. The present successful extension of the model beyond the temperature range of its calibration illustrates its robustness, because the parameterisation for s was calibrated independently of considerations of Ag–Cu exchange equilibrium. The model parameter ($\Delta\bar{G}^{o}_{34}$) that expresses the crystallochemical incompatibility between Ag and As in fahlore is observed to be temperature independent. This indicates that the model can be successfully applied to problems of sulfide petrology encountered in certain ore deposits.

In Fig. 3 we present a graphical calibration of the Ag–Cu exchange reaction for several compositions of coexisting (Fe,Zn)S to illustrate such applications. The strong dependence of isotherms of constant $\mathrm{Ag(Cu)_{-1}}$ exchange potential on X_3 reflects the arsenic–silver incompatibility in fahlore. In general, isotherms of a given $X^{\mathrm{EL}}_{\mathrm{Ag}}$ are displaced to lower values of X_4 with decreasing $X^{\mathrm{SPH}}_{\mathrm{FeS}}$. This displacement reflects the incompatibility between zinc and silver in fahlore as expressed by a positive energy of the reaction

$$\mathrm{Cu_{10}Zn_2Sb_4S_{13} + Ag_{10}Fe_2Sb_4S_{13} = Cu_{10}Fe_2Sb_4S_{13} + Ag_{10}Zn_2Sb_4S_{13}}. \quad (4)$$

It is consistent with the common observation that there is a positive correlation between iron and silver in fahlores in specific systems. Fig. 3 is also consistent with the inference that high-silver fahlores are restricted to lower temperature environments. In accordance with the reaction

$$\mathrm{FeS + Ag_2S = FeS_2 + 2\ Ag}, \quad (5)$$

argentite ($\mathrm{Ag_2S}$) saturation limits the maximum permitted silver contents of both fahlore and electrum to progressively lower values with increasing temperature and decreasing $X^{\mathrm{SPH}}_{\mathrm{FeS}}$. The production of very Ag-rich zincian fahlores is therefore limited to subassemblages of those examined in Fig. 3 (e.g. Paar *et al.*, 1978).

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Notes

Note 1: Use of the group name fahlore emphasises the crystal–chemical similarity of these minerals, and reduces the cumbersome application of end-member names (e.g. tetrahedrite, $\mathrm{Cu_{12}Sb_4S_{13}}$; see Makovicky and Skinner, 1979), with their plethora of modifiers. Exact compositions are quoted where appropriate. End-member names merely specify restricted subsets of the fahlore composition range, where their use will not detract from their meaning.

Note 2: Throughout, the bar ($\bar{\ }$) above refers to a standard unit of matter (gram-formula weight, or moles). The ^{o} superscript refers to standard state quantities incorporating both vibrational and configurational terms, while the * superscript refers to those incorporating only non-configurational components.

Note 3: Tables 1 and 2 of Ebel and Sack (1989) summarise this model, however (cf. Sack, 1991) the expression in parameters equivalent to the Taylor expansion coefficient g_{4s} in their Table 1 is egregiously in error.

Note 4: Paar *et al.* (1978) report graphically that a similar phenomenon complicates reflectance—X_4 systematics in natural argentian fahlores.

Note 5: Here Q is the thermodynamic analog of the distribution coefficient. The subscript x as used in Q_x^* refers to Ag–Cu exchange. The quantity Q_x^* simply represents the expression which defines it (Table 1), as a convenient way to express the results of Ag–Cu partition in the mineral system studied here.

Note 6: Values of compositional variables are insensitive to the normalisation method (13 sulfurs, 29 atoms, etc.) chosen for recalculating formulae from element weight percent data.