

Origin of high-Ag fahlores from the Galena Mine, Wallace, Idaho, U.S.A.

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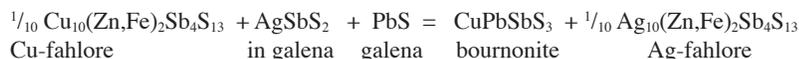
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ABSTRACT

Tetrahedrite fahlores from the Galena Mine of the Coeur d'Alene Mining District (Wallace, Idaho) have been found to be enriched in Ag by the Ag-Cu exchange reaction:



which occurred during cooling following fahlore mineralization. This solid-state reaction produced a distinct population of high-Ag fahlores found in galena-rich samples, quantitatively removed Ag (in an AgSbS₂ component) from galena, and accounts for all of the bournonite mineralization. This reaction has produced the most argentian fahlore yet found [molar Ag/(Ag + Cu) = 0.443] in the district, and forms a secondary overprint on any primary fahlore zoning that may have existed. The results obtained here indicate that the galena and fahlore-siderite stages of mineralization were virtually synchronous, as this reaction has produced the same result despite the opposite relative age relationships of these mineralization stages exhibited in two of the mines studied. Multiple lines of evidence suggest a temperature between 320 and 350 °C for this “stage.” Based on the Ag/(Ag + Cu) of fahlores and Fe-Zn partitioning between fahlore and sphalerite, we estimate that fahlore compositions were frozen in by about 235 °C, roughly 40 °C above corresponding temperatures obtained for the Gold Hunter vein of the Lucky Friday Mine. This result and the absence of readily detectable diaphorite (~Pb₂Ag₃Sb₃S₈) in the Galena Mine sample containing the highest Ag fahlore indicate a faster cooling rate for the terrane in the vicinity of the Galena Mine.

INTRODUCTION

The Coeur d'Alene mining district, northern Idaho, has produced in excess of one billion ounces of Ag (e.g., White 1998) and is one of the most extensively studied Ag districts in the world. Mineralization is of Cretaceous age (Fleck et al. 2002), and includes the extensive Ag-Pb-Zn orebodies exploited by most of the recently active mines, and gold-quartz veins currently being evaluated and mined by the New Jersey Mining Company (NJMC). Lead isotopic data indicate that the respective sources of these ores are rocks of the Proterozoic Belt Supergroup and granitic rocks possibly underlying or nearby the district (Fleck et al. 2002; Sack and Brackebusch 2004). Ag-Pb-Zn ore is concentrated in narrow, steep, west- to northwest-trending veins in deformed argillites and quartzites of the Middle Proterozoic Belt Supergroup, and is found in mineral belts immediately north and south of a major right-lateral, strike-slip fault (Osburn fault) that has some 25 km of post-mineralization displacement. Ag-Pb-Zn ore mineralization occurred during a dip-slip tectonic event accompanied by localized greenschist-facies metamorphism (e.g.,

White 1989, 1998; Wavra et al. 1994) and proceeded in stages that include early silicate, Fe-carbonate (±barite), and Fe-oxide, followed by sulfide stages dominated by sphalerite, the sulfosalt tetrahedrite-tennantite fahlore, and galena (e.g., Fryklund 1964; Mitcham 1952). Other sulfides/sulfosalts reported in the Ag-Pb-Zn ores include minor bournonite, chalcocopyrite, and arsenopyrite; trace amounts of boulangerite, pyrargyrite, polybasite, stibnite, chalcostibite, and gersdorffite (e.g., Fryklund 1964); and recently discovered diaphorite and matildite (Sack et al. 2002).

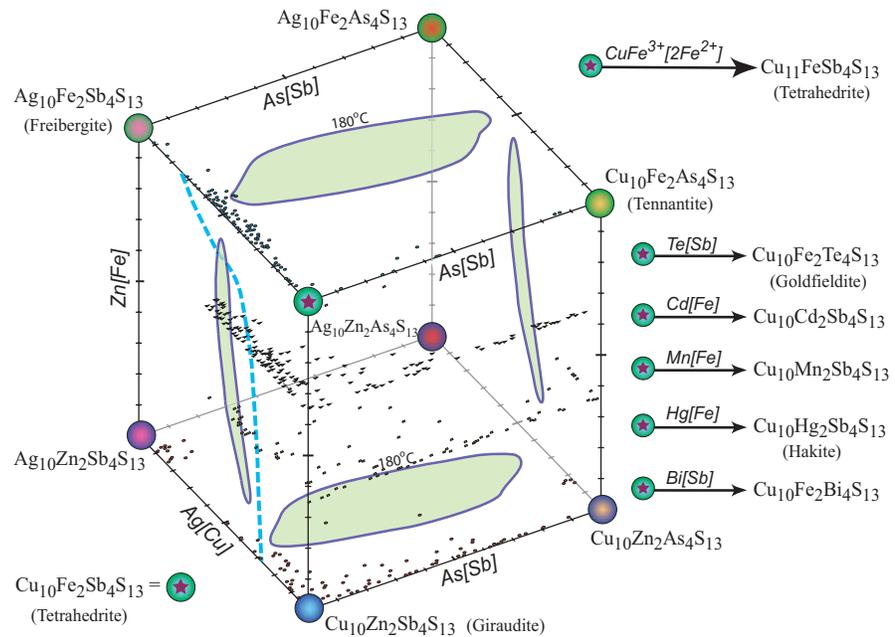
In this paper, we report microprobe analyses of tetrahedrite-tennantite fahlores and associated sulfides/sulfosalts from the Galena Mine (Wallace, Idaho) and analyze our findings in light of the recently developed thermochemical database for sulfides/sulfosalts (Sack 2000, 2005). This database is the product of over 20 years of experimental, theoretical, and petrological studies focused on characterizing the thermodynamic properties of tetrahedrite-tennantite fahlore [a complex solid-solution series typically approximating the chemical formula (Cu,Ag)₁₀(Zn,Fe)₂(Sb,As)₄S₁₃] and the sulfides and sulfosalts with which it coexists.

Fahlores approximating this simplified formula may be displayed in a cube (Fig. 1) whose vertices correspond to the

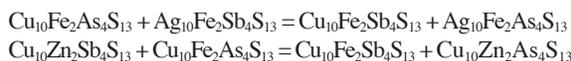
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FIGURE 1. Cubic representation of the compositional range of $(\text{Cu}, \text{Ag})_{10}(\text{Fe}, \text{Zn})_2(\text{Sb}, \text{As})_4\text{S}_{13}$ fahlores derived by fully substituting Zn for Fe ($\text{Zn}[\text{Fe}]$), As for Sb ($\text{As}[\text{Sb}]$) and Ag for Cu ($\text{Ag}[\text{Cu}]$) in a $\text{Cu}_{10}\text{Fe}_2\text{Sb}_4\text{S}_{13}$ end-member basis component. Shaded areas on the Fe-, Zn-, As-, Sb-free faces of the cube represent areas of intrinsic instability of fahlore with respect to unmixing at 180 °C. The calculated gaps on these cube faces merge to form a continuous miscibility gap within the cube that is of slightly greater width in $\text{Ag}/(\text{Ag} + \text{Cu})$ ratios than that the gaps on the top and bottom faces (cf., O'Leary and Sack 1987, their Fig. 7). The dashed curve on the As-free (front-left vertical) face defines the maximum Ag-content of $(\text{Cu}, \text{Ag})_{10}(\text{Fe}, \text{Zn})_2\text{Sb}_4\text{S}_{13}$ fahlores that are extrinsically stable in the simple system $\text{Ag}_2\text{S}-\text{Cu}_2\text{S}-\text{ZnS}-\text{FeS}-\text{Sb}_2\text{S}_3$ at 180 °C (cf., Fig. 5). Assemblages coexisting with $(\text{Cu}, \text{Ag})_{10}\text{Zn}_2\text{Sb}_4\text{S}_{13}$

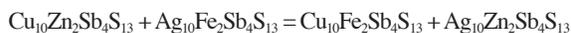
fahlores (bottom left edge of cube) and ZnS sphalerite at 300 °C are illustrated in Figure 2. $\text{Ag}/(\text{Ag} + \text{Cu})$ and $\text{As}/(\text{As} + \text{Sb})$ ratios of points plotted on the top and bottom faces of the cube are those of representative natural Fe- and Zn-rich fahlores with $1.0 \geq \text{Fe}/(\text{Fe} + \text{Zn}) > 0.8$ and $0.2 > \text{Fe}/(\text{Fe} + \text{Zn}) \geq 0.0$ from the compilations from sources cited in Sack et al. (1987), Sack (1992), and Sack and Ebel (1993); $\text{Ag}/(\text{Ag} + \text{Cu})$ and $\text{As}/(\text{As} + \text{Sb})$ ratios of fahlores from these compilations with $0.8 \geq \text{Fe}/(\text{Fe} + \text{Zn}) > 0.5$ and $0.5 \geq \text{Fe}/(\text{Fe} + \text{Zn}) \geq 0.2$ are represented on planes with $\text{Fe}/(\text{Fe} + \text{Zn}) = 0.65$ and 0.35, respectively. Arrows connecting the $\text{Cu}_{10}\text{Fe}_2\text{Sb}_4\text{S}_{13}$ end-member basis component with other end-member components in the full fahlore composition space, shown on the right of the diagram, illustrate other common substitutions: $\text{CuFe}^{3+}[\text{2Fe}^{2+}] \text{Te}[\text{Sb}]$, $\text{Cd}[\text{Fe}]$, $\text{Mn}[\text{Fe}]$, $\text{Hg}[\text{Fe}]$, and $\text{Bi}[\text{Sb}]$. Representative varietal names for end-members are enclosed in parentheses.



eight end-member components that may be derived by performing the Ag for Cu, Zn for Fe, and As for Sb substitutions on a $\text{Cu}_{10}\text{Fe}_2\text{Sb}_4\text{S}_{13}$ end-member basis component. This representation is analogous to the prismatic representation commonly employed for $(\text{Mg}, \text{Fe}^{2+})(\text{Al}, \text{Cr}, \text{Fe}^{3+})_2\text{O}_4$ spinels and the analogy between these and other solid solutions extends to a multiplicity of physical phenomena including strong energetic coupling between their independent elemental substitutions and compositionally induced changes in cation site preferences or manifestations of the so-called “fahlore effect” (cf., Robbins et al. 1971; Sack and Ghiorso, 1991, 1998; Sack, 1992). In fahlores, these energetic couplings between element substitutions are the consequence of positive Gibbs energies of the reciprocal reactions that express the incompatibilities between Ag and As, Zn and As, and Ag and Zn in fahlore:



and



(cf., Sack 1992). These incompatibilities and the inferred changes in site preferences of Ag and Cu appear to account for the distribution of fahlore compositions observed in nature, miscibility

gaps features, and volume-composition systematics (cf., Fig. 1; Sack et al. 1987; Sack 1992).

The thermodynamic database for sulfides/sulfosalts that we employ to analyze our mineralogical data from the Galena Mine consists of models for the Gibbs energy of mixing and of formation of minerals and their end-member components. This database has been used to calculate phase equilibria involving the phases fahlore, sphalerite, galena, miargyrite, polybasite-pearceite, pyrrargyrite-proustite, skinnerite, body-centered cubic-, face-centered cubic-, and hexagonally close-packed- $(\text{Ag}, \text{Cu})_2\text{S}$ solid solutions, stibnite, smithite, trechmannite, pyrite, chalcocopyrite, and electrum in the system $\text{Ag}_2\text{S}-\text{Cu}_2\text{S}-\text{ZnS}-\text{FeS}-\text{Sb}_2\text{S}_3-\text{As}_2\text{S}_3-\text{PbS}-\text{FeS}_2-\text{Au}$ (cf., Fig. 2; Sack 2000, 2005; Sack and Brackebusch 2004). Recent petrological studies (Sack et al. 2002, 2003; Sack and Goodell 2002; Sack and Brackebusch 2004; Chutas and Sack 2004) have demonstrated the adequacy of various predictions of the database [e.g., unmixing of $(\text{Cu}, \text{Ag})_{10}(\text{Fe}, \text{Zn})_2\text{Sb}_4\text{S}_{13}$ fahlores below 190 °C], and shown that the database is a powerful new tool for mining geologists to evaluate Ag and Au resources.

We undertook this study to evaluate whether high-Ag fahlores reported for the Galena Mine by Hackbarth (1984) are the products of advanced stages of fluid fractionation as suggested by Hackbarth and Petersen (1984), or whether they are the result of the retrograde reactions with galena shown to account for the population of high-Ag fahlores from the Sunshine (Kellogg,

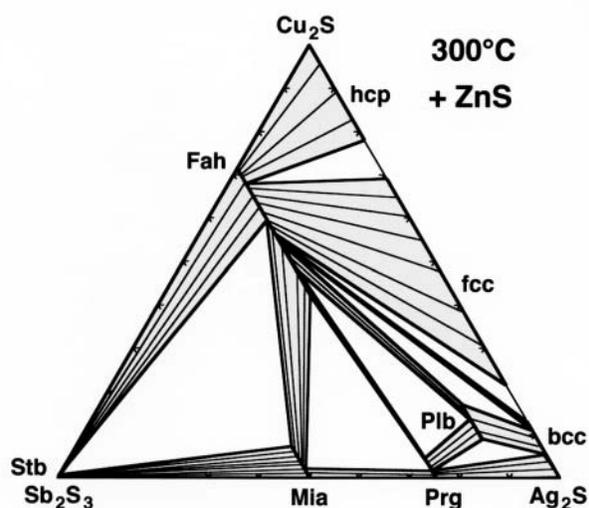


FIGURE 2. Stability relations at 300 °C for $\text{Ag}_2\text{S-Cu}_2\text{S-ZnS-Sb}_2\text{S}_3$ sulfides and sulfosalts coexisting with ZnS sphalerite (Sack 2005) represented (projected) on the composition plane $\text{Ag}_2\text{S-Cu}_2\text{S-Sb}_2\text{S}_3$. Abbreviations: hcp, fcc, and bcc are hexagonally close packed, face-centered cubic, and body-centered cubic (Ag,Cu) $_2\text{S}$ solid solutions; Prg, pyrargyrite, $\sim(\text{Ag,Cu})_3\text{SbS}_3$; Plb, polybasite, $\sim(\text{Ag,Cu})_{16}\text{Sb}_2\text{S}_{11}$; Mia, miaragrite, $\sim(\text{Ag,Cu})\text{SbS}_2$; Stb, stibnite, $\sim\text{Sb}_2\text{S}_3$; Fah, fahlore, $\sim(\text{Cu,Ag})_{10}\text{Zn}_2\text{Sb}_4\text{S}_{13}$; Sph, sphalerite, $\sim\text{ZnS}$.

Idaho) and Lucky Friday Mines (Mullan, Idaho) by Sack et al. (2002). A secondary objective of this study was to shed light on the issue of the relative timing of siderite-fahlore and galena-quartz mineralization events. Macroscopic textures indicate that siderite-fahlore veins crosscut pre-existing galena-quartz veins in the Galena Mine and are, thus, younger. The opposite relative age relations have been observed in the West Chance vein of the Sunshine Mine, a fahlore-siderite vein with an overprint of galena shoots. Consequently, the samples from the Galena Mine might be expected to present a different picture of the interaction between fahlore and galena than that seen at the Sunshine or Lucky Friday Mines.

Throughout this paper we use the term “fahlore” (german fahlerz = “gray ore”) with the modifiers “tetrahedrite,” “tennantite,” and “freibergite,” or their elemental equivalents (i.e., Sb-fahlore, As-fahlore, and Ag-rich, Sb-fahlore), to describe minerals with the $\bar{I}43m$ structure approximating the structural formula $^{\text{III}}(\text{Ag,Cu})_6^{\text{IV}}[(\text{Ag,Cu})_{2/3}(\text{Fe,Zn})_{2/3}]_6^{\text{III}}(\text{Sb,As})^{\text{IV}}\text{S}_3]_4^{\text{VI}}\text{S}$ (e.g., Johnson 1986). We do this following ample historical precedent (e.g., Cronstedt 1758; Ramdohr 1969; Mosgova and Tsepin 1983; Spiridonov and Okrugin 1985; Förster et al. 1987; Mosgova et al. 1987; Ebel and Sack 1989; Sack 1992) and to preserve the concept of the group when referring to thermodynamic models including tetrahedrite, tennantite, hakite, giraudite, goldfieldite, annivite, freibergite, argentotennantite, and other end-member isometric sulfides, selenides, and tellurides with the general formula $\text{M}_{12}\text{X}_4\text{Y}_{13}$ [where $\text{M} = \text{Cu, Ag, Fe, Mn, Hg, Zn, Cd}$; $\text{X} = \text{As, Sb, Bi, Te}$; and $\text{Y} = \text{S, Se}$ (e.g., Gaines et al. 1977, p. 162–165)]. The term “fahlore” has deep historical roots in mineralogy (cf., Ford 1929; Palache et al. 1944, p. 374 et seq.), and its use by Ramdohr (Fahlerzgruppe, cf., 1969, p. 554)

may reflect the fact that he was one of the very few who could tell these species apart (G. Kullerud, pers. comm.). As far as is known, all of these “fahlore” end-members and varieties are of the same $\bar{I}43m$ structure and they exhibit substantial solid solution with each other, forming a complete solid solution above about 270 °C in $(\text{Cu,Ag})_{10}(\text{Fe,Zn})_2(\text{Sb,As})_4\text{S}_{13}$ “fahlore” composition space (Sack 1992, 2005; Sack et al. 2003).

Although attempts have been made to discredit “fahlore” as a mineral name in favor of “tetrahedrite” (e.g., Nickel and Mandarino 1987), these are quite problematic! For one thing, Russian and other mineralogists have used the term “tetrahedrite” to refer to the $\text{Cu}_{12-14}\text{Sb}_4\text{S}_{13}$ end-member(s) (e.g., Mozgova 1982; Mackovicky and Skinner 1978, 1979; Klein and Hurlbut 1993), and the natural “tetrahedrite-tennantite” “fahlore” solid solution appears to extend only so far as $\text{Cu}_{11}\text{Fe}(\text{Sb,As})_4\text{S}_{13}$ from $\text{Cu}_{10}(\text{Zn,Fe})_2(\text{Sb,As})_4\text{S}_{13}$ (Charnock et al. 1989; Mackovicky et al. 1990; Mackovicky and Karup-Møller 1994; Sack and Goodell 2002). Furthermore, Spiridonov (1984) summarized observed composition limits for the general group formula $\text{M}_{10}^{\text{I}}\text{M}_2^{\text{II}}\text{X}_3^{\text{III}}\text{Y}_4^{\text{IV}}\text{S}_{13}^{\text{V}}$ ($\text{M}^{\text{I}} = \text{Ag, Cu}$; $\text{M}^{\text{II}} = \text{Fe, Zn, Cu, Hg, Cd, Sn, Mn}$; $\text{X}^{\text{III}} = \text{As, Sb, Bi, Te}$; $\text{Y}^{\text{IV}} = \text{S, Se}$) and most fahlores from nature closely approximate this formula (e.g., Johnson and Jeanloz 1983; Jeanloz and Johnson 1984). Also, many papers in the 1980s in Doklady Akademii Nauka refer to “fahlore” in their titles, and only one contains “tetrahedrite-tennantite” as a parenthetical modifier (GEOREF search, *fahlore*). Therefore, it would appear to be in the interests of international scientific communication, clarity, and brevity to retain the group name “fahlore,” with “tetrahedrite-tennantite” for the $\text{Cu}_{12-14}\text{Sb}_4\text{S}_{13}\text{-Cu}_{12-14}\text{As}_4\text{S}_{13}$ subgroup that are interesting materials but do not appear to exist as true minerals, or for the $\text{Cu}_{11-x}\text{Fe}_{1+x}(\text{Sb,As})_4\text{S}_{13}$ series subgroup as in Gaines et al. (1977) (cf., Fig. 1).

EXPERIMENTAL METHODS

Samples

Nine samples from the Galena Mine (Wallace, Idaho) were examined, two of which were collected by Claudia Hackbarth from the 164 vein (3040) and the Ag vein (3267). These are galena-rich samples and contain fahlores with the highest Ag-contents (Hackbarth 1984). Three samples were collected at 7, 13, and 33 m from the core of diamond drill hole 30–92 (collar on 3000 level) drilled down a Pb vein named the “4 Vein” with minor siderite and trace fahlore. The 4 Vein is one of about eight east-west vein zones that occur in a 120–180 m wide Pb zone that also trends east-west, and appears to be a set of steep, en echelon structures in the footwall of a branch off of the major Polaris Fault. The “vein” is not discrete; rather, it consists of variable, finely disseminated galena, with streaks of fine- and coarse-grained galena, stringers of quartz vein, patches of siderite, streaks of pyrite, and traces of fahlore and sphalerite. Two samples contain visible blebs of fahlore (3092-13 and 3092-33) and one does not (3092-7). Finally, two pairs of samples (the control samples) were collected from two different, proximal areas on the 4300 and 5200 levels where small (5–13 cm) quartz-galena-siderite veins are cut by later siderite-quartz-fahlore veins that were being mined. Samples designated with an “A” (4300-A and 5200-A) contain trace to negligible galena, whereas galena is abundant in samples designated with a “B” (4300-B and 5200-B). Polished sections were prepared using cold-setting epoxy to mount samples on glass slides.

Microprobe analysis

Microprobe analyses of fahlores and associated sulfosalts and sulfides were performed on the JEOL 733 Superprobe in the Department of Earth and Space Sciences at the University of Washington. Analytical conditions, standards, and correction procedures were identical to those reported in Sack et al. (2002). Analyses of internal standards are accurate to better than $\pm 2\%$ for elements present in concentrations of greater than 3 wt%.

TABLE 1. Averaged sulfosalt and sulfide compositions (wt%)

Label*	phase†	N	Ag	Cu	Fe	Zn	As	Sb	Bi	Pb	S	Sum
4300-A	fah	4	9.69(16)	30.67(18)	5.01(15)	2.33(01)	0.62(07)	27.48(24)	0.09(06)	n.d.	24.23(37)	100.10
4300-A	gn	1	0.62	0.06(09)	0.19	0.07	0.03	0.08	1.71	85.03	12.59	100.38
4300-B	fah	6	17.04(30)	24.74(41)	4.29(30)	2.70(24)	0.61(21)	26.76(21)	0.12(13)	n.d.	24.17(20)	99.88
4300-B	bno	2	n.d.	13.12(01)	n.d.	n.d.	0.26(04)	24.62(30)	0.18(12)	42.80(28)	20.79(18)	101.75
4300-B	gn	3	0.09(15)	0.02(01)	0.04(03)	n.d.	0.01(02)	0.02(03)	0.57(21)	87.27(107)	13.03(11)	101.04
5200-A	fah	7	8.05(45)	31.93(65)	5.16(38)	2.30(20)	1.24(31)	26.70(54)	0.19(14)	0.03(04)	24.71(47)	100.31
5200-B	fah	5	16.13(49)	25.58(41)	4.82(10)	2.26(51)	1.04(06)	26.13(29)	0.10(06)	0.05(06)	23.48(35)	99.61
5200-B	gn	3	0.21(19)	0.01(02)	0.01(02)	0.01(01)	0.01(02)	0.15(12)	0.69(30)	86.81(84)	12.62(23)	100.51
3092-33	bno	4	n.d.	12.92(23)	0.28(10)	0.01(01)	0.72(87)	23.79(13)	0.07(11)	42.10(34)	20.52(29)	100.41
3092-33	gn	3	0.06(10)	n.d.	n.d.	0.01(02)	n.d.	0.13(12)	0.34(14)	85.36(72)	14.14(34)	100.04
3092-13	fah	8	14.41(69)	26.76(52)	2.08(32)	5.33(25)	1.55(49)	25.16(69)	0.12(10)	0.05(07)	23.99(14)	99.46
3092-13	sph	5	0.01(01)	0.15(16)	1.38(48)	65.71(41)	0.01(01)	0.01(01)	0.10(07)	0.06(09)	31.88(68)	99.32
3092-13	bno	3	n.d.	13.23(15)	0.01(02)	2.74(59)	0.71(16)	27.15(46)	0.01(01)	41.50(27)	20.29(44)	100.10
3092-13	gn	2	0.02(03)	0.01(01)	n.d.	0.04(02)	n.d.	0.21(13)	0.09(01)	85.78(159)	13.57(113)	99.73
3092-7	sph	6	0.02(03)	0.02(03)	1.50(70)	65.85(63)	n.d.	0.03(02)	0.06(07)	0.05(06)	32.15(93)	99.70
3092-7	gn	1	n.d.	n.d.	n.d.	n.d.	0.02	n.d.	0.20	87.01	13.22	100.73
3040	fah	6	19.62(310)	21.39(239)	2.53(42)	4.60(51)	0.31(40)	26.76(37)	0.04(04)	0.08(11)	22.65(38)	97.97
3040	sph	4	0.06(08)	0.05(04)	0.45(13)	65.25(48)	0.01(02)	0.02(02)	0.10(05)	0.15(04)	31.75(52)	97.82

* 4300-A and -B and 5200-A and -B are samples 4300-26E 6th + 5' and 5200-170 370; 3092-33, -13, and -7 are samples obtained at 33, 13, and 7 meters along ddh 30-92 down the 4 vein; 3040 is Hackbarth's (1984) sample 040 from the 164 vein. Fahlore was not observed in four sections of 3267.

† Mineral abbreviations: fah, fahlore; sph, sphalerite; bno, bournonite; gn, galena. Standard deviations for N analyses are number in parentheses and are 1 σ ; n.d. indicates not detected.

RESULTS

Mineralogy-petrography

Several features of the sections examined are striking. First, bournonite is confined to near the contacts between pockets or veins of galena and siderite-fahlore veins (cf., Figs. 3a–3c). These bournonites have nearly the ideal stoichiometric formula for the Sb-end-member component, CuPbSbS_3 , with minor As substituting for Sb (Table 1). Fahlores are also found at interfaces between pockets or veins of galena and siderite-fahlore veins (e.g. Figs. 3b and 3e), and these fahlores are within analytical uncertainty of the ideal fahlore formula, $(\text{Ag,Cu})_{10}(\text{Fe,Zn})_2(\text{Sb,As,Bi})_4\text{S}_{13}$, with minor amounts of As, negligible Bi, and sums of (Ag+Cu) slightly less than the ten atoms per ideal formula unit, possibly due to components of the Fe for Cu or Fe for Cu_2 substitutions inferred by Sack and Loucks (1985) or a slight amount of Ag and Cu diffusion under the focused microprobe beam (e.g., Harlov and Sack 1994). These interfacial fahlores, and fahlores adjacent to galena concentrations, are notably enriched in Ag relative to fahlores found in siderite-fahlore veins not in contact with, or containing, volumetrically significant galena. This Ag-enrichment is readily illustrated for pairs of samples designated with an "A" (4300-A and 5200-A) and with a "B" (4300-B and 5200-B) in a plot of the $\text{Ag}/(\text{Ag} + \text{Cu})$ vs. $\text{Zn}/(\text{Zn} + \text{Fe})$ molar ratios of Galena Mine fahlores (Fig. 4).

As is evident from Figure 4 (open symbols), fahlores from the control samples from siderite-fahlore veins with minor galena [4300-A and 5200-A] have only roughly half the molar $\text{Ag}/(\text{Ag} + \text{Cu})$ [0.157 \pm 0.003 and 0.129 \pm 0.008] as those associated with pockets of coarse-grained galena in the corresponding samples 4300-B and 5200-B [molar $\text{Ag}/(\text{Ag} + \text{Cu})$ of 0.289 \pm 0.006 and 0.264 \pm 0.029, respectively]. Coincidentally, the extent of Ag-enrichment inferred for the control samples from the Galena Mine corresponds almost exactly to that inferred by Sack et al. (2002) for two galena-rich samples from the West Chance (WC-7) and Gold Hunter (GH-5) veins of the Sunshine and Lucky Friday Mines. This inference was based on the assumption that

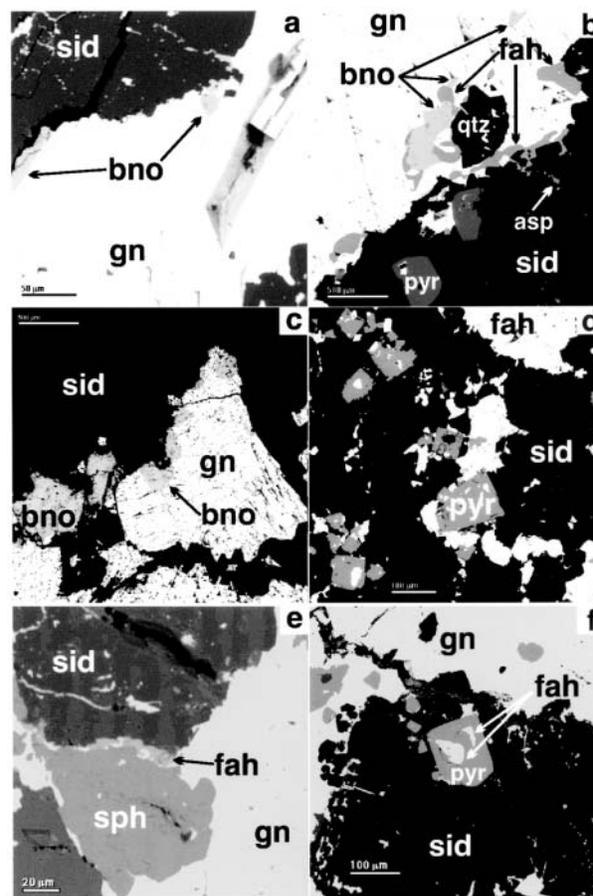


FIGURE 3. Back-scattered electron (BSE) images of samples from the Galena mine. (a) Bournonite (bno) selvages between siderite (sid) and galena (gn) in 3092-33. Bar = 50 μm . (b) Bno and fahlore (fah) associations at the margins between gn and sid in 3092-13. Additional minerals include pyrite (pyr), quartz (qtz) and arsenopyrite (asp). Bar = 500 μm . (c) Bournonite (bno) selvages between siderite (sid) and galena (gn) in 4300-B. Bar = 500 μm . (d) Typical texture of the sid-fah vein in 5200-A. Bar = 100 μm . (e) Selvage of fah between sid and sphalerite (sph) in 3040. Bar = 20 μm . (f) Prominent fah inclusions in pyr in 3040. Bar = 100 μm .

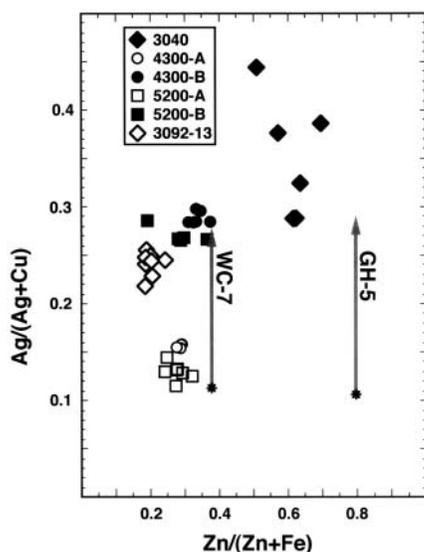
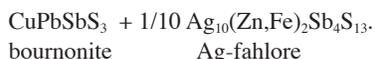


FIGURE 4. Molar $\text{Ag}/(\text{Ag} + \text{Cu})$ and $\text{Zn}/(\text{Zn} + \text{Fe})$ of fah from the Galena Mine compared with paths of Ag-enrichment (vertical arrows) inferred for samples WC-7 and GH-5 from West Chance and Gold Hunter veins of the Sunshine and Lucky Friday Mines. Arrow tips represent the mean molar $\text{Ag}/(\text{Ag} + \text{Cu})$ and $\text{Zn}/(\text{Zn} + \text{Fe})$ ratios of fah from WC-7 and GH-5. Asterisks at tails of arrows indicate original, primary $\text{Ag}/(\text{Ag} + \text{Cu})$ ratios for fah in these samples inferred from mass-balance by Sack et al. (2002).

all of the bournonite in WC-7 and GH-5 was produced during cooling by the reaction:



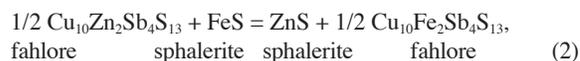
(1)

Further evidence that this reaction has produced a distinct population of high-Ag fahlores found in galena-rich samples, and may account for all of the bournonite mineralization, is found in the fahlores in samples 3092-13 and 3040. Sample 3040 provides particularly conclusive evidence in this regard. Not only does it contain fahlores with the highest molar $\text{Ag}/(\text{Ag} + \text{Cu})$ reported for the Coeur d'Alene district (~ 0.45), but fahlores encapsulated in pyrite in this sample (Fig. 3f) have significantly lower molar $\text{Ag}/(\text{Ag} + \text{Cu})$ (~ 0.29).

Galena has concentrations of Ag varying from below the minimum detection limit of about 0.1 wt% (Knowles 1983) to as high as 0.62 wt% in the most Bi-rich of the 13 domains analyzed (4300-A, Table 1). All analyses have $\text{Ag} < (\text{Sb} + \text{Bi})$, and $\text{Bi} > \text{Sb}$ in all but 2 of them. Based on metal ratios, the departure of galena stoichiometry from the $\text{Pb}_2\text{S}_2\text{-AgSbS}_2\text{-AgBiS}_2$ plane is roughly 1 mol% (0.0097 ± 0.0039) and involves a $\square_{2/3}(\text{Bi},\text{Sb})_{4/3}\text{S}_2$ component. This stoichiometric impropriety is within the limits on such departures established by Van Hook (1960) and Hoda and Chang (1975). The average mol fraction of the AgSbS_2 component, 0.0024 ± 0.0034 , is virtually identical to that guesstimated

for other Coeur d'Alene galenas by Sack (2005), 0.0022 , and the average mol fraction of the AgBiS_2 component, 0.0034 ± 0.0069 , is slightly greater than these estimates.

Finally, sphalerites were observed in sections prepared for only three of these samples, 3092-7, 3092-13, and 3040. Analyses of fahlores in contact with sphalerites were obtained only in the section from sample 3092-13, as 3092-7 lacked fahlore and 3040 lacked adequate sphalerite-fahlore contacts (e.g., Fig. 3e). Three sphalerite-rim + fahlore pairs from the 3092-13 section yield an average blocking temperature of 225 ± 22 °C for the Fe-Zn reaction between sphalerite and fahlore:



according to the calibration of O'Leary and Sack (1987). This result is slightly higher than that obtained for the Lucky Friday system by Sack et al. (2002), 174 ± 21 °C, and it may well support the inference that the veins from the Galena Mine cooled more rapidly than those from the Lucky Friday system.

Additional support for this inference comes from the maximal Ag-contents of fahlores from these mines. The maximal observed molar $\text{Ag}/(\text{Ag} + \text{Cu})$ ratios of fahlores from sample 3040 indicate that Reaction 1 proceeded at temperatures of at least 250 °C (cf., Fig. 5), whereas the corresponding maximal molar $\text{Ag}/(\text{Ag} + \text{Cu})$ ratios in fahlores from Gold Hunter sample GH-2 place lower bounds of only slightly above 200 °C on the temperature at which Reaction 1 proceeded. Furthermore, the diaphorite produced by the reaction:

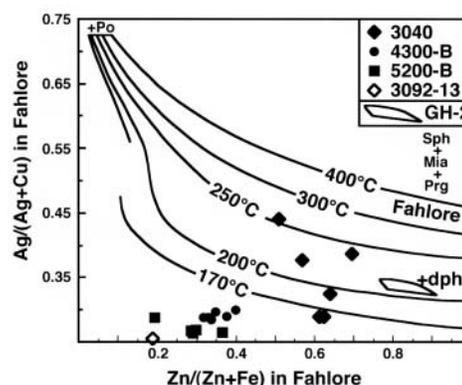
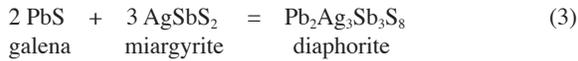


FIGURE 5. Molar $\text{Ag}/(\text{Ag} + \text{Cu})$ and $\text{Zn}/(\text{Zn} + \text{Fe})$ of high-Ag fah from the Galena Mine compared with curves calculated for the maximum solubility of Ag in fah in the system $\text{Ag}_2\text{S-Cu}_2\text{S-ZnS-FeS-Sb}_2\text{S}_3$ at 170, 200, 250, 300, and 400 °C [fah in equilibrium with pyrrhotite (Prg), sphalerite (Sph), and miargyrite (Mia)] by Sack (2005). These curves define minimal temperatures at which a fahlore of a given molar $\text{Ag}/(\text{Ag} + \text{Cu})$ formed, if it did not coexist with Prg, Sph, and Mia (cf., Sack et al. 2003). These isotherms are terminated at low $\text{Zn}/(\text{Zn} + \text{Fe})$ and high $\text{Ag}/(\text{Ag} + \text{Cu})$ as a consequence of saturation with respect to pyrrhotite (Po) and this occurs at a roughly constant fahlore $\text{Ag}/(\text{Ag} + \text{Cu})$ ratio (~ 0.725) as inferred from the calibration of the sphalerite-hexagonal pyrrhotite two-phase region given by Balabin and Sack (2000, their Fig. 4). Open irregular symbol labeled GH-2 is defined by fahlore compositions from a diaphorite (dph)-bearing sample from the Gold Hunter vein of the Lucky Friday Mine determined by Sack et al. (2002).



and abundant in GH-2 (Fig. 3d, Sack et al. 2002) is not present in 3040, at least not at a scale coarse enough to be obvious in back-scattered electron (BSE) images. In addition, the sphalerites in the Galena Mine samples are more strongly zoned in relative amounts of FeS component in sample 3092-13 than those examined from the Gold Hunter vein, and an average temperature of 355 ± 44 °C may be calculated from the partitioning of Zn and Fe between fahlores and the more FeS-rich cores of the large sphalerite grains in this sample. This estimate would appear to define a lower bound on the original temperature of mineralization, and this inference is in accord with a mineralization temperature of about 320 °C inferred from fluid-inclusion studies (cf., Arkadaskiy 2000; Sack and Brackebusch 2004), or a temperature of 350 °C inferred from estimated primary fahlore and galena compositions by Sack (2005).

DISCUSSION

Several issues merit further discussion. First is the issue of to what extent the bournonite in the district is of secondary origin. Second is the issue of how Reaction 1 depends on the timing of galena mineralization relative to siderite-fahlore mineralization. Third is the issue of the proportion contributed by galena to the Ag that has been mined in the district. Finally, there remains the question of what was the extent of primary metal zoning in the district.

Based on the data presented here and by Sack et al. (2002), it appears that bournonite is an entirely secondary product of Reaction 1, at least in the sulfide veins of the Galena and Lucky Friday Mines, and in the West Chance vein of the Sunshine Mine. This inference is completely consistent with the previous microscopic examinations of Rasor (1934), Anderson (1940), and Willard (1941), who all noted that bournonite appears to be replacing fahlore. It may not, however, account for the observation of Fryklund (1964, p. 18) that bournonite “also occurs as veinlets in galena away from tetrahedrite contacts,” unless Reaction 1 is envisioned to operate on scales much larger than that of a hand specimen or such bournonite is in contact with fahlore out of the plane of observation. Given that substantial post-mineralization deformation features have been noted in Coeur d’Alene ores (e.g., slickensides developed in some Galena Mine fahlores), it appears likely that deformation may have enabled the production of such veinlets. Such deformation would also help explain the fact that Reaction 1 does not appear to have proceeded in all locations where galena precipitated adjacent to fahlore. This feature also was noted by Sack et al. (2002), who observed that the partial corona of bournonite grains surrounding a fahlore grain in a galena matrix (their Figs. 3a and 3b) was atypical, and that bournonite grains were typically associated with shear zones in galena where post-mineralization deformation was evident. Thus it would appear that, at present, there is no compelling evidence to indicate that any of the bournonite in the district is primary.

Second, it appears that Reaction 1 has operated to remove Ag and Sb from galena independent of the order in which siderite/fahlore- and galena-bearing veins were introduced. For example, the reaction occurs prominently in the West Chance vein of the

Sunshine Mine, a fahlore-siderite vein with an overprint of galena shoots, and the Galena Mine where fahlore-siderite veins cut pre-existing galena veins. In the former case, the operation of Reaction 1 does not require that these two episodes of mineralization were closely linked temporally. In the latter case, however, the post-emplacement, Ag-enrichment of fahlores requires that siderite-fahlore and galena mineralization were virtually synchronous, as any extensive cooling after galena mineralization would have resulted in Ag-loss from galena prior to fahlore mineralization and would thus have rendered Reaction 1 virtually inoperative on fahlores in the siderite-fahlore veins. As discussed above, a temperature in the range 320–350 °C may be assigned to this “event,” and this temperature estimate is in agreement with fahlore and galena composition systematics for other Coeur d’Alene ores (Sack 2005). Based on these systematics (e.g., Fig. 6 for As-free subsystem) and the average compositions of fahlores in 4300A and 5200A given in Table 1, we predict that galenas that would have been equilibrium with these fahlores at 320–350 °C would have had $X_{\text{AgSbS}_2} = 0.0114 \pm 0.0010$ and 0.0094 ± 0.0009 , or would have had 0.258 ± 0.024 and 0.212 ± 0.020 wt% Ag, respectively.

Third, the proportion of Ag that galena contributed to the Ag mined in the Coeur d’Alene district remains an open question. Hardy (2002), for example, has estimated that about half of the 1.1 billion ounces of Ag mined as of 2002 has been produced from macroscopic fahlores in siderite-fahlore veins and that the

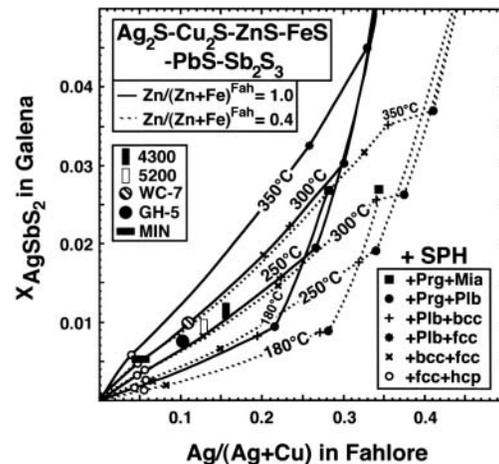
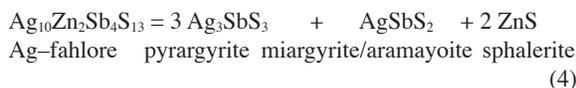


FIGURE 6. Ag/(Ag + Cu) ratios of primary fahlores (fah) and mole fractions of AgSbS_2 in primary galenas (X_{AgSbS_2}) from Coeur d’Alene Ag-Pb-Zn deposits compared with curves for fah and gn coexisting with sph and one of the phases Mia, Prg, Plb, or bcc-, fcc-, or hcp-(Ag,Cu)₂S solid solution in the simple system $\text{Ag}_2\text{S-Cu}_2\text{S-ZnS-FeS-PbS-Sb}_2\text{S}_3$ calculated by Sack (2005). Points defined by four-phase curve intersections are labeled as indicated in legend. Vertical rectangles indicate ranges of X_{AgSbS_2} in $\text{AgSbS}_2\text{-Pb}_2\text{S}_2$ gn calculated using the database of Sack (2005) for the average compositions of fahlores in 4300A and 5200A in Table 1 and for temperatures between 320 and 350 °C. Larger circles are estimates for original gn and fah compositions for samples WC-7 and GH-5 from the West Chance vein of the Sunshine Mine and from the Gold Hunter vein of the Lucky Friday Mine (Sack et al. 2002; Sack 2005). Horizontal bar represents the minimum in Ag-contents in primary gn and fah in $\text{Ag}_2\text{S-Cu}_2\text{S-ZnS-FeS-Sb}_2\text{S}_3$ analogs of Coeur d’Alene ores estimated by Sack (2005).

remaining production has been derived from galena ores. It is astonishing that the nature of the silver phases in the galena ores have not been characterized adequately. Derivation of Ag from galena appears to be the case in many other major Ag districts as well, cases in point being the Mexican Ag-belt and the fissure-vein deposits of the Peruvian Andes (e.g., Lueth et al. 2000; Chutas and Sack 2004; Goodell and Petersen 1974; Wu and Petersen 1977; Hackbarth and Petersen 1984; Sack and Goodell 2002). In the Mexican Ag-belt, significant Ag is concentrated in galena exsolution products such as diaphorite and Ag-sulfosalts in manto-type deposits like Santa Eulalia (Lueth et al. 2000), and it appears that virtually all of the Ag now contained in fahlores, polybasite-pearceites, pyrrargyrite-proustites, and (Ag,Cu)₂S phases in La Colorada, a major producer of the Pan American Silver Corporation (PAAS), could have been derived from the galenas originally deposited by hydrothermal solutions (Chutas and Sack 2004).

Compared with the Mexican deposits, ores of the Coeur d'Alene district may be considered anomalous, in that they record discrete stages of fahlore mineralization. Perhaps the Peruvian fissure-type deposits may be considered intermediate to the Mexican and Coeur d'Alene types. Fahlore is an essential constituent in the Peruvian ores studied by Goodell and Petersen (1974), Wu and Petersen (1977), Hackbarth and Petersen (1984), and Sack and Goodell (2002). At Julcani, fahlore becomes Ag-enriched as a result of Reaction 1, except in the bonanza Ag-zone where original high-Ag galena (up to ~90% AgSbS₂) has decomposed into low-Ag galena and various combinations of aramayoite [~(Ag,Cu)₅(Sb,Bi)₄(Bi,Sb)S₁₀, Sb-Bi analog of miargyrite], bismuthian diaphorite, diaphorite, and pyrrargyrite (Sack and Goodell 2002; Sack 2005). In this zone, and in other pyrrargyrite-bearing Ag-Pb-Zn ores such as those from the Keno Hill District, Yukon (Sack et al. 2003), zincian fahlores undergo retrograde Ag-depletion as a result of the reaction:



illustrated for the system Ag₂S-Cu₂S-ZnS-FeS-Sb₂S₃ in Figure 5. At present, one can only speculate about the extent to which Reaction 1 or similar reactions operated at Casapalca and the other pyrrargyrite-free, Peruvian ores examined by Wu and Petersen (1977) and Hackbarth and Petersen (1984). It can, however, be confidently assumed that Reaction 1 has played an important role in producing the high-Ag fahlores in these deposits, as it is very difficult, if not impossible, to account for the production of these ores by a fluid fractionation model (e.g., Hackbarth and Petersen 1984), even when thermochemical incompatibilities between Ag and As and between Zn and As in fahlore are taken into account (e.g., Ebel and Sack 1989, 1991; Sack 1992).

Finally, there remains the question of what was the extent of primary metal zoning in the Coeur d'Alene district. Because these ore deposits are retrograde metamorphic rocks that have undergone post-mineralization reactions that altered the compositions of the primary minerals and introduced new phases, this is a question for the future. In the least, it will be necessary to reconstruct (or identify) the initial compositions of minerals

such as fahlore, galena, and sphalerite. Although primary sphalerite and fahlore compositions may be identified from nearly monomineralic sulfide domains or inclusions in quartz, pyrite, or other refractory phases, determining primary compositions of galena will require additional modal and compositional data. If samples have behaved as closed systems, the initial Ag-contents of galena may be estimated from mass-balance considerations as outlined by Sack et al. (2002). Alternatively, they may be estimated from primary fahlore compositions and mineralization temperatures utilizing calibrations of mineral equilibria such as that illustrated in Figure 6.

CONCLUDING REMARKS

We have shown that Reaction 1 produced the population of high-Ag fahlores in the Coeur d'Alene Ag-Pb-Zn District, and that the database of Sack (2005) may be used to calculate compositions of primary hydrothermal sulfides in these ores when explicit provision is made for this reaction and Reaction 2. More generally, it will be necessary to account for additional retrograde reactions (e.g., Reactions 3 and 4) to reconstruct primary mineral compositions for similar polymetallic hydrothermal ore deposits. Such reconstructions will be possible in detail only when the thermodynamic properties of additional Ag₂S-Cu₂S-ZnS-FeS-PbS-Sb₂S₂-As₂S₂-Bi₂S₃ sulfides (e.g., bournonite, diaphorite, bismuthian diaphorite, aramayoite) are added to the database to complete the thermodynamic description of common sulfide assemblages. Nevertheless, the current database may be successfully integrated into studies of hydrothermal ore-forming processes and used to construct calibrations of mineral equilibria useful for evaluating resource potential and unraveling retrograde evolution (e.g., Figs. 5 and 6).

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REFERENCES CITED

- Anderson, R.J. (1940) Microscopic features of ore from the Sunshine Mine. *Economic Geology*, 35, 659–667.
- Arkadaskiy, S.V. (2000) Fluid inclusion and stable isotopic study of precious and base metal veins from the Coeur d'Alene Ag-Pb-Zn district, Idaho, U.S.A. M.Sc. thesis, University of Alberta, Edmonton, Alberta, Canada, 156 pp.
- Balabin A.I. and Sack R.O. (2000) Thermodynamics of (Zn,Fe)S sphalerite: a CVM approach with large basis clusters. *Mineralogical Magazine*, 64, 923–943.
- Charnock, J.M., Garner, C.D., Patrick, R.A.D., and Vaughan, D.J. (1989) EXAFS and Mössbauer spectroscopic study of Fe-bearing tetrahedrites. *Mineralogical Magazine*, 53, 193–199.
- Chutas N.I. and Sack R.O. (2004) Ore genesis at La Colorada Ag-Zn-Pb deposit in Zacatecas, Mexico. *Mineralogical Magazine*, 68, 923–937.
- Cronstedt, A. (1758) *Mineralogie; eller Mineral-Rikets Upställning*. Magellan, Stockholm.
- Ebel, D.S. and Sack, R.O. (1989) Ag-Cu and As-Sb exchange energies in tetrahedrite-tennantite fahlores. *Geochimica et Cosmochimica Acta*, 53, 2301–2309.
- (1991) As-Ag incompatibility in fahlore. *Mineralogical Magazine*, 55, 521–528.
- Fleck, R.J., Criss, R.E., Eaton, G.F., Cleland, R.W., Wavra, C.R., and Bond, W.D. (2002) Age and origin of base and precious metal veins of the Coeur d'Alene mining district, Idaho. *Economic Geology*, 97, 23–42.
- Ford, W.E. (1929) *Dana's Manual of Mineralogy*, 14th ed. 476 p. Wiley, New York.
- Förestér, von H.-J., Hunger, H.-J., and Grimm, L. (1987) Elektronenstrahlmikroanalytische untersuchungen von erzmineralen aus der Zinn-Lagerstätte Altenberg (Erzgebirge, DDR) 4. Mitteilung; Fehlerze - chemismus und nomenklatur. *Chemie Erde*, 47, 111–115.

- Fryklund, V.C., Jr. (1964) Ore deposits of the Coeur d'Alene district, Shoshone County, Idaho. U.S. Geological Survey Professional Paper 445, 103 p.
- Gaines, R.V., Skinner, H.C.W., Foord, E.E., Mason, B., Rosenzweig, A., King, V.T., and Dowty, E. (1997) *Dana's New Mineralogy*, 8th ed. 1819 p. Wiley, New York.
- Goodell, P.C. and Petersen, U. (1974) Julcani mining district, Peru: a study of metal ratios. *Economic Geology*, 69, 347–361.
- Hackbarth, C.J. (1984) Depositional modeling of tetrahedrite in the Coeur d'Alene district. Ph. D. thesis, 298 p. Harvard University, Cambridge, Massachusetts.
- Hackbarth, C.J. and Petersen, U. (1984) Systematic compositional variations in argentine tetrahedrite. *Economic Geology*, 79, 448–460.
- Hardy, L.S. (2002) Characterization of silver in Coeur d'Alene District ores: the missing component. In J.K. Duff and R.O. Laidlaw, Eds., *Coeur d'Alene District Symposium, Northwest Mining Association 108th Annual Meeting, Exposition and Short Courses*. Spokane, WA.
- Harlov, D.E. and Sack, R.O. (1994) Thermochemistry of polybasite–pearceite solutions. *Geochimica et Cosmochimica Acta*, 58, 4363–4375.
- Hoda, S.N. and Chang, L.L.Y. (1975) Phase relations in the system $PbS-Ag_2S-Sb_2S_3$ and $PbS-Ag_2S-Bi_2S_3$. *American Mineralogist*, 60, 621–633.
- Jeanloz, R. and Johnson, M.L. (1984) A note on the bonding, optical spectrum and composition of tetrahedrite. *Physics and Chemistry of Minerals*, 11, 52–54.
- Johnson, M.L. and Jeanloz, R. (1983) A brillouin–zone model for compositional variation in tetrahedrite. *American Mineralogist*, 68, 220–226.
- Johnson, N.E. (1986) The crystal chemistry of tetrahedrite. Ph.D. thesis, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, 216 p.
- Klein, C. and Hurlbut, C.S., Jr. (1993) *Manual of Mineralogy*, 21st ed, 681 p. Wiley, New York.
- Knowles, C.R. (1983) A microprobe study of silver ore in northern Idaho. In R. Gooley, Ed., *Microbeam Analysis*, p. 61–64. San Francisco Press, California.
- Lueth, V.W., Megaw, P.K.M., Pingatore, N.E., and Goodell, P.C. (2000) Systematic variation in galena solid solution at Santa Eulalia, Chihuahua, Mexico. *Economic Geology*, 95, 1673–1687.
- Makovicky, E. and Karup-Møller, S. (1994) Exploratory studies on substitution of minor elements in synthetic tetrahedrite Part I. Substitution by Fe, Zn, Co, Ni, Mn, Cr, V, and Pb. Unit-cell parameter changes on substitution and the structural role of “Cu²⁺”. *Neues Jahrbuch für Mineralogie Abhandlungen*, 167, 247–261.
- Makovicky, E. and Skinner, B.J. (1978) Studies of the sulfosalts of copper. VI. Low temperature exsolution in synthetic tetrahedrite solid solution, $Cu_{12+8}Sb_{4+3}S_{13}$. *Canadian Mineralogist*, 16, 611–623.
- — — (1979) Studies of the sulfosalts of copper. VII. Crystal structures of the exsolution products $Cu_{12+3}Sb_4S_{13}$ and $Cu_{13+3}Sb_4S_{13}$ of unsubstituted synthetic tetrahedrite. *Canadian Mineralogist*, 17, 619–634.
- Makovicky, E., Forcher, K., Lottermoser, W., and Amthauer, G. (1990) The role of Fe²⁺ and Fe³⁺ in synthetic Fe-substituted tetrahedrite. *Mineralogy and Petrology*, 43, 73–81.
- Mitcham, T.W. (1952) Indicator minerals, Coeur d'Alene silver belt. *Economic Geology*, 47, 414–450.
- Mosgova, N.N. (1982) A new interpretation of the isomorphism of divalent metals in tetrahedrite. *Doklady Akademii Nauka SSR*, 265, 128–131.
- Mosgova, N.N. and Tsepin, A.I. (1983) Gray Ores: Aspects of Chemical Composition and Properties. 279p. Nauka, Moscow. Note that “Gray Ores” is equivalent to “Fahlores”.
- Mosgova, N.N., Mikuionis, V., Valiukenas, V.I., Tsepin, A.I., and Orliukas, A. (1987) Some electrical properties of fahlore $Cu_{10}(Zn,Fe)_2(As,Sb)_3S_{13}$. *Physics and Chemistry of Minerals*, 15, 171–172.
- Nickel, E.H. and Mandarino, J.A. (1987) Procedures involving the IMA Commission on New Minerals and Mineral Names, and guidelines on mineral nomenclature. *Canadian Mineralogist*, 25, 353–377.
- O'Leary, M.J. and Sack, R.O. (1987) Fe-Zn exchange reaction between tetrahedrite and sphalerite in natural environments. *Contributions to Mineralogy and Petrology*, 96, 415–425.
- Palache, C., Berman, H., and Frondel, C. (1944) *Dana's System of Mineralogy*, 7th ed., vol. 1: Elements, Sulfides, Sulfosalts, Oxides. 834 p. Wiley, New York.
- Ramdohr, P. (1969) *The Ore Minerals and their Intergrowths*. 1174p. Pergamon, London.
- Rasor, C.A. (1934) Silver mineralization in the Sunshine mine, Coeur d'Alene district, Idaho. M.S. thesis, University of Idaho, Moscow, Idaho, 16p.
- Robbins, M., Wertheim, G.K., Sherwood, R.C., and Buchanan, D.N.E. (1971) Magnetic properties and site distributions in the system $FeCr_2O_4-Fe_3O_4$ ($Fe^{2+}Cr_2^{3+}Fe^{3+}_2O_4$). *Journal of Physics and Chemistry of Solids*, 32, 717–729.
- Sack, R.O. (1992) Thermochemistry of tetrahedrite-tennantite fahlores. In N.L. Ross and G.D. Price, Eds., *The Stability of Minerals*, p. 243–266. Chapman and Hall, London, England.
- — — (2000) Internally consistent database for sulfides and sulfosalts in the system $Ag_2S-Cu_2S-ZnS-Sb_2S_3-As_2S_3$. *Geochimica et Cosmochimica Acta*, 64, 3803–3812.
- — — (2005) Internally consistent database for sulfides and sulfosalts in the system $Ag_2S-Cu_2S-ZnS-FeS-Sb_2S_3-As_2S_3$: Update. *Geochimica et Cosmochimica Acta*, in press.
- Sack, R.O. and Brackebusch, F.W. (2004) Fahlore as an indicator of mineralization temperature and gold fineness. *CIM Bulletin*, 97, 78–83.
- Sack, R.O. and Ebel, D.S. (1993) As-Sb exchange energies in tetrahedrite-tennantite fahlores and bourmonite-seligmannite solutions. *Mineralogical Magazine*, 57, 633–640.
- Sack, R.O. and Ghiorso, M.S. (1991) Chromian spinels as petrogenetic indicators: Thermodynamics and petrological applications. *American Mineralogist*, 76, 827–847.
- — — (1998) Thermodynamics of feldspathoid solutions. *Contributions to Mineralogy and Petrology*, 310, 256–274.
- Sack, R.O. and Goodell, P.C. (2002) Retrograde reactions involving galena and Ag-sulfosalts in a zoned ore deposit, Julcani, Peru. *Mineralogical Magazine*, 66, 1043–1062.
- Sack, R.O. and Loucks, R.R. (1985) Thermodynamic properties of tetrahedrite-tennantites: Constraints on the interdependence of the $Ag \leftrightarrow Cu$, $Fe \leftrightarrow Zn$, $Cu \leftrightarrow Fe$, and $As \leftrightarrow Sb$ exchange reactions. *American Mineralogist*, 70, 1270–1289.
- Sack, R.O., Ebel, D.S., O'Leary, M.J. (1987) Tennantite thermochemistry and zoning. In H.C. Helgeson, Ed., *Chemical Transport in Metasomatic Processes*, p. 701–731, D. Reidel, Dordrecht.
- Sack, R.O., Kuehner, S.M., and Hardy, L.S. (2002) Retrograde Ag-enrichment in fahlores from the Coeur d'Alene mining district, Idaho, USA. *Mineralogical Magazine*, 66, 215–229.
- Sack, R.O., Lynch, J.G.V., and Foit, F.F., Jr. (2003) Fahlore as a petrogenetic indicator: Keno Hill Ag-Pb-Zn district, Yukon, Canada. *Mineralogical Magazine*, 67, 1023–1038.
- Spiridonov, E.M. (1984) Species and varieties of fahlore (tetrahedrite-tennantite) minerals and their rational nomenclature. *Doklady Akademii Nauka SSR*, 279, 166–172.
- Spiridonov, E.M. and Okrugin, V.M. (1985) Selenium goldfieldite, a new fahlore variety. *Doklady Akademii Nauka SSR*, 280, 476–478.
- Van Hook, H.J. (1960) The ternary system $Ag_2S-Bi_2S_3-PbS$. *Economic Geology*, 55, 759–788.
- Wavra, C.S., Bond, W.D., and Reid, R.R. (1994) Evidence from the Sunshine Mine for dip-slip movement during Coeur D'Alene district mineralization. *Economic Geology*, 89, 515–527.
- White, B.G. (1989) Superposed map-scale folds and subsequent veins unrelated to Osburn strike-slip fault, Coeur d'Alene mining district, Shoshone County, Idaho. *Geological Society of America Abstracts with Programs (Rocky Mountain Cordilleran Section)*, 21, 158.
- — — (1998) New tricks for an old elephant: Revising concepts of Coeur d'Alene geology. *Mining Engineering*, August, 27–35.
- Willard, M.E. (1941) Mineralization at the Polaris mine. *Economic Geology*, 36, 539–550.
- Wu, I. and Petersen, U. (1977) Geochemistry of tetrahedrite-tennantite at Casapalca, Peru. *Economic Geology*, 72, 993–1016.

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