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COMPOSITIONAL VARIATION IN MERCURIAN TETRAHEDRITE–TENNANTITE FROM THE EPITHERMAL DEPOSITS OF THE STEENS AND PUEBLO MOUNTAINS, HARNEY COUNTY, OREGON

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ABSTRACT

Mercury-bearing tetrahedrite–tennantite (tetrahedrite$_{ss}$), $^{III}(Cu^+)_6\ ^{IV}[(Cu^+)_4(R^{2+})_2]\ ^{III}(Sb,As)_4{}^{IV}S_{12}{}^{VI}S$, where R^{2+} = Hg, Fe, Zn, Cu … is a minor but important constituent in the epithermal deposits of the Steens–Pueblo Mining District of southeastern Oregon. Electron-microprobe analyses of tetrahedrite$_{ss}$ from 12 of the deposits reveal complete substitution between the tetrahedrite and tennantite end-members with extensive substitution of Hg (up to 21.3 wt.%) and, in one deposit, silver (up to 49.7 wt. %). The Hg content is negatively correlated to the both the Fe and, especially, the Zn content, and positively but weakly correlated to the Sb content. Thus samples with the highest Hg contents (~2 atoms per formula unit) tend to be tetrahedrite$_{ss}$ with only minor to trace amounts of Fe and Zn and approximately 10 atoms per formula unit of Cu. Samples from the O'Keefe claims contain the highest Hg and Ag contents, $Ag_{6.00}[(Ag_{4.00})\ (Cu_{0.62}\ Hg_{0.60}Zn_{0.40}Fe_{0.12}Co_{0.05}Cd_{0.04})]\ (Sb_{2.35}As_{1.72})\ S_{13.09}$, ever reported for an intermediate member of the tetrahedrite–tennantite series, with substitution extending to the end member in which Cu is entirely replaced by Ag. This end member corresponds to the Sb-dominant analogue of argentotennantite. The antipathetic relationships between Ag and As, and between Ag and S, often reported in natural tetrahedrite$_{ss}$, is not observed. The accommodation of large amounts of Ag in both the trigonal and tetrahedral sites in the structure seems facilitated by the presence of significant Hg and Zn in the tetrahedral framework rather than by the formation of S defects and octahedral metallic clusters.

Keywords: mercurian tetrahedrite, argentian tetrahedrite, tetrahedrite–tennantite series, argentotennantite, Steens–Pueblo District, Oregon.

SOMMAIRE

La solution solide tétraédrite–tennantite mercurifère (ou tétraédrite$_{ss}$), $^{III}(Cu^+)_6\ ^{IV}[(Cu^+)_4(R^{2+})_2]\ ^{III}(Sb,As)_4{}^{IV}S_{12}{}^{VI}S$, avec R^{2+} = Hg, Fe, Zn, Cu … est un composant accessoire mais tout de même important des gisements épithermaux du camp minier de Steens–Pueblo, dans le sud-est de l'Oregon. Les analyses de la tétraédrite$_{ss}$ provenant de douze gisements avec une microsonde électronique révèle une substitution complète entre les pôles tétraédrite et tennantite, avec incorporation importante de mercure (jusqu'à 21.3% en poids) et d'argent (jusqu'à 49.7% dans un gisement). La teneur en Hg montre une corrélation négative avec la teneur en Fe et surtout en Zn, et une corrélation positive mais relativement faible avec la teneur en Sb. Ainsi, les échantillons contenant le maximum de Hg (~2 atomes par unité formulaire) ont tendance à être des compositions de tétraédrite$_{ss}$ avec de faibles teneurs en Fe et Zn, et environ 10 atomes par unité formulaire de Cu. Les échantillons provenant de la propriété dite O'Keefe contiennent les teneurs les plus élevées en Hg et Ag, $Ag_{6.00}\ [(Ag_{4.00})(Cu_{0.62}Hg_{0.60}Zn_{0.40}Fe_{0.12}Co_{0.05}Cd_{0.04})]\ (Sb_{2.35}As_{1.72})\ S_{13.09}$ qui soient connues dans le cas d'un membre intermédiaire de la série tétraédrite–tennantite, la substitution menant à un pôle dans lequel le Cu est entièrement remplacé par Ag. Ce pôle correspondrait à l'analogue à dominance de Sb de l'argentotennantite. Les relations antipathétiques entre Ag et As, et entre Ag et S, souvent citées dans les descriptions de tétraédrite$_{ss}$ naturelle, ne sont pas observées. L'accommodation de quantités importantes de Ag à la fois dans les sites trigonaux et tétraédriques de la structure semble facilitée par la présence d'une proportion importante de Hg et Zn dans le réseau de tétraèdres de la trame, plutôt que par la formation de défauts dans le site S ou d'agglomérations de métaux dans les sites octaédriques.

(Traduit par la Rédaction)

Mots-clés: tétraédrite mercurifère, tétraédrite argentifère, série tétraédrite–tennantite, argentotennantite, district de Steens–Pueblo, Oregon.

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INTRODUCTION

The mercury deposits of the Steens–Pueblo Mining District in southeastern Oregon are very unusual in that the dominant ore mineral is a rare mercury-bearing member of the tetrahedrite–tennantite solid-solution series, $(Cu,Ag)_{10}(Hg,Zn,Fe)_2Sb_4S_{13}$ – $(Cu,Ag)_{10}(Hg,Zn,Fe)_2As_4S_{13}$. Although members of this series (hereafter, tetrahedrite$_{ss}$) are important primary ores of Cu and Ag, their recovery as an ore of Hg coupled with their known propensity for cation substitutions of great extent and diversity made them attractive candidates for further study. Indeed, this series exhibits the most extensive chemical substitutions and widespread occurrence of all of the sulfosalt mineral groups.

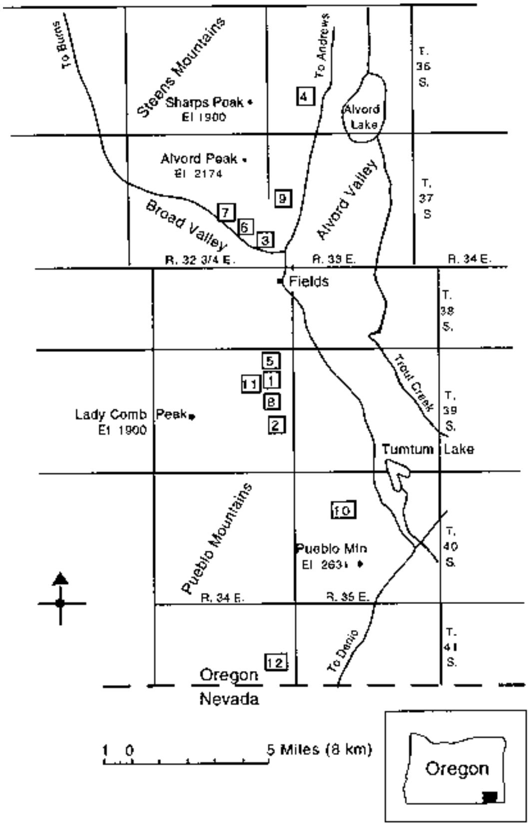

FIG. 1. Map showing the location of the tetrahedrite$_{ss}$ deposits, after Brooks (1963) and J.G. Evans (pers. commun., 1997). Mine and prospect locations (latitude 42° and longitude 118°): (1) Ajax North claims 12.80', 41.38', (2) Blue Bull mine 10.66', 40.57', (3) Blue Boy mine 17.60', 41.45', (4) Fisher Group claims 23.33', 39.27', (5) Harmony Group claims 13.50', 41.27', (6) Mogul mine 17.97', 42.23', (7) O'Keefe claims 18.33', 43.12', (8) Rabbit Hole mine 12.00', 40.60', (9) Red Dome claims 19.66', 40.57', (10) Spring Creek claims 7.30', 37.92', (11) Surprise Group claims 13.37', 41.32', and (12) Tiller Cabin claims 1.42', 40.93'.

All accessible mines and pits (over 90 sites) in the Steens–Pueblo District were examined for tetrahedrite$_{ss}$ mineralization (Ulbricht 1997, Ulbricht & Foit 1998). Samples from 12 deposits (Fig. 1) were found to contain visible Hg-bearing tetrahedrite$_{ss}$, the crystal chemistry of which is the focus of this study.

BACKGROUND INFORMATION

Regional geology

The Steens–Pueblo Mining District is a 65-km long, 5- to 8-km-wide belt of epithermal copper, gold, and mercury deposits located along the eastern margin of the Steens–Pueblo Range (Fig. 1). The mineralization has been linked (Rytuba & McKee 1984, Roback *et al.* 1987, Minor *et al.* 1987, Orr *et al.* 1992, Rytuba 1994) to hydrothermal events associated with the formation of the Pueblo caldera, the western margin of which coincides with the Pueblo Range front. The Pueblo caldera is one of 22 calderas in the McDermitt complex, which formed after the eruption (16.1–15.0 Ma) of seven large-volume ash-flow sheets that cover 20,000 km^2 in southeastern Oregon and northwestern Nevada. The mercury-bearing tetrahedrite$_{ss}$ occurs as a minor but important constituent in a large-scale northwest- to northeast-trending silicified fissure–fault system cutting pre-Tertiary metamorphic rocks and Miocene andesites, rhyolites and basalts along the western margin of the caldera. Faulting associated with caldera collapse and later tectonic activity likely provided conduits for hydrothermal fluids. The silicified reefs, being more resistant to erosion than the host rocks, form prominent ridges up to 8 meters wide and a kilometer in length.

The earliest recorded commercial exploitation of these deposits took place in 1919, with the bulk of the mining spanning the late 1930s to the early 1950s. The amount of mercury mineralization was very limited, and the economics were driven by war-time needs. The largest producer, the Mogul mine, produced only 30 flasks of mercury by crudely roasting the ore and condensing the mercury vapor.

Mineralogy of the deposits

The mineralogy of most of the deposits is very similar. The tetrahedrite$_{ss}$ occurs in siliceous veins primarily as micrometric- to millimetric disseminated anhedral grains and blebs most commonly associated with massive chalcopyrite (Fig. 2). The intimate intergrowth and absence of replacement textures suggest that they were deposited early and contemporaneously. In some of the veins, masses of tetrahedrite$_{ss}$ enclose bornite overgrown with chalcocite and covellite. In the northernmost deposits (Fisher claims), minor amounts of cinnabar also occur. Hand samples and outcrops show evidence of

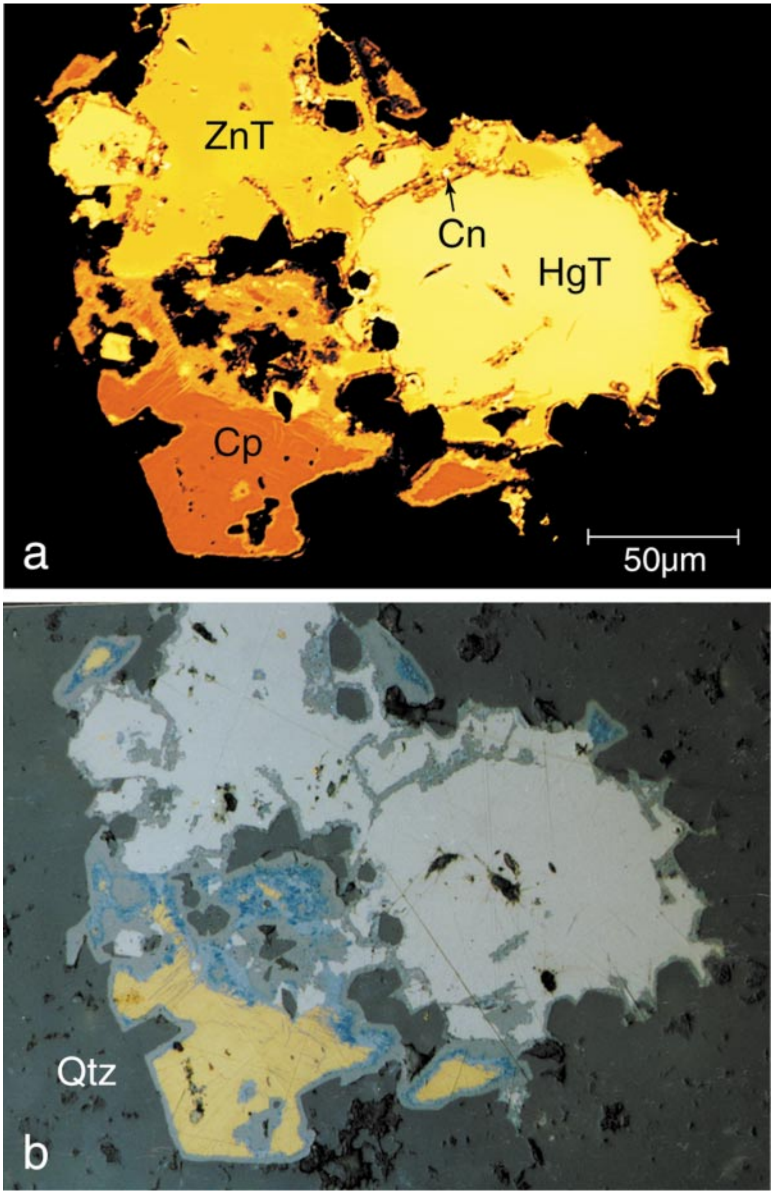

FIG. 2. Tetrahedrite$_{ss}$ from the Spring Creek claims. a) Back-scattered electron image of Hg-rich tetrahedrite$_{ss}$ (HgT), Zn-rich tetrahedrite$_{ss}$ (ZnT), chalcopyrite (Cp), and cinnabar (Cn). The cinnabar appears as nearly white dots in the Fe-oxide coatings on the tetrahedrite$_{ss}$ and chalcopyrite. b) Reflected-light image showing a light gray tetrahedrite$_{ss}$, medium gray Fe-oxide coating, dark gray quartz matrix (Qtz), dark blue covellite, and pale blue digenite.

supergene alteration in the form of characteristic blue-green staining due to abundant azurite, malachite, and chrysocolla. These minerals, along with covellite, digenite, chalcocite and, especially, goethite–lepidocrocite and chalcedony, occur as fracture fillings and overgrowths on chalcopyrite and, to a lesser extent, on tetrahedrite$_{ss}$.

A sample from the Spring Creek claims (Fig. 2) contains tetrahedrite$_{ss}$ of two different compositions, a Hg-rich, Zn- and Fe-poor phase (HgT, Fig. 2a) and a

Zn-rich, Hg- and Fe-poor phase (ZnT), chalcopyrite (Cp), and cinnabar (Cn). Covellite (bright blue, Fig. 2b) and digenite (pale blue) replacing the chalcopyrite and tetrahedrite$_{ss}$ are coated with an Fe-oxide – hydroxide (medium gray), which hosts finely disseminated tetrahedrite$_{ss}$ and an occasional cinnabar crystal. There is commonly a thin layer of covellite + digenite between the chalcopyrite and Fe-oxide layer.

ANALYTICAL DATA

Carbon-coated polished thin sections were prepared from at least two samples from each deposit. The samples of tetrahedrite$_{ss}$ were analyzed in the Department of Geology's GeoAnalytical Laboratory (Washington State University) using a Cameca Camebax electron microprobe equipped with four wavelength-dispersion spectrometers, an acceleration voltage of 20 keV, a beam current of 16 nA, and a beam diameter of 5 μm. Only Ag, As, Cu, Cd, Co, Fe, Hg, S, Sb, and Zn were found to be present in detectable amounts, and initially they were measured using the following calibration standards (and emission lines): $CuFeS_2$ (Cu$K\alpha$, Fe$K\alpha$, S$K\alpha$), FeAsS (As$K\alpha$), elemental Sb (Sb$L\alpha$), ZnS (Zn$K\alpha$), elemental Ag (Ag$L\alpha$), HgS (Hg$M\alpha$), CdS (Cd$L\alpha$), elemental Co (Co$K\alpha$). During the course of data reduction, the recurrence of high analytical totals and anomalously high sulfur contents suggested the presence of a serious systematic analytical error similar to that encountered by Trudu & Knittel (1998).

The problem, which will be encountered in any X-ray fluorescence analysis of compounds containing appreciable Hg and S, involves the relatively large absorption corrections necessitated by the proximity of the Hg$L\alpha$ and S$K\alpha$ emission lines (Harris 1990). The S$K\alpha$ line is greatly absorbed by Hg. Inspection of tables of mass-absorption coefficients in several of the computer correction routines revealed considerable variation in the Hg mass-absorption coefficients for S$K\alpha$, suggesting this as an important contributor to the problem. The best choice of these coefficients was determined by analyzing a series of stoichiometric Hg- and S-bearing compounds covering a range of Hg:S values, alternately using one then the other as the standard and unknown. The conventional ZAF correction using the mass-absorption coefficients of Heinrich (1987) provided the best results. To further minimize matrix effects and improve the quality of the data, livingstonite, $HgSb_4S_8$, a stoichiometric mineral containing approximately the same ratio of Hg:S as observed in Hg-rich tetrahedrite$_{ss}$, was chosen as a new Sb and Hg standard.

Formulas of the Steens–Pueblo tetrahedrite$_{ss}$ used in the following evaluations were calculated on the basis of 29 atoms per formula unit (*apfu*) conforming to $^{III}M(2)_6{}^{IV}M(1)_6[^{III}X^{IV}Y_3]_4{}^{VI}Z$ where $M(1)$ = Fe, Zn, Hg, Cu^{2+}, Cd …; $M(2)$ = Cu^+, Ag; X = Sb, As, Bi, Te; Y and Z = S, Se. Hg is assumed to be divalent in these calculations, which is consistent with previous studies and the resulting expected stoichiometry. The quality of the results is confirmed by the fact that for the 420 point analyses, the analytical totals average 99.83 ± 0.85 wt%, and the number of S and (Sb + As) atoms per formula unit, *apfu*, based on a total of 29 *apfu*, averages 13.00 ± 0.10 and 4.00 ± 0.06, respectively, which matches the expected stoichiometry. The average composition of tetrahedrite$_{ss}$ from each of the sites is presented in Table 1. The standard deviation (in parentheses) for each element provides a measure of the compositional variability in each deposit. Table 2 contains averaged data for tetrahedrite$_{ss}$ of unusual composition.

COMPOSITIONAL VARIATIONS

Regional variations

Hg is most abundant in tetrahedrite$_{ss}$ from the most northerly (Fisher Group claims, #4 in Fig. 1) and southerly deposits (Spring Creek and Tiller Cabin claims, #10 and #12 in Fig. 1; Table 1). In these deposits, Hg ranges from 0.21 to 2.02 *apfu* and averages 1.50–1.71 *apfu*. The Zn content varies inversely with Hg, and the highest Zn values are observed in the centrally located deposits, just north and south of Fields, Oregon. Tetrahedrite$_{ss}$ from

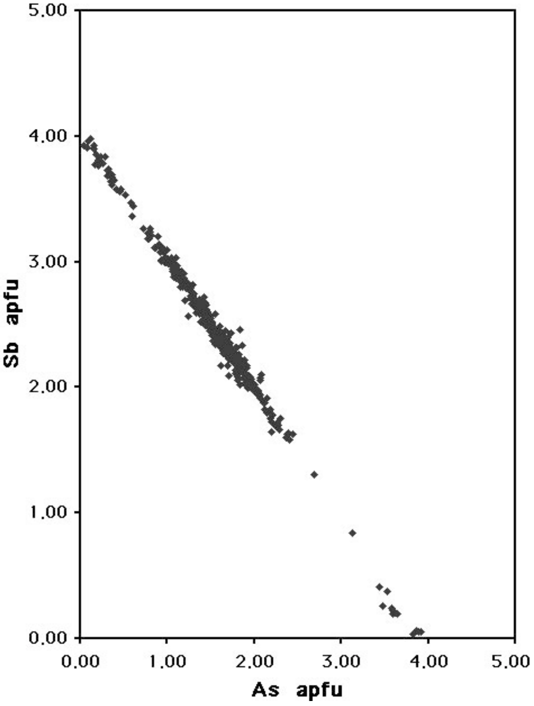

FIG. 3. Variation of Sb with As in tetrahedrite$_{ss}$ of the Steens–Pueblo suite.

TABLE 1. MEAN COMPOSITION OF TETRAHEDRITE$_{ss}$* FROM EACH OF THE STEENS–PUEBLO DEPOSITS

Zn	Cu	Co	Fe	Sb	As	Cd	Ag	S	Hg	As+Sb	ΣMetal cations
1. Ajax North claims											
sample 1 (vein), *n* = 21											
1.09(9)	10.10(5)	0.02(1)	0.33(7)	2.33(17)	1.67(17)	0.01(0)	0.02(0)	13.07(5)	0.34(8)	4.00(3)	11.91(5)
sample 2, *n* = 24											
0.74(19)	10.19(9)	0.03(1)	0.45(14)	2.16(64)	1.82(61)	0.01(1)	0.02(1)	13.02(8)	0.57(21)	3.98(5)	12.01(7)
2. Blue Bull mine, sample from dump, *n* = 26											
0.58(31)	10.33(24)	0.01(0)	0.28(28)	2.15(32)	1.83(31)	0.01(1)	0.01(1)	13.00(6)	0.82(49)	3.98(3)	12.04(4)
3. Blue Boy mine, sample from dump, *n* = 21											
0.54(30)	10.13(13)	0.01(1)	0.06(3)	2.54(65)	1.44(61)	0.00(0)	0.01(1)	13.00(7)	1.27(41)	3.98(5)	12.02(2)
4. Fisher Group claims											
pit 1, *n* = 30											
0.13(7)	10.19(20)	0.01(1)	0.20(38)	3.25(1.26)	0.76(1.23)	0.00(0)	0.01(1)	12.89(7)	1.58(49)	4.01(6)	12.12(10)
pit 2, sample 1, *n* = 4											
0.42(3)	10.01(7)	0.01(1)	0.01(0)	2.61(16)	1.40(13)	0.01(1)	0.01(1)	13.01(5)	1.52(2)	4.01(6)	11.99(6)
pit 2, sample 2, *n* = 22											
0.34(7)	10.01(5)	0.00(0)	0.01(1)	2.85(29)	1.18(26)	0.00(0)	0.01(1)	12.97(8)	1.62(9)	4.03(4)	11.99(5)
pits 4 and 5, *n* = 20											
0.59(38)	10.33(27)	0.01(1)	0.45(44)	2.35(83)	1.60(91)	0.00(0)	0.02(1)	13.00(7)	0.65(37)	3.95(10)	12.05(8)
5. Harmony Group claims, sample from one pit, *n* = 18											
0.96(15)	10.06(7)	0.02(1)	0.12(3)	2.62(21)	1.37(22)	0.02(1)	0.04(1)	13.02(6)	0.78(16)	3.99(3)	12.00(7)
6. Mogul mine, sample from dump, *n* = 5											
0.74(43)	10.17(15)	0.01(1)	0.04(3)	2.56(84)	1.45(80)	0.03(2)	0.01(0)	13.00(4)	0.99(51)	4.01(8)	11.99(8)
7. O'Keefe claims											
pit 1, sample 1, *n* = 38											
0.76(20)	10.21(19)	0.03(1)	0.17(8)	2.13(40)	1.87(38)	0.00(0)	0.09(5)	13.04(10)	0.69(18)	4.00(6)	11.95(11)
pit 1, sample 2, *n* = 37											
0.45(26)	4.65(§)	0.03(2)	0.18(8)	2.31(17)	1.72(17)	0.01(1)	5.78(¶)	13.05(19)	0.83(33)	4.03(11)	11.93(24)
8. Rabbit Hole mine, sample from dump, *n* = 28											
0.89(29)	10.16(5)	0.01(1)	0.09(3)	2.11(27)	1.88(27)	0.03(1)	0.01(1)	13.05(6)	0.80(31)	3.99(3)	11.99(6)
9. Red Dome claims, pit 1, *n* = 21											
1.35(10)	10.11(5)	0.07(1)	0.35(6)	3.03(19)	0.96(18)	0.00(0)	0.00(0)	13.06(6)	0.06(1)	3.99(3)	11.94(6)
10. Spring Creek claims											
pit 1, *n* = 22											
0.55(27)	10.09(9)	0.01(1)	0.07(8)	2.72(29)	1.32(30)	0.00(0)	0.01(1)	12.94(8)	1.29(42)	4.04(4)	12.02(9)
pit 2, *n* = 20											
0.24(6)	10.04(13)	0.00(0)	0.01(0)	2.81(29)	1.22(28)	0.00(0)	0.01(1)	12.95(7)	1.71(14)	4.03(3)	12.01(7)
11. Surprise Group claim, *n* = 24											
0.97(15)	10.05(9)	0.01(1)	0.11(4)	2.62(16)	1.39(15)	0.07(3)	0.08(6)	12.98(9)	0.72(17)	4.01(5)	12.01(9)
12. Tiller Cabin claim, *n* = 19											
0.44(32)	10.01(7)	0.01(1)	0.04(3)	2.28(31)	1.73(31)	0.00(0)	0.01(1)	12.97(8)	1.50(38)	4.01(6)	12.01(7)

n: number of point-analyses made. Standard deviation is shown in parentheses. * Normalized to 29 atoms per formula unit. § ±3.24. ¶ ±3.12.

the Red Dome claims is particularly high in Zn, with values averaging 1.35 *apfu* and ranging from 1.20 to 1.51 *apfu*. No systematic regional variations were observed for any of the other elements.

Coupled substitutions

Electron-microprobe data reveal the presence of stoichiometric amounts of As and Sb and the existence of complete solid-solution between the tetrahedrite and tennantite end-members. Most of the crystals are of intermediate composition, containing between 1 and 2 As *apfu* (Fig. 3) and showing extensive incorporation of mercury and, in some crystals, mercury and silver. Although Mozgova *et al.* (1979) reported the existence of end-member tennantite containing 2 Hg *apfu*, the data in Figure 4 confirm the suggestion of Johnson *et al.* (1986) that Hg-rich tetrahedrite$_{ss}$ tends to be Sb-rich.

TABLE 2. SELECTED COMPOSITIONS OF TETRAHEDRITE$_{ss}$ FROM THE STEENS–PUEBLO SUITE*

Zn	Cu	Co	Fe	Sb	As	Cd	Ag	S	Hg	As + Sb	ΣMetal cations
Cu-rich tetrahedrite (average of samples with >10.6 Cu *apfu*)											
Fisher Group claims, *n* = 8											
0.07(6)	10.72(8)	0.01(0)	0.99(17)	0.26(25)	3.60(24)	0.00(0)	0.01(1)	13.03(9)	0.32(14)	3.86(8)	12.12(5)
Blue Bull mine, *n* = 3											
0.06(2)	10.87(9)	0.01(1)	0.91(6)	1.68(36)	2.29(38)	0.00(0)	0.00(0)	13.01(8)	0.17(8)	3.97(2)	12.02(6)
O'Keefe pit, *n* = 1											
0.08	11.06	0.02	0.24	0.04	3.82	0.00	0.11	13.12	0.52	3.86	12.02
Ag-rich tetrahedrite (average of samples with Cu < 2 and Ag > 8.5 *apfu*)											
O'Keefe pit, *n* = 10											
0.47(16)	0.95(59)	0.04(1)	0.18(6)	2.30(14)	1.80(17)	0.02(1)	9.25(59)	13.13(10)	0.87(15)	4.10(7)	11.80(13)

n: number of point-analyses made. Standard deviation is given in parentheses. * Normalized to 29 atoms per formula unit.

Approximately 90% of the crystals analyzed contain 10 Cu *apfu* (Fig. 5), and generally the highest concentrations of Hg were found in these crystals, an observation also made by Johnson *et al.* (1986) in their literature survey on tetrahedrite$_{ss}$. Samples of tetrahedrite$_{ss}$ in the Steens–Pueblo suite with less than 10 Cu *apfu* contain the highest concentrations of Ag, and those with more than 10 Cu *apfu*, the lowest concentrations of divalent cations (Hg + Zn + Fe + Cd + Co). The data to the right of the 10 Cu *apfu* line correspond to crystals that contain as many as 11 Cu *apfu* with a corresponding deficiency in divalent cations (Table 2). The deviation from stoichiometric amounts of divalent cations (Zn + Fe + Cd + Co) at low Hg contents (Fig. 6) is due, in part, to the presence of excess Cu, with charge balance maintained by the presence of Cu^{2+} or Fe^{3+}, both of which have been reported in natural samples (Charnock *et al.* 1989, Pattrick *et al.* 1993, Marcoux *et al.* 1994). The presence of excess Cu in natural tetrahedrite$_{ss}$ is common, especially in the presence of Fe (Charlat & Lévy 1974, Pattrick & Hall 1983, Johnson *et al.* 1986). Although there is sufficent Fe (if present as Fe^{3+}) in the Cu-excess tetrahedrite$_{ss}$ from the Fisher Creek claims and the Blue Bull mine (Table 2) to balance the charges, one Cu-excess crystal from the O'Keefe pit contains virtually no Fe, which suggests the presence of significant Cu^{2+} in the structure. This is consistent with the observation of Makovicky *et al.* (1990) that the presence of Zn and Hg favors the presence of Fe^{2+}, even at low Fe contents.

The data points to the left of the 10 Cu *apfu* line in Figure 5 correspond to the Ag- and Hg-rich tetrahedrite$_{ss}$ from the O'Keefe claims (Fig. 1) and reflect a one-for-one substitution of Ag^+ for Cu^+ (Fig. 7). The substitution seems to be complete, extending to the Ag end-member composition, $(Ag^+)_6[(Ag^+)_4\ (R^{2+})_2]$ $(Sb,As)_4S_{13}$ (Riley 1974, Balitskaya *et al.* 1989, Li & Wang 1990). The average composition of the 10 most

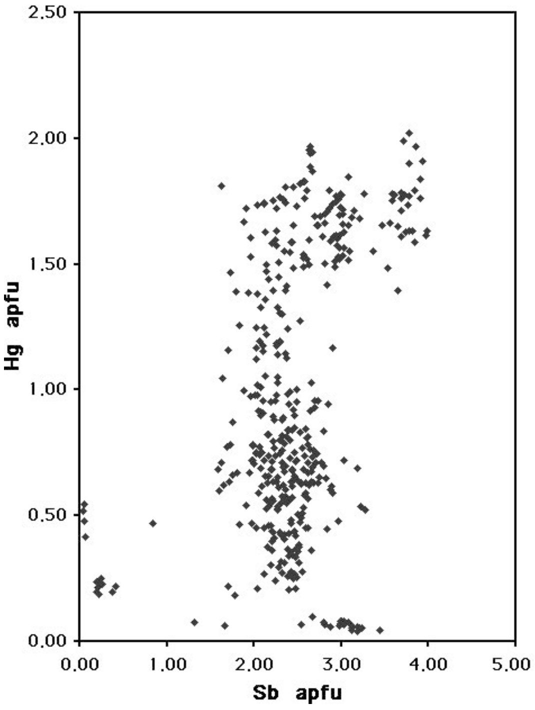

FIG. 4. Variation of Hg with Sb in tetrahedrite$_{ss}$ of the Steens–Pueblo suite.

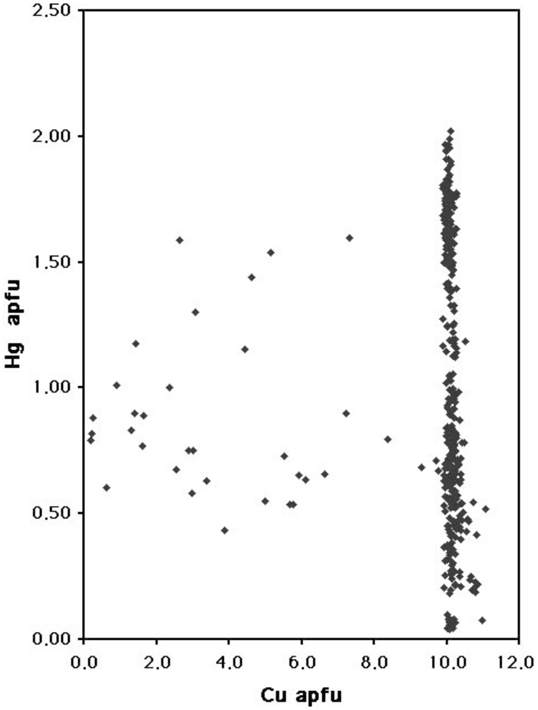

FIG. 5. Variation of Hg with Cu in tetrahedrite$_{ss}$ of the Steens–Pueblo suite.

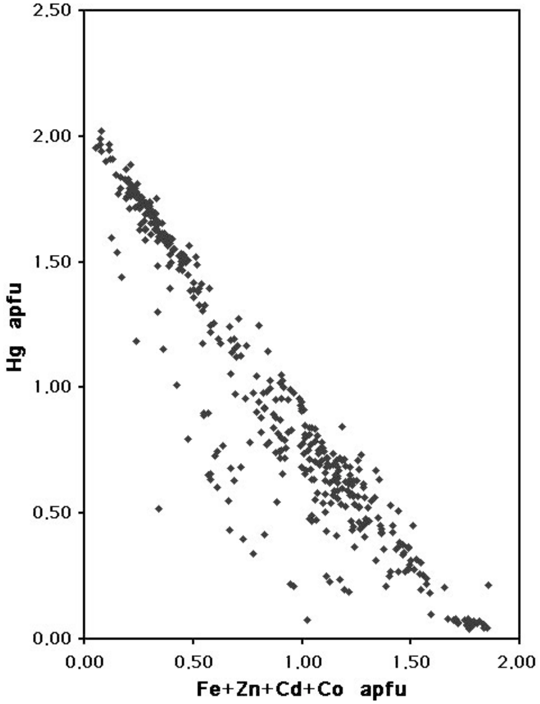

FIG. 6. Variation of Hg with Fe + Zn + Cd + Co in tetrahedrite$_{ss}$ of the Steens–Pueblo suite.

Cu-deficient (Cu < 2 *apfu*, Fig. 5) and Ag-rich (Ag > 8.5 *apfu*, Fig. 7) crystals is given in Table 2. The Ag-rich tetrahedrite$_{ss}$ contains between 0.43 and 1.59 Hg *apfu* (Fig. 8) and is intermediate along the tetrahedrite–tennantite join, with a nearly constant Sb:As ratio (Fig. 9). The Ag content appears to be correlated with the Cu content only, and there is no evidence of the antipathetic relationships between either Ag and Hg (Fig. 8) or Ag and As (Fig. 9) reported by Johnson (1986). Unfortunately, these Ag-rich crystals were found to be too small to examine the variation of the *a* lattice parameter with Ag substitution using conventional X-ray-diffraction techniques.

The Hg content is negatively correlated to both the Fe, and especially the Zn content (Fig. 10), and positively but weakly correlated to the Sb content (Fig. 4). Unlike the Zn-rich Steens–Pueblo tetrahedrite$_{ss}$, most tetrahedrite$_{ss}$ is Fe-rich, and Johnson *et al.* (1986) reported a strong negative correlation between Hg and Fe contents. As observed by Johnson *et al.* (1986), the sum of the divalent cations rarely, and then only slightly, exceeds 2 *apfu*. Samples with the highest Hg contents (~ 2 *apfu*) tend to be tetrahedrite$_{ss}$ with only minor to trace amounts of Fe and Zn and approximately 10 *apfu* of Cu. This further confirms that Fe, Zn, and Hg compete for the same site in the tetrahedrite structure, and that the Hg antipathy to either Zn or Fe is more likely due to physical or chemical conditions during formation rather than crystal-chemical preferences. The data in Figure 4 suggest that the accommodation of significant Hg in the structure is facilitated by the presence of Sb. This is more compelling given the apparent abundance of As in the Steens–Pueblo ore-forming fluids; the composition of tetrahedrite$_{ss}$ in a single hand-sample from the Fisher Group claims (Fig. 1) was observed to span almost the complete range of As:Sb substitution.

DISCUSSION

Natural mercury-free samples (*e.g.*, Paar *et al.* 1978, Imai & Lee 1980, Sandecki & Amcoff 1981, Ixer & Stanley 1983, Augsten *et al.* 1986, Spiridonov *et al.* 1986, O'Leary & Sack 1987, Lynch 1989) and synthetic equivalents (*e.g.*, Pattrick & Hall 1983) approach the end-member composition, $^{III}Ag_6\,^{IV}[Ag_4(R^{2+})_2](Sb,As)_4S_{13}$, proposed by Hall (1972) and Riley (1974). However, tetrahedrite$_{ss}$ from the O'Keefe deposit is unique in that it contains some of the highest levels of Ag and Hg, $Ag_{6.00}[(Ag_{4.00})(Hg_{0.60}Zn_{0.40}Cu_{0.20}Fe_{0.12}Co_{0.05}Cd_{0.04})](Sb_{2.35}As_{1.72})S_{13.09}$, ever reported for an inter-

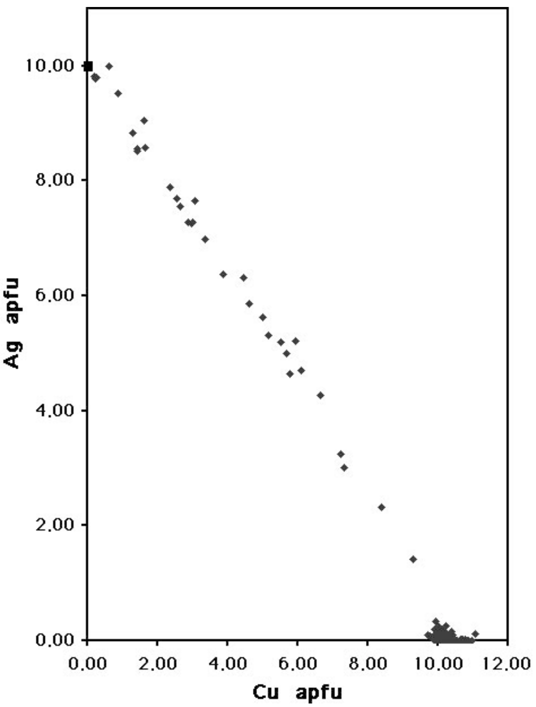

FIG. 7. Variation of Ag with Cu in tetrahedrite$_{ss}$ of the Steens–Pueblo suite. Filled square represents the Ag-rich end-member, $(Ag^+)_6[(Ag^+)_4(R^{2+})_2](Sb,As)_4S_{13}$ of Riley (1974).

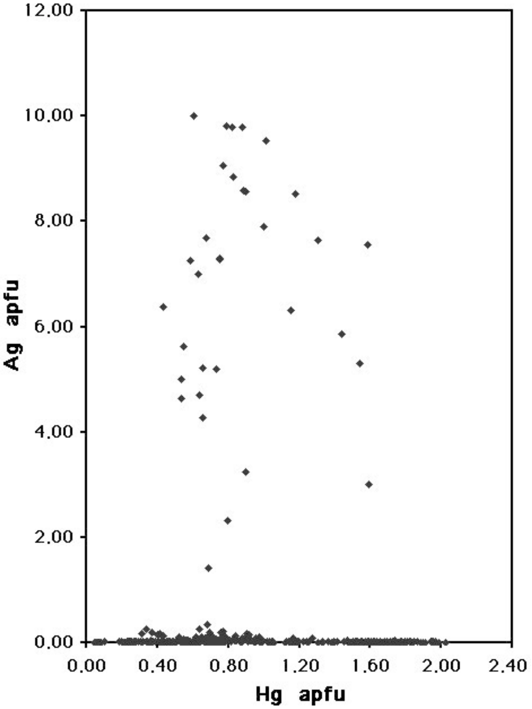

FIG. 8. Variation of Ag with Hg in tetrahedrite$_{ss}$ of the Steens–Pueblo suite.

mediate member of the tetrahedrite–tennantite series and is one of only a few examples of the Ag-rich end-member.

Tetrahedrite$_{ss}$ from the O'Keefe claims contains Ag in significant excess of the 6 apfu allowed by some current structural models based on the preference of Ag for trigonal coordination (Charnock *et al.* 1988). This suggests that Ag occupies both trigonally and tetrahedrally coordinated sites; indeed, Kalbkopf (1972) suggested that the Ag preferentially substitutes for Cu^+ in the $^{III}M(2)$ site and, when this site is full, the Ag enters the $^{IV}M(1)$ site. Crystal-structure refinements of synthetic argentian tetrahedrite (Johnson & Burnham 1985) and freibergite (Peterson & Miller 1986) containing modest amounts of Ag (2.12 and 4.22 *apfu*, respectively) confirm the presence of Ag^+ exclusively in the $^{III}Cu^+$ site. More extensive incorporation of Ag appears to be accompanied by formation of defects at the ^{VI}Z (sulfur) site and metallic Ag-clusters (Samusikov & Leskova 1988, Samusikov *et al.* 1988, Rozhdestvenskaya *et al.* 1989a, b).

Johnson *et al.* (1986) reported that "Ag and As have little tolerance for each other in the tetrahedrite structure and that the presence of only one atom of As decreases (neglecting scatter) the maximum number of Ag atoms contained from six to one." Although a distinct negative correlation between Ag and As contents has been widely observed in natural samples (Wu & Petersen 1977, Johnson & Burnham 1985, Johnson 1986), there are many examples (Ixer & Stanley 1983, Spiridonov 1988, this study) in which both Ag and As are abundant in a particular crystal. This would suggest that either environmental factors (*e.g.*, composition of the ore-forming fluid) or the presence of other substituents (*e.g.*, Hg, Zn or Fe) might promote the concomitant incorporation of Ag and As. Most natural Ag-rich tetrahedrite$_{ss}$ is also Fe-rich (Johnson *et al.* 1986), and the Ag content of synthetic tetrahedrite appears to be controlled by the nature and amount of divalent substituents, principally Fe, Cd, and Zn (Pattrick & Hall 1983). In contrast (Fig. 10), the predominant divalent cations in the Steens–Pueblo tetrahedrite$_{ss}$ are Hg and Zn. Although no distinct positive covariance was observed between Ag and Zn + Hg, crystals containing large amounts of Ag also contain >0.89 *apfu* of Hg + Zn (Fig. 11). Pattrick & Hall (1983) observed that the extent of silver incorporation in synthetic tetrahedrite increases with the covalent radius of the "divalent" cation (Fe < Zn < Cd ≈ Hg) substituting for $^{VI}Cu^{2+}$. The maximum substitution observed was 7.02 Ag atoms in a syn-

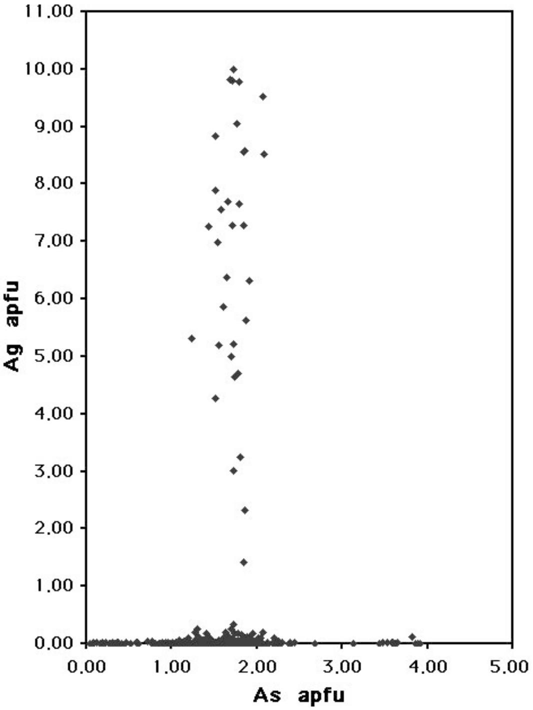

FIG. 9. Variation of Ag with As in tetrahedrite$_{ss}$ of the Steens–Pueblo suite.

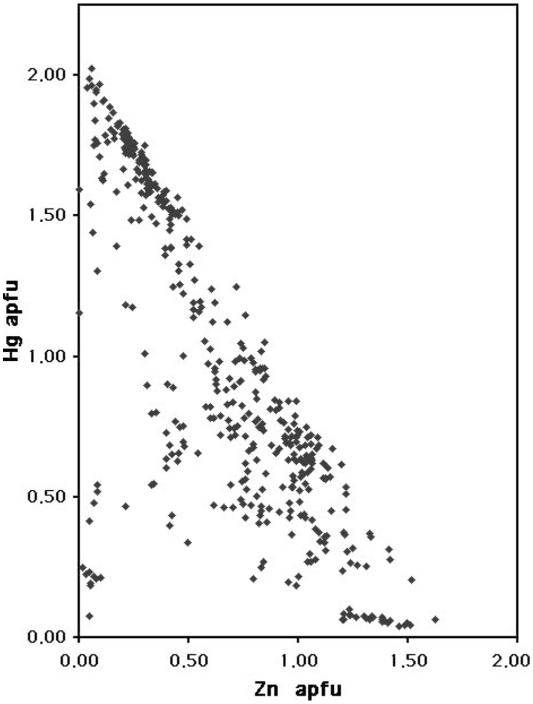

FIG. 10. Variation of Hg with Zn in tetrahedrite$_{ss}$ of the Steens–Pueblo suite.

thetic Cd-rich tetrahedrite. O'Leary & Sack (1987) suggested that a maximum in the configurational Gibbs energy of the Fe–Zn exchange reaction between sphalerite and tetrahedrite (corrected for nonideality of sphalerite) at ~4 Ag *apfu* can be explained simply if the trigonal–tetrahedral site-ordering variable is a maximum here and "Ag prefers trigonal coordination more strongly in iron tetrahedrites than zincian tetrahedrites". This explanation suggests that the presence of Zn promotes entry of Ag into the tetrahedral site, as must be the case in Ag-rich O'Keefe tetrahedrite$_{ss}$ containing more than 6 Ag *apfu*.

A survey (Foit 1999) of silver-rich tetrahedrite$_{ss}$ (most of which is not Hg-bearing) published in the literature reveals a gap in composition between ~7 and 8 Ag *apfu* in the series $(Cu^+)_6[(Cu^+)_4(R^{2+})_2]$ $(Sb,As)_4S_{13}$ – $(Ag^+)_6[(Ag^+)_4$ $(R^{2+})_2]$ $(Sb,As)_4S_{13}$ and a negative correlation between Ag and S content (Mosgova *et al.* 1996). The gap is consistent with a maximum incorporation of 7.3 Ag *apfu* observed in synthesis experiments and the maximum Ag-content (< 8 Ag *apfu*) of tetrahedrite coexisting with pyrargyrite, miargyrite, and sphalerite or pyrrhotite (Ebel & Sack 1994). Thus in some cases, extensive incorporation of Ag in the tetrahedrite structure may not only be accompanied by formation of defects in the sulfur and metallic octahedral clusters (Samusikov & Leskova 1988, Samusikov *et al.* 1988, Rozhdestvenskaya *et al.* 1989a, b), but also by a structural transformation (Foit 1999). This adjustment would help explain the anomalous behavior of the *a* lattice parameter and inadequacy of a current structural model (Johnson 1986, Johnson *et al.* 1988) for very Ag-rich compositions. However, there is no corresponding gap in the Ag^+ for Cu^+ substitution (Fig. 7) or a negative correlation between levels of Ag and S in either the O'Keefe tetrahedrite$_{ss}$ (Fig. 12) or argentian mercurian tetrahedrite$_{ss}$ described by Atanasov (1975). Even the most Ag-rich crystals contain close to a stoichiometric content of S (13 *apfu*), suggesting that the incorporation of Ag in the O'Keefe tetrahedrite$_{ss}$ may not result in the creation of a defect at the sulfur site and metallic octahedral clusters. Back-scattered electron (BSE) and scanning electron (SEM) images at 4000× of crystals containing 5–10 Ag *apfu* are essentially featureless, showing no evidence of exsolution. In addition, X-ray line scans across four 50–100 μm crystals using a 1-μm electron beam revealed compositional homogeneity in three of them and a slight enrichment in Hg and depletion in Ag at the rim of the fourth.

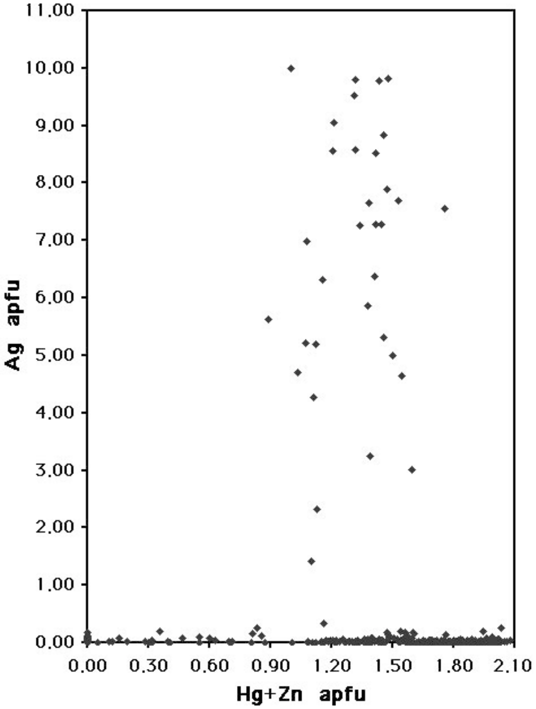

FIG. 11. Variation of Ag with Hg + Zn in tetrahedrite$_{ss}$ of the Steens–Pueblo suite.

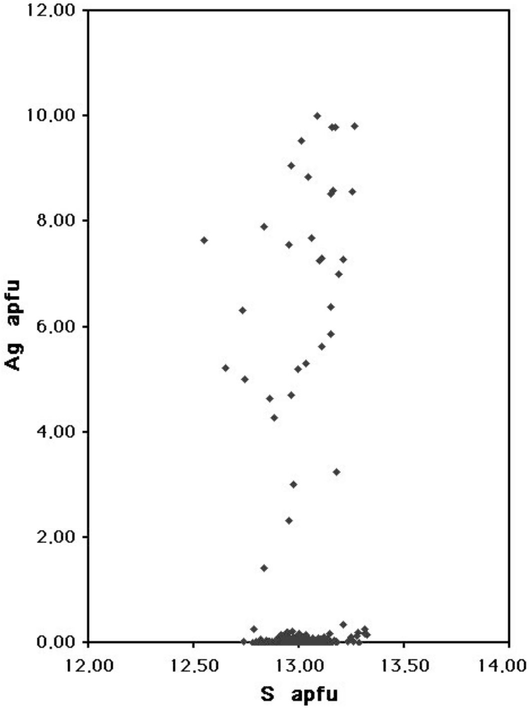

FIG. 12. Variation of Ag with S in tetrahedrite$_{ss}$ of the Steens–Pueblo suite. Samples with more than 1.0 Ag *apfu* are from the O'Keefe claims.

It has been suggested (N. Johnson 1999, pers. commun.) that the O'Keefe tetrahedrite$_{ss}$ might represent the Ag-rich tetrahedrite-like melts observed by Johnson (1982) in her synthesis experiments. Given that the valence-electron summations (Johnson & Jeanloz 1983) for the O'Keefe argentian tetrahedrite$_{ss}$ (Fig. 13) are characteristic of (crystalline) tetrahedrite, whereas the low- and high-pressure melts fall considerably off or contain Ag in excess of the maximum amount permitted in the structure, makes this unlikely. On the other hand, tetrahedrally coordinated Zn and Hg may stabilize the structure during incorporation of Ag in the tetrahedral framework.

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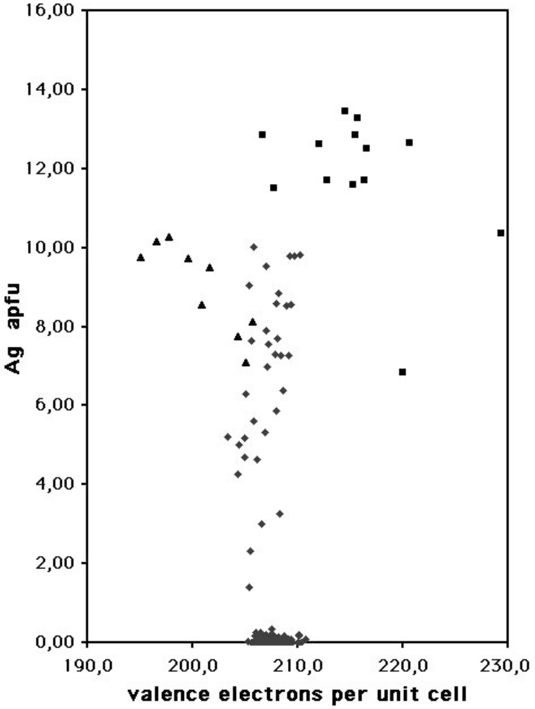

FIG. 13. Variation in number of valence electrons per unit cell with Ag content for the O'Keefe argentian tetrahedrite$_{ss}$ (filled diamonds), high-pressure tetrahedrite-like melt (filled triangles; Johnson 1982) and low-pressure melts (filled squares; Johnson 1982).

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