

Structural variations in mercurian tetrahedrite

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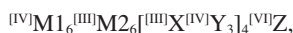
ABSTRACT

The structures of four mercurian tetrahedrite samples, $^{[IV]}[(Cu^+)_4(Hg,Zn,Fe)_2]^{[III]}(Cu^+)_6^{[III]}(Sb,As)_4^{[IV]}S_{12}^{[VI]}S$, with Hg-contents ranging from 0.32 to 1.15 apfu were refined by least-squares in space group $I\bar{4}3m$ to agreement factors $R < 0.027$. The a cell dimension varied from 10.3310(2) to 10.4033(2) Å; both the a cell dimension and the size of the $^{[IV]}M1$ site vary linearly with the Hg content. The magnitude of the observed variation in the a cell dimension partially validates the empirical relationship developed by previous investigators. The degree of distortion and amount of rotation of the $^{[IV]}M1$ tetrahedron as a function of the M1-S1 bond length is comparable to that predicted by the empirical relationships of previous investigators when the As content is taken into account. The spinner blade length remains virtually unchanged because the Hg substitution takes place at M1 and the As:Sb ratio varies only slightly. The structural trends as a function of composition in these mercurian tetrahedrites closely follows those previously predicted by modeling using ionic radii and

INTRODUCTION

The tetrahedrite group of minerals has been long recognized for its diversity of substitution, which involves virtually all of the crystallographic sites in the structure. The structures of many end-members have been determined (tetrahedrite: Wuensch 1964; argentian tetrahedrite/freibergite: Kalbskopf 1972; Johnson and Burnham 1985; Peterson and Miller 1986; goldfieldite: Kalbskopf 1974; mercurian tetrahedrite: Kalbskopf 1971; Kaplunnik et al. 1980) and structural relations have been modeled using lattice parameters and ionic radii (Johnson 1986; Johnson et al. 1988).

Stoichiometry and site occupancies of tetrahedrite-group minerals can be represented by the following structural formula proposed by Johnson et al. (1988):



where M1 = Cu, Fe, Hg, Cd, Mn, Co; M2 = Cu, Ag; X = Sb, As, Bi, Te; Y and Z = S, Se.

The tetrahedrally coordinated $^{[IV]}M1$ cations form a three-dimensional framework with large cavities analogous to those found in the framework silicate sodalite (Fig. 1a). These large cavities, termed Laves polyhedra or truncated tetrahedra, house the $^{[III]}M2$ cations that are three-coordinated by two framework S atoms (Y) and the thirteenth S atom (Z) in the center of the polyhedron (Fig. 1b). The As and Sb atoms are pyramidally coordinated to the three S atoms which form the truncations of the Laves polyhedron and their lone pair electrons project into neighboring polyhedra.

The most recent structure refinement (Kaplunnik et al. 1980) of a mercurian tetrahedrite, $(Cu_{4.4}Hg_{1.6})Cu_6As_4S_{12}$, was carried out assuming stoichiometry that included 12 S atoms per formula unit (apfu), despite electron microprobe analyses of material from the same deposit that indicated the presence of 13 S apfu.

The likely presence of the thirteenth S atom at the Z site in the center of the Laves polyhedron was dismissed “owing to the lack of room for the large S^{2-} anion” and thus it was not included in the structure refinement. This omission clearly rendered the results incorrect. This combined with the fact that no systematic examination of the response of the tetrahedrite structure to a single substituent has been undertaken, urged further study. In this paper structural variations occurring in tetrahedrites having extensive Hg substitution are described and related to predictions based on the modeling of Johnson et al. (1988).

EXPERIMENTAL METHODS

Sample preparation and electron microprobe analysis

The tetrahedrite crystals examined in this study were extracted from hand samples from the Spring Creek Claims (latitude 40° 7.30', longitude 118° 37.92') in Harney County, Oregon (Ulbricht 1997; Ulbricht and Foit 1998; Foit and Ulbricht 2001). Polycrystalline masses that ranged from 0.5 to 2.0 mm in dimension were imbedded in a quartz matrix. Tetrahedrite from these deposits exhibits a wide range of Hg-Zn substitution with the presence of lesser amounts of other divalent cations (e.g., Fe, Cd; Ulbricht 1997; Foit and Ulbricht 2001). Obtaining crystals representing a wide range of Hg content and physically suitable for single crystal structure analysis involved selecting a large number of chonchoidal fragments and mounting them on a glass slide. The intensity of the $HgM\alpha$ line for each was then measured using the electron microprobe, and four crystals representing a broad range of counts (Hg content) were selected for structure refinement. After collection of the single crystal X-ray data, each crystal was mounted in epoxy and polished to produce a cross section for quantitative chemical analysis. The analyses were conducted in the Department of Geology's GeoAnalytical Laboratory at Washington State University using a Cameca Camebax electron microprobe equipped with four wavelength dispersive spectrometers, an acceleration voltage of 20 Kv, a beam current of 16 nA, and a beam diameter of 5 microns. Only Ag, As, Cu, Cd, Co, Fe, Hg, Sb, and Zn were present in detectable amounts and they were measured using the analytical standards and correction routine described in Foit and Ulbricht (2001). The compositions of the crystals used in the structure refinements are given in Table 1. Although compositional variation within crystals C2 and E3 appears small, as reflected in the relatively low standard deviations of the atom weight percents, there is indication of compositional zoning in samples A2 and E5. For this reason the microprobe-determined compositions were not

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used in the structure refinement.

The tetrahedrite formulae were calculated on the basis of 13 S apfu. In these calculations Hg is assumed to be divalent, consistent with previous studies (Foit and Ulbricht 2001) and the resulting expected stoichiometry; the validity of this assumption was confirmed by subsequent structure analyses. The calculations yielded As + Sb, and metal apfu values (Table 1) closely conforming to the structural formula and site occupancies given above.

X-ray data collection and crystal structure refinements

Intensity data were collected using a Bruker Platform goniometer equipped with an APEX 4K CCD detector and MoK α radiation. Data were integrated using the Bruker program SAINT, and absorption was corrected using the program SADABS. For all samples, a frame width of 0.20°, a scan time of 15 s/frame, and a nominal detector distance of 5 cm was employed; a total of 4500 frames were collected for each sample, yielding redundancy factors >25 for all data sets.

Least-squares refinement was undertaken using the Bruker program SHELXTL version 6.10, using neutral-atom scattering factors and corrections for anomalous dispersion. Because of the similarity of Fe, Cu, and Zn scattering factors as compared to Hg, the occupancy of the Cu sites was modeled with Cu and Hg exclusively. The refinements were routine, and all atomic thermal ellipsoids were positive-definite.

Table 2 contains crystal data and results of the structure refinement for the four mercurian tetrahedrites. Tables 3, 4, and 5¹ contain positional parameters, selected interatomic distances and angles, and structure factors, respectively.

DISCUSSION

The differences in the site occupancies obtained from the electron microprobe data (Table 1) and site refinement (Table 3) are likely due to the inadequate characterization of the compositional zoning by electron microprobe analysis. For this reason, where

¹For a copy of Table 5, document item AM-04-051, contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. Deposit items may also be available on the American Mineralogist web site at <http://www.minsocam.org>.

TABLE 1. Compositions of mercurian tetrahedrite samples used in structure refinements

| | A2 | E3 | C2 | E5 |
|-----------------|---|--------------|--------------|--------------|
| | Values in wt% | | | |
| Cu | 39.93(0.44) | 38.59(0.69) | 37.68(0.25) | 36.46(0.45) |
| Ag | 0.01(0.02) | 0.02(0.02) | 0.02(0.02) | 0.02(0.03) |
| Hg | 3.90(0.20) | 7.08(0.61) | 8.22(0.19) | 13.18(0.60) |
| Fe | 1.38(0.28) | 0.96(0.10) | 0.14(0.03) | 0.09(0.02) |
| Zn | 3.44(0.54) | 3.17(0.18) | 3.94(0.08) | 2.50(0.17) |
| Cd | 0.01(0.01) | 0.01(0.02) | 0.02(0.03) | 0.02(0.03) |
| Co | 0.06(0.02) | 0.08(0.02) | 0.04(0.01) | 0.04(0.01) |
| As | 6.50(0.83) | 5.07(0.27) | 5.00(0.27) | 5.80(0.95) |
| Sb | 19.10(1.14) | 20.85(0.40) | 20.67(0.25) | 18.29(1.34) |
| S | 25.58(0.20) | 24.69(0.23) | 24.39(0.16) | 23.73(0.27) |
| Total | 99.93(0.48) | 100.53(0.91) | 100.12(0.50) | 100.14(0.81) |
| Points analyzed | 13 | 14 | 12 | 14 |
| | Atoms based on 13 S per formula unit | | | |
| Cu | 10.24(0.07) | 10.26(0.14) | 10.14(0.08) | 10.08(0.10) |
| Hg | 0.32(0.02) | 0.60(0.08) | 0.70(0.01) | 1.15(0.06) |
| Fe | 0.40(0.08) | 0.29(0.03) | 0.04(0.01) | 0.03(0.01) |
| Zn | 0.86(0.14) | 0.82(0.04) | 1.03(0.03) | 0.67(0.04) |
| Co | 0.02(0.01) | 0.02(0.01) | 0.01(0.00) | 0.01(0.00) |
| As | 1.41(0.17) | 1.14(0.06) | 1.14(0.06) | 1.36(0.21) |
| Sb | 2.56(0.17) | 2.89(0.06) | 2.90(0.04) | 2.64(0.21) |
| S | 13.00 | 13.00 | 13.00 | 13.00 |
| As+Sb* | 3.97 | 4.04 | 4.04 | 4.00 |
| Metals* | 11.84 | 11.99 | 11.93 | 11.95 |
| apfu* | 28.81 | 29.02 | 28.97 | 28.95 |

* Stoichiometric values: As + Sb = 4, metals = Cu + Ag + Hg + Fe + Zn + Cd + Co = 12, apfu = 29

applicable, site occupancies obtained from the site refinement were using in the modeling of the structure which follows.

As expected, the Hg atom resides exclusively at the four-coordinate M1 site (Fig. 1a, Table 3) and clearly controls its size (Fig. 2) and the magnitude of the *a* cell parameter (Fig. 3) as reflected in the high correlation coefficients. Despite the fact that the ratio of Fe:Zn in this site varies significantly (0.04 to 0.47), these strong linear covariances confirm earlier suggestions (Hall 1972; Charlat and Levy 1975; Johnson et al. 1987) that variation in the Fe:Zn ratio has a negligible effect on the *a* cell parameter. These data also validate the empirical equation, $a(\text{\AA})_{\text{natural}} = 10.379 + 0.082(\text{Ag}) - 0.01(\text{Ag}^2) - 0.009(\text{Cu}^*) + 0.066(\text{Hg}) - 0.038(\text{As}) + 0.144(\text{Bi})$ where $\text{Cu}^* = 2.0 - (\text{Fe} + \text{Zn} + \text{Hg} + \text{Cd})$, formulated by Johnson et al. (1987). The values calculated using this equation are very close to those observed in this study (Fig. 3). The reader should note that the coefficient for the Hg content in the equation has been changed from 0.66 to 0.066. This typographical error was first recognized by DiBenedetto et al. (2002) and it is needed to reproduce the values of *a* in Table 4 of Johnson et al. (1987) as well as to create the data for our Figure 3.

The crystal structure data (Kaplunnik et al. 1980) for a very

TABLE 2. Crystal data and results of structure refinement for four mercurian tetrahedrite samples

| | A2 | E3 | C2 | E5 |
|------------------------|--------------|--------------|--------------|--------------|
| Space group | $I\bar{4}3m$ | $I\bar{4}3m$ | $I\bar{4}3m$ | $I\bar{4}3m$ |
| <i>a</i> = | 10.3310(2) | 10.3794(3) | 10.3777(3) | 10.4033(2) |
| Hg content (apfu) | | | | |
| EMPA | 0.32(2) | 0.60(8) | 0.70(1) | 1.15(6) |
| XRD | 0.20(2) | 0.72(6) | 0.72(5) | 1.23(5) |
| Measured reflections | 12,783 | 25,809 | 12,904 | 13,000 |
| Unique reflections | 325 | 330 | 331 | 335 |
| Refined parameters | 21 | 21 | 21 | 21 |
| R1*, all reflections | 0.022 | 0.027 | 0.022 | 0.023 |
| Difference peaks (+,-) | 0.70, 0.74 | 0.67, 1.01 | 0.62, 0.74 | 0.58, 0.59 |
| Goodness-of-Fit | 1.302 | 1.373 | 1.449 | 1.333 |

*R1 = $\sum |F_o| - |F_c| / \sum |F_o|$

TABLE 3. Atomic positions, equivalent isotropic thermal parameters, and site occupancies for four mercurian tetrahedrite samples

| Atom | x | y | z | <i>U</i> _{eq} | Occupancy |
|---------------------|------------|-----|-----------|------------------------|--|
| (IV)M1 Cu,Hg | | | | | |
| A2 | 1/4 | 1/2 | 0 | 0.0209(5) | Cu _{0.967(3)} Hg _{0.033} |
| E3 | 1/4 | 1/2 | 0 | 0.0217(6) | Cu _{0.880(1)} Hg _{0.120} |
| C2 | 1/4 | 1/2 | 0 | 0.0221(5) | Cu _{0.880(8)} Hg _{0.120} |
| E5 | 1/4 | 1/2 | 0 | 0.0243(4) | Cu _{0.795(8)} Hg _{0.205} |
| (III)M2 Cu | | | | | |
| A2 | 0.2168(2) | 0 | 0 | 0.0559(8) | Cu _{0.97(1)} |
| E3 | 0.7839(3) | 0 | 0 | 0.054(1) | Cu _{1.02(2)} |
| C2 | 0.7840(2) | 0 | 0 | 0.0543(9) | Cu _{1.01(1)} |
| E5 | 0.7849(2) | 0 | 0 | 0.0515(8) | Cu _{0.99(1)} |
| (III)X Sb,As | | | | | |
| A2 | 0.26566(4) | x | x | 0.0168(2) | Sb _{0.58(2)} As _{0.42} |
| E3 | 0.73414(5) | x | x | 0.0160(3) | Sb _{0.79(4)} As _{0.21} |
| C2 | 0.73436(4) | x | x | 0.0163(3) | Sb _{0.73(3)} As _{0.27} |
| E5 | 0.73550(5) | x | x | 0.0173(3) | Sb _{0.70(3)} As _{0.30} |
| (IV)Y S1 | | | | | |
| A2 | 0.1169(1) | x | 0.3581(1) | 0.0176(4) | S _{1.00} |
| E3 | 0.8834(2) | x | 0.6417(2) | 0.0158(6) | S _{1.00} |
| C2 | 0.8835(1) | x | 0.6421(2) | 0.0170(5) | S _{1.00} |
| E5 | 0.8836(1) | x | 0.6433(2) | 0.0184(5) | S _{1.00} |
| (IV)Z S2 | | | | | |
| A2 | 0 | 0 | 0 | 0.020(1) | S _{1.00} |
| E3 | 0 | 0 | 0 | 0.017(1) | S _{1.00} |
| C2 | 0 | 0 | 0 | 0.018(1) | S _{1.00} |
| E5 | 0 | 0 | 0 | 0.018(1) | S _{1.00} |

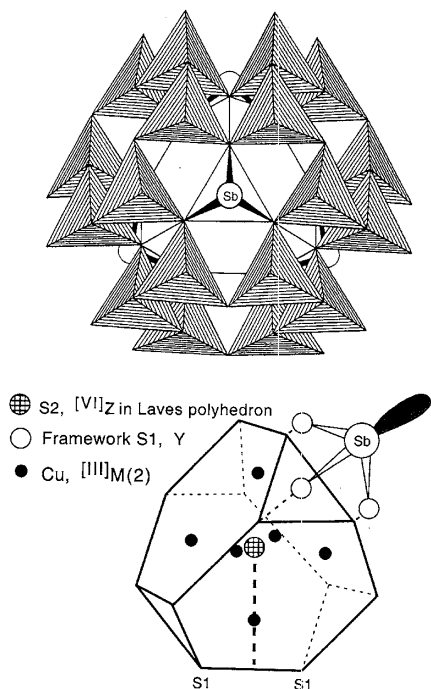


FIGURE 1. (a) The tetrahedral framework, $[^{VI}]M-S1$, portion of the tetrahedrite structure (after Johnson et al. 1988). (b) Cavity (Laves polyhedron) in the tetrahedral framework. Bold dashed line designates the length and orientation of the spinner blade and the shaded lobe represent the orientation of the lone pair electrons (after Johnson et al. 1988).

TABLE 4. Selected interatomic distances in four mercurian tetrahedrite samples

| Parameter | A2 | E3 | C2 | E5 |
|-------------------------------------|------------|------------|------------|------------|
| Bond distances (Å) | | | | |
| M1-S1 ⁸ | 2.3384(9) | 2.3550(13) | 2.3573(11) | 2.3708(11) |
| M2-S1 ² | 2.2533(18) | 2.2601(24) | 2.2570(20) | 2.2588(19) |
| M2-S2 | 2.2398(23) | 2.2426(28) | 2.2413(24) | 2.2374(21) |
| Sb-S1 | 2.3784(16) | 2.3917(22) | 2.3882(19) | 2.3813(19) |
| S1-S1 | 3.415(2) | 3.423(3) | 3.421(3) | 3.424(2) |
| S1-S2 | 4.084(1) | 4.094(1) | 4.089(1) | 4.087(1) |
| Spinner Blade | 3.7099 | 3.7186 | 3.7137 | 3.7110 |
| Bond angles (°) | | | | |
| S1 ⁵ -M1-S1 ⁸ | 110.23(4) | 110.22(5) | 110.19(4) | 110.11(4) |
| S1 ⁷ -M1-S1 ⁸ | 107.95(7) | 107.98(10) | 108.04(9) | 108.19(9) |
| S1 ² -M2-S1 ⁴ | 98.55(13) | 98.25(17) | 98.56(14) | 98.56(14) |
| S1 ⁴ -M2-S2 | 130.72(6) | 130.77(9) | 130.72(7) | 130.72(7) |
| S1-Sb-S1 ⁵ | 96.14(5) | 95.74(7) | 95.71(6) | 95.74(7) |
| Sb-S1-M2 ⁵ | 115.33(8) | 115.58(11) | 115.65(9) | 115.53(9) |
| M2 ⁵ -S1-M1 ¹ | 116.39(6) | 116.59(8) | 116.62(7) | 116.80(6) |
| Sb-S1-M1 ¹ | 101.91(5) | 101.69(6) | 101.69(6) | 101.78(5) |
| M1 ¹ -S1-M1 ² | 102.70(6) | 102.36(8) | 101.74(6) | 102.20(7) |
| M2-S2-M2 ⁶ | 90.00 | 90.00 | 90.00 | 90.00 |

1 = $-x + 1/2, -y + 1/2, z + 1/2$; 2 = z, x, y ; 3 = $-x, -y, z$; 4 = $z, -x, -y$; 5 = y, z, x ; 6 = $-y, z, -x$; 7 = $-x + 1/2, -y + 1/2, z - 1/2$; 8 = $-x + 1/2, y + 1/2, -z + 1/2$; 9 = $y, -z + 1, -x$

Hg-rich tetrahedrite, $(Cu_{4.4}Hg_{1.6})Cu_6Sb_4S_{12}$, is suspect. In addition to conducting their refinement using an incorrect 12 S apfu, their M1-S1 distance (2.354 Å) is more in keeping with the 1.02 Hg apfu reported in their electron microprobe analysis of the crystal whereas their reported a cell parameter and the 1.6 Hg apfu reported for their site refinement falls on an extension of

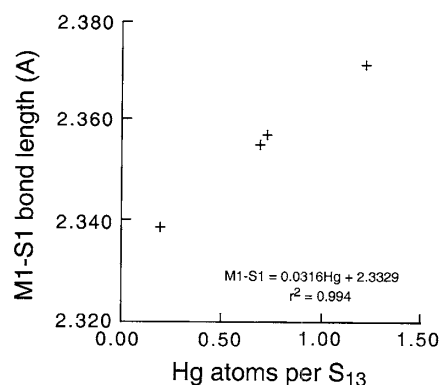


FIGURE 2. Variation of the M1-Y bond length with Hg content per formula unit. The regression equation was calculated using the Hg values from the site refinements.

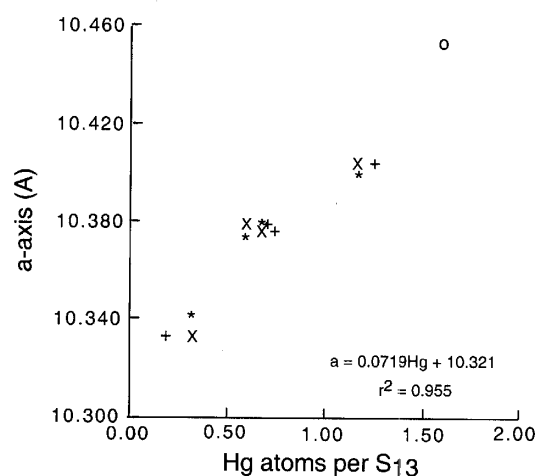


FIGURE 3. Variation of the a unit cell parameter with Hg content per formula unit: X = the mercury Hg determined by electron microprobe analysis; + = Hg content from site refinement; o = data from Kaplunnik et al. (1980); * = data calculated using microprobe data and the equation of Johnson et al. (1988). The regression equation was calculated using the Hg values from the site refinements.

our linear trend in Figure 3.

The degree of framework rotation is linearly dependent on the M1-S1 bond length (and amount of Hg substitution at the $[^{VI}]M1$ site) as predicted by Johnson et al. (1988). This linear trend (Fig. 4) is parallel to and displaced from the trend of the tetrahedrite (Sb) end-member toward the tennantite (As) end-member by precisely the average amount of As substitution ($As/As + Sb = 0.32$) in these Hg-bearing tetrahedrites. The amount of polyhedral distortion of the framework tetrahedra due to Hg substitution is small, of the same type (extension) and follows the same trend (a slight decrease with M1-S1 bond length, Fig. 5) as predicted by the Johnson et al. (1988) model.

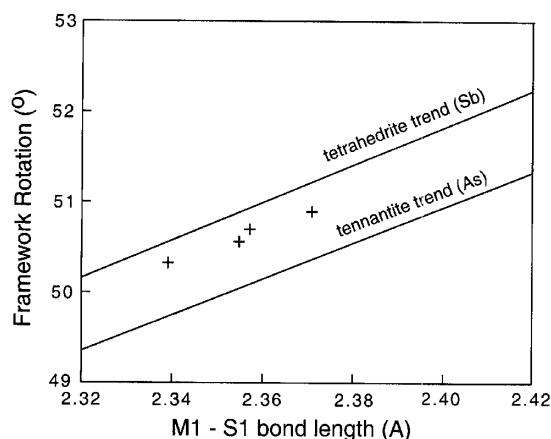


FIGURE 4. Variation of rotation of the M1 tetrahedral site with M1-S1 bond length. The diagram is modified after Johnson et al. (1988) and the tetrahedrite and tennantite trends are those calculated on the basis of ionic radii.

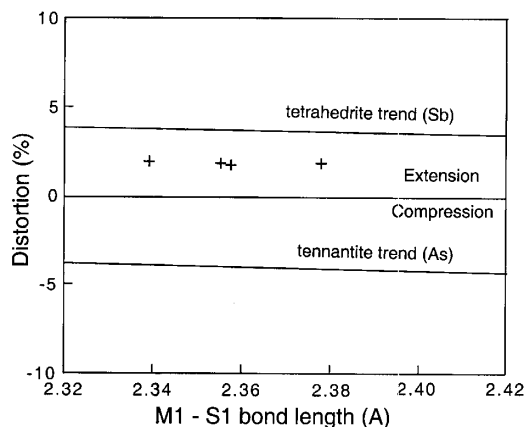


FIGURE 5. Variation of % distortion of the M1 tetrahedral site with the M1-S1 bond length. The diagram is modified after Johnson et al. (1988) and the tetrahedrite and tennantite trends are those calculated on the basis of ionic radii.

The displacement of the mercurian tetrahedrite data from the curves for the Sb- and As-end-members is again proportional to the amount of As substitution.

The length of the spinner blade (Fig. 1b), which is the distance from S2 through M2 to the midpoint between two S1 atoms defining an edge of the Laves polyhedron, has been used to model the degree of expansion and contraction of the structure due to ion substitution (Wuensch 1964; Johnson et al. 1988). There is little change (total range of variation = 3.709 to 3.719 Å, Table 4) in the spinner blade length in these mercurian tetrahedrites. This is because Hg substitution takes place at the M1 site in the tetrahedral framework rather than at the trigonal planar M2 site in the Laves polyhedron and because of the relatively small variation (0.29–0.35) in As/As + Sb in these samples, both of which have a significant effect on the spinner blade length. The relatively small changes in tetrahedral distortion (Fig. 6) and rotation (Fig. 7) are

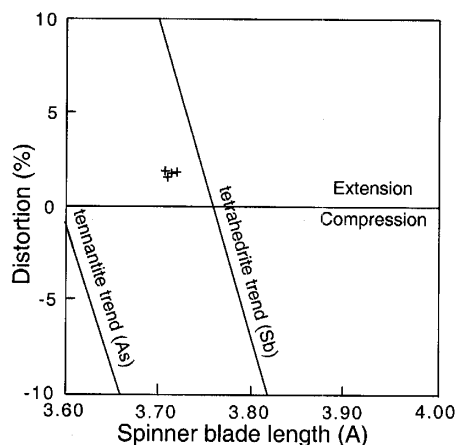


FIGURE 6. Variation of % distortion of the M1 tetrahedral site with spinner blade length. The diagram is modified after Johnson et al. (1988) and the tetrahedrite and tennantite trends are those calculated on the basis of ionic radii.

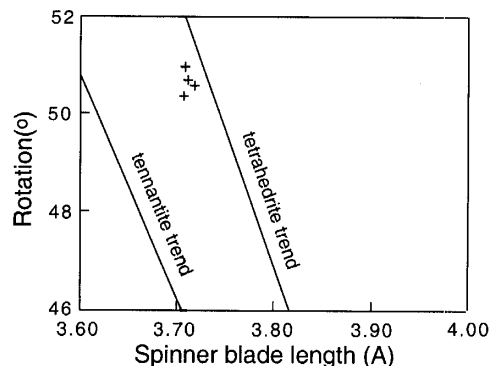


FIGURE 7. Variation of rotation of the M1 tetrahedral site with spinner blade length. The diagram is modified after Johnson et al. (1988) and the tetrahedrite and tennantite trends are those calculated on the basis of ionic radii.

thus consistent in nature and extent with the principal substitution (Hg into M1) taking place in these samples.

The structural trends observed in these mercurian tetrahedrites as a function of compositional variation closely follows those predicted in previous modeling using ionic radii (Johnson et al. 1988) and largely serve to confirm the validity of this approach.

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