

Crystal structure and crystal chemistry of perroudite: A mineral from Coppin Pool, Western Australia

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ABSTRACT

Perroudite, from Coppin Pool, Western Australia, having the composition $\text{Hg}_{4.6}\text{Ag}_{4.4}\text{S}_{4.6}(\text{Cl}_{2.0}\text{Br}_{0.8}\text{I}_{1.6})$, is orthorhombic, $a = 17.43$, $b = 12.24$, $c = 4.35$ Å, space group $P2_12_12$. In the four asymmetric units, 9.2 Hg and 0.8 Ag are in flattened octahedral coordination with respect to S and halogens, and 8 Ag are tetrahedrally coordinated. Chains of face- and edge-shared Hg (predominantly) octahedra wind their way through the structure in a direction parallel to [010]. Central to each chain are continuous $-\text{S}-\text{Hg}-\text{S}-$ linkages formed from the short diagonal (linear) bonds in the individual flattened octahedra. Vertically stacked columns of octahedral chains in the structure form corrugated layers parallel to (100). The Ag tetrahedra act as bridges between the octahedral chains and layers. $\text{Hg}_5\text{Ag}_4\text{S}_5(\text{Cl},\text{Br},\text{I})_4$ is proposed as the ideal structural formula for the mineral. A range of composition, based on the ideal structure and interpreted from the results of electron-microprobe analysis, is expressed by the general formula $\text{Hg}_{5-x}\text{Ag}_{4+x}\text{S}_{5-x}(\text{Cl},\text{Br},\text{I})_{4+x}$, $-1.4 < x < 1.4$.

INTRODUCTION

The bright red-colored sulfide-halide (Cl, Br, and I) of Hg and Ag from Coppin Pool, W.A., discussed in this paper, was originally described (with the composition corresponding to $\text{Hg}_{5.18}\text{Ag}_{4.75}\text{S}_6\text{Cl}_{2.40}\text{I}_{1.81}\text{Br}_{0.98}$) by Nickel (1985). Analysis of the results of a recent study of a distinctive red-colored mineral from Broken Hill by Dr. W. D. Birch, Melbourne (pers. comm.) showed the two to be the same mineral species, but with I dominant for the Broken Hill occurrence, rather than the approximately equal Cl and I dominance that is generally the case for the Coppin Pool mineral. Structure analysis and least-squares refinement of X-ray data from a single crystal of the Coppin Pool mineral determined a composition of $\text{Hg}_{4.6}\text{Ag}_{4.4}\text{S}_{4.6}(\text{Cl}_{2.0}\text{Br}_{0.8}\text{I}_{1.6})$ for that particular crystal. The crystal-structure analysis supports evidence from electron-microprobe analysis that a range of composition exists for an ideal structural formula of $\text{Hg}_5\text{Ag}_4\text{S}_5(\text{Cl},\text{Br},\text{I})_4$. This range may be expressed as $\text{Hg}_{5-x}\text{Ag}_{4+x}\text{S}_{5-x}(\text{Cl},\text{Br},\text{I})_{4+x}$, $-1.4 < x < +1.4$. Both the Coppin Pool and the Broken Hill minerals are considered to be the same as the new mineral (perroudite) from Cap-Garonne, France, concurrently described by Sarp et al. (1987).

EXPERIMENTAL DETAILS

Electron-microprobe analysis

The mineral was found to be somewhat unstable under the beam of the electron-microprobe, but this problem was minimized when care was taken to use low accelerating voltages and a slightly defocused beam. The effect of the instability, together with the chemical variability of the mineral, made it difficult to define its chemical composition. Electron-microprobe studies done at CSIRO, Division of Minerals and Geochemistry, Perth (on polished specimen 18445, further to those reported in 1985) yielded the average composition $\text{Ag}_{1.68}\text{Hg}_{1.78}\text{S}_{2.0}\text{Cl}_{0.78}\text{Br}_{0.40}\text{I}_{0.63}$ [Ag 24.2, Hg 47.8, Cl 3.7, Br 4.3, I 9.7, S 8.6, total 98.3 wt%]. A set of results obtained from other Coppin Pool material (specimen GM57) at CSIRO, Division of Mineral Chemistry, Melbourne, are plotted in Figure 1a. In addition, a second set of measurements was made on specimen 18445 in Melbourne, and these are plotted in Figure 1b. The individual halide proportions are plotted in Figure 1c. Although these later results (more particularly those in Fig. 1a, when taken in conjunction with the original study) suggested that a chemical composition of $(\text{Ag},\text{Hg})_5\text{S}_5(\text{Cl},\text{Br},\text{I})_3$ was the more probable for the mineral, the microprobe studies to determine its composition (summarized in Table 1 and Fig. 1) were by no means conclusive. A single-crystal X-ray investigation performed at CSIRO, Melbourne, has determined the crystal structure of the mineral and has also helped

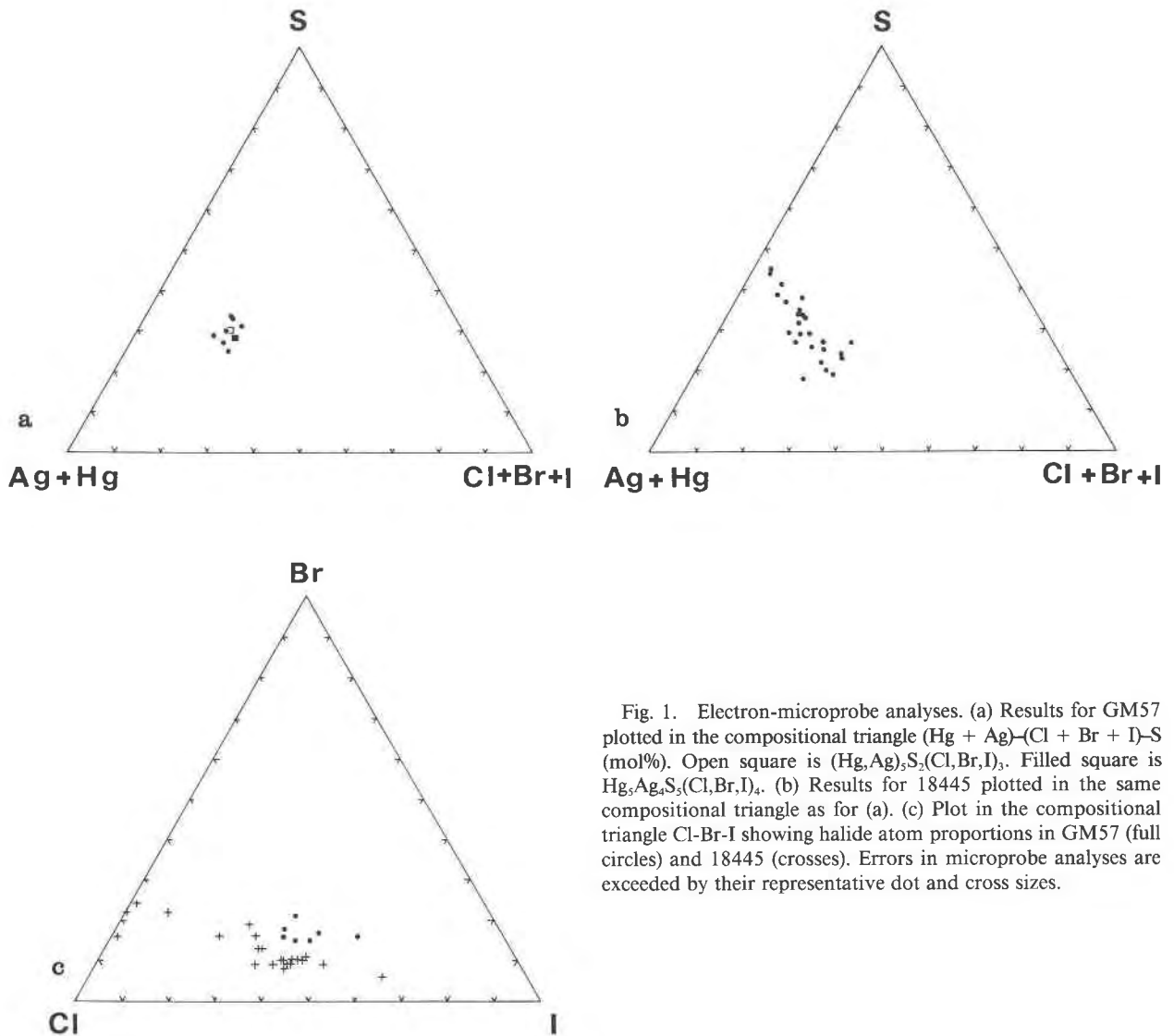


Fig. 1. Electron-microprobe analyses. (a) Results for GM57 plotted in the compositional triangle (Hg + Ag)-(Cl + Br + I)-S (mol%). Open square is $(\text{Hg}, \text{Ag})_5\text{S}_2(\text{Cl}, \text{Br}, \text{I})_3$. Filled square is $\text{Hg}_5\text{Ag}_4\text{S}_3(\text{Cl}, \text{Br}, \text{I})_4$. (b) Results for 18445 plotted in the same compositional triangle as for (a). (c) Plot in the compositional triangle Cl-Br-I showing halide atom proportions in GM57 (full circles) and 18445 (crosses). Errors in microprobe analyses are exceeded by their representative dot and cross sizes.

to resolve some of the problems in the interpretation of the mineral's chemical composition.

X-ray study

Several specimens of material containing tiny crystals of the Coppin Pool mineral were available for study. Although a true single crystal was not obtained, it proved possible to collect mea-

surable Weissenberg data from a "fused" bundle of several small crystals, all of which were closely aligned with each other. Unit-cell parameters, refined from powder data (presented in Table 3, Sarp et al., 1987) indexed from the Weissenberg films, are given in Table 2. The symmetry was found to be orthorhombic, and the space-group alternatives were observed to be $P2_12_12$ or $P2_12_12_1$. Multiple film packs of the 0, 1, and 2 levels for the crystal mounted along the *b* axis were collected using an integrating Weissenberg camera and $\text{CuK}\alpha$ radiation.

Structure solution

Although the space group could not be uniquely determined from the Weissenberg data and the upper level data were of only moderate quality owing to some smearing of those reflections, it was anticipated that there was at least a reasonable chance of solving the structure in projection by virtue of the short *c* axis. A Patterson projection $P(u, v, 0)$ was calculated, and, by reference to it, the structure projection was solved in plane group Pgg . Atoms were found to be at special positions: an Hg atom

TABLE 1. Electron-microprobe analyses

	Average (wt%)	Range (wt%)
Ag	19.43	4.52–43.60
Hg	57.68	35.85–80.17
S	8.79	5.77–12.51
Cl	3.56	0.49–9.32
Br	2.11	0.17–5.74
I	6.45	0.18–15.20

Note: Values are average composition and associated ranges (wt%) of 32 different point measurements on polished sections 18445 and GM57.

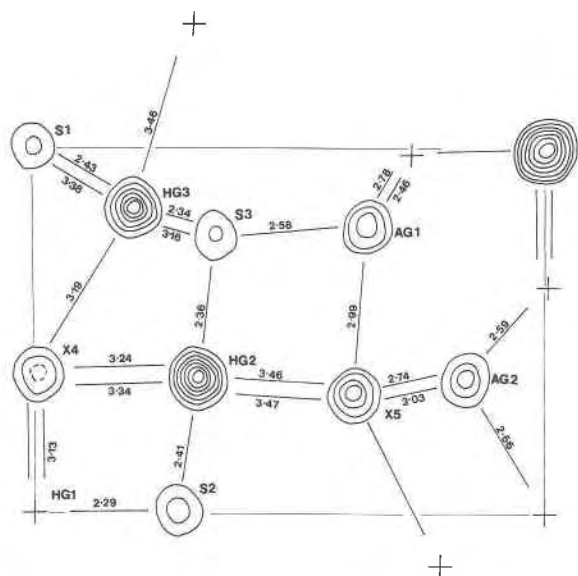


Fig. 2. Electron-density projection onto (001) of an asymmetric unit of $\text{Hg}_{4.6}\text{Ag}_{4.4}\text{S}_{4.6}(\text{Cl}_{2.0}\text{Br}_{0.8}\text{I}_{1.6})$. Contouring is at intervals of 15 electrons.

was located at (0, 0) and an anion at $(\frac{1}{2}, 0)$. In the final Fourier projection, all the atoms were clearly resolved, with the results indicating an asymmetric unit content of $\text{Me}_x\text{X}_{4.5}$, where Me and X represent cations and anions, respectively. Further emendment of this formula to $\text{Hg}_{2.5}\text{Ag}_{2.0}\text{S}_{2.5}(\text{Cl}, \text{Br}, \text{I})_{2.0}$ was encouraged because two of the cation peaks (other than the one at the origin) were much stronger than the other two cation peaks and that two of the anion peaks located in general positions and the one in the special position at $(\frac{1}{2}, 0)$ were much weaker than the other two anion peaks. At this point, the three-dimensional Patterson map was consulted. In conjunction with the projected structure, it was possible to use it to deduce the z coordinates of the Hg atoms in $P2_12_12$. Structure factor and Fourier map recycling procedures (together with stereochemical considerations) were then applied using the three-dimensional data to determine the positions of all the other atoms (Fig. 2). A satisfactory refinement was achieved in this space group, and the stoichiometry deduced from the structure projection was confirmed. All cal-

TABLE 2. Chemical and crystallographic data for perrouditite

Crystal size	0.15 × 0.04 × 0.04 mm
Space group	$P2_12_12$
a (Å)	17.43(2)
b (Å)	12.24(2)
c (Å)	4.35(1)
Z	2
D_{calc}	6.60 g/cm ³
Radiation	$\text{CuK}\alpha$
μ	1288 cm ⁻¹
Total no. of reflections	559
R	0.10
Derived formula	
$\text{Hg}_{5-x}\text{Ag}_{4+x}\text{S}_{5-x}(\text{Cl}, \text{Br}, \text{I})_{4+x}$, $-1.4 < x < 1.4$	
Structural formula	
$\text{Hg}_{4.6}\text{Ag}_{4.4}\text{S}_{4.6}(\text{Cl}_{2.0}\text{Br}_{0.8}\text{I}_{1.6})$	

TABLE 3. Relative electron densities

Atom	Peak height
Hg1	323
Hg2	324
Hg3	291
Ag1	133
Ag2	122
S1	55
S2	55
S3	54
X4	70
X5	171

culations were carried out with a VAX computer using the SHELX76 library of programs (Sheldrick, 1976).

Refinement of the structure

The atomic distribution in the structure could not be assessed very accurately because of the problem of getting a probe analysis of the crystal used for intensity measurement. Individual crystals were too small to prepare in polished mounts. Therefore, for the least-squares refinement, site occupancies were chosen and adjusted on the basis of the electron densities revealed in the Fourier maps as the refinement progressed (Table 3). The electron densities associated with Hg1 and Hg2 were greatest and were observed to be almost equal; therefore these were refined as Hg-occupied sites. For Hg3, the electron density was observed to be 10% less than that of Hg1 and Hg2, and this was refined as 0.8Hg + 0.2Ag. The reduced electron density in Hg3 was assumed to be due to Ag substitution in that site, as Ag may readily adopt a flattened octahedral coordination with bond distances similar to those for Hg in this configuration (see later). Atoms S1, S2, and S3 all had equal electron densities and were refined as S. Atom X4 had a higher density, and X5 was represented by a peak half the size of Hg1 and Hg2. It was therefore assumed that Br and I occupied X5 and that Cl, Br, and maybe some S occupied X4.

The structure was eventually refined to an R value of 0.10, using isotropic temperature factors and absorption corrections for a small prism size. The final occupancies determined by this approach are given in Table 4, together with the refined atomic coordinates and isotropic temperature factors. The composition finally determined from the structure refinement, $\text{Hg}_{4.6}\text{Ag}_{4.4}\text{S}_{4.6}(\text{Cl}_{2.0}\text{Br}_{0.8}\text{I}_{1.6})$, is one that lies well within the compositional range of the mineral. It should be stressed, however, that its derivation was also based on the premise that the substitution of Hg^{2+} by Ag^+ is coupled to a substitution of S^{2-} by $(\text{Cl}, \text{Br}, \text{I})^-$.

The asymmetric unit (Fig. 2) contains 4.5 metal-atom sites and 4.5 anion sites. Atoms Hg1 and Hg2 have flattened octahedral coordinations with two short linear diagonal bonds and four longer equatorial bonds. The coordination of Hg3, although distorted, is still (overall) the same flattened octahedral configuration possessed by Hg1 and Hg2. Atoms Ag1 and Ag2 both have tetrahedral coordinations. Bond lengths and angles are listed in Table 5.

DESCRIPTION OF THE STRUCTURE

The crystal structure of (ideal) $\text{Hg}_5\text{Ag}_4\text{S}_5(\text{Cl}, \text{Br}, \text{I})_4$ is shown in Figure 3. Groups of three face-shared Hg octahedra (Hg2-Hg1-Hg2) are joined together through edge-sharing with an edge-shared combination (or pair) of octahedra (Hg3-Hg3). All of these octahedra build around continuous crankshaft-shaped $-\text{S}-\text{Hg}-\text{S}-$ chains ($-\text{S}2-\text{Hg}2-$

TABLE 4. Atomic coordinates, occupancies, and isotropic U values (\AA^2) for perroudite

Atom	Occupancy*	x	y	z	U	Ideal occupancy†
Hg1	0.5Hg	0	0	0.3399(32)	0.0231(27)	0.5Hg
Hg2	Hg	0.1589(4)	0.1743(7)	0.3776(30)	0.0225(20)	Hg
Hg3	0.8Hg + 0.2Ag	0.0931(4)	0.4230(7)	0.9988(30)	0.0195(19)	Hg
Ag1	Ag	0.3112(10)	0.3967(14)	0.1328(44)	0.0426(45)	Ag
Ag2	Ag	0.4213(12)	0.1853(19)	0.4229(41)	0.0665(49)	Ag
S1	0.5S	0	$\frac{1}{2}$	0.6441(95)	0.0194(70)	0.5S
S2	0.9S + 0.1Cl	0.1304(22)	-0.0173(33)	0.3229(73)	0.0147(55)	S
S3	0.9S + 0.1Cl	0.1787(22)	0.3658(33)	0.3793(75)	0.0153(53)	S
X4	0.8Cl + 0.2Br	0.0180(18)	0.1897(29)	0.8599(68)	0.0241(44)	Halide
X5	0.2Br + 0.8I	0.3135(6)	0.1694(11)	0.8781(31)	0.0218(20)	Halide

* Occupancy for $\text{Hg}_4\text{Ag}_4\text{S}_4\text{S}_4(\text{Cl}_2\text{Br}_0\text{I}_1)_4$; composition determined by single-crystal refinement.

† Occupancy for ideal composition $\text{Hg}_3\text{Ag}_4\text{S}_5(\text{Cl}, \text{Br}, \text{I})_4$.

S3–Hg3–S1–Hg3–S3–Hg2–S2–Hg1–S2–Hg2–S3–). Equatorial atoms (which are mostly halide, with some S) complete flattened octahedral coordinations typical of Hg, at much longer distances. Adjacent chains of octahedra are corner-joined to each other through X5. The remaining space between the chains of octahedra is filled in by the paired Ag tetrahedra, Ag1 and Ag2. The face-shared elements of the Hg octahedral chains may be considered to be fragments of the face-shared chains in corderoite [i.e.,

$\alpha\text{-Hg}_3\text{S}_2\text{Cl}_2$ (Frueh and Gray, 1968)], CuHgSCl , and CuHgSBr (Guillo et al., 1979). The edge-sharing is typical of cinnabar, where the infinite spiral chains characteristic of the structure are formed by just such a (continuous) articulation of octahedra.

CRYSTAL CHEMISTRY AND SUBSTITUTION LIMITS

Ideal composition

Rather than the empirical composition $(\text{Ag}, \text{Hg})_3\text{S}_2(\text{Cl}, \text{Br}, \text{I})_3$, the ideal composition that results from the structure analysis is $\text{Hg}_3\text{Ag}_4\text{S}_5(\text{Cl}, \text{Br}, \text{I})_4$. The site occupancies in the unit cell required for this ideal structure are also listed in Table 4. The Ag content in excess of two atoms per asymmetric unit found for the particular crystal used in the X-ray study is explained by means of Ag substitution in Hg3. Both Ag and Hg regularly adopt octahedral coordination. For example, Ag has octahedral (or more strictly a linear-pseudo-octahedral coordination) in pavonite (Makovicky et al., 1977) and benjaminite (Makovicky and Mumme, 1979); Hg has a similar coordi-

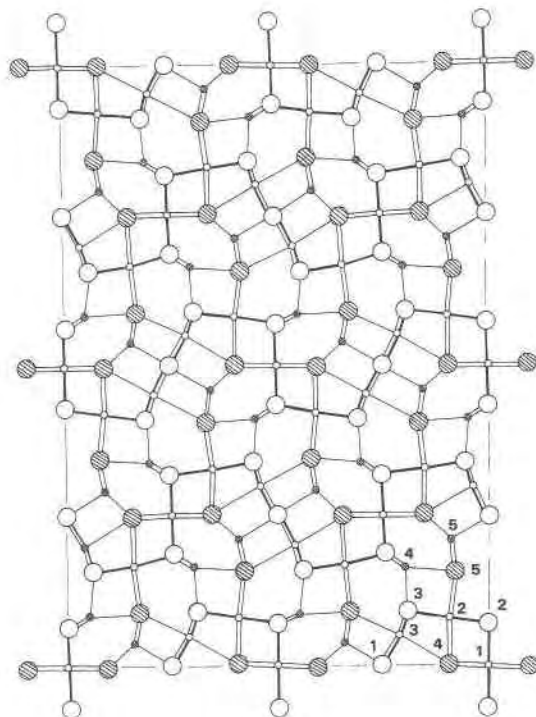


Fig. 3. Projection onto (001) of the structure of (ideal) $\text{Hg}_3\text{Ag}_4\text{S}_5(\text{Cl}, \text{Br}, \text{I})_4$, showing the chains of Hg octahedra built around continuous $-\text{S}-\text{Hg}-\text{S}-$ bonds (drawn as heavy lines). Cross-linking of chains is via the Ag tetrahedra and the X5 atom. A block of four unit cells is shown. Small circles are (open) Hg and (hatched) Ag; large circles are (open) S and (hatched) Cl, Br, and I.

TABLE 5. Bond lengths (\AA) and angles ($^\circ$) in perroudite

	Hg1–S2	2.29 (2)	
	–X4	3.13 (4)	
Hg2–S3	2.36	Hg3–S3	2.34
–S2	2.41	–S1	2.43
–X4	3.24	–S3'	3.16
–X5	3.46	–X4	3.19
–X5'	3.47	–S1'	3.38
–X1'	3.34	–X5	3.46
Ag1–S2	2.46	Ag2–X4	2.59
–S3	2.58	–S1	2.66
–S2'	2.78	–X5	2.74
–X5	2.99	–X5'	3.03
S2–Hg1–S2'	176	Hg1–S2–Hg2	96
S3–Hg2–S2	174	Hg3–S3–Hg2	102
S3–Hg3–S1	173		
S3–Ag1–S2'	92	X4–Ag2–S1	97
S3–Ag1–S2	140	X4–Ag2–X5	146
S2–Ag1–S2'	112	X4–Ag2–X5'	94
S2–Ag1–X5	95	S1–Ag2–X5	112
S3–Ag1–X5	92	S1–Ag2–X5'	100
S2'–Ag1–X5	131	X5–Ag2–X5'	98

Note: Estimated standard deviations for bond distances are 0.05 \AA , for bond angles 1.0 $^\circ$.

nation in the pavonite homologue-related HgBi_2S_4 (Mumme and Watts, 1980) and in cinnabar (Aurivillius, 1950). Furthermore, in the sulfosalts christite (Edenharter, 1976), galkhaite (Divjakovic and Nowacki, 1975), and vrbaite (Ohmasa and Nowacki, 1971), Hg adopts tetrahedral coordinations that are also typical of Ag. Edenharter (1976) found mean linear (pseudo-octahedral) bonds for Hg-S and Ag-S of 2.27 and 2.46 Å, respectively. By comparison, the mean values he found for tetrahedral coordinations are 2.55 and 2.66 Å. Hg-halide bonds range from 2.23, 2.27 Å in HgCl_2 (linear-pseudo-octahedral), through 2.48 Å in HgBr_2 (linear-pseudo-octahedral), to 2.78 Å in red HgI_2 (tetrahedral), and 2.68, 2.62 Å in yellow HgI_2 (linear-pseudo-octahedral). Ag-halide bond distances are 2.77 and 2.89 Å in AgCl and AgBr (equi-octahedral) and 2.81 Å in AgI (tetrahedral). The Hg bonding arrangements displayed in the structure of perroudite (linear S-Hg-S groups with longer equatorial bonds to the predominantly halide atoms) is characteristic of that found in other mercuric sulfide halides, such as the already-mentioned $\alpha\text{-Hg}_3\text{S}_2\text{Cl}_2$, CuHgSCl , and CuHgSBr .

These overall bonding equivalences support the concept of coupled substitutions, with partial substitution by Ag^+ for Hg^{2+} balanced by the equivalent substitution by $(\text{Cl}, \text{Br}, \text{I})^-$ for S^{2-} . This coupled substitution, assuming no vacant sites, can be expressed by the formula $\text{Hg}_{5-x}\text{Ag}_{4+x}\text{S}_{5-x}(\text{Cl}, \text{Br}, \text{I})_{4+x}$ with $x = 0.8$, as was invoked during the refinement of the structure.

The question of atomic site vacancies

Although the overall bonding pattern found in this mineral (Fig. 3) does not lend support to partial occupancies of atomic sites, for the Hg3 site in particular it can be argued that the reduced electron density associated with that site, rather than representing partial substitution by Ag for Hg, indicates only 90% occupancy by Hg. This is one case where a substitution by Ag^+ for Hg^{2+} is not coupled by a substitution by $(\text{Cl}, \text{Br}, \text{I})^-$ for S^{2-} . Assuming that all the Hg is divalent, the most acceptable composition for the crystal, based on the results of least-squares structure refinement, would be $\text{Hg}_{4.8}\text{Ag}_{4.0}\text{S}_{4.6}(\text{Cl}, \text{Br}, \text{I})_{4.4}$; and, in such a case, the general formula (which includes a variable occupancy factor to describe part of the apparent composition range) is $\text{Hg}_{5-x}\text{Ag}_{4+x}\text{S}_{5-2x}(\text{Cl}, \text{Br}, \text{I})_{4+2x}$ with $x \geq 0$.

It should be noted that a partial metal vacancy in Hg3, based on this interpretation of the results of the structure analysis, implies a metal-to-anion (Me/X) ratio less than unity at compositions with $\text{S}/(\text{Cl}, \text{Br}, \text{I})$ values less than the value found for the ideal composition (1.25). This is not confirmed by the electron-microprobe analytical results (Fig. 4a), where the (approximate) mean value of $\text{Me}/\text{X} = 1.0$ persists from values of $\text{S}/(\text{Cl}, \text{Br}, \text{I}) > 1.25$ to lower values of $\text{S}/(\text{Cl}, \text{Br}, \text{I})$, with no trend to lower Me/X values. Further to this, the plot of Hg/Ag vs. $\text{S}/(\text{Cl}, \text{Br}, \text{I})$ in Figure 4b (which shows graphically the 1:1 relationship between the cation and anion ratios) is also taken as evidence that the overall composition is based on the simple mixing formula $(10 \pm x)\text{HgS} \cdot (8 \mp x)\text{Ag}(\text{Cl}, \text{Br}, \text{I})$. However, the

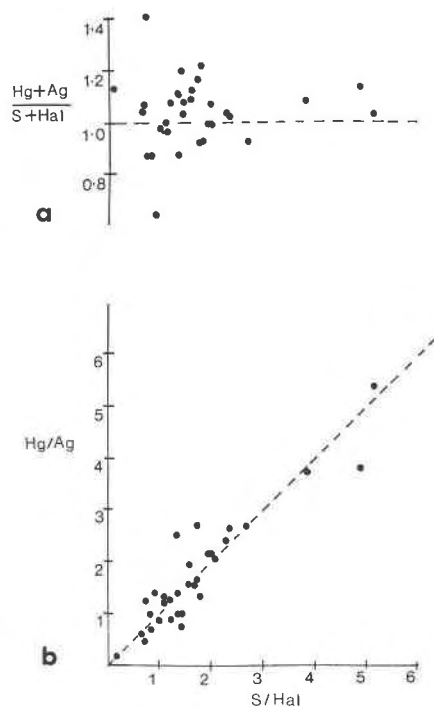


Fig. 4. Plots of atom-ratio values based on the atom concentrations derived from electron-microprobe analysis (as previously depicted in Fig. 1). (a) Total metals to total anions. (b) Hg/Ag, plotted against $\text{S}/(\text{Cl}, \text{Br}, \text{I})$.

case for or against vacancies in Me3 when $\text{S}/(\text{Cl}, \text{Br}, \text{I}) < 1.25$ is fairly inconclusive because of the difficulties encountered in obtaining accurate analytical data (owing to the unavoidable problems of specimen instability and contamination by cinnabar) and better-quality single-crystal X-ray data. These problems also inhibit assessment of the likelihood of a second substitution mechanism where the proposed coupled substitution does not occur. In this situation, the other part of the experimentally assumed composition range may be explained by independent partial substitution by Hg for Ag and substitution by S for $(\text{Cl}, \text{Br}, \text{I})$; the formula would be of the form $\text{Hg}_{5+x}\text{Ag}_{4-2x}\text{S}_{5+y}(\text{Cl}, \text{Br}, \text{I})_{4-2y}$, with x and $y \geq 0$, and there would be $x + y$ vacancies overall. The presence of Hg^+ is not considered very likely because the linear S-Hg-S coordinations of all the Hg atoms in the structure are quite typical of Hg^{2+} , not of Hg^+ , which characteristically forms Hg_2^{2+} pairs.

Preferred substitution mode

The mechanism and range of chemical substitutions in the mineral, based on the structure and unit-cell contents, are derived using the following interpretations. The electron-microprobe data in Figure 1b are interpreted to lie (within the experimental errors) at the 50 mol% (Ag + Hg) line between the limits (45% S + 5% halide), and (20% S + 30% halide). The limits based on frequency of observation are approximately (35% S + 15% halide) and

(20% S + 30% halide). In particular, the analyses close to the HgS point are considered to be the result of such above-mentioned contamination by cinnabar, and the scatter about 50 mol% (Hg + Ag) is also considered to be due to experimental errors such as those described above. The composition is therefore interpreted to vary between $(\text{Ag,Hg})_{9,0}\text{S}_{6,4}(\text{Cl,Br,I})_{2,6}$ and $(\text{Ag,Hg})_{9,0}\text{S}_{3,6}(\text{Cl,Br,I})_{5,4}$; more strictly, the variation is between $\text{Hg}_{6,4}\text{Ag}_{2,6}\text{S}_{6,4}(\text{Cl,Br,I})_{2,6}$ and $\text{Hg}_{3,6}\text{Ag}_{5,4}\text{S}_{3,6}(\text{Cl,Br,I})_{5,4}$, which is expressed generally as $\text{Hg}_{5-x}\text{Ag}_{4+x}\text{S}_{5-x}(\text{Cl,Br,I})_{4+x}$ with $-1.4 < x < +1.4$. The upper limit is achieved by the progressive substitution of Ag into the Hg3 site; the lower limit is achieved by Hg substitution into the tetrahedral Ag1 and Ag2 sites. Charge balancing is achieved by a (Cl,Br,I) and S interchange in the anion sites that has the same magnitude as the Ag-Hg replacement. More variable substitutions seem to be permitted among Cl, Br, and I.

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