Capgaronnite, HgS·Ag(Cl,Br,I), a new sulfide-halide mineral from Var, France

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Abstract

Capgaronnite, ideally HgAg(Cl,Br,I)S, is a new mineral from the Cap-Garonne copper-lead mine, Var, France. The mineral is orthorhombic, space group $P2_12_12$, with $a = 6.803(8)$, $b = 12.87(1)$, $c = 4.528(7)$, and $Z = 4$. The composition and crystal structure of capgaronnite are related to those of perroudite [$5HgS·4Ag(Cl,Br,I)$] previously reported from the Cap-Garonne locality. Like perroudite, capgaronnite probably crystallized following decomposition of Hg- and Ag-bearing tennantite by halide-bearing solutions of marine origin.

Capgaronnite is pleochroic in very thin splinters, with α = dark brown and γ = gray to clear purple. The optical orientation is $\alpha = c$, $\beta = b$, and $\gamma = a$. Indices of refraction measured by reflectance measurements on oriented crystals in polished section were $\alpha \sim 2.2$, $\gamma \sim 2.3$; β could not be measured because the crystals are very thin parallel to $\beta = b$.

A preliminary solution of the capgaronnite atomic arrangement ($R = 0.17$) was obtained from X-ray film intensities. In capgaronnite, (010) layers of face-shared Hg octahedra built around chains of continuous -S-Hg-S- bonds are joined by cross-linked, paired groups of Ag tetrahedra.

Introduction

Capgaronnite occurs in the Cap-Garonne (Var, France) copper-lead mine (Guillemin, 1952; Mari and Rostan, 1986) and forms small tufted aggregates or isolated crystals (maximum width 0.02 mm and maximum length 0.1 mm) within cavities in Triassic conglomerates and sandstone. The mineral is associated with secondary Cu minerals such as olivenite, cyanotrichite, brochantite, parnauite (Sarp et al., 1978), tennantite containing Ag and Hg, strueverite, tourmaline, and perroudite (Sarp et al., 1987; Mumme and Nickel, 1987).

Electron microprobe analysis indicated the ideal formula HgS·Ag(Cl,Br,I) when an Ag deficiency and a halide excess were assumed. Powder X-ray film data for the mineral were observed to be similar to those reported in the JCPDS file for tocornalite, a poorly defined Hg,Ag iodide with no definite recorded composition or unit-cell data. However, the substantial amount of S observed in analyses of the mineral from Cap-Garonne had not been previously reported in the case of tocornalite.

From the data available at this early stage it was decided that this mineral was a new Hg,Ag sulfide-halide, probably related to perroudite but with affinities to tocornalite. Although now surmised, any close relationship to tocornalite cannot be substantiated because a type specimen of that mineral does not exist for comparison (private communications, Paris Museum).

Preliminary crystal structure analysis determined the ideal composition to be HgS·Ag(Cl,Br,I); new mineral status and name were approved for capgaronnite by the International Mineralogical Association Commission on New Minerals and Mineral Names in May 1990.

Physical and optical properties

Capgaronnite crystals are translucent to opaque, black with a subadamantine-submetallic luster and black-gray streak. They are fragile, and the hardness could not be measured because of the small crystal size. The fracture is irregular; the cleavage {010} is perfect.

Crystals of capgaronnite are prismatic, elongated along [001] and flattened on {010}. The observed forms are {010}, {100}, {110}, and {h0l}. Contact twinning is present with the composition plane {h0l}.

The mineral is probably optically negative, but this is very difficult to confirm because of the poor quality of the convergence figure and the submetallic character. The refractive indices, which are high, could not be measured because of reaction between the crystals and index oils. They were determined by reflectance measurements on oriented crystals in a polished section and yielded $\alpha \sim 2.2$, $\gamma \sim 2.3$; β could not be measured because the crystals are very thin parallel to $\beta = b$.

Optical orientation is $\alpha = c$, $\beta = b$, and $\gamma = a$. The crystals are pleochroic in very thin splinters with α = dark

TABLE 1. EPMA results for capgaronnite

	1	2	3	4	5	6	7
Hg	56.61	53.20	52.97	52.83	53.98	53.92	52.24
Ag	19.96	22.11	26.97	21.66	29.27	23.99	28.09
S	8.07	8.37	8.26	8.99	6.10	7.96	8.35
Cl	10.81	10.38	10.64	11.11	9.97	10.58	7.57
Br	5.13	5.33	5.06	5.17	5.16	5.17	3.75
I	0.06	0.00	0.34	0.54	0.7	0.33	
Total	100.64	99.39	104.25	100.3	105.18	101.95	100.00

Note: Numbers 1–5, individual analyses; 6, mean of 1–5; 7, calculated values with Cl:Br = 0.82:0.18 for ideal composition HgAg(Cl,Br,I)S.

brown, γ = gray to clear purple. Density could not be measured because of the small grain size. Calculated density, based on the idealized formula with $Z = 4$ and unit-cell volume, is 6.43(1) g/cm³; on the basis of the empirical formula it is 6.19 g/cm³.

CHEMICAL RELATIONS

Electron probe microanalysis of capgaronnite presented significant difficulties (as was the case for perroudite)

TABLE 2. X-ray powder diffraction data for capgaronnite and tocornalite (JCPDS data)

Capgaronnite				Tocornalite (JCPDS)		
hkl	d_{calc}	d_{obs}	I	hkl	d_{calc}	d_{obs}
020	6.435	6.43	40	020	6.358	6.37
110	6.014	6.01	5			
120	4.674	4.67	10	120	4.638	4.67
001	4.528	4.527	10	001	4.497	4.510
101	3.769	3.762	60	101	3.747	3.760
130	3.629	3.637	60	130	3.594	3.610
				111	3.595	
200	3.402	3.386	10	200	3.390	3.390
210	3.289	3.283	30	210	3.276	3.290
040	3.218	3.218	5	040	3.179	3.190
220	3.007	2.996	5	220	2.991	2.998
140	2.909	2.905	10	140	2.878	2.894
201	2.720	2.712	5			
230	2.665	2.664	100	230	2.648	2.644
211	2.661			211	2.648	
221	2.505	2.488	5	221	2.491	2.468
240	2.337	2.319	10	240	2.319	2.309
002	2.264	2.265	40	002	2.248	2.254
102	2.148	2.144	10	102	2.134	2.127
060	2.145			320	2.129	
250	2.053	2.047	20	250	2.034	2.036
160	2.046					
202	1.885	1.886	10	202	1.874	1.877
340	1.854	1.851	5			
042	1.852			042	1.836	1.834
232	1.726	1.724	5			
071	1.703	1.700	15			
350	1.702					
400	1.701			400	1.695	1.695
052	1.700					
171	1.652	1.646	5	171	1.635	1.634
152	1.649			152	1.635	
420	1.644					
242	1.626					
270	1.617	1.614	5			
080	1.609					
302	1.602	1.591	5			
351	1.593			351	1.581	1.583
				321	1.582	

Note: Intensities are visual estimates of Gandolfi film.

TABLE 3. Atomic coordinates and isotropic temperature factors for capgaronnite

Atom	Occupancy*	x	y	z	U
Hg	1.0	0.134(5)	0.253(3)	0.464(6)	0.035(2)
Ag	1.0	0.291(8)	0.044(6)	−0.010(8)	0.110(6)
S	1.0	0.390(10)	0.114(8)	0.468(9)	0.038(9)
X	0.8Cl + 0.2Br	0.383(7)	0.355(6)	0.031(8)	0.110(9)

* Occupancy of X based on electron microprobe analyses.

because of the volatility of the elements. Ag is particularly mobile, and the average crystal size is very small.

Five analyses were carried out using the Cameca automated microprobe at Washington State University. The standards used were HgS (Hg, S), AgCl (Ag, Cl), KBr (Br), and RbI (I). The analytical conditions were 15 kV, 6-μm-diameter beam, 2.35-nA beam current, 10 s count time. The analytical results are listed in Table 1. From those results the empirical formula on the basis of a total of four atoms is $Hg_{0.98}Ag_{0.80}(Cl_{1.08},Br_{0.23},I_{0.01})S_{0.90}$. The simplified formula is HgAg(Cl,Br,I)S, which, with Cl:Br = 0.82:0.18, requires Hg 52.24, Ag 28.09, Cl 7.57, Br 3.75, S 8.35 wt%, total 100.0 wt%.

X-RAY STUDY

Crystallographic relations

X-ray single-crystal study by the precession and Weissenberg methods showed that capgaronnite is orthorhombic with space group $P2_12_12$ and $a = 6.803(8)$, $b = 12.87(1)$, $c = 4.528(7)$ Å, $V = 396.4$ Å³.

A powder pattern was obtained using a Gandolfi camera (114.6-mm diameter, Ni-filtered CuKα), and d values were indexed using the cell dimensions determined from the single-crystal precession data (Table 2).

A single-crystal X-ray investigation performed at CSIRO, Melbourne, has elucidated the crystal structure of capgaronnite. In addition to the precession data (obtained in Geneva), it proved feasible, using CuKα radiation, to measure Weissenberg film pack data for the 0, 1, and 2 levels for a crystal mounted along the **c** axis. The structure was solved by the traditional approach of calculating

TABLE 4. Bond lengths for capgaronnite in angstroms

Capgaronnite		Perroudite (average)
Hg-S¹	2.40	2.35
-S	2.49	2.42
-X	2.90	3.20
-X¹	3.14	3.27
-X²	3.17	3.42
-X³	3.34	3.47
Mean	2.91	3.02
Ag-S	2.44	2.53
-S²	2.61	2.62
-X⁴	2.71	2.76
-X¹	3.05	3.01
Mean	2.70	2.73

Note: S¹ = −1 + (½ + x), ½ − y, 1 − z; S² = x, y, −1 + z; X¹ = −1 + (½ + x), ½ − y, − z; X² = −1 + (½ + x), ½ − y, 1 − z; X³ = x, y, 1 + z; X⁴ = ½ − x, −1 + (½ + y), −z.

a 3-dimensional Patterson function $P(u,v,w)$ to determine the position of the heavy Hg atom. Fourier map and structure-factor calculation recycling methods were then used to locate, and least-squares to refine, the positions of the other atoms in the asymmetric unit. Overall, a satisfactory refinement was achieved in space group $P2_12_12$ when one considers that the reflections on the films were substantially smeared, particularly in the case of the upper level data, and the extremely high absorption coefficient ($\mu_1 = 1374$ cm^{-1}). All calculations were made using a VAX computer and the SHELX76 library of programs (Sheldrick, 1976).

The structure was eventually refined to an agreement R value of 0.17 using isotropic temperature factors and absorption corrections for a thin prism shape. During these refinements the occupancy factor of the halide site was fixed at that determined by the EPMA study. Refined atom coordinates are given in Table 3, bond lengths in Table 4, and structure factors in Table 5.[1]

Crystal structure

The crystal structure of capgaronnite is illustrated in Figure 1. Parallel layers of face-shared Hg octahedra built around vertically stacked zig-zag chains of continuous -S-Hg-S- bonds are joined by cross-linking (paired) groups of Ag tetrahedra. As such, capgaronnite has a very simple layer structure with the layers of Hg octahedra extending parallel to (010).

The composition and crystal structure of capgaronnite are related to those of perroudite, which was also found at the Cap-Garonne locality. Capgaronnite, similar to perroudite, most likely crystallized following decomposition of Hg and Ag bearing tennantite by halide-bearing solutions, probably of marine origin. Perroudite, with the ideal composition 5HgS·4Ag(Cl,Br,I), has three-member groups of face-shared Hg octahedra in its structure (Mumme and Nickel, 1987). In the elimination of Hg octahedra to create the 1:1 HgS:AgCl stoichiometry, the extremely regular layerlike arrangement of capgaronnite is realized. As in the case of perroudite, the face-sharing element in capgaronnite is similar to that observed in corderoite [α-Hg$_3$S$_2$Cl$_2$ (Frueh and Gray, 1968)], CuHgCl, and CuHgSBr (Guillo et al., 1979). The type of edge sharing of Hg octahedra typical of cinnabar, and observed in perroudite, is not found in the crystal structure of capgaronnite.

REMARKS ON CRYSTAL-CHEMICAL RELATIONS

Neither the analytical data nor the results of crystal structure refinement yield data accurate enough to detect any substitution of Ag^{1+} for Hg^{2+} in the metal sites in capgaronnite. Such substitution could be inferred from the halide:S ratios that are consistently greater than 1.0.

[1] Copies of Table 5 may be ordered as Document AM-92-489 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit $5.00 in advance for the microfiche.
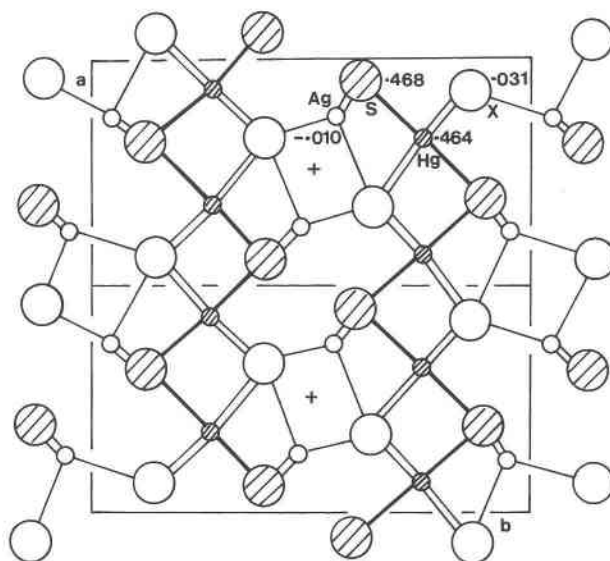

Fig. 1. Projection onto (001) of the structure of capgaronnite showing the sheets of Hg octahedra joined by Ag tetrahedra. Continuous -S-Hg-S- bonds are drawn with heavy lines. Small circles are (open) Ag, (hatched) Hg; large circles are (open) S, (hatched) Cl,Br. Vertical coordinates given indicate that open atoms are at approximately $z = 0$, hatched atoms at approximately $z = \frac{1}{2}$. The symbol (+) denotes the origin.

That is to say, any (Cl,Br,I)$^{1-}$ substitution for S^{2-} that occurs in the anion site should be coupled with an equivalent Ag^{1+} for Hg^{2+} substitution in the octahedral cation site (Hg). However, Ag contents are consistently low in the EPMA results, probably because it becomes mobile when the electron beam strikes the polished surface of the crystals (charge repulsion effect) and cannot be measured accurately in the sample. In the same way, it is felt that the measured halide excess may also be the result of shortcomings in the analytical method rather than excessive substitution trends in the anion sites. However, it is probable that such a coupled substitution does exist over a limited range of composition, and the overall composition of capgaronnite is more accurately given by the formula $(1 + x)$HgS·$(1 - x)$Ag(Cl,Br,I).

RELATIONSHIP TO "TOCORNALITE"

In the course of the new mineral proposal to IMA, it was pointed out that the powder X-ray diffraction data for the minerals capgaronnite and tocornalite are strikingly similar. The JCPDS data reported for tocornalite may be indexed using the slightly smaller cell $a = 6.78$, $b = 12.72$, $c = 4.50$ Å (Table 2). The X-ray data obtained by Mason (1972) and reported in his note to have derived from Broken Hill tocornalite and sample C906 in the U.S. National Museum labeled tocornalite, Chanarcilla, Chile, may not in fact have been obtained from tocornalite cotypes. Domeyko (1867) originally reported tocornalite to be a silver-mercury iodide. Some of the Broken Hill mineral (USNM 134015) was donated by B.M.

for EPMA study at CSIRO, and several (good) analyses yielded the average formula $Hg_{1.07}Ag_{0.87}S_{1.09}(Cl_{0.88},Br_{0.09}, I_{0.01})$. Most of the analyses yielded very low totals because of the fine-grained nature of the material.

Thus the Broken Hill (and presumably the Chilean) specimen is chemically different from Domeyko's tocornalite and may well be identical to capgaronnite (in fact most probably it is, judging from the above analyses). An attempt was made by B.M. to obtain some of Domeyko's type specimen from the National Museum in Paris, but the reply from H.-J. Schubnel of that institution stated that the museum does not possess a type specimen of tocornalite, and he actually considers the mineral to be a mixture, not a species in its own right. Thus it seems most appropriate that tocornalite should be abandoned as an inadequately described mineral. Its identity with the more realistically characterized capgaronnite may remain unsolved for the present.

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