

Perroudite, a new sulfide-halide of Hg and Ag from Cap-Garonne, Var, France, and from Broken Hill, New South Wales, and Coppin Pool, Western Australia

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ABSTRACT

Perroudite is a new sulfo-halide of Hg and Ag from Cap-Garonne, Var, France; Broken Hill, New South Wales; and Coppin Pool, Western Australia, Australia. Averaged microprobe analyses gave the following formulae: $\text{Hg}_{5.04}\text{Ag}_{4.03}\text{S}_{3.96}(\text{Cl}_{1.55}\text{I}_{1.55}\text{Br}_{0.87})_{23.97}$ (Cap-Garonne), $\text{Hg}_{5.0}\text{Ag}_{4.2}\text{S}_{5.45}(\text{I}_{1.6}\text{Cl}_{1.55}\text{Br}_{0.25})_{23.4}$ (Broken Hill), and $\text{Hg}_{5.7}\text{Ag}_{3.5}\text{S}_{5.4}(\text{Cl}_{2.0}\text{I}_{1.0}\text{Br}_{0.5})_{23.5}$ (Coppin Pool). A structure determination of a Coppin Pool crystal gave the general formula $\text{Hg}_{5-x}\text{Ag}_{4+x}\text{S}_{5-x}(\text{Cl,I,Br})_{4+x}$ ($-1.4 < x < 1.4$) (Mumme and Nickel, 1987). The mineral is orthorhombic, space group $P2_12_12$, with $a = 17.47(3)$, $b = 12.23(2)$, $c = 4.29(2)$ Å, $V = 917.5$ Å³, and $Z = 2$. The averaged calculated density is 6.92 g/cm³. The strongest seven lines in the X-ray diffraction pattern are (d in Å, (hkl) , I/I_0) 3.012,(140)(321),100; 2.965,(430)(411)(031),80; 3.945,(111),60; 2.638,(511)(331)(620),35; 3.694,(230)(211),30; 2.740,(421),30; 2.446,(710),30 (Cap-Garonne data). Perroudite forms bright red, transparent prismatic crystals to 0.07 mm in length, elongated along [001] and often flattened on {100}. The main forms present are {100} and {001}, and some crystals from Broken Hill and Coppin Pool are fluted with hollow terminations. Luster vitreous to adamantine; streak orange-red; brittle with one perfect cleavage on (100); fracture irregular. The refractive indices are in the range 2.3–2.4; the mineral is biaxial positive; $2V_{\text{meas}} = 70^\circ$; dispersion $r > v$ (very strong); pleochroism marked from brownish-red to yellow to brownish-yellow.

Perroudite forms from the alteration of Hg- and Ag-bearing tennantite at the type locality (Cap-Garonne). At Broken Hill it occurs in massive white kaolinite associated with silver halides, native silver and native gold, and possibly other mercury-bearing minerals. At Coppin Pool, perroudite occurs with supergene minerals such as covellite, cerussite, anglesite, phosgenite, etc., derived by the weathering of galena in a quartz vein. Halide-rich solutions are implicated in the formation of perroudite at all three occurrences.

The mineral is named for Mr. Pierre Perroud, of Geneva, Switzerland. Type specimens are lodged in the Natural History Museum, Geneva, Switzerland. Material representative of the two Australian localities has been deposited in the Museum of Victoria and the Western Australian Government Chemical Laboratories, Perth, Western Australia.

INTRODUCTION

In 1983, a red fibrous mineral on a rock specimen collected from the Cap-Garonne mine, Var, France, by Mr. Gerard Davenne, was sent to one of us (H.S.) for identification.

The X-ray powder-diffraction pattern of the mineral did not correspond to any known species, nor to any synthetic inorganic material. Electron-microprobe analysis revealed an unusual combination of elements—

Hg, Ag, S, Cl, I, and Br—which defied accurate quantitative determination for several years until special techniques, outlined below, were adopted in the Sandia National Laboratories that enabled satisfactory quantitative analyses to be obtained. In 1986, all data were forwarded to the IMA Commission on New Minerals and Mineral Names (CNMMN), and the new mineral species and the name, perroudite, were approved prior to publication.

The existence of at least one unusual, undefined, red, Hg-bearing mineral at Broken Hill, New South Wales, Australia, had been recognized since the early days of mining (Birch et al., 1982), but the physical nature of the material, generally earthy patches in kaolinite, made its full characterization difficult. However, the discovery within the Museum of Victoria mineral collections of several kaolinite specimens containing aggregates of red microcrystals enabled one of us (W.D.B.) to obtain an X-ray powder-diffraction pattern and quantitative microprobe analyses of this enigmatic mineral. Soon thereafter, the occurrence of an unusual red Hg-Ag-S halide at Coppin Pool, in the Pilbara district of Western Australia, was described by Nickel (1985). A chance conversation between W.D.B. and W. G. Mumme (CSIRO, Division of Mineral Chemistry, Melbourne), who was attempting structural and microprobe analyses of the Coppin Pool mineral, revealed its close similarity with the Broken Hill mineral. A joint submission to the CNMMN for approval of a new species was in the final stages of preparation when the perroudite data from the French locality was received for voting by W.D.B., the Australian member of the CNMMN. It became immediately evident that the mineral from France and the mineral from the two Australian occurrences were one and the same.

Thus, by a curious chain of coincidence, data on an unusual new mineral from three widely separated localities were being accumulated simultaneously, yet the avenues of communication were sufficiently open to prevent three separate submissions to the CNMMN and to enable a cooperative approach to be adopted. The authors considered that a single descriptive paper on all three occurrences was in the best interests of mineralogy.

Perroudite is named in honor of Mr. Pierre Perroud (1943–), Professor in the Voltaire College, Geneva, Switzerland, and President of the Mineralogical Society of Geneva, for his work on Cap-Garonne minerals. Material from the type locality (Cap-Garonne) is preserved in the Mineralogy Department of the Natural History Museum, Geneva, Switzerland. Specimens representative of the Broken Hill and Coppin Pool occurrences are lodged in the Mineralogy Department of the Museum of Victoria, Melbourne, Australia, and in the collections of the Western Australian Government Chemical Laboratories, Perth, Australia.

OCURRENCE

Perroudite from the Cap-Garonne copper-lead mine (Guillemain, 1952; Mari and Rostan, 1986) forms fibrous, tufted aggregates of crystals up to 0.07 mm long by 0.02

mm wide within cavities in sandstones and conglomerates of Triassic age. Secondary copper minerals such as olivenite, brochantite, cyanotrichite, and parnauite (Sarp et al., 1978), as well as Hg- and Ag-bearing tennantite, also occur in these sedimentary rocks.

At Broken Hill, perroudite occurs within massive white kaolinite as aggregates of prismatic microcrystals up to 0.03 mm long and as single crystals intimately associated with iodargyrite to form slightly photosensitive, earthy to waxy reddish-orange grains and patches. Seams containing tiny crystals of native gold also occur within the perroudite-bearing kaolinite, along with relict euhedra of spessartine.

Extensive deposits of white compact kaolinite occurred in the upper levels of the Proprietary, Block 14, and other spatially associated mines at Broken Hill. They were often richly impregnated with films, veins, and plates of silver halides (iodargyrite and bromian chlorargyrite), seams and films of native silver, and patches of reddish Hg-bearing minerals showing varying degrees of photosensitivity. Cinnabar and “coccinite,” a term used for an inadequately described mercury iodide, were thought to be present (Smith, 1926), but have not been confirmed. Perroudite is most probably a major constituent of these reddish patches.

At the Coppin Pool occurrence (Nickel, 1985), a suite of supergene minerals including anglesite, cerussite, phosgenite, covellite, pyromorphite, cinnabar, and at least six new species, have formed by weathering of a galena-bearing quartz vein. Perroudite occurs as coatings of prismatic crystals up to 0.05 mm long by 0.025 mm wide on the walls of small cavities in a heterogeneous supergene assemblage.

PHYSICAL AND OPTICAL PROPERTIES

Perroudite crystals are transparent and bright red with a vitreous to adamantine luster and a reddish-orange streak. They are brittle and soft—the hardness could not be measured owing to the small crystal size—with an irregular fracture. Perfect (100) cleavage is observed on crystals from Cap-Garonne.

Crystals are prismatic along [001] and tend to be flattened on {100}. The observed forms are {100}, {001}, and minor {010} and {0 h l} (Fig. 1). Crystals from Broken Hill and Coppin Pool tend to be fluted and frequently show hollow terminations (Fig. 2). Crystals from Cap-Garonne may be contact-twinning with composition plane 0 h l (Fig. 3).

Optical properties were determined only on crystals from Cap-Garonne. The mineral is biaxial positive, with a measured $2V$ close to 70° . The very high refractive indices could not be measured owing to reaction between the crystals and index oils. Instead they were determined by reflectance measurements on oriented crystals in a polished section and gave $\alpha = 2.3$, $\beta = 2.4$; dispersion $r > v$, very strong. The optical orientation is $X = c$, $Y = b$ and $Z = a$. Pleochroism is very intense with $X =$ dark brownish-red, $Y =$ yellow, and $Z =$ brownish-yellow.

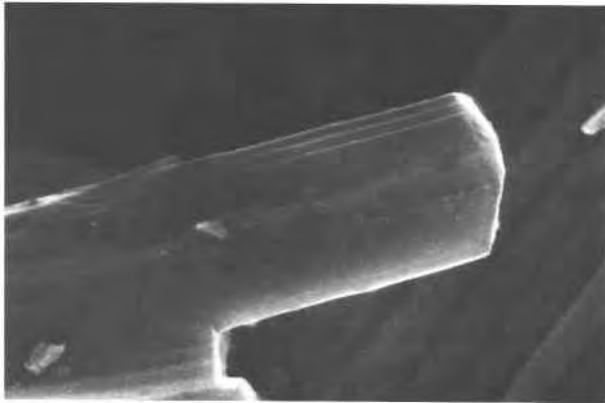


Fig. 1. SEM photomicrograph showing a single crystal of perroudite from Cap-Garonne. Crystal is 0.016 mm wide.

The density could not be determined on material from any of the three localities owing to the small crystal size. Calculated densities, based on the respective empirical formulae and unit-cell volumes, vary from 6.60 g/cm³ (Coppin Pool) through 6.86 g/cm³ (Cap-Garonne) to 6.92 g/cm³ (Broken Hill). The wide range of calculated densities reflects the effects of solid solution (see below).

CHEMISTRY

Quantitative electron-microprobe analysis of perroudite from all three localities presented significant difficulties because of the volatility of the elements, especially the halides (I, Cl, and Br), and the very small crystal size, which restricted both the movement and the defocusing of the microprobe beam in order to minimize surface damage. Special precautions were taken to achieve satisfactory results.

For the Cap-Garonne perroudite, analyses were performed using a Cameca MBX electron microprobe with Tracor-Northern automation run by the Sandia TASK 8 computer program (Chambers, 1985). Standards selected were natural HgS (Hg, S), silver metal (Ag), synthetic NaCl (Cl), synthetic RbI (I), and synthetic KBr (Br). All analyses were carried out at 15 kV with a beam current of approximately 0.064 μ A. The X-ray lines measured were the $K\alpha$ lines of S and Cl, the $L\alpha$ lines of Br, Ag, and I and the $M\alpha$ line of Hg. The most volatile elements (Br, Cl, and I) were analyzed first, and the counting times for each element were adjusted so that the three wavelength-dispersive spectrometers completed the full 66-s analysis nearly simultaneously. Corrections for instrumental errors and matrix effects (Bastin et al., 1984; Chambers, 1985) were then applied. Analyses from five different points on two crystals are shown in Table 1.

For the Broken Hill mineral, analyses were obtained using a JEOL electron-microprobe operating at 15 kV and with a specimen current of about 0.013 μ A. Under these conditions, surface damage was minimized, but the count rate for Hg was very low (100 cps). Only single crystals mounted in epoxy resin and then polished could be ana-



Fig. 2. SEM photomicrograph showing aggregates of perroudite crystals from Broken Hill, New South Wales. The crystals average about 0.025 mm long.

lyzed, as interference effects for Ag and I were considerable for crystals enclosed within iodargyrite. Standards were similar to those used for the Cap-Garonne mineral, except that a natural crystal of marshite (CuI) was used for I. Elements were analyzed on three wavelength-dispersive spectrometers in the following combinations: Hg ($M\alpha$); S ($K\alpha$), Cl ($K\alpha$), Ag ($L\alpha$) and I ($L\alpha$); Br ($L\alpha$). From a total of 17 analyses, 7 were selected on the basis of satisfactory totals and charge balances and are presented in Table 2.

For perroudite from Coppin Pool, several sets of microprobe data showing considerable variation were obtained using low accelerating voltages and a slightly defocused beam (Mumme and Nickel, 1987). The averaged composition, given in column 10 of Table 2, was obtained from 32 point measurements on two polished sections.

A comparison of the analytical data in Tables 1 and 2 reveals the following: (1) The Cap-Garonne perroudite is quite uniform in composition, whereas the Broken Hill



Fig. 3. SEM photomicrograph of a contact twin of perroudite from Cap-Garonne. Each arm of the twin is 0.08 mm long.

TABLE 1. Microprobe analyses of perroudite from Cap-Garrone, France

wt%	1	2	3	4	5	6	7	8
Hg	54.45	52.39	52.72	53.31	52.55	53.08	0.296	52.29
Ag	22.07	25.03	23.60	22.06	21.54	22.86	0.237	22.50
S	6.77	6.18	6.55	6.96	6.89	6.67	0.233	8.36
I	10.23	9.79	10.08	10.09	11.39	10.32	0.091	9.92
Cl	2.94	2.91	2.91	2.87	2.82	2.89	0.091	2.77
Br	3.58	3.44	3.68	3.96	3.67	3.67	0.051	4.16
Total	100.04	99.74	99.55	99.25	98.86	99.49	0.999	100.00

Note: 1–5, individual analyses; 6, mean of 1–5; 7, atomic proportions for mean (6); 8, theoretical values for ideal structural formula. Formula (based on 17 atoms): $\text{Hg}_{5.04}\text{Ag}_{4.03}\text{S}_{3.96}(\text{Cl}_{1.55}\text{I}_{1.55}\text{Br}_{0.87})_{23.97}$.

mineral shows variation in terms of Hg:Ag, S:(Cl,Br,I) and Cl:Br:I. (2) For the Broken Hill perroudite, individual analyses show either I or Cl dominant in the halide position. (3) The averages for the Cap-Garonne and Broken Hill perroudites are very similar, but the Cap-Garonne mineral is poorer in S and richer in halides, notably Br, than the Broken Hill material.

The empirical formula for the Cap-Garonne perroudite was initially calculated on the basis of 17 atoms and gave $\text{Hg}_{5.04}\text{Ag}_{4.03}\text{S}_{3.96}(\text{Cl}_{1.55}\text{I}_{1.55}\text{Br}_{0.87})_{23.97}$ or, ideally, $\text{Hg}_5\text{Ag}_4\text{S}_4(\text{Cl,I,Br})_4$. However, if Hg is divalent, charge balance is not satisfied by this formula.

A formula for the Broken Hill mineral was calculated on the basis of 18 atoms and gave $\text{Hg}_{5.0}\text{Ag}_{4.2}\text{S}_{3.45}(\text{I}_{1.6}\text{Cl}_{1.55}\text{Br}_{0.25})_{23.4}$.

A formula for the Coppin Pool perroudite, based on 6 S atoms, was given by Nickel (1985) as $\text{Hg}_{5.18}\text{Ag}_{4.75}\text{S}_{6.00}(\text{Cl}_{2.40}\text{I}_{1.81}\text{Br}_{0.98})_{25.19}$.

The differences between these formulae could only be resolved by a structural study. This was undertaken on a single crystal of perroudite from Coppin Pool (Mumme and Nickel, 1987) and indicated that the ideal structural formula is $\text{Hg}_5\text{Ag}_4\text{S}_5(\text{Cl,I,Br})_4$.

A range of composition is permitted by coupled substitution, with partial replacement of Hg by Ag, balanced by the equivalent substitution of S by halide. This gives rise to a general formula of $\text{Hg}_{5-x}\text{Ag}_{4+x}\text{S}_{5-x}(\text{Cl,Br,I})_{4+x}$, with $-1.4 < x < 1.4$ (Mumme and Nickel, 1987).

The less restricted substitution within the halide position suggests that distinct I-, Cl-, and Br-dominant perroudites may exist. We consider that the chemical data presented here are inadequate to establish end-member species at this stage, since some of the apparent compo-

sitional variation may arise from the difficulties encountered during the microprobe analysis.

There appears to be no clear relationship between perroudite and other sulfide-halides of Hg, such as lavrentievite $\text{Hg}_3\text{S}_2(\text{Cl,Br})_2$ and "arkazite" (a nonapproved species) $\text{Hg}_3\text{S}_2(\text{Br,Cl})_2$ (Vasil'yev et al., 1984), and corderoite $\text{Hg}_3\text{S}_2\text{Cl}_2$. Its relationship to toconalite, a poorly characterized Hg-Ag iodide reported from Broken Hill (Mason, 1972), is uncertain. However, on one specimen in the Museum of Victoria collection, perroudite occurs mixed with iodargyrite and a mineral with the same X-ray powder-diffraction pattern as that given by Mason (1972) for toconalite.

X-RAY CRYSTALLOGRAPHY

X-ray powder-diffraction data for perroudite from all three localities are shown in Table 3. Unit-cell parameters, refined from the powder data, are as follows: Cap-Garonne— $a = 17.47(3)$, $b = 12.23(2)$, $c = 4.29(2)$ Å, $V = 917.5$ Å³. Broken Hill— $a = 17.46(5)$, $b = 12.22(4)$, $c = 4.29(3)$ Å, $V = 916.5$ Å³. Coppin Pool— $a = 17.43(2)$, $b = 12.24(2)$, $c = 4.35(1)$ Å, $V = 928.5$ Å³.

Perroudite is orthorhombic, with space group $P2_12_12$, assigned from inspection of X-ray single-crystal photographs (Mumme and Nickel, 1987). Using the ideal formula $\text{Hg}_5\text{Ag}_4\text{S}_5(\text{Cl,I,Br})_4$, with the Cl:I:Br ratio of the Cap-Garonne perroudite (1.56:1.56:0.88), an average unit-cell volume of 920.8 Å³, and $Z = 2$, gives an averaged calculated density of 6.92 g/cm³.

Details of the crystal structure of perroudite, based on the Coppin Pool mineral, are given by Mumme and Nickel (1987).

TABLE 2. Microprobe analyses of perroudite from Broken Hill and Coppin Pool, Australia

wt%	1	2	3	4	5	6	7	8	9	10	11
Hg	54.69	52.57	51.72	51.62	51.21	49.56	52.30	51.95	0.259	57.68	0.288
Ag	20.16	22.41	26.99	21.95	23.19	26.92	23.15	23.54	0.218	19.43	0.180
S	8.72	9.44	9.29	8.64	9.21	9.23	8.98	9.07	0.283	8.79	0.274
I	13.53	8.33	10.43	11.49	10.63	10.66	10.54	10.80	0.085	6.45	0.051
Cl	2.56	2.79	3.35	2.77	2.80	2.92	2.63	2.83	0.080	3.56	0.100
Br	1.13	0.97	0.73	0.99	0.89	0.92	1.08	0.96	0.012	2.11	0.026
Total	100.79	96.51	102.51	97.46	97.93	100.21	98.68	99.15	0.937	98.02	0.919

Note: 1–7, individual analyses (Broken Hill); 8, mean of 1–7; 9, atomic proportions for mean (8); 10, average of 32 point analyses (Coppin Pool) (Mumme and Nickel, 1987); 11, atomic proportions for Coppin Pool average (10). Formulae (based on 18 atoms): $\text{Hg}_{5.0}\text{Ag}_{4.2}\text{S}_{3.45}(\text{I}_{1.6}\text{Cl}_{1.55}\text{Br}_{0.25})_{23.4}$ (for 8 and 9) and $\text{Hg}_{5.7}\text{Ag}_{3.5}\text{S}_{5.4}(\text{Cl}_{2.0}\text{I}_{1.6}\text{Br}_{0.5})_{23.5}$ (for 10 and 11).

TABLE 3. X-ray powder-diffraction data for perroudite

hkl	Cap-Garonne			Coppin Pool*			Broken Hill		
	d_{calc}	d_{obs}	$ l_0$	d_{calc}	d_{obs}	$ l_0$	d_{calc}	d_{obs}	$ l_0$
200	8.735	8.74	<5						
210	7.108	7.10	<5				7.146	7.145	<10
220	5.010	5.01	25	5.009	5.016	10	5.008	5.009	20
400	4.368	4.36	5				4.366	4.369	20
001	4.290	4.303	<5						
101	4.166	4.170	<5				4.168	4.170	<10
011	4.048	4.052	<5				4.050	4.050	<10
111	3.944	3.945	60	3.989			3.945	3.949	60
201	3.851	3.860	<5		3.948	30	3.852	3.851	<10
130				3.973					
230	3.694	3.694	30						
211	3.673						3.674	3.676	20
021	3.512	3.520	<5				3.513	3.512	<10
301	3.454								
121	3.443	3.458	25						
510	3.360	3.372	25				3.444	3.446	20
221	3.259	3.264	<5				3.358	3.358	<10
140	3.012			3.014			3.259	3.259	10
321	3.007	3.012	100	3.026					
411	2.969			2.985			3.008	3.012	100
430	2.980	2.965	80	2.978	2.982	100	2.969	2.969	80
031	2.955			2.975					
131	2.914						2.914	2.911	10
600	2.912	2.914	5						
240	2.886	2.885	<5				2.885	2.884	10
610	2.833	2.831	<5				2.832	2.830	10
421	2.737	2.740	30	2.750			2.737	2.737	60
501	2.709			2.720	2.724	40			
340	2.707	2.710	<5	2.707					
511	2.645			2.655					
331	2.635	2.638	35	2.648	2.629	20	2.635	2.635	20
620	2.629			2.625					
431				2.457					
710	2.445	2.446	30	2.440	2.442	20	2.444	2.444	35
150	2.422	2.423	5	2.424					
720	2.311	2.307	<5				2.310	2.307	10
800	2.184								
441	2.163	2.176	5						
701	2.157								
810	2.150	2.146	<5	2.145					
450	2.134			2.134					
051	2.125	2.130	<5	2.133	2.141	20			
102				2.141					
012	2.113	2.113	<5				2.114	2.114	<10
112	2.098	2.086	<5	2.125					
212				2.079					
251	2.065	2.060	5	2.072	2.071	20			
820	2.057								
060	2.038	2.041	<5						
402									
830	1.925	1.931	10						
232									
821	1.855	1.850	5						
920	1.850								
061	1.843								
422	1.837	1.834	5						
502	1.828								

Note: Conditions for data collection: Cap-Garonne—114.6-mm Gandolfi camera, Ni-filtered $\text{CuK}\alpha$, intensities influenced by perfect 100 cleavage. Coppin Pool—114.6 mm, Debye-Scherrer, Ni-filtered $\text{CuK}\alpha$, intensities estimated. Broken Hill—Guinier camera, Si internal standard, $\text{CuK}\alpha$, intensities visually estimated.

* Data provided by W. G. Mumme and E. H. Nickel (see Mumme and Nickel, 1987).

PARAGENESIS

At Cap-Garonne, the perroudite has crystallized following decomposition of Hg- and Ag-bearing tennantite by halide-bearing solutions, probably of marine origin.

At Broken Hill, the white kaolinite that hosts the Ag-

and Hg-bearing halides was locally derived by alteration of primary aluminosilicates such as sillimanite and feldspars. The original metamorphic rocks, mainly granitic gneisses, were weakly to strongly mineralized, mainly with galena and sphalerite. Release of S, Ag, and Hg during sulfide alteration, probably influenced by halide-rich so-

lutions, provided the necessary ingredients for perroudite crystallization. The source of the Hg is uncertain, as primary sulfides carrying significant Hg are not known within the ore bodies. However, Ag-rich tetrahedrite inclusions within galena are common in the primary ore, and this mineral may also be the source of the Hg. The high I concentrations in the oxidized zone at Broken Hill have not been satisfactorily explained, although it is possible that the presence of sea water has influenced mineralization during the long and complex history of development of the secondary zone.

At Coppin Pool, the presence of a number of Cl-bearing secondary minerals suggests that this element was present in abundance in the groundwater that was responsible for alteration of the primary sulfides (Nickel, 1985). Perroudite, cinnabar, and several new Hg-Ag sulfides indicate locally rich, but so-far unidentified, primary sources of Hg.

Whereas perroudite is obviously a rare and unusual mineral, its close physical similarity to cinnabar suggests that other occurrences may have gone unnoticed.

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