

Argentian mercurian tetrahedrite, a new variety, from the Chiprovtsi ore deposit, Western Stara-Planina mountains, Bulgaria

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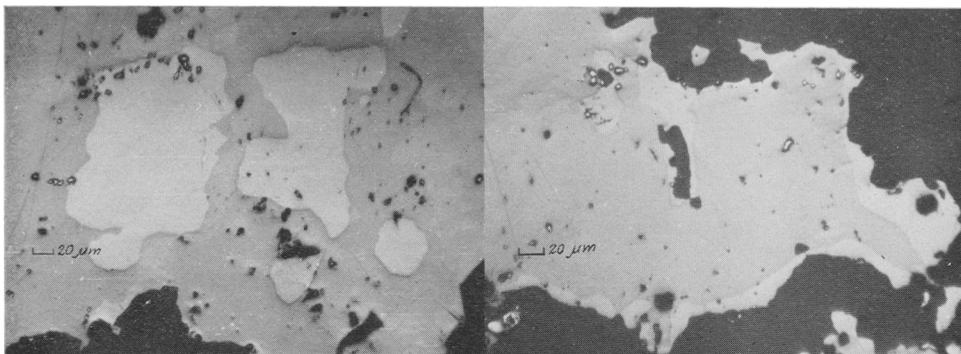
SUMMARY. An electron-probe microanalysis of tetrahedrite occurring together with the latest-deposited pyrite-cinnabar association in the Chiprovtsi lead-silver deposit yielded more than 16 wt. % Ag and more than 18 wt. % Hg. X-ray powder examination established an extremely large unit-cell edge, $a\ 10.64 \pm 0.01$ Å. Vickers microhardness 223 to 237 kg/mm². The chemical formula derived on the basis of the analyses made is quite near to $\text{Cu}_6^+(\text{Cu}^+, \text{Ag}^+)_4(\text{Hg}, \text{Zn})_2(\text{Sb}, \text{As})_4\text{S}_{13}$. There is not any antiparallelism between Ag and Hg in tetrahedrite. The name proposed for all stages of simultaneous isomorphic replacement along the Cu^+-Ag^+ and $\text{Cu}^{2+}-\text{Hg}^{2+}(\text{Zn}^{2+}, \text{Fe}^{2+})$ directions is argentian mercurian tetrahedrite. The upper limits of the Ag and Hg content are expected to be $\text{Cu}_6\text{Ag}_4\text{Hg}_2(\text{Sb}, \text{As})_4\text{S}_{13}$. It is the six copper atoms ($\text{Cu}_1^+, \text{Cu}_2^{2+}$), sited in the Laves' polyhedra, that are replaced by Ag^+ and Hg^{2+} respectively.

In conformity with X-ray chemical data, as well as structural considerations (Pauling and Neuman, 1934; Belov, 1952; Wuensch, 1964) the generally accepted formula of tetrahedrite is $(\text{Cu}, \text{Ag}, \text{Zn}, \text{Fe}, \text{Hg})_{12}(\text{Sb}, \text{As})_4\text{S}_{13}$. N. V. Belov (1952), E. K. Lazarenko (1956), and recently G. Springer (1969) and N. Shimada and F. Hirowatari (1972) emphasized the constancy of the ratio 10:2 between monovalent and divalent cations in the first part of the formula. In agreement with this I. Kostov (1957) has noticed a pronounced antiparallelism between Zn^{2+} and Fe^{2+} . So far there are no reliable data on the coexistence of mercury and the other elements. As for mercury and silver it should be pointed out that all of the analyses of freibergites quoted in the literature are practically without mercury and the same is valid for schwartzites, in which only traces of silver have been yet reported. Thus, the antiparallelism postulated to exist between Ag and Hg (Mincheva-Stefanova *et al.*, 1964) appeared to be justified.

Mode of occurrence. The Chiprovtsi lead-silver deposit is situated in the vicinity of the town of Chiprovtsi, Western Stara-Planina mountains, North-west Bulgaria. It is located in the strongly folded Pre-Cambrian and Lower-Palaeozoic core of the Berkovitsa anticlinorium, in which phyllites, graphite schists, diabases, diabasic tuffs, quartzites, albitophyres, marbles, and metamorphosed dioritic and gabbroid rocks take part (Dimitrov, 1964). These are intruded by non-metamorphosed gabbro, diorites, granodiorites, and granites.

All the ore bodies are confined to a well-expressed, but broken band of marbles. The ore mineralization is of a metasomatic origin. The commercial ores consist mainly of galena, sphalerite, pyrite, tetrahedrite, jamesonite, bournonite, stibnite, silver sulpho-salts, acanthite, and native silver. A body of about 10 m in size, almost

isometric in shape, was discovered in the easternmost part of the deposit, called either the Velin Dol or the Staina Chuka section. It consists mostly of pyrite, marcasite, cinnabar, fluorite, quartz, and calcite. Small amounts of tetrahedrite and sphalerite are also present in the ore body. The minerals mentioned above are younger than those of the main lead–silver mineralization and should be designated as a pyrite–cinnabar association. Tetrahedrite belonging to this typical mercury paragenesis occurs as grains, less than 0.5 mm in size, mostly included in cinnabar (fig. 1), but in places to be found outside it. Tetrahedrite rims around cinnabar grains are also

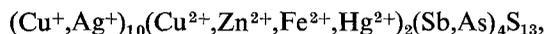


FIGS. 1 and 2: FIG. 1 (left). Argentian mercurian tetrahedrite (light grey) in cinnabar (grey). Reflected light without analyser. FIG. 2 (right). Argentian mercurian tetrahedrite (light grey) rimming and partly replacing cinnabar (grey). Reflected light without analyser.

to be frequently seen (fig. 2). Apparently this generation of tetrahedrite is deposited during the latest stages of deposition of cinnabar and sometimes partially replaces it. Our investigations concern tetrahedrite from the pyrite–cinnabar association only.

Chemical composition. Data on the chemical composition of tetrahedrite from the pyrite–cinnabar association in the Chiprovtsi ore deposit were obtained by electron-probe microanalysis. Three individual grains from a single polished section were analysed with a 'Cameca MS-46' apparatus in the Institute of Geology and Geophysics, Novosibirsk, USSR. The results are shown in Table I.

Natural chalcocopyrite (Cu), cinnabar (Hg), realgar (As), synthetic sphalerite (Zn), stibnite (Sb,S), and metallic silver (Ag) were used as standards. The intensity ratios measured were corrected for background, atomic number, absorption, and dead time by applying the formula described by G. Springer (1967). Radiation, accelerating voltage and probe current: Cu- $K\alpha$, 30 kV, 10 nA; Ag- $L\alpha$, 15 kV, 30 nA; Hg- $L\alpha$, 30 kV, 10 nA; Zn- $K\alpha$, 30 kV, 12.5 nA; Sb- $L\alpha$, 15 kV, 30 nA; As- $K\alpha$, 30 kV, 20 nA; S- $K\alpha$, 15 kV, 30 nA. No Fe, Bi, and Pb were found. The chemical formula of each grain analysed was calculated on the basis of 29 atoms per molecule. Two of the analyses gave an almost ideal formula,



as proposed by E. K. Lazarenko (1956) and confirmed by G. Springer (1969) and

N. Shimada and F. Hirowatari (1972). Analysis 3 shows certain deviations from the formula, which may be due to the inaccuracy of the electron-probe microanalysis. Nevertheless, the sum of the atomic quantities of divalent cations Hg and Zn is almost 2 and that of Sb and As is very near to 4 in all three analyses. It is the simultaneous high content of silver and mercury that is peculiar and new in the chemical composition of tetrahedrite from the mercury mineralization in the Chiprovtsi ore deposit. Thus, it cannot be denoted either as freibergite, or as schwartzite. There are no data for tetrahedrites of analogous composition in the literature.

TABLE I. *Chemical composition of tetrahedrite from pyrite-cinnabar association.*
Anal. Y. G. Lavrentiev

	1	2	3	1'	2'	3'
Cu	22.70	22.60	21.30	7.03	7.01	6.59
Ag	16.00	15.70	16.90	2.92	2.87	3.08
Hg	18.70	18.90	18.30	1.83	1.86	1.80
Zn	0.55	0.54	0.61	0.17	0.16	0.18
Sb	20.80	20.60	21.00	3.36	3.34	3.39
As	2.57	2.77	2.75	0.68	0.73	0.72
S	21.20	21.20	21.60	13.01	13.03	13.24
Total:	102.52	102.31	102.37	29.00	29.00	29.00

1, 2, 3: Electron-probe analyses of three grains from the Chiprovtsi deposit
1', 2', 3': Atomic ratios on a basis of 29 atoms

The *X-ray investigations* were carried out in the Higher Institute of Mining and Geology, Sofia, with a TUR-M60 apparatus. Due to the small amount of material available and the small size of the grains the X-ray powder data were obtained from a rubber ball preparation of 0.2 mm diameter. Material for preparation was taken from a single grain with a diameter of 0.15 mm in polished section. Filtered copper radiation was used in a 57.3 mm camera. Internal standard NaCl. The results are listed in Table II.

All the spacings known for tennantite, tetrahedrite, and freibergite were recorded, except for d_{066} , the latter being present in the powder pattern of typical freibergites (Berry and Thompson, 1962; Shimada and Hirowatari, 1972). Its absence is probably due to the extremely small quantity of the material analysed. The X-ray powder pattern exhibits a very large unit-cell edge a 10.64 ± 0.01 Å. It was calculated from the d_{356} , d_{266} , and d_{048} . In addition, 8 other grains of argentine mercurian tetrahedrite from the same ore body were examined and gave a values ranging from 10.62 to 10.67 Å. Evidently they also indicate a simultaneous and high content of Ag and Hg. So far the biggest unit-cell measured for the minerals of tetrahedrite-tennantite series was that of freibergite, a 10.564 ± 0.005 Å (Shimada and Hirowatari, 1972).

Physical properties. Argentine mercurian tetrahedrite is steel-grey with metallic lustre. No cleavage was observed. Under the microscope it is white-grey, with a yellowish tint. Polishing hardness is greater than that of cinnabar and almost equals

that of sphalerite. Internal reflections were not observed. The Vickers microhardness determined from 50 measurements is 223 to 237 kg/mm². It is considerably lower than that of the typical tetrahedrites and tennantites, and is slightly lower than freibergite with silver content of 22.2 wt. % (Atanasov, 1973). The measurements were carried out with a PMT-3 equipment, using a load of 50 g. Under a load of 5 g a value of 20.5 kg/mm² was measured for natural NaCl standard.

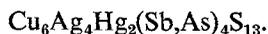
Diagnostic etch reactions: HCl 1:1, KOH 40 %, FeCl₃ 20 %, all without effects. HNO₃ 1:1, a brown, easily wiped off coating. HgCl₂ 5 %, slight surface etching. KCN 20 %, slight surface etching and a display of cracks and polishing scratches.

TABLE II. X-ray powder pattern of argentine mercurian tetrahedrite

<i>hkl</i>	<i>d</i> _{meas}	<i>I</i>	<i>d</i> _{calc}	<i>hkl</i>	<i>d</i> _{meas}	<i>I</i>	<i>d</i> _{calc}
1	2	3	4	5	6	7	8
112	4.35 Å	3	4.34 Å	136	1.569 Å	1	1.569 Å
022	3.77	2	3.76	444	1.538	2	1.536
222	3.08	10	3.07	017, 055, 345	1.507	1	1.505
123	2.85	2	2.84	127, 255, 336	1.448	1/2	1.448
004	2.66	5	2.66	246	1.422	1/2	1.422
033, 114	2.52	3	2.51	237, 156	1.352	1	1.351
024	2.38	1	2.38	008	1.332	1	1.330
233	2.26	1	2.27	118, 147, 455	1.309	1	1.309
224	2.17	1/2	2.17	356	1.273	2	1.272
015, 134	2.085	3	2.086	057, 138, 347	1.238	1	1.237
125	1.941	3	1.942	266	1.221	3	1.220
044	1.883	8	1.881	048	1.189	1	1.190
035, 334	1.826	1	1.824	019, 338	1.176	1/2	1.175
006, 244	1.778	1/2	1.773	129, 167, 556	1.148	1	1.147
116, 235	1.727	3	1.726	039, 158, 457	1.123	1	1.122
026	1.684	1	1.682	239, 367	1.097	1/2	1.097
145	1.646	1	1.642	448	1.087	4	1.086
226	1.605	6	1.604				

Discussion. The chemical data in Table I indicate beyond doubt that there is no antiparallelism between Ag and Hg in tetrahedrite. The fact that the sum of divalent metals Hg and Zn is so close to 2.00 suggests that they occupy the positions of divalent copper in the ideal formula of the mineral. For this reason it could be suggested that 2 formula units are the upper limit of Hg in the tetrahedrite structure, and the antiparallelism between Zn and Fe (Kostov, 1957) should be extended, including Hg. At the same time the percentage of Hg in Table I is the highest known for natural tetrahedrites (schwartzites). The amount of silver (about 3 formula units) in the argentine mercurian tetrahedrite from the Chiprovtsi ore deposit is lower than the highest known; N. Shimada and F. Hirowatari (1972) reported 23.85 wt. % in mercury-free tetrahedrite, which is close to 4 formula units, a figure that can be suggested for an upper limit of the monovalent copper-silver isomorphism. Thus, argentine mercurian tetrahedrites containing larger amounts of Ag than those in Table I could be expected. To this effect it is interesting to note that the sum of the atomic units

involved in the Cu^+-Ag^+ and $\text{Cu}^{2+}-\text{(Zn}^{2+}, \text{Fe}^{2+}, \text{Hg}^{2+})$ isomorphism is six, half the total copper in the formula $(\text{Cu}_6^+)^{\text{iv}}(\text{Cu}_4^+\text{Cu}_2^{2+})^{\text{iii}}(\text{Sb, As})_4\text{S}_{13}$. So far there are no direct data as to which group of six copper atoms can be replaced by Ag, Hg, Zn, and Fe, whether those in the tetrahedral positions (iv), or those of trigonal coordination (iii) in the Laves' polyhedra. Nor is there any agreement concerning the particular positions of divalent copper. N. V. Belov (1952), E. K. Lazarenko (1956), and Mincheva-Stefanova *et al.*, (1964) consider that Cu^{2+} is trigonally coordinated. An alternative opinion has been advanced by M. S. Sakharova (1966) and L. N. Indolev *et al.* (1971). It should be noted that in sulphides containing copper in a tetrahedral coordination the Cu–Ag–Hg isomorphism, if present, is confined in very narrow limits. On the contrary, the Cu–Ag and Cu–Hg isomorphism are quite well represented in sulphosalts, where copper atoms may occupy different positions. Thus, it can be expected that not the copper of tetrahedral coordination in tetrahedrite structure, but all of the monovalent copper (up to 4 atomic units) and all of the divalent copper (up to 2 atomic units) in the Laves' polyhedra could be replaced by Ag^+ and $(\text{Zn}^{2+}, \text{Fe}^{2+}$ and $\text{Hg}^{2+})$ respectively leading to the formula



The name suggested for all stages of simultaneous isomorphic replacement along the Cu^+-Ag^+ and $\text{Cu}^{2+}-\text{Hg}^{2+}$ ($\text{Zn}^{2+}, \text{Fe}^{2+}$) directions is argentine mercurian tetrahedrite.

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