

# THE AMERICAN MINERALOGIST

JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

Vol. 56

NOVEMBER–DECEMBER

Nos. 11 and 12

## HEMUSITE—A COMPLEX COPPER-TIN-MOLYBDENUM SULFIDE FROM THE CHELOPECH ORE DEPOSIT, BULGARIA

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### ABSTRACT

Hemusite, a new mineral with the formula  $\text{Cu}_6\text{SnMoS}_8$ , was found in the copper ore deposit of Chelopech, Bulgaria, in association with enargite, luzonite, colusite, stannoidite, renierite, tennantite, chalcopyrite, pyrite, and other minerals. It occurs as rounded isometric grains and aggregates usually about 0.05 mm in diameter.

Hemusite has a gray color, metallic luster, and moderate hardness (about 4, Mohs). In reflected light it is violet-gray to ash-gray, isotropic, with low reflectivity (469 nm 23.4, 518 nm 24.9, 589 nm 24.2, 668 nm 23.4%).

Microprobe analyses indicate small amounts of Fe, V, As, and Se in the mineral.

The X-ray pattern is indexed on a cubic lattice,  $a = 10.82 \text{ \AA}$ . The strongest lines are 3.11(10)(2.22), 1.919(5)(044), 1.858(3)(035), 1.632(3)(226). Single crystal studies could not be made.

The name is from the ancient name of the Balkan Mts., in the Southern slope of which the Chelopech ore deposit occurs.

### INTRODUCTION

During microscopic studies of the copper ores from the Chelopech deposit in Bulgaria in 1963, small grains of a mineral with unusual optical properties were observed. Further detailed investigations of the chemical composition and properties of the mineral confirmed the original assumption that it is an independent species. The mineral was named hemusite after the locality of its finding.<sup>1</sup>

### PHYSICAL AND OPTICAL PROPERTIES

Hemusite has a gray color and metallic luster. It is non-magnetic. A microhardness of 210–215 kg/mm<sup>2</sup> was determined with a Hanemann's indenter, corresponding to approximately 4 on the Mohs scale.

In reflected light the mineral is violet-gray to ash-gray, isotropic, with a low reflectivity. The results of reflectivity measurements, taken with

<sup>1</sup> The mineral and the name have been approved by the Commission on New Minerals and Mineral Names, International Mineralogical Association.

TABLE 1. REFLECTIVITY OF HEMUSITE IN AIR

$\lambda m\mu$	R%
433	21.8
469	23.4
482	23.8
518	24.9
559	24.7
589	24.2
624	23.8
668	23.4
691	23.3

an apparatus with a photomultiplier of the Bernstein system, are shown on Table 1.

Hemusite polishes well. Etch tests with  $\text{HNO}_3(1:1)$ ,  $\text{HCl}(1:1)$ , KCN, KOH,  $\text{HgCl}_2$ , and  $\text{FeCl}_3$  are negative.

#### CHEMICAL COMPOSITION

The composition of hemusite was determined by electron-probe analysis. Several different types of instruments were used. Variations in the conditions of the analyses and standards were also applied. The results so obtained showed satisfactory agreement. The deviations of the measurements from their average were as follows: Cu:3.0 percent, Sn:0.8 percent, Mo:6.8 percent, S:6.3 percent. Three of the analyses are presented on Table 2. They were repeated and the values confirmed after repolishing the sections in order to make sure that the hemusite grains were larger than the depth of penetration of the electron beam. The results include corrections for the absorption of the X rays and for the atomic number effect. The distribution patterns of the elements, obtained by scanning of the portion of the polished section containing hemusite grains (Fig. 1), are shown on Figure 2.

The chemical composition of hemusite closely corresponds to the formula  $\text{Cu}_6\text{SnMoS}_8$ .<sup>1</sup> The small amounts of Fe, V, and As, detected in the mineral, probably replace Sn-atoms, and Se replaces S-atoms.

<sup>1</sup>In the early stages of the investigation some difficulties in determination of the chemical composition of the mineral arose in connection with the small size of the grains. The first analyses indicated high content of As and Fe (later established to be due to the excitation of the surrounding enargite and pyrite) and no Mo. I reported the progress of the study at the 7th Congress of the Carpatho-Balkan Geological Association in 1965 which led to the publication of the name and the tentative formula with a question mark, in the proceedings of the Congress (Terziev, 1965) and also in some later publi-

Table 2. Electron-microprobe analyses of hemusite

Numbers of analyses	Elements - Weight %								
	Cu	Sn	Fe	V	As	Mo	S	Se	Total
1	45.3	12.8	1.2	0.1	0.1	11.2	29.8	0.1	100.6
2	47.6	12.9	1.8	-	-	10.5	29.0	-	101.8
3 <sup>+</sup>	43.6	12.8	2.6	-	0.1	11.7	28.0	-	98.8
Theoretical values	44.73	13.92	-	-	-	11.26	30.09	-	100.00

<sup>+</sup> Analyst T. Padfield.

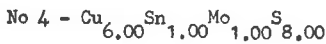
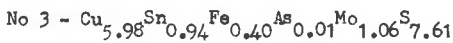
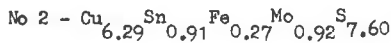
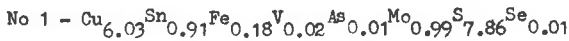
Conditions of the analyses:

No 1 - instrument Cameca-46, acc. volt. 20 kV,  
standards pure metals, stannite, chalcopyrite, and pyrite;

No 2 - instrument Cameca-46, acc. volt. 15 kV,  
standards pure metals and chalcopyrite;

No 3 - instrument AEI, acc. volt. 15 kV,  
standards stannite and molybdenite.

Formulas:



#### X-RAY INVESTIGATIONS

The X-ray powder diagram of hemusite was obtained from a few micrograms of the mineral in a spheroidal rubber-paste sample with 0.4

cations (Terziev, 1966b, 1968). The name was included in some lists of new mineral names (Bonshtedt-Kupletskaya, 1968, Fleischer, 1968) with a formula (and without any question mark), slightly different from that published previously by me.

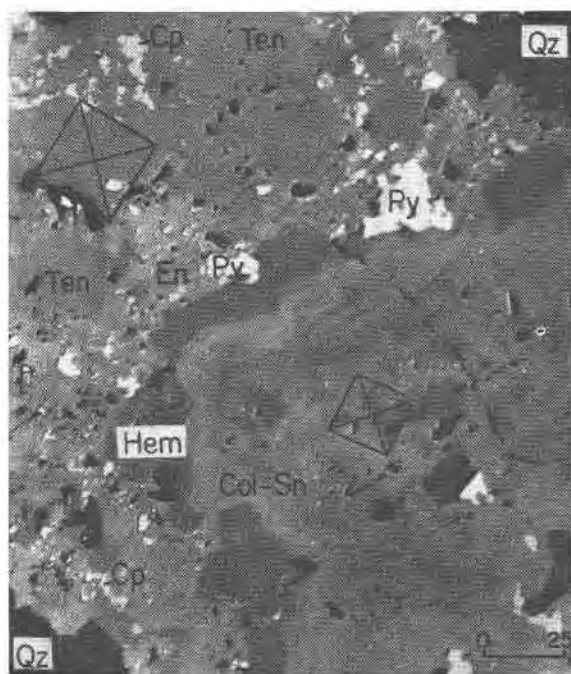


FIG. 1. Hemusite-containing portion of the surface of the polished section, which was examined by an electron-probe X-ray microanalyzer. Photomicrograph, air. Hem—hemusite, Col-Sn—colusite-stannoidite aggregate, Py—pyrite, Ch—chalcopyrite, En—enargite, Ten—tennantite, Qz—quartz, crossed squares—indication marks made by a diamond pyramid.

mm diameter, applying the method of Hiemstra (1956) as improved by Ghenkin and Korolev (1961). Three samples were analyzed separately and later amalgamated in a single sample in order to increase the quantity of the mineral in the sample. The results were similar. All the X-ray powder diagrams show a relatively small number of lines. The results of the calculations of one of the diagrams are presented in Table 3.

The X-ray diagrams were indexed in the cubic system with  $a$  10.82 Å. The small dimensions of the grains did not allow a more detailed structural investigation. The X-ray data however suggest a close relation to the stannite group. A probable structural model of the mineral is a stannite type of lattice with a unit cell of 4 ( $\text{Cu}_6\text{SnMoS}_8$ ) where each S-atom is surrounded by three Cu- and one Sn- or Mo-atom, as illustrated in Figure 3. The slight increase in the value of  $a$  = 10.82 Å in hemusite in comparison with the value of  $c$  = 10.72 Å in stannite may be due to the

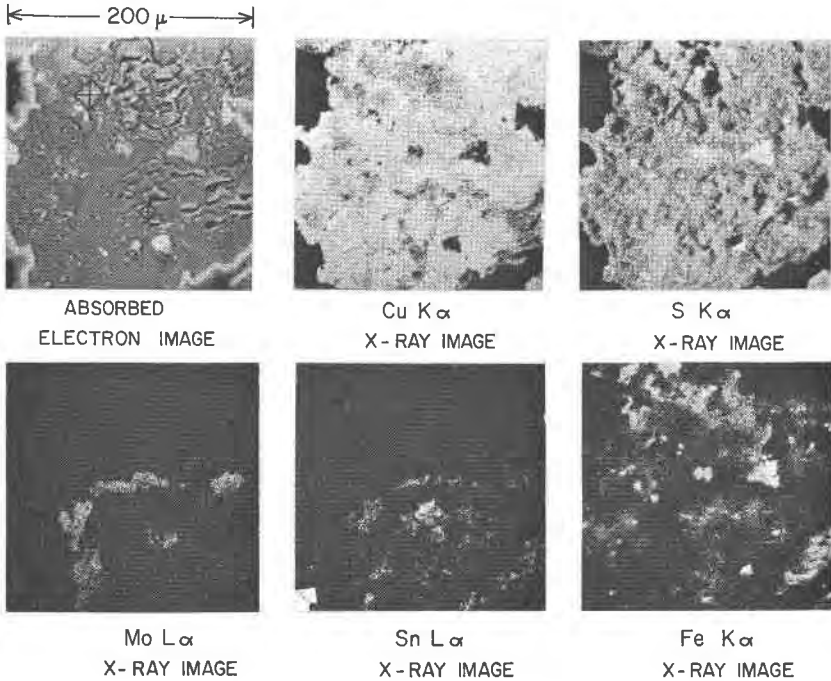


FIG. 2. Scanning images of the hemusite-containing portion of the surface of the polished section, shown on Fig. 1, with the distribution patterns of the elements. Electron-probe microanalyzer JXA-3, acc. volt 15 kV.

increased number of Cu-atoms in the lattice, replacing the smaller Fe-atoms.

#### OCCURRENCE AND PARAGENESIS

The ore deposit of Chelopech in which the mineral was found is complex. It contains predominantly copper, but also lead-zinc and barite bodies, represented by irregular replacements of Upper Cretaceous propylitized andesites. The main ore minerals are pyrite, chalcopyrite, tennantite, enargite, luzonite, bornite, galena, and sphalerite. A considerable number of minerals in small amounts is also present (Terziev, 1966a; 1968). The ores contain Au, Ag, Se, Te, Bi, Tl, Sn, Ga, Ge, Mo, and other trace elements.

There is a distinct horizontal and vertical zoning in the distribution of the minerals (Terziev, 1965; 1966b; 1968): copper ore bodies are found in the deeper levels while the lead- and zinc-containing minerals

Table 3. X-ray powder diffraction data for hemusite

I	d Å (meas.)	hkl	d Å (calc.)
2	3.61	{003} {112}	3.61
2	3.38 $\beta$	222	-
10	3.11	222	3.12
2	2.87	123	2.89
1	2.71	004	2.71
2	2.55	{033} {114}	2.55
1	2.22	224	2.21
2	2.09	{115} {333}	2.08
2	2.00	{025} {234}	2.01
5	1.919	044	1.914
3	1.858	035	1.856
1	1.757	{116} {235}	1.756
3	1.632	226	1.632
1	1.595	136	1.596

Intensities by visual estimate. Camera TuR (2R 57.3 mm), 35 kV, 16 mA. Unfiltered Cr radiation. Calibrating substance silicon.

are above and around them. Uppermost is a barite zone locally enriched in fluorite. Within the copper zone, a chalcopyrite-tennantite-pyrite association gradually gives way at depth to a luzonite-enargite-pyrite association which in turn is locally replaced by a bornite-pyrite zone at the deepest levels.

Hemusite was established in the luzonite-enargite-pyrite zone of

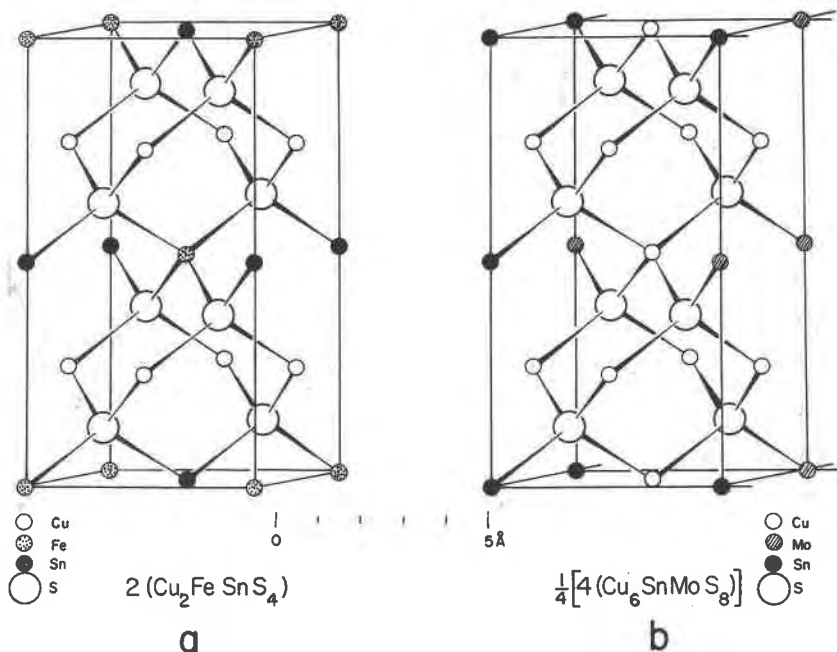


FIG. 3. A model of the structure of hemusite (b) compared with stannite (a).

copper ores in close association with other minor minerals such as colusite, stannoidite ( $\text{Cu}_5\text{Fe}_2\text{SnS}_8$ ), renierite, chalcopyrite, and tennantite. Hemusite occurs in rounded isometric grains and aggregates of irregular shape. The size of the grains is usually about 0.05 mm in diameter. In some cases hemusite surrounds the zonal colusite-stannoidite aggregates forming relatively large accumulations up to 0.1 mm wide and 1.0 mm long in cross sections (Fig. 4). Hemusite is one of the first to be formed amongst the minerals in the association.

#### NAME AND TYPE MINERAL

The name of the mineral is from the ancient name of the Balkan Mts., in the Southern slope of which the Chelopech ore deposit occurs. The name of the mountains, probably of Thracian origin, was spelled in Greek as  $\chi\alpha\mu\upsilon\sigma$  and passed to Latin as *Hæmus*. In some 18th century, and more recent, French literature it was spelled as *Hémus*. The spelling *Hémus* is accepted in modern European languages with the Latin alphabet. In languages with the Cyrillic alphabet the original spelling *Xemyc* is still preserved.

Samples of the mineral are kept in the Mineralogical Museum of the

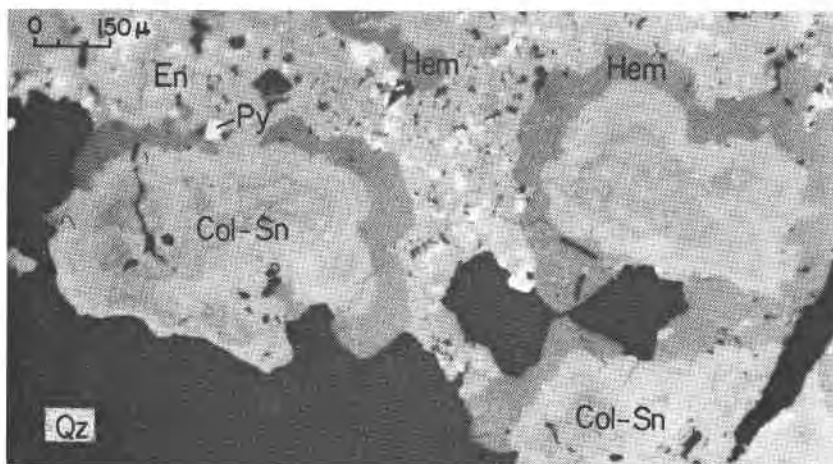


FIG. 4. Hemusite (Hem) surrounding spheroidal zonal colusite-stannoidite aggregates (Col-Sn). Py—pyrite, En—enargite, Qz—Quartz. Photomicrograph, air.

University of Sofia, Bulgaria and in the mineralogical collections of the Geological Institute of the Bulgarian Academy of Sciences.

#### ACKNOWLEDGMENTS

The author is indebted to T. Padfield from the Department of Earth Sciences, the University of Leeds, England, who analyzed a sample of hemusite, and also to the management of the CAMECA and JEOLCO in Paris, France, for the facilities provided for the microprobe analyses of the mineral.

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*Manuscript received, April 10, 1971; accepted for publication, May 24, 1971.*