



HETAEROLITE FROM MADJAROVO AU-BASE-METAL DEPOSIT, EASTERN RHODOPE

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Hetaerolite is a Zn-Mn oxide mineral with composition corresponding to the formula $ZnMn_2O_4$; it has a tetragonal spinel-type structure and according to Frondel and Heinrich (1942) represents a Zn analogue of hausmannite ($Mn^{2+}Mn^{3+}_2O_4$). The mineral is quite rare. It was discovered in Sterling Hill, New Jersey and was later found in Franklin, New Jersey and Leadville, Colorado (Frondel and Heinrich, 1942), as well as in some other deposits in the USA (Bevins et al., 1987).

Only few findings of this mineral in Europe have been reported: Rodna, Romania (Udubasa et al., 1973); Moresnet, Belgium (Fransolet and Melon, 1975); Eastern Cliff, Cornwall, UK (Bevins et al., 1987) and Mont Chemin, Switzerland (Meisser and Perseil, 1993).

In Bulgaria, hetaerolite was diagnosed in two Pb-Zn deposits from Madan ore field, Central Rhodopes: Kechi Kaya (data from N. Zidarov, after Kostov et al., 1964) and Varba (Kolkovski, 1966).

Hetaerolite was determined in samples from the oxidizing zone of quartz-sulphide veins from Madjarovo deposit (Patronkaya section, ore vein No 5) in association with quartz, chalcophanite, coronadite, pyrolusite, goethite and other Mn and Fe oxides and hydroxides.

Madjarovo Au-base metal deposit is situated in the Eastern Rhodopes and is related to the central part of an Oligocene volcano-plutonic structure. Volcanic rocks are represented mainly by shoshonitic and high-K Ca-alkaline rocks, latite predominating. The ore mineralization is of vein type, epithermal, low-sulphidation, located along radiate faults. Ore veins are quartz, quartz-barite and quartz-calcite in composition with different quantity of sulphides. The mineral forming process is a poly-stage one. Different researchers describe various stages of mineralization (Radonova, 1960; Atanasov, 1962; Kolkovski, 1971 – after Breskovska et al., 1976; Breskovska and Gergelchev, 1988; Breskovska and Tarkian, 1993). Kolkovski et al. (1974) divide the following hypogene stages: quartz-specularite, quartz-chalcopyrite, quartz-galena-sphalerite, quartz-chalcedony-barite and calcite-quartz. Most often the oxidizing zone is well expressed, reaching in depth up to 300 m. Over 50 supergene mineral phases are determined – goethite, Mn oxides and hydroxides, phosphates, carbonates, sulphates and others.

The chemical composition and infrared spectrum of the mineral were examined and the paragenetic, morphological and structural peculiarities were studied. X-ray powder diffraction patterns are obtained on DRON-1 diffractometer (CuK α , Ni filter) and TUR-M-60 equipment (III 57.3 mm camera) in UMG "St. Ivan

Rilski". Quantitative microprobe analyses are accomplished using scanning electron microscope JEOL JSM 35 CF with Tracor Northern TN 2000 EDEX system in the laboratory of EUROTTEST Plc., Sofia. The following standards were used: for Mn, Fe, Zn – pure metals, for Mg, Ca, Si – diopside, for K – biotite, for Al – corundum, for Pb – PbTe. Infrared spectrum is registered on infrared spectrophotometer Perkin Elmer FTYR PE-1600 within region 400 – 1600 cm^{-1} .

Samples, in which hetaerolite was found have a porous fabric, set up mainly by quartz and black banded to lens-like aggregates from Mn oxide and hydroxide minerals. The mineral forms massive, radiate or fibrous aggregates with black to black-brown colour, semi-metallic lustre, yielding a dark brown streak. It shows high hardness (6 according to Mohs scale). Observed in reflected polarized light, hetaerolite is grey in colour, with distinct anisotropy and red internal reflections. Single hetaerolite individuals are isometric, with rectangular, rhombic or rounded shape and size up to 250 μm (Plate I – a, b). The mineral also occurs as granular, feather-like, radiated, needle-like and fibrous aggregates (Plate I – d) often with developed crystal faces. It is associating with quartz, chalcophanite, coronadite, pyrolusite and semi-amorphous Mn-hydroxides with desiccation cracks in some cases. In some investigated polished sections it is in close association with goethite and relicts from sulphide minerals, mainly pyrite. In general the mineral is earlier formed, compared with accompanying Mn oxide and hydroxide minerals – chalcophanite, coronadite, pyrolusite (Plate I – c). A manifested tendency in the succession of mineral forming is hetaerolite – coronadite – chalcophanite – pyrolusite – chalcophanite and it is connected with initial increase of O $_2$ partial pressure in supergene zone and consecutive restriction of oxygen regime.

Quantitative microprobe analyses data (Table 1) show that hetaerolite from Madjarovo deposit is quite similar in composition to the hetaerolite from Eastern Cliff, Cornwall, UK (Bevins et al., 1987), as well as to that from Sterling Hill, New Jersey, USA (Frondel and Heinrich, 1942). Compared with its theoretical composition small deficit of Zn $^{2+}$ is observed, compensated probably by presence of Mn $^{2+}$ as structural admixture (Dana et al., 1946; Frenzel, 1980). Insignificant deviation in stoichiometry is typical for hetaerolite and is mentioned by different authors. A single case of Zn $^{2+}$ excess and Mn $^{3+}$ deficit is described about Pb-bearing

hetaerolite from Rodna deposit, Romania (Udubasa et al., 1973).

Hetaerolite is a mineral with spinel type structure and formula $A^{2+}B^{3+}O_4$, where Zn^{2+} is taking A position in tetrahedral coordination, while Mn^{3+} is in B position in octahedral coordination with oxygen anions (Frenzel,

1980). It is considered that isomorphic replacement of Zn^{2+} by Mn^{2+} is possible, due to the similar ionic radius of the two types cations.

X-ray powder diffraction data obtained coincide with the standard pattern (JCPDS 24-1133).

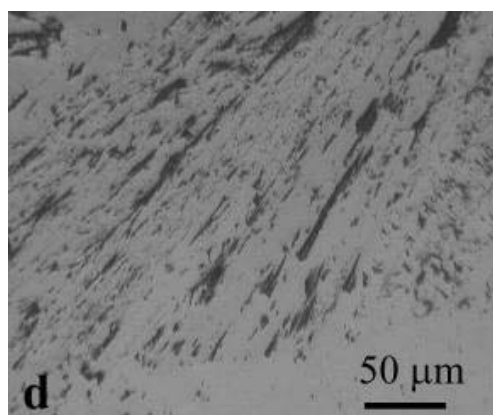
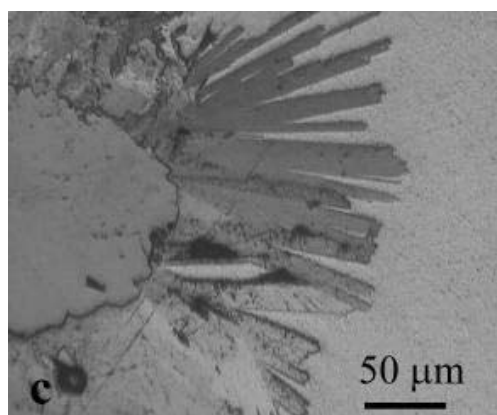
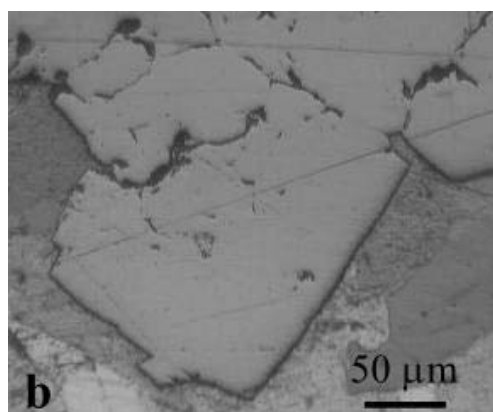
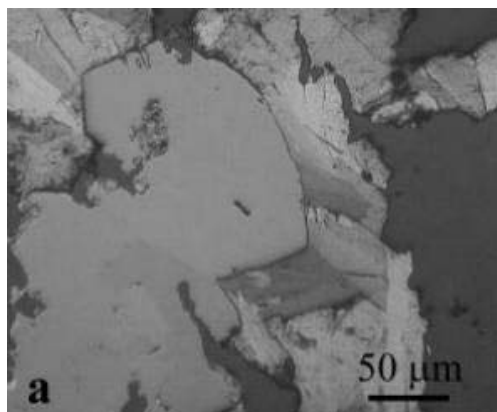


PLATE I. Morphology of hetaerolite from Madjarovo deposit. Reflected polarized light, N //.

a – Hetaerolite (grey) – hypidiomorphic individuals and granular aggregates, corroded by flaky chalcophanite (grey-whitish) and quartz (dark grey).

b – Hetaerolite (grey with high relief) among mass of chalcophanite.

c – Growth of elongated prismatic chalcophanite individuals on hetaerolite ground (grey with high relief at the left). Whitish mineral at the right represents Mn-hydroxide.

d – Two varieties of hetaerolite – radiate-fibrous and massive (at the bottom).

The infrared spectrum (IRS) of hetaerolite from Madjarovo deposit is quite similar to those registered by other authors for this mineral (Kulig, 1972, 1973; Udubasa et al., 1973). Two intense absorption bands are characteristic with maximums at 627 and 534 cm^{-1} and two poorly expressed ones at 422 and 405 cm^{-1} . In the IRS obtained several additional bands with low intensity are observed, determined by the presence of impurities from different mineral phases – chalcophanite and quartz.

In the oxidizing zone of Madjarovo deposit hetaerolite is found in close association with quartz, chalcophanite, coronadite, pyrolusite, goethite and other Mn and Fe oxide and hydroxide minerals. Most commonly hetaerolite is accompanied by chalcophanite, but compared with the latter one it is in minor amount. The source of Zn for both minerals is ZnS from primary sulphide mineralization in the deposit.

Table 1. Representative electron microprobe analyses of hetaerolite.

Oxides	Samples (wt. %)						
	1	2	3	4	5	6	7
Mn ₂ O ₃	65.98	64.21	64.17	67.20	66.99	67.89	68.37
MnO	-	1.86	-	-	-	-	-
ZnO	34.02	32.46	31.98	32.60	31.99	31.77	31.07
Fe ₂ O ₃	-	0.24	0.15	0.17	0.57	0.05	-
CaO	-	-	-	-	0.01	-	0.12
MgO	-	0.49	-	-	-	-	-
SiO ₂	-	0.18	2.26	-	0.44	0.21	0.41
TiO ₂	-	-	0.38	-	-	-	-
K ₂ O	-	-	-	-	-	0.07	0.02
CuO	-	-	0.58	-	-	-	-
H ₂ O	-	0.19	-	-	-	-	-
Σ	100.00	99.63	99.52	99.97	100.00	99.99	99.99
Cations	Formula proportions based on four oxygen atoms						
Mn ³⁺	2.00	1.97	2.00	2.03	2.02	2.05	2.06
Mn ²⁺	-	0.06	-	-	-	-	-
Fe ³⁺	-	0.01	-	0.01	0.02	-	-
Zn ²⁺	1.00	0.97	0.97	0.95	0.94	0.93	0.91
Cu ²⁺	-	-	0.02	-	-	-	-
Σ	3.00	3.01	2.99	2.99	2.98	2.98	2.97

1. ZnMn₂O₄ (Dana et al., 1946); 2. Hetaerolite, Sterling Hill, New Jersey, USA (Fron del and Heinrich, 1942); 3. Hetaerolite, Mont Chemin, Switzerland (Meisser and Perseil, 1993); 4. Hetaerolite, Eastern Cliff, Cornwall, UK (Bevins et al., 1987); 5, 6, 7. Hetaerolite from Madjarovo deposit, Eastern Rhodopes.

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