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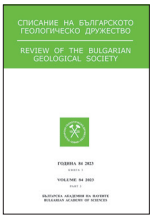

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Millerite from the Madan ore field

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Милерит от Маданско рудно поле

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Abstract. Millerite is discovered in samples from Krushev Dol and Mogilata deposits in the Madan ore field. It was found in two associations different in appearance and mineral composition. One of them is with light green ferrodolomite, and the other with bright green mariposite (chromium-bearing phengite). Only cobalt and iron are detected as impurity elements in some analyses. They are in small concentrations (below 0.01 apfu). The Ni/S ratio is 0.95. The nickel source is associated with bodies of serpentinized ultramafics cut by ore-bearing veins.

Keywords: millerite, mariposite, Madan ore field.

Introduction

Millerite is found in several deposits in Bulgaria. It was described as small needles around chromite grains in serpentinitized ultrabasic rocks in Gornoslav (Kostov et al., 1964) and among chromite bodies and serpentinitized ultrabasic rocks near the village of Dobromirtsi (Kerestedjian et al., 2007). Millerite, associating with chromium-bearing muscovite (fuchsite) was found in the hydrothermally altered rocks around the ore bodies at Sveta Marina, Haskovo region (Atanassov, Vitov, 1981). In all listed above cases, millerite is hydrothermal in origin and the source of nickel is associated with the serpentinized ultramafics.

So far, the presence of millerite has not been detected in Madan ore field. There aren't any data for the presence of serpentinized ultramafics, nevertheless Bonev et al. (1996), describing chromium-bearing mica-mariposite in the Madan hydrothermal deposits, suggested that because of the limited mobility of chromium in hydrothermal conditions, small ultramafic bodies intersected by the ore zones are most likely the source of chromium.

During the fieldwork in the Madan mines, millerite mineralization and several small bodies of serpentinized ultramafics (ophiolites) intersected by the ore-bearing faults are found in Krushev Dol (level 650) and Mogilata Sever deposits (level 760).

Geological setting

The hydrothermal Pb-Zn deposits are situated in the central part of the Rhodope Massif in Bulgaria, referred as the Central Rhodope (Madan) Dome (Ivanov et al., 2000). The core of the dome consits of high-grade otho- and parametamorphic rocks distingusihed as the Arda unit (Ivanov et al., 2000). Small bodies of metamorphosed ultramafics (parts of an ophiolite complex) were found among the metamorphites of the unit.

Studies on the main ore minerals: galena, sphalerite, pyrite and chalcopyrite and less common ones such as arsenopyrite, tetrahedrite, tennantite, pyr-

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rhotite, silver and bismuth sulfosalts have been carried out by many authors, and the results have been published in dozens of works. A summary of the results of these studies can be found in Kolkovski and Manev (1988) and Vassileva et al. (2009). No nickel minerals were established in this ore field.

Materials and methods

The samples from the Krushev Dol mine represent pale green carbonate druse on a matrix and a piece of green sericite. They were collected by the mine geologists in 2012. A pale green carbonate druse from the Mogilata deposit was collected by Mehmed Karadzhov in 2023 and donated by Georgi Bozoukov.

Photos of the material were taken with SONY alfa 6000 camera at daylight illumination. To study the NiS structure an X-ray single crystal diffractometer Bruker D8 Venture was used. The data collection and data reduction were performed by CrysAlisPro. The crystal structure was solved ab initio with program for crystal-structure refinement SHELXT and refined by the full-matrix least-squares method of F2 with ShelxL programs. Scanning Electron Microscope (SEM) fitted with Energy Dispersive Spectrometer (EDS) performed the SEM investigations and chemical analysis of the samples. Internal standards are used. Apparatus JEOL – model JSM-6010PLUS/LA with a 20 kV accelerating voltage, spot size 70 nm and EDS detector with resolution over 129 eV MnKa were used.

Results and discussion

Millerite in the Madan ore field is found in two associations different in appearance and mineral composition. One of them is with light green ferrodolomite. It was observed in samples from both the Krushev Dol and Mogilata deposits. The average carbonate composition is $Ca_{0.46}Mg_{0.47}Fe_{0.06}CO_3$, with the concentration of iron in the dolomite varying from 0 to 0.09 apfu. In the sample from the Krushev Dol deposit, individual millerite needles are more common than radial aggregates (Fig. 1b). The cross-section of the needles varies from 20 to 100 μm, and the length from 0.2 to 1 mm. The sizes of the aggregates reach up to 2 mm. At the Mogilata deposit, millerite occurs as radial fans of acicular crystals of bronze colour in a base of white dolomite or covered with free-grown green ferrodolomite crystals. Millerite crystals are thin, long prismatic to whisker-like (Fig. 1a). The cross-section of the crystals varies between 20 and 200 μm, and their length can reach up to 6 mm. No complete crystal terminations were observed.

In the other association millerite is among flakes of bright green mariposite – chromium-bearing phengite. The crystal chemical formula of the mica is $K_{0.68}(Al_{1.66}Cr_{0.18}Mg_{0.15}Fe_{0.01})(Si_{3.49}Al_{0.51}O_{10})(OH)_2$. The mica flakes, up to several millimetres in size, are bent probably by tectonics. Millerite crystals among the mica are very often also bent and deformed (Fig. 1d). Lengthwise striation is noticeable in most of the crystals (Fig. 1d). The colour of millerite is light bronze to dark grey on an oxidized surface. In this association, among the white dolomite, the millerite crystals are smaller and of a long-prismatic to acicular habit, and among the mica they are larger and of a prismatic to long-prismatic habit (Fig. 1b, c). Crystals of different size are often found together in a single radial aggregate. As a rule, there are not many other sulphide minerals around the millerite crystals, or if there are, they are scarce sphalerite (cleophane) or pyrite crystals up to 2 mm in size. Black chromite grains up to 2–3 mm

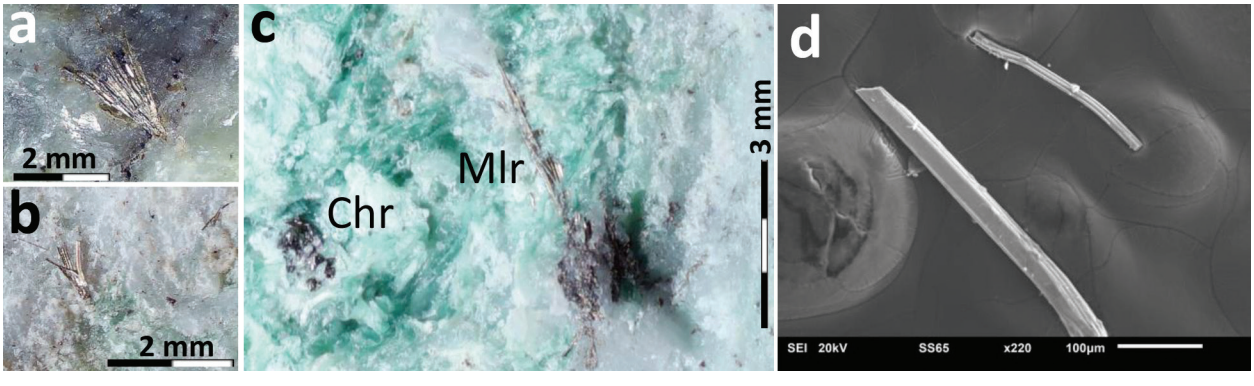

Fig. 1. *a*, millerite radial fan of acicular crystals within dolomite (Mogilata deposit); *b*, millerite within dolomite (Krushev Dol deposit); *c*, millerite and chromite within green mariposite (Krushev Dol deposit); *d*, SEM microphotographs of millerite crystals (Krushev Dol deposit)

Table 1. SEM-EDS analyses of millerite from the Madan ore field (in wt %)

Deposit	Krushev Dol, mean of 7		Mogilata, Mean of 14		Madan ore field, Mean of 21	
		Stand. deviation		Stand. deviation		Stand. deviation
Fe	0.20	0.35	0.00	0	0.07	0.21
Co	0.52	0.19	0.08	0.16	0.23	0.27
Ni	62.55	2.25	63.67	2.02	63.30	2.07
S	36.73	2.03	36.25	1.94	33.41	1.89
	apfu		apfu		apfu	
Fe	0.003	0.006	0.000	0	0.001	0.003
Co	0.008	0.003	0.002	0.002	0.003	0.004
Ni	0.96	0.05	0.98	0.04	0.97	0.04
S	1.03	0.04	1.02	0.04	1.02	0.04
Ni/S	0.93	0.09	0.96	0.08	0.95	0.07

in size are relatively common (Fig. 1c). The composition of chromite is $(Fe^{2+}_{0.89}Mn_{0.11})(Cr_{1.79}Fe^{3+}_{0.21})O_4$.

The source of nickel and chromium is assumed to be bodies of serpentinized ultramafics found in the mines. It is likely that their number is greater than currently established because mariposite has a fairly wide distribution and chromium does not migrate long distances in hydrothermal systems.

The single crystal diffractometry shows typical for a millerite cell parameters a: 9.589(5)Å, b: 9.589(5)Å, c: 3.141(2)Å, V = 250.2(3) Å^3. RRUFF ID**:** R070323 – Millerite from Orford, Quebec, Canada has cell parameters a: 9.604(6)Å, b: 9.604(6) Å, c: 3.145(1)Å, V=250.03(5) Å^3 (Lafuente et al., 2015).

The chemical composition of millerite is shown in Table No. 1. The only impurity elements - cobalt and iron are found in very small quantities. Iron is found only in millerite in dolomite from Krushev Dol. The concentration of cobalt varies from 0 to 0.82 wt %, being again the highest in millerite in dolomite from Krushev Dol. Cobalt was found in only 3 analyses in Mogilata.

The average element chemistry of millerite corresponds to the average formula $Ni_{0.97}S_{1.03}$ (based on 2 atoms per formula unit).

Some alteration products after millerite have been found there. They are under study.

Conclusions

A new mineral for Madan ore field – millerite was discovered in two associations different in appearance and mineral composition. One of them is with light green ferrodolomite. It was observed in samples from both the Krushev Dol and Mogilata deposits. In the other association millerite is among flakes of bright green mariposite – chromium-bearing phengite.

The composition of the millerite is very close to the theoretical, almost impurity-free, with a Ni/S ratio of 0.95.

Several bodies of serpentinized ultramafics found in the mines are assumed to be the source of nickel and chromium.

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