50 years University of Mining and Geology "St. Ivan Rilski"
Annual, vol. 46, part I, Geology and Geophysics, Sofia, 2003, pp.177-182

CHARACTERIZATION OF THE SULFIDE MINERALIZATION IN METAMORPHOSED SERPENTINITES NEAR ZHIVKOVO VILLAGE, CENTRAL SREDNA GORA, BULGARIA

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ABSTRACT
Sulfide mineralization manifested by monosulfide solid solutions (*mss*) of pentlandite and pyrite is studied. *MSS* include troilite and pyrrhotite (monoclinic and hexagona). The minerals are found in an artificial outcrop in the central part of a small serpentinite body at about 3 km SW of Zhivkovo village (Ihtiman region). The serpentinites are built by antigorite, chrysotile, carbonate, and relics of orthopyroxene and olivine. The widespread minerals, which give the outlook of the ore mineralization are *mss* and pentlandite embedded in serpentinite and observed as intimately interweaved aggregates of elongated (veinlets, lamellae) or irregular form. Their size varies in wide ranges with the length of the former reaching 5 to 6 cm while the irregular ones display 0.6 cm width and up to 1.5 cm length. Pyrite is met more rarely that the other minerals and is represented by individual grains of irregular or crystal (mostly cubic crystals) form. Initial phase of oxidation of pyrite is rarely observed and, if this case, it associates with Fe-oxides (or hydroxides). Other ore minerals are found very rarely represented mainly by spinelides (magnetite and chromite).

INTRODUCTION

On many places in the Precambrian metamorphites of Central Sredna Gora plenty of small ultrabasite bodies (single or groupings) are found the predominant part of them being strongly altered or almost entirely serpentinized. The data about these bodies in the Bulgarian geological literature are scarce and as concerns the sulfide mineralizations only the presence of pentlandite has been discussed (Kozhoukharov et al., 1980). The present study presents data for the mineralogical features of a sulfide mineralization found in a relatively small body cropping out at about 3 km SW of Zhivkovo village (Ihtiman region), quite near to the road Ihtiman-Samokov. Petrographic characterization of the studied metamorphosed serpentinites is also performed. The mineralization is found in an artificial outcrop in the central parts of the body sized some tens of m^2. In the past, many of the serpentinite bodies in the region have been prospected for manual production of small amounts of talc (Zhelyaskova-Panayotova and Bozhinov, 1989). During the last years this production has been stopped. At present, for juvenille-decoration purposes only manual processing of small blocks of relatively fresh serpentinite from separate bodies is performed. Due to the past activity the studied body is with removed cover of weathered mass and in depth fresh metamorphosed serpentinites crop out in which the sulfide mineralization is observed.

GEOLOGICAL SETTING

The serpentinized bodies in Ihtiman Sredna Gora are localized among Precambrian metamorphites in the rims of boudinage structures among gneisses and migmatites (Kozhoukharov et al., 1980). The above authors note that bodies are embedded in the rocks of the Boturche Group (in the frame of the Western Sredna Gora these rocks are related to the Garvanitsa series), which are represented by biotite gneisses, amphibolites, muscovite and two-mica schists, kyanite schists, and gneisses and biotite gneisses. According to the same authors, during the regional metamorphism new mineral association developed in a zonal manner over ultrabasites. The hydration of the primary rock-forming minerals afterwards has caused the formation of chrysotile, antigorite, serpophite, bastite, chlorite, and ore minerals (magnetite, chromite, and pentlandite).

METHODS OF STUDY

The microscopic observations in transmitted light was performed with microscope Amprival. Ore minerals were studied with optical microscope Leitz Orthoplan-Pol and electron microscope Philips SEM-515 in a regime of secondary and back scattered electron emission. The electron microprobe analyses (point and area quantitative scans) were performed on analytical attachment EDAX PV 9100 under the following conditions: U – 20-25 kV, I - 0.5 mA, beam diameter of 5 μm, count time of 80 s; lines and standards: Fe$K\alpha$ and S$K\alpha$ (marcasite), Ni$K\alpha$ (pentlandite), Co$K\alpha$ (cobaltite). Powder X-ray diffraction (XRD) studies of serpentinites and sulfides were fulfilled on a DRON 3M diffractometer (Co$K\alpha$ radiation; 40 kV, 28 mA). A sample taken from the richest ore part of the body was milled and a trial was made to separate a heavy mineral concentrate but the applied gravitational enrichment did not give any result. Applying electromagnetic separation, a sample was isolated, which contains mainly serpentinite minerals with inclusions of sulfides and magnetite.

PETROGRAPHIC CHARACTERIZATION

The studied body is located among Precambrian metamorphites – two-mica schists, biotite schists, gneisses, and amphibolites.

Mica schists are the prevailing rock varieties, which display a clearly expressed crystallization schistosity and homoblastic (lepidoblastic, granolepido-blastic) textures and are built by a fine-grained aggregate of quartz (30-40 wt.%), which is xenoblastic, isometric, or elongated along the schistosity as well as by preserved, in some cases partially serpentinized, fine-lamellar plagioclase (5-15 wt.%) represented by albite-oligoclase, $An_{8-10} \div An_{12-24}$). Quartz is observed also as monomineral stripes and lenses and displays a wavy, rarely mosaic darkening. Mica (30-35 wt. %) is with a sub-parallel orientation and is localized in bands, which determine the clear crystallization schistosity of the rock. The mica quantity ratio varies but biotite always prevails above muscovite. Chloritoid occurs as sporadic, strongly elongated lens-like aggregates, which are parallel to the schistosity. It is greenish, weakly pleochroic, fresh or partially chloritized along the cleavage surfaces. Kyanite is colorless, prismatic and platy, fresh, but in cases intensively sericitized with only separate relics remaining preserved. It was observed only in some of the mica schists. In cases, when the kyanite quantity increases it is observed that the mica schists go into kyanite schists. Garnet is rare but is always found. It is isometric and sized predominantly in the range 0.1-0.4 mm. The accessory minerals are represented by apatite, zircon, and rutile. Typical feature of the schists is the local manifestation of K-feldspar mineralization expressed in formation of thin bands and lens-like parts of pink K-feldspar.

Rare layers of pegmatite veins (thick from 0.5 to 1.0 m) are observed among the mica schists in the region. They are built by K-feldspar, plagioclase, quartz, muscovite, and accessory apatite.

The gneisses (biotite and two-mica) are schistous and on places display “eye”-like structure. They are composed of rare porphyroblasts of fresh or partially serpentinized plagioclase sized up to 1.5 cm, which determines the “eye”-structure of the rock. A fine-grained aggregate fills the space between porphiroblasts composed of xenoblastic quartz, plagioclase (oligoclase, An_{22-28}), and slightly pelitized K-feldspar. Quartz builds also not well-formed bands and lenses. Mica is represented by elongated biotite scales, which, together with muscovite, surround the plagioclase porphyroblasts. The accessory minerals are apatite and rutile as well as included in biotite zircon, around which there are formed pleochroic courts. The texture is granoblastic (for the stripes built mainly by quartz) and granolepidoblastic (in the places where mica prevails) and also porphyroblastic in respect to plagioclase.

Amphibolites crop out in the region of the studied body but no immediate contact between them and serpentinites is observed. They are dark-green to black with a banded structure and granoblastic and poikiloblastic texture. Composed are mainly of plagioclase (with plenty of zoisite inclusions) and amphibole, subordinate amount of zoisite and garnet as well as of accessory titanite, apatite, and magnetite.

Ultrabasites are intensively but irregularly serpentinized. The outer parts of the bodies are relatively fresher with preserved relics of the primary rock. In their peripheral parts there are developed talc-chlorite, talc-tremolite-chlorite, and talc rocks without clear spatial relations between them. Similar rocks are described by Kozhoukharov et al. (1980). According to the authors the smaller bodies are entirely replaced by tremolite, tremolite-chlorite, talc-tremolite-chlorite, and talc rocks, formed during the regional metamorphism.

The serpentinites from the inner parts of the bodies are built mainly by serpentine (antigorite and chrysotile) with admixtures of talc, chlorite, carbonate (in varying quantities), relics of ortopyroxene and olivine and accessory magnetite. In some cases the quantity of secondary minerals is great. Antigorite is colorless, platy, scaly or is coarse fibrous with a perfect cleavage and is developed on ortopyroxene. Chrysotile occurs in subordinate quantity and forms fibrous (most frequently cross fibrous) veinlets and cryptocrystalline aggregates replacing olivine at the periphery or along the fissures. Talc is scaly with perfect cleavage and high birefringence. Carbonate forms irregular bodies and associates with serpentine and talc. Chlorite is in a subordinate quantity and is colorless, with perfect cleavage and typical anomalous gray-green and yellow-green interfering colors. Along the cleavage surfaces it is partially replaced by talc. XRD analysis defines this phase as clinochlore. The texture is fibrous, cross-fibrous, and unclearly expressed ladder-like.. The mineral composition of serpentinites and the established relics of primary minerals give reason to propose a peridotite composition of the primary rock.

The talc-chlorite rocks are gray-green to dark green and on places with a rusty-brown color caused by the presence of iron hydroxides. They are built mainly by fine- to medium-scaly talc and clinochlore replaced by talc and serpentine along the cleavage surfaces. The secondary minerals are antigorite, lizardite, and tremolite. With the increase of talc content the rocks gradually go into talc ones.

The mineral composition of the talc-tremolite-chlorite rocks (talc, clinochlore, tremolite, antigorite, and lizardite) is determined in a transmitted light and confirmed by XRD phase analyses. Tremolte is colorless, thin-prismatic to needle-like and without clearly expressed contours. Characteristic cleavage below 124^{o} is observed in cross sections. On places along the cleavage surfaces it is replaced by talc.

The chemical composition of the metamorphosed serpentinites is given in Table 1. The content of SiO_2 is between 41.33 and 50.07 % with lowest quantities displayed for the serpentinites in the inner parts of the body and highest ones are typical for the peripheral parts - in the talc-tremolite-chlorite and most of all in the talc rocks. (Table 1). Inverse tendency is observed in respect to MgO content.

Table 1. Chemical composition of metamorphozed serpentinites

Oxides (%)	CS-11	CS-11/1	CS-9	CS-8	CS-10
SiO_2	41.33	41.59	46.90	49.47	50.07
TiO_2	0.02	0.10	0.02	0.06	0.06
Al_2O_3	2.16	2.84	2.04	2.54	2.98
Fe_2O_3	4.26	4.98	5.40	3.45	2.99
FeO	4.30	4.47	3.06	2.45	1.35
MnO	0.12	0.11	0.06	0.04	0.01
MgO	36.35	34.94	32.39	32.92	34.52
CaO	1.64	1.83	1.09	1.94	0.06
Na_2O	0.11	0.18	0.13	0.10	0.12
K_2O	0.08	<0.05	<0.05	0.08	0.08
P_2O_5	<0.03	<0.03	<0.03	<0.03	<0.03
ЗПН	9.57	9.05	9.01	6.67	7.59
Сума	99.94	100.09	100.10	99.72	99.83
(g/t)					
Cr	1880	1840	1940	1790	1920
Ni	1335	1341	1648	684	915
Cu	22.6	29.4	34.2	47.1	18.8
Co	60.6	63	40.3	20	19.9
Ag	<1	<1	<1	<1	<1
Au	<0.03	<0.03	<0.03	<0.03	<0.03

CS-11, CS-11/1 – serpentinites ;
CS-8, CS-9 – talc-tremolite-chlorite rocks;
CS-10 – talc-chlorite rocks.

MINERALOGY OF SULFIDES

The sulfide mineralization in the studied body is represented by monosulfide solid solutions of iron (*mss*), pentlandite, and pyrite and is incorporated in the serpentinite matrix of the rock. Minerals of widest distribution, which give the outlook of the ore mineralization are those of *mss* and pentlandite being in most cases intimately interweaved in complex aggregates, which build veinlets or single grains with irregular form. The latter are with size up to 0.6x1.5 cm, while the veinlets are wide up to 0.8-1.0 cm and long up to 5-6 cm. Dominating in this association are the *mss* minerals. Pyrite is the most rare mineral among sulfides and is represented by single grains of irregular or crystal form. It rarely associates with Fe-oxides (hydroxides).

Mss are represented by troilite and pyrrhotite (monoclinic and hexagonal), which always form complex aggregates of structure type "dissociation of solid solutions" (varieties - plate-like and framework). According to Kostov and Minceva-Stefanova (1984) the phases $Fe_{1-x}S$ are the widely distributed minerals of nickeline-type structure (NiAs) and play the role of an example for sulfides with varying superstructures and non-stoichiometric compositions. They are formed at various conditions and in nature three different pyrrhotites are formed: monoclinic, Fe_7S_8, hexagonal, Fe_9S_{10} - $Fe_{10}S_{11}$ - $Fe_{11}S_{12}$, and finally hexagonal troilite FeS. The similarity in chemical composition and structure results in a significant equality in optical properties of these minerals making them hardly differentiated in optical light (Reference book…). The studied monosulfide aggregates in reflected light are light-yellow in color and with unclear boundaries between the separate phases. The criterions for their differentiation are in the strongly expressed anisotropy of troilite while pyrrhotite is with richer color effects in the region of the yellow-brown and reseda-green nuances. The investigation of polished samples with magnetic suspension for diagnosis of monoclinic pyrrhotite gave a negative result. The XRD data, however, registered its presence in the complex aggregates. The powder XRD pattern in the interval 50 - 52^0 2θ (Fig. 1) displays the diffraction maxima of 1 1 4 peak (2.093 Å) characteristic of troilite, of 1 0 0 peak (2.072 Å) typical of hexagonal) pyrrhotite and of 3 2 2 peak (2.060 Å) - intense peak of monoclinic pyrrhotite. The broadening in the base of diffraction maximum 1 0 0 (of hexagonal pyrrhotite) is caused probably by partial overlapping with the peak 2 0 4 of monoclinic pyrrhotite. Also, in the XRD pattern at about 35^0 2θ there exists another peak, 1 2 2 (2.9710 Å), which belongs to monoclinic pyrrhotite. Despite the low intensity of these peaks they confirm the presence of monoclinic pyrrhotite, which is of less quantity than the other monosulfides in the sulfide aggregates and falls in the detection limits of the method. The obtained d-values for the studied *mss* are given in Table 2.

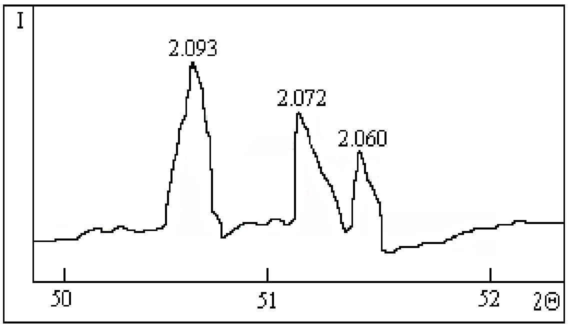

Figure 1. d-values (Å) 2.093 (troilite), 2.072 (hexagonal pyrrhotite) and 2.060 (monoclinic pyrrhotite) in the interval 50 - 52^0 2θ of the XRD pattern of mss from ultrabasites of Central Sredna Gora

Mss are most often intimately intergrown with pentlandite and rarely form single grains and veinlets. The form of the individuals is irregular, almost isometric (Fig. 2a) or profoundly elongated (lamellar) (Fig. 2b, c). The veinlets are composed of separate sub-parallel or oblique oriented fine lamellae with length of up to several mm. The polished surfaces of the separate monosulfides are homogeneous and without optically visible zoning.

Table 2. d-values (Å) of *mss* from ultrabasites of Central Sredna Gora

pyrrhotite				troilite	
monoclinic		*hexagonal*			
d, Å	I	d, Å	I	d, Å	I
2.971	10	2.985	8	4.748	9
2.640	8	2.647	9	2.983	8
2.629	8	2.072	10	2.668	7
2.068	7	1.723	7	2.093	10
2.060	9			1.720	6
2.052	7				

Their composition is simple and includes only the constitutional elements with only small variations in the composition of the separate grains (Table 3). The composition of the studied grains varies from $Fe_{1.01}S_{0.99}$ to $Fe_{0.98}S_{1.02}$. The studied pyrrhotite does

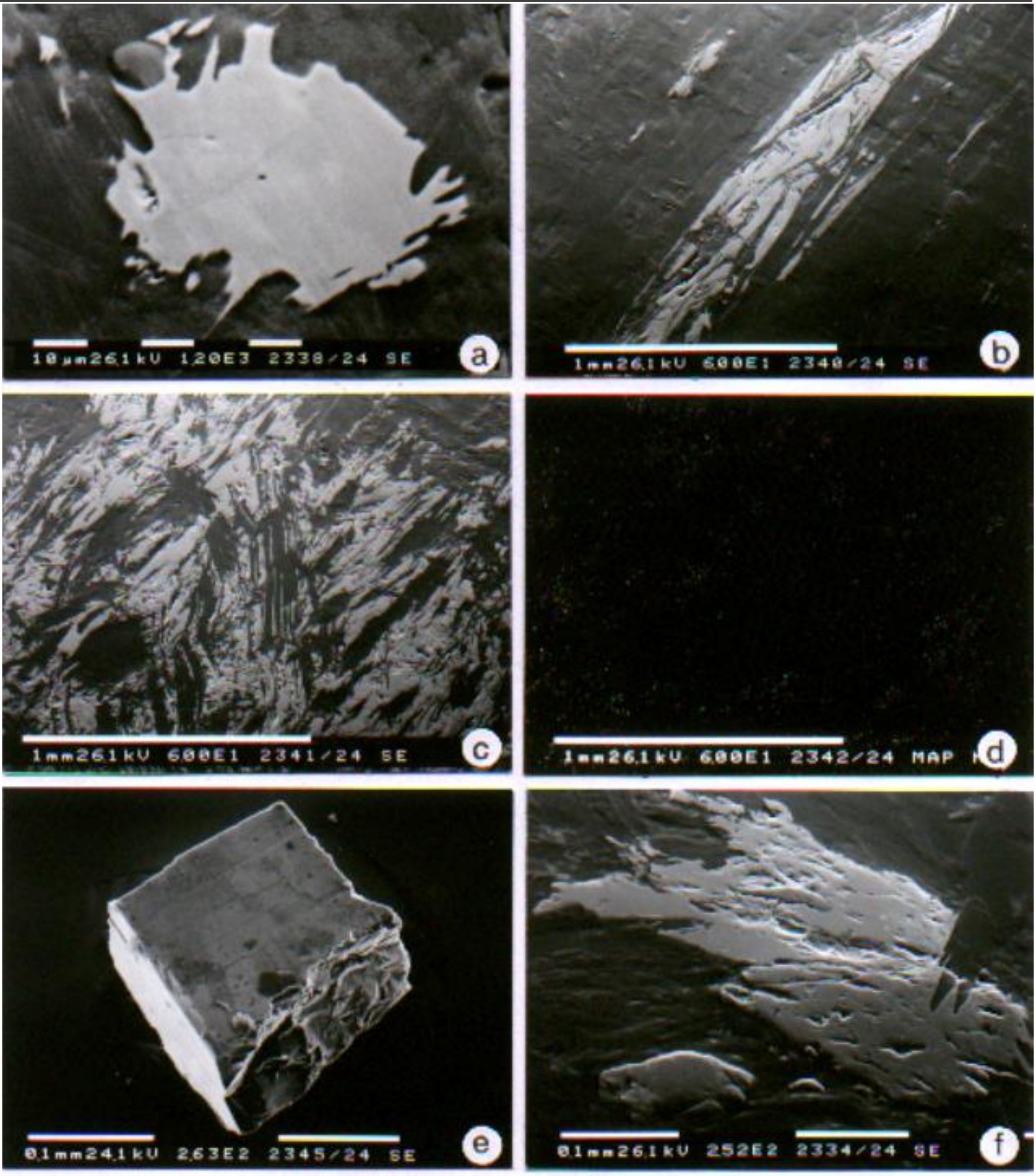

Figure 2. SEM micrographs of sulfides in ultrabasites from Zhivkovo village, Central Sredna Gora. a – irregular grain of mss; b - vein of mss; c – association mss-pentlandite; d – single element scans for Ni; e - cubic crystal of pyrite; f – association pyrite and Fe-oxide/ hydroxides. *Polished sections – a-d, f; native surface – e. Scale bars: 10 μm – a; 100 μm – e, f; 1 mm – b-d.*

not display metasomatic replacements like the one described for Martinovo deposit (Tarassova, 1987). Troilite is found principally in meteorites, while in the rocks of the Earth it is very rarely met - mainly in ultrabasites. The studied troilite is a first find in mother rocks in Bulgaria. Such mineral sample with meteoritic origin has been found in the third specimen of the meteoritic rain "Gumoshnik" (Dimov, 1972).

Pentlandite is found always intergrown with *mss* but in this association the mineral is of a subordinate significance. Most frequently it builds e definite segment of the periphery of the obtained aggregates and more rarely it is found as fine needles among *mss*. The size of the separate individuals varies in wide ranges - their width most often being several microns (in some cases up to 15 μm), while their length reaches several mm. The polished surfaces of the grains are dense (rarely displaying small caverns), uniform and without zoning, which indicates that the system Fe-Ni-S had not been influenced by phase transformations from later metamorphic processes. The composition of pentlandite is constant and the variations in the contents of the elements in different points of the separate individuals are very small and between separate grains these variations are in narrow ranges (Table 3).The atomic ratio Ni/Fe is from 0.99 to 1.05 and the content of Co is from 1.23 to 1.30 at %. According to Kostov et al. (1986) when this ratio is close to 1 (our case) we can define the mineral as low-cobalt normal pentlandite. The stoichiometry of the mineral is from $(Fe_{4.43}Ni_{4.38}Co_{0.22})_{9.03}S_{7.97}$ to $(Ni_{4.53}Fe_{4.31}Co_{0.22})_{9.06}S_{7.94}$.

The *mss*-pentlandite association is characterized by interrelations, which show that the aggregates are formed as a result of a dissociation. Following the nomenclature of Durazzo and Taylor (1982) the resulting structure can be determined as cell or lamellar type.

Table 3. Chemical composition of the sulfide mineralization in ultrabasites from Zhivkovo village, Central Sredna Gora

N	Fe	Co	Ni	S	Total
Monosulfide solid solutions					
1	63.62			35.39	99.01
2	64.85			35.71	100.56
3	62.41			37.45	99.87
4	63.78			35.40	99.18
5	62.97			37.24	100.21
Pentlandite					
6	30.92	1.64	34.17	32.73	99.47
7	31.77	1.67	33.03	32.80	99.27
8	31.23	1.68	34.15	32.86	99.92
9	30.96	1.64	34.12	32.85	99.57
10	31.03	1.58	33.96	32.79	99.36
Pyrite					
11	46.74			53.59	100.33
12	47.26			52.91	100.17
13	46.91			52.78	99.69
14	47.15			52.66	99.81
Formulae coefficients					
Monosulfide solid solutions					
1	1.01			0.99	
2	1.02			0.98	
3	0.98			1.02	
4	1.01			0.99	
5	0.98			1.02	
Pentlandite					
6	4.31	0.22	4.53	7.94	
7	4.43	4.38	0.22	7.97	
8	4.51	4.31	0.22	7.96	
9	4.51	4.31	0.22	7.96	
10	4.51	4.32	0.21	7.96	
Pyrite					
11	1.00			2.00	
12	1.02			1.98	
13	1.01			1.99	
14	1.02			1.98	

Pyrite is the less distributed sulfide and is observed in only one sample. This is probably due to its restricted distribution in the studied body. Morphologically it is represented by cubic crystals or by grains of irregular form (Fig. 2e, f). The surface of the former is uniform, dense, sometimes disrupted by small caverns of predominant ellipse-like form. The color of the crystals is light-yellow. Partial replacement of pyrite by Fe-hydroxides due to oxidation processes is very rarely observed. Also, there are no observations of its association with the other sulfides. The stoichiometry of pyrite is in the range $Fe_{1.00}S_{2.00}$ to $Fe_{1.02}S_{1.98}$.

ISCUDSSION

The interpretation of the ore structures is the most difficult, but at the same time the most important aspect in the study of rocks, which are carriers of Fe-Ni-sulfide mineralization. The intergrowth relations between pyrrhotite and pentlandite give a rich genetic information (Durazzo and Taylor, 1982). Data up to now give reason to consider that only *mss* and pentlandite from the studied sulfide mineralization display a paragenetic relation, while pyrite is formed in other more restricted spatial conditions. The post-magmatic processes impose a very high degree of serpentinization of the primary ultrabasites in the region of Ihtiman Sredna Gora where the low-temperature hydrothermal metamorphism had played a definite role (Kozhoukharova, 1986). The restricted presence of sulfides and magnetite observed in the studied body indicate for local changeable conditions for $f(S_2)$ and $f(O_2)$ during the process of crystallization (Oberthür et al., 1997). The association *mss*-pentlandite had been probably formed in conditions of primary hydrothermal alteration of ultrabasites. Firstly, the mineralization had been widely manifested in the body. The formed structures of dissociation of the solid solutions of the two minerals allow to propose that the processes had started at about 300^0C (Durazzo and Taylor, 1982). The lowering of temperature had led to structural changes in the high-temperature hexagonal pyrrhotite, which below 300^0C had resulted in the formation of substructures and monoclinic pyrrhotite. Then, at 142^0C dissociation between troilite and hexagonal pyrrhotite had taken place in compositions poor in S (Naldrett et al., 2000). Together with those processes an inversion in the conditions had taken place - locally increased $f(S_2)$ had been replaced by high $f(O_2)$ resulting in the formation of magnetite. The later stages in their transformations had led to destruction of a part of these sulfides and to a new increase in $f(S_2)$ in separate parts where pyrite had crystallized. The needed iron for the formation of the sulfide mineralization had been released from the primary rock-forming minerals of ultrabasites being present there in divalent form (Zhelyaskova-Panayotova, 1965). The earlier formed pentlandite and Ni-containing minerals could be considered as a probable sources of Ni (Atanassov and Vitov, 1981; Kostov et al., 1986).

Sulfide mineralization represented by pyrrhotite + pentlandite + chalcopyrite + pyrite has been described as a carrier of platinum-group elements (PGE) for the ores of Great Dyke (Zimbabwe) where among sulfides there have been observed also minerals of the platinum-group element (PGM) represented by sperrylite ($PtAs_2$), cooperite (PtS), moncheite ($PtTe_2$), and merenskyite ($PdTe_2$) (Oberthür et al., 1997). The ultrabasite body Baula Complex (India) is a carrier of analogous Ni-Fe-S association also accompanied by PGM (dominated by sperrylite) and formed in hydrothermal conditions (Augé et al., 2002). On the basis of these data it seems very probable to expect during detailed mineralogical studies on sulfides in the ultrbasites in the region of Ihtiman Sredna Gora the finding of PGM and some other sulfides like chalcopyrite, cubanite, etc. Most probably PGM should be represented by sulfides and related compounds of Pt and Pd, which are very mobile hydrothermal conditions. As a confirmation of this statement can be considered the finds of mineralizations of PGE with a probable hydrothermal origin reported for the placers from the upper parts of Iskar river, region being close to the studied ones (Tsintsov, 2003).

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Recommended for publication by Department of Mineralogy and Petrography, Faculty of Geology and Prospecting