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Bismuth minerals in the postskarn sulphide-arsenide mineralization in the Martinovo iron deposit, NW Bulgaria

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Abstract. Rare bismuth minerals were found in the postskarn sulphide-arsenide mineralization in the Martinovo iron deposit, Northwestern Bulgaria. The postskarn mineralization has direct relation to the Sveti Nikola collisional granite intrusion into the rocks of the Diabase Phyllitoid Complex. The observed bismuth minerals spatially associate with the pyrrhotite and chalcopyrite from the pyrrhotite-chalcopyrite assemblage of the postskarn mineralization. According to their chemical composition, the bismuth minerals are identified as native bismuth, bismuthinite, pilsenite (?) and hedleyite. Two elemental associations - Bi-S and Bi-Te-S are distinguished on chemical and textural criteria. In the Bi-Te-S association, native bismuth, bismuthinite and hedleyite are observed as larger and more abundant grains. Two bismuthinite varieties (Bs1 and Bs2) are distinguished according to textural peculiarities, physical and optical properties. Native bismuth and Bs2 occur as close myrmekite-like intergrowths, which probably result from a decomposition of a preceding mineral phase with composition Bi_4S_3 (?). The co-existence of these bismuth tellurides and sulphides reveals the conditions of ore forming processes, i.e. temperature below 266°C, $\log f\mathrm{Te}_2 \geq -14.9$ and $f\mathrm{S}_2 \geq -16.1$. The established hedleyite is the Bi-richest ever found. This fact either extends the range of compositional variations of hedleyite or gives a clue to a new mineral species in the Bi-Te system.

Key words: Native bismuth, bismuth tellurides and sulphides, postskarn mineralization, Martinovo iron deposit

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Димитрина Димитрова, Томас Керестеджиян. Бисмутови минерали в постскарновата сулфидно-арсенидна минерализация в железорудното находище Мартиново, СЗ България

Резюме. Редки бисмутови минерали са установени в постскарновата сулфидно-арсенидна минерализация в железорудното находище Мартиново, северозападна България. Постскарновата минерализация е пряко свързана с внедряването на Св. Николския колизионен гранит в скалите на диабаз-филитоидния комплекс. Бисмутовите минерали тясно асоциират с пиротина и халкопирита от пиротин-халкопиритовата парагенеза на постскарновата минерализация. Въз основа на химичния състав бяха идентифицирани самороден бисмут, бисмутинит, пилзенит (?) и хедлеит. Минералните взаимотношения и химичeният състав определят две елементни асоциации, в които се срещат бисмутовите минерали – Bi-S и Bi-Te-S. В Bi-Te-S асоциация самородният бисмут, бисмутинитът и хедлеитът се наблюдават като по-едри и по-изобилни зърна. Въз основа на текстурни особености, физични и оптични характеристики се разграничават две разновидности на бисмутинита - (Bs1 и Bs2). Самородният бисмут и Bs2 се наблюдават като фино-прораснали агрегати, вероятно резултат от разпад на богата на Bi по-ранна фаза - Bi_4S_3 (?). Едновременното присъствие на бисмутовите телуриди и сулфиди определя условията на формиране на минералите: температура под 266°C, $\log f\mathrm{Te}_2 \geq -14{,}9$ и $f\mathrm{S}_2 \geq -16{,}1$. Хедлеитът установен в находище Мартиново е с най-високо съдържание на Bi досега известно в литературата, което разширява обхвата на вариациите в химичния състав на минерала или предполага съществуването на неизвестна до момента нова минерална фаза в системата Bi-Te.

Introduction

Bismuth minerals – native bismuth, bismuthinite, pilsenite (?) and hedleyite have been found in the postskarn sulphide-arsenide mineralization from the Perchinki and Mali Dol mine sections of the Martinovo iron deposit - part of the Martinovo-Chiprovtsi ore zone, situated in Northwestern Bulgaria. The native bismuth and bismuthinite are first mentioned here by Dragov (1971), Velchev (1973) and later on by Atanassov and Pavlov (1983), but no sufficient chemical data are provided. Based on light microscopy, Dragov (1971) determined ikunolite, galenobismuthite and joseite-A as well. Later, in his Dr. Sc. thesis Dragov (1992) provided some standardless microprobe analyses of the Bi-Te-S minerals. The bismuth minerals were observed only in several polished sections from the Mali Dol mine section, among almost 50 studied samples.

Materials and analytical methods

Polished sections were made of samples from Zhazhkov Dol, Mali Dol and Perchinki mine sections, Martinovo deposit. Additional polished sections received from Prof. Peter Dragov have been studied too. The mineral relationships in about 50 polished sections were studied by reflected light microscopy. Microprobe analyses were performed by a JEOL JSM 35 CF electron microprobe equipped with a Tracor Northern TN-2000 analyzing system at the laboratory of Eurotest Control AD, Sofia and by JEOL Superprobe 733 electron microscope equipped with an ORTEC energy-dispersive system at the Geological Institute, BAS. The operating conditions were as follows: accelerating voltage 25 kV and probe current 2.10^{-9}A. The spectral lines for each element are CuKα, PbLα, AgLα, AuLα, BiLα, SbLα, TeLα, SeKα, FeKα and SKα. The following standards were used: pure metals Ag, Au, Bi, Se and Te, PbS (for Pb), Sb_2S_3 (for Sb), FeAsS (for As), $CuFeS_2$ and $Cu_{12}As_4S_{13}$ (for Cu, Fe and S). ZAF corrections were made. In most cases, back scattered electron images (BSEI) were used to distinguish different phases because some of the grains, looking homogeneous under the microscope, turned out to be multiphase in BSE images.

Geological setting and mineralizations

The Martinovo iron ore deposit is located NW of the Martinovo village, in the western part of the Balkan Mountains and its underground mine was operated until 1999. It is hosted in the low-grade metamorphic rocks of the Diabase Phyllitoid Complex, which constitutes the Paleozoic core of the Alpine Berkovitsa anticline (Fig. 1). According to Haydoutov (1991) this complex is considered as a construction of three regionally metamorphosed

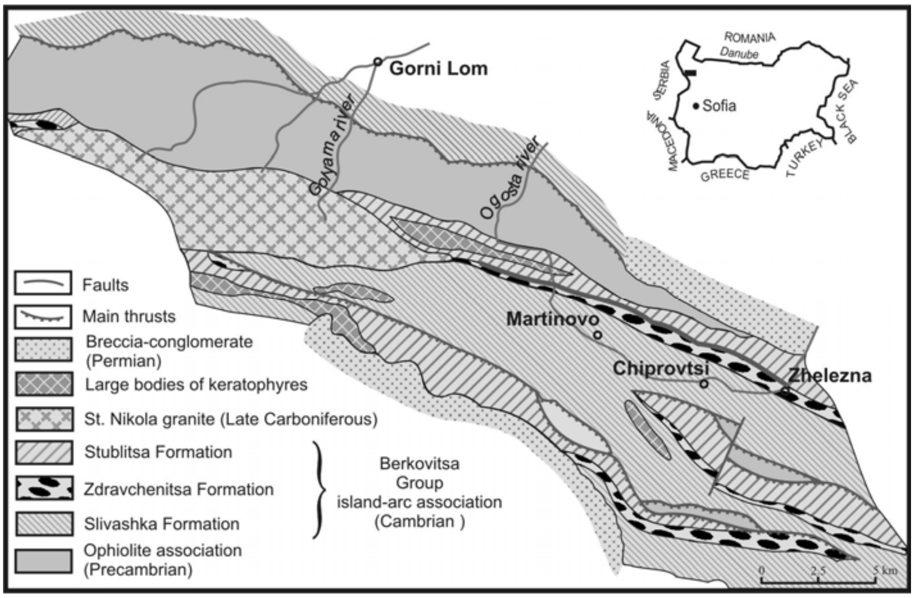

Fig. 1. Simplified geological map of the Martinovo and Chiprovtsi deposits, modified after Haydoutov (1991)

Фиг. 1. Опростена геоложка карта на находищата Мартиново и Чипровци по Haydoutov (1991), с изменения

metamorphosed to greenschist facies units: 1) Tcherni Vruh Group, a well stratified ophiolite association (tectonized peridotites, layered cumulates, sheeted dykes and pillow lavas) with Precambrian age; 2) Berkovitsa Group, an island-arc association (sedimentary-volcanic sequence – turbidites and pelites) with Cambrian age; 3) Dulgi Del Group, an Early Ordovician olistostrome sequence, composed mainly of terrigenous rocks and olistolites of the ophiolites and island-arc igneous rocks. Diabase Phyllitoid Complex is a part of the Balkan-Carpathian ophiolite segment, which also comprises the Zaglavach, Deli Jovan and South Banat massifs in Serbia and Romania, respectively. Recently published data about Pilatovets gabbro, part of the island-arc association, indicates its Cambrian – Early Ordovician age - 493.0 ±6.6 Ma (Carrigan et al., 2003).

The metasomatic ore bodies have irregular, pipe-like, vein-like and nest-like shapes and are lithologically controlled by large siderite and marble bodies in the low-grade metamorphic series. Most of the economically important magnetite-bearing ore bodies are represented of siderite bodies, fully or partially metamorphosed, owing to the influence of the Sveti Nicola collisional granite intrusion. Recently determined U-Th-Pb zircon ages of the Sveti Nicola granite present 313.8 ± 3.5 Ma, i.e. Late Carboniferous age (Carrigan et al., 2003), that gave reason to Carrigan et al. (2005) to suppose that the Sveti Nikola granite is involved in the Variscan orogeny in SE Europe. Both the host rocks and the ore bodies have been intensely tectonized during the Pre-Alpine and Alpine folding (Dragov, 1991).

Generally, three mineralization types, subsequently formed by the granite intrusion into Diabase Phyllitoid Complex are represented in the Martinovo deposit (Atanassov, Pavlov, 1983; Tarassova, Tarassov, 1988, and

Dragov, 1992): 1) Garnet-amphibole-pyroxene skarns with molybdenite and scheelite (to the northwest of the Martinovo village – Prekop and Perchinki mine sections); 2) Garnet-biotite skarns with magnetite, pyrrhotite, pyrite and arsenopyrite (Perchinki, Mali Dol and Zhazhkov Dol mine sections); 3) Siderite-magnetite mineralization (Kamaka mine section), where siderite have been transformed to magnetite as a result of thermal metamorphism. The skarns are formed in calcite marbles, i.e. calcic garnet-pyroxene skarns. According to Tarassova and Tarassov (1988), the garnets belong to the grandite series with grossular content up to 72.3 mole% and andradite content – up to 90.2 mole%. The pyroxenes belong to the salite series, with predominantly diopside-hedenbergite composition, but contain johannsenite up to 14.8 mole%. A magnetite-pyrrhotite mineralization is spatially attached to the gar-net skarn zone. The main ore minerals preferably replace firstly garnet and then pyroxenes, thus pyroxene relicts are frequently observed together with pyrrhotite (Tarassova, 1989).

According to Dragov (1992), aside of the main magnetite ore mineralization, a later postskarn, high- to medium-temperature sulphide-arsenide mineralization occurs in the eastern part of the deposit. It is represented mainly by pyrite, pyrrhotite, arsenopyrite, magnetite and less lölingite, cobaltite, chalcopyrite, marcasite and small quantities of galena and is accompanied by insignificant quantities of native gold and bismuth minerals. It is observed as fine, short metasomatic veinlets, nests and inclusions, embraced in magnetite, siderite and silicate bodies within or adjacent to the marble layer. Dragov et al. (1991) analyzed $\delta^{34}S$ in 34 samples of molybdenite, pyrrhotite, pyrite and arsenopyrite from the postskarn sulphide-arsenide mineralization and proved its magmatic origin.

Einaudi et al. (1981), Einaudi and Burt (1982) and Meinert (1992) classified the skarn deposits based upon the dominant economically important metals. Concerning this, the economically important molybdenite-scheelite mineralization in the garnet-pyroxene skarns in Prekop lot (Kanourkov, 1988), could be assigned to the Mo-W skarn type category of deposits. The presence of other, less significant metals – Pb, Bi, Cu and Au in Mo-W skarns is common, which could be very likely the reason for the formation of bismuth minerals within the postskarn sulphide-arsenide mineralization.

Bismuth minerals

Bismuthian hedleyite, bismuthinite, pilsenite (?) and native bismuth were found in only few samples in two similar elemental associations. The term elemental association is used here to describe the products of a late depositional phase in the frames of the pyrrhotite-chalcopyrite assemblage of the postskarn sulphide-arsenide mineralization. Relatively uniform physicochemical conditions and specific chemical composition of the fluid is supposed for each of the associations derived on textural and chemical grounds.

The first association (Bi-S) is represented mainly by native bismuth and less bismuthinite and very rarely contains pilsenite (?). It is found at the grain boundaries of pyrrhotite and chalcopyrite (Figs. 2e, f and 3e). The second (Bi-Te-S) association (Figs. 2a, b, d and 3a-d) consists of native bismuth, bismuthinite and hedleyite, which according to the microprobe data (Table 1) should be considered bismuthian. Mineral grains in this association are also formed at pyrrhotite and chalcopyrite grain boundaries, but are larger in size and much more abundant. The gangue minerals here are quartz and calcite. Bi-Te-S minerals are probably re-precipitated later in quartz veins as consolidated irregular-shaped grains.

Both associations are rare within the postskarn mineralization and do not have economic significance, but are genetically important.

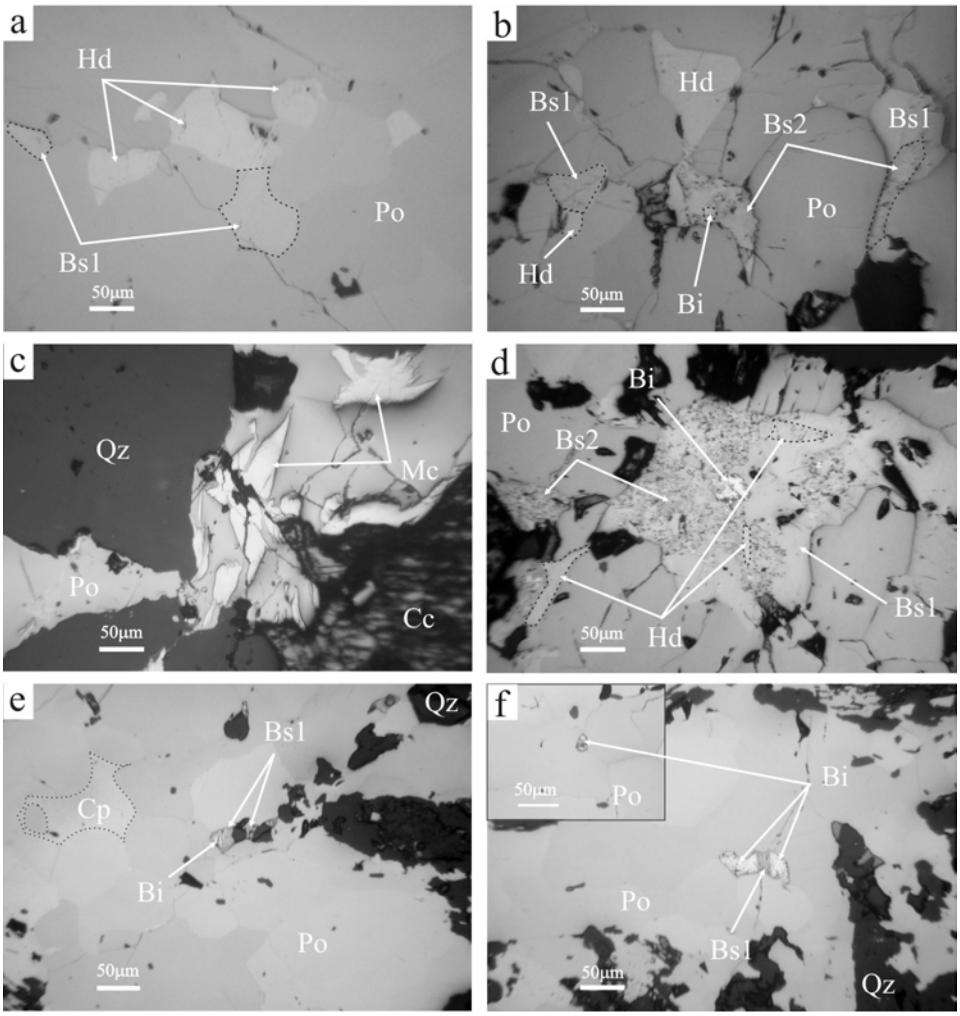

Fig. 2. Microphotographs of Bi-S and Bi-Te-S associations: a) bismuthinite 1 and hedleyite from the Bi-Te-S association amongst pyrrhotite grains; b) and d) native bismuth and bismuthinite 2 intergrowths accompanied by hedleyite and bismuthinite1 from Bi-Te-S association amongst pyrrhotite grains; c) marcasite flake-shaped grains within pyrrhotite surrounded by quartz and calcite; e) and f) native bismuth and bismuthinite1 from the Bi-S association at pyrrhotite grain boundaries. Abreviations: Bi – native bismuth, Hd – hedleyite, Bs1 – bismuthinite 1, Bs2 – bismuthinite 2, Cp – chalcopyrite, Po – pyrrhotite, Mc – marcasite, Qz – quartz, Cc – calcite

Фиг. 2. Микрофотографии на Bi-S и Bi-Te-S асоциации: a) бисмутинит 1 и хедлеит от Bi-Te-S асоциация всред пиротинови зърна; b) и d) прораствания от самороден бисмут и бисмутинит 2 съпроводени от хедлеит и бисмутинит 1 от Bi-Te-S асоциация всред пиротинови зърна; c) марказитови пластинчати зърна в пиротин всред кварц и калцит; e) и f) самороден бисмут и бисмутинит 1 от Bi-S асоциация, разположени на междузърновите граници на пиротина

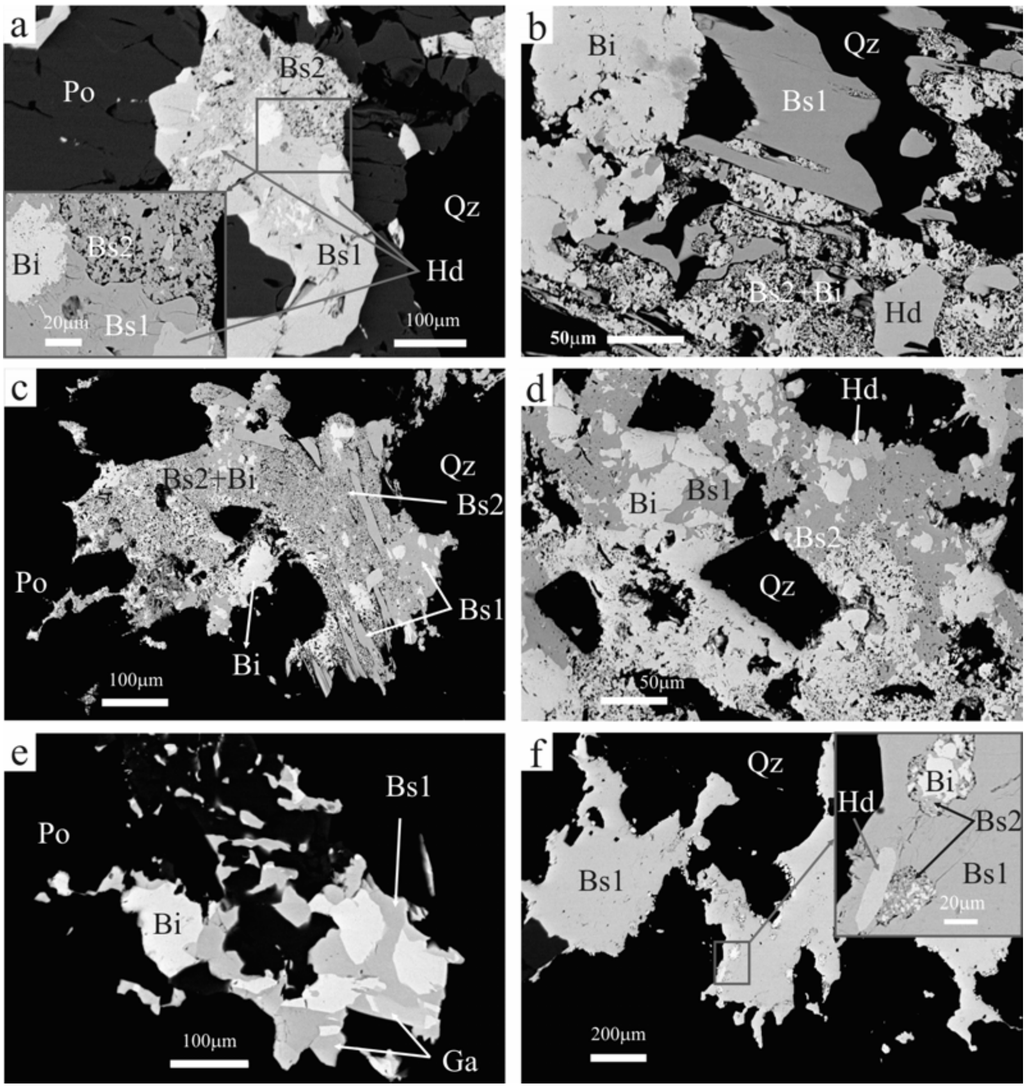

Fig. 3. BSE images of bismuth minerals from the Bi-S and Bi-Te-S associations: a-d) and f) intergrowths of native bismuth and bismuthinite 2 together with hedleyite and bismuthinite 1 within pyrrhotite and quartz; e) co-existing native bismuth, bismuthinite 1 and galena within pyrrhotite. Abreviations: Bi – native bismuth, Hd – hedleyite, Bs1 – bismuthinite 1, Bs2 – bismuthinite 2, Ga – galena, Po – pyrrhotite, Qz – quartz

Фиг. 3. BSEI изображения на бисмутови минерали от Bi-S и Bi-Te-S асоциации: a-d) и f) прораствания от самороден бисмут и бисмутинит 2 заедно с хедлеит и бисмутинит 1 всред пиротин и кварц; e) едновременно образувани самороден бисмут, бисмутинит 1 и галенит всред пиротин

Native bismuth from the Bi-S association is observed as tiny blebs, up to 10 µm in size, close to pyrrhotite and chalcopyrite grain boundaries, sometimes showing euhedral shapes (Fig. 2f). Very scarcely it is found together with bismuthinite (Fig. 2e,f) and native gold. Unlike the Bi-S association, the native bismuth from the Bi-Te-S association is observed as irregularly shaped grains, up to 100 µm in size. It is usually observed together with bismuthinite 2 as close myrmekite-like intergrowths, probably formed by a decomposition of a previous Bi-rich phase (Figs. 2d and 3a-d). It rarely occurs also as separate, isolated irregular grains at pyrrhotite and chalcopyrite grains. According to microprobe analyses of bismuth grains in both associations, the chemical composition does not show any significant amounts of impurities. The total amount of impurities (Fe, Cu, Sb, and in two different samples - Te and Ag respectively) does not exceed 2.00-3.00 wt.% (Table 1). Only in one sample, Cu up to 3.75 wt.% was determined.

Bismuthinite in the Bi-S association is found rarely, together with native bismuth (Fig. 2e,f) and does not show any specificity in chemical composition, unlike bismuthinite in the Bi-Te-S association. Two phases, determined as bismuthinite by electron microprobe analysis (EPMA) but clearly distinguishable on their physical, optical and textural properties were observed in the Bi-Te-S association. In order to discriminate them, the following abbreviations will be used in the text and figures – Bs1 and Bs2. Bismuthinite 2 has slightly higher hardness and darker colour compared to bismuthinite1 and is characterized by very specific porous surface (Fig. 3). It is observed in specific myrmekite-like intergrowth relations with native bismuth (Fig. 3a-c and 3f). This is probably a result from a decomposition of a preceding mineral phase, stable at higher temperature. The composition of this phase could probably be Bi_4S_3, i.e. seleneless ikunolite. Supposedly, with temperature drop down, this phase became unstable and broke down to native bismuth and bismuthinite, according to the reaction:

$$2Bi_4S_3 + 1.5S_2 = 3Bi_2S_3 + 2Bi.$$

Ramdohr (1980) reports similar intergrowths between bismuth and bismuthinite. Chatterjee and Smith (2000) and Koszowska (2004) also found such intergrowth textures between native bismuth and other bismuth tellurides and sulphides and interpreted them as exsolved phases too. Bismuthinite in the Bi-S association and bismuthinite 1 in the Bi-Te-S association do not contain significant amounts of impurities, except Cu, Fe and Sb, which sum up below 1.6 wt.%. The calculated crystal chemical formulae are included in Table 1.

Hedleyite is first found and described in the Good Hope gold bearing claim, Hedley District, British Columbia, Canada, by Warren and Peacock (1945). They determined the crystal structure of the mineral and proposed the simplified chemical formula $Bi_{14}Te_6$ or Bi_7Te_3. Zavyalov et al. (1976) refined the unit cell parameters of hedleyite and based on structural considerations proposed another chemical formula – $Bi_{2+x}Te_{1-x}$, where x = 0.13-0.19. Both authors' teams accepted hexagonal $\bar{3}2/m$ point group, but as it is shown in Table 2, they accepted different space groups - $R\bar{3}m$ and $P\bar{3}m1$ respectively. Further studies add even more uncertainty about the hedleyite crystal structure and composition. Different published data about unit cell parameters, composition and proposed chemical formulae are summarized in Table 2. There are certain disagreements about hedleyite crystal-chemical formula yet. Gu et al. (2001) concerning hedleyite chemical composition derived from numerous microprobe analyses among samples from different deposits in China, proposed the formula – Bi_8Te_3, which was officially accepted by the Commission of New Minerals and Mineral Names (CNMMN) of the International Mineralogical Association (IMA) (Jambor et al., 2002).

Table 1. *Composition of the main ore minerals and the Bi-Te-S assemblage, wt. %*

Таблица 1. *Състав на основните рудни и Bi-Te-S минерали, тегл. %*

№	Sample №	Mineral	Au	Ag	Cu	Pb	Fe	Bi	Sb	Te	S	Total	Formula
1.	JD 4	native gold	89.89	9.49	0.62	-	-	-	-	-	-	100.00	$(Au_{0.82}Ag_{0.16}Cu_{0.02})_{1.00}$
2.	Ch-461b	native bismuth	-	-	0.45	-	1.14	98.13	0.39	-	-	100.11	$(Bi_{0.94}Cu_{0.01}Fe_{0.04}Sb_{0.01})_{1.00}$
3.	Ch-461b	native bismuth	-	-	0.66	-	1.33	96.80	0.24	0.25	-	99.28	$(Bi_{0.92}Cu_{0.02}Fe_{0.04}Sb_{0.01}Te_{0.01})_{1.00}$
4.	JD 4	native bismuth	-	-	3.75	-	-	96.06	-	-	-	99.81	$(Bi_{0.89}Cu_{0.11})_{1.00}$
5.	JD 4	native bismuth	-	0.91	0.58	-	-	97.94	0.38	-	-	99.81	$(Bi_{0.95}Cu_{0.02}Ag_{0.02}Sb_{0.01})_{1.00}$
6.	Ch-85	bismuthinite 2	-	-	0.31	-	1.77	80.24	-	-	16.98	99.30	$(Bi_{2.03}Fe_{0.17}Cu_{0.03})_{2.23}S_{2.77}$
7.	Ch-85	bismuthinite 2	-	-	0.54	-	0.78	80.66	-	-	17.45	99.43	$(Bi_{2.03}Fe_{0.07}Cu_{0.04})_{2.14}S_{2.86}$
8.	Ch-85$_2$	bismuthinite 2	-	0.49	0.60	-	0.56	78.74	-	-	19.39	99.77	$(Bi_{1.87}Fe_{0.05}Cu_{0.02}Ag_{0.02})_{1.99}S_{3.01}$
9.	Ch-85	bismuthinite 1	-	-	0.56	-	0.63	82.99	0.36	-	16.76	101.29	$(Bi_{2.10}Sb_{0.02}Fe_{0.06}Cu_{0.05})_{2.23}S_{2.77}$
10.	Ch-461b	bismuthinite 1	-	-	0.52	-	0.88	79.94	-	-	17.70	99.04	$(Bi_{2.00}Fe_{0.08}Cu_{0.04})_{2.12}S_{2.88}$
11.	Ch-85	bismuthinite 1	-	-	0.74	-	0.21	80.70	-	-	18.10	99.75	$(Bi_{2.00}Fe_{0.02}Cu_{0.06})_{2.08}S_{2.92}$
12.	Ch-85$_2$	bismuthinite 1	-	-	0.90	-	0.17	81.12	-	0.21	17.63	100.02	$(Bi_{2.03}Fe_{0.01}Cu_{0.07})_{2.12}(S_{2.87}Te_{0.01})_{2.88}$
13.	Ch-85	hedleyite	-	-	0.41	-	-	85.77	-	13.01	-	99.18	$(Bi_{8.70}Cu_{0.14})_{8.84}Te_{2.16}$
14.	Ch-85	hedleyite	-	-	0.53	-	0.32	85.87	-	12.96	-	99.67	$(Bi_{8.58}Cu_{0.18}Fe_{0.12})_{8.88}Te_{2.12}$
15.	Ch-85	hedleyite	-	-	0.57	3.79	-	83.93	-	11.37	-	99.65	$(Bi_{8.53}Cu_{0.19}Pb_{0.39})_{9.11}Te_{1.89}$
16.	Ch-85	hedleyite	-	-	0.63	1.86	0.36	87.22	-	9.16	-	99.22	$(Bi_{8.93}Cu_{0.21}Fe_{0.13}Pb_{0.19})_{9.46}Te_{1.54}$
17.	Ch-85	hedleyite	-	-	0.52	1.72	0.22	85.44	-	12.25	-	100.14	$(Bi_{8.56}Cu_{0.17}Fe_{0.08}Pb_{0.18})_{8.99}Te_{2.01}$
18.	Ch-85	hedleyite	-	-	0.44	-	-	86.72	-	12.67	-	99.83	$(Bi_{8.76}Cu_{0.14})_{8.90}Te_{2.10}$
19.	Ch-85$_2$	hedleyite	-	-	0.84	-	0.12	88.68	-	10.75	-	100.39	$(Bi_{8.91}Cu_{0.27}Fe_{0.05})_{9.23}Te_{1.77}$
20.	JD 4	pilsenite	-	0.34	0.22	-	-	72.13	-	26.53	-	99.22	$(Bi_{4.93}Ag_{0.05}Cu_{0.05})_{5.03}Te_{2.97}$
21.	JD 4	pilsenite	-	-	-	-	-	71.24	-	28.39	-	99.63	$Bi_{4.84}Te_{3.16}$
22.	Ch-461b	galena	-	-	-	85.17	-	-	-	-	14.38	99.54	$Pb_{0.96}S_{1.04}$
23.	Ch-461b	galena	-	-	0.04	82.77	0.92	1.30	-	-	14.62	99.65	$(Pb_{0.91}Fe_{0.04}Bi_{0.01})_{0.96}S_{1.04}$
24.	MD 46	chalcopyrite	-	0.43	34.40	-	30.20	-	-	-	34.90	99.93	$Cu_{0.998}Ag_{0.007}Fe_{0.997}S_{1.997}$
25.	MD 46	chalcopyrite	-	-	34.39	-	30.15	-	-	-	34.77	99.31	$Cu_{0.999}Fe_{0.997}S_{2.003}$
26.	JD 4	pyrrhotite	-	-	-	-	63.61	-	-	-	36.25	99.86	$Fe_{1.00}S_{1.00}$
27.	JD 4	pyrrhotite	-	-	0.09	-	63.19	-	-	-	35.89	99.17	$Fe_{0.99}S_{1.00}$
28.	JD 4	pyrrhotite	-	-	-	-	63.53	-	-	-	36.20	99.72	$Fe_{0.99}S_{1.00}$
29.	MD 46	pyrrhotite	-	0.07	-	-	61.32	-	0.03	-	38.58	100.00	$Fe_{0.95}S_{1.05}$

Bismuthinite is calculated on the basis of 5 *apfu*, as it is adopted by CNMMN of IMA; pilsenite - on the basis of 8 *apfu*, as bismuthian pilsenite, accepted by Gu et al. (2001); hedleyite – on the basis of 11 *apfu*, as it is accepted by Jambor at al. (2002)

Table 2. *Published crystallographic and compositional data of hedleyite*

Таблица 2. *Публикувани данни за кристалографските особености и химичния състав на хедлеита*

Authors/ Deposits	Symmetry		Unit cell dimensions			Composition wt. %									(Bi+Cu+Fe +Pb+Sb)/ (Te+S+Se)	Proposed formula
	Point group	Space group	*a* Å	*c* Å	*z*	Bi	Te	Se	Cu	Fe	Pb	Sb	S	Σ		
Warren and Peacock (1945) Good Hope, Hedley District, Canada																$Bi_{14}Te_6$
	$\bar{3}2/m$	$R\bar{3}m$	4.46	118.8	3	80.60	18.52	-	-	-	-	-	0.12	99.24	2.59	$Bi_{14.32}(Te_{5.39}S_{0.15})_{5.54}$
			4.46	5.94		81.55	17.60	-	-	-	-	-	0.04	99.19	2.80	$Bi_{14.49}(Te_{5.13}S_{0.05})_{5.18}$
Zavyalov et al. (1976) Vostok 2, Russia																$Bi_{2+x}Te_{1-x,\ x=0.12-0.14}$
	$\bar{3}2/m$	$R\bar{3}m$	4.47	119.2	3	81.30	19.20	0.60	-	-	-	-	-	101.10	2.46	$Bi_{2.12}(Te_{0.82}Se_{0.04})_{0.86}$
		$P\bar{3}m1$	4.472	17.82		81.10	17.90	0.70	-	-	-	-	-	99.70	2.60	$Bi_{2.14}(Te_{0.77}Se_{0.05})_{0.82}$
Bayliss (1991)	$\bar{3}2/m$	$P\bar{3}m1$	4.475	5.367	3	no compositional data included in Bayliss (1991)										Bi_5Te_2 Bi_8Te_3
Dobbe (1993) Tunaberg, Sweden																BiTe
	after Bayliss (1991)					78.40	18.50	-	0.20	0.10	1.30	0.90	0.20	99.60	2.60	$*(Bi_{1.38}Pb_{0.02}Cu_{0.01}Fe_{0.01}Sb_{0.03}Te_{0.53}S_{0.02})_{2.00}$
						78.90	18.80	-	0.30	0.10	0.30	1.20	-	99.60	2.68	$*(Bi_{1.39}Pb_{0.01}Cu_{0.01}Fe_{0.01}Sb_{0.04}Te_{0.54})_{2.00}$
						77.10	19.90	-	0.20	0.10	0.30	1.10	-	98.70	2.46	$*(Bi_{1.36}Pb_{0.01}Cu_{0.01}Fe_{0.01}Sb_{0.03}Te_{0.58})_{2.00}$
Gu et al. (2001) Huangshaping and Datuanshan, China																Bi_8Te_3
	after Zavyalov et al. (1976)					82.46	18.00	0.01	-	-	-	0.10	-	100.56	2.80	$*(Bi_{8.09}Sb_{0.02})_{8.11}(Te_{2.892}Se_{0.002})_{2.894}$
						80.08	16.96	1.73	0.01	0.40	0.37	0.12	0.11	99.78	2.49	$*(Bi_{7.64}Cu_{0.003}Fe_{0.14}Pb_{0.035}Sb_{0.02})_{7.84}(Te_{2.65}Se_{0.44}S_{0.07})_{3.16}$

* Chemical formulae calculated according to published chemical compositions in Dobbe (1993) based on two *apfu* and Gu et al. (2001) – based on eleven *apfu*, as considered in the respective papers

Hedleyite is typically a late-stage, rare hydrothermal mineral in quartz veins and massive sulphides, associated with skarns and breccias and less common in pegmatites. It usually associates with native bismuth, bismuthinite, gold, pyrrhotite and chalcopyrite as observed in the Martinovo deposit. Hedleyite is difficult to distinguish by reflected light microscopy, because it has similar physical and optical properties (colour, tinge, reflectivity, anisotropy) to the other bismuth tellurides, such as tellurobismuthite, pilsenite, joseite, etc., as stated by Ramdohr (1980). In this study, it was determined by scanning electron microscopy (SEM) and EPMA. In reflected light microscopy it possesses silver white colour with slight yellowish tinge, clear anisotropy and high reflectivity compared to bismuthinite. It is soft, with Moos hardness two and shows smooth surface in polished sections. Sometimes its grains have irregular shapes, but more often they form rounded and elongated blebs, ranging from several to 100 µm in size (Figs. 2 and 3).

Compositional data of hedleyite are shown in Table 1. Although the IMA approved Bi richest formula of Gu et al. (2001) was accepted for stoichiometric our results show significant overstoichiometric Bi contents. This fact is better visualized on Fig. 4, showing the Martinovo analyses grouped well aside of both the stoichiometric and reported by other authors values. Small amount of impurities - Cu and Fe about 0.30-0.80 wt.%, Pb – up to 3.79 wt.%, are detected too.

A Bi-Te phase with composition corresponding to pilsenite was found as minute (2-2.5 µm), triangle-shaped inclusion within pyrrhotite (Table 1) in one sample, containing Bi-S association. Although this mineral is a common constituent of such assemblages and its existence here is logical, the minute size of the grain casts some doubts on the correct mineral identification.

The pyrrhotite-chalcopyrite assemblage

Main ore minerals in the assemblage are pyrrhotite and chalcopyrite, which rarely associate with marcasite, pyrite and magnetite. *Pyrrhotite* is coarse-grained and has irregular shapes, sometimes fractured. According to Tarassova (1989), it is observed in two polymorphic modifications - hexagonal and monoclinic, but they are not discernable in reflected light microscopy. *Chalcopyrite* usually occurs as irregular grains, often crosscutting pyrrhotite aggregates. *Pyrite* is a rare mineral in this assemblage. It is usually observed as small euhedral grains with cubic or cubo-octahedral shape and rarely associates with marcasite in aggregates, which replace pyrrhotite. *Marcasite* is comparatively rare and is formed metasomatically after pyrrhotite as orientated, elongated, fine-grained poly-synthetic aggregates (Fig. 2c). *Magnetite* is observed as rare, fine relics within pyrrhotite.

Discussion

A homologous series of five Bi-Te phases (tellurobismuthite, tsumoite, pilsenite, hedleyite and unnamed Bi_2Te) are synthesized in the Bi-Te system (Afifi et al., 1988). All of them exist in nature (Warren, Peacock, 1945; Zavyalov et al., 1976; Shimazaki, Ozawa, 1978; Gamyanin et al., 1982; Ozawa, Shimazaki, 1982; Goncharov et al., 1984; etc.). In natural occurrences however, the majority of them show non-stoichiometric compositions getting out of the limits, outlined by the synthetic analogues. Dobbe (1993) suggested the existence of single solid solution phase in the Bi-Te-S system with atomic ratio (Bi +Pb + Sb)/(Te + S) between 1.35 and 2.61, covering the chemical compositions of all known pilsenites and hedleyites. Gu et al. (2001) on the contrary, proposed the existence of five limited solid solutions in Bi-Te system, corresponding to Bi_2Te_3, Bi_2Te_2, Bi_4Te_3, Bi_2Te, and Bi_8Te_3.

As seen, there is significant uncertainty about the limits of the possible compositions in the Bi-Te system. The reason for this situation most probably lies in the crystal structure specifics of this group of minerals. According to Strunz (1963), Zavyalov et al. (1976), Shimazaki and Ozawa (1978), Yamana et al. (1979), Ozawa and Shimazaki (1982) and Bayliss (1991), Cook and Ciobanu (2004) all structures of Bi-Te minerals can be described as series of hexagonal close packed layers of Bi or Te atoms, with differences only attributed to different patterns of layer stacking. These patterns can be pretty complex and respectively can produce a rather large number of possible resulting compositions. This phenomenon can be traced in structure solution results (Warren, Peacock, 1945; Zavyalov et al., 1976), some of which show *c* values up to 25 times larger than the respective *a* values, proving this way rather long series of non-periodic layer stacking.

Our results only confirm the wider range of possible compositions in the Bi-Te system. The pilsenite from Martinovo (Table 1, Fig. 4) corresponds to the Bi-richest variety, reported by Gu et al. (2001) and proposed for the name bismuthian pilsenite.

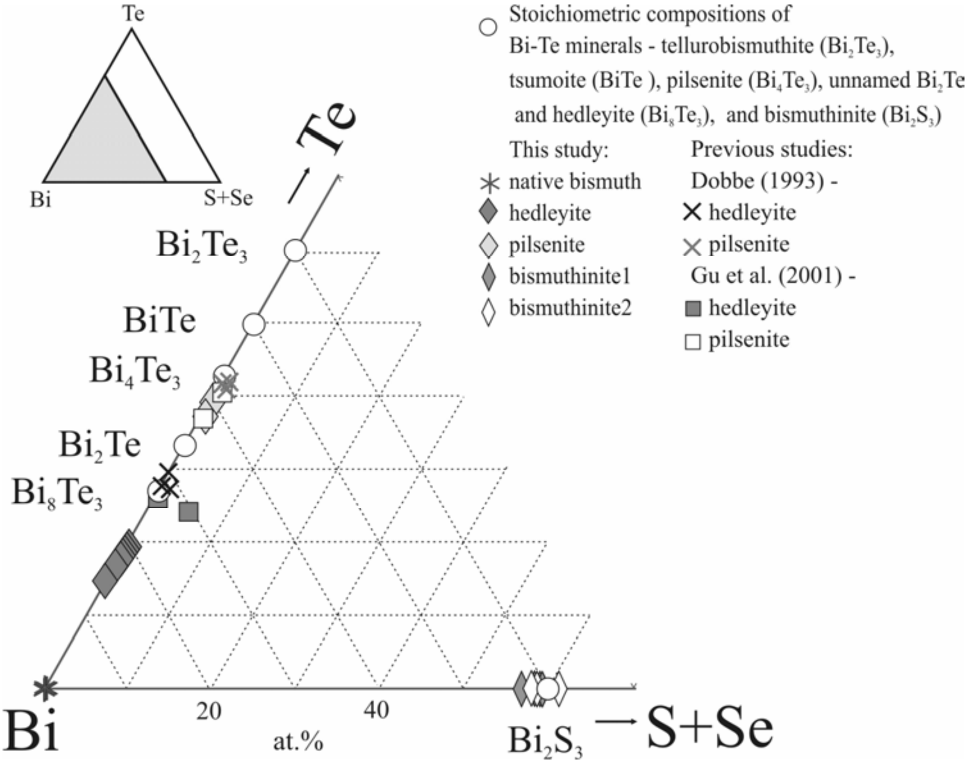

Fig. 4. Compositions of native bismuth, bismuthinite, hedleyite and pilsenite(?), compared to the data of Dobbe (1993), Gu et al. (2001) and stoichiometric compositions, marked with circle (○)

Фиг. 4. Състави на самороден бисмут, бисмутинит, хедлеит и пилзенит (?) сравнени със състави на същите минерали по данни на Dobbe (1993) и Gu et al. (2001) представени в Таблица 2, и със стехиометрични състави, означени с кръгче (○)

The calculated formulae for hedleyite, based upon eleven *apfu*, as proposed by Gu et al. (2001) show a variation range $(Bi_{8.53-8.93}Cu_{0.14-0.27}Fe_{0.05-0.13}Pb_{0.18-0.39})_{8.84-9.46}Te_{1-54-2.16}$. In order to agree with the 11 *apfu* concept we need to comply with a supposed substitution of Te by Bi as high as 1.46 *apfu*. This substitution is rather high. On the other hand, observed Bi/Te atomic ratio is much closer to 4:1 rather than to 8:3. This is why formulae were re-calculated on the basis of five *apfu* for a hypothetical phase Bi_4Te (Table 3). As seen, the composition is well stabilized over a Bi_4Te formula (in the limits of analytical accuracy and impurity treatment), but such phase is unknown in the Bi-Te system. This fact either significantly enhances the range of hedleyite definition or gives a clue to a new mineral species in the Bi-Te system. Unfortunately, the small size of the available grains prevents any X-ray studies required for precise solution of the pending questions.

The minerals from the Bi-S and Bi-Te-S associations (native bismuth, bismuthinite, hedleyite and pilsenite) in the Martinovo deposit commonly occur in similar postskarn environments (Nysten, 1990; Dobbe, 1993; Gu et al., 2001). Co-existence of native bismuth, hedleyite and bismuthinite is also considered characteristic for gold deposits, particularly for the Au-skarn type (Warren, Peacock, 1945; Meinert, 1992; Cook et al., 2002; Rombach, 2004).

Table 3. *Formulae of the hedleyites in Table 1 (13-19), re-calculated on five apfu basis, according to the proposed composition Bi_4Te*

Таблица 3. *Формули изчислени въз основа отношението Bi/Te от анализите за хедлеит в Таблица 1(13-19) при сума от 5 apfu за предполагаема формула Bi_4Te*

№ in Table 1	Sample №	Calculated Formula
13.	C-85	$(Bi_{3.955}Cu_{0.062})_{4.017}Te_{0.983}$
14.	Ch-85	$(Bi_{3.902}Cu_{0.079}Fe_{0.054})_{4.035}Te_{0.965}$
15.	Ch-85	$(Bi_{3.877}Cu_{0.086}Pb_{0.176})_{4.139}Te_{0.860}$
16.	Ch-85	$(Bi_{4.057}Cu_{0.095}Fe_{0.062}Pb_{0.087})_{4.301}Te_{0.699}$
17.	Ch-85	$(Bi_{3.892}Cu_{0.078}Fe_{0.037}Pb_{0.079})_{4.086}Te_{0.914}$
18.	Ch-85	$(Bi_{3.981}Cu_{0.066})_{4.047}Te_{0.953}$
19.	Ch-85$_2$	$(Bi_{4.051}Cu_{0.125}Fe_{0.021})_{4.197}Te_{0.803}$

According to Brown and Lewis (1962) and Elliott (1966), bismuth+hedleyite and hedleyite exist below 266°C and 312°C, respectively. Compared with the $f\mathrm{Te}_2$ - $f\mathrm{S}_2$ diagram calculated for 200°C in Afifi et al. (1988) is outlined an area of stability at log $f\mathrm{Te}_2 \geq -14.9$ and $f\mathrm{S}_2 \geq -16.1$, determined by reaction Bi_2Te_3/Bi_2S_3. The fact that hedleyite, pilsenite and bismuthinite show maximum Bi contents, is an evidence for a low Te fugacity in the hydrothermal fluid. Furthermore, Cook et al. (2002) also believed that liquid Bi (in higher *T*°C) may scavenge chalcogenides, e.g. Te, and precipitated them later as blebs of intermediate Bi tellurides and sulphides, where the resulting assemblages typically have Bi/(Te +S+Se) > 1, for example hedleyite and pilsenite. The Cook et al. (2002) hypothesis also states, that the observed phases therefore may have non-stoichiometric composition too.

Conclusions

Native bismuth, bismuth tellurides and sulphides, particularly hedleyite and bismuthinite, often exist together with pyrrhotite and chalcopyrite in skarn environments. Thus, their presence in the postskarn sulphide-arsenide mineralization in Martinovo deposit is explicable. The co-existence of these minerals reveals some of the ore-forming conditions, such as temperature below 266°C and Te fugacity and S fugacity equal or above -14.9 and -16.1, respectively. The observed Bi/Te atomic ratio in hedleyite could substantiate the existence of bismuthian variety of hedleyite, or the existence of another Bi_4Te phase in the bismuth-tellurium system. Furthermore, the compositions of previously mentioned mineral phases by Dragov (1971, 1992), such as bismuthinite, galenobismuthite and joseite-A proved to refer to bismuthinite (Bs1 and Bs2) and bismuthian hedleyite.

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