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HYDROTHERMAL NICKEL MINERALIZATION FROM THE BLACK SHALES IN ČIERNA LEHOTA (WESTERN CARPATHIANS, SLOVAKIA)

Black shales hosted syngenetic metamorphosed pyrrhotite-pyrite mineralization is environment for epigenetic hydrothermal mineralization, where the pararammelsbergite is the main ore mineral. Pararammelsbergite features spherules, colloform, botryoidal textures as well as subhedral grains. The structural formula of pararammelsbergite could be written as $(Ni_{1.00}Fe_{0.03})_{\Sigma 1.03}(As_{1.84}S_{0.11})_{\Sigma 1.95}$ which indicates limited cation substitution but substantial anion substitution of As by S. Ni—As—Fe—S paragenesis contains furthermore löllingite, gersdorffite and arsenopyrite. The mineral assemblage typically shows complex textural and compositional variation, reflecting an environment of rapid changes in physicochemical conditions of its formation.

Keywords: Ni, Fe diarsenides, pararammelsbergite, mineralogy, black shales, Slovakia.

Geological settings and ore mineralization. The minerals of the Fe—Co—Ni—As—S system occur in many different types of geological environments. These range from droplets in podiform chromites to framboids in black shales or chalk. Fe and S are, in most cases, the dominant constituents, although there are numerous deposits where the ore-forming system is rich in Ni, Co and As. The described mineralization occurs in the Tatric tectonic unit of Strážovské vrchy Mts. (crystalline basement of the Suchý Mts.). The Tatric tectonic unit is an extensive thick-skinned crustal sheet composed of a pre-Alpine (generally Variscan) crystalline basement and its sedimentary cover. The Tatric basement has a generally well-preserved Variscan structures without a significant Alpine overprint. Investigated mineralization occurs in the crystalline basement of the Suchý Mts which is build by Variscan granitoid rocks (S-type), paragneisses and migmatitic complexes. The metamorphic rocks are mainly high temperature paragneisses and quartz-rich paragneisses. The age of granitoidic rocks from the Suchý Mts. determined by Rb-Sr isochron is 393 ± 6 Ma [10, 12]. Variscan tectogenesis is dominant with temperatures and pressures about 540—560 °C/4—5 Kbar, respectively and X (H_2O) = 0.6—0.8 [3]. The Alpine restructuring of the crystalline complex is relatively poor [13].

The investigated mineralization is situated approximately 2 km SSE from village of Čierna Lehota (Fig. 1). Mineralization is situated in a narrow zone (about 20 m thick, SSW—NNE direction) of

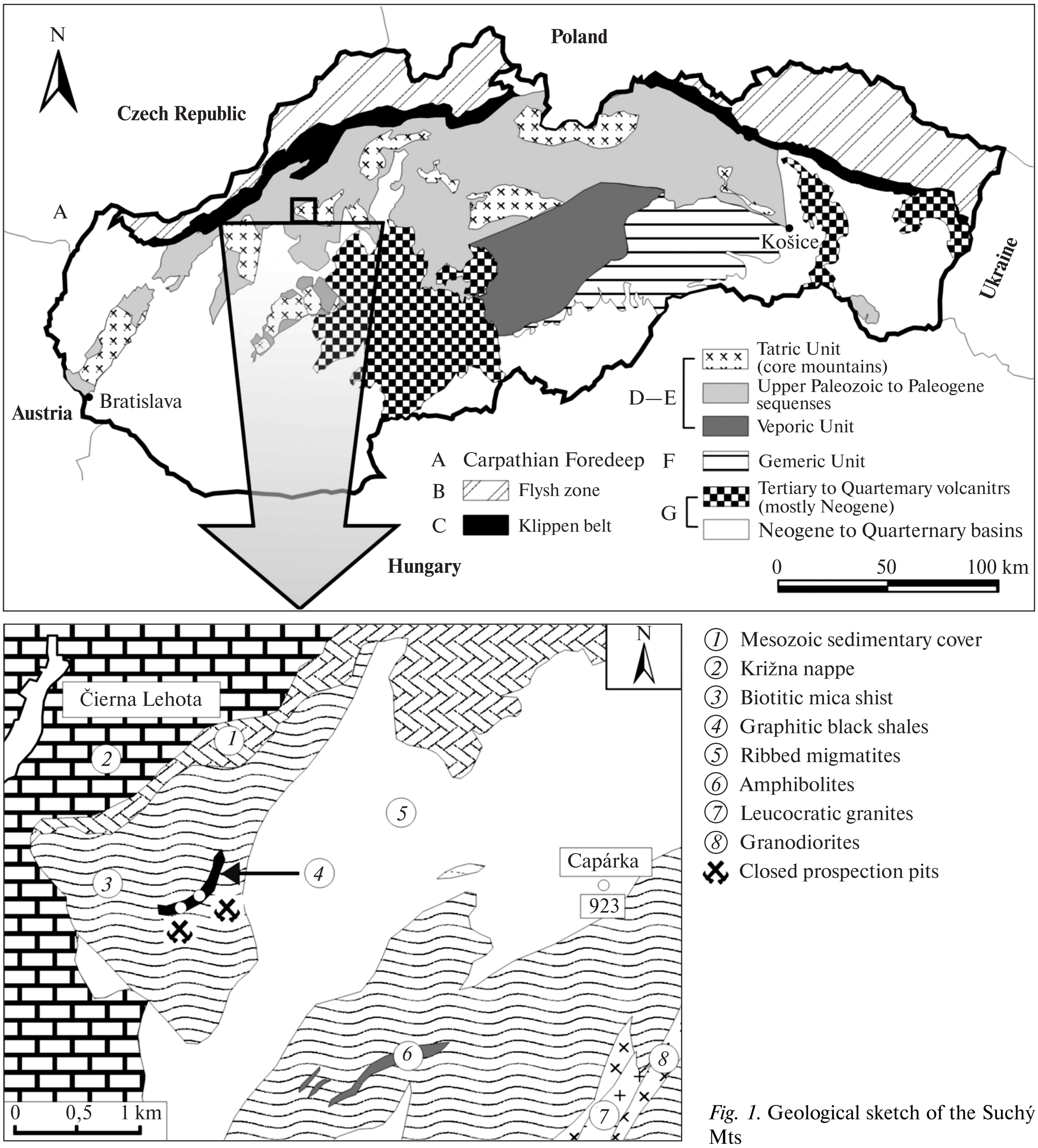

Fig. 1. Geological sketch of the Suchý Mts

black shales and intensive graphitized rocks (graphitic-biotitic gneisses, graphitic metaqaurtzite). This zone occurs in the quartz-biotitic paragneisses.

Nickel mineralization is developed in the environment of metamorphic syngenetic pyrite — pyrrhotite mineralization with sphalerite (± galena, chalcopyrite) in the black shales. Syngenetic pyrite — pyrrhotite mineralization was formed during volcano-sedimentary processes, presumably of Devonian age. Later on, during Variscan tectono-metamorphic processes pyrite-pyrrhotite ores were recrystallized. These ores exhibit banded impregnation and massive textures. Massive pyrrhotite is the most prevailing. Mineralogy of the area was studied by Mikuš et al. [15] and Pršek et al. [19].

According to ICPMS analysis (Geological Survey, Spišská Nová Ves) black shales, as host rocks for Ni-Bi mineralization, are enriched in Mo, V, Cr, Ba and organic carbon. Hydrothermally altered rocks are enriched in elements that are present in hydrothermal mineralization such as Cu, Ni, Bi, As, Zn, and carbonate-bound carbon.

Mineral associations and paragenetic study of hydrothermal mineralization. The hydrothermal mineralization was developed during Variscan tectono-metamorphic evolution of the area. Several mineralization stages were distinguished. The first, oldest one consists predominantly of Ni and Fe arsenic minerals with quartz and Fe-dolomite as gangue. This assemblage is typical by predominance of pararammelsbergite; löllingite, arsenopyrite and gersdorffite are rare. Paragenetical evidence suggests that arsenides formed initially and gradually, with increase in sulphur fugacity and decreasing temperature, arsenopyrite and gersdorffite were formed. Chemical composition of minerals from the first stage is shown in Table.

Bismuth minerals — native bismuth, bismuthinite, aikinite, Cu-bearing matildite together with Bi sulphosalts (cuprobismutite, hodrushite, kupčíkite) form the second stage of mineralization and are accompanied by Bi-Fe bearing tennantite, chalcopyrite, pyrite, sphalerite and galena with quartz gangue [19].

The third, epigenetic stage is represented by Pb-Zn mineralization (galena, sphalerite and chalcopyrite) with carbonate gangue and the fourth stage is characterized by hematite and magnetite with calcite. Secondary minerals are especially represented by Ni arsenates and sulphates, e. g. annabergite, retgersite, native copper, cuprite, chrysocolla, gypsum and many X-ray amorphous phases [14].

Ni mineralization. The samples are mainly composed of Ni minerals. Four different Ni-Fe phases (two arsenides and two sulfarsenides) collectively referred to as arsenides have been found in Čierna Lehota. The most abundant of them is the *pararammelsbergite* occurring as mostly massive, colloform concentrically zoned aggregates and spherules as well as subhedral needle-shaped crystals (Fig. 2) *Löllingite* is present as xenomorphic tiny lamellar grains (up to 70 μm) closely associated (intergrown) with pararammelsbergite. Textural relationships indicate that pararammelsbergite with other arsenides and sulphoarsenides are older than the Bi sulphosalts. The name pararammelsbergite is used, because it has been possible to distinguish this mineral from rammelsbergite and krutovite. In reflected light it shows pure white color and strong anisotropy.

The X-ray diffraction pattern of pararammelsbergite from Čierna Lehota could be matched with the published pararammelsbergite data (JCPDS) [1] and its lattice parameters (a = 5.7794; b = = 5.8469; c = 11.4520 Å) correspond to tabulated data [6]. Compositional data (Table) reported below and plotted in Fig. 3 are based on a compilation of electron microprobe analyses carried out at the Faculty of the Natural Sciences (Comenius University, Bratislava), M.P. Semenenko Institute of Geochemistry, Mineralogy and Ore Formation of the NAS of Ukraine (Kyiv). Most of the ana-

Microprobe analyses of diarsenides and sulphoarsenides from Čierna Lehota

Mineral	Sample	Compositions, wt. %							Atomic proportions					
		As	S	Fe	Co	Ni	Cu	*Total*	As	S	Fe	Co	Ni	Cu
Pararammelsbergite	305/17	64.18	4.51	3.63	0.47	25.29	0.08	98.16	1.71	0.28	0.13	0.02	0.86	0.00
	305/5a	69.09	1.25	0.56	0.08	29.1	0.27	100.34	1.88	0.08	0.02	0.00	1.01	0.01
	305/17	69.96	0.74	0.44	0.04	28.51	0.11	99.8	1.93	0.05	0.02	0.00	1.00	0.00
	305/5a	64.4	4.8	2.06	0	29.53	0	100.93	1.66	0.29	0.07	0.00	0.97	0.00
	305/17	62.7	4.91	2.25	0	29.16	0	99.02	1.64	0.30	0.08	0.00	0.98	0.00
	305/14*	71.25	0.07	0.66	0.26	28.21	0.04	100.49	1.97	0.00	0.02	0.01	0.99	0.00
Gersdorffite	305/17*	46.59	17.48	11.84	0.04	22.63	0	98.68	1.06	0.93	0.36	0.00	0.66	0.00
	305/7	49.39	13.22	7.33	0.13	29.37	—	99.81	1.16	0.73	0.23	0.00	0.88	0.00
	305/7	49.04	16.41	6.23	0.34	28.19	—	100.2	1.11	0.87	0.19	0.01	0.82	0.00
Löllingite	305/5a	66.28	3.15	31.4	0	0.7	0.14	101.6	1.70	0.19	1.08	0.00	0.02	0.00
	305/5a	62.89	3.3	31.67	0	0.7	0.13	98.63	1.65	0.20	1.12	0.00	0.02	0.00
	305/5a	65.59	2.69	30.6	0	0.39	0.16	99.71	1.73	0.17	1.08	0.00	0.01	0.00
	305/5a	63.71	3.12	32.75	0	0.51	0.17	100.26	1.65	0.19	1.14	0.00	0.02	0.01
	305/5a	63.84	3.4	31.7	0	0.65	0.13	99.72	1.66	0.21	1.11	0.00	0.02	0.00
Arsenopyrite	305/6a*	43.22	21.04	34.65	0.08	1.04	0.04	100.07	0.92	1.05	0.99	0.00	0.03	0.00
	305/17	45.23	19.13	35.29	0.06	0.12	0.08	99.91	0.99	0.97	1.03	0.00	0.00	0.00

Note. Analyses were carried out on: 1 — Cameca SX-100 in Department of Electron Microanalysis, Geological Institute of Dionyz Stur, Bratislava, Slovak Republic and 2* — JXA-8200 in Technical centre of NAS of Ukraine, Kyiv, Ukraine.

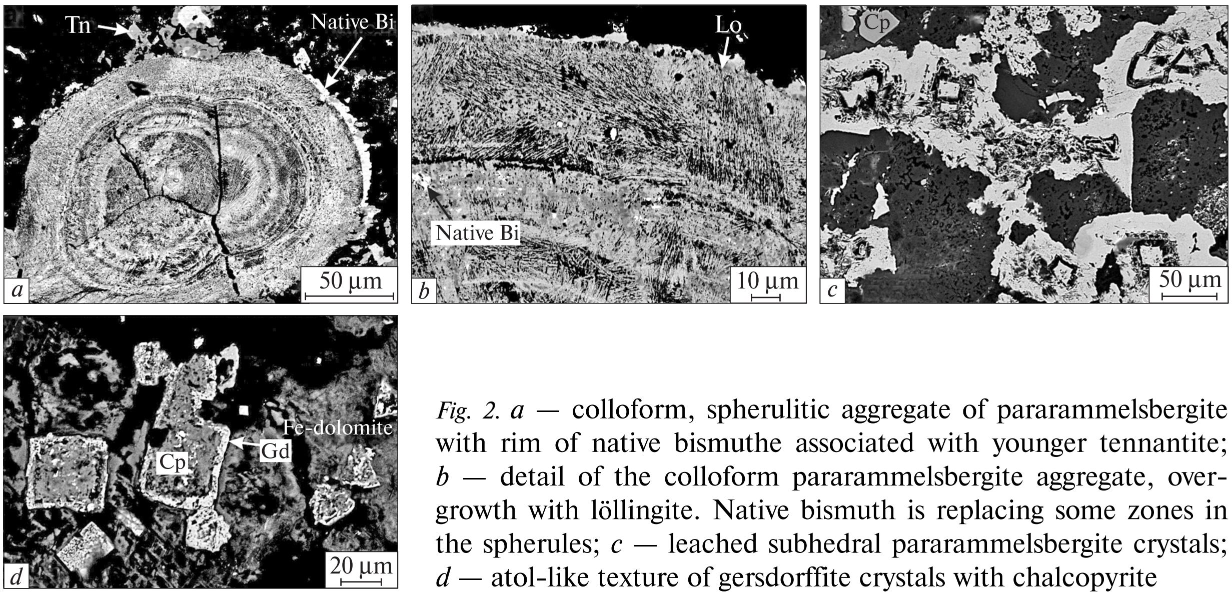

Fig. 2. a — colloform, spherulitic aggregate of pararammelsbergite with rim of native bismuthe associated with younger tennantite; *b* — detail of the colloform pararammelsbergite aggregate, overgrowth with löllingite. Native bismuth is replacing some zones in the spherules; *c* — leached subhedral pararammelsbergite crystals; *d* — atol-like texture of gersdorffite crystals with chalcopyrite

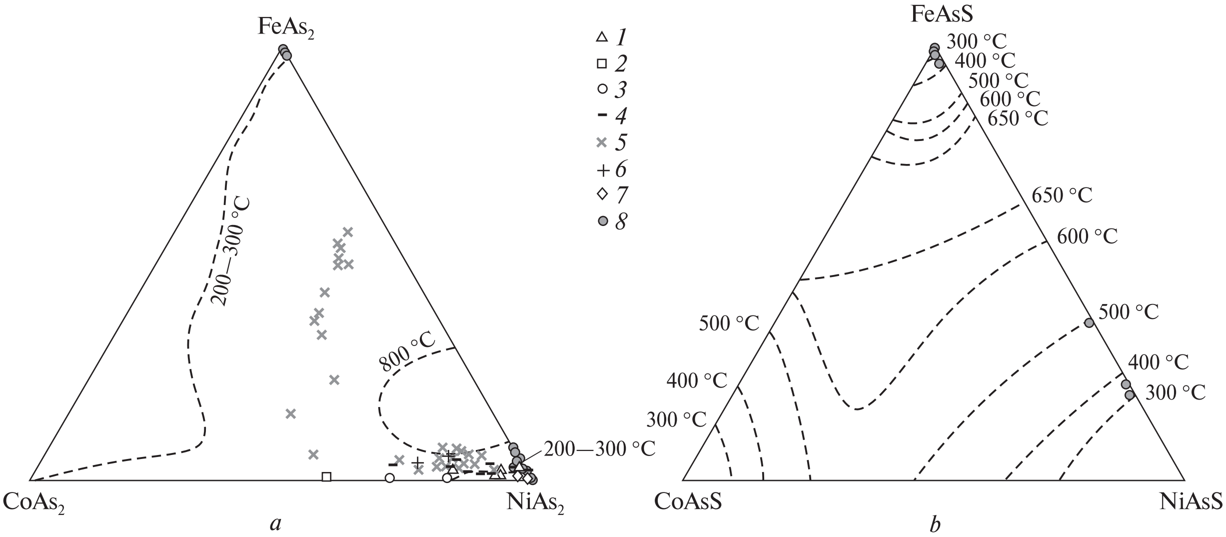

Fig. 3. Composition of (*a*) diarsenides and (*b*) sulphoarsenides from Čierna Lehota. Miscibility fields at various temperature in (*a*) after Gervilla and Rønsbo (1992). Isotherms for sulphoarsenides (*b*) are after Klemm (1965). Data after: *1* — San Juan de Plan, Spain (Fanlo et al., 2004); *2* — Bou Azzer, Morocco (Vinogradova et al., 1972); *3* — Brunflo, Sweden (Nyström and Wickman, 1991); *4* — Atrevida, Spain (Parviainen et al., 2008); *5* — Ishkinino, Russia (Nimis et al., 2008); *6* — Malaga, Spain (Gervilla and Rønsbo, 1992); *7* — Crescencia, Spain (Fanlo et al., 2006); *8* — authors own analyses

lyses of diarsenides approaches almost pure endmember from the point of view of diarsenides solid solution (dss). They lack the cobalt. There is not so distinct substitution in the pararammelsbergite (average 0.03 apfu $FeAs_2$) and löllingite (average 0.02 apfu $NiAs_2$) of Čierna Lehota. On the other hand, diarsenides display significant and variable extents of S-for-As substitution. Sulfur contents are particularly high in pararammelsbergite, ranging from 0.05 to 0.32 apfu (atoms per formula unit), As-S substitution in löllingite is less extended (up to 0.21 apfu of S).

Sulphoarsenides are represented by *gersdorffite* and *arsenopyrite*. Less abundant gersdorffite forms up to a few hundreds of μm sized, sometimes atoll-like aggregates with younger chalcopyrite and rarely skeletal aggregates. Gersdorffite shows increased Fe content (up to 11.84 wt. %) and similar to diarsenides lacks Co (Table; Fig. 2). *Arsenopyrite* forms euhedral crystals up to 1mm in size and aggregates in ferrous dolomite and in silicified hydrothermal alteration zones in wallrock. It occurs with gersdorffite and pyrite. Arsenopyrite shows negligible Ni and Co content. Similar to pararammelsbergite and löllingite, As and S contents in arsenopyrite and, especially, gersdorffite tend to be mutually correlated.

Discussion and conclusion. There are three naturally occurring polymorphs of $NiAs_2$; the most common is rammelsbergite (the Ni end member of the diarsenide solid solution), the other two, krutovite and pararammelsbergite, are rare. Recently, the only published analyses of pararammelsbergite we have found in the literature are from the Crescencia deposit [5] and it shows similar chemical composition (low Fe, Co content) but lower content of S (up to 0.66 wt. %). Chemical composition of pararammelsbergite from Čierna Lehota was compared also with more widespread rammelsbergite. The only chemically similar rammelsbergite is from the Atrevida mine (Fig. 2), although most rammelsbergite from Atrevida show some Co content [18]. All literature published about rammelsbergite display significant fractions of Co, Ni, and Fe components in solid solution (Fig. 3) [9, 16, 17, 22]. There are also some textural similarities: pararammelsbergite from Čierna Lehota and rammelsbergite from Atrevida [18] appear as spherules, and colloform textures, as well as subhedral crystals.

The chemical compositions of these arsenide minerals exhibit limited cation substitution but substantial anion substitution of As by S, exceeding the expected theoretical values at low temperatures. This suggests that most of them formed under disequilibrium conditions.

Because of the low Co content in the pararammelsbergite and löllingite the $CoAs_2$ — $NiAs_2$ — $FeAs_2$ system can be regarded as pseudobinary. Roseboom [21] reported that at 800 °C there is complete miscibility between synthetic rammelsbergite and safforite and that a miscibility gap appeared at lower temperatures. Rammelsbergite has been reported to transform to pararammelsbergite at temperatures lower than 590 °C [23], although the stability relations between these phases and krutovite are unknown. The low mutual solubility of Fe, Co and Ni diarsenides from Čierna Lehota would also be consistent with a relatively low temperature of formation for Ni paragenesis (Fig. 3) [7, 20].

The data discussed above suggest that the depositional environment of the Ni arsenides in the Čierna Lehota occurrence was characterized by the presence of Ni and Fe-rich fluids, or fluids with a Ni and Fe solubility lower than that of Co, promoting the formation of nearly pure Ni phase (pararammelsbergite, löllingite), and by crystallization conditions partly far from equilibrium. In fact, Canals et al. [2] interpreted the skeletal, botryoidal and spherulitic textures as formed rapidly from supersaturated solutions.

Hem [8] summarized, that members rich in Co or Ni are mostly found in almost S-free deposits, in assemblages dominated by arsenides and Fe-rich members mostly occur in S-richer assemblages with minerals such as pyrrhotite, chalcopyrite, sphalerite, and rarely pyrite. Ni-rich members developed in the environment of syngenetic pyrrhotite-pyrite mineralization from Čierna Lehota suggest some discussion.

Possible source of Ni, As and Bi can be found in the surrounding (host) rocks of the mineralization. During Variscan tectonometamorphic events, these components could have been leached and transported to form the studied mineralization.

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ГІДРОТЕРМАЛЬНА НІКЕЛЕВА МІНЕРАЛІЗАЦІЯ ЧОРНИХ СЛАНЦІВ РЕГІОНУ ЧЕРНА ЛЕХОТА (ЗАХІДНІ КАРПАТИ, СЛОВАЧЧИНА)

За допомогою мікрозондового аналізу досліджено нікелеву епігенетичну гідротермальну мінералізацію в палеозойських чорних сланцях, яка, в свою чергу, накладається на сингенетичну пірит-піротинову. Головним нікелевим рудним мінералом є парарамельсбергіт, який утворює глобули з коломорфними і гроноподібними структурами, а також гіпідіоморфні зерна. Кристалохімічна формула парарамельсбергіту, $(Ni_{1,00} \times \times Fe_{0,03})_{\Sigma 1,03}(As_{1,84}S_{0,11})_{\Sigma 1,95}$, свідчить про обмежені заміщення в катіонній частині та істотні заміщення аніона As на S. Поширений парагенезис Ni—As—Fe—S представлений переважно льолінгітом, герсдорфітом і арсенопіритом. Варіації хімічного складу та особливості структур згаданих мінералів вказують на швидкі температурні зміни в середовищі мінералоутворення.

Ключові слова: Ni, Fe діарсеніди, парарамельсбергіт, мінералогія, чорні сланці, Словаччина.

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ГИДРОТЕРМАЛЬНАЯ НИКЕЛЕВАЯ МИНЕРАЛИЗАЦИЯ ЧЕРНЫХ СЛАНЦЕВ РЕГИОНА ЧЕРНА ЛЕХОТА (ЗАПАДНЫЕ КАРПАТЫ, СЛОВАКИЯ)

С помощью микрозондового анализа изучена никелевая эпигенетическая гидротермальная минерализация в палеозойских черных сланцах, которая формируется вслед за сингенетической пирит-пирротиновой. Главным никелевым рудным минералом является парараммельсбергит, представленный глобулами с колломорфными и гроздеподобными структурами, а также гипидиоморфными зернами. Кристаллохимическая формула парарамельсбергита, $(Ni_{1,00}Fe_{0,03})_{\Sigma 1,03} \times \times (As_{1,84}S_{0,11})_{\Sigma 1,95}$, свидетельствует об ограниченных замещениях в катионной части и существенных замещениях аниона As на S. Распространенный парагенезис Ni—As—Fe—S представлен преимущественно леллингитом, герсдорфитом и арсенопиритом. Вариации химического состава и особенности структур упомянутых минералов указывают на быстрые температурные изменения в среде минералообразования.

Ключевые слова: Ni, Fe диарсениды, параммельсбергит, минералогия, черные сланцы, Словакия.