МІНЕРАЛОГІЧНИЙ ЖУРНАЛ
MINERALOGICAL JOURNAL
(UKRAINE)

UDC 549.328/.334 (437.6+477)

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COMPARATIVE STUDY OF Bi-Te-Se-S MINERALIZATIONS IN SLOVAK REPUBLIC AND TRANSCARPATHIAN REGION OF UKRAINE. PART 1. LOCALITIES, GEOLOGICAL SITUATION AND MINERAL ASSOCIATIONS

Comparative analysis of telluride occurrences found in the territory of Slovakia and Transcarpathians (Ukraine) has shown that there is distinct difference between the mode of Au-Ag-Bi-Te-Se mineralization of these regions. But within the area of distribution of neovolcanites Bi-Te-Se-S mineralization is generally represented by similar mineralogical phases. In the Transcarpathian region bismuth tellurides (tsumoite, pilsenite, joseites, native bismuth and poorly studied sulpho-seleno-tellurides of bismuth) were found only in metasomatites as secondary quartzites of the Vyghorlat-Guta ridge area. (Il'kivtsy, Podulky, Smerekiv Kamin'). The similar mineralization have been also found in some neovolcanites of Slovakia (Poruba pod Vigorlatom, Remetska Hamra).

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Introduction. Associations of non-ferrous and precious metals occurred due to geochemical differentiation of elements in the upper mantle and earth crust. There is a certain relation between "composition" of association of chalcophile elements and conditions of their formations [18]. So, for example, association of Ag-Au-Hg metals and satellite association of Bi-Te-Se occurs at low temperature, forming characteristic paragenesises in epithermal polymetallic deposits. Among compounds of chalcophile metals the (Pb, Ag, Au, Cu) tellurides and selenides occupy special position because of their genetic relation with gold [8, 9, 18]. Owing to the large size the ion of bismuth takes special position in the range of three "semimetals" As-Sb-Bi. It is also manifested by distinct affinity of tellurium to bismuth and genetic association of bismuth with large atoms such as tellurium and selenium. At the same time, genetic relation between Bi and S is also obvious, which is manifested in formation of a great number of bismuth sulphosalts [18]. Because of strong dispersion of selenium in widespread sulfides it rarely forms separate minerals. As the significant amount of selenium and sulfur can be traced into the structure of tellurides (polar isomorphism), it is necessary to describe their composition in the triple system Te-Se-S. Crystallochemical restriction on replacement of tellurium by sulfur does not prevent accommodation of sulfur in independent positions such as, for example, in the structure of tetradymite and joseite. Therefore among sulfotellurides it is possible to expect the discovery of new mineral varieties of stoichiometric composition.

Tellurides can be subdivided into three crystallochemical types: 1. Tellurides of transitive metals and platinoides. 2. Tellurides of silver, gold and copper. 3. Tellurides of bismuth, lead, antimony and mercury. Such subdivision approximately corresponds to transition from high-temperature to low-temperature paragenesises. As mineralization processes frequently occur at a wide range of temperatures, telluride associations of different crystallochemical type can often be formed. In addition, this wide temperature interval of crystallization observed for some telluride means that they might be refered as passing-through minerals. Tetradymite, tellurobismuthite and tsumoite are present at paragenesises occurring at different temperature. The composition of tellurides reflects geochemical specificity of the mineralization environment. They can play the role of some indicators of possible useful (economic) mineralization that also can be used in practical geology. For epithermal gold among such indicators it can be not only silver and gold tellurides, but also bismuth and lead ones. But for these conditions of mineralization till the present time the layered tellurides of bismuth as minerals of variable composition and the peculiarities of their typochemistry have not been studied enough.

There are some certain problems in studying the mineralogy of tellurides, especially their classification and studying some chemical and structural characteristics of their mineral varieties. At present about 75 tellurides have been found but considerable number of them is not thoroughly studied. It is known that the major varieties of tellurides are minerals of the variable composition that form segregations on submicroscopic scale. The use of microprobe analysis can solve the problem of studying their composition, but it is difficult to measure structural parameters of these microsegregations. At the same time only X-ray analysis can confirm authenticity of certain mineral. Without using structural data a number of problematic phases arises increasingly. Many tellurides are related to the rare and insufficiently studied minerals. Therefore repeated investigation of old (museum and field) material with application of modern method of investigations can lead to new findings. One possible decision for the problems mentioned above still remains. It is necessary to carry out some comparative mineralogical investigations in the regions with similar mineragenetic histories.

This article discusses the results of comparative analysis of mineralogy of tellurides of Slovakia and Transcarpathian region of Ukraine. The amount of data available from both sides are not comparable because tellurides have been found at more than 20 manifestations within territory of Slovakia and only 7 telluride occurrences (but 4 of which are thoroughly studied) have been described till the present time in the Transcarpathian region of Ukraine. Two types of hydrothermal mineralization of tellurides are distinguished within the territory of Slovakia: 1) hydrothermal veins in (Paleozoic and more older underlying) rocks of non-volcanic origin; 2) hydrothermal veins and zones of argillization in neovolcanites. The first type of mineralization was found confined to the region of Western Carpathians, and the second type was described in the central and eastern part of Slovakia. Conditionally enough among possible analogues of these types of mineralization in the Transcarpathian region of Ukraine we can mention such occurrences as gold mineralization at Sauliak [7] and secondary quartzites and argillizates in neovolcanites of the Vyghorlat-Guta ridge [21, 22]. Comparative mineralogical investigation carried out on tellurides from Slovakia and Ukrainian Transcarpathians has shown, that there are some differences and similarities as well, manifested in character of Au-Ag-Bi-Te-Se mineralization occured in these regions.

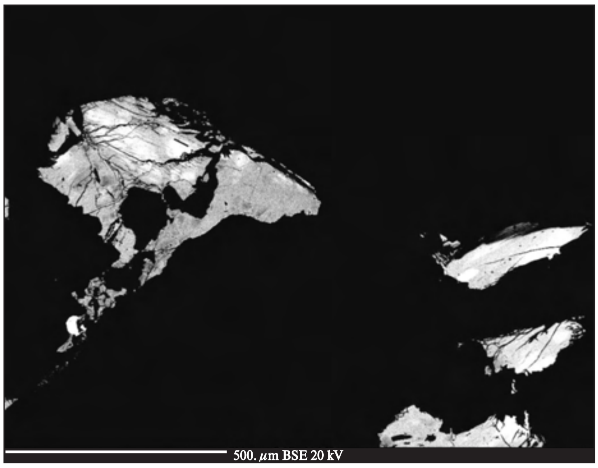

Fig. 1. Small inclusion minerals of tetradymite group (mostly tetradymite) in zonal bismuthinite (Dúbrava deposit)

Bi-Te mineralization of Slovak Republic. ***Hydrothermal veins with Bi-Te mineralization in non-volcanic rocks of Western Carpathians***. Te-Se mineralization apart from the neovolcanic rocks occurs in hydrothermal veins of older (mostly Carboniferous) tectonic units of the Western Carpathians (Table 1). These units represent Tatric, Veporic and Gemeric Units that are predominantly comprised by granitoid and metamorphic rocks. Bi-Se-Te minerals are often found mostly in association with bismuthinite in white quartz. Specific type is representeed by Bi-Se-(Te) minerals found at Smolník where predominant Se-rich phases and selenides forms myrmekite overgrowths.

Dúbrava. The largest stibnite deposit in the Slovak Republic Dúbrava is situated in north part of Nízke Tatry Mts. within granitoid rocks (Devonian age) of crystalline basement of Tatric Unit. The stibnite of Dúbrava deposit occurs in veins of milky quartz in which tetradymite have been described [27]. Tetradymite inclusions were found in bismuthinite crystals in quartz in which

Table 1. **Tellurides of Slovakia and their localities**

Locality	Forms of occurrences and host rocks	Minerals
Non-volcanic rock of Western Carpathians		
Dúbrava	Veins of milky quartz in granitoides	Joseite-A, Bi_2TeS_2 (S-skippenite), bismuthinite, bismuth
Jasenie	Veins in migmatites, gneisses	Tellurobismuthite, tellurantimony, joseite-B, tsumoite, pilsenite, tetradymite
Hnúšťa	Magnesite-talc lenses in mica-schists	Bismuthinite, hessite, pilsenite, tsumoite, laitakarite, bismuth, Se-gustavite ($PbAgBi_3S_6$)
Chy né	Hydrothermalites in granite, alternating sondstones, phylitic schists	Baksanite, joséite-A, joséite-B
Katarínska Huta	Disseminated impregnation in phyllites, mica schists, quartzites	Tetradymite
Kokava nad Rimavicou	Quartz veins in gneisses	Tellurobismuthite, tetradymite, montanite
Krokava	Gold-bearing veins in migmatites, gneisses and amphibolites	Tetradymite (?)
Rochovce	Quartz veins in phyllites	Bismuthinite, bismuth, ikunolite
Gemerská Poloma	Magnetite-garnet-pyroxenic skarns	Bismuthinite, tetradymite, joseite-B, joseite-A, ingodite, sulfotsumoite, galenobismuthite, gladite
Smolník and Úhorná	Siderite and quartz-sulphidic veins in rocks of greenschist facies	Tetradymite, tsumoite (?), ikunolite- laitakarite, phase $(Bi, Sb, Cu)_3S_4$, hedleyite and Se-hedleyite (Bi_7Te_2Se)
Central Slovakian Neovolcanics		
Kremnica	Epithermal Au-Ag quartz ± carbonate veins in hydrothermal altered andesite	Hessite, altaite, petzite, stützite, native tellurium
upkov	Hydrothermal altered andesitic tuffs	Tetradymite, montanite
Banská Štiavnica and Hodruša ore field	Epithermal Au-Ag-base metal quartz ± ± carbonate veins in hydrothermal altered andesite	Hessite, tetradymite, petzite, tellurobismuthite
East Slovakian Neovolcanics		
Zlatá Baňa	Epithermal precious and base metal veins and veinlets	Hessite, altaite, petzite, sylvanite, weissite, rickardite
Byšta	Mineralized zones in hydrothermal altered neogene sediments, gneisses and mica schists of crystalline complex	Stützite
Poruba pod Vigorlatom and Remetské Hámre	Secondary quartzites and argillites in volcanic rocks	Tetradymite, telluronevskite, vihorlatite

pyrite and scheelite occur (Fig. 1). Recently Ozdín and Chovan [30] have informed about new findings in Dúbrava, indicating the presence besides tetradymite in bismuthinite, of more joseite-A and unknown phase Bi_2TeS_2 from tetradymite group, probably S-rich analogue of skippenite. Some analyses of bismuthinite and sulphotellurides indicate their enrichement with stibium. Joseite-A occurs in assemblage with bismuth and bismuthinite.

Jasenie. The largest tungsten deposit of Slovak Republic, Jasenie-Kyslá one was found at the southern part of Nízke Tatry Mts. Deposit of scheelite occurs in high-metamorphic rocks of crystalline basement of Tatricum Unit (migmatites, gneisses). Bi-Te mineralization is represented by tellurobismuthite, tellurantimony [6], joseite-B, tsumoite, pilsenite and tetradymite [5]. These minerals occur in association with gold, bismuth, scheelite and wolframite. Tellurium minerals were precipitated during final tungsten stage before carbonate-sulphidic one [6].

Hnúšťa. Large magnesite-talc deposit, Mútnik that is situated near Hnúšťa in the Central Slovakia area occurs in mica-schist of the Veporic Unit. In magnesite-talc lenses sulphide mineralization of Alpine age is locally developed. The oldest mineral assemblage is comprised by pyrite I, arsenopyrite and cobaltite and younger one does pyrite II, pyrrhotite, chalcopyrite, sphalerite, galena, tetrahedrite, gold, bismuth, bismuthinite, gustavite, cosalite (?), marcasite, ullmanite, willyamite and minerals from linnéite-siegenite series [35].

M. Ragan described tetradymite in this deposit [35]. S. Ferenc confirmed the presence of tetradymite and described some other Ag- and Bi-tellurides (hessite, pilsenite, tsumoite) [12]. Pilsenite and tsumoite occur in assemblage with chalcopyrite, pyrrhotite and sphalerite in magnesite. Locally was observed intergrowing of hessite with tsumoite and pilsenite-pyrrhotite myrmekitic intergrowths. Se-gustavite (Se content about 2 wt. %) is associated with chalcopyrite, bismuth and bismuthinite.

Chy né. T. Bálintová and D. Ozdín described accessory occurrence of Bi-Te minerals on stibnite-tungsten locality of Herichová near village Chy né in central part of Slovak Republic [4]. The locality is situated in the western part of the Spišsko-gemerské rudohorie Mts. near the contact zone of two significant tectonic units of the Western Carpathians — Gemericum and Veporic Unit. The host rocks that comprise hydrothermal mineralization are Carboniferous granite and metamorphosed fine-grained sandstones cyclically alternating with phyllite schists. Bi-tellurides found in final stage of mineralization after precipitation of arsenopyrite-pyrite, stibnite and carbonates. Joséite-A, joséite-B and baksanite occur in association with bismuth, bismuthinite and Ag-Pb-Bi-(Sb) sulphosalts in galena. Content of Se in these tellurides is very low. Content of tellurium varies (a. p. f. u.): 1.23—1.36 for joséite-A; 1.49—1.54 for joséite-B and 1.82—2.02 for baksanite.

Katarínska Huta. By studying borehole KH-1 at Katarínska Huta S. Ferenc described mostly disseminated type of mineralization of Alpine age [12]. Host rocks are represented by phyllites, mica schist and quartzites. Sulphidic mineralization represents arsenopyrite, pyrite, pyrhotite, molybdenite, marcasite, ullmannite, chalcopyrite, tetrahedrite, sphalerite, galena, jamesonite and boulangerite. Tetradymite forms short veins and grains in quartz and tetrahedrite.

Kokava nad Rimavicou. Quartz veins with tellurides probably of Alpine age occur in gneisses near the Kokava nad Rimavicou in Veporic Unit. Old mines are situated at Bohaté, Bohaté-východ and Sinec-Strieborná Studnička localities. Layered tellurobismuthite crystal up to 0.6 mm in size was identified at the locality Sinec-Strieborná studnička in eluvial-deluvial placers in aggregates with gold. Tetradymite forms irregular aggregates of layered crystals of up to 6 mm in quartz with dravite, clinochlore and gold. Tetradymite is homogenous and sulphur content is little increased. Montanite is abundant product of hypergene conditions and intensively replace tetradymite. Sometimes it forms entire pseudomorphoses after tetradymite [13].

Krokava. Hydrothermal gold-bearing veins described by Bakos et al. [3] are situated near Krokava in the Central Slovakia. Mineralization is represented by quartz with gold, pyrite, galena, bismuth, Bi-Te minerals, rutile and tourmaline in migmatites, gneisses and amphibolites of crystalline basement of Veporic Unit. Unknown very small tellurides of bismuth (tetradymite ?) were identified by EDS method.

Rochovce. At the village Rochovce quartz veins with sulphidic mineralization were found in borehole RO-9. Mineralization is confined to fine grained Paleozoic phyllites, occured at hanging wall of the Rochovce granitoid intrusion. Jeleň [15] in Pauliš et al. [32] described quartz veins containing joseite-B in assemblage with chalcopyrite, bismuthinite, bismuth and Bi-ullmannite. Pauliš et al. [31] mentioned about finding in this occurrence of ikunolite and Jeleň [15] about sulphosalt with Se-wittite.

Gemerská Poloma. In the Gemeric Unit sulphotellurides were occasionallly identified in boreholes at Dlhá dolina Valley where small grains of joseite-A, joseite-B, ingodite and sulfotsumoite occur rarely in magnetite- or garnet-pyroxenic skarns. Skarns represent products of contact-metasomatic metamorphosis caused by granite. Sulphotellurides were found in assemblage with bismuthinite, chalcopyrite and Bi-Pb sulfosalts or sphalerite, galena. Sometimes tellurides are found inclosed in gersdorffite. Recently we identified in bismuthinite small crystals of tetradymite and joseite-B in assemblage with galenobismuthite ($PbBiS_4$) and gladite ($PbCuBi_5S_9$) (D. Ozdín, unpubl. data).

Smolník and Úhorná. Unknown Bi-Se-Te minerals with crystallochemical formula $(Bi_{1.77}Cu_{0.16} \times \times Pb_{0.09})_{2.02}(Te_{0.89}Se_{0.72}S_{0.37})_{1.98}$ are described by D. Peterec [33] from hydrothermal siderite and quartz-sulphidic veins between villages Smolník and Úhorná. Vein type mineralization occur in metamorphic rocks of Gemeric Unit metamorphosed in greenschist facies. Dominant minerals of these veins are siderite and quartz, from sulphides are most abundant pyrite, chalcopyrite and tetrahedrite. As less abundant occur pyrhotite, arsenopyrite, ullmanite, gersdorffite, galena and other minerals. Bi-Se-(Te) phases were precipited in final stages of mineralization. Selenium enter into structure of sulphosalts. Se-content in

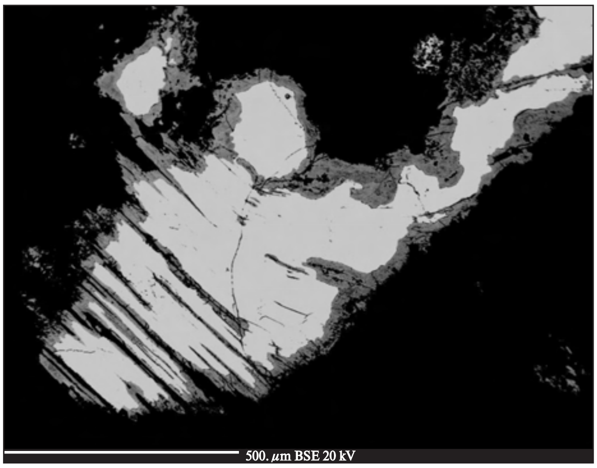

Fig. 2. Laminar tetradymite crystal covered by montanite (Župkov)

sulphosalts (jamesonite, stibnite var. horobetsuite and pekoite) reaches up to ~2.5 wt. %. Most abundant Bi-Se-(Te) sulphides are from series ikunolite-laitakarite. In assemblage with unknown Bi-Se-Te phase and Se-minerals occur bismuth and Te-rich galena. Bi-Se-(Te) minerals form small myrmekite overgrowths. The most recent investigation of this mineralization was made J. Pršek and D. Peterec [34] who discovered Bi-Se- and Te-minerals in chalcopyrite and tetrahedrite. Se-bearing sulphosalts (jamesonite, tintinaite, bournonite), tetradymite, ikunolite, laitakarite, hedleyite and Se-rich analogue of hedleyite (Bi_7Te_2Se) were identified in association with bismuth and unknown phase ($(Bi, Sb, Cu)_3S_4$. Bi-Se-Te minerals and bismuth form both complex decomposition products of pre-existing unknown phase and small (<50 μm) needles or laths enclosed in tetrahedrite, jamesonite and tintinaite.

Central Slovakian Neovolcanics. Neogene volcanic rocks in Slovakia host numerous precious-metal and base metal epithermal mineralizations, both of low-sulfidation and high-sulfidation type. The mineralizations mostly occur in the central zones of andesite stratovolcanoes, located in the central and eastern Slovakia, being a part of an extensive volcanic region of the Carpathian arc and the Pannonian Basin (Table 1). The origin of the hosting volcanic rocks is related to subduction and back-arc extension, associated with development of the Carpathian arc during Neogene. Some of the Au-Ag epithermal deposits belong to the largest ore districts in the Carpathian arc and are famous for its long silver and gold mining history since at least the early Middle Ages.

Kremnica. Au-Ag epithermal deposit is the only locality in Slovakia with a significant presence and the largest amount of Se-Te minerals. The deposit is associated with marginal faults of a young resurgent horst in the Kremnica volcanotectonic graben within the central zone of an older stratovolcano. Kremnica is a typical low-sulfidation deposit, associated with late stage rhyolite magmatism. The Au-Ag vein mineralization is represented here by microscopic gold (electrum) in pyrite and quartz with minor Ag-sulfosalts and base metal sulphides (1^{st} vein system). Visible (bonanza-type) gold is also present here in cavernous quartz-carbonate gangue, accompanied by minor Ag-sulfosalts (2^{nd} vein system). Ag-, Au- and Pb-tellurides (hessite, altaite, petzite, stützite, goldfieldite, Te-tetrahedrite, Te-tennantite, benleonardite and native tellurium) have been identified especially in deeper parts of the 1^{st} vein system (250—1000 m) together with sulfides and gold of high fineness (>800). The highest content of Te is in the depth of 300—500 m, where the veins are enriched by galena (average Te content >10 g/t). In selected parts of the veins Te content reached up to 58 g/t Te and 27 g/t Se. Many minerals contain here increased amount of isomorphic Se (in wt. %): up to 5.3 in acanthite, 2.1 in miargyrite, 1.2 in pyrargyrite, 4.8 in pearceite, 2.6 in polybasite, 1.6 in tetrahedrite and 2.9 in galena [16].

Župkov. The occurrence of Bi-Te mineralization bonded to strongly altered andesite near Župkov (Vtáčnik Mts., Slovak Republic) is known for a long time (1830—1831) and represents a type locality for Bi-sulfotellurides [14, 37]. The Te-Bi mineralization is represented by relatively abundant occurrence of tetradymite and supergene Bi-tellurate — montanite (Fig. 2). Tetradymite forms well-formed trigonal crystals 0.1—7.0 mm in size, some skeletal or with striated crystal faces. The electron microprobe chemical analysis gave Bi — 58.10, As — 0.08, Cd — 0.06, Au — 0.04, Te — 36.00, S — 4.33, Se — 0.68, Cl — 0.02, *total sum* — 99.29 wt. %.

Banská Štiavnica and Hodruša. The Štiavnica-Hodruša ore district also contains a number of Te-Se bearing minerals. This large ore district is located in the central zone of the extensive Štiavnica stratovolcano, the largest volcano in the whole Carphatho-Pannonian area. Epithermal mineralization of low-sulfidation type is related to structures resulting from caldera subsidence (the Rozália mine Au deposit) and from long-lasting resurgent horst uplift in the center of caldera, accompanied by rhyolite volcanic activity (zoned system of precious- and base metal veins covering an area of 100 km^2). The Rozália mine Au mineralization is represented by banded veins with gold (81—96 % Au) in the form of inclusions in base metal sulfides and less commonly disseminated in quartz and carbonates. Rare telluride minerals (hessite, petzite and altaite) occur here in the latest stage of mineralization, accompanied by gold of lower fineness (74—79 % Au), base-metal minerals and rare Ag-sulfosalts. Within the large system of horst uplift-related veins three types of veins are distinguished: (1) sulfide-rich base metal veins in the eastern part of the horst ("Štiavnica type"), (2) silver ± base-metal veins in central and eastern part of the horst ("Hodruša type"), (3) precious-metal veins in marginal parts of the horst ("Kremnica type"). In the Štiavnica type veins, rare Te-Se minerals occur in deep, Cu-enriched, parts of veins (hessite, naumannite), associated with base-metal minerals and accessory native gold (72—74 % Au). Naumanite contains here isomorphic Te (up to 2.8 wt. %), while Se is included also in galena (up to 3.5 wt. %), chalcopyrite (0.63 wt. %), bornite (0.59 wt. %), acanthite (1.2 wt. %), stefanite (0.9 wt. %). Various Ag-Bi, Cu-Bi and Cu-Pb-Bi sulfosalts very often contain here increased concentrations of Se (1—1.5 wt. % in average), e. g. in wittichenite (up to 3.2 wt. %) and bismuthine (1.7 wt. %). In the Hodruša-type veins rare Te-bearing minerals (hessite, Ag-benleonardite, petzite, tellurobismuthite and some Ag-Bi sulphotelluride) accompany base-metal minerals, electrum, native gold and Ag-sulfosalts in upper parts of veins. In deep parts of the Kremnica-type veins tetradymite and hessite have been identified associated with Bi and Mo-bearing minerals and with base metals. Rare grains of tetradymite and ingodite have been discovered also in precious-metal replacement mineralizations in carbonate sediments (locality Bukovec), associated with native gold and Bi minerals. Te-Se minerals have been also identified at some other localities within Neogene volcanic rocks. They include the type locality of tetradymite upkov [14] also with secondary montanite and represent low-sulfidation precious-metal mineralizations [16].

The K-Ar data of illite from various vein zones of the Kremnica deposit lies in the interval of values 10.1—11.7 Ma. Rb-Sr isochron age of the same samples is equal to 11.1 ± 0.6 Ma. For the Rozália mine in the Hodruša deposit the K-Ar age values of 2 illite samples are 11.9 ± 0.3 and 11.5 ± ± 0.3 Ma. The Rb-Sr dating of these samples yields value 12.8 ± 0.6 Ma. The assumed age of the mineralization from Banská Štiavnica deposit is 12.1—11.2 Ma (K-Ar), and 12.8—11.2 Ma (Rb-Sr), respectively [24].

East Slovakian Neovolcanics. *Zlatá Baňa*. Zlatá Baňa deposit is situated in north part of the Slanské vrchy Mts. in central part of Zlatá Baňa stratovolcano and represents a zoned system of epithermal veins and veinlets with assumed genetic link to diorite porphyry intrusion. Te-mineralization was identified in borehole KS-2. Mineralization is bond on the stockwork zone of base metal ores. Rare telluride minerals (petzite [19], altaite [10], sylvanite, hessite, rickardite, weissite [11], cervelleite [31] occur both in upper and deeper parts of veins and are accompanied by native gold, silver and Ag-sulfosalts. Te-phases created microscopic inclusions in galena and rare in pyrite.

Byšta. In near Byšta were identified base-metal mineralization in the Byšta formation in high-metamorphic gneisses and mica schists of Proterozoic crystalline basement of Zemplín Unit. Mineralizations represent fossil hydrothermal system of Neogene Age. Base metal veins and veinlets transect rocks of Proterozoic Age of Zemplín Unit to the Middle Badenian claystones. Stützite creates microscopic inclusions in association with galena [17]. Fragment of mineralization was found at the surface in lithogeochemical sample. These samples contain only one Te-phases, stützite which created microscopic inclusions in association with galena [17].

Poruba pod Vihorlatom and Remetské Hámre. Bi-Se-Te mineralization related with magmatic and later hydrothermal processes were described near Poruba pod Vihorlatom in the Vihorlat Vrchy Mts. Mineralization is joined with bodies of secondary quartzites of the Central volcanic zone in the Porubský Potok valley. Theses metasomatic bodies are strongly argillitized and partially silicified.

Massive white to grey secondary quartzites are composed of quartz, opal, kaolinite, tridymite, boehmite, diaspore, topaz, andalusite, mullite, dumortierite, dickite, fluorite, zunyite, hematite and corundum [1]. Bi-Se-Te phases occur as flaky to granular aggregates in quartz-opal veinlets (Fig. 3). Main Bi-Se-Te minerals identified on these localities are telluronevskite (Fig. 4, 5) and vihorlatite in association with tetradymite, scheelite and stannite [36].

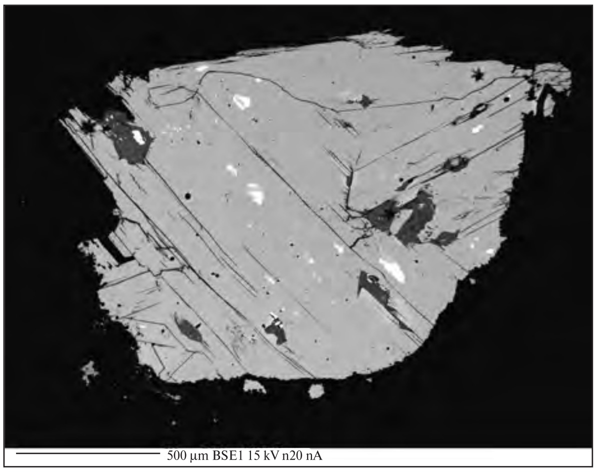

Fig. 3. Chemical homogeneous unknown Bi-Te-Se phase (grey) together with Bi-phases (white) (native bismuth, bismuthinite (?), bismuth telluride) and montanite (dark grey) (Poruba pod Vihorlatom)

Fig. 5. White layered crystal of tellurunevskite with secondary mineral related to montanite (?) (Poruba pod Vihorlatom)

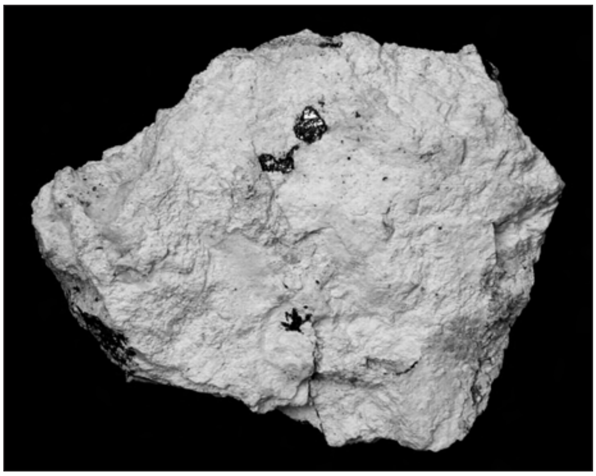

Fig. 4. Layered crystal of telluronevskite in secondary quartzite; size of specimen ~5.5 cm (Poruba pod Vihorlatom)

Bi-Te mineralization of Transcarpathian region of Ukraine. The number of tellurides in Transcarpathian region of Ukraine is much less in comparison with their numerous varieties, which have been found in Slovakia region. This fact is possible to be explained by much thorough level of mineralogical investigations carried out in Slovakia. But at the same time, telluride mineralization shows common association with gold occurrences, a lot of which have been found, within the territory of Slovakia [2]. As to the tellurides of Transcarpathian gold deposits of Ukraine they are either extremely rare minerals in it (Sauliak) or even absent as a whole (Beregovo). This phenomenon demands more careful study. Among known tellurides established within Transcarpathian region of Ukraine there are mostly bismuth tellurides associated with metasomatites of the Vyghorlat-Guta ridge [21, 22, 25, 26]. This mineralization has some similarities to occurrences of Bi-tellurides well-known in neovolcanites of Slovakia (Poruba pod Vigorlatom, Remetska Hamra). Some characteristic features of the two types of Bi-telluride occurrences found in Transcarpathian region of Ukraine is followed below (Table 2).

Gold deposit Sauliak. This deposit is localised within Rahovsk and Chivchinsk areas of Transcarpathian region of Ukraine, on the right bank of the river Tisa. Structurally it is localised in the northwest part of the Marmaroshsk allochthon of the Carpathian Ridge. Endogenic gold occurred only in rocks of greenshist facies metamorphism, namely Delovetsk and Belopotoksk suites. Ore bodies are represented by gold-bearing quartz-carbonate veins and zones of quartz and carbonate lead veins. Free gold of 0.01—0.1 mm prevails in ore, occasionally reaching 2—4 mm in size. Such minerals as galena, pyrrhotite and sphalerite show the presence of gold as microinclusions. Here tellurides form complex intergrowths with native gold. The number of telluride species is limited to altaite, hessite and tellurobismuthite [7]. Here altaite is the predominate telluride, with hessite and tellurobismuthite being rarely found. Altaite forms microscopic (10—200 mc) segregations in galena. The morphology of these segregations indicates their possible formation during decomposition of Pb(S, Te) solid solution. Microprobe investigations gives the following values of compo-

Table 2. **Tellurides of Transcarpathian region of Ukraine**

Location	Host rocks	Minerals
North-Eastern part of Marmarosh massif		
Sauliak	Quartz-carbonate veins and lenses in crystalloshists	Altaite, hessite, tellurobismuthite
Vyghorlat-Guta ridge		
Podulky	Quartz-turmaline "stockworks" in kaolinite-hydromica metasomatites; quartz-topaz — montmorillonite metasomatites	Tsumoite, Ag-tsumoite, pilsenite
Il'kivtsy	Hydromica-montmorillonite metasomatites	Pilsenite, tsumoite, bismuth, phase Bi_2Te
Smerekiv Kamin'	Hydromica-montmorillonite metasomatites with lenses of secondary quartzites	Bismuthinite, varieties of tsumoite, Te-sulfonevskite, joseite-A, pilsenite, phase $Bi_3Te_{1.5}S_{0.5}$ and $Bi_2Te_{0.5}S_{0.5}$

sition for this mineral (wt. %): Pb — 58.89, Te — 38.10, Sb — 1.3, Ag — 0.45, Bi — 0.56, S — 0.06, with *total sum* — 93.36 %. Its structural formula is similar to stoichiometric one: $(Pb_{0.95}Bi_{0.01}\times\times Ag_{0.01})_{0.97}(Te_{0.99}Sb_{0.04})_{1.03}$. Hessite, like altaite, forms microscopic inclusions in galena with which gold and altaite are associated. The hessite from rich ores has the following values of composition (wt. %): Ag — 61.84, Te — 37.06, Au — 0.14, Fe — 0.07, *total sum* — 99.11. Tellurobismuthite was found in the form of single grains in ore-quartz but any interrelations of it with other tellurides have not been distinguished yet. The results obtained on single grain analysis of this mineral indicates for its possible formula as $(Bi_{1.53}Pb_{0.54})_{2.07}\times\times(Te_{2.51}Sb_{0.42})_{2.93}$. So, this mineral can be interpreted as species of tellurobismuthite that is highly enriched in lead and antimony up to ~0.5 a. p. f. u.

Metasomatites of Vyghorlat-Guta Ridge. Neovolcanites of the Vyghorlat-Guta ridge show the presence of tellurides only in metasomatically altered rocks (mainly in andesites and their tuffs). Unlike telluride occurrences of Slovakia and Sauliak deposit, tellurides of the Vyghorlat-Guta ridge are represented by exclusively bismuth tellurides. Metasomatites such as argillizites and secondary quartzites are the most widespread here. They are confined to the centres of eruptions with intensive process of fumarolic-solfataric activity. Wide fields of metasomatites have been found at mount Syniak, Podulki tract and village Il'kivtsy areas.

Fig. 6. Globule of native bismuth containing bismuth tellurides — Se-tsumoite, joseite-A, joseite-B (Smerekiv Kamin')

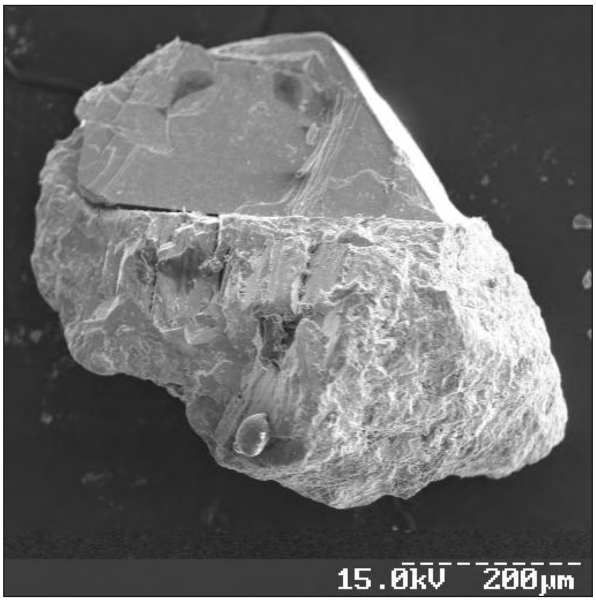

Fig. 7. Crystal of joseite-A in native bismuth (Smerekiv Kamin')

First findings of bismuth tellurides in Transcarpathian region have been described as mineral "vehrlite" [20, 23]. But multi-phase nature of this mineral composition has been established much later [28, 29, 38], so the term "vehrlite" is used as collective term for layered bismuth tellurides of unknown composition. Geologists that work in Transcarpathian region used term "vehrlite", at the case when the nature of telluride is difficult to establish completely, for example, at the stage of field-work.

"Vehrlite" can be occasionally found in the form of crystals, but more often it forms hexagonal or oval plates. It is not clear, whether the lamellar shape is its natural shape of growth, or it obtains this shape as a result of splitting crystals on cleavage plane.

Most often Bi-Te-mineralization (vehrlite and occasionally bismuth) is associated with quartz-tourmaline metasomatites. Large assemblages of "vehrlite" are found at apical part of quartz-tourmaline "stockworks" localised in kaolinite-hydromica metasomatites [21, 22]. Such type of mineralization is established in the northern part of Podulky tract. The following investigations showed that among Bi-tellurides the tsumoite is prevailing species, with pilsenite and their mixtures being found less often. Plates of bismuth tellurides (up to 5 mm in size), thin-needled turmaline and small crystals of pyrite were found in the mass of amorphous silicate that fills cavities within thin veins (3—5 cm). The content of Bi-tellurides reaches some percent as compared to the mass of amorphous substance. In quartz-topaz metasomatites, secondary quartzite zone is preceded by hydromica one. Bismuth tellurides in association with galena, sphalerite, sometimes arsenopyrite fill thin cracks in the rock, which formed before their replacement by hydromica. Quartz-fluorite and quartz-dumortierite metasomatites are represented mainly by montmorillonite. The sphalerite and single plates of "vehrlite" are found in quartz-fluorite veins formed before the metasomatic processes. Lenses of fine-grained quartz and opal with some small crystal of metacinnabar and "vehrlite" among quartz-kaoline metasomatites have been found at tract Podulki area. Pilsenite is predominant, with tsumoite and native bismuth being present at much smaller amount in hydromica-montmorillonite metasomatites of village Il'kivtsy [25, 26].

Montmorillonite metasomatites of *Smerekiv Kamin'* are characterised by the presence of absolutely different type of bismuth-telluride mineralization. Here lamellar shapes of tellurides are almost absent and spherical segregations from 0.1 to 1—3 mm in the size are predominant (Fig. 6). Sometimes spheres show the presence of flat surfaces ("faces") and as a result the globule gets polyhedral shape. These globules are comprised on 50—80 % by native bismuth with remained volume occupied by segregations of bismuthinite, tsumoite, joseite and other tellurides [25, 26]. They also show significant content of sulfur and selenium (10—13 wt. %) that distinguish them from tellurides of Il'kivtsy-Podulky area. The smallest segregations of pyrite and pyrrhotite are rarely found inside these globules. The plate crystals of joseite are found in intergrowths with native bismuth (Fig. 7).

Conclusions. About 25 mineral species of tellurides and sulfo-tellurides are established in the territory of Slovakia. And only 8 mineral species are found in the Transcarpathian region of Ukraine.

Comparative mineralogical investigation carried out on tellurides from Slovakia and Ukrainian Transcarpathians has shown, that there are some differences and similarities as well, manifested in character of Au-Ag-Bi-Te-Se mineralization occurred in these regions.

The number of tellurides in Transcarpathian region of Ukraine is much less in comparison with their numerous varieties, which have been found in Slovakia region. But at the same time, telluride mineralization shows common association with gold occurrences, a lot of which have been found, within the territory of Slovakia [2]. As to the tellurides of Transcarpathian gold deposits of Ukraine they are either extremely rare minerals in it (Sauliak) or even absent as a whole (Beregovo). Among known tellurides established within Transcarpathian region of Ukraine there are mostly bismuth tellurides associated with metasomatites of the Vyghorlat-Guta ridge [21, 22, 25, 26]. This mineralization has some similarities to occurrences of Bi-tellurides well known in neovolcanites of Slovakia (Poruba pod Vigorlatom, Remetska Hamra).

Acknowledgements. This paper has been prepared according to the project of international cooperation between M.P. Semenenko Institute of Geochemistry, Mineralogy and Ore Formation, NAS of Ukraine and Geological Institute of Slovak Academy of Sciences. The title of the project is "Comparative mineralogical-geochemical analysis of Au-Ag-Bi-Te-Se neovolcanic mineralization of Ukraine and Slovakia (Carpathian region)". This study was supported by of VEGA grant UK/231/2009.

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Received 14.09.2009

РЕЗЮМЕ. Порівняльний аналіз проявів телуридів на території Словаччини і Закарпаття (Україна) показав, що існує помітна відмінність в характері Au-Ag-Bi-Te-Se мінералізації цих регіонів. Але в областях розвитку неовулканітів Bi-Te-Se-S мінералізація представлена в основному аналогічними мінеральними фазами. Телуриди вісмуту (цумоїт, пильзеніт, жозеїти, самородний бісмут і маловивчені сульфо-селено-телуриди бісмуту) знайдені на території Закарпаття тільки в метасоматитах типу вторинних кварцитів Вигорлат-Гутинського пасма (Ільківці, Подулки, Смереків Камінь). Подібна мінералізація встановлена в деяких неовулканітах Словаччини (*Poruba pod Vigorlatom, Remetska Hamra*).

РЕЗЮМЕ. Сравнительный анализ проявлений теллуридов на территории Словакии и Закарпатья (Украина) показал, что существует заметное различие в характере Au-Ag-Bi-Te-Se минерализации этих регионов. Но в областях развития неовулканитов Bi-Te-Se-S минерализация представлена в основном аналогичными минеральными фазами. Теллуриды висмута (цумоит, пильзенит, жозеиты, самородный висмут и малоизученные сульфо-селено-теллуриды висмута) найдены на территории Закарпатья только в метасоматитах типа вторичных кварцитов Выгорлат-Гутинской гряды (Ильковцы, Подулки, Смерекив Каминь). Подобная минерализация установлена в некоторых неовулканитах Словакии (*Poruba pod Vigorlatom, Remetska Hamra*).