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## COMPARATIVE STUDY OF Bi-Te-Se-S MINERALIZATIONS IN SLOVAK REPUBLIC AND TRANSCARPATHIAN REGION OF UKRAINE. PART 2. CRYSTAL CHEMISTRY AND GENESIS OF LAYERED BI-TELLURIDES

Bismuth tellurides of layered structure (tetradymite group) are characteristic minerals of metasomatically altered neovolcanites of Slovakia and Ukrainian Transcarpathians. Tsumoite, pilsenite and joseite (*A* and *B*) are established in both regions, but the tetradymite is not found in Transcarpathians. Two new minerals, telluronevskite and vihorlatite, are found in Slovakia. Phase  $\text{Bi}_2\text{Te}$  (X-ray, microprobe) that forms epitaxial intergrowths with pilsenite is determined in Transcarpathians (Il'kivtsy). Se-joseite-*B*, Se-tsumoite, Te-bismuthite, phase  $\sim \text{Bi}_2\text{SeS}$  (intermediate phase between nevskite and ingodite) and phase with stoichiometry of  $A_3X_2$  ( $A = \text{Bi}$ ;  $X = \text{Te, Se, S}$ ) are determined in globules of native bismuth (Smerekiv Kamin') by microprobe analysis, but the number of anions  $X$  varies from  $\text{Bi}_3\text{Te}_{1.5}\text{S}_{0.5}$  to  $\text{Bi}_3\text{TeSe}_{0.5}\text{S}_{0.5}$ . The temperature of formation of layered bismuth tellurides is estimated within the interval 350–100 °C.

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The data of localisation of tellurides within the territory of Slovakia and Transcarpathian region of Ukraine and typical mineral associations found here were discussed in the first part of the article [13]. As layered tellurides of bismuth are established both in Transcarpathian region of Ukraine and Slovakia they can be taken as the object to do comparative study of their crystallochemistry. Table 1 and 2 show crystallochemical formulas of bismuth tellurides found in both these regions. We would like to note, that chemical analyses are not given for all minerals listed in [13] (Table 1). Therefore, the data summarized in Table 1 do not completely display all the crystallochemical features of bismuth tellurides of Slovakia. Predominant mineral varieties are related to such structural types as tetradymite ( $A_2X_3$ ), tsumoite ( $AX$ ) and pilsenite ( $A_4X_3$ ). There are also some problematic species of bismuth tellurides that have not been studied enough yet. The same situation is observed with

tellurides of Transcarpathians which crystallochemical formulas are listed in Table 2.

**Tetradymite and tellurobismuthite.** In spite of the fact that tetradymite and tellurobismuthite are the most widespread tellurides in Slovakia a number of chemically characterised samples is limited to several manifestations (Table 1). Their compositions are close to stoichiometric, but tetradymite from Smolník and Úhorná localities shows high selenium content (0.26 Se on f. u.). Tetradymite from Zupkov is the first finding of this mineral (A. Wehrle, 1831). The parameters of the trigonal unit cell ( $a = 4.2496(7) - 4.2463(6) \text{ \AA}$ ,  $c = 29.576(6) - 29.560(4) \text{ \AA}$ ,  $V = 462.6(1) - 461.6(1) \text{ \AA}^3$ ) are in accordance with calculated formula  $(\text{Bi}_{1.97} \times \text{As}_{0.01})_{1.98} (\text{Te}_{2.00} \text{S}_{0.96} \text{Se}_{0.06})_{1.02}$  [16]. Strangely enough but tetradymite has not been found in the Transcarpathian region of Ukraine till now. Sulphur bearing tellurobismuthite from Sauliak shows significant amount of lead (0.54 Pb p. f. u.) (Table 2).

**Tsumoite and similar minerals.** Tsumoite from Smolník and Úhorná contains about 0.16 Cu on

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f. u. As the replacement of large Bi by transitive elements (Ni, Co, Fe, Cu) is rather limited, high contents of copper seem strangely enough. Telluronevskite is the new bismuth telluride found in Slovakia [15]. Formula  $\text{Bi}_3\text{TeS}_2$  represents stoichiometrically idealized composition, but ratio Bi : (Te + Se + S) = 1 : 1 indicates its relation to minerals of tsumoite subgroup. The ratio of Te : (Se + S)  $\approx$  1 : 2 is rather similar to nevskite than to tsumoite. Vihorlatite  $\text{Bi}_{21.90}\text{Se}_{17.40}\text{Te}_{4.10}\text{S}_{1.60}$  shows stable chemical composition with low contents of Sb, Au and Ag [17]. Based on the ratio of Bi : (Te + Se + S)  $\approx$  1 : 1 vihorlatite is much closer to nevskite, which formula can be represented as Bi  $(\text{Te}_{0.19} \times \text{Se}_{0.79} \text{S}_{0.07})_{1.05}$  ( $AX$  type of structure). However more structural investigations to substantiate this assumption are necessary.

In the Transcarpathian region of Ukraine the composition of tsumoites is different for three different types of metasomatites (Table 2). Tsumoite from quartz-turmaline metasomatites of tract Podulky contains small amount of silver (up to 0.18 Ag p. f. u.) and insignificant admixtures of Pb and Sb. Tsumoite from montmorillonite-hydromica metasomatites of Il'kivtsy is characterized by complete absence of any Se and S admixtures. But one interesting feature typical of lamellar bismuth tellurides is observed in this area. Very often the plates of this mineral are comprised by pilsenite and tsumoite, but single-phase plates were also

found here. In the area of Smerekiv Kamin' tsumoite was found in bismuth globule separated from montmorillonite. Tsumoite shows wide range of tellurium, selenium and sulfur contents (in p. f. u.): Te — 0.18—0.72, Se — 0.40—0.17, S — 0.37—0.03. Thus, formally these minerals should be named as seleno-sulfo-tsumoites, and phases with the minimum contents of tellurium show their similarity to sulfonevskite (Table 2).

**Pilsenite, joseite and similar minerals.** The selenium bearing pilsenite from Hnúšť'a location is interesting to study due to its high arsenic contents that reach 0.22 As p. f. u. (Table 1). Two joseites (*A* and *B*) from Chyžne contain lead (0.16 p. f. u.) that indicates to the isomorphism between Pb and Bi in pilsenite structural type ( $A_4X_3$ ). Wide isomorphism between S and Se is found in ikonulite-laitakarite series (Smolník and Úhorná), but there are no data available about tellurium contents in these minerals (Table 1).

In Transcarpathians layered tellurides of pilsenite subgroup are represented by pilsenite and joseites (Table 2). The whole absence of any admixtures of S and Se is typical for pilsenite, as well as for tsumoite from metasomatites of Podulky and Il'kivtsy areas.

Bismuth globules from Smerekiv Kamin' do not contain pilsenite (Table 2), but selenium bearing joseite is usually found in them (Fig. 1). Joseite-*A* shows selenium content ranging from 0.1 to 0.83 of

Table 1. The crystallochemical characteristics of layered tellurides of bismuth of Slovakia

$A_mX_n$	Mineral	Formula	Location
$A_2X_3$	Tetradymite	$(\text{Bi}_{1.82}\text{Sb}_{0.13}\text{Cu}_{0.06})_{2.01}(\text{Te}_{1.96}\text{Se}_{0.04}\text{S}_{0.99})_{2.99}$ $(\text{Bi}_{1.84}\text{Sb}_{0.05}\text{Cu}_{0.05}\text{Pb}_{0.04})_{2.00}(\text{Te}_{1.78}\text{Se}_{0.26}\text{S}_{0.84})_{2.88}$ $(\text{Bi}_{1.97}\text{As}_{0.01})_{1.98}(\text{Te}_{2.00}\text{S}_{0.96}\text{Se}_{0.06})_{3.02}$	Katarínska Huta Smolník and Úhorná Župkov
	Tellurobismuthite	$(\text{Bi}_{2.01}\text{Ag}_{0.07}\text{Au}_{0.02}\text{Cd}_{0.01})_{2.11}(\text{Te}_{2.84}\text{Se}_{0.03})_{2.87}$	Kokava nad Rimavicom
$AX$	Tsumoite	$(\text{Bi}_{0.97}\text{As}_{0.03}\text{Pb}_{0.03}\text{Fe}_{0.03}\text{Cu}_{0.02})_{1.08}(\text{Te}_{0.80}\text{Se}_{0.14}\text{S}_{0.02})_{0.96}$ $(\text{Bi}_{1.77}\text{Cu}_{0.16}\text{Pb}_{0.09})_{2.02}(\text{Te}_{0.89}\text{Se}_{0.72}\text{S}_{0.37})_{1.98}$	Hnúšť'a Smolník and Úhorná
	Telluronevskite	$(\text{Bi}_{2.92}\text{Pb}_{0.02})_{2.94}(\text{Te}_{1.01}\text{Se}_{1.73}\text{S}_{0.32})_{3.06} \approx \text{Bi}_{0.95}(\text{Te}_{0.33}\text{Se}_{0.57}\text{S}_{0.11})_{1.01}$	Poruba pod Vihorlatom, Remetske Hamre
	Vihorlatite	$\text{Bi}_{21.90}(\text{Se}_{17.40}\text{Te}_{4.10}\text{S}_{1.60})_{23.1}$	
$A_4X_3$	Pilsenite	$(\text{Bi}_{3.50}\text{Sb}_{0.03}\text{As}_{0.22}\text{Au}_{0.01}\text{Pb}_{0.07}\text{Cu}_{0.13})_{4.04}(\text{Te}_{2.72}\text{Se}_{0.35}\text{S}_{0.08})_{3.15}$	Hnúšť'a
	Joseite- <i>A</i>	$(\text{Bi}_{4.11}\text{Sb}_{0.01}\text{Pb}_{0.16})_{4.28}(\text{Te}_{1.29}\text{S}_{1.41})_{2.70}$	Chyžne
	Joseite- <i>B</i>	$(\text{Bi}_{3.97}\text{Sb}_{0.01}\text{Pb}_{0.16})_{4.1498}(\text{Te}_{1.55}\text{Se}_{0.02}\text{S}_{1.30})_{2.87}$	
	Ikonulite-laitakarite	$A_{4.00}(\text{S}, \text{Se})_{3.08}$ up to $A_{4.00}(\text{Se}, \text{S})_{2.86}$ $A = \text{Bi} (+\text{Sb}, \text{Pb}, \text{Cu}, \text{Fe})$	Smolník and Úhorná
$A_7X_{3+x}$	Hedleite	$(\text{Bi}_{6.15}\text{Sb}_{0.69}\text{Cu}_{0.16})_{7.00}(\text{Te}_{2.49}\text{Se}_{0.88}\text{S}_{0.25})_{3.62}$	Smolník and Úhorná

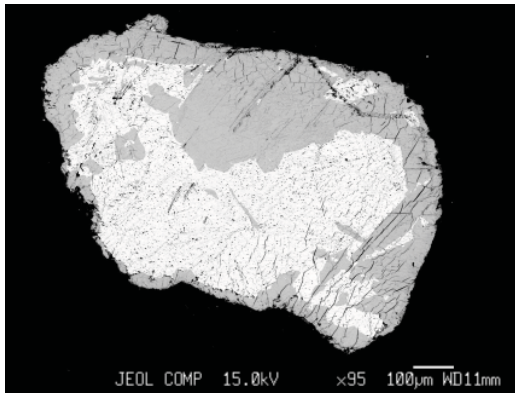


Fig. 1. Globule of bismuth (white) with margin of phase  $\text{Bi}_{4.04}\text{Te}_{1.81}\text{Se}_{0.57}\text{S}_{0.58}$  (grey). Smerekiv Kamin'

Se p. f. u. Joseite-*B* is characterized by steady values of selenium content (0.5–0.6 Se p. f. u.), with ratio  $\text{Se/S} \approx 1$ . The compositions of jositites indicate that, despite fluctuations of sulphur/selenium ratio there is a tendency to maintain values of  $\text{Te} : (\text{Se} + \text{S})$  ratio close to 1 : 2 for jositite-*A* and to 2 : 1 for jositite-*B*.

**Insufficiently distinguished phases.** Some tellurides enriched in bismuth ( $\text{Bi} > X = \text{Te, Se, S}$ ) which composition is close to stoichiometry of  $\text{Bi}_6\text{X}_5$ ,  $\text{Bi}_3\text{X}_2$ ,  $\text{Bi}_2\text{X}$  or  $\text{Bi}_7\text{X}_3$  should be related to this group. Baksanite ( $\text{Bi}_6\text{Te}_2\text{S}_3$ ) was established at Chyžné location (Table 1). This sulfotelluride is enriched by Bi and its structural formula can be rewritten as  $(\text{Bi}_2\text{TeS})(\text{Bi}_4\text{TeS}_2)$ . Thus the baksanite

Table 2. Crystallochemical characteristic of layered Bi-tellurides of Transcarpathian region of Ukraine

$A_mX_n$	Mineral	Formula	Location
$A_2X_3$	Tellurobismuthite	$(\text{Bi}_{1.53}\text{Pb}_{0.54})_{2.07}(\text{Te}_{2.51}\text{S}_{0.42})_{2.93}$	Sauliak
	Bismuthite	$\text{Bi}_{2.06}(\text{Te}_{0.51}\text{Se}_{0.04}\text{S}_{2.39})_{2.94}$	
$AX$	Nevskite-ingodite	$\text{Bi}_{1.05}(\text{Te}_{0.18}\text{Se}_{0.40}\text{S}_{0.37})_{0.95}$	Smerekiv Kamin'
		$\text{Bi}_{1.07}(\text{Te}_{0.51}\text{Se}_{0.26}\text{S}_{0.16})_{0.93}$	
		$\text{Bi}_{1.09}(\text{Te}_{0.54}\text{Se}_{0.22}\text{S}_{0.16})_{0.92}$	
	Se-tsumoite	$\text{Bi}_{1.08}(\text{Te}_{0.72}\text{Se}_{0.17}\text{S}_{0.03})_{0.92}$	
	Tsumoite	$(\text{Bi}_{0.920}\text{Ag}_{0.05})_{0.97}\text{Te}_{1.034}$	Podulky
		$(\text{Bi}_{0.850}\text{Ag}_{0.18})_{1.03}\text{Te}_{0.970}$	
$\text{Bi}_{0.96}\text{Te}_{1.04}$		Il'kivtsy	
$\text{Bi}_{3.00}\text{Te}_{0.92}$			
$A_4X_3$	Joseite- <i>A</i>	$\text{Bi}_{4.01}(\text{Te}_{0.86}\text{Se}_{0.10}\text{S}_{2.03})_{3.00}$	Smerekiv Kamin'
		$\text{Bi}_{4.04}(\text{Te}_{0.85}\text{Se}_{0.22}\text{S}_{1.86})_{2.93}$	
		$\text{Bi}_{4.00}(\text{Te}_{1.01}\text{Se}_{0.21}\text{S}_{1.78})_{3.00}$	
		$\text{Bi}_{4.09}(\text{Te}_{1.30}\text{Se}_{0.83}\text{S}_{0.78})_{2.91}$	
	Joseite- <i>B</i>	$\text{Bi}_{4.04}(\text{Te}_{1.81}\text{Se}_{0.57}\text{S}_{0.58})_{2.96}$	
		$\text{Bi}_{4.05}(\text{Te}_{1.75}\text{Se}_{0.55}\text{S}_{0.65})_{2.95}$	
	Pilsenite	$(\text{Bi}_{3.80}\text{Ag}_{0.10})_{3.90}\text{Te}_{3.06}$	Podulky
$\text{Bi}_{3.96}(\text{Te}_{2.91}(\text{Se, S})_{0.15})_{3.06}$		Il'kivtsy	
$A_3X_2$	Phase $\text{Bi}_3\text{Te}_2$	$\text{Bi}_{2.98}(\text{Te}_{0.84}\text{Se}_{0.55}\text{S}_{0.63})_{2.02}$	Smerekiv Kamin'
		$\text{Bi}_{2.93}(\text{Te}_{1.20}\text{Se}_{0.11}\text{S}_{0.67})_{2.07}$	
		$\text{Bi}_{2.99}(\text{Te}_{1.51}\text{S}_{0.50})_{2.01}$	
		$\text{Bi}_{3.02}(\text{Te}_{1.47}\text{S}_{0.50})_{1.97}$	
$A_2X$	Phase $\text{Bi}_2\text{Te}$	$\text{Bi}_{1.92}(\text{Te}_{0.51}\text{S}_{0.57})_{1.08}$	Il'kivtsy
		$\text{Bi}_2\text{Te}$	

Notes. The samples were analyzed with microprobe JXA-8200 in Analytical centre of NAS of Ukraine.

structure represents the interlaying of ingodite ( $\text{Bi}_2\text{TeS}$ ) and joseite-*A* ( $\text{Bi}_4\text{TeS}_2$ ) blocks [14]. The presentation of structure of sulfotellurides as sequence of simple structural blocks (as example  $\text{Bi}_2\text{Te}_3$  and  $\text{Bi}_2$ ) is useful for interpretation of their interrelation [11, 12]. Taking into consideration the fact, that ingodite has structure similar to tsumoite, and joseite does of pilsenite, the sequence of blocks in baksanite is possible to be represented as:  $2 \text{Bi}_2\text{X}_3 \cdot \text{Bi}_2 \cdot \text{Bi}_2\text{X}_3 \cdot \text{Bi}_2 = 2\text{Bi}_2(\text{Te}_{0.5}\text{S}_{0.5})_3 \times \text{Bi}_2 \cdot \text{Bi}_2(\text{Te}_{0.33}\text{S}_{0.66})_3 \cdot \text{Bi}_2$ . Having designated blocks as in [12],  $\text{Bi}_2\text{X}_3 = m$  and  $\text{Bi}_2 = n$ , we will receive the formula for baksanite as  $5m + 4n$ . If S be substituted by Te we will receive composition of hypothetical bismuth telluride,  $\text{Bi}_6\text{Te}_5$ . This formula can be expressed as  $\text{Bi}_3\text{Te}_{2+x}$  ( $x = 0.5$ ). Tellurides of such composition are established in bismuth globules of occurrences from Smerekiv Kamin' [11].

However, as it is easy to see that the proportion of different blocks may be slightly changed. That disproportion may be a reason of the deviation of the telluride composition from stoichiometry.

Microprobe analyses of the Bi-tellurides often show the existence of the phase composition of which close to  $\text{Bi}_2\text{Te}$ . The following phase of  $\text{Bi}_2\text{Te}$  is distinctly fixed on X-ray pattern of pilsenite from Il'kivtsy area (Fig. 2, *a*, *b*). This phase forms thin intergrowths in pilsenite, with orientation along plane (0001) that is common for these phases (mixed-layering in Bi-tellurides [10]). Its composition was estimated on parameter with  $c \approx 18 \text{ \AA}$ . Moreover, phase  $\sim\text{Bi}_4\text{TeS}$  was found in globules of bismuth from the Smerekiv Kamin' (Table 2). In addition, mineral  $\text{Bi}_2\text{Te}$  is described in the Ergeliach deposit (The Indigirka river, Siberia) in association with tellurobismuthite and native bismuth [3]. It is worth to note that the phase  $\text{Bi}_2\text{Te}$  does not necessary to be matched with hedleyite ( $\text{Bi}_7\text{Te}_3$ ), which composition and parameters are considerably different [19]. The reality of the structure of the phase  $\text{Bi}_2\text{Te}$  was justified by HREM investigation [2].

The phase  $\text{Bi}_3\text{Te}_2$  has been and still remains as a subject of discussions since such composition was assumed for "vehrlite" [4, 6, 7]. The possibility of existence of compounds as  $\text{Bi}_3\text{X}_2$  ( $X = \text{Te}, \text{S}$ ) has been shown in some papers [4, 5, 10]. Natural phases with idealized composition  $\text{Bi}_3(\text{Te}_{1.33}\text{S}_{0.67})_2$  (mineral-*K*) and  $\text{Bi}_3(\text{Te}_{0.5}\text{S}_{1.5})_2$  (mineral-*P*) were described in the paper by A. Godovikov et al. [4, 5]. And finally, phase  $\text{Bi}_3(\text{Te}_{1.5}\text{S}_{0.5})_2$  was found in globules from the Smerekiv Kamin' (Fig. 3; Table 2). The main disadvantage of all investigations

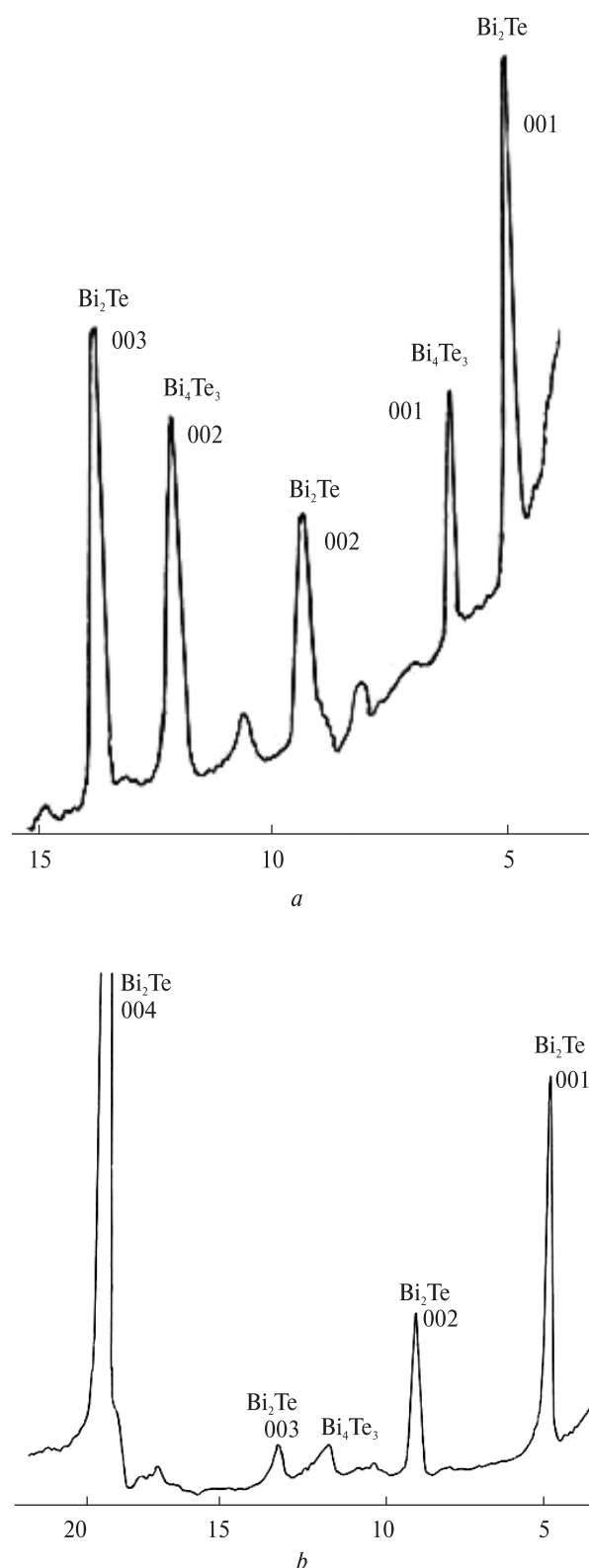


Fig. 2. X-ray diffraction patterns of pilsenite samples (Il'kivtsy) containing  $\text{Bi}_2\text{Te}$  phase: *a* — intergrowth of pilsenite  $\text{Bi}_4\text{Te}_3$  and phase  $\text{Bi}_2\text{Te}$  along plane (0001) of lamellar crystals. Diffraction pattern of plate oriented along cleavage plane; *b* — diffraction pattern of more clear phase  $\text{Bi}_2\text{Te}$ ; the weak reflections of pilsenite might be found

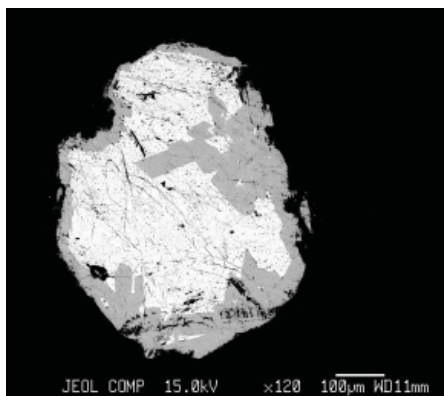


Fig. 3. Crystallisation of phase  $\text{Bi}_{2.92} \times (\text{Te}_{0.93}\text{Se}_{0.59}\text{S}_{0.56})_{2.08}$  on boundary with native bismuth. Stoichiometric formula is  $\text{Bi}_6\text{Te}_2\text{SeS}$  (Smerekiv Kamin')

carried out at studying phase  $\text{Bi}_3\text{X}_2$  is the whole absence of reliable structural characteristics. It is mainly caused by the submicroscopic size of grains.

**Genesis.** Detailed discussion of genesis of tellurides was not the main aim of this paper. However the preliminary analyses of the available data allow us to make some conclusions. We note that there is dependence between composition of telluride and geochemical environment at which this mineral was crystallized. It looks naturally, because compositions of the mineral phases that form mineral association should reflect association of chemical elements at certain environment of mineralization. So, tellurides of silver, lead or bismuth can be formed only at the presence of these elements in hydrothermal solution and at the same time for their formation tellurium should be present in this solution at certain concentration values. For example, Beregovo gold deposit shows the presence of bismuth sulphosalts and bismuthinite, but bismuth tellurides have not been found here till now [8].

In [13] (Table 1) have been indicated the existence of three types of telluride mineralization in Slovakia that corresponds to different degrees of S, Se and Te fugacity.

1. Mineralization with the high fugacity of sulfur. The characteristic minerals of this type are represented by bismuthinite ( $\text{Bi}_2\text{S}_3$ ), ikonolite ( $\text{Bi}_4\text{S}_3$ ), tetradymite ( $\text{Bi}_2\text{Te}_2\text{S}$ ), sulfö-skippenite ( $\text{Bi}_2\text{TeS}_2$ ), joseite ( $\text{Bi}_4\text{TeS}_2$ ). Telluride occurrences are localized in Dubrava, Katarínska Huta, Kokava and Rimavicou, Krokava, Rochovce, Banská Štiavnica and Hodruša areas. All these occurrences do not show any close association with volcanic processes.

2. Mineralization without manifestation of any separate fugacity of sulfur, selenium or tellurium.

For this type telluride associations with different relations S, Se and Te in their compositions are observed: a) Layered structures are represented by tetradymite, tsumoite, ikonolite ( $\text{Bi}_4\text{TeS}_2$ ), pilsenite, laitakarite ( $\text{Bi}_4\text{Se}_2\text{S}$ ), joseite-A, joseite-B and Se-hedleyite ( $\text{Bi}_7\text{Te}_2\text{Se}$ ), native bismuth; b) Some other structures observed are bismuthinite, phase ( $\text{Bi,Sb,Cu}$ ) $_3\text{S}_4$  (raklidgeite type), gustavite ( $\text{Bi}_3 \times \text{PbAgS}_6$ ), baksanite ( $(\text{Bi,Pb})_6\text{Te}_2\text{S}_3$ ), gladite ( $\text{Bi}_3\text{PbCuS}_9$ ), hessite ( $\text{Ag}_2\text{Te}$ ).

The following occurrences were found in Hnúšťa, Chyžné, Gemerská Poloma areas. For this type any association with volcanic processes have not been found.

3. Mineralization with high fugacity of tellurium. For this type it is possible to distinguish two groups of minerals: a) Layered tellurides of bismuth represented by tetradymite ( $\text{Bi}_2\text{Te}_2\text{S}$ ), tsumoite ( $\text{BiTe}$ ), pilsenite ( $\text{Bi}_4\text{Te}_3$ ), joseite-B ( $\text{Bi}_4\text{Te}_2\text{S}$ ), ingodite ( $\text{Bi}(\text{Te, Se})$ ); b) Some other tellurides found represented by hessite ( $\text{Ag}_2\text{Te}$ ), altaite ( $\text{PbTe}$ ), petzite ( $\text{Ag}_3\text{AuTe}_2$ ), stutzite ( $\text{Ag}_5\text{Te}_2$ ), silvanite ( $\text{AgAuTe}_4$ ), cervelleite ( $\text{Ag}_4\text{TeS}$ ), weissite ( $\text{Cu}_3\text{Te}_3$ ), rickardite ( $\text{Cu}_3\text{Te}_2?$ ). All these tellurides are tellurides of Bi, Ag, Pb and Cu.

Telluride mineralization of this type is localised in Jasenie, Kremnica, Zupkov, Banská Štiavnica and Hodruša, Zlata Bana, Bysta, Poruba pod Vihorlatom and Remetske Hamre areas [13]. These occurrences are found to be confined to neovolcanites.

It is also worth to note that manifestations of tellurides with predominantly layered structures (namely tellurides of tetradymite group) show close association with secondary quartzite and argillizite formations.

Some interesting interrelation between minerals that form paragenetic association is observed in bismuth globules sampled from the Smerekiv Kamin' area. Besides native bismuth bismuth sulfotellurides and tellurides, bismuthinite and pyrite are found to be present in these globules. All mineralogical phases found in globules show close contact relation with native bismuth.

This fact indicates high bismuth abundance in mineral-forming environment with high activity of sulfur. It also results in the crystallization of bismuth rich phases such as joseite, pilsenite,  $\text{Bi}_3(\text{Te, Se, S})_2$  and  $\text{Bi}_2(\text{Te, S})$  (Table 2). The fact of occurrence of low-temperature association of  $\text{Bi}_2\text{Te}$  phase and bismuth rich tellurides were described in early paper [3]. It is possible that there is direct relation not only between amount of S and Se in structure

of bismuth tellurides but also between temperatures of their formation. The similar conclusion might be partly related to the values of bismuth content found in telluride, notably the more high bismuth content the more low temperature is.

The data on temperatures of telluride formation are rather rare. And only few publications represent data on composition of hydrothermal solutions. Some results are obtained after carrying out some complex investigation of hydrothermal veins of the Štiavnica-Hodruš ore district and discussed in paper by Maťo [9]. The phase relations in the Au-Ag-Te-(Se) and Bi-Te-S-(Se) systems compared with data on the thermometry of fluid inclusion indicate that: *a* — the temperature of the precipitation of tellurides was commonly between 310–150 °C; *b* — the fluid composition of solutions corresponds to the systems of H<sub>2</sub>O — NaCl and H<sub>2</sub>O — NaCl — KCl; *c* — the solution concentration values vary from 0.7 to 3.9 equiv. wt. % NaCl. Variable pressure (195–45 bars) indicates continuous opening of the system and transition from hydrostatic + litostatic to hydrodynamic conditions at shallow depths. Oxygen isotopic data on quartz (–4.0 to 15.2 ‰) and carbonates (+3.5 to 25.1 ‰), as well as the δD values of chlorite and kaolinite indicate progressively increasing percentage of meteoric waters during the later mineralization stages (–52 to –113 ‰). The values of the δ<sup>34</sup>S of sulphides show that isotopic composition corresponds to the δ<sup>34</sup>S of fluids, which were separated from the uncontaminated granitic magmas, the δ<sup>34</sup>S values of melt varied from –3 to +3 ‰ [9].

Temperatures of the formation stages of the main mineral associations found in Saulak deposit were determined with the help of studying of gaseous-liquid inclusions and mineral parageneses: 1 — gold-pyrite-quartz: 390–320 °C; 2 — gold-sulfide-telluride: 270–200 °C; 3 — gold-mica-carbonate: 220–160 °C [1]. Thus, lead and silver tellurides were formed at middle tempera-

tures. Since the tellurobithmutite is commonly found as separated from other tellurides, gold and sulfides this fact allows us to assume, that its crystallization occurred at more low temperatures.

According to the data published in [18] the homogenization of essentially gaseous inclusions found in quartz sampled from quartz-turmaline metasomatites occurred at temperatures more than 250 °C. So it is possible to assume, that the tsumoite crystallization temperature was also high. This facts indicates possible tsumoite crystallization at the stage of pre-metasomatic cracks formation and its close association with pyrite and arsenopyrite. These cracks played a role of conduits for the fluid saturated with gases, that cause the processes of metasomatic alteration. Thus, bismuth tellurides are possible to be crystallized in the range from the middle (350–300 °C) to the lowest (150–100 °C) temperatures.

**Conclusions.** Tellurides and sulfotellurides of layered structure are found widespread in locations of gold associated with epithermal alteration processes of volcanic rocks. Their composition depends on environment conditions, first of all, geochemical features, S and Te activity and crystallization temperatures. The deviation from stoichiometrical composition is typical of tellurides and sulfotellurides that commonly cause the uncertainty at their classifications. More detailed structural and chemical investigations are needed for many mineral phases to be precisely distinguished.

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1. Bobrov O.B., Sivoronov A.O., Gursky D.S. et al. Geological and genetical typification of Ukraine gold deposit. — Kyiv, 2004. — 386 p. (in Russian).
2. Ciobanu C.L., Pring A., Cook N.J. et al. Chemical-structural modularity in the tetradymite group : A HRTEM study // Amer. Miner. — 2009. — 94. — P. 517–534.
3. Gamyarin G.N., Leskova N.V., Vyal'sov L.N., Laputina I.P. Bismuth tellurides — Bi<sub>2</sub>Te and BiTe — in deposits North-East USSR // Proc. All-Union Miner. Soc. — 1980. — Pt. 109, No 2. — P. 230–235 (in Russian).
4. Godovikov A.A., Kochetkova, K.V., Lavrentyev, Y.G. Bismuth tellurides from the deposit Sokhondo // Ibid. — 1971. — Pt. 109, No 3. — P. 257–265 (in Russian).
5. Godovikov A.A., Kochetkova, K.V., Lavrentyev, Y.G. On the systematization of bismuth sulfotellurides and tellurides // Ibid. — 1971. — 100, No 4. — P. 417–428 (in Russian).
6. Kukovsky E.G., Lazarenko E.A. Wehrlite from Transcarpathians // Geol. Journ. — 1959. — 19, No 4. — P. 91–92 (in Ukrainian).

7. Lazarenko E.K., Lazarenko E.A., Baryshnikov E.K., Malygina O.A. Mineralogy of Transcarpathians. — Lvov : Publ. House of Lvov. Univ., 1960. — 140 p. (in Russian).
8. Matkovsky O.I., Yasinskaya A.A., Stepanov V.B. Lead and silver tellurides on Transcarpathians // Rept. Acad. Sci. SSSR. — 1979. — **245**, No 2. — P. 444—449 (in Russian).
9. Maťo L., Ferenc Š., Jeleň S., Kovalenker V.A. Te-Se mineralization of neovolcanites and crystalline complexes of Slovakia // Understanding the genesis of ore deposits to meet the demands of the 21st cent., 12th IAGOD Quadren. Symp. (21—24 aug. 2006) : Extended abstr. — M., 2006.
10. Melnikov V.S. A variation of Bi/Te ratio, polytypism and mixed-layering in Bi-tellurides (Transcarpathians, Ukraine) // 32nd Intern. Geol. Congr., Florence : Abstr. vol. — 2004. — Pt. 1. — P. 275.
11. Melnikov V., Bondarenko S., Grinchenko A. Bi-tellurides of Transcarpathians (Ukraine) : Mineralogy and genesis. Gold-Silver tellurides Deposits of the Golden Quadrilateral, South Apuseni Mts., Romania / Eds. N.J. Cook, C.L. Ciobanu. — 2004. — P. 214—216. — (IAGOD Guidebook. Ser. 12).
12. Melnikov V., Bondarenko S., Grinchenko A. Conditions of Bi-telluride formation in Vyhorlat-Huta volcanic ridge (Transcarpathian region, Ukraine) // Geochemistry, mineralogy and petrology. Vol. 43. Au-Ag-Te-Se deposits. — Sofia, 2005. — P. 124—127. — (IGCP Project 486. 2005 Field Workshop, Kitten, Bulgaria).
13. Melnikov V., Jeleň S., Bondarenko S. et al. Comparative study of Bi-Te-Se-S mineralizations in Slovak Republic and Transcarpathian region of Ukraine. Pt. 1. Localities, geological situation and mineral associations // Mineral. Journ. (Ukraine). — 2009. — **31**, No 4. — P. 38—48.
14. Pekov I.V., Zav'yalov E.N., Fedushchenko S.V. et al. Baksanite  $\text{Bi}_6(\text{Te}_2\text{S}_3)$ , a new mineral species from Tyrnyauz (Northern Caucasus) // Trans. Rus. Acad. Sci., Earth Sci. Sect. — 1996. — **347A**. — P. 419—423 (in Russian).
15. Řídkošíl T., Skála R., Johan Z., Šrein V. Telluronevskite,  $\text{Bi}_3\text{TeSe}_2$ , a new mineral // Eur. J. Miner. — 2001. — **13**. — P. 177—185.
16. Sejkora J., Litochleb J., Černý P., Ozdín D. Bi-Te mineral association from Župkov (Vtáčnik Mts., Slovak Republic) // Miner. Slov. — 2004. — **36**, No 3—4. — P. 303—315 (in Slovak).
17. Skála R., Ondruš P., Veselovský F. et al. Vihorlatite,  $\text{Bi}_{24}\text{Se}_{17}\text{Te}_4$ , a new mineral of the tetradymite group from Vihorlat Mts., Slovakia // Eur. J. Miner. — 2007. — **19**. — P. 255—265.
18. Sobolev V.S., Kostjuk A.P., Bobrievich A.P. et al. Petrography of Neogene volcanic and hypabyssal rocks of the Soviet Carpathian mountains. — Kyiv : Publ. House Acad. Sci. Ukraine, 1955. — 247 p. (in Russian).
19. Zav'yalov Y.N., Begizov V.D., Nechelustov G.N. New data on hedleite // Rept. Acad. Sci. SSSR. — 1976. — **230**, No 6. — P. 1439—1441 (in Russian).
20. Zav'yalov Y.N., Begizov V.D., Stepanov V.I. Redetermination of wehrlite and the first find of tsumoite in the USSR // Proc. All-Union Miner. Soc. — 1978. — Pt. 107. — P. 544—553 (in Russian).

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**РЕЗЮМЕ.** Телуриди бісмуту шаруватої структури (група тетрадиміту) — характерні мінерали метасоматично змінених неовулканітів Словаччини і Українського Закарпаття. Цумоїт, пильзеніт і жозеїт (*A* і *B*) відомі в обох регіонах, але тетрадиміт не знайдений в Закарпатті. У Словаччині відкриті два нових мінерали — телуроневскіт і вигорлатит. У Закарпатті (Льківці) в епітаксичному зростанні з пильзенітом визначена фаза  $\text{Bi}_2\text{Te}$  (рентген, електронний зонд), що утворює епітаксичні зростання з пильзенітом. У глобулах самородного бісмуту (Смереків Камінь) за допомогою електронно-зондового аналізу виявлені Se-жозеїт-*B*, Se-цумоїт, Te-бісмутиніт, фаза  $\sim\text{Bi}_2\text{SeS}$  (проміжна між невскітом й інгодитом) і фаза зі стехіометрією  $\text{A}_3\text{X}_2$  ( $\text{A} = \text{Bi}$ ;  $\text{X} = \text{Te}, \text{Se}, \text{S}$ ), але кількість аніонів *X* змінюється від  $\text{Bi}_3\text{Te}_{1,5}\text{S}_{0,5}$  до  $\text{Bi}_3\text{TeSe}_{0,5}\text{S}_{0,5}$ . Температурний інтервал утворення шаруватих телуридів бісмуту — 350—100 °C.

**РЕЗЮМЕ.** Теллуриды висмута слоистой структуры (группа тетрадимита) — характерные минералы метасоматически измененных неовулканитов Словакии и Украинского Закарпатья. Цумоит, пильзенит и жозеит (*A* и *B*) установлены в обоих регионах, но тетрадимит в Закарпатье не найден. В Словакии открыты два новых минерала — теллуроневскит и вигорлатит. В Закарпатье (Ильковцы) определена фаза  $\text{Bi}_2\text{Te}$  (рентген, электронный зонд), образующая эпитаксические сростки с пильзенитом. В глобулах самородного висмута (Смерекив Каминь) с помощью электронно-зондового анализа определены Se-жозеит-*B*, Se-цумоит, Te-висмутинит, фаза  $\sim\text{Bi}_2\text{SeS}$  (промежуточная между невскитом и ингодитом) и фаза со стехиометрией  $\text{A}_3\text{X}_2$  ( $\text{A} = \text{Bi}$ ;  $\text{X} = \text{Te}, \text{Se}, \text{S}$ ), но количество анионов *X* изменяется от  $\text{Bi}_3\text{Te}_{1,5}\text{S}_{0,5}$  до  $\text{Bi}_3\text{TeSe}_{0,5}\text{S}_{0,5}$ . Температурный интервал образования слоистых теллуридов висмута — 350—100 °C.