Bismuth sulphosalts from the siderite–sulphidic and As-Co mineralization in Medzev area, Slovakia

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Abstract: Two interesting associations of Bi minerals were found in the vicinity of the town of Medzev in Slovenské rudohorie Mts. The first one occurs with quartz and arsenopyrite at Kobaltová vein and is represented by native Bi, bismuthinite, ikunolite, ingodite, benjaminite, matildite and gustavite. The second one was found at Oriešok vein associated with pyrrhotite, arsenopyrite, cobaltite, sphalerite and galena. The sulphosalts identified there are: izoklakeite, tintinaite, Bi-rich boulangerite and Bi-rich jamesonite. An extensive $Bi^{3+} \leftrightarrow Sb^{3+}$ substitution was observed among studied sulphosalts. The Co anomalies, determined previously by geochemical methods, were explained by cobaltite and Co-rich arsenopyrite. Studied sulphosalts belong to the latest stages of the quartz-sulphidic mineralization in the Gemeric Superunit.

Key words: Western Carpathians, Slovenské rudohorie Mts., izoklakeite, matildite, gustavite, benjaminite, Bi-rich boulangerite and Bi-rich jamesonite

1. INTRODUCTION

The exact beginning of mining around the village of Medzev area is not known because the smaller Medzev deposit was overshadowed by the near larger Cu deposits Smolník and Gelnica. Manually chiseled tunnels at the Fichtenhübel deposit (Konštancia, Krištof and Michal veins) indicate mining already in the Medieval times. Based on a mining map of the Christofory adit from 1764, Návesňák and Kotras (1959) estimated the earliest mining in Medzev area cautiously in the 18th century. The first brief written documents about the ore veins were published by Tóth (1882), Maderspach (1880) and Papp (1915), followed by later studies by Horal (1971) and Varček (1973). The latest information about the mineral content of the veins, with emphasis on the high-temperature mineralization was given by Malachovský et al. (1983).

There are more than 40 ore bodies in the area of Medzev. They are dominated by siderite and contain variable amount of sulphides. Chalcopyrite and less abundant tetrahedrite are typical for most of the bodies (e.g., ore veins in the Fichtenhübel deposit). Some veins (Hummel, Gregori) are known for their association of sphalerite, galena and Pb-Sb-Bi sulphosalts. Other veins contain stibnite (Kloptaň, Hummel parallel) and some even Co mineralization (Kobaltová vein). The aim of our research is a detailed description of the mineralization at the Kobaltová vein for the purposes of exploration company European Cobalt and Oriešok vein for its unusual massive sulphide texture (VMS-like), unusual bedding and the problematic historical data.

2. GEOLOGICAL SETTINGS

Ore mineralization is hosted by metamorphosed greywacke, metamorphosed rhyolite tuff and sericite-graphite phyllites which were members of an Early Palaeozoic Drnava Formation (Fig. 1). The rock sequence includes also porphyroids and sericite-chlorite phyllite, metamorphosed rhyolite tuff, quartz-sericite and graphite phyllite to black shales of the Bystrý potok Formation formation and was intruded by a body of Gemeric granite (so-called Humel granite). Ore veins are located in the strike slip, fold and thrust zones which belong to Jedľovec nappe (Grecula ed., 1995).

The Kobaltová vein lies on the SE margin of the siderite-copper deposit Fichtenhübel. Its thickness varies from 10 to 30 cm, strike is E-W and it was opened with 2 galleries (Grecula ed., l. c.). Lateral and vertical extent are not precisely known. The mineral content of the Kobaltová vein is dominated by quartz, with additional arsenopyrite, glaucodot, cobaltite, chalcopyrite, pyrite, marcasite, pyrrhotite, tetrahedrites, sphalerite, bismuth and non-specified Bi minerals.

Grecula ed. (1995) reported that the Oriešok vein is a siderite-quartz body of E-W direction, with a length of 50 m and thickness of 5-60 cm. Zábranský and Radzo (1966) reported that the vein contains siderite, quartz, ankerite, pyrite, chalcopyrite, tetrahedrites, marcasite, pyrrhotite and kobellite. Oriešok vein could represent the western continuation of the Hummel vein (Kalte Rinne), with elevated content of base-metal sulphides (Bajaník, 1960; Eliáš, 1977).

3. METHODS

Samples for the mineralogical study were collected in 2018 from the waste dumps of the Kobaltová and Oriešok vein. The chemical composition of sulphides and sulphosalts was determined by wavelength-dispersive spectrometry (WDS) on an electron probe microanalyzer (EPMA) JEOL JXA 8530FE (at Earth Sciences Institute of Slovak Academy of Sciences in Banská Bystrica) with the following conditions: accelerating voltage 20 kV, probe current 15 and 20 nA, beam diameter 2-3 µm, ZAF correction, counting

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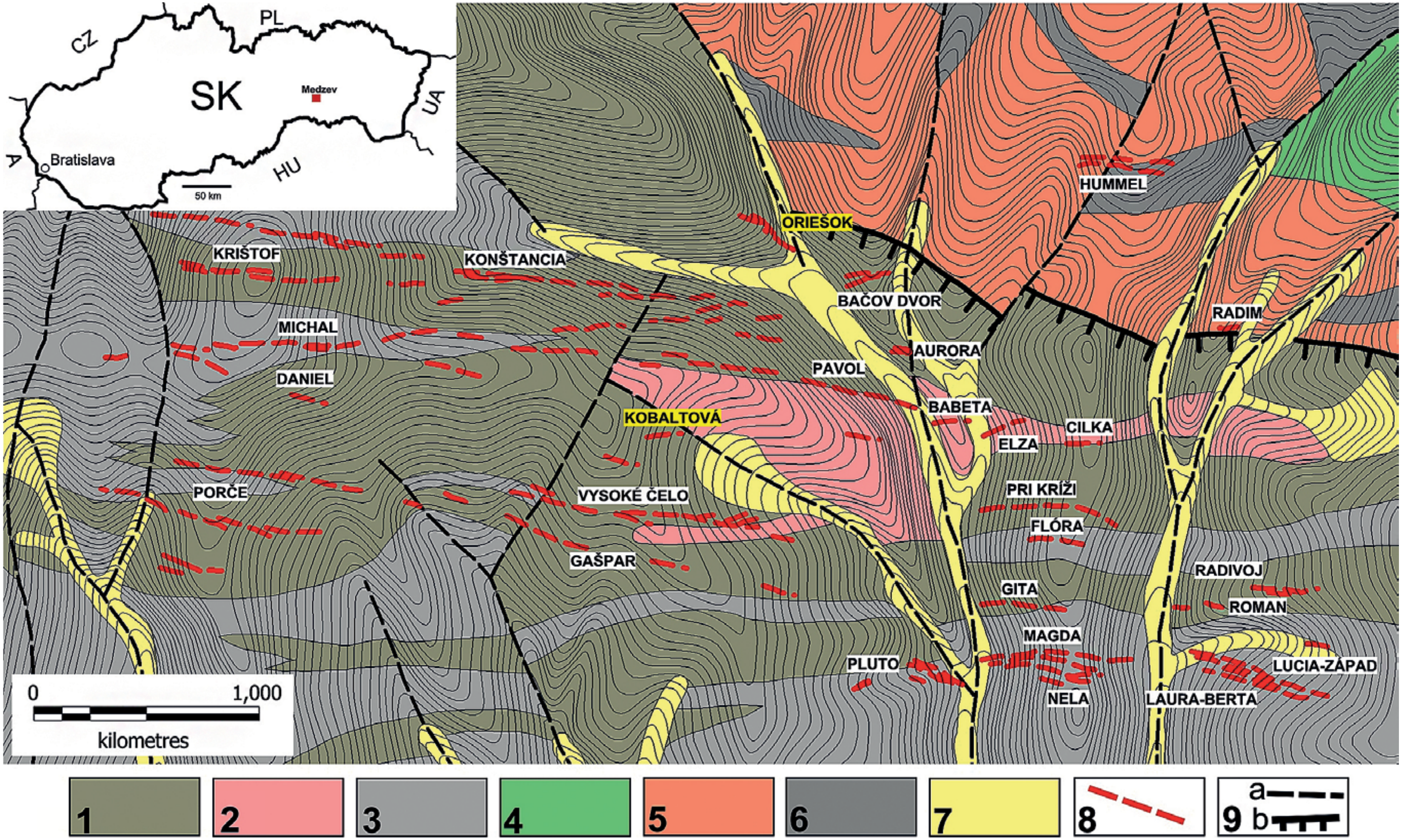

Fig. 1 Simplified geological map of Medzev ore field and location of studied veins (modified after http://apl.geology.sk/gm50js). Legend: 1. – 3. Early Paleozoic, Drnava formation, Gemeric unit (1. Metamorphosed greywacke; 2. Metamorphosed rhyolite tuff; 3. Sericite and graphite phyllite); 4. – 6. Early Paleozoic, Bystrý potok formation, Gemeric unit (4. Sericite-chlorite phyllite; 5. Metamorphosed rhyolite tuff; 6. Quartz-sericite and graphite phyllite); 7. Quaternary alluvial sediments; 8. Ore veins; 9. a, faults; b, thrust fault.

time 20 s on peak, 10 s on background. For WDS analyses the following standards were used: Ag($L\alpha$) - pure Ag, S($K\alpha$) - pyrite, Cu($K\alpha$) and Fe($K\alpha$) - chalcopyrite, As($L\beta$) - GaAs, Se($L\beta$) - Bi_2Se_3, Cd($L\alpha$) an Te ($L\alpha$) - CdTe, Sb($L\alpha$) - stibnite, Hg($M\alpha$) - cinnabar, Bi($L\alpha$) - Bi_2S_3, Pb($M\alpha$) - galena, Ni($K\alpha$) - gersdorffite, Co($K\alpha$) - pure Co, Zn ($K\alpha$) – sphalerite, Mn ($K\alpha$) – rhodonite, Au ($M\alpha$) – pure Au. The detection limits are between 0.02 - 0.05 wt. %.

Bulk chemical composition of ore samples from the dumps was determined in the laboratory ALS Global Rosia Montana – Romania. The samples were weighed, dried and milled so that minimum 70 % of each sample was in the fraction < 2 mm. Later, quartered parts of samples with weight of 250 g were milled so that minimum 85 % of each sample has reached the grain size <0.075 mm. Gold was analysed by fire assay from samples with weight 30 g, followed by Au content determination by AAS (methodology code Au-AA24). The detection limit of this method is 0.005 ppm. Other elements from the Oriešok vein were analysed in the lab Loughrea (Ireland) by ICP-AES using a strong oxidizing acid digestion (analytical code ME-ICPORE). Samples from the Kobalt vein were analyzed in Loughrea (Ireland) lab from weight of 0.2 g using aqua regia digestion with ICP-MS (analytical code ME-MS41).

4. RESULTS

The entrances of the mine galleries of the Kobaltová vein are collapsed and the tectonic settings of the studied mineralization cannot be studied. Deducing from the volume of the waste dumps, the vein are at least 100-150 m long. Three types of mineralization were found in the waste dump material (sulphosalts-bearing quartz, arsenopyrite-bearing quartz and carbonates). Carbonates are rare, lack visible sulphides and were not further considered. Sulphosalts form aggregates up to 1-2 cm or occur as veinlets (thick up to 5 mm) on the contact with the silicified host rock. Arsenopyrite forms dense impregnations of grains up to 2 mm arranged in up to 5 cm thick bands. The richest ores contain three bands of massive arsenopyrite. The common occurrence of arsenopyrite and sulphosalts was also confirmed by correlation of As and Ag, Bi, Pb in the bulk geochemical data. The Kobaltová vein was most likely exploited historically for silver. A sample rich in sulphosalts shows Ag content of 2460 g/t, >1 % Bi, 0.24 % Pb, 0.34 % As, 0.05 % Co and 1.11 g/t of Au. Two samples with arsenopyrite show in average >1 % As, 0.56 % Co, 0.18 % Bi, 0.05 % Pb, 550 g/t Ag and 0.44 g/t Au.

At the Kobaltová vein, we identified microscopically only quartz, arsenopyrite, pyrite and Ag-Pb-Bi sulphosalts. *Arsenopyrite* forms aggregates up to 1 cm in size and often shows cataclastic textures with oscillatory zoning, with variable Sb and Co content (Table 1) and Sb up to 1.9 wt% (0.03 apfu) and Co up to 5.5 wt% (0.16 apfu). Arsenopyrite is replaced by pyrite and sulphosalts (Fig. 2a).

Sulphosalts of the Kobaltová vein

Bismuthinite Bi_2S_3

Bismuthinite is a rare phase. It forms irregular grains up to 10 µm large and usually replaces matildite, gustavite and native bismuth. Chemical compositions of bismuthinite from Medzev and the corresponding formulae are given in Tab. 2. There are

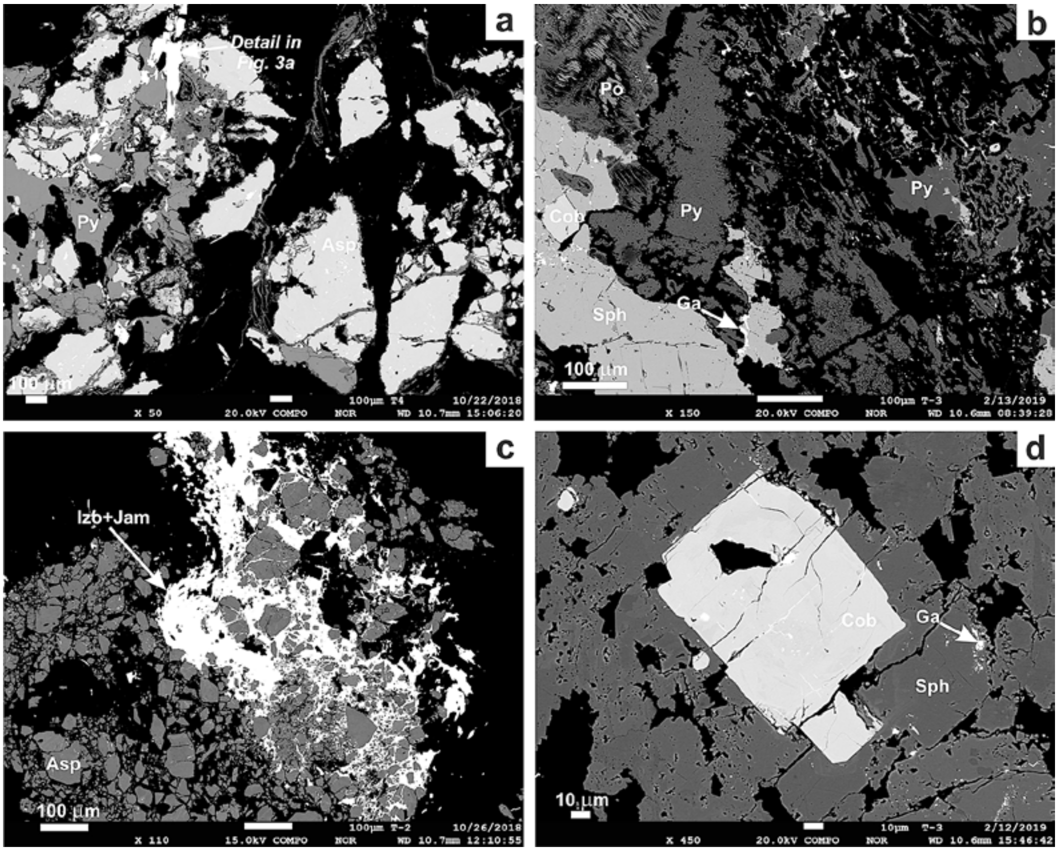

Fig. 2a – **Allotriomorphic grains of arsenopyrite (Asp) associated with pyrite (Py) and sulphosalts (detail description is given in Fig. 3a), Kobalt vein. b – Assocation of sulphides from the Oriešok vein; pyrrhotite – (Po), cobaltite – (Cob), pyrite, sphalerite – (Sph) and galena (Ga). c – Tectonically brecciaed arsenopyrite aggregates rejuvenated with sulphosalts, Oriešok vein. d – Idiomorphic grain of cobaltite enclosed in sphalerite, Oriešok vein. Back-scattered images (BSE).**

only limited $Bi^{3+} \leftrightarrow Sb^{3+}$ and $S^{2-} \leftrightarrow Se^{2-}$ substitutions, with Sb content up to 0.01 apfu and Se <0.08 apfu.

Ikunolite $Bi_4(S,Se)_3$

Ikunolite forms rare irregular grains up to 10 μm in size (Fig. 3a). It is usually associated with native Bi and replaced by matildite and benjaminite. The crystallization sequence was: native Bi → ikunolite → bismuthinite. The calculated formula is $Bi_{3.98}(S_{2.76-2.89}Se_{0.13-0.22})_{\Sigma 2.98-3.01}$ and corresponds to Se-poor ikunolite (Tab. 2), with minor Te (up to 0.32 wt %). Ikunolite from Medzev belongs to the Bi_4S_3–$Bi_4S_{1.5}Se_{1.5}$ solid solution (Parafiniuk et al. 2008). Se-poor or Se-free ikunolite was described from Stanos, Greece (Voudouris et al. 2013) or Kutná Hora, Czech Republic (Pažout et al. 2017).

Ingodite $Bi(S,Te)$

Ingodite forms acicular or anhedral inclusions in benjaminite or gustavite up to 40 μm large (Fig. 3c). It is replaced by benjaminite and gustavite. Te content is up to 0.40 apfu and S content ranges from 0.49 to 0.73 apfu. There is also partial $S^{2-} \leftrightarrow Se^{2-}$ substitution, with max. 0.08 apfu of Se. Crystal chemical formula can be expressed as $Bi_{0.98-1.04}(S_{0.49-0.73}Te_{0.23-0.40}\,Se_{0.05-0.08})_{\Sigma 0.95-1.01}$ (Tab. 2).

Matildite $AgBiS_2$

Matildite is a common phase and usually associates with gustavite and benjaminite (Fig. 3a, 3b, 3d). It forms reaction zones between benjaminite and gustavite (Fig. 3a) or needle-shape grains up to 100 μm intimately intergrown with gustavite (Fig. 3b, 3d).

It is usually replacing benjaminite, itself being replaced by gustavite. The crystallization sequence was: native Bi → bismuthinite → ikunolite → ingodite → benjaminite → matildite → gustavite. Chemical compositions of matildite from Medzev and the corresponding chemical formulae are given in Tab. 3. Average (13 points) crystal chemical formula can be written as $Ag_{0.96}Pb_{0.01}Bi_{1.02}(S_{1.92}Se_{0.06}Te_{0.01})_{\Sigma 1.99}$. Most of the analytical points project near the theoretical composition of matildite (Fig. 4). Matildite shows partial $S^{2-} \leftrightarrow Se^{2-}$ substitution (up to 0.10 apfu of Se); solid solution

Tab. 1 Chemical composition of arsenopyrite and cobaltite from Kobalt and Oriešok vein, Medzev (formula based on 3 apfu).

locality	Kobalt vein						Oriešok	vein		
sample	T4-1	T4-3	T9-4	T9-5	T9-6	T9-7	T2-117	T2-119	T2-119	T2-123
Fe	30.22	28.21	31.96	35.16	31.16	32.48	34.12	4.43	4.53	7.25
Sb	0.82	0.90	1.76	0.10	1.91	0.91	0.65	0.00	0.00	0.00
As	44.91	44.11	44.88	44.30	44.43	44.51	42.22	45.44	44.99	44.03
Ni	0.05	0.38	0.09	0.00	0.09	0.03	0.18	0.30	0.29	0.34
Co	4.07	5.50	2.16	0.07	3.04	2.15	1.43	28.96	28.82	27.69
S	18.84	18.94	18.53	20.08	18.46	19.02	21.07	19.63	19.99	20.61
Au	0.01	0.02	0.19	0.00	0.08	0.09	0.07	0.00	0.09	0.00
total	98.92	98.07	99.58	99.70	99.17	99.21	99.76	98.75	98.71	99.92
Fe	0.90	0.85	0.95	1.02	0.93	0.96	0.98	0.13	0.14	0.21
Sb	0.01	0.01	0.02	0.00	0.03	0.01	0.01	0.00	0.00	0.00
As	1.00	0.99	1.00	0.96	0.99	0.98	0.91	1.01	1.00	0.96
Ni	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01
Co	0.11	0.16	0.06	0.00	0.09	0.06	0.04	0.82	0.82	0.77
S	0.98	0.99	0.96	1.02	0.96	0.98	1.06	1.02	1.04	1.05
Au	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Tab. 2 Chemical composition of ingodite, ikunolite and bismuthinite from Kobalt vein in Medzev (apfu – the basis for calculation of empirical formula).

phase	Ingodite					Ikunolite			Bismuthinite	
point	17	18	19	25	32	7	31	109	36	110
Ag	0.02	0.08	0.20	0.14	0.17	0.04	0.08	0.14	0.05	0.02
Sb	0.27	0.18	0.15	0.04	0.18	0.02	0.00	0.00	0.22	0.27
Se	1.75	2.13	2.36	1.57	1.92	1.84	1.06	1.69	1.16	1.14
Bi	75.04	76.80	78.70	78.04	78.54	88.42	88.91	88.71	81.14	80.96
Te	17.47	11.69	11.05	11.01	11.10	0.32	0.08	0.35	0.00	0.00
S	5.46	7.14	7.50	8.86	7.91	9.42	9.90	9.44	18.14	17.98
Pb	0.06	0.79	0.09	0.03	0.08	0.04	0.02	0.08	0.12	0.11
total	100.08	98.80	100.05	99.69	99.91	100.06	100.05	100.40	100.83	100.48
apfu	2.00	2.00	2.00	2.00	2.00	7.00	7.00	7.00	5.00	5.00
Ag	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00
Sb	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01
Se	0.06	0.08	0.08	0.05	0.07	0.22	0.13	0.20	0.08	0.07
Bi	1.04	1.03	1.03	0.99	1.02	3.98	3.98	3.99	2.00	2.01
Te	0.40	0.26	0.24	0.23	0.24	0.02	0.01	0.03	0.00	0.00
S	0.49	0.62	0.64	0.73	0.67	2.77	2.89	2.77	2.91	2.90
Pb	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

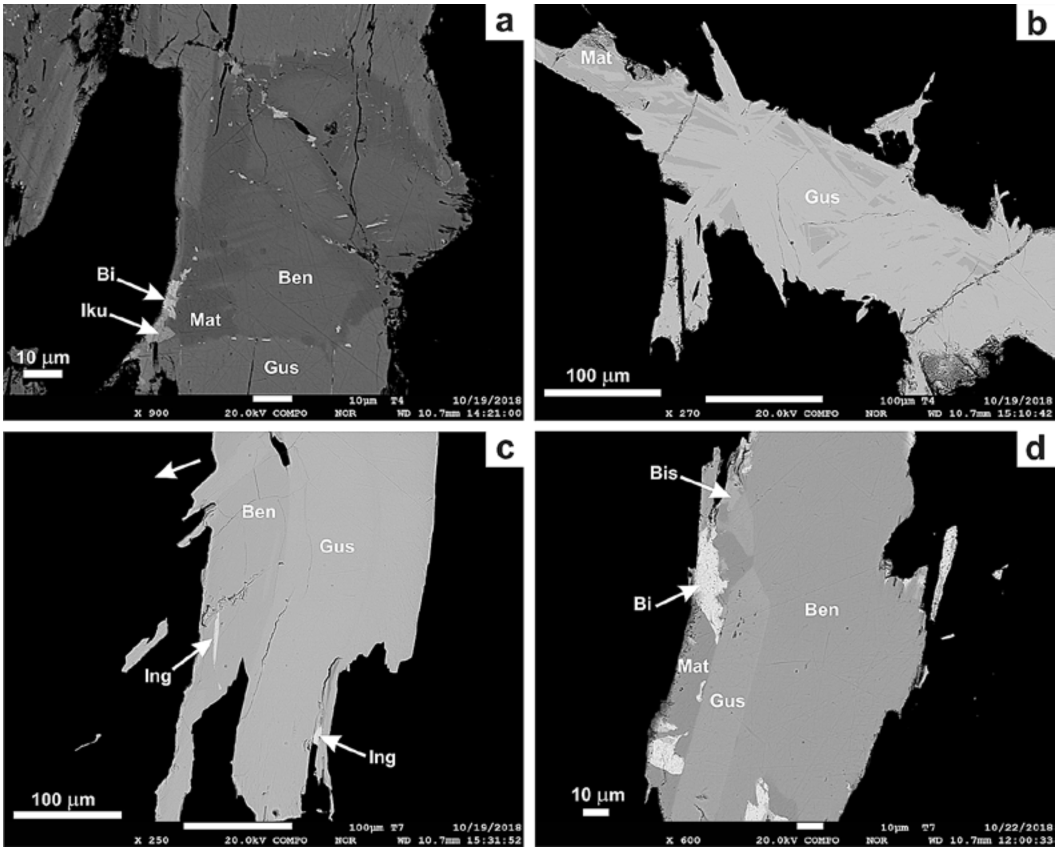

Fig. 3a – Allotriomorphic grains of benjaminite (Ben) replaced by matildite (Mat) and gustavite (Gus), associated with native bismuth (Bi) and ikunolite (Iku). **b** – Relics of matildite replaced by gustavite needles. **c** – Benjaminite replaced by gustavite, both encloses needles of ingodite (Ing). **d** - Allotriomorphic grains of benjaminite replaced by matildite and gustavite needles. Benjaminite and matildite are replacing bismuth and bismuthinite (Bis). BSE images from Kobalt vein.

composed 95% of matildite and 5% of bohdanowiczite ($AgBiSe_2$ isostructural with matildite). Higher Se content in matildite (up to 0.22 apfu) was reported from Ikuno deposit, Japan (Shimizu et al., 1998). Some analyses show elevated Pb (1.27–2.57 wt. %) corresponding to 0.96–1.99 mol. % PbS, suggesting a solid solution between matildite and galena, otherwise galena was not found associated with matildite. Pažout et al. (2017) report 6.25 mol. % PbS in matildite from Kutná Hora, Czech Republic.

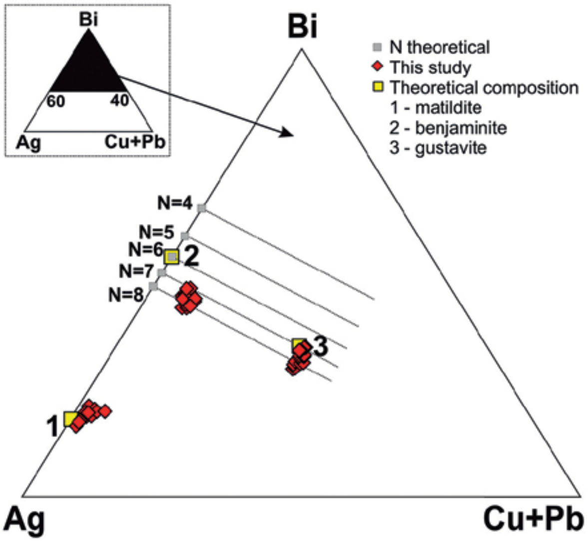

Fig. 4 Projection in the system Ag-(Cu+Pb)-Bi of analytical results for the Ag-Bi±Pb sulphosalts. N is order number for the pavonite homologue series (Makovicky et al. 1977, Mumme 1990).

Gustavite $AgPbBi_3S_6$

Gustavite is the most common sulphosalt in Medzev. It forms irregular, more often euhedral acicular grains up to several hundreds µm long (Fig. 3a, 3b, 3c). It is usually replacing matildite and benjaminite (Fig. 3b, 3c, 3d). It is the last phase in crystallization sequence among Bi minerals. Gustavite shows extensive $Sb^{3+} \leftrightarrow Bi^{3+}$ substitution and partial $Se^{2-} \leftrightarrow S^{2-}$ substitution (up to 0.23 apfu Se). The Sb content in gustavite is up to 0.51 apfu what suggest solid solution with terrywallaceite, ideally $AgPb(Sb,Bi)_3S_6$ which is isostructural with gustavite (Yang et al., 2013). Gustavite belongs to the lillianite homologous series with *N* = 4 (^4L). The *N* values determined from our analytical data vary from 3.95 up to 4.8, with the highest *N* values correlating well with the highest Sb contents. Its chemical composition (Tab. 4) gave the formula (based on 11 apfu) $Ag_{1.03}Pb_{0.95}(Bi_{2.61}Sb_{0.51})_{\Sigma 3.12}(S_{5.81}Se_{0.07})_{\Sigma 5.88}$ for Sb-rich gustavite.

Benjaminite $Ag_3Bi_7S_{12}$

Benjaminite is common and closely associated with matildite and gustavite. It forms anhedral grains up to 300 µm in size (Fig. 3d). Benjaminite is replaced by matildite and gustavite. It belongs to pavonite homologous series (^7P). The calculated *N* values vary from 7.17 to 8.63 (Fig. 4). Benjamite shows distinct substitution of Se for S (up to 0.50 apfu of Se). The mean (average of 12 analyses) formula is $Cu_{0.04}Ag_{2.87}Fe_{0.13}Pb_{0.38}Bi_{6.52}S_{11.48}Se_{0.31}$. Chemical compositions of benjaminite from Medzev and corresponding chemical formulae are given in Tab. 5.

Ore mineralization at the Oriešok vein was historically exploited with 3 galleries and by 15-20 small exploration shafts.

Tab. 3 Chemical composition of matildite from Kobalt vein in Medzev (formula based on 4 apfu).

point	9	22	29	33	37	38	45	48
Ag	27.00	28.30	27.46	27.13	27.21	27.13	26.99	25.21
Sb	0.27	0.38	0.47	0.31	0.28	0.23	0.10	0.61
Se	1.68	2.05	0.80	0.11	1.01	1.45	0.38	0.23
Bi	55.44	54.03	55.19	55.59	55.21	55.26	55.98	54.21
Te	0.16	0.36	0.20	0.38	0.16	0.26	0.26	0.57
S	15.58	15.18	16.17	16.28	16.08	16.03	16.21	16.24
Pb	0.51	0.01	0.32	0.55	0.39	0.13	1.25	2.57
total	100.63	100.32	100.61	100.35	100.34	100.49	101.17	99.61
Ag	0.97	1.02	0.98	0.97	0.97	0.97	0.97	0.91
Sb	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.02
Se	0.08	0.10	0.04	0.01	0.05	0.07	0.02	0.01
Bi	1.03	1.01	1.02	1.03	1.02	1.02	1.03	1.01
Te	0.00	0.01	0.01	0.01	0.00	0.01	0.01	0.02
S	1.89	1.85	1.94	1.96	1.94	1.92	1.95	1.98
Pb	0.01	0.00	0.01	0.01	0.01	0.00	0.02	0.05
Bi/(Bi+Sb)	0.99	0.99	0.99	0.99	0.99	0.99	1.00	0.98

Tab. 4 Chemical composition of gustavite from the Kobalt vein, Medzev (formula based on 11 apfu). The order number N was calculated to lillianite homeotypic series (${}^4L$).

point	1	13	20	27	28	35	39	41	43	49
Ag	9.16	9.32	9.57	9.51	9.70	9.44	9.57	9.48	9.46	9.99
Sb	4.10	3.82	4.43	3.79	4.26	3.93	3.66	4.36	3.58	5.62
Se	1.07	0.80	1.11	0.64	0.54	0.26	1.15	1.02	0.02	0.53
Bi	51.23	50.15	49.61	51.14	50.39	51.33	50.93	50.37	52.03	49.09
S	16.23	16.67	16.60	16.66	16.94	16.98	16.58	16.80	16.92	16.73
Pb	18.02	18.50	17.97	18.30	17.91	18.13	18.00	18.56	18.19	17.64
total	99.80	99.24	99.30	100.04	99.74	100.08	99.88	100.59	100.21	99.59
Ag	0.96	0.97	0.99	0.99	1.00	0.98	0.99	0.98	0.98	1.03
Sb	0.38	0.35	0.41	0.35	0.39	0.36	0.34	0.40	0.33	0.51
Se	0.15	0.11	0.16	0.09	0.08	0.04	0.16	0.14	0.00	0.07
Bi	2.78	2.70	2.66	2.75	2.68	2.74	2.73	2.67	2.79	2.62
S	5.74	5.85	5.81	5.83	5.88	5.91	5.80	5.82	5.91	5.81
Pb	0.99	1.01	0.97	0.99	0.96	0.98	0.97	0.99	0.98	0.95
Bi/(Bi+Sb)	0.88	0.88	0.87	0.89	0.87	0.88	0.89	0.87	0.89	0.84
N	4.20	4.41	4.56	4.38	4.52	4.32	4.41	4.46	4.27	4.80

Layout of the shafts indicates NW-SE direction of the ore zone with the length of 250 m. The structures in a short exploration adit and 2 open pits show NW-SE to WNW-ESE direction with dip to SW to SSW. The mineralized zone, visible in several mine galleries, consists of veins and veinlets with a total thickness of 15-20 m. The thickness of individual veins is less than 20-30 cm and they contain pyrite, pyrrhotite, siderite and quartz. Siderite occurs in minor amounts in the lowest adit. The four samples of sulphidic ore show following average and maximal elemental concentrations: S 12.8 %, 38 % Fe, 1.16 % As, 0.12 % Co (max. 0.2 %), 0.22 % Cu (max. 0.34 %), 0.37 % Pb (max. 0.75 %), 0.82 % Zn (max. 2.33 %), 0.03 % Sb (max. 0.11 %), 248 ppm Bi (max. 680 ppm), 27 ppm Ag (max. 64 ppm) and 0.1 ppm Au (max. 0.18 ppm). Three limonite-rich samples gave: S 1.3 %, 45 % Fe, 1.59 % As, 0.01 % Co, 0.09 % Cu, 0.37 % Pb (max. 1.04 %), 0.16 % Zn (max. 0.26 %), 0.02 % Sb, 140 ppm Bi (max. 370 ppm), 16 ppm Ag (max. 42 ppm) and 0.14 ppm Au (max. 0.25 ppm). Samples of quartz veins and veinlets with iron-oxide coatings and scarce pyrite impregnations show negligible amounts of metals other than Fe.

The mineral content of the Oriešok vein is more varied than at the Kobaltová vein (Fig. 2b). The crystallization sequence of the Oriešok vein was quartz → pyrrhotite → arsenopyrite → cobaltite → pyrite → sphalerite → carbonate (siderite) → galena → sulphosalts (PbSbBi).

Pyrrhotite occurs as only relics with typical texture (Fig. 2b) massively replaced by pyrite and iron oxides. Its chemical composition obtained from EPMA is $Fe_{0.95}S_{1.05}$.

Arsenopyrite forms crushed veinlets and aggregates or euhedral crystals, replaced by siderite and sulphosalts. Sulphosalts also commonly fill and heal the fractures (Fig. 2c). Apart from the major elements (Tab. 1), there is minor Co (up to 1.43 wt%, 0.04 apfu) and Sb content (0.6 wt%, 0.01 apfu).

Cobaltite forms euhedral grains up to 150 μm large, associated with sphalerite aggregates (Fig. 2d). Chemical compositions and the corresponding formulae are given in Tab. 1. Its Ni content is limited to 0.34 wt%, Fe content reaches up to 7.2 wt% (0.21 apfu).

Pyrite occurs as massive aggregates or anhedral grains up to several hundreds μm, usually replaced by sphalerite. Its chemical composition (EPMA) is simple and identical to the nominal composition.

Sphalerite is a common phase and occurs as veinlets or massive aggregates. It is replacing pyrite, itself being replaced by galena. Zinc is substituted by Fe (up to 6.63 wt%) and Cd (up to 0.37 wt%). Contents of the other M^{2+} cations are negligible. The crystal chemical formula is $(Zn_{0.88}Fe_{0.12})_{\Sigma 1}S_1$.

Galena forms irregular grains up to several hundreds μm large. It is the latest simple sulphide and is replaced by sulphosalts. Galena hosts some Ag (up to 0.51 wt%, 0.01 apfu), rarely also Sb (up to 1.2 wt%, 0.02 apfu) and Bi (up to 2.2 wt%, 0.03 apfu). Sulphur is partly replaced by Se (up to 0.26 wt%, 0.01 apfu). The crystal chemical formula is $(Pb_{0.97}Ag_{0.01}Sb_{0.01}Bi_{0.01})_{\Sigma 1}(S_{0.99}Se_{0.01})_{\Sigma 1}$.

Sulphosalts of the Oriešok vein

Izoklakeite – Giessenite series $(Cu,Fe)_2Pb_{26}(Sb,Bi)_{20}S_{57}$ $N = 4$

Minerals of this series belong to the kobellite homologous series (Moëlo et al., 2008). Within this series, the members of the kobellite-tintinaite solid solution can be identified by $N = 2$ (Zakrzewski and Makovicky, 1986), where $N = 4$ for the izoklakeite-giessenite solution. The limiting composition between izoklakeite and giessenite is still questionable (Makovicky and Karup-Møller, 1986; Zakrzewski and Makovicky 1986); according to these authors, the name "izoklakeite" is applied to all samples with Sb/Bi atomic ratio close to 1 (i.e. Bi/(Bi + Sb) close to 0.50), even for samples with Bi > Sb.

Minerals of the izoklakeite-giessenite series are relatively rare in nature, however, izoklakeite is the most common sulphosalt at the Oriešok vein. Izoklakeite was found as acicular to prismatic crystals or irregular grains up to several hundreds μm in length in association with tintinaite, Bi-rich jamesonite, Bi-rich boulangerite and galena (Fig. 5a, 5b, 5c). The crystallization sequence was galena → izoklakeite → tintinaite → Bi-rich boulangerite → Bi-rich jamesonite.

Bi/(Sb + Bi) ratios for izoklakeite are confined to a narrow range of 0.43-0.48 and correlate well with published data (Fig. 6a). Fe + Cu content in the studied samples (average 2.16 apfu) is close to ideal (Fe + Cu = 2 apfu). Cu content is more variable than Fe (Fig. 6b). Silver content is up to 1.66 wt.% (1.62 apfu, Fig. 6c) what correspond to usual Ag content in izoklakeite (2.19 apfu, Moëlo et al., 1995; 1.95 apfu, Harris et al., 1986). The Pb vs. Ag plot shows (Fig. 6d) a negative correlation corresponding to the common substitution in sulphosalts or galena: Ag + (Bi,Sb)→2Pb. Chemical analyses of izoklakeite from Medzev and their structural formulae are given in Tab. 6. An average formula (15 analyses) for izoklakeite can be written as $(Cu_{1.64}Fe_{0.52})_{\Sigma 2.16}(Pb_{23.87}Ag_{1.30})_{\Sigma 25.17}(Sb_{11.52}Bi_{9.67})_{\Sigma 21.19}(S_{56.40}Se_{0.05})_{\Sigma 56.45}$ with chemically calculated N=3.62.

Kobellite - Tintinaite series $(Cu, Fe)_2Pb_{11}(Sb, Bi)_{15}S_{35}$ $N = 2$

Sulphosalts of this series occur rarely at this site. It forms exsolved irregular aggregates or needle-like crystals in izoklakeite up to 100 μm. It replaces izoklakeite and is replaced by Bi-rich jamesonite (Fig. 5b, 5c). The chemical composition and chemical formula of tintinaite from Medzev are given in Tab. 7. The Sb/(Sb+Bi) ratio varies from 0.54 to 0.58. Sb content in tintinaite reaches up to 8.66 apfu and Bi content is up to 6.95 apfu. The tintinaite lies on ideal Bi-Sb substitutional trend (Fig. 7). Silver content is up to 0.27 apfu, in comparison to the highest Ag content reported by Moëlo et al. (1995) from the Les Chalances (up to 0.54 apfu). The Fe + Cu content is close to the ideal one (Fe + Cu = 2 apfu) for the kobellite-tintinaite series (Zakrzewski and Makovicky, 1986). The maximum content of Fe + Cu is 2.27, 2.11 in average. The formula for the studied phase can be written as $(Cu_{1.12}Fe_{0.96})_{\Sigma 2.08}(Pb_{10.95}Ag_{0.27})_{\Sigma 11.18}(Sb_{8.53}Bi_{6.77})_{\Sigma 15.3}S_{34.33}$ with chemically calculated N = 1.98.

Bi-rich jamesonite $FePb_4Sb_6S_{14}$

Bi-rich jamesonite is quite common phase in studied samples. Usually forms anhedral or needle-like aggregates up to 100 μm

Tab. 5 Chemical composition of benjaminite from the Kobalt vein, Medzev (formula based on 22 apfu). The order number N was calculated to pavonite homologous series (^7P).

point	**5**	**6**	**16**	**21**	**24**	**26**	**34**	**40**	**42**	**46**
Ag	14.35	14.67	13.67	14.84	14.15	14.19	14.09	13.93	14.17	14.22
Fe	0.27	0.19	0.35	0.33	0.39	0.41	0.40	0.38	0.30	0.35
Sb	1.27	1.45	1.73	1.63	1.76	1.43	1.37	1.41	1.17	1.05
Se	1.73	1.62	1.63	1.81	1.13	1.13	0.59	0.92	0.32	0.00
Bi	63.09	61.63	63.22	60.91	62.10	63.42	62.86	62.70	62.87	63.38
Cu	0.00	0.39	0.19	0.21	0.06	0.08	0.00	0.04	0.08	0.00
Te	0.20	0.18	0.21	0.31	0.12	0.11	0.09	0.16	0.12	0.18
S	16.72	16.63	17.01	16.42	16.87	17.07	17.20	16.82	16.97	17.37
Pb	3.58	3.21	3.00	3.14	4.30	3.47	3.78	3.47	4.70	3.42
total	101.22	99.97	101.00	99.60	100.90	101.29	100.38	99.82	100.70	99.97
Ag	2.89	2.97	2.73	3.01	2.85	2.84	2.84	2.83	2.87	2.87
Fe	0.10	0.08	0.13	0.13	0.15	0.16	0.16	0.15	0.12	0.14
Sb	0.23	0.26	0.31	0.29	0.31	0.25	0.24	0.25	0.21	0.19
Se	0.48	0.45	0.45	0.50	0.31	0.31	0.16	0.25	0.09	0.00
Bi	6.56	6.43	6.53	6.39	6.45	6.55	6.53	6.59	6.58	6.61
Cu	0.00	0.13	0.07	0.07	0.02	0.03	0.00	0.01	0.03	0.00
Te	0.03	0.03	0.03	0.05	0.02	0.02	0.02	0.03	0.02	0.03
S	11.33	11.31	11.44	11.22	11.43	11.49	11.65	11.51	11.58	11.80
Pb	0.38	0.34	0.31	0.33	0.45	0.36	0.40	0.37	0.50	0.36
N	7.72	8.39	7.17	8.63	7.85	7.54	7.59	7.45	7.76	7.54

Tab. 6 Chemical composition of izoklakeite from Oriešok vein, Medzev (formula based on 105 apfu). N (homologue number) was calculated according to Zakrzewsky and Makovicky, (1986).

point	52	53	54	57	62	64	89	94	95
Ag	1.30	1.47	1.56	1.62	1.66	1.55	0.99	1.14	1.25
Fe	0.25	0.29	0.29	0.30	0.30	0.31	0.27	0.28	0.26
Sb	12.90	13.25	13.63	14.11	13.69	13.31	13.25	13.76	13.48
Se	0.12	0.00	0.09	0.01	0.22	0.07	0.00	0.00	0.00
Bi	19.46	19.60	20.04	19.57	19.41	19.68	18.41	17.81	18.79
Cu	0.98	0.96	1.09	1.14	1.03	1.06	0.91	0.92	0.95
S	17.21	17.18	17.23	17.17	17.11	17.36	17.12	17.18	17.18
Pb	47.08	46.69	45.47	45.34	45.56	46.73	48.71	48.79	48.11
total	99.36	99.48	99.40	99.27	99.09	100.05	99.66	99.99	100.03
Ag	1.27	1.43	1.51	1.57	1.62	1.50	0.97	1.11	1.21
Fe	0.46	0.54	0.54	0.56	0.56	0.57	0.51	0.52	0.49
Sb	11.16	11.45	11.73	12.14	11.82	11.39	11.49	11.88	11.62
Se	0.17	0.00	0.12	0.01	0.29	0.09	0.00	0.00	0.00
Bi	9.81	9.87	10.05	9.81	9.77	9.82	9.30	8.95	9.44
Cu	1.62	1.59	1.80	1.88	1.70	1.73	1.51	1.52	1.58
S	56.55	56.39	56.27	56.10	56.11	56.40	56.38	56.29	56.25
Pb	23.94	23.72	22.98	22.92	23.12	23.50	24.83	24.73	24.38
Sb/(Sb+Bi)	0.53	0.54	0.54	0.55	0.55	0.54	0.55	0.57	0.55
N	3.68	3.60	3.44	3.42	3.52	3.61	3.74	3.76	3.70

(Fig. 5a, 5b, 5c, 5d). It is usually replacing izoklakeite, Bi-rich boulangerite, tintinaite and galena (Fig. 5a, 5b). Electron probe microanalyses revealed a significant amount of Bi in jamesonite, 12.66 to 15.02 wt% what corresponds to 1.33-1.59 apfu. The Bi/(Bi+Sb) ratio varies from 0.226 to 0.265. Chemical compositions of Bi-rich jamesonite and the corresponding formulae are given in Tab. 8. The formula for the Bi-richest jamesonite (based on 25 apfu) is $Fe_{1.09}Pb_{4.06}(Sb_{4.4}Bi_{1.59})_{\Sigma 5.99}S_{13.83}$. Bi-rich jamesonite with similar composition is mentioned also from Kutná Hora (Pažout et al., 2017) or Brezno-Hviezda (Pršek et al., 2008).

Bi-rich boulangerite $Pb_5Sb_4S_{11}$

Bi-rich boulangerite occurs quite commonly as needles or acicular to anhedral grains up to 500 μm (Fig. 5b, 5d). It is replacing galena, izoklakeite and tintinaite and is replaced by Bi-rich jamesonite. Chemical composition and chemical formula of Bi-rich boulangerite from Medzev are given in Tab. 9. The amount of Bi for Sb substitution is up to 0.64 *apfu*. Similar contents of Bi in boulangerite are quite rare in nature. Bi-rich boulangerite is known from the Apollo mine, Germany (Wagner and Cook 1996), the Damajianshan deposit, China (Zhang et al. 2015) and also from Kutná Hora (Pažout et al., 2017). The formula for the Bi-richest boulangerite (based on 20 apfu) is $Pb_{5.05}(Sb_{3.3}Bi_{0.64})_{\Sigma 3.94}S_{10.92}$.

Tab. 7 Chemical composition of tintinaite from Oriešok vein, Medzev (formula based on 63 apfu). N (homologue number) was calculated according to Zakrzewsky and Makovicky, (1986).

point	56	58	61	102	103	105
Ag	0.49	0.42	0.47	0.38	0.42	0.42
Fe	0.89	0.97	1.04	0.93	0.99	1.47
Sb	17.19	17.08	17.54	16.68	17.04	16.99
Hg	0.19	0.17	0.08	0.09	0.20	0.06
Se	0.00	0.00	0.14	0.00	0.00	0.11
Bi	23.44	23.64	22.17	24.10	23.04	22.43
Cu	1.18	1.12	1.12	1.10	0.97	1.04
S	18.23	18.50	18.28	18.33	18.57	18.38
Pb	37.56	37.20	38.45	38.07	38.90	39.01
total	99.15	99.09	99.27	99.67	100.12	99.88
Ag	0.27	0.23	0.26	0.21	0.23	0.23
Fe	0.96	1.04	1.11	1.01	1.06	1.56
Sb	8.53	8.42	8.66	8.25	8.36	8.32
Hg	0.06	0.05	0.02	0.03	0.06	0.02
Se	0.00	0.00	0.10	0.00	0.00	0.08
Bi	6.78	6.79	6.37	6.95	6.59	6.40
Cu	1.12	1.06	1.06	1.04	0.91	0.97
S	34.34	34.63	34.26	34.44	34.59	34.18
Pb	10.95	10.78	11.15	11.07	11.21	11.23
Sb/(Sb+Bi)	0.56	0.55	0.58	0.54	0.56	0.57
N	1.98	1.95	2.01	1.99	2.02	2.00

5. DISCUSSION AND CONCLUSIONS

Sulphosalts are typical accessory minerals of the hydrothermal sulphide mineralizations in Western Carpathians. An interesting associations of sulphosalts (native Bi, bismuthinite, ikunolite, ingodite, benjaminite, matildite, gustavite and izoklakeite, tintinaite, Bi-rich boulangerite, Bi-rich jamesonite) has been described in this work at Kobaltová and Oriešok veins near Medzev.

Silver-bearing minerals in the Gemeric superunit represent usually Ag-bearing tetrahedrite (e.g. Chovan et al., 1994, Pršek and Lauko, 2009, Mikuš et al., 2018). Silver at the Kobalt vein is hosted in rare sulphosalts which have not been determined in the Gemeric superunit yet and are represented by matildite, benjaminite (pavonite homologous series ^7P) and gustavite (lillianite homeotypic series ^4L). Matildite is a rare accessory mineral of ore mineralizations with increased Bi-Ag content

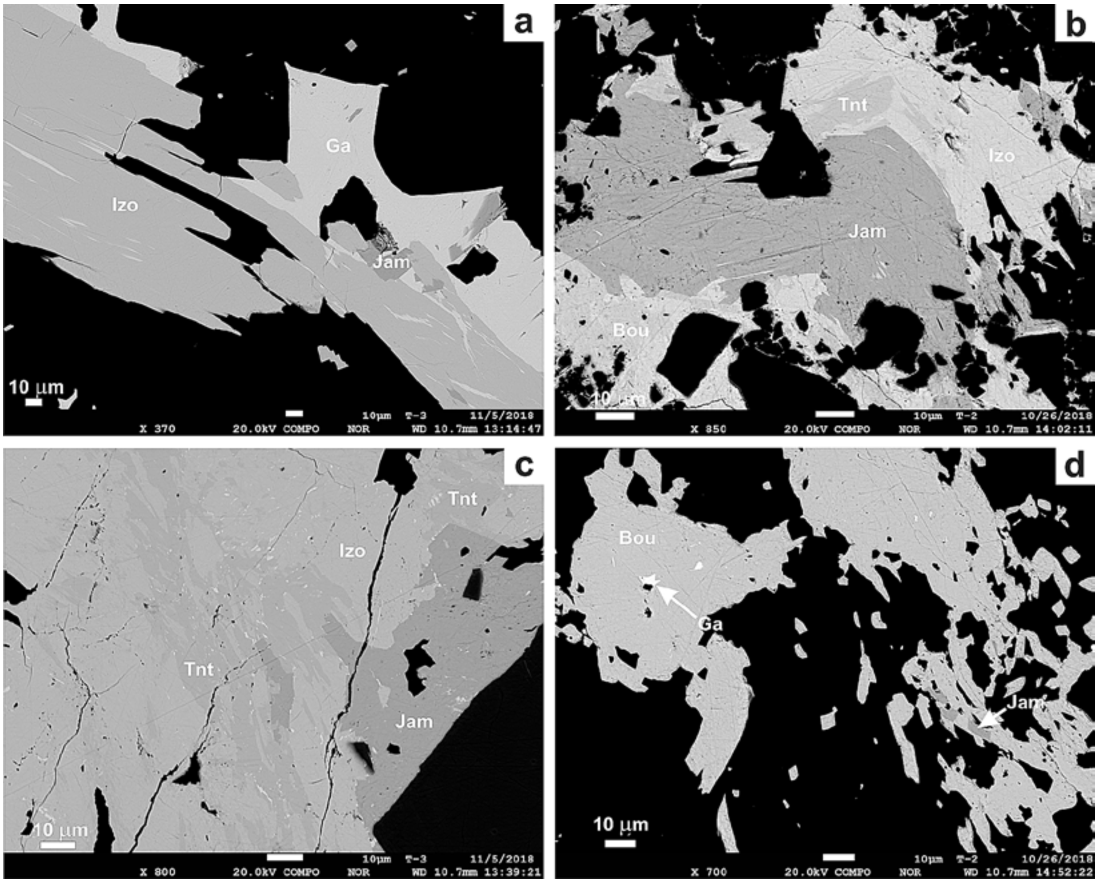

Fig. 5a – Izoklakeite (Izo) needles associated with Bi-rich jamesonite (Jam) replacing galena. **b** – Allotriomorphic grain of izoklakeite intensively replaced by tintinaite (Tnt), Bi-rich boulangerite (Bou) and Bi-rich jamesonite. **c**- Izoklakeite grain replaced by tintinaite and Bi-rich jamesonite. **d** – Relics of galena almost completely replaced by Bi-rich boulangerite. BSE images from Oriešok vein.

Tab. 8 Chemical composition of Bi-rich jamesonite from the Oriešok vein, Medzev (formula based on 25 apfu).

point	51	55	60	63	87	96	100	101	106
Fe	2.65	2.58	2.87	2.75	2.61	2.60	2.78	2.52	2.76
Sb	24.80	24.80	24.74	25.50	25.32	25.37	24.80	24.30	24.23
Bi	13.84	14.21	14.33	13.00	12.66	13.03	13.97	14.77	15.02
S	20.38	19.99	20.07	20.17	20.31	20.29	19.99	20.10	20.07
Pb	38.30	38.29	38.03	38.42	38.79	38.57	37.55	38.40	38.07
total	99.97	99.87	100.04	99.84	99.70	99.87	99.10	100.08	100.15
Fe	1.04	1.02	1.13	1.08	1.03	1.02	1.11	1.00	1.09
Sb	4.48	4.52	4.49	4.61	4.58	4.58	4.53	4.43	4.40
Bi	1.45	1.51	1.51	1.37	1.33	1.37	1.49	1.57	1.59
S	13.96	13.84	13.82	13.85	13.94	13.92	13.85	13.90	13.85
Pb	4.06	4.10	4.05	4.08	4.12	4.10	4.03	4.11	4.07
Bi/(Bi+Sb)	0.25	0.25	0.25	0.23	0.23	0.23	0.25	0.26	0.27

Tab. 9 Chemical composition of Bi-rich boulangerite from the Oriešok vein, Medzev (formula based on 20 apfu).

point	65	66	68	78	86	92	93	98
Fe	0.18	0.35	0.19	1.04	0.44	0.28	0.15	0.22
Sb	20.55	20.56	21.64	21.08	21.57	21.27	21.17	21.28
Bi	6.85	6.57	5.21	6.14	5.27	5.33	5.87	5.47
S	17.93	17.86	18.06	17.96	18.00	17.99	17.93	18.15
Pb	53.62	53.39	54.37	54.02	54.05	54.13	53.98	54.64
total	99.15	98.71	99.47	100.24	99.34	99.00	99.11	99.81
Fe	0.06	0.12	0.07	0.36	0.15	0.10	0.05	0.08
Sb	3.30	3.31	3.45	3.32	3.43	3.40	3.40	3.38
Bi	0.64	0.62	0.48	0.56	0.49	0.50	0.55	0.51
S	10.93	10.91	10.92	10.75	10.87	10.92	10.92	10.94
Pb	5.06	5.05	5.09	5.00	5.05	5.09	5.09	5.10
Bi/(Bi+Sb)	0.16	0.16	0.12	0.15	0.12	0.13	0.14	0.13

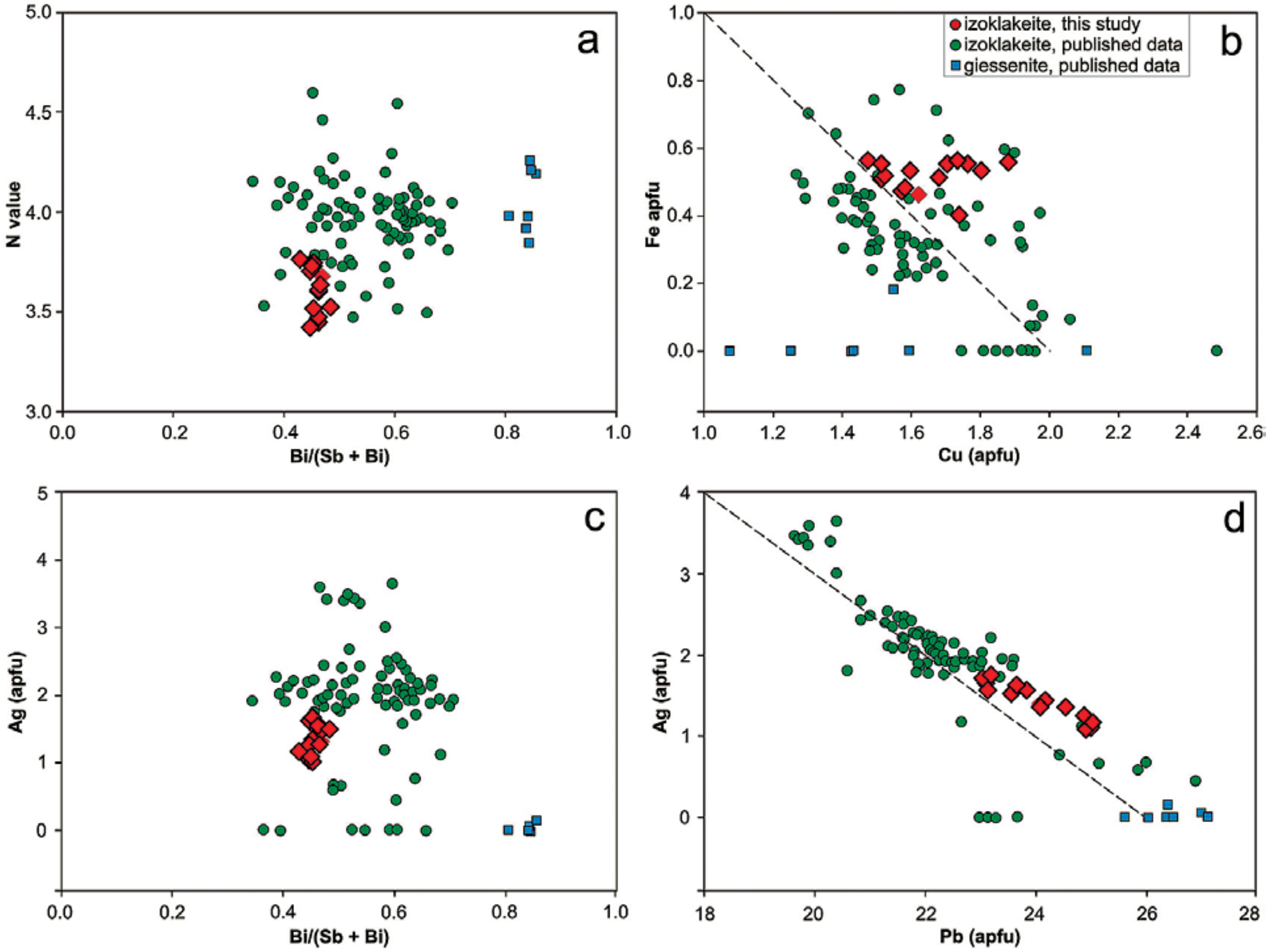

Fig. 6 Substitution diagrams for members of the izoklakeite–giessenite series (apfu): a – Bi/(Sb + Bi) vs. N value; b – Cu vs. Fe plot; line indicates ideal content Fe + Cu = 2; c- Bi/(Sb + Bi) vs. Ag plot; d - Pb vs. Ag plot; line indicates ideal 2Ag – Pb correlation. Published data for izoklakeite are from Armbruster and Hummel (1987), Harris et al. (1986), Zakrzewski and Makovicky (1986), Moëlo et al. (1995), Ozawa et al. (1998), Orlandi et al. (2010) and Zhang et al. (2015), Pažout et al., (2017) ; for giessenite from Karup-Møller (1973), Graeser and Harris (1986), and Makovicky and Karup-Møller (1986).

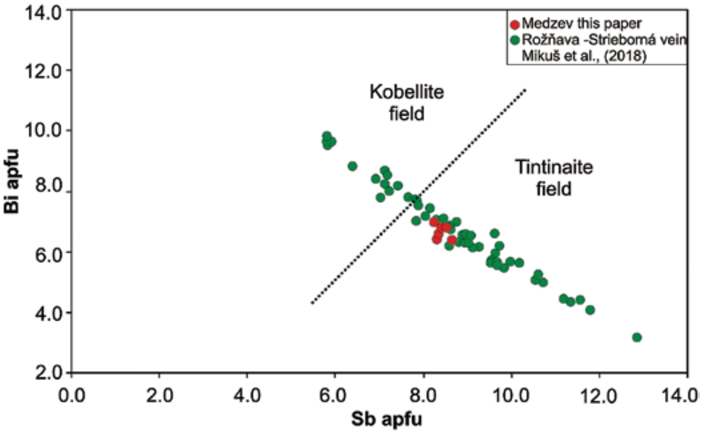

Fig. 7 Sb vs. Bi (apfu) plot for tintinaite-kobellite series from the Medzev – Oriešok vein. Dashed line represents a formal border between kobellite and tintinaite. Published analyses are from Mikuš et al., (2018).

in the Western Carpathians and occurs with various members of lillianite homologous series. Benjaminite and matildite are known from the Rozália mine - epithermal Au deposit (Jeleň et al., 2012) and matildite occurs in Ni-As-Bi mineralization in Čierna Lehota (Pršek et al., 2005). Sulphosalt corresponding to benjaminite is reported from the Kokava – Bohaté in the Veporic unit (Ferenc, 2008). Gustavite is known from the siderite mineralization in Bacúch (Pršek and Chovan, 2001) and from Chyžné locality (Bálintová et al., 2006). The compound $AgBiS_2$ has two polymorphs stable below the temperature of its congruent melting of 801° ± 4 °C (Craig, 1967), a high-temperature cubic phase is called shapbachite and low-temperature hexagonal phase called matildite. The temperature of the shapbachite – matildite equilibrium varies from 215 °C (Kovaleva and Chukov, 1975) to 289 °C (Gather and Blachnik, 1980). For matildite associated with bismutihinite and Bi the equilibrium temperature can be constrained to be ~ 120–220 °C (Voronin and Osadchii, 2013). Experimental work documented that matildite is able incorporate various amounts Cu_2S into its structure between 300-450 °C (Chen and Chang, 1974). Matildite from Medzev contain no Cu, therefore, its crystallization temperature could be bellow 300 °C according to these experimental studies. Another alternative is that fluid was Cu-poor, therefore the Cu content in matildite is determined geochemically and is not controlled by temperature.

Sulphosalts of the kobellite-tintinaite series are usual and typical for the siderite-sulphidic mineralization in the Western Carpathians whereby most occurrences are known from the Gemeric superunit (e.g. Kupčík et al., 1969, Klimko et al., 2009). Outside of the Gemeric superunit, these minerals known from Hviezda (Majzlan and Chovan, 1997), Dúbrava (Chovan et al., 1998) and Ľubietová-Kolba (Pršek and Mikuš, 2006). Otherwise, sulphosalts of the izoklakeite-giessenite series belong to rare minerals. In the Western Carpathians, they were mentioned by Pršek (2008) from a few localities of the siderite mineralization in the Tatric superunit in Nízke Tatry Mts. (Jarabá, Vyšná Boca and Mlynná dolina) and from Rožňava – Aurélia vein (Gemeric superunit). Members of the izoklakeite-giessenite series are typical for their silver content which distinguishes them from chemically similar jaskolskiite (Makovicky and Nørrsestam, 1985).

An interesting association of Bi-Se-Te minerals (laitakarite, ikunolite, ingodite etc.) was described from Smolník – locality Úhorná from the Gemeric superunit (Peterec, 1996). Laitakarit-ikunolit associated with native bismuth occurs also in Hnúšťa-Mútnik in the Veporic unit (Ferenc, 2008).

Cobalt mineralization at Kobaltová and Oriešok vein is represented only by Co-bearing arsenopyrite or cobaltite whereas other occurrences of Ni-Co mineralization in Western Carpathians show more variable developed associations of Ni-Co minerals (e.g. Kiefer et al., 2017, Mikuš et al., 2013).

Bi-rich jamesonite occurs in Gemeric unit quite often with Bi content up to 1.31 apfu (Mikuš et al., 2018) at Strieborná vein (Rožňava) and up to 0.84 apfu at the Aurelia vein, Rožňava (Pršek and Biroň, 2007) and is reported also from Veporic from the Klenovec – Medené and Kokava (Ferenc, 2008) where the Bi content reach up to 1.38 apfu. Bi content over 2 apfu is reported from the Hviezda (Majzlan and Chovan, 1997).

Similar association of bismuth sulphosalts was described from the Kutná Hora ore district by Pažout et al. (2017) who identified aramayoite, bismuthinite, cosalite, ikunolite, izoklakeite, matildite, galena, Bi-rich jamesonite, Bi-rich boulangerite, Bi-rich owyheeite and Bi-rich semseyite. Pažout et al., (2017) supposed that origin of the Bi-rich mineralization is related to the penetration of lower temperature fluids (c. 100–250 °C) into tectonically opened fractures in older filling of the ore veins.

A characteristic feature of the studied sulphosalts from Medzev is the extensive Bi–Sb substitution. Their chemical composition suggests that the hydrothermal fluids must have been relatively rich in Bi, Pb, Ag and Sb and poor in Cu. High Bi and Ag content was characteristic in of the initial stages of the mineralization and the final pulses produced Bi-rich Pb-Sb sulphosalts with distinctly less Ag.

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