

# Mineral phases of the berthierite-garavellite series from the Klenovec-Medené occurrence (Slovenské Rudohorie Mts – Veporic Unit), Slovak Republic

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## AGEOS Minerálne fázy berthieritovo-garavellitového radu z lokality Klenovec-Medené (Slovenské rudohorie – veporikum), Slovenská republika

**Abstract:** The Klenovec-Medené occurrence is an example of the Alpine carbonate and quartz-sulphidic mineralization in the Veporic Unit, Slovakia. Locality lies in western part of the Slovenské Rudohorie Mts., 25 km to NNW from the Rimavská Sobota district city. Mineralization is bound to the shear zone, located in biotite-albitic paragneisses of the Klenovec Complex. In frame of the quartz-sulphidic stage of vein filling development, there was found next-to complete transition from Bi enriched berthierite (formula:  $\text{Fe}_{0.96}(\text{Sb}_{1.81}\text{Bi}_{0.19})_{2.00}\text{S}_{4.01}$ ) to Sb-rich garavellite with formula:  $\text{Fe}_{0.96}(\text{Sb}_{1.48}\text{Bi}_{0.53})_{2.01}\text{S}_{4.03}$ . They were found in tetrahedrite aggregates, near by the interfaces with chalcopyrite, in association with arsenopyrite and gold. Berthierite-garavellite series minerals form two morphologic types: I) elongated/isometric grains and veinlets in tetrahedrite; II) irregular aggregates/veinlets, as a part of myrmekite intergrowths with chalcopyrite and tetrahedrite. Association and microstructural relationships of berthierite and garavellite suggest, that these originated by precipitation from Bi enriched residual solutions of tetrahedrite crystallization, or/and from solutions of slightly younger hydrothermal process.

**Key words:** Western Carpathians, Slovenské Rudohorie Mts, Veporic Unit, Klenovec, sulphidic mineralization, berthierite, garavellite

## 1. INTRODUCTION

The Klenovec-Medené is one of the most known occurrences of carbonate and quartz-sulphidic mineralization in the Veporic Unit. First archival reference about locality (exploitation of copper and precious metals ores) dates from the second half of the 18th century; mining activities were terminated at the beginning of 20<sup>th</sup> century (Žilák, 1993). Sporadic geological survey, focused mainly on precious metals, was made here mainly in the second half of 20th century.

Mineralogy and geological settings of the Klenovec-Medené locality were studied by Šuf (1937), Sombathy (1950), Petro (1961), Lázníčka (1962; 1963; 1964), Galko (1982), Ragan (1989), Horal (1997) and Ferenc (2008).

Orthorhombic berthierite ( $\text{FeSb}_2\text{S}_4$ ), garavellite ( $\text{FeSbBiS}_4$ ), and clerite ( $\text{MnSb}_2\text{S}_4$ ) belong to the berthierite isotypic series (Moëlo et al., 2008). This group of minerals can also include newly discovered graňianite ( $\text{MnBi}_2\text{S}_4$ ) which represents monoclinic analogue of the above mentioned minerals (Ciobanu et al., 2014). Graňianite is isostructural with monoclinic grumiplucite ( $\text{HgBi}_2\text{S}_4$ ) and kudriavite ( $\text{Cd,PbBi}_2\text{S}_4$ ), members of pavonite homologous series.

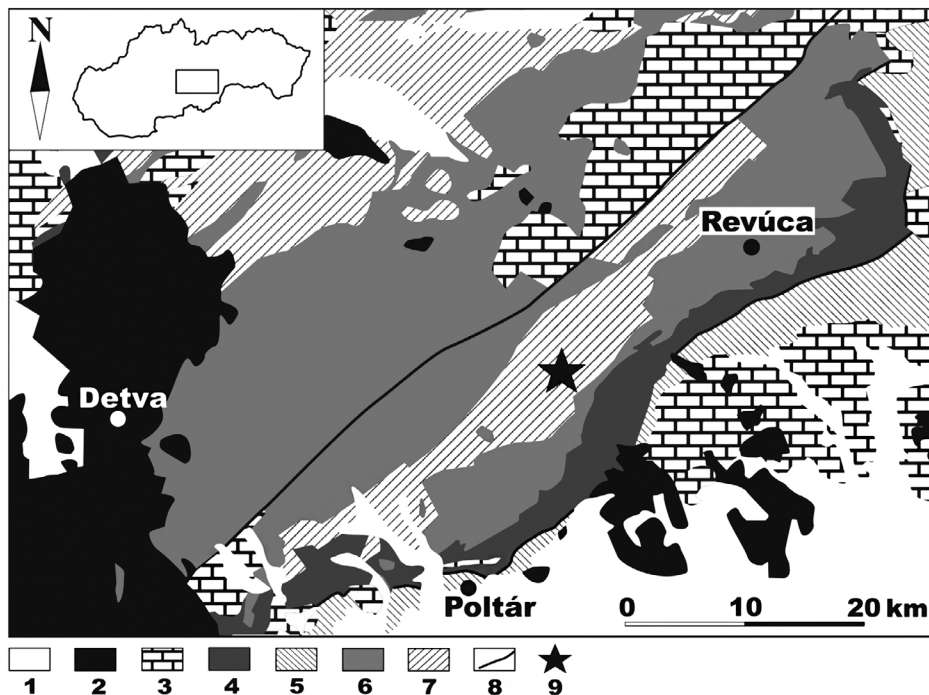
At the Klenovec-Medené, Bi-enriched berthierite up to Sb-rich garavellite were found within the quartz-sulphidic mineralization stage. This contribution is devoted to study of paragenetic relationships and chemical composition of these mineral phases.

## 2. GEOLOGICAL AND MINERALOGICAL CHARACTERISTICS

The Klenovec-Medené locality lies in the western part of Slovenské rudohorie Mts, 25 km NNW of Rimavská Sobota district town. Occurrence of the Cu ores is situated about 1.2 km SW of Klenovec village centre, at the left slope of the Bártova dolina Valley (altitude of 500 m asl.). Geographic coordinates of locality (Július adit) are:  $\text{E}19^\circ52'41.37''$ ,  $\text{N}48^\circ35'20.57''$ . Ore occurrence was opened in the past by several pits and the Július adit with the length of 335 m. Based on the regional geological division, the Klenovec-Medené locality lies in the Kohút Zone of the Veporic Unit (sensu Zoubek, 1957; Vass et al., 1988; Fig. 1). NW surroundings of the studied occurrence are built mainly by Hercynian granites, granodiorites, and tonalites of the Kráľova Hoľa Complex that is southward in contact with garnet mica schists of the Ostrá Complex. Mineralization at the Klenovec-Medené occurrence is located in the biotite-albitic paragneisses of the Klenovec Complex. Hanging wall of the paragneisses is formed by the muscovite-chloritic schists with basic metavolcanites and magnesite bodies of the Sinec Complex (Bezák, 1988; Bezák et al., 1999). These complexes represent Hercynian and Alpine deformed Lower Paleozoic sediments and products of volcanism.

Vein or veinlet-disseminated type of mineralization is concentrated into shear zone with the NE-SW direction and 45–70° south-eastward dipping. Veins have a lenticular shape and they

Fig. 1. Schematic sketch of geological building of the Slovenské Rudohorie Mts., western part. Explanation: 1 – Quaternary, Neogene and Paleogene sediments (gravels, alluvial sediments, clays, sands, claystones, sandstones, conglomerates), 2 – products of the Neogene volcanism (andesites, pyroclastics), 3 – the Mesozoic sedimentary rocks (limestones, dolomites, slates, quartz sandstones), 4 – the Paleozoic rocks of the Veporic Unit (sandstones, conglomerates, quartz sandstones, slates, volcanic rocks), 5 – the Paleozoic rocks of the Gemeric Unit (sandstones, conglomerates, slates, volcanoclastics), 6 – granitic rocks of the Veporic Unit, 7 – metamorphosed rocks of the Veporic Unit (phyllite, mica schists, migmatites, gneisses), 8 – important tektonic lines, 9 – Klenovec-Medené locality.



Obr. 1. Schéma geologickej stavby západnej časti Slovenského rudohoria. Vysvetlivky: 1- kvartérne, neogénne a paleogénne sedimenty (štrky, riečne sedimenty, íly, piesky, ílovce, pieskovce, zlepence), 2 – produkty neogénneho vulkanizmu (andezity, pyroklastiká), 3 – mezozoické sedimentárne horniny (vápence, dolomity, bridlice, kremence), 4 – paleozoikum veporika (pieskovce, zlepenec, kremence, bridlice, vulkanické horniny), 5 – paleozoikum gemerika (pieskovce, zlepenec, bridlice, vulkanoklastiká), 6 – granitoidy veporického kryštalinika, 7 – metamorfované horniny veporického kryštalinika (filyty, svory, migmatity, ruly), 8 – dôležité tektonické línie, 9 – lokalita Klenovec-Medené.

are up to 15 m long with thickness from several cm up to 1.5 m. Carbonates and quartz are main minerals of vein infill. Ore minerals form disseminations or small veinlets in gangue, massive sulphidic ore bodies are locally developed, too.

The following mineralization stages can be distinguished within the vein filling development (Ferenc, 2008): I) quartz-carbonate stage (muscovite, monazite-(Ce), quartz, ilmenite, calcite, dolomite); II) quartz-sulphidic stage (quartz, pyrite, arsenopyrite, gold I, gudmundite, ullmannite, pyrrhotite, chalcopyrite, tetrahedrite, sphalerite, berthierite, garavellite, Fe dolomite, gold II, marcasite, galena, bismuth); III) quartz-carbonate stage II (quartz, calcite). Oxidation zone is represented by: spionkopite, geerite, malachite, erythrite, goehite, gypsum, and scorodite (?). Fluorite, ankerite, pentlandite, boulangerite, chrysocolla, and Sb ochres from the Klenovec-Medené were reported by Láznicka (1963). Mineralization is metamorphic-hydrothermal and originated during the paleo-Alpine orogenesis (Lexa et al., 2007).

### 3. METHODS

Samples for mineralogical study were taken from dump of the Július adit. Polished sections were observed under the polarization microscope (AMPLIVAL, State Geological Institution of Dionýz Štúr, Banská Bystrica) in reflected light.

An electron microprobe CAMECA SX 100 (State Geological Institution of Dionýz Štúr, Bratislava) was used for determination of chemical composition of studied minerals (WDS) and

for documentation of their microstructural relations (BSE). Polished sections were covered with a carbon layer (JEOLJEE-4X, State Geological Institution of Dionýz Štúr, Bratislava) before analyzing. Conditions for WDS microanalysis were: accelerating voltage 20 kV, beam current 15 nA and a beam spot size in the range of 1 to 5  $\mu\text{m}$ . Used standards and spectral lines:  $\text{CuFeS}_2$  (CuK $\alpha$ , FeK $\alpha$ , SK $\alpha$ ),  $\text{Sb}_2\text{S}_3$  (SbL $\beta$ ),  $\text{Bi}_2\text{Se}_3$  (BiL $\alpha$ ), arsenopyrite (AsK $\beta$ ), PbS (PbL $\alpha$ ), Cd (CdL $\alpha$ ), rhodonite (MnK $\alpha$ ) and Ag (AgL $\alpha$ ). Detection limits for individual elements varied between 0.04–0.1 wt. %. Silver, arsenic, and manganese contents were quantitative analyzed, but their concentrations were under device detection limit. Obtained data were corrected by PAP software (Pouchou & Pichoir, 1985).

### 4. NATURE OF THE BERTHIERITE-GARAVELLITE MINERAL PHASES

Mineral phases of the berthierite-garavellite series occur within the varied quartz-sulphidic stage of the vein filling development. They were found in tetrahedrite aggregates associated with chalcopyrite, always nearby their interfaces with chalcopyrite. More rarely, arsenopyrite and gold were found in the association.

Minerals of the berthierite-garavellite series form the two base morphologic types: I) elongated, or isometric grains and veinlets (0.001–0.06 mm in size) in tetrahedrite (Figs. 2, 3); II) irregular aggregates/veinlets, as a part of myrmekite intergrowths with chalcopyrite and tetrahedrite (Figs. 3, 4). These intergrowths

were observed explicitly only in close vicinity of massive chalcopyrite and tetrahedrite aggregates border.

Studied mineral phases are interesting especially for relatively high bismuth content (8.69–18.33 wt. %; Tab. 1). Zones with more significant bismuth content, have an irregular shape, with diffuse interfaces. Locally they form hairline veinlets intersecting of Bi depleted berthierite aggregates, or individual grains at their edges (Fig. 4). Antimony is the dominant element, its content ranges from 37.67 to 49.25 wt. %. From divalent elements, iron is prevailing (11.25–11.95 wt. %), copper and lead are present only as a minor admixtures (max. 0.68 wt. % of Cu + Pb; Tab. 1).

#### 4. 1. Discussion and conclusions

In contrast to the significantly widespread berthierite ( $\text{FeSb}_2\text{S}_4$ ), garavellite ( $\text{FeSbBiS}_4$ ) represents only rare mineral of hydrothermal mineralizations. The type locality is in Miniera del Frigido (Tuscany, Italia), where garavellite was found in the siderite-sulphidic mineralization (Gregorio et al., 1979). Bindi & Menchetti (2005) reports garavellite from a historic sample (berthierite with minor garavellite, bismuthinite, chalcopyrite, and siderite) from the Caspari mine (Germany). In Czech Republic, garavellite is known from the gold bearing quartz veins

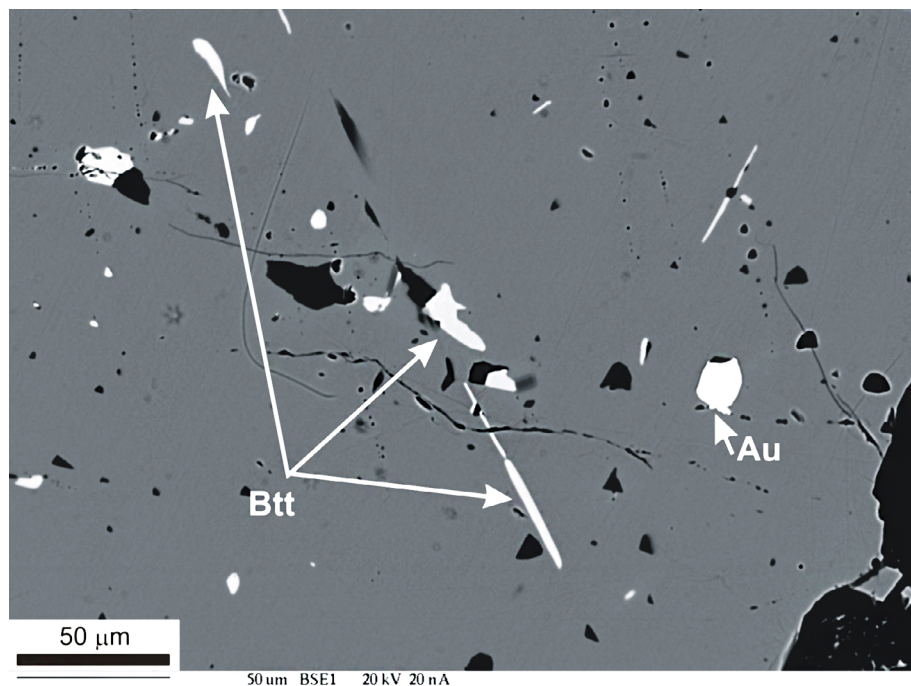


Fig. 2. Elongated and isometric grains of Bi-rich berthierite (Btt) in tetrahedrite (dark grey). Gold (Au) forms isometric inclusion in tetrahedrite (BSE).

Obr. 2. Pozdĺžne a izometrické zrná Bi bohatého berthieritu (Btt) v tetraedrite (tmavosivý). Zlato (Au) tvorí izometrickú uzavreninu v tetraedrite (BSE).

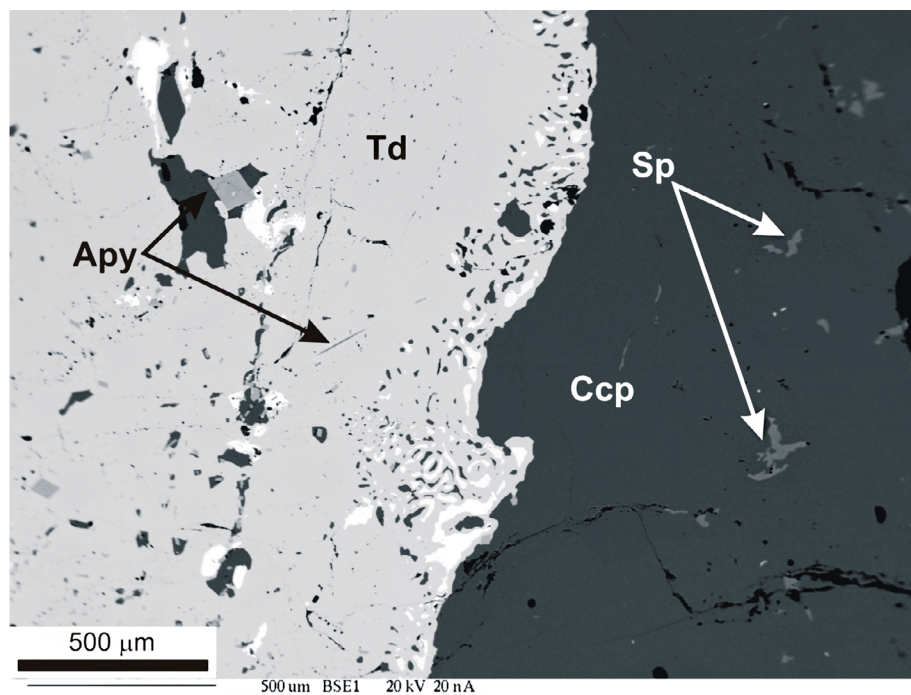


Fig. 3. Myrmekitic intergrowths of tetrahedrite (Td), chalcopyrite (Ccp), Bi-rich berthierite and Sb-garavellite (both white) in tetrahedrite aggregate. Bi-rich berthierite also forms irregular grains and veinlets in tetrahedrite. Arsenopyrite (Apy) forms idiomorphic crystals of orthorhombic and long prismatic shape, enclosed by tetrahedrite. Sphalerite (Sp) forms exsolutions in chalcopyrite (BSE).

Obr. 3. Myrmekitické prerastanie tetraedritu (Td), chalkopyritu (Ccp), berthieritu bohatého na Bi a Sb-garavellitu (obidva biele) v tetraedritovom agregáte. Bi-bohatý berthierit tiež tvorí nepravidelné zrná a žilky v tetraedrite. Arzenopyrit (Apy) tvorí idiomorfne kryštály kosoštvorcového a dlhoprizmatického prierezu uzavreté v tetraedrite. Sfalerit (Sp) vytvára odmiešninu v chalkopyrite (BSE).

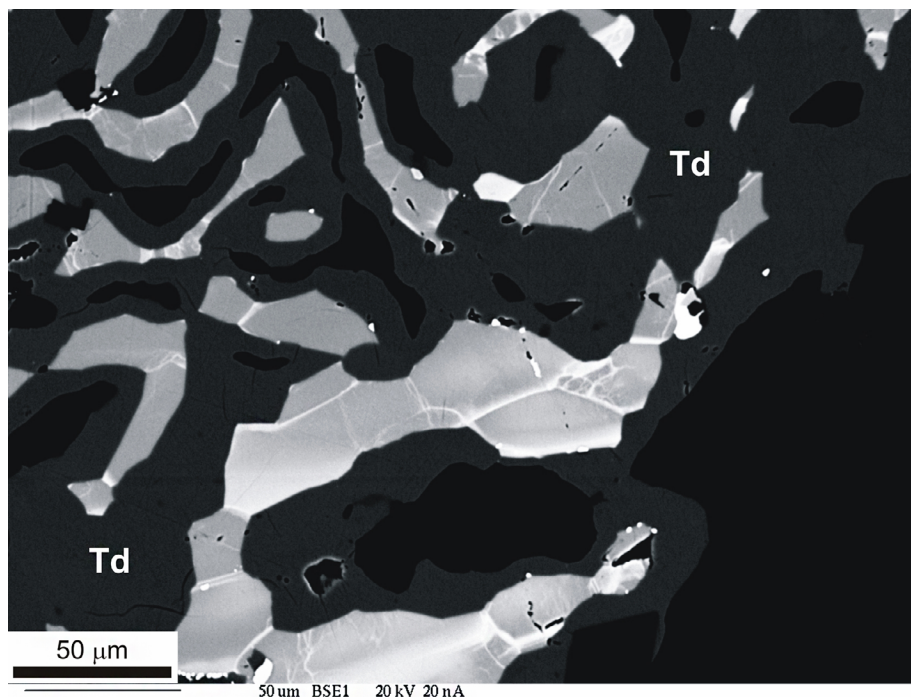


Fig. 4. Detail from the previous picture. Myrmekitic intergrowths of chalcopyrite (black), tetrahedrite (Td) and berthierite-garavellite series minerals (light grey to white). Zones with significant Bi content (white) form irregular grains, veinlets and diffuse domains in Bi depleted berthierite (light grey), BSE.

Obr. 4. Detail predchádzajúceho obrázka. Myrmekitické prerastanie chalkopyritu (čierny), tetraedritu (Td) a minerálov berthieritovo-garavellitového radu (svetlosivé až biele). Zóny s významným obsahom Bi (biele) tvoria nepravidelné zrná, žilky a difúzne domény v Bi ochudobnenom berthierite (svetlosivý), BSE.

of the Kasejovice deposit (Litochleb et al., 1990). Garavellite is also present in Pb-Zn deposits Shaanxi (Wei et al., 1985) and Sn-base metal ore field of the Dachang (Li et al., 1998) in China. It was found in shear zone related gold bearing quartz veins of the Aprelkovskii deposit, Russia (Borovikov et al., 1990). In Slovakia garavellite was previously described from the Tatric Unit on the Pezinok Sb-Au deposit (Andráš et al., 1993) and the

Bystrá-Hviezda occurrence in the Nízke Tatry Mts. (Majzlan & Chovan, 1997). In the Pezinok deposit, garavellite was found as a component of separate Bi mineralization in association with native bismuth, Sb-rich bismuthinite (so-called horobetsuite), and stibnite. In the quartz-stibnite veins (Bystrá-Hviezda) association of Bi minerals (garavellite, Bi-rich jamesonite, horobetsuite, kobellite, glädite and krupkaite) which represents a part

Tab. 1. Electron microanalyses of Bi-berthierite (an. 1–7) and Sb-garavellite (an. 8) from the Klenovec-Medené locality.

Tab. 1. Elektronové mikroanalýzy Bi-berthieritu (an. 1–7) a Sb-garavellitu (an. 8) z lokality Klenovec-Medené.

analyse	Fe	Pb	Cu	Cd	Bi	Sb	S	Σ wt. %
1	11.95	0.30	0.38	0.02	8.69	49.25	28.69	99.19
2	11.93	0.22	0.09	0.05	10.95	47.01	28.40	98.66
3	11.62	0.40	0.19	0.03	15.53	43.18	27.84	98.78
4	11.67	0.22	0.21	0.03	15.69	43.69	27.94	99.45
5	11.66	0.28	0.18	0.03	17.01	42.22	27.76	99.14
6	11.66	0.16	0.14	0.01	18.11	40.95	27.60	98.63
7	11.63	0.14	0.04	0.07	18.33	41.16	27.59	98.96
8	11.25	0.18	0.04	0.02	23.27	37.67	27.07	99.50
atomic proportions (calculated on basis of 7 atoms)								
	Fe	Pb	Cu	Cd	Bi	Sb	S	
1	0.959	0.006	0.027		0.186	1.812	4.009	
2	0.970	0.005	0.006		0.238	1.754	4.024	
3	0.964	0.009	0.014		0.344	1.643	4.024	
4	0.963	0.005	0.015		0.346	1.654	4.016	
5	0.970	0.006	0.013		0.378	1.610	4.021	
6	0.977	0.004	0.010		0.406	1.574	4.029	
7	0.974	0.003	0.003		0.410	1.581	4.025	
8	0.960	0.004	0.003		0.531	1.475	4.026	

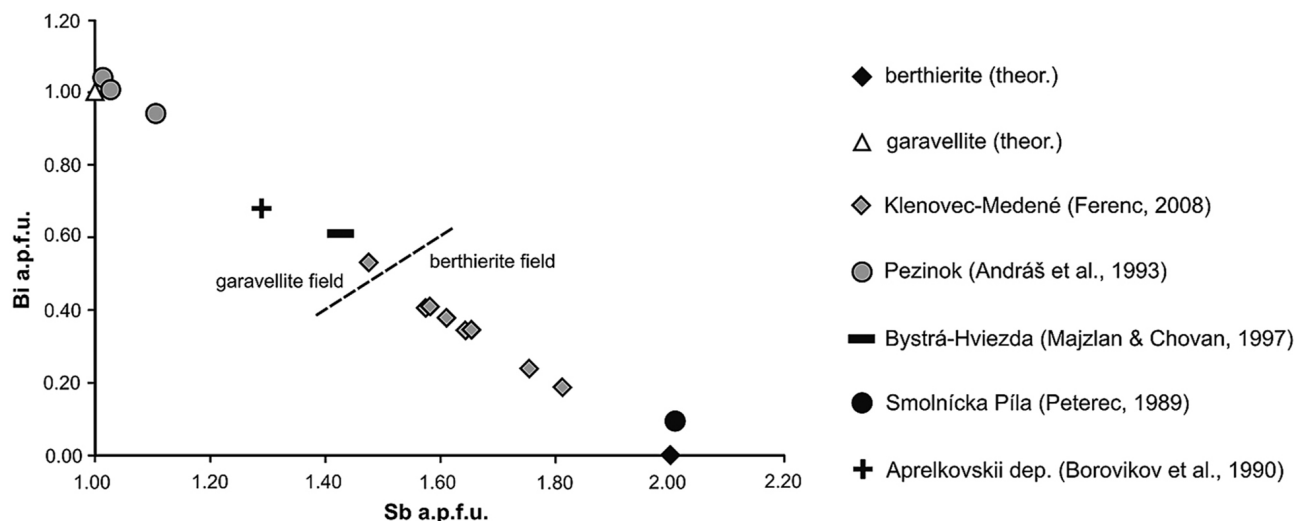


Fig. 5. Plot Sb vs. Bi (a.p.f.u.) in studied mineral phases from the Klenovec-Medené, compared to some other published data.

Obr. 5. Graf Sb vs. Bi (a.p.f.u.) v študovaných minerálnych fázach z Klenovca-Medeného v porovnaní s niektorými inými publikovanými údajmi.

of the youngest chalcopyrite-tetrahedrite mineralization stage was identified.

Berthierite with composition of  $\text{Fe}_{1.00}(\text{Sb}_{2.05}\text{Bi}_{0.09})_{2.14}\text{S}_4$  (Bi content 4.4 wt. %) was described from the quartz-stibnite veins in the Gemeric Unit near Smolnícka Píla, Slovakia (Peterec, 1989). It occurs here within the Sb-Pb-Bi mineral association (Bi-rich stibnite, Bi-rich jamesonite, pyrite, pyrrotite) which is, as for the veins development, placed to the end of sulphidic stage. Majority of berthierites from Slovakia is characterized by very low  $\text{Sb}^{3+} \rightarrow \text{Bi}^{3+}$  substitution. Bi content varies mostly in hundredths, more rarely in the first tenths of weight %. Berthierite with Bi content up to 0.36 wt. % was found in the Chyžné-Herichová Sb mineralization occurrence, Veporic Unit (Bálintová et al., 2006). Bi content up to 0.28 wt. % was reported in berthierite from the Gemeric quartz-stibnite veins at Betliar and Poproč (Klimko et al., 2009). From the chemical point of view, mineral phases from the Klenovec-Medené belong to, more or less, the complete transition from Bi-enriched berthierite ( $\text{Fe}_{0.96}(\text{Sb}_{1.81}\text{Bi}_{0.19})_{2.00}\text{S}_{4.01}$ ) to Sb-rich garavellite with formula:  $\text{Fe}_{0.96}(\text{Sb}_{1.48}\text{Bi}_{0.53})_{2.01}\text{S}_{4.03}$  (Fig. 5).

In the Western Carpathians, Bi mineralization with garavellite or Bi-rich berthierite in association with other Bi minerals is connected with the end of sulphidic stage of the siderite-sulphidic, quartz-stibnite vein, and stockwork/disseminated types of mineralization. In the Klenovec-Medené site, Bi-rich berthierite to Sb-rich garavellite occurs in close association with tetrahedrite, chalcopyrite, arsenopyrite, and gold but without any other Bi minerals. Their formation took place at the final phases of quartz-sulphidic stage of mineralization development. Based on association and microstructural relationships of berthierite and garavellite from the Klenovec-Medené, it can be assumed that these minerals could originate by two following ways:

a) Forming of Bi-berthierite and Sb-garavellite could be completely or partially caused by decomposition of Bi rich tetrahedrite with Fe and Cu excess. This alternative is not supported by the composition of tetrahedrite associated with Bi-bearing

phases (in wt. %): Cu 37; Ag 1; Fe 5.5; Zn 1.4; Bi 0.1, Sb 28.4; As 0.4; S 25.3;  $\Sigma$  99.1 – which is, in terms of chemical composition, ordinary. Bi content is too low in this tetrahedrite. Furthermore, in case of unstable tetrahedrite decomposition, sphalerite would also have to occur in myrmekites. Moreover, As is not present in any minerals of the myrmekite paragenesis.

b) Most probably, myrmekites with Bi-rich phases originated by the precipitation from residual solution of tetrahedrite crystallization, and/or from solution of slightly younger hydrothermal process – when tetrahedrite has not yet been completely crystallized. These solutions were enriched in bismuth and other elements. This hypothesis is supported by the occurrence of a separate Bi-rich berthierite in tetrahedrite aggregate (Fig. 2), without myrmekite formation.

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**Resumé:** Lokalita Klenovec-Medené je jedným z najznámejších výskytov karbonátovej a kremenno-sulfidickej mineralizácie v kohútskej zóne veporika (Obr. 1). Tento výskyt medených a drahokmových rúd je situovaný asi 1,2 km na JZ od obce Klenovec, v nadmorskej výške okolo 500 m n. m. V 18. až 19. storočí bol otvorený niekoľkými ťažbami a štôľňou Július.

Žilný resp. žilnikovo impregnačný typ mineralizácie sa koncentruje do strižnej zóny SV–JZ smeru, so sklonom 45–70° k JV. Okolité horninu predstavujú biotiticko-albitické pararuly klenoveckého komplexu. Jednotlivé žily majú šošovkovitý tvar, sú max. 15 m dlhé, s hrúbkou od prvých cm do 1,5 m. Hlavnými rudnými minerálmi sú kremeň a karbonáty. Tieto sprevádza muskovit, monazit-(Ce), ilmenit, kalcit, dolomit, pyrit, arzenopyrit, zlato, gudmundit, ullmannit, pyrotit, chalkopyrit, tetraedrit, sfalerit, berthierit, garavellit, markazit, galenit a bizmut. Supergénná zóna je reprezentovaná spionkopitom, geeritom, malachitom, erytritom, goethitom, sádrovcem a skoroditom (Ferenc, 2008). Láznicka (1963) uvádza z lokality ešte fluorit, ankerit, pentlandit, boulangerit, chryzokol a Sb okry. Mineralizácia vznikla počas paleoalpínskeho (vrchná krieda) neskoroorogénneho štádia metalogenetického vývoja Západných Karpát (Lexa et al., 2007).

Mineralogickým štúdiom vzoriek kremenno-sulfidickej mineralizácie z Klenovca-Medeného (odrazené svetlo, elektrónový mikroanalýzátor) boli zistené dva minerály izotypovej série berthieritu, berthierit a garavellit. Boli nájdené v tetraedritových agregátoch, vždy v blízkosti ich rozhrania s agregátmi chalkopyritu. Tvoria principiálne dva morfológické typy: I) predĺžené, alebo izometrické zrná veľkosti 0,001–0,06 mm v tetraedrite (Obr. 2), II) nepravidelné agregáty a žilôčky ako súčasť myrmekitových prerastov s chalkopyritom a tetraedritom (Obr. 3, 4). Myrmekity boli zistené len v tetraedrite, v tesnej blízkosti hranice s chalkopyritovými agregátmi.

Študované minerálne fázy sú zaujímavé zvýšeným obsahom Bi (8,96–18,33 hm. %, Tab. 1, Obr. 5). Zóny s významnejším obsahom Bi majú nepravidelný tvar, s difúznymi okrajmi, niekedy tvoria vlásočnice pretínajúce bizmutom chudobnejší berthierit, alebo individuálne zrná (Obr. 4). Antimón je dominantným prvkom (37,67–49,25 hm. %), z dvojmocných prvkov prevažuje Fe (11,25–11,95 hm. %), Cu a Pb sú zastúpené iba ako nevýrazné prímеси (max. 0,67 hm. % Cu + Pb, Tab. 1).

Oproti pomerne rozšírenému berthieritu predstavuje garavellit iba mineralogickú vzácnosť hydrotermálnych mineralizácií. Vyskytuje sa na lokalite Miniera del Frigido v Taliansku (Gregorio et al., 1979) a v bani Caspari v Nemecku (Bindi & Menchetti, 2005). V Čechách je známy z Au ložiska Kasejovice (Litochleb et al., 1990). V Ázii je známy z ložísk Shanxi a Dachang (Wei et al., 1985; Li et al., 1998) v Číne, tiež z ložísk Aprelkovskoe v Rusku (Borovikov et al., 1990). Na Slovensku bol garavellit v minulosti opísaný len z Sb ložiska pri Pezinku (Andráš et al., 1993) a z lokality Bystrá-Hviezda v Nízkych Tatrách (Majzlan & Chovan, 1997). Berthierit so zvýšeným obsahom Bi (4,4 hm. %) bol opísaný zo Smolníckej Píly

(Peterec, 1989). Väčšina berthieritov na Slovensku sa vyznačuje veľmi nízkou substitúciou  $Sb^{3+} \rightarrow Bi^{3+}$ . Obsah Bi sa pohybuje prevažne v stotínach, vzácnejšie v prvých desatinách hm. %.

Garavellit ako aj Bi obohatený berthierit vznikali v závere sulfidického štádia vývoja mineralizovaných štruktúr. Tieto minerály sa vždy vyskytujú v úzkej asociácii s inými bizmutovými resp. bizmutom obohatenými minerálnymi fázami (Sb-bizmutinit, kobellit, gladiť, Bi-jamesonit, Bi-antimonit...).

Študované minerálne fázy z Klenovca sú charakterizované takmer kompletným prechodom od berthieritu bohatého na Bi ( $Fe_{0,96}(Sb_{1,81}Bi_{0,19}/2,00)S_{4,01}$ ) k Sb bohatému garavellitu so vzorcom:  $Fe_{0,96}(Sb_{1,48}Bi_{0,53}/2,01)S_{4,026}$  (Obr. 5). Vyskytujú sa v asociácii s tetraedritom, chalkopyritom, arzenopyritom a zlatom, avšak nie s inými Bi minerálmi. Ich vznik spadá do záveru kremenno-sulfidického štádia

vývoja mineralizácie. Na základe mikroštruktúrnych vzťahov a zistenej asociácie možno vysloviť predpoklad, že Bi-berthierit a Sb-garavellit mohli vzniknúť dvoma spôsobmi. Ich úplný alebo aspoň čiastočný vznik rozpadom tetraedritu bohatého na Bi s prebytkom Cu a Fe je málo pravdepodobný. Svedčí proti tomu zloženie samotného tetraedritu v asociácii s Bi minerálnymi fázami (nízky obsah Bi, "štandardné" chemické zloženie), neprítomnosť sfaleritu v myrmekitoch a tiež neprítomnosť arzénu v myrmekitových mineráloch. Pravdepodobnejšie je, že berthierit a garavellit precipitovali zo zvykových roztokov (obohatených o Bi) kryštalizácie tetraedritu a/alebo z roztokov o niečo mladšieho hydrotermálneho procesu, kedy tetraedrit ešte nebol kompletne vykryštalizovaný. Táto teória je podporovaná aj vznikom samotného Bi-berthieritu vo vnútri tetraedritových agregátov, bez toho aby sa vytvorili myrmekitové agregáty (Obr. 2).