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# Polymetallic Cu-Bi-(Pb-Zn-Co-Ag) mineralization of the Perin Potok locality near Bor, Serbia

Aleksandar Pačevski[1], Kristina Šarić[1] & Vladica Cvetković[1]

**Abstract.** Complex polymetallic Cu-Bi-(Pb-Zn-Co-Ag) mineralization of the Perin Potok locality occurs as disseminations and fine nests in quartz-ankerite-(sericite) veins. The veins are located in metamorphic rocks of the outer contact zone of the Variscan Gornjane Granitoid. The mineralization consists of (in decreasing abundance): chalcopyrite, aikinite, bismuth, galena, Ag,Bi-bearing tetrahedrite, sphalerite, cobaltite and an unnamed $Bi_2Te$ mineral. All these phases form distinctive exsolutions and intergrowths and they simultaneously precipitated from a very complex hydrothermal fluid. Silver shows elevated contents in tetrahedrite (3.3–4.4 wt. % Ag), galena (0.9–1.1 wt. % Ag) and in the unnamed $Bi_2Te$ mineral (0.9 wt. % Ag). Such high Ag concentrations can imply that Ag minerals could be also present. Minor amounts of rutile showing fine intergrowths with sericite also occur in this paragenesis. This is W-bearing rutile that shows zoning caused by up to 2.2 wt. % W. The studied mineralization is probably genetically related to the Variscan Gornjane Granitoid, although the possibility of derivation from the metamorphic basement should be also taken into account.

**Key words:** aikinite, bismuth, tetrahedrite, rutile, Variscan metallogeny, Gornjane Massive, east Serbia.

**Апстракт.** Комплексна полиметалична Cu-Bi-(Pb-Zn-Co-Ag) минерализација откривена на локалитету Перин поток образује импрегнације и гнездашца у кварц-анкерит-(серицитским) жицама које се налазе у контактној зони горњанског гранитоида с околним метаморфитима. Минерализацију чине (у опадајућој количини): халкопирит, ајкинит, самородни бизмут, галенит, Ag,Bi-тетраедрит, сфалерит, кобалтин и неименовани $Bi_2Te$ минерал. Сви ови минерали образују изразита издвајања и прорастања и истовремено су депоновани из једног веома комплексног хидротермалног флуида. Сребро показује повећане концентрације у тетраедриту (3,3–4,4 мас. % Ag), галениту (0,9–1,1 мас. % Ag) и неименованом $Bi_2Te$ минералу (0,9 мас. % Ag). На основу ових повишених концентрација Ag може се претпоставити да на испитивном терену постоје и минерали сребра. Рутил, који је у мањој количини такође присутан у овој парагенези, показује фина прорастања са серицитом. Овај W-обогаћени рутил показује зонарност узроковану садржајем волфрама до 2,2 мас. %. Испитивана минерализација вероватно је генетски повезана с горњанским гранитоидом, мада би могућност њеног порекла из околних метаморфита такође требало узети у разматрање.

**Кључне речи:** ајкинит, самородни бизмут, тетраедрит, рутил, херцинска металогенија, горњански масив, источна Србија.

## Introduction

The locality of Perin Potok, situated about 10 km north-eastward of the town of Bor, has long been known as one of the occurrences of W-Mo mineralization in north–east Serbia. The mineralization is mostly represented by scheelite and molybdenite and, apart of these minerals, the presence of sulphides – chalcopyrite, pyrite and rarely arsenopyrite - was also reported (Savić 1956; Janković 1990). This W-Mo mineralization is generally interpreted as genetically related to the Gornjane Granitoid. This granitoid belongs to a belt of NE Serbia granitoids that were formed by Variscan orogenic/post-orogenic events (Urošević 1908; Simić 1953; Mihajlović-Vlajić & Markov 1965; Divljan & Divljan 1972). Both Variscan gran-

[1] University of Belgrade, Faculty of Mining and Geology, Department of Mineralogy, Crystalography, Petrology and Geochemistry, Đušina 7, 11000 Belgrade, Serbia. E-mails: aleksandar.pacevski@rgf.bg.ac.rs; kristinas@rgf.bg.ac.rs; cvladica@rgf.bg.ac.rs

itoids and their metamorphic basement are found to host numerous ore-bearing quartz veins with W, Au and sporadically with Cu, Fe and Pb-Zn mineralizations (Simić 1953; Kalenić *et al*. 1973, 1976). In this context, the true origin of these mineralizations (either magmatic or metamorphism-related?) remained poorly constrained.

In this study we report new data on the polymetallic mineralization occurring in the Perin Potok locality, in particular on the assemblage dominated by Cu-Bi-(Pb-Zn-Co-Ag) metallogeny. To our best knowledge, this locality represents the very first occurrence of such type of mineralization in north-east Serbia. By presenting textural and mineral chemistry characteristics of the observed ore paragenesis we want to provide better understanding of the formation of W-Mo-dominated mineralization in north–east Serbia. We also have reasons to believe that this association of metals could be present in economically significant proportions in this area, and can shed new light on the whole metallogeny of the entire region.

## Geological Setting

The studied polymetallic mineralization occurs in a very complex area of the East Serbian Carpatho-Balkanides that represents an assemblage of the Lower Paleozoic terranes intruded by the late Variscan granitoids (e.g. Karamata & Krstić, 1996; Karamata, 2006). The Perin Potok mineralization is found along the southern contact zone between the Variscan Gornjane Granitoid and the surrounding metamorphic rocks of the Stara Planina–Poreč terrane. Further to the west there are occurrences of the Upper Cretaceous andesitic volcanics and volcaniclastics of the Timok Magmatic Complex that is famous of large porphyry-copper and epithermal-gold systems (e.g. Banješević, 2006; Kolb *et al*. 2013). A simplified geological sketch of the area is shown in Fig. 1.

Gornjane is a NNW–SSE elongated lens-shaped granitoid pluton that consists of quartz monzonite, granodiorite, quartz diorite, diorite and syenite displaying gradual transitions in composition (Divljan & Mićić 1960; Kalenić *et al*. 1976; Vasković *et al*. 2012). Central parts of the magmatic body are composed of quartz monzonite surrounded by granodiorite, while in the peripheral parts and contact zones dioritic rocks generally occur. This granitoid pluton contains numerous quartz veins, veins of pegmatite and aplite, and younger shallow granite intrusions. Vasković *et al*. (2012) reported the U-Pb zircon ages of 323.3 ±2.6 Ma to 305.8 ±3.6 Ma. These ages confirm that the emplacement of this granitoid massive occurred during the late Variscan events.

The metamorphic basement consists of the Rifeo--Cambrian to the Lower Palaeozoic units (Kalenić *et al*. 1976) composed of various metabasic and metasedimentary rocks. The locality of Perin Potok is located along the contact zone between the Gornjane Granitoid and the Lower Palaeozoic unit. The latter unit starts with conglomerates and continues with sandstones, siltstones, metamorphosed clays and phyllites.

The mineralization is found in up to 30 cm thick quartz-ankerite and subordinate sericite veins. The

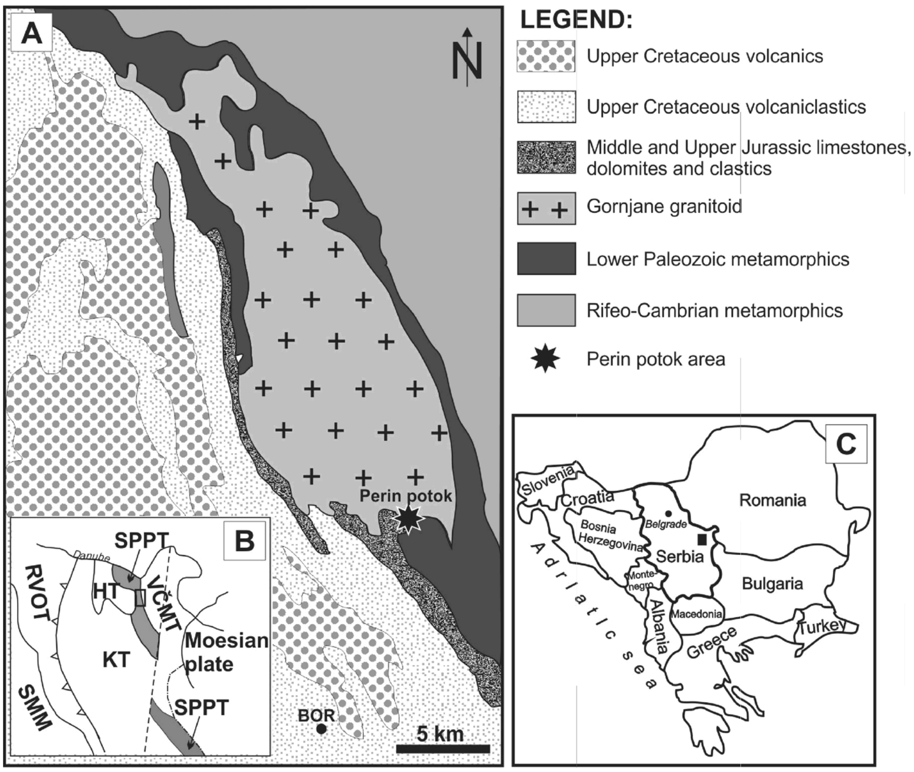


Fig. 1. **A,** Simplified geological map (Kalenić *et al*., 1976), **B,** Geotectonic division (Karamata & Krstić, 1996) and **C,** Geographical position of the studied area. Explanations: **SPPT,** Stara planina–Poreč terrane; **VČMT,** Vrška čuka–Miroč terrane; **HT,** Homolje terrane, **KT,** Kučaj terrane; **RVOT,** Ranovac–Vlasina–Osogovo terrane; **SMM,** Serbo-Macedonian massif.

veins can be found only in stream beds as stream flanks are covered by humus. They are mainly enclosed in adjacent metamorphic rocks. Sulphide minerals form disseminated mineralization and nests up to 5 mm in size in these veins.

**Materials and Methods**

Representative samples of the mineralized veins were routinely studied macroscopically and by reflected-light microscopy. Electron microprobe analyses (EMPA) of the ore minerals were obtained at the University of Belgrade – Faculty of Mining and Geology, using a JEOL JSM–6610LV scanning electron microscope (SEM) connected with INCA energy-dispersion X-ray analysis (EDX) unit. An acceleration voltage of 20 kV was applied. The following standards and analytical lines were used: pure copper (Cu*K*α), pyrite (Fe*K*α, S*K*α), ZnS (Zn*K*α), InAs (As*L*α), $Ag_2Te$ (Ag*L*α, Te*L*α), InSb (Sb*L*α), PbS (Pb*M*α), pure bismuth (Bi*M*α), pure cobalt (Co*K*α), pure nickel (Ni*K*α), CdS (Cd*L*α), TiO (Ti*K*α) and pure tungsten (W*L*α). Detection limits of the applied EDX measurements were $2\sigma \sim 0.2$ wt. %. Gangue minerals were determined by semi-quantitative analysis using internal standards.

## Results

This complex mineralization is characterized by fine intergrowths of many sulphides (Fig. 2), among which chalcopyrite and aikinite predominate, whereas bismuth, galena, sphalerite, tetrahedrite and locally cobaltite are less abundant. In addition, fine exsolutions of an unnamed $Bi_2Te$ mineral also occur in this assemblage, but only as rare grains up to 10 μm in size. Chalcopyrite and aikinite occur as irregular grains mainly up to 1–2 mm in size. Exceptionally,

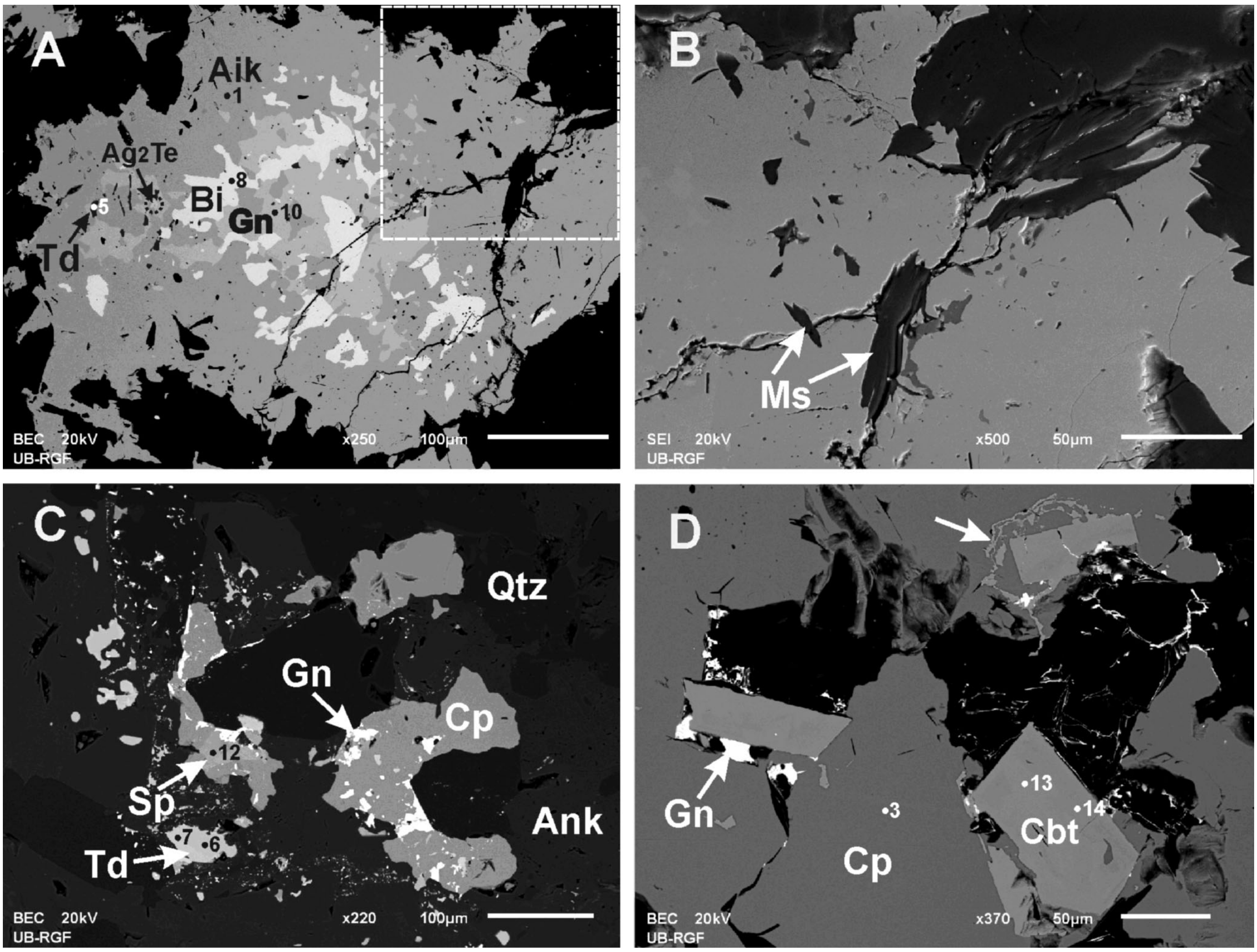


Fig. 2. Studied mineral assemblages from the Perin Potok locality (**A, C, D,** backscattered electron images; **B,** secondary electron images of detail marked by rectangle in A). Fine intergrowths of cobaltite with chalcopyrite in **D** are marked by the arrow. Dots and numbers represent single electron microprobe analyses given in Table 1. Symbols: **Aik,** aikinite; **Ank,** ankerite; **Bi,** bismuth; **Cbt,** cobaltite; **Cp,** chalcopyrite; **Gn,** galena; **Ms,** muscovite; **Qtz,** quartz; **Sp,** sphalerite; **Td,** tetrahedrite.

chalcopyrite can be up to 4–5 mm in size. Bismuth forms characteristic exsolutions in the central parts of aikinite grains (Fig. 2a). Tetrahedrite also forms exsolutions in aikinite (Fig. 2a), but it mainly appears as intergrowths with chalcopyrite, sphalerite and galena (Fig. 2c). Cobaltite forms individual subhedral to euhedral grains up to 0.1 mm in size or shows intergrowths with chalcopyrite (Fig. 2d).

wt.% Bi). The presence of these metals characterizes this mineral as a variety of Ag,Bi-bearing tetrahedrite. The unnamed $Bi_2Te$ mineral contains 0.9 wt.% Ag and shows Bi:Te ratio close to 2:1. There is no known mineral of such composition. However, as this mineral occurs in very small grains, its detailed determination was not possible. Galena contains 0.9–1.1 wt.% Ag. Sphalerite contains common amount of iron (1.6 wt.%

Table 1. Results of electron microprobe analysis (wt.%) of the ore minerals from the Perin Potok locality.

| Spot | Mineral | S | Fe | Cu | Zn | As | Ag | Sb | Pb | Bi | Co | Ni | Cd | Te | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Aikinite | 15.3 | | 11.0 | | | | | 39.0 | 35.3 | | | | | 100.6 |
| 2 | | 15.0 | | 11.2 | | | | | 39.1 | 35.1 | | | | | 100.4 |
| 3 | Chalcopyrite | 35.1 | | 34.0 | | | | | | | | | | | 99.0 |
| 4 | | 35.4 | 29.9 | 34.1 | | | | | | | | | | | 99.6 |
| 5 | Tetrahedrite | 23.9 | 30.1 | 32.1 | 4.1 | 0.4 | 4.4 | 26.3 | | 6.1 | | | | | 99.3 |
| 6 | | 25.0 | 2.0 | 35.2 | 5.1 | 6.5 | 3.3 | 19.8 | | 3.3 | | | | | 99.9 |
| 7 | | 24.3 | 1.8 | 34.0 | 5.8 | 4.1 | 4.0 | 22.3 | | 3.5 | | | | | 99.4 |
| 8 | Bizmuth | | 1.4 | | | | | | | 100.2 | | | | | 100.2 |
| 9 | Unnamed $Bi_2Te$ | | | | | | 0.9 | | | 76.2 | | | | 22.0 | 99.1 |
| 10 | Galena | 12.7 | | | | | 0.9 | | 85.6 | | | | | | 99.2 |
| 11 | | 12.8 | | | | | 1.1 | | 85.3 | | | | | | 99.3 |
| 12 | Sphalerite | 33.1 | 1.6 | | 57.2 | | | | | | | | 7.5 | | 99.4 |
| 13 | Cobaltite | 21.0 | 3.8 | | | 43.6 | | | | | 31.2 | 1.0 | | | 100.6 |
| 14 | | 22.4 | 6.8 | | | 41.7 | | | | | 28.1 | 1.3 | | | 100.3 |

Chemical compositions of all the above-mentioned ore minerals are given in Table 1. Aikinite, chalcopyrite and bismuth do not contain EMPA-detectable trace elements. Tetrahedrite displays chemical zoning caused by Sb-As solid solution. Apart of the essential elements, this mineral contains considerable amounts of silver (3.3–4.4 wt.% Ag) and bismuth (3.3–6.1

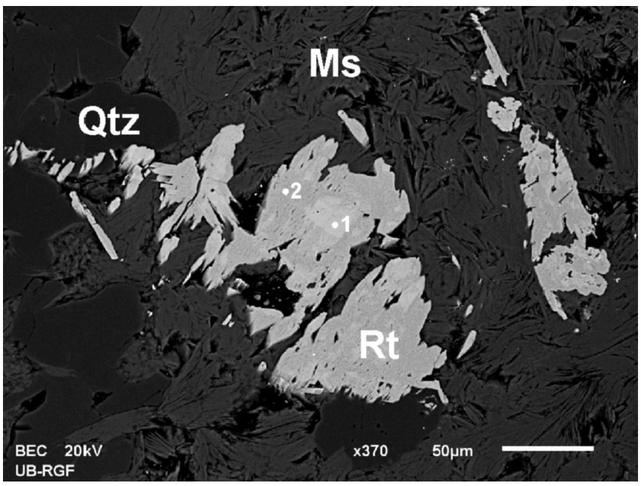


Fig. 3. Occurrence of W-bearing rutile at the Perin Potok locality (backscattered electron image). Dots and numbers represent single electron microprobe analyses given in Table 2. Symbols: **Ms,** muscovite; **Qtz,** quartz; **Rt,** rutile.

Fe) and relatively higher amounts of cadmium (7.5 wt.% Cd). Cobaltite shows slight zoning caused by its common impurities of iron (3.8–6.8 wt.% Fe) and nickel (1.0–1.3 wt.% Ni).

Negligible amounts of pyrite and pyrrhotite are also present. Pyrite occurs in anhedral to subhedral individual grains and in aggregates up to 0.3 mm in size, while pyrrhotite forms rare subhedral to euhedral grains up to 50 µm in size.

Minor amounts of rutile occur as irregular grains and aggregates up to 0.2 mm in size. Rutile shows fine intergrowths with sericite and displays crystal zoning caused by uncommonly high tungsten contents of up to 2.2 wt.% W (Fig. 3 and Table 2).

Table 2. Results of electron microprobe analysis (in wt.%) of W-bearing rutile from the Perin Potok locality.

| Spot | O | Ti | Fe | W | Total |
|---|---|---|---|---|---|
| 1 | 39.3 | 56.5 | 1.3 | 2.2 | 99.3 |
| 2 | 40.0 | 59.3 | 0.3 | | 99.6 |

Sericite, i.e. fine-grained muscovite that is coeval with rutile (Fig. 3), appears within cracks in sulphide-bearing mineral aggregates (Fig. 2b). Thus, it could be concluded that this mineral assemblage formed in the stage of mineralization where sulphide minerals are simultaneously deposited with quartz and ankerite, whereas sericite and rutile precipitated in a subsequent paragenetic sequence of the same stage.

**Discussion and conclusions**

The above reported data suggest that minerals carrying Cu and Bi - chalcopyrite and aikinite, are the most abundant ore phases in the studied sample suite, whereas bismuth, galena, sphalerite, cobaltite and tetrahedrite are subordinate. All these ore minerals of Cu, Bi, Pb, Zn and Co, which form distinctive exsolutions and intergrowths, simultaneously precipitated from a complex hydrothermal fluid. This fluid was enriched also in additional elements of interest, especially in Ag, and in lesser degree in Ni and Te. The presence of Ag minerals is not revealed in this assemblage, but this precious metal occurs is considerable amounts in other ore minerals, principally in tetrahedrite and galena. Nickel occurs in cobaltite, while tellurium forms fine exsolutions of an unnamed $Bi_2Te$ mineral. Sphalerite contains elevated contents of cadmium. Additionally, minor amounts of W-bearing rutile are also found. Thus, it could be suggested that this paragenesis was formed under high- to middle-temperature hydrothermal conditions from a complex Cu-Bi-Fe-Pb-Zn-Ag-Co-Ni-Ti-W-As-Sb-S-Te-bearing fluid. The presence of such very complex ore paragenesis indicates that, in addition to already known occurrences of W-Mo mineralization (SAVIĆ 1956), this area probably contains other types of mineralization. These types can be variable at relatively short distances and they may host so far undiscovered ore phases, especially Ag-bearing minerals. This is inferred from elevated contents of this metal, which are found in some minerals investigated by this study.

The metal budget of the studied mineralization probably derived from the Gornjane granitoid. However, as this mineralization was revealed in adjacent metamorphic rocks, it lacks clear spatial and genetic relationships of the mineralization with the granitoid. Thus, the origin of the mineralization from the metamorphic basement could be also considered. It is much less plausible that this mineralization is related to the Upper Cretaceous Timok Magmatic Complex because, this very well-studied Cu-dominated mineralization is not characterized by the presence of Bi minerals or by the ore mineral assemblage present here.

As already stated above, Cu, W, Mo and in lesser degree Pb mineralization is widespread in quartz- and pegmatite veins of the Gornjane Granitoid. Moreover, SIMIĆ *et al*. (1953) found the presence of cassiterite in some placers of the streams surrounding the Gornjane granitoid. They reported an association of W, Mo and Sn, and presumed that the presence of still undiscovered Bi minerals could complete the already known metal assemblage typical of granitoid rocks. The occurrence of Bi minerals reported by this study supports their speculation.

Partly similar mineralization regarding predominant metals was discovered in east Serbia only in the region of Stara Planina Mt. It is the Cu-Bi ore deposit of Aljin Do where vein ore bodies are found to occur in the large gabbro massive of Zaglavak, and this deposit is interpreted as having derived from the adjacent Variscan granitoids (JANKOVIĆ 1990).

On the other side, the Perin Potok mineralization occurs in quartz-ankerite-(sericite) veins located in metamorphic rocks that are generally rich in quartz and sericite. These metamorphic rocks are widespread in NE Serbia and represent also the basement of other granitoids in this region (SIMIĆ *et al*. 1953). Numerous ore-bearing quartz veins with W-, Au- and various polymetallic mineralizations are found in the metamorphic basement in other parts in NE Serbia (SIMIĆ 1953; KALENIĆ *et al*. 1973, 1976). For instance, there is a similarity of the ore vein type found in Perin Potok with those occurring near Neresnica because both contain ankerite (SIMIĆ 1953). All these occurrences were often explained as genetically related to Variscan granitoids, even though a clear spatial relationship between the mineralized veins and the granitoids lacks in many cases.

It is clear that the complex mineral association found in the contact zone of the Perin Potok locality needs further investigations. These studies must aim at better and more unequivocal constraining the genetic relations between the ore-bearing quartz veins and either the Variscan granitoids or the metamorphic basement. Moreover, the future investigations should examine the possibility that the associations of metals reported in this study may have economically significant occurrences in a wider area.

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## Резиме

## Полиметалична Cu-Bi-(Pb-Zn-Co-Ag) минерализација на локалитету Перин Поток у близини Бора, Србија

На локалитету Перин поток, који се налази у атару села Топла, око 10 km североисточно од Бора, а који је раније био познат по присуству W-Mo орудњења, откривена је комплексна полиметалична Cu-Bi-(Pb-Zn-Co-Ag) минерализација у кварц-анкерит-(серицитским) жицама. Ове жице дебљине до 30 cm налазе се у јужној контактној зони горњанског гранитоидног масива варисцијске старости и метаморфита који чине његову основу, при чему су жице откривене у метаморфитима који су у овом делу контактне зоне претежно изграђени од филита (сл. 1).

Ова комплексна минерализација карактерише се финим прорастањем сулфидних минерала (сл. 2), међу којима су најзаступљенији халкопирит и ајкинит, док се самородни бизмут, галенит, сфалерит, тетраедрит и кобалтин јављају у мањој количини. Поред наведених минерала, овај рудоносни полиминерални агрегат садржи и ретка зрна (до 10 μm) неименованог минерала $Bi_2Te$ састава. Електронска микроанализа поменутих рудних минерала дата је у табели 1. Ајкинит, халкопирит и бизмутинит не садрже хемијске примесе. Тетраедрит показује зонарност узроковану Sb-As чврстим раствором, а овај минерал сложеног састава садржи у значајнијој количини и сребро (3,3–4,4 мас.% Ag) и бизмут (3,3–6,1 мас.% Bi), услед чега се може закључити да је реч о Ag,Bi-тетраедриту. Галенит такође садржи сребро у концентрацијама 0,9–1,1 мас.% Ag. Сфалерит садржи уобичајене примесе гвожђа (1,6 мас.% Fe) и релативно високе концентрације кадмијума (7,5 мас.% Cd). Кобалтин показује слабу зонарност узроковану примесама гвожђа (3,8–6,8 мас.% Fe) и никла (1,0–1,3 мас.% Ni). У испитиваној минерализацији присутне су и мање количине рутила, као и ретка зрна пирита и пиротина. Рутил показује фина прорастања са серицитом и зонарност узроковану неуобичајеним примесама волфрама до 2,2 мас.% W (сл. 3, таб. 2). Рудни минерали бакра, бизмута, олова, цинка и кобалта, који образују карактеристична међусобна прорастања и издвајања, образовани су истовремено, а заједно с њима депоновани су и кварц и анкерит, као пратећи

минерали. Рутил и серицит су образовани у наредној парагенетској сукцесији истог стадијума минерализације. На тај начин, може се закључити да је испитивана минерална парагенеза образована у високо- до средњотемпературном хидротермалном стадијуму из једног веома комплексог флуида обогаћеног Cu-Bi-Fe-Pb-Zn-Ag-Co-Ni-Ti-W-As-Sb-S-Te асоцијацијом метала.

Ова минерализација је вероватно генетски повезана с горњанским гранитоидом. Међутим, с обзиром да је откривена у метаморфитима који се јављају близу контакта с гранитоидом, не постоји непосредна просторна веза минерализације с гранитоидским масивом. Из тог разлога, треба узети у разматрање и могућност генетске повезаности минерализације са филитима из метаморфне основе.

Полиметалична минерализација откривена у Перином потоку представља, према сазнањима аутора, прву појаву оваквог типа Cu-Bi-(Pb-Zn-Co-Ag) минерализације у североисточној Србији. Овакав тип минерализације може бити и економски интересантан, посебно ако се има у виду који су све метали присутни у асоцијацији (Cu, Bi, Pb, Zn, Ag, Co, итд.). Овај тип минерализације може имати и значајан допринос металогенези овог рудоносног дела Србије, у којем се јављају бројне Au, W, Mo и друге полиметаличне рудне жице у варисцијским гранитоидима и метаморфној основи у којима се ови гранитоидни масиви налазе. Даљим испитивањима ове минерализације у Перином потоку и осталих појава које се јављају на сличан начин у овом делу Србије, требало би јасно установити њихову генетску повезаност са варисцијским гранитима и/или околним метаморфитима.