391 GEOME 2 Manuscript received: August 15, 2022 Accepted: October 31, 2022 Geologica Macedonica, Vol. 36, No. 2, pp. 177–195 (2022)
On print ISSN 0352 – 1206
On line ISSN 1857 – 8586
UDC: 553.4.065(497.74)
https://doi.org/10.46763/GEOL22362177gj

Original scientific paper

TYPIZATION OF HYDROTHERMAL ALTERATIONS IN THE BOROV DOL DEPOSIT

Lazar Gjorgjiev

Faculty of Natural and Technical Sciences, "Goce Delčev" University in Štip, Blvd. "Goce Delčev" 89, Štip, Republic of North Macedonia lazar.gorgiev@ugd.edu.mk

A b s t r a c t: For the study of hydrothermal alterations in the Borov Dol deposit, a total of 12 samples were taken, of which 10 samples from boreholes BD-335, BD-320 and BD-322, and 2 samples from the open pit mining of Borov Dol. The material for the X-ray diffraction analyses was also prepared from the samples from which petrographic preparations were made. The following types of alterations have been determined from the conducted investigations: propylitization, chloritization, epidotization, argillitization, kaolinization, calcitization, silification, sericitization, biotitization, adularization, and K-feldsparization. Some of the alterations are pre-ore or follow the formation of copper mineralization (silicification, sericitization and K-feldsparization), and some are post-ore (argillitization, calcitization, and kaolinization). The model of alterations follows the examples of porphyry systems, and the most significant alterations for the spatial distribution of copper mineralization in the Borov Dol deposit are sericitization, silicification, and K-metasomatism. Surface alterations are due mainly to limonitization and in places to argillite alteration. Propylitization gives the segment of the outer halo of alterations in this area.

Key words: hydrothermal alterations; porphyry mineralizations; alteration halo; quantification

INTRODUCTION

Many ore deposits, especially epigenetic ones, may have a zone or zones of altered surrounding rock adjacent to or surrounding them. These alterations of the surrounding rocks are characterized by changes in color, textures, mineralogy, and chemical changes. The spatial distribution of alteration can vary considerably. Namely, it can sometimes be limited only to a few centimeters on each side of the vein, or it can form a powerful halo around the ore body (Tasev & Serafimovski, 2017).

The hydrothermal alterations of the surrounding rocks in the Borov Dol deposit are among the most significant features that characterize this porphyry copper deposit and they actually model the spatial and temporal relationships between different types of hydrothermal alterations represented on a significant surface, as well as the possible spatial and temporal relationship between hydrothermal alterations and ore mineral zoning. Such connections indicate that the porphyry copper mineralization and the alterations of the surrounding rocks are in a close genetic connection and are of special importance in the phase of the exploration of the deposit, because the halos of the hydrothermal alterations

are widespread and they allow easier locating of ore bodies and the provision of their genetic characteristics. With the first drillings in the area of Borov Dol, which were carried out in the middle of the last century, it was established that hydrothermal alterations in combination with geochemical research represented a guide for the design of the investigative drill holes. This was confirmed by the intensification of the investigative drilling, where at that stage a more serious treatment of the hydrothermal alterations was planned, which resulted in the preparation of a Study by Knežević-Djordjević et al. (1975).

The significance of the alterations in the spatial arrangement of mineralization was emphasized by Serafimovski (1990), and a little later by Tudžarov (1993). More recently, Lehmann et al. (2012) emphasized the alterations in the presentation of the Borov Dol mine. Alterations are also a challenge in today's explorations of the open pit of the Borov Dol mine, where with the development of individual projects (Serafimovski, 2021) special emphasis is placed on alterations as an important segment in the exploitation of copper ores.

GEOLOGICAL CHARACTERISTICS OF THE BOROV DOL DEPOSIT

The porphyry copper deposit of Borov Dol is located in the southern part of the Bučim–Damjan–Borov Dol mining area (Čulev et al., 1984), within the Vardar zone on the border with the Serbian-Macedonian massif from the east.

Neogene sediments, Paleogene sediments, volcanogenic-sedimentary rocks and volcanic rocks – a product of the Tertiary magmatism in this area (Serafimovski, 1990) (Figure 1) take part in the geological structure of the immediate vicinity of the Borov Dol deposit.

Neogene sediments-conglomerates occupy the northern and north-eastern parts of the Borov Dol deposit. The conglomerates are made up of heterogeneous material dominated by quartz pebbles, crystalline schists and Paleogene limestones. In the composition of the Neogene conglomerates there is a sandy fraction of the Paleogene flysch as well as fragments of the magnetite-hematite ore, which indicate that the mineralization in the Damjan deposit was largely affected by erosion.

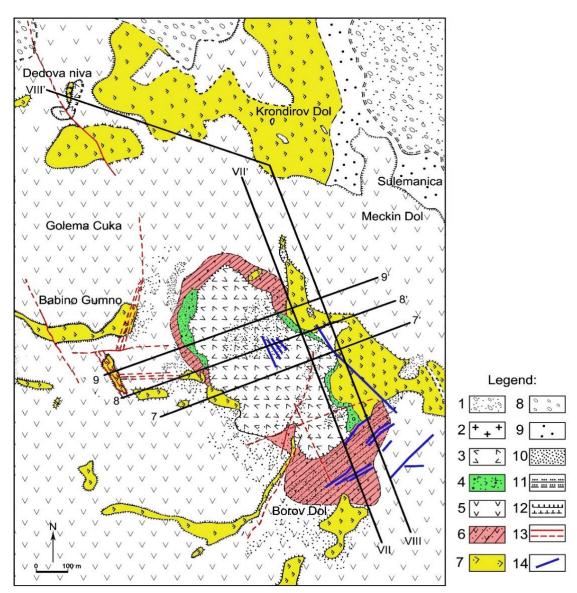


Fig. 1. Geological map of the Borov Dol deposit (modified, after Tudžarov, 1973)

1 – Neogene (conglomerates, sandstones and gravels); 2 – Vein rocks; 3 – Andesites; 4 – Volcanic breccia; 5 – Latites and quartzlatites; 6 – Cu mineralization; 7 – Volcanogenic sedimentary rocks and andesite tuff; 8 – Conglomerates; 9 – Paleogene flysch (marl, sandstone, limestone, marly sandstone and conglomerates); 10 – Hydrothermal alterations; 11 – Transgressive border (confirmed and assumed); 12 – Intrusive border (confirmed and assumed); 13 – Fault (confirmed and assumed); 14 – Quartz-sulphide ore veins

Paleogene sediments occupy a large part of the area of Borov Dol. They mainly occur in the northern and northeastern part of the deposit with a NNW-SE direction with a dip to the NE of 40–60°. All members of the Paleogene are present here: conglomerates, Paleogene flysch and a series of tuffites and sandstones (Tudžarov, 1993).

Volcanogenic-sedimentary formations are determined as a tuffaceous-sandy series, built of sandstones, marly sandstones and limestones, and pelitic tuffs and tuffites. These formations represented a unique covering that was later penetrated by the volcanites and pinched or covered by them (Tudžarov, 1993). In several places, they are tectonically crushed, which is why their layering is hardly noticeable, and is best expressed in the present sandstones. The series dips towards NE with dip angles of 40-60°. From the analysis of the pyroclastic material, the tuffs are determined as andesitic. The presence of tuffs in the series indicates volcanic activity synchronous with the sedimentation of Paleogene sediments. Moreover, the tuffs lying around Borov Dol originated from a different and earlier eruption (Lehmann and Barcikowski, 2012).

Igneous rocks in the Borov Dol deposit are represented by subvolcanic and volcanic facies of latites, quartz latites and andesites. Based on the regional and detailed geological surveys and the volcanological-petrological surveys carried out on the Borov Dol deposit, it has been established that two volcanic phases can be distinguished. The first phase consists of gray-white coarse porphyry intensively hydrothermally altered andesites, that is, latites and quartz latites, where the copper mineralization in Borov Dol is located (Figure 1). With the microscopic examination of the latites and quartz latites, it has been established that the hornblende is mostly transformed into epidote and chlorite, while the rest of the ingredients are mostly fresh. These rocks, as a product of the older phase, appear as negative forms in the relief in this area. The second, younger phase is represented by fresh dark gray fine porphyry andesites that break through the rocks from the older phase and appear as positive forms in the relief (volcanic necks) (Figure 1).

The grey-white coarse porphyry intensively hydrothermally altered and mineralized latites and quartz latites appear in the central part of Borov Dol and extend to the west. They gradually pass into hydrothermally altered and slightly mineralized rocks, and further into propylitized rocks. The crite-

rion for separating these varieties is the appearance of ore minerals as a result of the decomposition of colored ingredients (in the form of nests), and the hydrothermal activity when copper minerals appear in the form of impregnations and veinlets.

Dark gray fine porphyry andesites occur northwest of the Borov Dol stream and have a NW-SE extension. According to their mineral composition, they are the same as the propylitized andesites, but femic minerals are more represented (biotites and amphiboles). Along the entire length of the contact with the older latite-quartz latite rocks, especially towards the north-eastern part, volcanic-tectonic breccias were formed from the older volcanic rocks and tuffs.

Morphological characteristics of mineralization

The mineralization in Borov Dol is paragenetically related to the dark gray fine porphyry andesites and is localized in the gray-white coarse porphyry andesites. It forms a ring around the dark gray fine porphyry andesites that form a neck.

Figure 2 shows a transverse profile through the Borov Dol deposit; from the profiles it can be seen that the ore body with Cu porphyry mineralization is arranged in the form of a ring and mainly lies in the eastern part of the volcanic structure screened by volcanic tuffs.

The width of the ring around the andesite neck is not the same everywhere. Based on the research so far, three ore bodies can be distinguished: South ore body, which is in direct contact with the andesite neck and is located around Borov Dol itself, Central ore body, that is still underexplored, but is indicated by several drillings in the deeper parts of the deposit below the andesite neck, and the North ore body, which is indicated by several drillholes in the northern part below the andesite neck at a depth of over 100 m (Figure 2).

In terms of the scale of the ore bodies based on the knowledge so far, in the South ore body, 32 Mt of ore have been calculated, in the Central ore body 15 Mt of ore have been calculated, and in the North 15 Mt of ore. The ore bodies are medium to small in size. The ore mineralization is of the stockwork-impregnation type in which impregnations take a dominant place, where chalcopyrite is the main ore mineral and the most significant carrier of the sulfide copper mineralization in the deposit.

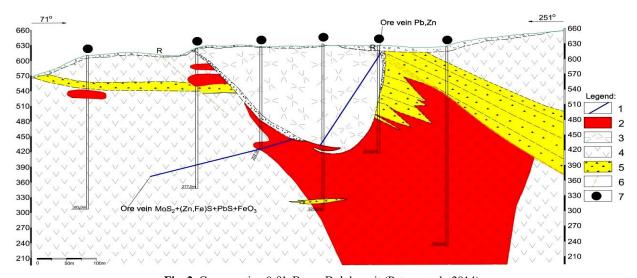


Fig. 2. Cross section 9-9', Borov Dol deposit (Petrov et al., 2014)

1) Veins of Pb-Zn; 2) Ore body; 3) Dark grey fine-porphyry andesites; 4) Grey white coarse-porphyry andesites; 5) Volcanic tuff; 6) Faults; 7) Investigation boreholes

MATERIALS AND METHODS

For the study of hydrothermal alterations at depth, 10 samples were selected from drillholes BD-335 (Z = 572.24 m; D = 200.2 m; geological profile 3A-3A'), BD-320 (Z = 593.17 m; D = 249.6 m; geologic profile 5-5'), and BD-322 (Z = 618.12 m; D = 206.2 m; geologic profile 5-5'). Also, 2 samples from the Borov Dol open pit mine were taken for the study of hydrothermal alterations. Material for X-ray diffraction analyses was also prepared from the samples from which petrographic preparations were made.

The petrographic preparations were made in the preparation laboratory of the Geological Institute "Strashimir Dimitrov" in BAS, Sofia. The petrographic research was done on 12 petrographic preparations by using a transmitted light microscope model Amplival Pol-U by the chief assistant PhD Anna Lazarova, Geological Institute at BAS.

For a more concrete understanding of the types of hydrothermal alterations, the examination with the method of quantitative X-ray-structural analysis was applied.

12 rock samples, hydrothermally altered to varying degrees, were analyzed. The samples were pre-crushed and ground in an agate mortar up to 200

mesh with alcohol for better homogenization. Photographing of the diffraction images was performed using a Huber Image Plate Guinier Camera G670 in the asymmetric emission mode and monochromatic copper X-ray radiation (CuK α 1, λ = 1.540598 Å) in the angular range from 4° to 100° 2 Θ simultaneously and a step of 0.005 2 Θ .

The collected diffraction data were processed with the X-ray phase analysis software package Match! of CRYSTAL IMPACT, including the database of the International Center for Diffraction Data (ICDD PDF-2) and the Crystallography Open Database (COD). The quantitative phase analysis is performed based on the so-called RIR method (Reference Intensity Ratio), comparing the intensities of the identified crystal phases with those of the "Corundum Standard" (I/Ic).

According to the received complex diffractograms, the mineral types, their percentage content and the parameters of the elementary cell were determined.

This research was carried out at the Geological Institute in BAS, by the main assistant Ivanina Sergeeva with the direct participation of Asst. Prof. Slavcho M'nkov from the University of Mining and Geology "St. Ivan Rilski".

CHARACTERISTIC HYDROTHERMAL ALTERATIONS

From the aspect of studying hydrothermal alterations, the area of Borov Dol was covered by detailed investigations. Here, in addition to the field

research conducted through surface geological mapping and geological mapping of the core from the drillholes, study research was also carried out on the

hydrothermal alterations of the samples that were taken on a 100×100 m grid (on the surface) and at an interval of 2 m from the core of certain drillholes (BD-11 and PS-11). Within Borov Dol, an area of 400 ha was covered with detailed investigations of hydrothermal alterations (Knežević-Djordjević et al., 1975). All chemical and optical tests were performed in the petrology laboratory at the Faculty of Mining and Geology in Belgrade.

Knežević-Djordjević et al. (1975) determined the alkali content and calculated the ratio of potassium and sodium on all 402 samples of altered rocks. The finding has been confirmed, as in many other places, that with the introduction of potassium there is a depletion of sodium, especially in those places where we have an increased concentration of Cu.

Within this paper, a reinterpretation of the analyzed values of K_2O and Na_2O and their relationship has been carried out. The data were processed using the Surfer 9.0 software, and isolines of the degree of potassium metasomatism in the Borov Dol deposit were obtained (Figure 3). On the isoline map of the K_2O and Na_2O ratio, the andesite neck is plotted, the contour of the ore bodies of Borov Dol

and Popova Šapka, extracted on the basis of the chemical analyses of the drillhole core and the locations of the quartz-galena-sphalerite ore veins. From the attached picture it can be seen that K-metasomatism has an extensive character within the Borov Dol ore deposit, referring to the studies of the samples taken from the surface. Strong K-metasomatism can be observed west of the Popova Šapka locality, that is, south of the Damjan mine.

The examination of 29 samples from the BD-11 drillhole (Z = 630,0 m; D = 329.0 m; geological profile 13–13') has established the existence of potassium metasomatism with moderate to strong intensity in the deeper parts of the deposit, more precisely at an interval of 290–329 m, where the K₂O/Na₂O ratio is greater than 10, where intensive pyritization was found, with the sulfur content being up to 2% (Knežević-Djordjević et al., 1975).

During 1993, a detailed examination of the mineralogical-petrographic and geochemical characteristics of the materials taken from the core of the PS-11 drillhole ($Z=647,05~\mathrm{m};~D=241,0~\mathrm{m};$ geological profile 17–17', Popova Šapka) was carried out (Boev et al., 1994).

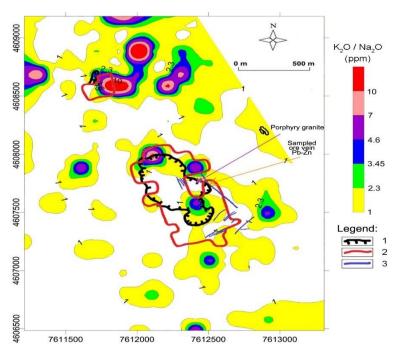


Fig. 3. Isolines of the ratio of K₂O and Na₂O (1) Andesite neck; 2) Contour of the ore bodies; 3) Quartz-sulphide ore veins (modified after Knežević-Djordjević et al., 1975)

The samples taken from the core of the borehole PS-11 in an interval from 1 to 180 m were prepared in the laboratories of the Faculty of Mining and Geology in Štip and they were later subjected to various laboratory tests. First, petrographic preparations were made from all the samples taken, which gave an answer to the question of what types of rocks were present in the treated area, what their

mineral composition was and what types of alterations were represented. For a more specific understanding of the types of hydrothermal alterations, tests using the X-ray diffraction method were applied in the laboratories of the University of Mining and Geology in Sofia.

The following types of alterations were found in the above investigations: propylitization, chloritization, epidotization, argillitization, kaolinization, calcitization, silification, sericitization, biotitization, adularization, and K-feldsparization (Figures 4 and 5).

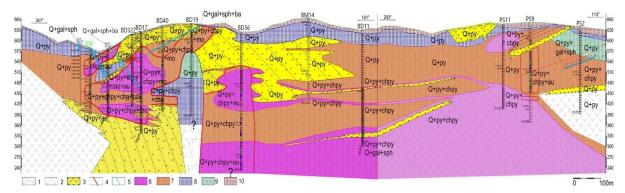


Fig. 4. Schematic model of the more important hydrothermal alterations and ores associated with each zone of alteration in the ore of the Borov Dol deposit.

- 1) Gray-white large porphyritic andesites; 2) Dark gray fine porphyritic andesites; 3) Volcanic tuffs; 4) Contours of ore body;
- 5) Quartz-galena-sphalerite veins; 6) Potassium-feldspatization (biotitization in Borov Dol, adularization in Popova Šapka);
- 7) Quartz-sericite-pyrite (phyllitic) alteration with presence of intermediate argillitic alteration; 8) Advanced argillitic alteration;
- 9) Propylitic alteration; 10) Limonitic hat. (Q quartz; py pyrite; chpy chalcopyrite; gal galena; sph sphalerite; au gold; mo molybdenite; cha chalcocite; cov covellite; ba barite).

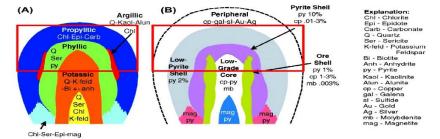


Fig. 5. Zones of hydrothermal alterations associated with the porphyry copper deposits (completed by Lowell and Guilbert, 1970). **(A)** Schematic profile of zones of hydrothermal alterations with minerals which consist of propylitic, phyllitic, argilitic and potassic alteration zones. **(B)** Schematic profile of ores associated with each zone of alteration. The red squares indicate the position of the topic ore deposit in the schematic profiles.

All the above-mentioned alterations are present in the treated rocks, but with different degrees and intensity. Some of the alterations are the result of autohydrothermal processes (propylitization, chloritization and epidotization), and most of them are the product of hydrothermal activity.

Within the framework of hydrothermal alterations, some of them are pre-ore or they follow the formation of copper mineralization (silicification, sericitization and K-feldsparization), and some are post-ore (argillitization, calcitization, and kaolinization).

These two groups of alterations are very difficult to separate in practice without additional and complex laboratory and chemical tests. This is primarily the case with sericitization, silicification and kaolinization.

RESULTS AND DISCUSSION

Within the Borov Dol deposit, the existence of **potassium metasomatism** was determined, including a series of hydrothermal alterations that are the product of the transformation of feldspars and the

intensive feldspathization of plagioclases. This primarily includes adularization, potassium feldsparization and biotitization.

Adularization is registered in a larger number of samples from the PS-11 drillhole, but mostly as extensive, and only in places does adular appear as a typical hydrothermal product. This alteration is a consequence of the influence of potassium-rich hydrothermal solutions at a temperature between 180 and 300° C (Reyes, 1990), during which primary feldspars are suppressed by the low-temperature feldspar – adular. This type of alteration occurs in some epithermal deposits in vulcanites, where adular (gold deposits) dominate (Tasev and Serafimovski, 2017).

Potassium feldsparization is found in two levels in the studied interval of the PS-11 drillhole (from 30 to 80 m and after 170 m), in the BD-11

drillhole it is found after 290 m, in the BD-335 drillhole from 10.0 to 106.0 m, in the drillhole BD-320 from 10.0 to 87.0 m, and in the drillhole BD-322 in two levels (from 80 to 160 m and after 196 m). It is manifested by the creation of a clear potassium feldspar, mostly in the form of jets and only in places in veins. It suppresses the plagioclase phenocrysts and the groundmass mineral constituents. In the places where it is quite intensive, this process also affects the biotite. The potassium alteration zone in the Borov Dol deposit is characterized by orthoclase \pm biotite + quartz \pm magnetite \pm sericite (or muscovite) \pm albite \pm chlorite \pm apatite \pm rutile \pm epidote \pm chalcopyrite \pm pyrite (Figures 6 and 7).

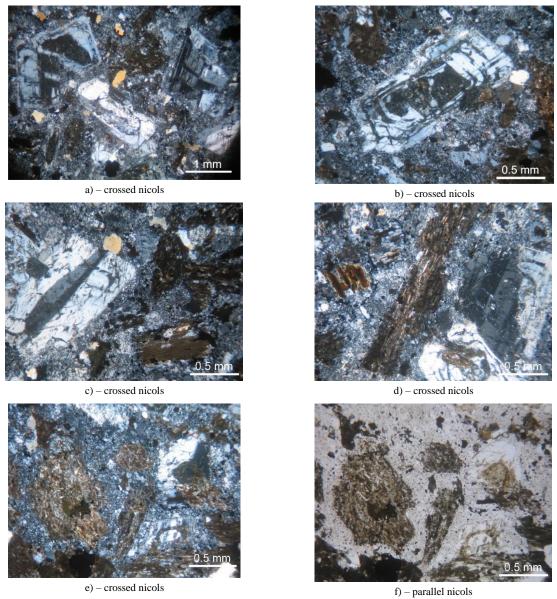


Fig. 6. a) Complexly fused aggregates of feldspars and zonally formed single phenocryst.

b) Zonal idiomorphic feldspar, selectively substituted from fine- crystalline aggregate of clay minerals.

c), d), e) and f) Quartz-kaolinite-sericite groundmass in the hydrothermal mineral association BD-6

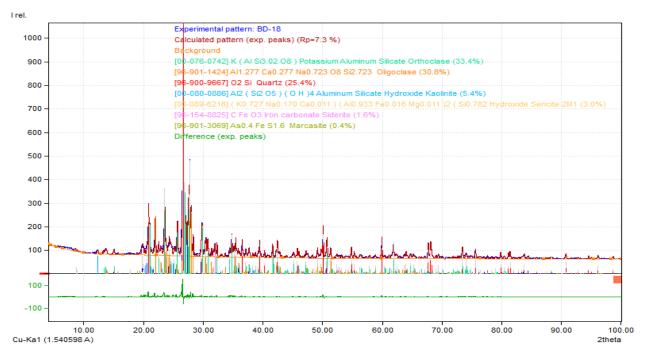


Fig. 7. X-ray diffractogram of the sample BD-18 (BD-320, D = 87.1 m)

In sample BD-6 (BD-320, D = 87.1 m), by composition the average subvolcanic rock has about 50% porphyry mainly of feldspar - K-feldspar, plagioclase and secondary biotite and another femic mineral, probably amphibole, completely replaced by secondary minerals. Phenocrysts are included in the fine-grained groundmass of secondary minerals - primary sericite and clay minerals, quartz, dark colored and ore minerals. Feldspars are represented by single finer (2-3 mm), mostly hypidiomorphic grains or fragments of grains, but much more often they form complex aggregates of several individuals, with some reaching up to 1 cm. They are characterized by complex zonation, unbalanced structures (network-like structure, corroded internal parts) and complex joints. These characteristics reflect the dynamics in the magmatic crystallization process. The feldspars are unevenly altered. Sometimes within a single phenocryst, unchanged zones and ones completely replaced by secondary minerals are determined. Many of the grains are penetrated by systems of fine microcracks, filled mainly with red carbonate, sericite and illite (?) (Figure 6).

Biotitization was found in samples from the BD-335 drillhole at the level from 10 to 91 m, in one sample from the DB-320 drillhole at 87,1 m and in the BD-12 sample from the open pit (near the BD-43 drillhole, level 615) located in the dark gray fine porphyry andesite (Figures 8, 9 and 10).

The subvolcanic rock from sample BD-1 (BD-335; D = 32.0 m) is about 50% phenocrysts, mainly

of feldspar (K-feldspar > plagioclase) and in smaller amount of amphibole and biotite, included in the fine-grained groundmass. Feldspars are represented by smaller (2-3 mm), mostly hypidiomorphic individuals and more often by complexly arranged aggregates of several grains, with some reaching up to 1 cm. They are characterized by complex zonation, unbalanced structures (net-like structure) and complex intergrowths. Feldspars are throughout penetrated by systems of fine microcracks, filled primarily with hydrothermal biotite ± sericite (Fig. 8c and 8d). Some of the finer grains are almost completely biotitized, but others are relatively fresh. Amphiboles form long and short-prismatic and often xenomorphic individuals (from 3 to 4 mm parallel to spreading), as without exception almost all are replaced entirely by fine-grained flakes (< 1 mm) hydrothermal biotite. Igneous biotite is in roughly equal amounts and proportions to amphibole. Some of the individuals are also partially transformed into an aggregate of secondary biotite. Some of the biotites show inclusions of biotitized feldspars. A pseudohexagonal morphology can be seen locally. The main mass is built mainly from secondary phases – clay minerals, quartz and ore phases. Carbonate and chlorite are also present in small quantities. Quartz and ore minerals often form morphologically irregular but coarser-grained aggregates in the groundmass and thin veins. There is a large quantity of ore minerals and they impregnate the rock-forming independent grains (rarely), aggregates (ore or quartz-ore) and veinlets.

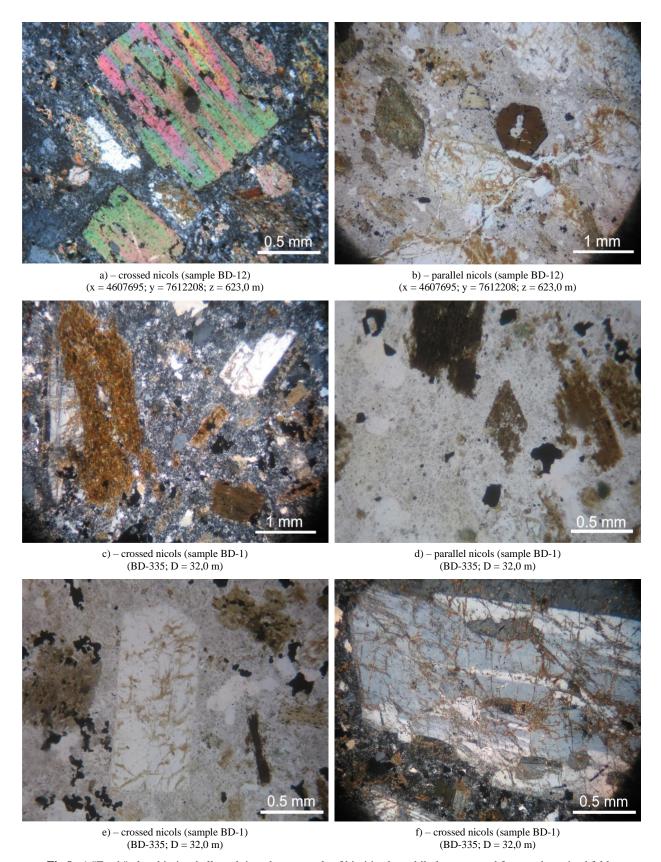


Fig 8. a) "Fresh" plate biotite shells and tiny phenocrystals of biotitized amphibole penetrated from carbonatized feldspar.
b) Short-prismatic biotitized and in extension weakly chloritized amphibole and pseudohexagonal "fresh" biotite.
c) Porphyritic feldspar, biotitized amphibole and biotite in latite porphyry with signs of high-temperature biotitization.
d) Biotitized amphibole – hypidiomorphic and xenomorphic phenocrystals.
e) and f) Idiomorphic feldspar phenocryst – weakly cracked, where the secondary biotite is deposited after the microcracks (?).

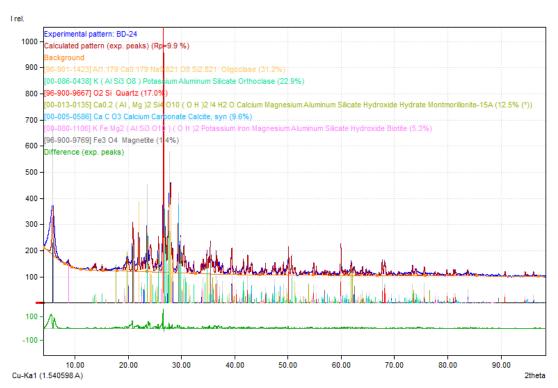


Fig. 9. X-ray diffractogram of the sample BD-24 (x = 4607695; y = 7612208; z = 623,0 m)

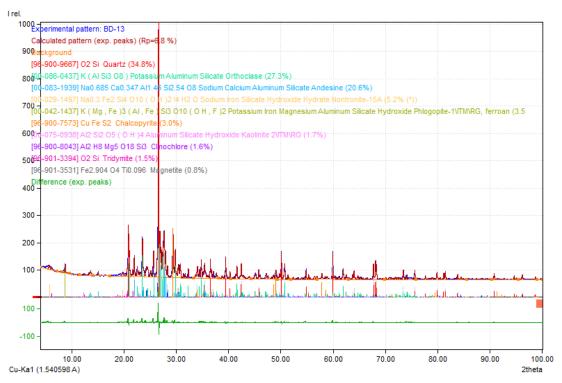


Fig. 10. X-ray diffractogram of the sample BD-13 (BD-335, D = 32,0 m)

Strong biotite alteration, implying partial or complete replacement of specific minerals by biotite in the surrounding rock and in the porphyry intrusive body, has been described in numerous porphyry copper deposits (Titley, 1982). Horblende biotitization, the most common alteration of this type, occurs in broad halos that in some deposits extend well beyond the limits of mineralization. The zone of biotitization is generally symmetrical with respect to zones containing the earliest hydrothermal stages of copper and molybdenum sulfide deposition, which have scattered fracture-controlled occurrences (Roberts, 1973).

In more detail, near the outer edges of this zone, where islands of unaltered surrounding rock persist, biotitization of the hornblende can show clear association with veinlets that control the haloes of potassium or potassium-silicate type alteration; these veinlets contain alkali feldspar, muscovite, andalusite, biotite, quartz and anhydrite (Roberts 1973; Brimhall, 1977). The use of different geothermometers indicates the relatively high range of temperatures and is indicative of early hydrothermal systems (570–700°C) (Brimhall, 1977; Roberts, 1973; Jacobs and Parry, 1979). This suggests that the process of biotitization is associated with the initial development of control fractures and represents the first hydrothermal phase in the longterm fracturing sequence during which convective solution circulation occurs (Titley, 1982), followed by the creation of solution composition (Brimhall, 1977).

A close genetic connection with the late impulse of dark gray fine porphyry andesites is indicated by the strong biotitization observed in the apical parts of gray-white coarse porphyry andesites that are near the contact with the dark gray fine porphyry andesites, where the density of hydrofractures is the highest. The first introduction of copper into the gray-white coarse porphyry andesites occurred in this environment in the Borov Dol deposit. Its existence as a high-temperature alteration is almost always overlaid by one of the other lower-temperature types of alterations present in this system (lower-temperature processes of sericitization, silicification, and carbonatization). In this context is also the confirmation of the finding of Titley (1975), Carson and Jambor (1974), Cheney and Trammell (1975) that although a potassium alteration is usually manifested in or near the "porphyry center", the halo of the biotite alteration that covers the surrounding igneous rocks is wide.

In drillholes BD-335, BD-322, and BD-11, hydrobiotite was observed with K-feldsparization. In the PS-11 drillhole, the presence of hydrobiotitization and hydromica was also observed. Hydrobiotitization is a process present in this space and it is manifested by the appearance of hydrobiotite that was probably created in the process of contact changes of andesites and some deeper plutonic body (leucocratic granitoporphyry), and it usually goes together with K-feldsparization, which in the BD-11 and PS-11 drillholes is also a favorable indication of the existence of porphyry-type mineralization.

Hydromica from the drillhole PS-11 were noticed only by X-ray diffraction and they probably represent the decomposition product of feldspars when in those processes the adular passes into hydromica.

Quartz-sericite-pyrite ("phyllite") alteration with the presence of intermediate argillite alteration is distinguished, which is the result of overlapping of these two types of changes.

The quartz-sericite-pyrite (phyllite) alteration is one of the more significant alterations in the Borov Dol deposit, mainly located above the potassium feldsparization zone. This alteration is very intensive and builds a very wide halo around the mineralized zones. Although this alteration can also be related to the period of consolidation of the andesitic rocks, it is intensive practically only in the case when it is related to the hydrothermal solutions that carry the ore. Sericite (Lowell and Guilbert, 1970) or phyllite alteration (Meyer and Hemley, 1967; Rose, 1970) affects the potassic feldspars, then the plagioclases – the peripheral parts, then the central parts, the groundmass, and finally the colored minerals, especially biotite. This transformation is characterized by the replacement of these minerals with fine-grained sericite (or muscovite minerals) and clay minerals and it is carried out by hydrothermal solutions with low pH value and rich in potassium at temperatures between 150 and 400°C (Boev et al. 1994). At the same time, these reactions can lead to the creation of larger amounts of excess silicon, which enables the formation of quartz. The formation of the quartz-sericite association occurs under the influence of meteoric waters, so that association also represents the limit of the influence of juvenile waters in hydrothermal solutions. Also, iron released by the alteration of iron-bearing minerals, as well as iron and sulfur added by hydrothermal solutions, form pyrite, which is more abundant in the deeper levels of this zone. Pyrite is in the form of veinlets and impregnations. Those veinlets have been replaced in places by chalcopyrite.

The phyllite alteration in the examined samples from the drillholes (BD-335, BD-320, BD-322, BD-11 and PS-11) is characterized by the appearance of fine-grained, and in some cases also coarsegrained sericite, which is present in the entire rock. This alteration typically characterizes the center of the mineralization activity with its progressive replacement into kaolinite (argillitic alteration) as moving toward the outer zones (Misra, 2000) (Figures 11, 12, and 13). In the case of the Borov Dol deposit these two changes overlap.

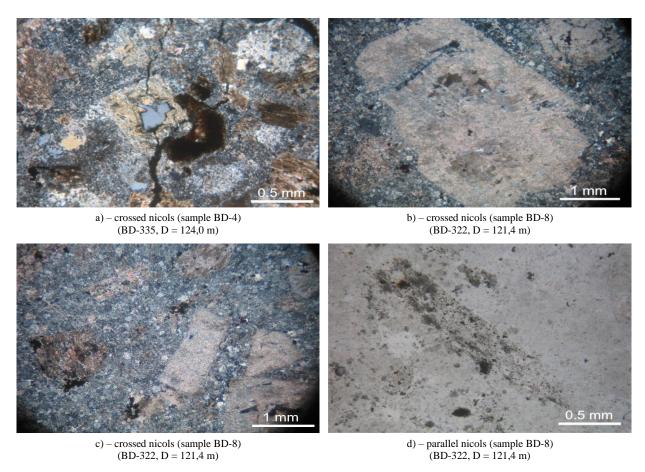


Fig. 11. a) "Fresh" biotite shell with partially developed pseudohexagonal morphology and fully sericitized feldspar phenocrystal in intensively sericitized, silificized and argillitized latite porphyry. b) Fine-grained aggregate of sericite and carbonate, which imitating has altered the feldspar. c) Fine-grained aggregate of sericite and carbonate, which imitating has substituted the feldspars.

d) An aggregate of clay minerals and dark-colored minerals, which imitating has probably substituted the amphibole

The rock from the sample BD-8 (BD-322, D =121,4 m) is intensively hydrothermally altered, with only rare, fine grains of accessory apatite and zircon remaining from the original minerals. Former feldspar porphyries are recognized only by the preserved grain morphology – often hypidiomorphic, prismatic. They are completely replaced by a fine-crystalline aggregate of sericite, carbonates, clay minerals and some quartz, and, in some cases, an ore mineral participates in the aggregate. This gives the impression that some porphyries have been replaced by a coarser-grained aggregate of white mica, similar to muscovite, coarse grains of carbonate and ore mineral. The presence of amphibole in the protolith can also be assumed – long prismatic and rhombohedral features of some grains, darker grains at parallel nicols, representing a fine-grained aggregate of clayey and dark-colored minerals, ± ore mineral (Figure 11).

The rock is permeated by veins of various sizes (1–4 mm thick) with quartz, carbonate, K-feldspar (?) and white mica. This gives the impression of the

presence of detached flakes of coarser white mica/ hydromuscovite (?) in the groundmass. In some of the veins, the quartz forms rare, poorly formed radial aggregates.

Within the petrographic preparation, there are ore minerals in moderate quantity. They are represented by fine-grained and morphologically irregular aggregates, unevenly distributed in the rock – independently in the groundmass or developed upon the replaced former phenocrysts. Rare, very fine non-continuous veinlets with ore mineral are also visible.

The intermediate argillite alteration is characterized by the appearance of kaolin and minerals from the montmorillonite group, but montmorillonite is represented with a lower intensity than kaolinite. Also, X-ray analyses confirmed that kaolinite is dominant and accompanied by montmorillonite and illite. Argillitic alteration is a process of acid leaching (relatively intense hydrogen-ion metasomatism) at a temperature of 100 to 300°C, of rocks with almost complete removal of alkaline cations

and complete destruction of feldspars and femic minerals. Under conditions when limited amounts of K, Ca and Mg remained in the altered rock, enough to form montmorillonite, illite, hydromicas, chlorite and kaolinite, it is a question of intermediate argillitization (Beane and Titley, 1981). Within its framework, plagioclase is replaced by kaolin (usually close to the upper parts of the intrusion at the peripheral part), that is, montmorillonite in the higher levels (where ore mineralization is insignificant). The location of the kaolinite alteration helped reveal the place of greatest decomposition. That argillitization can develop on top of earlier potassium and

sericitic alteration was first confirmed by Brimhall (1979) and Gustafson and Hunt (1975).

The intermediate argillite zone overlaps the quartz-sericite-pyrite zone and represents a transition to deeper and higher-temperature alterations.

Shallow alteration levels can also be interpreted as a supergene (zone of secondary sulfide enrichment) cover over the deposit, so the possibility that the deeper clay alteration of the feldspars have the same origin is not excluded. In this zone, in some parts, chalcocite also occurs in the form of impregnations and veinlets, created by the suppression of chalcopyrite.

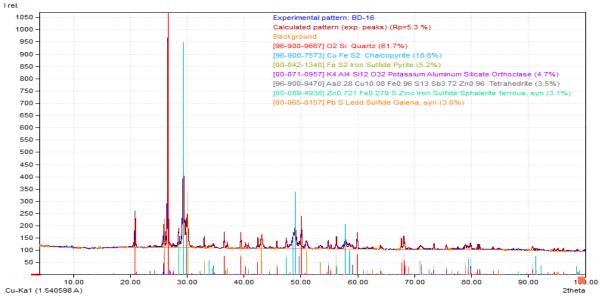


Fig. 12. X-ray diffractogram of the sample BD-16 (BD-335, D = 124,0 m).

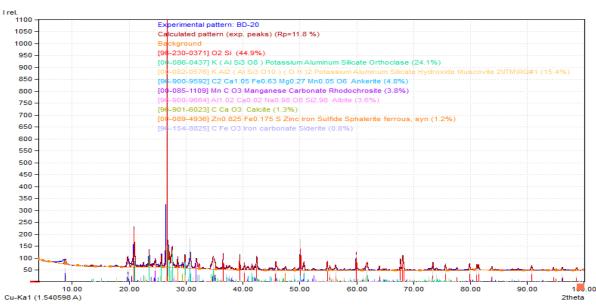


Fig. 13. X-ray diffractogram of the sample BD-20 (BD-322, D = 121,4 m)

Advanced argillite alteration in the Borov Dol deposit extends immediately above the Cu-Au-Mo porphyry system, i.e., in the peripheral parts of the intrusive. Its occurrence is structurally controlled by the presence of deep normal faults. It includes kaolinite and quartz, as well as nontronite, sericite, limonite, and pyrite.

It also represents a spatial association with the mineralization in the deposit, and above all for the vein mineralization.

It is accompanied by silicification, which is manifested by a structurally controlling occurrence, whereby silicification or siliceous-sulphide-limonite alteration is associated with zones of clay alteration and bleaching, observed in the near-surface grey-white coarse porphyry andesites.

The advanced argillitic alteration assemblage was developed under highly acidic conditions by intensive hydrolytic leaching of the bases. This system is characterized by an early stage of massive or breccia-like, advanced quartz-dominated argillic alteration. Phase relations indicate that the early advanced quartz-dominated argillitic alteration developed at temperatures of < 275°C (Allibone et al., 1995).

In the case of the Borov Dol deposit, the advanced argillite change occurs with the transfor-

mation of the rocks at the expense of the alkaline feldspars, during the alternating action of the ascending alkaline sulfate solutions and surface waters. At the same time, kaolinite and other clay minerals are created by the destruction of different minerals, above all feldspars (Figures 14 and 15).

Intensively hydrothermally altered subvolcanic rock (sample BD-11; x = 4607505; y = 7612702; z = 635.0 m) is built almost entirely of secondary minerals. Relics of incompletely replaced feldspar and biotite, as well as accessory apatite and zircon, are retained from the original mineral composition. Feldspars were the main porphyry phase in the protolith. The feldspars have retained their original prismatic morphology and hypideomorphic forms, with complex joint relations between several individuals, visible in a number of places. They are almost completely replaced by fine crystalline aggregates mainly of clay minerals and sericite, \pm quartz. In very rare cases, during incomplete replacement, relics of former feldspar grains are visible. Biotite is found in a significantly smaller amount compared to feldspars and due to intensive alteration it is difficult to distinguish it from them. It is almost completely replaced by a red-brown aggregate of clayey and dark colored minerals (Figure 14).

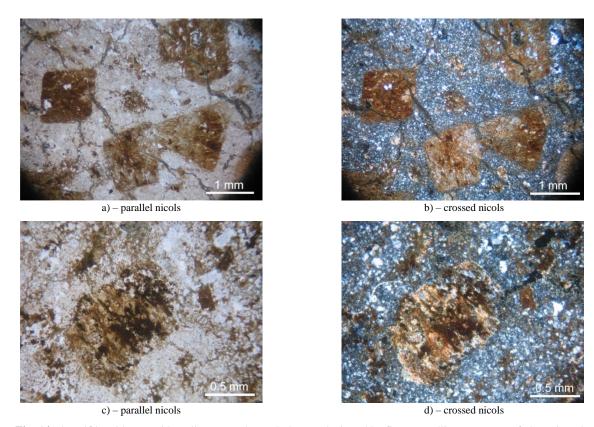


Fig. 14. a) and **b)** Feldspars with well-preserved morphology, substituted by fine-crystalline aggregate of clay minerals and sericite ± quartz. **c)** and **d)** Red-brown aggregate of clay minerals and dark-colored minerals, which has almost completely substituted the biotite (sample BD-11).

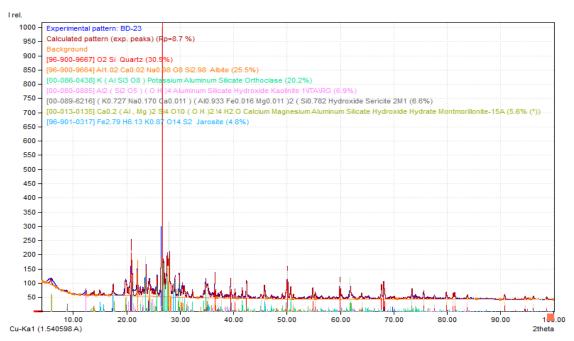


Fig. 15. X-ray diffractogram of the sample BD-23 (x = 4607505; y = 7612702; z = 635,0 m)

The groundmass is fine and unevenly grained, made up of quartz and clay minerals. In respective domains, those secondary minerals form coarsergrained depositions, with the clay phases often forming radial aggregates. In order to appropriately define the mineral composition of the rock, an X-ray structural analysis was made (Figure 15).

Within the framework of the petrographic preparation, the ore minerals are found in moderate quantity, where they grow upon the altered femic minerals, they fill the fine veinlets and are rarely present as independent grains.

Propylitization is a regional phenomenon in the examined area (Popova Šapka locality), that is, it is basically an autohydration change that affects the products of volcanic activity, most often andesites and tuffs.

As a phenomenon, propylitization basically takes place under the influence of water, which after the crystallization of petrogenic minerals stays behind in the intergranular spaces at a temperature of around 400°C. It is manifested through changes in colored minerals (mainly biotites and amphibolites), which are transformed most often into chlorite, epidote, calcite and through the release of iron sulfides (mainly pyrite) (Boev et al., 1994). It should be mentioned that in the process of propylitization, the chemism of the rock changes very little, that is, an increased amount of sulfur appears, as well as an increased amount of chemically bound water, which was also confirmed by the chemical

tests of the volcanic rocks from the PS-11 drillhole. In general, it can be said that propylitization as a phenomenon indicates that the products of the magmatic activity were enriched with easily volatile components and that the system was closed without the possibility of draining water into the surrounding environment.

Chloritization and epidotization – these types of changes within the studied rocks can be treated ambiguously. Namely, on the one hand, they are the product of regional propylitization of volcanic rocks and in such cases they are usually extensive, but with low intensity. The second case is when they are the result of hydrothermal processes and in certain levels they are more intensively present.

Chloritization is basically the replacement of colored minerals with chlorite and it occurs under the influence of moderately basic solutions at temperatures between 100 and 400°C (Reyes, 1990). However, both chloritization and epidotization within the study area can be treated as changes surrounding ore that are not directly related to mineralization.

Silicification is a hydrothermal change that has repeatedly manifested itself in the area of Borov Dol. Namely, in most cases, silicification manifests itself as syn-ore, i.e., syn-mineralization when it occurs mostly in the form of veinlets with sulphide mineralization and it metasomatically suppresses the minerals from the base rock and usually goes

together with sericitization, while causing an indicative quartz-sericite change characteristic of the spaces above the porphyry copper mineralizations (Boev et al., 1994). Another phase of silicification is significantly later and is manifested by the appearance of chalcedony finer veinlets, and often the chalcedony can be found on quartz margins.

Pyritization occurs extensively in simultaneously propylitized and hydrothermally altered andesites. Most likely, the pyrite that occurs in the form of fine-grained aggregates is of a regional character and is not related to the chalcopyrite ore-bearing phase. Pyritization occurring in gray-white coarse porphyry andesites and dark gray fine porphyry andesites that are only propylitized is quite intensive, especially in the extreme southern parts of the Borov Dol deposit (drillholes BD-4 and BD-8), the extreme northern parts of the Borov Dol deposit (drillholes BD-69, BM-14 and BM-15), as well as the Popova Šapka locality and north of it, to the open pit of the Damjan mine (drillholes PS-6, PS-4 and BD-20). Intensive pyritization was found there, and the sulfur content is up to 10%.

Carbonation in the rocks in Borov Dol is twofaceted both genetically and materially. In the phase of contact metamorphic changes, some carbonate was created on these rocks, and in the phase of deposition of ore-bearing substances, mainly no carbonate yield took place (Knežević-Djordjević et al., 1975). Calcitization, which often affects the rocks in this area, is most likely a post-mineralization alteration related to descending solutions and is manifested mostly by small irregular depositions and small veins and veinlets in the bedrock (Figures 16 and 17).

Sample BD-9 (BD-322, D = 168.0 m) is an intensively hydrothermally altered subvolcanic rock with a preserved porphyry structure, but the proportional phenocryst-matrix ratio is difficult to be determined. Of the original minerals, feldspars and biotite porphyries, as well as accessory phases, are partially preserved. Feldspars are mainly represented by aggregates of several individuals (4–7 mm parallel to elongation), strongly cracked and partially or almost completely replaced by clay minerals and carbonates.

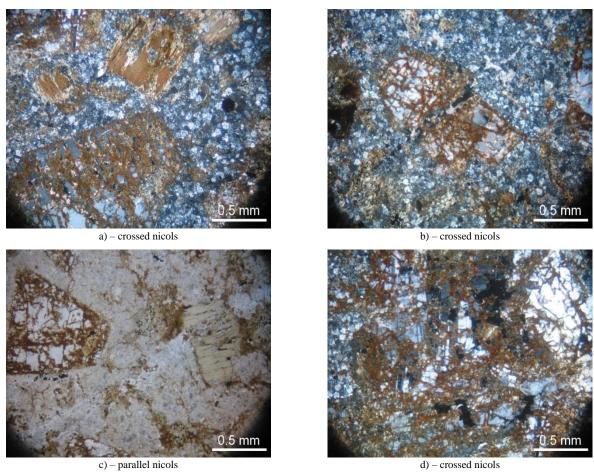


Fig. 16. a), b), c) and d) Quartz-kaolinite-calcite groundmass in a hydrothermal mineral association which completely or partially suppresses the feldspars (BD-9)

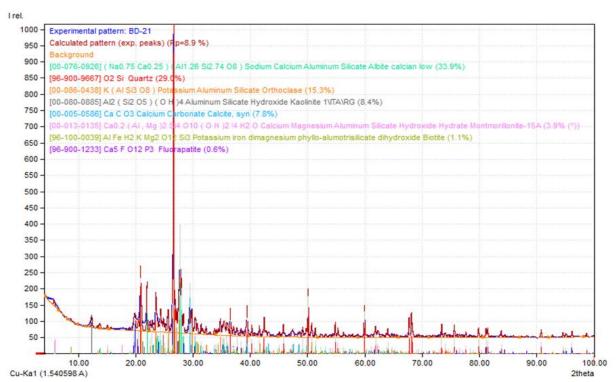


Fig. 17. X-ray diffractogram of the sample BD-21 (BD-322, D = 168,0 m)

In many cases the primary hypidiomorphic features of the phenocrysts in the aggregates are clearly visible (Figure 16). Biotite crystals are small (1–3 mm), tabular, partially replaced by chlorite. They are locally split from carbonates and quartz veinlets. Rims of dark colored and ore minerals are rarely seen parallel to the surfaces of split. Other femic minerals are impossible to distinguish, but their presence can be assumed from the existence of fine-grained accumulations of chlorite and ore minerals.

The groundmass is a fine-grained aggregate mainly of quartz, clay minerals, carbonates, dark colored and ore minerals. Fine carbonate veinlets are frequent. In order to correctly determine the mineral composition of the groundmass, an X-ray structural analysis was made (Figure 17)

It should be noted that finely sprinkled calcites are observed in the rocks in places, which probably represent a product of the regional propylitization in these areas (Boev et al., 1994).

CONCLUSION

Field and laboratory (petrographic and XRF) investigations of hydrothermal alterations have shown that in the deposit there are:

- pre-ore hydrothermal changes or autohydration processes (propylitization, chloritization and epidotization),
- syn-ore hydrothermal changes (potassium metasomatism including adularization, K-feldsparization and biotitization, sericitization and silicification), and
- post-ore hydrothermal changes (silification, argillitization and calcitization).

The hydrothermal alteration system in the deposit is extremely complex, as evidenced by the complex interrelationships of the various types of alterations, as well as the fact that certain characteristic minerals are present at a wide range of depths. Such spatial arrangement of those minerals indicates the fact that the system was of a complex and multiphase character.

The spatial position and morphology of the alterations surrounding ores are controlled by the same structural and lithological factors as the mineralization itself, and the close genetic and temporal connection between magmatic activity and hydrothermal mineralization is also indicated by the presence of intermineral intrusions and breccias.

REFERENCES

- Allibone, H. A., Cordery, R. G., Morisson, W. G., Jaireth, S. and Lindhorst, W. J. (1995): Synchronous advanced argillic alteration and deformation in a shear zone-hosted magmatic hydrothermal Au-Ag deposit at the Temora (Gidinbung) mine, New South Wales, Australia. *Economic Geology*, Vol. 90, No. 6, pp. 1570–1603.
- Beane, R. E., and Titley, S. R., (1981): Porphyry copper deposits: Part II. Hydrothermal alteration and mineralization. *Economic Ggeology*, 75th Anniversary Volume (eds. Skinner, J. B.), pp. 235–269.
- Boev, B., Serafimovski, T., Lepitkova, S. (1994): Results of the mineralogical-petrographic investigations of the core of the borehole PSH-11 (Popova Šapka), University "St. Cyril and Methodius" Skopje, Faculty of Mining and Geology Štip, 48 pages. + attachments. [In Macedonian: Боев, Б., Серафимовски, Т., Лепиткова, С. (1994): Резулиайи од минеролошко-йейрографскийе исйийувња на јадройо на дуйнайшнайй ПШ-11 (Пойова Шайка), Универзитет "Св. Кирил и Методиј" Скопје, Рударско-геолошки факултет Штип, 48 стр. + прилози.]
- Brimhall, G. H., Jr., (1977): Early fracture-controlled disseminated mineralization at Butte, Montana. *Econ. Geol.* Vol. **72**, pp. 37–59.
- Brimhall, Jr. G. H. (1979): Lithological determinations of the mass transfer mechanism of multiple-stage porphyry copper mineralization at Butte, Montana. Vein formation by hypogene leaching and enrichment of potassium-silicate protore. *Economic Geology*, Vol. **74**, pp. 556–589.
- Carson, D. J. T., and Jambor, J. L. (1974): Mineralogy, zonal relationships and economic significance of hydrothermal alteration at porphyry copper deposits, Babine Lake area, British Columbia. *Canadian Institute Mining Metall. Bull.*, Vol. 67, pp. 1–24.
- Cheney, E. S., and Trammell, J. W. (1975): Batholitic ore deposits [abs.] *Economic Geology*, Vol. **70**, pp. 1318–1319.
- Čulev, G., Mitevski, G., Tudžarov, N. (1984): Study of the calculation of ore reserves of Borov Dol Radoviš. Bučim's professional fund. [In Macedonian: Чулев, Ѓ., Митевски, Ѓ., Туџаров, Н., (1984): Елаборат за пресметката на рудните резерви на Боров Дол Радовиш. Стручен фонд на Бучим.]
- Gustafson, L. B., Hunt, J. P. (1975): The porphyry copper deposit at El Salvador, Chile. *Economic Geology*, Vol. 70, pp. 857–912.
- Jacobs, D. C., and Parry, W. T. (1979): Geochemistry of biotite in the Santa Rita porphyry copper deposit, New Mexico. *Econ. Geol.*, 74, 860–887.
- Knežević-Djordjević, V., Karamata, S., Djorgjević, P. (1975):
 Study of Hydrothermal Changes Around ore Phenomena in the Locality of Borov Dol, Faculty of Mining and Gelogy, Laboratory of Petrology Belgrade, 29 pp. + attachments. [In Serbian: Knežević-Djordjević, V., Karamata, S., Djorgjević, P. (1975): Studija hidrotermalnih izmena oko rudnih pojava na lokalnosti Borov Dol. Rudarsko geološki fakultet, Laboratorija za petrologiju Beograd, 29 str. + prilozi.]

- Lehmann, S. T., Barcikowski, J., Von Quadt, A., Heinrich, C. A., Schmid, S., Serafimowski, T. (2012): Magmatic evolution of the Bučim-Damjan-Borov Dol ore district, Macedonia. Unpubl. MSc Thesis, ETH, Zürich.
- Lowell, J. D., and Guilbert, J. M., (1970): Lateral and vertical alteration-mineralization zoning in porphyry ore deposits. *Economic Geology*, Vol. **65**, pp. 373–408.
- Meyer, C. and Hemley, J. J. (1967): Wall rock alteration. In: Barnes, H. L., ed., *Geochemistry of Hydrothermal Ore Deposits*. New York, Holt Rinehat and Winstop, pp. 166–235.
- Misra, K., (2000): *Understanding Mineral Deposits*. Kluwer Academic Publishers, Dodrecht, Netherland, 845 p.
- Petrov, D. et al. (2014): Study of the performed detailed geological surveys, with calculation of the geological ore reserves, of copper mineral raw material at the "Borov Dol" locality, municipality of Konche and municipality of Štip. Contractor "Geoengineering-M" DOOEL Skopje, investor DPTU "Borov Dol" DOOEL Radoviš, 205 p. + graphic attachments. [In Macedonian: Петров, Д. и др. (2014): Елаборай од изведенийе дейални теолошки исйражувања, со йресмейка на теолошкийе рудни резерви, на минерална суровина бакар на локалийейой "Боров Дол", ойшйина Конче и ойшйина Шйий, изведувач "Геоинженеринг М" ДООЕЛ-Скопје, инвеститор ДПТУ "Боров Дол" ДООЕЛ Радовиш, 205 стр. + графички прилози.]
- Reyes, A. G. (1990): Petrology of Philippine geothermal system and the application of alteration mineralogy to their assessment. *Journal of Volcanology and Geothermal Research*, **43**, 279–304.
- Roberts, S. A. (1973): Pervasive early alteration in the Butte District, Montana. Soc. Econ. Geol. Guide-book, Butte Field Mtg. HH1-HH8.
- Rose, A. W., (1970): Zonal relations of wallrock alteration and sulfide distribution at porphyry copper deposits. *Economic Geology*, Vol. **65**, pp. 920–936.
- Serafimovski, T., (1990): Metalogenija na zonata Lece-Halkidiki (Metallogeny of the Lece-Chalkidiki Zone (in Macedonian). – Ph.D. thesis, Faculty of Mining and Geology, Štip, 390 p.
- Serafimovski, T. (2021); Project for detailed geological research research of the Borov Dol deposit. Investor: DPTU Borov Dol DOOEL Radoviš, Execution: "Goce Delčev" University Štip, Faculty of Natural and Technical Sciences, Štip, 59 p.
- Tasev, G., Serafimovski, T. (2017): Alterations and Mineral Parageneses, Textbook. "Goce Delčev" University Štip, Faculty of Natural and Technical Sciences, 292 pp. [In Macedonian: Тасев, Г., Серафимовски, Т. (2017): Алшерации и минерални йара тенези. Учебник. Универзитет "Гоце Делчев" Штип, Факултет за природни и технички науки, 292 стр.]
- Titley, S. R. (1975): Geological characteristics and environment of some porphyry copper occurrences in the south-western Pacific. *Economic Geology*, Vol. 70, pp. 499–514.
- Titley, S. R. (1982): Mineralization and alteration in porphyry copper systems. In: *Advances in Geology of the Porphyry*

Copper Deposits in Southwestern North America (S. R. Titley, ed.). University of Arizona Press, Tucson, Arizona. pp. 37–53.

Tudžarov, N. (1973): Annual Report on the Geological Investigation Works on Borov Dol. Bučim's professional fund. [In Macedonian: Туџаров, Н. (1973): Годишен извешшај за теолошкише исшражни рабоши на Боров Дол. Стручен фонд на Бучим.] Tudžarov, N. (1993): Metallogeny of the Borov Dol Deposit.

Doctoral dissertation, Faculty of Mining and Geology —
Štip, University "St. Cyril and Methodius" — Skopje, 195
р. [In Macedonian: Туџаров, Н., (1993): Мешало тенија на нао талиштето Боров Дол, Докторска дисертација, Рударско-геолошки факултет — Штип, Универзитет "Кирил и Методиј" — Скопје, 195 стр.]

Резиме

ТИПИЗАЦИЈА НА ХИДРОТЕРМАЛНИТЕ АЛТЕРАЦИИ ВО НАОЃАЛИШТЕТО БОРОВ ДОЛ

Лазар Ѓорѓиев

Факулійет за йриродни и технички науки, Универзитет "Гоце Делчев" во Штий, бул. Гоце Делчев 10-А, й. фах 201, 2001 Штий, Рейублика Северна Македонија lazar.gorgiev@ugd.edu.mk

Клучни зборови: хидротермални алтерации; порфирски минерализации; венец на алтерација; квантифицирање

За проучување на хидротермалните алтерации во наоѓалиштето Боров Дол беа одбрани вкупно 12 примероци, од кои 10 примероци од дупнатините BD-335, BD-320 и BD-322 и 2 примерока од површинскиот коп Боров Дол. Од примероците од кои беа изработени петрографски препарати беше подготвен и материјал за анализи на рендгенска дифракција. Од спроведените испитувања се констатирани следните типови алтерации: пропилитизација, хлоритизација, епидотизација, аргилитизација, каолинизација, калцитизација, силификација, серицитизација, биотитизација, адуларизација и К-фелдспатизација. Дел од алтерациите се предрудни или го следат образувањето на бакарната минерализација (силификација, серицитизација и Кфелдспатизација), а дел се пострудни (аргилитизација, калцитизација и каолинизација). Моделот на алтерации ги следи примерите на порфирските системи и најзначајни алтерации за просторниот распоред на бакарното оруднување во наоѓалиштето Боров Дол се серицитизацијата, силификацијата и К-метасоматозата. Површинските алтерации отпаѓаат главно на лимонитизацијата и наместа на аргилитската алтерација. Пропилитизацијата го дава сегментот на надворешниот венец на измени во овој простор.