

## MINERAL ASSEMBLAGES GROUP OF MAJOR AND ASSOCIATED MINERAL PHASES IN THE KADIICA PORPHYRY COPPER DEPOSIT, EASTERN MACEDONIA

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**A b s t r a c t:** Several representative mineral associations and mixed mineral phases have been detected within the Kadiica porphyry copper deposit. It was studied mineral association in oxidation and cementation zones, where were confirmed primary relics of chalcopyrite, pyrite, magnetite, pyrrhotite, enargite, etc. In the oxidation zone were determined magnetite, rutile, hematite and sphene relics, followed by transformed limonite, goethite and unclassified Fe-oxides. In the cementation zone have been confirmed chalcocite, covellite, bornite and series of rare mixed phases of emplectite, wittichenite, mawsonite etc. Studied compositions of particular minerals shown steadiness at primary mineral phases close to the theoretical values with minor presence of admixture elements, while at mixed sulphosalt phases such as emplectite-wittichenite we witnessed irregular compositions and theoretically undefined mineral phases. In the case of wittichenite compositions ranged 38.32–39.4 % Cu, 0.27–0.83% Fe, 0.33–0.46% Zn, 38.72–39.97% Bi and 19.98–21.66% S, while for emplectite they were 13.88% Cu, 0.15% Fe, 0.09% Zn, 24.91% Bi and 60.96% S.

**Key words:** porphyry deposit; Kadiica; mineral phases; composition; Macedonia

### INTRODUCTION

The Kadiica deposit as an integral part of the mineralized area Delčevo–Pehčevo–Berovo was subject of numerous geochemical explorations and mineralogical studies during the past 4 decades. Preliminary studies of this kind started in 1974–1975 when the Geological Survey in Skopje performed preliminary explorations, on the net-like scheme (one sample per a square kilometer). After that period, during 1980–1990, some sporadically explorations took place in the Kadiica deposit wider area also by the Geological Survey in Skopje. Findings of those explorations can be found in Hadži-Petrušev (1985). Special interest was shown by the Western Company Phelps

Dodge PDX from USA, which performed detailed geological explorations of the area during 2002–2007 (Alexandrov and Bombol, 2007). Some of the later studies concerning this area of interest can be found in the works of Stojanov et al. (1995) and Hadži-Petrušev (2008a; 2008b). Some of the latest findings about the genesis of the Cu-porphyry mineralization in the Kadiica deposit were given in Volkov et al. (2008) and Tasev (2010). An serious update of mineralogical explorations of the Kadiica deposit can be found in Tasev (2010), Tasev et al. (2011), Serafimovski et al. (2013), Grudev et al. (2013), etc.

### GEOLOGICAL FEATURES

The Kadiica–Bukovik ore district is located in the easternmost Surdulica–Osogovo–Thassos metallogenic zone (Janković and Petković, 1974; Janković et al., 1980; Serafimovski, 1990; Serafimovski et al., 1995; Janković and Serafimovski, 1997, etc.), which used to be characterized by the wide development of Pb-Zn mineralization. This

regional metallogenic unit is 250 km long (Janković, 1997; Janković et al., 1997) and controlled by major fracture zones, spatial distribution of Tertiary magmatism and presence of numerous polymetallic mineralizations. The mineralizations are related to the Oligo-Miocene to Lower Pliocene, 25 to 14 Ma (Harkovska et al., 1989; Stojanov et

al., 1995; Boev et al., 1997; Boev and Yanev, 2001) calc-alkaline complexes (rhyolite-quartzlatite-dacite/andesite), which occur in intervals along the fractured zone. Although base metals mineralizations (lead and zinc sulfides) dominate within this metallogenic zone with local occurrences of molybdenite and scheelite (stockwork-disseminated type of mineralization as well as hydrothermal quartz veins), recent discovery of the porphyry copper mineralization in the Kadiica ore district exhibited inconsistency with its metallogenic specialization and previous metallogenic model of this belt (Tomson et al., 1998).

From the geological and structural aspects, the Bukovik-Kadiica area belongs to the well-known Serbo-Macedonian mass. It is built up mainly of Riphean-Cambrian and Palaeozoic metamorphic rocks represented by metadiabases and schists (*diabase-phyllitoid complex, Vlasina complex*) and diorites. The Paleozoic rocks have experienced green schist facies metamorphism and display a well-developed schistosity. Near Berovo they directly cover gneisses of the amphibolite facies (Karamata, 1974; Kockel et al., 1975, Grubić, 1980; Dumurdžanov et al., 2005).

Formation of metadiabase and schist is represented by epimetamorphic (green schist facies) basic igneous rocks and sedimentary rocks, which were defined as Kadiica formation (Zagorchev, 1987). Metadiabase and schist are cross-cut by dikes of younger gabbro and diabase. The age of the Kadiica Formation is post-Vendian and pre-Permian (Zagorchev, 1987), metadiabases and schists covering discordantly the older Frolas Formation (Vlasina complex) 530–550 Ma. At Macedonian part the metadiabase and schist built up a monocline, with foliation dipping west-southwest. To the west the belt is bounded by a Tertiary graben filled with Eocene and Pliocene sediments.

North of Belo Brdo towards Kriva Buka and Pančarevo granitoids are dominating. They are represented by granites, granite porphyries and granodiorites. These igneous rocks build up north of Belo Brdo a belt along the Macedonian-Bulgarian border. To the west they subsided into the Pehčevo-Delčevo graben, and are covered with Tertiary (Paleogene and Neogene) sedimentary formations. The oldest rocks present are diorites, and they are cross-cut by granite-porphyries and granodiorites (Figure 1). All they are referred to the Paleozoic (Stojanov et al., 1995).

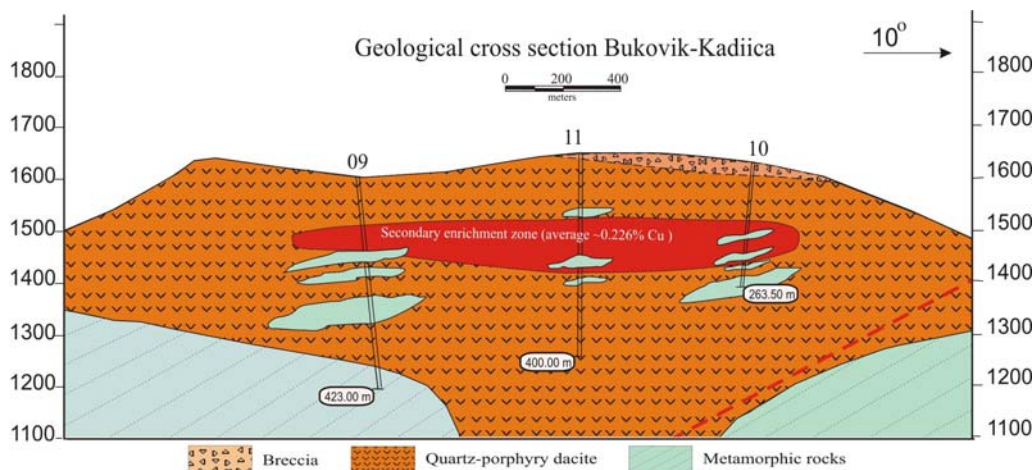


Fig. 1. Geological cross-section of the Bukovik-Kadiica locality, scale 1: 50 000 (Tasev, 2010)

The granite-porphyries are a margin facies of the Hercynian Delčevo granites. The age is proven by the presence of granite fragments within the Permian and Triassic conglomerates. The granitoids are cross-cut by diabase dikes near Pančarevo. Along an orthogonal fault system, the granitoids are hydrothermally altered. It is most probable that the hydrothermal alterations in the granitoids were related to the post-magmatic hydrothermal processes of the Tertiary volcanic rocks.

Permian sediments (sand and claystone) lie transgressively over metagabbrodiabases and granodiorites. They are distinctively red, yellow to gray, while the facial changes in vertical and horizontal direction gives them colorful look.

Triassic products are represented by masses of Lower and Middle Triassic age. The Lower Triassic has been represented by conglomerates and sandstones. Middle Triassic is concordant rela-

tive to Lower Triassic, but at several locations shows tectonic relations with granites and Paleogene sediments.

Paleogene products are represented by Eocene sediments that in accordance to their lithological features and superposition of layers can be distinguished into: gray conglomerates facies (conglomerate, breccia, sand, clay and marl), flysch facies (yellow sand with occasional intercalations of silty clays and microconglomerates with rhythmic alternation).

The Tertiary volcanism in the Bukovik-Kadiica area is represented by the volcanic dome Bukovik (1722 m) and small subvolcanic bodies of dacites and rhyodacites at Belo Brdo and Kadiica (1932 m) at a surface of about 4 km<sup>2</sup>. Small dacite bodies and dikes have been found also on Bulgarian territory within a zone of NW–SE direction as well as an extrusive dome with subvolcanic breccias at the intersection of faults with north-south and NE-SW strike (Harkovska, 1984). The Kadiica subvolcanic intrusive center is one of several Neogene dacitic plugs that have intruded a variety of metamorphic rocks of the Serbo-Macedonian massif. Several of these intrusives are associated with quartz vein stockwork development and widespread hydrothermal alteration. The subvolcanic intrusive complex is poorly exposed on Bukovik hill (1722 m a.s.l.) and consists of flow banded dacite and massive fine crystalline aphyric dacite that have been intruded by a coarser equigranular dacite phase, a quartz-, biotite- and plagioclase-phyric dacite porphyry and a postulated second dacite porphyry at depth. Near-surface pyroclastics and dacitic autobreccias are exposed along the southwest side of Bukovik hill. According to Harkovska (1984), Harkovska et al. (1989), Stojanov et al. (1995) the Kadiica intrusive complex is likely to have an age between 35 and 27 Ma (Oligocene). An extensive area of brecciation consists predominantly of tectonic breccias associated with a north-south striking major fault zone. Late stage phreatic or phreato-magmatic breccias are intercepted at shallow levels in exploration drill holes (KC-1 and KC-8).

The subvolcanic intrusive complex has been intensely altered and is cut by numerous quartz,

quartz-sulfide and sulfide veins and veinlets. Surface alteration is dominated by silicification with strong limonites as disseminations and in veins with lesser amounts of kaolinite, sericite and local alunite. Petrography of selected samples shows the presence of a near surface advanced argillic overprint characterized by alunite with local diaspore and andalusite. Alteration and metal zoning suggests the presence of a deeper dacite porphyry phase that was responsible for the formation of the large stockwork exposed at Bukovik hill. Alteration and weak copper mineralization are hosted by an Oligocene dacitic volcanic complex (Tasev, 2010), that has intruded into Paleozoic sediments, andesites and gabbros.

Copper mineralization near the town of Pehchevo was recently discovered and preliminarily estimated. The Kadiica deposit is localized at the contact between neogene quartz latites and volcanosedimentary rocks of the Vlasina Group. The host rocks represent hydrothermally altered quartzlatites and partially schists (rocks subjected to alunite, sericitization, and silicification). Copper mineralization in quartzlatites is developed as stockworks and dissemination. The known copper mineralization mainly occurs as supergene chalcocite and lesser covellite coatings on pyrite and rare chalcopyrite. Traces of chalcocite occur far below the base of oxidation. Primary copper grades are probably around 0.1% Cu or less and chalcopyrite is decidedly scarce. The copper distribution clearly defines the leached zone and an enriched copper zone. The copper distribution in the deeper part of most holes drilled does not define a well developed positive copper gradient. Major ore minerals are represented by pyrite, chalcopyrite, magnetite, and hematite. Enargite, pyrargyrite, tetrahedrite, galena, sphalerite and pyrrotite are less common. Quartz is the main gangue mineral. In terms of morphology, link with porphyry intrusion, and composition, the deposit is classed with the copper porphyry type. Some of the aforementioned minerals and wallrock alterations are also typical of sulfidized epithermal deposits. The zone incorporates systems of sheeted bodies and discordant dikes of quartzlatites with an absolute age within 24–12 Ma.

## METHODOLOGY

An intensive field sampling programme took place within the boundaries of an active Kadiica prospect, near the city of Pehčevo. Samples were

taken from cores of exploration drill holes. In total 27 ore samples were taken and were prepared the same number of polished sections. Study started

with microscopic observations under a Zeiss Axio-lab Pol reflected light polarized microscope equipped with ZEISS MC 80 DX (Databack D4) analogue camera and state of the art LEICA DMP 4500 reflected light polarized microscope equipped with digital camera LEICA DFC 450 (at magnifications within range  $\times 100$  to  $\times 630$ ) in the optical laboratory of the Faculty of Natural and Technical Sciences, University "Goce Delčev" – Štip, R. Macedonia. Microscopic observations of the most interesting polished sections were subjected to the quantitative elemental electron microanalysis (EPMA/EDS) in two stages. First of all we used an older JEOL Superprobe 733 with the following standards; for Bi-synthetic  $\text{Bi}_3\text{S}_3$ , for Ag-synthetic Ag, for Cu, Fe and S-synthetic  $\text{CuFeS}_2$ , for Se-synthetic PbSe, for Pb-synthetic PbS, for As-chemically

analyzed and checked for homogeneity  $\text{FeAsS}$ ,  $I = 0.8 \text{ A}$ ,  $U = 25 \text{ kV}$ . As the study proceeded we have switched to the JEOL JXA-8200 Electron Probe Micro-Analyser WD/ED Combined Microanalyser (equipped with a SE- and BSE-detector, five-WDS crystal spectrometer and an EDS analyser) in the analytical facilities at the Institute of Geochemistry and Petrology, ETH-Zurich, Switzerland. The selected electron beam conditions were a beam current of 20 nA at an acceleration voltage of 15 kV. The microprobe of this type and model was able to analyze elements from Be through U with the analytical sensitivity ranges from a low of a few parts per million for optimum cases, to a typical detection limit of several hundred ppm while the precision was in the range of 0.X% relative and accuracy as good as 1–2%.

## RESULTS AND DISCUSSION

The latest findings of the current study of the Kadiica deposit have confirmed that the main ore minerals were an iron and iron-titanium ones: magnetite and ilmenite at higher hypsometric levels and pyrite in depth. The quartz-pyrite-chalcopyrite assemblage was deposited in the form of veinlets, disseminated minerals and nests through the entire deposit.

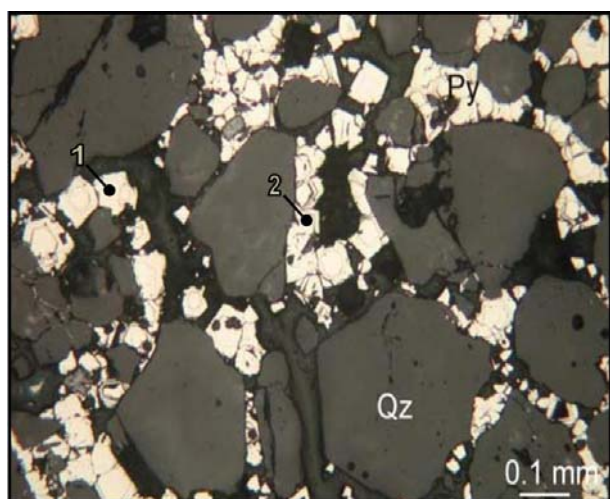
Primary copper sulfides determined within this study were chalcopyrite and bornite, and also a certain sulfoarsenides – enargite and tennantite, deposited simultaneously with pyrite and in most cases fully included in pyrite grains. Occasionally chalcopyrite (probably later generation) fills spaces or fissures in pyrite. In regards to quantitative ratio, primary copper minerals are of secondary importance or sporadic. Quantitatively their occurrence in different forms varies significantly from sample to sample. As secondary products of chalcopyrite and chalcocite occur covellite and secondary chalcocite. In quantitative ratio chalcocite is secondary to sporadic. Also, within the sporadic minerals group were determined copper sulfobismutides – emplectite and wittichenite. Copper mineralization is poor, which is typical of porphyry systems. However, having in mind data from the identified types of hydrothermal alterations (Tasev, 2010; Serafimovski et al., 2013), indicative for peripheral parts of the porphyry system and low copper concentrations in chemical analyses, we assume that samples were taken from exploration drill holes that did not reach the real copper porphyry mineralization in fact.

### *Mineralogy*

The mineralogy of the Kadiica deposit is complex (Stojanov et al., 1995) and the latest data about the mineralogical composition of the Kadiica deposit can be found in detailed electron microprobe study of Tasev (2010), where the mineral presence and their association has been brought to an higher level of knowledge. With up to date studies has been confirmed that within the Kadiica deposit can be found the following ore minerals: pyrite, pyrrhotite, chalcopyrite, magnetite, rutile, hematite, bornite, enargite, tetrahedrite, tennantite, chalcocite, digenite, covellite, malachite, azurite, luzonite, mawsonite, stannoidite, arsenosulvanite, sylvanite etc. (Alexandrov and Bombol, 2007; Tasev, 2010). Traces of colusite (Cu-Sn-V-As-Fe sulphide), sphalerite and galena have also been reported (Tasev, 2010) quite similar to genetically same deposits worldwide (Madera, 2000). The most common copper sulfides display a very distinctive replacement sequence from bornite  $\rightarrow$  digenite  $\rightarrow$  chalcocite  $\rightarrow$  exsolution covellite. Pyrite is by far the most abundant 'ore' mineral present, but chalcopyrite, sphalerite, tennantite-tetrahedrite and enargite are also abundant. Gold occurs as small grains dispersed in sulphides (pyrite, chalcopyrite, enargite, galena). Zoning and replacement textures are common, pointing to numerous, discrete, mineralizing events. Petrographical and textural studies suggest the following main stages of mineralization: (i) pyrrhotite, pyrite, chalcopyrite; (ii) magnetite, hematite, rutile, scheelite; (iii) molybdenite, chalcopyrite, pyrite, sphalerite, native gold, tetrahedrite, enargite, bornite; (iv) enargite,

bornite, chalcocite, chalcopyrite, pyrite, galena, sphalerite, tetrahedrite, tennantite, luzonite, selligmanite, proustite, pearceite, (v) calcite, barite, siderite (including the Mn-variety, 'oligonite'), hematite (after magnetite-'martite'). Of the nonmetallic minerals the most common were quartz, calcite, barite etc.

The most common ore mineral is **pyrite** ( $\text{FeS}_2$ ), which occurs in different massive, net-like and irregular aggregates (Figure 2a and b). In reflected light can be seen zonal growth of pyrite meta-crystals. Massive pyrite crystals sometimes reach up to 0.5 cm. At higher magnifications we observed that often pyrite crystals are strongly cracked and metasomatically interlaced with secondary minerals. Another feature noticed during the microscopic observations was that chalcopyrite grains were enclosed within massive pyrite minerals (Figure 5a and b).



a)



b)

**Fig. 2.** a) Pyrite (Py) net-like structure in quartz (Qz) matrix; b) xenomorphic structure of pyrite (Py).

Electron microprobe analyses of pyrite have shown relatively uniform composition (Table 1).

Table 1

*Chemical composition of pyrite (points 1, 2 and 3) from the Kadiica deposit*

Element	Chemical analysis (%)		
	1	2	3
Cu	0.09	0.21	0.23
S	52.77	51.75	53.18
Fe	45.8	46.99	45.91
Sb	0.02	0.02	n.d
As	0.04	0.02	0.05
Co	0.01	0.15	0.04
Pb	0.34	0.32	0.13
Ni	n.d.	0.21	0.32
Zn	n.d.	0.11	0.03
$\Sigma$	99.07	99.78	99.89

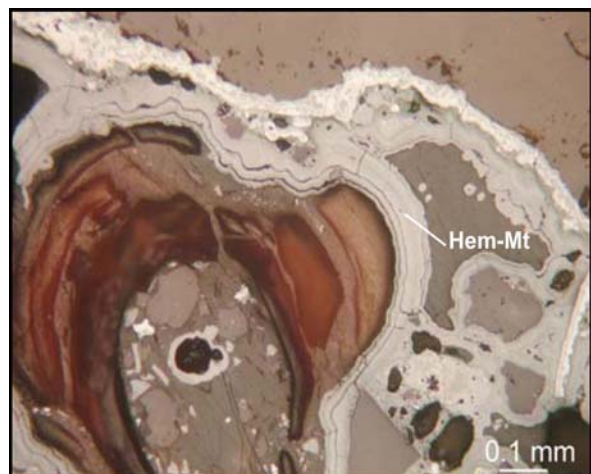
Unlike As (here ranging 0.02–0.05 wt%), very few studies have documented high Cu concentrations in pyrite, also known as “cuprian pyrite”. Although at some samples it was obvious that most Cu occurs in pyrite as inclusions of Cu-sulfides (e.g. chalcopyrite; see Figures below), our study confirmed that Cu can be accommodated within the pyrite structure in significant amounts (in our study 0.09–0.23 wt%), which is similar or close to findings of some other authors studying this matter elsewhere (Frenzel and Ottemann, 1967; Einaudi, 1968; Clark, 1970; Radcliffe and McSween, 1970; Pacevski et al., 2008). As it is already known, in hypogene Cu deposits, copper is usually supersaturated with respect to Cu-bearing sulfides forming chalcopyrite ( $\text{CuFeS}_2$ ), bornite ( $\text{Cu}_5\text{FeS}_4$ ) and chalcocite ( $\text{Cu}_2\text{S}$ ). Relatively high contents of Cu reported in pyrites from the Kadiica deposit, which can reach up to parts of wt.%, indicate that pyrite may act as an important Cu scavenger, and therefore play an unforeseen control on this element during ore system evolution similarly as it was mentioned by Reich et al., (2013).

**Hematite ( $\text{Fe}_2\text{O}_3$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ )** in general occur in form of fine lamellar boundary depositions over the rock-forming minerals (Figure 3).

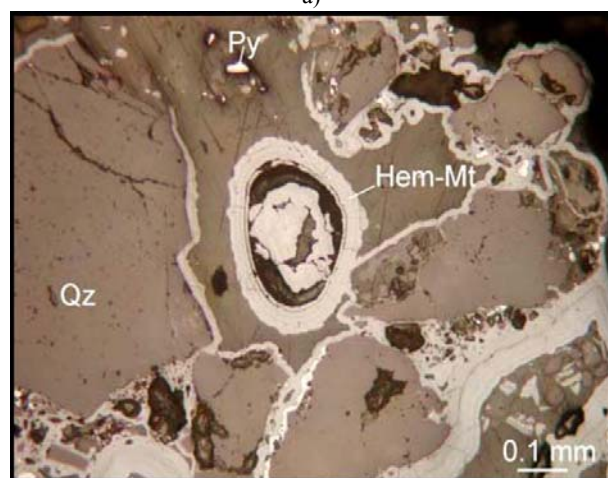
This is in accordance with the fact that the final porphyry mineralization was controlled by sulfate reduction, which started with magnetite crystallization (probably accompanied by decreasing pH and correspondingly increasing  $f\text{O}_2$ ) while



hematite formed after sulfate reduction lowered the pH sufficiently and the  $fO_2$  reached the hematite–magnetite oxygen fugacity buffer (Sun et al., 2013; 2015). Also, we would like to stress out that reducing wallrocks may also contribute to sulfate reduction and porphyry mineralization. Further, we have to mention that hematite and magnetite occurred as regular mineral within massive pyrite grains, too. At the more advanced stages of magnetite alteration forms spongy hematite, with cemented rutile (lamella or grains).



a)



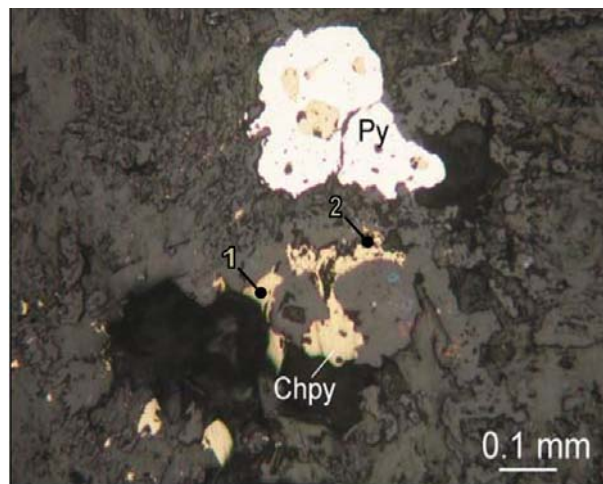
b)

**Fig. 3.** a) Collomorph structure of hematite-magnetite (Hem-Mt); b) collomorph structure of hematite-magnetite (Hem-Mt) associated with pyrite (Py) in quartz (Qz) matrix

Although rarely **ilmenite** ( $FeTiO_3$ ) was identified as grains of white-grayish color light brown internal reflections and low degree of polishing while at crossed polars (nicols).

**Chalcopyrite** ( $CuFeS_2$ ) can be found in several forms, as an independent mineral, as fillings in pyrite, droplet-like inclusions in pyrite. At places chalcopyrite occur all together with bornite and

chalcocite (see Figures 4a and 4b and below). These observations confirmed existence of two independent minerals assemblages: an earlier (quartz-magnetite-bornite-chalcopyrite) and later one (quartz-pyrite-chalcopyrite).



a)



b)

**Fig. 4.** a) Association of pyrite (Py) and chalcopyrite (Chpy) in massive quartz (grey); b) droplet-like inclusions of chalcopyrite (Chpy) in pyrite (Py)

Immediately after the formation of the first ore assemblage (quartz-magnetite), the deposition of the quartz-magnetite-bornite-chalcopyrite assemblage followed in form of veins, veinlets and lenses. It is the most probable that first chalcopyrite, magnetite and bornite were deposited during its formation and then again chalcopyrite in which inclusions of magnetite, bornite, tennantite and pyrrhotite can be observed (see Figures below). At that time a number of rare minerals were deposited, primarily wittichenite, sylvanite etc. (Tasev, 2010; Serafimovski et al., 2013). This assemblage formation conditions probably were low-sulfur and low-oxide, which explains the formation of telluride and selenide that is very similar to study elsewhere (Georgiev, 2009a, 2009b).

Before the beginning of the next stage, intensive cracking and faulting of the orehosting rocks occurred in the deposit (Figure 4b). The rock faulting and cracking was followed by the deposition of the economically most significant quartz-pyrite-chalcopyrite assemblage. Temperature of the solutions probably was in the range 450–330°C (Tasev, 2010). The quartz-pyrite-chalcopyrite assemblage was deposited in the form of veinlets, disseminated minerals and nests through the entire orebody. During its formation it penetrated the area of quartz-magnetite-bornite-chalcopyrite assemblage thus enriching it in Cu, Au and Mo. The main ore minerals are chalcopyrite and pyrite, pyrite being in larger quantities than chalcopyrite. The secondary minerals observed are bornite and Cu-rich pyrite, and the rare ones are enargite, tennantite-tetrahedrite, sphalerite, galena, magnetite, hematite, molybdenite, marcasite, arsenopyrite, etc. (Tasev, 2010; Serafimovski et al., 2013).

Table 2

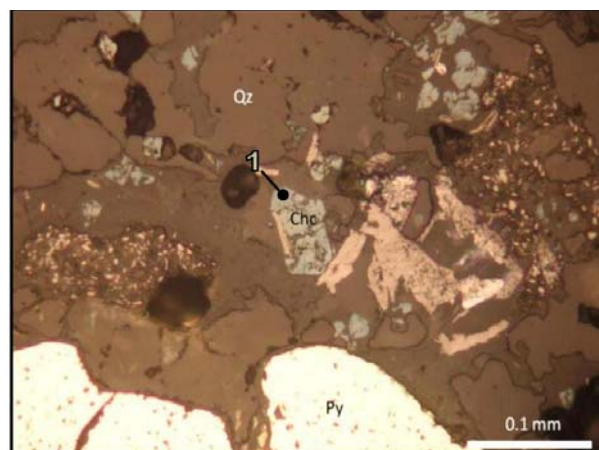
*Chemical composition of chalcopyrite (points 1, 2 and 3) from the Kadiica deposit*

Element	Chemical analysis (%)		
	1	2	3
Cu	32.80	36.61	35.72
Fe	29.70	29.53	28.68
Zn	0.27	0.02	0.07
S	37.21	33.62	34.65
Σ	99.98	99.78	99.12

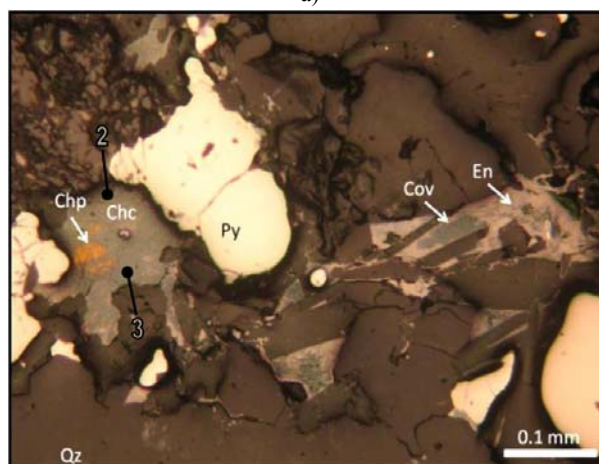
**Chalcocite (Cu<sub>2</sub>S)** was observed and determined along fissures and spaces within pyrite where it has been deposited as late chalcocite (Figure 5). This mineral often occurs in association with chalcopyrite where it forms fine veinlets within. It is not rare situation where chalcocite was replaced by covellite.

These chalcocite microscopic observations were confirmed by electron microprobe analysis findings, as shown in Table 3.

Also, very often it cuts through chalcopyrite and bornite aggregates and forms fine veinlets in them. Chalcocite occurs in association with enargite, tennantite and mawsonite. At places chalcocite has been replaced completely by covellite. Chalcocite is later than chalcopyrite and bornite and formed simultaneously with enargite, tennantite and mawsonite.



a)



b)

**Fig. 5.** a) Association of pyrrhotite (Po) in massive pyrite (Py) and Cu-sulfides (bornite – Bor, chalcocite – Chc); b) droplet-like inclusions of chalcopyrite (Chp) and chalcopyrite-pyrrhotite (bird's eye) in pyrite (Py)

Table 3

*Chemical composition of chalcocite (points 1, 2 and 3) from the Kadiica deposit*

Element	Chemical analysis (%)		
	1	2	3
Cu	75.82	77.39	78.23
Fe	1.39	1.02	0.11
Zn	0.57	0.13	0.07
As	0.02	0.03	0.08
Co	0.02	0.01	0.01
Pb	0.01	0.24	0.05
S	22.16	22.46	21.87
Σ	99.99	101.28	100.42

**Pyrrhotite (Fe<sub>1-x</sub>S)** was another high temperature mineral that was confirmed by the chemical analysis (electron microprobe) to be present in Kadiica's mineral association (Table 4).

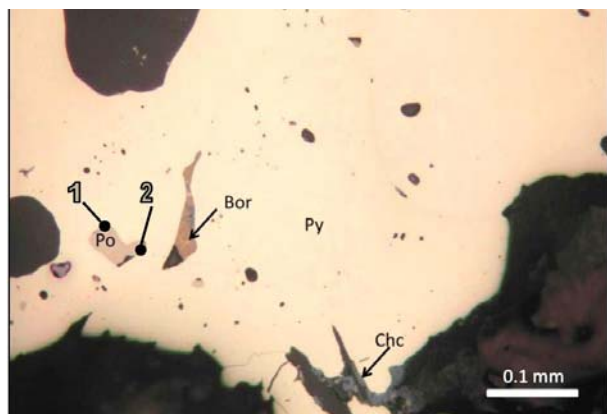


Table 4

*Chemical composition of pyrrhotite (points 1, 2 and 3) from the Kadiica deposit*

Element	Chemical analysis (%)		
	1	2	3
Cu	1.31	0.11	0.19
Fe	57.67	60.43	59.38
Zn	0.66	0.13	0.33
Sb	n.d.	0.05	0.19
As	n.d.	0.09	0.06
S	40.09	38.61	38.93
$\Sigma$	99.73	99.42	99.08

In general microscopic observations showed that it occurs mainly as droplet-like forms included in pyrite grains (Figure 6a), although occasionally were determined so-called bird's eye textures formed as fine mixture of pyrrhotite and later chalcopyrite (Figure 6b).



a)



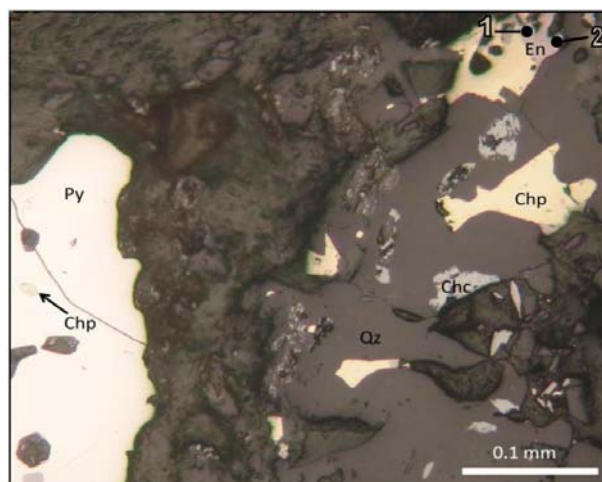
b)

**Fig. 6.** a) Association of pyrrhotite (Po) in massive pyrite (Py) and Cu-sulfides (bornite – Bor, chalcocite – Chc); b) droplet-like inclusions of chalcopyrite (Chp) and chalcopyrite-pyrrhotite (bird's eye) in pyrite (Py)

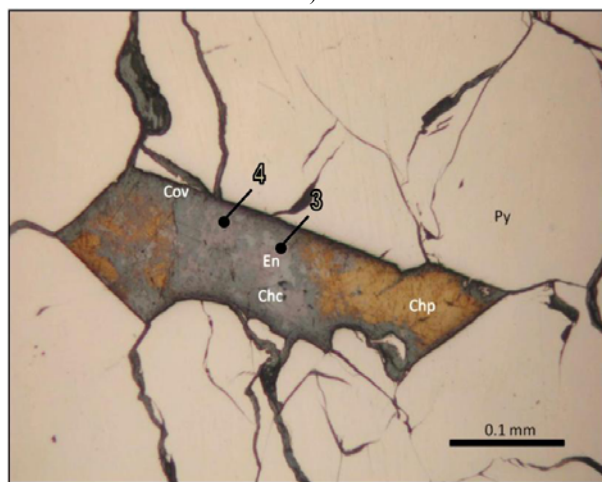
The aforementioned bird's eye texture resulted as development of an intimate intergrowth of compositionally distinct phases, due to unstable

conditions pyrrhotite has been replaced by chalcopyrite, very similar as mentioned for the elatsite deposit (Dragov and Petrunov 1994, 1996; Georgiev 2005, 2009a, 2009b).

**Enargite ( $\text{Cu}_3\text{AsS}_4$ )** occurs exclusively in pyrite and chalcopyrite (Figure 7a) in form of irregular fine-grained aggregates while scarcely it occurred in chalcocite, too (Figure 7b).



a)



b)

**Fig. 7.** a) Association of enargite (En) with massive chalcopyrite (Chp); b) fine-grained enargite (En) within chalcocite (Chc) and covellite (Cov) replace massive grain of chalcopyrite (Chp)

Enargite observed microscopically was subjected to an analysis, which results are given in Table 5.

Abundant pyrite accompanied by enargite, lesser chalcopyrite, chalcocite and occasional molybdenite point out to an hypogene origin of components, being related to the sericitic alteration, and thus providing the highest grade hypogene ore, which is similar to deposits elsewhere (Sillitoe, 1973)



Table 5

Chemical composition of enargite (points 1, 2, 3 and 4) from the Kadiica deposit

Element	Chemical analysis (%)			
	1	2	3	4
Cu	51.03	51.66	49.54	49.69
Fe	0.40	0.45	0.31	0.97
Zn	0.45	0.26	0.07	0.01
As	14.54	14.70	16.81	17.21
Sb	0.49	0.28	1.03	0.05
S	32.98	32.64	32.12	32.01
Σ	99.89	99.99	99.88	99.94

**Tennantite ( $\text{Cu}_{11}\text{FeAs}_4\text{S}_{13}$ )** forms single irregular form grains in pyrite and chalcocite as well (Figure 8).

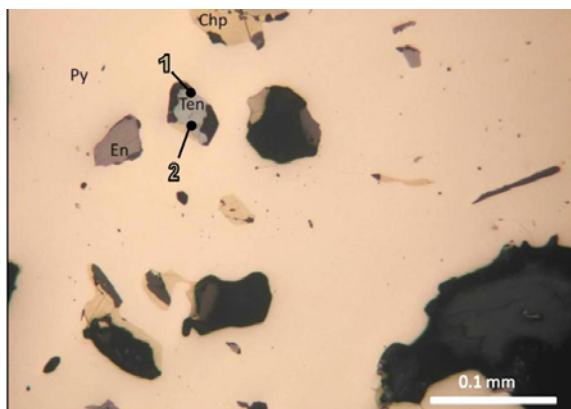


Fig. 8. a) Association of tennantite (Ten) with enargite (En), chalcocopyrite (Chp) and pyrrhotite (Po) in massive pyrite (Py).

Electron microprobe analyses of the microscopically observed tennantite have shown that this mineral exhibits compositional variations in which base metals substitute for copper, Sb for As, while absence of Te from the mineral composition speaks itself for the mineralizing fluid (Table 6).

As we already know porphyry copper deposits can be grouped into an arsenic-poor class, without arsenic minerals, and an arsenic-rich class, of equal size, with arsenic minerals. The presence of tennantite-group minerals, which are the most frequently observed arsenic minerals, beside enargite/luzonite and arsenopyrite that are less common, classifies the Kadiica deposit in the later ones. The occurrence of arsenic minerals is closely related to hydrogen metasomatism (sericitic, intermediate argillic, and advanced argillic alteration). It is the most probable that fluid evolution paths were leading to low  $\text{K}^+$ ,  $\text{Na}^+$ , and  $\text{Cu}^+$  versus  $\text{H}^+$  ion activity ratios, which promoted deposition of arsenic sulfosalts (Schwartz, 1995). The As concentrations of hydrothermal fluids generally

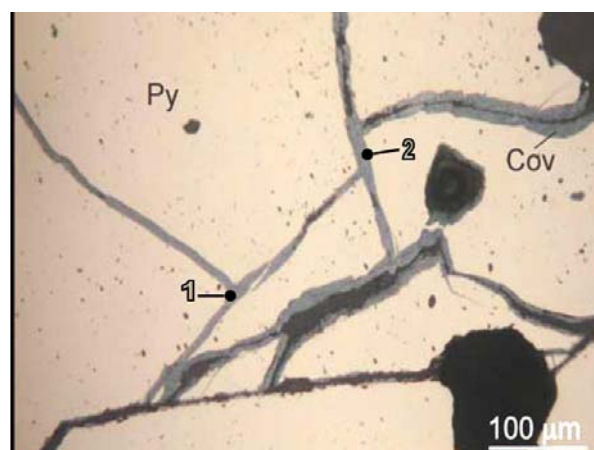
were sufficiently high to allow precipitation of tennantite as a stable phase at low temperatures and low  $\text{Cu}^+/\text{H}^+$  activity ratios of the hydrothermal fluid (Tasev, 2010).

Table 6

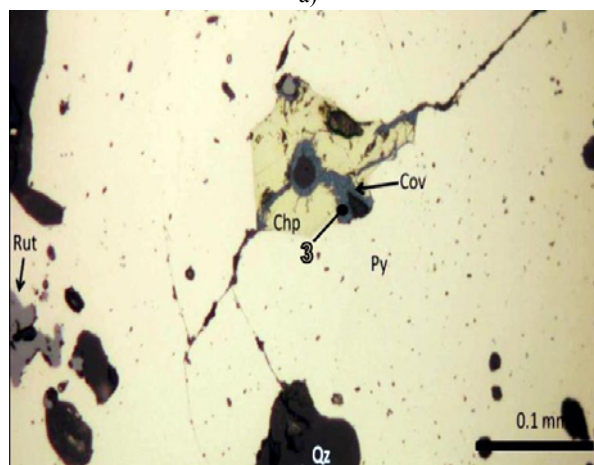
Chemical composition of tennantite (points 1 and 2) from the Kadiica deposit

Element	Chemical analysis (%)	
	1	2
Cu	45.06	44.66
Fe	5.69	2.05
Zn	0.69	0.20
As	16.42	16.90
Sb	0.72	0.38
S	31.41	35.80
Σ	99.99	99.99

**Covellite ( $\text{CuS}$ )** as secondary mineral occurs along cracks within pyrite and around chalcocopyrite distinguished by its dark blue to blue-greenish color (Figure 9).



a)



b)

Fig. 9. a) Covellite (Cov) veinlets network in massive pyrite (Py); b) massive rutile grain (Rut) locked in pyrite (Py) as alteration of magnetite while in the center massive chalcocopyrite (Chp) has been transformed into covellite (Cov)

Microprobe analyses have shown almost theoretical composition of covellite with up to 3.40% wt Fe as an impurity (Table 7).

Table 7

*Chemical composition of covellite  
(points 1, 2 and 3) from the Kadiica deposit*

Element	Chemical analysis (%)		
	1	2	3
Cu	66.39	70.20	68.80
Fe	n.d.	1.31	3.40
Zn	n.d.	0.09	0.07
Ag	0.001	n.d.	n.d.
Bi	0.0001	n.d.	0.0003
Se	0.0001	n.d.	n.d.
Te	0.0001	n.d.	n.d.
S	33.45	28.70	27.83
Σ	99.84	100.30	100.10

Otherwise, covellite, as microscopic observations and chemical analyses have shown, sometimes occurs in association with pyrite, enargite, chalcocite while the most common association was chalcocite, covelite and bornite, which is direct product of supergene enriched ores (layer) at the Kadiica deposit similar to some deposits elsewhere (Schwartz, 1966; Milu et al., 2004). All this different copper-ore mineral assemblages are a function of the chemical composition of the fluid phase and the pressure and temperature conditions affecting the fluid. Thus, specific mineral associations may vary in a deposit as a function of space and time as the composition of the hydrothermal fluid changes.

**Bornite ( $\text{Cu}_5\text{FeS}_4$ )** occurs very rarely and it has been associated to chalcopyrite and chalcocite (Figure 10).

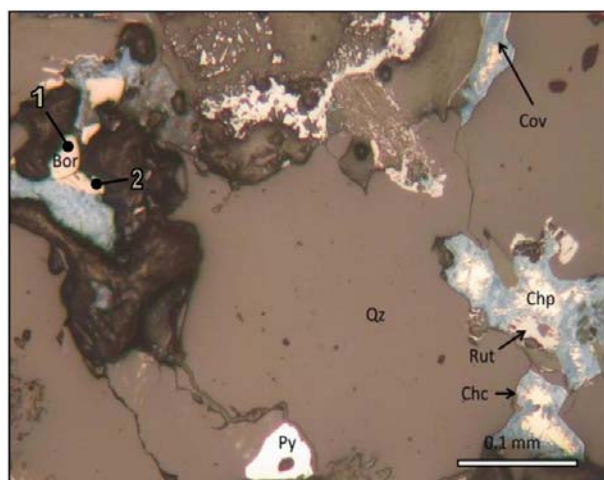


Fig. 10. Association of massive pyrite – (Py) and Cu-sulfides (chalcopyrite – Chp; bornite – Bor; chalcocite – Chc; covellite – (Cov) and rutile – (Rut)

Its forms are irregular mainly. It occurs within pyrite in form of inclusions and as mawsonite decomposition, too. Electron microprobe analyses have shown almost ideal composition of bornite with very small impurities of Zn, As and Sb (Table 8).

Table 8

*Chemical composition of bornite  
(points 1, 2, 3 and 4) from the Kadiica deposit*

Element	Chemical analysis (%)			
	1	2	3	4
Cu	64.15	62.92	63.10	63.13
Fe	8.09	11.20	9.23	11.21
Zn	0.44	0.02	0.22	0.05
As	0.03	0.11	0.05	n.d.
Sb	0.02	0.10	0.07	0.06
S	27.25	25.40	27.20	25.60
Σ	99.89	99.75	99.87	100.05

Transitions from chalcopyrite to bornite and from bornite to chalcocite, as in Figure 10 above (and Figure 11 below; analysis points 3 and 4 in Table 8), suggest that multiple episodes of sulfide deposition occurred. Chalcopyrite precipitated first while bornite replaced chalcopyrite.

**Mawsonite ( $\text{Cu}_6\text{Fe}_2\text{SnS}_8$ )** forms a single teardrop grains within bornite and chalcopyrite (Figure 11).

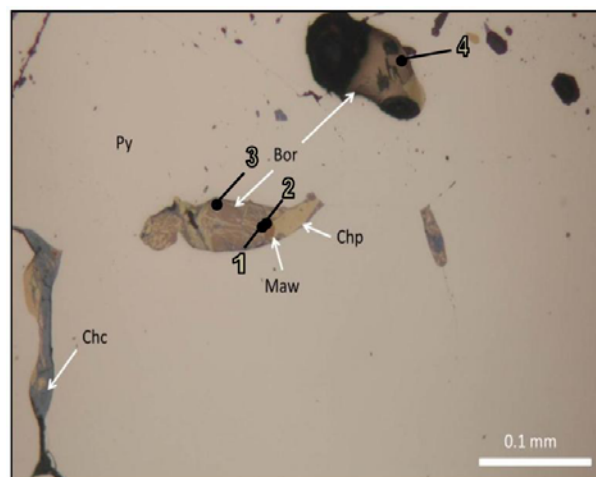


Fig. 11. Association of mawsonite (Maw), bornite (Bor) and chalcopyrite (Chp). In left part of the photo chalcocite (Chc) aggressively replaces chalcopyrite (Chp)

Mawsonite microscopically observed was analyzed at two points under the electron microprobe (Table 9).

Table 9

*Chemical composition of mawsonite (points 1 and 2) from the Kadiica deposit*

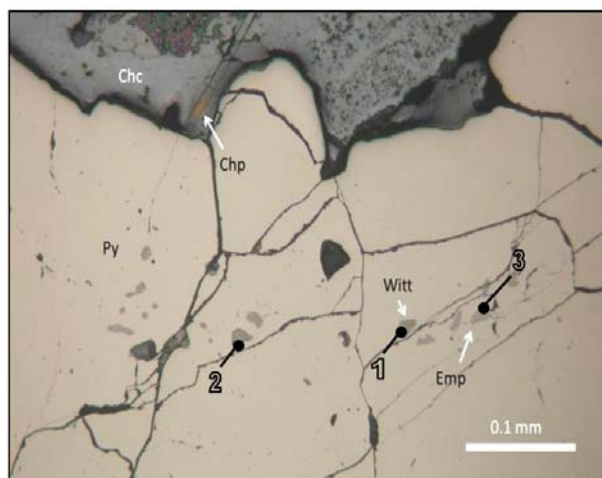
Element	Chemical analysis (%)	
	1	2
Cu	43.20	44.20
Fe	13.10	13.87
Sn	13.70	11.90
Se	1.10	1.00
S	28.80	29.20
Σ	99.90	100.17

As can be seen from the table above, mawsonite shows almost ideal chemical composition with slight selenium impurities not more than 1.10% wt Se.

The mineralogical setting as shown above (mawsonite-bornite-chalcopyrite) is very similar to findings of Lee et al. (1975) where it is clearly stated that mawsonite is stable at temperatures below 390°C and that it decomposes to bornite and chalcopyrite ( $\pm$ stannoidite) above this temperature, which in our case is an indication of upper temperatures range.

**Wittichenite ( $\text{Cu}_3\text{BiS}_3$ ) and emplectite ( $\text{CuBiS}_2$ )** were determined as single or aggregate teardrop-like inclusions within pyrite (Figure 12). However their occurrence was of limited character.

Electron microprobe analysis results of points 1, 2 and 3 plotted at Figure 12 is given in Table 10.



**Fig. 12.** Association of wittichenite and emplectite teardrop-like minerals in pyrite, while in the uppermost part [the chalcopyrite has been intensively replaced by chalcocite

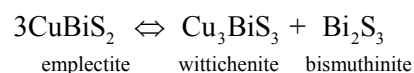
Table 10

*Chemical composition of wittichenite (points 1 and 2) and emplectite (point 3) from the Kadiica deposit*

Element	Chemical analysis (%)		
	1	2	3
Cu	38.32	39.43	13.88
Fe	0.83	0.27	0.15
Zn	0.46	0.33	0.09
Bi	38.72	39.97	24.91
S	21.66	19.98	60.96
Σ	99.99	99.98	99.99

As we already know the Cu-Bi-S system, an essential part of several multicomponent sulphosalt systems, contains four mineral species: wittichenite ( $\text{Cu}_3\text{BiS}_3$ ), cuprobismutite ( $\text{Cu}_{10}\text{Bi}_{12}\text{S}_{23}$ ), emplectite ( $\text{CuBiS}_2$ ) and hodrushite ( $\text{Cu}_8\text{Bi}_{12}\text{S}_{22}$ ). Within this particular system are present, and as can be seen from results in Table 10 above, wittichenite and emplectite, which are known to have stability ranges extending from higher temperatures down to below 200°C, more probably within range 200–300°C (Wang, 1989, 1994). Also the absence of hodrushite excludes probability of very low temperatures (Buhlmann, 1965, 1971; Sugaki and Shima, 1971; Sugaki, 1972; Chen and Chang, 1974; Sugaki et al., 1978; Wang, 1994).

In this direction we would like to point out to the work of Chen and Chang (1971), which reported that in the system  $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_2-\text{Bi}_2\text{S}_3$ ,  $\text{CuSbS}_2$  and  $\text{CuBiS}_2$  do not form a complete solid solution series, rather an immiscibility gap was reported at the Bi-rich end. Also, because the synthesis of emplectite from pure elements, or from  $\text{Cu}_2\text{S} + \text{Bi}_2\text{S}_3$ , is very sluggish, particularly if the high temperature form, the re-equilibration processes may occur (Wang, 1989). The analysis showed a composition effect related to changing Bi content. In pure emplectite, the first strong endothermic reaction detected was initiated at about 472°C and has an energy of 2.45 kJ/mol. One sample was heated in the DSC to just above the 472°C heat effect and then cooled. X-ray study showed the presence of wittichenite plus bismuthinite consistent with the decomposition reaction:





## CONCLUSION

Studied mineral groups within the Kadiica deposit clearly point out to an existence of three types of mixed mineralization dictated by the spatial distribution of mineral phases. In the near surface parts dominate oxide-hydroxide parageneses lead by limonite with magnetite-hematite-rutile relics etc. In the cementation zone, which basically defines the porphyry character of mineralization in the Kadiica deposit, dominant are covellite, chalcocite, bornite and undefined mixed phases, followed by relics of pyrite, chalcopyrite, enargite,

pyrrhotite etc., associated with sulfosalt phases where has been determined emplectite, mawsonite, wittichenite and undefined transformation of wittichenite. At depth dominate vein and disseminated chalcopyrite, pyrite and magnetite.

Defined mineral groups reflect the porphyry character of the deposit, mainly, vertically, while the lateral range has been defined by the cementation mineralization with chalcocite and covellite as dominant minerals.

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## Резиме

**ГРУПА НА МИНЕРАЛНИ СОСТАВИ НА ГЛАВНИТЕ И ПРИДРУЖНИ МИНЕРАЛНИ ФАЗИ ВО НАОЃАЛИШТЕТО НА БАКАР КАДИИЦА, ИСТОЧНА МАКЕДОНИЈА**

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**Клучни зборови:** порфирско наоѓалиште; Кадица; минерални фази; состав; Македонија

Неколку репрезентативни минерални асоцијации и мешани минерални фази беа одредени во рамките на порфирското наоѓалиште на бакар Кадица. Беа проучувани минерални асоцијации во зоните на оксидација и цементација, каде беа потврдени примарни реликти на халкопирит, пирит, магнетит, пиротинт, енаргит и др. Во зоната на оксидација беа потврдени реликти на магнетит, рутил, хематит и сфен проследени со трансформиран лимонит, гетит и недодефинирани Fe-оксиди. Во зоната на цементација беше потврдено присуство на халкоцит, ковелит, борнит и серија ретки мешани минерални фази на емплектит,

витихенит, маусонит и др. Проучуваните минерални состави на одредени минерали покажаа стабилност кај примарните минерални фази блиски до теоретските вредности со мало присуство на елементи примеси, додека кај мешаните сулфосолни фази како што е емплектит-витихенит бевме сведоци на неправилни состави и теоретски недодефинирани минерални фази. Во случајот на витихенитот составите се движеа во опсег 38.32–39.4 % Cu, 0.27–0.83% Fe, 0.33–0.46% Zn, 38.72–39.97% Bi и 19.98–21.66% S, додека кај емплектитот тие изнесуваа 13.88% Cu, 0.15% Fe, 0.09% Zn, 24.91% Bi и 60.96% S.