

Faculty of Natural and Technical Sciences, University “Goce Delčev”-Štip, R. Macedonia with a grant from the CEI-ES Know How Programme organize



**1st INTERNATIONAL WORKSHOP
ON THE PROJECT**

**Environmental Impact assessment of the Kozuf
metalogenic district in southern Macedonia in
relation to groundwater resources, surface
waters, soils and socio-economic
consequences (ENIGMA)**

PROCEEDINGS

**Edited by:
T. Serafimovski & B. Boev
Kavadarci, 10th October 2013**

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METALLOGENY OF THE KOZUF ORE DISTRICT, R. MACEDONIA

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Abstract

Metallogeny of the Kozuf ore district have been related to the Alpine Neogene tectonic structures, recent Kozuf volcanism (1.8-6 Ma), representative morphostructural forms related to that young volcanism and jasperoids as a setting where have been localized the major gold mineralizations. The Alshar Au-Sb-As-Tl-Hg and Dudica Cu-Au-Ag-Pb deposits are the most representative ore-bearing localities within the complex Kozuf ore district. The northern most part of this district shows higher mineralizing potential than the southern one, adjacent to the Area region in the Republic of Greece. The Carlin type of Au deposits related to the silicified tuffs and jasperoids are the major goal of the recent explorations and definition of new types of mineralization. The gold concentrations in that mineralization are within the range 1-20 g/t Au or in general are approximately around 3 g/t Au. Copper mineralization at the Dudica is the most important. Two different types of copper mineralization have been determined within the Dudica deposit: quartz-pyrite-enargite veins with interesting concentrations of lead and zinc at the Mircevic Valley where in particular samples were determined concentrations of 0.2 to 5.08% Cu and stockwork-impregnated low grade ore bodies (0.52 % Cu) formed at the contact between the hydrothermally altered andesite and Paleozoic schist.

Key words: Metallogenic units, Kozuf volcanic area, ore district, gold, copper.

Introduction

The ore mineralizations in the Kozuf ore district were known and studied since the second half of the XIX-th century, mainly from the aspect of arsenic and antimony, when even exploitation from the Alshar mine took place, too. With certain interruptions exploration (and exploitation) of the Alshar and Dudica localities lasts up to today. At the beginning of this century explorations were performed mainly by foreign companies such as Nassau, Rio Tinto etc.

Productive arsenic and antimony mineralizations with up to 500 000 t of ore with 2.5% Sb and 2% As have been determined at the Alshar deposit, while explorations of the Carlin type gold mineralization shown flexible values of up to 20 t gold metal.

At the Dudica area explorations have been performed shortly after the end of the Second World War and during the 1960 and 1961 when were submitted the first official reports (Ivanov, 1961). Unlike Alshar here are not validated ore reserves, but have been determined existence of copper ore mineralization in form of quartz-pyrite-enargite veins with lead and zinc and stockwork-impregnated copper mineralization with up to 0.5% Cu in particular ore bodies.

Along with explorations, studies of polymetals within the Kozuf ore district were performed too. There we would like to accent workings of Boev and Lepitkova (1990), Boev and Percival (1990), Boev and Serafimovski (1990, 1993), Boev et al. (1993), Ivanov (1965, 1986), Jankovic (1960, 1979, 1988, 1993), Johan et al. (1970, 1975), Percival et al. (1990), Jankovic et al (1997), Kochneva et al., (2006), Volkov et al., (2006) and some other. Within this paper we would like to emphasize the potentiality of the

Kozuf ore district from aspect of copper, gold and other polymetals, especially in regards to different morphogenetic types of mineralization, which opens possibilities for discovery of new ore bodies.

Regional Geotectonic and Metallogenic Setting

The Alshar deposit is located in the Kozuf metallogenic area (according to Ivanov, 1986) or the Kozuf - Aridea metallogenic area (according to Jankovic, 1993). This metallogenic area is situated within Mount Kozuf volcanic complex on both sides of Macedonian - Greek border.

Ore mineralization is related to the Pliocene volcano-intrusive complex which developed after tectono-magmatic processes in the unstable Vardar zone and the strong crystalline mass of the Pelagonian massif during the formation of the Kozuf - Kilkis transverse structure during Miocene-Pliocene (Boev, 1988). Mineralization includes Cu, Pb-Zn, and Au in the central parts (Alshar and Smrdliva Voda) and Sb, As, Tl, Au, and Ba (Alshar) (Figure 1).

The Kozuf volcano-intrusive complex which is present as intermediary to acidic igneous rocks developed in a basement composed of Triassic sediments, Jurassic ophiolite formations (gabbro-peridotitic) and Cretaceous carbonates and clastic sediments. Magmatic activity took place during the Miocene - Pliocene (6.5 to 1.8 m.y.), Boev (1988), Kolios (1980). Rocks are dacite-quartzlatitic to trachy-rhyolitic mainly enriched in LIL elements (Boev, 1988).

Extrusive magmatic activity was intense and represented by various types of tuffs, breccias and lacustrine volcanic-sediments. The intrusive phase of the magmatic activity is represented by subvolcanic bodies which were entirely hydrothermally altered by later hydrothermal processes.

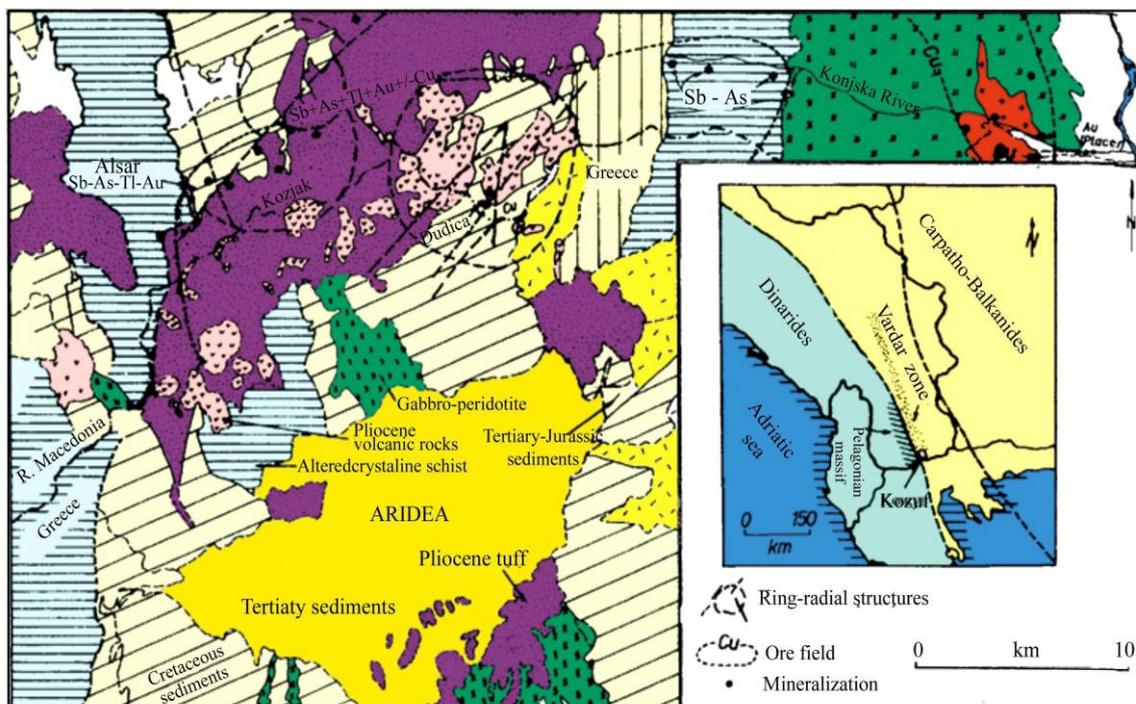


Fig. 1. The position of the metallogenic district of Kozuf (Jankovic, 1993)

Geology of the Kozuf-Aridea ore district and tectonic setting

The Pliocene volcanic-plutonic complex of calc-alkaline rocks of the Kozuf-Arid Zone was formed on a basement of Precambrian gneisses, Triassic rocks (dominant), Jurassic ophiolites (gabbro-peridotite), and Cretaceous sequences.

The Precambrian albite gneiss with sporadic lenses of amphibolite forms the oldest rocks of the Kozuf-Arid Zone. Marble blocks are sporadically incorporated in gneiss. Paleozoic schist, phyllite, metasandstone, shale, and quartzite occur locally. The Triassic sequence occupies most of the area and is composed of two main facies: (1) marmorized limestone and dolomite and (2) mudstone and sandstone with sporadic dolerite and greenschist. The Jurassic sequence consists of limestone, sandstone, shale, quartzite, cherty shale, and a severely serpentinized dunite-harzburgite complex that hosts small podiform chromite bodies. Serpentinite is exposed as narrow tracts that have tectonic boundaries with adjacent rocks. Their emplacement is related to diapiric processes. The Cretaceous sediments are represented by Barremian-Albian conglomerate and Turonian limestone. The Upper Eocene sequence is composed of basal conglomerate overlain by flysch sediments (siltstone, clay, and sandstone with limestone interbeds). Pliocene sedimentary and pyroclastic rocks are widespread around the Alshar deposit. They are composed of conglomerate and clayey sandstone with calcareous clay interbeds. Volcanosedimentary and pyroclastic rocks and clayey sandstone occur in some Pliocene basins north of the Alshar deposit. Quaternary sediments form river terraces.

The Alshar deposit is located at the intersection of the Vardar and Kozuf-Arid metallogenic zones (Fig. 1) at the western flank of the Vardar Graben and the Pelagonian crystalline massif approximately 50 km southwest of the town of Kavadarci and 3 km from the Greek-Macedonian border. The ore field is 21 km² in area.

The tectonic setting of the ore district and the Alshar deposit itself was deduced from the results of morpho-structural analysis and interpretation of satellite images. First, the present-day structural grain of southern Macedonia was outlined. For this purpose, the traditional method of morphotectonic contour lines was used to generalize the topographic contour lines and drainage pattern. Structural features of different ranks were contoured from the analysis of present-day land-forms of several orders.

The Alshar deposit is located in the upper reaches of the Rozdenska River (the right tributary of the Crna River). The streams in the Rozdenska River basin form a radial-centripetal pattern (Figure 2). The branched radial rivers and creeks are surrounded by arcuate ridges up to 1500-1800 m in height with arcuate valleys along their outer framework. Such an orographic pattern fits an endogenic ring structure 18 x 15 km² in size with a relatively subsided inner part and an elevated outer belt. This ring structure is located at the intersection of two extended diagonal through fault zones. The northwestern fault zone is an element of the Vardar Zone. Another (northeastern) fault zone was deduced from linear shade anomalies in satellite images. This fault zone is emphasized by the rectilinear valley of the Bosavica River, by the present-day slope elements, and by a chain of dome-shaped structural features up to 10 km across. In addition, a system of very young NE-trending faults controls the Pliocene lava flows here. The Alshar ring structure is surrounded by a belt of daughter domes up to 5 km across. Each of these domes is comparable with associated ore-bearing central-type structures (Fig. 2). The three second-order domes located in Greece south of the Alshar ring structure are characterized by the most complex structure and are contrastingly expressed in the present-day topography. By

analogy with other regions studied previously, such structures control large ore districts and deposits (Volkov and Sidorov, 2001).



Fig. 2. Morphostructures of southern Macedonia (Kochneva et al., 2006).

Hypsometric levels (m): (1) 1500–2000, (2) 1000–1500, (3) 500–1000, (4) below 500; (5) zones of diagonal dislocations; (6) boundaries of ring structures; (7) orthogonal deep-seated faults; (8) other faults; (9) geochemical halos; (10) Alshar deposit.

The tectonic position of the Alshar deposit is emphasized by the configuration of geochemical halos. An Fe-Ni halo extends along the Vardar Zone and an Sb-As-Tl-Pb-Zn-Cu halo corresponds to the young NE-trending fault system that crosses the Oligocene and Miocene metallogenic zones (Figure 2).

In the opinion of Jankovic (1993), the extended and wide meridional fracture zone radial relative to the center of the ring structure serves as a main ore-controlling tectonic line. We also traced a latitudinal fault zone as a fragment of an extended system interpreted in a satellite image.

The Alshar deposit

The Alshar deposit is composed of various rocks that belong to three lithostratigraphic complexes: 1) a complex of pre-Tertiary sedimentary and metamorphic rocks; 2) Tertiary carbonate rocks and 3) Pliocene volcano-sedimentary rock complexes.

Volcanics are widespread at the deposit. Two stages of volcanic activity are recognized. The older stage, probably Miocene in age, is represented by subvolcanic dikes, which are completely altered at the Alshar deposit and in the Dudica ore field. Relics of

primary rocks are retained only locally. The Ar-Ar age of plagioclase relics was determined at 1.2 Ma (Frantz, 1994).

The younger stage corresponds to the Pliocene (Boev, 1988). Most volcanics that were formed during this stage are fresh and suitable for detailed petrographic examination. This volcanic stage was accompanied by a vigorous explosive event, which resulted in the formation of an extensive pyroclastic complex composed of tuff, tuffite, and ignimbrite. Products of Pliocene volcanism overlie the igneous rocks of the older stage, although the *contact is* completely obscured by hydrothermal metasomatic alteration. Latite, trachyandesite, trachyte, andesite, and dacite were identified among the volcanic rocks.

Silicification at the Alshar deposit also affects Tnassic and Tertiary carbonate rocks south of adits (Figure 3). As was noted, silicification varies in intensity from weak to very high, in which case carbonate rocks are replaced by jasperoids. Silicified rocks are spatially related to variably oriented faults and fracture zones and make up stock works and slightly silicified fracture zones. Jasperoids are usually brecciated and crossed by quartz veins and thin veinlets. The rocks are composed of fine-grained microcrystalline quartz, which obscures the primary structure of carbonate rocks. Although jasperoids are rather common at the Alshar deposit, they are second in abundance relative to slightly silicified host rocks.

Ore mineralization at the Alshar deposit is developed as mineralized breccia at the contact of volcanic cover with dolomites, jasperoid beds in the carbonate rocks (Figure 3), and vein-disseminated zones in dolomites and Tertiary volcanic rocks. The Alshar deposit includes several ore bodies with specific geochemical association of elements and composition.

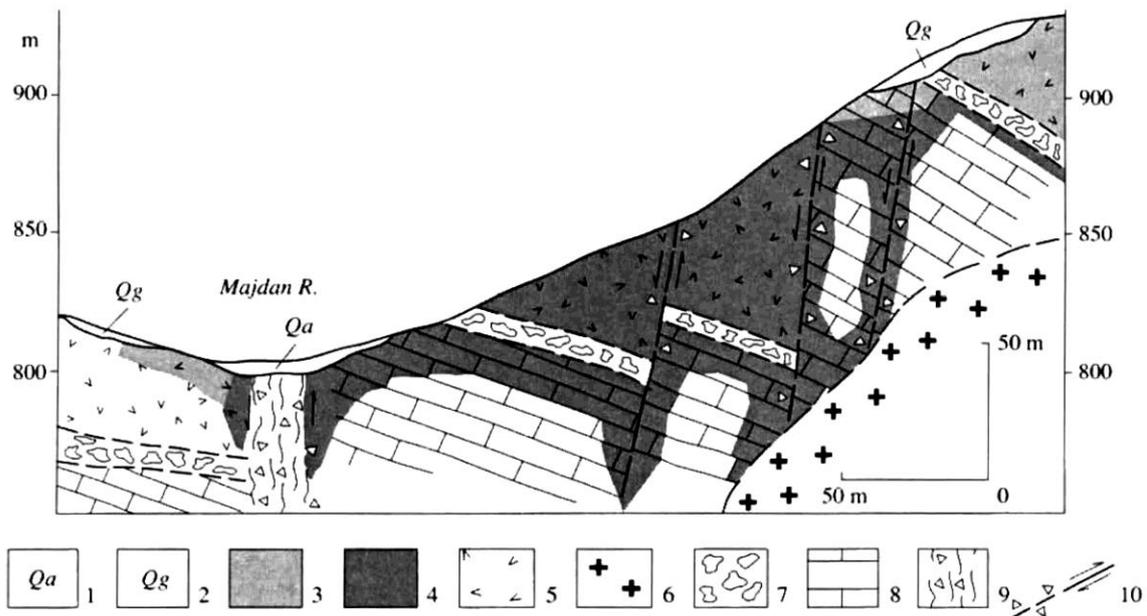


Fig. 3. Geological section across the Alshar deposit (modified after Percival and Radtke, 1994)
 1. Quaternary alluvial sediments; 2. Quaternary glacial (moraine) sediments; 3. Zone of argillic alteration; 4. Siliceous rock (jasperoid); 5. Pliocene latite tuff; 6. Pliocene hypoabyssal porphyry intrusion; 7. Unconformity zone; 8. Triassic marble and dolomite; 9. Main fault breccia; 10. Auxiliary faults and relative displacements and breccia along them

Namely, a few morphostructural types of orebodies are distinguished within the deposit: (1) mineralized breccia zones along contacts of subvolcanic intrusions with dolomite and tuffaceous dolomite and mineralized fault zones in carbonate rocks; (2) systems of mineralized veins and fissures in Tertiary tuffaceous dolomite and Triassic dolomite; (3) stratiform sulfide lodes hosted in tuffaceous dolomite; and (4) disseminated Sb mineralization (stibnite is prevalent) in association with gold-bearing pyrite and marcasite as stratiform bodies along the contact between the volcanosedimentary sequence and Triassic carbonate rocks and hosted in silicified volcanics and jasperoids as well. It should be noted that the geological exploration conducted at the deposit is insufficient for the ultimate estimation of reserves.

This is the only deposit in Macedonia, which has economic-grade contents of Tl (0.1–0.5%), Sb (up to 2.5%), As (1.5%), and gold (>1 g/t). It should be noted that gold is unevenly distributed in the ores. The highest Au contents (3–4 g/t; occasionally, up to 20 g/t or more) were found in jasperoid zones in the southern part of the deposit (Percival and Radtke, 1994). By analogy with the Carlin-type deposits in Nevada, Percival and Radtke [3] distinguished four economic-grade types of gold ores at the Alshar deposit: (1) Sb–Au jasperoid ore (+ Au + As + Tl); (2) siliceous gold ore (+Au + Sb + Tl); (3) As–Au ore (+ Tl + Hg + Sb + Au); and (4) Tl ore. The ores form three mineral assemblages of different ages: pyrite–marcasite, antimonite, and orpiment–realgar–lorandite.

The Dudica ore field

The Dudica ore field is located about 2 km far from the Macedonian border with Greece. It was explored in the period (1916-1917, 1940-1944, 1946-1948), but no mining operations were undertaken except for native sulphur to an insignificant extent. The explorations were of considerable scope: tunnelling (one adit more than 400 m long) and diamond drilling (individual holes were several hundreds of meters long). The explorations have been conducted on the basis of the concept that Dudica is a deposit of massive sulphide copper ore such as Bor, and the preliminary explorations in the 1985 were aimed at gold mineralization.

Although the Dudica ore field has been explored by several explorers, the only published information can be found in the papers of Hiessleintner, (1945), Ivanov (1965) and Jankovic (1967).

The Dudica ore field is situated in the western margin of the Vardar zone, within its contact with the Pelagonian massif. Within that area, regional dislocation structures as well as the geotectonically labile zones associated with Jurassic peridotitic complex were developed. The Dudica ore field lies within a metallogenic complex formed inside a Pliocene volcano-intrusive andesite and quartz latite complex of Aridea in Greece and Kozuf in the Republic of Macedonia; at present only the north portion of this regional metallogenic unit is known.

Upper Palaeozoic crystalline schists belong to the oldest rocks. In the area of the Tethyan Ocean closing were developed the representatives of gabbro-peridotite formations overlain by Cretaceous sediments, partly metamorphosed. The major part of the former Aridea crater is overlain by Pliocene sediments.

From the aspect of metallogeny, the volcano-intrusive complexes of Aridea and Kozuf is of particular interest. The characteristics of Kozuf volcanic complex have been discussed in detail by Boev (1988). In terms of composition, it is represented by different types of andesites and quartz latites. Pyroclasts are by far more abundant. The proportion

of intrusive outcrops is insignificant, most probably, as a consequence of a low erosion level. The volcano-intrusive activity within the areas of Kozuf and Aridea lasted from 7 to 1.8 million years.

The immediate surroundings of the deposit, covering an area of several square kilometers, consist of Paleozoic formations (phyllite, schists, sandstones, green schists, etc.) and Mesozoic crystalline limestones sporadically transformed into marble (Figure 4). These rocks have been intruded and/or overlain by the products of magmatic activity during Pliocene. These are dacite-andesite-quartz rhyolite subvolcanic intrusions extending northwards into a thick series of tuffs. Vein equivalents of calc-alkaline magma can be recognized locally. The magmatic rocks include the products of the alterations related to volcanic activity (propylitization), as well as the alterations caused by hydrothermal solutions (silicification, kaolinization, etc.). Under the effect of hydrothermal solutions, limestones and marbles underwent alterations, resulting in the formation of larger masses of metasomatic quartz (jaspilite) along the contact between the propylitized andesites and limestones. Within the broader area around Dudica, several occurrences are known of ore mineralization of pyrite, copper (enargite, chalcopyrite), lead (galena), as well as the occurrences of native sulphur.

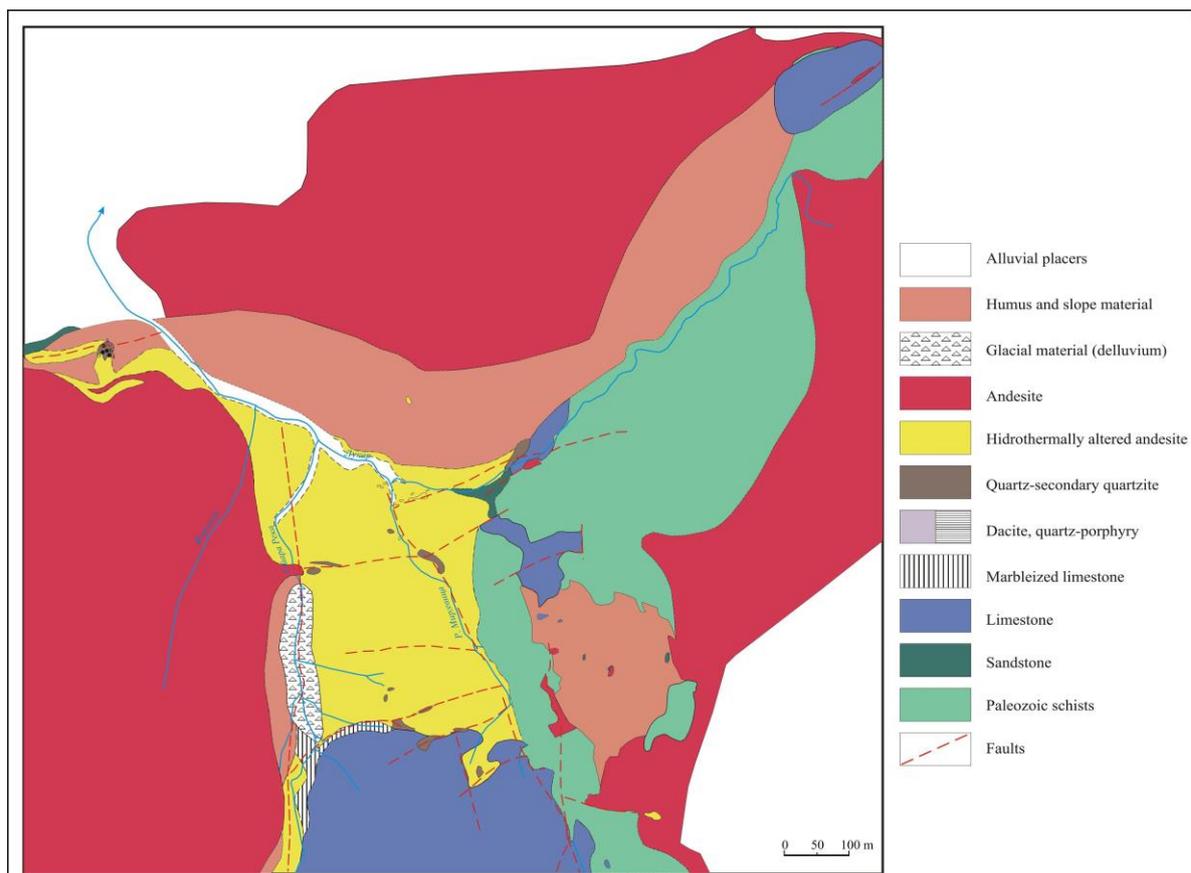


Fig. 4. Geological map of the Dudica ore deposit

Copper ore occurrences located along Mircevic Reka, associated with intensive hydrothermal rock alterations, caused further phase of investigation and exploration activities to be carried out.

The mineralization consists of wide scale mineral occurrences (more than fifty minerals), with only few minerals dominant. The mineral occurrences are hosted by altered andesite rocks and, to a lesser extent, Cretaceous limestones. The mineralization is dominantly fracture controlled and occurs as a small sulphides (quartz-pyrite-enargite, pyrite-enargite, etc.) filling in veins and small fractures, or as disseminations in the sheared zones. Within the veins, the ore has a breccia like texture or is deposited in open spaced fractures. In some places the ore has a banded texture. The ore bodies lay in the linear structures with some discontinuity of extension and are small in size within the linears (Figure 5). Some ore lenses were traced to 30 m., varying in thickness from a few centimetres to one meter. The mineralised contact zone varied in thickness from 0.2 m to almost 20m. The depth of the extension has not been explored in details.

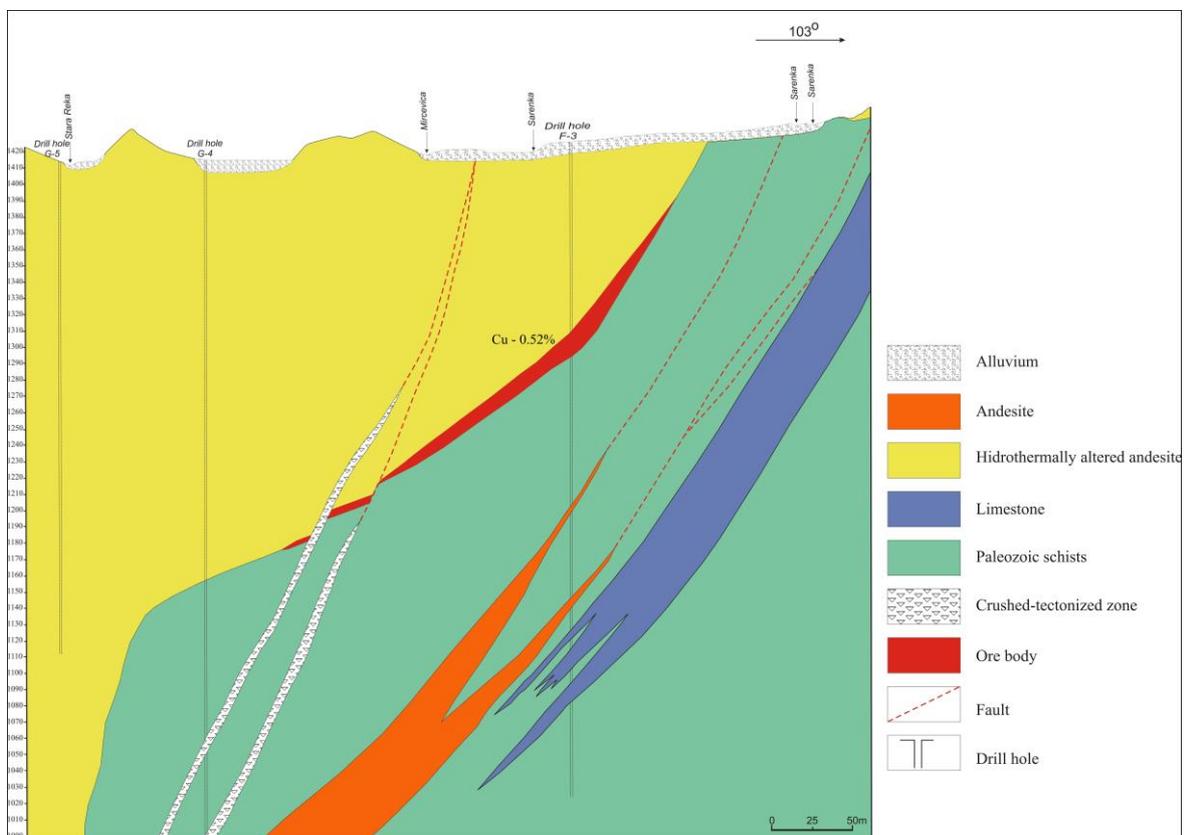


Fig. 5. Geological cross section through the Dudica copper deposit

The mineral composition appeared relatively simple. Pyrite and enargite are clearly recognizable with the naked eye. The polished section revealed more complex composition (Ivanov, 1961) and numerous minerals were identified. The frequency in appearance of the minerals was calculated on the basis of their presence in the studied polished sections. Pyrite and chalcopyrite were found to be present most often, followed by pyrrhotine. The next most often appearing minerals are ranked as follows: sphalerite, galena, valerite, bravoite, tetrahedrite, bornite, enargite, marcasite etc. (Figure 6).

No.	Stage	Propylitic stage	Stage of hydrothermal alterations	Ore-bearing stage							Oxide stage
	Minerals			I sub-stage	II sub-stage	III sub-stage	IV sub-stage	V sub-stage	VI sub-stage	VII sub-stage	
1	Magnetite	██████████									
2	Pyrite	██████████	██████████			██████████					
3	Chlorite	██████████									
4	Calcite	██████████									
5	Sericite		██████████								
6	Quartz		██████████				██████████				
7	Kaolinite		██████████								
8	Zeolite		██████████								
9	Rutile		██████████								
10	Chalcopyrrhotite			██████████							
11	Chalcopyrite			██████████		██████████					
12	Sphalerite			██████████							
13	Bornite				██████████						
14	Galena					██████████					
15	Bournonite						██████████				
16	Tennantite						██████████				
17	Enargite						██████████	██████████			
18	Covellite							██████████			
19	Pink chalcocite							██████████			
20	Blue chalcocite							██████████			
21	Germanite							██████████			
22	Stibnite								██████████		
23	Marcasite								██████████		
24	Native sulfur									██████████	
25	Anhydrite										██████████
26	Alunite										██████████
27	Chalcedony										██████████
28	Gold										██████████
29	Native silver										██████████
30	Cuprite										██████████
31	Malachite										██████████
32	Azurite										██████████
33	Chrysocolla										██████████
34	Anglesite										██████████
35	Limonite										██████████
36	Deposition of Fe	██████████	██████████			██████████					██████████
37	Deposition of Cu			██████████	██████████	██████████	██████████	██████████			
38	Deposition of As						██████████	██████████			
39	Deposition of Pb					██████████					
40	Deposition of S										
41	Deposition of Sb								██████████		
42	Deposition of Au								██████████		
43	Deposition of Ag									██████████	

Fig. 6. Succession diagram of ore minerals and major ore metals in the Dudica copper deposit

The spatial distribution of a number of minerals was of particular interest to Ivanov (1961). He studied the extension of a mineral or group of minerals from the surface (having an elevation of 1800m) to a depth of 700 m. They determined that:

- Hydrothermal alteration: the clay minerals illite, kaolinite, sericite and the silica minerals anhydrite and pyrite were discovered to a depth of at least 850 m, from the surface (having an elevation of 1700m.);

- Chalcopyrite, the principal copper-bearing ore mineral was discovered at an elevation of the 1400 m to a depth of 850m. Copper porphyry or metasomatic type ore deposits could potentially also be present within this range;
- The other copper-bearing group of minerals, consisting of bornite, covellite, chalcocite, tetahedrite and enargite was discovered only in the relatively short range of between 1500 m. down to 1220 m. (the first four minerals) and 1650 m. to down 1230 m. (enargite).

Mineralised structures such as veins and other mineralisation types were explored (Figure 7), as were the inside of drill holes, where the mineralised zones intersected. Obtained data suggests that the thickness of the mineralised structure ranges from 0.1 m to 0.5 m with copper contents ranging from 0.2% to 5.08% Cu. Gold and silver were sporadically assayed and it was determined that their contents varies from traces to 1.1 g/tAu, and 0.0 to 18 g/t Ag.

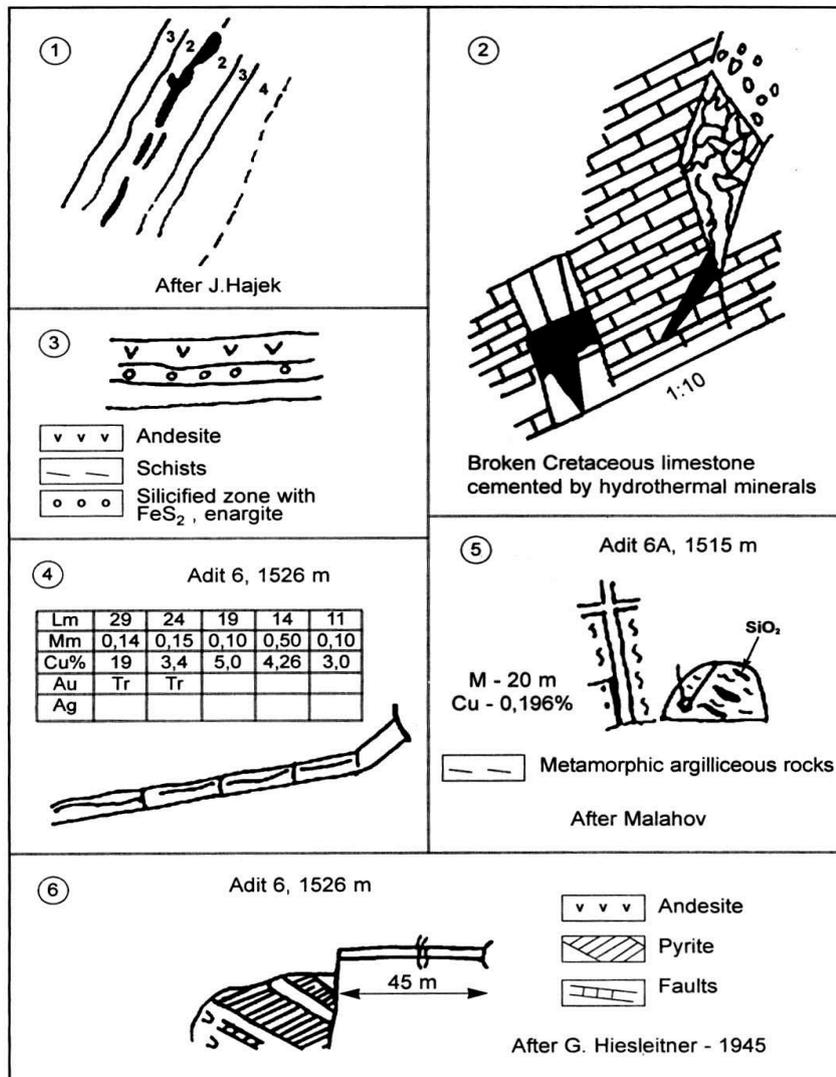


Fig. 7. Structure types of Dudica ore mineralization

The mineralized contact point was intersected at the end of adit 6. The mineralisation was hosted by schist rocks. Within the assayed interval of 8 m., a copper content of 0.206% was recorded. Within another mineralised zone of 20 m hosted by schists, assayed data indicated a copper content of 0.196% Cu. Gold content was not analysed.

Conclusion

The Kozuf ore district have been characterized by youngest Alpine metallogeny within the Serbo-Macedonian Metallogenic Province, related to the Neogene volcanism (6-1.8 Ma) in the Kozuf-Aridea area. Metasomatic mineralizations of arsenic, antimony, thallium and gold as well as Carlin types of gold are the most significant features of the mineralizations within the Alshar deposit while quartz-pyrite-enargite veins and stockwork-impregnated copper mineralizations are the most representative of the Dudica deposit. Structural-morphostructural and magmatic control gave positive indications that within the Kozuf ore district can be expected new potential areas for some of the formerly mentioned metals, especially gold in eastern-southeastern parts of the Kozuf complex, in the adjacent vicinity of the Smrdliva Voda locality.

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