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Напомена: Аутори су одговорни за садржај и квалитет својих саопштења, за припрему рада према дефинисаном упутству, као и за сва мишљења, тврдње и резултате објављене у њима. Издавач не преузима одговорност за ставове и мишљења изнета у радовима, нити их нужно дели. Превод на енглески језик извршили су сами аутори. Сви радови су рецензирани од стране чланова научног одбора или рецензената. Појединачни радови су објављени на језицима и писмима на којима су их аутори доставили приликом пријављивања.

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GEOHEMICAL CHARACTERISTICS OF THE POLYMETALLIC Cu–Au–Mo DEPOSIT ILOVICA, EASTERN REPUBLIC OF NORTH MACEDONIA

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ABSTARCT

The conducted geochemical researches of the Ilovica deposit have confirmed the presence of Cu–Au–Mo mineralization, where it has been established that the greatest potential occurs between the Ilovica River (Jazga) and west of the Anovi–Chukar ridge. In this area, a quartz, quartz–iron-oxide, and quartz–magnetite with gold have been identified, which at greater depth transitions into a quartz–magnetite–sulfide, while volcanic breccia appears at the highest elevations. The top of the system is represented by a silica–alunite alteration zone (silica–alunite lithocap) and intense silicification. For a more complete overview of the results from the conducted research, this paper briefly presents the results of lithogeochemical, metallometric, and stream-sediment analyses separately.

INTRODUCTION

The Ilovica deposit it is located in southeastern part of Republic of North Macedonia, more precisely on Ograzden mountain, at about 17 km at a distance from Strumica city, near Ilovica village (*Figure1*). In the Republic of North Macedonia even and broader, "Ilovica" deposit represents one of the more significant porphyry deposits of Cu- Au-Mo. This deposit represents a part of several porphyry systems in eastern parts of North Macedonia and northern Greece, which are in association with igneous complexes and is one of deposits of the type of the deposit Bucovik- Kadiica in Republic of North Macedonia and Scurries in Greece. In view of the regional geotectonic position, "Ilovica" deposit belongs to Serbian-Macedonian Massif (Zagorchev et al., 2008) and the Serbian-Macedonian Metallogenic Zone (Jankovic, 1977), in belt, in whose geological construction participate late Proterozoic to Palaeozoic metasediments and granitoids. The processes that took place in the frame of the SMM have caused structure of the volcanic apparatus, domes and regional dislocations, as the Tupal dislocation and dislocation Besna Kobila-Osogovo (Aleksandrov, 1992). Actually, creation and spatial distribution of the magmatism and the ore are in function of the structural factor of a control or disjunctive-depth structures that are present in the Ograzden granite massif and have direction along the borders of the basic geotectonic units: Serbian-Macedonian Massif and the Vardar Zone.

GEOLOGICAL SETTING

Ilovica is a porphyry copper-gold deposit, located in a northwest-southeast striking Cenozoic magmatic arc, that covers large areas of Central Romania, Serbia, Republic of North Macedonia, Southern Bulgaria, Northern Greece and Eastern Turkey (Tomić, 1936; Stojanović, 1971; Westra, 2005; Schefer et al., 2011; Schmid et al., 2013).

The Illovica porphyry system is about 1.5 km in diameter and is associated with a poorly exposed dacite-granodiorite plug, emplaced along the north eastern border of the northwest-southeast elongate Strumica graben (Rakičević et al, 2008; Sinclair, 2008). The exact location of the deposit is controlled by major north-south cross cutting faults and minor northwest-southeast faulting, parallel to the faulted border of the graben.

Figure 1. *Geographic location of the Ilovica deposit.*

At surface, the Ilovica intrusive complex con sists of a central dacitic breccia diatreme, approximately 1.3 km in diameter (Bird and Morris, 2012; Wheeler, 2015). The diatreme is intruded by at least one dacite and two granodiorite porphyry stocks that have generated several hydrothermal pulses, resulting in widespread multi-phase veining within a mineralized (Janković et al., 1995).

The Ilovica porphyry is centred on a hill of more than 400 metres (m) of absolute relief, surrounded at lower elevations by numerous small dykes and irregular bodies of dacitic tuff and breccias and intermediate volcanic rocks (*Figure 2*).

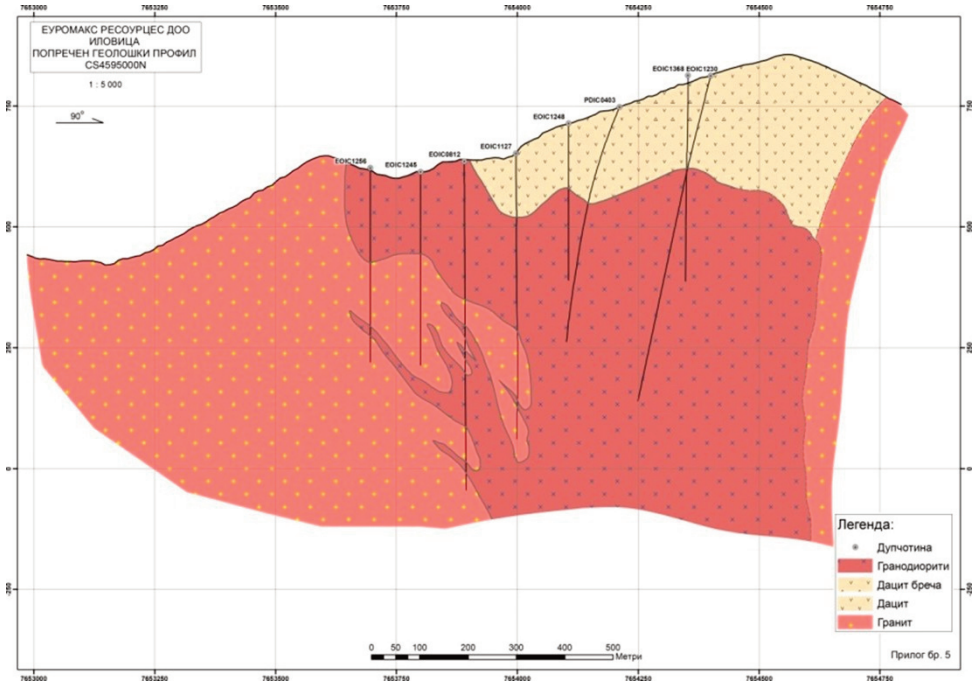

Figure 2. *Cross-sectional geological profile.*

The Ilovica magmatic complex is emplaced into lower Palaeozoic granite. The granite is locally weakly foliated, coarsely porphyroblastic, and forms a roughly northwest-elongate body some 4 by 12 km in size, intruding Precambrian mica schist and gneiss. Portions of the main dacitic diatreme locally contain abundant xenoliths of basement granite near the lithological contact.

Geochemical characteristics

The lithogeochemical investigations were methodologically carried out according to the principle of rock chip sampling, conducted on surface areas evaluated as interesting for this type of research. The prepared samples were analyzed for about 20 elements in a reference laboratory. Particular attention was given to the contents of Cu, Au, Mo, Ag, As, Sb, Pb, Zn, Bi, Fe, S, Ba, Ga, Ge, and other elements that characterize the geochemical association typical for this type of deposit.

Copper (Cu) – Copper concentrations range from 10–3909 ppm. Of the analyzed samples, 65 samples (63.72%) contain up to 100 ppm, 33 samples (32.35%) contain 101–1000 ppm, and only 5 samples (4.17%) contain more than 1000 ppm.

The samples with the highest copper contents are sample G134482 with 2580 ppm (taken west of Chukar and Anovi in granodiorites) and sample IR006 with 3909 ppm, taken from the waste dump between the two World Wars, south of Chukar, near Shtucka River. The most significant copper anomalies are located east of the Ilovica River (Jazga) and west of Anovi and Chukar, within the granodiorites and their contact with dacites and dacite-andesites, while only a minor part of the anomalies occurs in granites.

Gold (Au) – Gold contents from 102 samples range from <5 to 3100 ppb, with analyses performed using the AAS method. Of all analyzed samples, 59 samples (57.84%) contain up to 100 ppb, 12 samples (11.76%) contain 0.10–0.20 g/t (anomalous contents), and 22 samples (21.57%) contain more than 0.21 g/t (highly anomalous contents). Samples with the highest Au contents are 28044 (1.73 g/t) and 28045 (2.07 g/t)—taken in granodiorite where magnetite and quartz-magnetite are strongly developed—as well as IR006 (3.10 g/t), taken from the dump of old mining works.

Molybdenum (Mo) – Molybdenum contents range from 2–128 ppm, where 96 samples contain 2–20 ppm (not anomalous), 16 samples contain 21–100 ppm (anomalous contents), and 4 samples contain more than 100 ppm. The anomalous Mo contents largely coincide with the Cu anomalies and partly with Au anomalies.

Silver (Ag) – Silver contents range from the detection limit of the method up to 60.0 ppm. In 65 samples the contents are below 1 ppm, in 22 samples the contents are 1–2 ppm, and in 15 samples the contents are higher than 3 ppm. The highest Ag contents were determined in sample 28044 (46.2 ppm – the same sample also contains 1730 ppb Au), G13277 (59 ppm), and 21805 (60 ppm Ag). Such Ag contents are typical for porphyry Cu–Au–Mo deposits.

Metallometry – Soil Sampling of the "B" Horizon

Soil sampling was carried out in the northwestern part of the Ilovica Concession, where a total of 540 sampling points were investigated during the period 2004–2007. Soil sampling was conducted in order to identify anomalous zones that cannot be detected by other methods due to the absence of rock outcrops suitable for sampling.

The samples were analyzed using the ICP method (Inductively Coupled Plasma), while Au and elevated contents of Cu and Mo were analyzed using AAS (Atomic Absorption Spectrometry). The obtained results from the chemical analyses showed anomalous concentrations of several elements, the most significant being Cu, Au, Mo, Ag, As, Pb, Zn, Ba, Bi, Ni, and others. Below, the geochemical characteristics of the most important elements and their associations are described.

Copper (Cu) – Copper concentrations within the developed 100 × 100 m sampling grid range from 10 to 1055 ppm. Statistical processing of the obtained data determined a local background value of 46 ppm, a standard deviation of 0.8060, and an anomaly threshold of 47.62 ppm (accepted as 48 ppm).

Based on the calculations, four classes were defined:

- Class I: 48–96 ppm
- Class II: 97–192 ppm
- Class III: 193–384 ppm
- Class IV: >385 ppm

Based on these defined classes, a geochemical anomaly map was prepared (*Figure 3*). The Cu geochemical anomalies in the Ilovica deposit reflect the geological structure of the investigated area (dacites, dacite-andesites, granodiorites, and granites affected by various types of alteration), the formed oxidation zone in the surroundings of Chukar and Anovi, and definitively the mobility of Cu and its other geochemical characteristics.

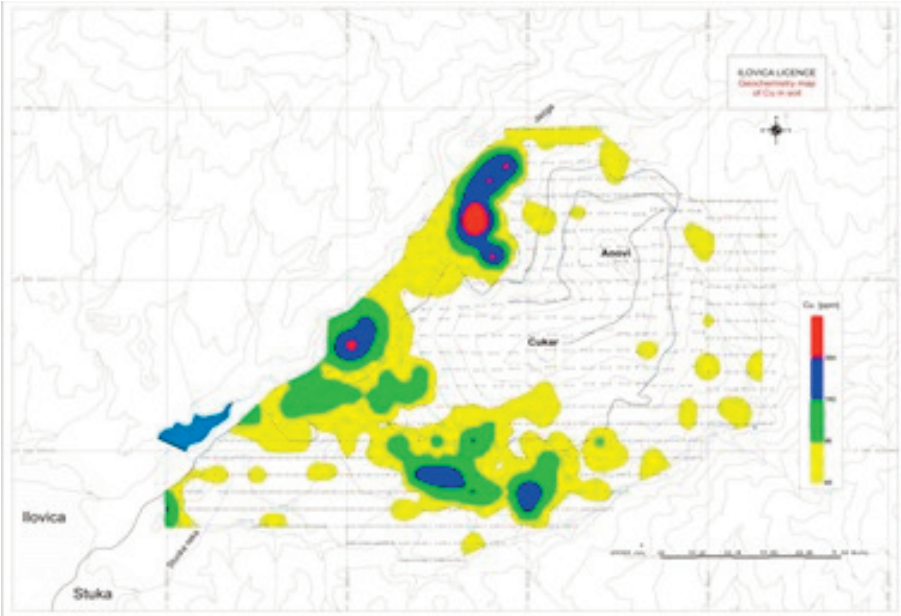

Figure 3. *Geochemical map of Cu anomalies.*

The anomaly located northwest of Chukar–Anovi is the most significant and most likely marks a mineralized stock controlled by a tectonic node.

The anomaly near Kremen Chuka indicates mineralization controlled by a fault following the Ilovica River and its intersection with an east–west trending fault, which is long and is one of the major faults bounding the Strumica basin from the north.

The anomaly at the Domus Gaber site and north of Shtucka River may be caused by a small intrusion and the intersection of an east–west trending fault with quartz–alunite veins trending almost north–south. This anomaly requires additional geophysical investigations and subsequent verification through deep drilling.

Gold (Au) – Gold contents in the analyzed samples range from <5 to 230 ppb. In 234 samples, Au is below the detection limit of the method (<5 ppb), 277 samples contain 5–100 ppb, and only 6 samples contain >100 ppb Au, representing the anomalous concentrations.

Statistical processing determined a standard deviation of 0.7431 and an anomaly threshold of 27.403 ppb (accepted as 27 ppb). Four classes were defined:

- Class I: 0.027–0.054 ppm
- Class II: 0.055–0.108 ppm
- Class III: 0.109–0.218 ppm
- Class IV:>0,218 ppm

Based on these classes, a geochemical anomaly map was prepared (Figure 4). The main anomaly is located west of the Anovi–Chukar ridge, in higher elevations within dacites, dacite-andesites, and granodiorites (here, the highest Au contents are observed), while in peripheral areas anomalous concentrations are also found in granites, especially those with a developed hematite–magnetite stockwerk.

Molybdenum (Mo) – Mo contents range from <3 to 69 ppm. Of the 540 analyzed samples, 430 samples contain more than 3 ppm. Statistical processing determined a local background of 3.46 ppm, a standard deviation of 0.800, and an anomaly threshold of 5.0 ppm. Four classes were defined:

- Class I: 5–10 ppm
- Class II: 11–20 ppm
- Class III: 21–40 ppm
- Class IV: >40 ppm

The resulting Mo geochemical anomaly map shows that anomalous Mo areas largely overlap with Au anomalies. The Mo anomaly is located on the northwestern slopes of Chusar and west of Anovi. The highest anomalous values occur at the contact between granodiorites and granites (south) and between granodiorites and volcanic rocks – dacites and dacite-andesites (east). The Mo and Au anomalous zones are almost identical and lie over the porphyry mineralization, although Au shows a wider geochemical dispersion. Based on these geochemical results, Mo may also have economic significance under exploitation conditions.

Silver (Ag) – Silver contents range from <0.1 to 46.2 ppm. Of all analyzed samples, 247 samples have <0.1 ppm, and 47 samples contain 1–20 ppm, which are typical for porphyry Cu–Au–Mo deposits.

Arsenic (As) – Arsenic contents range from 3–225 ppm. In 215 samples, As is 3–20 ppm, 203 samples contain 21–50 ppm, and 56 samples contain >50 ppm. The highest As contents were found in sample IS-17-4 (154 ppm), IS-22-4 (180 ppm), KC57 (196 ppm, Kremen Chuka), P45 (213 ppm), and R8/8 (225 ppm). A comparison of Au and As analyses clearly shows that there is no correlation between gold and arsenic.

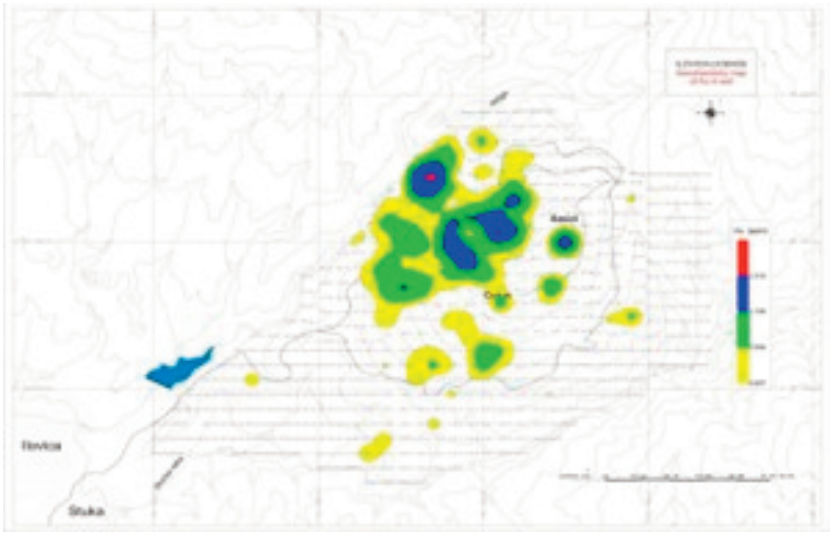

Figure 4. *Geochemical map of Au anomalies.*

Stream Sediments

To evaluate the potential of the Ilovica Concession, a method of stream-sediment investigation was also applied. The technique for sampling river sediments was modified and refined by the Company. Since the stream-sediment results were used for eco-geochemical studies, the samples were collected in Phase I in July 2004 and in Phase II in March–April 2005. All sampling locations were recorded using GPS. In total, 39 samples were collected from an area of 35 km^2 within the catchment areas of the Ilovica and Shtucka Rivers, representing more than 1 sample per km^2.

All samples were analyzed using ICP for 35 elements, while Au was analyzed using AAS. During sampling, elevation and coordinates were recorded for all samples, and a protocol was completed noting geological settings, hydrogeological characteristics, potential contamination, riverbank type, possible sample depletion, and each sample was photographed with a digital camera. The distance between samples was 500 m, which is considered acceptable for determining the characteristics of river catchments.

For dry sediments, the material was sieved on-site using an -80 mesh sieve, while for wet sediments, 5–10 kg samples were collected. The collected samples were air-dried, sieved, and a 250 g sub-sample and duplicate were prepared for laboratory pulverization and analysis.

The results from the stream-sediment sampling confirmed and complemented the results from the lithogeochemical and soil (metallometric) surveys. The combined results from lithogeochemistry, metallometry, and stream sediments indicate a complex geochemical association of elements with anomalous values, suggesting the presence of porphyry mineralization.

From the results, it can be concluded that the stream sediments show a complex geochemical association of elements, with the most significant being Cu, Mo, As, Pb, Zn, Co, Ni, Ba, Ga, and others.

Copper (Cu) – Copper contents in both phases are almost identical, ranging from 2–996 ppm (Phase I) and 2–839 ppm (Phase II). In Phase I, 30 samples had Cu ≤ 10 ppm, 7 samples 10–100 ppm, and 2

samples >100 ppm. In Phase II, 22 samples had ≤ 10 ppm, 16 samples 10–100 ppm, and 1 sample >100 ppm. The highest Cu values, 996 ppm (Phase I) and 839 ppm (Phase II), were observed in samples SS-36 and SS3-36, confirming the reliability of the method.

Molybdenum (Mo) – Most samples are below the method detection limit of 0.5 ppm in Phase I (only 4 samples at 0.5 ppm), but low values were recorded except in SS-13, which had 13.3 ppm in Phase I and 10.7 ppm in Phase II, representing a significant indicator of porphyry mineralization.

In addition to detailed analyses of Cu, Au, and Mo, these investigations covered element packages characteristic for such deposits, including Pb, Zn, As, Co, Ba, etc., which show elevated concentrations relative to background values, though without significant economic importance.

CONCLUSION

The results from the geochemical studies (lithogeochemistry, metallometry, and stream sediments) indicate a complex geochemical association of elements with anomalous values. The most significant elements include Cu, Au, Mo, Ag, Pb, Zn, As, Bi, Co, Ni, Ba, and others, suggesting the possible presence of porphyry mineralization.

The Ilovica Cu–Au–Mo porphyry system is located within a volcanic apparatus, where the developed quartz–magnetite–sulfide hosts the potential porphyry mineralized area.

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