

Journal of the Geological Institute at the Faculty of Natural and Technical Sciences, University "Goce Delčev"-Štip, R. Macedonia



Geologica Macedonica	Vol.		No		pp.		Štip	
Geologica Macedonica	Год.	32	Број	1	стр.	1 -90	Штип	2018

UDC 55 CODEN – GEOME 2 In print: ISSN 0352–1206 On line: ISSN 1857–8586

GEOLOGICA MACEDONICA

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Published by: – Издава:

"Goce Delčev" University in Štip, Faculty of Natural and Technical Sciences, Štip, Republic of Macedonia Универзитет "Гоце Делчев" во Штип, Факултет за природни и технички науки, Штип, Република Македонија

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Faculty of Natural and Technical Sciences P. O. Box 96 MK-2000 Štip, Republic of Macedonia Tel. ++ 389 032 550 575 E-mail: todor.serafi GEOLOGICA MACEDONICA РЕДАКЦИЈА

Факултет за природни и технички науки пошт. фах 96 МК-2000 Штип, Република Македонија Тел. 032 550 575 ovski@ugd.edu.mk

E-mail: todor.serafimovski@ugd.edu.mk

400 copies Published twice yearly

> Printed by: 2^{ri} Avgust – Štip

Price: 10 € The edition is published in June 2018 Тираж: 400 Излегува два пати годишно

Печати: 2^{ри} Август – Штип

Цена: 500 ден. Бројот е отпечатен во јуни 2018

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Упатство за авторите	89–90
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336 GEOME 2 Manuscript received: December 11, 2017 Accepted: April 25, 2018

Original scientific paper

NATIVE GOLD COMPOSITION AND MORPHOLOGY THROUGH THE MINERAL PROCESSING STAGES AT THE BUČIM COPPER MINE, REPUBLIC OF MACEDONIA

Violeta Stefanova, Todor Serafimovski, Goran Tasev

Geology Institute, Faculty of Natural and Technical Sciences, "Goce Delčev" University in Štip, Blvd. Goce Delčev 89, 2000 Štip, Republic of Macedonia violeta.stefanova@ugd.edu.mk

A b s t r a c t: The native gold is a common by-product in many Cu-porphyry deposits, although its distribution and chemistry in many deposit remains not well understood. The aim of this paper is to analyze chemistry and morphology of individual gold grain. In this study we examine the gold chemistry and morphology from mineral processin, flotation and tailings from Bučim deposit. Five grains from the mine level, seven aggregates from the material of flotation, nine aggregates from the concentrate, three from the canalletes and four aggregates from the tail were subject of study. Fineness ranging from 805 to 995. Silver is the most common trace constituent in the studied gold grains from 0.27 to 19.24%. The Cu and Fe are common trace constituent that range in average for iron about 2.5% Fe and copper max. 4% Cu. It is noted that iron and coper as impurities are not present in all tested aggregates. Titanium and tellurium are present only in one analyzed gold aggregates (2.82%). Studied gold grain appear in various morphological forms, characterized by more or less rounded edges. Elongated gold grain with rounded edges have been commonly observed, while flat and anhedral grains are more rarely found.

Key words: gold grains; chemical composition; morphological forms; mineral processing

INTRODUCTION

Porphyry copper deposits are among the largest gold reservoirs in the upper crust and are important potential sources of gold in low temperature epithermal deposits (Kerrich, 2000). In porphyry copper deposits, gold is found in a solid solution in Cu-Fe and Cu sulphides and as small grains of native gold usually around the boundaries of bornite, which in some deposits (e.g. Skouries, Hiau, etc.) may contain about 1 ppm Au. Chalcopyrite usually contains less than 1 ppm Au (Kessler et al., 2002).

Studies of the gold bearing porphyry deposits according to these authors suggest that gold is most commonly associated with early potassium alterations and is associated with bornite in the form of inclusions with about 5 to 100 microns in size, inside the grains or on the sulphide grains. Gold also occurs with chalcopyrite in porphyry copper-rich ores rich in chalcopyrite, especially when there is lateral chalcopyrite-pyrite phyllite alteration.

Experiments of the Cu-Fe-S-Au system show that bornite and chalcopyrite may contain about 1000 ppm of gold at typical temperatures for the formation of porphyry copper deposits of 600 to 700 °C and suggest that the bornite and chalcopyrite in these deposites are saturated in terms of gold at a temperature of only 200–300 °C.

This suggests that the maximum dosage of gold in porphyry copper deposits is probably determined by the amount of gold that goes into the solid solution of Cu-Fe sulphides when the deposit is formed at high temperature and that gold is usually not added later from other sources, although it can be redistributed during cooling or later stages. Experimental data also suggests that high temperature vapors (600–700 °C) can extract significantly more gold from the porphyry copper systems than the low temperature (300 °C) alterations (Kessler et al., 2002).

Studies of the microchemical and morphological features of gold aggregates refer to the combined use of the chemical composition and the morphology of Au-grains to define the mineral bonds, genetic types of mineralization and conditions of precipitation. The mineral featuress of golden grains in combination with chemistry can be used to define the "microchemical signature", which may indicate the most likely type of mineralization of the source (Moles et al., 2011). Such studies are also used in the studies of placer gold, in order to explain the physical and chemical changes that occur during the water transport of the native gold aggregates. (Chapman et al., 2000, 2010, 2011; Florencia et al., 2004; Knight et al., 1994, 1999; Nakagawa et al.,

This deposit belongs to the Bučim–Damjan– Borov Dol metallogenic zone. Spatially, this ore zone occupies parts of two geotectonic units: the Vardar zone and the Serbian-Macedonian zone. Magmatism in this ore region is characterized by Tertiary volcanism, for which mineralization of copper, iron, gold, lead-zinc etc. spatially and paragenetically is associated. Magmatism in the Bučim block is represented by subvolcanic-volcanic facies of latite and trachy-rhyolite in the form of dykes and necks that are intruded into the crystalline complex along the faulting zones.

Geological setting

In the geological setting of the Bučim deposit, mainly participate Precambrian metamorphic rocks: gneiss, mica, amphibolites and Tertiary volcanic rocks (Rakičević et al., 1969; Ivanov, 1982). The most common are the gneisses, which are also the setting in which the ore mineralization was deposited. Tertiary magmatic rocks are represented by subvolcanic-volcanic breakthroughs of latite and andesite-latite around which the ore bodies in the Bučim deposit have been contoured. The age of these Tertiary volcanic rocks had been determined from 24.5 to 27.5 Ma (Serafimovski, 1993; Serafimovski et al., 2016) and 24.04 ± 0.77 and $24.51 \pm$ 0.89 Ma as indicated by chemical-annealing (CA)-LA ICP-MS zircon dating (Lehmann et al., 2013). Copper mineralization was located in four ore bodies: the Central part, Bunardžik, Vršnik and Čukar (Figure 1).

Ore mineralization

The primary mineralization in the Bučim ore deposit consists of major useful minerals: chalcopyrite followed by chalcocite, magnetite, native gold, gold minerals and accompanied minerals. Such are: pyrite, hematite, molybdenum and other rare minerals such as selenium and bismuth (Serafimovski, 2005; Townley et al., 2003; Tishcenko, 1981; Dumula et al., 2001; Mortensen et al., 2004, 2005; Bonev et al., 2002).

The most explicit way to examine these features of native gold from solid deposits is its separation from the ore and the use of appropriate methods for detailed studies including chemical, physical and microscopic studies. This research approach was also applied in these studies of the native gold from the Bučim porphyry deposit of copper and gold.

THE BUČIM DEPOSIT

1990; Serafimovski et al., 2006). Native gold and golden tellurides were determined, too. Spatial distribution and the way of occurences of gold at the Bučim deposit were studied by several researchers (Čifliganec, 1986, 1993; Serafimovski, 1992; Serafimovski et al., 2016).



Fig. 1. Generalized geologic map of the Bučim ore deposit and its particular ore bodies:
1) Central body; 2) Vršnik; 3) Čukar; 4) Bunardžik

Studies have shown that gold occurs in association with copper minerals such is chalcopyrite, where it does not appear as classical adhesion, but in the form of inclusions, droplets and rod-like shapes. Also, gold occurs with pyrite, usually as a binder material around small pyrite aggregates. A small part appears in the form of a fixed grain with the magnetite. The most often it occurs in the form of agglomerated grains with the waste minerals, and often these minerals make a boundary around the gold or in the form of veinlets that cut across the gold. Literature data of porphyry copper deposits studies (Batu Hijau Indonesia; Kessler et al., 2002) indicate that the most common gold in the quartz veins bound to sulfides or as native gold along the quartz or silicate grains boundaries. It can also be called "invisible gold" (in the structure of sulfides). From the performed studies (Pavičević et al., 1982) on samples from the Central part ore body were obtained certain findings that indicate some of the features of the gold minerals.

The sampled material originates from the drillholes from which polished sections were made and some of them are selected for a detailed study under an electron microprobe. The results showed that gold is present as native gold, in form of telluride and is most often related to chalcopyrite or more precisely about 95% of the native gold and telluride were found within chalcopyrite. The dimensions of the gold are very small, 5–10 microns (0.01–0.005 mm), and some of them could not be analyzed under the electron microprobe. The results of the performed analysis of the natural gold are given in Table 1.

Table 1

Chemical composition of natural gold aggregates within the polished sections (%)

Probe	Au	Fineness	Ag	Cu	Sn	Fe	Те	V
2	89.7	922	7.5	2.4	0.3	1.1		
6	85.7	870	12.7	2.3		1.0	0.3	
34	92.3	909	9.2	2.7		1.3		0.1
56	93.3	942	5.7	1.6	0.2	1.4		
98	86.2	897	9.8	2.4	0.4	1.1	0.4	
99-1	87.8	895	10.3	2.0		1.0		
99-2	89.4	894	10.5	2.4	0.2	1.3		
99-3	89.3	893	10.7	2.4		1.1		
99-4	97.2	982	1.7	0.9	0.4	4.0		

The sampling that was carried out for the purposes of this study was systematically organized to cover all phases of the processing of the porphyry ore in the Bučim mine. For this purpose, firstly, the primary ore was sampled from the open pit mine Bučim, where a sample was taken from the mine level 555/540 (Figure 2-a) for the formation of The results showed that native gold belongs to the group of moderate high grade gold (6 aggregates of gold), while two aggregates fall into the group of high-grade gold with a 901–950 probability and one belongs to the group of very high-grade gold. The silver content ranges from 1.7–12.7%. As for the impurities, the presence of copper is dominant in all samples with concentrations ranging from 0.9 to 2.7% Cu followed by iron with much lower concentrations, usually about 1% Fe. Telluride, tin and vanadium are very rarely present and in very low contents 1%. In addition to native gold, the gold in Bučim occurs in the form of electrum (sample 5) and pecite (sample 6), as can be seen from the Table 2 (Serafimovski,1992).

Table 2

Quantitative X-ray microanalysis of minerals of gold from the Bučim deposit (%)

Probe	Au	Ag	Cu	Fe	Te
1	92.06	5.60	1.57	0.62	-
2	84.66	15.34	-	-	-
3	86.00	13.90	0.46	-	-
4	80.30	18.68	0.35	0.87	-
5	72.53	25.42	1.26	0.68	-
6	26.84	41.09	0.52	-	31.23

Studies conducted in 1993 at the Central ore body confirmed the fact that gold most often occurs as a native gold, closely related to the chalcopyrite, in part with pyrite, magnetite and quartz. The gold contents within the chalcopyrite are variable, in the earlier generations they are higher compared to the smaller concentrations in the younger generations of chalcopyrite (Čifliganec et al., 1994). According to the data from the laser spectral microanalysis, the concentration of gold in the chalcopyrite was from 0.01 to 300 g/t Au and it was distributed irregularly. Gold in chalcopyrite occurs as thin inclusions of native gold and intergrowths in some crystal structures as atomic and finely dispersed.

MATERIALS AND METHODS

artificial schlich, which was further processed according to the scheme.

The next phase of sampling was carried out within the flotation of the Bučim mine, and the samples were taken from the active flotation cells where the flotation concentration of the primary ore was carried out (Figure 2-b), the next samples were taken from the concentrate immediately after completion of the flotation process of the primary ore (Figure 2-c). In the next phase, the slug was treated after the exit from the flotation. The first artificial samples were taken from the canalette through which the pulp from the flotation was transferred to the flotation tailing dam (Figure 2-d). The last samples were formed on the flotation tailing itself (Figure 2-e). Of all the samples whose sampling position was photographed in Figure 2, the necessary quantities of material (minimum 10 kilograms from the primary ore up to about 1 kg of flotation cells) were taken, which were further treated with a schlich procedure. Namely, each probe, depending on the quantity and nature of the material, was treated with the schlich method through a procedure for production of an artificial schlich. The obtained technical schlichs in the further procedure were treated for the magnetic separation of the magnetic fraction. Both derived fractions were examined under a stereoscope-binocular. Gold grain size was measured by the SEM.

The golden aggregates found were separated manually. Such segregated gold aggregates were subjected to further laboratory processing. A scanning electron microscopy (SEM) was used to determine the morphological characteristics as well as the chemical composition of the gold.









d)



Fig. 2. Position of the sampling points for monitoring of gold in the Bučim mine processing
a) Panoramic image of the northern part of the open pit mine Vršnik with microlocation where microsample was taken for artificial schlich (mine level 555/540). b) Illustration of a flotation cell from the Bučim mine, a site of flotation sampling.
c) Illustration of a concentrate in the flotation of the Bučim mine with locations of samples taken from the concentrate.
d) Illustration of the sampling of the canalette through which the pulp moves in the vicinity of the Bučim mine.
e) Illustration of the sampling of the hydrotailing at the Bučim mine flotation dam.

RESULTS AND DISCUSSION

The latest study was carried out on ore originating from the Vršnik mine, from a milled material prepared for flotation, from the flotation material, from the channels where flotation waste material flows into the flotation dam and from the flotation tailing dam. The performed study of morphology (shape and size) and the chemical composition of the gold aggregates showed certain differences.

Primary gold from the open pit mine level. For the examination of the primary gold, the material from the open pit mine level 600/615 was taken and an artificial schlich was prepared. After gently agitated in water the heavier fraction sinked to the bottom of the pan. That heavier material was subjected to laboratory treatment, whereby the golden aggregates found were manually separated. The gold aggregates, a total of five, found in the material, are characterized by a small size ranging from about 100 microns to about 490 microns. These aggregates were further subjected to morphological and chemical analysis.

Studies have shown that the form of the found gold aggregates is irregular, with the edges being rounded. The aggregates B1 and B2 are characterized by an elongated shape, B3 is characterized by irregular rounded form. The surface of aggregates B4 and B5 shows porosity (Figure 3). Such a porous surface in primary gold can be explained as a result of the dissolution of silver, or as a result of direct precipitation of gold with high purity (Petrovskaya, 1973; Groen et al., 1990). According to Bonev et al., 2002, such structure in the golden aggregates of the Čelopek deposit is not due to the extraction of silver, but is probably formed during the primary dendrite growth. Morphological analysis of aggregates can define specific conditions that are directly related to the mechanism of crystallization of primary gold.





B4. Rounded spherical gold grain with porous surface

B5. Golg grain showing irregular rounded porous surface partial flattened

Fig. 3. Morphology of gold aggregates from material taken from the open pit mine level 555/540.

The golden aggregates found were also analyzed from the aspect of chemistry as well. Each golden aggregate was analyzed in the rim parts and in the central parts in order to determine whether there is a zonation in the distribution of silver as an admixture (Table 3). Fineness in gold aggregates can be seen in Figure 4.

Table 3

Chemical composition of gold aggregates of material from the open pit mine level 555/540 (%)

		Au	Fineness	Ag	Fe	Ti Te	Cu
	Center	98.94		0.58	0.48		-
B1	Rim	99.40	995	0.37			0.24
	Mean	99.17		0.47	0.48		0.24
	Center	99.53		0.06			0.02
B2	Rim	99.30	997	0.49			0.21
	Mean	99.41		0.27			0.11
	Center	98.21		0.75	0.68		0.35
B3	Rim	96.22	979	3.41	0.37		-
	Mean	97.21		2.08	0.52		0.35
	Center	99.00		0.26	0.75		_
B4	Rim	99.27	996	0.34	0.22		0.18
	Mean	99.13		0.30	0.48		0.18
	Center	92.83		7.11			0.06
B5	Rim	99.89	963	0.11			
	Mean	96.36		3.61			0.06



Fig. 4. Plot of fineness in gold aggregates from samples taken from the open pit mine level 555/540

As can be seen from the plot there is no zonation in relation to the distribution of silver as a mineral impurity in the gold aggregates. There is a uniform distribution of gold and silver. The gold aggregates of this primary gold are characterized by high purity ranging from 963 to 997 (Table 3). This chemical composition turns this gold into a group of very high-grade gold (Zakharova, 1994).

Of the other impurities, silver is found with medium content of 0.27 - 3.61% Ag, or an average content of 1.34% Ag. Iron with medium content ranging from 0.27 to 3.61% Fe and average content of 0.29% Fe. Copper is much lower among content ranging from 0.06 to 0.35% Cu, and an average of 0.19% Cu.

Compared with the analysis of gold made on gold aggregates from the central ore (Table 1), the gold aggregates from Vršnik, which were the subject of the latest study, are characterized by much greater purity. This means that the gold aggregates differ in their "microchemical signatures".

Study by Moles, et al., 2013, shows that some "microchemical signatures" can be diagnostic for the appropriate types of Au mineralization, while other such signatures can be associated with a number of geological parameters, as chemical precipitation areas are repeated. The notion that a "different signature" does not have to be equated with a "different style of mineralization" or even a "different mineralization event" has profound implications for how microchemical signatures are seen.

For example, gold-copper oxisulfides may be related to primary hydrothermal ores and is present in the form of inclusions in gold and in microfractures within tetrahedrite, while the second type of oxisulfides can be formed during weathering of tetrahedrite-rich ores and associates with cuprite, malachite and limonite. Analysis of the data shown in this study shows that, in a number of samples, the atomic ratio (Au+Cu+Ag)/S is close to either two or one, which may indicate the existence of copper and gold phases, similar to the binary sulfides of silver and gold such as uytenbogaardtite (Ag₃AuS₂), petrovskaite (AgAuS) etc.

Knight et al. (1999), suggests in its researches that the existence of a difference in golden fineness ((Au/Au+Ag)×1000) can indicate different phases, changes between phases or differences in a phase of mineralization. However, as pointed out by Henley (1975), the calculation of the fineness does not take into account the small proportions of other elements which may be present. Also, the true fineness should be distinguished from "apparent fineness" which is derived from gold and silver assays of whole-ore samples and which may differ from the true fineness of the native gold if other gold- or silver-bearing minerals are present in the ore. The fineness of gold and its relation to the genesis of gold deposits has been studied by numerous workers (Harris, 1990). According to Knight et al. (1999), the homogeneity and the range of values at last may be in accordance with gold from mesothermal sources. Also, certain minerals (Tauson et al., 2017) can be formed both in hypogene and supergene conditions, and their precursors are solid solutions (Ag,Au)₂S with a primitive cubic unit cell, stable in the conditions of formation of the main-stage mineralization at 220-250°C. Thus, the problem is not formation, but preservation of Au-Ag sulfides, especially under oxidizing environment, in associations with sulfates and hydroxides in supergene conditions (Palyanova et al., 2014). The data obtained indicate that the surface of the native gold from an epithermal deposit has a complex structure: thin Ag- and S-enriched layer may be followed by a \sim 30–60 nm thick layer containing SiO₂ as a protective coating for Ag,Au sulfides, causing compositional discrepancies (Tauson et al., 2017).

According to Morrison et al., 1991, gold aggregates showing a homogeneous alloy composition indicate uniform precipitating conditions. Such aggregates, although often, but not exclusively, are related to orogenic precipitation of gold as a result of the same Au (HS) evaluation mechanism, e.g. H₂S is lost through sulphidation of lateral rocks. In complex deposition settings, some porphyry and epithermal systems include transport of gold from two types of complexes – chloride complexes and bisulphide complexes, and precipitation of the metal through pH change, redox change, temperature change, and interaction with surrounding rocks.

Gold aggregates in material prepared for flotation. Laboratory had shown that large-scale gold (50–60% of the total gold in the ore) is released by rough grinding of ore by finishing up to 53%. Only a small part of the gold about 5% is obtained from a class of size less than 10 microns. Also, studies have shown that the largest use of gold, up to 74%, in the harsh copper concentrate, was achieved in the rough grinding of the ore, i.e. at the final of about 46% minus 0.074 mm. For other finishes, the use of gold is reduced.

After gentle water panning and rinsing of this roughly brittle material that was prepared for flotation with our study, 9 gold aggregates were found. Dimensions of the golden aggregates found, unlike the gold originating from storey block, are larger and ranged from 300 microns to 1.4 mm (Figure 5).

When it comes to the shape of the golden aggregates found in the flotation material, it can be said that the elongated shape (F6 and F9) is present, where part of the grains are spliced (F1 and F4), then the irregular shape in which the grains are rounded or partially rounded edges (F2). On the surface of some grains, a porous structure (F3, F5, F8) was observed, which was also observed in the analyzed gold grains from the material of the open pit mine level.

The study of the chemical composition of the gold aggregates (Table 4) showed that it is a native gold which is characterized by a lower purity compared to the gold aggregates that originated from the material of the open pit mine level. Gold content here ranges from 81 to 97% Au or average content of 86–95% Au. It can be seen (Table 4) that most of the investigated gold aggregates can be found in the group of very high-grade gold with contents of 951-998, and much less in the group of high-grade gold with a purity of 900-950 (Figure 6). Only one golden aggregate belongs to the group of moderate highgrade gold (800-899). Of the present impurities, silver appears in higher content that reach up to 10% Ag (F7), and in two aggregates, titanium and tellurium appear as impurities. It is also noticed that the copper as an admixture is not present in all aggregates. Silver from impurities, is the most common, with an average content of 1.88-10.44%. The distribution of the gold and silver contents is given in Figure 6.

Table 4

Chemical comp	position of gold	aggregates
from material	prepared for flo	otation (%)

		Au	Fineness	Ag	Fe	Ti	Те	Cu
F1	Center	90.78		6.90	2.31	_	-	_
	Rim	94.97	953	2.21	_	2.82	_	_
	Mean	92.87		4.5	2.31	2.82	_	_
	Center	94.96		1.56	1.92	_	1.56	_
F2	Rim	96.45	980	2.20	1.35	_	_	_
	Mean	95.70		1.88	1.63	_	1.56	_
	Center	95.29	922	4.71	_	—	—	—
F3	Rim	89.30		10.70	_	_	_	_
	Mean	92.29		7.7	_	_	_	_
	Center	95.00		3.93	1.07	_	-	-
F4	Rim	91.71	953	5.30	2.99	_	-	-
	Mean	93.35		4.6	2.03	_	_	_
	Center	97.61	957	2.39	_	-	-	—
Е5	Rim	86.97		5.56	3.97	_	-	3.49
гэ	Rim	93.76		4.18	1.25	_	-	0.81
	Mean	92.78		4.1	2.61	-	-	2.15
	Center	92.13	922	7.87	_	_	_	_
F6	Rim	90.11		7.52	1.38	_	-	0.99
	Mean	91.12		7.69	1.38	_	-	0.99
	Center	95.42		4.58	_	_	_	_
F7	Rim	93.07	952	4.76	0.95	-	-	1.22
	Mean	94.24		4.67	0.95	_	-	1.22
	Center	90.66		8.52	0.83	—	—	—
F7 '	Rim	81.41	891	12.36	4.30	-	-	1.93
	Mean	86.03		10.44	2.56	_	-	1.93
F8	Center	93.67	927	6.33	_	_	-	-
	Rim	91.88		8.12	-	-	-	-
	Mean	92.77		7.22	-	_	-	-
F9	Center	93.91	972	3.04	3.05	—	—	_
	Rim	96.78		2.39	0.83	_	-	-
	Mean	95.34		2.71	1.94	_	_	_



F5.1. Gold grain showing elongated, flattned partially rounded surface features



F2. Gold grain with irregular rounded surface feature



F3. Porous partially rounded gold grain



F4. Elongated, flattened, partially rounded gold grain



F5. Irregular porous partially rounded gold grain



F6. Elongated, partially rounded gold grain



F7 and 7. Gold grains with well rounded edges and corners





F8. Golg grain showing irregular rounded porous surface

F9. Elongated, partially rounded gold grain

Fig. 5. Morphology of gold aggregates from material prepared for flotation

In regards to some other impurities, iron is commonly represented with an average of 1.38 - 2.56% Fe. Copper, titanium, and tellurium are present only in some of the tested aggregates with contents less than 3%.

Bearing in mind the fineness of the golden aggregates (Table 2), are classified in the group of very high-grade gold (Zakharova, 1994), which is characterized by the fineness of 951–998 (F1, F2, F4, F5, F7, F9) and gold with high grade from 900 fo 950 (F3, F6, F8). In addition, a certain zonation in the distribution of silver as a mineral impurity can be observed in those aggregates.



Fig. 6. Plot of fineness in gold aggregates from material taken from the flotation

In aggregates that are characterized by lower fineness, the center of gold aggregates is with higher content of silver than the rims of the aggregates. Gold-rich rims are very commonly observed in gold grains from placers and oxidized zones of gold deposits worldwide. Many researchers believed that the grain rim (in contrast to the grain core) does not reflect the gold grain composition of the original hypogene source (Svetlitskava et al., 2018). While in the higher-grade aggregates the situation is reversed, the rims of the aggregates are more rich in silver. According to Svetlitskaya et al., 2018, although gold grains with such zonality are poorly documented in the literature, they can be found in research. Such grain zoning where silver increase from core to margin is rarely observed and seems to be attributed exclusively to an increase of the Ag/Au ratio in solution during the gold grains growth. This zoning type is common for epithermal environments (Desborough et al., 1971, and Carrillo Rosúa et al., 2002, in Svetlitskava et al., 2018).

Compared to the golden aggregates of the material from the mine level, it can be seen that the purity of gold decreases and the silver and iron contents as the admixture increases. Also, certain zonation of silver, which phenomenon is missing in the gold from mine level material.

Gold aggregates from concentrate material. Two samples were taken from the material from the concentrate in which 28 grains were found in total. For some of these aggregates chemical composition and forms of gold aggregates were analyzed. From the analyzed grains it can be seen that the irregular elongated shape of gold aggregates with rounded sides prevails (K1.2, K1.3, K2.4, K2.3, K2.5, K2.7). Fewer aggregates are golden aggregates with a composite rounded shape (K1.1, K2.1 K2.9). The size of the grains ranges from about 120 microns to about 300 microns (Figure 7).

The chemical composition analyses (Table 5) of these gold aggregates showed that it is a native gold where the average gold content ranges from 80.58 to 97.22% Au, or the average gold content in all investigated gold aggregates is 88.21% Au.

Table 5

Chemical composition of gold aggregates of concentrate material (%)

		Au	Fineness	Ag	Fe	Ti	Те	Cu
	Center	83.24		16.76	_	_	_	_
K1.1	Rim	77.92	805	22.08	_	_	_	_
	Mean	80.58		19.42	_	_	_	_
	Center	95.29		4.71	_	_	_	_
K1.2	Rim	97.51	964	2.49	-	_	_	_
	Mean	96.40		3.6	_	_	_	_
	Center	89.14		10.86	_	_	_	_
K1.3	Rim	83.93	874	13.91	2.16	_	_	_
	Mean	86.53		12.38	2.16	_	_	_
	Center	87.28		12.72	_	_	_	_
K1.4	Rim	83.97	856	16.03	-	_	_	_
	Mean	85.62		14.37	_	_	_	_
	Center	87.46		9.91	2.63	_	_	_
K 2.1	Rim	86.71	884	12.74	0.55	_	_	_
	Mean	87.08		11.32	1.59	_	_	_
	Center	96.75		3.25	_	_	_	_
K 2.3	Rim	97.70	972	2.30	-	_	_	_
	Mean	97.22		2.77	_	_	_	_
	Center	88.91		9.97	1.12	_	_	_
K 2.5	Rim	77.80	842	21.09	1.12	_	_	_
	Mean	83.35		15.53	1.12	_	-	-
	Center	85.32	876	14.68	_	_	_	_
K 2.7	Rim	89.88		10.12	-	_	_	_
	Mean	87.6		12.4	-	-	-	-
K 2.9	Center	88.38	898	10.95	0.67	_	_	_
	Rim	90.67		9.33	-	-	-	_
	Mean	89.52		10.14	0.67	-	-	_



K1.1: Gold grain showing complex partially rounded surface morphology



K1.4: Rounded elongated gold grain showing minor abrasion polishing



K2.3: Rounded elongated gold grain



K2.6: Irregular elongated gold grain rounded



K1.2: Elongated, flattned, partially rounded gold grain



K2.1: Complex elongated, flattned, partially rounded gold grain



K2.4: Irregular elongated gold grain rounded



K2.7: Irregular elongated gold grain rounded



K2.9: Gold grain showing complex partially rounded surface morphology



K1.3: Irregular elongated gold grain partly rounded



K2.2: Elongated, flattned, partially rounded gold grain



K2.5: Irregular elongated gold grain rounded



K2.8: Gold grain showing complex partially rounded surface morphology

Fig. 7. Morphology of gold aggregates from a material taken from a concentrate in the gold aggregates with reduced gold content, we have an increase in the content of silver whose contents range from 2.22 to 19.42% Ag or an average content of 11.32% Ag.

On the Figure 8 we can see the distribution of silver in the gold aggregates. The distribution of silver is relatively uniform. Only in a few aggregates there is small silver enrichment in the central parts and it can be said that the zonality is poorly expressed.



Fig. 8. Plot of fineness in gold aggregates from material sampled from the concentrate

Of the other impurities in the gold aggregates, only iron is present (only in half of the analyzed aggregates) with an average content of 1.38% Fe, while the titanium, tellurium and copper are not present at all in the gold aggregates of this material. According to the fineness of the gold aggregates which varies from 805 to 972, it can be said that only one sample belongs to the group of very highgrade gold (951–998), while the rest fall into the group of moderate high-grade gold (800-899) (Zakharova, 1994). As can be seen from the data provided, the purity of gold compared to the previous gold aggregates is further reduced.

Golden aggregates from material taken from the canalettes. In the canals, after the flotation processing of the concentrate, gold aggregates were also found. These are, in fact, golden aggregates glued along the walls of the canals that move the material from flotation to the tailing. From the large number of gold aggregates, only three grains were analyzed (Figure 9).

Most of the gold aggregates of this group are characterized by an elongated irregular shapes, which also permeate structures, mostly with partially rounded edges. There are also present flat shapes with well-rounded and sharp edges. According to Bulatović et al., 2000, gold and its alloys during crushing take various forms: plate, corpuscles, scales, etc. Gold particles that are characterized by sharp edges tend to unravel the air bubbles that result in gold loss during the flotation process. On this basis, it can be said that the gold found in the channels is actually the "lost" gold in the flotation process.



1. Elongated, partially rounded gold grain









3. Porous partially rounded gold grain



Fig. 9. Morphology of golden aggregates from material sampled from the tailing flow channels

7. Irregular dendritic gold grain

The size of tested aggregates ranges from about 300 up to 700 microns. Most of the golden aggregates from the tailing flow channels are characterized by a flat shape. According to studies, the flattening of the grains grows with the increase in the length of the transport (Knight et al., 1999; Youngston and Craw, 1999; Tishcenko, 1981, etc.). This assumption that the flattening is related to changing the shape of the grains during sediment transport is not generally proven, since the presence of flattened forms in the primary sources is noticeable (Bonev et al., 2002).

From the chemical analyses (Table 6) it can be seen that two of the grains are with gold content ranging from 92 to 93% Au, and a silver content ranging from 3.0 to 7.34% Ag (falls into the group of high-grade gold). The fineness in gold aggregates is given in Figure 8. In the golden aggregate № 2 in the peripheral parts were detected high iron (16.64%) Fe) and copper contents (18.6% Cu) compared to the central part of the aggregate. Titanium and tellurium as secondary elements are not present in these particular specimens.

Gold aggregates from material sampled from the tailing. In the material that was sampled







J1.6: Irregular porous well rounded gold grain

from the tailing, 17 gold aggregates were found. Some of these gold aggregates were used for further laboratory study. Studies of the morphology of the gold aggregates (Figure 10) showed that these grains are characterized by irregular shapes with well-rounded sides where the porous structure of the surface of the aggregate was observed J1.5).

Table 6

Chemical composition of golden aggregates of material from tailing flow channels (%)

		Au	Fineness	Ag	Fe	Ti Te	Cu
1	Center	96.13	926	3.87	_		-
	Rim	89.18		10.82	-		-
	Mean	92.65		7.34	-		-
2	Center	97.31	963	2.69	_		_
	Rim	62.42		2.33	16.64		18.60
	Mean	79.86		3.00	16.64		18.60
3	Center	93.19		4.78	2.03		_
	Rim	93.06	944	6.06	0.88		-
	Mean	93.12		5.46	1.45		_



J1.5: Porous partially rounded gold grain



J1.8: Gold grain with well rounded corners and edges

Fig. 10. Morphology of golden aggregates from material sampled from the tailing

The size of the grains ranges from about 100 to 200 microns. These gold aggregates are the smallest in size compared to all previously found and studied gold aggregates. Apart from the size of these aggregates, there is a noticeable curvature of the edges. This crushing and rounding of aggregates arise as a result of the "transport" of aggregates in the process of processing this material to the final destinationthe tailing, and due to the fact that gold has a small hardness.

The chemical analysis was made of four of the golden aggregates found (Table 7). From the Table 7 it can be seen that it is a native gold where the contents range from 83 to 95%. The silver content range from 4 to 16.24%. Fineness of gold ranges from 837 to 956, which means it can be turned into a group of moderately high-grade (JI.8, Jl.1) and high-grade gold.

Table 7

Chemical composition of gold aggregates of tail material (%)

		Au	Fineness	Ag	Fe	Ti	Te	Cu
J1.1	Center	85.93		14.07	-	_	_	-
	Rim	81.59	837	18.41	_	-	_	_
	Mean	83.76		16.24	_	_	_	_
J1.5	Center	94.71		4.48	0.81	_	_	_
	Rim	85.75	930	9.11	1.08	_	_	4.06
	Mean	90.23		6.79	0.94	_	_	4.06
	Center	96.31		3.69	_	_	_	_
J1.6	Rim	94.90	956	5.10	-	_	_	-
	Mean	95.60		4.39	_	_	_	_
J1.8	Center	88.91	888	11.09	_	—	_	_
	Rim	87.11		11.01	_	_	_	1.88
	Mean	88.01		11.05	_	-	-	1.88

The fineness in the analyzed aggregates is given in Figure 11. Of the remaining impurities there are the iron in one gold aggregate with an average content of 0.94% Fe and copper in two gold aggregates with contents of 1.88% and 4.06% Cu. The table shows that there are somewhat higher contents of silver in the two aggregates than in the peripheral parts, while in the other two aggregates it is not noticeable. These data, however, are not enough to draw a conclusion on the existence of zonation.

If the correlation between the golden aggregates is made, it can be concluded that the golden aggregates derived from a flotation material have

The elongated shape prevails, where sharp edges of the aggregates are observed. According to the report, the aggregates (6) that belong to the group of very high-grade gold (950 - 998) prevail, 3 aggregates fall into the group of high-grade gold (901 - 950) and only one aggregate is moderately highgrade (850 - 900). Of the remaining impurities, iron prevails in almost all gold aggregates the second is copper, while titanium and tellurium are present in only two aggregates.

the largest dimensions from 300 microns to 1.3 mm.



and tailing flow channels (1-3)

As this material passes through the process of flotation, certain changes in gold aggregates are also noted. The size of the gold aggregates in the material of the concentrate is smaller, i.e. ranges from 120 up to 300 microns. The shape of the golden aggregates also changes, i.e. the elongated shape dominates but with much more radiant edges. The fineness which now amounts to most of the gold aggregates (7 aggregates) to 900 and only two grains are at last over 951. The other impurities can be noted that their content drastically changes, that is, the iron is most present while there is no presence of copper, tellurium and titanium.

In the aggregates that were found in the tailing material, the irregular forms dominate. These are smaller aggregates compared to the previous, with a size of 100–200 microns. Two of these aggregates belong to the group of high-grade (930 and 956) and two aggregates are moderately high-grade (850–900). The impurities in the studied aggregates are the least represented compared to the previous ones. The iron was detected only in one aggregate, while the copper in two aggregates is present. Titanium and tellurim were not detected at all.

Gold in the Bučim deposit as a whole is characterized by high purity without any characteristic zonality in relation to the content of silver as an admixture in gold aggregates. The remaining impurities – copper, iron, titanium and tellurium, are of very low contents or sometimes were not detected at all.

Study of the impurities that may be present in the homogeneous gold, showed that in some porphyry deposits, the native gold that was associated with sulphide minerals contained higher copper content than free gold (Kessler et al., 2002). The silver content is higher in gold that it is associated with chalcopyrite than that is related to the bornite, while the content in free gold is between these two contents. From our study it may be seen that the contents of copper and silver vary in a wide range that can indicate that these gold aggregates may originate from gold associated with chalcopyrite, but as native gold, too.

Morphological forms of gold from the open pit mine level are likely to reflect the conditions of the environment in which the gold aggregates crystallized. The size and shape of the rest of the gold depends on the length of the process, but also on the changes that occur in the process of crushing and grinding the ore during the preparation of the material in the flotation process. Apart from the forms, the application of reagents during flotation certainly has an impact on the chemical composition of the native gold. This means that as the material moves during the processing, starting from the crushed material through the concentrate to the golden aggregates, there are changes related to the size of the gold aggregates, their shape and the chemical composition.

CONCLUSION

Based on the presented data, several conclusions can be drawn:

- Schlich study showed the presence of gold in the material of the mine level which is characterized by size from about 100 microns to about 490 microns. The shape is mostly irregular with rounded edges. The gold aggregates of this primary gold are characterized by high purity ranging from 963 to 997. Of the impurities, silver is present with an average content of 1.34% Ag, iron with medium content of 0.29% Fe and copper is represented with an average content of 0.19% Cu.

- The size of the golden aggregates found from the material prepared for flotation ranges from 300 microns to 1.4 mm. There are an elongated and irregular shapes. The gold aggregates are of purity ranging from 810 to 970. Of the impurities the most represented are: silver with average contents of 1.88–10.44% Ag, iron with average 1.38–2.56% Fe, while copper, titanium and tellurium are present only in some of the tested aggregates with contents less than 3%.

- The gold aggregates of the material taken from the concentrate are with the grains sizes from about 120 microns to about 300 microns. The irregular elongated shape prevail, the gold aggregates with a complex rounded shape are less represented. The chemical composition of these gold aggregates has shown that it is a golden gold with an average gold content of 88.21% Au.

- Studied gold aggregates from a material taken from the tailing flow channels are with sizes ranging 300–700 microns. The golden aggregates of this group are characterized by an elongated irregular and a spliced form. The fineness of these golden aggregates is from 926 to 963. The average silver content ranges from 3.0 to 7.34% Ag. Of the other impurities are present iron and copper.

- The gold aggregates sizes of the material sampled from the tailing ranged 100–200 microns. Grains are characterized by irregular shape. According to the chemical composition, these aggregates are native gold of high purity ranging from 837 to 956, which means it can be formed in the group of very high-grade and high-grade gold. The silver content ranges from 4 to 16.24% Ag. Of the remaining impurities, there are iron in one gold aggregate with average content of 0.94% Fe and copper in two gold aggregates with contents of 1.88% and 4.06% Cu.

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Резиме

СОСТАВ И МОРФОЛОГИЈА НА САМОРОДНОТО ЗЛАТО НИЗ ФАЗИТЕ НА МИНЕРАЛНОТО ПРОЦЕСИРАЊЕ ВО РУДНИКОТ ЗА БАКАР БУЧИМ, РЕПУБЛИКА МАКЕДОНИЈА

Виолета Стефанова, Тодор Серафимовски, Горан Тасев

Институт за теолотија, Факултет за природни и технички науки, Универзитет "Гоце Делчев" во Штип, бул. "Гоце Делчев" 89, 2000 Штип, Република Македонија violeta.stefanova@ugd.edu.mk

Клучни зборови: златни зрна; хемиски состав; морфолошки форми; минерално процесирање

Самородното злато е чест нуспроизвод во многу Сипорфирски наоѓалишта, иако неговата дистрибуција и хемизмот во многу наоѓалишта остануваат недоволно проучени. Целта на овој труд е да се анализира хемискиот состав и морфологијата на одделни златни зрна. Во овие проучувања се испитуваше хемизмот и морфологијата на златото во минералниот процес, флотацијата и јаловината во наоѓалиштето Бучим. Беа анализирани пет зрна од етажниот блок, седум агрегати од материјалот за флотација, девет агрегати од концентратот, три од каналетите и четири агрегати од јаловината. Чистотата е во ранг од 805 до 995. Среброто е најчест спореден елемент и неговата содржина се движи во ранг од 0,27 до 19,24%. Си и Fe се среќават поретко, во просек железото околу 2,5% Fe. а бакарот максимално до 4% Cu. Забележано е дека железото и бакарот како нечистотии не се присутни кај сите анализирани агрегати. Титан и телуриум се присутни само во еден анализиран златен агрегат (2.82%). Проучуваните златни зрна се појавуваат во различни морфолошки форми, кои се карактеризираат со повеќе или помалку заоблени рабови. Најчесто се забележани издолжени златни зрна се поретко пронајдени.