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Original scientific paper

MORPHOLOGICAL AND CHEMICAL CHARACTERISTICS OF GRAINS OF PLACER GOLD FROM THE OTINJA RIVER

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A b s t r a c t: In the Serbo-Macedonian metallogenic province in the Republic of North Macedonia, numerous occurrences of Au have been found in alluvial sediments. Placer gold originates from known genetic types of Cu-Au porphyry deposits (Bučim and Borov Dol) and epithermal Au deposits (Plavica and Allchar). However, in the Otinja river, the primary source of Au still remains unclear. Twenty-three Au grains collected from the river of Otinja alluvion were primarily analyzed on a scanning electron microscope (SEM) to investigate their morphological and chemical characteristics. The gold aggregates that were found range in size from about 120 μm to 2 mm, they have mostly sub-rounded to rounded shapes, rarely irregular shapes, with microtextures indicating a source at a distance of several km. Chemical composition tests show mainly Au-Ag mixtures, with Au contents ranging from 94.45 to 100%. By chemism, Au grains belong to the group of very high grade gold with high purity (951 to 1000). In general, impurity contents are very low. In order of representation, the following are most present: Ag (0.02–4.89%), Fe (0.02–4,74%), Cu (0.02–0.54%), Te (0.09–0.55%), and Se (0.29%).

Key words: Au grains; morphology; chemical composition; primary sourcre

INTRODUCTION

Gold has attracted people's interest since ancient times and numerous investigative methods and approaches have been introduced in gold exploration over time. In that sense, it is important that the studies of morphology and chemical composition of Au grains are widely used in gold exploration (Chapman et al., 2021; Dos Santos Alves et al., 2020; Liu et al., 2021; Svetlitskaya and Nevolko, 2017). Morphological features of Au grains may indicate the distance they traveled during transport from the primary source, chemical compositions of Au grains may represent the hypogene source and may possibly distinguish between primary sources (Masson et al., 2021).

In regions of low intensity of rock dissolution, morphological and microchemical studies of placer Au grains from alluvial sediments have been more used to identify original hypogene sources. In accordance with the defined relationship between shape and hypogene source, the determination of the distance traveled by Au grains from their source can be made based on their morphological characteristics and their surface textures (Dos Santos Alves et al., 2020). In a fluvial environment, the shape and size of sediment grains reflect the history and evolution during transport. (Youngson and Craw, 1999). As a result, estimation of the transport distance in streams and rivers is possible by examining the degree of flatness, roundness, polish, bending, and surface texture of Au grains (Masson et al., 2021). Identification of hypogene sources and types of Au deposits that contribute to the formation of Au deposits from many areas around the world is a challenging task. Hypogene source types and their interaction with primary mineralization have been revealed using the microchemical characterization technique of placer Au grains worldwide (Svetlitskaya et al., 2018), even though the primary ore sources are still unknown.. Chapman and Mortensen (2006) improved this method on the basis of several compilations of microchemical characteristics of Au grains around the world, defining characteristic Ag and Au contents in each type of Au mineralization. A number of studies have attempted to identify potential sources, mostly using electron microprobe analyses (EMPA), and have shown good results worldwide (Chapman and Mortensen, 2016; Dos Santos Alves et al., 2020; Liu et al., 2021). In the eastern parts of the Republic of North Macedonia, research on eluvial-alluvial Au, which undoubtedly bears some of the marks of hypogene sources, has been intensified in the last two decades. Here we will the first of all mention the investigations of the morphological forms of Au grains and the investigations of chemical composition. First such investigations were carried out on Au grains from several localities in which the presence of endogenous Au mineralization was determined by previous investigations (Stefanova et al., 2007, 2013, 2014, 2015; Volkov et al., 2008; Kovacev et al., 2007). Then tests were carried out on other alluvions. For some of them, there was previous data from certain preliminary surveys that indicated the presence of Au, while others were investigated for the first time, such as the schlich prospecting on the river of Otinja (Stefanova et al., 2021).

The primary source(s) of placer Au in the river of Otinja remain(s) undiscovered due to the lack of studies, even in terms of the morphology and the chemical study of gold. This is the second paper on the morphological and chemical characteristics of placer Au in the Otinja river.

This paper provides a detailed analysis of the morphology and chemical characteristics of Au grains from the Otinja river in order to estimate the distance to the primary source, including the genetic type of mineralization. The morphology of the Au grains and the chemical composition were analyzed by scanning electron microscope (SEM); to determine if there is zoning in the gold aggregates, measurements were made in the cores and rims of the grains themselves. The chemical characteristics of placer Au, which is the subject of investigations in this paper, are a useful tool for researching the hypogenic environment of an unknown primary source that can greatly help in the research of metallic mineral deposits in the Republic of North Macedonia.

GEOLOGICAL CHARACTERISTICS OF THE BUČIM-DAMJAN-BOROV DOL ORE AREA AND THE RESEARCH TERRAIN

In the southern parts of the Balkan Peninsula there are several larger metallogenic provinces, within the boundaries of which there are metallogenic zones that include important deposits and occurrences of polymetals. What is important is the metallogeny of the Vardar zone and the Serbo-Macedonian massif, which are within the Serbo-Macedonian metallogenic province (Figure 1), distinguished by Janković, 1967. This large metallogenic province with a NNW-SSE orientation is located in the central parts of the Balkan Peninsula, between the Dinarido-Hellenides in the west and the Carpatho-Balkanides in the east (Serafimovski, 1990).

The basic metallogenic feature of the Serbo-Macedonian metallogenic province consists of polymetallic ores (Pb, Zn, Ag, Cu, Au, Mo, As-Sb, etc.) distributed in several metallogenic zones, areas and regions, and spatially, temporally and genetically-paragenetically associated with Tertiary intermediate to acidic volcanogenic-intrusive magmatism (Serafimovski, 1990; Serafimovski et al., 2016). The creation and spatial arrangement of magmatism and mineralization in this large metallogenic unit are controlled mainly by deep dislocation structural zones, directions of extension of which coincide with the boundaries of the basic geotectonic units (the Dinarides, the Vardar zone, the Serbo-Macedonian massif, etc.).

The most important metallogenic zones in the Republic of North Macedonia are Lece-Chalkidiki and Besna Kobila-Osogovo-Thassos (Figure 1), which fully reflect the structural-geological, tectonomagmatic and metallogenic structure of the Serbo-Macedonian metallogenic province (Serafimovski, 1990; Serafimovski et al., 2016). Spatially, the Lece-Chalkidiki metallogenic zone is localized in the border area between the Serbo-Macedonian massif and the Vardar zone, occupying the eastern peripheral parts of the Vardar zone and the western peripheral parts of the SMM (Figure 1).

The Bučim-Damjan-Borov Dol ore area is part of the Lece-Chalkidiki metallogenic zone, i.e., it occupies its central parts, and with an area of about 200 km^2 it is one of the smallest ore areas in this zone (Čifliganec, 1987; Serafimovski, 1990; Lehmann and Barcikowski, 2012) (Figure 1).

The Bučim-Damjan-Borov Dol ore area is characterized by the occurrence of intense tectonic-magmatic and mineralization processes, the manifestations of which are mainly related to the late stages of the Alpine orogenic cycle, that is, the Young Alpine mineralization epoch (Serafimovski et al., 2016; Lehmann and Barcikowski, 2012). Volcanic activity began at the end of the Oligocene, while mineralization occurred during the Miocene (Serafimovski et al., 2016; Boev and Yanev, 2001; Lehmann at al., 2013). Significant concentrations of

Fe-skarn type (Damjan and Šopur), Cu, Au, Ag-porphyry type (Bučim and Borov Dol) and occasionally Pb-Zn, Ba, etc. were formed. – hydrothermal vein type.

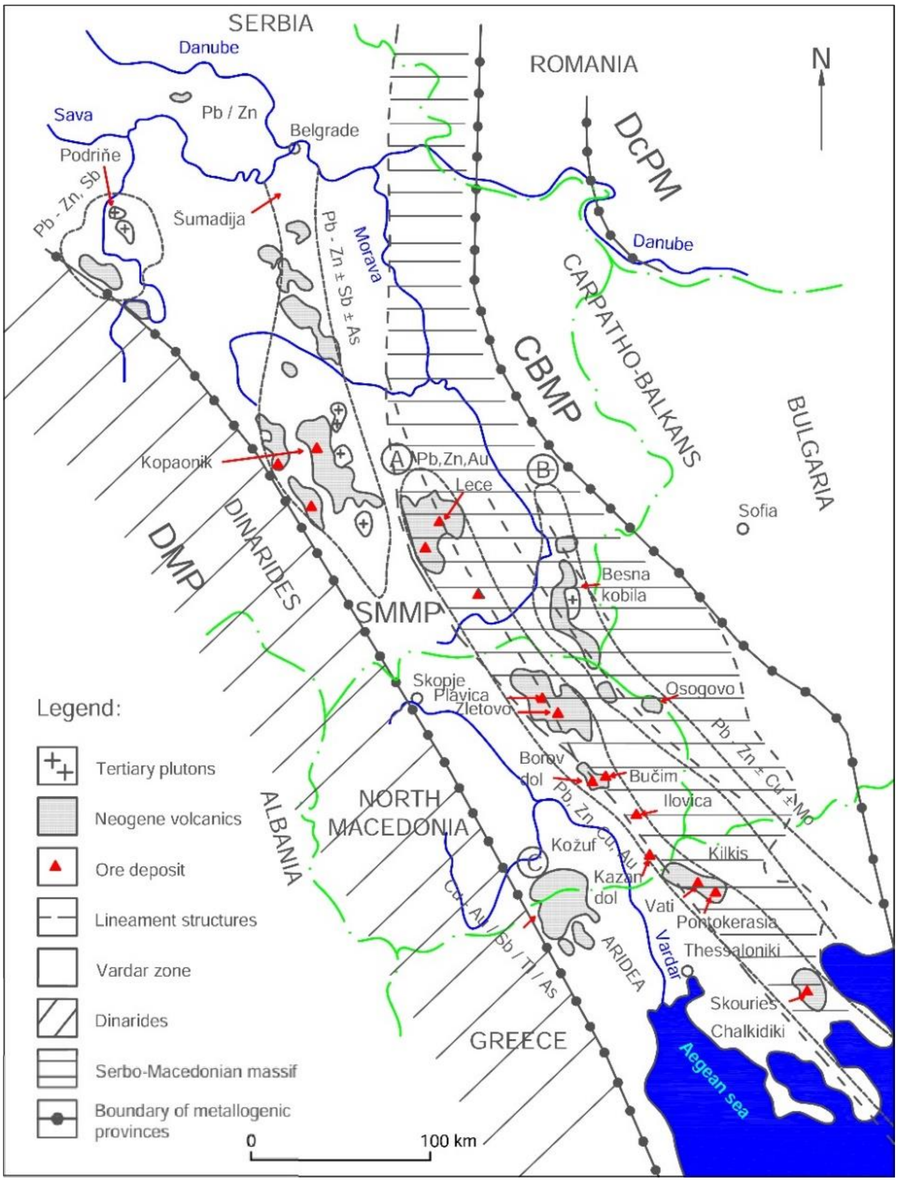


Fig. 1. Main metallogenic zones in the Serbo-Macedonian metallogenic province (modified, according to Janković, 1990). A – Metallogenic zone Lece-Chalkidiki, B – Metallogenic zone Besna Kobila-Osogovo-Thassos, and C – Metallogenic area Kožuf-Aridea. (DcPM – Dacian metallogenic province, CBMP – Carpatho-Balkan metallogenic province, SMMP – Serbo-Macedonian metallogenic province, DMP – Dinaridic metallogenic province).

In the Bučim-Damjan-Borov Dol mining area, there are three systems of differently oriented fault lines (the first system of fault structures NW-SE, the second system of fault structures NE-SW, and the third system of fault structures NNW-SSE to almost N-S), as well as numerous tectono-magmatic morphostructural forms characteristic of the structures of volcanic apparatuses from the order of volcanic calderas, volcanic domes, dyke structures, etc. (Serafimovski, 1990).

Rocks of different ages are found in the geological structure of the research area (Figure 2). The Otinja river drains an area that is mostly built of Precambrian rocks represented by several varieties of gneisses, amphibolites and micaschists, amphibolite schists and leptinolites. The Paleozoic is represented by serpentinites, chlorite amphibole schists, marbles and carbonate schists. Jurassic magmatism is represented by aplitoid and biotite granites and adamellites. The Cretaceous sediments are represented by conglomerates, sandstones, claystones, marls and limestones. In the Paleogene, the sedimentation of Eocene conglomerates, sandstones, claystones, and marls.

Tertiary magmatism within the boundaries of the Bučim ore field is represented by small subvolcanic-volcanic intrusions of andesites and trachytes (Lehmann and Barcikowski, 2012). Pliocene sediments represented by sands, loams and gravels are also found on this terrain. The Otinja river drains a part of the Bučim-Damjan-Borov Dol ore area, *i.e.*, from the Bučim ore field, within the boundaries of which is also the porphyry Cu-Au deposit of Bučim (Figure 2).

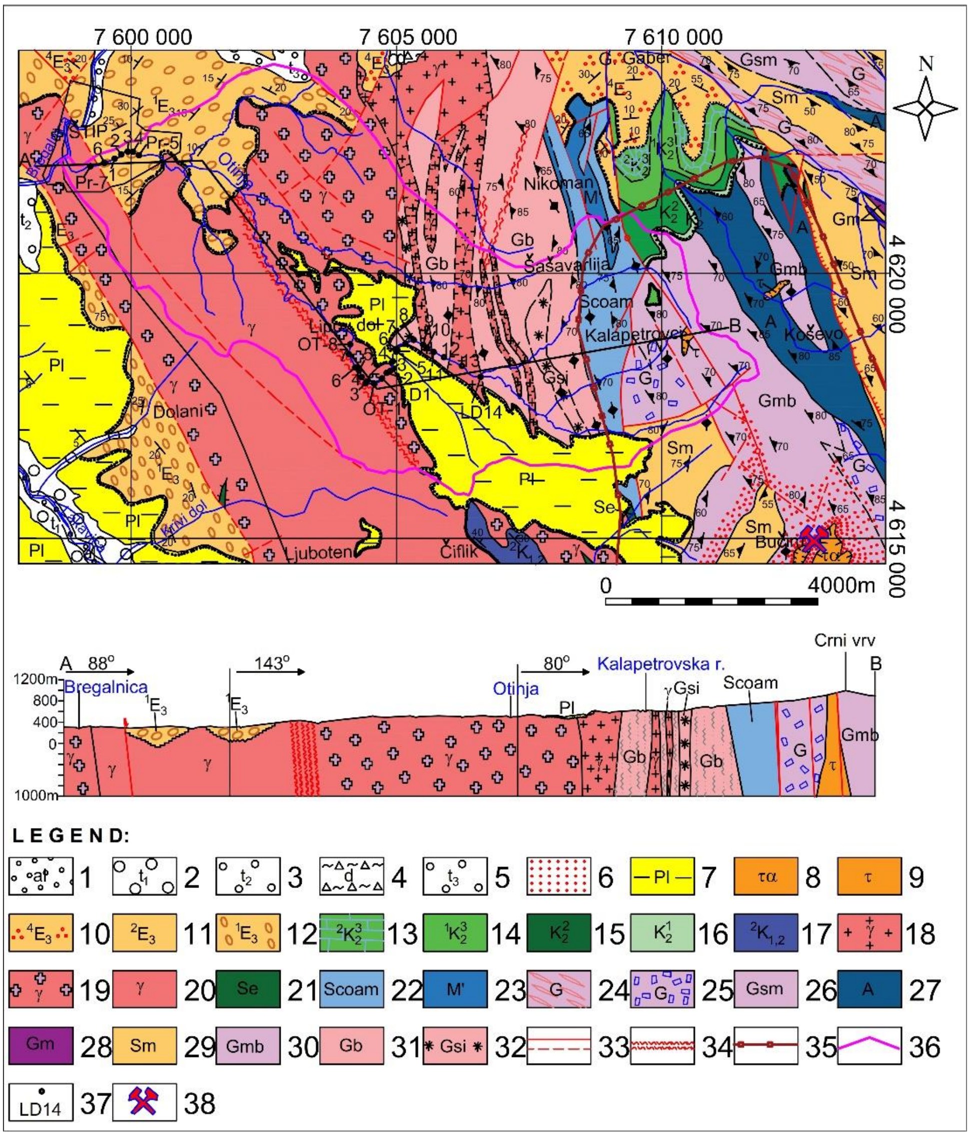


Fig. 2. Geological map of the wider environment of the catchment area of the river of Otinja.
Legend: 1 – Alluvium; 2 – Lower river terrace; 3 – Higher river terrace; 4 – Deluvium; 5 – Old river terrace; 6 – Hydrothermal changes [1 – 6 Quaternary]; 7 – Sands, loams and gravels; 8 – Andesites; 9 – Trachytes [7 – 9 Neogene]; 10 – Upper zone of the flysch: claystones and sandstones; marls, limestones and claystones; 11 – Lower zone of the flysch: gray sandstones and purple claystones; conglomerates, sandstones and claystones; 12 – Basal series: sandstones, marls and conglomerates [10 – 12 Paleogene]; 13 – Limestones and marls (senon); 14 – Clays, sandstones and siltstones (senon); 15 – Sandstones (turon); 16 – Conglomerates and sandstones (Cenomanian); 17 – Sandstones and claystones (Albian-Cenomanian) [13 – 17 Cretaceous]; 18 – Aplitoid granites; 19 – Biotite granites; 20 – Adamelites [18 – 20 Jurassic]; 21 – Serpentinites [21 – Younger Paleozoic]; 22 – Chlorite-amphibole schist; 23 – Marbles and carbonate schists [22 – 23 Old Paleozoic]; 24 – Eye-like-amygdaloid gneisses; 25 – Porphyroblastic gneisses; 26 – Gneisses, amphibolites and micaschists; 27 – Amphibolites and amphibolite schists; 28 – Muscovite gneisses; 29 – Micaschists and leptinolites; 30 – Two-mica banded gneisses; 31 – Biotite fine-grained gneisses; 32 – Sillimanite-cordierite gneisses [24 – 32 Precambrian]; 33 – Fault: established and presumed; 34 – Mylonite; 35 – Border of the mining area Bučim-Damjan-Borov Dol; 36 – Border of the catchment area of the Otinja river; 37 – Location of a tested schlich sample; 38 – Location of the Bučim Cu-Au mine

The Tertiary magmatism in the Bučim deposit produced the copper mineralization that is followed by Au and is distributed in several ore bodies located around the intrusions, and the gneisses are the depositional environment (Čifliganec, 1987; Serafimovski et al., 2016). Also, copper mineralization is located in andesites and trachyandesites. The faults present in this terrain with a NNW-SSE orientation and NE-SW oriented fault structures of a lower order allowed the ore-bearing hydrothermal solutions to move, and at the same time delayed mineralization in gneisses as a favorable environment. In addition to the Bučim deposit, numerous porphyry Cu occurrences are known in the northern part of the Bučim ore field (Vranjak, Orljak, Crn Vrv – Kalapetrovci, Koševo, Koševska Reka, etc.) (Čifliganec et al., 1993) (Figure 2).

Specifically, the Crn Vrv-Kalapetrovci ore occurrences are within the research area drained by the Otinja river (Figure 2). These ore occurrences are localized in the northwestern parts of the Bučim ore field, *i.e*., in close proximity to the village of Kalapetrovci and the locality Crn Vrv. With the past geological research, intrusion magmatic bodies were discovered here, which in the form of small dykes intruded into the Precambrian complex, along the intersection zones of the fault structures with direction of extension NNW-SSE and NE-SW. Wide zones of hydrothermal metasomatic changes such as sericitization, silicification, K-feldspathization, chloritization, etc., have been determined around and in the trachytic dykes themselves, which indisputably represent a favorable indication of the existence of copper mineralization of the porphyry type (Čifliganec et al., 1993).

With geochemical research carried out in the past, data were obtained on high anomalies (primarily) of Cu and Mo, while Pb and Zn anomalies are somewhat less pronounced and form mostly circular anomaly zones. At the places of strongly pronounced anomalies of Cu and Mo (around the magmatic intrusions) veined pyritic-chalcopyritic mineralizations are also registered. These are the ore occurrence immediately next to the trachytic intrusion on Crn Vrv and the ore occurrence north of the village of Kalapetrovci (Čifliganec et al., 1993).

APPLIED METHODOLOGY

The schlich prospecting was carried out in the lower and middle course of the river of Otinja, which has a length of about 18 km. The surface of the catchment area drained by this river is about 53 km^2 (Figure 3). Au grains from the Otinja river were obtained by gold panning random schlich samples. Schlich sampling points were selected from the active river channels based on the evaluation of the alluvial sediments (Figure 4).

All schlich sampling points were located in positions of the riverbed where the water flow energy is the lowest so as to allow precipitation of heavy minerals including Au grains (Figure 4). Along the course of the Otinja river, a total of 29 schlich samples were taken on three occasions. On the first occasion, 7 samples were taken in the lower course of the Otinja river, up to the mouth of the river of Bregalnica. A total of 8 samples were taken in the middle course of the Otinja river with the second schlich prospecting. The geographic coordinates of each test were recorded using a GPS device. Holes were excavated in the riverbed to remove the surface sandy material (30 cm to 50 cm in depth) in order to expose and test a sample from the middle gravel zone. Gold panning of the tested gravel and sand was classical using a basin to concentrate the Au grains. The resulting black schlich from each test was packed in plastic bags, marked with appropriate labels, and air-dried. Furthermore, the black schlich from each sample was subjected to laboratory processing. The separation of the magnetic series was performed manually with a magnet and the material was examined with an electronic stereoscope-binocular. Au grains were separated manually, and in the laboratory for electron microscopy at the Goce Delčev University, Štip, they were subjected to microchemical and morphological analyses.

Morphological characteristics of gold, primarily flatness, roundness and bending of the grains, were determined using a scanning electron microscope (SEM). This method is also applied to determine the chemical composition of Au grains.

SEM analyses were recorded using a VEGA3 LMU scanning electron microscope and an INCA Energy 250 microanalysis system, for quantitative sample analysis. SEM analyses were performed with an SE (Scattered Electrons) detector at a voltage of 20 kV. First, an Au grain is placed on the sample holder which has a carbon double-sided adhesive tape on it. The grain placed on the Modular Coater, Quorum Q150R ES was analyzed in high vacuum mode at more than 0.018 Pa. The surface of the grain is analyzed on a motorized sample holder in 5 axes (x, y, z rotation and tilt). VegaTC software was used for SEM. The energy dispersive X-ray (EDX) system for SEM is a fully quantitative SDD with excellent performance at low and high counts, which is able to achieve better than 125 eV resolution of the MnK_α, FK_α and CK_α peaks. The working distance for X-rays was 15 mm. Detector control and data processing were performed with the INCA software. SEM-EDS analyses were performed on unpolished surfaces. The elements Ag, Au, Fe, Cu, Te, and Se were analyzed.

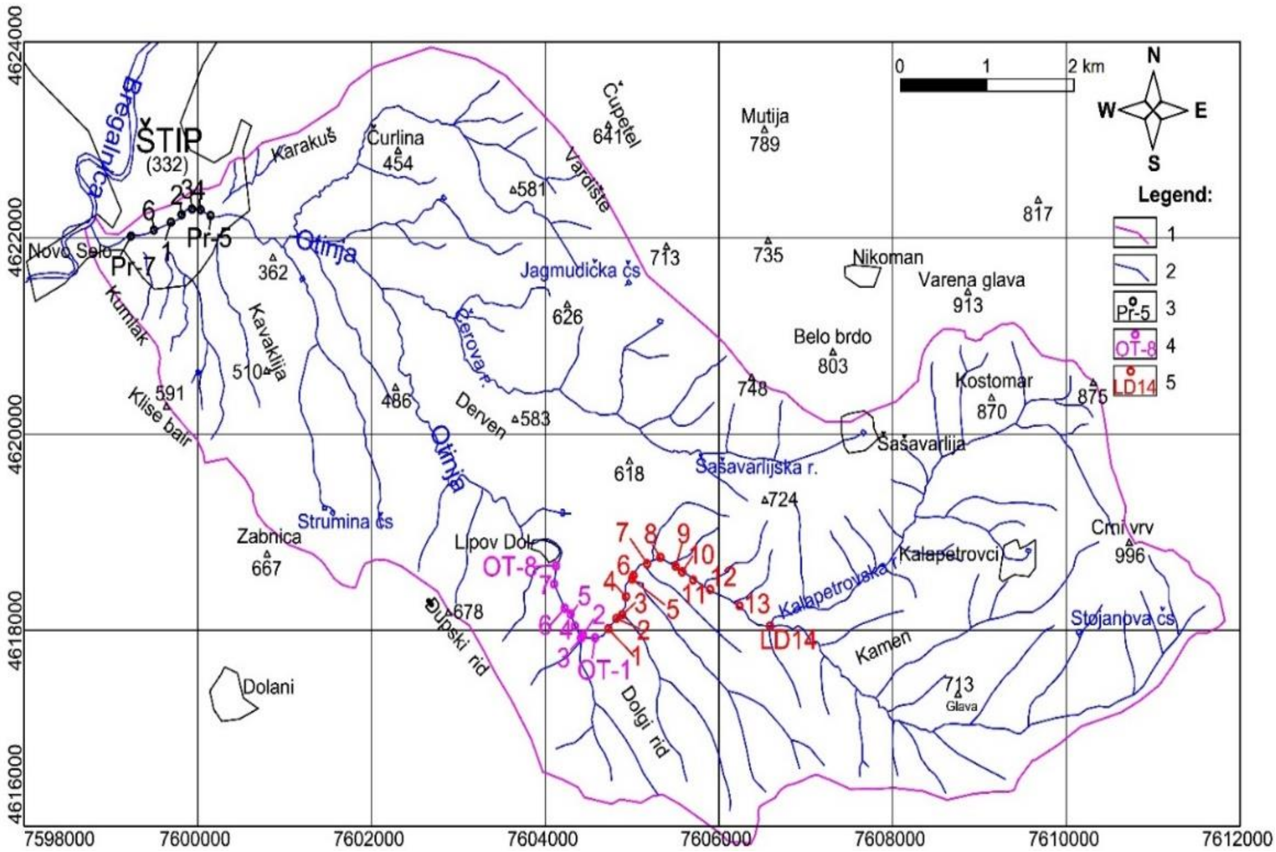


Fig. 3. Schematic map of the catchment area of the Otinja river with the locations of the tested schlich samples.
Legend: 1 – Boundary of the catchment area of the Otinja river; 2 – Drainage system;
3–5 – Locations of tested schlich samples on three occasions

Fig. 4. Field photographs of the sampling points of schlich samples (LD-1 and LD-8) from the bed of the river of Otinja

RESULTS AND DISCUSSION

Morphology of Au grains

Native Au is a very malleable mineral and therefore many of the physical characteristics such as grain size will depend on the type of primary mineralization, the type and length of transport, and the erosion processes to which the terrain is subjected (Mudaliar et al., 2007). However, the morphology of Au grains is a less reliable indicator than the chemical composition of Au grains in determining whether it is a single source or multiple sources of the found placer Au (Nakagawa et al., 2005).

Of a total of 29 samples taken from the Otinja river on three occasions, 23 grains of Au were found, 7 of which with the last schlich prospection realized in 2022.

Figure 5 shows grains of Au from the Otinja river. The size of the Au grains found ranges from about 120 µm (grain LD-3) up to 2 mm (grain OT-1), that is, they are composed of small (<1.5 mm) and rarely of large grains (>1.5 mm).

Fig. 5. Photographs of Au grains from the river of Otinja

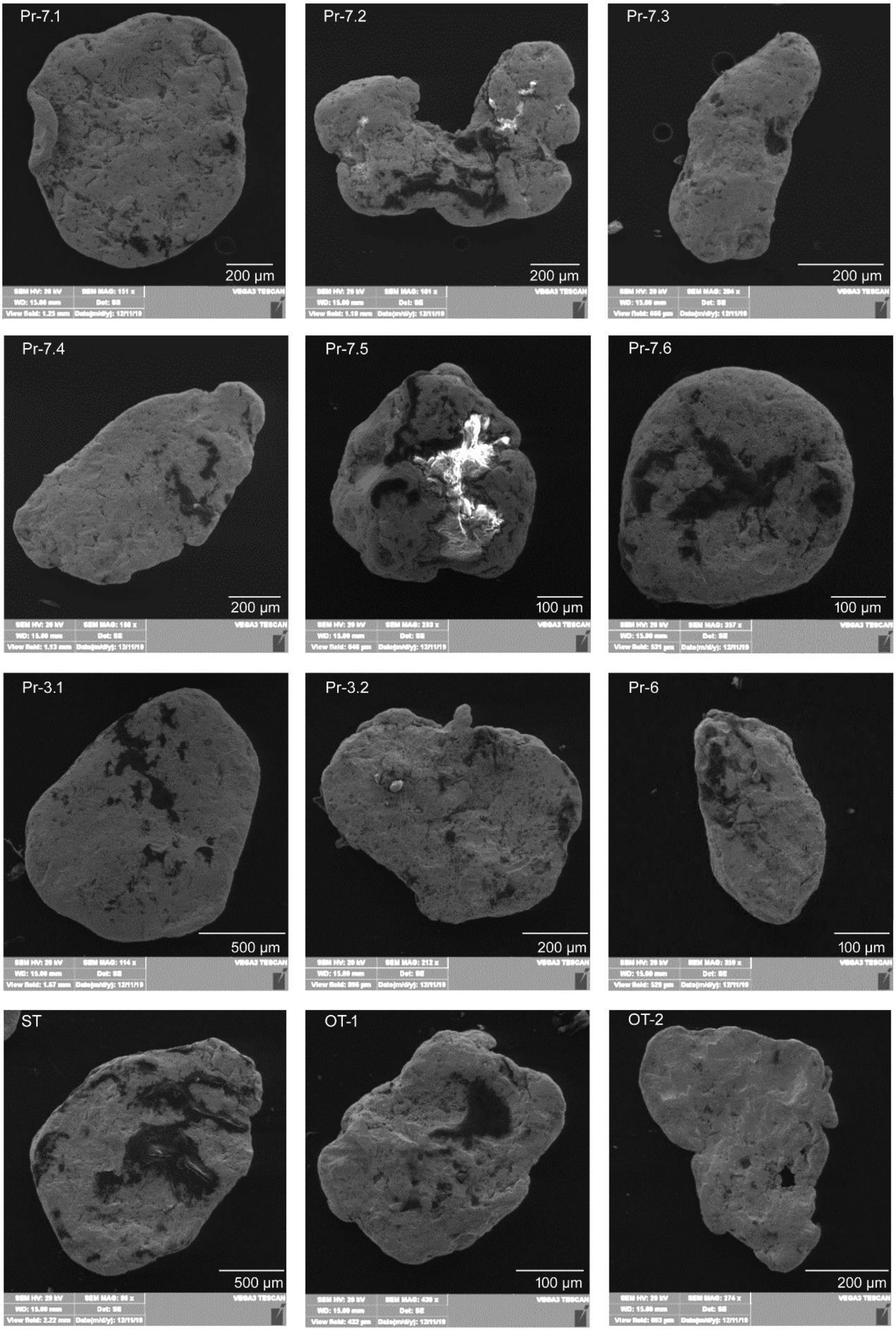
From the scanning electron microscope (SEM) photographs (Figure 6) of the selected Au grains, it can be seen that they are sub-rounded to rounded, and rarely elongated. These Au grains show a regular shape. Most of the Au grains lack or are Ag-poor in both cores and rims, i.e., there is no strong evidence for supergene precipitation. This phenomenon of supergene precipitation is common for Au grains in tropical areas and is often attributed to surface processes (Suh and Lehmann, 2003; Nono et al., 2021).

In these Au grains, a smoothing of the grain surface has been observed, and, at the same time, the flatness increases, which may also be due to significant transportation of grains, and above all, due to the small hardness and malleability of gold as a mineral (Townley et al., 2003). Flatness can also be explained by the fact that during transport Au grains collide with grains of other harder rock minerals leading to an increase in flatness as a function of transport length (Knight et al., 1999; Townley et al., 2003; Tishcenko, 1981). Flatness also varies with grain size as larger grains (>1.5 mm) are flattened much more than smaller grains (<1.5 mm). Grains less than 60 µm undergo much less flattening (Knight et al., 1994). Grain flatness is the greatest in high-energy places, and changes in grain size and flatness depend partly on downstream movement and partly on sorting of the material during fluvial transport.

Highly angular and irregular shapes indicate that the alluvial gold is close to its primary source, while abrasive and circular shapes indicate transport of several km (Mudaliar et al., 2007).

Most of the Au grains from the Otinja river are of almost uniform size and are rounded (circular), flattened and smoothed; this may indicate the fact that the grains underwent longer transport.

Chemical and mechanical alteration of the Au grains led to a reduction in size and rounding of shape after they were removed from the mineralized veins in the cycle of alteration/transport (Suh and Lechmann, 2003; Townley et al., 2003).


Pr-7.1
200 µm
Pr-7.2
200 µm
Pr-7.3
200 µm
Pr-7.4
200 µm
Pr-7.5
100 µm
Pr-7.6
100 µm
Pr-3.1
500 µm
Pr-3.2
200 µm
Pr-6
100 µm
ST
500 µm
OT-1
100 µm
OT-2
200 µm

(Fig. 6)

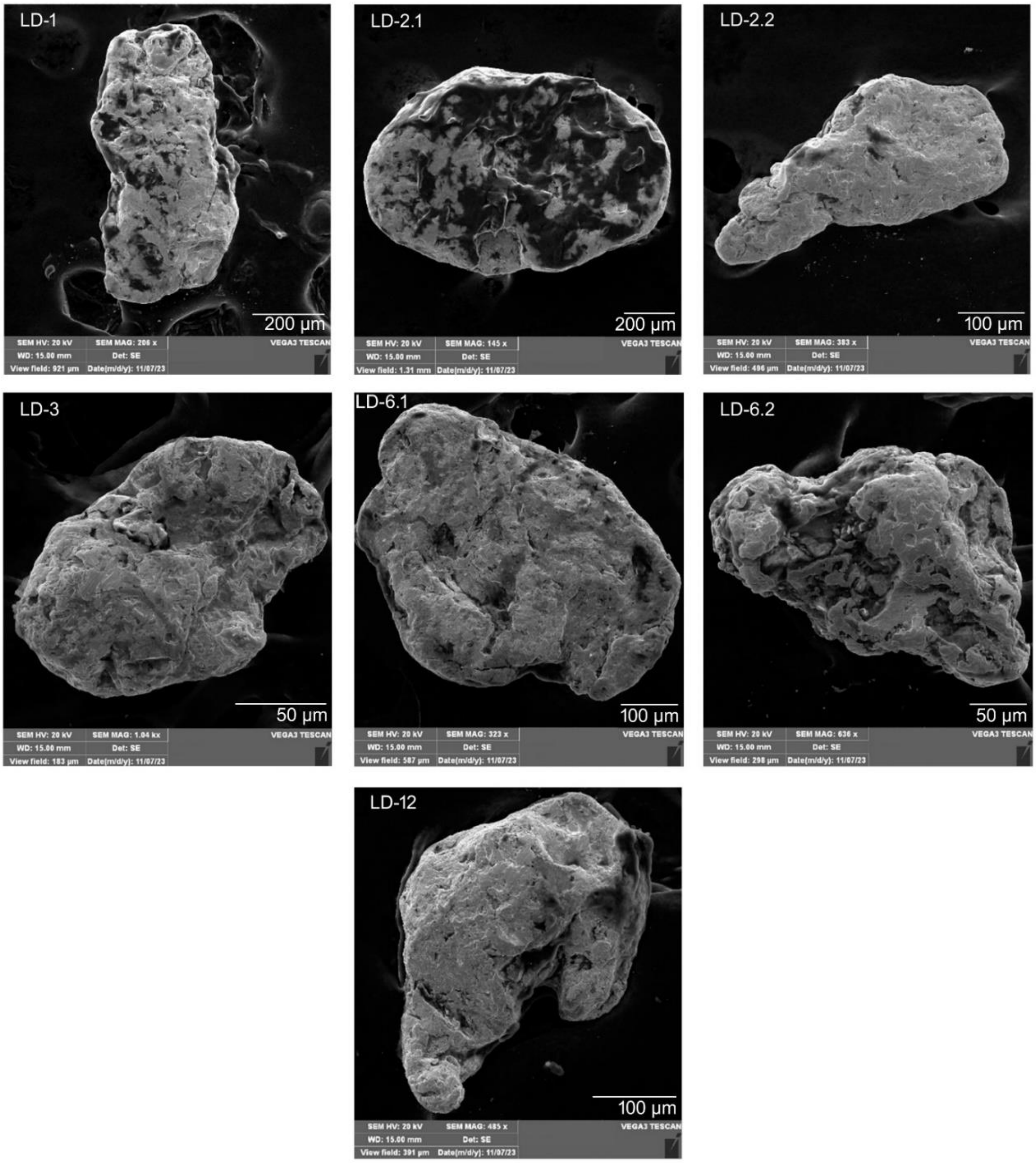


Fig. 6. Scanning electron microscope (SEM) photographs of Au grains from the Otinja river.

CHEMICAL COMPOSITION OF Au GRAINS

The quantitative data on the chemical composition of Au grains from the river of Otinja from SEM-EDS analyses are given in Table 1.

Au grains from the Otinja riverhave impurities of Ag and Fe and smaller amounts of Cu, Te, and Se. The content of Au in grains from the Otinja river ranges from 94.45 to 100 % (Table 1).

The Ag content is in the range from 0.02 to 4.89 %. The Fe content ranges from 0.02 to 4.74%. The content of Cu in Au grains is below the detection limit in most of them; in those grains where the presence of Cu has been determined, the measured contents are in the range from 0.02 to 0.54% Cu (Table 1).

T a b l e 1

Chemical composition of Au grains from the Otinja river

		Au	Ag	Fe	Cu	Te	Se
Pr-7.1	rim	99.93	–	0.07	–	–	–
	core	99.67	–	0.31	0.02	–	–
	medium content	**99.80**	–	**0.19**	**0.02**	–	–
Pr-7.2	rim	99.76	–	0.14	0.10	–	–
	core	99.96	–	0.04	–	–	–
	medium content	**99.86**	–	**0.09**	**0.10**	–	–
Pr-7.3	rim	99.09	0.88	0.02	–	–	–
	core	99.70	0.18	0.12	–	–	–
	medium content	**99.39**	**0.53**	**0.07**	–	–	–
Pr-7.4	rim	99.77	–	0.23	–	–	–
	core	99.88	–	–	0.12	–	–
	medium content	**99.82**	–	**0.23**	**0.12**	–	–
Pr-7.5	rim	99.79	0.21	–	–	–	–
	core	94.95	0.32	4.74	–	–	–
	medium content	**97.37**	**0.26**	**4.74**	–	–	–
Pr-7.6	core	99.86	0.14	–	–	–	–
Pr-3.1	rim	99.17	–	0.47	0.36	–	–
	core	99.42	–	0.58	–	–	–
	medium content	**99.29**	–	**0.52**	**0.36**	–	–
Pr-3.2	rim	99.69	0.14	0.18	–	–	–
	core	99.19	–	0.81	–	–	–
	medium content	**99.44**	**0.14**	**0.49**	–	–	–
Pr-6	core	100.00	–	–	–	–	–
ST	rim	99.69	–	0.03	0.28	–	–
	core	99.67	0.02	0.31	–	–	–
	medium content	**99.68**	**0.02**	**0.17**	**0.28**	–	–
OT-1	rim	99.65	0.09	–	0.27	–	–
	core	99.35	0.16	0.25	0.24	–	–
	medium content	**99.50**	**0.12**	**0.25**	**0.25**	–	–
OT-2	rim	97.56	2.36	–	0.08	–	–
	core	99.83	0.09	0.06	0.11	–	–
	medium content	**98.69**	**1.22**	**0.06**	**0.09**	–	–
LD-1	rim	99.13	–	0.08	0.28	0.51	–
	core	98.65	–	0.98	0.37	–	–
	medium content	**98.89**	–	**0.53**	**0.32**	**0.51**	–
LD-2.1	rim	99.36	–	0.64	–	–	–
	core	99.79	–	0.21	–	–	–
	medium content	**99.57**	–	**0.42**	–	–	–
LD-2.2	rim	99.76	–	0.06	0.09	0.09	–
	core	99.52	–	0.12	–	0.36	–
	medium content	**99.64**	–	**0.09**	**0.09**	**0.22**	–
LD-3	rim	99.24	0.19	–	–	0.27	0.29
	core	98.87	1.13	–	–	–	–
	medium content	**99.05**	**0.66**	–	–	**0.27**	**0.29**
LD-6.1	rim	99.89	–	–	0.11	–	–
	core	99.13	–	0.56	0.08	0.24	–
	medium content	**99.51**	–	**0.56**	**0.09**	**0.24**	–
LD-6.2	rim	95.65	4.01	0.03	0.30	–	–
	core	94.45	4.89	–	–	0.55	–
	medium content	**95.05**	**4.45**	**0.03**	**0.03**	**0.55**	–
LD-12	rim	99.44	–	0.56	–	–	–
	core	99.27	–	–	0.54	0.19	–
	medium content	**99.35**	–	**0.56**	**0.54**	**0.19**	–

Under an electronic stereoscope-binocular, coalescence with a quartz grain was observed only in one Au grain. Au grains that are usually associated with accompanying basic minerals, most often with inclusions of quartz and/or Fe oxides, according to Townley et al., 2003, belong to the group of Au grains that underwent short transport, 50 m downstream from the primary source, whereas granites and gneisses are rocks that carry more quartz veins and are high-potential source rocks.

The content of gold or purity of Au grains from the Otinja river ranges from 951 to 1000 with an average value of 996. This parameter is usually used to describe the Au content in the Au-Ag alloy in various types of hypogene mineralization (Ketchaya et al., 2022). The purity of Au grains from the study area has a very high range of 951 to 1000, which corresponds to the Au purity of the studied orogenic deposits defined by Liu and Beaudoin (2021) and is consistent with the mesothermal Au purity values obtained by McInnes et al. (2008).

Au grains from the Otinja river are in the gold group with a low content of silver. According to Wierchowiec (2002), the boundary between gold with a low silver content and gold with a high silver content is Ag = 8 %.

Microchemical characteristics of Au grains are often used to determine the type of mineralization in various mining areas (Huang et al., 2013). When determining the microchemical characteristics of placer gold, the Ag content is the first criterion considered (Chapman et al., 2017), especially because the Ag content in the Au grains allows the type of deposit to be determined (Chapman et al., 2009). The Ag content in mesothermal gold mineralizations is lower than that of epithermal gold mineralization (Chapman and Mortensen, 2006).

The Ag contents in Au grains from the Otinja river are clustered in gold with low silver content (<8 %) (Nono et al., 2021), which could mean that the grains were from the same source or were formed by one single geological process. Most Au grains lack or are Ag-poor in both cores and rims, indicating no evidence for supergene precipitation. This suggests that the grains were transported directly from the hypogene source from the land surface and the fluvial system.

Gold purity is an important criterion that is used to characterize Au grains (Morrison et al., 1991). Ag is usually leached from the edges of Au grains during transport in stream sediments which leads to an increase in the purity of gold as the distance from the source increases (Dumula и Mortensen, 2002). According to Morrison et al. (1991), Au grain purity values vary among different types of gold deposits. The ranges are: 780–1000 for aArchaic vein gold ore deposits; 800–1000 for mesothermal deposits in a shale belt; 650–970 for plutonic deposits; 650–1000 for porphyry deposits, and 0-1000 for epithermal deposits. Gold from mesothermal environments shows a narrow range of purity with average values of 800–1000 and primary deposition by sulfidation (Morrison et al., 1991). These tests show that Au grains from the Otinja river have a narrow range of purity from 951 to 1000. All values cluster towards the upper limit closer to the average for mesothermal deposits in a shale belt (920–940) rather than intrusion-related deposits (825) (Morrison et al., 1991). Low Ag content and high gold purity values in the studied gold deposits indicate that sulfidation may be the dominant mechanism in ore deposition. Au grains with Cu contents less than 1 % may indicate a primary hydrothermal vein type of deposit (Vishiti et al., 2015).

The compositions of Au grains from the river of Otinja were plotted on Au-Ag*10 vs. Cu*100 three-component diagram for the determination of ore-bearing systems; Au grain composition fields are according to Townley et al., 2003, and include epithermal, porphyry deposits rich with gold and gold-rich porphyry copper deposits (Figure 7).

Au grains from the Otinja river fall into the zone of orogenic gold deposits (Figure 7). They coincide with the orogenic gold deposits defined by Chapman и Mortensen (2006), Suh et al. (2006) and Liu and Beaudoin (2021). From Au-Ag*10 vs. Cu*100 three-component diagram for determination of the ore-bearing systems (Figure 7) during these tests, the contents of Ag < 5 % and Cu < 1 % were obtained. The points in the diagram for the Otinja river are clustered in the field of epithermal/mesothermal orogenic gold suggesting that the gold in the Otinja river basin originates from a mesothermal orogenic gold ore field (mesothermal orogenic gold locality), where Au mineralization is likely spatially, temporally, and genetically-paragenetically related to the Tertiary intermediate to acidic volcanogenic-intrusive magmatism, i.e., trachytic dykes. A similar ternary discrimination plot of Au-Ag*10 vs. Cu*100 was obtained from the studies of alluvial gold grains in an East Cameroon region, where gold is clustered in the field of epithermal/mesothermal orogenic gold, with the difference that its age is Archean (Eon, Precambrian) (Nono et al., 2021).

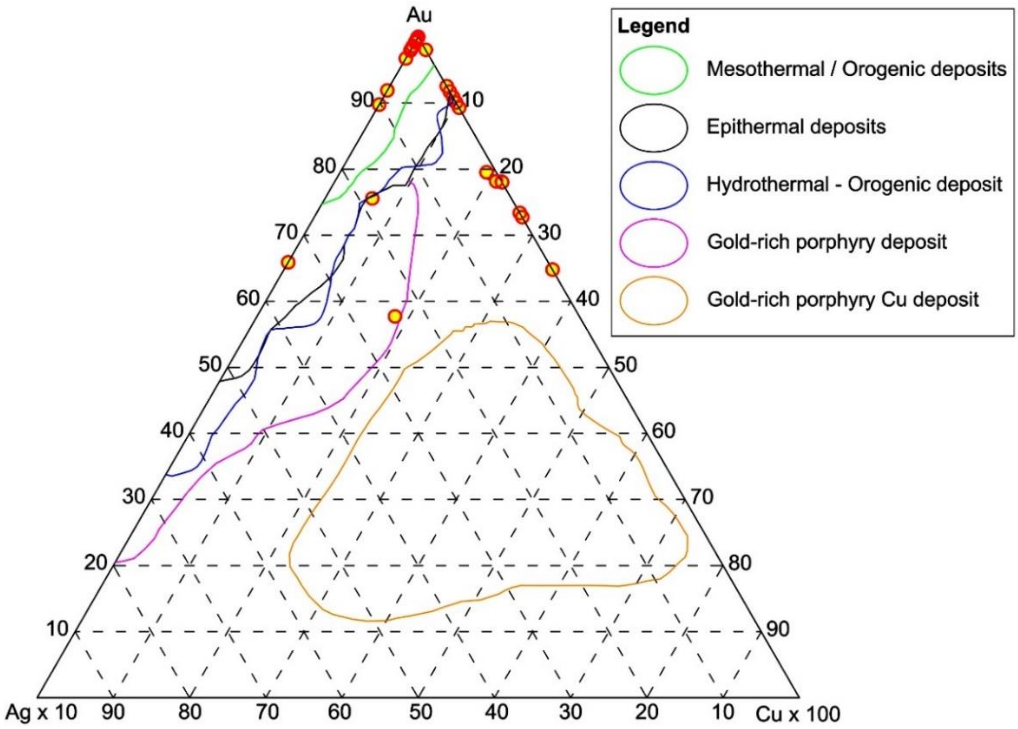


Figure 7. A three-component separation diagram Au–Ag*10 vs. Cu*100 with the composition of Au grains from the Otinja river (*n* = 36)

The alloy compositions of the Au grains from the Otinja river are two-component gold-silver, with copper contents <1 %. Such compositions indicate that the area of the Otinja river basin is an orogenic gold locality.

Morphological characterization of Au grains from stream sediments has emerged as an important tool for exploring orogenic gold localities (Antweiler and Campbell, 1982; Grant et al., 1991; Rubin and Kyle, 1997). This is important in providing added value to existing research methods, such as rock and soil sampling, drilling exploratory wells, excavations, geological mapping, etc. (Chapman and Mileham, 2016).

The results presented so far from this schlich prospecting initiate the need for further research, primarily geochemical and geophysical, in order to discover the primary source of gold in this area where Au grains are found in most of the stream sediments.

Based on the geomorphology and drainage system of the Otinja river, the areas between the villages of Lipov Dol, Shashavarlija, Kalapetrovci and the Crn Vrv locality can be of interest. The defined prospect space is composed of trachytes, granites and gneisses, rocks that carry multiple quartz veins, and are high potential source rocks. All these rocks are involved in several stages of deformation. Research should focus on fault zones and also contact zones between trachytes, granites and gneisses. Also, special attention should be paid to the Pliocene sediments represented by sands, loams and gravels that cover a large part of the terrain in question.

CONCLUSIONS

– In the catchment area of the Otinja river, the presence of small and rarely large grains of Au was determined by schlich prospecting. A total of 29 Au grains were determined.

– Morphological analysis showed that the Au grains are of sub-rounded to rounded shapes, and less often elongated forms with regular shapes. Some of the grains are flattened. Such morphology of the examined gold aggregates indicates that they underwent a longer transport.

– Microchemical tests of the Au grains show that it is very high-grade gold with a fineness ranging from 951 to 1000. Among the impurities, silver with contents of less than 5% and very small amounts of Fe, Cu, Te, and Se are found. Most Au grains do not have Ag-leached rims.

– The alloy compositions of the Au grains from the Otinja river are two-component gold-silver, with copper contents <1 %. Such compsitions indicate that the area of the river basin of Otinja is an orogenic gold locality.

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Р е з и м е

МОРФОЛОШКИ И ХЕМИСКИ КАРАКТЕРИСТИКИ НА ЗРНА НАНОСНО ЗЛАТО ОД РЕКАТА ОТИЊА

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Клучни зборови: зрна на Au; морфологија; хемиски состав; примарен извор

Во Српско-македонската металогена зона во Република Северна Македонија се пронајдени бројни појави на Au во алувијалните седименти. Наносното злато потекнува од познати генетски типови на порфирски наоѓалишта на Cu-Au (Бучим и Боров Дол) и епитермални наоѓалишта на Au (Плавица и Алшар). Сепак, кај реката Отиња примарниот извор на Au сѐ уште останува нејасен. Дваесет и три зрна на Au собрани од алувионот на реката Отиња за прв пат беа анализирани на скенирачки електронски микроскоп (SEM) за да се истражат нивните морфолошки и хемиски карактеристики. Пронајдените златни зрнца се со димензии од околу 120 μm до 2 mm, имаат главно суб-заоблени до заоблени форми, ретко неправилни форми, со микротекстури што укажуваат дека изворот се наоѓа на растојание поголемо од неколку километри. Испитувањата на хемискиот состав покажуваат главно смеси на Au-Ag, при што содржината на Au се движи од 94,45 до 100%. Според хемизмот зрната на Au спаѓат во групата на многу висококвалитетно злато со голема чистота (951 до 1000). Примесите се главно со многу мали содржини. Според застапеноста се присутни најмногу: Ag (0,02–4,89%), Fe (0,02–4,74%). Cu (0,02–0,54%), Te (0,09–0,55%) и Se (0,29%).