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GOLD PROSPECTION IN STREAMS AND RECENT ALLUVIONS IN THE WESTERN PARTS OF THE KRATOVO-ZLETOVO VOLCANIC AREA

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A b s t r a c t: Two methods were used in the prospection study of streams and recent alluvium in the western parts of the Kratovo-Zletovo volcanic area (BLEG and stream sediments). The research and samples analysis by the BLEG method determined gold content in all samples in the locality Borović, within the range from 0.00031 to 0,248 ppm Au, and in the locality Plavica gold content ranged from 0.00047 to 0,0667 ppm Au. Examined and studied stream sediments from localities of the recent alluvium Borović (Povišnica river) and Plavica localities determined characteristic geochemical associations of elements that were statistically processed that obtained appropriate groups of equivalent elements, which form cluster systems. Cluster analysis identified associations that can be divided into ore associations and associations originating from rocks, which built adjacent setting around the mineralization. From ore associations in the locality Borović were determinated three element associations:{[(Y-Co)-(Ta-Nb)]-Ni}; ‖∫{[(Sn-Pb)-S)-Ga]-Bi]}-[(Te-In)-Ag]-As∫-(U-Sb)‖; {[(Cd-Zn)-(Au-Cu)]-(Ge-W)]}-(Fe-V)]}-{[(Mo-Hg)-(Pb-Sn)]-(Re-Tl)-Se]}. From associations constituting petrogene minerals were allocated following associations: {[(Rb-K)-Li]-Cs}; {[(Zr-Hf)-Sr]-Ba-[(Y-Mg)-(Na-Be)]-(Ti-P)]}; [(La-Ce)-Hg]-Th. In the locality Plavica were determinated three elemental associations: [(Ni-Co)-Ca]; ‖∫{[(Hg-Sb)-Ag]-Tl}-Mn∫-{[(Zn-Cd)-Pb]-[(Ge-Ga)-(Nb-Ta)]}∫‖; ∫{[(W-Mo)-Re]-Au}-[(Cu-Fe)-Cr]-∫{[(Sn-As)-In]-Bi}-Te∫-[(Se-S)-U]}∫. From associations that build petrogene minerals were allocated four elemental associations: ∫{[(La-Ce)-Th]-S}-(P-Ba)∫; {[(Mn-Cs)-(Rb-K)]-Li}; [(Mg-Ca)-Na]; [(Hf-Zr)-Al]. These associations were sorted by level of relationship that exists between certain elements.

Key words: gold; stream sediments; ore association; cluster analysis

INTRODUCTION

The Kratovo-Zletovo volcanic area represents a remarkable volcanic complex in the center of the Balkan Peninsula, which covers an area of 1250 km^2 (Serafimovski, 1990) where are present almost all types and representatives of extrusive-effusive equivalents of the Tertiary magmatism, which pulsations took place in the interval from Ma 37 to Ma 12 (Petkovrić, 1982; Serafimovski, 1993; Serafimovski and Boev, 1996; Zlatkov, 2016). Within this area were discovered productive mineralization of lead, zinc, silver, copper, gold, uranium and another within the mining area Kratovo-Zletovo which covers an area of approximately 400 km^2 (Serafimovski, 1990; Tomson et al., 1998).

Beside numerous geological studies within this ara preliminary samples were taken for analysis and schlich stream sediments (Klajn 1977; Denkovski, 1984; Fish, 1998), but more quantitative results of those trials were not given except for individual samples in report of Fish (1998). The analysis of stream-sediments with more specific results for individual parts of the Plavica caldera are given in the works of Stefanova (2005, 2008 and Stefanova et al. (2012), while other information on this type of studies were not given.

Foregoing was a reason to perform the research and study of river sediments from upstream rivers that drain the area of Kartovo-Zletovo volcanic area specifically the Borović locality and Plavica deposit. The goal was to determine the correlation between the geochemical stream sediment and parental rocks and the distribution of elements in river sediments along streams. For this purpose were used complex methods such as petrological research, chemical analyses of river sediments and cluster analysis. There was determined a relation between river sediments and adjacent rocks in this ore-bearing area.

Stream sediments are a mix of sediments, soil and rocks from the catchment areas downstream from locations that are subject to research (Mikoshiba et al., 2006). Study of stream sediments recently became one of the main methods of prospection (Ottesen et al., 1994). Experience shows that based on these studies can draw conclusions from a wider area and their wide application. For getting maximum performance from geochemical surveys it is necessary to establish a balance between the minimum density of the number of samples versus the maximum length of the investigated area in order to reduce the factor cost/time (Cohen et al., 2005). In particular the results of geochemical research of stream sediments allow to determine the relationship with rocks and mineralization provided by these sediments.

Also, it can be studied the degree of alteration of minerals in stream sediments during the exogenous processes, especially of gold nuggets. Establishing a relation between the geochemical characteristics of stream sediments and minerals entering their composition as well as the correlation between minerals from primary ores and rocks and those contained in the stream sediments can give dependence that will directly help prospection examination and get away definite conclusions about the genesis. This is confirmed by some studies carried out on certain sites in the Republic of Macedonia (Stefanova, 2005; Kovachev et al., 2002, 2006). These studies had shown that in certain types of ore (e.g Carlin type-Alshar) analyses of stream sediments have not yielded good results because gold aggregates are of submicroscopic size (less than 5 microns) which is not the case with sediments originating from coppergoldfields sites where this method has proved satisfactory results.

Endogenous gold in the Republic of Macedonia has been the subject of many studies (Bogoevski, 1998; Stefanova, 2005; Čifliganec et al., 1994; Čifliganec and Serafimovski, 1994; Serafimovski and Rakić, 1998; Persival et al., 1990, 1992, 1994). On the other hand, the possibility of finding gold aggregates in heavy fractions of copper and copper-gold-bearing deposits opens vast field of research. Studies of geochemical characteristics of eluvial-deluvial gold and concurrent minerals and geochemical characteristics of stream sediments containing gold aggregates are the subject of this paper. These studies are a step forward in its ability to define the type of ore based on the analysis of endogenous and exogeniuos gold.

GEOLOGICAL FEATURES

Terrains of the Kratovo-Zletovo volcanic area are characterized by complex composition, which mainly consists of Tertiary volcanogenic-sedimentary complex imposed on the Serbian-Macedonian massif foundations. With up to date numerous and long-term geological studies (Pendžerkovski et al., 1960; Hristov et al., 1969; Pantić et al., 1972; Ristić and Klajn, 1973; Ivanov and Denkovski, 1978; Rakić, 1982; Petković, 1982), as well as complex studies by Stojanov (1980), Ivanov and Denkovski (1980), Serafimovski (1990), Stojanov and Serafimovski (1990), Serafimovski (1993), Serafimovski and Boev (1996), were confirmed complex lithostratigraphic relations that are introduced by several types of rocks with different composition, age and conditions of formation. Nevertheless, at this area its representatives have Precambrian metamorphic rocks, Paleozoic, Mesozoic and Cenozoic types of rocks, but however over 90% of the geological composition of the Kratovo-Zletovo volcanic area consists of Tertiary volcanic rocks. We would like to emphasize that partially geological composition has been subject in the latest studies of alterations and mineralizations in the Plavica and Borović locations, where special contribution was done by works of Serafimovski and Rakić (1998, 1999), Alderton and Serafimovski (2007), Stefanova et al. (2007, 2013, 2015); Tasev and Serafimovski (2012); Serafimovski et al. (2012, 2015a, 2015b); Zlatkov et al. (2014); Ivanovski et al. (2015); Ivanovski (2016); Zlatkov (2016),

As we already mentioned the foundation of these terrains is represented by Precambrian complex that comprise of various types of gneiss, mica schist, amphibolite schist etc., which are occupying northern and northeastern parts of the area (Fig. 1).

Also, the Paleozoic rocks don't have significant impact on the composition of the Kratovo-Zletovo volcanic area because they occur far north and are represented by chlorite-sericite schist and phyllite, somewhere intercalated with carbonaceous schist and marble. Sometimes as enclaves in the volcanics appear quartz-graphite schist.

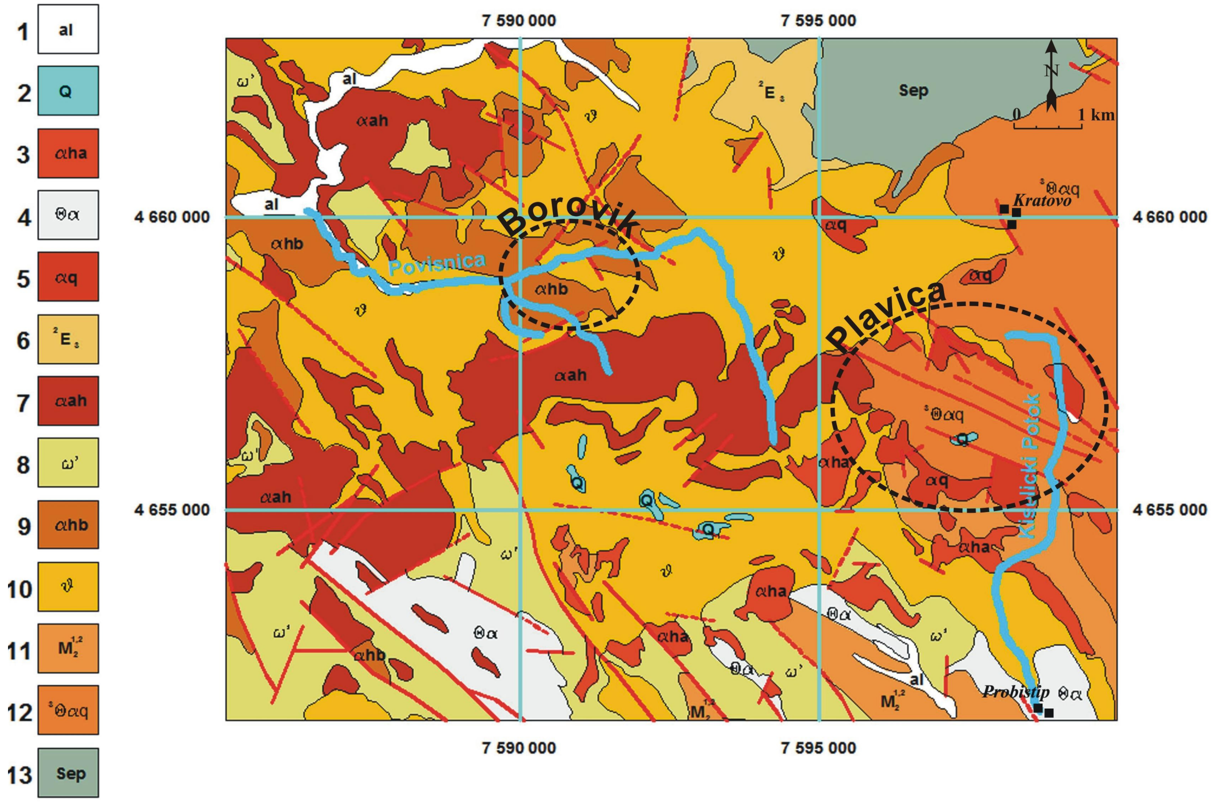

Fig. 1. Simplified and digitalized geological map (1 : 100 000) of the western part of the Kratovo-Zletovo volcanic area according to data from the Basic geological map (OGK-1), sheet Kratovo.
1. al – Alluvium (*Holocene*); 2. Q – Hydrothermal quartzite/silex (*Pleistocene*); 3. αha– Hyaloandesite (*Pleistocene*); 4. Θα – Hornblende-augite-andesite (*Pleistocene*); 5. αq – Ignimbrite of andesite composition (*Pleistocene*); 6. $^2E_2$ – Dacite and dacitoide (*Pliocene*); 7. αah – Augite-hornblende-biotite andesite (*Pliocene*); 8. ω' – Andesite breccia (*Pliocene*); 9. αhb – Hornblende-augite-biotite andesite (*Pliocene*); 10. ϑ – Tuff (*Miocene*); 11. $M_2^{1,2}$ – Limestone, tuffaceous sandstone and claystone (*Miocene*); 12. ^3Θαq – Plate-like gray-greenish ignimbrite of dacite composition (*Miocene*); 13. Sep – Albite-epidote schists

Mesozoic rocks in the Kratovo-Zletovo area are represented mainly by magmatic representatives. They are found in eastern parts where should be emphasized gabbro near the village of Pantelej and granodiorite enclaves discovered within ignimbrite complex near Dobrevo (Šoptrajanova, 1965), which by their composition and terms of its formation, are considered similar to so-called Štip granites (Djordjević et al., 1982).

Cenozoic products are widely present in the Kratovo-Zletovo area and represented by Tertiary volcanics and volcano-sedimentary complexes (Fig. 1) of Middle Miocene age. The most common within the vertical lithological column is ignimbritite of dacite-andesite composition, stratified tuffs, andesite and dacite intrusions with their lava outflows, as well as younger quartz-latite and latite dikes and diorite dikes near the Borović.

At the studied terrains of the Povišnica river and Borović locality, as the most common volcanic representatives appear andesite flows intercalated with thin tuff beds. This sequence is intruded by dikes and necks of augite andesite and porphyrytic diorite (Klajn, 1977). All volcanic rocks are strongly altered to form hydrothermal quartzite, argillic rocks (illite, kaolinite, sericite), and jarosite rocks. Quartz-alunite lithocap covers hilltops composed of hydrothermal quartzite, which are the main bearers of primary gold mineralization. Also, the fault structures are related with intensive hydrothermal alterations and post-volcanic manifestations. Up to date data have shown that within the Borović mineralized system are present numerous hydrothermally altered zones that occasionally are mineralized, mainly with copper and gold mineralization and sporadically with lead and zinc. All the facts are pointing out that the major focus should be given to the exploration of copper and gold mineralizations (Stefanova et al., 2015). Present data displayed that contents of copper in individual drill core samples reach 0.1 % Cu and individual samples taken from secondary quartzites and silicified fault zones at the Povišnica river have 0.45 g/t Au in average (Serafimovski et al., 2012).

As well as at the Borović area and its main drainage Povišnica, at the Plavica locality and its main drainage Kiselički Potok as the most common volcanic rocks appear thick section (nearly 500 m) of intercalated volcanic flows, tuffs, debris flows and subvolcanic intrusions. The flows and massive tuffs ranging in composition from andesite to latite, comprise the basal portion of the volcanic sequence and are overlain by a series of debris flows with intercalated water-lain tuffs, tuffs and volcano-clastic sediments. Tertiary rocks are the dominant lithology at the Plavica area (Serafimovski et al., 2015): ignimbrite of dacite-andesite composition, propylitized dacite-andesite rocks (northern slopes of the Plavica and southern part of the Maricanski Rid locality), quartzlatite neck, stock and dyke that break-through dacite-andesite (Karac, Dogandžiski Kamen, Plavički Potok) as well as so-called silex-secondary quartzite in the central part of the Plavica. The most representative rock from the aspect of primary gold mineralization within the Plavica deposit is secondary quartzite, which in average contain 3 g/t Au (Serafimovski and Rakić, 1998, 1999), while in some individual samples gold concentration reached up to 12 g/t Au. Also, primary gold concentrations were determined in intensively altered volcanic rocks (unidentified) where had been determined copper mineralization of approximately 0.2 % Cu. Those are areas that are drained by several creeks and small rivers, where in their watercourse had been determined gold in the BLEG and stream sediment samples.

MATERIALS AND METHODS

During the actual study were applied fieldwork activities when was sampled geochemical material for geochemical and mineralogical analyses.

The material for geochemical studies was sampled from sediments that were formed by decomposition and transport using waterways in the wider area, which are draining studied volcanic area. From the Borović locality were sampled 6 samples in total (Fig. 2), while from the Plavica were sampled 9 samples (Fig. 3).

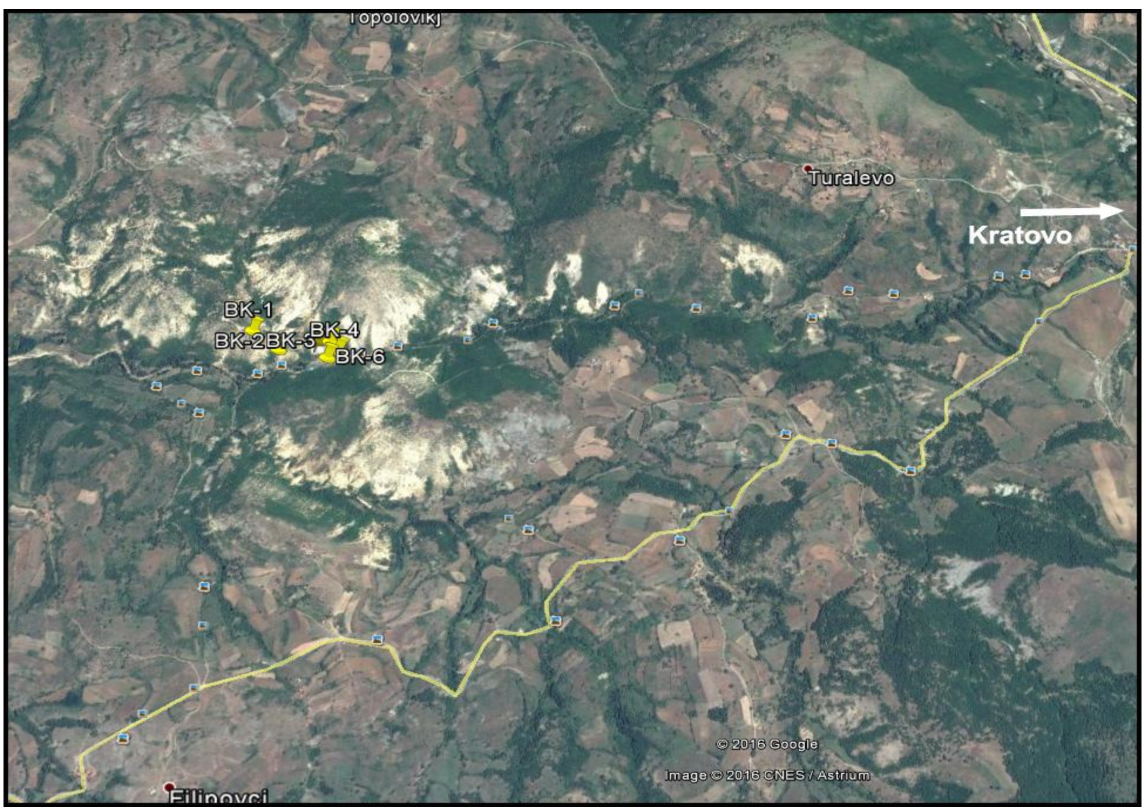

Fig. 2. Sampling points of stream sediments from the Borović locality

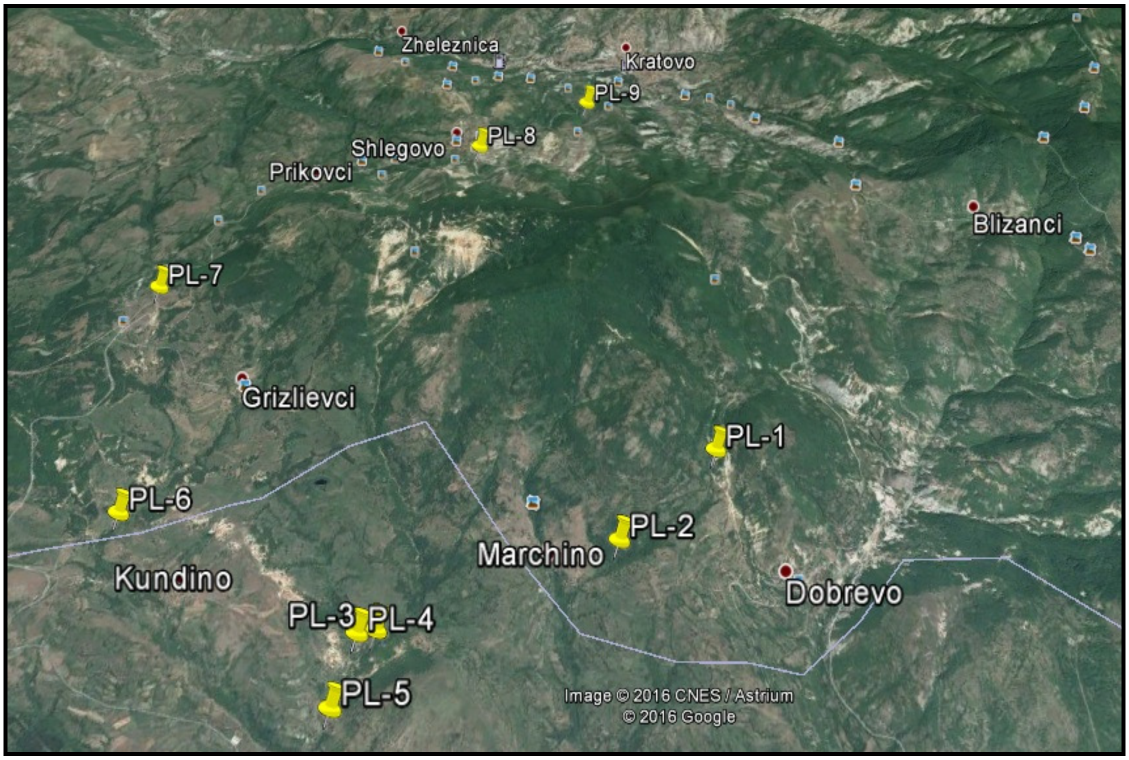

Fig. 3. Sampling points of stream sediments from the Plavica locality

From each sampling point was collected material weighing 15 kg that was later sieved, which procedure gave us two fractions. The first fraction finer than 0.17 mm (minimum quantity of 500 g) was used to test ISP-AES and MS and the second fraction (finer than 0.5 mm) with a minimal amount of 2.5 kg was used for test by the BLEG analysis.

The chemical analysis of stream sediments (49 elements) was performed by ICP-AES and MS at the ALS Chemex Laboratory in Australia. To more accurately determine the content of gold, silver and copper all samples were analyzed by BLEG analysis (Bulk Leach Extractable Gold; cyanide leaching) to extract gold from the material. Analyses were made in SGM Welshpool Minerals Laboratory, Australia.

Statistical methods were performed in the processing of the analysis data. Cluster analysis was used to interpret them by their classification according to the similarity variables. To apply cluster analysis was used Pearson's coefficient as a measure of distance of the sample or chemical element. Also, this ratio was used as an initial index correlation coefficient of variables which eliminates the influence of the units in which were expressed elements (percentage, ppm, etc.). The correlation in the cluster analysis was performed by weighted pair-group average meaning remote measurement between potential clusters is based on their average values.

RESULTS AND DISCUSSION

Stream sediments are formed by minerals that occur as a result of destruction of rocks that built up the drained area of the volcanic area. One of the methods used for testing the stream sediments was the BLEG method (liquid extraction of gold from large tables). This method has the effect of lumps suppression or "nugget" to a level that any coarse-grain aggregates of gold in the sample is only partially affected (Mazzucchelli, 1994). Bulk cyanide leaching (BLEG method) of large samples (2 kg) exceeds finegrain problem of gold that can be deployed in heterogeneous samples (Yilmaz, 2003). Therefore more material for these tests is more appropriate (Radford, 1996). Moreover, this method is attractive because it is relatively inexpensive and also a sensitive technique prospect of regional (Wood et al., 1990).

BLEG analysis on samples from these localities was performed on three elements in order to determine the content of gold, silver and copper. The results indicate the presence of gold in the locality Borović with an average content of 0.1 ppm (Table 1). These results were in accordance with the results of schlich prospection which was conducted at this area when was determined presence of gold in river sediments (Stefanova et al, 2015).

The average content of gold in the Plavica deposit is 0.02 ppm. (Table 2). The average content of gold is lower compared to locally Borović, while the content of copper and silver are higher.

Table 1

Statistical parameters of elements analyzed by the BLEG method, Borović locality (ppm)

Elements	Probe	Mean	Minimum	Maximum	Std. dev.
Au	6	0.109178	0.000310	0.248000	0.121345
Ag	6	0.045000	0.010000	0.090000	0.026646
Cu	6	2.798333	0.005000	7.620000	3.769664

Table 2

Statistical parameters of elements analyzed by the BLEG method, Plavica locality (ppm)

Elements	Probe	Mean	Minimum	Maximum	Std. dev.
Au	9	0.02023	0.000470	0.06670	0.02446
Ag	9	1.20500	0.005000	8.44000	2.72940
Cu	9	10.40944	0.005000	29.10000	10.66144

Also, the gold content in this deposit was determined by the schlich prospection when were discovered of gold aggregates (Stefanova et al., 2013).

Stream sediments were analyzed by the ICP-AES method in order to determine the chemical composition of rocks and main ore mineralization, as well as other elements in order to compare their composition in stream sediments.

The results obtained from the analysis were statistically processed and results for the Borović locality are shown in Table 3.

Also, data from the Plavica locality was statisticaly processed and the results are shown in Table 4.

Table 3

Statistical parameters for chemical elements in Borović locality (ppm)

Variable	Mean	Minimum	Maximum	Std. dev.
Au	0.221	0.0010	0.661	0.2699
Ag	0.125	0.0400	0.260	0.0894
Al	8.152	7.4000	8.920	0.6897
As	12.267	5.8000	21.700	5.3969
Ba	743.333	700.0000	840.000	50.8593
Be	1.985	1.7000	2.240	0.2394
Bi	1.170	0.2900	2.850	1.1542
Ca	2.872	0.2300	5.820	2.4320
Cd	0.463	0.1800	1.230	0.3834
Ce	56.117	46.5000	67.300	8.0728
Co	9.567	2.3000	15.500	5.0989
Cr	10.667	9.0000	14.000	1.9664
Cs	10.633	7.6800	17.800	3.7611
Cu	55.333	12.4000	154.000	56.1747
Fe	4.663	3.4600	6.260	0.9647
Ga	17.942	15.5500	20.300	1.8529
Ge	0.152	0.1200	0.200	0.0313
Hf	1.717	0.4000	3.800	1.2336
In	0.159	0.0500	0.453	0.1568
K	2.162	1.8500	2.880	0.4100
La	25.133	20.5000	31.500	4.2917
Li	13.133	6.8000	18.000	3.9893
Mg	0.815	0.5500	1.180	0.2260
Mn	961.333	161.0000	1575.000	554.7845
Mo	10.512	1.0100	29.600	11.9073
Na	0.910	0.5200	1.090	0.1995
Nb	8.383	7.1000	9.500	0.9766
Ni	3.450	2.2000	4.300	0.8142
P	1215.000	720.0000	1640.000	313.7356
Pb	111.567	33.5000	207.000	66.5383
Rb	97.933	81.8000	131.500	17.9982
Re	0.020	0.0010	0.082	0.0315
S	0.432	0.0200	0.800	0.3586
Sb	1.320	0.5400	1.860	0.4858
Se	2.167	1.0000	3.000	0.7528
Sn	5.333	2.3000	9.700	3.3423
Sr	484.333	289.0000	893.000	213.3070

Variable	Mean	Minimum	Maximum	Std. dev.
Ta	0.753	0.6100	0.910	0.1285
Te	0.150	0.0500	0.380	0.1200
Th	12.167	9.4000	15.100	2.3045
Ti	0.379	0.3390	0.462	0.0454
Tl	1.517	0.9000	3.000	0.8042
U	2.650	1.5000	3.600	0.8735
V	144.833	105.0000	173.000	25.4434
W	2.617	1.4000	4.300	1.1686
Y	17.750	12.8000	22.600	3.7993
Zn	143.167	90.0000	289.000	73.0053
Zr	46.367	12.1000	98.600	30.9565
Hg	0.057	0.0010	0.135	0.0499

Table 4

Statistical parameters for chemical elements in the Plavica deposit

Variable	Units	Mean	Min.	Max.	Std. dev.
Au	ppm	0.04	0.0010	0.20	0.065
Ag	ppm	3.94	0.005	19.40	6.15
Al	%	7.92	6.97	9.11	0.816
As	ppm	116.4	22.00	267.00	103.63
Ba	ppm	1541.1	800.00	2430.00	556.96
Be	ppm	1.90	1.30	2.41	0.31
Bi	ppm	3.19	0.39	6.31	2.67
Ca	%	1.17	0.20	3.68	1.30
Cd	ppm	1.47	0.07	4.61	1.67
Ce	ppm	62.1	43.30	82.70	12.20
Co	ppm	10.1	2.20	15.70	4.12
Cr	ppm	13.5	5.00	20.00	5.07
Cs	ppm	18.6	6.87	74.60	21.57
Cu	ppm	126.5	22.60	296.00	113.85
Fe	%	4.99	3.85	6.51	0.85
Ga	ppm	17.52	16.60	18.60	0.75
Ge	ppm	0.15	0.13	0.17	0.015
Hf	ppm	3.64	2.10	4.50	0.72
In	ppm	0.33	0.07	0.72	0.27
K	%	2.57	1.89	3.99	0.64
La	ppm	28.86	19.50	41.90	7.06
Li	ppm	16.74	10.20	23.30	4.16
Mg	%	0.41	0.26	0.67	0.15
Mn	ppm	2175.66	349.00	10001.00	3052.06
Mo	ppm	6.05	1.95	17.20	6.08
Na	%	0.51	0.21	0.90	0.21
Nb	ppm	10.01	7.50	12.00	1.36
Ni	ppm	4.61	2.10	6.90	1.33
P	ppm	1315.55	840.00	1910.00	369.56
Pb	ppm	1568.82	42.20	4580.00	1618.76
Rb	ppm	181.06	71.60	440.00	106.24
Re	ppm	0.002	0.001	0.00	0.001
S	%	0.41	0.10	0.72	0.24
Sb	ppm	31.27	0.67	157.50	49.96
Se	ppm	1.44	1.00	2.00	0.52
Sn	ppm	3.51	2.10	5.60	1.41
Sr	ppm	772.22	263.00	1190.00	355.56
Ta	ppm	0.92	0.78	1.15	0.10
Te	ppm	0.84	0.07	2.22	0.82
Th	ppm	18.78	14.00	24.30	3.43
Ti	%	0.39	0.32	0.46	0.04
Tl	ppm	3.48	1.69	8.48	2.06
U	ppm	6.37	4.80	8.20	1.00
V	ppm	154.33	95.00	199.00	37.01
W	ppm	9.00	2.90	26.10	9.58
Y	ppm	17.12	12.80	22.50	3.34
Zn	ppm	408.11	76.00	1150.00	395.33
Zr	ppm	114.18	58.50	147.50	26.84
Hg	ppm	0.18	0.001	0.94	0.29

The area that was the target of study is generally made up of andesites, latite, andesite-dacite and their transitional types (Stefanova et al., 2007). They are built of the following main oxides: plagioclase (SiO_2, Al_2O_3, CaO, Na_2O; less than 1% FeO, K_2O); potassium feldspate (SiO_2, Al_2O_3, K_2O, Na_2O; about 1% BaO); clynopiroxene (SiO_2, CaO, Na_2O, MgO, FeO, about 1% TiO_2, Al_2O_3, MnO, K_2O); biotite (SiO_2, Al_2O_3, K_2O; MgO, FeO, and 3% TiO_2). These oxides are the main oxide phase in geochemical associations. From previous and recent studies were determined these ore minerals: pyrite (Fe, S), chalcopyrite (Cu, Fe, S), pyrrhotite (S, Fe), enargite (S, Fe, As), tennantite-tetrahedrite association (S, Sb, Fe, Cu, Zn, As); galena and sphalerite (S, Fe, Cu, Zn, Pb).

Stream sediments geochemistry

Taking into account the data, a comparative analysis of the geochemical similarities between stream sediments and rocks of origin can be done. Table 5 shows the values obtained from tests that were made of rocks and values obtained from studies of stream sediments in the Borović locality. The results of the Plavica deposit study are given in Table 6.

T a b l e 5

Contents of petrogene (%) and ore elements (ppm) in the rocks and stream sediments in the Borović locality

Element.	Element content in rocks						Element content in stream sediments							Rocks/str. sedim
	1	2	3	4	5	Mean	BK-1	BK-2	BK-3	BK-4	BK-5	BK-6	Mean	
Si	28.25	27.99	25.5	26.75	26.17	26.93	–	–	–	–	–	–		–
Ti	0.38	0.37	0.42	0.27	0.5	0.38	0.34	0.36	0.46	0.37	0.39	0.35	0.38	1.02
Al	1.209	1.209	0.37	0.24	0.44	0.69	8.87	8.92	8.48	7.49	7.75	7.4	8.15	0.08
Fe	0.02	0.104	1.17	1.42	2.07	0.95	4.78	4.15	6.26	4.23	5.1	3.46	4.66	0.2
Mn	0.09	0.1	0.07	0.07	0.62	0.19	402	161	1095	1310	1575	1225	961	1.9
Mg	1.36	1.42	1.01	1.09	0.91	1.15	0.61	0.55	0.86	0.79	1.18	0.9	0.81	1.4
Ca	4.07	3.88	5.31	4.51	4.21	4.39	0.79	0.23	1.12	4.26	5.82	5.01	2.87	1.5
Na	2.06	2.23	2.79	2.25	2.29	2.32	0.95	0.52	1.01	1.09	0.93	0.96	0.91	2.55
K	3.25	3.13	3.25	3.12	3.53	3.25	1.97	1.95	1.85	2.43	1.89	2.88	2.16	1.5
P	0.11	0.09	0.12	0.14	0.15	0.12	1100	1110	1370	1640	1350	720	1030	0.00
Cr	44	34	18	20	36	30.4	10	10	12	14	9	9	10.6	2.9
Ni	5	<5	10	<5	5	5	2.9	2.2	4.3	4.3	3.5	3.5	3.45	1.4
Co	12	13	15	18	14	14.4	4.5	2.3	10.4	12.1	15.5	12.6	9.5	1.5
Li	22	24	12	15	9	16.4	11.4	13.6	12.4	16.6	6.8	18	13.3	0.8
Rb	127	116	100	111	130	116.8	99.6	97.4	83.3	94	81.8	131.5	97.9	1.2
Zn	1038	82	104	1761	1348	866.6	136	118	289	118	90	108	143	6
Pb	59	15	9	118	48	49.8	157.5	207	137.5	76.2	33.5	57.7	112	0.4
Sr	17	1228	1986	7	68	661.2	363	398	289	473	893	490	484	0.8
Cu	81	83	129	176	1496	393	90.3	36.4	154	14.8	24.1	12.4	55	7.1

T a b l e 6

Contents of petrogene (%) and ore elements (ppm) in the rocks and stream sediments in Plavica deposit

Elem.	Element content in rocks						Element content in stream sediments										Rock/ stream sediments
	1	2	3	4	5	Mean	Pl-1	Pl-2	Pl-3	Pl-4	Pl-5	Pl-6	Pl-7	Pl-8	Pl-9	Mean	
Si	28.25	27.99	25.53	26.75	26.17	26.93	–	–	–	–	–	–	–	–	–	–	–
Ti	0.38	0.37	0.42	0.27	Pl1	0.38	0.32	0.394	0.403	0.374	0.46	0.431	0.418	0.354	0.438	0.40	0.97
Al	1.20	1.20	0.37	0.24	0.44	0.69	7.29	7.90	7.03	9.11	7.49	9.04	8.54	6.97	7.94	7.92	0.09
Fe	0.02	0.10	1.17	1.42	2.07	0.95	3.95	4.66	5.46	4.6	6.51	5.04	5.79	3.85	5.12	5.00	0.19
Mn	0.09	0.1	0.07	0.07	0.62	0.19	1870	1285	816	482	883	349	10000	770	3080	2175	0.00
Mg	1.36	1.42	1.01	1.09	0.91	1.15	0.59	0.67	0.36	0.26	0.34	0.59	0.31	0.26	0.35	0.41	2.79
Ca	4.07	3.88	5.31	4.51	4.21	4.39	3.17	3.68	0.6	0.97	0.7	0.54	0.23	0.2	0.5	1.18	3.74
Na	2.06	2.23	2.79	2.25	2.29	2.32	0.57	0.75	0.5	0.9	0.57	0.48	0.28	0.21	0.39	0.52	4.50
K	3.25	3.13	3.25	3.12	3.53	3.25	2.81	2.29	2.51	1.89	2.44	1.95	3.99	2.32	3.01	2.58	1.26
P	0.11	0.09	0.12	0.14	0.15	0.12	1350	1290	1610	840	1630	850	990	1910	1370	1315	0.00
Cr	44	34	18	20	36	30.4	11	9	20	5	20	13	14	12	18	13.56	2.24
Ni	5	<5	10	<5	5	5	6.9	5.3	3.8	4.1	4.4	4.8	4.4	2.1	5.7	4.61	1.08
Co	12	13	15	18	14	14.4	11.6	15.7	7.7	9.7	9.2	8.4	11.9	2.2	15.3	10.19	1.41
Li	22	24	12	15	9	16.4	19.9	19.8	17.4	10.2	17	11.4	23.3	14.6	17.1	16.74	0.98
Rb	127	116	100	111	130	116.8	148.5	114	191.5	71.6	175	112	440	169	207	180.96	0.65
Zn	1038	82	104	1761	1348	866.6	342	132	285	83	271	76	1150	324	1010	408.11	2.12
Pb	59	15	9	118	48	49.8	177	544	2580	42.2	2560	75.8	4580	2610	1440	1623	0.03
Sr	17	1228	1986	7	68	661.2	495	606	984	1190	1115	775	367	1155	263	772	0.86
Cu	81	83	129	176	1496	393	22.6	39	291	67.8	296	59.8	240	52.9	69.4	126.50	3.11

It can be concluded that there is a similarity between the obtained data or that the composition is similar to with small variations. For this purpose, it was calculated relationship between the content of elements in rocks and stream sediments. It can be allocated several groups of elements. When this ratio is close to one, then it means that there are no signficant changes in the concentration of elements in rocks and stream sediments.

In the Borović locality in the first group where the ratio is 0.6 belong the following elements: Al, Pb, Fe, Rb. This ratio shows that these elements are with higher concentration in stream sediments than in the rocks. The second group of elements with a ratio of 0.8–1.2. These elements have not significant change in concentration in the stream and rocks. These are: Ti, Sr, Li. The third group characterized by a ratio greater than 2.12 features content that is larger than the rocks in stream sediments. These elements are: Na, Cr, Zn, Cu.

From the Plavica deposit study we have received very similar results. Here we also can divide the elements into three groups. The first group includes elements where the relationship between rock and stream sediments ranged up to 0.6 where the concentration of elements in stream sediments is greater than in the rocks. That are Al, Fe, Rb, Pb. This suggests further enrichment of sediments with these elements. A second group of elements whose relative ranges were from 0.8 to 1.2 are Ni, Ti, Li, Sr. This group includes elements that have approximately the same content in rocks and stream sediments. The third group includes elements that have a relationship greater than 2.12 or content in rocks is much greater than in stream sediments. This group includes petrogene elements Mg, Ca, Na, K and the ore elements Cr, Zn, Cu.

This geochemical behavior of elements analyzed mainly due to their transformation into soluble form during the chemical decomposition as the differences in specific gravity between minerals hosts of these elements in stream sediments. It can be assumed that in the acidic environment as a result of the dissolution of sulphides and increasing the acidity of the water under the influence of sulfuric acid, manganese and phosphorus will pass in solution, and taken by the stream and some of copper and lead will accumulate in the form of ore due to their high specific gravity.

Cluster analysis

Cluster analysis (Symons, 1981) is used to group elementss according to the level of similar spatial distributioned, i.e this is a method of grouping elements in order to obtain meaningful organizational structures. Data processed using cluster analysis were done in accordance to Weathed procedure pair-group average using it as a measure of the closeness of the elements is used the correlation coefficient.

Study of geochemical characteristics of stream sediments showed that as a result of the disintegration of rocks occur two sets of elements: elements derived from ore mineralization in this area and elements derived from petrogene minerals contributing into the composition of the rocks that built studied area. Since one mineral in principle consists of two or more elements, the expectation is that spatial associations which were distinguished by the cluster analysis reflect the closeness of the elements that form the element or elements. So based on all the elements of the cluster analysis we can make conclusions about minerals that occur in stream sediments.

The preliminary classification of elements into two groups is due to the fact that in the studied area were distinguished two types of rocks: Tertiary volcanic rocks and ore bodies. As typical elements of the first group are: K, Mg, P, Th, Zr, Y, Be, Al, Rb Na, Ba, Li, Hf, Cs, Ce, Sr, Al. For the second group may be allocated the following elements: Au, Ag, Cu, As, Bi, Co, Cr, Cd, Ga, Ge, Mo, Ni, In, Tl, Pb, Re, Nb, Sb, Se, Sn, Ta, Te, U, V, W, Zn, Hg. Other elements such as Ca, Mn, and S are associated with the two groups that enter into the composition of rocks and ore bodies.

Ore elements in Borović are divided into three clusters (Table 7). The first cluster includes two subclusters. In the first subcluster enters yttrium and cobalt, and the second subcluster which is characteristic for rare elements includes: tantal and niobium. These two subclusters are followed by the nickel. Chromium is beyond the level of significance of cluster which for 6 samples is 0.73.

The second cluster include three subclusters: subcluster Sn-Pb followed by sulfur, then subcluster Te-In followed by silver, and the third subcluster U-Sb. This cluster includes elements with high affinity for sulfur.

Gold as an element enters the third cluster which occurs in association with copper (Au-Cu). This cluster enters the subcluster Cd-Zn, then Ge-W and subcluster Fe-V, which is typical of high iron oxides from the group of magnetite. This cluster also includes subcluster of Mo-Hg, then subcluster of Pb-Sn, and the subcluster Re-Tl followed by selenium. These items usually build sulfide or native elements (Fig. 3).

Table 7

Element clusters of rock-forming and ore elements in stream sediments from the Borović locality

Elements group	Cluster	Elements association	Elements out of cluster
Ore forming elements	I	{[(Y-Co)-(Ta-Nb)] – Ni}	Cr
	II	‖∫{[(Sn-Pb)-S)-Ga] – Bi]}-[(Te-In)-Ag]-As ∫ - (U-Sb) ‖	
	III	{[(Cd-Zn)-(Au-Cu)]-(Ge-W)]}-(Fe-V)]}-{[(Mo-Hg)-(Pb-Sn)]-(Re-Tl)-Se]}	
Rocks forming elements	I	{[(Rb-K)-Li]-Cs}	
	II	{[(Zr-Hf)-Sr]-Ba- [(Y-Mg)-(Na-Be)]- (Ti-P)]}	
	III	[(La-Ce)-Hg]-Th	Al

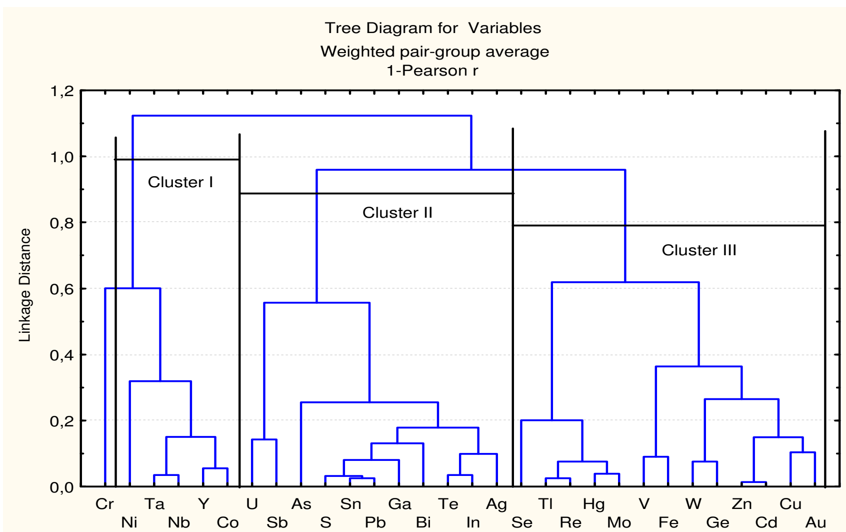

Fig. 3. Ore elements clusters in the Borović locality

The elements that built petrogene minerals form three clusters (Fig. 4). Outside the clusters remains aluminum that likely shows no correlation with neither element. In the first cluster comes only subcluster of rubidium and potassium followed by lithium and cesium. These are typical elements for the Rare Earth Elements. The second cluster can be distinguished subcluster of zirconium and hafnium which is considered a stable association. These elements with the elements of the first cluster associations that upon closer geochemical properties of elements commonly occur frequently. In the third cluster comes only subcluster of lanthanum, cesium, followed by mercury and thorium.

Ore elements in the Plavica deposit were divided into three clusters (Table 8). The first cluster includes subcluster of nickel and cobalt, while vanadium like element is outside the level of significance of cluster which for 9 samples was 0.58. Common occurrence of nickel and cobalt geochemicaly is justified (Fig. 5). In the second subcluster enters subcluster of mercury and antimony followed by silver. Here comes another subcluster with association of lead-zinc and cadmium, which made a sulphide association of minerals which is characteristic for polymetalic mineralization that is present in the deposit.

The other two subclusters: subcluster of germanium and gallium and subcluster of niobium and tantalum, geochemical often appear together.

Gold as an element enters the third cluster which occurs in association with subcluster of molybdenum, tungsten and rhenium. In this cluster still enters subcluster of copper and iron, tin and arsenic, and subcluster of selenium and sulphur, which may indicate the possible association of gold with copper sulphides, having in mind that the mineralization of the site includes the copper as a valuable raw material. The elements of this cluster show an affinity for sulphur (Fig. 5).

T a b l e 8

Element clusters of rock-forming and ore elements in stream sediments from the Plavica deposit

Elements group	Cluster	Elements association	Elements out of cluster
Ore forming elements	I	[(Ni-Co) - Ca]	V
	II	‖ ∫{[(Hg-Sb)-Ag]-Tl}-Mn∫-{[(Zn-Cd)-Pb]-[(Ge-Ga)-(Nb-Ta)]}∫ ‖	
	III	∫{[(W-Mo)-Re]-Au}-[(Cu-Fe)-Cr]- ∫{[(Sn- As)-In]-Bi}-Te∫-[(Se-S)-U]}∫	
Rocks-forming elements	I	∫ {[(La-Ce)-Th]-S}-(P-Ba)∫	Ti, Sr
	II	{[(Mn-Cs)-(Rb-K)]-Li}	Be
	III	[(Mg-Ca)-Na]	
	IV	[(Hf-Zr)-Al]	

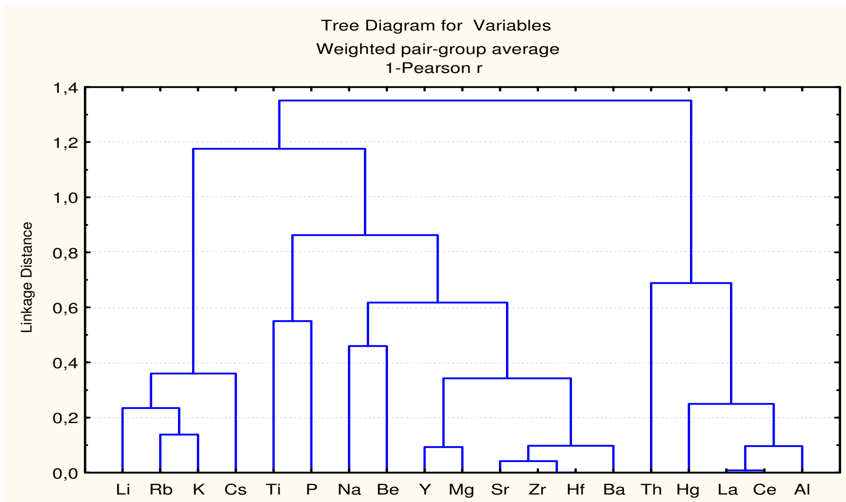

Fig. 4. Rock forming elements clusters in the Borović locality

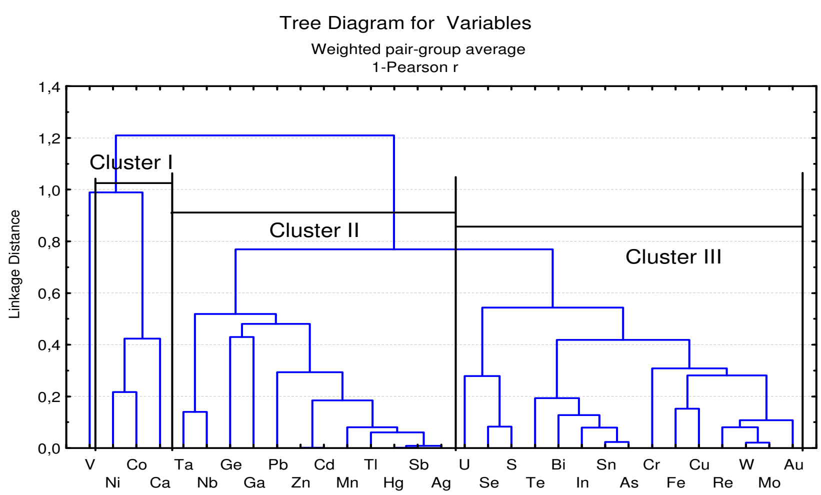

Fig. 5. Ore elements clusters in the Plavica deposit

The elements entering the construction of petrogene minerals formed four clusters (Fig. 6). Outside the clusters remain titanium, strontium and beryllium that do not have correlation about each element of the cluster. In the first cluster enters subcluster of lanthanum and cerium followed by thorium. This association is characteristic of the very rare elements.

Magnesium, calcium and sodium in the third cluster are associations that upon closer geochemical properties of the elements usually appear together frequently.

Other subcluster such as rubidium and potassium, lithium followed by hafnium and zirconnium can be said that are stable geochemical associations, so their appearance is geochemicaly justified.

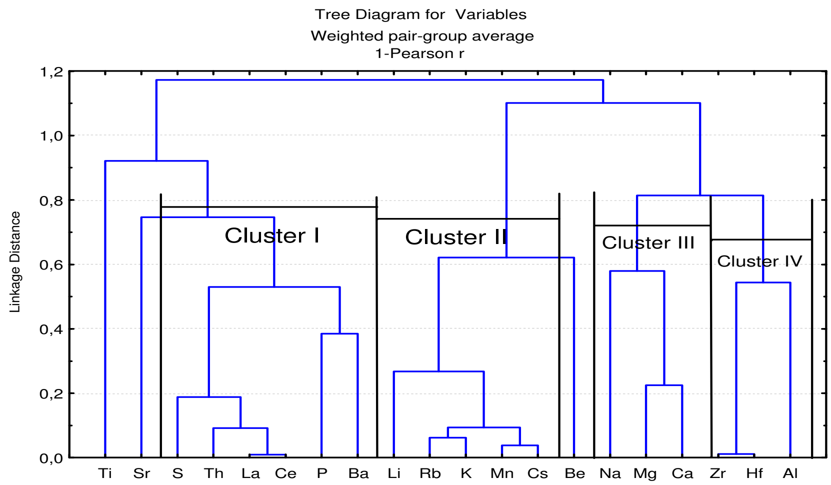

Fig. 6. Rock forming elements clusters in the Plavica deposit

Correlation analysis

Gold contents that were determined by the BLEG analysis were quite low in both localities. The average contents of gold at the Plavica deposit were lower compared to those of the Borović locality, while the contents of copper and silver are higher.

Both localities from the metallogenetic point belong to the Kratovo-Zletovo volcanic area. Because of that it is expected to have similar geochemical associations and certain differences due to individual geological features of the localities. In terms of geochemical features, there is a high similarity between the chemical composition of rocks and stream sediments in the two localities, so that the chemical composition of stream sediments can specify rocks that build up the studied area. If we correlate the results, can be seen that there is a similarity in the separate groups of elements.

In the first group were classified four elements that appear in both sites: Al, Fe, Pb, Rb. The content of these elements in stream sediments is greater than in the rocks. The second group, which has uniform composition in stream sediments and rocks, includes Ti, Li, Sr, Ni, or from four elements three elements appear in both localities as follows: Ti, Li, Sr. In the third group, where the content in rocks is greater than in stream sediments includes the following elements which are appear in the Borović and the Plavica localities: Na, Cr, Zn, Cu. In this group from seven elements, previously mentioned four elements are found in both localities. This means that the composition of stream sediments is correlated with the composition of the rocks in both studied localities. The greatest similarity in composition exists in the first group where all the elements appear at both localities. The second group has 75% of the same elements and the third group the proportion of elements that exist in both localities is 57%. The Mn, Mg, Ca, K, Ni, Co show a tendency of reduction in stream sediments in the Borović locality. At the Plavica locality only Co shows tendency of reduction.

Cluster analysis displayed similarities in the geochemical associations and specific differences. What is important is that gold as an element in both localities is found in the third cluster with a similar association of elements such as volfram, molybdenum, then rhenium, copper, iron, tin and selenium. Of the remaining clusters as similar can be accented the first cluster: {[(Y-Co)-(Ta-Nb)]-Ni}; [(Ni-Co)-Ca] with similar association of nickel and cobalt. The second cluster in both localities rather varies according to the geochemical associations. Common association that is found in both localities is the association of Ta-Nb.

The most of nonmetallic elements associations occur in both localities. Such subclusters are: La-Ce, Hf-Zr and Rb-K followed by lithium.

When comparing the clusters in terms of linkage distance, apart three groups. The first group are the following clusters with linkage distance to 0.2 and for them it can be said that high reliability. The second group with linkage distance of 0.2–0.4. Such clusters are less reliable but still adequate. The third group with over 0.4 linkage distance is unreliable (Mladenov et al., 2007).

When comparing the clusters of the two localities we can see that most of the mineral elements (over 90%) at the Borović locality are in group with linkage distance to 0.2 which points to highly reliable associations. The 63% of nonmetallic elements belong to the group with linkage distance to 0.2 while only 15% belongs to the group of linkage distance over 0.4. These associations are considered to be geochemicaly unreliable. Those established in linkage distance of 0.2 to 0.4 are less reliable. At the Plavica deposit 66% of the mineral elements are in the group of credible associations, 25% in the group with less reliability or linkage distance from 0.2 to 0.4. Only 9% of the elements are in the group of linkage distance over 0.4 and are considered to be unreliable associations. From nonmetallic elements, 20% are in group with linkage distance of 0.2 to 0.4. The group of more than 0.4 linkage distance is only 10%, the rest of the group has linkage distance to 0.2.

Using cluster analysis it was performed grouping of samples which were analyzed in both localities (Fig. 7). From the figure it can be seen that there are three separate clusters.

Accordance to linkage distance, it can be said that the best correlation there is between samples Pl-Pl-3 and 8 of the second cluster which includes samples from the site Plavica. The first cluster is composed only of samples from the Plavica. The third cluster are grouped samples from the two localities. The image also shows that there is a better correlation relationship between the second and third clusters.

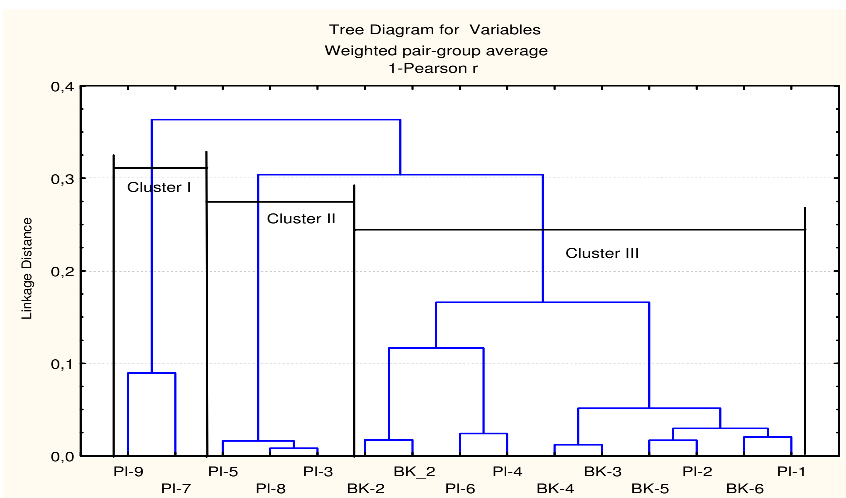

Fig. 7. Linkage distance betwen samples from Borović locality and Plavica deposit

CONCLUSION

Conducted studies by the BLEG and stream sediments confirmed the presence of gold in the treated sites in the western parts of Kratovo-Zletovo volcanic area, which highly coincides with previous preliminary analyses of this area.

Three groups of elemental associations were determined by processing of the results of stream sediment: a group of elements whose content in stream sediments are greater than them in primary rock, a group of elements where no significant change in concentration in the stream and rocks and a group characterized by a content greater than the rocks in stream sediments.

With cluster analysis in the Borović locality were allocated three ore clusters and three clusters that build up minerals which entering the construction of petrogenic minerals. In the Plavica deposit were allocated three clusters of one and other group as well. From ore subcluster in Borović locality can be distinguished subcluster of: (Au-Cu), (Cd-Zn), (Fe-V), (Mo-Hg), (Sn-Pb)-S, (Te-In)-Ag. By nonmetallic clusters can be distinguished: (Zr-Hf)-Sr, [(La-Ce)-Hg, (Zr-Hf). In the Plavica deposit can be distinguished ore subcluster of [(W-Mo)-Re]-Au, [(Zn-Cd)-Pb], [(Hg-Sb)-Ag]. By nonmetallic subcluster can be distinguished following subclusters: [(La-Ce)-Th]), (Rb-K)]-Li, (Hf-Zr).

Performed correlation between samples from the two localities it can be seen that the best correlations are between samples Pl-Pl-3 and 8 from the second cluster that is in a better correlation relationship with the third cluster than the first cluster.

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Р е з и м е

ПРОСПЕКЦИЈА НА ЗЛАТО ВО СТРУЈНИ СЕДИМЕНТИ И РЕЦЕНТНИ АЛУВИОНИ ВО СЕВЕРНИОТ ДЕЛ НА КРАТОВСКО-ЗЛЕТОВСКАТА ВУЛКАНСКА ОБЛАСТ

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Клучни зборови: злато, струјни седименти, рудна асоцијација, кластерна анализа.

Во проспекциските испитувања во потоците и современите алувиони во западните делови од Кратовско-Злетовската вулканска област беа користени два метода (BLEG и струјни седименти). Со испитувањата и анализата на пробите со методот BLEG е утврдена содржина на злато во сите примероци од локалитетот Боровиќ, во опсег од 0,00031 до 0,248 ppm Au, а во локалитетот Плавица содржината на злато се движи во опсег од 0,00047 до 0,0667 ppm Au.

Во испитуваните и проучувани струјни седименти од локалитетите на рецентните алувиони во месноста Боровиќ (реката Повишница) и локалитетот Плавица се утврдени карактеристични геохемиски асоцијации на елементи кои статистички се обработени, при што се добиени соодветни групи еквивалентни елементи кои формираат кластерни системи. Со кластерната анализа се утврдени асоцијации кои можат да се поделат на рудни асоцијации и асоцијации кои потекнуваат од карпите кои ја градат околината на орудувањето.

Од рудните асоцијации од локалитетот Боровиќ се одредени три асоцијации на елементи:

{[(Y-Co)-(Ta-Nb)]-Ni};

‖∫{[(Sn-Pb)-S)-Ga]-Bi]}-[(Te-In)-Ag]-As∫-(U-Sb)‖;

{[(Cd-Zn)-(Au-Cu)]-(Ge-W)]}-(Fe-V)]}-{[(Mo-Hg)-(Pb-Sn)]-(Re-Tl)-Se]}.

Од асоцијациите кои ги градат петрогените минерали се издвоени следниве асоцијации:

{[(Rb-K)-Li]-Cs};

{[(Zr-Hf)-Sr]-Ba-[(Y-Mg)-(Na-Be)]-(Ti-P)]};

[(La-Ce)-Hg]-Th.

Во наоѓалиштето Плавица се утврдени три елементни асоцијации:

[(Ni-Co)-Ca];

‖∫{[(Hg-Sb)-Ag]-Tl}-Mn∫-{[(Zn-Cd)-Pb]-[(Ge-Ga)-(Nb-Ta)]}∫‖;

∫{[(W-Mo)-Re]-Au}-[(Cu-Fe)-Cr]-∫{[(Sn-As)-In]-Bi}-Te∫-[(Se-S)-U]}∫.

Од асоцијациите кои ги градат петрогените минерали се издвоени четири елементни асоцијации:

∫{[(La-Ce)-Th]-S}-(P-Ba)∫;

{[(Mn-Cs)-(Rb-K)]-Li};

[(Mg-Ca)-Na];

[(Hf-Zr)-Al].

Овие асоцијации се подредени според степенот на врската која постои меѓу одредените елементи.