

UDC 55

CODEN – GEOME 2

ISSN 0352 – 1206

# GEOLOGICA MACEDONICA



Geologica Macedonica	Год.	12	стр.	1-78	Штип	1998
Geologica Macedonica	Vol.		pp.		Štip	

## THE SECONDARY QUARTZITES HOSTING GOLD MINERALIZATION IN THE CRN VRV - PLAVICA VOLCANIC AREA

Todor Serafimovski<sup>1</sup> and Stevo Rakić<sup>2</sup>

<sup>1</sup>*Faculty of Mining and Geology, Štip, Republic of Macedonia*

<sup>2</sup>*Silex Company, Kratovo, Republic of Macedonia*

**Abstract:** The paper presents the latest results of the chemical examination and geochemical investigations carried out on the secondary quartzites in the Crn Vrv – Plavica area. The area under consideration consists of volcanic areas (volcanic calderas) in whose central parts secondary quartzites of variable gold concentrations were determined. The surface manifestations of the secondary quartzites occur as small lenses and nests, grading into wedge-like shapes to depth. Chemical examinations showed that they contain high SiO<sub>2</sub> (96.34 – 98.78%) contents. Geochemical examinations indicated the presence of gold concentrations accompanied by a large number of elements such as Cu, Ag, Bi, Sb, Se, Te, Hg etc. Gold content is variable ranging from traces to over 20 ppm Au in individual samples. Lower contents have been found in the Crn Vrv area (5 to 467 ppb), and an average of 1.29 ppm Au (from 0.186 to 0.506 ppm Au) were found in Plavica. The results obtained were interpreted by appropriate computer software. They showed significant correlation relationships between individual pairs such as Au-Cu, Cu-Mo, Au-Sb, Au-Hg, Au-Fe etc., indicating to a common primary mobilization and evolution within the epithermal mineralization system.

**Key words:** Crn Vrv – Plavica area; secondary quartzites; volcanics; gold mineralization; volcanic calderas

### INTRODUCTION

The Kratovo–Zletovo volcanic area is characterized by various specific features with regard to their structural and geological composition as well as different types of polymetallic mineralization styles. The central parts consist of several old volcanic apparatuses hosting large masses of secondary quartzites. These specific, commonly quartz alunite, rocks are related to significant gold mineralization styles accompanied by Cu, Mo, Fe, Sb, Bi, Hg, etc. The largest masses of secondary quartzites, the most intensely hydrothermally altered rocks and extensive occurrences of polymetallic mineralization are found in the central parts of Mts. Plavica and Crn Vrv not far from Kratovo. The spatial and genetic relationships of secondary quartzites and the mineral raw materials mentioned give grounds for further investigations.

Although these silicified rocks formed as a result of hydrothermal silicification, they are not uniform, and differ in terms of their chemical, mineralogical and petrographic composition and their physical-mechanic characteristics. It should

be mentioned that highly silicified rocks in the Kratovo – Zletovo area formed either near earlier volcanic apparatuses or commonly in the volcanic apparatuses themselves.

The extent of investigation of the volcanic rocks, silicified masses and accompanying mineral raw materials is not the same. Most samples were collected from the central part of Kratovo – Zletovo or the Crn Vrv – Plavica areas where investigations of polymetallic and non-metallic mineral raw materials are still in progress.

Numerous results and discussions can be found in the papers of Ivanov and Denkovski (1978, 1980), Stojanov (1980), Rakić (1982), Serafimovski (1990, 1993), Serafimovski and Mudrinić (1991), and lately in the papers of Janković et al., (1997), Serafimovski and Boev (1996), Serafimovski et al. (1997) etc. These data make possible the overall understanding of the geology, structural composition, genesis and the economic significance of the polymetallic mineralization and secondary quartzites in the Crn Vrv – Plavica area. As

it was mentioned earlier, complex geological investigations have been carried out either by joint domestic and foreign companies or exclusively by

foreign companies. The major goal of this investigation is understanding the epithermal gold mineralization in the area.

## GEOLOGICAL CHARACTERISTICS

The central part of the Kratovo – Zletovo volcanic area (where Mts. Plavica and Crn Vrv are situated) is built of complex volcanic, subvolcanic and volcanogenic-sedimentary occurrences whose composition corresponds to a granodiorite magma or dacitic and andesitic equivalents. However, the common occurrence of subvolcanic intrusions of rhyodacites (quartzlatites) as acid ones and the occurrence of labrador-augite andesites (andesite-basalts) extrusions as basic component parts classify this association as rhyolite-dacite-andesite-basalts, with numerous, commonly unclear transitions (from acid to basic or vice versa).

Three major phases of rock formation can be distinguished. The first phase includes amphibole-biotite and pyroxene-biotite dacite-andesites; the second – subvolcanic solidified sanidine dacites (quartzlatites), and the third – labrador-augite andesites (andesite-basalts) extrusions. Pyroclastic rocks formed mainly during the formation of dacite-andesite, but their formation continued, to a lesser extent, until the last phase of formation of volcanics (Fig. 1).

The volcanic rocks in the central part of the Kratovo-Zletovo area were affected by regional propylitization with common occurrences of hydrothermally altered rocks, particularly in parts of previous volcanic apparatuses (Plavica, Crn Vrv, Borovik etc.) the most pronounced being sericitization, kaolinization, silicification, alunization and pyritization and, to a lesser extent, other kinds of hydrothermal alterations.

Fracture zones with regional and local features are present in the central part of the area. Zones of intense fracturing extending E–W and NW–SE are the most common. Nevertheless, the basic feature of the structural composition, particularly in the area of Plavica (the area of Crn Vrv is less investigated), is the presence of a large number of fractures radially distributed relative to the central part (Fig. 1). Large masses of strongly silicified rocks which, because of their great physical resistance outcrop in the area forming characteristic "riffs", were formed inside the old calderas, along fracture of W–E strike in the central parts of Plavica and Crn Vrv. In Plavica they

appear in an area of some 0.2 km<sup>2</sup>, and in Crn Vrv in an area of over 0.4 km<sup>2</sup> (Fig. 1). They have sub-vertical extension and become smaller in size to depth. Deep-drillings have indicated that their "roots" go down to over 400 m in depth where they gradually wedge out (Fig. 1). Their boundaries with surrounding volcanic rocks are gradual or the degree of silicification gradually gets lower when going far from "pure silex masses" (meaning the silex masses possessing over 95% SiO<sub>2</sub>, most commonly 97–98% SiO<sub>2</sub>).

The genesis of secondary quartzites is closely related to hydrothermal alterations of intermediary rocks in volcanic apparatuses and their immediate vicinity. Their formation started after paroxysm activity of the volcanic apparatus or in the late hydrothermal stage.

Fumarolic-sulphataric alterations took place not only along joints, but along horizons of porous eruptive products distributed several hundreds meters from the apparatuses.

Secondary quartzites are metasomatic products developed without supply of SiO<sub>2</sub> from the magma (nor Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, K<sub>2</sub>O and Fe). This means that redeposition of the component and transport to the place of hydrothermal activity took place with the supply of only water, S, F, Cl, P, B and heavy metals (except for Fe). This is evidenced by residual structures and textures of previous rocks found in them. They were formed by complex and long term activity of hydrothermal solutions and multiple occurrences of tectonic activities which is related to multiple and pulzational movement of hydrothermal solutions that resulted in the formation of other non-metallic raw materials and polymetallic mineralization.

The silex ore in the Crn Vrv and Plavica deposits is composed of amorphous to microcrystalline silicic mass and some opal. It is light-grey to bluish in colour and reddish when it is brecciated. It is found as dense, very hard and tenacious rocks, very difficult to work, resistant to abrasion and shock, of very little porosity and resistant to chemicals. The ore always possesses high contents of SiO<sub>2</sub> (making it different from other secondary quartzite types) and permissive content of harmful components (Table 1).

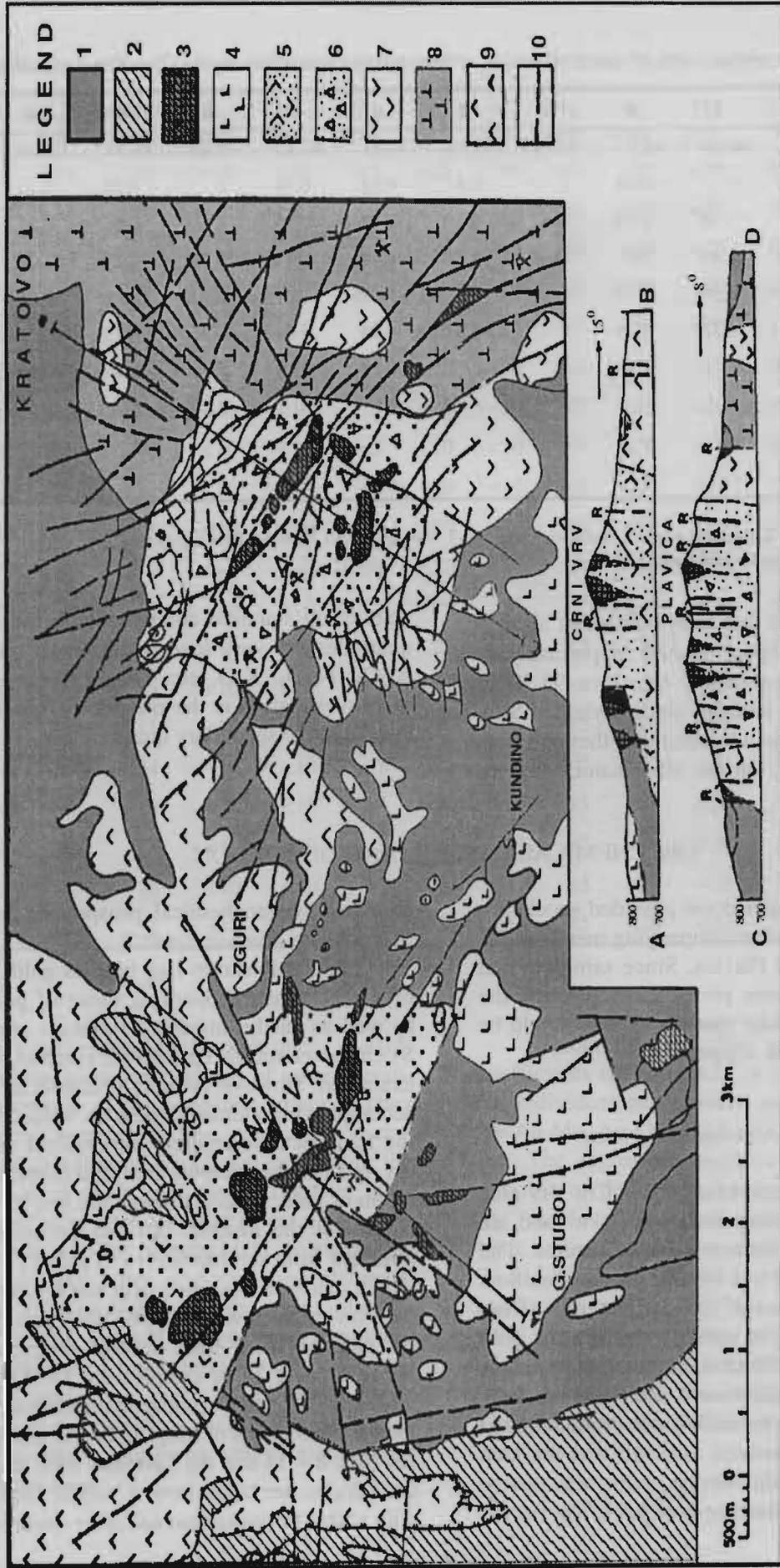


Fig. 1. Geological map and cross section through Crm Vrv-Plavica area

1. Miocene-Pliocene volcano-sedimentary rocks;
2. Oligocene sedimentary rocks;
3. secondary quartzites;
4. labrador-augitic andesites;
5. andesitic volcanic tuffs at Crm Vrv;
6. hydrothermally altered volcanics;
7. dacito-andesites;
8. ignimbrites;
9. augite-biotite andesites;
10. faults (partially mineralized)

Table 1

Chemical composition of some varieties of secondary quartzites in the Crn Vrv area (%)

Components	1	2	3	4	5	6	7	8	9	10	11
SiO <sub>2</sub>	98.63	94.94	93.7	98.78	98.53	97.61	97.47	98.67	96.34	97.68	98.54
TiO <sub>2</sub>	trace	/	0.08	/	0.4	0.52	0.16	/	0.38	0.12	0.14
Al <sub>2</sub> O <sub>3</sub>	0.1	1.54	1.72	0.57	0.2	1.02	0.76	/	0.51	0.25	0.38
Fe <sub>2</sub> O <sub>3</sub>	0.83	1.43	2.5	0.08	/	0.29	0.37	0.06	2.29	1.07	0.29
MgO	/	0.56	0.75	/	0.015	0.016	0.016	0.32	0.025	0.04	0.02
CaO	0.07	0.32	0.25	/	0.07	0.08	0.04	0.25	0.13	0.21	0.11
Na <sub>2</sub> O+K <sub>2</sub> O	0.09	/	/	/	/	0.15	0.16	/	trace	trace	trace
MnO	trace	/	/	/	/	/	/	/	/	/	/
P <sub>2</sub> O <sub>5</sub>	/	/	/	/	/	/	/	/	/	/	trace
H <sub>2</sub> O (110°C)	0.13	/	/	/	/	/	/	/	/	/	/

Note: 1. Light gray silex. 2. Reddish silex. 3. Yellowish silex. 4–7. Samples from Ajdučko Kladenče area; 8–11. Samples from Gradište area

The table shows that SiO<sub>2</sub> content in all secondary quartzite samples studied is permanently high. The contents obtained are from 93.70 to 98.78%. Most of the samples studied yielded SiO<sub>2</sub> contents of over 98% indicating that they are high quality raw material. On the other hand, the con-

tents of all standard components in the secondary quartzites are very low. Such are the contents of Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, etc. Of particular interest to this investigation is the presence of gold spatially related to the secondary quartzites.

## GEOCHEMICAL RESULTS AND DISCUSSION

Examinations carried out provided geochemical results of gold and accompanying metals in the area of Crn Vrv and Plavica. Since sampling and data interpretation were performed separately the present authors consider that the results should be presented for each site separately.

### *The Crn Vrv prospecting area*

The secondary quartzites in the Crn Vrv area can be found in an area of about 0.4 km<sup>2</sup> and are characterized by numerous specific features. The examinations carried out by the presents authors included a smaller part of the raw materials (from the area of Gradište), in order to establish its gold mineralization. Individual sampling consisted of 20 samples (all of which were analyzed) on Au + 13 standard elements for such kinds of mineralized areas. Notably, the authors assumed that the area represented a high sulphidation epithermal system or standard acid sulphate type of gold. The results

obtained by geochemical prospecting in the Crn Vrv area are given in Table 2.

The Table shows that besides gold, a number of other elements including those of polymetallic as well as easily migrating elements (As, Hg, Se, S) characteristic of epithermal systems, were also examined. However, results obtained for gold and accompanying elements indicate values located at the flank of a completely mineralized area. Notably, most of the samples analyzed contain less than 5 ppb of gold, which is below the low limit of sensitivity of the method. An interesting result was obtained from sample No. 13 (Table 2) of 467 ppb which can well compare with the results obtained for Plavica. It is worth mentioning that the results for gold obtained from several samples close to No. 13 (Table 2), or samples 8 – 13 (Table 2) can correlate with other accompanying elements. A close look at the contents of Mo, Cu, Fe, As and S in analyses Nos. 8 – 14 and the sampling sites illustrate that the samples are taken from a smaller fault structure with visible limonitization and other alterations.

Table 2

## Contents of gold and some associated metals in the "secondary quartzites" of the Crn Vrv area

Sample number	Au ppb	Ag ppm	Cu ppm	Mo ppm	Pb ppm	Zn ppm	Bi ppm	As ppm	Hg ppm	Se ppm	Te ppm	Fe %	Mn %	S ppm
1	<5	<5	14	<10	<10	<5	<20	34	<5	<20	<20	0.82	<0.01	277
2	17	<5	8	<10	<10	9	<20	<10	<5	<20	<20	0.91	0.02	611
3	<5	<5	6	<10	<10	<5	<20	<10	<5	<20	<20	0.71	0.01	123
4	<5	<5	7	<10	<10	<5	<20	<10	<5	<20	<20	0.77	0.01	160
5	<5	<5	11	<10	<10	<5	<20	11	<5	<20	<20	1.08	0.02	114
6	<5	<5	14	<10	<10	<5	<20	20	<5	<20	<20	0.86	0.01	110
7	<5	<5	7	<10	<10	5	<20	<10	<5	<20	<20	0.79	0.01	228
8	22	<5	12	<10	<10	<5	<20	<10	<5	<20	<20	0.86	<0.01	1373
9	<5	<5	10	<10	<10	<5	<20	<10	<5	<20	<20	0.79	0.01	1895
10	12	<5	18	<10	<10	9	<20	12	<5	<20	<20	0.97	<0.01	634
11	8	<5	10	<10	<10	10	<20	27	<5	<20	<20	1.17	0.01	555
12	23	<5	121	15	<10	15	<20	51	<5	<20	<20	5.05	<0.01	1268
13	467	<5	75	18	<10	11	25	43	<5	<20	<20	4.75	<0.01	610
14	<5	<5	38	<10	<10	7	<20	19	<5	<20	<20	1.35	<0.01	95
15	7	<5	11	<10	<10	<5	<20	19	<5	<20	<20	1.04	<0.01	126
16	<5	<5	31	<10	<10	7	<20	52	<5	<20	<20	1.93	0.01	114
17	<5	<5	18	<10	<10	7	<20	33	<5	<20	<20	1.36	<0.01	64
18	<5	<5	8	<10	<10	5	<20	11	<5	<20	<20	1.00	<0.01	95
19	<5	<5	28	<10	<10	12	<20	12	<5	<20	<20	1.77	0.01	317
20	<5	<5	11	<10	<10	8	<20	<10	<5	<20	<20	0.86	<0.01	385

As it was said earlier the area under consideration also contains low contents of other accompanying elements of no economic interest. They are of interest in terms of their geochemistry, correlation and distribution which can be used in the interpretation of their evolution. Computer software support were used in order to get a complete understanding of the geochemical relationships between gold and other accompanying elements, correlation relationships and the extent of their distribution. The method applied was regression analysis with use of linear model  $y = a + B \cdot x$  and exponential model:  $y = \exp(a + b \cdot x)$ . Investigation of correlation relationships included Au-Cu, Au-Mo, Au-As, Au-Hg, Au-Fe as well as many variations between them.

Results illustrate that sufficient correlation coefficients (of over 0.58 or > 58%) are obtained for individual geochemical pairs. With gold they are Au-Mo, Au-Cu and Au-Fe pairs.

The regression analysis linear model made possible to define the linear correlation between the Au-Mo geochemical pair. The R-squared statistic indicates that the model as fitted explains 73.5152% of the variability in Au. The correlation coefficient equals 0.85741, indicating a moderately strong relationship between the variables. The standard error of the estimate shows the standard deviation of the residuals to be 54.3407. Graphic relationships between these two elements are shown in Fig. 2.

Plot of fitted model

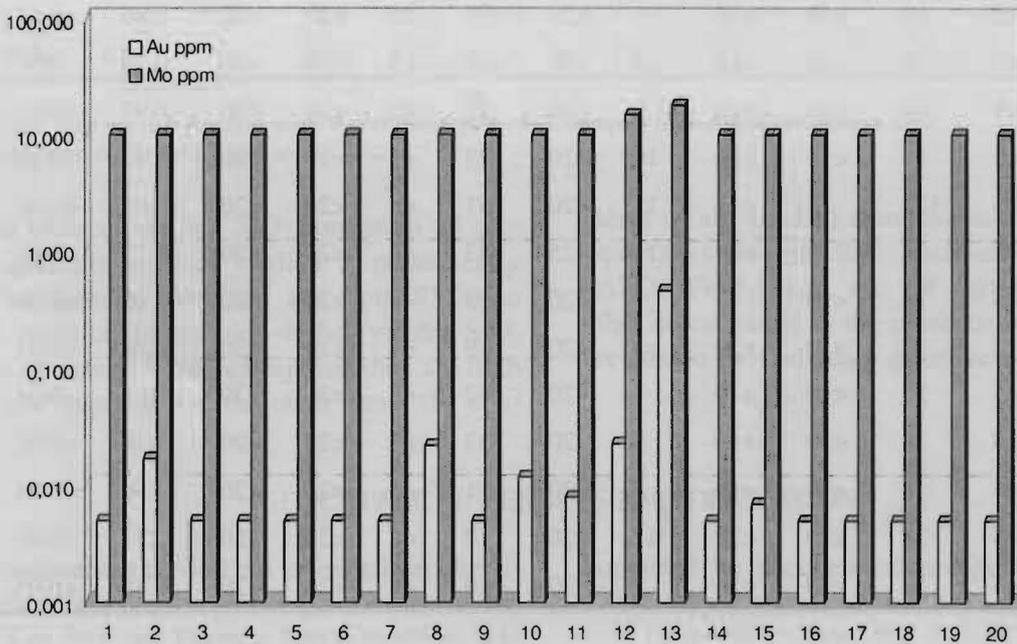
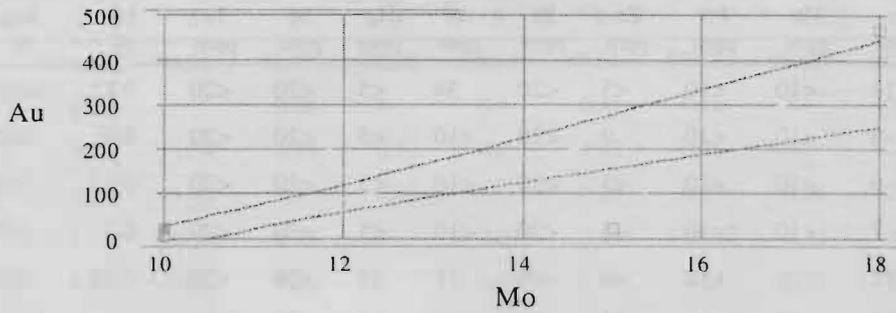


Fig. 2. Correlation diagram and histogram of distribution of Au and Mo from the Crn Vrv area

The correlation diagram between Au-Mo shows that a small number of data is plotted despite the high correlation. This is due to uniformity of a large number of data (Mo contents are below 10 ppm) which can be seen better from the distribution diagram for Au and Mo.

The Au-Cu geochemical pair examined is typical of this ore-bearing area. It indicated a correlation dependence that is not strongly pronounced. The R-squared statistic indicates that the model as fitted explains 34.1589% of the variability in Au after transforming to a logarithmic scale

to linearize the model. The correlation coefficient equals 0.584456, indicating a moderately strong relationship between the variables. The standard error of the estimate shows the standard deviation of the residuals to be 0.902049.

The correlation diagram and histogram of distribution (Fig. 3) display that data plotting as basis for regression analysis – exponential model explain only part of the samples (from 8 to 15, Table 1) that was put forward earlier. This is also proved for the Au-Cu geochemical pair.

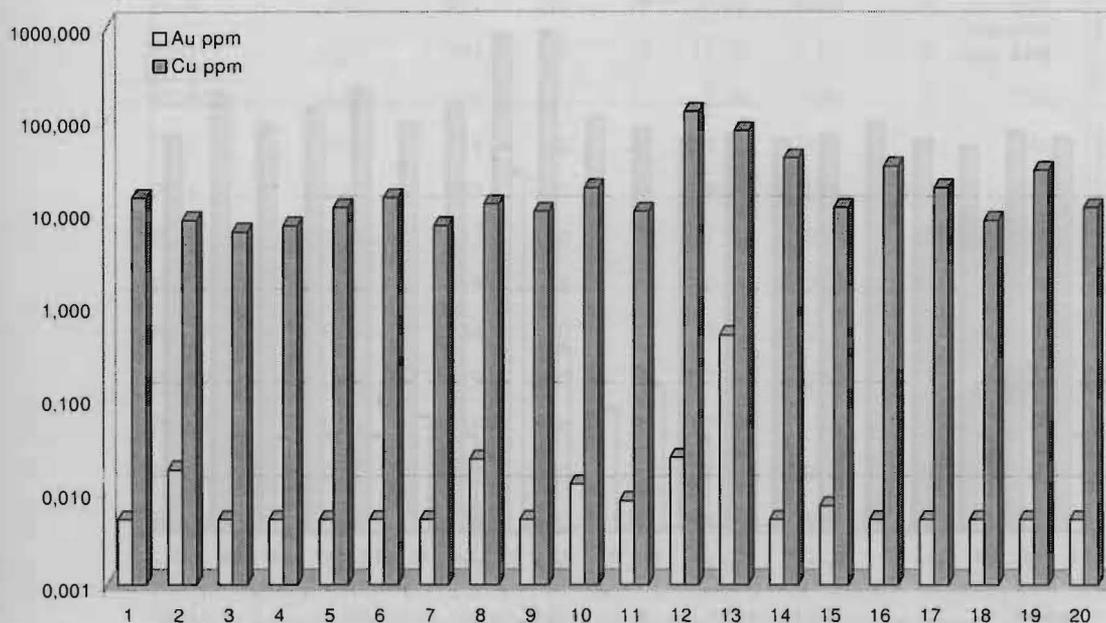
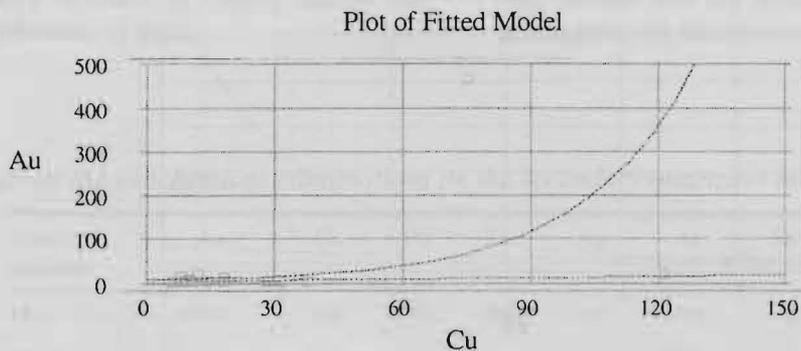


Fig. 3. Correlation diagram and histogram of distribution of Au and Cu from the Crn Vrv area

An interesting correlation relationship was obtained for the Au-Fe geochemical pair which is not the usual standard for mineralization styles of this kind. The high correlation relationship obtained is probably due to the similar geochemical evolution during the processes of mineral formation noticed during selecting the samples. The R-squared statistic indicates that the model as fitted explains 52.7233% of the variability in Au after transforming to a logarithmic scale to linearize the model. The correlation coefficient equals 0.726108, indicating to a moderately strong relationship between the variables. The standard error of the estimates shows the standard deviation of the residuals to be 0.764372.

The correlation and distribution diagrams of Au and Fe (Fig. 4) indicate that there is a logical plotting of data that essentially provide a high correlation coefficient, and pronounced distribution of these two elements in a certain number of samples (from 8 to 14) which practically contribute most to the pronounced correlation.

In addition to the correlation relationships between gold and accompanying elements presented, there is a clear correlation dependence between other elements as well. Such are the Cu-Mo pair with the correlation coefficient of 0.8260, Fe-Mo with 0.9267, Fe-Zn, Cu-Zn, Zn-Mo and some others.

Plot of fitted model

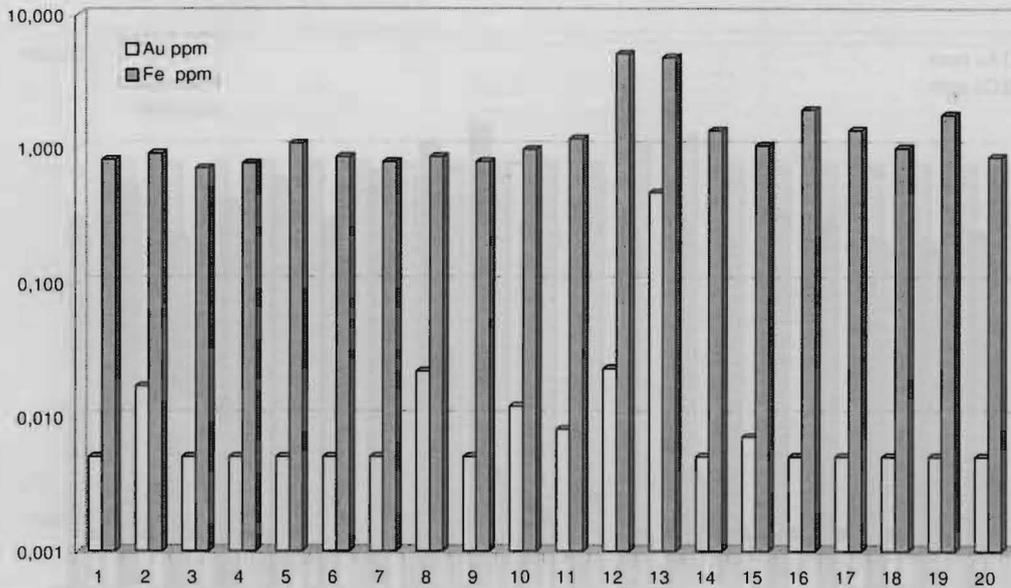
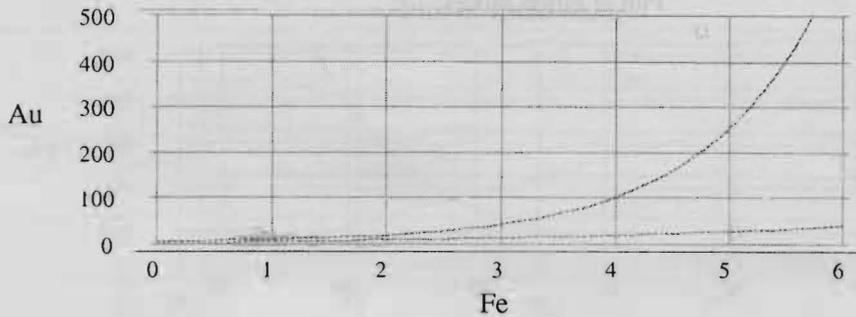


Fig. 4. Correlation diagram and histogram of distribution of Au and Fe from the Crn Vrv area

The increased contents of the whole series of elements and their pronounced correlation relationships with no correlation between gold and easily migrating elements such as As, Sb, Hg, Se, etc. lead to the conclusion that gold and its accompanying elements are close to the relationship of the Plavica porphyry mineralization system (only its north-west flanks) rather than a separate epithermal system of the order of "acido-sulphate" or a high sulphidation epithermal system.

This conclusion is also inferred based on the data from individual diagrams, standard increased contents of almost all elements from samples Nos. 8 to 14 which coincides with our observations in the terrain that this is a small fault structure that is limonitized and altered on the surface. This probably explains the close correlation relationships

between Au and Fe which are not commonly standard for epithermal mineralization systems with Au.

#### *The Plavica prospecting area*

Prospection carried out in the central parts of the Plavica volcanic structure included 26 samples for gold and other metal analyses. Sampling was made the surface outcrops from the secondary quartzites. Previous sampling indicated that the most significant gold contents were related to the silicified zones or secondary quartzites (Fig.1). All samples were quantitatively analyzed for Au and associated metals, particularly elements As, Sb and Hg. The results obtained are shown in Table 3. In order to get a complete knowledge the results are

subjected to statistical analysis using Excel, Surfer, Stat Graph in order to clearly define the content and distribution of gold.

Table 3 shows that, besides gold, Cu, Pb, Zn, Ag, As, Sb and Hg were also analysed as major accompanying elements in the Plavica deposit.

Table 3

*Results of the geochemical examinations on the secondary quartzites in Plavica (ppm)*

Elements Samples	Au	Cu	Pb	Zn	Ag	As	Sb	Hg
PL-1	0.18	339	1140	98	3.00	196	9	0.31
PL-2	1.08	112	460	11	7.00	1330	26	0.39
PL-3	0.43	56	215	8	8.80	600	5	0.41
PL-4	1.72	411	240	10	27.80	6600	54	1.04
PL-5	0.74	341	118	13	11.20	21	19	1.43
PL-6	4.53	171	250	21	8.00	980	33	2.27
PL-7	0.65	444	189	29	4.60	7400	62	0.46
PL-8	2.82	363	270	11	19.90	2.16	183	4.11
PL-9	1.71	335	800	32	1.50	930	32	0.56
PL-10	3.68	119	198	12	10.40	2290	24	0.31
PL-11	0.27	34	420	8	13.30	213	31	0.33
PL-12	0.19	19	330	8	7.50	380	3	0.20
PL-13	0.31	36	270	9	17.70	64	9	0.49
PL-14	0.07	62	630	25	7.50	910	39	0.80
PL-15	5.67	1150	1090	42	4.50	2940	78	0.51
PL-16	3.72	417	870	41	5.80	4200	77	0.93
PL-17	0.32	186	141	16	4.40	1100	9	2.64
PL-18	0.50	575	370	94	2.30	1550	28	0.67
PL-19	1.00	286	720	22	1.00	4020	170	1.47
PL-20	1.00	105	139	14	3.30	680	23	0.54
PL-21	0.21	205	470	14	2.20	1090	33	1.94
PL-22	0.40	90	790	21	5.60	560	14	0.36
PL-23	0.16	195	630	17	20.20	490	7	0.41
PL-24	0.59	61	300	11	3.60	112	7	0.17
PL-25	1.12	87	2900	15	13.60	870	19	0.59
PL-26	0.43	100	3500	9	9.00	137	6	0.21

Gold contents in some samples exceeding 5.5 ppm. Correlate with high values of more mobile elements (As and Hg) undoubtedly point to the development of epithermal systems which carries gold in secondary quartzites. It should also be

mentioned that the bulk of the samples were taken from topographic highs of the Plavica system (Fig. 5). The silicified bodies are mainly found in this level.

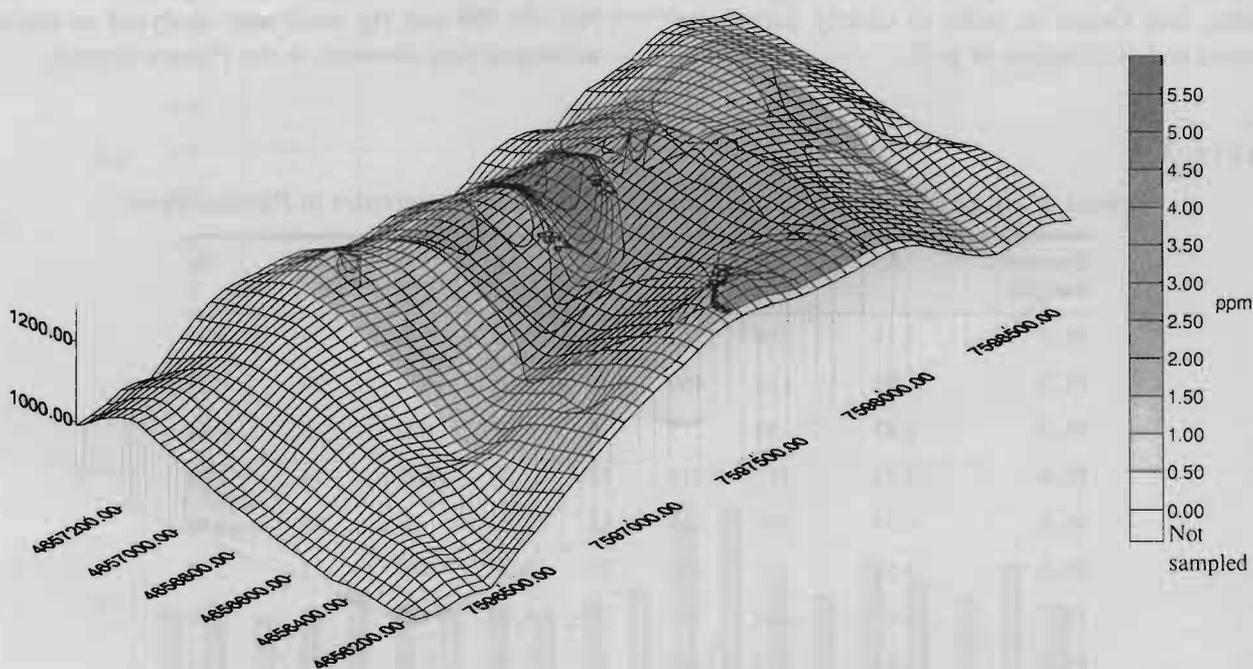


Fig. 5. Hypsometric review of gold contents in secondary quartzites of Plavica

Increased amounts of Cu, Pb, and Ag in particular, are apparent, and can be related to the polymetallic stockwork-disseminated mineralization styles which form a wide halo both laterally and to more than 1,000 m vertically. Statistical

analysis of data and investigation of correlation relationships were applied in order to get a detailed knowledge of individual relationships between gold contents and other metals (Table 4).

Table 4

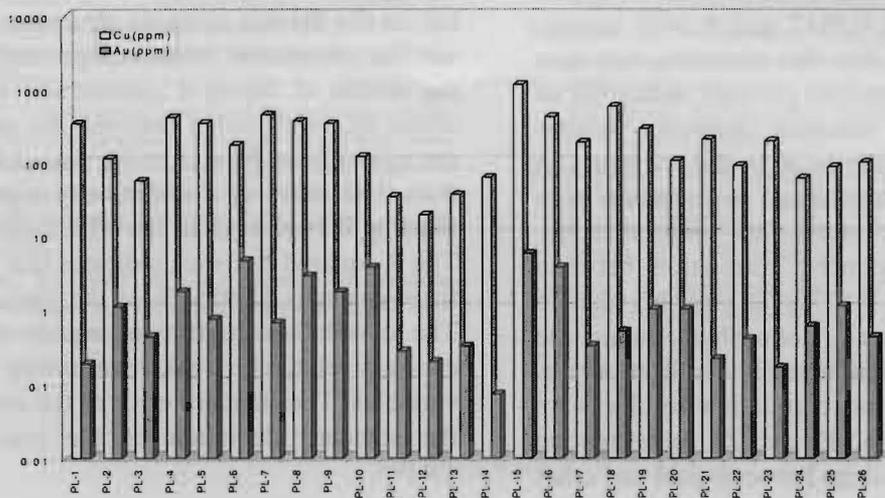
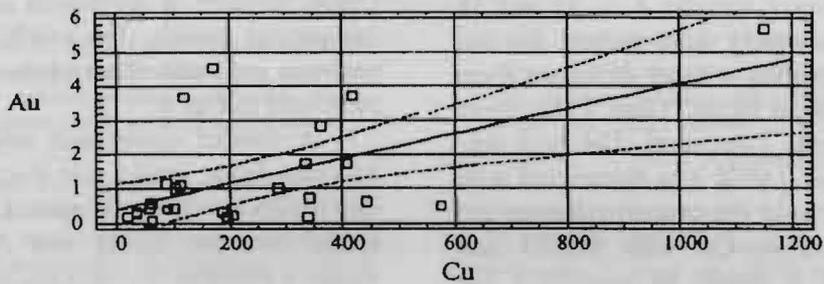
*Statistical data and correlation relationships between elements in the analyzed secondary quartzites in Plavica*

Analysis	<i>n</i>	<i>X</i>	$\sigma$	Low	High	$X + \sigma$	$X + 2\sigma$	$X + 3\sigma$
Cu (ppm)	26	242.30	240.500	19	1150	482.90	723.500	963.80
Pb (ppm)	26	671.10	803.800	118	3500	1474	2278	3082.50
Zn (ppm)	26	23.50	23.380	8	98	46.88	70.270	93.64
Ag (ppm)	26	8.95	6.505	1.50	27.80	15.45	21.960	28.47
As (ppm)	26	2435	4355	64	21600	6790	11146	15 500
Sb (ppm)	26	38.46	45.720	3	183	84.19	129.900	175.62
Hg (ppm)	26	0.90	0.924	0.17	4.11	1.83	2.755	3.68
Au (ppm)	26	1.29	1.5171	0.07	5.67	2.81	4.324	5.84

*Correlation coefficients*

	Cu (ppm)	Pb (ppm)	Zn (ppm)	Ag (ppm)	As (ppm)	Sb (ppm)	Hg (ppm)	Au (ppm)
Cu (ppm)	1							
Pb (ppm)	-0.0139	1						
Zn (ppm)	0.5095	0.0567	1					
Ag (ppm)	-0.1188	-0.0099	-0.4209	1				
As (ppm)	0.3127	-0.1753	-0.0747	0.3996	1			
Sb (ppm)	0.4084	-0.1017	0.0075	0.2285	0.7918	1		
Hg (ppm)	0.1244	-0.2465	-0.1313	0.2030	0.6806	0.5879	1	
Au (ppm)	0.5779	-0.0273	0.0508	0.0220	0.2837	0.5573	0.2497	1

Plot of fitted model



Plot of fitted model

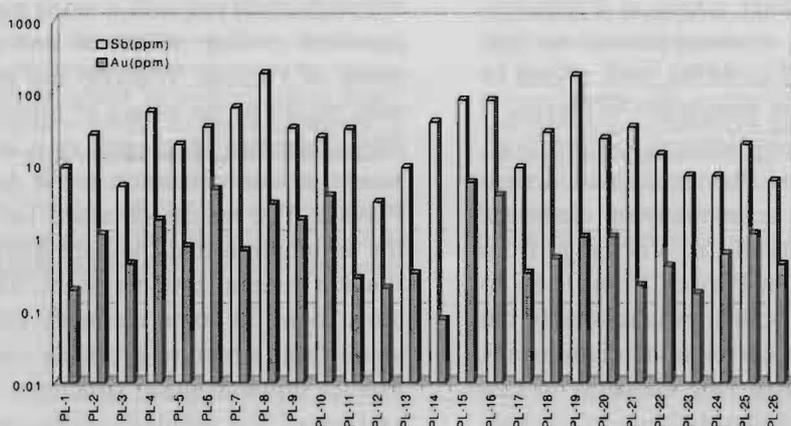
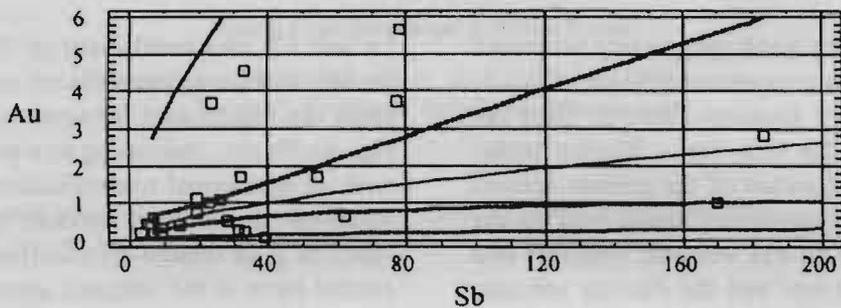


Fig. 6. Correlation diagrams and histograms of distribution of Au-Cu and Au-Sb pairs from the Plavica area

The Table shows that besides  $x$ ,  $\sigma$ ,  $x + \sigma$ ,  $x + 2\sigma$  and  $x + 3\sigma$  since samples 4, 7, 15 and 18 (Table 4) show extremely high values for individual elements creating a large deviation from normal distribution to be larger. Table 4 also gives correlation coefficients calculated. The best correlation coefficient of 0.6806 was discovered with the Hg-As pair. For gold the best correlations are between Au-Sb and Au-Cu with 0.5573 and 0.5779, respectively. It should be mentioned that gold has a positive correlation coefficient with both As and Hg (of 0.2837 and 0.2497 respectively) this indicates that these elements may also show a genetic relationship perhaps indicative of shared hydrothermal transport chemistry. Alteration mineralogy and deposit style and chemistry in the "secondary quartzites" seem to be of the high sulphidation type of epithermal mineralization. The close and pronounced correlation between gold and copper (of 0.5779) is probably due to their close geochemical relationships within the stockwork Cu-Au disseminated mineralization present at depth. Negative correlation results were found between gold and Pb and Zn. Investigation of correlation relationships between gold and other

accompanying elements was assessed using Stat-Graph program or regression analysis was carried out various models. The results of this correlation between gold and other elements are graphically presented in Fig. 6.

A distinct correlation relationship, obtained by using linear model was discovered with Cu-Au and Au-Sb geochemical pairs. Correlation was also found between As-Hg and As-Sb pairs which makes it possible to constrain the genetic evolution of Au mineralization related to "secondary quartzite" in the Plavica volcanic structure. In this manner the correlation relationships carried out give the results of fitting a geometrical model to describe the relationship between Au and Sb. Since the values from Plavica in the Anova table are less than 0.01 there is a statistically significant relationship between Au at the 95% confidence level. The R-squared statistics indicates that the model as fitted explains 15.9556% of the variability in Au. The correlation coefficient equals 0.3994, indicating a relatively weak relationship between the variables. The standard error of the estimate shows the standard deviation of the residuals to be 1.4195.

## CONCLUSION

The results of the latest prospecting presented in the paper cover an area of some 50 km<sup>2</sup> (Fig. 1) in the central parts of Kratovo-Zletovo. They belong to the area of the Crn Vrv – Plavica strike. The subject of investigation of the present authors was only secondary quartzites established in the central parts of the Crn Vrv volcanic structure that cover an area of 0.4 km<sup>2</sup> and the Plavica volcanic caldera which covers an area of 0.2 km<sup>2</sup>.

The secondary quartzites are metasomatic occurrences, a product of later stages of hydrothermal activity, whose SiO<sub>2</sub> contents amount to over 98% (most commonly 93 to 98%), with regard to the significant gold contents, particularly in Plavica.

The results of the geochemical examinations carried out in Crn Vrv and Plavica indicate a variety of gold contents and accompanying elements. Notably, the gold contents in Crn Vrv range from 5 to 467 ppb, and those in Plavica from 0.186 to 5.67 ppm. Gold found in both sites is related to the secondary quartzites. The correlation relationships between gold and accompanying elements in Crn Vrv indicated pronounced correlation relationships with Au-Cu, Au-Mo, Au-Fe, particularly between

Fe and Cu (the coefficient of 0.9562) as well as Fe-Mo. In Plavica pronounced correlation relationships are established between Au-Cu, Au-Sb, As-Hg, As-Sb etc., indicating to a possible connection with an epithermal mineralization system that corresponds to standard models of acido-sulphatic types of gold related to silicified zones within the central parts of old volcanic apparatuses. Plavica is part of these complex volcanic apparatuses.

The relationships established for Crn Vrv, although analyzed with a small number of samples, provided similar structural and geologic data to those of Plavica. The two are probably different with regard to the extent of mineralization. Secondary quartzites developed in a wider area but the extent of mineralization is far lower than that in Plavica. The results obtained for Crn Vrv lead to the assumption that they are marginal parts of the Plavica mineralization system. The increased contents found in some elements indicate that it is a small fault structure probably connected with the Plavica mineralization structures. It should also be mentioned that definite conclusions require precise terrain and laboratory investigations.

## REFERENCES

- Иванов, Т., Денковски, Ѓ., 1978. *Геолоџија на метало-џенейскиот јазел Пластица–Златица во крайовско–златовската металоџенейска област*. Зборник радова IX конгрес геолога Југославије, стр. 767–777, Сарајево.
- Иванов, Т., Денковски, Ѓ., 1980: *Хидротермални алтерации во порфирској бакарно лежнито Пластица–Златица во крайовско–златовската вулканска област*. Симпозиум: Алтерација стена и минерала, 139–163, Београд.
- Janković, S., Serafimovski, T., Jelenković, R., Čifliganec, V., 1997: *Metallogeny of the Vardar zone and Serbo-Macedonian mass.* Symposium – Annual Meeting, Proceedings, pp. 29–69, Dojran.
- Ракиќ, С., 1982. *Секундарни кварцити централног дела крайовско–златовске вулканске области: Значајне неметаличне сировине, са којима су везане и значајне појаве полиметаличног и неметаличног оруђења*. X конгрес геолога Југославије, кн. II, 337–349. Будва.
- Серафимовски, Т., 1990: *Металоџенија на зоната Леце – Халкидик*, докторска дисертација, 391 стр. Рударско-геолошки факултет, Штип.
- Serafimovski, T., Mudrinić, C., 1991. *Mineralogical and geochemical characteristics of Cu-polymetallic deposits Plavica-Zlatica (Eastern Macedonia)*. XXIII oktobarsko savetovanje rudara i metalurga, p. 27–30, Bor.
- Serafimovski, T., 1993. *Structural-Metallogenic Features of the Lece–Chalkidiki zone : Types of Mineral Deposits and Distribution*. Faculty of Mining and Geology, Spec. issue, № 2, p. 328, Štip.
- Serafimovski, T., Boev, B., 1996: *Metallogeny of the Kratovo-Zletovo volcano-intrusive complex*. Proceedings, Terrains of Serbia, 343–353, Belgrade.
- Serafimovski, T., Thomson, I. N., Kocneva, N. T., 1997: *Alpine orogenic structures and metallogeny in the Serbo-Macedonian massif and the Vardar zone of the territory of Macedonia*. Symposium – Annual Meeting, Proceedings, pp. 113–119, Dojran.
- Стојанов, Р., 1980. Вулканската купа Пластица, полиметалните минерализации и околурудните промени во неа. Симпозиум: Алтерација стена и минерала, 122–138, Београд.
- Stojanov, R., Denkovski, Dj., 1997: *The Plavica supervolcanic structure in the Kratovo–Zletovo volcanic area and its metallogeny*. Symposium – Annual Meeting, Proceedings, pp. 215–221, Dojran.

## Резиме

## СЕКУНДАРНИТЕ КВАРЦИТИ СО МИНЕРАЛИЗАЦИИ НА ЗЛАТО ВО ВУЛКАНСКАТА ОБЛАСТ ЦРН ВРВ – ПЛАВИЦА

Тодор Серафимовски<sup>1</sup> и Стево Ракиќ<sup>2</sup><sup>1</sup>Рударско-геолошки факултет, Штип, Република Македонија<sup>2</sup>"Силекс", Крайово, Република Македонија

**Клучни зборови:** област Црн Врв – Пластица; секундарни кварцити; вулканити; минерализација на злато; вулкански калдери

Во трудот се прикажани најновите резултати од хемиските и геохемиските испитувања на секундарните кварцити од подрачјето на Црн Врв–Пластица. Станува збор за вулкански простори (вулкански калдери) во чии централни делови се утврдени секундарни кварцити со променливи концентрации на злато. Површинските манифестации на секундарните кварцити се во вид на леќи и гнезда со мали димензии, а кон длабочина добиваат клинеста форма. Хемиските испитувања покажаа дека тоа се стени со многу високи содржини на SiO<sub>2</sub> (96,34 – 98,78%), а геохемиските испитувања покажаа дека во нив постојат и концентрации на злато придружувани со поголем број еле-

менти како што се Cu, Ag, Bi, Sb, Se, Te, Hg и др. Содржината на злато е променлива и се движи од траги до преку 20 g/t Au во индивидуални проби. Пониски содржини се констатирани во областа Црн Врв (5–467 ppb), додека на Пластица во просек се утврдени 1.29 g/t Au (0,186 – 0,506 ppm Au). Добените резултати се интерпретирани со соодветни софтверски поддршки, при што се констатирани интересни корелативни врски помеѓу поедини парови: Au–Cu, Cu–Mo, Au–Sb, Au–Hg, Au–Fe и др, кои неоспорно упатуваат на заедничка примарна мобилизација и заедничка еволуција во рамките на епитермалниот минерализационен систем.