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GEOCHEMICAL STUDY OF THE MINERALIZED SYSTEM BUKOVIK–KADIICA, EASTERN MACEDONIA

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A b s t r a c t: In accordance with the performed regional and detailed geochemical studies of the stream sediments, soils and rock chips, at the wider area of the Bukovik–Kadiica locality near Pehčevo town, Eastern Macedonia, regional and local polymetallic geochemical anomalies of elements such are Cu, Fe, S, Mo, Au, Pb, Zn, Sn, As, Sb, Ti, V, Co etc were detected. However, copper, molybdenum, silver, lead and zinc, appeared to have most standard values which coincides with the former geochemical studies. This data directly point to an existence of the copper mineralization in a wider area that coincides with the structural-metallogenic features of the Bukovik–Kadiica area, also. Detailed studies allowed calculation of the correlation factors of the most frequent elements in the area of interest. Especially significant correlation factors were detected for the elemental pairs such as Cu-Ag, Fe-Cu, Zn-Au, Pb-Ag and Pb-As.

Key words: primary halos; stream sediments; metalometry; polymetallic mineralizations; Bukovik–Kadiica locality

INTRODUCTION

The mineralized area Delčevo–Pehčevo–Berovo has been subject of numerous geochemical explorations and studies during the past 4 decades. The first studies of this kind were performed in 1974–1975 when the Geological Survey–Skopje performed preliminary explorations, on the net-like scheme, it was sampled with one sample per a square kilometer. Some of the later geochemical studies concerning this area of interest can be found in the works of Hadži-Petrušev (1985), Stojanov et al. (1995) etc.

Synthesized up to date numerous and complex studies in which geochemical studies took special place, have shown all the complexity of the area, in question as well as findings concerning perspective areas from the mineralization(s) point of view.

Geochemical studies have confirmed the existence of large dislocations, where along them were intruded magmatites and volcanites, as well as post-magmatic hydrothermal processes deposited mineralization and sometimes remobilized them (Hadži-Petrušev, 2008). Geochemical explorations and studies of this region could be divided to:

– systematic regional (and half-regional) explorations and studies of the whole region, and

– separate detailed explorations of particular localities.

Geochemical explorations outlined in this manner enabled regionalization of the terrain in regard of metallic mineral resources, lithological, structural and temperature factors. The existence of the mega-structure of northwest-southeast direction was defined in that manner while at the same time the activities of northeast-southwest and east-west direction were highlighted. Also, the problems of erosion processes were opened where it the presence of copper mineralization was sensed. As very characteristic areas appeared Bukovik–Kadiica, Dvorište and a wider area around the town of Berovo (Vladimirovo, Rusinovo). In that direction was the existence of the aforementioned mega-structure.

REGIONAL GEOCHEMICAL RESEARCH

Geochemical half-regional studies were performed for the necessities of the OGK-2 (Basic Geological Map-2) of the ore region Delčevo–Pehčevo–Berovo (Hadži-Petrušev et al., 2008). Geochemical studies were performed on heavy fractions panning material and soil material (secondary halos of dispersion) along the stream network. Separate geochemical studies from the half-regional and detailed point of view were performed several times at different terrains and localities. Most important of them appeared to be the studies of lead-zinc occurrences in the northern parts of the area, then primary and secondary studies of copper and other mineral resources near Dvorište, Pančarevo, Bukovik–Kadiica, presence of Fluor in Berovo (Maleševo area) and Delčevo (Stamer–Dzvegor–Grat) region. Special attention during the half-regional studies was given to the rare elements (tungsten, tin, molybdenum) near Delčevo (Kulata) and Berovo (Maleševo Mountains). Also, the studies of gold along the Pekljanska river, Bukovik, Dvorište, Laki and other streams were of great importance.

Information obtained from the statistical analysis of the studied elements enabled preparation of graphical interpretation of each element, getting an idea about their lithogeochemical features in comparison to the adjacent areas, as well as about their spatial distribution and concentration within particular localities (Figure 1).

In regards to their spatial distribution and paragenetic grouping of elements and mineral association, the studied region could be divided into four segments: Vetren–Dzvegor–Bukovik–Kadiica –Dvorište; Plačkovica-Maleševo Mountain, southeastern part of the Sasa zone (Kostin Dol), Mitrašinci–Virče. In this preview we are going to pay special attention to the most important geochemical features of the first zone mentioned above, where the copper anomalies around the Bukovik–Kadiica mineralized system stand out. The Vetren–Dzvegor–Bukovik–Dvorište anomalous zone has been characterized by volcanic emanations of dacite to andesite composition, intensive alterations and hydrothermal changes within the volcanic aparatuses and adjacent lithological settings where they have been intruded. Geochemical association has been represented by wide range of elements such as Cu, Pb, Zn, Mo, Ag, Ba, Au and Fe. Mineral associations are represented by chalcopyrite, chalcocite, bornite, covellite, tetrahedrite, lead and zinc sulfides, molybdenite, malachite, azurite, pyrite, native gold and some other minerals. The mineralogical diversity allowed distinction of three geochemical sub-groups:

Dvorište metallogenic field with Cu, Pb, Zn, Mo, Ba ± native Au.

Vetren–Dzvegor–Istevnik metallogenic field with Cu, Pb, Zn, Mo, Ag, Ba.

Bukovik metallogenic field with Cu, Pb, Zn, Mo, Ba, Ag ± native gold and W.

At Maleševo Mountains, around 2.5 km SE from the Dvorište village the so called Dvorište formation composed of dacite, tuff, breccia and aglomerates has been developed. Within this formation and its close vicinity polymetallic Cu, Pb, Zn, Mo, Fe, Au mineralization determined. The polymetallic mineralizations were deposited along the faulting structures located in two-mica and muscovite gneiss. The most important occurrences are: Zabelski Potok, Vrli Čukar, Džuarec, Slivata, Srbnica and Bela Voda. Within all the aforementioned occurrences identical hydrothermal alterations and ore veins filled with pyrite appear, chalcopyrite, chalcocite, bornite, Pb-Zn sulfides, Mo, Ag etc. All of them should be studied in more detail. The volcanic activity around the Vlaina area has been determined as the bearer of polymetallic mineralizations grouped around the volcanic masses at Gabrovo–Dzvegor, enclosed in rocks of the Riphean-Cambrian complex and Triassic limestones and within the volcanic products itself. Near the Gabrovo and Dzvegor villages intensive hydrothermal alterations such are kaolinitization, silicification, and limonitization of the localities occur: Lazovi Kući, Belite Kamenja, Popov Čukar, Karakol, Turćinska Maala, Čukata–Ostrec, Grčina, Okno etc. The mineral paragenesis has been represented by pyrite, chalcopyrite, chalcocite, covellite, sphalerite, galena, magnetite, hematite, titanite, ilmenite, secondary malachite, azurite etc. Minerals at particular localities appear in form of veins while at some other appear they as impregnations.

The volcanic activity at the Bukovik–Orlovec –Kadiica–Kadan Bunar is the bearer of the primary mineralization. At the source area of the Pehčevska River at the contact between volcanics with green schists of the Rusinovo formation hydrothermal alterations with polymetallic mineralizations of pyrite, chalcopyrite, tetrahedrite, galena, sphalerite, molybdenite, malachite, limonite, magnetite and gold occur.

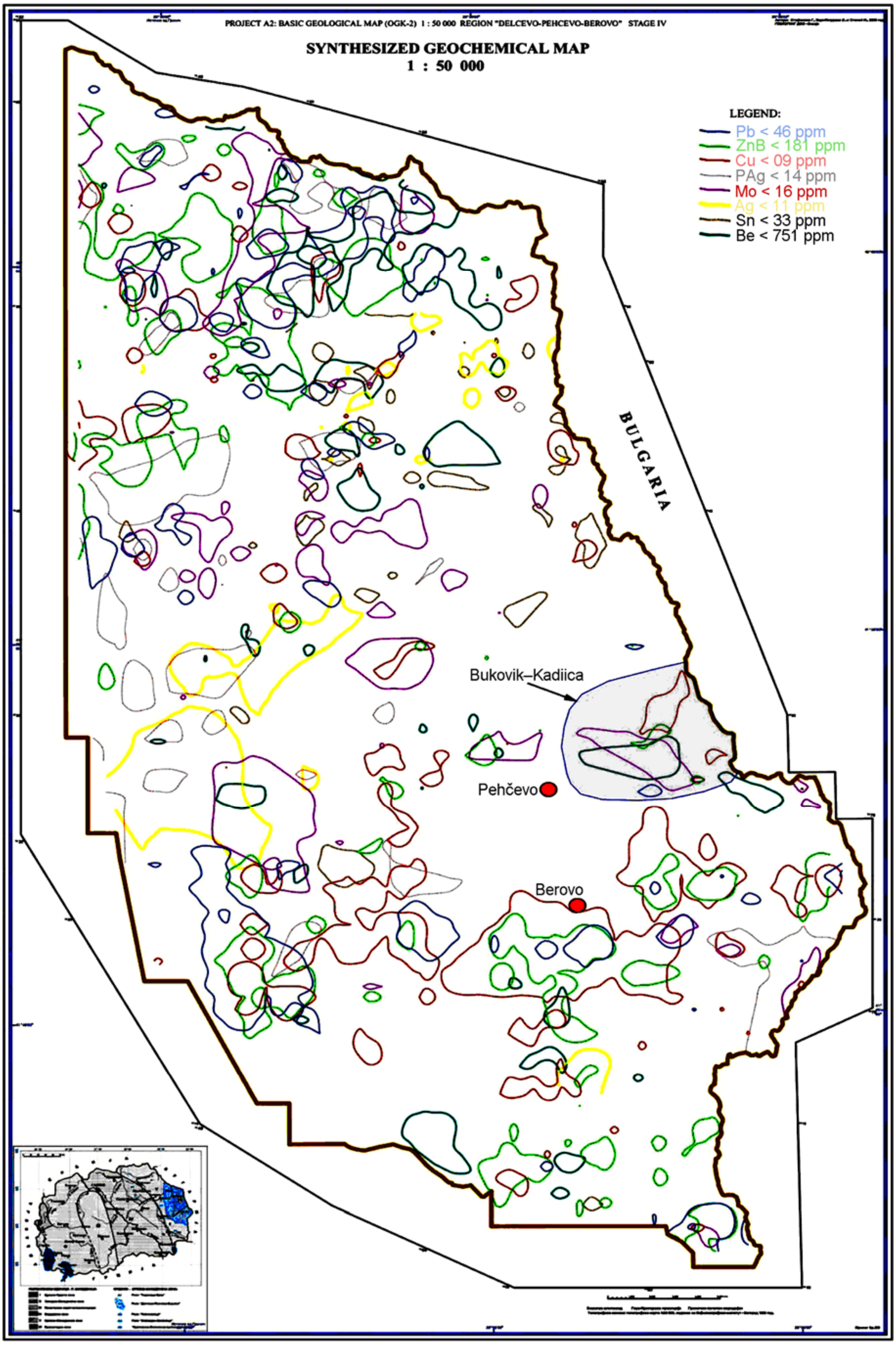


Fig. 1. Synthesized geochemical map of the ore-bearing region Delčevo–Pehčevo–Berovo (Hadži-Petrušev et al., 2008)

This locality has been studied a few times and there are serious indications of the discovery of ore deposit of polymetallic ores of economic significance. Those findings were also confirmed by the results from the geophysical studies conducted within this metallogenic field. Namely, the geomagnetic and aeromagnetic measuremens pointed to the presence of large masses characterized by magnetic susceptibility. Geophysical measurments of SP and IP pointed to an expressed electrical conductivity that spreads with the increase of the depth.

Geochemical interpretation of copper

Copper represents one of the main basic elements that were studied within the Delčevo–Pehčevo–Berovo area. Its presence was registered in most of the analyzed samples. In analyzed 12255 samples copper presence was registered within the 12143 samples. The copper concentrations ranged from 2 up to 2.000 ppm depending strongly on the lithological setting of the sampling location (Hadži-Petrušev et al., 2008).The copper concentrations all over the area of interest were of different values and intensities (Figure 2).

The most frequent bearers of the mineralization are volcanics and granitoids, while metamorphic rocks were the most suitable setting for mineralization deposition were. The statistical parameters such as mean value, standard deviation, and treshold of anomaly are pointing to the fact that the copper is present in enriched concentrations compared to the Clark values in similar lithological settings. Anomalous values were grouped in four categories. It was kept in mind that the samples with concentrations of least 250 ppm should ein the fourth category, which according o today's trends at World's copper markets represents a significant anomaly for initiating more detailed research. Of all the samples, 250 of them were with values higher than 250 ppm, which is a significant confirmation of the previously stated. For more illustrative view of the anomalous fields and zones a copper geochemical map was prepared over the topographic layer. Interpretations of the spatial setting of the anomalous fields and zones have been correlated to the geological composition of the studied region. Also, this kind of interpretation gives an idea about the most prospective and least prospective ones for further geochemical studies (Figure 2).

The biggest anomalous zone, composed of large number of anomalous fields has been registered in southern parts of the terrain (wide 8 km, long 25 km with E-W direction), while spatially it has been located in two different structural-lithological elements. The western parts of this zone were located in southern parts of the Plačkovica mountain, within the localities such as Laskov Čukar, Vaskov Čukar, Brankov Čukar, Zariski Rid, Sredni Rid, Mangovec and westward of Vladimirovo. These anomalous fields were located in the Plačkovica's granitoide complex, which is in direct connection to the gneiss-schists complex of the particular terrain. Anomalous fields have been generated within labile zones caused by faults of NW-SE and NE-SW direction.

The central and eastern parts of this zone were located at the area occupied by the Maleševo Mt. This part of the anomalous zone is composed of numerous anomalous field. The most representative ones are those at Vladimirovo, Rusinovo and Ratevo villages, southern, southeastern and eastern of Berovo up to the Macedonian–Bulgarian border. All of them, in general, have NW-SE direction and point to the cross-cutting knots between the NW-SE and NE-SW structural directions.

The second anomalous zone has been located in the northwestern part of the area and it is of lower intensity compared to the previous one. It has been located in contact parts between the Delčevo granitoide with meta-quartz keratophyres and meta-rhyolites. The most representative anomalous fields were located at the localities such as Kalankova Čuka, Bumbarci, Vitandžik and Kalinova Čuka. These anomalous fields are of NW-SE direction or at the cross-section knots of faults of NW-SE and NE-SW direction.

The third group of anomalous fields has been located in the eastern part of the area. From the spatial and lithological point of view they were located in two complexes. Anomalous fields around Pehčevo (Crnik, Ostri Rid and Bukovik) are located in metamorphic amphibolite-epidote complex intruded by dacite-andesite volcanics. Anomalous fields eastern of Delčevo were located around Virče, Grad and Dzvegor. From the lithological point view they were located at peripheral parts of the Delčevo granitoids intruded by younger dacite-andesites. The lowest anomalous fields were located in the southern parts of studied area. Located in the closest vicinity of Dvorište they represent direct consequence of younger dacite volcanism intruded in th gneiss complex of the Maleševo Mt. and northernmost parts of the Ogražden granitoide.

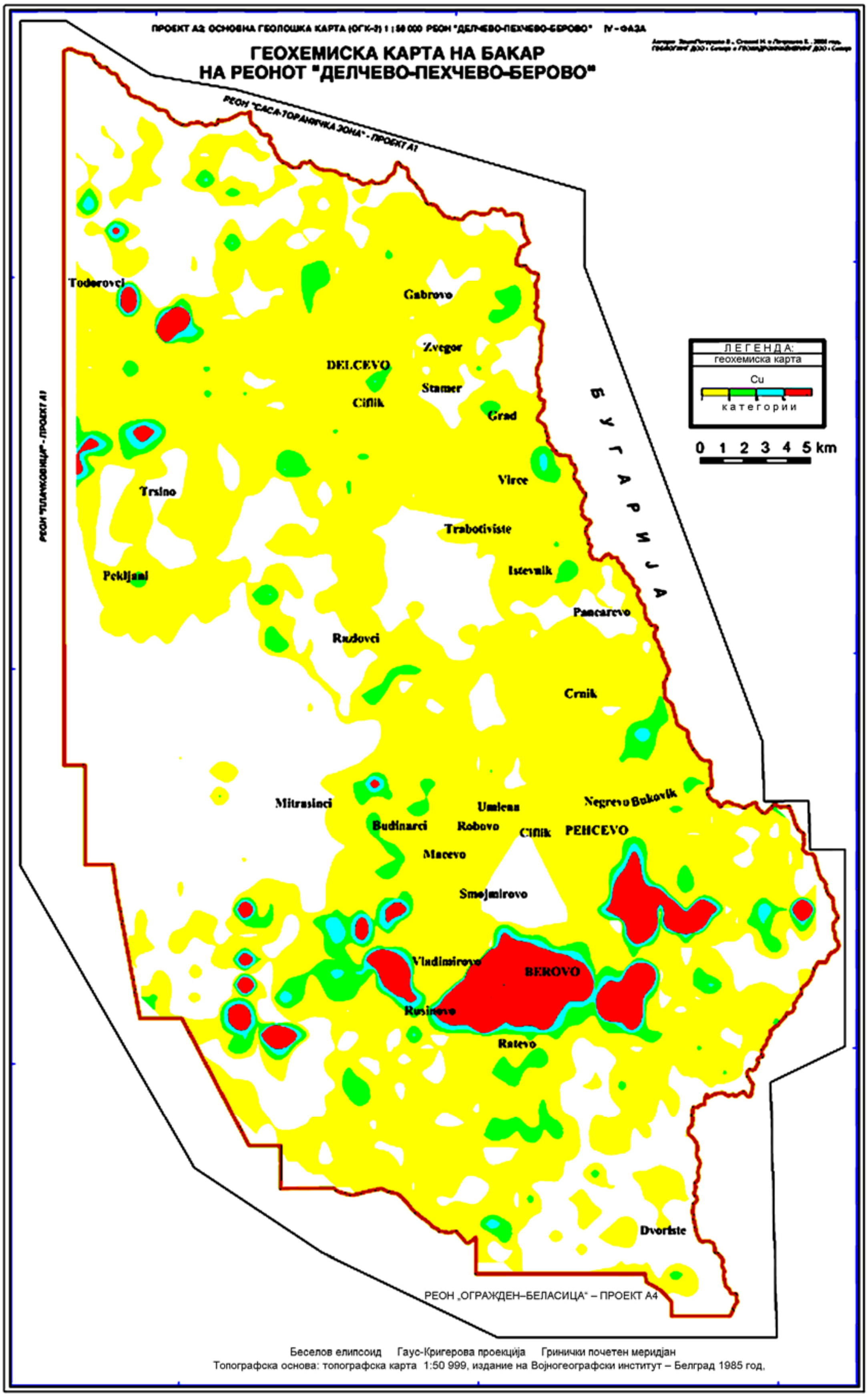


Fig. 2. Regional geochemical copper map of the studied area (Hadži-Petrušev et al., 2008)

DETAILED GEOCHEMICAL STUDIES OF THE BUKOVIK–KADIICA LOCALITY

Significant volume of detailed sampling of lithogeochemical, metalometric and stream sediments was performed during the detailed studies and geological mapping by the Geological Survey–Skopje, in the period 1981 up to 1985, as well as by the US company Phelps Dodge Exploration (through its subsidiary company here in Macedonia the Phelps Dodge Vardar) during the period 2002–2007. The first detailed studies performed by the Geological Survey have resulted with a few geochemical maps at scale 1 : 2 500, compatible with the detailed geological map 1 : 2 500, where alteration zones were shown and some of the mineralization occurrences. Especially interesting have been copper anomalies in the wider area between the Bukovik–Kadiica peaks, but interesting anomalies of Pb, Zn, Ag, Mo etc., also (Hadži-Petrušev, 1985) have been registered. These results served as a background to the further geochemical and mineralogical studies by the US based company Phelps Dodge Exploration, which during the few years period have preformed geochemical study programme combined with geophysical studies and exploration drilling (Aleksandrov and Bombol, 2007). In the text below we will focus in more detail to the results obtained by the Phelps Dodge Exploration.

Primary dissemination halos-lithogeochemistry

The geochemical sampling has been performed by the lithogeochemical method (rock samples). The total weight of the each separate sample was 2–3 kg, enough to be representative for the respective sampling point. All the occurrences of altered and/or stockwork rocks were sampled in order to determine the surface geochemistry features of the area. For better determination, some of the occurrences with complex geological composition have been represented by few samples. Particular small volcanic intrusions were sampled in a more detailed manner because of the possibility of presence of mineralization in them. In total at this stage 236 rock samples of altered rocks evenly distributed all over the area were sampled.

The preparation of rock samples was performed by crushing, grinding, pulverizing and shortening up to the weight of 150 g for each sample and providing a duplicate, also. Chemical analysis has been performed on an ICP-AES (35 elements) while AAS/FA has been used to determine Au, Cu, Mo and some other elements with increased concentrations.

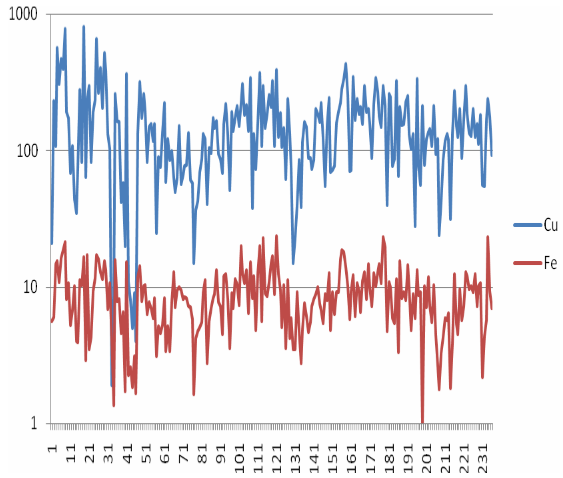
Obtained data have shown a whole array of different values for different elements. For example, values for particular elements were in the ranges as follows: 1.91÷809 ppm Cu, 1÷1447 ppm As, 2÷485 ppb Au, 0.441÷319 Mo, 1÷5012.33 ppm Pb, 0.1÷8120 ppm, 1÷23.47 % Fe, 0.052÷23.115 ppm Ag, 0.76013÷32 ppm Co, 8÷335.99 ppm Cr, 4–6400 ppm Mn, 1÷85 ppm Ni, 0.01÷3395 ppm Ti and 4÷364 ppm V. In our efforts for better understanding of the geochemical cycle and relations between certain elements we have performed an ANOVA statistical analysis (Table 1).

Table 1

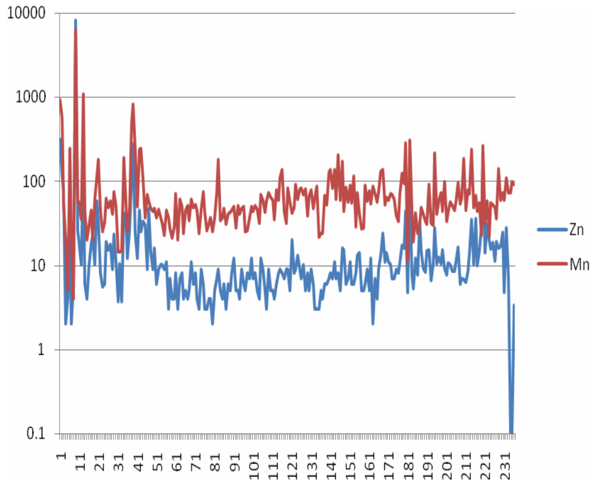
Elemental correlation factors for lithogeochemical samples from the Bukovik–Kadiica locality

	Cu	Au	As	Mo	Pb	Zn	Fe	Ag	Co	Cr	Mn	Ni
Cu	1											
Au	0,190	1										
As	0,272	0,157	1									
Mo	–0,009	–0,109	0,380	1								
Pb	0,116	0,303	0,463	0,019	1							
Zn	0,011	0,633	0,093	–0,057	0,236	1						
Fe	0,719	0,158	0,305	0,022	0,143	–0,012	1					
Ag	–0,080	0,285	0,056	–0,094	0,191	0,331	–0,088	1				
Co	–0,021	0,299	0,006	–0,147	0,089	0,453	0,008	0,142	1			
Cr	0,280	0,187	0,089	–0,147	0,258	0,091	0,125	–0,105	0,304	1		
Mn	–0,028	0,607	0,066	–0,072	0,220	0,973	–0,039	0,322	0,560	0,123	1	
Ni	–0,188	0,033	–0,147	–0,034	–0,043	0,140	–0,289	–0,041	0,511	0,363	0,239	1

The outcomes of the statistical study are represented as correlation factors. The highest correlation factors in this media were achieved for the elemental pairs Zn–Mn with correlation factor of 0.973 and Cu-Fe with correlation factor of 0.719. In that direction we have proceeded with preparation of plots for more illustrative preview of those correlations (Figure 3).



a)



b)

Fig. 3. Shape of the most representative plots of elements with highest correlation factors, Fe-Cu and Zn-Mn, Bukovik–Kadiica lithogeochemistry

As can be seen from the figure above the shape of one element almost ideally follows the shape of the other element with which it strongly correlates. Also, we would like to stress that elemental pairs such are Cu-Fe and Zn-Mn reflect their strong correlation in primary mineralizations as well as in hydrothermally related ones (Kroll et al., 2002). Detailed rock chip geochemistry around mineralization reveals that S and Cu show the highest geochemical contrast, with halos extending up to 0.5 km from mineralized zones. Of these two elements, S shows the more consistent pattern, which is very similar to those shown by Barnes (1997) and Deksissa and Koeberl (2004). Also, the dispersions of the lithophile elements (Rb, Sr, Ba, K, Ca, Na) are controlled "by type and intensity of wall-rock alteration, with halos extending slightly beyond ore zones but within the alteration envelope. Distribution of the femic elements (Zn, Mn, V, Ti, Ni, Co, Fe, Mg) is controlled principally by primary lithology.

Metallometry (horizon"B")

Sampling the secondary dissemination halos (soil sampling – horizon"*B*") has been performed in separate parts of the volcano-intrusive complex, estimated as the most promising ones based on the geological mapping, but without low extent occurrence at the surface. Sampling has been performed along profile lines of NS or EW direction, at mutual distance of 100 m, while the distance between the profiles for surface estimate was set to 200 m. For setting up the profiles the so called "heap chain" and GPS units of high accuracy were used. The mass of the sample used was around 500 g and with special tool was taken from the "B" soil horizon. 13 profile lines were sampled, long between 600 m and 2.1 km. In total, 181 samples including 7 blank samples were sampled. Parts of the area covered by network 200 × 100 m were located to the north and southwest of the Bukovik peak. Separate profiles characterize the area on the north of the Bukovik peak (profile X), as well as those to the south (southern part of the profile C) and southeast of the same area (eastern parts of the profile A and F). All the sampling profiles have been shown at Figure 4. Samples were dried at room temperature and sieved through the sieve of –80 mesh. From the sieved material by quatering material was separated with mass up to 70–80 g, which was later sent to analysis under the ICP for 30 elements and AAS for gold.

Obtained results have shown anomalous values for Cu, Mo, As, Au, Pb and partially for Ag. Based on these results geochemical maps for aforementioned elements were prepared. Few anomalies of copper were contoured (Figure 5).

The lowest limit for contour lines was determined at >100 ppm Cu. The most important anomaly has been located at W-SW of the main sheepfold at the Bukovik peak. It is long 800 m, 350–500 m wide and elongated in N-NW direction and separated at two parts in southern corner and with maximal value of 262 ppm Cu at the eastern part. Very characteristic were the anomalies determined at border parts of the area, below the level of 1400 m, covered by geochemical study of secondary halos.

The highest anomaly at the west is with the maximum value of 296 ppm Cu, while to the south the maximal value is 380 ppm Cu. Small anomalies (>100 ppm) were contoured at north and east near the end of the profile lines. This phenomenon could be described by the leaching of copper by the surface waters and its re-deposition close to the present water level, which overlaps with the existing wells.

Molybdenum anomalies have been contoured at values higher than 50 ppm. It has an irregular shape around the northern slope and almost overlaps the surface occurrences of the quartz-porphyry intrusion or lies below its occurrences. Maximal values toped up at 189 ppm Mo. At 20 ppm as the lowest limit values of the anomaly, the highest part of the Bukovik peak and its NW, N and NE slopes are within the anomaly with an exception of one small part to the north of the highest point. There is no correlation between Cu and Mo.

One gold anomaly has been determined with values higher than >80 ppb. It has been located on the high parts of the Bukovik peak close to the southern slope (Figure 6).

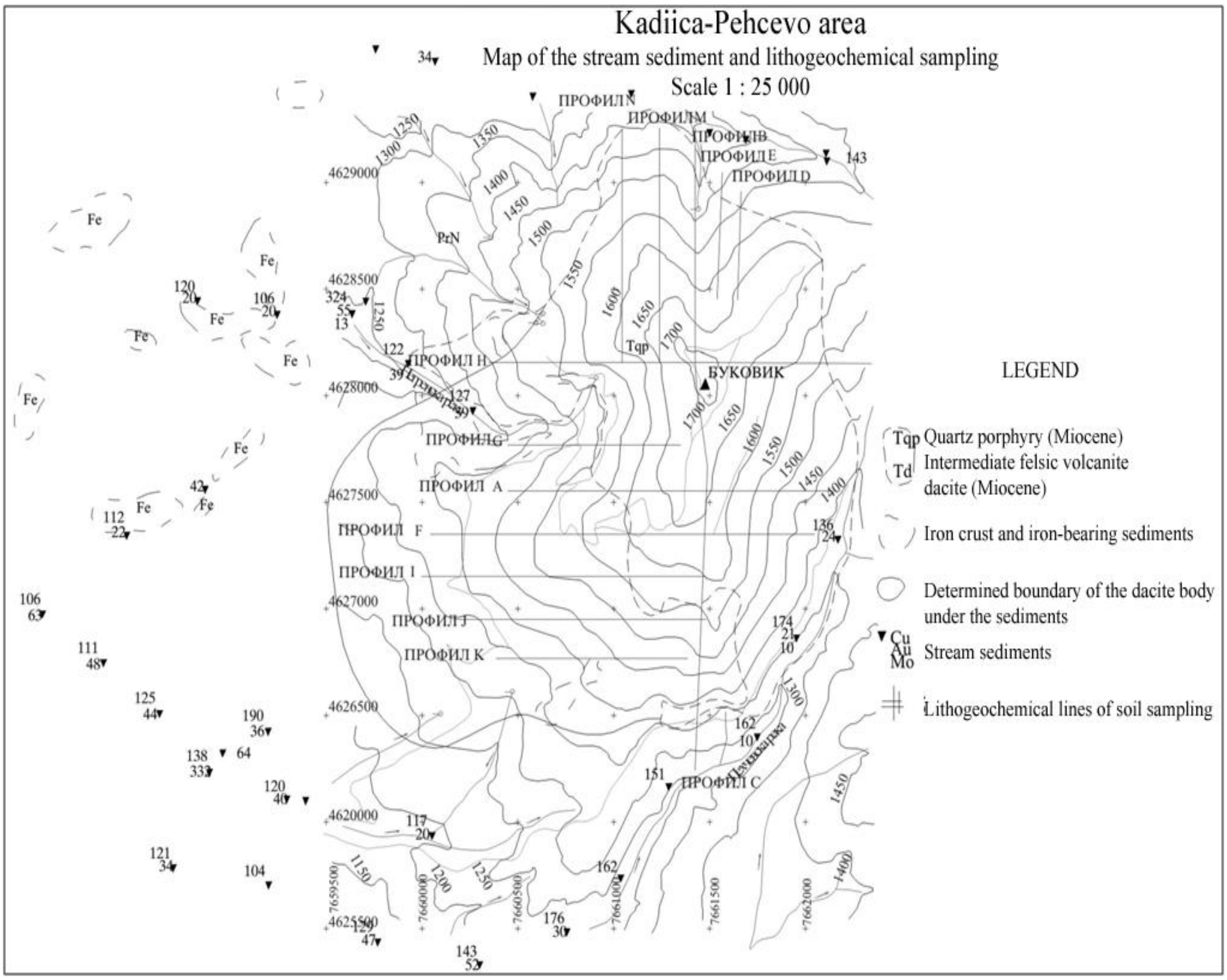


Fig. 4. Map of the lithogeochemical sampling and stream sediments (Aleksandrov and Bombol., 2007)

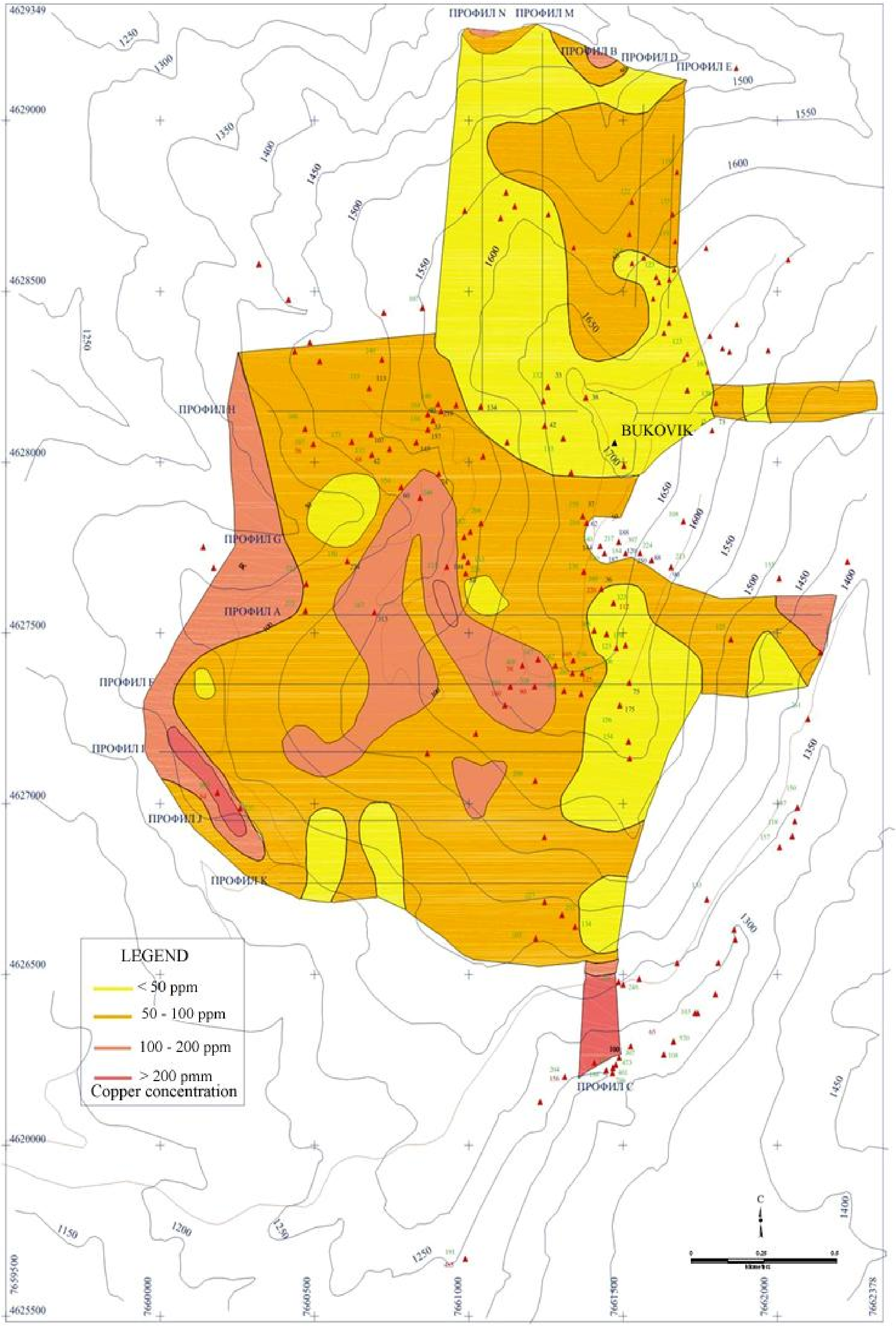


Fig. 5. Map of geochemical anomalies of Cu at the locality Bukovik–Kadiica (Aleksandrov and Bombol, 2007)

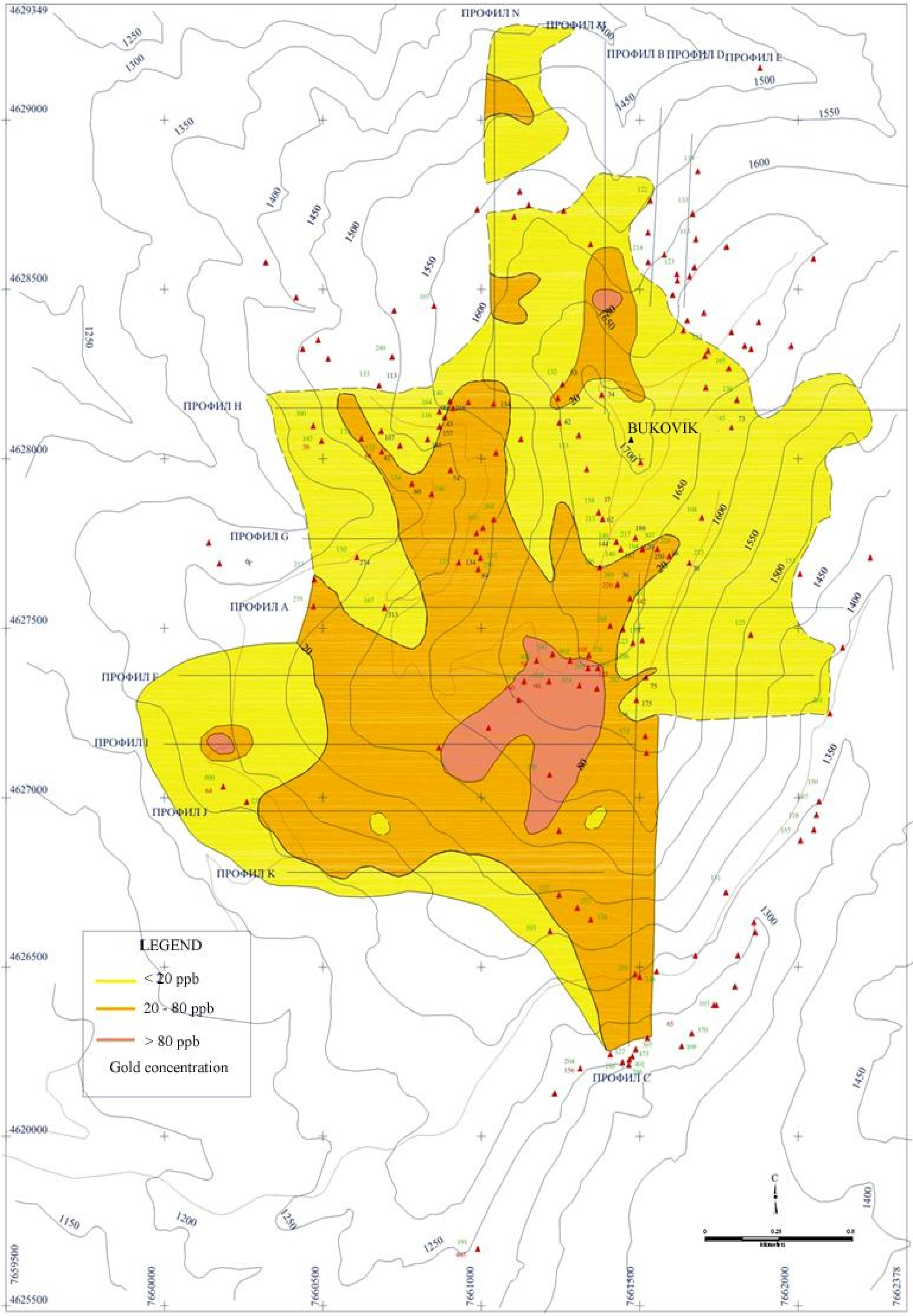


Fig. 6. Map of geochemical anomalies of Au at the locality Bukovik–Kadiica (Aleksandrov and Bombol, 2007)

The SW part of the anomaly has been divided into two parts. Northwestern part of the anomaly is with maximal value of 267 ppb and it overlaps with the SE part of the copper anomaly.

This anomaly is oval in shape with small elongation in NNE-SSW direction and it is long 500 m long and 350 m wide.

Wide arsenic anomaly was outlined at SW and S using lower limit concentration of 100 ppm As. The anomalies of second order, >200 ppmAs, were determined in two separate areas. One of them was with dimensions 500 × 400 m, while the other one was with 600 × 400 m, both with concentrations higher than 300 ppm As (max 475 ppm). The easternmost of these two anomalies overlaps with the formerly described Au anomaly.

For lead values above 90 ppm Pb were accepted as anomalous ones. In such case the lead anomalies almost overlap the As ones. This element anomaly covers the southern part of the mountain and it is open to its southernmost part.

The lowest limit concentration for cobalt was set to 190 ppm. Samples with higher concentrations than that have formed a narrow and elongated zone with N-S direction and maximal concentration of 600 ppm Co. Silver has shown only sporadical anomalous values.

In total, the obtained data have shown a whole array of different values for different elements. Values for particular elements were in the ranges as follows: 13÷433.3 ppm Cu, 2.3÷267 ppb Au, 0.5÷132 ppm Mo, 1.4÷11.8% Fe, 9.4÷600.1 ppm Pb, 7.7÷198.5 ppm Zn, 0.1÷58 ppm Ag, 3÷487.2 ppm As, 159÷15398 ppm Mg, 0.1÷2.3 ppm Cd, 1÷23.8 ppm Co, 5.2÷226.7 ppm Cr, 18.5÷1347.8 ppm Mn, 1.9÷47.4 ppm Ni, 151÷1100 ppm Ti and 17.9÷218.8 ppm V.

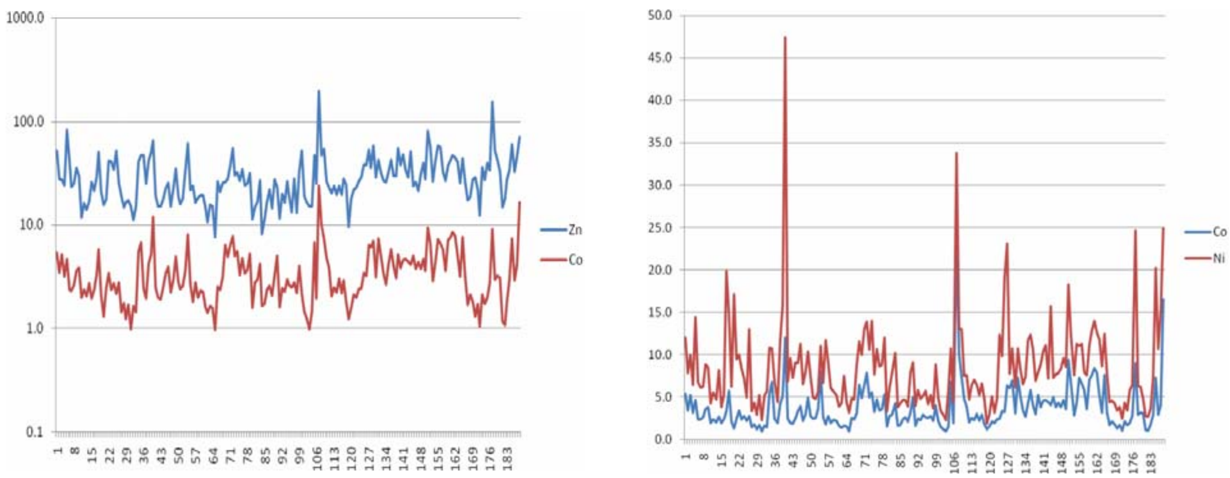
As well as for the lithogeochemical studies our efforts for better understanding of the geochemical cycle and relations between certain elements in soils resulted in an ANOVA statistical analysis (Table 2).

Table 2

Elemental correlation factors for soil samples from the Bukovik–Kadiica locality

	Cu	Au	Mo	Fe	Pb	Zn	Ag	As	Mg	Cd	Co	Cr	Mn	Ni
Cu	1													
Au	0,250	1												
Mo	–0,126	–0,079	1											
Fe	0,484	0,081	–0,358	1										
Pb	0,280	0,446	–0,387	0,292	1									
Zn	0,224	–0,026	–0,300	0,382	0,009	1								
Ag	0,684	0,090	0,015	0,079	0,074	–0,007	1							
As	0,352	0,603	–0,368	0,339	0,708	0,051	0,052	1						
Mg	0,097	–0,134	–0,273	0,417	–0,154	0,574	–0,057	–0,116	1					
Cd	0,154	0,180	–0,224	0,407	0,161	0,492	–0,096	0,340	0,321	1				
Co	0,206	–0,037	–0,377	0,402	0,107	0,811	–0,012	0,117	0,576	0,462	1			
Cr	0,206	–0,172	–0,236	0,505	–0,159	0,341	0,017	–0,158	0,796	0,219	0,340	1		
Mn	0,124	0,002	–0,373	0,172	0,245	0,530	–0,007	0,244	0,294	0,509	0,689	0,132	1	
Ni	0,186	–0,056	–0,363	0,405	0,014	0,702	0,003	0,052	0,822	0,340	0,787	0,604	0,516	1

The outcomes of the study are represented as correlation factors. The most representative correlation factors in this media were obtained for the elemental pairs Zn–Co wih correlation factor of 0.811 and Co-Ni with correlation factor of 0.787. In that direction we have proceeded with preparation of plots for more illustrative preview of those correlations (Figure 7).



a) *b)*

Fig. 7. Shape of the most representative plots of elements with most representative correlation factors, Zn-Co and Co-Ni, Bukovik–Kadiica metalometry-soils

As can be seen from the figure above the shape of one element almost ideally follows the shape of the other element with which it strongly correlates. Also, we would like to stress out that elemental pairs such as Zn-Co and Co-Ni reflect their strong correlation in primary mineralizations as well as in hydrothermally related ones. This is in strong correlation with the findings of the Barnes (1997) and Aliani et al. (2009).

Stream sediments sampling

For more precise estimate of the mineralization potential the method of stream sediments sampling has been performed. In dry conditions the sample with weight of 200–250 g was taken and sieved at place with sieve of –80 mesh. The wet ones were with weight of 5–10 kg, later on they were dried at room temperature, sieved and by quartering final sample with weight of 150 g was formed, as well as the duplicate sample with the same weight. The sampling always took part at modern river sediments and sample was taken perpendicular to the water flow along the whole width and maximal depth. For each sampling point was conducted a description of the geological setting of the stream-river, possible pollution, character of the river banks, etc. To be able to reach optimal coverage of the area of interest it was agreed that the distance between the samples should be 500 m. The 36 samples in total were sampled. Those samples alloweds to follow the drainage areas at the middle and lower part of the Pehčevska River until its entrance to the city of Pehčevo, Negrevska River from its source parts (Negrevo village) and all its left tributaries, Želevica River from its source parts up to the black road between the Crnik and Negrevo villages.

All the dry samples were quartered up to the mass of 150 g, making two identical samples, that were sent to a multielemental analysis (ICP) and for gold (AAS). The results of the most important elements are given in the Table 3.

Results from the river sediments sampling have confirmed findings of other types of research and studies. Copper anomalies (>100 ppm Cu) in drainage parts of the Pehčevska River Negrevska River, as well as in its left tributaries were with maximums of 324 ppm Cu in upper parts of the Negrevska River, whose sources are washing parts of proved anomaly of secondary halos of dispersion. Especially distinctive were the anomalies of Au in Negrevska River and its left tributaries that are constantly present, while at the Pehčevska River anomalies occur sporadically. The highest (anomalous) concentrations of Au occurred in the large left tributary of the Negrevska River, northern of Pehčevo, whose source parts have been located beneath the anomaly of secondary halos of Au. Maximal anomalous value for Au was obtained in the formerly mentioned stream and reached values of up to 332 ppb Au. Anomalous contents of molybdenum (>30 ppm Mo) were registered in upper parts of the Negrevska River, SW of the formerly mentioned secondary halos molybdenum anomaly, but molybdenum's absence in the stream of Želevica River is surprising. Zinc has shown interesting anomalies (>100 ppm Zn) along the margins of th volcanic body in Pehčevska River and Želevica River.

Table 3

Results of chemical analysis (ICP) of samples from river sediments at the Bukovik–Kadiica locality (Aleksandrov and Bombol, 2007)

Sample No.	Cu ppm	Au ppb	Mo ppm	Fe %	Pb ppm	Zn ppm	Ba ppm	Ag ppm	As ppm	Sb ppm
SMK–001	67	3	1,5	6,29	100	52	79	0,3	138	8
E12102	117	20	0,9	4,45	1358	461	136	5	105	17
E12103	55	16	0,5	4,92	975	795	78	1,4	57	4
E12104	190	36	3,9	5,32	128	140	150	0,3	71	5
E12105	91	64	2,2	4,36	182	38	86	0,7	225	12
E12106	138	332	1,6	7,38	694	322	161	3,3	173	13
E12107	120	40	1,5	7,2	575	331	146	1,8	131	10
E12108	125	44	2,1	6,99	478	224	146	1,1	197	14
E12109	111	48	2,4	5,84	613	229	181	1,5	153	11
E12110	106	63	4,9	8,05	234	97	155	0,8	88	5
E12111	57	42	6,4	4,45	67	46	111	0,7	39	1
E12112	112	22	2,7	8,01	56	78	90	0,2	22	2
E12113	106	21	2,7	2,9	58	124	121	0,2	54	2
E12114	324	55	13	5,9	19	87	37	0,2	21	2
E12115	122	17	39	8,47	16	33	23	0,3	18	1
E12116	127	14	39	9,23	16	20	23	0,6	14	1
E12117	56	16	1,9	4,44	14	99	42	0,3	18	2
E12118	120	20	6,5	4,29	38	159	120	0,3	32	1
E12119	121	34	3,2	5,2	119	444	171	0,7	66	4
E12120	104	17	4	4,82	70	432	71	0,3	16	2
E12121	129	47	4	5,68	74	527	67	0,4	19	1
E12122	143	52	5,1	6,7	72	544	61	0,3	19	1
E12123	176	30	5,2	6,75	85	597	58	0,4	20	1
E12135	174	21	10	6,31	59	111	44	0,2	15	1
E12136	186	24	9,3	6,95	46	113	37	0,3	12	1
E12137	162	5	10	5,63	54	101	50	0,2	15	2
E12138	151	10	8,3	5,83	67	142	50	0,4	19	2
E12139	162	9	9	6,06	61	148	44	0,4	20	2
G13448	143	4	3,6	5,26	46	129	58	0,4	16	1
G13449	57	7	1	5,12	45	176	48	0,3	19	1
G13451	70	3	1,5	4,32	32	163	37	0,1	10	1
G13452	85	7	1,4	4,38	42	140	107	0,4	17	1
G13453	85	6	1,8	5,45	39	157	44	0,3	17	1
G13454	90	11	3,2	5,5	32	137	40	0,3	15	2
G13455	57	34	1,2	5,38	31	170	40	0,2	16	1
G13456	50	4	3,2	3,61	24	92	56	0,1	11	2

The absence of the Zn in drainages that wash away in the central part of the hydrosystem is a logical consequence. Its higher concentrations (up to ~600 ppm Zn) in lower parts of the sampled flow of the Pehčevska River are probably due to the presence of polymetallic veins and stockwork-impregnated occurrences uncovered by erosion processes. The absence of the anomalous concentrations of any other elements probably may be described by very fast flow of waters and steep relief and respectively fast change of the river sediments in the river beds and large dissemination along the river banks.

In total the obtained data have shown a whole array of different values for different elements. Values for particular elements were in the ranges as follows: 50÷324 ppm Cu, 3÷332 ppb Au, 0.5÷39 ppm Mo, 2.9÷9.23% Fe, 14÷1358 ppm Pb, 20÷795 ppm Zn, 0.1÷5 ppm Ag, 10÷225 ppm As, 1÷17 ppm Sb.

In order to get a more detailed insight about the relation between certain elements, similar to the lithogeochemical and metalometry programme, for stream sediments we have performed statistical analysis-correlation (Table 4).

The outcomes of the statistical study of stream sediments programme are represented as correlation factors. The most representative correlation factors in this media were obtained for the elemental pairs Pb-Ag wih correlation factor of 0.9099 and As-Sb with correlation factor of 0.9039. In that direction we have proceeded with preparation of plots for more illustrative preview of those correlations (Figure 8).

As can be seen from the figure above, the shape of one element almost ideally follows the shape of the other element with which it strongly correlates. Also, we would like to stress out that elemental pairs such are Pb-Ag and As-Sb reflect their strong correlation as it is in primary mineralization.

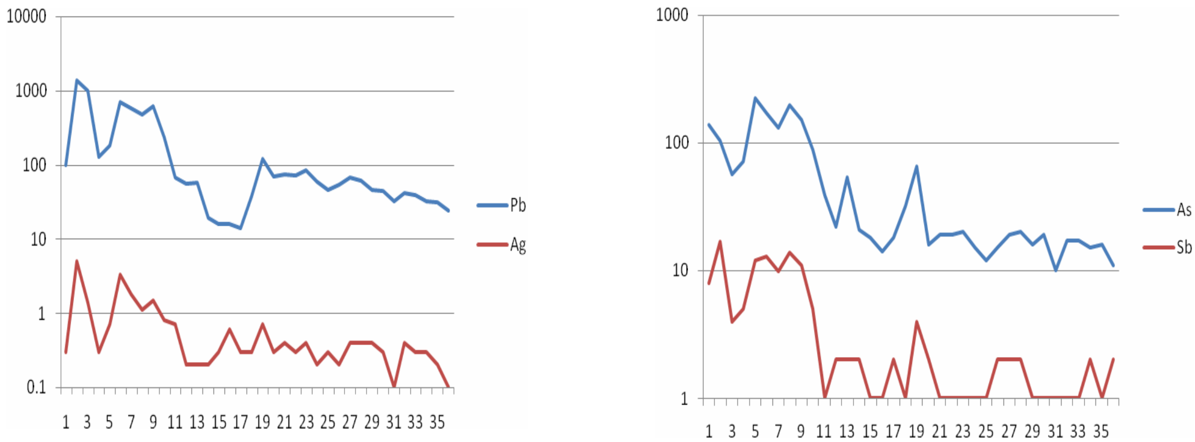
From all the aforementioned facts related to the conducted geochemical studies of the Bukovik–Kadiica locality we may to conclude that the geochemical associations of elements are very close to the ones given by Jankovic et al., (1995) for the Kadiica, as well as data for porphyry deposits Bučim (Čifliganec, 1987; Serafimovski, 1990) and Borov Dol (Tudzarov, 1993). Similar findings were also detected for numerous deposits and occurrence around the globe. Just to name few of them, Okote area in Ethiopia (Deksissa and Koeberl, 2004), Skouries deposit in Greece (Kroll et al., 2002), Tongshankou and Yinzu deposits in

China (Wang et al., 2004), Meiduk deposit in Iran (Aliani et al., 2009) etc.

Table 4

Elemental correlation factors for stream sediments samples from the Bukovik–Kadiica locality

	Cu	Au	Mo	Fe	Pb	Zn	Ba	Ag	As	Sb
Cu	1									
Au	0,15400	1								
Mo	0,29079	–0,10854	1							
Fe	0,32261	0,25262	0,56464	1						
Pb	–0,09151	0,32622	–0,26346	0,00208	1					
Zn	–0,01765	0,14800	–0,31880	–0,06641	0,52324	1				
Ba	–0,06255	0,41612	–0,40494	–0,06175	0,53254	0,21153	1			
Ag	–0,02954	0,48423	–0,17336	0,05437	0,90995	0,37253	0,52237	1		
As	–0,08607	0,48614	–0,27443	0,08635	0,55936	0,04903	0,67156	0,53012	1	
Sb	–0,03762	0,44598	–0,28127	0,06690	0,78226	0,16024	0,65268	0,79150	0,90388	1



a) *b)*

Fig. 8. Shape of the most representative plots of elements with the most representative correlation factors, Pb-Ag and As-Sb, Bukovik–Kadiica stream sediments sampling programme

CONCLUSION

With the realization of the extensive geochemical explorations and studies of the wider area of the Bukovik–Kadiica locality important information have been obtained in regard to the distribution of characteristic elements, which have been of high importance for the estimate of the potentiality of the studied area from the polymetallic mineralizations point of view. Namely, in the elemental association of the Bukovik–Kadiica deposit were determined: Cu, Fe, S, Mo, Au, Pb, Zn, Sn, As, Sb, Ti, V, Co etc. The group of major elements that constitute their own minerals or contribute significantly to the composition of other elements minerals stand out in this association. Such elements are: Cu, Fe, V, Sn, Sb, Pb, Zn, Ti, S, As etc. The rest of the elements occur in certain ore or rock forming minerals or hydrothermally altered zones and they appear asymmetrically without any consequential order.

The obtained data coincide with up to date information related to the geological, structural and mineralizing features of the Bukovik–Kadiica system. They would certainly be of interest during the planning of detailed mineral explorations for assessment of the ore-bearing potential of this very prospective locality.

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Р е з и м е

ГЕОХЕМИСКИ ПРОУЧУВАЊА НА МИНЕРАЛИЗИРАНИОТ СИСТЕМ БУКОВИК–КАДИИЦА, ИСТОЧНА МАКЕДОНИЈА

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Клучни зборови: примарни ореоли; стрим-седименти; металометрија; полиметални минерализации; локалитет Буковик–Кадиица

Во изведените регионални и детални геохемиски проучувања на стрим-седименти, почви и карпи во пошироката околина на локалитетот Буковик–Кадиица во близина на градот Пехчево, источна Македонија, беа детекти-

рани регионални и локални полиметалични аномалии на елементи како што се Cu, Fe, S, Mo, Au, Pb, Zn, Sn, As, Sb, Ti, V, Co и др. Со најстандардни вредности се појавија бакарот, молибденот, оловото и цинкот, што се совпаѓа со поранешните геохемиски проучувања. Овие податоци директно укажуваат на постоењето на бакарна минерализација во пошироката област, што исто така коинцидира со структурно-металогенетските карактеристики на областа Буковик–Кадиица. Деталните проучувања овозможија пресметка на корелационите фактори за најчестите елементи во областа од интерес. Особено изразени корелациони фактори беа одредени за парови елементи како што се Cu-Ag, Fe-Cu, Zn-Au, Pb-Ag and Pb-As.