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TRACE ELEMENTS IN WINES PRODUCED AT HOME IN THE TIKVEŠ AREA

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A b s t r a c t: In this paper the results of the geochemical research of the presence of trace elements (Al, As, Ba, Ca, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sr, V и Zn) in the wines produced at home in the Tikveš area with the application of the methods of ICP-AES and (ETAAS) are shown. The paper also presents the correlations made on the basis the presence of certain trace elements in the soil on which the specified variety of grape wine is grown and the same elements in the wine which is produced from that type of grape. The correlations basically point to the fact that there is no great correlation between the presence of the determined trace elements in the soil and wine produced at home. Namely, these correlations for the determined geochemical pairs are the following: Al_{soil}/Al_{vine} (0.04); As_{soil}/As_{vine} (0.11); Ba_{soil}/Ba_{vine} (0.23); Ca_{soil}/Ca_{vine} (0.02); Cd_{soil}/Cd_{vine}(–0.06); Co_{soil}/Co_{vine} (–0.26); Cr_{soil}/Cr_{vine} (–0.04); Cu_{soil}/Cu_{vine} (0.04); Mg_{soil}/Mg_{vine} (–0.30); Mn_{soil}/Mn_{vine} (–0.40); Na_{soil}/Na_{vine} (0.11); Ni_{soil}/Ni_{vine} (0.03); Pb_{soil}/Pb_{vine} (0.27); The lack of significant correlations between the given geochemical pairs is a result of a few moments such as: (1) the presence of trace elements in the soil is determined up to the depthof 30 cм. (2) trace elements in soils are present mainly in the silicate matrix from which the elements are not easily excreted into aqueous solutions. (3) the root system of the grape vine is at a much greater depth of 30 cm.

Key words: wine; geochemistry; elements in traces; correlations

INTRODUCTION

Wine is a drink that is an integral part of the human diet and it has played a significant role in the development of the society, religion and culture. Like any other skill, the production of wine was based on empirical findings, perception of some external phenomena, without getting into the essence of the process. This way of producing wine for centuries until Pasteur opened the doors of science for understanding the processes that occur while producing wine with his book, "Study on Wine" (1866).

The wine as a product of alcoholic fermentation of the must contains a number of compounds, some of which are in the must, while others occurred during the alcoholic fermentation, with the transformation of sugar into some other compounds. All of these compounds enter the geo-chemical composition of the wine, thus defining the quality that is manifested by the organolepthic properties of the wine. For the quality of wine not only qualitative composition is important, but also the quantification of compounds and elements in it. The determination of the geochemical analysis of the composition of wine is made by using analytical methods. Some of these analytical methods are simple and fast, and some are complex and require more time for analysis.

The results concerning the determination of the presence of trace elements in wines that are produced at wineries in the area Tikveš, as in other wine regions in the country, can be found in the works of: Cvetković et al. (2002a); Cvetković et al. (2002b); Cvetković et al. (2002c); Stafilov et al (2009); Karadjova et al. (2007); Karadjova et al. (2004); Cvetković et al. (2001); Tasev et al. (2004, 2006, 2005). Likewise, the results concerning the geological, pedo-genetical and the geochemical characteristics of the region of Tikveš and its wider surrounding can be found in the works of: Boev et al. (2005), Stafilov et al. (2008).

Physical-geographic characteristics of the Tikveš area

Among the valleys in Macedonia which by their position differ from one another, the Tikveš Valley stands out as a separate entity with its geographical, geomorphologic, and the anthropological-geographical features. With an area of 2120 km^2 the region Tikveš occupies a significant part of the territory of Macedonia. The Tikveš valley is constrainedin the southby the Mariovsko-Meglanski Mountains, whose ranges are up to 1700 meters. The mountain heights are also well expressed in the east and west. To the west of the valley is the mountain "Borila" of 1500 meters and in the south is the mountain "Ballina" with 1400 m and Karadak with 750 meters height. This Tikveš valley constrained with mountains is cut by the river Varda on the northern side, in the west by the river Crna Reka, while the river Luda Mara runs through the middle of the valley.

In a narrower geographical sense, the Tikveš valley lies: in the north by the river basin Bregalnica opposite the villages Viničani and Nogaevci and then turns above the villages Gradsko and Dolno Čičevo, then above the villages Sirkovo, Mrzen Oraovec, Fariš, Raec up to the village Nikodin, to the hill Nozhot and up to the village Toplice.

The western boundary of the valley begins from the locality Toplice across the road Gradsko–Prilep to the villages Raec and Drenovo towards the Tikveš Lake. It covers the localities Suva Gora with the surroundings of the villages Begnište, Košani and Dabnište. The area continues southward the villages Vataša, Moklište and the Vitačevo plateau. This section covers the villages of the locality Belgrade with the villages Gorni and Dolni Disan, Prždevo and Demir Kapija. The south side ends with the village Dren.

The East side moves across the river Vardar in the direction of the village Korešnica, cuts the Lipkovska river and goes toward the villages Brusnik and Pepelište, then passes the river Vardar and the railway line Skopje–Gevgelija to the village Ulanici and ends with the mouth of the rivers Vardar and Bregalnica.

Climate

The climate has a great impact on the development of the grapevine in terms of quantity and quality of the grapes. As an important factor in the development of the grapevine, the climate consists of the air temperature, the sunlight, and the humidity of the air currents which are present in a given area. Each of these factors has its own influence upon the grapevine which is seen through the growth of the grapevine, the level of ripening of the fruit and the production of quality ingredients which from grapes pass into vine.

The geographical position and the relief of the Tikvešh area are the main factors which affect the totality of the climate characteristics. The Tikveš area is an area of two intersected climates – continental and Mediterranean. The local mountain climate has less impact.

The influence of the continental climate comes from the north along the Vardar River and the Bregalnica River. As a result, we have short and quite cold periods.

On the other hand, the Mediterranean climate comes from the Aegean Sea in the south along the valley of the river Vardar and it results in warm winters with relatively high temperatures.

The influence of the local mountain climate is limited and if there is any, it is highly felt in the mountain part of the area. Under the influence of these climates a special modification of the Mediterranean climate is produced in this region. As a result, the Tikveš region is rich in vegetation.

Temperature

The grapevine is a domestic plant which can vegetate and live in extremely high temperatures in the areas with warm climate, as is the case in the Tikveš area. This region belongs to very warm areas and this factor has a very favorable influence on the development of viticulture. The mean annual temperature in Kavadarci is 18.9 °C, and 19.5 °C in Demir Kapija. The warmest month in Kavadarci are July and August with an average temperature of 24.7 °C, and the coldest is January with an average temperature of 1,5 °C.

The Tikveš region is characterized by relatively high temperatures, especially during the summer months. The highest temperature of 44.5 °C in the Republic of Macedonia was registered in Demir Kapija on 22.07.1952 year, whereas in Kavadarci it was 41°C. The absolute minimum of the air in Kavadarci was noticed on 27.01.1952 and it was –17°C, and in Demir Kapija it was –22 °C.

The mean number of summer days when the air temperature is over 30 °C for Demir Kapija is 68, and it is a bit less for Kavadarci.

Rainfalls

The largest part of the Tikveš region is characterized by small amounts of rainfall and the territory around Gradsko is considered to be the site with the least rainfall per square meter in the Republic of Macedonia. The mean amount of rainfall is 484 mm in Kavadarci. July and August are the most arid summer months in Kavadarci with the mean monthly amount of 23 to 27 mm.

The average annual days with rainfalls in Kavadarci range from 63 to 112 days. If the total amount of rainfall is divided by the number of rainy days, the average is 5 mm of rain on a rainy day.

Geological characteristics of the Tikveš area

The geological characteristics of the area Tikveš have so far been the subject of research by a growing number of geologists, but the most complete description can be found in the works of Rakićević et al. (1965) and Hristov et al. (1965). Based on these studies made within the development of the basic geological map of the Republic of Macedonia in Tikveš area the litho-stratigraphic sequence has the following order (Fig. 1).

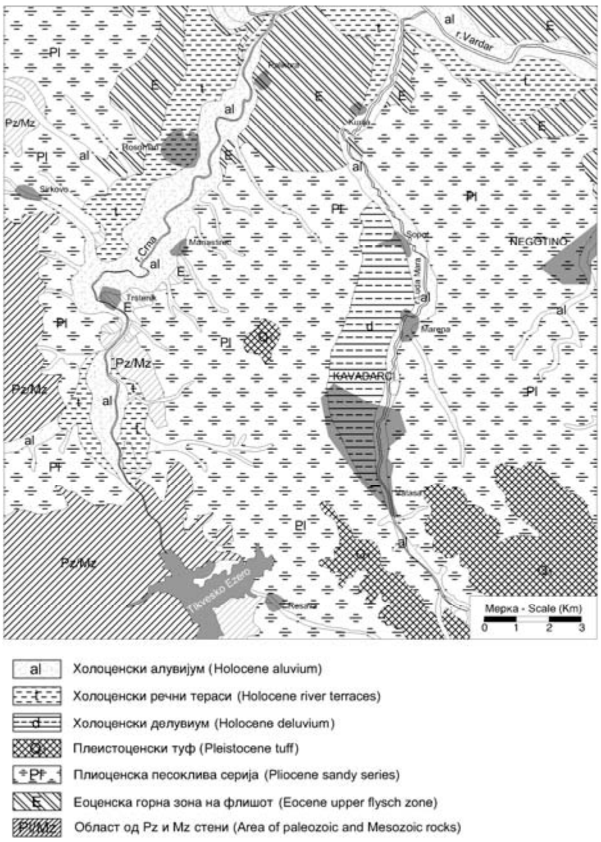

Fig. 1. Geological map of Tikveš area

The oldest formations have northwest-southeast direction delineation (NW-SE) and belong to the inner part of the Vardar zone. The lowest Paleozoic (Pz) metamorphic complex is represented by two series as follows: a series of amphibole and amphibole-chlorite schists with layers of marbles and a series of quartz-schist with quartz-sericite pro-layers of marble and filities. Along the rupture structures in the Vardar zone in the form of elongated tapes and interspersed lenses serpentinities appear. The furthest south-west of the area Tikveš is represented with marbles and dolomites, which are probably of Devonian age.

Through a series of Paleozoic metamorphic rocks developed the Mesozoic (Mz) formations, mainly from the Late Cretaceous age. The Turonian (K2) sandstones, massive conglomerates and limestone extend to the southwest and the west Tikveš of the area. The diabases and the submarines outbursts of spilites are common in the lower parts of this sequence, where also smaller masses of gabbros appear. The Paleozoic and Mesozoic rocks cover nearly 39 km^2 in the southwest and west part of the area Tikveš.

The complex of Tertiary and Quaternary sediments covers most of the Tikveš area. The Upper Eocene (4E3) flysch sediments and yellow sandstones occur along the valleys of the rivers Vardar, Crna River and Luda Mara, as well as in a fraction of the Tikveš basin. These sediments with depth to 3500 m cover about 34 km^2 mainly in the northern part of the Tikveš area.

The Tikveš basin is filled with Pliocene (Pl) sediments, bordering with the Vardar River in the north and the Paleozoic-Mesozoic formation which covers the north-west-southeast. This area is mainly represented by sandy series of different sands. These series are homogeneous, containing mostly yellow sands with low content of coarse sandy clay (pebble sandy clay) and fine-bean gray sandstone, poor in fossil remains. The Pliocene (Pl) sediments cover most (about 182 km^2) of the central part of the area Tikveš.

Southeast of Kavadarci there were Quaternary (Q) pyroclastic volcanites with tuffs, Brecias and agglomerates, which covered around 25 km^2.

The Quaternary period is represented by diluvium (d), river terraces (t) and alluvium (al). The diluvial sediments (12 km^2) contain coarse material from the surrounding rocks, mixed with sand and clay material. Along the rivers Vardar, Crna and Luda Mara terrace sediments are formed (23 km^2). The terraces contain gravel, sand and clay. Alluvial sediments (40 km^2) cover the flooding plains of the rivers Vardar and Crna and Luda Mara and consist mainly of sand and clay.

Pedo-genetical characteristics of the Tikveš area

The pedo-genetical characteristics of the area Tikveš are shown based upon the detailed pedological description of the present types of soils (Fig. 2):

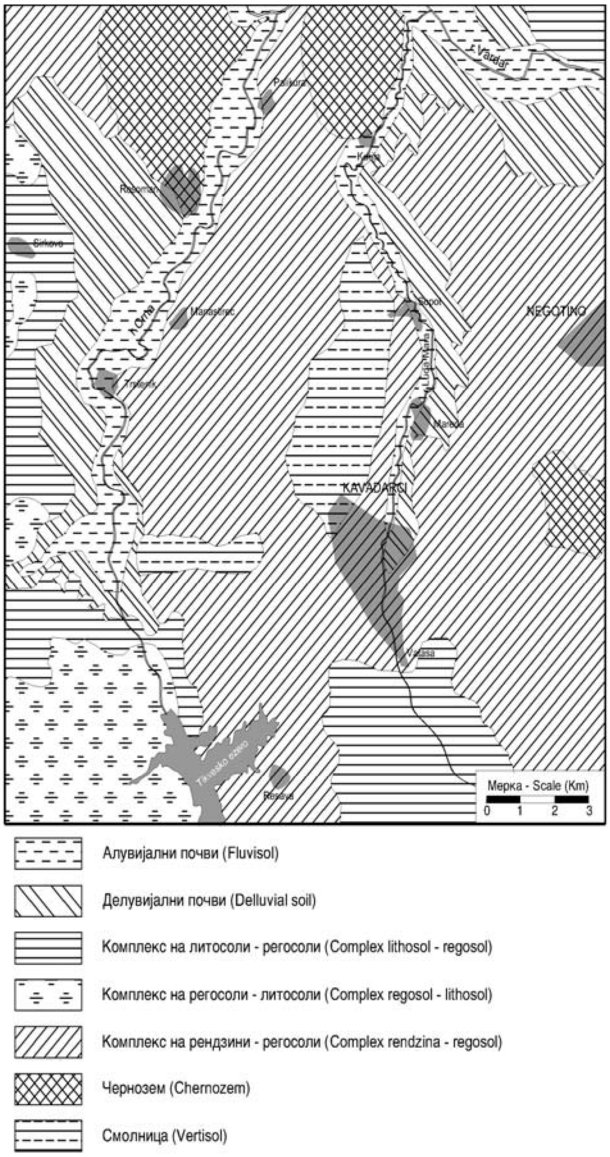

Fig. 2. Pedological map of Tikveš area

Automorphyc soils

Lithosols with the profile type (A)-R1-R2 are developed or poorly developed soils with a maximum depth of 20 cm of the solum, formed on a strong or weak cracked rock. These soils have low productive capacity due to the shallow solum, high skeleton content and low content of clay. These soils have no importance for the agricultural production.

Rogosols with the profile type (A)-C are formed on loose sediments. They are formed by accelerated erosion of the soil profile of previously developed soils with initial pedogenetical processes that lead to the creation of poorly developed horizon (A). These soils are prone to erosion, so we recommend anti erosive safeguards. Regosols are characterized by lower fertility than the neighboring soils from which they were made by erosion.

Soil complex from regosols and litosols in Tikveš appears on the terrains that are characterized by a greater slope, west of the Lake Tikveš in the areas of the villages Debrište, Kamen Dol and Kruševica and northwest up to the village of Dolno Čičevo.

The soil complex of litosols, regosols and renzines appears quite often. Litosols are noted on the highest parts of the ground. Very often on the surface where there is a presence of litosols solid rocks can be notised as well. Regosols appear on fields that are characterized by a slightly larger slope where erosion by the solum is progressively rejuvenating, whereas the rendzinas appear on flat fields and at the foot of the hills where there is an outbreak of frequent change of regosols at small distances. This soil complex is widespread in the area of the village Drenovo, then in the villages Sirkovo, Kamen Dol, Mrzen, Oreovec, Debrište and east of the district Gradsko on the left side of the river Vardar.

Soil complex litosols, regosols and rankers appears on the plateau Vitačevo near Kavadarci. Litosols and rankers are formed on the basis of compact volcanic tuffs, and the regosols are formed by erosion of the humus-accumulative horizon of the rankers.

Diluvial (coluvial) soils are defined as undeveloped and poorly developed soils with the possible (A) or Ar horizon. They have a simple construction of the profile of the type (A)-C. They are formed by erosion and transportation of substrates and soils from higher terrain by means of surface waters and water from torrential streams and modern sedimentation of the such eroded material in the foot parts of the ground. Horizon (A) contains a slightly larger amount of humus horizon than (C), but there are no visible signs of the formation of structural aggregates. The diluvial soils have large horizontal and vertical (in depth profile) heterogeneity of all properties. In comparison with the alluvial bordering soils they have lower productive capacity.

Renzins are soils with profile of the type-A-AC-C. They are formed upon the bulk silicate-carbonate substrate with a mollic A horizon. The depth of humus horizon is 40 cm it has a dark gray, dark brown to black color with well-expressed structure. The carbonates emerge from the surface or at a certain depth. Most renzins are extensively used in the agriculture and one part of them is under pastures. On a map they are represented as a complex of rendzines and regosols, and a complex of litosols, regosols and rendzines. The complex of rendzines and regosols occupies the largest surface of the Tikveš area. In the vicinity of the village of Dolno Čičevo small areas of cinnamon forest soils and regosoli appear.

Vertisols are loamy soils formed on clay sediments with more than 30% of clay, which gives them a property of swelling (smektites) or on acidic rocks or ultra-acidic rocks whose decay provides larger quantities of clay. Vertisols in the Tikveš area are developed on tertiary clay sediments of a low wave relief with low inclination. They have the type of profile A-AC-C. The soil contains more than 30% of the clay horizon and has vertical properties: prismed cracks and distinctive structure. A horizon has a depth greater than 30 cm and AC horizon is typically 20–30 cm deep. In the Tikveš area thevertisols are isolated as an independent soil type. They prevail in the immediate vicinity of villages Ribarci, Trstenik and Vozarci and north of Kavadarci.

Chernozem is a soil type of the semiarid steppe regions with typical molic A_0 horizon which is thicker than 40 cm and with a front horizon AC (25–0 cm). They contain $CaCO_3$ mostly from the surface and in the lower part of horizon A or AC. The horizon A has well expressed stable grain structure. In the Tikveš area chernozems often contain carbonates from the surface, and in some sections they are washed to some depth in solum. Chernozems were singled out as special pedological units (Fig. 2) north of the village Rosoman, whereas smaller areas are located east of the village Palikura and between the villages Timjanik and Dolni Disan.

Cinnamonic forest soils are soils with a profile of the type Ar-(B)-C or Ar-(B)C-C. They are characterized by the cambic horizon (B), which lies between A and C horizons. Cambic horizon (B) always contains more clay than the A horizon. It is more compact, with reduced capillary porosity, reduced stability of the structural aggregates and reduced presence of water. The production capacity of these soils is not great.

Hydromorphic soils

Alluvial soils are contemporary (recent) river or lake sediment layers, and they can have a horizon (A) or (Ar), and even G. Unlike the diluvial soils they are characterized by good assortment. The suspended materials from which these soils are formed have heterogeneous mineralogical-petro graphic composition. According to mechanical properties they are light soils. The macro structure is poorly expressed, and therefore the physical properties depend on the mechanical composition. They have good water, air and heat regime. They are a very fertile type of soil and they are used for intensive agricultural production. They are represented as an independent soil type along the rivers Vardar, Crna Reka and Luda Mara.

METHODOLOGY OF WORK

The sample of wine (15.0 mL) is placed in a quartz furnace and ethanol is slowly added until the sample reaches a volume of 8 ml, then quantitatively it is placed in 25 ml calibrated volumetric bottle and made up to the mark with concentrated HCl.

Instrumentation

The elements are analyzed through the application of atomic spectrometric method with dual plasma (AES-ICP) and the method of electro thermal spectrometric atomic absorption (ETAAS). With the method of AES-ICP the following elements were also measured: Al, As, Ba, Ca, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sr, V and Zn. The concentrations of As, Cd, Co, Cr, Ni and Pb in wine samples were below the detection limits of AES-ICP and therefore were analyzed by ETAAS. Instruments such as: Varian 715-ES Series ICP Optical Emission Spectrometer (Varian, USA) and Zeeman ETAAS Varian SpectrAA-640Z were used for the analysis.

OBTAINED RESULTS AND COMMENT

The results of the geo-chemical determination of concentrations of macro elements and trace elements in wines that are produced at home in the Tikveš area by applying the methods of ICP-AES and ETASS are shown in Table 1.

The spatial position of samples taken from the wines produced at home and the correlation between the presence of definite geo-chemical pairs of elements in wines/soils is shown in the images (Figs. 3–8), and statistical parameters are shown in Tables 2 and 3.

Table 1

Concentration of macro elements and trace elements in wines produced at home in the Tikveš area

Samp No.	Sort of vine	Region – attar	Samples of soils lattitude / longitide	Al	Ba	Ca	Cu	K	Mg
				mg/l					
I-1	Kratošija	Debrište-Ramnište	41.459362° / 21.895683°	0.11	0.17	62.23	0.046	851.7	102.87
I-2	Smederevka	Debrište-Ramnište	41.459362° / 21.895683°	0.22	0.11	39.77	0.318	582.6	88.86
I-3	Smederevka	Ljubaš		0.25	0.68	55.73	0.051	742.0	87.87
I-4	Kavadarka	Ljubaš		0.39	0.21	125.15	0.049	895.0	106.71
I-5	Burgundec	Glišicki atar	41.460129° / 22.014170°	0.10	0.06	19.77	0.036	431.0	23.92
I-6	Smederevka	Poroj (nad otpad)	41.453508°/ 21.997288°	0.17	0.08	34.11	0.093	636.8	57.14
I-7	Smederevka	Drenovo	41.432973°/ 21.881231°	0.96	0.15	99.74	0.036	868.0	70.15
I-8	Kratošija	Drenovo	41.432892°/ 21.889044°	0.27	0.10	51.57	0.127	897.2	96.18
I-9	Burgundec	Sirkovo	41.445288°/ 21.907220°	0.55	0.07	22.25	0.020	323.5	26.24
I-10	Rizling	Ribarci	41.507803°/ 21.976810°	2.43	0.10	105.16	0.277	698.5	95.27
I-11	Kratošija	Goligaz	41.445470°/ 21.986805°	0.29	0.22	49.02	1.081	442.1	116.22
I-12	Vranec	Ovcka Reka	41.436889°/ 22.054705°	0.89	0.19	82.09	0.051	983.4	88.19
I-13	Smederevka	Kurii-Lazarica	41.521023°/ 22.023823°	0.87	0.24	81.64	0.058	829.3	87.08
I-14	Kaberne	Sopotsko	41.483175°/ 22.043180°	0.78	0.34	78.40	0.065	1109.4	90.66
I-15	Smederevka	Krivi Dol Resava	41.403094°/ 21.977884°	1.08	0.22	32.12	0.127	748.8	81.15
I-16	Kratošija	Kalnica	41.421496°/ 22.021953°	0.81	0.47	35.66	0.077	819.8	113.34
I-17	Smederevka	Korija-Resava	41.409952°/ 21.977952°	0.26	0.12	43.40	0.009	1002.6	72.63
I-18	Kaberne	Sopot	41.508380°/ 22.006101°	0.44	0.34	85.01	0.034	1115.0	130.52
I-19	Belan	Kopacot	41.418623°/ 22.003520°	0.43	0.16	25.49	0.881	415.3	89.50
I-20	Kratošija	Kurii	41.527615°/ 22.005905°	1.38	0.20	36.99	0.043	1374.3	79.59
I-21	Šardone	Kurii	41.527615°/ 22.005905°	0.96	0.11	26.02	0.030	1253.2	93.60
I-22	Smederevka	Gradevica	41.393553°/ 21.986142°	0.29	0.14	57.67	0.029	606.0	74.54
I-23	Smederevka	Dabnište	41.384672°/ 22.006563°	0.27	0.22	37.81	0.085	813.2	78.53
I-24	Vranec	Begnište	41.358727°/ 21.994742°	0.65	0.09	60.66	0.023	956.1	86.18
I-25	Merlo	Krnjevo (Ploštovo)	41.310944°/ 22.125286°	0.27	0.25	57.87	1.389	805.5	83.90
I-26	Stanešina	Dabnište	41.384672°/ 22.006563°	0.34	0.27	44.87	0.115	824.7	100.37
I-27	Kratošija	Kruška	41.465574°/ 22.044982°	0.65	0.47	47.29	0.031	1174.3	122.32
I-28	Vranec	Moklište	41.387880°/ 22.046183°	0.16	0.38	49.47	0.090	1182.5	66.86
I-29	Smederevka+Kratošija	Rosoman (Konjarovec)	41.520796°/ 21.931591°	0.63	0.18	39.16	0.135	666.9	90.13
I-30	Kratošija	Dolni Disan	41.448101°/ 22.090495°	0.24	0.18	29.79	0.050	778.6	101.88
I-31	Rekaciteli	Krnjevo (Ploštovo)	41.313702°/ 22.125842°	0.19	0.17	35.37	0.184	397.2	87.53
I-32	Kaberne	Krnjevo (Poleto)	41.310946°/ 22.131133°	4.93	0.43	42.10	0.134	1626.4	88.97
I-33	Kratošija	Ljubaš	41.443418°/ 21.987745°	0.35	0.38	48.81	0.079	867.9	113.37
I-34	Smederevka	Belgrad	41.424559°/ 22.041539°	1.09	0.10	43.94	0.874	544.7	82.06
I-35	Belan	Sivec		1.55	0.25	37.59	0.873	571.2	73.03
I-36	Vranec	Palikura	41.527579°/ 21.975896°	1.05	0.16	62.65	0.045	1470.1	88.39
I-37	Smederevka+Temjanuga	Goligaz		0.27	0.10	25.92	0.490	454.5	82.53
I-38	Kratošija	Bel Kamen	41.430558°/ 21.997249°	1.27	0.38	32.85	0.319	883.5	114.85

Table 1. Continue

Sample No.	Sort of vine	Region – attar	Samples of soils lattitude / longitide	Co	Cr	Ni	Pb	Zn
				µg/l				
I-1	Kratošija	Debrište-Ramnište	41.459362° / 21.895683°	1.81	7.18	92.58	81.17	0.31
I-2	Smederevka	Debrište-Ramnište	41.459362° / 21.895683°	7.24	8.65	313.83	<5	0.15
I-3	Smederevka	Ljubaš		2.12	3.09	41.62	80.28	1.12
I-4	Kavadarka	Ljubaš		3.72	7.48	62.71	25.22	0.59
I-5	Burgundec	Glišicki atar	41.460129° / 22.014170°	0.48	1.37	22.18	15.56	0.23
I-6	Smederevka	Poroj (nad otpad)	41.453508°/ 21.997288°	0.84	6.48	60.46	28.09	0.57
I-7	Smederevka	Drenovo	41.432973°/ 21.881231°	2.24	19.70	119.95	53.18	0.23
I-8	Kratošija	Drenovo	41.432892°/ 21.889044°	5.58	13.52	108.52	21.55	0.66
I-9	Burgundec	Sirkovo	41.445288°/ 21.907220°	0.96	<1	23.02	16.42	<0.1
I-10	Rizling	Ribarci	41.507803°/ 21.976810°	10.57	15.06	26.68	36.92	0.35
I-11	Kratošija	Goligaz	41.445470°/ 21.986805°	3.86	8.90	58.19	103.57	0.70
I-12	Vranec	Ovcka Reka	41.436889°/ 22.054705°	3.50	9.81	9.35	18.33	0.78
I-13	Smederevka	Kurii-Lazarica	41.521023°/ 22.023823°	3.38	4.68	11.99	12.61	0.66
I-14	Kaberne	Sopotsko	41.483175°/ 22.043180°	1.39	4.46	17.98	59.09	0.12
I-15	Smederevka	Krivi Dol Resava	41.403094°/ 21.977884°	6.63	21.79	75.89	28.02	0.30
I-16	Kratošija	Kalnica	41.421496°/ 22.021953°	0.58	11.85	23.56	47.42	<0.1
I-17	Smederevka	Korija-Resava	41.409952°/ 21.977952°	0.38	4.84	16.44	<5	<0.1
I-18	Kaberne	Sopot	41.508380°/ 22.006101°	2.79	4.00	6.71	<5	0.13
I-19	Belan	Kopacot	41.418623°/ 22.003520°	1.70	3.21	12.39	22.29	0.26
I-20	Kratošija	Kurii	41.527615°/ 22.005905°	4.84	13.23	10.96	6.38	0.28
I-21	Šardone	Kurii	41.527615°/ 22.005905°	3.10	12.64	<5	<5	0.14
I-22	Smederevka	Gradevica	41.393553°/ 21.986142°	<0.1	22.06	37.19	37.15	<0.1
I-23	Smederevka	Dabnište	41.384672°/ 22.006563°	0.39	5.30	19.17	24.45	0.11
I-24	Vranec	Begnište	41.358727°/ 21.994742°	2.80	6.61	13.09	40.94	0.11
I-25	Merlo	Krnjevo (Ploštovo)	41.310944°/ 22.125286°	0.18	5.41	15.52	66.80	0.33
I-26	Stanešina	Dabnište	41.384672°/ 22.006563°	0.74	12.50	13.10	6.02	0.10
I-27	Kratošija	Kruška	41.465574°/ 22.044982°	3.33	19.82	31.73	218.34	0.77
I-28	Vranec	Moklište	41.387880°/ 22.046183°	<0.1	2.45	33.73	<5	<0.1
I-29	Smederevka+Kratošija	Rosoman (Konjarovec)	41.520796°/ 21.931591°	1.85	10.44	21.21	72.69	0.26
I-30	Kratošija	Dolni Disan	41.448101°/ 22.090495°	0.43	2.71	<5	<5	<0.1
I-31	Rekaciteli	Krnjevo (Ploštovo)	41.313702°/ 22.125842°	<0.1	1.87	<5	218.99	0.24
I-32	Kaberne	Krnjevo (Poleto)	41.310946°/ 22.131133°	2.02	99.53	56.05	26.89	0.04
I-33	Kratošija	Ljubaš	41.443418°/ 21.987745°	1.35	13.16	44.07	54.60	0.90
I-34	Smederevka	Belgrad	41.424559°/ 22.041539°	3.40	8.16	27.29	289.79	0.59
I-35	Belan	Sivec		6.73	30.09	93.29	156.75	0.37
I-36	Vranec	Palikura	41.527579°/ 21.975896°	0.78	12.49	31.84	25.44	<0.1
I-37	Smederevka+Temjanuga	Goligaz		<0.1	4.04	<5	90.70	0.32
I-38	Kratošija	Bel Kamen	41.430558°/ 21.997249°	1.50	18.46	37.26	49.56	0.18

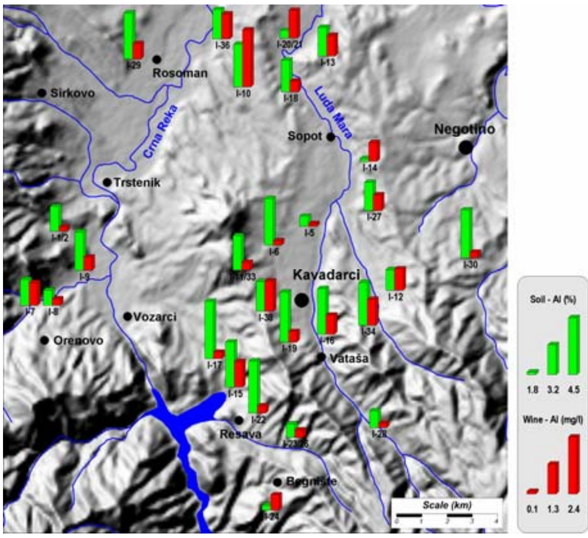

Fig. 3. Spatial position of samples taken from soils and wines and their geo-chemical correlation (Al_{soil}/Al_{vines})

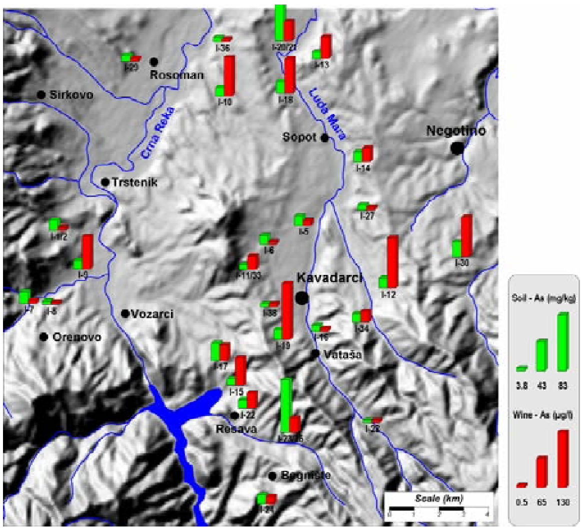

Fig. 4. Spatial position of samples taken from soils and wines and their geo-chemical correlation (As_{soil}/As_{vine})

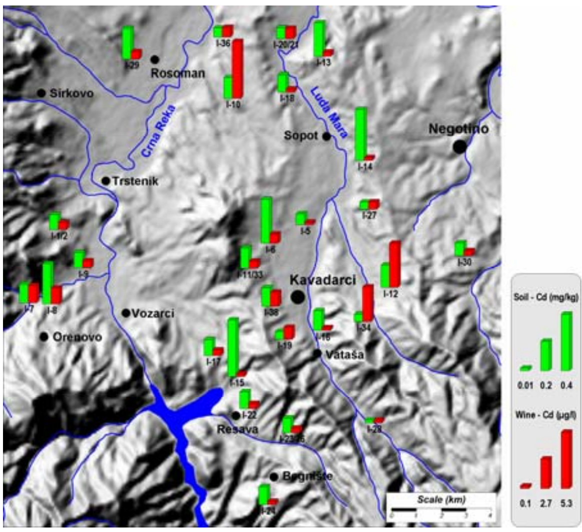

Fig. 5. Spatial position of samples taken from soils and wines and their geo-chemical correlation (Cd_{soil}/Cd_{vine})

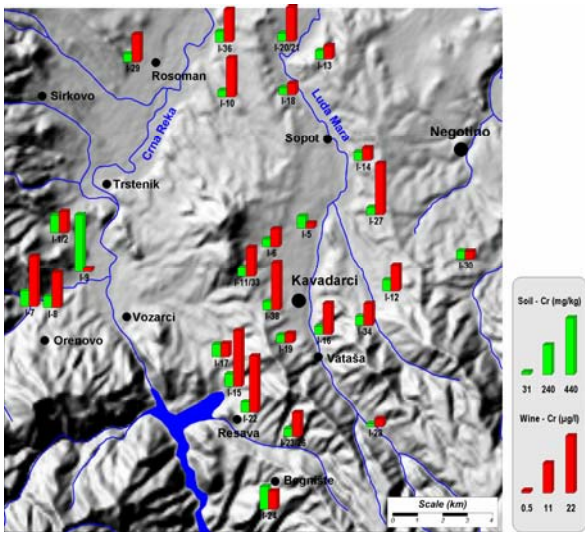

Fig. 6. Spatial position of samples taken from soils and wines and their geo-chemical correlation (Cr_{soil}/Cr_{vine})

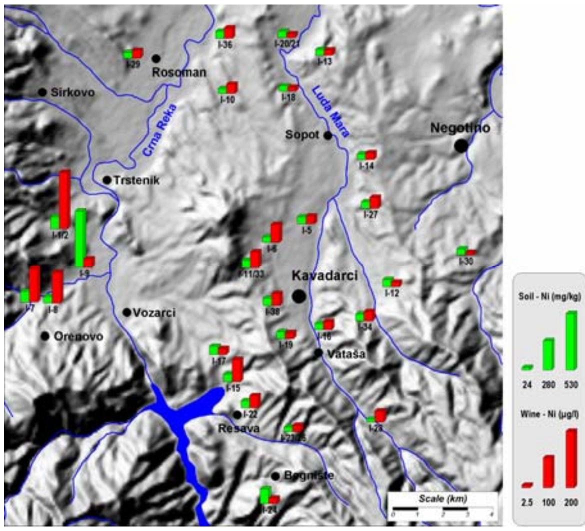

Fig. 7. Spatial position of samples taken from soils and wines and their geo-chemical correlation (Ni_{soil}/Ni_{vine})

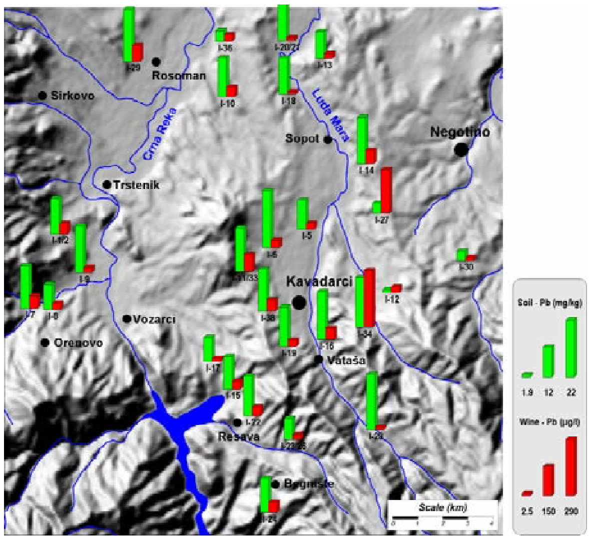

Fig. 8. Spatial position of samples taken from soils and wines and their geo-chemical correlation (Pb_{soil}/Pb_{vine})

Table 2

The statistical parameters of the vine geochemistry

Basic statistical parameters

	X	Xg	Md	min	P10	P25	P75	P90	max	*s*	A	E
Al	0.7700	0.5100	0.5500	0.1000	0.1700	0.2700	0.9600	1.2000	4.9000	0.9100	3.5200	14.9200
As	34.0000	9.9000	28.0000	0.5000	0.5000	0.5000	53.0000	87.0000	130.0000	36.0000	1.0300	0.3800
Ba	0.2200	0.1900	0.1800	0.0580	0.0920	0.1200	0.3400	0.3800	0.4700	0.1200	0.7800	–0.5500
Ca	51.0000	47.0000	47.0000	20.0000	30.0000	34.0000	61.0000	82.0000	110.0000	22.0000	0.9500	0.2800
Cd	0.8700	0.3800	0.4600	0.0500	0.0500	0.1200	0.9200	1.5000	5.3000	1.2000	2.5200	6.3700
Co	2.3000	1.2000	1.7000	0.0500	0.1800	0.5700	3.4000	4.5000	11.0000	2.3000	1.8000	4.4100
Cr	12.0000	7.6000	8.9000	0.5000	2.4000	4.5000	14.0000	20.0000	100.0000	17.0000	4.4800	22.7400
Cu	0.2200	0.0930	0.0790	0.0087	0.0290	0.0360	0.1800	0.8700	1.4000	0.3500	2.3800	4.8700
K	840.0000	790.0000	820.0000	320.0000	430.0000	637.0000	1000.0000	1200.0000	1600.0000	310.0000	0.5300	0.2600
Mg	87.0000	83.0000	88.0000	24.0000	67.0000	81.0000	96.0000	120.0000	130.0000	23.0000	–0.9200	1.9900
Mn	1.4000	1.3000	1.2000	0.4800	0.7400	1.1000	1.5000	1.9000	3.0000	0.5400	1.1300	2.0300
Na	9.5000	5.5000	3.6000	1.0000	2.0000	2.5000	11.0000	20.0000	64.0000	13.0000	3.0700	11.4600
Ni	38.0000	24.0000	24.0000	2.5000	6.7000	13.0000	44.0000	76.0000	200.0000	42.0000	2.5800	7.8600
Pb	53.0000	27.0000	28.0000	2.5000	2.5000	16.0000	55.0000	100.0000	290.0000	68.0000	2.4300	5.6200
Sr	1.1000	0.8200	0.9500	0.1500	0.3500	0.4400	1.4000	2.4000	2.9000	0.7400	0.9700	0.0900
Zn	0.3000	0.1900	0.2300	0.0360	0.0500	0.0500	0.5700	0.7000	0.9000	0.2600	0.9300	–0.4400

Table 3

The statistical parameters of the vine geochemistry

Correlation coefficients

Al	1.00															
As	0.18	1.00														
Ba	0.28	–0.10	1.00													
Ca	0.18	0.11	0.04	1.00												
Cd	0.44	0.37	–0.23	0.44	1.00											
Co	0.33	0.20	–0.17	0.42	0.59	1.00										
Cr	0.88	0.01	0.37	0.01	0.18	0.12	1.00									
Cu	–0.06	0.14	–0.05	–0.08	0.09	0.05	–0.09	1.00								
K	0.50	–0.12	0.50	0.28	–0.01	0.01	0.51	–0.34	1.00							
Mg	0.11	0.04	0.60	0.26	0.05	0.25	0.13	0.14	0.32	1.00						
Mn	0.21	–0.03	0.12	0.55	0.43	0.64	0.10	0.15	0.11	0.52	1.00					
Na	0.03	0.18	0.19	0.26	0.02	0.01	–0.07	–0.09	0.11	0.38	–0.02	1.00				
Ni	0.01	–0.38	–0.11	0.10	0.01	0.31	0.20	–0.03	–0.03	0.01	0.24	–0.30	1.00			
Pb	–0.03	–0.25	0.08	–0.07	0.19	0.04	–0.03	0.35	–0.24	0.20	0.07	0.16	–0.04	1.00		
Sr	0.07	–0.11	0.51	0.28	–0.09	0.19	0.01	–0.05	0.39	0.72	0.44	0.39	–0.19	0.07	1.00	
Zn	–0.14	0.02	0.03	0.17	0.33	0.37	–0.10	0.24	–0.16	0.26	0.27	0.02	0.12	0.37	0.09	1.00
	Al	**As**	**Ba**	**Ca**	**Cd**	**Co**	**Cr**	**Cu**	**K**	**Mg**	**Mn**	**Na**	**Ni**	**Pb**	**Sr**	**Zn**

From the presented results concerning the correlation between the presence of the macro elements and trace elements in soils and wines that are produced at home in Tikveš we can conclude that there is no marked correlation in certain element pairs. The lack of significant correlation between analyzed soils analysis and analyzed wines should be explained by the small number of samples that are the subject of the research, as well as through the very processes of concentration of the micro-elements in wines.

On the other side, another interesting part are the correlations which refer to the concentration of respective trace elements in the wines produced at homes, and the wines produced at the wineries in the Republic of Macedonia.

The pictures 9 and 13 show the concentrations of As (Fig. 9) and the concentrations of Pb (Fig. 13) from where it can be noted that there are higher concentrations of these two elements in the wines produced at home in relation to the wines produced at the wineries (Tašev et al. 2005, Karadzova et al. 2007) with an exception of the wine vranec and the content of Pb which is nearly identical to both wine types.

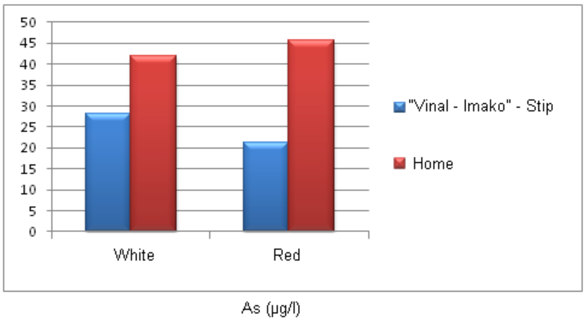

Fig. 9.

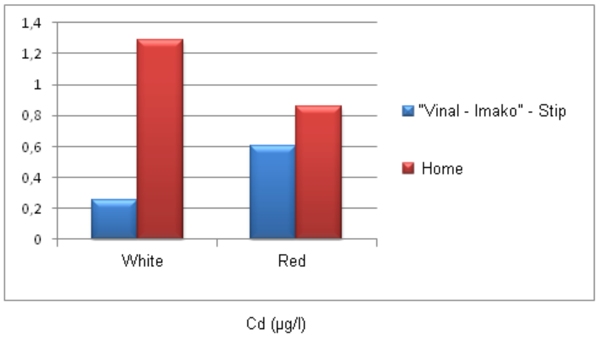

Fig. 10

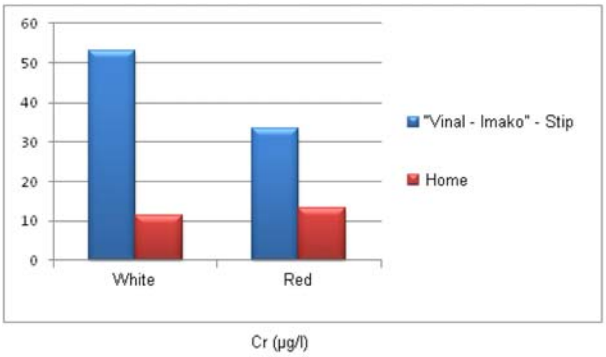

Fig. 11

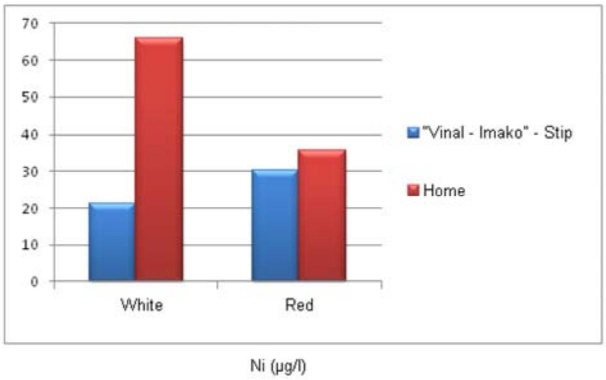

Fig. 12.

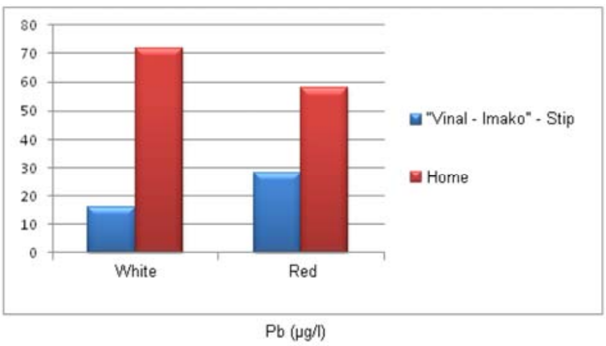

Fig. 13

Fig. 9–13. Correlationsof trace elements concentration in the wines produced at homes, and the wines produced at the wineries in the Republic of Macedonia

Figure 11, 12, 13 shows the relation of the contents of Cd, Ni, Cr in the white and red wine produced in home conditions and in the conditions at the Tikveš winery. From this picture it can be concluded that we have bigger concentrations of Cd and Ni in the white and red wine produced in home conditions in relation to the wines produced in the winery. It should be noted that this trend of bigger concentrations of the elements in the wines produced in home conditions does not follow the concentration of Cr.

CONCLUSION

The studies made about the presence of trace elements in wines produced at home in Tikveš suggest the following conclusions:

– The presence of trace elements such as As, Pb, Cd, Ni is higher in wines produced in home conditions in relation to the presence of these trace elements in wines produced in industrial conditions.

– There are no correlations between the presence of trace elements in wines produced at home and the elements that are present in soils.

The non-existence of correlations between element pairs (N_{soil}/N_{vine}) is the result of: the small depth at which samples are taken from the soil (30 cm): the presence of trace elements in soil is mainly in the silicate structure from which it is very difficult to perform the excretion the elements: the root systems of grape vine are very deep.

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Р е з и м е

МИКРОЕЛЕМЕНТИ ВО ВИНАТА ПРОИЗВЕДЕНИ ВО ДОМАШНИ УСЛОВИ ВО ТИКВЕШКО

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Кеѕ њордс: вино; геохемија; микроелементи; корелации

Во овој труд се прикажани резултатите од геохимиските истражувања на присуство микроелементи (Al, As, Ba, Ca, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sr, V и Zn) во вината произведени во домашни услови во Тиквешко со примената на методите на ICP-AES и (ETAAS) Во трудов се прикажани и корелациите направени врз основа на присуство на некои микроелементи во почвата на која се одгледува одредената сорта на грозје и истите елементи во виното кое се произведува од таков вид на грозје. Корелациите во главно укажуваат на фактот дека не постои голема поврзаност помеѓу присуството на одредени микроелементи во почвата и виното произведено во домашни услови. Имено, овие корелации за испитувањето на определена геохимиски парови се следните: $Al_{почва}$ / $Al_{вино}$ (0.04); $As_{почва}$ / $As_{вино}$ (0.11); $Ba_{почва}$ / $Ba_{вино}$ (0.23); $Ca_{почва}$ / $Ca_{вино}$ (0.02); $Cd_{почва}$ / $Cd_{вино}$ (–0,06); $Co_{почва}$ / $Co_{вино}$ (–0,26); $Cr_{почва}$ / $Cr_{вино}$ (–0,04); $Cu_{почва}$ / $Cu_{вино}$ (0.04); $Mg_{почва}$ / $Mg_{вино}$ (–0,30); $Mn_{почва}$ / $Mn_{вино}$ (–0,40); $Na_{почва}$ / $Na_{вино}$ (0.11); $Ni_{почва}$ / $Ni_{вино}$ (0.03); $Pb_{почва}$ / $Pb_{вино}$ (0.27); што укажува на дека отсуството на значајни корелации помеѓу дадените геохимиски парови е резултат на неколку моменти како што се: (1) присуството на микроелементи во почвата на длабочина до 30 cm. (2) микроелементите во почвата се присутни претежно во силикатна матрица од која елементи не можат лесно да се издвојуваат во водни раствори. (3) на корениот систем на винова лоза кој е во многу поголема длабочина од 30 cm.

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ARTESIAN MINERAL WATER OF THE RAOTINCE SITE, TETOVO

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A b s t r a c t: A number of mineral springs occur on the west and east peripheral part of the Polog valley. Their appearance is connected with the Western Polog fault that stretches west to the brim of the valley NE–SW direction and east direction of Polog fault stretches in NW–SE. This paper presents the results of detailed hydrogeological investigations of mineral water at the site Raotince Tetovo. Based on data obtained on two operational investigative boreholes at the site in Raotince of the pleistocene limnic sediments at a depth of 38–67 m is founded artesian aquifer with low mineralized water.

Key words: artesian aquifer; mineral water; Raotince; Polog valley; limnic sediments

INTRODUCTION

Raotince site is situated in the western part of Macedonia, 20 km north-east of Tetovo (Fig. 1). The occurrences of mineral and low mineral waters in this area appears in the left and the right banks of the river Vardar from the village Kopance to the village Raotince. In the immediate vicinity of the site Raotince passes the river Vardar. Mineral waters from the wider environment Raotince were investigated by several authors: (Bajic, 1929, Kekic, 1973, 1986, Kotevski, 1980, 1987, Loncar 1996).

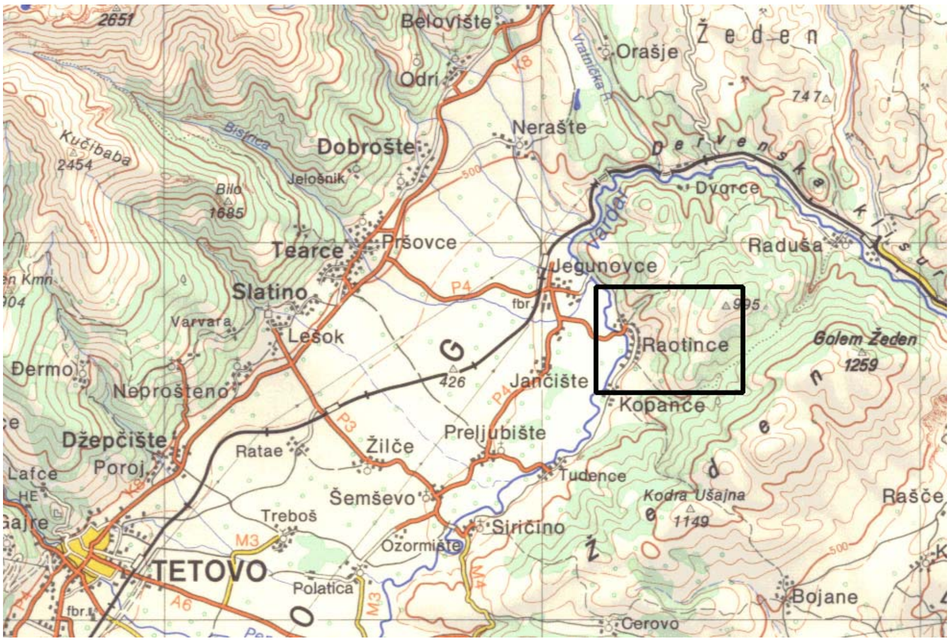

Fig. 1. Geographical possition of the investigated area

GEOLOGICAL COMPOSITION OF THE WIDER REGION

The geology of the region is made up of Paleozoic, Permotriasic, Mezozoic, Tertiary and Quarternary rocks (Petkovski, Karovic, 1977) (Fig. 2).

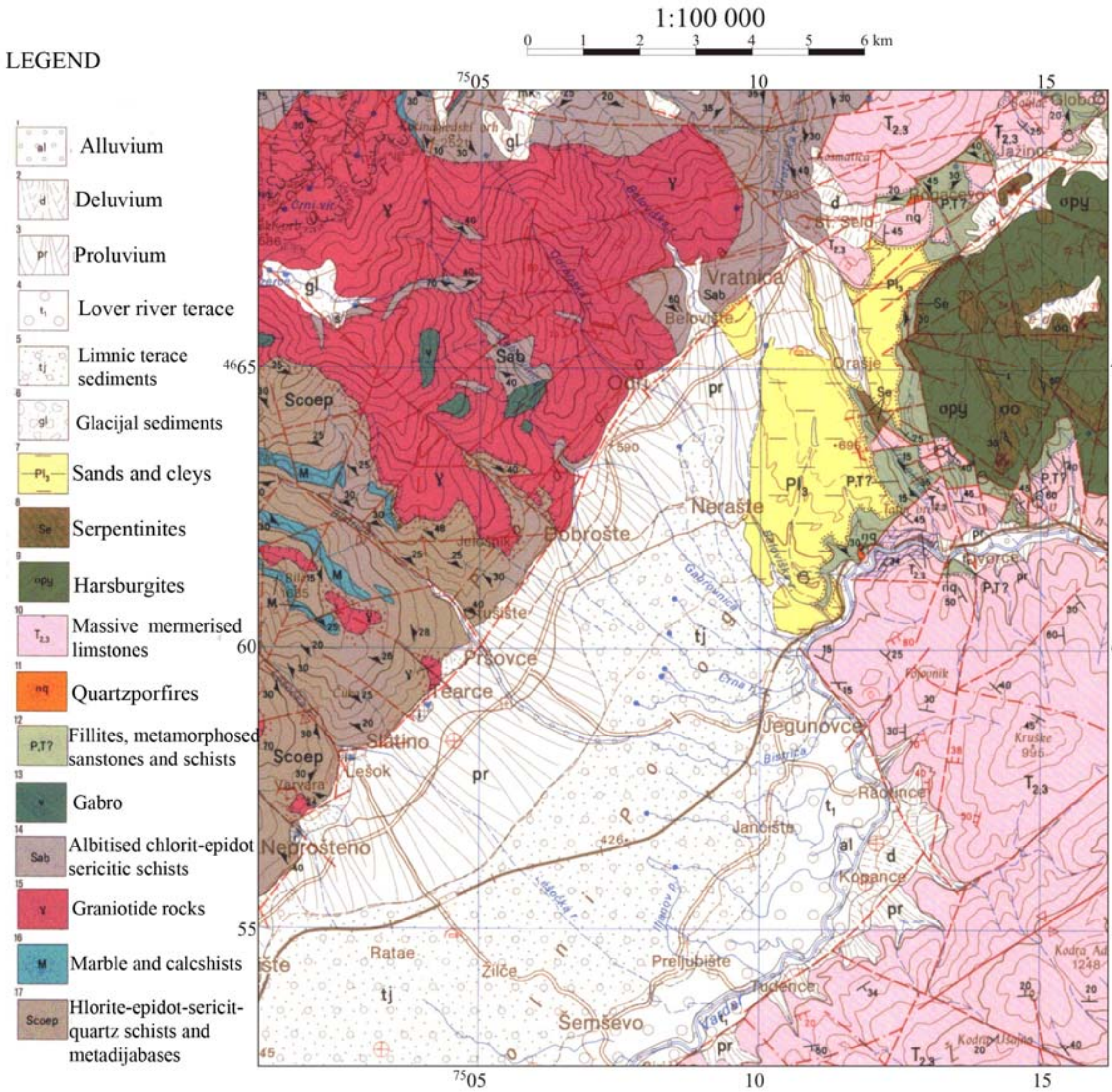

Fig. 2. Geological map of the investigated area. (Petkovski nad Karovic 1977)

The oldest rocks are represented of Paleozoic rocks present of: epidote – chlorite – sericite – quartz schist and metadijabases (Scoep), marbles and kalkshists (M), granite rocks (γ), albitized – chlorite – epidiot – quartz schist, and gabbros (ν). Permotriasic rocks are represented by: filites, metamorphosed cleystones, sandsstones and schists (P, T) and quartz porphyry (π q).

Mezozoic is present of Trijasic massive marble (T 2.3), jurasic harcburgites (σpy) and serpentinites (Se).

Tertiary is made up of only Pliocene sediments.

Quarterly rocks are represented of: moraine material (gl), limnic terace sediments (tj), lower river terraces (t1), proluvijal (pr), deluvijal (d) and alluvial sediments (al).

The investigated area by geotectonic regional aspect belongs to the Western Macedonian zone (Arsovski, 1997).

HYDROGEOLOGICAL INVESTIGATIONS

Two exploration drill holes with a depth of D_1 = 50 m and D_3 = 70 m. were made for the determination of the mineral water at the Raotince site .

With both boreholes artesian water were discovered bearing horizons with low mineral water. Based on data obtained by investigations drilling, was designed hydrogeological profile clearly presented lithological members (Fig. 3). From the hydrogeological profile it can be seen that the topmost parts of the site-built of alluvial terace sediments which thickness ranges up to 10 meters. In the terace alluvial sediments that are built of gravel and sand aquifer is formed by free level. Under the alluvial terace sediments down to the final depth are determined limnic sediments, presents of gravels, sands and clays and a varieties of their mutual transition. After drilling and purification drill holles have been done galvanized perforated pipes with a diameter 3" have been filled. By measuring the yield of the drill holles artesian mineral water with capacity of: D1–Q= 8 l/s D3 – Q = 2.6 l/s is obtained.

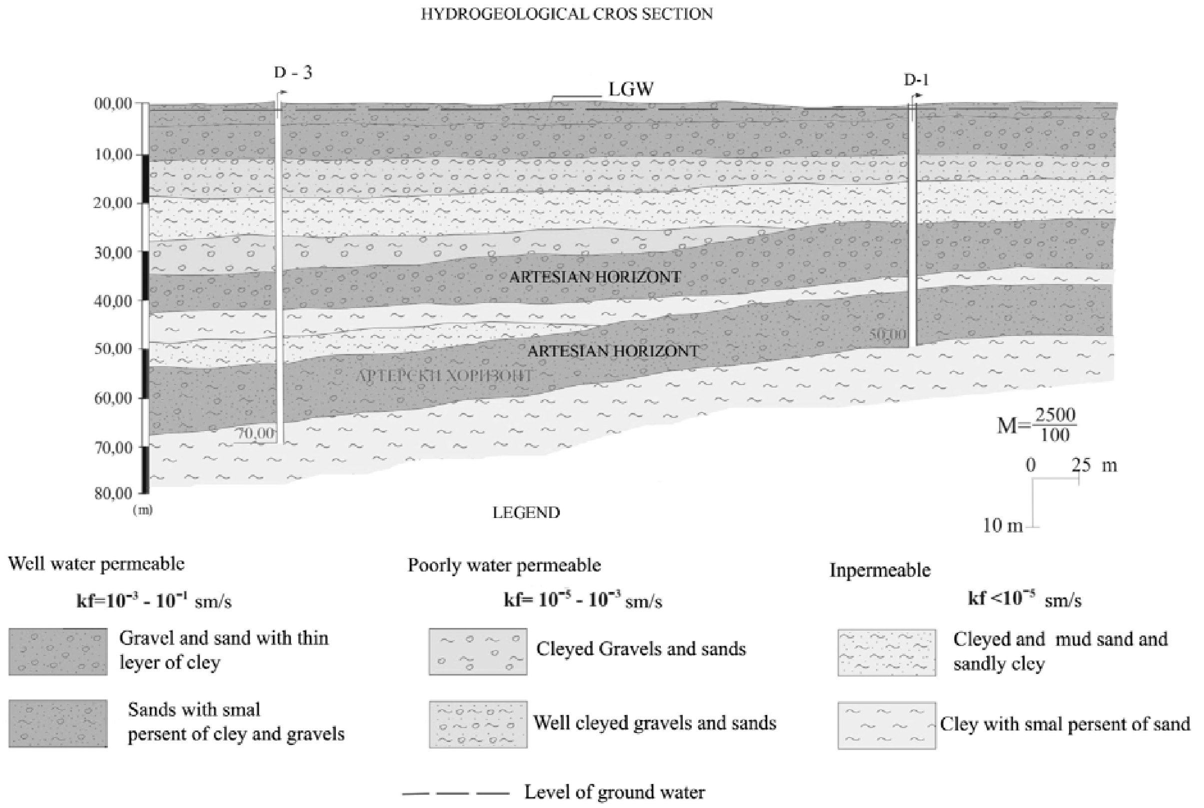

Fig. 3. Hydrogeological profile

On the bases of D1 drill hole there is greater yield in it so technical exploration is prepared for exploration as well (Fig. 4). The drill hole is located about 400 meters downstream of the bridge of river Vardar Raotince village.

Based on field observations on known data as a potential zone in which there is mineralisation water zone it is located on both sides of the river Vardar in NW–SE direction. The width of this zone ranges of 250–500 meters in length and can be traced right to the village Kopance

Fig. 4. Artesian drill hole of Raotince site

CALCULATION OF THE HYDROGEOLOGICAL PARAMETERS

According to the data of the investigation work done a calculation has been made of the hydrogeological parameters of the water bearing environment:

K – coefficient of filtration

T – trasmissivity coefficient

Q – yield of drill hole

N– hydrostatic pressure of aquifere

l – thickness of water–baring leyer

Filtration coefficient

Filtration coefficient is determined based on determination of granulometric composition of samples from the artesian water-baring layer which in the drill holle D1 is in the interval from 38.00 to 49.00 meters and the results obtained by the tests carried out on the well.

The results obtained from the granulometric analyses were used for calculation according to the formula of "USBR".

$$K_f = 0.36 \cdot d_{20}^{2.3}$$

Where is: *K* – coefficient of filtration, d_{20} – diameter of grains (mm), with representation from 20% to granulometric curve.

According to this formula the filtration coefficient was obtained by the following value:

$Kf = 1.60 \times 10^{-1}$ sm/s, sm/s or 138 m/dey

Static water level is located at + 4.5 m above the surface of the ground. The testing of the well obtained the following values of the capacity of the well Q and lowering the water level S in the well Table 1.

Table 1

Data from the test well

Height of LGW over field *H* m	Capacity *Q* *l*/s	Lower level $H_0 - H) = S$
$H_1 = 3.20$	$Q_1 = 2.40$	$S_1 = 1.30$
$H_2 = 1.80$	$Q_2 = 5.75$	$S_2 = 2.70$
$H_3 = 0.60$	$Q_3 = 8.05$	$S_3 = 3.90$

Based on the obtained parameters for Q and S, calculation of the filtration coefficient has been made according to Krasnopolski (1980), for conditions when artesian aquifer is away from surface waters, there is not monitoring well and when the well radius (r) is very small regarding the radius of its influence (R).

$$K = \frac{0,16\,x\,Q}{m\sqrt{r \cdot S}}$$

Input parameters are:

Q = 8.05 l/s – Well capacity

*S*3 =3.90 m – Lowering the water level

m = 11 m – Thickness of water-bearing layer

r = 3"– Radius of well pipe

$K = 8.35\times10^{-2}$ cm/s = 72 m/dey

m = 11 m

$T = 72 \times 11 = 792$ m^2/dey

Transmissivity coefficient

Transmissivity coefficient (T) was calculated according to the formula for the non stationary conditions of streams in the water-bearing artesian layer:

$$T = K \times m$$

K – coefficient of filtration

m – thickness of the water-bearing layer

K = 72 m/dey

m = 11 m

T = 792 m^2/dey.

Capacity of the drill hole

After the drill hole has been technically equiped, testing of its capacity has been made.

The measurement was conducted for a period of 13. 5 months and the results are shown in Table 2.

A granulated gravel has been placed around the drill hole and over it until the surface of the clay court built as a buffer layer which acts to isolate the mineral waters from the penetration of water from upper layers. The mouth of the drill hole was equipped and protected by concrete manhole and plate.

This equipped drill hole was washed with water and e measuring of the capacity was conducted for a period of 10. 22. 1995 to 05. 04. 1996.

Table 2

Capacity of the artesian drill hole

Date of measurement	Capacity Q l/s	Tmperature °C
22.10.1995	10.22	12.4
12.11.1995	10.06	12.3
05.04.1996	12.0	12.0
11.01.1996	9.70	12.0
10.02.1996	10.28	11.8
15.03.1996	9.55	12.0
14.12.1996	10.00	12.1

After the results of the capacity of the drill hole is concluded to be stable hydrogeological conditions. Based on measurements data the exploitation yield for the drill hole is

$$Q_{exp}. = 10.0 \text{ l/s}.$$

However yield over time will decrease because of the dynamic discharge aquifer and reducing the permeability of the filter tubes over time this will be monitored and analyzed.

Hydrostatic pressures in the aquifere

Hydrostatic pressures in the aquifere was measured at the outlet pipe, thus obtained values ranging from 1.6 – 2.2 bar.

QUALITY OF THE WATER

Quality ot the mineral water was analized by the National Institute for Health Protection in Skopje have been made two chemical analysis.

According to the chemical composition the water belongs to the group of hydrocarbonate, calcic- magnesian water.

It is characterized by a pleasant tartness, no smell and has increased mineralization ranging from 708–895 mg / l, according to which it belongs to the group of low mineralized water.

According to the pH value (pH = 6.32) water belongs to the group of weakly acidic waters.

CONCLUSION

In the area of Raotince which was covered by detailed hydrogeological investigations in the pleistocene limnic sediments at a depth of 38 – 67 m, was founded aquifer of two artesian horizonts with low mineralized water.

Exploitation drill hole D1 works in stable hydrogeological conditions with capacity of

$$Q_{exp} = 10.0 \text{ l/s}$$

According to the chemical composition water belongs to the group of hydrocarbonate, calcic-magnesian water.

According to the mineralization ranging from 708–895 mg / l water belongs to the group of low mineralized waters.

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Р е з и м е

АРТЕСКА МИНЕРАЛНА ВОДА ОД ЛОКАЛИТЕТОТ РАОТИНЦЕ, ТЕТОВО

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Клучни зборови: артески водоносник; минерална вода; Раотинце; Полошка котлина; езерски седименти

Поголем број на појави и минерални извори се појавуваат по западниот и источниот ободен дел на Полошката котлина. Нивното појавување е поврзано со западно Полошкиот расед кој се протега по западниот обод на котлината со правец СИ–ЈЗ и со источно Полошкиот расед со правец на протегање СЗ–ЈИ. Во овој труд се прикажани резултатите од деталните хидрогеолошки истражувања за минерална вода на локалитетот Раотинце Тетовско. Врз основа на податоците кои се добиени со две истражно експлоатациони дупнатини на локалитетот Раотинце во плеистоценските езерски седимнати на длабочина од 38 – 67 m е констатиран артески водоносник со слабо минерализирана вода.

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TYPES OF HYDROTHERMAL ALTERATION WITHIN THE ILOVITZA DEPOSIT

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A b s t r a c t: As a result of the recent detailed explorations, Ilovitza deposit is separated to the polymetallic Cu-Au-Mo porphyry deposit, located within Tertiary intrusive complex, whose mineralization is closely related to intensive hydrothermal alterations of surrounding rocks. This deposit represents a part of several porphyry systems in eastern Macedonia and northern Greece, which are in association with igneous complexes and is one of deposits of the type of the deposit Buković–Kadiica in Macedonia and Scouries in Greece. Hydrothermal alterations, as a special marc of the deposit, with our laboratory examinations, were determined as an alteration that characterizes porphyry systems. Between them are distinguished neobiotitization, quartz–sericitization, silicification, argillitization et al one of the most intensive alteration is silicification (around 49 %), which in association with alunitization (around 40%), encompasses the apical parts of intrusive complex.

Key words: porphyry system; intrusive complex; neobiotitization; quartz–sericitization; silicification; argillitization

INTRODUCTION

From the historical aspect, Ilovitza deposit, which is located in eastern Macedonia, in the vicinity of Strumica city, have always been interesting for exploring, as indicated by the data in the form of travel notes, as well as numerous papers submitted by Томич, 1936; Шоптрајанова, 1957; Стојанов, 1966; Stojanović, 1972 etc.. Recent investigation which started in 2004 were made by the company *Phelps Dodge*, and today, extended from the company *EurOmax*, on whose basis Ilovitza deposit is separated as deposit whit porphyry type of Cu-Au-Mo mineralization (Aleksandrov and Bombol, 2008). Shows characteristics of the connection with Tertiary magmatism and the same is considered as deposit of the type of deposits from the zone Lece-Chalkidiki (Serafimovski, 1990, 1993). Examinations which include X-ray and microscopic examinations of the samples, proved the presence of hydrothermal alterations which is closely related to the porphyry mineralization (Рогожарева, 2010). Between them could be separated: supergene sulphide alteration, weak propyllitic alteration, advanced argillic alteration, quartz-sericite-pyrite ("phyllic") alteration and potassium metasomatism with the presence of intermediate argillic alteration. In addition, in view of the mineralization especially are interesting deeper parts of the deposit, especially zones and their contact parts where the quartz-sericite-pyrite alteration is developed and potassium metasomatism with the presence of intermediate argillic alteration.

REGIONAL GEOLOGY, GEOTECTONIC AND METALLOGENIC POSITION

In the Republic of Macedonia even and broader, "Ilovitza" deposit represents one of the more significant porphyry deposits of Cu-Au-Mo.

It is located on the territory of the Republic of Macedonia, more precisely in its southeastern part, at about 17 km at a distance from Strumica city, in the immediate vicinity of the Ilovitza village.

In view of the regional geotectonic position, "Ilovitza" deposit belongs to Serbian-Macedonian Massif (Zagorchev et al. 2008) and the Serbian-Macedonian Metallogenic Zone (Janković, 1977; Serafimovski, 1990), in belt, in whose geological construction participate late Proterozoic to Palaeozoic metasediments and granitoids (Figure 1).

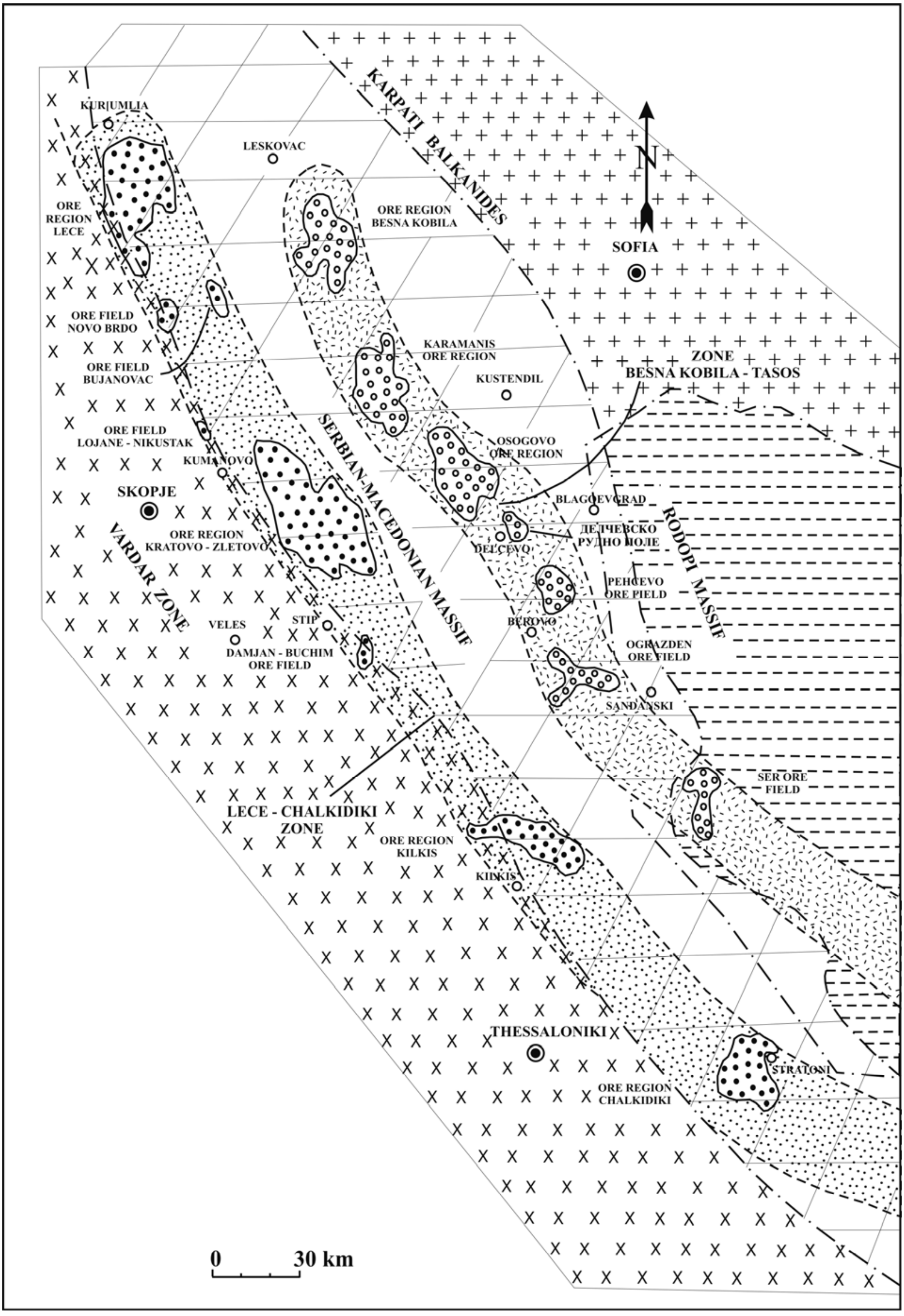

Fig. 1. Regional position of the "Ilovitza" deposit (Serafimovski, 1990)

The processes that took place in the frame of the SMM have caused structure of the volcanic apparatus, domes and regional dislocations, as the Tupal dislocation and dislocation Besna Kobila-Osogovo (Serafimovski, 1990; Aleksandrov, 1992). These regional dislocations are separated as very important in the structural control on the intrusive complexes of granitoides (Ракичевиќ et al. 1980; Janković et al. 1995; Janković and Serafimovski, 1997). Actually, creation and spatial distribution of the magmatism and the ore are in function of the structural factor of a control or disjunctive-depth structures that are present in the Ogražden granite massif and have direction along the borders of the basic geotectonic units: Serbian-Macedonian Massif and the Vardar Zone (Serafimovski, 1990).

GEOLOGICAL CHARACTERISTICS OF THE BROADER AREA

The Ogražden granite massif is located in the southeast part of the Republic of Macedonia, in to large-scale geotectonic unit of the Serbian-Macedonian Massif (Figure 2). The fundament in which the broken the Palaeosoic Variscan granite massif is represented by Precambrian and Rif-Cambrian rocks. The Precambrian lithological is represented by gneisses (the two mica, the biotite, the muscovite, the phorphyroblastic) micashists, amphibolites. The Rif-Cambrian is represented by the amphibole and epidote-quartz-sericite-chlorite shists. From the structural aspect, the massif Ogražden represent a batholite, which during the Variscan orogen phase was intrude in the fundament and is characterized by intense disjunctive tectonic or fault shape with general direction NW–SE.

During the Tertiary, along rupture structures in the consolidated Ogražden granite masses in the gneisses had volcanic acts that contributed to creation of dacite and andesite with which is connected hydrothermal changes. They represent subvolcanic to volcanic disruption in the granite and gneisses (Ilovitza, Dvorište, Štuka, Sušica).

Mineralogical-petrographic caracteristics of the Ogražden massif indicate that is it quite heterogeneous and is basically represented by calcalcaline granites. These granites shall occupy the central parts of the mountain Ogražden and is represented by: biotite coarse-grained granites, leucocrate coarse-grained granites, graniteporphyres, muskovite leucocrate granites, two mica medium grain granites, biotite porphyry granites and granodiorite, leucocrate schist granites.

From mineralogical aspect, the Ogražden massif is represented by large crystals of feldspar, a large amount of biotite and quartz. From petrographic aspect, the same are characterized by alotriomorfic grain to porphyry structure with massive, and sometimes the weaker schists texture.

Hydrothermal changes in the dacite–andesite caused almost completely destroyed primary structure and changes in the mineral composition. These changes are manifested in the form of silicification, sericitization, alunitization, kaolinitization and some places opalitization and chloritization.

The zone of intensive silicification and sericitization space is expressed on the west side of the dacite–andesite disruption.

The zone of intensive silicification and alunitization space is expressed on the east part of the dacite–andesite disruption, in which the presence of alunite varies from 20–50%.

Noticed that in the parts where alunite contains are moving within the limits of 20–48%, sulphide mineralization is missing, similar as well as in Plavica polymetallic systems (Stojanov, 1980) and Dudica (Ivanov and Ivanova, 1980). However , in the parts of intensive silicification and alunitization are registered and certain contents of gold (over 19 g/t), which mark one epithermal area, where the mineral components are products of acidly sulfate solutions (Serafimovski and Aleksandrov, 1995).

TYPES OF HYDROTHERMAL ALTERATIONS

According typomorphic minerals and on the basis of the results derived from X-ray examination of samples, as well as so far, the degree of explorations, within the Ilovitza deposit may be separated the following types of hydrothermal alterations (Figure 3).

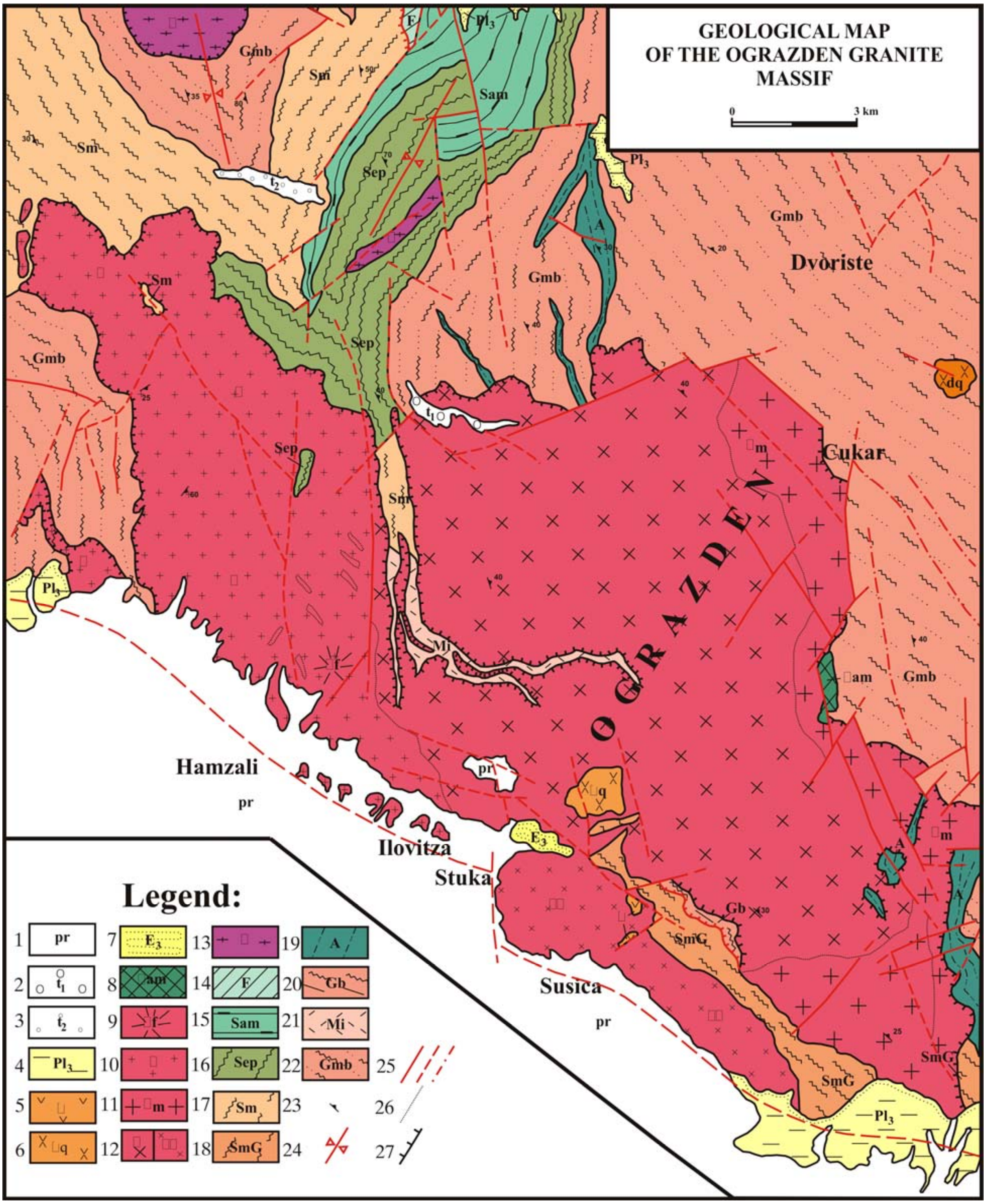

Fig. 2. Structural-geological map of the Ogražden granitoide massif
Quaternary – 1. Proluvium; 2. Lower terrace; 3. Higher terrace. Tertiary – 4. Clays; 5. Andesites; 6. Dacites; 7. Volcanic sediment sandstones, conglomerates and tuffs. Lower Palaeozoic – 8. Amfibole gabbro; 9. Leucocrate coarse–grained granites (metasomatic); 10. Aplitoide granites; 11. Muscovite leucocrate granites; 12a. Biotite porphyry granites; 12b. Biotite porphyry granodiotites; 13. Leucocrate shist granites; 14. Phyllites. Riphean-Cambrian – 15. Amphibole shists; 16. Epidote-quartz-sericite chlorite shists. Precambrian – 17. Micashists; 18. Micashists and leptinolites; 19. Amphibolites; 20. Biotite gneisses; 21. Migmatite (porphyryblastic gnaisses); 22. Two mica fibre gneisses; 23. Elements of the decline in the foliation; 24. Axis of syncline; 25. Faults (set, covered and fotogeological); 26. Gradual transition; 27. Lump of the flakes

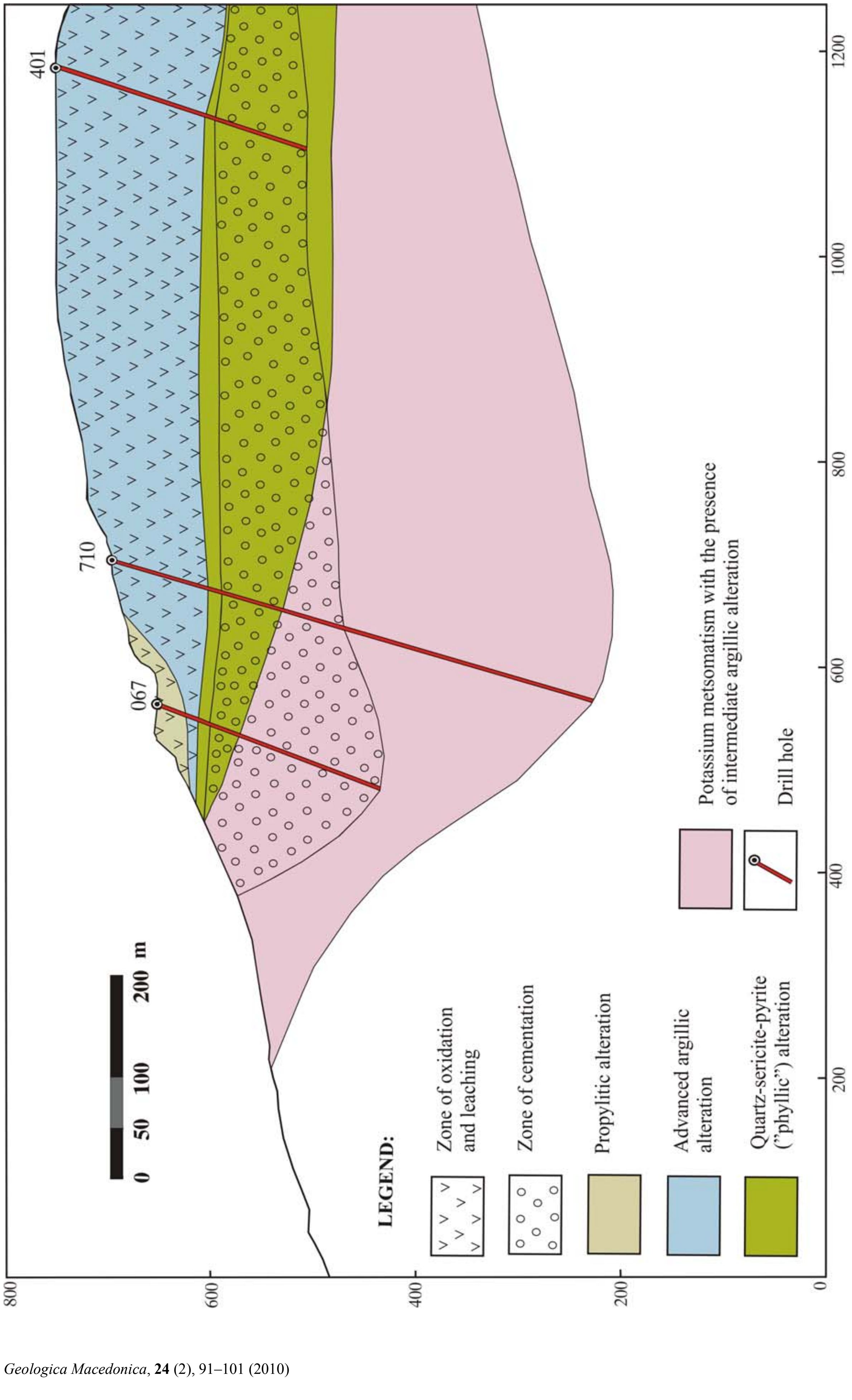

Fig. 3. Development of the types of the hydrochemical alterations in "Ilovitza" deposit

Supergene sulphide alteration

One of the important features of the “Ilovitza” porphyry Cu-Au-Mo depositis the presence of the deep supergene sulphide zone of alteration, which locally reaches a depth more then 150 m, similar to the appearances in the polymetallic system Bukovik–Kadiica (Tasev, 2010).

Is characterized by oxidation, leaching and intensive argillitization and includes the appearances of pyritization, limonitization and secondary sulphide enrichment.

Oxidized and leached zones on the surface are recognized by the "coverage" of metals in the supergene clay minerals, limonite (goethite, hematite and jarosite) and residual quartz. The secondary (supergene) zones containing chalcocite, covelline and other Cu_2S minerals (digenite et al.), hrizokol, native copper and copper oxides, as well as carbonate and sulfate minerals (Panteleyev, 1995; Tasev, 2010).

Pyritization is a direct indicator that there were conditions for sulphide mineralization. Limonitization is widespread, especially in quartz–alunite–limonite breccias (Figure 4).

Fig. 4. The core of silica–alunite–limonite breccia

Is manifested with occurrence of hematite, goetite and jarosite, which mark the zone of oxidation. Their occurrence is noticed at the surface of the terrain and also by microscopic and X-ray examinations, when it is determined that limonite meet cracks of the tectonic weaken rocks, so all rock mass is filled with them and simultaneously making pigmenting of the silica which is present in the rock (Figure 5).

In the products which occurred after the formation of the primary mineralization, and as a result of supergene sulphide oxidation is among the secondary sulphide enrichment, occur in the area of the oxidation-reduction zone (Emmons, 1917; Garrels, 1954; Čifliganec, 1993; Tasev, 2010). This area on the secondary sulphide ore in “Ilovitza” deposit, which in some parts is possible over and above 100 m (locally over 150 m) was built by chalcocite and covelline and the same has no particular economic significance.

Fig. 5. Intensely altered core of the drill hole PDIC-04-01

Propylitic alteration

This alteration phenomenon occurs in the end-edge areas of the zone of alteration and is characteristic of the andesite porphyry which are characterized by the presence of chlorite-epidote-clay with limonite veinlets and Mn oxides in outcrops (Donkova, 2006).

Occurs in the vicinity of the other alteration types and is characterized with very weak intensity associated with the zeolites, so in the individual parts almost is absent (Ivanov and Ivanova, 1980).

The zeolitization, which registered a low occurrence is manifested in the surface, more shallower parts of the terrain with appearance of analcime, who is the registered in PDIC-06-07 in sample number 1, with contents of 14 %.

Advanced argillic alteration

Advanced argillic alteration is widespread, immediately over Cu-Au-Mo porphyry system in the peripheral parts of the intrusive, controlled by the presence of deep normal faults.

Includes kaolinite and quartz, as well as alunite, natroalunite, natrolite, ilite, sericite, limonite and pyrite.

Associated with silicification and alunitization, which are manifested with structurally-controlled appearance, in which the silicification and silica- or silica-alunite-sulphide-limonite alteration is surrounded by narrow zones of clay alteration and bleaching, hosted in both fractured zones within basement granite, or within dikes/pods of Tertiary tuff-breccia (Carter, 2007).

The alunitization especially is characteristic for the apical parts of the intrusive, where it is developed silica-alunite litho-cap, while the process of alunitization is related to the mineralization, and especially with the zones of stock-work mineralization.

The alunitization also is registered in the core of drill hole, more precisely in drill hole PDIC-04-01, in which are determined the most contents of alunite presence in the sample number 1 (37%), where with the quartz represent the most dominant minerals in the sample (Table 1).

Table 1

Results of X-ray analysis of the more significant minerals (%) of drill hole PDIC-04-01

	Content (%)													
	Number of sample	Quartz	Alunite	Hidromuskovite	Fluoroapatite	Anortite	Hematite	Anhydrite	Microcline	Muscovite type of mica	Muscovite	Kaolinite	Pyrite	Muscovite + ilite
Drill hole PDIC-04-01	1	54	37	4	3	–	–	–	–	–	–	–	–	–
	2	59	–	25	–	7	5	2	–	–	–	–	–	–
	3	46	10	27	–	5	3	–	7	–	–	–	–	–
	4	48	5	32	–	4	7	2	–	–	–	–	–	–
	5	52	–	–	–	6	3	2	–	35	–	–	–	–
	6	53	–	–	–	7	4	2	–	–	22	10	–	–
	7	44	–	–	–	6		1	–	24	–	12	11	–
	8	42	–	–	–	4		1	–	–	–	17	13	21
	9	50	–	26	–	6		2	–	–	–	3	11	–

Among the rest, the intensity in his appearance shows and the silicification, which is probably a product of the completed leaching of the cations and the result of the decomposition of feldspars.

In the Ilovitza deposit, it is manifested by the presence of quartz in the form of two generations or more fine-grained, which appears in the base of the rock mass and than suppressed the primary mineralization and coarse-grained, in the form of vein-lets with varying thickness, which arise with fulfill of the cracks and fractures with silica matter.

Quartz-sericite-pyrite ("phyllic") alteration

Quartz-sericite-pyrite ("phyllic") alteration is located below the zone of the advanced argillic alteration and is represented byintense quartz–sericite-clay-FeOx alteration, which contains which contains larger bodies of quartz-alunite alteration, and the same represents proximal zone of significant ore changes. As such shall be determined in hosted in both basement granite and Tertiary magmatic rocks (Carter, 2007).

This zone of alteration in the deeper parts is associated of stock-work quartz-pyrite-FeOx alteration and intense clay-sericite alteration largely confined to Tertiary dacitic breccia and dacite-granodiorite intrusive rocks (Carter, 2007).

The silicification is the companion of the phillyte alteration and variable is influential in the most of part of stock-work and the most of the most of the dykes. The quartz veins show an environment of weak sericite halos.

The appearance of phillyte alteration is characterized by an increase in the contains of muscovite, which arises by replacing of the orthoclase and plagioclase and the same has gradually transition towards other alterations.

Also, iron free from the alterations of iron–bearing minerals, as well as iron and sulphor additions of the fluid, can formed pyrite, which increases in the deeper levels of this zone.

He is present in the form of veins and impregnations, so the pyrite vein-lets reach a thickness of (8–10 mm) and in some places they are replaced by chalcopyrite. The numeral sulphide vein-lets formed a stock-work which is accompanied by quartz-sericite-pyrite and the traces of chalcopyrite alteration with some content of kaolinite (Figure 6).

Fig. 6. Quartz-sericite-pyrite alteration with intensive quartz and pyrite vein stock-work

In the deeper parts and closer to the core of the system, there are occurrence of intensive stock-work with lateral quartz veins of older generation, crosscutting with younger quartz-pyrite and the youngest pure pyrite veins and vein-lets. Among the rest this zone is characterized by a higher degree of copper contents.

Potassium metasomatism with the presence of intermediate argillic alteration

Allocating of the potassium metasomatism with the presence of intermediate argillic alteration is a result of overlapping of these two alteration types.

Intermediate argillic alteration is characterized by the appearance of kaolin, which is determined and with the X-ray analisis. Arises as a result of the alteration changes of the plagioclase, which become replaced by kaolinite and appears near the ore body. The potassium feldspar is less afflicted with the processes of metasomatism, when it is formed sericite, while similar biotite formed chlorite. This alteration zone is represented by central quartz-magnetite-sulphide FeOx stockwork and dissemination, with matrix alteration of illite–sericite, chlorite ("intermediate argillic alteration") containing patches of residual secondary biotite and K-feldspar, hosted in dacite-granodiorite porphyry, and minor andesite and latite–andesite porphyry dikes (Carter, 2007).

The shallow level of the alteration may be interpreted as supergene (zone of secondary sulphide enrichment) cover over the deposit, so it is not excluded and probability and deeper clay alterations of the feldspar to have the same origin. In this zone in individual parts and chalcocite occurs in the form of impregnations and vein-lets arise with the suppression of the chalcopyrite (Figure 7).

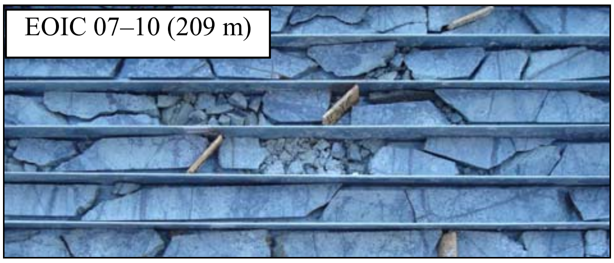

Fig. 7. Core of intensely altered stock-work with chalcocite in impregnations and veinlets

This zone is characterized by gradual transitions towards the potassium alteration, which represents the earliest and relatively high temperature alteration, which results in enrichment with potassium.

This type of alteration has a chance to be formed before the full crystallization of the magma, as indicates the presence of unrelated flexuous vein-lets.

Is represented by the appearance of orthoclase and secondary biotite, accompanied by a chlorite and sericite, but also we can notice the appearance of calcite and siderite in the deeper parts of the drill holes (Figure 8).

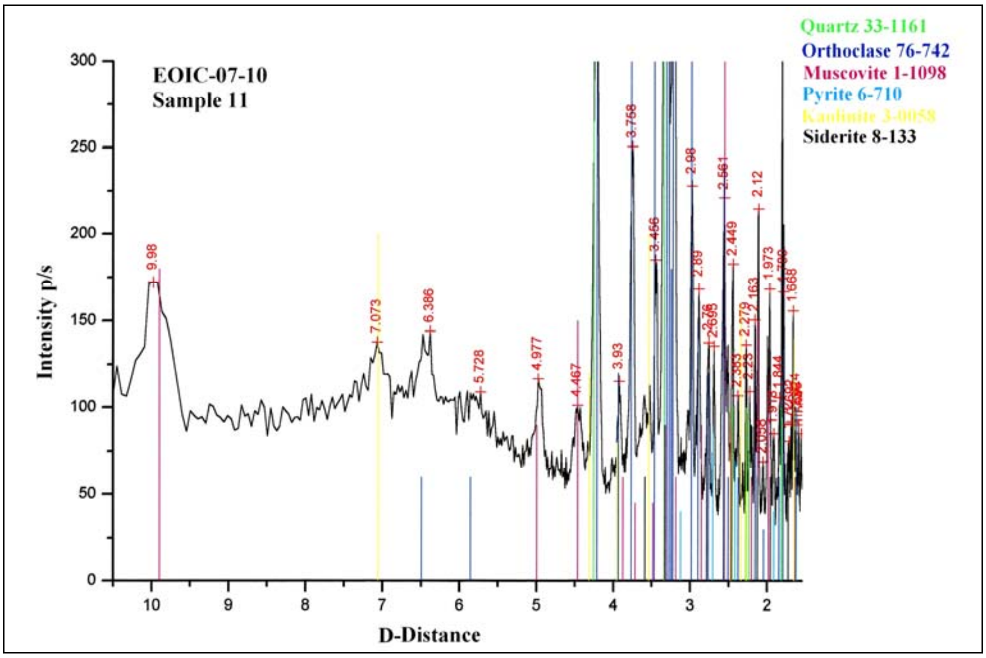

Fig. 8. Roentgenogram with the results of X-ray analysis of the sample number 11 of EOIC-07-10

Based on the X-ray analysis of the core of the several drill holes is found that the level of the occurrence of the potassium metasomatism starts from about 165.00 m, what exactly is determined by the appearance of the orthoclase, whose appearance with variable contents is present until the end of examinated drill holes.

Its genesis probably is a result of the metasomatism of the plagioclase in the K-feldspar, while secondary biotite with metasomatism of hornblende or chlorite.

Magnetite and hematite are general. The common sulphides are pyrite, molibdenite and chalcopyrite.

In the following are shown individually photographic images of the core of this zone, as well as mineralogical-alteration features of the core of the deeper parts of the drill holes.

On Figure 9 is given chlorite-sericite-clay-magnetite alteration with the quartz-magnetite vein-lets. In the deep parts, chlorite and magnetite become stable. Originally, the rock is altered to chlorite and magnetite. Replacement of the plagioclase by dark brown montmorillonite to the rock gives yellow-brown appearance.

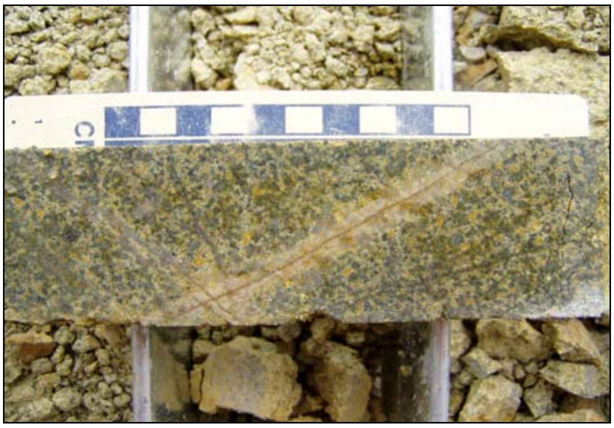

Fig. 9. Chlorite-sericite-clay-magnetite alteration with quartz-magnetite vein-lets

In the deepest levels of the examinated drill holes biotite has been preserved. At this level, is present facies of quartz veins (Figure 10), but, should be said that the density of the veins was reduced than in the stock-work zone of the higher level of the drill holes or the developed intensive stock-work go reaches its maximum in the periphery of the intrusive, while in the deeper parts more prevalent is the disseminated mineralization, which is accompanied by chlorite-sericite-magnetite–biotite alteration, which is covered with a late argillitization.

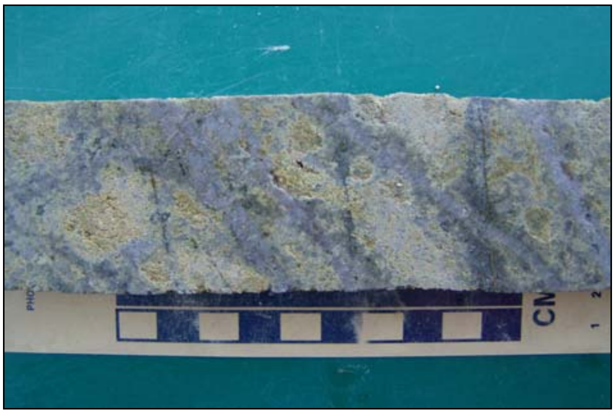

Fig. 10. Quartz veins with presence of argillitization of late stage

Among the rest, clearly can be noted that the deeper parts of the drill holes are characterized by late igneous occurrances as clasts of quartz veins, igneous breccias with quartz basis mass and some aplite structure. Also, should be said that at the top of this deep intrusive system is registered an appearance of typically developed system of alteration to the "worm-like" silicification.

Based on data derived from examinations and explorations, Ilovitza deposit by its characteristics can be set aside as copper porphyry deposit of type of deposit Scurries in Greece, which represents one of the first discovered porphyry deposits in Lecce–Chalcidice metallogenic zone.

Similar hydrothermal alterations, altered zones and mineralization which are present in Ilovitza deposit can meet and among many other porphyry deposits, such as Chukvikamata, Chile (Sinclair, 2009).

However, the characteristic mark of the Ilovitza deposit is its intense and widespread hydrothermal alterations, the deep zone of sulphide oxidation, leaching and argillitization.

CONCLUSION

The recent detailed explorations and examinations of the “Ilovitza” deposit pointed out on the presence of the polymetallic Cu-Au-Mo porphyry deposit, located within Tertiary intrusive complex, whose mineralization is closely related to intensive hydrothermal alterations of surrounding rocks.

The hydrothermal alterations are allocated on the basis of the typemorphic and characteristic follow minerals. Between them can be separated the following types of hydrothermal alterations: supergene sulphide alteration, weak propylitic alteration, advanced argillic alteration, quartz-sericite-pyrite ("phyllic") alteration and potassium metasomatism with the presence of intermediate argillic alteration. The ore mineralization in the biggest part is related to the zones where is developed the quartz-sericite-pyrite alteration and potassium metasomatism with the presence of intermediate argillic alteration, as well as in their contact parts. From aspect of the developed zones of hydrothermal alterations in "Ilovitza" deposit, may be noted that with him have can been developed the main zone of alterations that is also present almost in all porphyry deposits.

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Р е з и м е

ТИПОВИ НА ХИДРОТЕРМАЛНИ АЛТЕРАЦИИ ВО НАОЃАЛИШТЕТО „ИЛОВИЦА“

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Клучни зборови: порфирски систем; интрузивен комплекс; необиотитизација; кварц-серицитизација; силификација; аргилитизација

Како резултат на неодамнешните истражувања, наоѓалиштето „Иловица“ е издвоено како полиметалично порфирско наоѓалиште на Cu-Au-Mo, во рамките на Терциерниот интрузивен комплекс, чија минерализација пројавува карактеристики на тесна поврзаност со интензивните хидротермални алтерации на околните карпи. Ова наоѓалиште претставува дел од неколкуте порфирски системи во источна Македонија и северна Грција кои се во асоцијација со магматските комплекси и се вбројува во наоѓалиштата од типот на наоѓалиштето БуковиќКадиица во Република Македонија и Скуриес во Грција. Хидротермалните алтерации, како посебен белег на наоѓалиштето, со нашите лабораториски испитувања, беа одредени како алтерации кои ги карактеризираат порфирските системи. Помеѓу нив се издвојуваат необиотитизација, кварц–серицитизација, силификација, аргилитизација итн. Една од најинтензивните алтерациони промени е силификацијата (околу 49%), која во асоцијација со алунитизацијата (околу 40%), ги зафаќа апикалните делови на интрузивниот комплекс.

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Original scientific paper

HEAVY METALS IN THE WATER FROM THE DRAIN-BASIN OF THE MAVROVICA HYDRO-ACUMULATION – EASTERN MACEDONIA

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A b s t r a c t: In this paper the results and conclusions from the researches of the pollution of the water with heavy metals in the drain-basin of Mavrovica hydro-accumulation are given. With our analysis, there is an effort made to see the real conditions in the examinated area, and to determine the position of presence of heavy metals in the water of the above mentioned basin. The samples of water were taken from river Orelska and the smaller rivers (streams) near river Orelska. The analyses of the taken samples were made in the frames of one sequence of analysis of the instrument Atomic emissive spectrometry, with inductive harnessing plasma (AES-ICP). From the last examinations of contaminated areas as our area of interest, we can notice that the following group of elements should be kept track of: Mn, Fe, Al, Pb, Zn, As, Cd, Cu, Ni, Co, Ag, Cr, Ti with the possibility of several elements that will show higher concentrations of MAA (maximum allowed amounts). After the analysis and interpretation of the data, the assumptions were confirmed for increased values of the following metals: Al, Mn, Fe, Zn, As, Cd, Cu. The whole drainage system that gravitates trough river Orelska is contaminated. Increased concentrations of some of the metals were very often, several times above the maximum allowed concentrations.

Key words: heavy metals; pollutions; AES-ICP; water; river Orelska; river Makreska, river Kiseličkа, drainage area

INTRODUCTION

The pollution of the living environment in the past several decades is subject of which was given very little attention, but in the last several years this is very delicate subject with high priority. Very important is the problem of heavy metal and toxic metals presence – contaminates in the drinking water. Actualizing this question, we must say that the supply with drinking water, of the local population in the past period is strictly from the hydro-accumulation Mavrovica. Because of the suspicious quality of the water from the above mentioned accumulation during 2003 there was a decision made, for forbidding the further usage of the water of this accumulation for drinking water. Having this fact in mind there is a need for one more studious analysis of the water in this drainage-area.

There are more confluents of river Orelska that are used by the local inhabitants f or different needs. In the near by environment of the above mentioned area, there are large number of agricultural surfaces that are used for manufacturing different agricultural products. The last geological, geochemical and ecological researches showed the potential possibilities of natural pollution in the examined area. Even more significant reason for getting across this thesis is more and more strict legal standards for the quality of the living environment in which people lives, and work in this region.

In the research of the chemical and geochemical characteristics of the flowing water from the drainage area of the Mavrovica hydro-accumulation, and her near surrounding, in this period, were very little examinated. The data from this researches can be found in the papers of Ракичевиħ at al. (1968), Карајовановиħ at al. (1975a and 1975б), Думурџанов at al. (1976), Ѓузелковски (1997). Spasovski at al. (2007, 2009, 2010).

The area that was under research is covering river Kiselička, river Makreska and river Orelska until it's infusion in the Mavrovica accumulation (Fig. 1).

Fig. 1. Map of Republic of Macedonia with specified condition of the researched area

MATERIAL AND METHODS

In the frames of the researches there were preliminary field activities made, that were consisted from preliminary monitoring of the area, in order to gain preliminary impressions of the field.

Starting the field experiments there are the points of research defined, and in the same time the profile lines, which are defining basic field of research were defined. In the frames of foreseen activities, there are basic field researches made, that are consisted of preliminary tracking the field trough topographic determinations of the points of testing, and determination of the profile lines, from which the water samples will be taken. In the frames of this phase the field that embraces the flow of river Orelska and surrounding streams, starting from river Kiselička trough Blagin dol, to the inculcation of river Makreska in river Orelska, continuing to the inculcation to the mentioned hydro-accumulation were cultivated.

Starting phase of the experiment was taking samples from water from the named points of examination. Taking the samples from water is consisted from taking samples of water from the middle of the river flow, in clean plastic dish (plastic bottle from 1 L).

It is necessary to say that during assumption of the samples from the water, in the same time the filtration is done, trough paper filter with dimensions of the caliber of 45 μm. Before closing down the dishes, acidifying with 0.4 ml from 50% nitrogen acid (HNO_3) is done. This measure of caution is done in order to prevent sedimentation of the metals on the walls and the bottom of the dishes. Taking the samples was followed with certain determination of the points of experiment with help of topographic map in proportion 1 : 25 000. Laboratory examinations are consisted from analysis of taken samples with the method AES-ICP and interpretation of the gained results.

RESULTS AND DISCUSSION

In the frames of the foreseen examinations, samples from the water were taken from the middle of the river flow where the water shows calm flow. Every test is marked with unique number, and the places of the taken samples in the field are shown on the topographic map (Fig. 2).

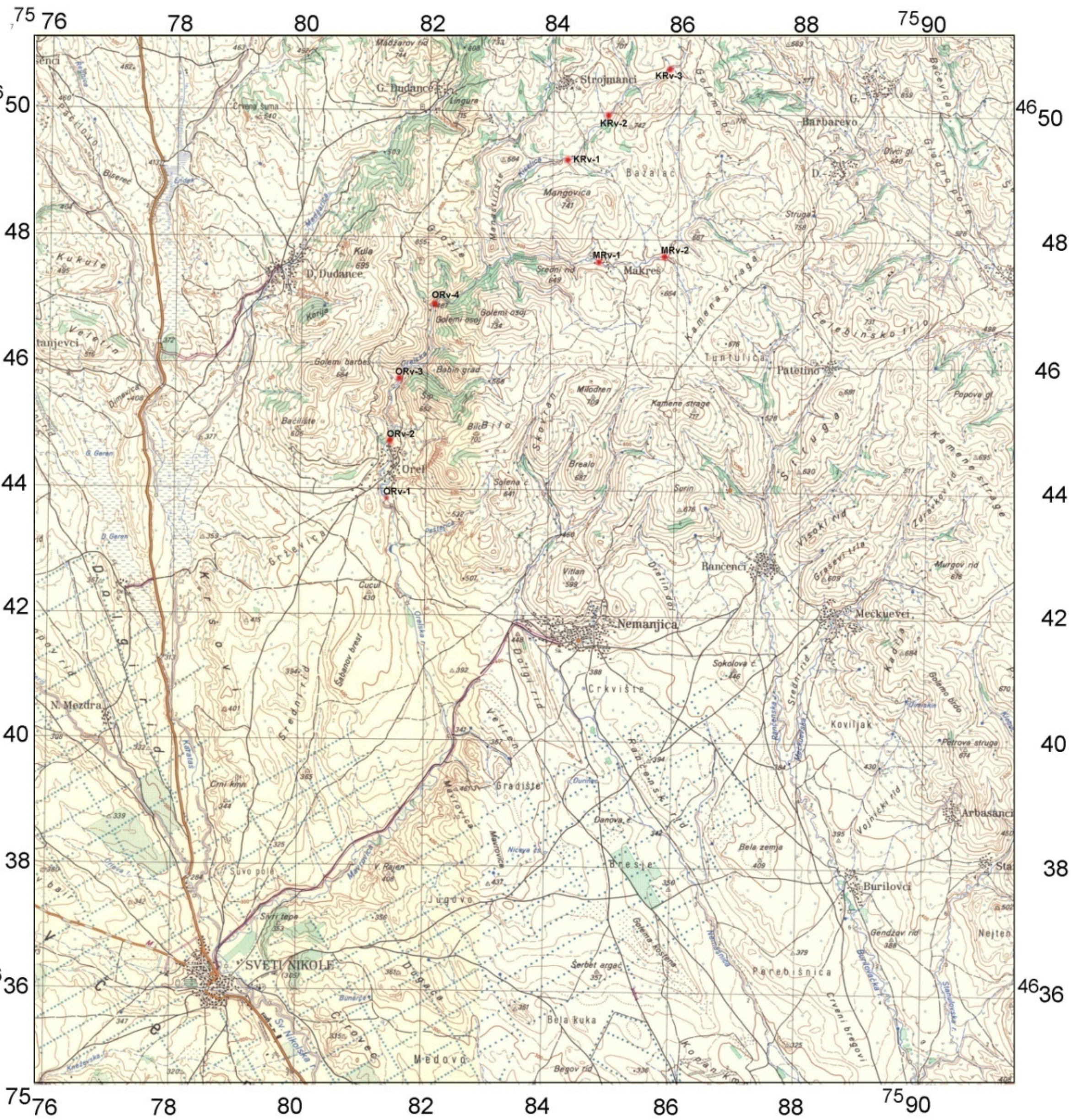

Fig. 2. Topographic map with pointed places of taken samples of water.

The results that are gained for the contents of the heavy metals in the water from the drainage basin of hydro-accumulation Mavrovica are given in Table 1.

To receive more complete impressions for the concentration of the analyzed elements, in the samples of water, taken from the drain area of Mavrovica hydro-accumulation, in the further examinations will be exhaustively presented and commented the results given in Table 1.

In the same table there are also given the standards for the contents of the analyzed elements in the moving water, in order to compare gained results with the standards.

In the basis on the data, given in Table 1, certain notes can be given, about the presence of certain heavy metals in the water from her confluents, and also the opinion for the reasons that redound to increased contents of certain metals.

Calcium in the tests taken from river Orelska and Makreska is showing in amounts, smaller than maximum allowed concentrations. In the tests taken from river Kiselička calcium is showed in values higher than maximum allowed concentrations. Highest values for magnesium are seen in the test KR-3 (279.60).

T a b l e 1

Content of heavy metals in the flowing water from the drainage basin of Mavrovica hydro-accumulation.

	ORv-1	ORv-2	ORv-3	ORv-4	MRv-1	MRv-2	KRv-1	KRv-2	KRv-3
As	0.008	0.005	0.111	0.001	0.004	0.035	0.0001	0.0001	0.0001
Stand	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Se	0.008	<0.005	0.035	0.004	0.005	0.004	0.0001	0.0003	0.0001
Stand	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Ag	0.012	<0.001	0.001	0.004	0.005	0.004	0.0001	0.0003	0.0001
Stand	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002
Al	0.003	0.002	0.012	0.238	4.67	5.21	69.15	71.12	72.89
Stand	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Ca	78.545	60.026	74.492	68.07	96.19	90.15	279.20	266.14	279.60
Stand	200	200	200	200	200	200	200	200	200
Ni	0.003	0.032	0.021	0.004	0.0054	0.0050	0.0050	0.049	0.052
Stand	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Mn	0.013	0.010	0.016	0.012	0.0049	0.005	4.41	4.93	5.47
Stand	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Fe	0.089	0.020	0.081	0.062	0.029	0.032	5.45	5.76	5.95
Stand	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Cr	0.001	<0.001	<0.001	0.001	0.004	0.004	0.001	0.001	0.001
Stand	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Mg	18.765	23.449	20.266	15.42	16.23	17.46	52.14	47.12	52.09
Stand	150	150	150	150	150	150	150	150	150
Na	20.700	21.526	19.198	22.46	29.06	29.20	66.79	63.45	66.79
Zn	0.009	0.011	0.081	0.579	0.012	0.010	0.61	0.55	0.71
Stand	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Cu	0.006	0.008	0.009	0.008	0.011	0.010	0.022	0.023	0.028
Stand	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Pb	0.001	0.001	0.010	0.017	0.007	0.006	0.002	0.001	0.002
Stand	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Cd	0.001	<0.001	<0.001	0.001	0.0017	0.0018	0.0032	0.0033	0.0048
Stand	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
Co	<0.001	0.001	0.014	0.026	0.017	0.019	0.142	0.145	0.150
Stand	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Na	20,700	21,526	19.198	22.46	28.12	29.06	55.14	58.15	66.79
K	4.041	3.503	5.588	5.852	6.976	6.986	9.451	9.392	9.426
pH	5.98	6.81	6.88	5.93	–	–	–	–	–

Symbols of taken samples: ORv – sample of water taken from river Orelska; MRv – sample of water taken from river Makreska; KRv – sample of water taken from river Kiselička

Magnesium, not like calcium, in all the tests is shown in concentrations lower than maximum allowed concentrations. What is interesting for this element is gradually increasing its values, going towards headwater of the studied rivers, and especially river Kiselička where are the highest values of 52.09 mg/l (sample KRv-3).

The values gained for alkaline metals Na and K are showing significant variation in the analyzed samples. The values that are gained for Na are moving in the frames from 19.198 mg/l in the sample ORv-3 to maximum of 66.79 mg/l in the sample KRv-3. Potassium is shown in concentrations significantly smaller compared to Na, and the same are moving in the frames from 5.03 in the sample ORv-2 to maximum 9.451 mg/l in the sample KRv-1.

The data for ferum (Table 1) are showing its small presence in the largest number of analyzed samples. The exception makes only the samples of water from river Kiselička, where the ferum is noted with values larger than maximum allowed concentrations and are moving in the frames from 5.45 mg/l (sample KRv-1) to 5.95 mg/l (sample KRv-3). Down the river Kiselička flow, a red deposit can be noticed, because of the presence of the oxides if ferum, but also the water is showing acetic taste.

Aluminum presents the biggest infector of the whole studied area. In the water samples taken from river Orelska, the values that are gained during the examination are lower than maximum allowed concentrations. The values gained for the aluminum in the samples of water in river Makreska and river Kiselička are showing its significant presence in this two rivers. Namely, the values for aluminum in the samples of water from river Makreska, are more than 10 times higher than maximum allowed concentrations. The results that are gained for the aluminum in the analyzed water samples from river Kiselička are showing very large contamination of this space with aluminum, indeed the values that are higher over 146 times compared to standards.

Significant infector of the studied area is also the zinc. The values gained for zinc in river Orelska (0.579 mg/l) and in the samples of water from river Kiselička (0.55 to 0.71 mg/l), are confirming very clearly its presence in the studied area. These values are showing that the concentrations of zinc are 7 times higher compared to the standards.

Manganese, like the zinc is significant infector of the researched area. The values that are gained for manganese in the river Kiselička are moving in the frames from 4.41 to 5.47 mg/l are around 10 times higher compared to the standards, and by that, it is confirmed its large presence in the examinated area.

Nickel, cobalt and cadmium are noted in every examinated samples, but the values that are gained in the largest number of the samples are lower than maximum allowed concentrations. In the samples of water taken from river Kiselička, of the above mentioned elements, the values that are gained that are higher, but also very close to the standard values.

Cuprum, plumbum and chrome in all tested samples are shown in concentrations that are lower than MDK and are not presenting contaminates in the researched area.

CONCLUSION

According the results that are gained, from the accomplished chemical researches for the content of heavy metals, in the flowing water from drainage basin of hydro-accumulation Mavrovica, it can be concluded that certain group of elements (Al, Mn, Zn, Fe), in biggest part from researched samples, are showing significant enlargement compared to MDK. Other group of elements (Ni, Co, Cd) is showed in concentrations very similar to the standard values, and the third group is elements (Cu, Pb, Cr) that are showing very low values according to MDK.

The researches are showing that there is legislative in the allocation of the elements that are infectors, in fact their continuous tracing and gradually enlargement of their values starting from river Orelska to Kiselička. This kind of appearance of the elements-contaminants, clearly can locate the natural source of contamination, the area around the source of river Kiselička.

For the metal concentrations in the flowing water, geological composition of the researched area has influence, geochemical characteristics of the elements-contaminates, as well as pH and Eh factors.

This conclusions and notes are based on relatively small number of researches (total 9 samples of water), but any way they are giving clear picture for presence of certain group of elements-contaminants. The values that are gained for the examinated elements, are initializing larger amount of problems (research of inculcation of river Orelska in hydro-accumulation Mavrovica, awareness for the composition of water in hydro-accumulation, monitoring of the water in different time periods, examinations of mineralogical and chemical composition of the environment trough where the flowing water are passing) with aim to see the source of contamination and the influence of the elements that are contaminants of the living environment.

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Р е з и м е

ТЕШКИ МЕТАЛИ ВО ВОДАТА ОД СЛИВНОТО ПОДРАЧЈЕ НА ХИДРОАКУМУЛАЦИЈАТА МАВРОВИЦА Ђ ИСТОЧНА МАКЕДОНИЈА

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Клучни зборови: тешки метали; загадување; AES-ICP; вода; Орелска Река; Макрешка Река; Киселичка Река; сливно подрачје.

Во овој труд се дадени резултатите и заклучоците од истражувањата на загадувањето со тешки метали во водата од сливното подрачје на хидроакумулацијата Мавровица. Со нашите испитувања, направен е обид да се согледаат реалните состојби во испитуваниот простор и да се утврди состојбата за присутноста на тешките метали во водите на споменатиот простор. Примероци на вода беа земени од Орелска река и помалите реки од нејзината непосредна околина. Анализата на примероците беше спроведена во рамките на една серија на анализи на инструментот Атомска емисиона спектрометрија со индуктивно спрегната плазма (AES-ICP). Од досегашните искуства на контаминирање на подрачја какво што е подрачјето од интерес, може слободно да се констатира дека треба да се следи следната група на елементи: Mn, Fe, Al, Pb, Zn, As, Cd, Cu, Ni, Co, Ag, Cr, Ti со можност и некои елементи кои ќе покажат поголеми концентрации од МКД (Максимално дозволени количества).

По анализата и интерпретацијата на податоците беа потврдени претпоставките за зголемени вредности на следните метали: Al, Mn, Fe, Zn, As, Cd, Cu. Контаминиран е целосниот дренажен систем кој гравитира кон Орелска река.

Зголемените концентрации на некои од металите многу често беа за неколку пати поголеми од максимално дозволените концентрации.

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Original scientific paper

THE POSSIBILITY OF USE OF KREMIĆ GRANITOID (SERBIA) AS AN ARCHITECTURAL STONE

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A b s t r a c t: The stone from the granitoid pluton of Kremić in southern Serbia has been examined in order to evaluate the possibility of its use as an architectural stone. Both field observations and laboratory testing of specimens have been performed. Although the specimens were collected from the field surface level, their physico-mechanical lab test results have shown that the rock mass itself fulfils all the requirements for use as an architectural stone set by the State through Serbian standards. Also, the stone quality is higher in deeper ground levels, where the weathering agents have less intense effects. This stone does not have high ornamental properties, but it has a fine-grained texture and low mica content which has a positive effect on its technical characteristics and susceptibility to processing.

Key words: granitoid; pluton; southern Serbia; architectural stone

INTRODUCTION

Kremić pluton is one of the many investigated under the author's dissertation whose theme is the potentiality of Vardar zone magmatic masses for use as an architectural stone. This plutonite is particularly interesting because it hasn't been investigated from this aspect before and the rock mass fulfills all the requirements for architectural purposes and, unlike other plutons in the Vardar zone, this rock does not contain excessive pyrite.

The Kremić granitoid pluton is situated in southern Serbia, NE from the city Raška. The majority of authors consider it the part of Kopaonik pluton (Urošević et al. 1973; Janković, 1990; Karamata et al. 1992), situated 2 km to the east, on the very border with Kosovo. A belt of schists and serpentinites separates these two plutons at the surface. The present level of erosion yields a Kremić granitoid plutonite surface of about 7 km^2. Due to poor accessibility and scarce outcroppings, Kremić granitoid is by far less examined compared to the near-by Kopaonik pluton. Also, the architectural stone has never been extracted in it, nor has its potentiality for this purpose been evaluated.

GEOLOGICAL SETTING

The oldest uncovered rocks belong to the upper Paleozoic low-metamorphic series of schists, metabasites, marble etc., known as Veleš series (Wilson, 1933). Magma that gave Kremić granitoid pluton intruded the Veleš series schists, serpentinites and volcanic complex, and metamorphosed them (Mićić, 1966, 1980). Serpentinized periodtites, mostly hartzburgites, represent a part of the "Ibar ultramafic complex". The proximity of the three main fault zones of the Vardar zone in Kopaonik area (Vukašinović, 2005) caused the intense magmatic activity. Volcanic rocks – dacito-andesites, lamproandesites, pyroxene-amphibole andesites, volcanic breccias etc., mostly hydrothermally altered, were formed in Oligocene-Miocene (Urošević et al. 1973). The geological setting is shown in Figure 1.

In geotectonic sense, all the plutonic masses of Kopaonik area (Kremić, Željin, Drenje, Crvanj etc.) belong to the Vardar zone, i.e. its sub-unit – Kopaonik unit or block-ridge terrane (Dimitrijević, 1995; Karamata, 1995, 2006; Robertson et al. 2009). This sub-unit spreads to north towards Belgrade and to the south continues into Paikon unit in Greece (Karamata, 2006; Robertson et al. 2009). Magma is intruded into so-called Kopaonik anticline which is disrupted by the east-west trending faults. This fault system was the main magma conduit (Karamata et al. 1992).

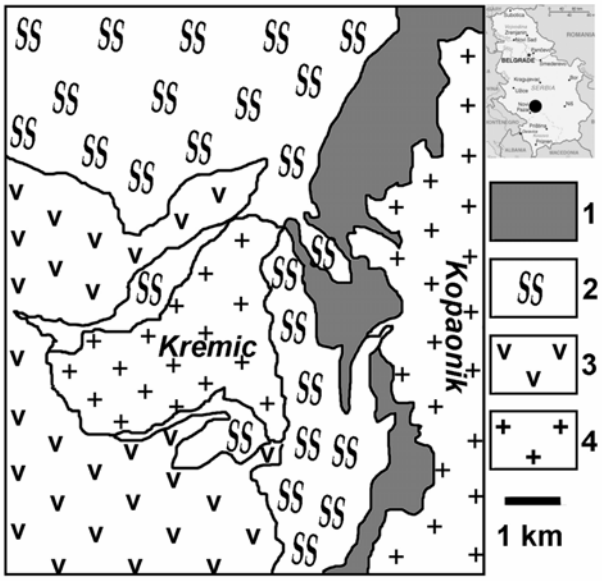

Fig. 1. Location of Kremić granitoid in Serbia (up, right). Simplified geologic map (left) of Kopaonik-Kremić area. Key: 1 – Veleš metamorphic series, 2 – serpentinized peridotites, 3 – volcanic rocks, 4 – plutonic rocks.

Petrologic and mineral composition and age

Many authors consider Kremić pluton to be a marginal facies of Kopaonik pluton, based on identical chemical (Table 1) and mineral compositions. Granodiorite, amphibole-biotite quartz-diorite and biotite quartz-monzonite with K-feldspar porphyroblasts show mutual transitional boundaries (Urošević et al. 1973; Janković, 1990; Karamata et al. 1992). Subvolcanic rocks (microgranodiorite, microquartzdiorite, aplite, pegmatite, lamprophyre) are also present (Mićić, 1966).

The rock texture is hypidiomorphic granular, in places grading into inhomogeneous granular close to porphyritic. General mineral composition: andesine (zonal, average An38.5 %), orthoclase (cryptopertite, sometimes partly transformed into microcline), quartz (undulate), biotite (more or less transformed into hornblende), hornblende, accessories (magnetite, apatite, zircon, ortite, sphene) (Karamata, 1957).

Table 1

Chemical composition of Kremić granodiorite (Mićić, 1980)

Component	Content (%)
SiO_2	60.56
TiO_2	0.70
Al_2O_3	17.69
Fe_2O_3	2.85
FeO	3.05
MnO	0.06
MgO	3.17
CaO	5.75
Na_2O	1.94
K_2O	2.96
P_2O_5	0.30
$H_2O^{+110°}$	1.22
$H_2O^{-110°}$	0.09

Tertiary granitoid rocks of Kopaonik area belong to the Dinaric suite of calc-alkaline magmatic formation of Serbian part of the Balkan peninsula, of late Paleogene-early Neogene age (Cvetković et al. 2002). According to Urošević et al. (1973), all the small plutonic masses in the area were formed in the same cycle of magmatic activity and are supposed to represent the parts of a larger, still covered pluton. All these granitoids are I-type, with identical trend from quartz-diorite to granodiorite and quartz-monconite, locally granite (Karamata et al. 1992).

Isotopic age analyses (Karamata et al. 1992) have shown that all the plutons in Kopaonik area were formed penecontemporaneously, in Oligocene (K/Ar age 29-35 Ma). K/Ar analysis for Kremić granitoid yielded the age of 32 Ma (on biotite).

TESTING METHODS

As a part of the PhD dissertation, and in accordance with regulatory provisions valid in the Republic of Serbia, the stone from Kremić granitoid pluton has been examined according to Serbian standards – SRPS.B.B3.200:1994 as the basic one and the standards cited therein. The testing is performed in The Stone and aggregate Laboratory of the Materials testing institute in Belgrade. Field examinations were performed during 2009, on available outcrops, on the regional prospecting works level (Vakanjac, 1976). Since the rock mass is not well uncovered, the specimens taken originate from the field surface. As a consequence, there were some hidden fractures in lab samples due to increased weathering level. However, the testing samples have shown plausible values of physico-mechanical characteristics. Undoubtedly the specimens from greater depth will show even better results.

Testing results

Field works. The available crop is situated near the granitoid-serpentinite contact. Granitoid rock has a grey colour, varying from darker to lighter shades. The heterogeneous look is due to more or less dense disposition of mafic minerals. The general look of this rock is very similar to marginal facies of Kopaonik pluton.

The rock has irregular and platy jointing. The plates are about 40 cm thick, cracked into smaller fragments of the longest axis up to 50 cm (Figure 2). Along some plate boundaries the weathering disintegration occurs. The deeper rock parts have blocky setting. Fracture systems have dip direction and dip angle: 127/56 (dividing the rock into plates); 198/50; 30/53 and 147/84 (dividing the plates into smaller pieces).

Topsoil is around 20 cm thick. In more weathered parts the feldspars become lustreless and stained with limonitic colouring and mafic minerals oxidized. On the granitoid-serpentinite contact, both rocks are intensely altered and powdery.

In spite the fact that the rock is exposed to weathering, it is compact and breaks hardly. Deeper parts are increasingly more fresh and compact.

Aplitic-pegmatitic veins are present, but far less than in adjacent plutons (Drenje, Željin).

Fig. 2. Platy jointing of Kremić granitoid rock.

Xenoliths of various shapes and sizes are present (Figure 3). Some look like the host rock, some are more mafic, others resemble schists. The most is up to 5 cm and isometric in shape.

The texture of the rock is fine-grained, the structure is homogenous. The hornblende grains show lineation only in the border zones.

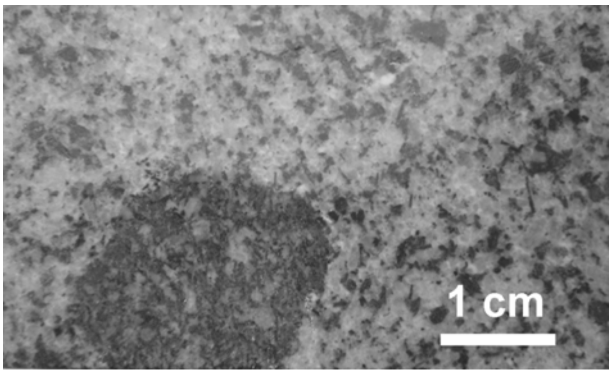

Fig. 3. Xenolite in Kremić granitoid rock.

Lab testing

Physico-mechanical properties testing and microscopic study. Some testing prisms when cut show cracks and fissures. They break mostly along these cracks during testing. Possibly also the presence of large grains predisposes the surface of break. Flexural strength prisms with no cracks have shown very high values, and those with cracks broke immediately and have therefore not been taken into account. The breaking surface is irregular and rough.

Table 2

Lab testing results of physico-mechanical properties for Kremić stone.

Property	Standard SRPS	Units	Testing results	
			variation range	average value
Frost resistance	B.B8.001	–	no visible changes	durable
Resistance to Na_2SO_4	B.B8.002	–	no visible changes mass loss 0.01–0.03%	durable 0.02% mass loss
Water absorption	B.B8.010	%	0.23–0.68	0.40
Compressive strength – dry – water saturated – after 25 freeze-thaw cycles	B.B8.012	MPa	 153–189 100–164 95–154	 169 136 134
Abrasion resistance	B.B8.015	$cm^3/50\ cm^2$	9.71–10.59	10.01
Flexural strength	B.B8.017	MPa	31.06–32.51	31.97
Apparent density	B.B8.032	g/cm^3	2.660–2.698	2.678
Real density		g/cm^3	2.703	2.703
Density coefficient		–	0.991	0.991
Porosity		%	0.9	0.9

MINERAL AND COMPOSITION

Macroscopic petrographic examination

Both felsic and mafic minerals can be observed. Felsic are feldspars and quartz, mafic comprise hornblende and biotite. Most grains are up to few millimetres. Only the largest K-feldspar porphyroblasts reach over 1 cm.

Feldspars are whitish-grey, translucent to opaque, sub- to anhedral. The samples from the greater depth contain more fresh and translucent feldspars. The largest porphyroblasts have pale purple colour. K-feldspar porphyroblasts occurrence is not rare in Vardar zone granitoid plutons; Divljan and Cvetić (1991) explain its origin by postgenetic K-metasomatosis on a regional scale.

Quartz is rare, probably due to increased basicity of these marginal parts of the intrusion. The grains are mostly isometric in shape, colourless, transparent and cracked.

Mafic minerals grains are mostly up to 1-2 mm in size. Hornblende grains are subhedral, sometimes up to (9x4) mm in size. Euhedral hornblende grains are more rare and up to (8x5) mm in size. In the samples taken from the surficial level, it shows oxidation signs but deeper in the rock mass it is more fresh.

Biotite content is smaller than hornblende; flakes are subhedral, fresh, black in colour, most often up to 2 mm, rarely up to 4 mm in length. Flake aggregates are up to 5-6 mm thick.

Microscopic study

The rock contains plagioclase, quartz, orthoclase, biotite, amphibole and pyroxene.

Plagioclase makes up around 50% of the rock. The grains are most often prismatic, rhombic and xenomorphic. Grains show minor alteration. Larger grains are poikilitic, containing metallic minerals, biotite and apatite. Synthetic and lamellar twins are present.

Quartz is intergranular, xenomorphic, rarely with cataclastic parts. Makes up about 20 % of the rock.

Orthoclase is present as large, xenomorphic to ellipsoidal grains, mostly up to (3x3) mm, with minor sericitization; poikilitic, containing plagioclase and mafic minerals.

Biotite is mostly fresh, tabular, with etched margins, rarely chloritized. Often spatially connected with hornblende into small aggregates of mafic minerals.

Amphibole is represented with hornblende of variable chemistry, reflected through colour changes from green to brown. Grains are xenomorphic to hypidiomorphic, altered in a variable degree.

Clinopyroxene has oval grains up to (0.3×0.2) mm, mostly altered.

Metallic minerals occur as grains under 0.1 mm, round or angular, sometimes making up the small piles. Apatite is most often poikilitically caught up in larger grains of other minerals.

Texture: hypidiomorphic granular.

Structure: homogenous

Rock type:

– according to mineral composition: granodiorite

– according to chemical composition: transition from granodiorite to quartz monzodiorite

Crystallization order: biotite, hornblende, clinopyroxene, plagioclase, orthoclase, quartz.

DISCUSSION – EVALUATION OF THE TESTING RESULTS

According to Bilbija (1984) criteria, physico-mechanical properties of the stone are characterizing the tested stone in the fallowing way:

– Density value characterizes it as a heavy stone.

– Porosity characterizes it as being compact.

– Water absorption is very low.

– Resistant to freeze and salt crystallization actions.

– Compressive strength is high.

– Abrasion resistance characterizes it as being on the boundary between hard and very hard.

According to the requirements prescribed in the standard SRPS B.B3.200, and the results of the physico-mechanical properties testing, this stone can be used for paving and cladding both in exteriors and interiors, for all load categories.

CONCLUSION ON USAGE AS AN ARCHITECTURAL STONE POTENTIALITY

The specimens for testing were taken from the surface where weathering was most intense, yet, lab testing results have shown that this stone is in full accord with the requirements of the Serbian standards. In the deeper ground levels, the rock mass passes from platy to blocky and is less affected by weathering, and will have even better results. Based on the results of all the examinations, it is concluded that the stone from Kremić granitoid pluton can be used as an architectural stone.

This rock is fine to medium-grained and has low mica content, which gives it a great potential to have plausible physico-mechanical properties and susceptibility to processing (cutting, polishing etc.). Absence of pyrite gives it a time perseverance for external applications. The flaws of this stone are the following: average ornamental value, heterogeneity of the appearance; xenoliths. However, this rock mass is barely opened by the erosion and there is a great possibility that is becomes more ornamental in its deeper parts, alike the nearby Kopaonik pluton that many authors consider Kremić pluton to be a part of. Kopaonik pluton is now included into the territory of a National park with no mining allowed; heterogeneity of the appearance becomes imperceptible after the stone is polished and also when the slabs are riven (Figure 4). It should be noted that in Serbia today, almost all the architectural stone comes from the import under the excuse that Serbia has no good quality stone deposits.

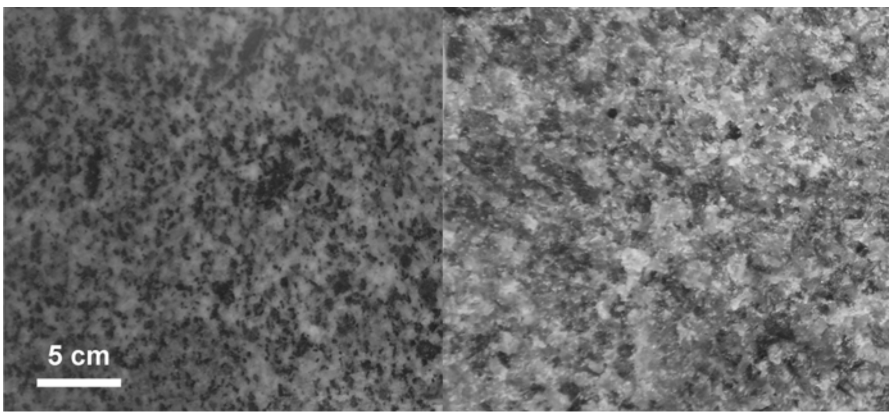

Fig. 4. The look of the polished (left) and riven (right) surface.

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Р е з и м е

МОЖНОСТ ЗА УПОТРЕБА НА ГРАНИТОИДОТ КРЕМИЌ КАКО АРХИТЕКТОНСКИ КАМЕН

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Клучни зборови: гранитоид; плутон; јужна Србија: архитектонско-градежен камен

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