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PALEOZOIC SODIUM METASOMATISM IN THE WESTERN BALKAN RANGE (BULGARIA)

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ABSTRACT

Low-temperature sodium metasomatites are established in many places of the Western Balkan Range. The deformed rocks of the diabase-phillite complex are affected mainly by sodium metasomatism. The metasomatites are composed of albite, quartz, sericite, chlorite, calcite, ferrodolomite, hematite and accessory minerals (apatite, zircon, leucoxene). The petrochemical and geochemical characteristics of the metasomatites are studied in this paper and the behaviour of the particular oxides and elements is traced during the metasomatic process. In comparison to the parent unaltereted rocks, sodium metasomatites have considerably higher contents of Na_2O, SiO_2, CaO, FeO, MnO and increased concentrations of U, Mo, Th, Ta, La, Sm, Ba, Hg , Nd, Hf.

INTRODUCTION

The low-temperature sodium metasomatites are rather widely developed in the exocontact parts of the Balkan Range calcium-alkaline intrusives. Their regional distribution and the rare metal mineralisation necessitated their detailed examination.

Sodium metasomatites were found in a lot of places in the Western Balkan Range: in the region of the villages of Chuprene and Stakévtsi, (Belogradchik district), between the villages of Kostentsi and Pesochnitsa, along the valleys of the Proboinoitsa, Gabrovnitsa, Elenov Dol rivers etc. Their regional distribution as well as the geological interest with regards to their metallogenic characteristics necessitated an extensive research (Marinov, Bakardjiev, 1988; Marinov, 1988; Marinov, 1991). These are a lot of data gathered from field and laboratory investigations which allow to characterize the metasomatic bodies, their morphology and geological affiliation.

GEOLOGICAL POSITION

Low-temperature sodium metasomatites are widely exposed in the exocontact parts of the Petrohan granitoid pluton between the villages of Kotenovtsi and Mezdrea (Berkovitza district) where they are studied in detail. They crop out in a region built up of Early Paleozoic granitoids, Triassic and Jurassic sediments.

Boyadjiev, 1970; Ivanov,1972; Kunov, 1974) relate the Early Paleozoic rocks to the so-called diabase-phillite complex. Recently two

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lithostratigraphic groups were specified in this complex - Berkoska and Dalgidelska (Hajdutov et al., 1979).

The Middle Paleozoic calc-alkaline magmatic rocks are represented by hypabyssal magmatic bodies, intruding the Early Paleozoic rocks (Fig. 1). Both Mezdrea and Kotenovtsi intrusives are considered by Dimitrov (1927, 1930) as a uniform body, formed during an individual magmatic impulse after the Petrohan intrusion. Recently these magmatic bodies are accepted

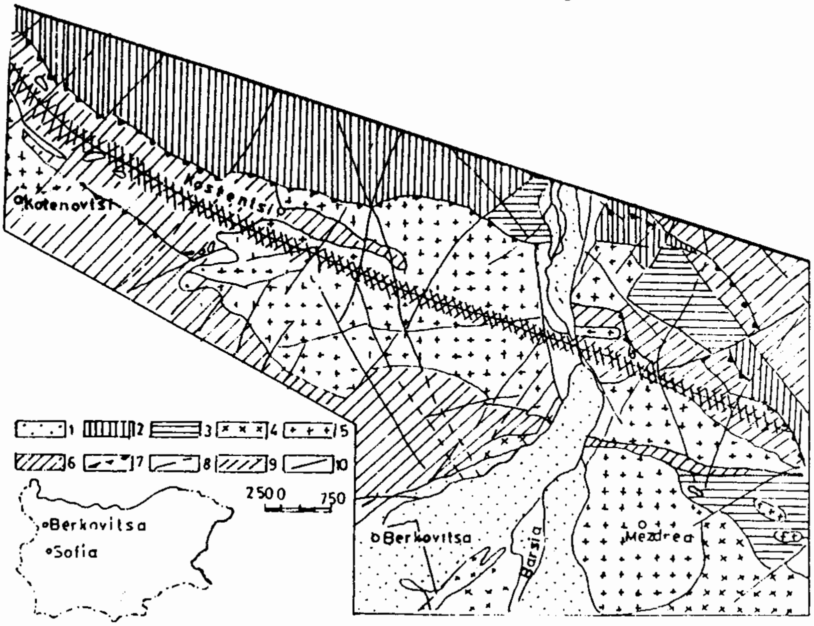

Fig. 1: Geological map of the region: 1 - Quaternary; 2 - Mesozoic sediments; 3 - Early Paleozoic rocks (Carboniferous - Permian); 4 - Petrohan intrusive; 5 - "Mezdrea type granites"; 6 - Rocks of the diabase-phillite complex; 7 - reverse fault; 8 - fault; 9 - Plakalnitsa dislocation; 10 - Profile line.

as metasomatic boundary parts with apophyses of the Petrohan intrusive (Marinov, 1975, 1977).

With regard to tectonism, the region is situated in the Paleozoic core of the Berkovitsa anticlinorium, particularly in the Chiprovtsi anticline defined by Bonchev (1971). The northern limb of the anticline is separated from the Paleozoic core by the Plakalnitsa dislocation (Fig. 1).

The sodium metasomatism affected mainly the rocks of the so called Dalgidelska group of the diabase-phyllite complex. They are represented by quartz-sericite-chlorite, sericite-chlorite and quartz-sericite schists. There are phillitized diabase tuffs alternating with thin diabase spills and graphitized schists among them.

The sodium metasomatites occurred in the boundaries of the Kotenovtsi-Pesochnitsa fault zone and in the transverse faults. The areas affected by sodium metasomatism are mainly composed of tectonized rocks (cataclasites, tectonic breccia and milonites). This determines their complicated morphology. They crop out as veins, mounts and lenses (Fig. 2). Very often the matrix of the breccia and milonitized rocks is albitized.

According to petrographic and geochemical data from borehole cores, the contact parts of the intrusives were subjected to more intensive sodium metasomatism. For example, the total thickness of the metasomatized rocks

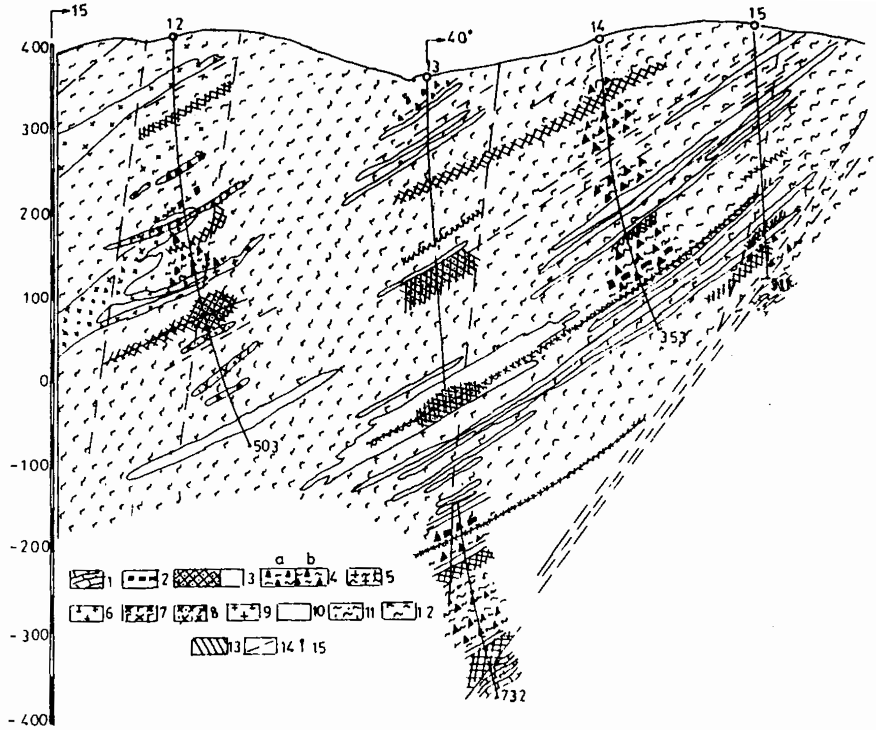

Fig. 2: Borehole geological section: 1 - Triassic limestones; 2 - Sulphide mineralization; 3 - Sodium metasomatites; 4 - Quartzitization: a - strong, b - weak; 5 - Potassium feldspatization; 6 - Alkaline metasomatites ("Mezdrea type granites"); 7 - Gabbrodiorites; 8 - Quartzdiorites; 9 - Granodiorites; 10 - Black graphite schists; 12 - Light-coloured quartz-sericite schists; 13 - Tectonic zone; 14 - Fault; 15 Borehole.

in the borehole, positioned most closely to the intrusive, is 65 - 70 m. To the north the thickness gradually decreases and at about 200 m from the intrusive contact it varies from 1 to 5 m.

The sodium metasomatites are pink-red, red-brown, compact rocks, sometimes with a breccia-like structure.

MINERALOGICAL AND PETROGRAPHIC COMPOSITION

The main mineralogical property of these rocks is the presence of the minerals albite, quartz, sericite, chlorite, calcite and ferrodolomite. Accessory minerals are apatite, zircon, xenotime, monazite, rutile, leucoxene, ilmenite. Ore minerals are pyrite, hematite and magnetite. Rocks with analogous peculiarities and mineral content were nominated as formational type - low-temperature sodium metasomatites or eisites (Omelianenko et al., 1974; Omelianenko, 1978).

Albite, hematite and calcite are the main minerals formed by the metasomatic process from the products of the low-metamorphosed rocks. The albite is a main typomorphic mineral for these rocks. Very often it possesses chess-like structure. It can be found as separate large crystals, mounts, lenses, porphyroblasts or veins. It is formed from plagioclase, quartz and K-feldspar. Albite, substituting for K-feldspar, is characterized by a chess-like structure. Among the carbonate matrix there is also a chess-like albite especially when the calcite crystals show dynamogenic twins, manifesting residual deformation. The sodium metasomatic process is also accompanied by the formation of apatite. Apatite crystals, among the microgranular main mass, occur with albite crystals, indicating that metasomatic apatite is related to the process of albitization.

The rocks described are densely meshed with ferrodolomites, calcite, quartz, hematite and chlorite veins. On the basis of their interrelation the order of their formation is as follows. First of all the ferrodolomites are formed followed by the albite, calcite and quartz-bearing rocks. The albite and chlorite veins are seldom crossed by the carbonate ones (Fig. 3).

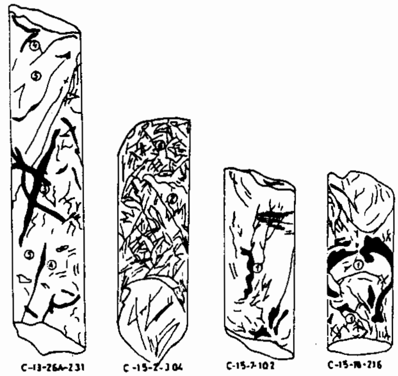

Fig. 3: Borehole cores, scale 1 : 1.1 - calcite; 2 - fissures; 3 - ferrodolomite; 4 - quartz; 5 - sodium metasomatites; 6 - fine veins (0.5 mm) - quartz, chlorite, hematite, carbonates, albite; 7 - hematite.

The colour of the albitized rocks is an important feature for their identification. The outcrops of high radioactivity rocks are mainly brown-red colour. The rock colour of different uranium deposits has been a subject of investigation of many authors (Ellsworth, 1932; Conybear, 1950). They have related the rock colour with the feldspatization by recrystallization or by addition of petrogenic elements.

PHYSICO-MECHANICAL PROPERTIES

With regard to the study of metasomatism, open capacity and bulk density of different rock varieties - unaltereted and metasomatized were determined. The character of the rock jointing was also determined (Marinov, Bakardjiev, 1988). The following conclusions can be drawn on the basis of the determined physico-chemical factors: a) The formation of the low-temperature metasomatites directly depends on the jointing and open rock capacity factors. The volume density depends on the open capacity, and to a certain extent it is a consequence of its magnitude. b) The correlation relationship between the open capacity and volume density is inversely proportional and significant; c) The open capacity and jointing factors differ not only in value but also in the interrelation each to a certain extent depressing the influence of the other. The high values of the tectonic jointing in comparison to those of background jointing are a precondition for both increasing the degree of the hydrothermal rock alteration, and for development of rare metal mineralization.

CHEMICAL COMPOSITION AND PECULIARITIES OF ROCK CHEMISTRY IN THE METASOMATIC PROCESS

The material collected about the chemistry of the initial and metasomatic rocks enables the description of a characteristic of their chemical composition as well as tracing the behaviour of particular petrogenic elements in the process of sodium metasomatism. The chemical analyses have been grouped according to the degree of the metasomatic rock alteration. As metasomatic rocks are treated sodium metasomatites and the hematitized quartz-sericite-chlorite schists. With the aim of expressing the general tendency in the behaviour of the main petrogenic oxides, petrochemical recalculations of the molecular quantities after the method of Kazitsin and Rudnik (1968) have been done and respective diagrams have been constructed (Table 1 - 3, Fig. 4).

By the mass balance (Fig. 4) it can be concluded that sodium metasomatism has a clear chemical trend. The metasomatically altered rocks have been enriched Na_2O, CaO, FeO and MnO, and have been depleted in K_2O and SiO_2 for the hematized rocks, and FeO and MgO for the sodium metasomatites. Na_2O was attending metasomatic solutions while a part of other oxides (CaO, MnO and TiO_2) were mainly mobilized from host rocks, and redistributed during the process of metasomatism. Because of the action of the solutions from the rocks affected by metasomatism, significant quantities of K_2O were permanently transported away. During the process of rock alteration the alkaline oxides had been exchanging each other, i.e. the higher sodium quantity in the metasomatites was compensated by lower potassium quantity. The ratio Na_2O/K_2O is the highest in the low-temperature sodium metasomatites - 3.18, and the lowest in non-alterated quartz-sericite-chlorite schists - 0.33. For the hematitized schists this ratio is 1.49. Red colour, caused by the ferroxides and the presence of hematite as inclusions in the minerals (albite, quartz, calcite) formed as a result of metasomatic process reveals that iron has been presented in both the solution and the relicts of the initial rocks.

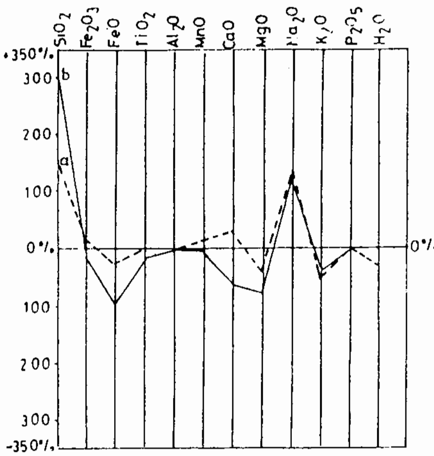

Fig. 4: Variation diagram of petrogenic oxides at sodium metasomatism of : a. quartz-sericite-chlorite schists; b. hematized quartz-sericite-chlorite schists.

GEOCHEMICAL FEATURES

With the aim of defining the element specificity of the initial and metasomatized rocks in the region data from borehole samples analysized by the NA method, the contents of the following elements are determined (ppm): Sm, Mo, Ce, Yb, Lu, U, Th, Cr, Hf, Ba, Nd, As, W, Cs, Ni, Tb, Sc, Rb, Zn, Ta, Co, Eu, La, Sb, Mn, K and Fe (Table 4).The comparison has been made on the basis of the average contents of the elements characterizing the particular rock types. The elements contained in the initial rocks have been compared to the same undergone sodium metasomatism.

The sodium metasomatites compared to the initial quartz-sericite schists present a higher content for the following elements (Fig. 5): U(27 times), Mo (15), Th (14), Ta (3.8), K (3.6), La (2.5), Sm, Ba and Nd (@ times), Hf (1.1), Zn and Sb are also of higher concentrations, 0.5 and 0.4 times respectively, and Ce, Yb and Eu - 0.8 times. Comparatively higher concentrations have the elements Lu and Tb. Lower concentrations with regard to

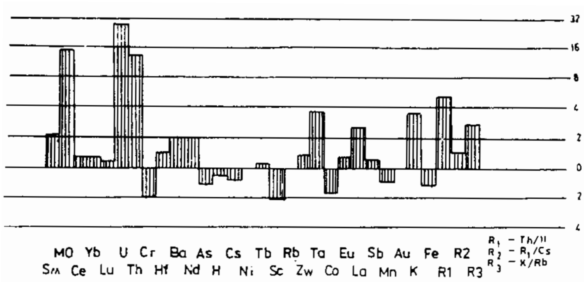

Fig. 5: Average element content in sodium metasomatites with respect to element content in initial quartz-sericite schists.

Table 1: Chemical composition of quartz-sericite-chlorite schists.

Ox.	SiO_2	Fe_2O_3	FeO	TiO_2	Al_2O_3	MnO	CaO	MgO	Na_2O	K_2O	P_2O_5	H_2O
x	57.19	1.43	2.84	0.74	15.00	0.09	4.09	2.74	1.51	3.62	0.14	0.35
min	45.74	0.35	0.98	0.33	10.83	0.03	1.93	0.97	0.32	2.09	0.04	0.06
max	71.56	4.37	6.15	1.15	21.53	0.13	7.54	6.10	4.47	4.98	0.57	1.00
sd	7.41	1.09	1.27	0.23	2.62	0.03	1.56	1.32	0.99	0.99	0.12	0.24
n	17	17	17	17	17	17	17	17	17	17	17	16

Table 2: Chemical composition of low-temperature sodium metasomatites

Ox.	SiO_2	Fe_2O_3	FeO	TiO_2	Al_2O_3	MnO	CaO	MgO	Na_2O	K_2O	P_2O_5	H_2O
x	61.37	2.12	2.07	0.58	14.95	0.31	4.67	2.01	4.86	1.55	0.09	0.19
min	52.92	0.37	0.60	0.19	11.18	0.02	0.97	0.76	3.61	0.54	0.02	0.08
max	74.62	12.16	5.57	1.83	18.60	3.72	11.12	3.39	7.00	4.23	0.35	7.72
sd	6.68	2.84	1.43	1,49	2.73	0.86	2.50	0.98	1.00	1.01	0.08	0.16
n	18	18	18	18	18	18	18	18	18	18	18	12

Table 3: Chemical composition of hematized quartz-sericite-chlorite schists.

Ox.	SiO_2	Fe_2O_3	FeO	TiO_2	Al_2O_3	MnO	CaO	MgO	Na_2O	K_2O	P_2O_5	H_2O
x	53.16	2.86	4.64	0.95	14.89	0.41	5.91	3.14	2.01	2.87	0.25	0.21
min	51.38	0.62	1.24	0.36	12.19	0.08	3.61	1.64	0.20	0.95	0.05	0.12
max	60.05	6.46	8.34	1.68	18.80	3.71	9.02	5.93	6.13	4.70	0.86	0.32
sd	4.23	1.73	2.21	0.44	2.08	1.04	1.68	1.26	1.73	1.22	0.28	0.23
n	12	12	12	12	12	12	12	12	12	12	12	9

NOTE: x - arithmetical mean; min-max - minimum and maximum values; sd- standart deviation; n - number of analyses.

the non-alterated schists have the elements Cr, Sc and Co - 2 times; As, Mn, Fe - respectively 1.1, 0.9, 1.1 times. The ratios Th/U; Rb/Cs and K/Rb are higher in the metamorphosed rocks: 5, 0.9 and 2.8 times.

The sodium metasomatites, compared to the slightly albitized or so called hematitized schists (Fig. 6) also show higher content of the elements U(12 times), Th (4.8 times), Sm, Ce, Nd and K (1.8) Yb and La (1.1), Eu (0.8), Tb and Rb (0.5). Comparatively higher concentrations have the elements As and W (2.4 times), Sc (2), Cr and Co (1.8), Ba, Mn and Fe (1.3), Ni (0.9), Zn and Sb (0.4).

In spite of the differences pointed out, the sodium metasomatites with

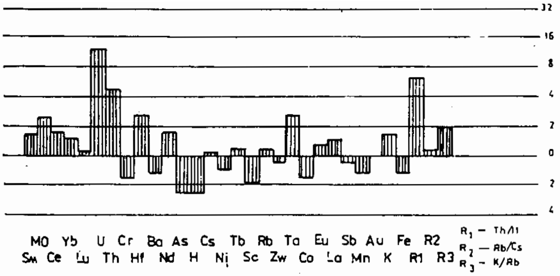

Fig. 6: Average element content in sodium metasomatites - with respect to the element content in hematized quartz-sericite schists.

Table 4: Rare elements quantity in low-temperature sodium metasomatites in the section Kotenovtsi - Pesochnitsa.

	Sm	Mo	Se	Yb	Lu	U	Th	Cr
N	23,0	8,0	23,0	23,0	11,0	23,0	23,0	14,0
x	8,52	26,63	78,49	2,83	0,31	51,19	72,82	59,36
sd	6,65	22,52	73,83	1,05	0,22	95,10	82,58	34,04
max	28,00	77,58	331,50	5,98	0,84	328,30	253,90	119,20
min	0,62	3,10	12,77	1,27	0,02	0,38	0,52	4,91
	Hf	**Ba**	**Nd**	**As**	**W**	**Cs**	**Ni**	**Tb**
N	22,0	21,0	4,0	18,0	9,0	23,0	9,0	23,0
x	8,57	707,76	103,49	9,49	2,45	2,50	42,06	1,09
sd	6,67	985,89	38,51	6,13	1,94	1,95	17,24	0,47
max	26,36	4449,00	167,80	22,65	5,01	7,39	78,95	2,40
min	1,01	39,52	64,57	0,10	0,02	0,25	21,80	0,35
	Sc	**Rb**	**Zn**	**Ta**	**Co**	**Eu**	**La**	**Sb**
N	23,0	21,0	17,0	22,0	23,0	23,0	23,0	18,0
x	7,84	77,19	83,53	1,87	11,26	1,33	40,15	1,43
sd	6,98	53,46	67,24	1,48	7,68	0,81	44,08	0,64
max	20,80	223,30	276,70	5,42	30,13	4,04	182,10	2,63
min	0,80	9,47	20,75	0,19	2,34	0,41	1,05	0,26

	Mn	Au	K	Fe	Th/Cz	Rb/Cz	K/Rb
N	23,0	0,0	6,0	23.0	23,0	21,0	6,0
x	284,83	0,0	35050,0	27308,0	19,84	35,85	422,71
sd	161,65	0,0	20337,0	16892,0	77,34	20,44	216,90
max	628,90	0,0	65000,0	64248,0	382,11	87,50	721,09
min	93,18	0,0	8720,0	6819,0	0,14	12,36	133,82

their element specificity show a certain closeness to the that of the hematized schists. This is another proof that the sodium metasomatites are final metasomatism products. In these or in intensively metasomatized phillites the content of rare earth elements La, Ce, Sm and Nb have increased from 0.8 to 2 times. That means that in the process of the albitization of the phillites from the diabase-phillitoid complex there had not been a significant supply of rare earth elements, and the metamorphogenic solutions had been enriched in these elements mainly on the account of the destructed minerals from these rocks.

In the initial low-metamorphic rocks from the diabase-phillite complex the content of the radioactive elements (U and Th) is low, but their content in the metasomatites is several times higher with a tendency of accumulation in the sodium metasomatites. Comparing the results the following dependence is noticed: With the increase of the quantity of SiO_2 and alkaline oxides, the concentration of U and Th increases, and with the increasing the quantity of Na_2O, the quantity of Nd increases as well. The high Uranium and Thorium content in the metasomatites correlates well with the high phosphorous content, which in some analyses reaches 1000 ppm. This is related to the presence of uranium-bearing apatite in the metasomatites.

For studying the character of the metasomatic process in detail a petrochemical and geochemical analysis has been made in depth. For this purpose all anomalous sections (indicated with J - logging) to a depth of 731 m have been sampled. Zoning has been found only in the range of the individual metasomatite bodies. There is no common vertical zoning in depth. As a peculaliarity of the zoning can be considered the quartz zones in the borehole columns that more often "crown" the metasomatite bodies.

CONCLUSIONS

1. The sodium metasomatism has taken place mainly in the exocontact parts of the Petrohan pluton, in the Berkovitsa district (region Kotenovtsi - Mezdrea) and weakly along the Gabrovnitsa and Proboinitsa rivers. The sodium metasomatism affected mainly the tectonized rocks from the diabase-phillite complex (phillites, diabase tuffs and diabases). As a result the morphology of the metasomatite bodies is rather variable - veins, nests, lenses.

2. The sodium metasomatites compared to unaltered rocks are of significantly higher content of Na_2O, SiO_2, CaO, FeO, MnO. They are with higher content of U(27 times) , Mo (15), Th (14), Ta (3.8), La(2.5), Sm, Ba, Hg and Nd (2) and Hf (1.1).

3. The sodium metasomatism and uranium-bearing metasomatites are localized mainly in the identified Kotenovtsi-Pesochnitsa fault zone, going mainly along the northern intrusive exocontact of the so-called "Mezdrea granites" and partially through them.

4. The alkaline metasomatites are separate geological features, with their own position in the tectonic and magmatic development of the Paleozoic. They are products of post-magmatic processes connected with the Paleozoic alkaline magmatism.

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