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SECONDARY DISPERSION HALOS AS A PROSPECTING INDICATOR OF PLATINUM METAL MINERALIZATION ON THE EXAMPLE OF THE KAMENUSHINSKY MASSIF (MIDDLE URALS)

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The paper discusses the results of bulk rock geochemical sampling of the Kamenushinsky massif eluvial-deluvial deposits and the massifs bedrocks spectral analysis data. Evaluation of secondary dispersion halos using two-dimensional modeling and multivariate statistic processing of the results have allowed establishing the spatial collocation of platinum and chromium anomalies and high correlation between these elements. These facts confirm the considerable contribution of chromite-platinum mineralization to the primary ores of the entire Kamenushinsky massif. The geological observations and rocks chemical composition analysis has revealed that uranium and barium anomalies are associated with the areas of gabbro and granitoids dike bodies. The insignificant overlapping of uranium and barium anomalies with platinum and chromium ones, as well as the negative correlation between these two groups of elements, is inconsistent with earlier conclusions on the spatial association of platinum mineralization with gabbro and granitoids dikes and a possible connection between these dikes and platinum metal mineralization zones.

Key words: Kamenushinsky massif; bulk rock geochemical sampling; secondary dispersion halos; platinum; chromite; mineralization; dikes

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Introduction. The depletion of alluvial platinum deposits in Russia raises the urgent question of prospecting and developing of primary platinum metal deposits. The raw material source is the zonal massifs of the Ural Platinum Belt, which served as the source of the world's largest platinum placers.

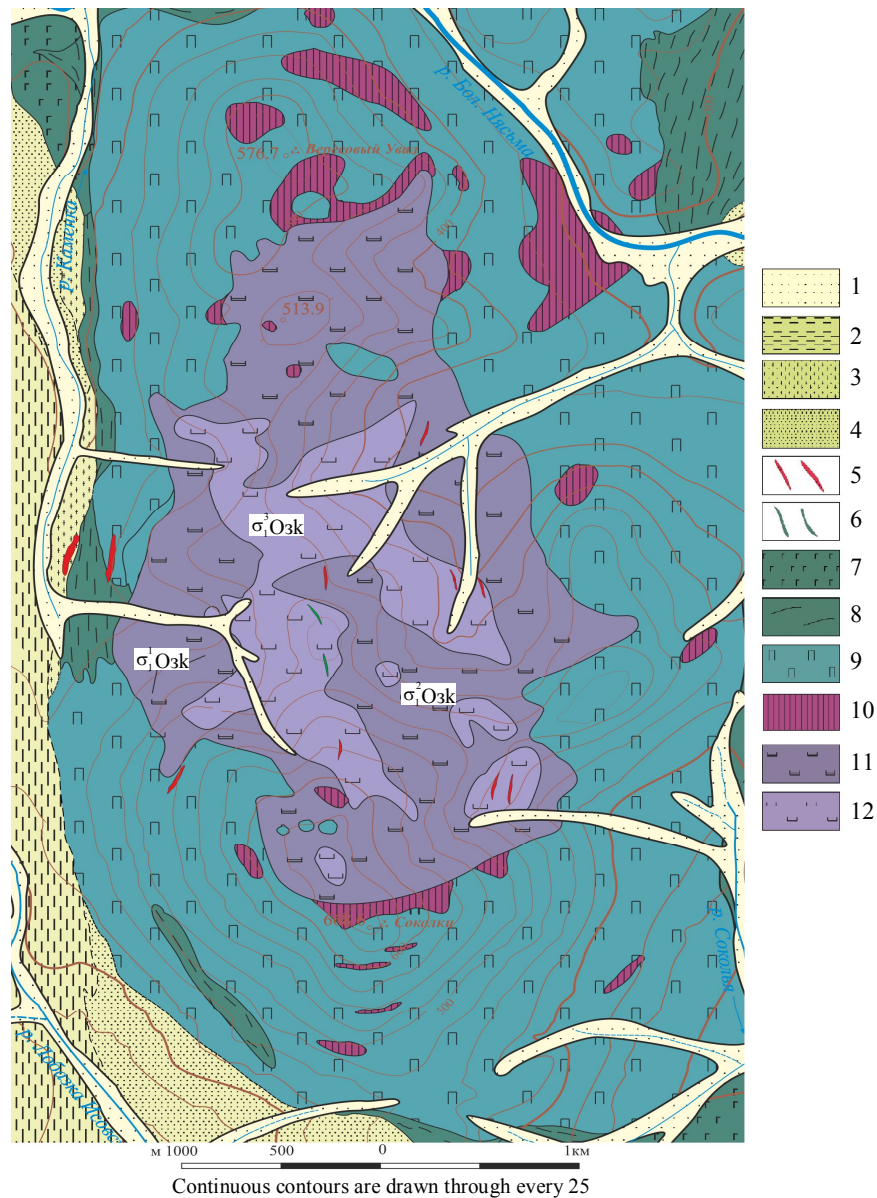
Not only PGE but also chromium (being considered as an indicator element) contents were determined at the exploration and evaluation stage, aimed at identifying primary platinum metal deposits. The use of this method is justified by the presence of chromite-platinum mineralization [1, 4, 7, 12], which is the most promising for the dunite-clinopyroxenite massifs of the Ural Platinum Belt.

Currently, the obtained data do not allow to determine and outline ore bodies within the dunite-clinopyroxenite massifs. This is largely due to the strong overlap of bedrock with eluvial and deluvial sediments, sodding and, in some cases, swampiness of zonal massifs, as well as an extremely uneven PGE mineralization.

The Kamenushinsky dunite-clinopyroxenite massif of the Ural-Alaskan-type is one of the promising arrays for the primary platinum-metal mineralization. At the same time, it has been poorly studied. Earlier studies have allowed distinguishing within the massif the Chromite Uval zone with platinum mineralization [3], many individual chromite bodies [6], and a number of mineralized chromitite zones [16, 17] in the Chromite Uval area. At the same time, based on numerous geological observations within the Chromite Uval area, it was assumed that the mineralized zones are spatially confined to gabbro and granitoids dikes, which can control platinum mineralization.

The obtained results allowed not only a new appreciation of the relationship between the platinum mineralization and dike bodies but also to highlight new chromitites zones with platinum mineralization in the 2017 field season.

Geological framework. The Kamenushinsky massif is located in the Middle Urals in the Sverdlovsk region and belongs to the dunite-clinopyroxenite-gabbro formation. The dunite core is elongated in the meridional direction and is framed by clinopyroxenites (Fig.1). The massif cut through the effusive Lower Silurian rocks in the west and is bordered by the Upper Ordovician gabbroids from the east, north, and south.



Continuous contours are drawn through every 25

Fig.1. The scheme of the Kamenushinsky massif (by O.K.Ivanov with additions and simplifications)

- 1 – technogenic and alluvial deposits; 2 – green schists;
- 3 – amphibolites; 4 – amphibole-plagioclase rocks (so-called «kytlymites»); 5 – plagiogranite dikes;
- 6 – hornblende gabbro dikes; 7 – hornblende gabbro; 8 – konzhakits (feldspathized pyroxenites);
- 9 – undifferentiated pyroxenites; 10 – wehrlite; 11 – fine-grained serpentized dunites;
- 12 – medium grained serpentized dunites

Fine-grained dunites compose a large northern part of the core and the peripheral zone of the southern part. The central part of the core is composed of medium-grained dunites. Coarse-grained dunites and dunite pegmatites are located in the central part of the massif, mainly in the saddle (Chromite Uval) between the Sokolinaya mountain in the south and the Veresovaya mountain in the north.

Dikes and veins of different composition are distributed within the Kamenushinsky massif. The most widespread are gabbro and granitoids dikes, to a lesser extent hornblendite, clinopyroxenite, and syenite dikes as well as veins of complex hydrothermal/metasomatic composition. Wide variety of chromitites bodies are also identified within the massif. Chromite bodies associated with platinum mineralization were found in the Chromite Uval site and the northern slope of the Sokolinaya mountain, as well as in the outcrops of the Bolshaya and Malaya Kamenushka rivers. The chromitite bodies form mineralized zones with a width of up to 3 m and length of up to 100 m, traced by the presence of segregations, schlier and vein bodies with a thickness of up to 0.4 m and a length of up to 3 m.



Analytical techniques. In 2014, a lithogeochemical survey on secondary dispersion halos was conducted within the Kamenushinsky massif using the well-known methodology [2, 14]. Sandy clayey and clayey eluvial-diluvial material weighing 200-300 g were sampled over a 200 × 20 m net. The lithogeochemical survey covered the entire dunite core from south to north, capturing part of the clinopyroxenite rim and effusive rocks framing the western part of the massif. The 23 sample profiles were passed from west to east. In some areas, especially in ravines and swamplands in the north-west of the territory, lithogeochemical sampling was not undertaken due to the technogenic and alluvial sediments cover, peat cover or the complete absence of eluvial and deluvial sediments and bedrock exposure. 1948 samples in all were taken and analyzed. Geological observations and rock chip sampling were also conducted during the lithogeochemical traverses.

The impurity elements content in the Kamenushinsky massif rocks were analyzed by ICP-MS technique. The ICP-MS analyses were performed in the central analytical laboratory of the A.P. Karpinsky Russian Geological Research Institute (VSEGEI) (St. Petersburg). A total of 14 rock chip samples were analyzed.

In order to carry out a comprehensive assessment of the Kamenushinsky massif ore potential, Pt, Pd, and Au content was determined in lithogeochemical samples, by the assay test (sensitivity is 0.002 g/t) on the basis of Stewart Laboratory, Moscow (Stewart Geochemical & Assay). The impurity elements content was determined using a semi-quantitative spectroscopy (sensitivity 0.002 g/t) in the analytical laboratory of AO «Mekhanobr Engineering», St. Petersburg.

The obtained geochemical data were processed by the mathematical statistics and graphic simulation according to the recommendations [19, 20] using Microsoft Excel 2010, Statistica 10.0, Surfer 13, and CorelDraw X7 software. For statistical analysis and mapping of anomalies, *statistically significant values* were distinguished, i.e. values below the detection limit and single anomalously high values were excluded from the data set. Maps of anomalies were generated on the basis of the Kamenushinsky massif schematic plan by determining the elements background content and contouring of anomalies along the isoconcentration lines based on the calculated parameters of the geochemical field.

26 elements were analyzed, including noble metals (Pt, Pd, Au, Ag), transition elements (As, B, Bi, Cd, Cu, Ge, Hg, Mo, Pb, Sb, Sn, W, Zn), iron group elements (Cr, Co, Mn, Ni, V), volatile elements (P), high field strength elements (U), and large-ion lithophile elements (Ba, Li). The elements are classified according to H.R. Rollinson [21]. The distribution law verification revealed the necessity of taking the elements values logarithm to bring the data to a normal distribution, after which a correlation matrix was compiled and the factor loadings were calculated.

Results. Obtained data (Table 1) shows the highest content of platinum among other noble metals, measured in lithogeochemical samples. Within the entire massif, platinum is characterized by a significant standard deviation, which is due to its extremely uneven distribution. Background values are 0.00-0.07 g/t. Elevated platinum concentrations (0.30-1.26 g/t) are mainly found in the central part of the massif, in particular within the Chromite Uval and the northern slope of Sokolinaya mountain, where coarse-grained dunites and dunite pegmatites are widespread. Platinum and chromium show strong direct correlation (Table 2) and their anomalies are spatially combined (Fig. 2, a).

Based on earlier conclusions on the spatial alignment of mineralized zones and dike bodies within the Kamenushinsky massif [9, 17], a number of elements associated with dike rocks were identified in order to determine the nature of the relationship between platinum mineralization and dikes. Thus, the secondary dispersion halos of uranium (U) and barium (Ba) are associated with gabbro and granitoid dikes (Fig. 2, c), which is confirmed by geological observations and trace element content data (Table 3).

Table 1

Impurity elements content in eluvial-deluvial deposits of the Kamenushinsky massif, g/t

Sr.№	Element	Number of statistically significant values	Analysis sensitivity	Content mean values	Standard deviation	Minimum	Maximum
Noble metals							
1	Au	315	0.002	0.005	0.0014	0	0.026
2	Pd	171	0.002	0.004	0.0024	0	0.073
3	Pt	1813	0.002	0.032	0.0423	0	1.262
4	Ag	68	0.002	≈0.002	0.0020	0	0.005
Transition elements							
5	As	645	0.005	≈0.005	0.0021	0	0.029
6	B	1558	0.001	12.2	4.3	5	36
7	Bi	1541	0.003	0.5	0.2	0	1
8	Cd	662	0.002	1.3	0.7	0	5
9	Cu	1716	0.001	17.0	5.8	6	57
10	Ge	1070	0.001	1.5	0.6	0	3
11	Hg	1278	0.001	2.6	1.4	0	9
12	Mo	1607	0.0005	1.9	2.0	0	19
13	Pb	1679	0.003	11.9	4.2	3	59
14	Sb	1784	0.0005	2.0	0.8	0	6
15	Sn	1573	0.002	4.4	3.2	0.5	37
16	W	1790	0.01	2.4	1.5	0	29
17	Zn	1462	0.05	55.6	36.5	2.5	190
Iron group elements							
18	Cr	1887	0.001	1023.4	761.1	46	6000
19	Co	1604	0.001	94.9	49.7	4	180
20	Ni	1802	0.0003	263.0	151.4	17	830
21	Mn	1773	0.4	972.8	505.8	200	3300
22	V	1814	0.0003	36.8	20.0	3	170
Volatile elements							
23	P	1392	0.1	122.4	62.9	50	430
High field strength elements							
24	U	1601	0.015	5.4	4.7	0	16
Large-ion lithophile elements							
25	Ba	1759	0.003	402.5	256.6	84	1500
26	Li	1770	0.03	27.2	9.7	8	95

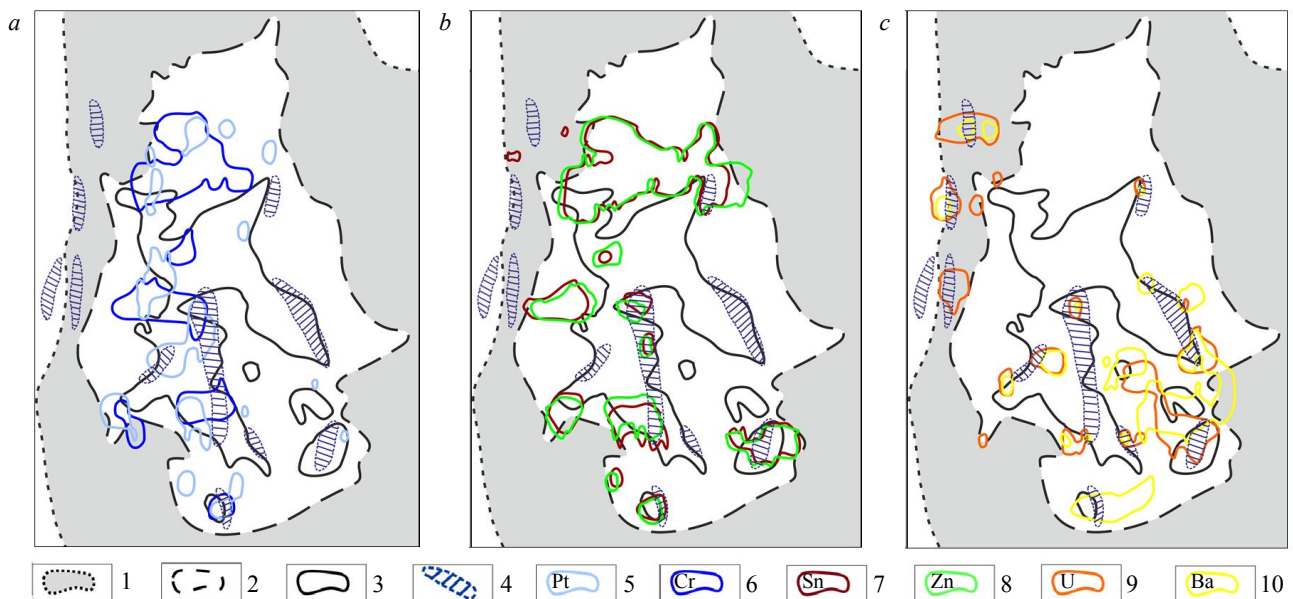


Fig.2. Secondary dispersion halos of the Kamenushinsky massif: a – Pt, Cr; b – Sn, Zn; c – U, Ba

1 – Kamenushinsky massif contour (clinopyroxenites); 2 – contour of fine-grained serpentinized dunites;
3 – contour of medium-grained serpentinized dunites; 4 – gabbro and granitoids dikes;
5-10 – secondary dispersion halos: 5 – platinum; 6 – chromium; 7 – tin; 8 – zinc; 9 – uranium; 10 – barium



Table 2

Correlation matrix of impurity elements of the Kamenushinsky massif eluvial-deluvial deposits

	lgPd	lgPt	lgBa	lgCr	lgCu	lgNi	lgP	lgSn	lgU	lgZn
lgPd	1.000									
lgPt	-0.045	1.000								
lgBa	0.005	-0.377	1.000							
lgCr	-0.089	0.666	-0.521	1.000						
lgCu	0.155	-0.092	0.124	-0.022	1.000					
lgNi	-0.140	0.480	-0.241	0.649	0.288	1.000				
lgP	-0.027	0.244	0.079	0.436	0.415	0.566	1.000			
lgSn	-0.083	0.573	-0.558	0.896	0.127	0.689	0.481	1.000		
lgU	0.090	-0.460	0.686	-0.595	0.153	-0.491	-0.125	-0.625	1.000	
lgZn	-0.038	0.390	-0.351	0.617	0.349	0.675	0.579	0.701	-0.417	1.000

Table 3

Mean values of impurity elements content in the Kamenushinsky massif rocks, g/t

Sr. №	Element	Coarse-grained gabbro	Granite pegmatite	Medium-fine-grained granite	Medium-fine-grained hornblendite	Vein-disseminated chromite	Serpentinized dunite	Coarse-grained wehrlite
Noble metals								
1	Au	<0.001	<0.001	<0.001	<0.001	0.0140	0.0086	0.0071
2	Pd	<0.002	<0.002	<0.002	0.0300	0.0068	<0.002	0.0065
3	Pt	<0.001	<0.001	<0.001	<0.001	1.1500	0.0610	0.0037
4	Ag	0.03	0.04	0.03	0.01	<0.01	<0.01	<0.01
Transition elements								
5	Bi	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
6	Cd	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
7	Cu	32.81	4.00	1.40	49.40	14.60	10.90	4.05
8	Ge	0.79	1.26	0.52	1.36	0.22	0.72	0.97
9	Mo	0.80	0.72	0.86	0.61	<0.60	<0.60	0.79
10	Pb	4.78	37.30	8.55	2.30	<1.00	<1.00	<1.00
11	Sb	0.39	1.06	0.34	<0.10	<0.10	<0.10	<0.10
12	Sn	1.48	2.47	1.68	1.59	0.81	0.73	0.88
13	W	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
14	Zn	48.27	7.94	3.71	106.00	14.90	54.50	61.80
Iron group elements								
15	Cr	17.20	16.90	19.10	288.00	12960.00	3580.00	1970.00
16	Co	10.30	0.83	<0.5	54.80	44.40	129.00	77.10
17	Ni	23.30	3.43	7.05	76.60	500.00	1710.00	500.00
18	V	145.00	4.13	4.77	382.00	132.00	8.44	105.00
High field strength elements								
19	U	25.00	50.00	16.00	<0.10	<0.10	<0.10	<0.10
Large-ion lithophile elements								
20	Ba	321.00	2870.00	473.00	114.00	<3.00	<3.00	8.21

Remarks. Two analyses were performed for each rock.

A comprehensive analysis of the correlation matrix, the factor load diagrams (Fig.3) and the mean content values of impurity elements in the rocks allowed us to identify elements that also characterize the platinum mineralization zones distribution within the Kamenushinsky massif. Thus, within the Kamenushinsky massif, the mean contents (Table 3) of such granophile elements as tin and zinc in ultrabasic rocks (dunites) are higher than the crustal abundance, and in basic and acidic rocks (gabbro and granitoids) are below the crustal abundance (Table 4). Also, there is a strong spatial alignment of platinum and chromium anomalies with tin and zinc ones (see Fig.2, a, b). Along with this, tin and zinc of the Kamenushinsky massif have an average positive correlation (0.39 and 0.57, respectively) with platinum and a strong positive correlation (0.61 and 0.89, respectively) with chromium.

Discussion. The geomorphological assessment of the Kamenushinsky massif based on geological observations and isohypse features (see Fig.1) allows describing its relief as wavy one, with secondary halos formed by moving rock clasts and diffusion of solutes in rocks moisture and are placed directly above the primary halos. The wavy relief causes weak defluction processes, mainly developed on the slopes, which indicates a slight displacement of secondary dispersion halos from the primary ones.

The significant role of chromite-platinum mineralization in the mineralization of the massif is evident. However, chromium anomalies are more widespread than platinum ones (Fig. 2, *a*). This can be explained, firstly, by the extremely low platinum content in some chromitites bodies, due to their accumulation in adjacent schlieren and chromitites segregations; secondly, a rare sampling net, insufficient to determine the distribution of such an unevenly distributed element as platinum. The presence of small local platinum anomalies that are not combined with chromium anomalies can be explained by the fact that the zonal dunite-clinopyroxenite massifs of the Ural Platinum Belt are characterized by a dunite-platinum mineralization type.

The data obtained within the Kamenushinsky massif give the strong relationship between platinum and chromium (both spatial and correlational) and allow to conclude that in this case platinum is predominantly concentrated in chromitites. The high correlation between platinum and chromium may indicate the platinum concentration in the extended mineralized chromitite zones typical for this massif. This is confirmed by geological observations, showing spatial coincidence of chromium anomalies and known mineralized chromitite zones, located on the Chromite Uval and the northern slope of Sokolinaya mountain.

In general, platinum and chromium anomalies are found in the western part of the massif, where they are most prevalent in the medium-grained dunites, as well as in the transition zones of fine- to medium-grained dunites (Fig.2, *a*). This confirms the conclusions about the location of the native chromite-platinum mineralization of the Kamenushinsky massif in the zones of dunites of various granularity [10]. A similar geological features of chromite-platinum mineralization has been established for Nizhnytagilsky, Svetloborsky, Veresoborsky zonal massifs of the Ural Platinum Belt [6, 8, 14, 15, 18]. The most widespread platinum and chromium anomalies (Fig.2, *a*) in the Chromite Uval and the northern slope of the Sokolinaya mountain are associated with coarse-grained dunites and dunite-pegmatites in the central part of the massif [9]. It is important to note that within the Nizhnetagilsky and Svetloborsky massifs, the richest chromite-platinum mineralization zones are confined to the coarse-grained dunites and dunite-pegmatites [6, 8, 15, 18].

Analysis of the elements mean contents in the composition of the rocks (see Table 3), their crustal abundance in various rocks types (Table 4), as well as the spatial distribution of the elements anomalies, indicates their unconventional distribution, namely, the connection of granophile elements (Sn, Zn) with ultramafic rocks, but not with the widely developed gabbro and granitoids dikes. This may be due to the high isomorphic capacity of ultramafic minerals, such as olivine, clinopyroxene, amphibole, chromspinelide, etc. (Table 5). For example, within the Nizhnetagilsky massif, one of the reference objects of the Ural Platinum belt, the high concentration of tin and zinc serves as a geochemical criterion of the platinum-bearing chromspinelides [11]. Thus, within the Kamenushinsky massif, a sufficiently high spatial and statistical correlation between the elements associated with platinum mineralization (Cr, Pt), tin and zinc can be explained by the following

facts: firstly, the joint accumulation of these elements in secondary halos; secondly, a higher content of tin and zinc in dunites with chromite-platinum mineralized zones, which as evidenced by the considerable superiority of dunites compared to the chromitites and dikes, and by the significant concentrations of tin and zinc (see Table 3) in dunites in general.

Table 4

Crustal abundance of granophile elements
in different rock types, g/t [5]

Element	Ultrabasic	Basic	Medium	Acidic
Sn	0.5	1.5	2.5	3.0
Zn	50	100	75	60



Table 5

Mean contents of granophile elements in mineral of ultramafic rocks, g/t

Element	Olivine*	Clinopyroxene*	Amphibole*	Basic plagioclase*	Chromspinelide with low PGE content**	Platinum-bearing chromspinelide**
Sn	2.6	4.2	27	4.0	1.26	9.36
Zn	50	60	250	50	974.39	1310.43

* In ultrabasic and basic rocks [5].

** In chromspinelides of Nizhnetagilsky massif [11]; PGE – platinum-group elements

In the central part of the Kamenushinsky massif (Chromite Uval), uranium and barium anomalies are partially combined with chromium and platinum ones (Fig.2, a, c), as evidenced by the spatial connection of mineralized zones with gabbro and granitoids dikes [9, 17]. However, a significant negative correlation is observed between the anomalies associated with dikes (U, Ba) and anomalies characterizing chromite-platinum mineralization (Cr, Pt) (see Table 2).

An analysis of the maps of anomalies throughout the entire massif suggests that the spatial combination of platinum mineralization anomalies and dikes is weak. Thus, in the eastern part of the massif, gabbro and granitoids dikes, as well as the associated uranium and barium anomalies are widespread. Along with this, anomalies of chromium and platinum are practically absent in the eastern part of the massif. Also in the western part of the massif, in the clinopyroxenite rim, within which there are no chromium and platinum anomalies, the anomalies of uranium and barium spatially coincide with the granitoids and gabbros dykes.

Partial combination of platinum and chromium anomalies with barium and uranium ones can be connected with the general confinement of dikes and platinum mineralization to the zones of internal primary heterogeneities of the massif. This is indicated by the most prevalent occurrence of dikes and associated barium and uranium anomalies in the facial contacts of fine-grained dunites with medium-grained ones (Fig.2, c), accompanied by porphyraceous dunites and the highest concentration of platinum and chromium anomalies in similar areas (Fig.2, a).

The principal component analysis data (Fig.3) also allow dividing barium and uranium with platinum and chromium into two groups. The first factor has a weight of 64.21 % and reveals two associations of elements: the first includes Pt, Cr, Sn, Zn, the second – U, Ba. Such a relationship may indicate a joint accumulation of elements within the selected associations. Secondary halos largely inherit the relationships of chemical elements from the primary mineralization, therefore, the first factor most likely reflects the differences in the nature of the initial melt of chromite-platinum mineralization and dike bodies.

Thus, the data obtained on the association of platinum and chromium anomalies with the uranium and barium ones allow us to conclude that there is a weak spatial relationship between the chromite-platinum mineralization and dikes. Negative correlation coefficient and principal components analysis data indicate that platinum and chromium, associated with platinum mineralization could not accumulate together with uranium and barium, associated with gabbro and granitoids dikes. Hence, the gabbro and granitoids dikes not genetically related to PGE mineralization, cannot be ore-controlling structures and serve as prospecting indicator.

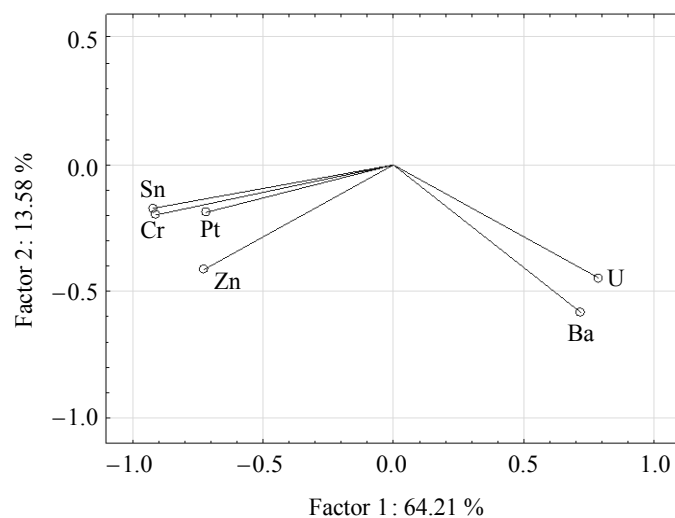


Fig.3. Factor loadings chart for the elements of litogeochemical samples (Pt, Cr, Sn, Zn, Ba, U)



Conclusion. Summarizing the obtained data, the following conclusions can be made about the platinum mineralization location within the Kamenushinsky massif:

1) The platinum and chromium anomalies are substantially correlated with the native mineralized chromite-platinum zones, which is confirmed by geological observations. This made it possible to identify new mineralized zones within the platinum and chromium anomalies, and especially in areas where there is dunites with granularity transition;

2) uranium and barium anomalies associated with gabbro and granitoids dikes cannot be signs of platinum mineralization, due to both the spatial incompatibility of uranium and barium with platinum and chromium, and the negative correlation between them;

3) tin and zinc can serve as indicators of PGE mineralization, as indicated by the spatial relationship of tin and zinc with platinum and chromium, and a strong correlation between them.

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