Classification on Morphological and Microanatomical Features of Zircon from Beshpagirsky Field of Rare Metal-Titanium Placers

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Abstract: Such parameters as crystal shape, elongation factor and cathodoluminescent image zoning used as petrogenesis indicators helped us to establish the following types of zircon from Beshpagirsky field: metamorphic (5 %), primary magmatic intrusive (S-granites of carbonate-alkaline series 55 %, I-granites of tholeiitic and alkalic series 15 %), primary magmatic effusive (alkaline rhyolite 15 %, alkaline basalts 10 %). At the same time 85 % of the studied zircon grains show signs of secondary changes of varying intensity, which may be due to metamorphism of the rocks from the source area. The first acquaintance with the morphology and microanatomy of zircon from rare metal-titanium placers of Stavropol shows the effectiveness of the chosen method as evidenced by the high incidence of 'typomorphic' zoning for each morphological group. Genetic types of zircon allocated using this method were compared with indigenous species from source areas located in the Greater Caucasus, thus confirming paleogeographic reconstructions made earlier, but also we used their quantitative proportion for specification and contouring of distributive province.

Keywords: zircon, morphological classification, cathodoluminescent microanatomy, types of zoning, distributive province
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One of the most common accessory minerals, occurring in almost all types of igneous, metamorphic and sedimentary clastic rocks is zircon. It has a wide range of typomorphic characteristics and is often used as an indicator mineral for petrogenesis. The composition of zircon is very sensitive to changes in the crystallization parameters and even within a single magma chamber may experience significant variations.

Interpretation of geochemical indicative features of zircon grains in the search for sources of supply for rare metal titanium placers is quite precise and time-consuming task. Therefore, available techniques (morphological and microanatomical typing) were used in this study to assess the ratio in placers of plutonic, volcanic and metamorphic zircons from crust, hybrid and mantle rocks.

To optimize the proposed method of morphological and microanatomical zircon typing, as indicator of supplying provenances, the most studied object is selected from a geological point of view – Beshpagirsky field of rare metal titanium placer, which is part of the Stavropol placer district. This placer district is confined to the eponymous arch separating the Terek and Kuban troughs in the Scythian Epihercynian plate.

Paleogeographically, Stavropol placers are located at the southern end of sublatitudinal strait of Medium-Upper Sarmatskian basin that separated the Russian plate from the insular land, which began to actively uplift a Greater Caucasus.

Position of placers in the Stavropol arch (Fig. 1) suggests the existence of a regressive series of shorelines, bending round the centerline of the arch and fixing stabilization phases of sea level in Medium-Upper Sarmatskian paleo-basin (Patyk-Kara, 2008; Kremenetsky, Veremeyeva et al., 2006; Boyko, 2004). It is possible to distinguish at least four such lines, to the south of which Beshpagirsky field is confined, and the two northern (the latest) – Kambulaksky field, Grachevsky and Tashlinsky areas (Rudyanov, 2001).

The ore deposit is confined to Beshpagshirskian suite of Upper Sarmatskian age, folded of layers of fine-grained sands with rare lenses and interlayers of quartz sandstone on carbonate cement and thin interbedded clays and clay sands. The heavy fraction includes ilmenite (40.1 %), leucoxene (10.9 %), rutile (13.0 %), zircon (10.7 %), as well as chromite, magnetite, garnet, epidote, staurolite, kyanite, sillimanite, monazite. The main ore minerals are concentrated in a narrow granulometric class – 0.1 + 0.044 mm.

Methodology of morphological and microanatomical classification of zircon from Stavropol rare metal titanium placers

The crystals of zircon, preserved elements of cut, were studied by means of widely used typological chart of J.P. Pupin (1980). In this diagram, zircon crystals are classified in accordance with the development in the faceted of individual prism {100} and {110} and pyramidal {211} and {101} forms. J.P. Pupin related the relative development of prismatic faces, mainly with crystallization temperature, while the development of pyramidal faces – with the chemistry of melted material decrystallization.

He drew attention to the fact that typological parameters of zircon populations can be used to describe the evolution of the magmatic system and suggested several genetic interpretations of the chart, adapted for the study of zircon crystals, not only of granitic plutonic origin, but also for zircon of volcanic and metamorphic rocks.

When classifying zircon by morphological features from sedimentary rocks, further features of the crystal structure need to be considered, allowing even conditionally allocate their main genetic varieties. One of these features is the coefficient of crystal elongation (EC). EC value is associated primarily with the growth rate of zircon crystal, as well as the features of chemistry and genesis of the rock, including this mineral. Many researchers noted that EC of intrusive granites often ranges from 2 to 3, EC 3-4 and above is characteristic for volcanic zircon, EC of intrusive crystals for zircon of medium, main substrate – 1,5-2, and metamorphic zircon – 1-1,5 (Liakhovich, 1979).

In the study of rounded grains of zircon at placers that did not keep the elements of cut, EC is the only morphological parameter that should be used for the genetic classification of this mineral. In sedimentary rocks rounded grains of zircon with EC 1 to 2 with equal probability may be of metamorphic, magmatic origin or be rounded fragments of larger crystals.

Therefore, the use of EC in the study of mostly rounded grains of zircon should be advantageously carried out in conjunction with the cathodoluminescence (CL) images of microanatomical structure of these grains. This method, compared to the labor-intensive geochemical methods, is the most affordable and effective enough at genetic classification of zircon from sedimentary rocks, where the identification of contribution share from volcanic, plutonic and metamorphic sources is already an important result.

Figure of zircon zoning reflects the evolution of the crystallization medium of each particular individual and in CL mode depends on the compositional changes of Zr and Si and, more importantly, changes of Hf, P, Y, REE, U, Th – up to the order of the absolute value for some of these elements (Koppel, Sommerauer, 1974; Benisek, Ringer 1993, Hanchar, Rudmck, 1995; Fowler et al., 2002, and many other studies). Along with the CL in the investigation of zircon reverse electron scattering method (BSE) is widely used. Element is mainly responsible for the change in the intensity of BSE, which is Hf with U, having a secondary effect (Hanchar and Miller, 1993).

Both methods identify similar features of the crystal structure; however, bright areas in CL appear as dark in BSE and vice versa (Hanchar and Miller, 1993; Koschek, 1993). With a full range of CL radiation intensity and further changes in color, this method is more informative. It allows identifying the different events of the crystal growth, which often have a characteristic color of CL radiation and allows scheduling areas with different isotopic age (Corfu, 2003).

Each texture segment of zircon retains a specific period in the history of this mineral. Therefore, the interpretation of CL image itself is quite a challenge. At the same time there are a number of ‘typomorphic’ signs of zoning, which can be confidently used in petrogenetic reconstruction – a complex spotty and patchy zoning, wavy zoning, presence of xenomorphic cores, as well as the width and contrast of oscillatory growth zoning, the nature of which is disclosed in sufficient detail in the “Atlas of zircon textures” by F. Corfu (Corfu, 2003).

Efficiency in using tandem parameters such as EC

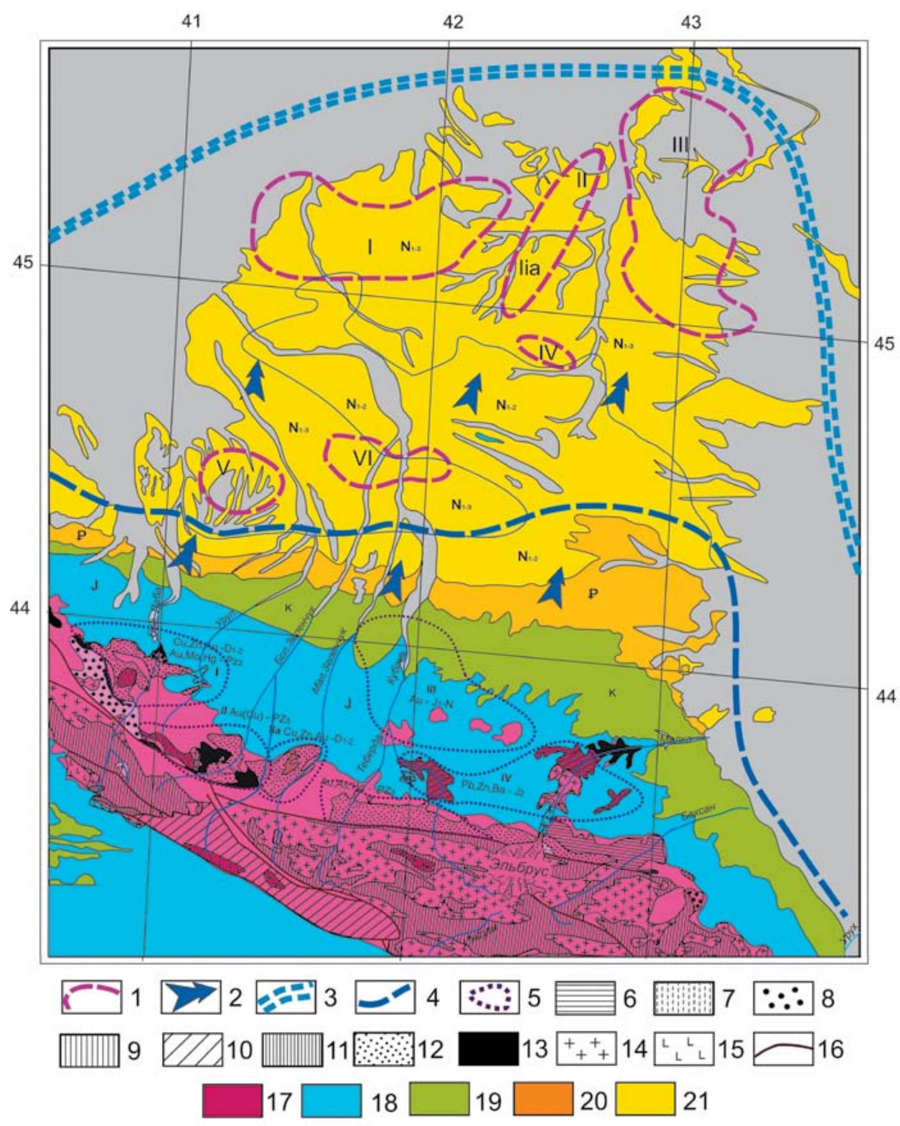


Fig. 1. Schematic map of geological structure of the Stavropol rare metal titanium placer district with elements of paleogeography of Middle-Upper Sarmatskian time (according to Yashchinin S.B. et al., FGUGP “Sevkavgeologiya” 2004, Somin M.L. (2000) as amended).
1 – Placer fields of Stavropol arch (I- Taishinskoe, II – Beitagirsky, IIa – Beitagirsky field, III – Pravoberezhny (Gofitsky, Kambulatsky field), IV – Kalaussky, V – Sinyukhinsky, VI – Nevinnomyssky); 2 – direction of terrigenous material ablation; 3 – average position of the boundary of lithological-facial complexes in shallow zone; 4 – estimated position of coastline of Middle-Upper Sarmatskian basin; 5 – location of ore nodes in the source area (I – Urupo-Labinksky and Andryuksky, II-Marukhisky, III-Mariysky polygenic-polychronic, IV – Kuban-Tyrzylsky, V-Kuchkur-Kishkitsky). Scheme of pre-Alpian base of the Great Caucasus: 6 – Bechasynsky area, Bechasynsky metamorphic complex; 7,8 – Front Ringe metamorphic complexes (1 -Atsgarinsky, 8- Blybsky and its analogues); 9-11 – Main Range metamorphic complexes (9 – Makersky and gneiss-migmatite, undivided, 10 – Buulgensky and its analogs, 11-Labinsky); 12 – Middle and Upper Paleozoic complexes unmetamorphosed complexes of Front Ridge; 13 – ophiolites; 14 – pre-Alpian granitoids; 15 – Batskian and more young granitoids; 16 – main faults. Development area of deposits: 17 – pre-Alpian base of the Greater Caucasus; 18 – Jurassic; – Cretaceous; 20 – Paleogene; 21 – Neogene system.

and CL-microanatomy as petrogenesis indicators is clearly displayed in this study. In case of petrogenetic classification, in varying rounded zircon crystals from the placers it is possible to allocate grain groups with similar conditions for crystallization by EC value and identify within these groups of grains with "typomorphic" signs and contrasting different patterns of zoning.

Results

Beshpagirsky placer is dominated in rounded grains of zircon, which did not preserve elements of the cut (56 % of the grains). The surface of most grains is smooth, less rough, with small holes; in a few cases there are grains of irregular shape (Fig. 2). The share of zircon that retained the crystallographic shape, with the ability to diagnose morphotype using chart of J.P. Pupin (1980) amounts to 44 % of the studied grains. The surface of crystals is smooth, often chipped in the form of thin regeneration rims. In accordance with EC value, the following morphological groups of zircon are allocated with EC 1-1,5 (11 %), EC – 1.5-2.2 (49 %), more than 2.2 (25 %), the fragments (15 %).

In the group with EC 1-1.5 rounded grains prevail (Fig. 1. 8-10). The microanatomical patterns of rounded grains of zircon (Fig. 3) are characterized by the following typomorphic features: complex spotted zoning (50 %), transformed primary-magmatic growth zoning (40 %), presence of xenomorphic core and regeneration rims (2 %), rounded fragments of large crystals (5 %).

Among the remaining crystals with EC 1-1.5 (3 %), diagnosed by a typological chart (Figure 4), zircon of morphotypes S8 and S14 is allocated (Fig. 2. 6-7), characteristic for granodiorite and monzogranites of carbonate-alkaline series (S-granites). Microanatomical pattern of such grains (Fig. 3i) retains the features of the primary growth zoning and has traces of superimposed

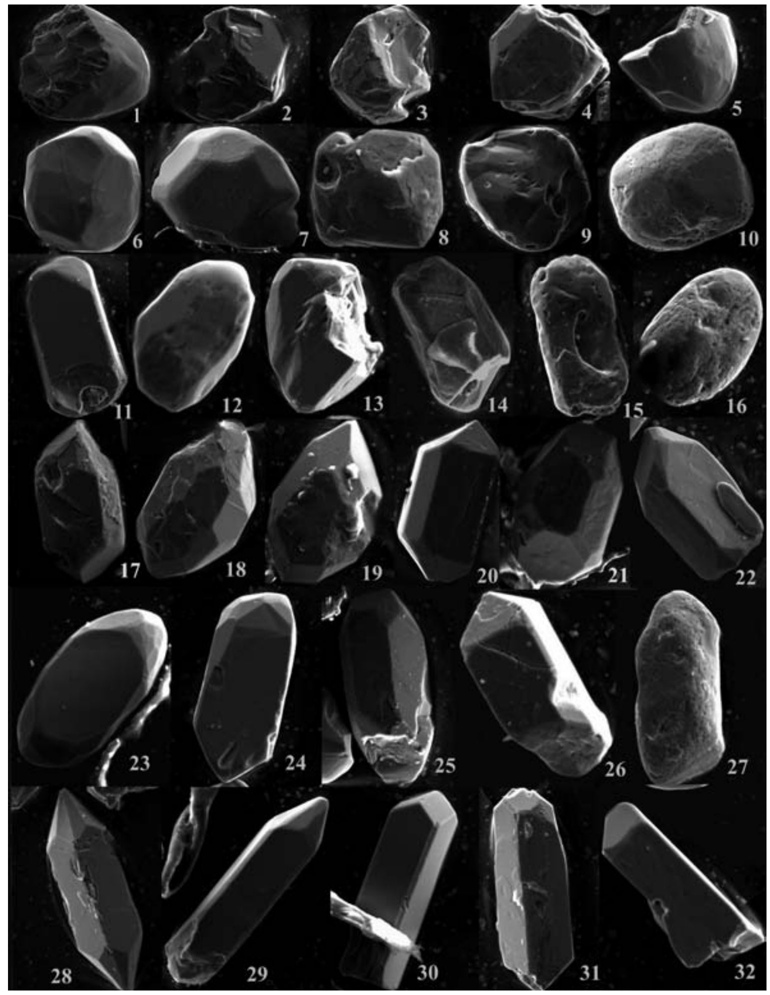


Fig. 2. Morphological features of zircon grains from Beitagirsky field of rare metal – titanium placers (grain size of 0.1 to 0.063 mm). 1-5 – fragments; 6-10 – EC 1-1.5 (grain 6-S_{14} and 7-S_8 with facet elements); 11-22 – EC 1.5-2.2 (11-13 grains with a smooth surface, 14-16 – grains with a rough surface and small holes, 17-21 grains with facet elements); 23-32 – EC over 2.2 (grains 23-26, 28-32 with elements of facet, grain 27 with a rough surface and small holes.

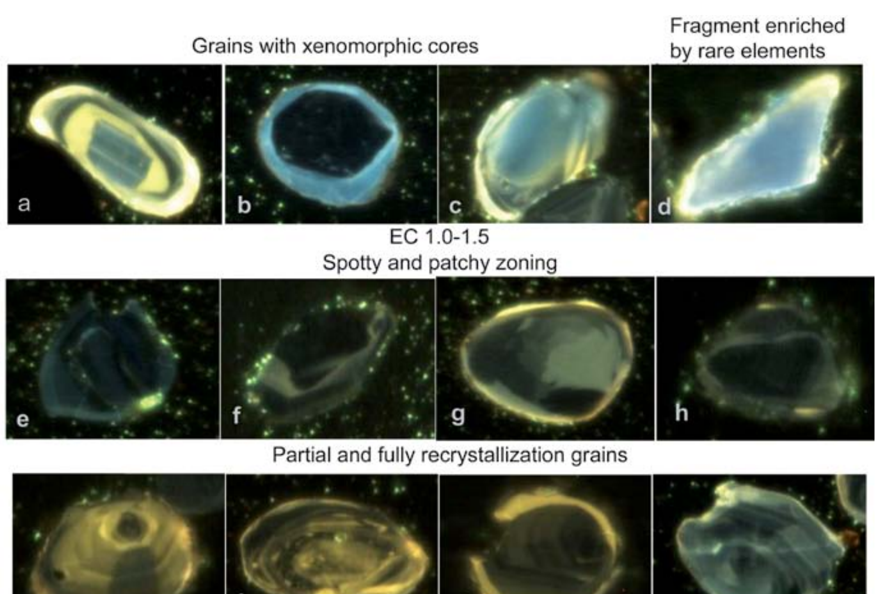


Fig. 3. Cl-pattern of polished zircon grains from Beshpagirsky field (grain size 0.1-0.071 mm). Grains f I – fragments are referred to this morphological group by zonation pattern. Grain j is referred to the group with EC 1.5-2.2 and exemplified as partial recrystallization grains.

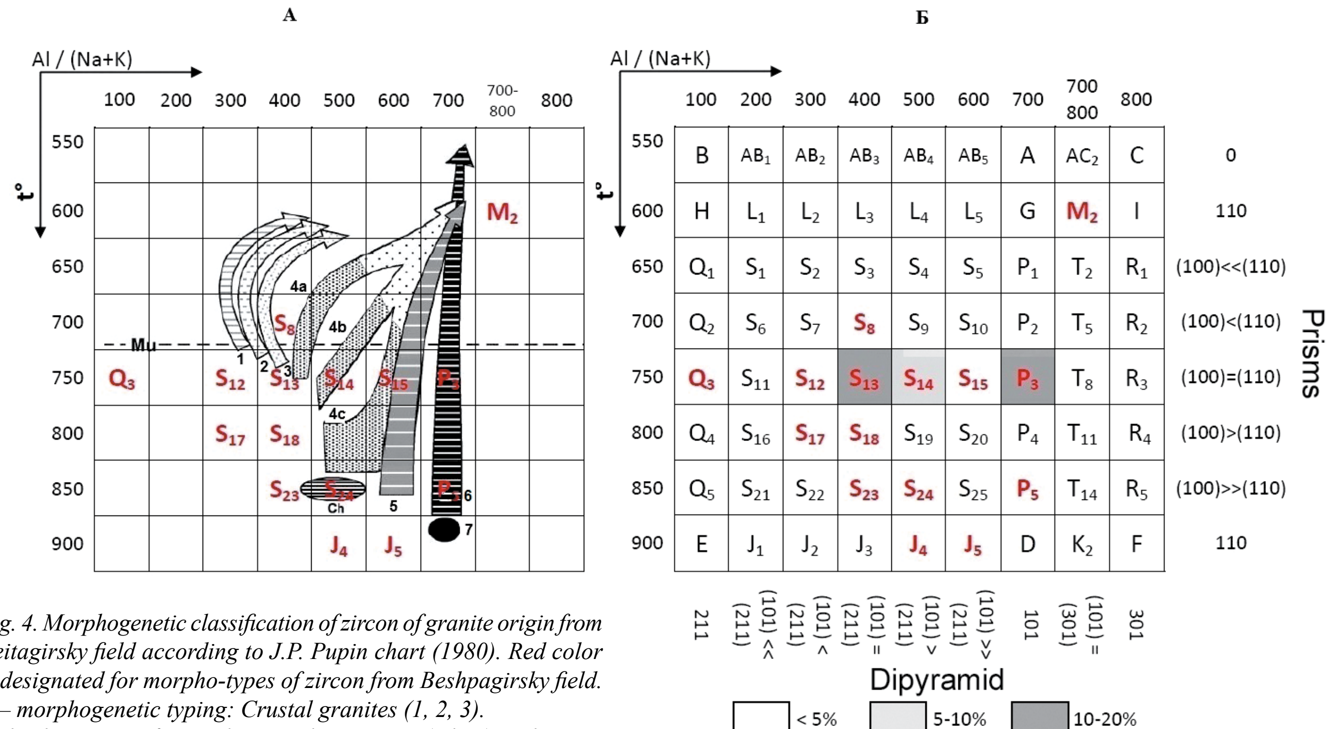


Fig. 4. Morphogenetic classification of zircon of granite origin from Beitagirsky field according to J.P. Pupin chart (1980). Red color is designated for morpho-types of zircon from Beshpagirsky field. A – morphogenetic typing: Crustal granites (1, 2, 3). Hybrid granites of crustal + mantle origin: 4 (a,b,c.) carbonate-alkaline series (dark field – granodiorite and monzogranites, bright field – monzogranites and alkaline granites), 5 – sub-alkaline series. Mantle granites: 6 – alkaline series; 7 – tholeiitic series. Ch – magmatic charnockites. B – Occurrence statistics of morphological types of zircon from Beshpagirsky field with EC 1.0-2.2.

conversion processes (dark spots and blurring of the primary sector).

The above typomorphic zoning of zircon with EC 1-1.5 testify in favor of the fact that 52 % of grains of this group have a metamorphic origin, and 43 % of grains are primary magmatic with traces of superimposed metamorphic effects of varying degrees.

In the group with EC 1.5-2.2 grains prevail that preserved appearance of crystals (65 %). Among the established morphological types of crystals (Fig. 4), the most widespread are S_{13} and S_{14}, (rarely S_{12} and S_8), characteristic to S-granites of carbonate-alkaline series, P_3 (with P_5, J_5, and J_4 in subordinate amount) corresponding to I-granites of alkaline and tholeiitic series. In small quantities zircon crystals are marked of subalkalic hybrid granites (S_{15}), magmatic charnockitic areas (S_{24}), tracheandesite (S_{23} and J_4), tonalite (S17, S_{18}), alkaline granites (M_2) and acidic granites (Q_3).

Microanatomical patterns of crystal zoning are growth oscillator, affected to varying degrees by later processes of alternation (Fig. 5). In 75 % of cases there is moderately uniform blur of zoning boundaries. The 25 % has a partial recrystallization with appearance of dark spots and locally modified areas of crystals. In a few cases there are rounded fragments of crystals with anatomical patterns characteristic

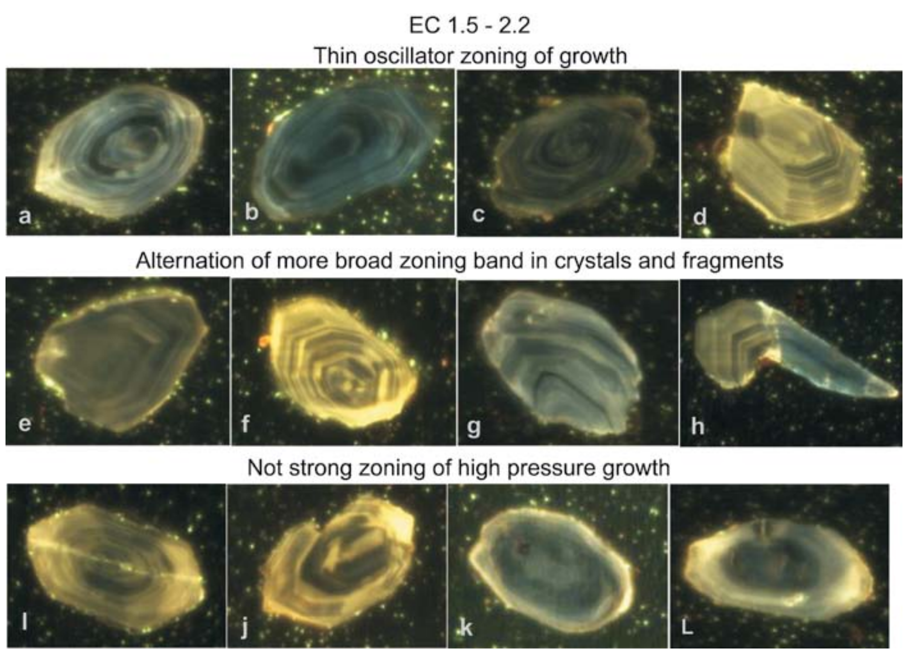
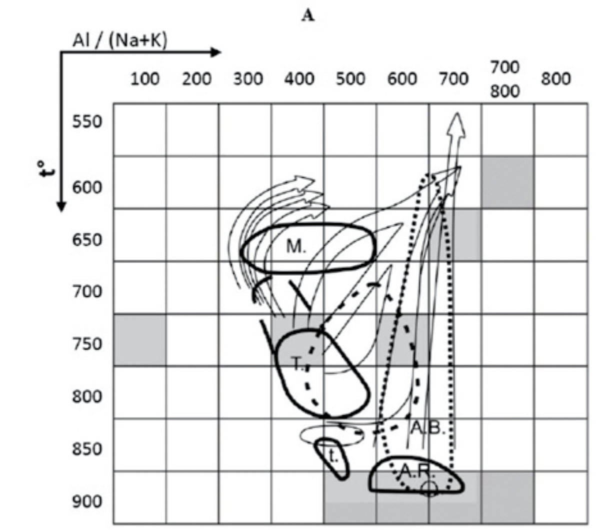


Fig. 5. Cl-patters of polished zircon grains from Beitagirsky field (grain size 0.1-0.071 mm).



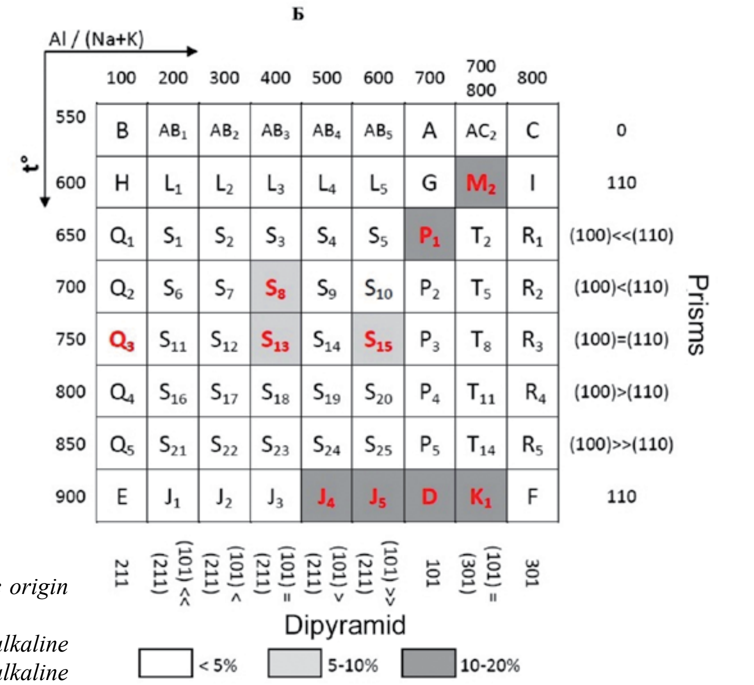


Fig. 6. Morphogenetic classification of zircon of non-granitic origin from Beitagirsky field according to J.P. Pupin chart (1980). A – morphogenetic typing: (A.B.) – alkaline basalts; (A.R.) – alkaline series of anorogenic rhyolite complexes; (C.A.R.) – carbonate-alkaline series of rhyolite (orogenic): (M) – migmatites, (t.) trachyandesites, (T) – tonalites. Grey color is designated for location of zircon types from Beitagirsky field with EC over 2.2. B – Occurrence statistics of morphological types of zircon from Beshpagirsky field with EC over 2.2. Red color is designated for zircon morphotypes of Beitagirsky field.

to zircon with EC over 2.2.

Rounded grains with EC 1.5-2.2 (35 %) have rough surface with small holes (Fig. 2. 11-16), and microanatomical patterns are signs of secondary changes in growth zoning.

From the above we can conclude that group of grains with EC 1.5-2.2 has a primary magma genesis and consists of zircon crystals of S-granites from calcareous-alkaline series (70 %), 1 – granites of alkaline and tholeiitic series (27 %) and granites of transitional series (3 %). Zircon grains of all types have traces of secondary modifications of magmatic growth zonation in varying degrees of intensity, as well as thin regenerative rim, covering the surface of crystals.

In the group of grains with EC over 2.2 crystals are marked with preserved elements of the cut (60 %), rounded grains (38 %), elongated-prismatic fragments (2 %).

Among the morphological types crystals are distributed with tetragonal prisms {110} and dipyramid {101} in combination with {211} and {301}, complicated by additional elements of the cut characteristic to morphotypes J_4-D-K (Fig. 2, grains 26, 31, 32). This morphological series, in our opinion, is effusive and according to the genetic chart, distribution of zircon of non-granite series by J.P. Pupin (1980) corresponds to the alkaline series of anorogenic rhyolite complexes (Fig. 6).

Morphotype P_1 is the second most common (Fig. 2. 30), corresponding to alkaline basalt. The same type includes zircon crystals of morphotype M_9. The smallest spread in the group with EC over 2 belongs to morphotypes S_{13} and S_{15} – calcareous-alkaline series of rhyolite from orogenic complexes and morphotype Q_3.

In the group of grains with EC over 2.2, crystals with recrystallized nucleus and unclear zoning are clearly distinguished (Fig. 7) from metamorphosed rocks (60 %), with banded zoning possibly from volcanic rocks of intermediate composition (40 %).

Zircon study using samples of morphological and microanatomical typomorphic features enabled to set in Beshpagirsky placer the following types of the described

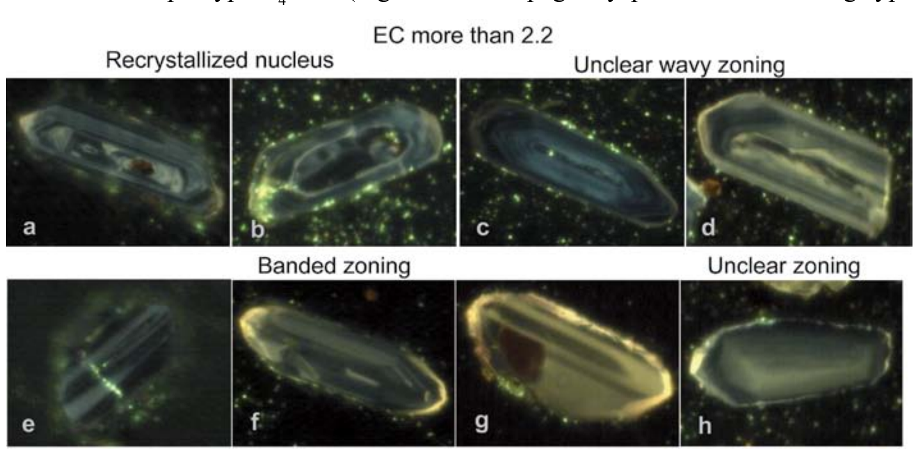


Fig. 7. Cl-pattern of polished zircon grains from Beshpagirsky field (grain size 0.1-0.071 mm). Grain is e-fragment, referred to the group according to zoning pattern.

	Crystallization temperature, C				
	600-650	700-750	800-850	900	Total, %
Metamorphogenic	2,5	2,5	n.d.	n.d.	**5**
Magmatic intrusive					
S-type	2,0	45,0	5,0	3,0	**55,0**
I-type	n.d.	13,00	0,8	1,2	**15,0**
Magmatic effusive					
S-type	n.d.	2,0	n.d.	n.d.	**2**
I-type	11,5	n.d.	n.d.	11,5	**23**
Total, %	**16**	**62,5**	**5,8**	**15,7**	**100**

Table. Petrogenetic types of zircon from Beshpagirky field of rare metal-titanium placers according to Pupin chart (1980).

mineral: metamorphogenic (5 %), primary magmatic intrusive (S-granites 55 %, I-granites 15 %), primary magmatic effusive (alkaline rhyolite 15 %, alkaline basalts 10 %). At the same time 85 % of the studied zircon grains show signs of secondary changes of varying intensity, which may be due to metamorphism of rocks of demolition source.

Another important feature is the absence of distinct metamorphic regeneration rims, with the exception of 4 grains with distinct contrast xenomorphic regeneration cores and rims (Fig. 4-c, k). On the surface of 3 % of grains relics of thin regeneration rims are marked of yellowish color (Figure 5. d, e; Figure 7. d, f, g). It is believed that part of the grains lost regenerative rims during transportation, as evidenced by thin chipped rims on the crystal surface (Fig. 2. 8, 18, 26, 28).

U-Pb dating of metamorphic and regeneration zircon rims (SHRIMP II) of Beshpagirsky field, carried by V.V. Kremenetsky et al (2011), has set the age of regeneration rims as 310 million years, which corresponds to the age of Variscan metamorphism in the Caucasus. Paleogeographic reconstructions (Fig.1) point out on the Caucasus, as the main source of clastic material ablation during the formation of Stavropol Neogene placers. This gives us the possibility of conditional comparison of the data with help of petrogenetic classification of zircon from Beshpagir with the conditions, in which they can be formed in the Caucasus.

Discussion of the results

The main criteria in determining the zircon provenance were crystallization temperature and geochemical belonging to granitoids of S – and I-type (Table). In the Caucasus, the nature of Variscan granite formation clearly correlates with the crust type: within sialic crust of Bechasynsky zone and especially Elbrus subzone of the Main Ridge S-granites were formed in ensimatic areas of the Front Ridge and crossover subzone of the Main Ridge – granitoids of I – and IM-type. In the first case there was remelting of sialic metasedimentary material, in the second – of mafic. In both cases, the contrast of compositions and P-T conditions of formation of metamorphic belts of these zones is emphasized: low-pressure – high-temperature in the Main Ridge and high-pressure – medium-temperature in the Front Ridge (the Great Caucasus in the Alpine epoch, 2007).

Analysis of the data indicates a predominance of medium-temperature intrusive zircon in Beshpagirsky placer, gravitating to the S-type granites with minor signs of secondary changes. Granites of this type are widely developed in the area of the Main Caucasus Ridge; they are syn – and postmetamorphic granitoids of carbonate-alkaline formation (Fig. 1). Temperature of crystallization of these granitoids is estimated by the authors (Somin, 2000; Petrology..., 1991) at 700-750 °C. Another source of zircon of this type may be unevenly metamorphosed of biotite facies in the north to biotite-garnet facies in the south of sedimentary and volcanic rocks of carbonate-alkaline series of Bechasynsky zone. Rocks of Bechasynsky complex can include effusive zircon of S-type (Table).

The Main Ridge area has widespread gneiss-migmatite metamorphic complex, with temperatures close to granulite. Rocks of this complex can include zircon grains with characteristic microanatomical metamorphic textures and high-temperature intrusive zircon of S-granites.

The second most common zircon in Beshpagirsky placers is zircon of I-granites. Its distinguishing feature is in the development of 'hybrid' elements of facet inherent to multiple high-temperature morphotypes, as well as increasing alkalinity due to cooling of the substrate (Fig. 6). Identified features are characteristic for associations of granitoids of I-type of the Front Ridge and saddle area of the Main Ridge (Fig. 1). Formation of these granitoids is genetically associated with an early stage of subduction zone development as a result of directional changes of the oceanic crust and is in its sequential enrichment of alkalis and magmatism change of tholeiitic series to granitoids of elevated potassium alkalinity (Petrology ..., 1991).

Thus, the source of high-temperature effusive and intrusive zircon of this type could be volcanic, genetically associated with ophiolite associations of the Front Ridge, composing independent zone of Variscan structures of the Great Caucasus. The source of medium-temperature zircon may have been both deep and igneous magma melts of high-alkalinity, which are processing products of ensimatic crust. This assumption may explain the presence of xenomorphic cores and signs of secondary changes in some zircon grains with EC of more than 2.2 (Fig. 7 a, b).

Without exaggeration, it can be noted that the identified genetic types of zircon in general reflect the picture of geological evolution of the whole region.

Statistically, according to the predominance of zircon type in a placer, it can be concluded on the contribution of structural zone in the Caucasus as provenance, provided that the zircon as an accessory mineral found in these rocks in approximately equal concentrations. Referring to the schematic structure of pre-Alpian base of Great Caucasus (Fig. 1) the source area can be conventionally distinguished.

Based on the fact that in studied placers intrusive granites of the S-type prevail, it can be assumed that the main contribution as the source falls on the area of the Main Ridge of the Great Caucasus. Within this zone there are also widespread outcrops of metamorphic rocks of gneiss-migmatite complex, which according to our estimates are a source of metamorphic zircon, the content of which is not large in placer (5 %).

Referring to the schematic structure of pre-Alpian base oucrops of the Greater Caucasus (Fig. 1) it is possible to note that rocks of gneiss-migmatite metamorphic complex in the most part is located in the southern part of this area, and could be water-collecting area from rivers with the southern direction of the flow, while a placer basin in the medium, upper Sarmatskian time was located to the north of the Great Caucasus. Thus, the rocks of this complex, located in the southern part of the Main Ridge were not source areas in Medium, Upper Sarmatskian time for Stavropol placer. While in the northern part, area of the outputs of metamorphic rocks roughly corresponds to the proportion of metamorphic zircon in Beshpagirsky placers.

The main suppliers of detritus from the Caucasus could be paleorivers with a northbound flow, such as paleo-Malka (possibly paleo-Baksan), paleo-Kuban, paleo-Teberda, paleo-Zelenchuki. The beds of these rivers drain the area of the Main Ridge, folded by magmatic and less high temperature metamorphic rocks, the Front Ridge area with ophiolites and associations of alkaline granites and Bechasynsky area with granite of S – type, in varying degrees of metamorphic changes. Outcrop areas of these structural zones roughly correspond to the proportion of zircon of each genetic type, defined in Beshpagirsky placers.

Participation of paleo-Laba, draining the western part of the Main Ridge with the prevailing development of gneiss-migmatite metamorphic complex, and approximately equal to it in size outcrop area of the Front Ridge to the metamorphic complexes and I-granitoids is not likely to have a significant impact on the typical composition of zircon from Beshpagirsky placers, since in its source area zircon of metamorphic genesis and granites of I-type should be present in roughly equal amounts, with the participation of subordinate granites of S-type. Products of paleo-Laba are probably present in placers of western Stavropol placer district, such as Sinyukhinsky and possibly Nevinnomyssky and Tashlinsky (Fig. 1).

Of course, such a comparison at this stage of the study is hypothetical in nature and requires a study of the composition of zircon at a more subtle geochemical level. Further research will not only benefit from more reliable geothermometer, but by means of spectrum of rare earth elements distribution and a set of micro-admixtures will help to detail the results already achieved.

The results of this study complement and coincide with the data obtained in the study of rutile and garnet from Beshpagirsky field (Chefranova et al., 2015). Optimized method of petrogenetic classification of zircon on morphological and microanatomical parameters is recommended for use on less studied placers of Taman Peninsula (Chefranova, Nalomov, 2013; Boyko, Korkoshko, 2003), Ergeny and Dagestan (Matsapulin, Yusupov, 2009; Lalomov, Bochneva, 2006), constituting the Neogene profile of the South Russian placer province.

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