ATLANTIS PRESS
Atlantis Highlights in Material Sciences and Technology (AHMST), volume 1
International Symposium "Engineering and Earth Sciences: Applied and Fundamental Research" (ISEES 2019)

Th/U Ratio in Zircons of Metamorphic Rocks and Granitoids of the Urals as an Indicator of Their Genesis

Pystina Yu.I.
Institute of Geology Federal State Budgetary Institution of Science Federal Research Center "Komi Scientific Center of the Ural Branch of the Russian Academy of Sciences", Syktyvkar, Russia
yuliya_pystina@mail.ru

Pystin A.M.
Institute of Geology Federal State Budgetary Institution of Science Federal Research Center "Komi Scientific Center of the Ural Branch of the Russian Academy of Sciences", Syktyvkar, Russia

Abstract – The paper presents the results of study of zircons of polymetamorphic and granitoid complexes of the Urals. The morphological features of the mineral characteristic of metamorphic and granitoid rocks are established. Morphotypes corresponding to the different physicochemical conditions of their formation and transformation of the host rocks have been identified. Geochronological data are obtained for individual morphotypes of zircons. Geochemical characteristics are established and a comparative analysis of the distribution of individual scattered elements in zircons is conducted, including an analysis of the Th / U ratio in zircons of polymetamorphic complexes and granitoids.

Keywords – polymetamorphic complexes; granitoids; zircons; geochronology.

I. INTRODUCTION

In recent years many publications on geochemical and geochronological studies of zircons from rocks of various genesis have appeared [1–6]. Analysis of published data shows that zircons of magmatic and metamorphic origin most reliably differ in their Th/U ratio, which is usually > 0.5 [4] for magmatic zircons and 0.1-0.3, significantly lower for metamorphic [2], according to Rubatto < 0.07 [6]. Although according to other data it may even be > 0.5, for example, 0.73 in zircons from the eclogite of the Maxutov complex [7]. But, despite some rebounds in the values of Th/U, the average indices for metamorphic zircons, as well as for magmatic ones, are fairly consistent.

Studying the polymetamorphic complexes of the Urals (Fig. 1) for many years, we collected a lot of material on the basis of which we attempted to make generalizations concerning both the morphology of zircons and their geochemical features. They allow the mineral to be used in the reconstruction of specific metamorphic events and the interpretation of geochronological data [8, 9, etc.]. Recently, we also have obtained new results on the morphology and geochemistry of zircons from granitoids of the northern part of the Subpolar Urals [10]. Together this has made it possible to compare different morphological types of magmatic and metamorphic zircons.

II. MORPHOLOGY OF ZIRCONES OF METAMORPHIC COMPLEXES

Precambrian formations, especially Pre-Riphean, which have underwent metamorphism as a rule, experienced it repeatedly, i.e. are polymetamorphic. Accordingly, the newly formed zircons, or transformed from the previously existing ones, in the course of these events should have acquired some new properties, expressed in changes in the morphology of the crystals, in the internal structure, and in the geochemical composition. What we observe in zircons from various polymetamorphic complexes of the Urals, where up to 5 morphological types of this mineral are distinguished (Fig. 2) [9].

The first morphological type is detritic zircons of various colors from colorless to dark pink (Fig. 2.1). The second morphological type is mainly rounded zircons with a clearly defined crystallographic shape due to the development of (311), (111), (110), (100) faces, dark pink, or light yellow. In foreign literature they received the name of the type of zircons – "soccer ball" [11] (Fig. 2.2). The third morphological type is irregular shaped zircons, formed, as it were, by intergrowths of two or more crystals, spontaneously germinating into each other, light colored or colorless. This type of zircon is usually present in the metamorphic rocks of the main composition and stands out as “a cauliflower” type zircons (Fig. 2.3) [12]. The fourth morphological type – zircons of prismatic habit, the main forms: (100), (110), (113), (112), are present (311), transparent, light colored (Fig. 2.4–2.5). AA Krasnobaev [13] distinguishes them as zircons of the “migmatite” type. And, finally, the fifth morphological type – zircons of prismatic habit due to the development of (100) and (111) faces, opaque or translucent of yellow or brownish brown color (Fig. 2.6). Detritic zircons determine the metamorphic affiliation to one or another source formation.

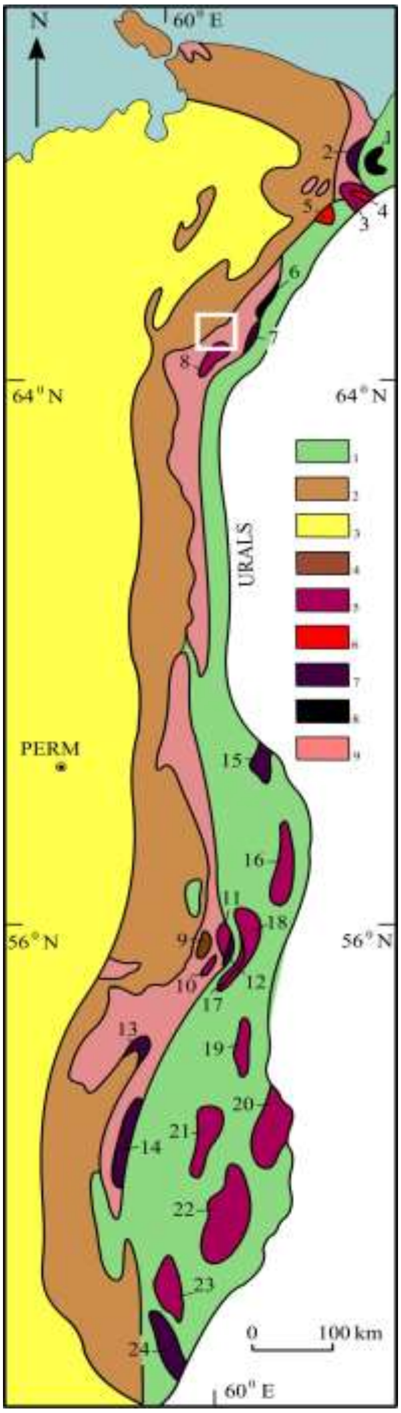

Fig. 1. Location map of polymetamorphic complexes of the Timan-Ural region: 1–2 – Paleozoic formations: 1 – paleooceanic; 2 – paleocontinental; 3 – sedimentary cover of the European platform; 4–7 – Lower Precocambrian (?) Polymetamorphic complexes: 4 – gneiss-granulitic, 5 – gneiss-migmatite, 6 – crystal-schists, 7 – eclogite-gneiss and eclogite-schists; 8 – granulite-metabasite; 9– Upper Proterozoic formations, mainly undergone green shale metamorphism. Polymetamorphic complexes: 1 – Malyk, 2 – Marunkeu, 3 – Hanmeikhoy, 4 – Parikvasshor, 5 – Kharamatalou, 6 – Khordyus, 7 – Nerkayu, 8 – Nyartin, 9 – Taratash, 10 – Alexandrov, 11 – Ufaley , 12 – Eastern Ufaley, 13 – Beloretsk 14 – Maksyut, 15 – Saldin, 16 – Murzin-Aduy, 17 – Selyankin, 18 – Sysert-Ilmenogorsk, 19 – Kochkar, 20 – Mariinsk, 21 – Adamovsk, 22 – Tekeldy-Tau, 23 – Kayrakta, 24 – Taldyk.

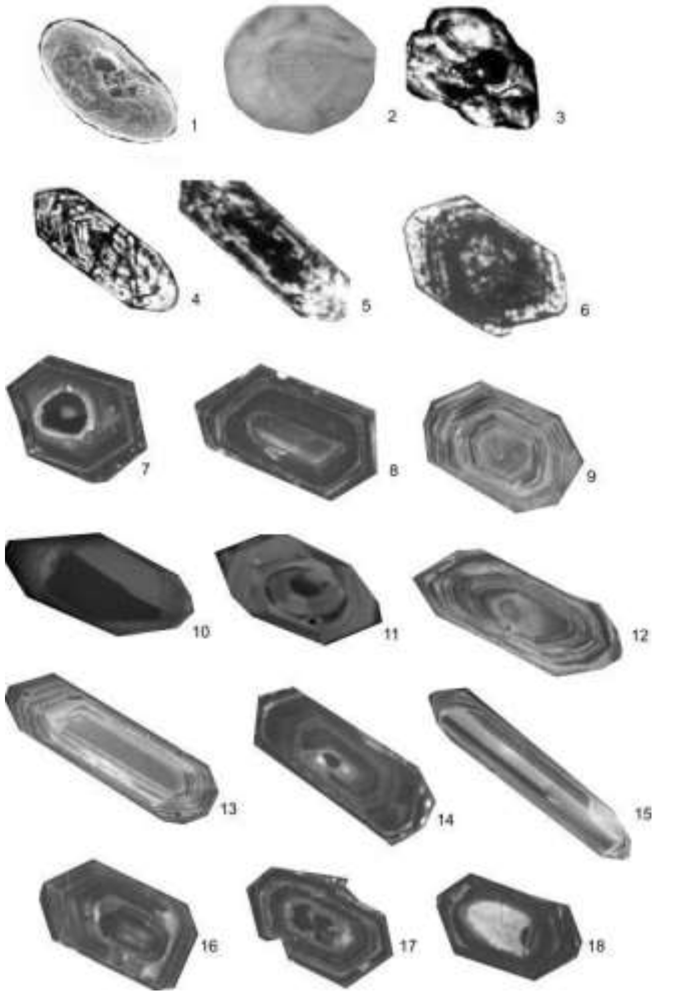

Fig. 2. Morphology of zircons from metamorphic rocks and granitoids of the North of the Urals. 1–6 – zircons from metamorphic rocks: 1 – detritus type zircons, 2 – “granulite” type zircons (“soccer ball”), 3 – irregular shaped zircons (“cauliflower”), 4–5 – “migmatite” type zircons (4 type), 6 – non-transparent zircons (5 type); 7–18 – zircons from granitoids: 7 – zircon type, 8–9 – hyacinth type. 10–12 – spear-shaped type, 13–15 – torpedo-shaped type, 16–18 – cyrtolithic type.

Zircons of the “soccer ball” type or, as is customary in the Urals, after A. Krasnobayev [13], call them "granulitic" (type 2), and also "migmatite" (type 4) fix the manifestation of high-temperature rock transformations. Zircon of irregular shape like “cauliflower” (type 3) is characteristic of rocks metamorphosed under conditions that do not exceed the low to medium stages of the amphibolite facies. In more high-temperature conditions it is found in the rocks of the main series. The reason for the emergence of such intricate forms of zircon may be the absence or deficiency of silicate melt. That is why, when P-T reaches the conditions of metamorphism, sufficient for the development of migmatization processes, such zircon can continue to crystallize only in metamorphic mafic composition, for which, as is known, the temperature threshold of migmatization is higher. Opaque zircons (type 5) are associated with the manifestation of medium temperature diaphtoresis. The internal structure of all morphotypes is characterized by the presence of nuclei of irregular or rounded shape, in the “migmatitic” type, oscillatory zonality is usually noted, the “granulitic” type is the most homogeneous.

It should be noted that among the detailed morphotypes of zircons in polymetamorphic complexes the “granulite” and “migmatite” types prevail. If, by morphological features and internal structure, the zircons of polymetamorphic complexes are confidently divided into morphotypes, which can be associated with certain metamorphic events, then the geochemical composition of the rare elements does not make a clear separation. On the one hand, this is due to the extremely low content of the elements themselves, most often zircon is enriched only in Hf, Y, U, P. On the other hand, the nature of the distribution of these elements in the crystal, their quantitative variations do not give reason to separate some zircon morphotypes from others. Although in some cases it is possible. For example, in “migmatite” zircons (type 4) from the gneisses of the Harbay complex, the distribution of Hf decreases from the center of the crystal to the edge, while in other morphotypes of zircons from the same rocks increases from the center to the edge. At the same time, in the gneisses of the Nyartin complex in all selected morphotypes, including the “migmatite” type, the content of Hf increases from the center of the crystal to the edge. The same picture, according to our data, is observed in zircons from the rocks of the metamorphic complexes of the Southern Urals: the Alexandrov and Ilmenogorsk (Selyankin block). But in general, the content and distribution of the scattered elements according to the data available today with morphological types of zircons are clearly not correlated. As noted above, metamorphogenic zircons differ from magmatogenic ones by a lower Th/U ratio: <0.5. This empirically established rule, in general, is confirmed by our data. As can be seen from table 1, in zircons from the Alexandrov complex rocks, the Th/U ratio does not exceed 0.41. All the grains analyzed belong to the “granulite” type and their crystallization is associated with the manifestation of the metamorphism of the granulite facies about 2.1 billion years ago [9, 14]. In zircons from the Nyartin complex rocks (Tab. 1), the Th/U ratio varies in the range of 0.02–0.75.

TABLE I. THE CONTENT OF TH AND U IN POLYMETAMORPHIC COMPLEXES OF THE URALS

№	Nyartin complex			№.	Alexandrov complex		
	ppm U	ppm Th	$^{232}Th/^{238}U$		ppm U	ppm Th	$^{232}Th/^{238}U$
1	91	66	0,75	1	609	136	0,23
2	66	44	0,68	2	485	116	0,25
3	123	36	0,31	3	143	32	0,23
4	316	7	0,02	4	156	41	0,27
5	360	104	0,30	5	223	77	0,36
6	402	212	0,54	6	167	66	0,41
7	289	25	0,09	7	187	70	0,38
8	313	104	0,34	8	60	20	0,34
9	444	166	0,39	9	255	82	0,33

At the same time, lower Th/U ratios (0.02–0.54) have crystals with Precambrian isotopic U/Pb datings, and elevated (0.75, 0.68) – with Paleozoic. Crystallization of zircons with a low Th/U ratio is associated with polymetamorphic rock transformations, and with a high Th/U ratio apparently with activation of magmatic processes in the early stages of development of the Uralides. The U-Pb-isotope age of zircons with a high Th/U ratio: 503±8 Ma (grain No. 1 in Tab. 1) and 498±8 Ma (grain No. 2 in Tab. 1) [9].

III. MORPHOLOGY OF ZIRCONES OF GRANITE COMPLEXES

Our studies show that accessory zircons from rocks of different granitoid complexes in the northern part of the Subpolar Urals, which occupy different geological positions and differ in isotopic age, differ in the set of morphotypes, their quantitative ratios, to some extent and geochemical features [10, 15]. Recently, we have studied the morphological features of zircons from granites from Nikolaishor (PR$_1$), Kozhim (PF$_3$), Badiau (RF$_3$–V) and Yarota (RF$_3$–V) massifs [10](Fig. 3).
In the samples of the granitic massifs studied by us, the presence of accessory zircons is very diverse in form, nature of zonality, presence of inclusions, color, degree of metamictization and other features. In total, they represent all the main morphological types of zircons according to I.V. Nosyrev [16]: zircon type, hyacinth, spear-shaped, torpedo-shaped and cyrtolithic (Fig. 2.7-18.). All of the above morphological types can be related to the generation of zircons of either synpetrogenic or superimposed genetic types [16].

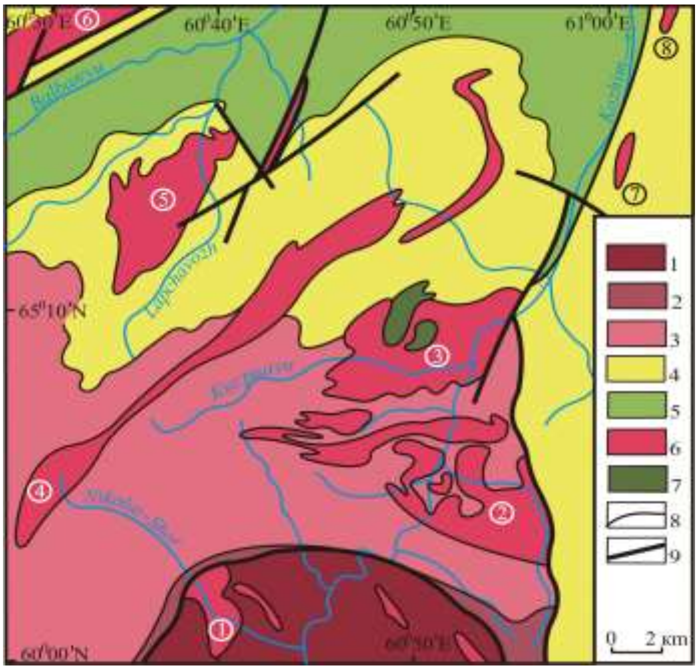

Fig. 3. Scheme of the geological structure of the northern part of the Subpolar Urals. 1 – Nyartin gneiss-migmatite complex (PR$_1$); 2 – schokurya suite (RF$_1$); 3 – the Puyva suite (RF$_2$?); 4 –Neoproterozoic deposits (RF$_3$–V), undivided; 5 – Paleozoic deposits (Є$_3$–O), undivided; 6 – granites; 7 – gabbro; 8 – boundaries of stratigraphic and intrusive divisions; 9 – faults. Massifs (numbers in circles): 1 – Nikolaishor; 2 – Kozhim; 3 – Kuzpuayu; 4 – Khatalambo-Lapchin; 5 – Lapchavozh; 6 – Maldin; 7 - Yarota; 8 – Badiau.

The zircon morphotype consists of transparent and translucent pale-colored, less often dark-brown crystals of short-prismatic habitus (Fig. 2.7). The hyacinth morphotype is represented by translucent less often transparent light-colored zircons of dipyramidal-prismatic habitus (Fig. 2.8–2.9.). Transparent, pale-colored zircons of a dipyramidal-prismatic and prismatic-dipyramidal habitus (Fig. 2.10–2.12) are highlighted in the spear-shaped morphotype. The torpedo-shaped morphotype consists of transparent colorless or pale-colored, rarely dark brown zircons of prismatic habitus. The combination of a sharp dipyramid and a well-pronounced blunt gives a torpedo-shaped crystal appearance (Fig. 2.13–2.15). The cyrtolithic morphotype is formed by opaque zircons of brownish yellow or brown prismatic and short prismatic habit. Crystals often have a flattened appearance (Fig. 2.16–2.18). The internal structure of all the detailed morphotypes of zircons is characterized by oscillatory zonality, sometimes round or irregularly shaped nuclei are noted. In unchanged granites, the zircon morphotype refers to early magmatic generation, hyacinth to late magmatic, co-shaped to pegmatite, torpedo-shaped to pneumatolytic, cyrtolithic to hydrothermal. The formation of the last two morphotypes (torpedo-shaped and cyrtolithic), rarely spear-like, may be associated with superimposed processes and in these cases they belong to the superimposed genetic type [16]. In addition, detritic zircons are present in the granites of the Nikolaishor massif, which lies among the deep-metamorphosed rocks of the Nyartin gneiss-migmatite complex. They are found in the form of rounded grains, in which the primary morphological features of the crystals are lost.

The maximum number of zircon morphotypes in the granites of the Nikolaishor massif is four: hyacinth, spear-shaped, torpedo-shaped, and detrital. Granitoids Kozhim, Badiau and Yarota massifs are characterized by the presence of three morphotypes of zircon, but if in granitoids Badiau and Yarota massifs are similar (zircon type, hyacinth and torpedo-shaped morphotypes), the rocks Kozhim massif – is zircon, torpedo-shaped and cyrtolithic morphotypes. Common to the granitoids of all the massifs is one morphotype – torpedo-shaped. Spear-shaped zircon is installed only in rocks of the Nikolashor granite massif. There are also detrital zircons, which are absent in the granitoids of other massifs. Granites of the Kozhim massif are distinguished from other granitoids by the presence of zircon of the cyrtolithic morphotype. The presence of this type of zircons is a sign of the metasomatic (or metamorphic) processing of rocks [17]. In addition, in contrast to the granites of the Badiau and Yarota massifs, they lack hyacinth type zircons.

Thus, as in the metamorphic complexes zircons of the granitoids studied by us are quite confident in their morphological features. As for the geochemical characteristics, the set of rare elements in zircons of different morphotypes is identical. The highest concentrations are characteristic for Hf, Y, Yb, Nd, Th, and U, but all of them, with the exception of Th and U in zircons of the cyrtolithic morphotype are very low. Only in some cases it is possible to establish some differences in the distribution of individual elements in different morphotypes. Thus an analysis of the distribution of U in the spear-shaped zircons of the Nikolaishor massif shows that with the prevailing development of the pyramid, the content of U decreases from the center of the crystal to the edge, and as the prism develops, on the contrary, it increases. According to some researchers [18], the enrichment of the edge parts of zircon crystals U can be explained by the influence of subsequent metamorphic transformations of rocks, which is quite consistent with the real situation. The Nikolaishor granitoids, as well as host rocks, have undergone several stages of metamorphism, also in the conditions of medium to high temperatures. The content of U in zircons of the cyrtolithic morphotype in granitoids of the Kozhim massif increases from the center of the crystal to the edge, which is probably due to metamorphic transformations of granitoids, as indicated by the inclusions in zircons (most likely newly formed) of thorite and uranothorite.

As noted above, the torpedo-shaped zircon morphotype is common for all granitoids of the territory under consideration. But according to the nature of the distribution of rare elements, zircons of this morphotype in the rocks of the Badiau and Yarota massifs differ, on the one hand, from similar zircons in the Nikolaishor and from Kozhim rocks, on the other.

TABLE II. THE CONTENT OF TH AND U IN GRANITOID COMPLEXES OF THE SUBPOLAR URAL

№	Nikolaishor			№	Kozhim		
	ppm U	ppm Th	$^{232}Th/^{238}U$		ppm U	ppm Th	$^{232}Th/^{238}U$
1	124	64	1	1	1450	945	0,67
2	912	831	0,94	2	907	524	0,60
3	381	234	0,63	3	1477	863	0,60
4	818	538	0,68	4	802	433	0,56
5	362	222	0,63	5	840	525	0,65
6	1049	741	0,73	6	522	246	0,49
7	721	487	0,70	7	874	516	0,61
8	424	270	0,66	8	1330	803	0,62
9	887	625	0,73	9	1450	945	0,67
10	582	376	0,67	10	907	524	0,60
	Khatalambo-Lapchin				**Lapchavozh**		
№	ppm U	ppm Th	$^{232}Th/^{238}U$	№	ppm U	ppm Th	$^{232}Th/^{238}U$
1	1778	1007	0,59	1	1766	1857	1,09
2	535	226	0,44	2	648	500	0,80
3	479	357	0,77	3	208	166	0,82
4	1451	546	0,39	4	294	169	0,59
5	274	96	0,36	5	178	159	0,92
6	1274	635	0,51	6	315	173	0,57
7	460	252	0,56	7	213	147	0,71
8	135	28	0,22	8	584	436	0,77
9	621	91	0,15	9	335	212	0,65
10				10	99	65	0,68

Moreover, in the rocks of the Nikolaishor and Kozhim massifs, torpedo-shaped zircons with similar geochemical characteristics differ markedly in Y content. Firstly, they have the lowest Y values for this zircon morphotype, and in the Kozhim granites, on the contrary, they are the highest.

Tab. 2 shows the contents of Th and U, as well as the values of Th/U ratios in zircons from the granitoids of Nikolaishor (PR_1), Kozhim (PF_3) Khatalambo-Lapchan (RF_3–V) and Lapchavozh (RF_3–V) massifs. The results in the table show that the Th/U ratio in zircons from granitoids of the northern part of the Subpolar Urals – Nikolaishor, Kozhim, Khatalambo-Lapchan and Lapchavozh massifs 0.73; 0.61; 0.51; 0.79, respectively.

These values are maintained and observed in all zircons of the studied granitoids. Only in some cases in the zircons from the granitoids of the Khatalambo-Lapchan massif, the Th/U values are knocked out of the general picture, amounting to 0.22 and 0.15, which is not at all characteristic of magmatic zircons. If we consider that the age of these zircon crystals obtained by the U-Pb SHRIMP-II method is 703.9±8 Ma and 795±41 million years, and the rest of the zircons are 550–580 Ma, we can assume that the formation of ancient zircons is due to more the early stages of granite formation. And the increased Th/U ratio is explained by the subsequent metamorphism of early generation granites.

IV. CONCLUSION

Thus, we have to state the validity of the fact that "... the only obvious systematic difference between the magmatic and metamorphic zircon is the Th/U ratio ..." [4]. It allows not only distinguishing between magmatic zircons from metamorphic, but taking into account the morphological features of individual crystals and isotopic age dating. It is more reliable to restore the history of the formation of specific metamorphic and magmatic complexes.

Acknowledgment

This work was supported by the Basic Research Program of the Russian Academy of Sciences, No. 18-5-5-19.

References

[1] I.L. Nedosekova, B.V. Belyatsky, E.A. Belousova, "Rare elements and isotopic composition of hafnium as indicators of the genesis of zircon during the evolution of the alkaline carbonatite magmatic system (Ilmen Vishnevogorsky complex, Ural, Russia)", Geology and Geophysics. vol. 57, no. 6, pp. 891–906, 2016.

[2] S.G. Skublov, S.B. Lobach-Zhuchenko, N.S. Guseva et al., "Rare earthand trace element distribution in zircons from miaskite lamproites of the Panozero complex, central Karelia", Geochemistry International, vol. 47, no. 9, pp. 901–913, 2009.

[3] G.B. Fershtater, A.A. Krasnobaev, F. Bea, P. Montero, "Zircon geochemistry from igneous and metamorphic rocks of the Urals", Lithosphere, no. 4, pp. 13–29, 2012.

[4] W.O. Hoskin, U. Schaltegger, "The Composition of zircon and igneous and metamorphic petrogenesis", Zirkon, vol. 53, Washington: Reviews in mineralogy & geochemistry, pp. 27–62, 2003.

[5] A. Liati, D. Gebauer, C.M. Fanning, "Geochronological evolution of HP metamorphic rocrs of the Adula nappe, Central Alps, in pre-Alpine and Alpine subductioncycles", J.Geol.Soc., vol. 166, pp. 797–810, 2009.

[6] D. Rubatto, "Zircon trace element geochemistry: partitioning with garnet and the link between U-Pb ages and metamorphism", Chem. Geol., vol. 184, pp. 123–138, 2002.

[7] A.A. Krasnobaev, P.M. Valizer, V.N. Anfilogov, E.V. Medvedeva, S.V.Busharin, "Zirconology of rutile eclogites of the Maksyutovsky complex (Southern Urals)", Dokllady Earth Sciences, vol. 477, no. 3, pp. 342–346, 2017.

[8] A.M. Pystin, V.L. Andreichev, O.V. Udoratina et al., The deep structure of the Timan-Northern Ural regione. Syktyvkar: Geoprint, 2011, p. 261.

[9] A.M. Pystin, Yu.I. Pystina, "Metamorphism and granite formation in the Proterozoic-Early Paleozoic history of the formation of the Subpolar Ural segment of the earth's crust", Lithosphere, no. 6, pp. 25–38, 2008.

[10] Yu.I. Pystina, Yu.V. Denisova, A.M. Pystin, "Typomorphic characteristics of zircon as a criterion for subdivision and correlation of granitoids (on an example of the northern part of the Subpolar Urals)", Proceedings of Institute of Geology, Komi SC, Ural Branch of RAS, no. 12, pp. 3–15, 2017.

[11] U. Schaltegger, C.M. Fanning, D. Gunther, J.C Maurin, K. Schulmann, D. Gebauer, "Growth, annealing and recrystlisation of zircon and preservation of monazite in high-grade metamorphism: conventional and in-situU-Pb isotope, cathodoluminescence and microchimical evidence", Contrib Mineral Petrol., vol. 134, pp. 186–201, 1999.

[12] F. Corfu, E.K. Ravna, K.A. Kullerud, "Late Ordovican U-Pb age for HP metamorphism of the Tromsdalstind eclogite in the Uppermost Allochthon of the Scandinavian Caledonides", Geochim Cocmochim Acta, vol. 77, A153, August, 2002 [12th Annual Goldschmidt Conference, 2002].

[13] A.A. Krasnobaev, Zircon as an indicator of geological processes. Moscow: Nauka, 1986, pp. 152.

[14] A. Pystin, J. Pystina, "The early Precambrian history of rock metamorphism in the Urals segment of crust", International Geology Review, vol. 57, iss. 11–12, pp. 1650–1659, 2015.

[15] A.M. Pystin, Yu.I. Pystina, "Archean and Paleoproterozoic history of rock metamorphism in the Urals crustal segment", Precambrian Geology Series, no. 7, pp. 3–18, 2015 [Proceedings of the Karelian SC of RAS].

[16] I.V. Nosyrev, V.M. Robul, K.E. Esipchuk, V.I. Orsa, Generative analysis of accessory zircon. Moscow: Nauka, 1989, p. 203.

[17] M.V. Fishman, N.P. Yushkin, B.A. Goldin, E.P. Kalinin, Mineralogy, typomorphism, and Genesis of accessory minerals of igneous rocks of the Northern Urals and Timan. Leningrad: Nauka, 1968, p. 250.

[18] B.M. Osovetskiy, Typohimism of schlichminerals, Reference book. Perm: Publishing house of Perm. State. University, 2001, 244 p.