E.V. Levashova, PhD (Geology & Mineralogy), Junior Research Fellow
Institute of Precambrian Geology and Geochronology of RAS
2, Makarova Emb., St. Petersburg, Russia, 199034
E-mail: levashova.kateryna@yandex.ru
https://orcid.org/0000-0002-0814-1428
H.O. Kulchytska, DrSc (Geology), Chief Research Fellow
M.P. Semenenko Institute of Geochemistry, Mineralogy and Ore Formation (IGMOF) of NAS of Ukraine
34, Acad. Palladin Ave., Kyiv, Ukraine, 03142
E-mail: kulchechanna@gmail.com
https://orcid.org/0000-0002-7206-4797
S.G. Skublov, DrSc (Geology & Mineralogy), Prof., Chief Research Fellow
Institute of Precambrian Geology and Geochronology of RAS
2, Makarova Emb., St. Petersburg, Russia, 199034
Saint Petersburg Mining University
2, 21st Line, St. Petersburg, Russia, 199106
E-mail: skublov@yandex.ru
http://orcid.org/0000-0002-5227-4260
I.M. Herasymets, PhD (Geology), Junior Research Fellow
M.P. Semenenko IGMOF of NAS of Ukraine
34, Acad. Palladin Ave., Kyiv, Ukraine, 03142
E-mail: Herasimets@i.ua
https://orcid.org/0000-0003-4670-0216
S.G. Kryvdik, DrSc (Geology & Mineralogy), Prof., Chief Research Fellow
M.P. Semenenko IGMOF of NAS of Ukraine 34, Acad. Palladin Ave., Kyiv, Ukraine, 03142
E-mail: kryvdik@ukr.net
https://orcid.org/0000-0002-8356-1115
O.L. Galankina, PhD (Geology & Mineralogy), Senior Research Fellow
Institute of Precambrian Geology and Geochronology of RAS
2, Makarova Emb., St. Petersburg, Russia, 199034
E-mail: galankinaol@mail.ru
Scopus ID: 7801578217
M.E. Mamykina, Student. Saint Petersburg Mining University 2, 21st Line, St. Petersburg, Russia, 199106
E-mail: emamikina@mail.ru
D.S. Levashov, PhD (Techn.), Associate prof. Saint Petersburg Mining University
2, 21st Line, St. Petersburg, Russia, 199106
E-mail: levashov_ds@pers.spmi.ru
https://orcid.org/0000-0003-2776-5153

TRACE ELEMENT GEOCHEMISTRY OF ZIRCONS
FROM THE VELYKA VYSKA SYENITE MASSIF, UKRAINIAN SHIELD

Zircon crystals from crushed syenite samples of individual intrusive bodies in the Velyka Vyska Massif were studied using the SEM-EDS (BSE images and chemistry) and SIMS methods. The results obtained were compared with early published data for zircon from the Azov and Yastrubets syenite massifs, Ukrainian Shield that host Zr-REE mineralization published earlier. Most of the zircon crystals analyzed are chemically inhomogeneous, but either azonal or show poorly-defined regular zoning. A darker

contrasting marginal zone is visible only in scarce crystals. The presence of solid silicate, sulphide, phosphate and carbonate inclusions support the assumption that the zircon crystallization medium was heterogeneous. The percentages of rare-earth, radioactive and other trace elements are below 1.6 wt.% and their mean value of 0.4% is smaller than in zircon from other massifs. The percentage of U + Th (average 0.07 wt.%) is too small for radioactive elements to be responsible for metamictization. Similar to zircon from other massifs, Y, which predominates over REE at a ratio of 1.3 : 1, plays the leading role. As the total amounts of Y and REE increase, REE composition becomes rich in LREE. Zircon from Velyka Vyska syenites has the highest HREE-content. The LREE/HREE mean ratio for this zircon is 0.06, while for Azov and Yastrubets zircons the ratio is 0.18 and 0.26, respectively. There are two types of REE distribution pattern for zircon crystals. Those of type I, characteristic of most crystals, are differentiated. They are identical to the pattern of central areas of crystals from other massifs and are typical of zircon which has crystallized from melt. Flattened spectra of type II are characteristic of crystal margins with a well-defined zonal structure. They are identical to those for the marginal parts of zircon crystals from other massifs and are characteristic of zircon crystallization in which a fluid phase was involved. The estimated zircon crystallization temperature calculated by Ti-thermometry is 600-1000 °C, commonly 700—800 °C, which is slightly lower than the values expected.

Keywords: *zircon, syenite, Velyka Vyska massif, yttrium, radioactive and rare-earth elements, REE deposit.*

Introduction. Zircon is a mineral occurring in practically all rock types. It plays a key role in solving many problems in mineralogy, geochemistry, geochronology and other fields of geology. Zircon is one of the best-studied minerals. However, the development of more sophisticated analytical methods opens up new prospects in the study of zircon. In spite of the relatively constant chemical composition of the mineral, it contains the impurities of rare-earth and many other trace elements. The trace element composition of zircon, together with the study of its internal structure, may cast light on the conditions of its formation. It is also widely used for reconstructing the conditions of formation of its igneous and metamorphic host rocks by analyzing the evolution pattern of melts and a fluid regime upon zircon crystallization.

Study area. There are syenite massifs of Proterozoic age with high-grade zircon deposits in the Ukrainian Shield (US). The best-known massifs are Yastrubets (Volyn Megablock), Azov and Octiabrsky (Priazov Megablock) [5]. The massifs display Zr and *REE* + Y mineralization. The Octiabrsky massif also exhibits Nb-mineralization [4].

In contrast to the Octiabrsky massif, in which syenites are typically alkaline [7], Yastrubets and Azov nepheline-free syenites are sub-alkaline rocks locally enriched in quartz. They are remarkable for the high iron content of femic minerals and the prevalence of alkaline monofeldspar of K-Na-composition (anorthoclase), which now occurs as perthitic albite ingrowths in orthoclase or microcline matrix. The formation of anorthoclase indicates that the rock has crystallized under hypersolvus conditions, hence the name hypersolvus given to the syenites [16, 17]. They are also known as nepheline-free, monofeldspathic and rare-metal syenites [6, 10]. Zircon from these massifs is unique not only due to its quantity in ore-hosting rocks

and crystal size but also to its trace and rare-earth element concentrations [15]. *REE* concentration in zircon is sometimes anomalously high (up to 4 wt.% *REE* and up to 8 wt.% Y from the Yastrubets ore occurrence).

Two more syenite massifs of this type known in the Ukrainian Shield are Velyka Vyska (Ingul Megablock) and Davydky (Volyn Megablock). Zircon mineralization in the latter is represented by baddeleyite. Zircon also occurs in small amounts in baddeleyite-bearing rocks (syenites and gabbroic rocks) from this massif.

The Velyka Vyska massif is a tentative name for individual, often linear, bodies intersected by boring on the southern margin of the Korsun-Novomyrgorod Pluton, US. These small (the biggest intrusions are up to 2 km long) syenite intrusions commonly occur among Korsun-Novomyrgorod granites. Dike-like fayalitic syenite bodies are also encountered outside the above pluton among older (ca. 2.0 Ga) biotite-garnet granites occurring in the Novoukrainian Massif. The composition of the rocks intersected varies from monzonite to leucocratic syenite, but fayalitic-hedenbergitic (with ferrohastingsite) medium- to fine-grained syenites predominate. Ilmenite- and zircon-enriched melanocratic (up to 35% dark-coloured minerals) varieties are occasionally encountered [6, 8]. Anorthoclase-microperthite, sanidine-microperthite, fayalite, hedenbergite, ferrohastingsite, ilmenite and quartz (5-10%) are rock-forming minerals in Velyka Vyska rocks. Zircon, apatite, chevkinite, allanite, britholite and lesser fluorite and bastnasite occur as accessories. Zircon is present in all rock types from the Velyka Vyska massif. It is closely associated with apatite and *REE*-minerals and, together with them, is confined to femic mineral aggregates [2]. Some of zircon crystals are up to 3 mm long, but no large-scale zircon or *REE*-mineral
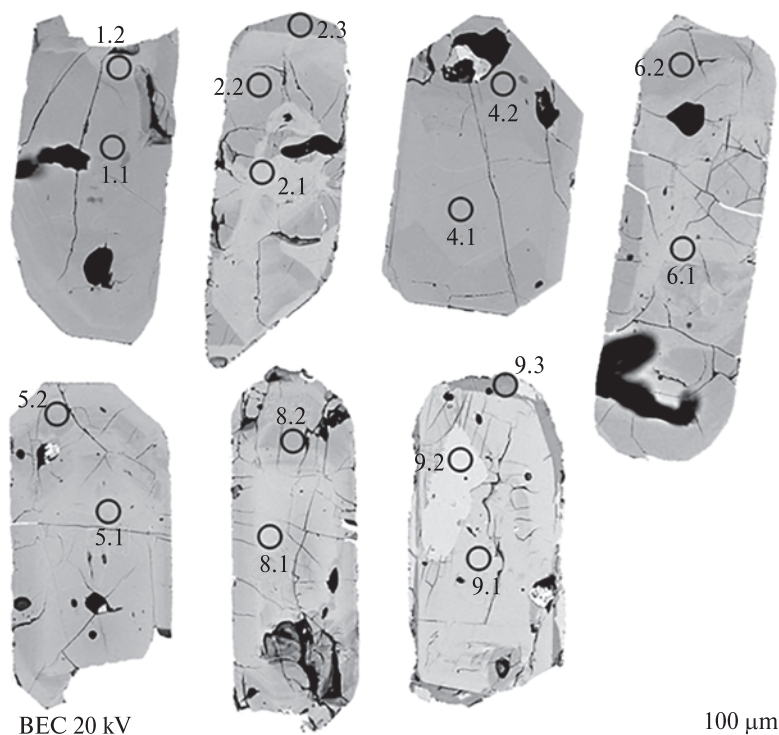
40

ISSN 2519-2396. Mineral. Journ. (Ukraine). 2020. 42, No. 3

Fig. 1. Zircon crystals from Velyka Vyska syenites. Image in a BSE regime. The ion probe crater diameter is ≈20 μm. Point numbers are consistent with numbers in Table

BEC 20 kV

100 μm

aggregates in the massif have been located — a feature used to distinguish between the Velyka Vyska and Azov and Yastrubets massifs. Velyka Vyska syenites have much in common with Azov and Yastrubets syenites, except for the aforementioned characteristics. The massifs are similar in chemical and mineral composition and the compositions of accessory minerals and ore constituents. Azov syenites are most similar to them.

The goal of the present study is to analyze the trace element composition of zircon from the Velyka Vyska massif and to compare it with that of zircon from the Azov and Yastrubets massifs. This will make it possible to assess the differentiation of the Velyka Vyska massif in more detail and to support and update earlier conclusions of the heterogeneity of the zircon crystallization medium [12] .

Methods. The chemical major element composition and internal structure of zircon were analyzed. The presence of mineral phase inclusions in zircon was checked and their composition was analyzed on a JEOL JSM-6510LA scanning electron microscope with an (EDS) JED-2200 energy dispersion spectrometer in a back-scattered electron (BSE) regime (IPGG RAS). *REE* and trace element concentrations in zircon were estimated using the secondary ion mass-spectrometry method (SIMS) on a Cameca IMS-4f ion microprobe (Valiev IPT RAS, Yaroslavl Branch) and standard techniques [19, 21]. Zircon crystallization temper-

ature was calculated with a "Ti-in-zircon" thermometer [24]. When constructing *REE* distribution spectra, zircon composition was normalized to chondrite CI composition [23].

Results. Ten zircon crystals, 0.2 to 0.7 mm in size, from ten 2—3 kg crushed ore-bearing syenite core samples from 7 boreholes that intersected individual bodies in the Velyka Vyska massif were studied. The crystals display a dipyramidal-prismatic habit (Fig. 1). Crystals of isometric habit with a complex external facet configuration are occasionally encountered. Most crystals are opaque and have a yellow or brown colour.

Their heterogenous structure, formed by alternation of parts with various shades of grey, is well defined on a BSE image. The zircons analyzed generally have a light grey central part and a darker margin. A well defined zonal structure is displayed by scarce crystals with very dark margins. The zones are either mottled or display an alternation of light and dark zones. Crystal colour intensity on a BSE image varies near solid-phase inclusions: the colour becomes lighter around some of them and gets darker near others (Fig. 1). Fracturing in the zircon samples is ubiquitous; it is best-developed near some of the inclusions and in the marginal part.

Solid-phase inclusions in zircon. It is known [11, 12] that zircon crystals from the Velyka Vyska massif contain a great variety of mineral microinclusions. Most of them are the accessory minerals of

The content of trace elements in zircon from Velyka Vyska syenite massif, ppm

Component	Sample, point of analysis												
	1.1	1.2	2.1	2.2	2.3	3.1	3.2	4.1	4.2	5.1	5.2	6.1	6.2
	200/858 BH		203/840 BH			205/840 BH		225/809 BH		236/859 BH		241/859 BH	
	dark center	light edge	light center	dark center	dark zone	light center	dark edge	light center	dark edge	light center	dark edge	light center	dark edge
La	0.09	0.31	0.19	0.11	0.04	0.24	0.03	0.10	0.02	0.43	0.08	6.25	0.20
Ce	10.2	9.91	6.38	10.1	2.87	25.2	11.1	10.1	7.28	23.4	13.5	53.1	12.2
Pr	0.15	0.17	0.18	0.15	0.04	0.98	0.11	0.96	0.09	1.24	0.13	3.63	0.35
Nd	2.55	0.76	2.04	1.42	0.71	14.3	1.93	15.6	1.25	19.0	1.61	30.2	2.60
Sm	5.15	0.77	2.71	2.02	1.35	22.6	3.92	19.3	2.75	27.0	2.83	29.0	3.66
Eu	0.22	0.02	0.40	0.26	0.12	0.44	0.15	0.95	0.12	0.59	0.07	1.20	0.21
Gd	26.4	4.70	13.3	10.2	6.09	111	17.2	70.9	14.0	124	13.6	99.2	15.7
Dy	82.5	21.0	50.8	38.2	20.6	378	52.0	192	51.9	360	51.0	305	49.6
Er	144	54.4	156	76.9	38.0	627	94.3	302	95.5	554	97.7	475	82.7
Yb	234	118	391	131	69.0	870	153	427	161	773	155	700	145
Lu	37.6	17.6	70.8	21.0	11.7	129	24.7	66.3	25.1	123	25.3	108	23.4
Li	0.14	1.00	0.45	0.05	0.07	0.74	0.32	0.40	0.28	0.88	0.42	0.73	0.29
P	67.0	130	46.9	75.2	49.0	101	100	81.4	26.3	129	54.1	86.4	311
Ca	24.9	316	35.7	115	43.5	37.4	20.3	24.6	21.5	59.0	1396	58.0	238
Ti	15.9	4.74	28.6	12.0	29.0	7.56	15.3	17.3	17.1	9.67	7.73	14.1	16.7
Sr	0.70	1.80	0.69	1.12	0.51	0.91	0.85	0.88	0.48	2.10	2.79	1.49	0.89
Y	746	254	650	402	202	3531	506	1676	560	3261	524	2672	499
Nb	66.4	32.2	46.8	37.0	35.5	42.3	32.2	19.4	31.3	39.6	33.1	94.6	51.6
Ba	1.65	10.2	3.64	1.17	1.76	2.46	3.36	7.48	1.53	4.43	1.68	32.7	10.0
Hf	11407	13379	12257	11924	10519	12250	10597	10165	11127	10614	11873	12483	9956
Th	82.8	74.7	114	59.1	17.7	419	82.3	118	52.5	381	76.0	409	63.0
U	125	345	672	146	57.1	634	133	153	97.4	449	153	486	114
Th/U	0.66	0.22	0.17	0.41	0.31	0.66	0.62	0.77	0.54	0.85	0.50	0.84	0.55
Eu/Eu*	0.06	0.03	0.20	0.17	0.13	0.03	0.06	0.08	0.06	0.03	0.03	0.07	0.08
Ce/Ce*	21.3	10.4	8.28	19.0	16.2	12.6	49.3	7.81	43.4	7.81	30.7	2.70	11.2
ΣREE	542	228	693	291	151	2179	359	1105	359	2006	361	1811	336
$\Sigma LREE$	13.0	11.2	8.79	11.7	3.67	40.7	13.2	26.7	8.64	44.1	15.3	93.2	15.4
$\Sigma HREE$	524	216	681	277	145	2115	342	1058	347	1934	343	1688	317
Lu_N/La_N	3953	543	3529	1851	2708	5242	8428	6290	12911	2788	2898	167	1134
Lu_N/Gd_N	11.5	30.3	43.1	16.6	15.5	9.44	11.6	7.56	14.5	8.05	15.0	8.83	12.1
Sm_N/La_N	90.1	3.97	22.5	29.5	52.1	152	223	304	235	102	53.9	7.42	29.5
T(Ti), °C	786	681	845	759	847	719	782	794	792	740	721	775	790

trace and rare-earth elements. Rock-forming mineral inclusions and unidentifiable solid phases of Al-Fe-silicate composition are also widespread.

The rock-forming minerals of syenites such as albite, K-feldspar, quartz and to lesser extent hedenbergite, annite and hastingsite that occur as inclusions in the zircon crystal samples were diagnosed by the SEM-EDS method.

Most of the inclusions are in the central zone of the zircon crystals and occur as individual mine-

rals and rock-forming minerals intergrowths, e.g. albite + K-feldspar, quartz + albite, and also form a common inclusion with an Al-Fe-silicate phase. The relationship between the amorphous phase and mineral inclusions is illustratedin [11, 12]. It should be noted that the Al-Fe-silicate phase has a complex, variable composition (FeO — 34—78, SiO_2 — 7—36, Al_2O_3 — 4—19, K_2O and CaO — 1—3 wt.%) and, therefore, cannot be diagnosted mineralogically. The variable composition of con-

42

ISSN 2519-2396. Mineral. Journ. (Ukraine). 2020. 42, No. 3

Sample, point of analysis								
7.1	7.2	8.1	8.2	9.1	9.2	9.3	10.1	10.2
168/860 BH		172/860 BH		178/865 BH			192/858 BH	
light center	dark edge	light center	dark zone	light center	light area in center	dark zone	light center	dark edge
0.49	4.99	16.1	6.16	44.3	0.02	58.9	0.20	0.11
133	56.1	123	24.2	103	3.42	134	9.43	7.34
6.11	3.85	8.14	2.47	7.51	0.02	16.2	0.97	0.13
100	38.3	95.6	12.8	26.4	0.13	58.7	13.8	2.15
122	36.5	97.9	4.32	16.7	0.43	27.2	23.5	4.40
2.57	0.89	2.35	0.32	0.32	0.02	1.57	1.33	0.14
408	126	298	8.62	79.6	5.48	57.6	95.9	19.2
1043	322	677	29.9	258	50.0	319	263	61.7
1354	468	925	57.5	461	202	821	390	109
1778	634	1230	92.0	669	624	1714	566	171
253	88.8	186	14.2	96.8	111	250	86.6	26.8
12.5	0.72	3.92	0.44	0.59	1.49	3.57	0.33	0.18
145	291	112	82.2	123	118	231	41.2	82.4
27.2	234	58.2	193	77.9	36.2	7970	19.4	32.3
11.9	16.6	11.6	9.61	7.30	0.77	11.5	15.1	11.0
1.55	3.07	1.78	2.73	1.75	2.14	167	1.00	0.49
8381	2348	5380	335	2543	873	4075	2267	600
104	59.9	44.5	30.0	109	118	192	29.0	25.3
2.34	147	11.3	292	9.55	4.16	194	2.47	3.12
7874	11236	8318	9976	12121	29440	21802	8136	8973
1113	272	713	32.9	436	63.3	570	133	34.1
741	284	467	90.7	756	2365	4332	167	65.1
1.50	0.96	1.53	0.36	0.58	0.03	0.13	0.80	0.52
0.04	0.04	0.04	0.16	0.03	0.03	0.12	0.09	0.05
18.6	3.10	2.59	1.50	1.37	45.8	1.05	5.17	15.0
5200	1780	3659	253	1763	997	3459	1451	402
240	103	242	45.6	181	3.59	267	24.4	9.73
4836	1639	3317	202	1564	993	3162	1401	387
4923	172	111	22.2	21.1	58905	40.9	4154	2393
5.01	5.70	5.05	13.3	9.84	164	35.1	7.31	11.3
393	11.7	9.74	1.12	0.61	37.5	0.74	187	65.3
758	790	757	739	716	558	755	781	751

stituents is more typical of amorphous substances such as silicate glass. Therefore, an Al-Fe-silicate phase is interpreted as having been produced by crystallization of conserved magmatic melt [12]. Trace and rare-earth minerals, such as thorite, baddeleyite, parisite, bastnasite, allanite and fluorapatite with 5—21 wt.% REE_2O_3, occur as inclusions. These minerals always form polymineral inclusions that also comprise chalcopyrite (lesser sphalerite) and an Al-Fe-silicate phase. Such polymineral in-

clusions occurring on zircon crystal margins are also regarded here as having been produced by crystallization of conserved magmatic melt [12]. The varied composition of inclusions formed by crystallization of conserved magmatic melts is indicative of medium heterogenization caused presumably by immiscibility in magma, particularly the subdivision of silicate melt into leucocratic and melanocratic and the separation of trace element-enriched salt (sulphide, phosphate and carbonate) melt from silicate melt [13].

The presence of baddeleyite in the zircon samples is noteworthy. Baddeleyite inclusions are worth discussing in a separate publication, because they are seldom found due to a difference in the crystallization conditions of two Zr-minerals.

Rare-earth composition of zircon. Electron microprobe (SEM-EDS) study has shown that most of the zircon samples contain small amounts of impurities; only hafnium (no more than 3 wt.% HfO_2) is often observed, and traces of Al_2O_3 (less than 1 wt. are encountered. FeO (2—3 wt.%), MnO (1), CaO (2), Na_2O (<1) impurities are seen only in the dark-grey areas of zircon on the BSE image.

Trace and rare-earth element concentrations were calculated by the SIMS method at 22 points in 10 zircon crystals (Table). The irregular distribution of impurity elements, which has resulted in the heterogenous structure of crystals on the BSE image, is noteworthy. Y and *REE* concentrations have changed tenfold, those of P and Nb by one order of magnitude and Ca, Th, U, Ti by two orders of magnitude.

Two types of *REE* distribution spectra in zircon are characteristic. For most of the crystals, the *REE* distribution patterns in the centre and on the margins of zircon display a kind of trend within one order of chondrite relations (Fig. 2). They commonly exhibit a differentiated light to heavy *REE* distribution spectrum (mean Lu_N/La_N ratio is 3462) with a distinct positive Ce-anomaly (Ce/Ce* from 2.70 to 49.3, average 15.8), a negative Eu-anomaly (Eu/Eu* from 0.03 to 0.20, mean value 0.07) and relatively low total *REE* concentration (200-5200 ppm), which depends mainly on *HREE* contribution.

However, there is a difference between the central and marginal areas of azonal crystals. The central parts of zircon crystals that are light grey on BSE images differ from slightly darker marginal zones in a markedly smaller Ce-anomaly value, although the Eu-anomaly value and higher *REE* concentration remain unchanged. The total *REE*
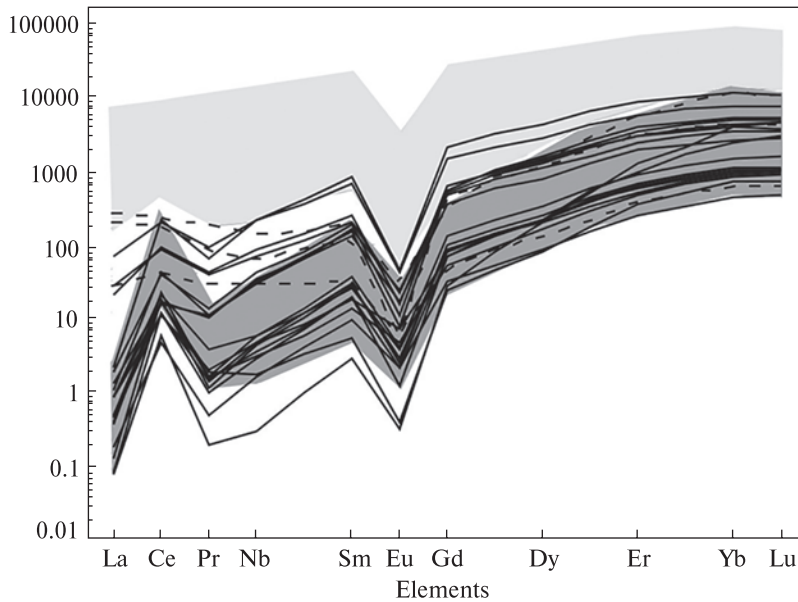
Fig. 2. REE distribution spectra in zircon. The solid line is for the central and marginal parts of most zircon crystals from Velyka Vyska syenites; the dotted line is for the dark marginal parts of scarce zircon crystals from Velyka Vyska syenites. Dark grey filling which indicates the REE distribution spectrum range is for the central parts of the zircon from Azov and Yastrubets syenites and light grey filling is for the marginal parts of zircon from Azov and Yastrubets syenites. REE concentration is normalized to chondrite CI [23]

concentration in the centre of the crystals is 400—5200 ppm against 200—2000 ppm in the marginal parts. The concentrations of other non-formula elements are generally higher in the central area of zircon but do not exceed the threshold values accepted [20], persisting in the range characteristic of igneous zircon. For example, Y concentration in the central area varies from 110 to 8400 ppm, showing a strong positive correlation with *HREE*. Nb concentration varies from 20 to 100 ppm, P — 25—255 ppm. The concentrations of zircon-incompatible elements such as Sr, Li and Ba are small, commonly varying within a few ppm. Ion mass-spectrometry has confirmed small radioactive element concentrations in zircon known earlier from the results of microprobe calculations [2]. Average Th and U concentrations are 277 and 352 ppm, respectively; Th/U ratio varies from 0.17 to 1.50 (mean value 0.73). It should be noted that only Ca and Ti did not tend to decrease their concentrations from the centre of a crystal to its margin. For example, Ca concentration in the central zone is 59 ppm and that in the marginal zone is 220 ppm, whole Ti concentrations are 25 and 56 ppm, respectively. Hf distribution within a crystal remains practically unchanged, averaging 10900 ppm, and only scarce crystals exhibit either a marked increase (up to 29 000 ppm) or a decline (to 8100 ppm) in Hf concentration. The above compositional characteristics are consistent with those of igneous zircon [22].

Different *REE* distribution spectra were obtained for zonal zircon crystals with a well defined marginal zone, much darker than the one on the BSE image (samples 8 and 9). They generally display *REE* patterns not typical of zircon, e.g. flattened spectra characteristic of zircon from intensive fluid reworking zones [18]. In this case, Ce-anomaly disappears (Ce/Ce*=1.05—1.50), the Eu-anomaly value remains almost the same or even increases slightly. The differentiation index of the *REE* spectra (Lu_N/La_N) is only 21—41 (Table), whereas the light central zone of this zircon typically displays a differentiated *REE* pattern similar to spectra for most zircon crystals from the Velyka Vyska massif and consistent with typical zircon of magmatic genesis (Fig. 2). Impurity concentrations in the dark marginal zones of zircon commonly increase. Ca, Ba, Th, U, Y and *REE* concentrations display the greatest increase. For example, Ca concentration in the darkest marginal zones increases 200 times (sample 9) in comparison with the central zones of zircon (8000 against 36 ppm), Y — 4.5 times; *REE* — 3.5 times and Th and U — 6—10 times. In this case, the Th/U ratio in such zones is as small as 0.03—0.56. Other impurity element concentrations vary slightly or even decrease from the centre to the periphery of the crystal (Table).

Approximate zircon crystallization temperature was calculated from the results of the Ti-Zr equilibrium in zircon using the method described in [24]. A value in excess of 1000 °C was obtained in one case, but it varies generally from 600 to 800 °C for all crystal parts, which is not consistent with the results of fluid thermometry [11] and the mineral paragenesis observed. This problem exists for zircon from Azov syenites [14], but this subject is beyond the scope of this paper.
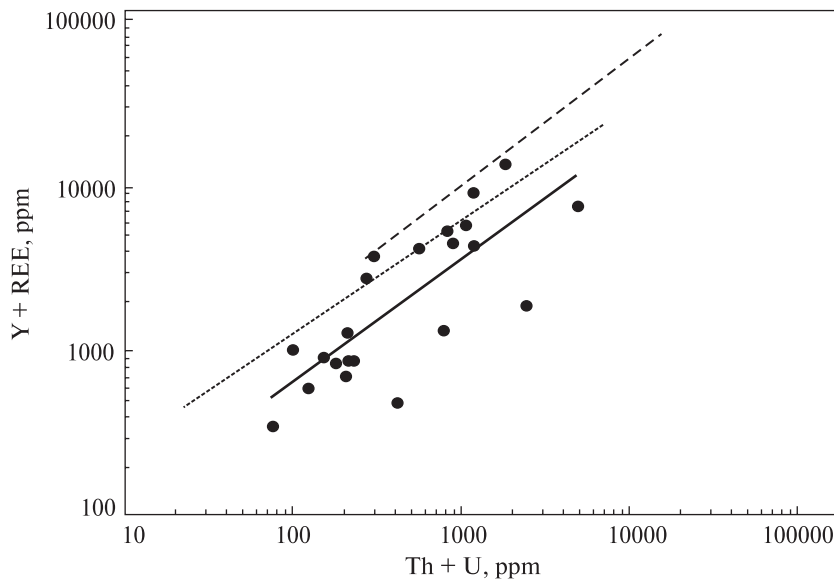
44

Fig. 3. Correlation of Th + U and *REE* + Y in zircon from the Velyka Vyska massif. The solid, dotted and broken lines show variation trends in Th + U and *REE* + Y concentrations in zircon from the Velyka Vyska, Azov [14, 15] and Yastrubets [15] massifs, respectively

Discussion. Zircon crystals from Velyka Vyska syenites are known to be structurally imperfect [2]. They are more similar in the degree of perfection, particularly the size of a coherent scattering zone (CHZ), to zircon from Yastrubets syenites and differ considerably from zircon in Azov syenites. The results obtained by the SIMS method do not support the assumption of radioactive radiation as the possible reason for crystal disorder. The crystals analyzed are almost identical in Th and U concentrations with zircon from Azov syenites and are much inferior to zircon from Yastrubets syenites (Fig. 3). Radioactive element concentration in zircon correlates with Y, *REE* and other impurities, as has been shown for other localities [2]. Considerable deviations of the figurative points of zircon composition from the trend developed are most probably provoked by the inclusions of own *REE*- and Th-minerals trapped by the probe.

However, the total impurity content of zircon from Velyka Vyska syenites is lower, which is not consistent with the conclusion of the effect of the total amount of impurity elements on the perfection of the crystalline lattice, as has been confirmed for zircon from the Yastrubets massif [2]. The crystals analyzed are most similar in the total amount of major impurities and their variation range to zircon from the Azov massif, as indicated by the length of corresponding trends (Fig. 3). However, substantial variations in the trace element composition of zircon from the Azov massif are caused by irregular impurity distribution between crystal parts and, to a greater extent, between crystals from the various rocks of the massif. The marginal parts of crystals from Azov melanosyenites and zircon from

pegmatoid (especially leucocratic) syenites are considerably enriched in Y and *REE* [15]. The central parts of crystals from the ore zones of the Azov massif vary in trace and rare-earth element concentrations within one order of magnitude [14], which is much less than in crystals from the ore-bearing zones of the Velyka Vyska massif. Comparing isomorphic Hf concentrations is demonstrative. The Hf content of Azov zircon varies from 0.6 to 0.7 wt.%, while that of Velyka Vyska zircon is 0.8—3 wt.%. Irregular trace element distribution is typical of Velyka Vyska syenites. Samples of almost identical rocks (158/860 and 228/809 [3]) exhibit marked variations in trace element composition, ppm: Zr — 2314 and 709; *REE* — 328 and 927, Nb — 57 and 187, Rb — 184 and 84; Sr — 9.9 and 219, respectively. The $^{86}Sr/^{87}Sr$ isotope ratio obtained (0.856) [9] is hard to explain genetically.

Most of zircon crystals from Azov and especially Yastrubets syenites are zonal and impurity constituents are accumulated in marginal zones, while in zircon from Velyka Vyska syenites they are distributed irregularly throughout the entire crystal. Most crystals (with few exceptions) on the BSE image are azonal with indistinct zone boundaries. It means that the redistribution of impurities and the perfecting of the crystal structure, most vigorous near crystallization temperature, were retarded in zircon from Velyka Vyska syenites. This suggests its short-term subjection to crystallization temperature provoked by the overcooling of the melt followed by the partial hardening of the mineral. As the intrusive bodies were small, favourable conditions for rapid cooling were provided. The same result could have been achieved by a rapid decline
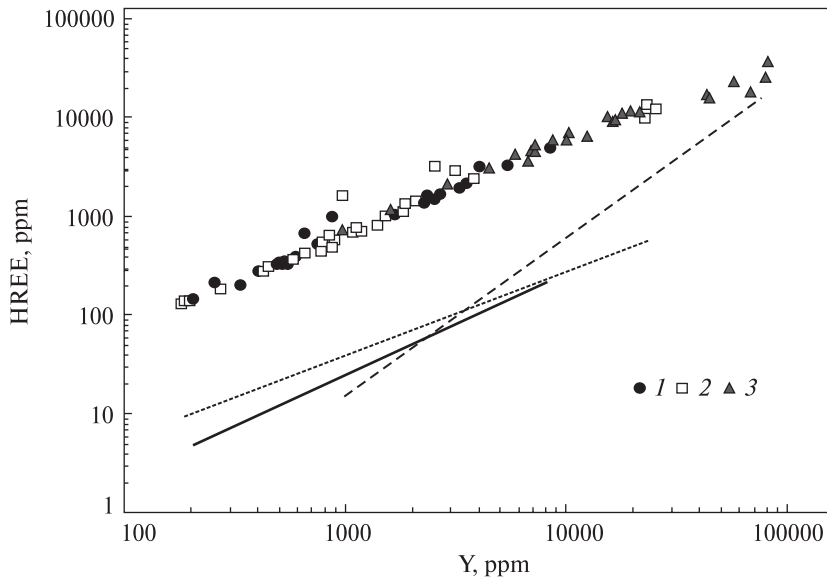
Fig. 4. Correlation of Y and *HREE* concentrations in zircon from hypersolvus syenites: *1* — Velyka Vyska massif, *2* — Azov massif, *3* — Yastrubets massif. The solid, dotted and broken lines indicate variation trends in the *LREE* content of zircon from Velyka Vyska, Azov [14, 15] and Yastrubets [15] syenites, respectively

in fluid pressure. The conclusion drawn explains the structural imperfection of zircon crystals and is consistent with earlier conclusions of the reason for the large-scale distribution of high temperature amorphous matter in Velyka Vyska syenites [1].

Yttrium is the most abundant impurity trace element. It is not surprising because Y is typically concentrated by zircon. Yttrium dominates over lanthanides, the Y/*REE* ratio is 0.8-1.6 (average 1.4). Almost the same mean values were obtained for zircon from Azov (0.9-2, average 1.3) and Yastrubets syenites (1-2.2, average 1.5), but the variation range of their Y/*REE* ratio is wider. Yttrium in zircon correlates with *REE*, as has been observed for other massifs [15], but its correlation with *HREE* is the closest (Fig. 4). There are some differences in the correlation of Y with *LREE* in zircon from various massifs (Fig. 4). *LREE* distributions in zircon from the Azov and Velyka Vyska massifs are almost identical (*REE* composition in the Velyka Vyska massif becomes slightly heavier), while *REE* composition in the Yastrubets massif obviously becomes "lighter" as the total amount of trace elements in zircon increases. As maximum amounts of impurity elements are accumulated in the marginal parts of zircon, it is in these parts that *REE* composition becomes "lighter". Zircon from Velyka Vyska syenites is the "heaviest" in *REE* composition. The average *LREE/HREE* ratio for this zircon is 0.06, while those for zircon from the Azov and Yastrubets massifs are 0.18 and 0.26, respectively. Judging by mineral parageneses, the Yastrubets massif displays the highest water and fluid saturation. The rockforming minerals of Yastrubets syenites are represented by water-bearing ferrosilicates and

syngenetic carbonates. Velyka Vyska syenites are the "driest"; they are dominated by anhydrous olivine and pyroxene and contain no carbonates. Available data suggest that variations in *REE* composition in zircon could only be due to the fluid saturation of the crystallization medium.

Zircon crystals with indistinct zoning display identical types of spectrum in both central and marginal parts. A different type of spectra was obtained only for crystals with distinct zoning. Similar types of spectra (differentiated in the central part of a crystal and flattened in its dark marginal parts) were obtained for zircon from Azov and Yastrubets syenites. The *REE* distribution spectrum in the central areas of zircon shows a differentiated *LREE* to *HREE* trend, while *REE* distribution in dark marginal parts exhibits a flat pattern with a reduced Ce-anomaly as long as a "bird wings spectrum" appears (Fig. 2). This type of spectrum is characteristic of zircon from rocks subjected to intensive fluid effect [18]. The marginal parts of zircon crystals from the Azov and Yastrubets massifs contain high, often anomalous concentrations of *REE*, Y and other incompatible elements (*REE* concentration increases to 40 600 ppm and Y concentration to 81 500 ppm), which is due to the increasing saturation level of trace and *REE* elements in the melt triggered by the differentiation of magmatic melt at the final stage of massif formation [15]. The marginal parts of zircon from Velyka Vyska syenites typically contain low trace and rare-earth element concentrations; their level in the marginal area occasionally decreases (sample 8). It seems that only the marginal parts of zircon, dark in BSE and showing flattened *REE* distribution

spectra, represent zircon subjected to fluid-triggered crystallization. This conclusion is consistent with the assumption of the contribution of fluid to the "lightening" of *REE* composition in zircon. Other crystals were produced by crystallization of magmatic melt followed by partial hardening upon a stepwise decline in pressure or temperature or both.

Conclusions. 1. Zircon crystals from Velyka Vyska syenites crystallized from heterogenous magmatic melt enriched in rare-earth and trace elements, as indicated by various inclusions of mineral and amorphous phases.

2. Most of the zircon crystals analyzed are chemically inhomogeneous, but either azonal or show poorly-defined regular zoning. Only a few crystals have dark-grey marginal parts contrasting on a BSE image with a light grey centre.

3. Zircon from the Velyka Vyska massif contains smaller amounts of trace elements (0.1 to 1.6 wt.%, average 0.4 wt.%) than that from the Azov (average 0.7 wt.%) and Yastrubets (4 wt.%) massifs, but their distribution in a crystal is more disordered. Low concentrations of radioactive elements and other impurities could not be responsible for the structural imperfection of the crystals analyzed. Their imperfection is assumed to be due to irregular impurity distribution. Probably a stepwise decline in temperature or fluid pressure immediately after zircon crystallization resulted in relatively fast cooling and partial crystal hardening and impeded impurity segregation in the marginal parts of the crystals.

4. *REE* distribution spectra in zircon from Velyka Vyska syenites are of a differentiated type; they are consistent with zircon that crystallized from magma and are similar to those in the central parts of the zircon crystals from the Azov and Yastrubets massifs. Spectra of a flattened type, typical of the marginal parts of zircon characteristic of zircon crystals from these massifs, were obtained in several cases for zircon from Velyka Vyska syenites. They were revealed in marginal crystal zones with well defined zoning.

5. Zircon from the Velyka Vyska Massif and other hypersolvus massifs of the Ukrainian Shield displays a distinct correlation between yttrium and *REE* (especially *HREE*) concentrations and the predominance of the former. The average Y/*REE* ratio varies from 1.3 to 1.5. *HREE* composition in zircon is observed to slightly "lighten" with a rise in impurity concentration triggered presumably by the increased fluid saturation level of the melt.

REFERENCES

1. Gerasimets, I.M., Kulchytska, H.O. and Belskyi, V.M. (2019), *Mineral. Journ. (Ukraine)*, Vol. 41, No. 1, Kyiv, UA, pp. 35-48 [in Ukrainian]. https://doi.org/10.15407/mineraljournal.41.01.035
2. Gerasimets, I.N., Kulchytska, H.O. and Grechanovska, O.Ye. (2018), *Mineral. Journ. (Ukraine)*, Vol. 40, No. 2, Kyiv, UA, pp. 17-26 [in Ukrainian]. https://doi.org/10.15407/mineraljournal.40.02.017
3. Dubyna, O.V. and Kryvdik, S.G. (2013), *Mineral. Journ. (Ukraine)*, Vol. 35, No. 3, Kyiv, UA, pp. 61-72 [in Ukrainian].
4. Kvasnytsya, V.M., Vyshnevskyi, O.A., Kvasnytsya, I.V. and Gurnenko, I.O. (2016), *Mineral. Journ. (Ukraine),* Vol. 38, No. 3, Kyiv, UA, pp. 9-23 [in Ukrainian]. https://doi.org/10.15407/mineraljournal.38.03.009
5. Kryvdik, S.G. and Tkachuk, V.I. (1990), *Petrologiya shchelochnyh porod Ukrainskogo shchita*, Nauk. dumka, Kyiv, UA, 408 p. [in Russian].
6. Kryvdik, S.G. (2002), *Geochemistry*, No. 7, Moscow, RU, pp. 707-716 [in Russian].
7. Kryvdik, S.G. (2005), *Mineral. Journ. (Ukraine)*, Vol. 27, No. 3, Kyiv, UA, pp. 41-49 [in Ukrainian].
8. Kryvdik, S.G. and Bezsmolova, N.V. (2011), *Geol. Journ.,* No. 3, Kyiv, UA, pp. 39-45 [in Ukrainian].
9. Kryvdik, S.G., Dubyna, O.V., Dovbush, T.I., Kotvytska, I.M., Vysotsky, O.B., Bezsmolova, N.V. and Amashukeli, Yu.A. (2011), *Mineral. Journ. (Ukraine)*, Vol. 33, No. 3, Kyiv, UA, pp. 55-62 [in Ukrainian].
10. Kryvdik, S.G., Zagnitko, V.M., Strekozov, S.M., Hurskyy, D.S., Vasil'chenko, V.V. and Matviychuk, M.V. (2000), *Mineral. Journ. (Ukraine)*, Vol. 22, No. 1, Kyiv, UA, pp. 62-72 [in Ukrainian].
11. Krochuk, V.M., Legkova, G.V., Galaburda, Yu.A., Orsa, V.I. and Usova, L.V. (1989), *Mineral. Journ. (Ukraine)*, Vol. 11, No. 5, Kyiv, UA, pp. 18-29 [in Russian].
12. Kulchytska, H.O., Gerasimets, I.N., Vyshnevskyi O.A. and Belskyi, V.M. (2019), *Mineral. Journ. (Ukraine)*, Vol. 41, No. 2, Kyiv, UA, pp. 34-44 [in Ukrainian]. https://doi.org/10.15407/mineraljournal.41.02.034
13. Kulchytska, H.O., Chernysh, D.S. and Herasymets, I.M. (2020), *Mineral. Journ. (Ukraine)*, Vol. 42, No. 1, Kyiv, UA, pp. 36-48 [in Ukrainian]. https://doi.org/10.15407/mineraljournal.42.01.036
14. Levashova, E.V., Voznyak, D.K., Skublov, S.G., Kaulina, T.V., Kulchytska, H.O. and Galankina, O.L. (2019), *Mineral. Journ. (Ukraine)*, Vol. 41, No. 2, Kyiv, UA, pp. 45-61 [in Russian]. https://doi.org/10.15407/mineraljournal.41.02.045

15. Levashova, E.V., Skublov, S.G., Li, X.H., Kryvdik, S.G., Voznyak, D.K., Kulchytska, H.O. and Alekseev, V.I. (2016), *Geol. Ore Deposits*, Vol. 58, pp. 239-362. https://doi.org/10.1134/S1075701516030065

16. Melnikov, V.S., Kulchytska, H.O., Kryvdik, S.G. and Strekozov S.M. (2001), *Mineral. Journ. (Ukraine)*, Vol. 23, No. 4, Kyiv, UA, pp. 19-33 [in Ukrainian].

17. Melnikov, V.S., Voznyak, D.K., Grechanovskaya, E.E., Gursky, D.S., Kulchytska, H.O. and Strekozov, S.N. (2000), *Mineral. Journ. (Ukraine)*, Vol. 22, No. 1, Kyiv, UA, pp. 42-61 [in Russian].

18. Skublov, S.G. (2005), *Geohimiya redkozemelnyih elementov v porodoobrazuyuschih metamorficheskih mineralah*, Nauka, St. Petersburg, RU, 147 p. [in Russian].

19. Fedotova, A.A., Bibikova, E.V. and Simakin, S.G. (2008), *Geochem. Intern.*, Vol. 46, No. 9, RU, pp. 912-927. https://doi.org/10.1134/S001670290809005X

20. Harley, S.L. and Kelly, N.M. (2007), *Elements*, Vol. 3, No. 1, pp. 13-18. https://doi.org/10.2113/gselements.3.1.13

21. Hinton, R.W. and Upton, B.G.J. (1991), *Geochim. et Cosmochim. Acta.*, Vol. 55, Iss. 11, pp. 3287-3302. https://doi.org/10.1016/0016-7037(91)90489-R

22. Hoskin, P.W.O. and Schaltegger, U. (2003), *Review Mineral. and Geochem.*, Vol. 53, No. 1, pp. 27-62. https://doi.org/10.2113/0530027

23. McDonough, W.F. and Sun, S.-S. (1995), *Chem. Geol.*, Vol. 120, Iss. 3-4, pp. 223-253. https://doi.org/10.1016/0009-2541(94)00140-4

24. Watson, E.B, Wark, D.A. and Thomas, J.B. (2006), *Contribs. Mineral. and Petrol.*, Vol. 151, pp. 413-433. https://doi.org/10.1007/s00410-006-0068-5

К.В. Лєвашова, канд. геол.-мін. наук, мол. наук. співроб. Інститут геології та геохронології докембрію РАН
199034, м. Санкт-Петербург, РФ, наб. Макарова, 2
E-mail: levashova.kateryna@yandex.ru; https://orcid.org/0000-0002-0814-1428

Г.О. Кульчицька, д-р геол. наук, гол. наук. співроб.
Інститут геохімії, мінералогії та рудоутворення (ІГМР) ім. М.П. Семененка НАН України
03142, м. Київ, Україна, пр-т Акад. Палладіна, 34
E-mail: kulchechanna@gmail.com; https://orcid.org/0000-0002-7206-4797

С.Г. Скублов, д-р геол.-мін. наук, проф., гол. наук. співроб. Інститут геології та геохронології докембрію РАН
199034, м. Санкт-Петербург, РФ, наб. Макарова, 2
Санкт-Петербурзький гірничий університет
199106, м. Санкт-Петербург, РФ, ВО, 21 лінія, 2
E-mail: skublov@yandex.ru; Scopus ID: 55918967400

І.М. Герасимець, канд. геол. наук, мол. наук. співроб. ІГМР ім. М.П. Семененка НАН України
03142, м. Київ, Україна, пр-т Акад. Палладіна, 34
E-mail: Herasimets@i.ua; https://orcid.org/0000-0003-4670-0216

С.Г. Кривдік, д-р геол.-мін. наук, проф., гол. наук. співроб. ІГМР ім. М.П. Семененка НАН України
03142, м. Київ, Україна, пр-т Акад. Палладіна, 34
E-mail: kryvdik@ukr.net; http://orcid.org/0000-0002-8356-1115

О.Л. Галанкіна, канд. геол.-мін. наук, старш. наук. співроб. Інститут геології та геохронології докембрію РАН
199034, м. Санкт-Петербург, РФ, наб. Макарова, 2
E-mail: galankinaol@mail.ru; Scopus ID: 7801578217

М.Є. Мамикіна, студент. Санкт-Петербурзький гірничий університет
199106, м. Санкт-Петербург, РФ, ВО, 21 лінія, 2
E-mail: emamikina@mail.ru

Д.С. Лєвашов, канд. техн. наук, доцент. Санкт-Петербурзький гірничий університет
199106, м. Санкт-Петербург, РФ, ВО, 21 лінія, 2
E-mail: levashov_ds@pers.spmi.ru; ResearcherID: AAI-1742-2019

ГЕОХІМІЯ РІДКІСНИХ ЕЛЕМЕНТІВ У ЦИРКОНІ З СІЄНІТІВ
ВЕЛИКОВИСКІВСЬКОГО МАСИВУ, УКРАЇНСЬКИЙ ЩИТ

Досліджено кристали циркону із проточок сієнітів розрізнених інтрузивних тіл Великовисківського масиву методами *SEM-EDS* і *SIMS*. Отримані результати зіставлені з опублікованими раніше даними для циркону із сієнітових масивів Українського щита з Zr-*REE* мінералізацією — Азовського і Яструбецького. На *BSE*-зображенні кристали азональні або зі слабко виявленою зональністю. Лише в поодиноких індивідах проявлена контрастно темніша крайова зона. Виявлені в кристалах силікатні, сульфідні, фосфатні і карбонатні тверді фази підтвердили гетерогенізацію середовища кристалізації циркону. Вміст рідкісних, у тому числі рідкісноземельних і радіоактивних, елементів не перевищує 1,6 мас. % за середнього значення 0,4 мас. %, що менше, ніж у цирконах із інших масивів. Вміст U + Th (середнє значення 0,07 мас. %) не дає змоги розглядати радіоактивні елементи як джерело руйнування структури кристалів. Подібно до циркону з інших масивів, провідна роль серед елементів-домішок

належить ітрію, який переважає над *REE* зі співвідношенням 1,3 : 1. Спостерігається деяке "полегшення" складу *REE* зі збільшенням загального вмісту Y і *REE*. "Найважчим" є циркон з великовисківських сієнітів. Середнє відношення *LREE/HREE* для цього циркону — 0,06, тоді як для цирконів з Азовського і Яструбецького масивів — 0,18 і 0,26 відповідно. Спектри розподілу *REE* у цирконі представлені двома типами. Перші — диференційовані, властиві більшості кристалів. Вони ідентичні спектрам центральних зон кристалів з інших масивів і характерні для циркону, що кристалізувався з розплаву. Другі — пологі, властиві крайовим ділянкам кристалів з чітко вираженою зональною будовою. Вони ідентичні спектрам для крайових зон кристалів циркону з інших масивів і характерні для циркону, кристалізація якого мала місце за участі флюїдної фази. Розрахована за Ti-термометром температура кристалізації циркону коливається у межах 600—1000 °C, більшість значень відповідає 700—800 °C, що дещо менше, ніж очікувалося.

Ключові слова: циркон, сієніт, Великовисківський масив, ітрій, радіоактивні та рідкісноземельні елементи, *REE*-родовище.