First Age and Geochemical Data on Zircon from Riebeckite Granites of the Verkhnee Espe Rare Earth–Rare Metal Deposit, East Kazakhstan

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Abstract—This paper is dedicated to the isotope-geochemical study of zircon from riebeckite granites of the Verkhnee Espe rare earth-rare metal deposit and the specification of its U–Pb age. Zircon from the Verkhnee Espe massif is peculiar in the high content of non-formula elements (up to 43000 ppm REE, up to 22000 Y, and others) and demonstrates a clearly expressed heterogeneous structure. The central and rim zones of the zircon show a “magmatic” rare-earth element (REE) distribution. The intermediate zones are characterized by a flattening of the REE patterns and an anomalous enrichment in REE, Y, Nb, and Ca. This compositional feature of the zircon may be caused by impact of fluid-saturated granite melts enriched in incompatible trace elements. The $\delta^{18}\text{O}$ values in the zircon are 5.83–7.16‰, which generally corresponds to zircon formed from granitoid melts. The age of zircon from the Verkhnee Espe rare earth–rare metal deposit is 283 ± 3 Ma, which indicates that there is no significant age gap between granite crystallization, on the one hand, and metasomatic processes and ore generation, on the other.

Keywords: zircon, U–Pb age, oxygen isotopic composition, rare-earth element geochemistry, rare earth–rare metal deposit, Verkhnee Espe

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INTRODUCTION

During P_1 – T_1 period of the Hercynian cycle, the East Kazakhstan region was spanned by intense granitoid magmatism formed in a post-collisional geodynamic setting, which is typical of the Central Asian Orogenic Belt (Dyachkov, 2015). The evolution of the granitoid magmatism was accompanied by a systematic compositional change of intrusive complexes and related mineralization: 300–310-Ma Kalguta and Kunush granodiorite–plagiogranite complex (Au–Ag); 292–297 and 281–288-Ma Kalba granite complex (Ta, Nb, Li, Be, Cs); 281–288-Ma Monastyrskii leucogranite complex (Ta, Sn, REE); and 250-Ma Keregetas–Espe alkaline granite complex (Nb, Zr, REE) (Khromykh et al., 2016; Dyachkov, 2015). The Verkhnee Espe granitoid massif is an important object of East Kazakhstan, because it is practically entirely

occupied by a promising complex rare-earth–rare metal (REE, Zr, Nb, Ta) deposit.

Numerous detailed studies have been carried out for the Verkhnee Espe massif. In particular, the geological position of the massif, petrography and geochemistry of rocks were reported in (e.g., Belov and Ermolov, 1996; Stepanov et al., 2011; Stepanov and Bekenova, 2009; Trace ..., 2011). The composition of rock-forming and accessory minerals and geochemistry of apogranites and ore lodes of the Verkhnee Espe deposit were described in (Baisalova, 2018; Frolova, 2018). At the same time, such important and informative accessory mineral as zircon remains insufficiently studied.

Zircon possesses a unique ability to retain isotope-geochemical fingerprints of important events in the formation of rocks and their sources. It is a key mineral for dating and deciphering the genesis of ore-bearing rocks. Zircon from this massif is also of great interest as ore mineral, because has extremely high content of

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trace and rare-earth elements. Zircon with such specific composition is relatively scarce and usually has a fluid-assisted hydrothermal-metasomatic genesis. Magmatic zircon with extremely high contents of trace elements is an extremely scarce phenomenon. It can be exemplified by zircon from the Yastrubets and Azov syenite massifs at the Ukrainian Shield (USh) (Levashova et al., 2016). This paper is aimed at unraveling the reasons of extreme contents of non-formula elements in zircon from the Verkhnee Espe granite massif and at determining the conditions of zircon crystallization. This study, in addition, will attempt to fill the gap in isotope-geochemical data on this massif. To this end, we have studied the trace and rare-earth element composition, morphology, and structure of the zircon as compared to zircons from highly evolved rocks (alkali feldspathic syenites of the Ukrainian Shield); determined the oxygen isotope composition of the zircon, which also provides insight into conditions of its crystallization, and established the zircon age, which can be used in geodynamic reconstruction for rare-metal complexes of the region.

GEOLOGICAL STRUCTURE

The Verkhnee Espe massif and eponymous complex rare-earth–rare-metal (REE, Zr, Nb, Ta) deposit are restricted to the outercontact of the large Akzhaylyautas granite massif in the southwestern margin of the Zharma–Saur ore belt, Eastern Kazakhstan. The massif is represented by two small domes (Bol'shoi and Malyi) of alkaline granites of the Keregetas–Espe Complex (second intrusive phase of the complex) (Fig. 1). The Verkhnee Espe massif is mainly made up of inequigranular rocks varying from fine to coarse-grained and pegmatoid alkaline granites (biotite–riebeckite, riebeckite, biotite, and aegirine–riebeckite), as well as porphyritic rocks (Stepanov and Bekenova, 2009). Host rocks are sandstones, siltstones, tuffstones, and schists. The massif comprises unaltered and metasomatically altered (apogranite) granites. Most intense metasomatic alterations occur in the apical part of the massif, which led to a change of the composition and structure of primary granitic rocks and formation of albite–riebeckite granites with elevated contents of trace elements (Zr, Nb, Th, Y, REE, and Sn, Pb, Zn, Ti et al.) (Stepanov et al., 2008; Stepanov and Bekenova, 2009). At the contact with metasomatically altered alkaline granites, host rocks were transformed in fenites (Stepanov and Bekenova, 2009).

Ore lodes are represented by stratal bodies confined to the near-contact zones of the massif (mainly quartz–albite, riebeckite–albite, and astrophyllite–aegirine varieties) and veinlike metasomatic bodies mainly in the domal parts of the massif. The trace element content gradually increases from the inner part of the massif to its apical part (Frolova et al., 2015). Ore mineralization is represented by fine dissemination of pyrochlore, bastnaesite, zircon, thorite, elpid-

ite, gagarinite (main REE carrier, first discovered in ores of the Verkhnee Espe deposit), and other trace minerals (Belov and Ermolov, 1996; Stepanov and Bekenova, 2009).

We studied zircons from fine-grained riebeckite granites of the Verkhnee Espe deposit, which were sampled in the outer zone of the Malyi Dome (Fig. 1). The fine-grained riebeckite granites forming small intrusions in the inner parts of the Bol'shoi and Malyi domes practically were not subjected to metasomatic transformations and have sharp intrusive contacts with granites of the inner part of the massif. According to petrochemical data, the riebeckite granites are alkaline K–Na, moderate-Mg peraluminous rocks, which consist mainly of quartz (35–40%), microcline (25–30%), albite (10–20%), riebeckite (10–15%), and aegirine (up to 5%). Accessory minerals are represented by zircon, pyrochlore, and fluorite. The granites have a patchy structure defined by the development of mafic minerals.

METHODS

The inner structure and major-element composition of zircon, as well as the composition of mineral inclusions were studied using back-scattered electron (BSE) imaging on a JEOL JSM-6510LA scanning electron microscope equipped with an EDS JED-2200 spectrometer (IPGG RAS).

Local U–Pb zircon dating was conducted on a SHRIMP-II ion microprobe (Center of Isotope Research, VSEGEI). The U–Pb measurements were carried out using technique (Williams, 1998). The intensity of O₂ primary beam was 4 nA, and the crater diameter, ~20 µm. Obtained U/Pb ratio was normalized to those of TEMORA and 91500 zircon standards. The errors are reported with 1σ error for single analyses (U/Pb ratio and age) and with 2σ error for calculated consistent ages and concordia intercepts. Concordia was plotted using an ISOPLOT/EX software (Ludwig, 2003). Prior to geochronological studies, zircon was studied with cathodoluminescence (CL) on a CamScan MX2500S electron microscope with a CLI/QUA 2 CL-detector at the CII, VSEGEI.

The REE and trace-element contents were studied on a Cameca IMS-4f ion microprobe at the Institute of Physics and Technology Yaroslavl Branch, Russian Academy of Sciences) using technique described in (Hinton and Upton, 1991; Fedotova et al., 2008). The measurement errors were 10–15% for elements with concentrations >1 ppm and 10–20% for elements with concentrations 0.1–1 ppm, the detection limit was 5–10 ppb. The crater size was approximately 20 µm. REE patterns of zircons were normalized to CI chondrite (McDonough and Sun, 1995). Crystallization temperature of zircon was calculated using Ti-in-zircon thermometer (Watson et al., 2006).

Fig. 1. Geological scheme of the Verkhnee Espe massif (after V.A. Belov and L.I. Semivragova). (1) Quaternary deposits; (2) sandstone, siltstone; (3) pegmatoid granite; (4) fine-grained alkali granite; (5) medium-grained riebeckite, riebeckite–biotite granite; (6) porphyritic biotite granite; (7) granosyenite and granodiorite; (8–10) vein rocks ((8) aplitic granite; (9) alkaline granite, (10) pegmatite); (11) ore-bearing riebeckite–albitite metasomatites; (12) first-order fractures; (13) second-order fractures; asterisks in the structural scheme shows sampling localities.

The oxygen isotope composition was analyzed on a Cameca-1280 ion microprobe (Institute of Geology and Geophysics, Chinese Academy of Sciences) in a maximally homogenous zircon domains using technique reported in (Gao et al., 2014). Primary Cs^+ beam determined the size of analyzed area as a square with sides of 15–20 μm . Each analysis involved 16 measurement cycles of $^{18}\text{O}/^{16}\text{O}$ ratio. The measured $^{18}\text{O}/^{16}\text{O}$ were normalized to VSMOW standard ($^{18}\text{O}/^{16}\text{O} = 0.0020052$). The instrumental mass fractionation (IMF) was determined using measurements

of TEMORA-2 zircon standard ($\delta^{18}\text{O} = 8.20\text{‰}$, $\text{SD} = 0.18$) (8 analyses) and was controlled by the independent measurement of 91500 standard ($\delta^{18}\text{O} = 10.04\text{‰}$, $\text{SD} = 0.29$) (4 analyses) implanted in the same sample.

RESULTS AND DISCUSSION

Extracted zircon is represented by euhedral grains reaching 100–250 μm across (Fig. 2). SEM-EDS data showed that the central part of the zircon contains

Fig. 2. BSE and CL images of zircon from riebeckite granites of the Verkhnee Espe massif. White circles show the position of analysis points for trace elements and U-Pb dating. Ion probe craters are shown beyond the scale. Numbers of analysis points correspond to those in Tables 1, 2.

large (up to 50–100 µm) microinclusions of albite and K-feldspar. In the BSE image, the zircon has a heterogeneous structure, which is also expressed in its trace-element composition. The crystal consists of light core and rim zones with relatively moderate trace element content and dark intermediate (between core and rim) zone with high content of trace and rare-earth elements. According to SEM-EDS data, BSE-dark intermediate zones of the zircon are peculiar in the elevated contents of FeO (up to 2–4 wt %), CaO, and Al₂O₃ (up to 0.5–1.5 wt %). The rim zone of zircon is broken by transverse fractures and practically devoid of admixtures.

The core zones of the zircon are characterized by the higher total REE content (12000–17000 ppm) compared to those typical of magmatic zircon (Harley

and Kelly, 2007). REE are dominated by HREE (12000–16000 ppm). The zircon also has elevated Y up to 10000–17000 ppm, as well as 800–1600 ppm P and 300–900 ppm Nb (Table 1). The core zones of zircon also have high U and Th contents: up to 1200–2000 ppm Th and 6000–8000 ppm U. The Th/U ratio is 0.16–0.33 (Table 1), which corresponds to the lower limit of values typical of magmatic zircon (Hoskin and Schaltegger, 2003). Based on Ti-in-zircon thermometer, zircon was formed at ~ 700–850°C (Table 1). The REE distribution pattern in the BSE-light central domain is highly differentiated, with HREE enrichment relative to LREE ($Lu_N/La_N = 400–46000$) at variable LREE content (Fig. 3a). The REE patterns show a pronounced negative Eu-anomaly having practically constant value ($Eu/Eu^* = 0.03–0.05$) and a positive widely varying Ce-anomaly ($Ce/Ce^* = 2–88$).

Table 1. Trace-element composition (ppm) of zircon from riebeckite granites of the Verkhnee Espe massif

Component	1.1	1.2	2.1	2.2	3.1	3.2	4.1	4.2
	dark intermediate zone	light rim	light core	light rim	light core	light rim	light core	light rim
La	171	0.07	0.02	0.08	5.26	0.85	0.13	0.36
Ce	7453	9.90	0.72	7.55	112	17.5	89.8	28.5
Pr	616	0.19	0.24	0.17	2.15	1.56	0.47	1.58
Nd	2962	1.11	0.68	0.76	15.4	8.13	7.53	7.38
Sm	2671	3.54	0.39	2.76	60.9	10.3	43.2	14.7
Eu	52.4	0.14	b.d.l.	0.08	1.86	0.24	1.28	0.28
Gd	3187	22.2	2.69	26.0	353	39.1	286	46.3
Dy	7740	271	19.1	324	2590	408	2263	480
Er	8189	681	65.7	832	4566	980	4068	1188
Yb	9456	1177	157	1449	6002	1672	5404	1982
Lu	1129	151	22.2	180	704	212	627	238
Li	1.24	2.20	0.16	1.78	6.45	2.03	4.39	2.30
P	793	86.0	b.d.l.	131	1008	135	827	156
Ca	7957	4.20	4.96	1.78	20.0	234	1.81	40.7
Ti	351	1.11	0.24	0.69	18.2	17.1	6.64	4.51
Sr	604	1.01	0.23	0.99	9.06	7.26	3.33	2.31
Y	22553	1798	113	2047	14832	2470	12489	2771
Nb	9426	83.8	20.8	85.1	436	133	340	148
Ba	159	1.62	1.15	0.40	2.79	2.22	1.92	2.42
Hf	8211	8796	11488	9529	6478	9340	6527	8396
Th	1956	70.0	6.58	66.0	1932	85.3	1206	112
U	8111	679	35.8	552	5793	668	4662	843
Th/U	0.24	0.10	0.18	0.12	0.33	0.13	0.26	0.13
Eu/Eu*	0.05	0.05	0.00	0.03	0.04	0.04	0.04	0.03
Ce/Ce*	5.55	20.7	2.64	15.9	8.07	3.68	87.9	9.20
ΣREE	43627	2317	269	2823	14414	3349	12791	3987
ΣLREE	11202	11.3	1.65	8.55	135	28.1	97.9	37.9
ΣHREE	29702	2302	267	2811	14216	3310	12648	3934
Lu _N /La _N	63.5	20168	11856	22359	1288	2393	46371	6425
Lu _N /Gd _N	2.87	55.0	66.6	56.1	16.1	43.8	17.7	41.5
Sm _N /La _N	25.0	78.8	35.0	57.0	18.5	19.4	530	66.1
T(Ti), °C	1198	580	495	552	799	793	708	677
δ ¹⁸ O, ‰	6.40	5.98	6.23	6.29	6.33	6.07	5.83	6.39
±, ‰	0.38	0.42	0.45	0.44	0.42	0.46	0.41	0.45

Table 1. (Contd.)

Component	5.1	5.2	6.1	6.2	7.1	7.2	8.1
	light core	light rim	light rim	light rim	light core	dark intermediate zone	light rim
La	2.54	10.2	0.39	n.d.	5.04	74.5	0.91
Ce	148	262	29.2	"	336	1309	82.4
Pr	8.34	34.4	1.09	"	17.2	297	3.40
Nd	64.6	193	6.37	"	104	1870	19.0
Sm	102	204	11.3	"	162	2026	33.2
Eu	2.37	4.69	0.08	"	3.14	32.7	0.89
Gd	375	260	46.3	"	479	1866	123
Dy	2931	1056	477	"	3177	4471	1106
Er	4858	1729	1028	"	5281	4734	2259
Yb	6942	2446	1649	"	5716	6342	3429
Lu	765	313	212	"	816	806	434
Li	14.8	2.81	2.61	"	6.15	3.04	3.68
P	1589	301	262	"	1655	1061	561
Ca	19.5	885	82.0	"	240	897	76.8
Ti	11.1	33.0	9.06	"	28.0	272	11.5
Sr	8.83	23.7	2.98	"	14.1	92.5	3.97
Y	15874	4782	3165	"	17048	15250	7115
Nb	423	611	177	"	688	2529	279
Ba	7.17	8.23	1.75	"	6.72	32.8	2.65
Hf	5782	6957	7016	"	5803	6842	6288
Th	1781	273	121	"	1710	836	381
U	7255	1497	942	"	6942	3085	2240
Th/U	0.25	0.18	0.13	"	0.25	0.27	0.17
Eu/Eu*	0.04	0.06	0.01	"	0.03	0.05	0.04
Ce/Ce*	7.77	3.39	10.9	"	8.74	2.13	11.3
ΣREE	16199	6512	3460	"	16096	23827	7491
ΣLREE	223	499	37.0	"	463	3551	106
ΣHREE	15872	5803	3412	"	15468	18218	7352
Lu _N /La _N	2904	295	5297	"	1560	104	4581
Lu _N /Gd _N	16.5	9.74	37.1	"	13.8	3.49	28.4
Sm _N /La _N	64.4	32.0	46.8	"	51.4	43.5	58.2
T(Ti), °C	752	861	734	"	843	1151	755
δ ¹⁸ O, ‰	6.53	6.55	6.54	6.37	6.31	7.16	6.22
±, ‰	0.36	0.37	0.41	0.62	0.38	0.38	0.47

Table 1. (Contd.)

Component	8.2	9.1	9.2	Z1.1	Z1.2	Z1.3	Z2.1
	dark intermediate zone	light rim	light core	light core	dark intermediate zone	light rim	dark core
La	n.d.	0.07	n.d.	1.19	31.8	6.62	227
Ce	"	16.3	"	76.4	984	184	4096
Pr	"	0.38	"	1.26	118	22.7	876
Nd	"	1.80	"	12.1	613	147	4978
Sm	"	4.57	"	44.5	639	187	4597
Eu	"	0.17	"	1.36	11.2	2.55	85.0
Gd	"	34.8	"	241	706	248	3331
Dy	"	390	"	1889	2355	982	5522
Er	"	936	"	3783	3413	1452	5203
Yb	"	1564	"	5674	4621	2137	7124
Lu	"	203	"	668	556	269	895
Li	"	1.72	"	77.6	27.8	10.5	5.91
P	"	332	"	954	675	226	797
Ca	"	11.1	"	165	1042	611	2801
Ti	"	2.42	"	117	135	491	693
Sr	"	1.45	"	19.9	63.4	11.8	336
Y	"	2801	"	10350	9554	4029	17648
Nb	"	128	"	418	1492	859	4377
Ba	"	1.45	"	24.3	27.0	14.3	154
Hf	"	8306	"	6058	6549	6610	6795
Th	"	132	"	1311	769	217	39243
U	"	828	"	8153	4613	1335	4239
Th/U	"	0.16	"	0.16	0.17	0.16	9.26
Eu/Eu*	"	0.04	"	0.04	0.05	0.04	0.07
Ce/Ce*	"	24.1	"	15.1	3.89	3.64	2.22
ΣREE	"	3150	"	12393	14047	5639	36934
ΣLREE	"	18.6	"	90.9	1746	360	10177
ΣHREE	"	3127	"	12256	11651	5089	22074
Lu _N /La _N	"	27706	"	5418	168	392	38.0
Lu _N /Gd _N	"	47.1	"	22.4	6.37	8.79	2.17
Sm _N /La _N	"	104	"	59.9	32.1	45.3	32.4
T(Ti), °C	"	631	"	1019	1039	1262	1335
δ ¹⁸ O, ‰	5.89	5.93	6.33	n.d.	n.d.	n.d.	n.d.
±, ‰	0.39	0.43	0.39	"	"	"	"

Table 1. (Contd.)

Component	Z2.1	Z2.2	Z3.1	Z3.2	Z3.3	Z4.1
	dark core	dark marginal zone	light core	light rim	light rim	light core
La	227	156	17.0	1.77	10.0	15.8
Ce	4096	4051	861	69.5	274	364
Pr	876	576	55.0	4.82	33.0	58.7
Nd	4978	3169	278	26.5	163	387
Sm	4597	3114	362	31.0	172	488
Eu	85.0	50.9	8.55	0.84	5.60	8.11
Gd	3331	3001	628	45.4	249	765
Dy	5522	6598	2998	156	1046	3249
Er	5203	6137	4515	192	2298	4674
Yb	7124	6947	5782	300	3315	6144
Lu	895	861	674	41.1	415	731
Li	5.91	2.32	8.98	5.52	23.6	98.1
P	797	784	829	43.6	358	1235
Ca	2801	4822	1082	271	358	263
Ti	693	442	226	414	397	140
Sr	336	258	60.4	6.36	17.2	36.1
Y	17648	16856	12665	457	6987	17152
Nb	4377	7008	940	182	715	689
Ba	154	115	33.7	9.03	7.50	14.8
Hf	6795	7249	6391	10135	7467	5649
Th	39243	31423	1260	86.9	540	2008
U	4239	5388	5678	113	2243	6666
Th/U	9.26	5.83	0.22	0.77	0.24	0.30
Eu/Eu*	0.07	0.05	0.05	0.07	0.08	0.04
Ce/Ce*	2.22	3.27	6.81	5.75	3.65	2.89
ΣREE	36934	34663	16177	869	7979	16885
ΣLREE	10177	7953	1211	103	479	826
ΣHREE	22074	23544	14596	735	7322	15562
Lu _N /La _N	38.0	53.0	382	223	399	447
Lu _N /Gd _N	2.17	2.32	8.68	7.33	13.5	7.73
Sm _N /La _N	32.4	31.9	34.1	28.0	27.5	49.6
T(Ti), °C	1335	1241	1120	1228	1221	1045
δ ¹⁸ O, ‰	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
±, ‰	"	"	"	"	"	"

b.d.l.—below detection limit. Measurement error of δ¹⁸O with confidence 95% interval. n.d.—not determined.

Fig. 3. REE distribution pattern in zircon from riebeckite granites of the Verkhnee Espe massif: (a) central and marginal zones of zircon; (b) intermediate zones of zircon. Numbers of points correspond to those in Fig. 2.

The value of Ce-anomaly in zircon is mainly controlled by oxygen fugacity in primary magma, i.e., is inherited from a melt (Hoskin and Shallegger, 2003), and correspondingly indicates a change of redox conditions in the latter.

Worth noting is the core zone of the crystal in analysis point 2.1, which significantly differs from the above described zircon in the lowest trace element contents (Table 1). The total REE content in this point is as low as 270 ppm, Y—110 ppm, Th—7 ppm, U—

36 ppm, and Th/U ratio is 0.18. The REE pattern in this point shows LREE to HREE fractionation, differing in the lowered content of these elements and a very deep negative Eu-anomaly, thus resembling a tetrad effect (Fig. 3a). Based on Ti-in-zircon thermometer, the crystallization temperature of zircon in this point is 500°C (Table 1), which is comparable with those of rare-metal granites of East Kazakhstan (Sokolova, 2014).

The trace-element composition of zircon in BSE-dark intermediate zones significantly differs. This zone is characterized by the high total REE content (14000–43600 ppm) mainly at the expense of LREE contribution (2000–11000 ppm) (Table 1). The content of other non-formula elements is also high. In particular, Y content varies from 10000 to 22500 ppm, Nb, from 1500 to 9500 ppm, Ca, from 900 to 8000 ppm, and Ti, from 130 to 700 ppm. It should be noted that ion microprobe study did not reveal microinclusions of REE phosphates (monazite, xenotime) and other accessory minerals. As suggested by some authors (Bindeman et al., 2014), the presence of rare-earth phosphate nanoinclusions invisible in electron microscope can be ignored since anomalous contents of REE, Y, and others are not supported by significant P increase. In spite of the fact that P content correlates with Y and Ca, at maximum U and Ca contents (22000 and 8000 ppm, respectively), the zircon contains only 800 ppm P. Such proportions of the considered elements excludes a “xenotime” scheme of isomorphism and entrapment of phosphate microinclusions in the analysis field. The intermediate zones are characterized by a nearly flat REE pattern with high LREE content ($\text{Lu}_N/\text{La}_N = 38\text{--}170$) (Fig. 3b), weakly expressed Ce-anomaly ($\text{Ce}/\text{Ce}^* = 2\text{--}5$), at preserved value of negative Eu anomaly ($\text{Eu}/\text{Eu}^* = 0.05\text{--}0.07$).

Zircon rims have light gray color in the BSE image (Fig. 2) and the lowest contents of trace elements within the grain. The Y and REE contents in them are 2000–7000 ppm and 2000–8000 ppm, respectively, which is no less than 2–3 times lower than in the core zone of the same crystal (Table 1). The content of other trace elements in zircon rims is on average by an order of magnitude lower (Th—130 ppm, U—900 ppm, P—240 ppm, Nb—160 ppm). In spite of different levels of trace and rare-earth elements, the REE patterns in rims are similar to those in their central part (Fig. 3a), bearing typical features of magmatic zircon (Hoskin and Schaltegger, 2003).

The oxygen isotope composition of zircon was analyzed in 25 points, 15 of which were preliminarily analyzed for trace and rare-earth elements (Table 1). The average $\delta^{18}\text{O}$ accounted for 6.30‰ at minimum content of 5.83‰ and maximum of 7.16‰, which is slightly higher than mantle values ($\sim 5.3\text{‰}$) and in general corresponds to those of zircon from Phanerozoic granitoids (Valley et al., 2005). The BSE-light core and rim zones of the zircon are characterized by

relatively low $\delta^{18}\text{O}$ values (5.83–6.55‰), whereas intermediate BSE-dark zones with elevated content of incompatible elements have slightly elevated $\delta^{18}\text{O}$ (6.40–7.16‰).

U–Pb dating was carried out for nine zircon grains (15 analysis points). The reliable age was obtained only for points from most homogenous (according to BSE and CL imaging) zircon domains (central and marginal parts of crystals). It is impossible to date the intermediate zone with elevated trace and rare-earth element contents (analysis points 1.1 and 7.2) due to the high content of unradiogenic lead (Table 2). Of 13 analyzed zircon points, only 7 points with moderate U (20–920 ppm) and Th (4–180 ppm) contents yield nearly concordant age values. The Th/U ratio in them is 0.13–0.20, which is typical of magmatic zircon (Hoskin and Schaltegger, 2003). The concordant age is 283 ± 3 Ma (MSWD = 0.50) (Fig. 4, Table 2). U–Pb age of zircon from the alkaline granites of the Verkhnee Espe massif coincides within the error with an age of apogranites from this massif (U–Pb age of 286 ± 4 Ma) (Baisalova, 2018) and is slightly lower than values established for albitized and finitized granites (U–Pb age of 291 ± 4 Ma) (Frolova, 2018). Thus, the age of alkaline granites of the Verkhnee Espe massif, which are associated with rare-earth–rare-metal deposit, indicates the absence of a significant age gap between metasomatic process and ore formation. In addition, obtained data indicate the simultaneous formation of granites of the Verkhnee Espe massif and granitoids of the Kalba, Zharmas, Preobrazhensky, and other Lower Permian complexes of the East Kazakhstan region, thus confirming (e.g., Khromykh et al., 2016) that the main stage of the granitoid magmatism in the region occurred in the Lower Permian.

The “flat” REE distribution pattern established for the intermediate zones of zircon from the Verkhnee Espe granites is a characteristic feature of “hydrothermal–metasomatic” zircon (Hoskin and Schaltegger, 2003; Hoskin, 2005; Geisler et al., 2007; Harley and Kelly, 2007; Schaltegger, 2007). However, zircon from riebeckite granites of the Verkhnee Espe massif shows no additional signs of metasomatic alterations (e.g., peculiar morphology and internal structure, enrichment in non-formula elements such as Ca, Ti, Sr, and others). Evidence for metasomatic alteration are also absent in host granite. In the studied zircon, the core and marginal parts display characteristic features of magmatic zircon (Hoskin and Schaltegger, 2003; Hoskin, 2005; Geisler et al., 2007; Harley and Kelly, 2007). The REE and trace element contents in the central part of the crystals and especially in its intermediate zone are sufficiently high, while the rim zone demonstrates a decrease of all admixtures. The high REE and Y contents (up to 22000 ppm Y and up to 43000 ppm REE) as in the zircon from the Verkhnee Espe massif were found in the rim zone of zircon from alkaline–feldspathic syenites of the Yastrubets and

Fig. 4. Concordia diagram for zircon from riebeckite granites of the Verkhnee Espe massif. Ellipses and values of U-Pb age correspond to 2σ , including error in decay constants.

Table 2. U-Pb age of zircon from riebeckite granites of the Verkhnee Espe massif

Analysis point	BSE characteristics	$^{206}\text{Pb}_c$, %	U, ppm	Th, ppm	$\frac{^{232}\text{Th}}{^{238}\text{U}}$	$^{206}\text{Pb}^*$, ppm	Age $^{206}\text{Pb}/^{238}\text{U}$, Ma	D, %	$\frac{^{207}\text{Pb}}{^{235}\text{U}}$	$\pm$, %	$\frac{^{206}\text{Pb}}{^{238}\text{U}}$	$\pm$, %	Rho
1.2	Light rim	0.26	367	48.9	0.14	14.1	281 ± 4	-3	0.309	2.8	0.045	1.4	0.494
2.1	Dark core	0.26	20.3	3.93	0.20	0.80	288 ± 8	12	0.373	8.6	0.046	2.8	0.329
2.2	Light rim	0.19	356	55.8	0.16	13.8	285 ± 4	0	0.325	2.6	0.045	1.4	0.532
3.1	Light core	0.09	3838	1739	0.47	163	311 ± 4	5	0.378	1.7	0.049	1.3	0.745
3.2	Light rim	0.14	448	73.1	0.17	17.3	283 ± 4	0	0.319	2.3	0.045	1.4	0.586
4.1	Light core	0.12	3302	1233	0.39	134	298 ± 4	-1	0.335	1.4	0.047	1.3	0.884
4.2	Light rim	0.35	872	176	0.21	33.4	281 ± 4	0	0.319	2.1	0.044	1.3	0.632
5.1	Light core	0.48	6431	1994	0.32	282	319 ± 4	2	0.383	2.9	0.051	1.3	0.442
5.2	Light rim	13.8	951	190	0.21	47.4	314 ± 4	169	1.290	10.0	0.050	1.4	0.134
6.1	Light rim	0.11	919	150	0.17	36.0	287 ± 4	0	0.327	1.8	0.046	1.3	0.728
7.1	Light core	0.02	5837	1788	0.32	249	312 ± 4	-2	0.353	1.4	0.050	1.3	0.930
8.1	Light rim	3.92	1240	150	0.13	51.7	294 ± 4	62	0.598	5.6	0.047	1.3	0.239
9.1	Light rim	0.14	509	100	0.20	19.6	283 ± 4	-2	0.315	2.1	0.045	1.3	0.633
1.1	Dark intermediate zone	31.4	7018	2126	0.31	1610	—	—	—	—	—	—	—
7.2	Dark intermediate zone	29.3	3074	983	0.33	987	—	—	—	—	—	—	—

Numbers of analytical spots corresponds to those of grain and crater within this grain (behind the point). Errors are given at 1σ . Pb_c and Pb^* are unradiogenic and radiogenic lead, respectively. 1σ is the calibration error of standard—0.49%. Isotope ratios were corrected for measured ^{204}Pb . D, %—Discordance: $D = 100 \cdot \{ [\text{Age}(^{206}\text{Pb}/^{238}\text{U})] / [\text{Age}(^{207}\text{Pb}/^{206}\text{Pb})] - 1 \}$. Dash means data are invalid due to the extremely high content of unradiogenic lead.

Azov massifs (Ukrainian shield), which are associated with rich rare-earth deposits (Levashova et al., 2016). The extremely high content of these elements in zircon (up to 36000 ppm REE and 81000 ppm Y) is caused by its crystallization at the late stages of the massif formation (riebeckite–aegirine quartz syenite) from a residual fluid-saturated melt enriched in Y, REE, U, Th, Nb, and other incompatible elements.

The HREE–Y diagram (Fig. 5a) clearly demonstrates a linear trend of zircon enrichment in HREE and Y, with a clear positive correlation, which is typical of this mineral. The trend starts in data point of zircon with extremely low contents of Eu and other trace elements (analysis point 2.1) and ends in data points of BSE-dark intermediate zones, which have flat REE pattern owing to the elevated LREE content (Fig. 5a). It is pertinent to mention that the Y and HREE contents in the central domains of the studied zircon are within a narrow range, whereas the contents of these elements in the marginal zones show a wider scatter. Similar distribution of elements is also observed in other diagrams (Figs. 5b–5d). Thus, the zircons demonstrate a systematic increase of trace elements from core to intermediate zones, which crystallized from a melt enriched in trace elements. At the final stages of crystallization, the rim zones of the zircon have been formed already from incompatible element-depleted melt, which resulted in the formation of a relatively depleted rim.

The studied zircons were compared with zircons from the Yastrubets and Azov massifs, which were crystallized from a residual fluid-saturated melt (Levashova et al., 2016). Zircons from the Yastrubets and Azov massifs, which host the eponymous rare-earth deposits, define own trend (Fig. 5) parallel to the trend of zircon from riebeckite granites of the Verkhnee Espe massif. The LREE and HREE contents and distribution pattern, as well as contents of Nb (Fig. 5c) and other trace elements (Th, U, Fig. 5d) in the intermediate zones of the studied zircon are similar to those of the rim zones of zircon from the Yastrebets and Azov rare-earth deposits (Fig. 5b). It was determined for natural conditions and experimentally that such incompatible elements as Zr, REE, Y, and Nb could be mobile in the alkali- and F-rich magmatic systems (Yang et al., 2014; and references therein), and could be accumulated in a highly evolved melt (Salvi and Williams-Jones, 1996, 2006; Jiang et al., 2005), as was established for the Azov massif (Voznyak et al., 2010, 2010a; Levashova et al., 2019). The enrichment in the aforementioned elements likely is a characteristic feature of zircon from alkaline granites and syenites, which crystallized during interaction with a fluid-saturated melt.

In the $\text{La}_N\text{--Sm}_N/\text{La}_N$ discriminant diagram (Fig. 5e), the majority of data points of zircon from riebeckite granites of the Verkhnee Espe massif fall in the region between distinguished fields of magmatic and hydro-

thermal-metasomatic zircon or in the field of magmatic zircon according to (Hoskin, 2005). Practically all data points from the core and intermediate zones of the studied zircon fall in the field of hydrothermal zircon according to (Kirkland et al., 2009), whereas data points of its rims correspond to magmatic zircon. In the $\text{Ce/Ce}^*\text{--Eu/Eu}^*$ discriminant diagram (Fig. 5e), data points show similar distribution, plotting mainly beyond the distinguished fields (Hoskin, 2005). The intermediate zones of zircon with high content of non-formula elements are plotted near the “hydrothermal” field. However, as mentioned above, the signs of hydrothermal origin and metasomatic alterations in zircon were not revealed.

The absence of significant influx of “external” fluids during zircon crystallization from a melt also follows from the study of its oxygen isotope composition. The core and rim zones of zircon show low $\delta^{18}\text{O}$ (5.83–6.55‰), while the intermediate zone has slightly higher $\delta^{18}\text{O}$ within 6.40–7.16‰. A shift of $\delta^{18}\text{O}$ in the melt–fluid system in a high-temperature magma is no more than 2‰ (Hoefts, 2009), whereas $\delta^{18}\text{O}$ variations in the studied zircon account for slightly more than 1‰. This indicates that the magmatic system was closed relative to the “external” fluid with essentially different isotope composition and that the studied zircon has a magmatic genesis. Thus, the oxygen isotope composition of zircon is consistent with above assumption that zircon enriched in trace and rare-earth elements was derived from evolved melt without contribution of “external” fluid.

CONCLUSIONS

Obtained U–Pb zircon age of 283 ± 3 Ma for riebeckite granites is regarded as the age of the Verkhnee Espe massif and associated eponymous rare-earth–rare-metal deposit. These data are consistent with previously published results of geochronological studies of the massif (Baisalova, 2018; Frolova, 2018).

Zircon from riebeckite granites of the Verkhnee Espe massif is characterized by the heterogeneous internal structure and composition. Its peculiar feature is the presence of an intermediate zone extremely enriched in REE (up to 43000 ppm) and having flat REE pattern, with high contents of Y (up to 22000 ppm), Nb (up to 9000 ppm), and other non-formula elements. No signs of metasomatic influence were found in the zircon from riebeckite granites of the Verkhnee Espe massif.

The studied zircon shows an increase of trace element contents from core to the intermediate zones, which were formed from a trace-element-enriched melt. In contrast, the rim zones of the zircon crystallized from an incompatible-element depleted melt. The study of oxygen isotope composition in zircon indicates that “external” fluids was not involved in its crystallization.

Fig. 5. Relations of HREE–Y (a), HREE–LREE (b), Y–Nb (c), U–Th (d), La–Sm_N/La_N (e), and Ce/Ce*–Eu/Eu* (f) in zircon from riebeckite granites of the Verkhnee Espe massif and in zircon from syenites of the Yastrubets and Azov rare-earth deposits (UA). The content of trace elements are given in ppm. Figures 4e and 4f demonstrate compositional fields of magmatic (1) and hydrothermal-metasomatic (2) zircons after (Hoskin, 2005), while diagram La–Sm_N/La_N (4e) additionally shows boundaries of zones (dashed lines) according to (Kirkland et al., 2009).

In terms of Y, REE, and other trace element contents, the intermediate zones of zircon from riebeckite granites of the Verkhnee Espe massif are similar to the “anomalous” zircon from the Yastrubets and Azov syenite massifs at the Ukrainian shield (Levashov et al., 2016). Zircon from the Verkhnee

Espe massif is most similar to zircon from the Yastrubets massif, which crystallized from a fluid-saturated residual melt. We suggest that the anomalous enrichment in incompatible elements is a characteristic feature of zircon from ore-bearing (Zr–REE–Y) alkaline granites and syenites.

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