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ANOMALOUS GEOCHEMISTRY OF ZIRCON FROM THE YASTREBETSKOE RARE METAL DEPOSIT (SIMS- AND TOF-STUDY)

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A detailed isotopic geochemical study (secondary ions mass-spectrometry – SIMS, time-of-flight mass-spectrometry – TOF) of zircon from ore-bearing syenites of the Yastrebetskoe rare metal-rare earth deposit (the Ukrainian Shield) has yielded proofs of magmatic genesis of the deposit: unaltered central parts of zircon grains typically feature characteristic magmatic spectra of REE distribution, their values of $\delta^{18}O$ staying somewhat higher than the mantle value (6.5 ‰, on the average). During the final stage of forming the deposit the role of fluorine-water-bearing fluids enriched with Y, REE, Nb, Be and heavy oxygen had increased, as directly reflected in the anomalous isotopic-geochemical characteristics of zircon rims and zones of zircon alteration (the contents of Y reaches 61874 ppm, that of Nb – 7976 ppm, Be – 1350 ppm, $\delta^{18}O$ reaches 12.42‰, F – 0.7 % mass, H_2O – 4% mass).

***Key words*:** zircon, rare earth elements, rare elements, ion microprobe, time-of-flight mass-spectrometry, isotopic composition of oxygen, Yastrebetskoe rare metal deposit.

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Introduction. Presently zircon is one of the most actively studied accessory minerals. Since zircon is considered to be one of the most stable minerals in secondary processes, it plays a dominating role in geochronological and isotopic studies. Modern experimental studies testify to considerable changes in the morphology, structure and composition of zircon during its interaction with water (hydrothermal) solutions and magmatic and metamorphic fluids.

The Ukrainian Shield is a unique province of Proterozoic alkaline magmatism. A particular feature of alkaline rocks of that region is the presence of nepheline-free alkaline syenites in their composition, rich ores of zircon, rare earths and yttrium associated with them. The study of zircon from rare metal-rare earth deposits of the Ukrainian Shield (Yastrebetskoe, Azovskoe and Perzhanskoe deposits) carried out previously has pointed to diverse morphologies and compositions of the mineral and revealed close age and similar conditions of formation of the Yastrebetskoe and Azovskoe deposits [1, 5]. A characteristic feature of zircon from Yastrebetskoe and Azovskoe deposits is its heterogenic structure, identical trends in the accumulation of its trace elements, considerable concentrations of REE and other elements. The study offers new data (the newly defined contents of light and volatile trace elements, mapped distributions of a number of trace elements across the whole area of zircon grain) that confirm the anomalous geochemical characteristics of composition of zircon from the Yastrebetskoe deposit.

Description of the Yastrebetskoe deposit. Rare metal and rare earth mineralization in the Ukrainian Shield is typical for its three megablocks: the North-Western, the Ingulo-Ingulets and the Azov ones [3]. Oustanding examples of such mineralization are the zirconium - rare earth Azovskoe and Yastrebetskoe and the complex rare metal Perzhanskoe deposits, the latter associated with granites and looking promising for mining Be, REE, HFSE (high field strength elements) and a number of other elements. The Yastrebetskoe zirconium deposit is similar to the Azovskoe deposit in many aspects and may be considered to be a petrological prototype of the latter. The Yastrebetskoe deposit is associated with the same-name massif that is considered to derive from the Korostenkiy anorthosite-rapakivi granite pluton and lie among the granites of the Perzhanskiy complex in the NW megablock of the Ukrainian Shield. The Yastrebetskiy massif is a differentiated layered intrusion; identified in it are endocontact syenites, syenites of the upper layered group, syenites of the main layered series, and also quartz-syenites and grano-syenites of the so-called central “core”, which are considered to be the last differentiates of syenite magma. Syenites of the massif, except for the tempered endocontact part, represent exclusively the alkaline feldspar types with high (90% and more) ferruginosity of mafic minerals [3]. The principal ore-bearing are the rhythmically stratified rocks of the main layered series, the alternating leucocrate and melanocrate syenites of varying granularity (all the way to pegmatoid ones) [2]. Leucocrate syenites dominate quite strongly over melanocrate syenites. Ore minerals of rare earth-syenites of the Yastrebetskiy massif are: zircon and, in slave amounts, britholite, allanite, bastnesite, parisite, fergusonite. Within the interval of 1050-550 m the Yastrebetskiy massif features a number of cumulative layer-by-layer ore beds ("horizons") up to several meters thick, rich in zircon, that compose the same-name deposit. Syenites of Yastrebetskiy and Azovskiy massif are considered to be the products of crystallization differentiation of trachyte magma (derivative of the basalt magma), while the interlayer beds of zirconium and rare earth ores are cumulative formations [3]. In contrast to the Azovkoe deposit similar in its mineral composition, the Yastrebetskoe deposit ores rich in Zr and REE are only zircon ores. The age of zircon from syenites of the Yastrebetskoe deposit, derived from the data of the local SHRIMP technique to be 1772 ± 19 Ma may be assumed as the age of formation of the deposit itself [1, 5].

The paper offers new data on the distribution of trace and rare earth elements in zircon from the riebeckite-aegirine quartz central "core" of Yastrebetskiy massif (the interval of 299-300 m; sample 20).

Study techniques. Particularities of the structure and composition of zircon in main elements, control of inclusions of mineral phases and their composition were studied using the composition contrast mode (BSE) of JEOL JSM-6510LA scanning electron microscope with the JED-2200 ED-spectrometer (Institute of Precambrian Geology and Geochronology RAS) and cathodoluminescence (CL), conducted at the Center for Isotopic Research of VSEGEI prior to U-Pb-dating. The contents of rare earth and trace elements in zircon was retrieved using the Cameca IMS-4f ion microprobe (Yaroslavl Branch of the Physical and Technological Institute RAS) and following the technique described in [9]. Measurements of the contents of light and volatile elements in zircon were taken during a separate session following a special technique discussed in [7]. The size of the analyzed spot of zircon free of micro-inclusions of other minerals did not exceed 20 μm in diameter; the relative measurement error for the majority of elements was 10-15 %; the detection limit for separate elements was 10 ppb on the average. When plotting the REE distribution spectra the composition of zircon was normalized to the composition of CI chondrite [10]. The isotopic composition of oxygen in zircon was studied at the same spots after the specimen was polished anew using the Cameca IMS-1280-HR ion microprobe (Institute of Geology and Geophysics, the Chinese Academy of Sciences) and following the technique presented in [11]. Mapping the distribution of a number of rare elements in the crystal of zircon was done using the time-of-flight mass-spectrometer (TOF-SIMS[5])

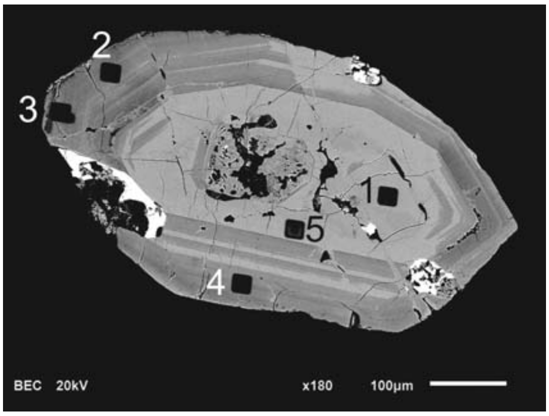

Fig.1. Image of zircon grain from Yastrebetskoe deposit in back-scattered electrons (BSE). Squares are indicated of analyzing zircon using the Cameca-1280-HR ion microprobe

Trace elements contents (ppm) and isotopic composition of oxygen, Yastrebetskoe deposit zircon

Component	Central part of the grain		Grain rim anomalous in composition		
	5	1	4	2	3
Li	8.94	6.82	6.64	2.56	4.26
Be	7.49	7.89	1013	1078	1350
B	1.86	0.80	354	319	381
H_2O	83.6	514	44358	42450	43298
F	34.0	13.8	4957	5310	7608
Cl	4.76	1.12	55.8	48.2	146
Y	–	2659	9606	61874	53528
P	–	68.8	204	956	492
Nb	–	48.9	2823	7667	7976
Ca	–	42.4	4869	7863	9858
REE	–	1943	8448	27667	23862
$\delta^{18}O$,‰	5.96	6.99	10.82	12.42	11.32

Comment. 1-5 are points of analysis (see Fig.1). Blank means no contents was measured. When calculating the contents of trace elements in the central part of the grain the averaged contents of SiO_2 was used over the zircon matrix, 30 % mass, while that for grain rims was taken at 25 % mass.

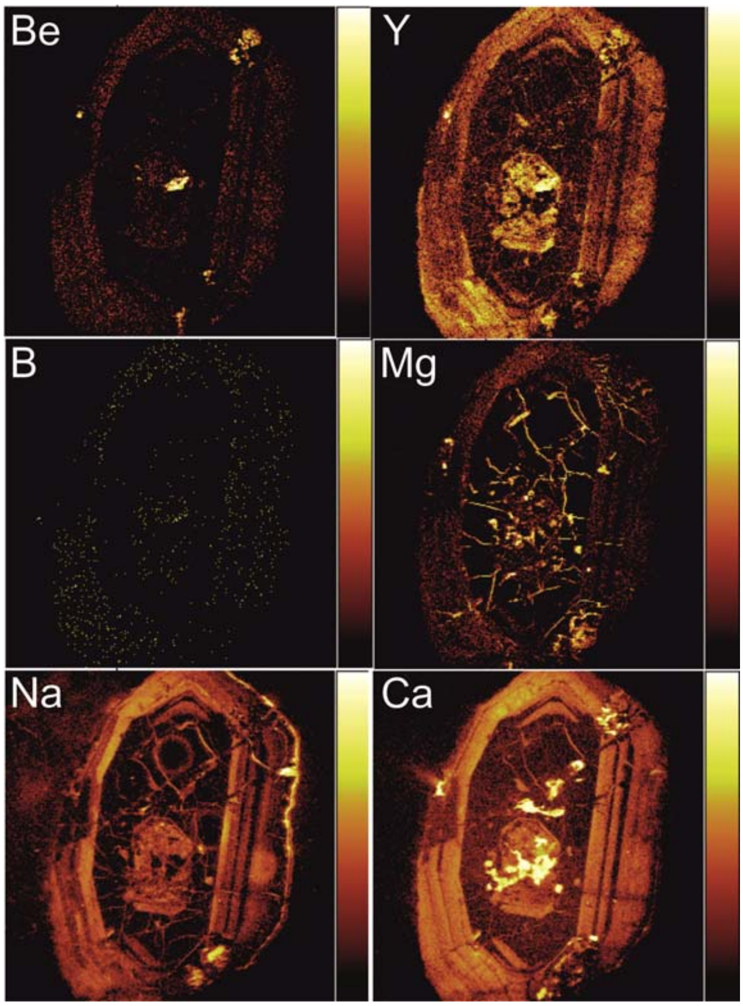

Fig.2. Distribution maps for trace elements in a zircon from the Yastrebetskoe deposit retrieved on the TOF-SIMS[5] time-of-flight mass-spectrometer. The size of mapped area was 500 × 500 μm. Relative scales of contents are given for each element separately (from the minimum level simulated by dark colors to the maximum contents presented by bright colors)

in Burst Alignment mode (lower mass and finer surface location resolution), at the resolution of 256 × 256 and the initial beam size of 3 μm [8].

Zircon geochemistry. A typical feature of all the studied grains of zircon from the Yastrebetskoe deposit is their large size (from 200-300 μm to several millimeters) and the presence of micro-inclusions of REE minerals (parisite, bastnesite, allanite) basically associated with the rim zone of zircon enriched with trace elements. Among the grains of zircon from riebeckite-aegirine quartz syenites (sample 20), the end product of differentiation of the massif [3], a grain was detected where its rim anomalous in composition and standing out by the dark coloration in its BSE-image reached the thickness of 100 μm while being mostly free from micro-inclusions of other mineral phases (Fig.1). The central part of the grain (Point 1 in the Table) is a strongly fractured homogeneous area with cumulative contents of REE (1943 ppm) typical for a zircon of magmatic genesis and an insignificant excess in the contents of some non-formula elements (Ca, Nb); the contents of Y and P is not high either (1659 and 69 ppm, respectively). The concentrically zonal rim of zircon grain is dark in color in BSE (Points 2-4 in the Table); it differs from the central part in its anomalously high contents of REE (up to 27667 ppm), Y (up to 61874 ppm) and non-formula elements: Ca (up to 9858 ppm), Nb (up to 7976 ppm), Be (up to 350 ppm), B (up to 381 ppm). The contents of Li grows insignificantly while moving from the central part of the grain (4.5 ppm on the average) to the grain rim (7.9 ppm on the average). What is most indicative is the increase in the contents of volatile components – water and F in the zircon rim (see the Table). The contents of water in the central part of the grain averages about 300 ppm, never exceeding the value of 514 ppm; in the rim it exceeds 4 % mass (averaging 43368 ppm). The contents of F increases more than 200-times, the respective averages being 24 and 5959 ppm. The contents of Cl grows towards the rim as well, though not as impressively, averaging 3 and 83 ppm, respectively.

Such a high contents of Y and REE in the rim of the studied zircon was found earlier in zircons from the zones of intense fluid reworking of Svecofennian age in the Fennoscandinavian Shield (their contents of Y reaches 84800 ppm, and that of REE up to 96800 ppm [6]) and in the yttrium-rare earth zircon from the Ichet'yu ore occurrence in Middle Timan (their Y contents exceeds 70000 ppm, and the REE exceeds 100000 ppm [4]). As for the Yastrebetskoe deposit the contents of Y in the anomalous zircon exceeds the total amount of REE more than two-times, which is extremely atypical even for metasomatic zircons where the contents of Y does not exceed 10000 ppm. Such an anomalous composition of the rim results from significant saturation of late riebeckite-aegirine quartz syenites by fluorine and water containing fluids enriched with Y, REE, Nb, Be, B and other elements incompatible for zircon.

Mapping the distribution of a number of trace elements in the zircon from the Yastrebetskoe deposit using the time-of-flight mass-spectrometer has confirmed heterogeneity of the internal structure of the mineral and systematic difference of rim composition from that of the central part of the zircon (Fig.2). Distribution maps for all the elements except B, its contents in the rim exceeding just insignificantly the sensitivity threshold of the time-of-flight mass-spectrometer reflect the enrichment of zircon rim with a wide spectrum of trace elements while underpinning a certain "banding" of rim structure. The observed banding somewhat resembles the oscillational zonality that is observed in the CL-images of zircons of magmatic genesis. Apparently, that "banding" reflects the oscillations of contents of trace elements in the melt (fluid) in the process of zircon crystallization. Besides, the maps of distribution of such elements as Ca, Mg and Na demonstrate that the altered spot in the center of the grain is linked with the rim by a whole network of veins and cracks enriched with those elements. It appears that the fluid enriched with incompatible elements was penetrating from the rim to the center of the grain along such veins and cracks affecting intensely the partially metamict porous center of the grain of zircon. The micro-tomographic study undertaken earlier, effective in studying the zircon anatomy has demonstrated extreme inhomogeneity of the considered grain which agrees in principle with its characteristic from BSE (see Fig.1). The grain core features a cavity of complex shape of about 30-40 μm size from which a number of twisted cracks spread out. In the rim part of the grain relatively temperate zones of lower and higher density alternate, 20-30 μm wide [5].

As compared to the central part of the grain, the REE distribution in zircon rim is characterized by a gently sloping weakly differentiated spectrum due to the contents of light REE increased by almost 2 orders of magnitude, while the negative anomaly in Eu evens out and the positive Ce-anomaly practically vanishes (Points 2-4 in Fig.3). The REE distribution spectrum in the central part of the grain is typical for a zircon of magmatic genesis: strongly excessive contents of light vs. heavy REE, clearly manifested negative Eu-anomaly and positive Ce-anomaly (Point 1 in Fig.3).

Studying the $\delta^{18}O$ in zircon from the Yastrebetskoe deposit revealed a considerable difference between the central parts of the grain from dark-CL rim zones and zones of zircon alteration [1]. For an unaltered zircon the characteristic value of $\delta^{18}O$ is 6.63 ‰, on the average (by 10 measurements). That value is somewhat higher than the mantle value (about 5.3 ‰) and points to the magmatic genesis of unaltered zircon [13]. Generally higher values of $\delta^{18}O$ are typical for zircon from alkaline rocks of Proterozoic age: zircon from the Brazilian shoshonites averages 8.73 ‰ of $\delta^{18}O$, and the zircon from the Wyoming, USA monzosyenites averages 7.35 ‰ in $\delta^{18}O$ [13]. As for the rim of the zircon in question coming from the Yastrebetskoe deposit featuring excessive contents of Y, REE, Nb and other incompatible elements, a sharply increased value of $\delta^{18}O$ was found in it, averaging 11.52 ‰ (see the Table). Growth in $\delta^{18}O$ correlates quite clearly with higher contents of Y: Point 2 with its 61874 ppm of Y yielded the maximum value of $\delta^{18}O$: +12.42 ‰.

To explain excessive values of $\delta^{18}O$ in zircon a mechanism was suggested of entrainment of sedimentary material in the process of crystallization or that of participation of metamorphic fluid in it [12]. However both petrologic data and composition particularities of zircon contradict that assumption in case of the Yastrebetskoe deposit with its high value of $\delta^{18}O$ in altered zircon rims: as a rule, metamorphic rims are depleted in trace elements as compared to zircon cores.

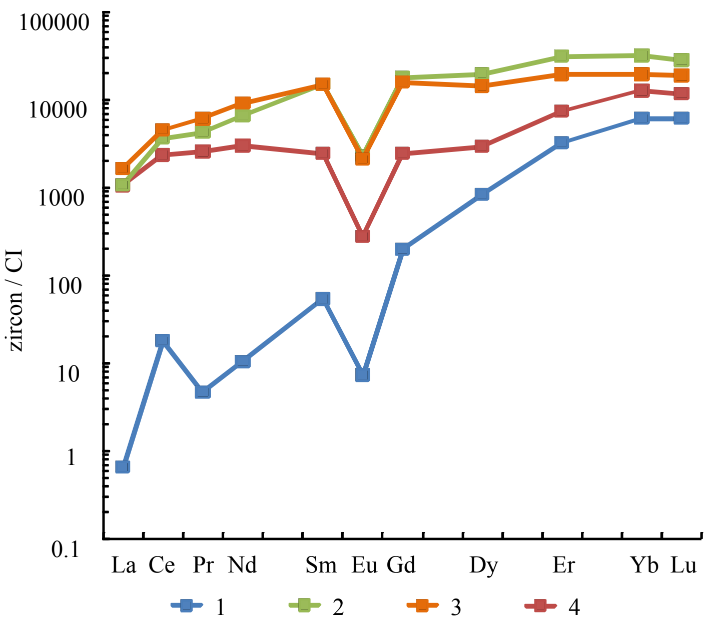

Fig.3. REE distribution spectra normalized by the composition of CI chondrite, zircon from the Yastrebetskoe deposit. Analyses point correspond to Fig.1 and the Table

Most probably, zircon rims record a sharp change in composition of the fluid enriched with incompatible elements and heavy oxygen, the fluid interacting with syenite melt during the final stage of forming the Yastrebetskoe deposit.

Conclusions. It appears that zircon with anomalous isotopic and geochemical characteristics of its rim composition has originated in the result of differentiation of magmatic melt during the final stage of forming of Yastrebetskoe deposit, when the role of fluids enriched in Y, REE and other trace elements and heavy oxygen increased. Rims of zircon from the Yastrebetskoe deposit feature an anomalous composition (see the Table): their contents of trace and rare earth elements is much higher than that in the rim parts of zircon from the Azovskoe deposit, both deposits similar in their genesis [1], which may be explained by stronger magmatic differentiation of the rocks of Yastrebetskoe deposit compare with that for the Azov deposit.

Studying the zircon from Yastrebetskoe deposit yielded proofs of the magmatic genesis of that Y-REE-deposit: unaltered zircon typically features a magmatic spectrum of REE distribution, it value of $\delta^{18}O$ somewhat higher than that for the mantle (6.63 ‰ on the average). During the final stage of forming the deposit the role of fluids enriched with Y, REE, Nb and heavy oxygen had increased, as directly reflected in the anomalous isotopic-geochemical characteristics of zircon rims and zones of zircon alteration (the contents of Y reaches 61874 ppm, that of Nb – 7976 ppm, Be – 1350 ppm, $\delta^{18}O$ reaches 12.42 ‰, F – 0.7 % mass, H_2O – 4 % mass).

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