High-Y zircon from the Yastrebetskoye Zr-REE deposit (the Ukranian Shield)

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The Ukrainian shield is a unique province of Proterozoic alkaline magmatism. Alkaline rocks in this region are characterized by the presence of nepheline-free alkaline syenites, associated with Zr, REE, Y bucked ores. A previous study of zircon from Zr-REE deposits of magmatic origin (Yastrebetskoye and Azovskoye deposits, the Ukrainian Shield) showed a variety of zircons morphology and composition, and revealed that these deposits were formed under the similar geological conditions (Levashova et al., 2016). A characteristic features of zircon from the Yastrebetskoye and Azovskoye deposits are its heterogeneous structure, high content of REE and other trace elements and the uniform trend of trace elements accumulation.

Zircon from the riebeckite-aegirine-quartz rocks of the Yastrebetskiy massifs core complex (depth interval 299-300 m, sample 20) was studied by SEM, EDS, WDS, SIMS (REE, TE, O), ToF-SIMS mapping and Raman spectroscopy. The central part of the grain (point 1, fig.1) is a highly fractured and rather homogeneous zone with a ΣREE content (1943 ppm) typical of magmatic zircon, slightly increased nonstoichiometry elements (Ca, Nb) content, and also low concentration of Y and P (1659 and 69 ppm, respectively). The concentric zonal rim compared to central part of the crystal is relatively dark in BSE (point 2, fig.1), abnormally enriched in REE (up to 27667 ppm), Y (up to 61874 ppm) and nonstoichiometry elements - Ca (up to 9858 ppm), Nb (up to 7976 ppm), Be (up to 1350 ppm), B (up to 381 ppm). The enhanced values of water and F (SIMS and WDS data) in zircon rim should be also pointed out: the water content in the central part of the grain averages about 300 pmm, but not exceeding 514 ppm, whereas in the rim zone this value exceeds 4 wt%; the F content increases more than two hundred times - from 24 to 5959 ppm on an average. Rim zone is also characterized by $\delta^{18}O$ (mean value=11.52 ‰) simultaneously increasing with Y content. ToF-SIMS maps of trace elements (except B, which concentration level in the rim zone slightly exceeds the detection limit), reflect not only the enrichment of the rim zone with trace elements, but also its zonal structure. The exposed zonation resembles oscillatory one, often observed in CL images of magmatic zircon. It appears that zonation reflects fluctuations in the rare elements content in the melt/fluid during the crystallization process.

Such a high content of Y and REE was previously found in zircon from PR fluid processed zones on the Fennoscandian Shield (Y up to 84800 ppm, REE - up to 96800 ppm, Skublov et al. 2011) and zircon from the Ichetju ore occurrence in Middle Timan (Y exceeds 70000 ppm, REE - 100000 ppm, Makeyev and Skublov 2016). ToF-SIMS trace elements mapping of zircon from the Yastrebetskoye deposit confirmed the heterogeneity of the crystals internal structure and the systematic difference in the composition of the zircons core and rim zones.

The Raman spectra profile across crystal elongation could be regarded under the aspect of zircon crystallinity: the only one relatively well-defined $\nu_3(SiO_4)$ band corresponds with crystal core; rim zone shows spectra with extremely broad to completely absent main peaks. The FWHM of the $\nu_3(SiO_4)$ band in the central zone is 11.6 cm^{-1}, which suggests only a partial amorphization of the crystal structure (so-called transit state) (Nasdala et al., 1995). It stands to mention that the intensity of characteristic bands is significantly reduced over the matter of the additional intense peaks, which may result from laser-induced fluorescence emission of the luminophor impurities, incorporated in zircons lattice. Significant structural radiation damage of rim zone could be a reason of the zircon reactive capacity enhancement and dramatic accumulation of REE.

The anomalous composition of the zircon rim derived from the considerable saturation of late riebeckite-aegirine-quartz syenites with fluorine-water-bearing fluids enriched with ^{18}O, Y, REE, Nb, Be, B and other trace elements.

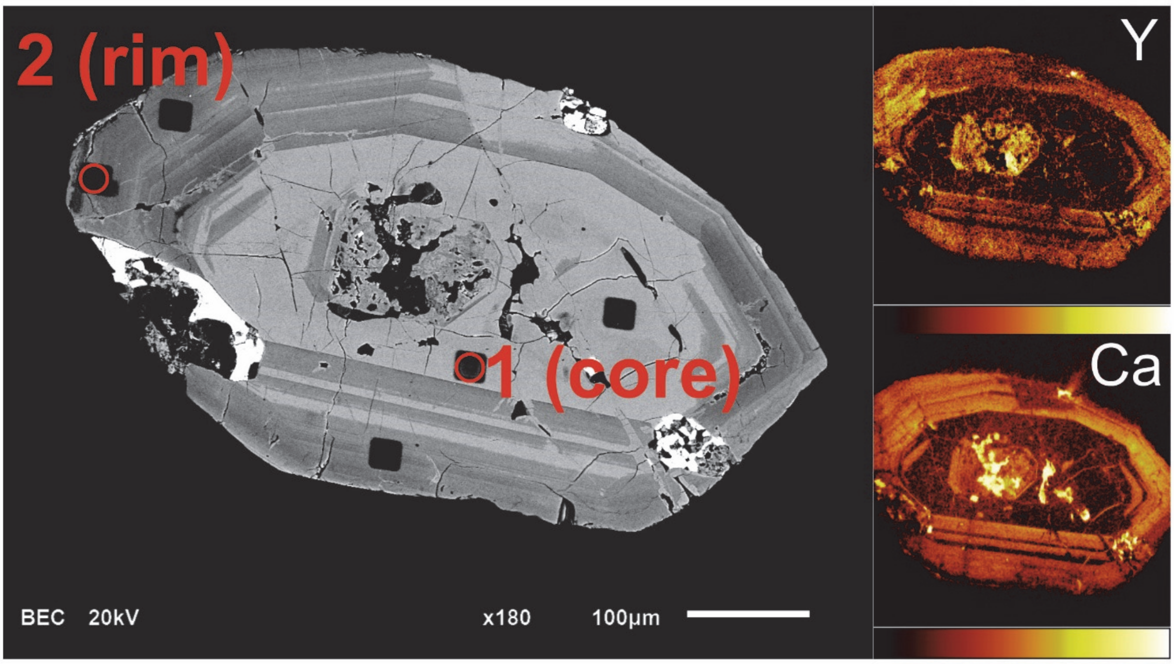

Fig. 1. *BSE image and Y and Ca maps (ToF-SIMS) for zircon from the Yastrebetskoye deposit*

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