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Lithium in low-temperature fluid-affected zircons. Paleoproterozoic weathering horizon (Karelia, the Baltic shield).

Nadezhda Alfimova (1), Ekaterina Klimova (2), Vjacheslav Matrenichev (3), and Tatjana Zinger (4)

(1) Institute of Precambrian geology and geochronology, Russian Federation , Institute of Earth Sciences SPbSU, Russian Federation (n.alfimova@spbu.ru), (2) Institute of Precambrian geology and geochronology, Russian Federation, (3) Institute of Precambrian geology and geochronology, Russian Federation , Institute of Earth Sciences SPbSU, Russian Federation, (4) Institute of Precambrian geology and geochronology, Russian Federation

Zircon is a mineral, which is widely used in geochronology. At the same time, low-temperature fluids had been shown to affect the inner structure, chemical and even isotopic composition of zircons (Geisler et al., 2007, Pidgeon et al., 2013).
Here we report changes in the inner structure and chemical composition of zircon grains, preserved in Paleoproterozoic weathering horizon from Karelia craton (N. Ladoga region, Russia) in spite of greenschist metamorphism. Detailed zircon SEM and CL study revealed that zircons in weathered samples can be classified into two groups depending on their microstructural characteristics: 1- the zircons with an unusual and complex (breccia-like) structure with almost no relics of magmatic zonation. The inner structure of that grains is often composed of a mosaic of angular crystal pieces cemented with silicates or even other generation of zircon itself. Group 2- zircons with clearly seen relics of magmatic (oscillatory) zonation. Both groups have outer rims which are forming the facets of the grains.
These two groups are also different in chemistry. Group 1 zircons contain more than 10 ppm of Ba and Sr, >1000 ppm U and Th/U there is $\leq$0.1, REE spectra show LREE/HREE > 0.5, positive Cen (<+2), Eu/Euan varies from +1.5 to 16. These grains also show an enrichment of non-formula elements (Ca, Mg, Fe, Al) and water. Lithium varies broadly - from 33 to 136 ppm (av.value around 60 ppm). Group 2 zircons are characterized by Th/U >0.3, Ba and Sr are less than 10 ppm each, LREE/HREE<0.5, Cen>+2.0, Eun $\leq$ +1.0, Li is from 19 to 73 ppm with average meaning 49 ppm.
A separate geochemical group can be identified within “a-structural” grains (group 1) –parts of zircons and grains light-colored in SEM. These part of group 1 zircons demonstrate specific REE spectra – LREE/HREE < 0.1, $\sum$REE $\leq$750 ppm, thus being lower, then LREE part of spectra from grains with magmatic structure. These group also has the highest concentration of Li (up to 136 ppm with av. 88 ppm) and lowest Ba/Sr ratio of all measured points, thus forming separate geochemical cluster.
Observed REE spectra, together with Ba/Sr ratio and Li concentration allow us to conclude, that pristine weathered horizon comprised two types of grains, not yet altered by weathering, with different amount of U and Li and thus, may come from diverse sources. Paleo-weathering had changed not only chemical composition (major element and REEs) but the inner structure of grains with higher U concentration more, then with low U content. Li had demonstrated strong ability to resist changes during the low-temperature fluid-mineral interaction.