High-Hf zircon from rare-metal pegmatites from the Vasin-Mylk deposit (Kola region, Russia)

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The Vasin-Mylk deposit is located within the Kolmozero-Voronya greenstone belt composed of sedimentary-volcanogenic rocks of 2.9-2.7 Ga Late Archean age. The massifs of tourmaline and microcline granites, together with granite pegmatites, intrude all the above complexes of the belt, completing its long evolution. An estimate of the age of pegmatites in the Vasin-Mylk deposit was determined by the U-Pb (ID TIMS) isotope composition of microlite and was 2454±8 Ma (Kudryashov at al. 2015).

The pegmatite field of the Vasin-Mylk deposit with the lepidolite-albite-microcline-spodumen-pollucite association is located among amphibolites in the northwestern part of the belt and is one of the largest cesium deposits in the world. The bulk of Cs is concentrated in the pollucite, the associated useful components of pegmatites are Li, Be, Ta, Nb. Among the great variety of accessory minerals in pegmatites, alongside with the pollucite, there are minerals of the columbite-tantalite group, simpsonite, torolite, behierite, holtite, microlite, zircon.

High-Hf zircon was found in the areas of fine-grained greisen with the albite-lepidolite-quartz composition. The zircon crystals are closely associated with holtite and stibiotantalite, representing idiomorphic, almost featureless, octahedral grains of about 500 μm with pinkish-yellow and yellow-orange color. High-Hf zircon is characterized by a very low content of uranium (<1 ppm) and rare-earth elements.

The researches of the internal structure of high-Hf zircon showed the presence of both a thin euhedral zonation, characterized by the alternation of the finest dark and light bands, and a rough zonation (Fig. 1). Light zones have increased Hf content compared to the dark ones. The nodules in zircon are mainly represented by tantalite, there are also small quartz and apatite nodules.

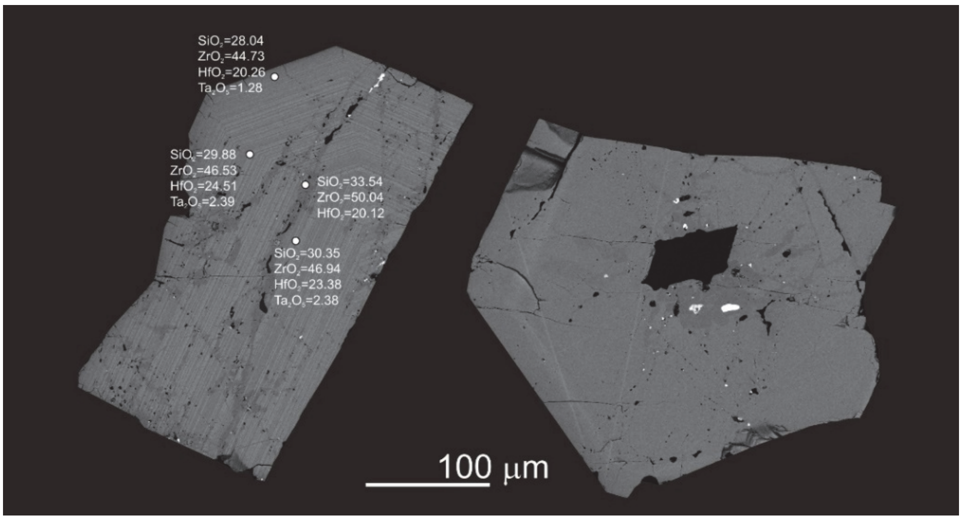

Fig. 1. *Microimages of zircon crystals in the reflected electrons mode. 1 - zircon with fine euhedral zoning; 2 - zircon with a rough zoning. The points are microprobe analysis areas and chemical composition*

The comparison of the position of Raman peaks of high-Hf zircon with the reference zircon and hafnon shows that the main peaks of the studied zircon are shifted toward higher values in relation to the reference zircon and toward lower values relative to the reference hafnon, thereby occupying the middle position (Fig. 2).

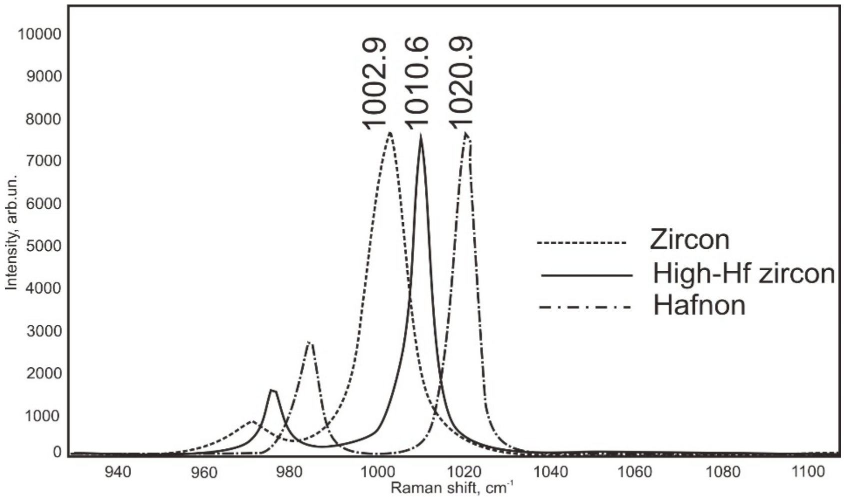

Fig. 2. *Raman spectra of the main peak for high-Hf zircon, reference zircon and hafnon*

Hafnium has a higher affinity for granite melt than zirconium. High concentrations of hafnium usually reflect Zr/Hf fractionation in granite magma, where zircon from pegmatites is considerably enriched by hafnium compared to granite (Černý et al. 1985). The main factor that can influence the solubility of zircon and hafnon in melts is the fractional crystallization of granite magma, where the composition of the melt and its temperature change. Other factors may be the buffer effects of Zr-bearing phases and the role of such fluxes as Li, F and B. The experimental works also showed that a low temperature of high-aluminous melt can result in high hafnium content in zircon (Linnen, Keppler, 2002).

The studied high-Hf zircon crystallized in Al-saturated melt because it was closely associated with albite, spodumene, lepidolite and holtite. Using a Ti-thermometer (Watson at al. 2006), the crystallization temperatures of high-hf zircon were measured in the range of 350-470 °C. This temperature is almost half the temperature of the zircon crystallized from magmatic melt. In the zones of development of high-Hf zircon, B-containing minerals including elbaite and holtite are widely distributed. Thus, the crystallization of aluminous minerals (spodumene, lepidolite) from alumina saturated melt with fluxing elements (B, Li and F) contributed to the strong fractionation of Zr/Hf ratio and the crystallization of the zircon with a high hafnium content during the late stages of the evolution of rare metal pegmatites at the Vasin-Mylk deposit.

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