## High-Hf zircon from the Snezhnoe deposit (Altai-Sayan province)

Machevariani, M.<sup>1,\*</sup>, Melnik, A.<sup>1,2</sup>, Skublov, S.<sup>2,1</sup>, Lukashova, M.<sup>3</sup>, Müller, D.<sup>4</sup>, Lupashko, T.<sup>5</sup>, Ilchenko, K.<sup>5</sup>

<sup>1</sup> Saint-Petersburg Mining University, Russia <sup>2</sup>Institute of Precambrian Geology and Geochronology, Russian Academy of Sciences <sup>3</sup> Tescan Orsay Holding, Russia <sup>4</sup> Ludwig-Maximilians-Universität München, Germany <sup>5</sup> M.P. Semenenko Institute of Geochemistry, Mineralogy and Ore Formation, National Academy of Science of Ukraine \* E-Mail: wmdmaria@gmail.com

This work presents a mineralogical study on high-Hf zircon (collection of Shuriga T.N.) from the albitized granite of Snezhnoe deposit, one of the richest beryllium deposits of the Altai-Sayan province with additional isolated tantalum-niobium mineralisation area (Kupriyanova and Shpanov 2011).

Literature review on high-Hf zircon from granite pegmatites and granitoids shows that maximum level of HfO<sub>2</sub> content in zircon from rocks of both types is quite similar: 18-44 wt% and 16-35 wt%, respectively (Kempe et al. 2004; Yin et al., 2013). The studied zircon contains up to 27 wt% HfO<sub>2</sub>, which is sufficient for entry in series of rare mineralogical findings. All the Hf-rich zircon grains show a patchy internal texture, sometimes combined with thin remnants ( $\sim$ 5µm) of oscillatory zoning on the edge of crystals (Fig.1). Since the "spongy" texture is considered to be specific for aqueous-fluid precipitated zircon (Corfu et al. 2003), the abundance of holes and cavities within all zircon grain with less corroded and vacuolized oscillatory rims suggested hydrothermal overgrowth after altered magmatic cores. Various mineral inclusions of albite, magnetite, limonite, xenotime, bastnaesite-(Y), and thorite are preserved within the zircon crystals and limited to zones with porous texture.



Fig. 1. BSE, CL, OM images and EBSD maps for zircon grain from the Snezhnoe beryllium deposit

The chondrite-normalised REE patterns of zircon appear to be typical for zircon of late magmatic or hydrothermal origin and are characterised by the steep positive slope from Sm to Lu with Ce/Ce\*~2.7 and Eu/Eu\*~0.2. The LuN/LaN varies within wide limits from 422 to 27098 and shows strong positive correlation with Hf content (r=0.85). Yet, all data points for the Hf-zircons fall within or near the field of hydrothermal zircons in the discriminant diagram of SmN/LaN – Ce/Ce\* coordinates (Fu 2009). The Zr/Hf ratio varies from 1.3 up to 5.0 and, consistently, the 100\*Hf/(Zr+Hf) characteristic ratio is between 17 and 42, which classifies zircon from the Snezhnoe deposit as hafnium one, according to nomenclature proposed by Correia Neves and Lopes Nunes (1974).

The Raman spectroscopy and EBSD data were used to identify the degree of crystallinity within the zircon grains, which could be a clue to understand if high-Hf zones are related to primary growth structures or affected by the secondary alterations. The positions of the most intensive zircon Raman peaks  $v_3(SiO_4)$  and  $v_1(SiO_4)$ , generally being used to evaluate zircon crystallinity degree (Nasdala 1995; Marsellos and Garver 2010), range within 1000.1-1009.7 cm<sup>-1</sup> and 967.1-975.7 cm<sup>-1</sup>, respectively, and show strong positive correlation with Hf content (r=0.7 in both cases). Hafnium concentration also negatively correlate with FWHM of  $v_3$  and  $v_1$  peaks: the bandwidth reduces and the Raman shift value of this bands increases substantially with elevation of Hf concentration. Since band parameters, significantly affected by impurities (mostly hafnium), could not be unambiguously used to measure the degree of zircon radiation-induced disorder, the evaluation of zircon crystallinity based on EBSD mapping is still possible. The angular fit between the EBSP at each point and the theoretical index solutions, given by the mean angular deviation, was generally good and the coefficient of coincidence came up to 78%. The obtained pattern quality and phase maps show that the zircon grains are generally presented by monocrystals with sufficiently stable unit cell parameters and without zones of amorphisation (Fig.1).

Thus, the overall study of high-Hf zircon shows that crystallinity degree and secondary alteration processes hardly regulate Hf distribution in zircon. Moreover, estimation of zircon lattice disorder by the parameters of characteristic Raman bands is not suitable for zircon with high Hf content.

*Acknowledgments:* This work was supported by the Russian Foundation for Basic Research (project no. 16-05-00125) and the Ministry of Education and Science of Russia (basic and design parts of the state task in the scientific sphere № 5.9248.2017/BY for 2017-2019).

## **References:**

- Corfu F, Hanchar JM, Hoskin PWO, Kinny P (2003) Atlas of zircon textures. In: Hanchar JM, Hoskin PWO (eds) Zircon. Rev Mineral Geochem, vol 53. Mineral Soc Am, Chantilly, pp 469–500
- Correia Neves JM, Lopes Nunes JE (1974) High Hafnium Members of the Zircon-Hafnon Series from the Granite Pegmatites of Zambezia, Mozambique. Contrib Mineral Petr 48:73-80
- Fu B, Mernagh TP, Kita NT, Kemp AIS, Valley JW (2009) Distinguishing magmatic zircon from hydrothermal zircon: A case study from the Gidginbung high-sulphidation Au–Ag–(Cu) deposit, SE Australia. Chem Geol 259:131–142
- Kempe U, Gruner T, Renno AD, René M (2004) Discussion on Wang et al. (2000) 'Chemistry of Hf-rich zircons from the Laoshan I-and A-type granites, Eastern China', Mineralogical Magazine, 64, 867-877. Mineral Mag 68:669-675
- Kupriyanova II, Shpanov EP (2011). Snezhnoe field. In: Kovalenko VI (ed) Russian beryllium deposits, GEOS, Moscow, pp 186-195
- Marsellos AE, Garver JI (2010) Radiation damage and uranium concentration in zircon as assessed by Raman spectroscopy and neutron irradiation. Am Mineral 95:1192–1201
- Nasdala L, Wolf D, Irmer G (1995) The degree of metamictization in zircon: a Raman spectroscopic study. Eur J Mineral 7:471-478
- Yin R, Wang RC, Zhang AC, Hu H, Zhu JC, Rao C, Zhang H (2013) Extreme fractionation from zircon to hafnon in the Koktokay No. 1 granitic pegmatite, Altai, northwestern China. Am Mineral 98:1714-1724