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Fractionation of Zr and Hf during the differentiation of peralkaline magmatic system (Lovozero rare metal deposit, Kola Peninsula)

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Zirconium and hafnium are valuable strategic metals. We assessed principal features of the distribution of these elements in peralkaline rocks, ores and rock-forming and accessory minerals of Lovozero complex. The accumulation of these elements during the evolution of alkaline magma of Lovozero deposit up to extremely high concentrations in eudialyte ores (5-8% ZrO2 and 1200-1800 ppm Hf) has been established. These ores represent valuable complex raw material not only for Zr and Hf, but for REE as well. We evaluated partition coefficients of these elements in alkaline pyroxenes (aegirines) from porphyry-like agpaitic lujavrites of Lovozero massif which are 0.40 for zirconium and 0.58 for hafnium. We assessed variations of Zr/Hf ratio for all the rocks of Lovozero alkaline massif. The growth of this ratio in the course of the evolution of alkaline magma has been observed from 38 in the earliest magmatic phase, to 44 in the second phase and to 51-53 in the latest manifestation of alkaline magmatsm. On the basis of the obtained data and equations of equilibrium and fractional crystallization the model of the fractionation of zirconium and hafnium during the evolution of Lovozero intrusion has been constructed. We have demonstrated that the source of strongly enriched magmatic systems similar to Lovozero rare metal deposit is short-lived enriched reservoir - metasomatized and carbonatized mantle substrate. We investigated the fractionation of zirconium and hafnium in carbonatized mantle xenoliths from East Antarctica. The elevated Zr/Hf ratios (up to 125) in metasomatized xenoliths by comparison with the chondritic value have been found. The main reactions of carbonate metasomatism lead to the replacement of primary orthopyroxene by clinopyroxene

 $2Mg2Si2O6 + CaMg(CO_3)2 = 2Mg2SiO4 + CaMgSi2O6 + 2CO_2$

 $3CaMg(CO_3)2 + CaMgSi2O6 = 4CaCO_3 + 2Mg2SiO4 + 2CO_2$

The substantial expansion of the clinopyroxene crystallization field results in increase of Zr/Hf ratio in equilibrium melt due to the higher value of Hf partition coefficient by comparison with Zr. The migration of active carbonate and carbonate-silicate melts equilibrated with the metasomatic wehrlites leads to the increase in Zr/Hf ratio in carbonatized mantle substrate.

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