

Fractionation between LREE and HREE in hydrothermal fluids associated with felsic magmatism

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As crustal abundances of heavy rare earth elements (HREE) are generally smaller than those of light rare earth elements (LREE), HREE are more expensive than LREE in the market. HREE-rich deposits (e.g., Longnan in China, Nechalacho in Canada) are associated with hydrothermally-altered felsic igneous rocks such as granite and syenite. This study aims to discuss what caused the fractionation between LREE and HREE in such igneous rocks.

Alkaline rocks, formed by magma with a low degree of partial melting, are significantly enriched in LREE and are weakly enriched in HREE because LREE are more incompatible than HREE in magma because of their larger ionic radii. Igneous rocks, which can be HREE-rich deposits, are probably formed by either process of alkaline magmatism enriched in certain elements and fractional crystallization. The former is represented by intercontinental alkaline rocks such as the Nechalacho deposit and is rich in REE, HFSE (high field strength elements), fluorine and carbonate. Previous experimental studies found that solubility of zircon is high when magma is rich in alkali elements and/or fluorine and this causes the residual melt to contain more HREE and Zr. On the other hand, calc-alkaline granite can be a source rock of HREE-rich deposits, as represented by the Longnan deposit. The intensive magmatic differentiation and fractionation of LREE-bearing minerals may cause the residual melt to be enriched in HREE relative to LREE. For REE ore formation, however, such deposits require further processes including the deuteric alteration, dissolution of REE-bearing minerals and adsorption of REE during weathering.

Fractionation between LREE and HREE by complexing with various ligands is likely to occur in hydrothermal fluids produced from felsic igneous rocks. Different previous works have suggested that REE³⁺ ions are complexed with carbonate, bicarbonate, fluorine, chlorine and sulfate ions. A recent study indicates that REE-fluoride complexes do not have a significant role in transportation or fractionation of REE because of their lower stability than REE-chloride and sulfate complexes above 150 °C (Migdisov et al., 2009). However, it appears that footprint of saline fluids or sulfate minerals are not very common compared to abundant carbonatite and fluorite in REE deposits.

The HREE-rich igneous rocks are commonly accompanied by alkali alteration and fluoritization in many ore deposits and prospects, however alkali igneous rocks containing high alkali or fluorine contents are not necessarily rich in HREE. REE-fluoride complexes are not significant in hydrothermal fluids, however there are insufficient data to determine an importance of chlorine or sulfate ions in complexing with REE. Fractionation between LREE and HREE in REE deposits still remains unclear and further studies are expected to elucidate which is the more significant process for the REE fractionation, magmatism or hydrothermal alteration.

Reference

Migdisov, A.A., Williams-Jones, A.E. and Wagner, T. (2009) *Geochimica et Cosmochimica Acta*, 73, 7087-7109.

Keywords: HREE, LREE, hydrothermal fluids, fractionation, ore deposits, felsic igneous rocks