ABSTRACT

The rare earth elements (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), including Y and Sc, constitute a strategic group of metals having high-tech applications. Worldwide, the bulk of the REEs are generally mined from deposits hosted in igneous rocks such as carbonatites and alkaline igneous rocks which constitute primary deposits. This dissertation attempts to characterize REE mineralization and hydrothermal alteration processes in peralkaline granites and carbonatites using the Kamthai carbonatite complex and peralkaline/A-type granites of the Malani Igneous Suite (MIS) in western India as case studies.

Peralkaline granites from the Siwana complex of the MIS in western India host mineralization of rare earth and other high field strength elements (REEs/HFSEs). The textural relations, major-trace element chemistry, and Li-isotope composition of minerals are used to constrain the magmatic evolution of the granites and the mechanism of hydrothermal REE mineralization. Three facies of peralkaline granites, viz., hypersolvus, transsolvus, and pegmatitic, are identified in the Siwana complex. Rayleigh crystal fractionation modeling using incompatible trace element abundances and Li isotopes in clinopyroxene and amphibole indicates that the hypersolvus and the transsolvus granites formed after 50–92% and >90% melt crystallization, respectively. Li-isotope variation in reequilibrated clinopyroxenes typically resembles a diffusion profile with a trough in Li and δ^7Li close to the boundary between the relict magmatic and hydrothermally reequilibrated zone marking the diffusion front. The Siwana granitoids are hydrothermally altered as evidenced from pseudomorphic re-equilibration of clinopyroxene, alkali feldspar megacrysts, vein and patch perthite formation, replacement of ferrorichterite/clinopyroxene by hydrothermal aegirine, alteration of primary fluorapatite, monazite, aenigmatite, eudialyte, and vlasovite. Three stages of hydrothermal alteration are identified in the granites: stage-I alteration was brought about by highly-saline high-temperature fluid that scavenged REEs, HFSEs, Ti, Na, and Fe from clinopyroxene and aenigmatite. This was followed by extensive replacement of ferrorichterite and arfvedsonite by aegirine, which decreased the pH and salinity of the fluid. The third stage alteration led to the replacement of vlasovite by calciocatapleiite, elpidite, and eudialyte and was accompanied by the replacement of alkali feldspar by aegirine, quartz, and secondary REE minerals. Secondary REE minerals precipitation was triggered by the fluctuation of pH primarily due to amphibole and alkali feldspar interaction with REE-bearing hydrothermal fluids.

The Siwana granitoids are characterized by the presence of rapakivi-like alkali feldspar megacrysts. The rapakivi texture found in many granitoids comprises alkali feldspar megacrysts mantled by plagioclase, usually of oligoclase composition. The existing models for their genesis involve magmatic or dry-subsolidus processes; however, using microtextural and geochemical evidence, this study demonstrates that rapakivi texture can form by subsolidus deuteric alteration of feldspar megacrysts through a coupled dissolution-reprecipitation replacement process. The feldspars in granites from the MIS crystallized at temperatures >720ºC and subsequently underwent coherent exsolution producing strain-controlled braid microperthite/antiperthite. At temperatures of

465-490°C, the feldspar megacrysts reacted with deuteric fluids, which led to the dissolution of the braid perthite/antiperthite along an inward moving reaction interface and coupled precipitation of oligoclase/albite mantle and patch perthite. At temperatures of 253-283°C, the feldspars were partially albitized, during which the oligoclase patches and the plagioclase mantle were partially pseudomorphically replaced by albite. These results conclusively demonstrate for the first time that in addition to magmatic processes, rapakivi feldspars can form by subsolidus fluid-induced dissolution-reprecipitation replacement reactions.

Recent models of hydrothermal REE mineralization in carbonatites advocate the exsolution of aqueous-carbonic fluids from the crystallizing carbonatite magma, which mobilizes the REEs. The precipitation of the REEs primarily as fluorocarbonates and phosphates is mainly in response to an increase in pH or decrease in temperature as a result of the interaction of the REE-bearing fluid with carbonates. While this model provides a broad overall genetic framework of REE mobilization and mineralization in carbonatites, there is little understanding of the role of non-carbonate minerals such as magnetite and apatite, which often constitute major components of many carbonatites, during the fluid-rock interaction leading to REE mineralization. Iron-oxide-bearing calciocarbonatites from the Kamthai alkaline complex in western India host REE mineralization comprising intergrowths of bastnäsite, hydroxyl-parisite, röntgenite, synchysite, and pyrochlore, with calcite that pseudomorphically replaces patches of hematite with cellular boxwork-type structure. The microtextural relations and trace element chemistry of hematite, magnetite, and calcite, and C-O isotope composition of carbonate are suggestive of extensive low-temperature hydrothermal alteration of the carbonatites. The hematite boxwork structure and the REE mineral-calcite intergrowths often have squarish outlines and are interpreted to have pseudomorphed primary magnetite during fluid-rock interaction. A new mechanism of hydrothermal REE mineralization is postulated involving an influx of acidic hydrothermal fluids, which scavenged the REEs and other trace elements from magmatic carbonates and apatite. These acidic fluids were responsible for the protonation of magnetite and leaching out of Fe^{2+}, converting them to hematite through a non-redox transformation. The reaction results in 32% volume reduction for every mole of magnetite consumed, generating significant rock porosity, which further aided fluid-rock reaction and hydrothermal alteration. More importantly, it consumed proton, which increased the fluid pH triggering precipitation of bastnäsite-group minerals (including bastnäsite, parasite, röntgenite, synchysite).

Keywords: Malani Igneous Suite, Kamthai carbonatite complex, peralkaline granite, carbonatite, rapakivi feldspar, REE mineralization, hydrothermal alteration, Li-isotopes, C-O isotopes, bastnäsite group minerals