REE and Uranium in Skarn Garnets and Other Phases: Constraints on the Transport of U and REE in Skarn Forming Fluids

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Introduction

The REE are commonly enriched during skarn metasomatism, prompting attempts to use them as indicators of fluid source and processes. Enrichments in actinide elements also occur in silicates, which are then of use for geochronology. It is therefore important to understand the hydrothermal behaviour of these elements. To further this aim we have initiated a study of the REE in skarn minerals from the Beinn an Dubhaich granite aureole, Skye, concentrating on trace element zonation in garnets.

Analysis

Three samples of garnet-bearing skarn were taken from around the Beinn an Dubhaich granite. Minerals were analysed for major elements using electron microprobe, and for trace elements using INAA and/or ion microprobe. The distribution of U was investigated by induced fission track mapping. Fluid inclusions were studied in order to characterise P-T conditions and fluid chemistry during metasomatism. Laser ablation ICP-MS analyses of zoned garnet are planned for the immediate future.

Fluid properties

Fluid inclusions in diopside indicate high temperature (600-620 °C) highly saline (45-50 wt.% NaCl eq.) brines, probably of magmatic derivation. Assuming a pressure of 500 bars fluid inclusions record cooling and dilution of fluids during garnet formation from around 350-400 °C and 20-25 wt.% NaCl eq., to 200-250 °C and 5-10 wt.% NaCl eq. Fluid inclusions in late stage fluorite show a wide range in salinity, possibly indicative of boiling or fluid mixing.

Chemistry of skarn garnets and other phases

All the garnets studied are andraditic. Oscillatory growth zoning and alteration textures are common. Pyroxenes are diopside-rich and show no zonation. Analyses of mineral separates show that garnets are the most REE-rich phase in all samples. Pyroxenes are typically light REE, and particularly La, enriched, with a negative Eu anomaly. A range of REE patterns occur in garnet, all showing LREE enrichment, and a flat HREE pattern. All garnets show a depletion in La relative to Ce and Nd. Chondrite normalised La/Nd and La/Lu ratios

range from ~0.5 to 3 and 5 to 35 respectively (Fig. 1a). Total REE abundances range from 17.2 ppm to 1277 ppm, with the highest values occurring in garnets with the lowest temperature and salinity fluid inclusion populations. Uranium concentrations in garnet separates from this sample range from 5 to 130 ppm. Induced fission track maps indicate that uranium is zoned within some garnets, and its distribution correlates with the major element zonation. Calculations also suggest that the distribution of U varies with changes in the ratio of Fe²⁺ to Fe³⁺. Preliminary ion microprobe analyses have been obtained from an area of the most U-rich sample that shows a continuous range in U concentration from ~0 to 25 ppm. The concentration of U shows a positive correlation with the sum of analysed REE (La+Ce+Pr) (Fig. 1b). Analyses of unzoned garnets separated by colour from the same sample show a range of U contents from 0 to 65 ppm, again with a positive correlation with REE content, but with a very different slope (Fig. 1b).

Discussion

The calc-silicate minerals of contact skarns from the Beinn an Dubaich granite aureole show varying absolute contents of the REE, and formed from fluids of different chemistry and P-T conditions. Differences in the bulk REE patterns of pyroxene and garnet are consistent with an external control on REE distribution. The adjacent granite is the most likely source of the REE at all stages, and therefore a speciation control on the uptake and deposition of the REE from hydrothermal fluids of different temperature and composition is the most likely explanation for this variation. The oscillatory nature of much of the zonation in garnet and the direct correlation of U with total REE suggests that one of the major controls on U and REE distribution was self organisation during disequilibrium growth from a super-saturated fluid (Ortoleva et al., 1987). However, less regular zoning, textural evidence for dissolution and overgrowth, the lack of a continuous correlation between U and the REE and changes in redox state inferred from major element chemistry all imply that external controls on the incorporation of trace elements into garnet, may also have affected REE and U distribution patterns. Further analyses of U and the full range of REE are planned using laser ablation ICP-MS in order to investigate the controls on their distribution.



Figure 1: (a) Chondrite normalised plot of the REE in garnet and pyroxene (data obtained by INAA). (b) Plot of La+Ce+Pr against U concentration in zoned garnet (data obtained by ion microprobe).

Ortoleva, P., Merino, E., Moore, C. & Chadam, J., *Am. J. Sci*, **287**, 979-1007, (1987).