

Lanthanide Tetrad Effects in Naegi granite and pegmatite, central Japan

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Lanthanide Tetrad Effects in Felsic Rocks

Lanthanide tetrad effects are observed as the concave or convex variations in chondrite-normalized REE abundance patterns for geochemical samples. Some felsic igneous rocks show pronounced convex REE patterns (Masuda and Akagi, 1989; Bau, 1996; Irber, 1999; Monecke et al., 2002; Zhao et al., 2002), suggesting the importance of the tetrad effect in felsic magmatic process. The present study reports REE characteristics of Naegi granite and pegmatite in view of tetrad effects in felsic magmatic conditions.

Results and Discussion

The Naegi granite is a biotite granite of the ilmenite-series intruded into the Nohi rhyolite and Jurassic clastic rock basements in central Japan. This granite often accompanies pegmatites yielding rare minerals of topaz, fluorite and others. We have made REE study of the Naegi granite and pegmatite, together with fine-grained sugary materials which occur in the border between relatively larger pegmatites and granite host. The granite and pegmatite samples, when normalized by chondrite, show convex tetrad effect variation of M-type at least in the first and third tetrads, although the fourth tetrads are not curved. All samples characteristically indicate huge negative Eu anomalies, suggesting significant fluid-silicate interaction. Pegmatite is enriched in HREE relative to granite, and pegmatite/granite pairs show the REE fractionation with obvious convex tetrad effects even in the fourth tetrad. The pegmatite and sugary material, when normalized by host granite, display convex and concave tetrad effect variations, respectively. In mineral separates of granite, REE are enriched in the order of heavy minerals > biotite >> K-feldspar = Plagioclase > quartz. The REE fractionation between the heavy minerals/bulk granite pair is similar to that of pegmatite/granite pairs, and distinctive from other mineral separate/bulk granite pairs. Naegi pegmatite has crystallized from the fluid segregated from felsic magma. We suggest that unmixing of fluid and melt in cooling supercritical hydrous melt is a key to understand the variable tetrad effects of Naegi granite and pegmatites.

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Direct determination of Ce(IV)/Ce(III) and Eu(II)/Eu(III) ratios in various natural samples and its geochemical implications

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Cerium and Eu are useful elements in geochemical studies. The abundances of Ce and Eu are sometimes out of trend in the normally smooth REE patterns, these being called Ce and Eu anomalies. The Ce and Eu anomalies are considered to be produced as a consequence of formation of Ce(IV) or Eu(II), respectively, during the genetic processes of the samples. However, few studies have identified Ce(IV) species in natural samples due to the low abundances of these elements, which cannot be detected by most physico-chemical methods. In this paper, we present our results on the direct determination of Ce(IV)/Ce(III) and Eu(II)/Eu(III) ratios in various natural samples by XANES (X-ray absorption near-edge structure). It is suggested that the ratios coupled with the degrees of Ce and Eu anomalies can provide various new geochemical information.

The Ce(IV)/Ce(III) and Eu(II)/Eu(III) ratios are determined by XANES using synchrotron radiation as an X-ray source and a multielement semiconductor detector for the measurement of fluorescent X-ray [1]. The detection limit is ca. 20 ppm for both elements. Therefore, the method can be applied to various samples regarding to Ce, but a limited application can be made for Eu.

The Ce(IV)/Ce(III) ratios have been measured for various samples such as weathered granites [2], ferromanganese nodules [3], cherts [2], deep-sea siliceous sediments, a soil-water system, and zircons [4]. Degrees of positive Ce anomalies in weathered granites and soils can be explained by the Ce(IV)/Ce(III) ratios. In contrast, the reduction of Ce(IV) is observed in cherts and zircons possibly by diagenesis and radiation effect, respectively, after their formations. Studies on ferromanganese nodules and siliceous sediments suggest the oxidation of Ce(III) by Mn oxides. The Eu(II)/Eu(III) ratio in ore deposits will be also discussed with Eu anomaly in the samples.

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