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Redistribution of U, Th and REE during zircon alteration in association with igneous thermal activities

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Thermal events associated with igneous and volcanic activities are one of the most common triggers for elemental redistribution in geological environments. Zircon $(ZrSiO_4)$ is an important host of U, Th, and rare earth elements (REE), especially heavy REE (HREE). Hydrothermal alteration of zircon during thermal metamorphism can lead to redistribution of these elements. In this study, we discuss the redistribution behaviors of U, Th, and REE during zircon alteration at the contact region where gabbro intrudes into granite in the Unazuki region of southwest Japan through in-situ isotopic analyses using an ion microprobe.

At the contact boundary between granite and gabbro, REE minerals such as monazite, xenotime, and REE oxides formed with Fe-Ti oxides in K-feldspar assimilated by gabbro. U was enriched in xenotime (UO₂> 0.72 wt.%) and REE oxides (UO₂> 0.10 wt.%), whereas Th was concentrated in REE oxides (ThO₂> 1.32 wt.%). Considering the similarity between the ionic radii of U^{4+} and Y^{3+} , U was incorporated into xenotime and REE oxides together with HREE. Th incorporation into xenotime (eightfold coordinated site) and monazite (ninefold coordinated site) was constrained by the lower contents of Gd and Dy, respectively. Saussuritization of plagioclase in gabbro and chloritization of biotite in granite at the contact boundary suggest low-temperature hydrothermal alteration at late stages of gabbro intrusion that occurred at 253 +/- 1 Ma. In contrast, zircon in the chloritized granite contained altered domains characterized by a dark response between backscattered electron and cathodoluminescence images; this was caused by a low average atomic number due to the release of Zr and Hf; the incorporation of non-formula elements such as Ca, Fe, and Al; and low crystallinity because of radiation damage. The altered domains showed enrichments of Th (ThO₂> 1.50 wt.%) and light REE (LREE) to middle REE (MREE) as well as positive Eu anomalies; this suggests the preferential incorporation of Th and LREE-MREE (particularly Eu2+) with Ca occurring during the hydrothermal alteration. The redistribution behaviors of U, Th, and REE during low-temperature hydrothermal alteration strongly depend on their ionic radii. Thorite in zircon was probably formed by the exsolution of high-Th altered domains.

Keywords: rare earth elements, uranium, thorium, hydorthermal alteration, zircon, Unazuki