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Formation of nanoscale Th-coffinite

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Abstract

U-thorite, $(Th,U)SiO_4$, from Ambohijatrova Masindray, Madagascar, was investigated to understand the behavior of Th and U during recrystallization of amorphous radiation-damaged, (Th,U)-orthosilicates. Optical microscopy and electron microprobe analyses reveal two types of U-thorite: (i) large (about 1 cm), orange, amorphous grains with composition: $(Th_{0.88\pm0.02}U_{0.09-0.01}Pb_{0.029\pm0.002}REE_{0.01\pm0.001})_{1.00\pm0.01}Si_{1.00\pm0.01}$; and (ii) green, microcrystalline U-thorite with composition: $(Th_{0.76\pm0.05}U_{0.08\pm0.01}Ca_{0.07\pm0.01}Pb_{0.014\pm0.005}REE_{0.009\pm0.001})_{0.92\pm0.07}Si_{1.12\pm0.06}$. Ca-free U-thorite-(i) is enriched in Th, U, and Pb (7.1, 1.2, and 1 wt%, respectively), and depleted in Si (3.0 wt%) compared to U-thorite-(ii). Recrystallization of U-thorite-(i) resulted in fracturing that facilitated migration of mobilized Th and U over a distance of about 300 μm, as evidenced by precipitation of U-thorite-(ii) in the fractures in associated apatite and garnet. Transmission electron microscopy observations and selected-area electron diffraction (SAED) patterns confirm that U-thorite-(i) is amorphous. U-thorite-(ii) forms: (1) single crystals (>1 μm in size) with variable amounts of amorphous material; or (2) randomly oriented, nanocrystalline aggregates (5–10 nm in size). TEM-EDX analyses show that the Th/U ratio in U-thorite-(i) and U-thorite-(ii) is ~6. High-angle annular dark-field scanning TEM (HAADF-STEM) and high-resolution TEM reveal that nanocrystalline Th-coffinite (20–40 nm in size) with Th/U ratio = 0.6, formed during recrystallization of U-thorite-(i). The calculated chemical Th-U-Pb ages of U-thorite-(i) range from 2.1–1.9 Ga and from 1.8–1.6 Ga, whereas U-thorite-(ii) ages range from 1.6–0.5 Ga. The calculated cumulative radiation dose for U-thorite-(i) varies from $1.6–1.8 \times 10^{18}$ α-decay events/mg, which is equivalent to 136–152 displacements per atom (dpa), and for U-thorite-(ii) from $3–4.4 \times 10^{17}$ (α-decay events/mg) (=27–37 dpa). The cumulative dose for Th-coffinite is 9.8×10^{17} α-decay events/mg (84 dpa).

Keywords: Thorite, coffinite, nanoparticles, amorphization, recrystallization, Madagascar