

Site preference of U and Th in Cl, F, and Sr apatites

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ABSTRACT

Crystals of U- and Th-doped fluor-, chlor-, and strontium-apatite have been synthesized from phosphate-halide-rich melts, and their structures were refined at room temperature with single-crystal X-ray diffraction intensities to $R = 0.0167\text{--}0.0255$. Structure refinements of U-doped fluorapatites indicate that U substitutes almost exclusively into the Ca2 site with site occupancy ratios U_{Ca2}/U_{Ca1} that range from 5.00 to 9.33. Similarly, structure refinements of Th-doped fluorapatites indicate that Th substitutes dominantly into the Ca2 site with Th_{Ca2}/Th_{Ca1} values that range from 4.33 to 8.67. Structure refinements of U-doped chlorapatites show that U is essentially equally distributed between the two Ca sites with U_{Ca2}/U_{Ca1} values that range from 0.89 to 1.17. Results for Th-doped chlorapatites show that Th substitutes into both Ca1 and Ca2 sites with Th_{Ca2}/Th_{Ca1} values that range from 0.61 to 0.67. In the Th-doped strontium-apatites with F and Cl end-members, Th is incorporated into both the Ca1 and Ca2 sites. The range of Th_{Ca2}/Th_{Ca1} values is 0.56 to 1.00 for the F end-member, and 0.39 to 0.94 for the Cl end-member. XANES measurements of the U-doped samples indicate that U in fluorapatite is tetravalent, whereas in chlorapatite it is heterovalent but dominantly hexavalent.

According to our calculation, the volume of the Ca2 polyhedron increases by about 5.8% from fluorapatite to chlorapatite, but that of Ca1 polyhedron increases by only 0.59%. We speculate that the much greater size of the Ca2 polyhedron in chlorapatite may diminish the selectivity of this position for U and Th. The incorporation of U and Th into fluorapatite results in a decrease in the size of both Ca polyhedra, but the incorporation of U and Th into chlorapatite results in an increase in the volume of both Ca polyhedra. We suggest that the preference of U and Th for both Ca sites in chlorapatite is attributable to the large increase in size and distortion of the Ca2 polyhedron upon substitution of Cl for F.

Keywords: Apatite, uranium, thorium, single-crystal XRD, uranium XANES in apatite