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 = 0.0167–0.0255. Structure refinements of U-doped fluorapatites indicate that U substitutes almost exclusively into the Ca2 site with site occupancy ratios UCa2/UCa1 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 ThCa2/ThCa1 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 UCa2/UCa1 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 ThCa2/ThCa1 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 ThCa2/ThCa1 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

INTRODUCTION

The crystal chemistry of trace metals in the apatite-group minerals, Ca5(PO4)3(F,OH,Cl), is of considerable significance in geology, biology, materials, and environmental sciences. Apatite can accommodate numerous substituents, including many radionuclides of environmental concern. Monovalent (Na+, K+), divalent (Sr2+, Pb2+, Ba2+, Mn2+, Cd2+), trivalent (REE3+), tetravalent (Th4+, U4+), and hexavalent cations (U6+) have been reported to substitute into Ca sites in the apatite structure (Pan and Fleet 2002). Up to 15.85 wt% ThO2 and 2.88 wt% UO2 have been reported as substituents in natural apatite structures, especially in the REE-rich varieties (Della Ventura et al. 1999; Oberti et al. 2001). Although scores of studies have focused on the crystal chemistry of substituents in apatite, little is known about the mechanism of incorporation and the structural response of apatite to substituent U and Th, despite the extensive use of those elements in geochronological and petrogenetic studies for over half a century (Larsen et al. 1952; Altschuler et al. 1958; Oosthuyzen and Burger 1973). Because of apatite’s high affinity for U and Th, its thermal annealing properties, and its relatively low solubility in most surface environments, there is great interest in apatite as a solid nuclear waste form and a contaminant sequestration agent (Chen et al. 1997a, 1997b; Carpena and Lacout 1998; Conca and Wright 1998; Bostick et al. 1999; Ewing and Wang 2002; Carpena et al. 2003; Knox et al. 2003; Conca et al. 2006; Raicevic et al. 2006). Rakovan et al. (2002) reported the structural characterization of U6+ in apatite as the first step in the investigation of U and Th in the apatite structure. Considerable work remains to characterize the structural response of apatite to substituent U and Th.

The structure of apatite was determined more than a half century ago (Mehmel 1930; Náray-Szabó 1930). Hughes et al. (1989) reported the most recent structure refinements on natural near-end-member fluorapatite, chlorapatite, and hydroxylapatite. There are two Ca polyhedra in the apatite structure that are hexagonally disposed about a central [001] hexad (Hughes and Rakovan 2002). Ca1 is coordinated to nine O atoms (3 × O1, 3 × O2, 3 × O3; Fig. 1) in a tricapped trigonal prism. Ca2 bonds to six O atoms (O1, O2, 4 × O3) and one column anion (X = F, Cl, OH; Fig. 1). The two Ca positions in apatite offer quite different stereochemical environments and are able to accommodate a variety of cations as substituents (Fleet et al. 2000).

Understanding the site preference and the structural response of apatite to U and Th substituents will help explore the mechanism of radionuclide retention and release in apatite, which is