Crystal chemistry of Th in fluorapatite

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ABSTRACT

Through the complementary use of single-crystal X-ray diffraction and X-ray absorption spectroscopy, we present in this paper the first direct results on the site occupancy of thorium in the fluorapatite structure and the structural distortion created by its substitution. Structure refinements based on single-crystal X-ray diffraction data from synthetic Th-doped fluorapatite indicates that Th substitutes almost exclusively in the M2 site. A single-crystal X-ray study of natural fluorapatite from Mineville, New York, also indicated that substituting heavy scatterers (including Th) are concentrated in the apatite M2 site, but definitive site assignments of specific elements were not possible. Extended X-ray absorption fine-structure spectroscopy (EXAFS) was used to probe the local structure of Th in the synthetic fluorapatite (single-crystal form) with a Th concentration of roughly 20 000 ppm, as well as Th in the natural Mineville fluorapatite (powder form) with a Th concentration of ~2000 ppm. The EXAFS fitting results also indicate that Th partitions into the M2 site and yield a ~0.05–0.08 Å decrease of average M2-O bond distances associated with local structure distortions that are not obtainable from single-crystal X-ray diffraction studies.

Keywords: Thorium, fluorapatite, single crystal, X-ray diffraction, X-ray absorption spectroscopy, EXAFS

INTRODUCTION

Thorium is found naturally in the Earth’s crust with the average concentration of ~10–15 ppm, which is about three times more abundant than uranium and almost as common as lead. At Earth surface conditions, naturally occurring thorium is tetravalent and is dominantly found as $^{232}$Th, with half-life of 1.40 × 10$^{10}$ years. The primary mineral sources of thorium are thorium silicates such as thorite and rare-earth phosphate minerals (e.g., monazite, xenotime, and apatite group minerals). Thorium has extensive industrial applications. For example, it is used in magnesium alloys to provide high strength and creep resistance at elevated temperatures. It is also used as an alloying agent in gas tungsten arc welding to increase the melting temperature of tungsten electrodes (Cary and Helzer 2005). Thorium oxide is used in the preparation of gas mantles because of its high emissivity in the visible spectrum; it also acts as a catalyst in the conversion of ammonia to nitric acid and the production of sulfuric acid (Patnaik 2002). In geology, Th in apatite and monazite is used for dating via the U-Th-Pb and (U, Th)/He geochronometers (Farley and Stockli 2002; Harrison et al. 2002). In the energy industry, thorium has been used in the production of nuclear power and in several compounds in the nuclear fuel cycle due to its natural abundance, attractive physical, chemical and nuclear properties, and reduced plutonium and actinide production (Lung and Gremm 1998). Because of its widespread industrial application, the disposal of thorium waste has become an important environmental concern.

Apatite has the general formula Ca$_x$(PO$_4$)$_y$X, where X can be F (fluorapatite), Cl (chlorapatite), or (OH) (hydroxylapatite). The apatite structure is remarkably tolerant of distortion and chemical substitution, and consequently there is a wide range of apatite group minerals (Hughes and Rakovan 2002; Pan and Fleet 2002; Pasero et al. 2010). Because of its common occurrence and its high affinity for many radionuclides (e.g., U, Th, REE, $^{88}$Sr, $^{90}$Y, etc.), apatite has been used in geochronological and petrogenetic studies for decades (Larsen et al. 1952; Altschuler et al. 1958; Oosthuyzen and Burger 1973). However, little is known about the mechanism of incorporation and structure response of apatite to substituent actinides. Geologically, fluorapatite is by far the most common of the apatite group minerals. It is a ubiquitous accessory phase in igneous, sedimentary, and metamorphic rocks. Because of fluorapatite’s high affinity for U, Th, and other radionuclides of environmental concern (Rakovan and Hughes 2000; Rakovan et al. 2002; Pan and Fleet 2002), its low solubility in most surface environments (Elliott 1994), and its resistance to radiation damage (Bros et al. 1996; Weber et al. 1997; Meis et al. 2000; Soulet et al. 2001), there is great interest in fluorapatite to sequester heavy metals and actinides and as a potential solid nuclear waste form (Chen et al. 1997a, 1997b; Carpena and Lacout 1998; Bostick et al. 1999; Ewing and Wang 2002; Carpena et al. 2003; Knox et al. 2003; Wright and Conca

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