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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