

Abstract No. rako430

### XAS Characterization of U in Fluorapatite

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Beamline(s): X18B

**Introduction:** Apatite,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{F},\text{OH},\text{Cl})_2$  is a ubiquitous accessory mineral in all major rock types, it is the main mineral constituent in bones and teeth, and it is widely used as a phosphor and lasing material. Thus, apatite has great significance in geology, biology and materials science. One unique characteristic of apatite that is of interest in all of these areas is the ability of its structure to accommodate many elemental substitutions. Indeed, more than half of the periodic table is known to substitute into apatite. Of particular interest is the ready incorporation of U. Uranium concentrations in apatites at the parts per million level are quite common and natural examples that contain as much as a few weight percent are known. In this study X-ray absorption spectroscopy (XAS) is being used to determine local structure of U within synthetic fluorapatite.

**Methods and Materials:** A powder sample of U-rich fluorapatite,  $\text{Ca}_{9.9}\text{U}_{0.1}(\text{PO}_4)_6\text{F}_{1.8}$ , was synthesized from  $\text{UO}_2$ , calcium orthophosphate and  $\text{CaF}_2$ . The starting material was ground and then annealed at  $\sim 1380^\circ\text{C}$  for 1-2 days in a Pt capsule under oxidizing conditions (in air). Powder X-ray diffraction showed that the final product is entirely fluorapatite. U  $L_3$  XAS data were obtained from the apatite in fluorescence mode using a PIPS detector and simultaneously from model compounds and standards in transmission mode.

**Results:** The X-ray absorption near-edge structures for U in fluorapatite, uraninite, and uranyl nitrate hexahydrate are shown in Fig. 1. The Fourier transform modulus of the extended X-ray absorption fine structure spectra (uncorrected for the EXAFS phase shift) and fit for the apatite are shown in Fig 2.

**Conclusions:** The fluorapatite XANES spectra shows an unusual structure in the U-absorption edge. Reference materials exhibit characteristic edge shapes with a 1 to 2 eV shift between U(IV) and U(VI). For the apatite there are two inflection points in the edge. The first inflection point coincides with the inflection point in the absorption edge in uranyl nitrate, indicating the presence of U(VI).

Preliminary analysis and fitting of the EXAFS spectra suggest that the U resides in the Ca1 site of apatite and leads to significant distortion relative to pure fluorapatite.

**Acknowledgments:** This work was supported by NSF grant EAR 9814691 and DOE EMSP grant DE-FG07-99ER15013.

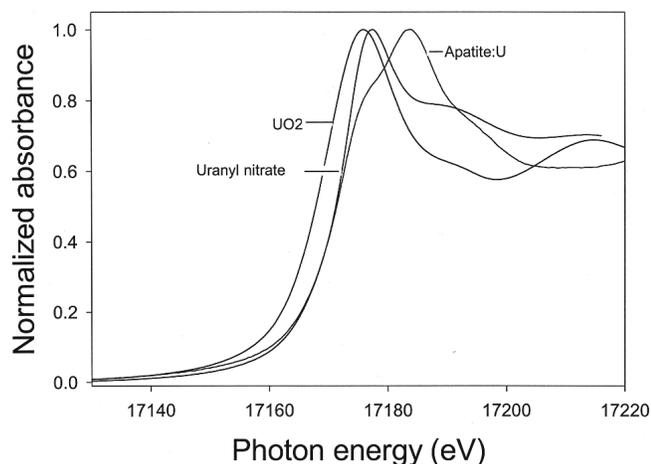


Figure 1. U  $L_3$  XANES data from apatite,  $\text{UO}_2$ , and uranyl nitrate hexahydrate.

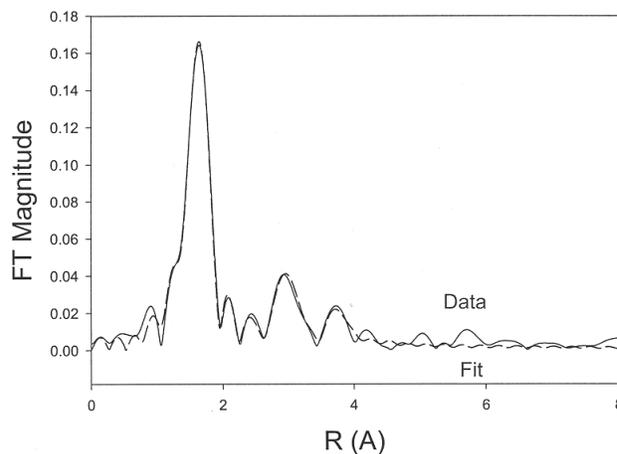


Figure 2. Fourier transform of the EXAFS spectra (uncorrected for phase shifts), solid line, and fit, dashed line.