

XAS Spectra of Hexavalent Uranium at 295K: A Study of Well-refined Structures

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Introduction

Uranyl minerals and compounds are currently receiving considerable attention owing to their significance to the environment [1]. They are important for understanding water-rock interactions in U deposits. They form as products of the oxidation of uranium mine and mill tailings, thereby affecting the release of radionuclides from mine wastes [2]. They occur in soils contaminated by actinides, such as the Fernald and Hanford sites, and are prominent alteration phases in laboratory experiments involving UO_2 and spent nuclear fuel in a moist, oxidizing environment, similar to the proposed repository at Yucca Mountain [3-7].

The crystal chemistry of U^{6+} is rich in diversity [8]. A comprehensive understanding of uranium minerals has lagged behind the understanding of most other mineral groups because of the complexity of their structures and chemistry and the lack of specimens suitable for study using conventional techniques. A thorough knowledge of these mineral structures is important in its own right and also because this information forms a basis from which to predict the fate and transport of uranium as well as neptunium and plutonium in the environment. The latter two elements have no natural mineral analogs, and an understanding of their behavior in the environment relies to a large degree on similarities with U chemistry.

Ideally, x-ray absorption near-edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) can provide a wealth of information on the oxidation states and coordination environments of U in samples of environmental interest [9-12]. We have undertaken a systematic study of the U L_{III} -edge XANES and EXAFS spectra for a series of crystalline uranium compounds that have well-refined structures and known valence states. This information will be used to address issues pertaining to spectral interpretation and will serve for testing the strengths and limitations of current analysis procedures, including principal component analysis, in extracting coordination environment information [13].

Methods and Materials

Our research focuses on U^{6+} , the most common oxidation state of uranium in nature. The U^{6+} cation usually occurs in crystal structures as part of a nearly linear $(\text{UO}_2)^{2+}$ uranyl ion, which is coordinated by anywhere from four to six ligands arranged at the

equatorial vertices of square bipyramids, pentagonal bipyramids, and hexagonal bipyramids, with the uranyl ion oxygen atoms located at the apices of the bipyramids [14]. A few structures have been reported to contain U^{6+} in regular octahedral coordination; in these cases, there appears to be no uranyl ion [15]. Rarely, U^{6+} has been reported in unusual sixfold geometry with two long bonds and four shorter bonds, as in Li_4UO_5 [16]. We have selected a group of synthetic and natural U compounds that display the range of coordination environments about U^{6+} for study.

The experiments involved the measurement of U L_{III} -edge x-ray absorption spectra, from 16.9 to 18.1 keV, of 13 separate compounds at the bending magnet beamline of the Basic Energy Sciences Synchrotron Radiation Center Collaborative Access Team (BESSRC-CAT) [17]. Each sample was prepared as a fine powder and was contained in Kapton®-sealed plastic sample holders. The radioactive samples were mounted in a sample containment system provided by the Actinide Facility. This sample containment system has received independent review and has been used previously at the BESSRC bending magnet line.

Both U L_{III} -edge absorption and fluorescence spectra were measured, the latter with a Lytle detector [18]. From five to eight spectra were acquired for each sample. The position of the U absorption edge at 17.166 keV was calibrated with Y metal (K edge at 17.038 keV). For selected samples, the Se and Cr K edges were also measured, and their absorption edge positions were calibrated with Au foil (L_{III} edge at 11.919 keV) and Cr metal (K edge at 5.989 keV) [19].

The compounds and minerals for which x-ray absorption (XAS) data were acquired were selected on the basis of the number and geometry of the uranyl sites in their crystal structures. They included the following:

1. A single distinct bipyramidal uranyl site:

Square: Chernikovite $(\text{H}_3\text{O})[(\text{UO}_2)(\text{PO}_4)](\text{H}_2\text{O})_3$

Pentagonal: Boltwoodite $\text{K}_2[(\text{UO}_2)\text{SiO}_3(\text{OH})_2](\text{H}_2\text{O})_3$

Hexagonal: Grimselite $\text{K}_3\text{Na}[(\text{UO}_2)(\text{CO}_3)_3](\text{H}_2\text{O})$ and uranyl selenite UO_2SeO_3

2. Two similar bipyramidal uranyl sites:

Square: Metatorbernite $\text{Cu}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_8$

Pentagonal:

Alpha-uranophane $\text{Ca}[(\text{UO}_2)\text{SiO}_3(\text{OH})_2](\text{H}_2\text{O})_5$

Beta-uranophane $\text{Ca}[(\text{UO}_2)\text{SiO}_3(\text{OH})_2](\text{H}_2\text{O})_5$

Uranyl phosphate hydrate $(\text{UO}_2)_3(\text{PO}_4)_2(\text{H}_2\text{O})_4$
Zippeite $\text{K}(\text{UO}_2)_2\text{SO}_4(\text{OH})_3(\text{H}_2\text{O})$ and
 KUCrO_6

3. Both square and pentagonal bipyramidal uranyl sites:

Curite $\text{Pb}_3(\text{H}_2\text{O})_2[(\text{UO}_2)_4\text{O}_4(\text{OH})_3]_2$

4. Regular octahedral coordination: Delta- UO_3

5. Unusual sixfold coordination: Lithium uranate Li_4UO_5 .

Crystal structure data for these compounds may be found in the following references: chernikovite [20], boltwoodite [21], grimselite [22], uranyl selenite [23], metatorbernite [24], alpha-uranophane [25], beta-uranophane [26], uranyl phosphate hydrate [27], zippeite [28], KUCrO_6 [29], curite [30], delta- UO_3 [15], and lithium uranate [16].

Results and Discussion

Data analysis and interpretation are currently underway.

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