

Comparison of U Valence State Ratio Determined from U L₃-Edge XANES to EXAFS Measurements

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Introduction

The ratio of U(IV) to U(VI) in samples is often determined by the energy value of the rise in the absorption edge at half the x-ray absorption edge step height. This methodology can be verified by analyzing the EXAFS data from these samples, as the first oxygen shells for U(VI) and U(IV) are easily distinguished. U(VI) is usually in the form of uranyl with two tightly bound oxygen atoms at a distance of ~ 1.8 Å, whereas U(IV) is usually coordinated by a uniform first oxygen shell with an oxygen distance of ~ 2.3 Å. To verify this methodology, we made XAFS measurements on anaerobic wet pastes with various ratios of U(IV) to U(VI).

Methods and Results

Data were collected at the MRCAT beamline [1] with a multielement detector in fluorescence mode. The second harmonic of the insertion device was tapered by 3.5 keV to reduce the variation in the incident x-ray intensity to 20% over the scanned energy range. The incident ion chamber was filled a mixture of with He and N₂ gases (50:50). A Rh mirror with a cutoff energy of 22 keV was used to eliminate higher harmonics. A reference spectrum from a uranium phosphate standard was measured by using scattered x-rays as described elsewhere [2].

The sample names (see Fig. 1) for abiotic and biotic Abbott's Pit sand are APSA and APSB, respectively. Sample names for biotic and abiotic control samples based on goethite are GEOA and GEOB, respectively. Additional information on the preparation of these samples can be found elsewhere [3].

The percent of U(VI) was determined by using U L₃-edge XANES and EXAFS data. All data sets were aligned accurately in energy by using the derivative of the edge of a uranyl phosphate standard measured simultaneously with the unknown samples, as described elsewhere [2]. For the XANES data, the energy value at 0.5 edge step in the normalized absorption data was compared to the value for U(IV) and U(VI) standards (Fig. 1A). The accuracy of this procedure is conservatively estimated at 15%. In addition, the inhomogeneity of the samples gave rise to some variation in the percent U(VI) from successive scans (3–7%) at different locations on the samples. The standard deviation of the values determined in each scan of each sample was added in quadrature to the 15% uncertainty estimate to determine the final uncertainty. The results indicated $88\% \pm 15.1\%$ and $81\% \pm 19.0\%$ U(VI) in the APSA and GEOA samples, respectively, and $65\% \pm 18.1\%$ and $24\% \pm 16.4\%$ U(VI) in the APSB and GEOB samples, respectively.

The percent of U(VI) was determined from the EXAFS data by fitting the first two coordination shells of O atoms around the U (Fig. 1B). Because the number of axial O atoms for U(VI) is 2, the percentage of U(VI) in the samples was determined as the ratio of the average number of O atoms axially coordinated to

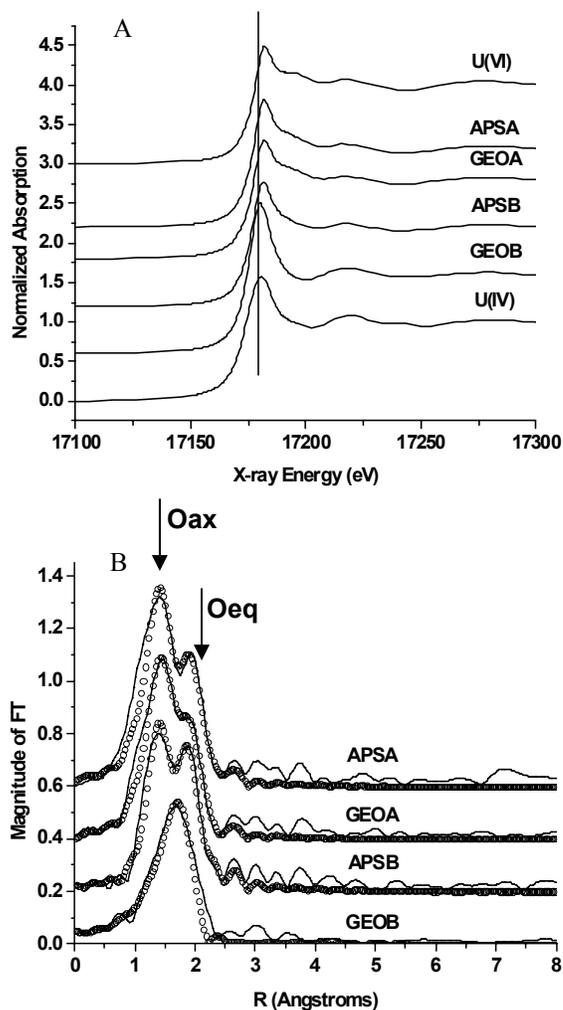


Fig. 1. Uranium XAFS data. A: Averaged normalized absorption data from each sample and from U(IV) and U(VI) standards. The vertical line shows the peak position of the U(IV) standard, at a position similar to that for the GEOB sample. The peak position for U(VI) is to the right of that for U(IV) and is similar for the abiotic samples. Samples with a mixture of U(IV) and U(VI), APSB, have a peak position between those of the U(IV) and U(VI) standards. B: Magnitude of the Fourier transform of the EXAFS data (line) and fits to the data (symbols). The first peak in the Fourier transform is due to the axial oxygens (Oax) bound to U(VI). The second peak contains a mixture of equatorial oxygen (Oeq) atoms from U(VI) and U(IV).

U, divided by 2. This analysis indicated $100\% \pm 10\%$ U(VI) in the APSA and GEOA samples and $50\% \pm 10\%$ and $0\% \pm 10\%$ U(VI) in the APSB and GEOB samples, respectively. Within the uncertainties, both procedures (EXAFS and XANES) are in agreement.

Discussion

In summary, we have described the results of determinations of the valence state of U by using the EXAFS region of the absorption spectra, relying on the uranyl configuration of U(VI) with two tightly bound axial oxygen atoms at a significantly shorter distance than the oxygen atoms of U(IV). Comparison of the percent of U(VI) in the biotic goethite and biotic Abbott's Pit sand indicates that indigenous microbes cannot reduce U(VI) in the presence of Abbott's Pit sand as readily as in the presence of goethite.

Acknowledgments

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References

- [1] C.U. Segre et al., Synchrotron Radiation Instrumentation: Eleventh U.S. Conference **CP521**, 419-422 (2000).
- [2] J.L. Cross, A.I. Frenkel, Rev. Sci. Instrum. **70**, 38-40 (1998).
- [3] B.H. Jeon et al., Environ. Sci. Technol. **38**, 5649-5655 (2004).