

Confocal μ -XRF and μ -XAFS Studies of an Uranium-Rich Sediment from a Nuclear Waste Disposal Natural Analogue Site

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We perform spatially resolved X-ray fluorescence and absorption fine structure investigations with a micrometer-scale resolution (μ -XRF and μ -XAFS) recorded in a confocal geometry on a bore core section from the uranium-rich tertiary sediment [1]. The aim of this study is to assess mechanisms leading to immobilization of the uranium during diagenesis of the uranium enriched horizon. In order to probe micro-volumes below the sample surface, a confocal irradiation-detection geometry is employed. For this purpose, two half-lenses are used; one is used to focus the primary beam and another collimating half-lens in front of the detector, perpendicular to the first lens [2]. By scanning sample areas at different depths, stacks of tomographic cross sections may be easily recorded. A polycapillary half-lens as well as planar compound refractive lenses are used to focus the beam to a 20 μ m diameter spot and to an ellipsoid spot with about 2.5 μ m vertical and 5 μ m horizontal dimensions, respectively. By varying the energy of the beam at a constant sample position, XAFS spectra are recorded. Both the near edge XAFS (XANES) region and the extended XAFS (EXAFS) energy region are investigated.

U L3 μ -XANES and μ -EXAFS results show uranium to be present as a tetravalent, poorly crystalline phosphate (or sulfate), possibly ningyoite (Fig. 1A&1B). The U L3 EXAFS is measured in a sample area bordering a lignite inclusion but does not resemble that expected for U ligation with organic material [3]. This suggests that lignite may have not been involved in U immobilization. Stacks of images at different depths reveal uranium to be near both framboidal Fe(II) nodules and to arsenic (Fig. 2). The arsenic present is either As(V) or As(0) (Fig. 3); we find no evidence for As(III). As(0) is observed to be intimately associated with the surface of Fe(II) nodules (Fig. 4) and likely arsenopyrite. The U(IV) is associated with As(V). That As(V) is found in addition to As(0), even in volumes probed below the surface, combined with the observation that the As(V) is associated with U hot spots allows to propose that arsenic was involved in the U(VI) immobilization during diagenesis. We propose a hypothesis for the mechanism of uranium immobilization, where arsenopyrite acted as reductant of ground water dissolved U(VI) leading to precipitation of less soluble U(IV) and thereby forming As(V).

References

- [1] M.A. Denecke, K. Janssens, K. Proost, J. Rothe, U. Noseck, *Environ. Sci. Technol.* (in print).
- [2] K. Janssens, K. Proost, G. Falkenberg, *Spectrochim. Acta B* 59 (2004), 1637.
- [3] See, e.g., M.A. Denecke et al., *Radiochim. Acta* 79 (1997)151.
- [4] HASYLAB and ANKA are gratefully acknowledged for allotment of beamtime.

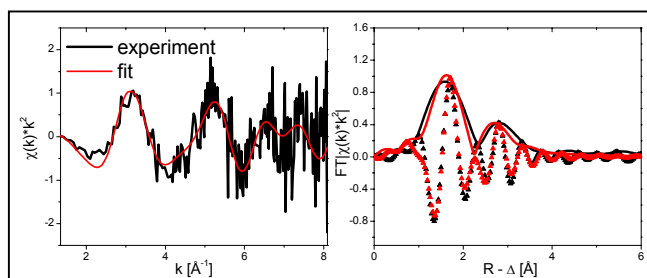


Fig. 1A. U L3 μ -EXAFS and corresponding Fourier transformed data. Best fit using ~ 8 O atoms at 2.33 Å and 6 P atoms at 3.65 Å.

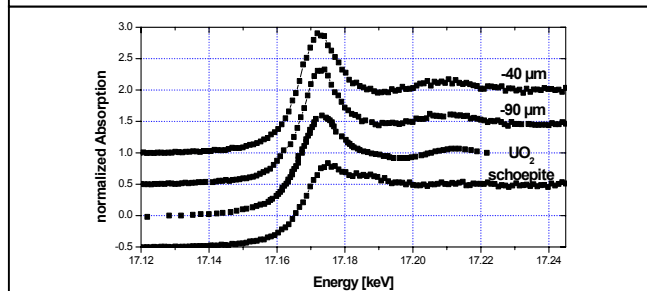


Fig. 1B. U L3 μ -XANES recorded at two different depths below the surface and compared to U(IV) and U(VI) reference sample XANES.

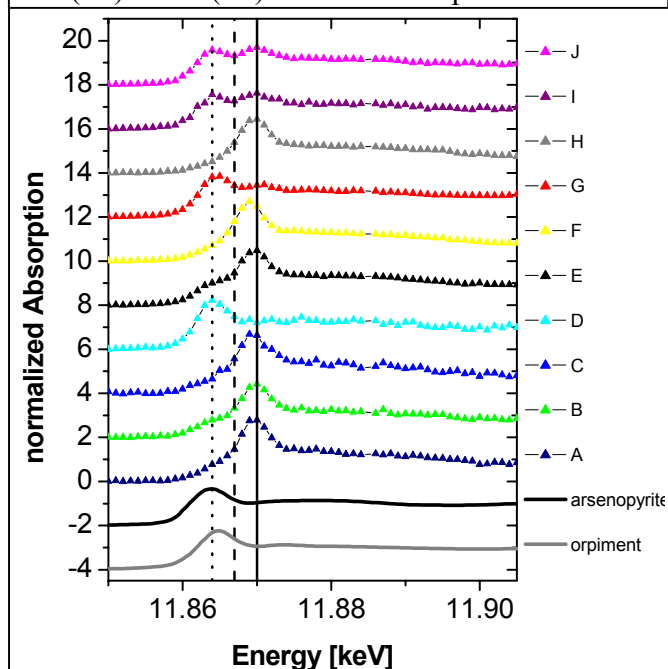


FIG. 3. As K μ -XANES recorded at various positions and depths below the sample surface (A-J) and compared to that of arsenopyrite and orpiment and energy positions expected for As(0) (dots), As(III) (dashed), and As(V) (continuous).

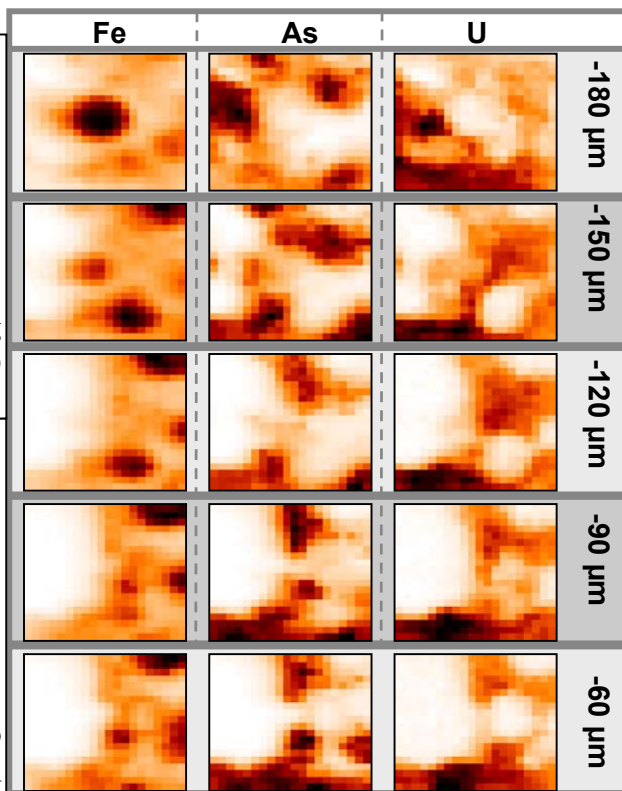


Fig 2. Fe, As, and U distribution maps at indicated depths below the surface of a $300 \times 300 \mu\text{m}^2$ sample section ($20 \times 20 \mu\text{m}^2$ step size); optical photograph at left.

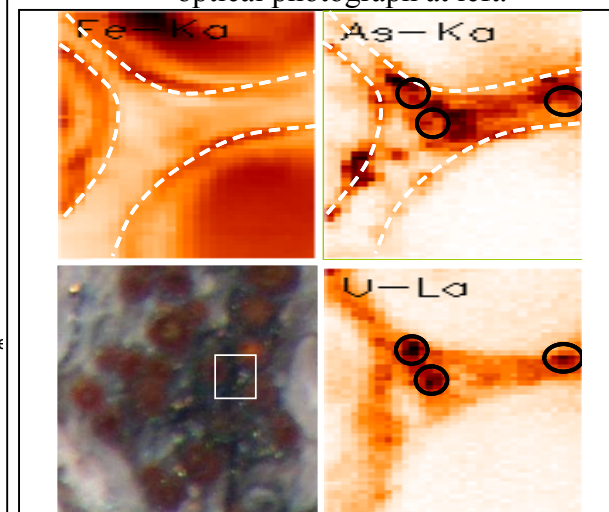


FIG. 4. Confocal μ -XRF maps of a $120 \times 120 \mu\text{m}^2$ section ($2 \times 4 \mu\text{m}^2$ step size) $-60 \mu\text{m}$ below the surface. Circles indicate U hotspots, dashed lines an As-rich rim on Fe(II)-nodules; optical image lower left.