

Supporting Information (SI)

TITLE: SPECTROSCOPIC EVIDENCE FOR URANIUM BEARING PRECIPITATES IN VADOSE ZONE
SEDIMENTS AT THE HANFORD 300-AREA SITE

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SI-1: Materials, Physiochemical Characterization, Batch Experiments, and μ -XRF, -XAS, and -XRD Analyses.

Materials and Physiochemical Characterization

A vadose zone sediment collected at a depth of 1.22 m (sample NPP2-4) below ground surface (bgs) was chosen for this study. This sediment contained the second highest concentration of U (~140 mg/kg) found in the vertical profile from ground surface to the water table at ~10 m bgs. Air-dried sub-samples of four sediments were passed through a 2 mm mesh prior to further analyses. Soil pH (1:1 sediment and deionized water ratio) was measured after equilibration for 48 hr. HF digestion with subsequent analysis was conducted to measure total elemental concentrations (1). Elements listed in SI-1 were analyzed using inductively coupled plasma mass spectrometry.

Batch Experiments.

These experiments document the amounts of U(VI) that can be released from the sediments by desorption and dissolution processes at a specific, fixed water-rock ratio (39 mL:1g) under conditions where carbonate ligand complexation controls U(VI) aqueous speciation. Air-dried sediment was suspended in artificial groundwater (AGW) (0.01M Ca(NO₃)₂, 0.0005M KNO₃, 0.0005M MgSO₄, and 0.005M NaNO₃) with NaHCO₃ added to achieve equilibrium with the desired pCO₂ at pH 7.2. Reaction vessels were shaken on an end-over shaker at 17 rpm for 30 days with sampling and analysis performed at intermediate time points. After centrifugation, filtrates through 0.45 μ m filters were analyzed for dissolved U, Al, and Cu using ICP-MS. Dissolved P was analyzed using the ammonium molybdenum method (2).

Literature Cited

- (1) Helmke, P. A.; Sparks, D. L. Method of Soil Analyses. In *Part 3 Chemical Methods*; Sparks, D. L., Ed.; Soil Sci. Soc. Am., Inc. Am. Soc. Agro., Inc. Madison, Wisconsin, USA: Madison, WI, 1996; Vol. 5, pp 551-601.
- (2) Strickland, J. D. H.; Parsons, T. R. *A Practical Handbook of Seawater Analysis*; Second ed.; Fisheries Research Board of Canada: Ottawa, 1972.

μ-XRF and μ-XAS Analyses.

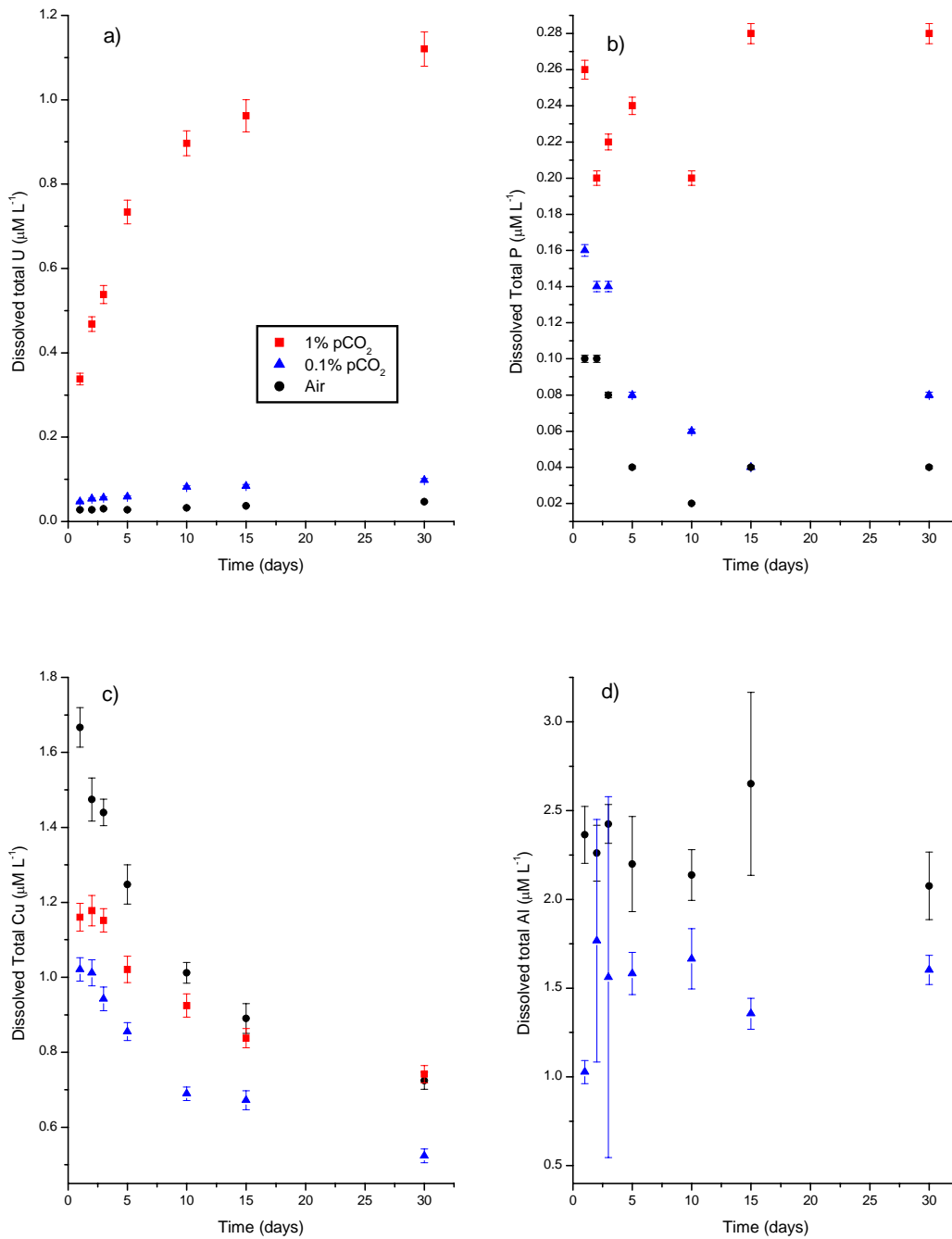
The samples were sectioned to 30 μm in thickness and mounted on Suprasil quartz slides using 3M electrical resin and superglue. These materials have proven to be nearly metal(loid) free, which is necessary for backing materials during SXRF analysis. The μ-XRF compositional maps of Ca, Cr, Zn, Cu, Fe, Mn and U (~3 x 3.5 mm) were collected at 17700 eV using a 7-element Ge solid-state detector. The incident beam energy was calibrated at 17174 eV at the whiteline peak. Beam size and dwell time were 10(H) x 5(V) μm, and 200 ms/pixel, respectively. U L_{III} edge μ-XAS measurements were performed at selected regions within U μ-XRF maps, and three to eight XANES and EXAFS scans per point were collected in fluorescence mode with the Ge detector.

μ-XRF and μ-XRD Analyses.

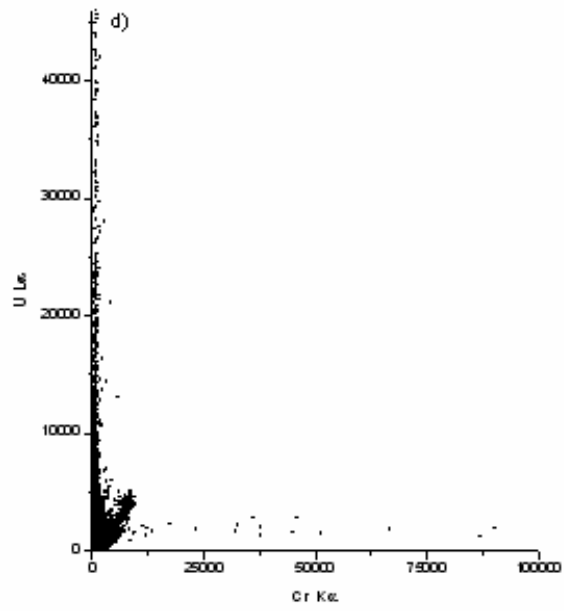
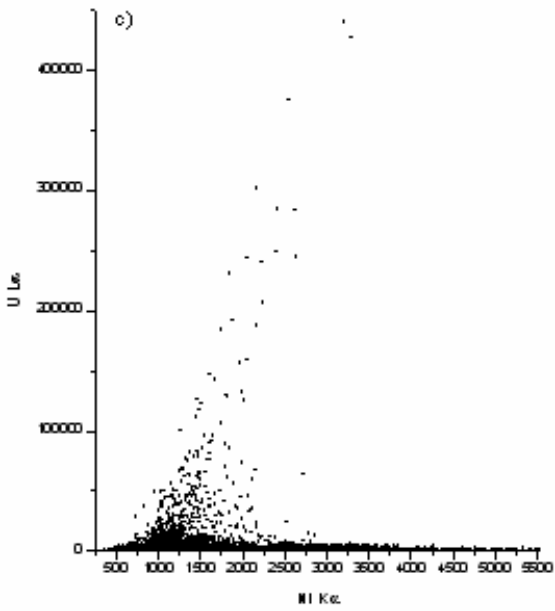
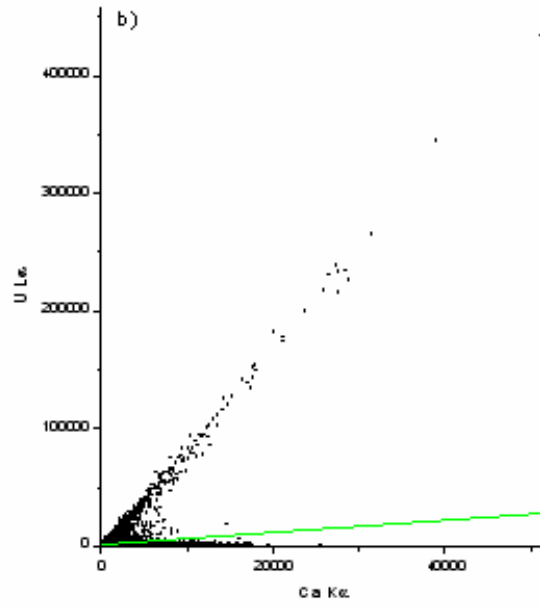
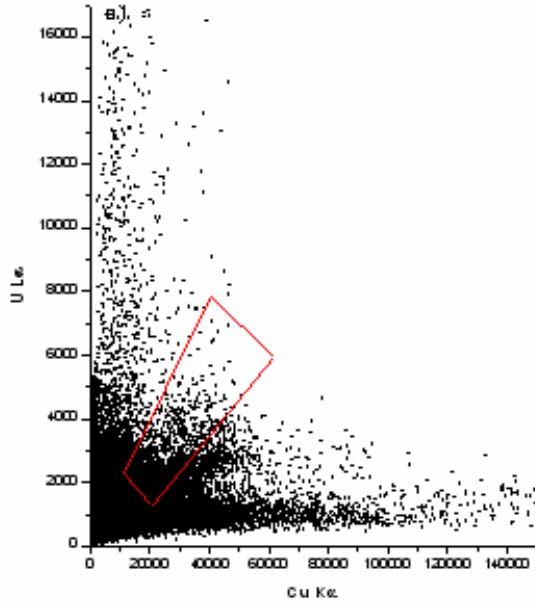
Cu fluorescence map was generated using the monochromatic beam (effective beam size of 10(H) x 25(V) μm on sample for a beam incidence angle of 10°) with an energy of 9000eV at BL 7.3.3, ALS, USA. Due to the energy limitation of BL7.3.3, we were unable to collect U μ-XRF maps (neither at M and L edge). X-ray fluorescence signals were recorded using a Ge solid-state detector. μ-XRD patterns were collected at selected regions in reflection mode using a Bruker SMART 6000 CCD area detector. 1024 x 1024 pixel (96 μm pixel size) patterns were collected with exposure times ranging from 300 to 500 seconds.

Depth (m)	pH	Na	Mg	Al	K %	Ca	Ti	Fe	Cu	P	V	Cr	Mn	Ni mg kg ⁻¹	Sr	Rb	Cs	Ba	U
0.61	7.18	1.6	1.8	6.1	0.9	4.0	1.1	7.1	0.36	1713	277.8	48.0	1164	26.04	297.28	33.31	1.38	558.86	89.41
1.22	7.21	1.7	2.1	7.2	0.9	4.6	1.3	8.5	0.52	1867	308.8	34.9	1373	28.97	310.23	37.82	1.45	586.31	125.9
2.44	7.46	1.8	1.9	6.8	1.0	4.3	1.2	7.7	0.01	1614	293.3	34.6	1282	22.88	345.16	41.06	1.63	640.12	16.67
3.66	7.53	1.8	2.1	6.9	1.0	4.9	1.3	8.5	0.008	1768	311.5	32.9	1350	19.80	331.45	37.25	1.24	756.21	16.3

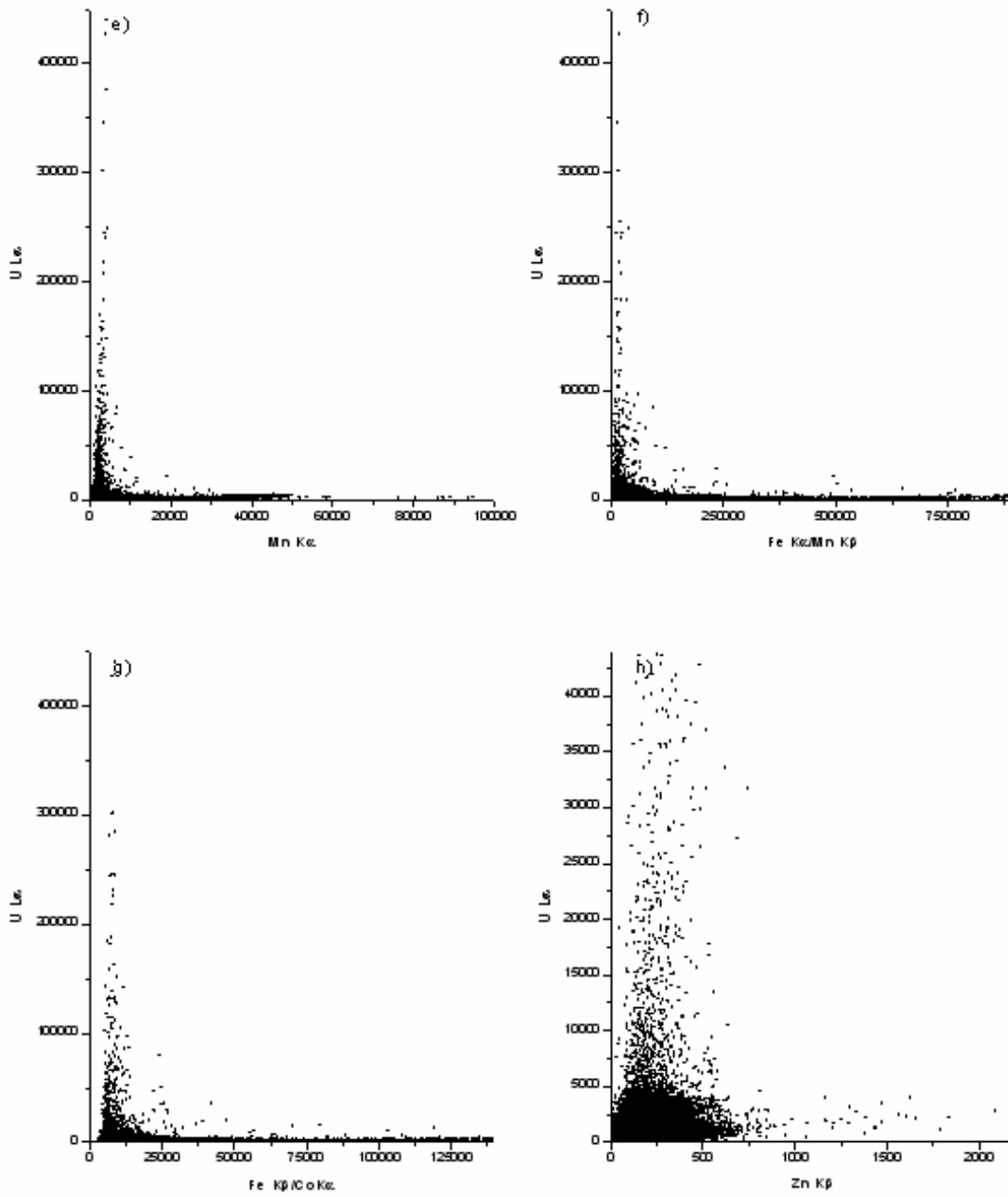
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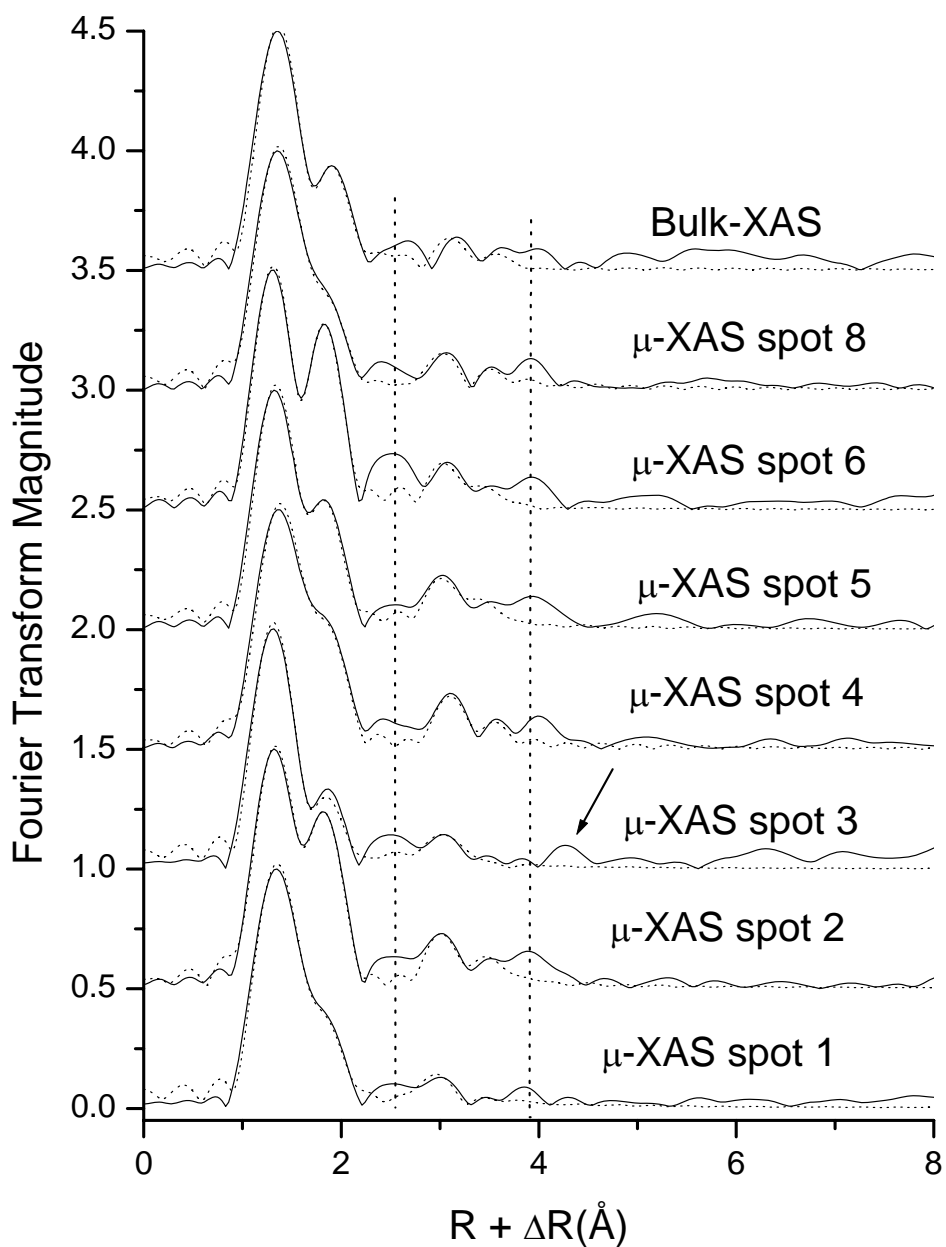
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SI-4. Scatterplots of fluorescence counts of U $L\alpha$ with $K\alpha$ counts of a) Cu, b) Ca, c) Ni, and d) Cr.



SI-4. Scatterplots of fluorescence counts of U $L\alpha$ with $K\alpha$ counts of e) Mn, f) Fe $K\alpha$ /Mn $K\beta$, g) Fe $K\beta$ /Co $K\alpha$, and h) Zn $K\beta$ /Au $L\alpha$.



SI-5: Fourier transformed k^3 -weighted U L_{III} -edge μ - and bulk-EXAFS spectra of the U-contaminated vadose zone samples NPP2-4 shown in Figures-2c and-2d. Solid lines are the experimental data and the dotted lines represent the theoretical fit with the structural parameters of metatorbernite.

SI-6: Acknowledgments:

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