Supporting Information

Quantitative separation of monomeric U(IV) from UO_2 in products of U(VI) reduction

Daniel S. Alessi[1], Benjamin Uster[1], Harish Veeramani[1,†], Elena I. Suvorova[1], Juan S. Lezama-Pacheco[2], Joanne E. Stubbs[2,§], John R. Bargar[2], Rizlan Bernier-Latmani[1,*]

[1]Environmental Microbiology Laboratory, Ecole Polytechnique Fédérale de Lausanne, CH-1015, Switzerland

[2]Chemistry and Catalysis Division, SLAC National Accelerator Laboratory, Menlo Park, CA 94025, USA

[†]Current address: Environmental Nanoscience & Technology Laboratory, Department of Geosciences, Virginia Polytechnic and State University, Blacksburg, VA 24061, USA

[§]Current address: Center for Advanced Radiation Sources, University of Chicago, IL 60637, USA

*Corresponding Author. Tel: +41 21 693 50 01, Email: rizlan.bernier-latmani@epfl.ch

Supporting Information Methods:

Electron Microscopy

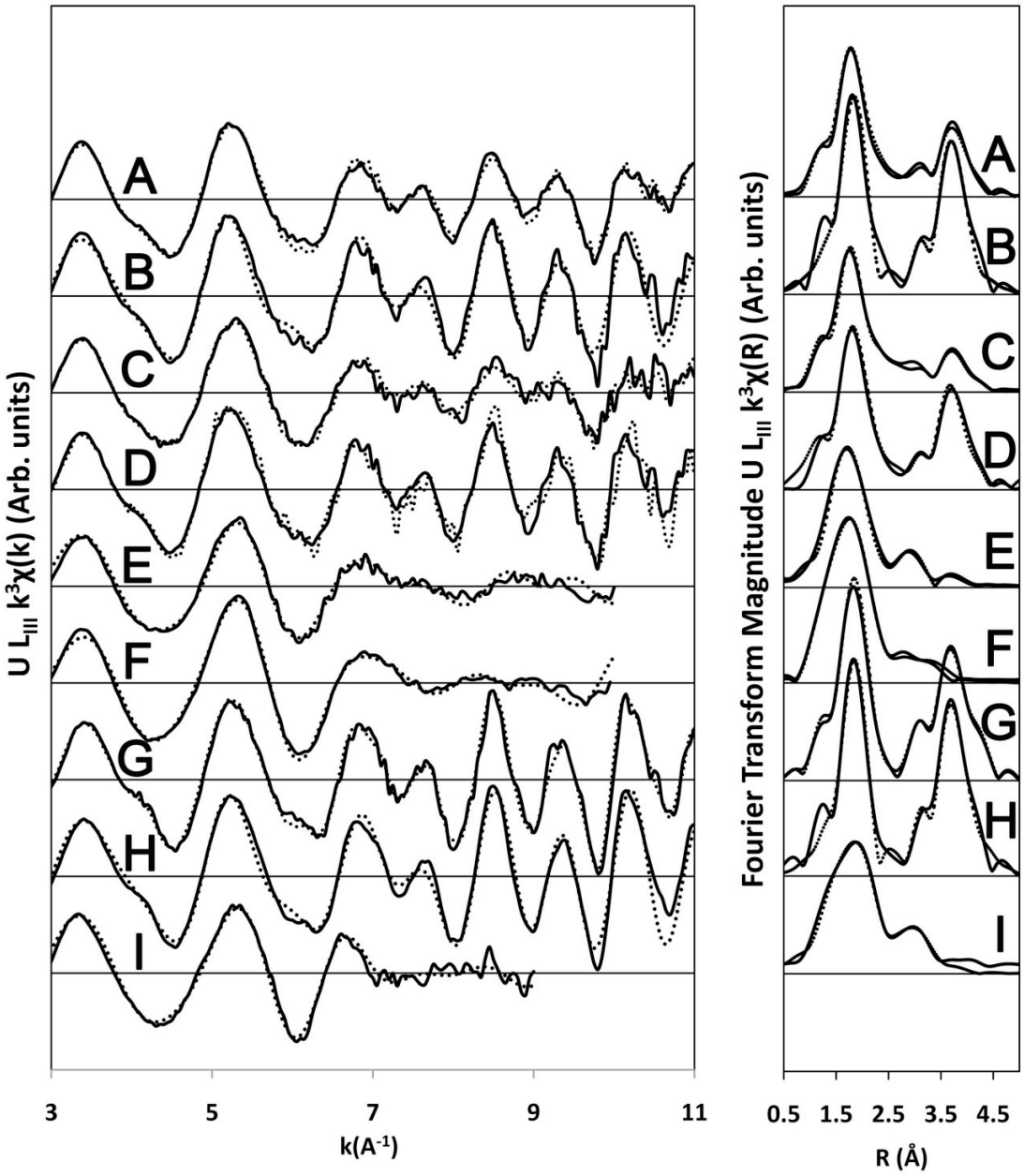
Transmission electron microscopy (TEM) was used to probe a sample treated with the bicarbonate extraction for traces of remaining biogenic UO_2 (sample Bio5 after bicarbonate extraction). The sample consisted primarily of monomeric U(IV) prior to extraction. After the extraction, the sample was centrifuged, the bicarbonate supernatant discarded, and the pellet washed repeatedly in deionized water. The pellet was then diluted to be 100 times more dilute than in the reduction and extraction experiments. A droplet of this suspension was placed in a spray apparatus, used to atomize the sample and mount it onto a standard carbon-coated copper grid (Quantifoil Micro Tools, GmbH, Jena, Germany) inside the anaerobic chamber. The rapid drying of the microdroplets formed by the spray apparatus prevented the formation of secondary crystals on the grids. Chemical information about the particles was collected using X-ray energy dispersive spectroscopy (EDS; INCA, Oxford). Images were recorded on a Gatan 797 slow scan CCD camera (1024 x 1024 pixels, 14 bits) and processed using Gatan Digital Micrograph 3.11.0 software (Gatan, Inc., Pleasanton, CA, USA), including Fourier filtering. Phase identification was performed by analyzing SAED patterns and Fourier transforms of HRTEM images (diffractograms). Diffraction patterns and images were calculated using the Java Electron Microscopy Software (JEMS) (43) for the electron-optical parameters of the microscope used in the study, and the structural data of all known U oxides and phosphates were taken from the Inorganic Crystal Structure Database (ICSD, FIZ Karlsruhe, 2011) and compared with the experimental ones. Accuracy of phase

identification was within 1% of interplanar spacings. The intensities of reflections were always taken into account.

Reference

(43) Stadelmann, P. A. EMS – A software package for electron-diffraction analysis and HREM image simulation in materials science. *Ultramicroscopy* **1987**, *21*, 131 – 145.

Supporting Information Figure 1: EXAFS data (left panel) and Fourier transforms of the same (right panel) for the following samples: A – Bio1 pre-extraction; B – Bio1 post-extraction; C – Bio3 pre-extraction; D – Bio3 post-extraction; E – Bio5 pre-extraction; F – vivianite pre-extraction; G – magnetite pre-extraction; H – magnetite post-extraction; I – RABS sediment pre-extraction. Dashed lines indicate linear combination fits (spectra A, C, D, G) and shell-by-shell fits for all other spectra (see also Supporting Information Table 2 and Supporting Information Figure 2). Fourier transforms were determined for the range 3<k<10.

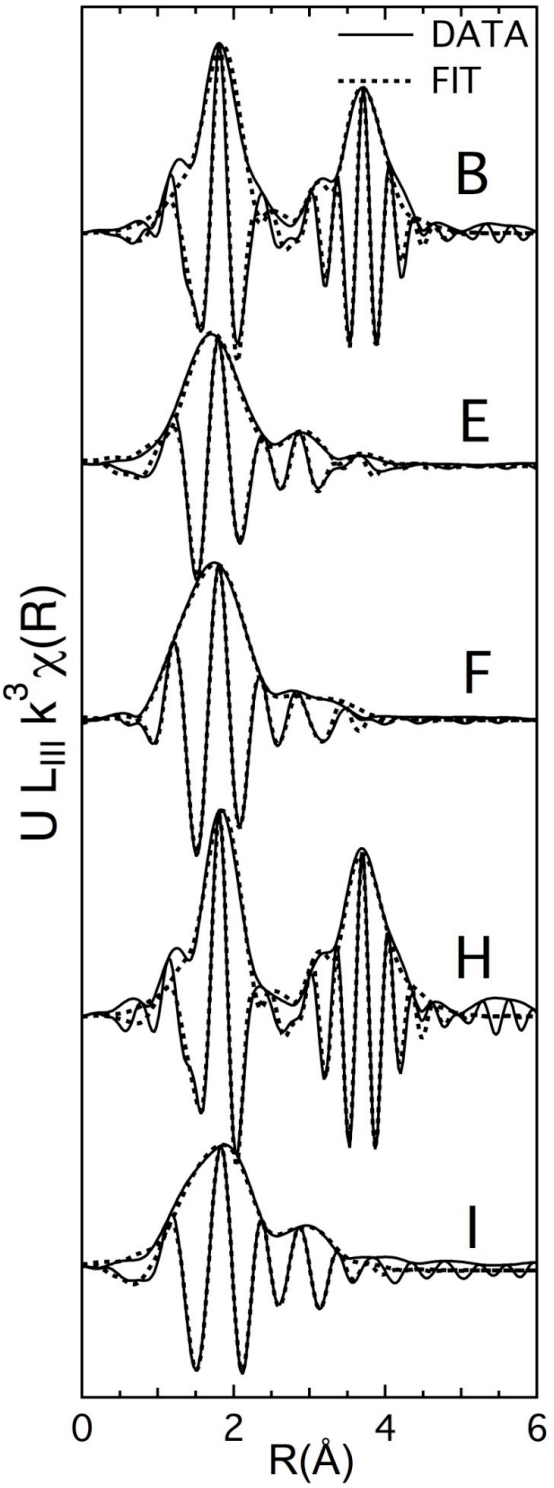


77

78 Supporting Information Figure 2: Shell-by-shell fits of samples B, E, F, H, and I (see

79 Supporting Information Figure 1), including the real part of the Fourier transform.

80 Fourier transforms were taken over the range $3<k<10$.



81

82

83

84

Supporting Information Table 1: Composition of Widell Low Phosphate (WLP) medium. WLP is comprised of 1 mL of solutions B, C, and D, added to 1 L of solution A.

A

Component	g L^{-1}
Calcium chloride	0.1
Potassium chloride	0.5
Monopotassium phosphate	0.03
Magnesium chloride	0.5
Sodium chloride	5.0
Ammonium chloride	0.25
Sodium bicarbonate	3.7
PIPES buffer	6.0
Lactic acid	1.8
Yeast Extract	0.5

B

Component	g L^{-1}
Hydrochloric acid	14.75
Ferrous sulfate	2.1
Boric acid	0.03
Manganese chloride	0.1
Cobalt chloride	0.19
Nickel chloride	0.024
Copper chloride	0.002
Zinc sulfate	0.144
Sodium molybdate	0.036

C

Component	g L^{-1}
4-aminobenzoic acid	0.04
D(+)-biotin	0.01
Nicotinic acid	0.1
Calcium D(+) pantothenate	0.05
Pyrodoxine dihydrochloride	0.15

D

Component	g L^{-1}
Sodium hydroxide	0.4
Sodium tungstate	0.008
Selenious acid	0.0025

Supporting Information Table 2: U L_{III}-edge EXAFS fits for spectra B, E, F, H, and I (see Supporting Information Figure 2).

		B	E	F**	H	I
U-O	*N*	7.6±0.9	3.8±1.6	4.5*	7.0±0.7	3.6±0.9
	D (Å)	2.36(1)	2.24(7)	2.25(3)	2.35(1)	2.21(4)
	σ^2 (Å^2)	0.010(2)	0.005*	0.005*	0.009(2)	0.005*
U-O			3.9±1.0	2.7*		7.0±1.0
			2.41(8)	2.49(4)		2.40(3)
			0.006*	0.006*		0.008*
U-P			1.2±0.5	1.8±0.9		2.0±0.4
			3.12(6)	3.15(4)		3.12(3)
			0.008*	0.008(6)		0.008*
U-P			2.4±1.0	2.7±0.9		4.0±0.8
			3.65(8)	3.77(4)		3.66(4)
			0.009*	§§0.009(12)		0.009*
U-U		9.3±1.7	1.2±1.1		11.3±1.3	
		3.85(2)	3.73(10)		3.85(2)	
		0.007*	0.007*		0.007*	
U-O		§22.8±2.7			§20.9±2.1	
		4.46(3)			4.46(2)	
		0.017(9)			0.009(4)	

***Fixed values**

****Contribution ~15-30% (from XANES) of U(VI)-O~1.75 Å with multiple scattering included in the model for this sample**

§Constrained value to coordination in UO_2 (3 times coordination of first U-O shell), , error was propagated accordingly

§§Constrained value $\sigma^2_{U\text{-}P1}=\sigma^2_{U\text{-}P1}+0.001$, error was propagated accordingly