

Supplementary Information:

From Adsorption to Precipitation of U(VI): What is the role of pH and Natural Organic Matter?

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Summary of Supporting Information

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Supplementary Notes: Additional Materials and Methods.

Micro X-Ray Fluorescence. Bulk chemistry analysis was performed on the unreacted samples using X-Ray Fluorescence (XRF) with a Rigaku ZSX Primus II with Rhodium X-ray tube that quantitatively determines major and minor elements, from B to U. The software is ZSX Primus II that performs both qualitative and quantitative analysis.

X-ray Absorption Spectroscopy. X-ray Absorption Spectroscopy measurements were performed at Beamline 7-3 at the Stanford Synchrotron Radiation Laboratory. Measurements were done at the U LIII edge in fluorescence mode using a 30 element Ge detector and a double crystal Si(220) Monochromator, calibrated at the first inflection point of a Y metal foil absorption at 17038.4 eV. Data steps across the U-LIII XANES was 0.35 eV to 17200 eV. The EXAFS spectra were taken in 0.05 k steps (\AA^{-1}) to 13.5 (\AA^{-1}). Measurements were performed at 10 K using a closed cycle cryostat. No change was observed through consecutive scans, nor changes in the absorption from the first and last scans of the series, ruling out beam damage during the measurement. Sample sets were reduced and analyzed using Athena and Artemis¹ with standard methods and benchmarks.

Inductively Coupled Plasma (ICP). Elemental concentrations in supernatant from the filtered acid digestion of the mineralized surface deposits from the Jackpile Mine samples and the batch experiments were measured using a PerkinElmer Optima 5300DV Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES). Trace elemental concentrations were measured using a PerkinElmer NexION 300D (Dynamic Reaction Cell) Inductively Coupled Plasma-Mass Spectrometer (ICP-MS). Both ICPs are calibrated with a 5-point calibration standards and QC samples were analyzed periodically to ensure quality results.

Identification of solids phases by Electron Diffraction. The identification of phases is based on the d-spacings and measurement of the angles between the three diffraction vectors in the zone

axis diffraction pattern, as well as the ratios of the lengths of the different diffraction vectors. There are four possible candidate phases that are likely for this phase, grimselite, schoepite, compreignacite, and clarkeite. We used the program Single Crystal to calculate the d-spacings for each of these phases using crystal structure data from the American Mineralogist Crystal Structure Database. We also calculated all the possible zone axis diffraction patterns for each of the four phases and compared our experimental zone axis diffraction pattern for the U-K-bearing crystallites (Figure 3I).

Table S1. Experimental design used for this study. All experiments were conducted in triplicate using 100 μ M U under environmentally relevant ionic strengths.²⁻⁴

ID	Reaction	KCl (M)	NOM (mgL ⁻¹)	pH adjust	Reaction time (h)	U _{aq} and DOC	TEM	μ XRF	XAS	Purpose
U- KCl-NOM	U+ KCl +NOM	0.01	0.2	NaOH	0.5, 24	Yes	Yes	Yes	Yes	Reaction to evaluate the U precipitation in the presence of NOM at ionic strengths observed in the field ²⁻⁴ (environmentally relevant).
Control U	U + KCl	0.01	0	NaOH	0.5, 24	Yes	Yes	Yes	No	Control to evaluate U precipitation in the absence of NOM.
Control NOM	NOM	0.01	0.2	NaOH	24	Yes	Yes	Yes	No	Control to evaluate the precipitation of POM in the absence of U.

Table S2. Reduced χ^2 values for the solids collected after the experiments of U-NOM and U-KCl-NOM after 24 h

Coordination	χ^2	
	U-NOM	U-KCl-NOM
Five	152.02	27.8
Six	199.6	22.2
Seven	92.8	19.2

Table S3. Statistical analyses to determine whether the U precipitation data with and without NOM is normally distributed by calculating p-values obtained using the Shapiro-Wilk Test. When the p-value of the Shapiro-Wilk Test is greater than 0.05, the data are normal, if it is below 0.05, the data significantly deviate from a normal distribution.

Reactor	Results Normality Test for Soluble U						Results Normality Test for DOC					
	pH 2	pH 4 0.5 h	pH 7	pH 2	pH 4 24 h	pH 7	pH 2	pH 4 0.5 h	pH 7	pH 2	pH 4 24 h	pH 7
NOM+U	0.46	0.50	0.13	0.47	0.43	0.14	0.36	0.36	0.92	0.31	0.57	0.35
U	0.31	0.46	0.18	0.25	0.38	0.29	0.11	0.69	0.37	0.84	0.36	0.17

Table S4. ANOVA tests for the soluble U data collected following U-precipitation experiments in the presence and absence of NOM.

**Anova: All pH values - time - U - UNOM
(Soluble U μM)**

Response: pH 2, pH 4 and pH 7

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
U	1	120.34	120.34	128.86	9.34E-13
U_NOM	1	1.43	1.43	1.53	0.22
time	1	0.35	0.35	0.37	0.55
Residuals	32	29.88	0.93		

**Anova: pH 2 pH 4 - time - U - UNOM
(Soluble U μM)**

Response: pH 2 and H 4

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
U	1	0.09	0.09	0.14	0.72
U_NOM	1	3.26	3.26	4.92	0.04
time	1	7.41	7.41	11.19	3.22E-03
Residuals	20	13.24	0.66		

**Anova: All pH values - time - NOM - UNOM
(DOC ppm)**

Response: pH 2, pH 4 and pH 7

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
NOM	1	83.76	83.76	461.21	3.18E-13
U_NOM	1	2.13	2.13	11.75	3.45E-03
time	1	4E-03	4E-03	0.02	0.89
Residuals	16	2.91	0.18		

Table S5. Comparison of measured d-spacings in Å (>4.7524 Å) from electron diffraction patterns from K-U bearing crystallites in the pH4 24hrs sample (e.g., Figure 3I) with possible K-U, and U-bearing minerals, showing that the d-spacings are uniquely consistent with the d-spacings for grimselite ($K_3Na[UO_2](CO_3)_3](H_2O)$), rather than schoepite $[(UO_2)8O_2(OH)_{12}](H_2O)_{12}$, compreignacite ($K_2((UO_2)3O_2(OH)_3)_2(H_2O)_7$), or clarkeite ($Na[(UO_2)O(OH)](H_2O)_{0-1}$). The d-spacings for each phase were calculated using SingleCrystal software (<http://crystallmaker.com/singlecrystal/>) based on crystal structure data from the American Mineralogist Crystal Structure Database (<http://rruff.geo.arizona.edu/AMS/amcsd.php>).

Reflection	U-K-bearing solid pH4 24 h	Grimselite	Schoepite	Compreignacite	Clarkeite
(010)			16.813		
(011)			11.0798		
(101)				9.4231	
(111)			8.7669		
(001)	<u>8.26</u>	<u>8.26</u>			
(020)			8.4065		
(100)	<u>8.002</u>	<u>8.0558</u>			
(200)				7.4296	
(002)			7.3655		
(021)			7.3013		
(200)			7.1685		
(012)			6.7465		
(210)			6.5941		
(102)			6.5515		
(121)			6.5062		
(110)				6.461	
(110)				6.1828	
(112)			6.1044		
(002)				6.0936	
(211)			6.0187		
(003)					5.8867
(111) (101)	<u>5.764</u>	<u>5.7671</u>			
(111)				5.7084	
(030)			5.6043		
(022)			5.5399		
(220)			5.4546		
(031)			5.2381		
(122)			5.1675		
(210)				5.161	
(211)				4.7524	

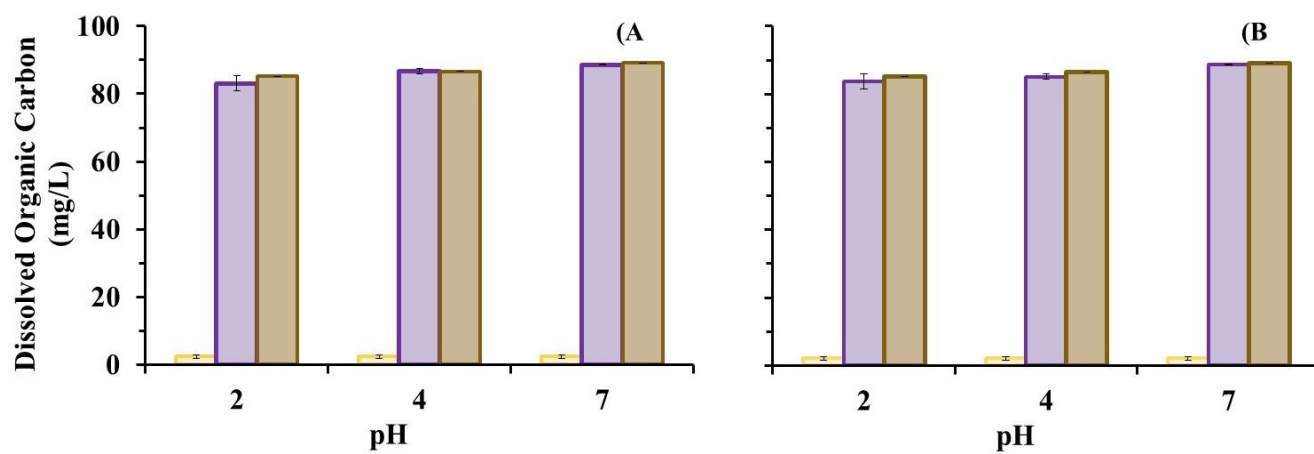


Figure S1. Concentration of dissolved organic carbon (DOC) in solution in batch reactors containing U-KCl-NOM (purple), U control reactor without NOM (yellow) and NOM control reactor without U (brown) after a reaction of A) 0.5 h, B) 24h.

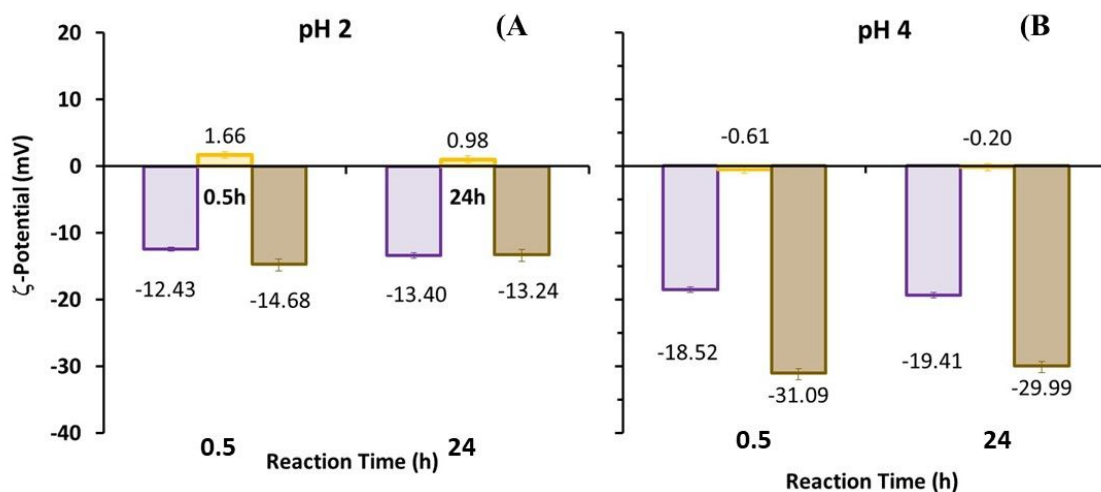


Figure S2. ζ-Potential for suspended solids present in supernatant from batch reactors U-KCl-NOM (purple), U control reactor containing (yellow) without NOM and NOM control reactor without U (brown) after a reaction time of 0.5 h. and 24 h. at A) pH 2, B) pH 4.

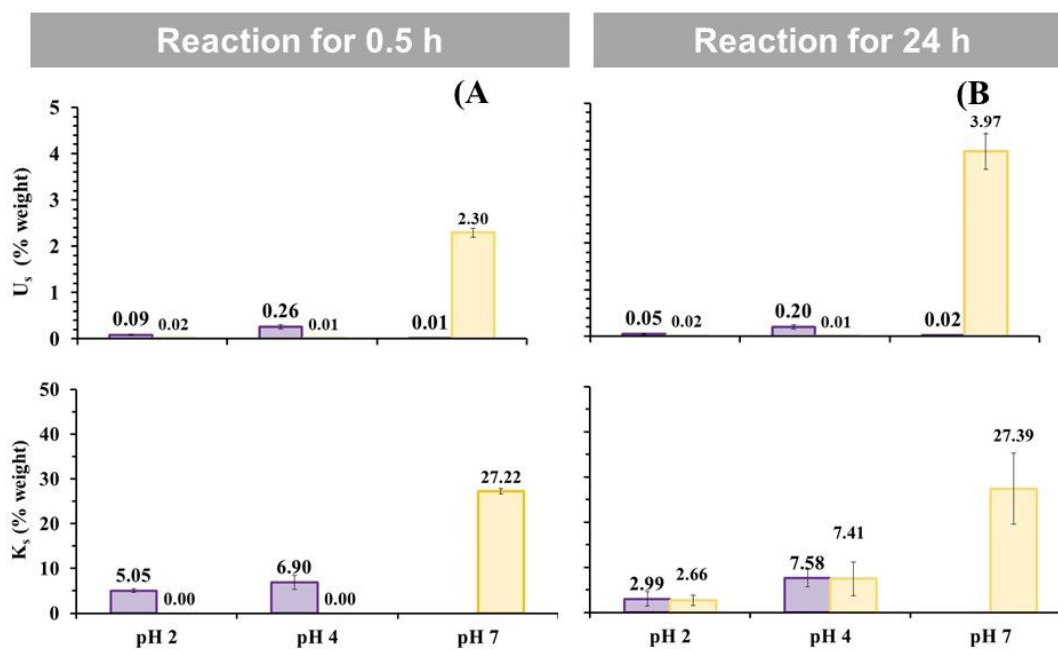


Figure S3. Solid analysis by μ -XRF on samples collected from batch experiments U-NOM-KCl (purple) and U control reactor without NOM (yellow) after a reaction of **A)** 0.5 h and **B)** 24 h. Concentration data for U and K shown as weight percent.

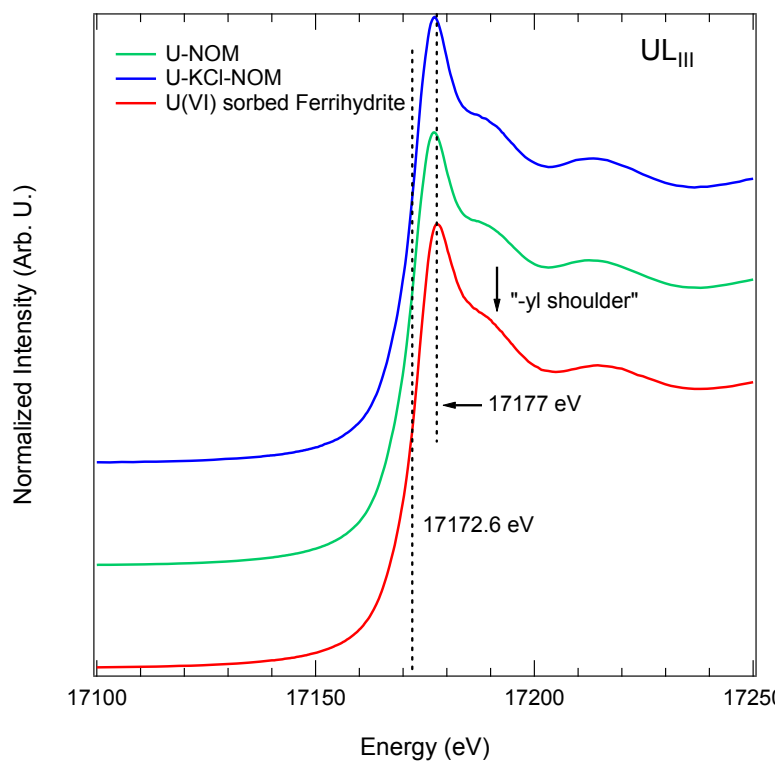
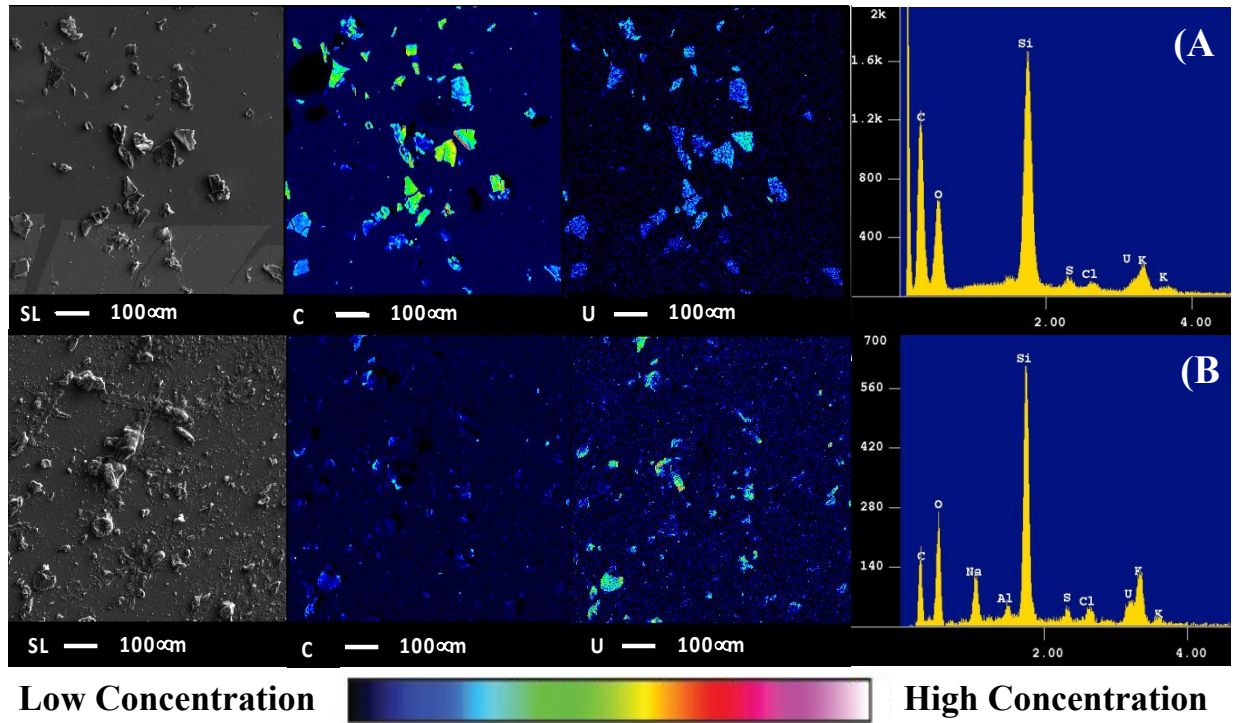


Figure S4. X-ray absorption near-edge structure (XANES) on solids collected after 24 h batch reactions of U-NOM and U-KCl-NOM at pH 4.



Sample at 0.5 hr.	Atomic %		
	U	C	O
pH 2	<1	68	25
pH 4	1	53	33

Figure S5. Secondary electron SEM images, electron microprobe WDS X-ray maps and qualitative energy dispersive X-ray spectra (EDS) on solids collected after 0.5 h batch reactions of SRNOM, uranium in 4% HNO₃ and KCl at A) pH 2, and B) pH 4.

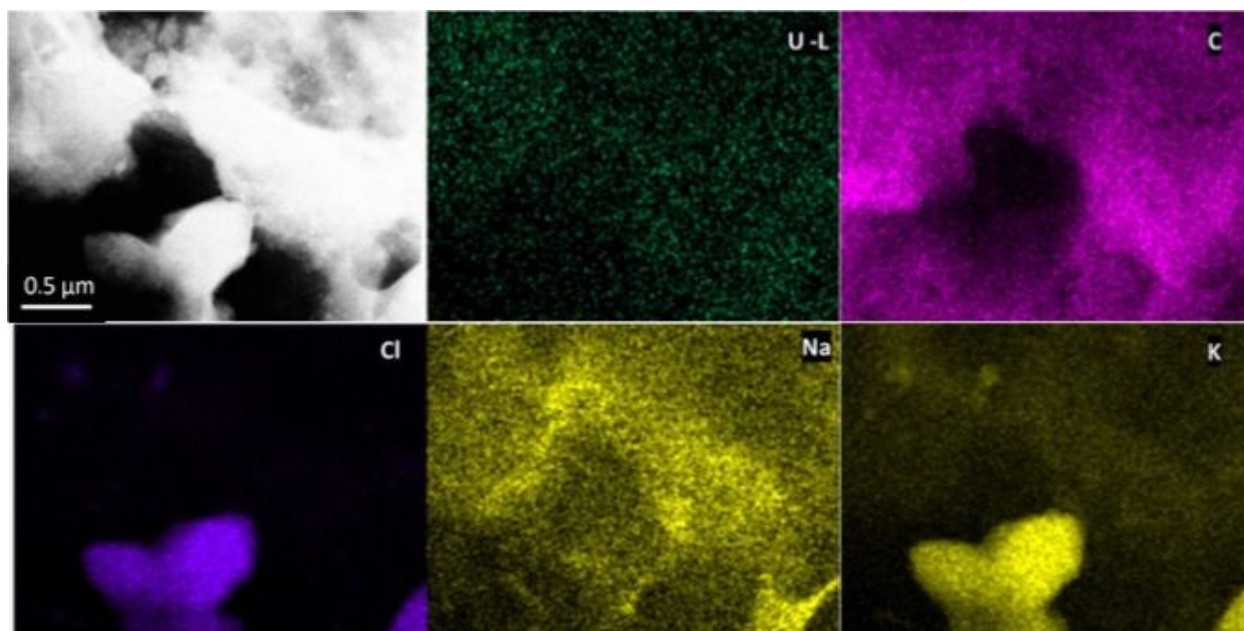


Figure S6. Scanning transmission electron microscope - energy dispersive spectroscopy (STEM-EDS) X-ray maps for solids collected from precipitation experiments in batch solutions of U-KCl-NOM after 24 at pH 2 indicating the association of U, C, Cl, Na, and K in these solids. U-rich particles are not detected in this sample.

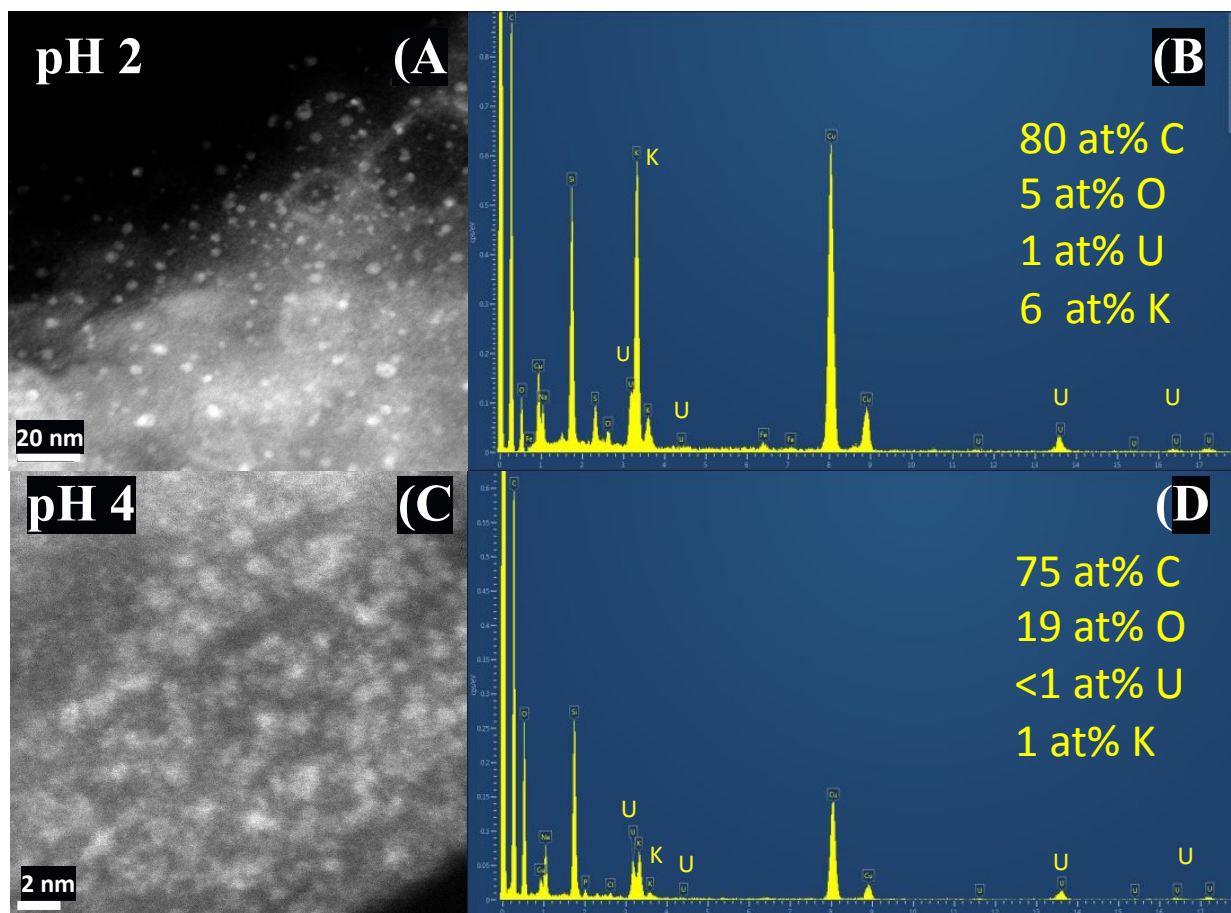


Figure S7. Dark-field scanning transmission electron microscope (DF-STEM) images and energy dispersive X-ray spectroscopy (EDS) spectra for solids collected from precipitation adsorption experiments in batch solutions of U-KCl-NOM after 0.5 hr. at pH 2 and pH 4 indicating the adsorption of U onto POM at pH 2 (A, B) and pH 4 (C, D) shown by the presence of distinct U peaks in the EDS spectra.

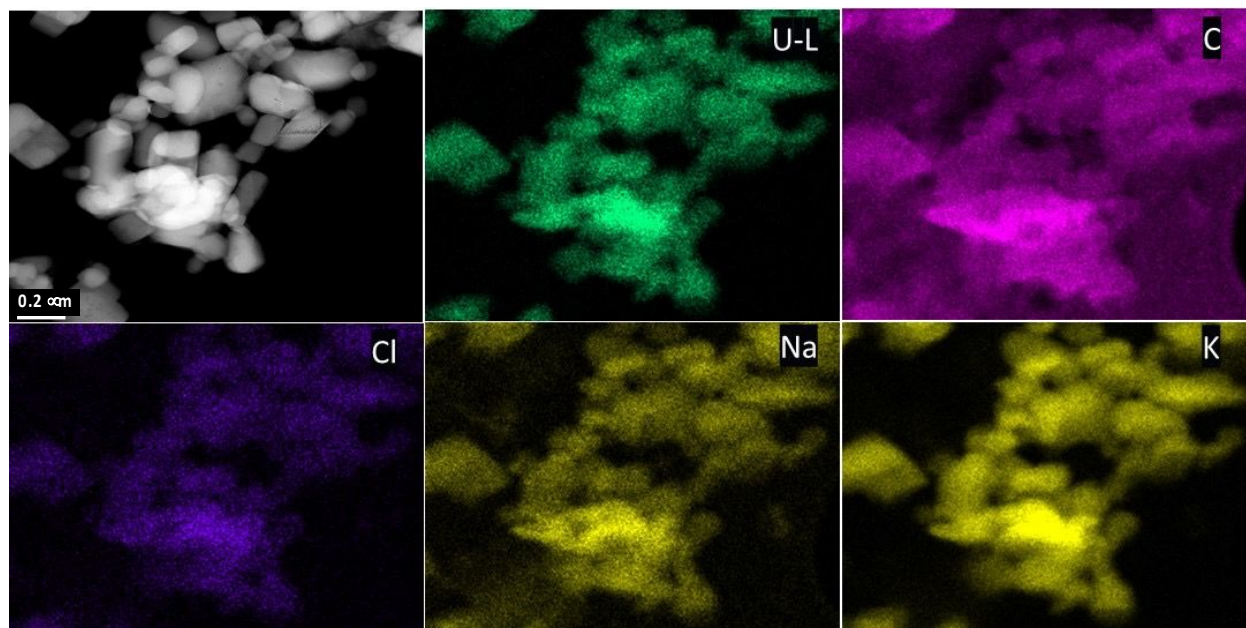


Figure S8. Scanning transmission electron microscope - energy dispersive spectroscopy (STEM-EDS) X-ray maps for solids collected from precipitation experiments in batch solutions of U-KCl-NOM after 24 at pH 4 indicating the association of U, C, Cl, Na, and K in these solids. Uranium- and K-rich particles are detected in this sample. The intensity of the color is correlated with the concentration of the element in the sample.

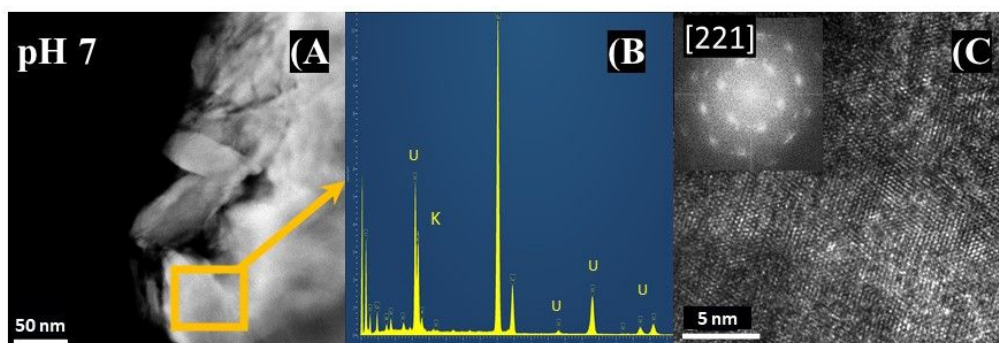


Figure S9. Dark-field scanning transmission electron microscope (DF-STEM) images, energy dispersive spectroscopy (EDS) spectra, high-resolution transmission electron microscopy (HRTEM) and (inset) Fast Fourier Transform extracted from HRTEM image. for solids collected from U control reactor containing (U-KCl) at pH 7 after 0.5 h indicating (A, B, C) the precipitation of U- and K-bearing nanocrystalline solids. The compositional and electron diffraction data are most consistent with clarkeite nanocrystals, but possibly with another U-bearing phase that remains unidentified.

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