SUPPORTING INFORMATION

Sequestering Uranium and Technetium through Co-precipitation with Aluminum in a Contaminated Acidic Sediment

Wensui Luo,[1] Shelly D. Kelly[2,3], Kenneth M. Kemner[2], David Watson[1], Jizhong Zhou,[4] Philip M. Jardine,[1] and Baohua Gu[1]

1. Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831.
2. Biosciences Division, Argonne National Laboratory, Argonne, IL, 60439.
3. Current Address: EXAFS Analysis, Bolingbrook, IL, 60440.
4. Institute for Environmental Genomics, Department of Botany and Microbiology, University of Oklahoma, Norman, OK 73019.

Environmental Science and Technology

August 1, 2009

Supporting Information Summary

Number of pages	7
Figures	5
Tables	1

EXAFS spectroscopic analysis

The X-ray absorption fine structure (EXAFS) spectra of a selected sediment sample following its batch titration (to pH ~6.7) were collected at room temperature in quick scanning fluorescence mode. The spectra were processed using Athena (*1*) with IFEFFIT and FEFFIT (*2,3*), and the theoretical spectra were produced using FEFF (*4*). The data are Fourier transformed over the range from 2.8 to 10.7 $Å^{-1}$, and modeled in R-space from 1 to 4 Å with a k-weight of 1, 2, and 3. These ranges give 17 independent points in the measured spectrum. The EXAFS model is based on the crystalline structure of dioxouranium sodium magnesium aluminium oxide (ICSD 73443). This structure has a uranyl bound to several alumina octahedral. Two of these U-Al distances were found in the measured spectra. The U-Al distances are 3.2 Å ($U\text{-}Al_1$) and 3.5 Å ($U\text{-}Al_2$). The EXAFS model includes 7 paths which are: $U\text{-}O_{ax}$ from the two tightly bound axial oxygen atoms of the uranyl, $U\text{-}O_{eq}$ from the 4 to 6 equatorial oxygen atoms of the uranyl, three different $U\text{-}O_{ax}$ multiple scattering (MS O_{ax}) paths, the $U\text{-}Al_1$ and $U\text{-}Al_2$ paths. The EXAFS parameters determined by optimizing the model to the measured spectrum for these paths are given in Table S1, and the EXAFS $\chi(k)$ spectrum in Figure S1.

Table S1. Uranium EXAFS spectroscopic analysis of a contaminated sediment following its titration to pH 6.7.

Path	CN[a]	R (Å)	σ^2 ($\cdot 10^{-3}$ $Å^2$)
$U\text{-}O_{ax}$	2[b]	1.749 ± 0.005	1.3 ± 0.5
$U\text{-}O_{eq}$	7.0 ± 0.8	2.35 ± 0.01	10.5 ± 1.5
$U\text{-}Al_1$	1.1 ± 0.7	3.20 ± 0.02	2.6 ± 5.6[d]
$U\text{-}O_{ax1}\text{-}O_{ax2}$	2[b]	3.50 ± 0.01[c]	2.5 ± 1.0[e]
$U\text{-}O_{ax1}\text{-}U\text{-}O_{ax2}$	2[b]	3.50 ± 0.01[c]	2.5 ± 1.0[e]
$U\text{-}O_{ax1}\text{-}U\text{-}O_{ax1}$	2[b]	3.50 ± 0.01[c]	5.1 ± 2.0[f]
$U\text{-}Al_2$	0.9 ± 0.6	3.73 ± 0.04	2.6 ± 5.6[d]

a: S_0^2 was held at 1.0 ± 0.1.

b: Coordination number for the U-O_{ax} paths were held at 2.

c: values constrained to be twice the distance of the single scattering U-O_{ax}.

d: σ^2 for the U-Al_1 and U-Al_2 paths were constrained to the same value.

e: σ^2 for these paths was constrained to be twice the value for the U-O_{ax} path.

f: σ^2 for this path is four times the value for the U-O_{ax} path.

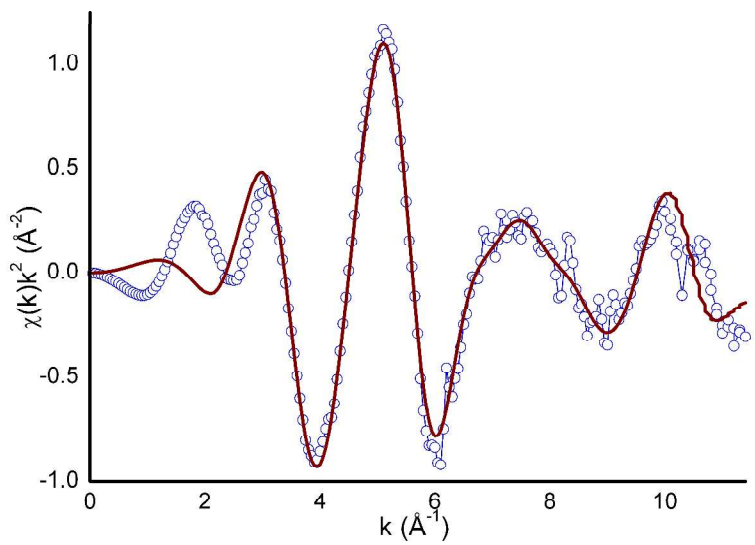


Figure S1. Uranium EXAFS spectral data (symbols) and model simulations (line) for the contaminated sediment, which was titrated to pH 6.7.

X-ray diffraction (XRD) analysis

Mineralogical analyses of the groundwater precipitates and sediment samples (from batch experiments, titrated to pH about 7) were performed using a Scintag XDS 2000 X-ray diffractometer operated at 40 kV and 35 mA (Scintag, Inc. Sunnyvale, CA). The samples after the batch titration were air-dried at room temperature and then transferred onto a glass slide for the XRD analysis. The scan rate was 2° 2θ/min using Co-Kα radiation (λ=0.17889 nm). No clear XRD pattern of Al-oxyhydroxides in both the groundwater precipitate and the sediment (after pH adjustment) can be observed (Figure S2), suggesting that the precipitated Al-oxyhydroxides are largely amorphous in nature.

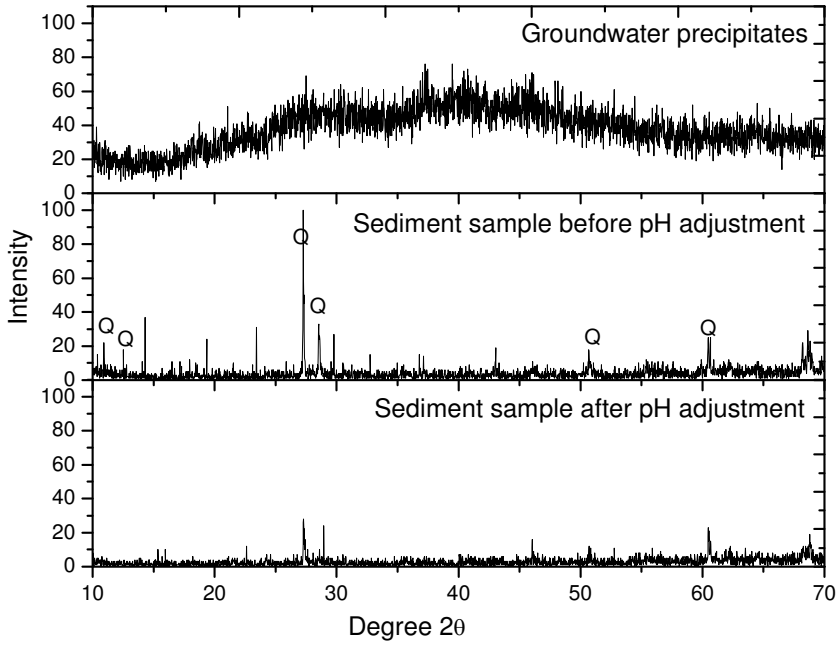
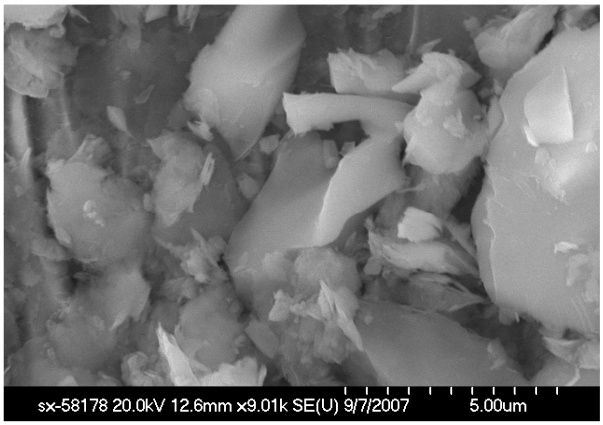


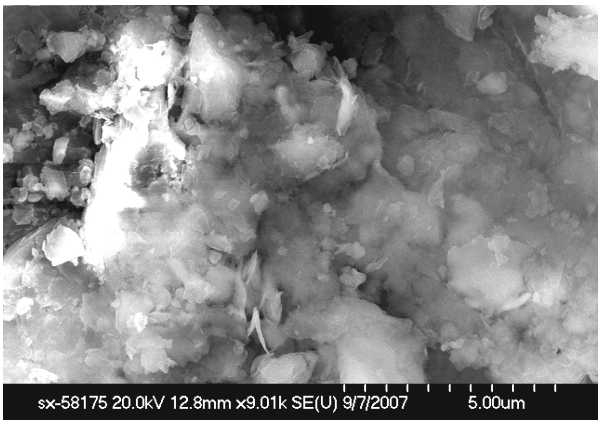
Figure S2. X-ray diffraction analysis of mineral precipitates following the batch titration of the contaminated sediment and the groundwater. Q = quartz.

Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analyses

Morphological properties and surface elemental compositions of sediment samples before and after pH adjustments were determined by means of scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) detector (JEOL JSM-35CF, Tokyo, Japan). Results are shown in Figures S3 and S4. SEM images indicate that the precipitated Al-oxyhydroxides (after pH adjustment) formed an amorphous coating on sediment minerals (Figure S3). The formation of Al-oxyhydroxide coatings was evidenced by a substantially increased Al signal in EDX analysis (Figure S4). The spectra also show a slightly increased U content in the sediment sample following its pH adjustment because of the co-precipitation of U with Al-oxyhydroxides (Figure S4).



Sediments before pH adjustment



Sediments after pH adjustment

Figure S3. Scanning Electron Microscope (SEM) images showing morphological properties and the precipitated Al-oxyhydroxide coatings on sediment minerals before and after pH adjustments.

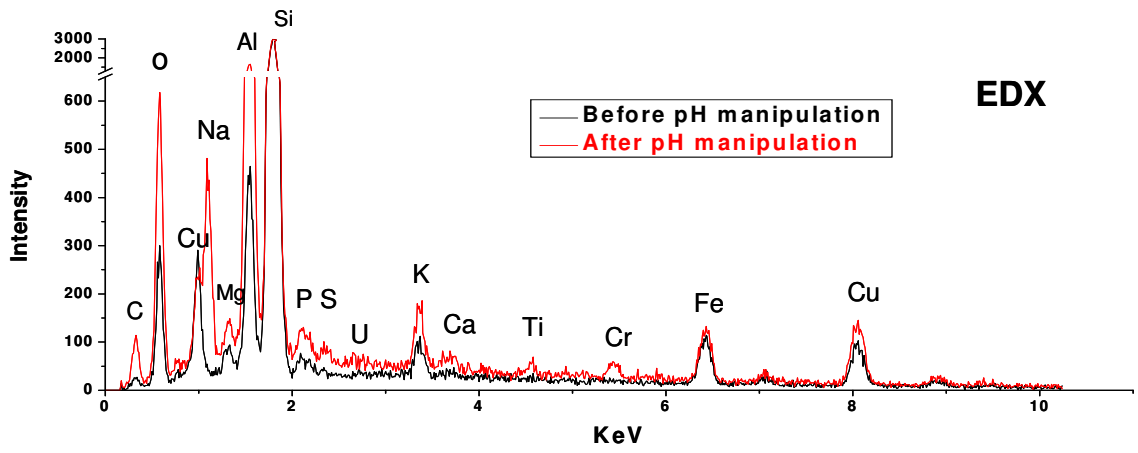


Figure S4. Energy Dispersive X-ray (EDX) analysis of the sediment samples before and after pH adjustments.

Activity Ratio Analysis of Al-OH-SO4 Precipitates

The formation of aluminum-hydroxyl-sulfate precipitates was analyzed by plotting the activity-ratio diagrams using methods of Sposito (*5*) (see Figure S5). Jurbanite [$Al(OH)SO_4.5H_2O$], Alunite [$KAl_3(OH)_6(SO_4)_2$], and basluminite [$Al_4(OH)_{10}SO_4.5H_2O$] are Al-sulfate minerals frequently found in environment with relatively high concentrations of sulfate and aluminum (*6,7*). The activity-ratio analysis indicates that the formation of jurbanite [$Al(OH)SO_4.5H_2O$] is thermodynamically favored under the given experimental conditions. The ratio of Al and sulfate removed in the groundwater titration was approximately 1:1, which is consistent with the Al and sulfate ratio of jurbanite. Therefore, the formation of jurbanite is most likely occurring for the co-precipitation of Al and sulfate under experimental conditions performed in this study.

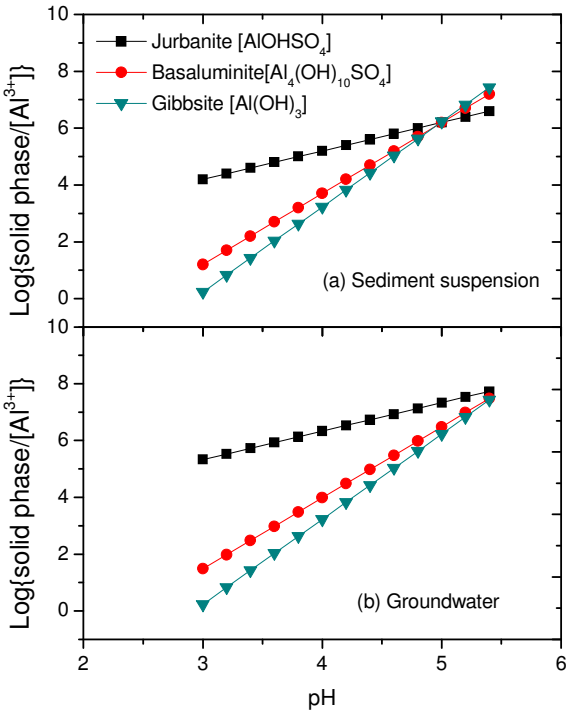


Figure S5. Activity ratio analysis of the precipitation of Al-oxyhydroxides in the presence of sulfate (a) in sediment suspension and (b) in groundwater.

Literatures Cited

(1) Ravel, B.; Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *J. Synchr. Rad.* **2005**, *12*, 537-541.

(2) Newville, M. IFEFFIT: interactive XAFS analysis and FEFF fitting. *J. Synchr. Rad.* **2001**, *8*, 322-324.

(3) Stern, E. A.; Newville, M.; Ravel, B.; Yacoby, Y.; Haskel, D. The UWXAFS analysis package - Philosophy and details. *Physica B Cond. Matter* **1995**, *208*, 117-120.

(4) Zabinsky, S. I.; Rehr, J. J.; Ankudinov, A.; Albers, R. C.; Eller, M. J. Multiple-scattering calculations of X-Ray absorption spectra. *Phys. Rev. B* **1995**, *52*, 2995-3009.

(5) Sposito, G. *The chemistry of soils*; Oxford University Press: New York, 1989.

(6) Adams, F.; Hajek, B. F. Effects of solution sulfate, hydroxide, and potassium concentrations on the crystallization of alunite, basaluminite, and gibbsite from dilute aluminum sulfate solutions. *Soil Sci.* **1978**, *126*, 169-173.

(7) Adams, F.; Rawajfih, Z. Basaluminite and alunite: a possible cause of sulfate retention by acid soils. *Soil Sci. Soc. Am. J.* **1977**, *41*, 686-692.