

DE-SC0002150

PI: Huifang Xu Department of Geoscience, University of Wisconsin – Madison (e-mail: hfxu@geology.wisc.edu)

Title: The role of nanopores on U(VI) sorption and redox behavior in U(VI)-contaminated subsurface sediments

co-PIs: Eric E. Roden, Department of Geoscience, University of Wisconsin – Madison; Kenneth M. Kemner, Biosciences Division, Argonne National Laboratory

Participants: Hun-Bok Jung, Yubing Sun, and Hiromi Konishi (Department of Geoscience, University of Wisconsin – Madison); Bhoopesh Mishra, and Maxim Boyanov (Biosciences Division, Argonne National Laboratory)

Source of Support: DOE, Subsurface Biogeochemical Remediation (SBR) Program

Total Award Amount: \$ 198,900 (to UW – Madison); \$112,945 (to ANL)

Award Period Covered: 09/01/2009 – 08/31/2011 (no cost extension to 08/31/12).

Summary

Most reactive surfaces in clay-dominated sediments are present within nanopores (pores of nm dimension). The behavior of geological fluids and minerals in nanopores is significantly different from those in normal non-nanoporous environments. The effect of nanopore surfaces on U(VI) sorption/desorption and reduction is likely to be significant in clay-rich subsurface environments. Our research objective is to test the hypothesis that U(VI) sorption on nanopore surfaces can be greatly enhanced by nanopore confinement environments.

U(VI) sorption affinity was evaluated with non-nanoporous alpha-alumina (SSA of 8 m²/g) and crushed natural goethite (SSA of 5 m²/g), as well as nanoporous natural goethite (SSA of 60 m²/g; nanoporosity of 30 μL/g for < 5 nm pore) and alumina materials with large nanopores (SSA of 147 m²/g; nanoporosity of 90 μL/g for < 5 nm pore) and small nanopores (SSA of 230 m²/g; nanoporosity of 145 μL/g for < 5 nm pore). Sorption of 100 μM U(VI) onto 0.2 g solid material in 10 mL of 5 mM HCO₃⁻ solution under near-neutral pH was rapidly completed for nanoporous goethite and Al oxides, whereas

only 30~60% sorption occurred on non-nanoporous oxides. Bicarbonate and pH exerted a minor effect on U(VI) sorption on nanoporous goethite and Al oxides, but played a significant role in hindering U(VI) sorption on non-nanoporous goethite and Al oxides. Majority of U(VI) remained on the surface of nanoporous goethite and Al oxides after extraction with 50 mM NaHCO₃, whereas nearly all U(VI) was released from non-nanoporous materials. Sorption and desorption results collectively suggest that nanoporous materials have significantly higher U(VI) sorption affinity than non-nanoporous materials (Figs. 1, 2, 3).

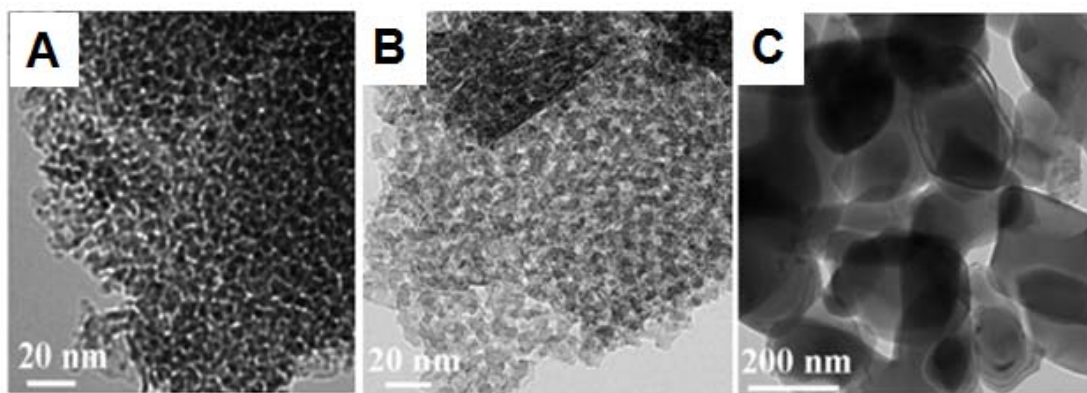


Fig. 1. TEM images of (A) sponge-like nanoporous alumina, (B) mesoporous alumina consisting of oriented stacking of hexagonal nano-crystals, and (C) non-nanoporous alumina clusters.

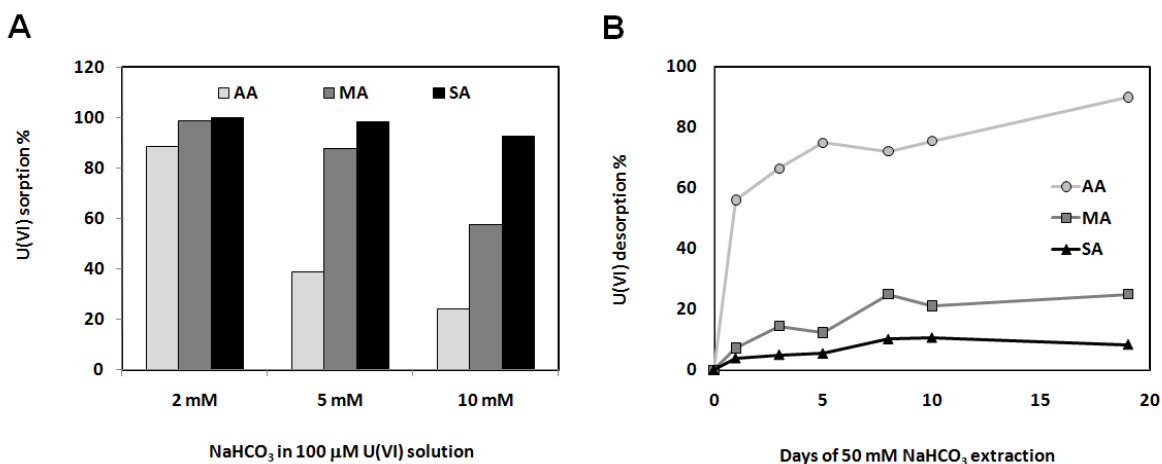


Fig. 2: **A:** The percentage of U(VI) adsorption (100 μ M U(VI) in 0.1M NaNO₃ containing 2, 5, or 10 mM NaHCO₃ XX day reaction time at fixed pH of XX) to non-nanoporous alpha alumina (AA), mesoporous alumina (MA), and nanoporous synthetic alumina (SA), **B:** Time-dependent desorption of U(VI) desorption from the types of alumina upon exposure to 50 mM NaHCO.

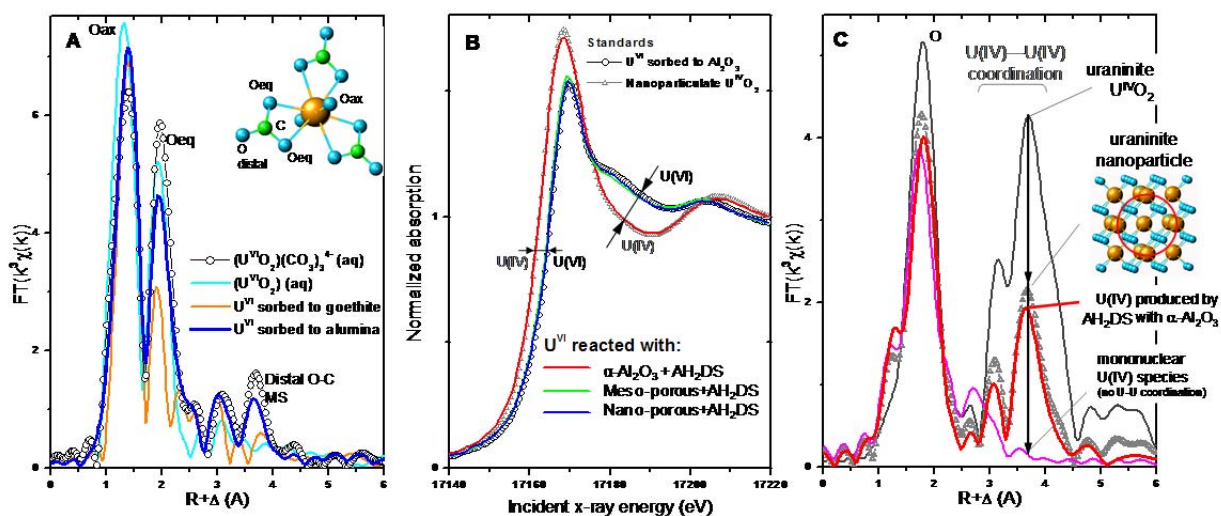


Fig. 3: **A:** Fourier transform of the EXAFS spectrum for the U(VI) species sorbed on all three types of Al oxides, compared to standards: hydrated uranyl and uranyl-tris-carbonato species in solution, and U(VI) sorbed to goethite (inner sphere complex). FT range is $k=2.6-12.0 \text{ \AA}^{-1}$ with a 1.0 \AA^{-1} Hanning window. The structure of an aqueous U(VI)-tris-carbonato complex is shown in the inset; **B:** Uranium L-edge XANES of U(VI) reacted with AH_2DS in the presence of the three types of alumina surfaces, compared to the U(VI) and U(IV) standards: U(VI) sorbed to Al_2O_3 and nanoparticulate UO_2 , respectively. **C:** Fourier transform of EXAFS data for uranium reduced in the presence of non-nanoporous Al oxide by 1 mM AH_2DS under anoxic condition for 1 week. FT range is $k=2.1-10.4 \text{ \AA}^{-1}$ with a 1.0 \AA^{-1} Hanning window.

Microbial reduction of soluble U(VI) to sparingly soluble uraninite (UO_2) is considered an efficient remediation technique for subsurface uranium contamination. An important unanswered question for in-situ bioremediation is whether U(VI) sorbed on a reactive mineral surface is subject to effective and rapid reduction, as is the case for aqueous U(VI). To investigate the chemical linkage between U(VI) sorption affinity and the redox reactivity on a mineral surface, U(VI) bound to the surfaces of non-nanoporous alpha-alumina and nanoporous alumina ($2\sim 5 \text{ \mu mole U/g}$) was reduced by 1 mM hydroquinone (AH_2DS) over 1 day to 3 weeks in an anaerobic chamber. The reduction of U(VI) sorbed on the alumina surfaces was estimated by comparing the U(VI) desorption in anoxic bicarbonate solution ($10\sim 1000 \text{ mM}$) between 1 mM AH_2DS - reduced and unreduced samples. Duplicate samples were analyzed by U L_{III} -edge x-ray absorption spectroscopy for uranium speciation. The results indicate complete reduction to

nanoparticulate uraninite of U(VI) sorbed on non-nanoporous alumina in 2 days, whereas little to no reduction was observed with U(VI) sorbed on nanoporous alumina with large pores (**15% U(IV)**) and small nanopores (**5% U(IV)**) after 1 weeks. This result is attributed to the higher sorption affinity of U(VI) to nanoporous surfaces than to non-nanoporous surfaces (Fig. 4).

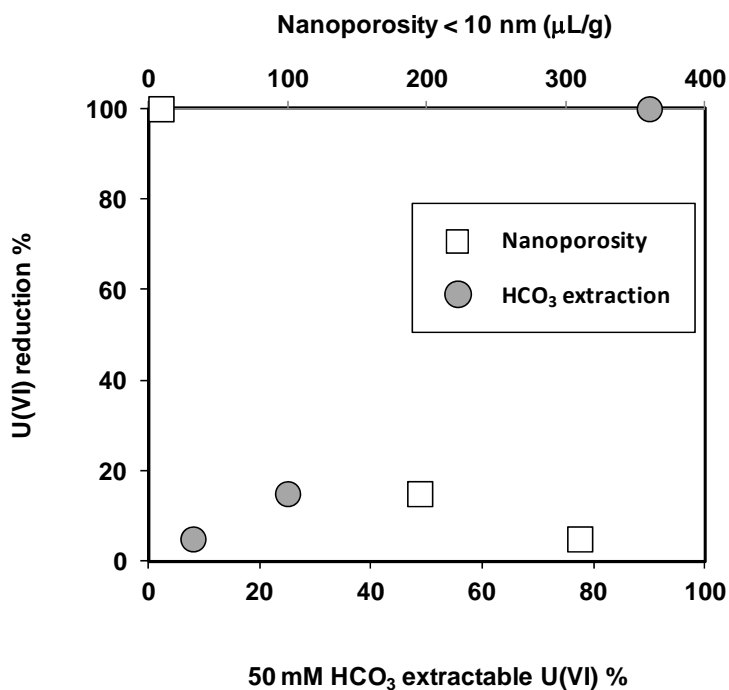


Fig. 4. Correlation between the extent of U(VI) reduction (determined by XANES) on aluminum oxide surfaces and U(VI) sorption affinity gauged by 50 mM NaHCO₃ extraction for 19 days (gray circle) or nanopore (< 10 nm) volume measured by BJH method (open square).

We also investigated sorption and desorption of uranium on both nanoporous and non-porous goethite. U(VI) Desorption experiments of nanoporous goethite and non-porous goethite model systems show that all the sorbed U(VI) on non-porous goethite can be easily desorbed with low bicarbonate concentration. However, the most sorbed U(VI) on nanoporous goethite cannot be desorbed even with high bicarbonate concentration (Figs. 5, 6). 50 mM bicarbonate solution can only desorb ~ 10% of sorbed uranium. The results also support that sorbed U(VI) in natural FRC sediments with nanoporous goethite (Fig. 7) are bonded to both nanopore surfaces (strong

sorption) and non-nanopore surfaces (weak sorption). Majority of sorbed U(VI) are associated with goethite nano-crystals. If we use Dithinote- Citrate-Bicarbonate (DCB) to remove goethite nano-crystals, it also removes more than 80% of U(VI). The amounts of labile Fe by BCD method is approximately 300 $\mu\text{mol/kg}$.

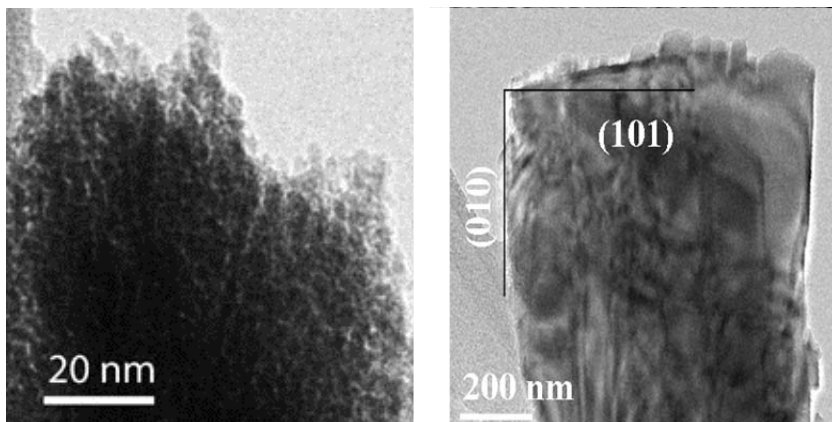


Fig. 5: TEM images showing natural nanoporous goethite (left) and crushed non-porous goethite crystals (right) as model systems.

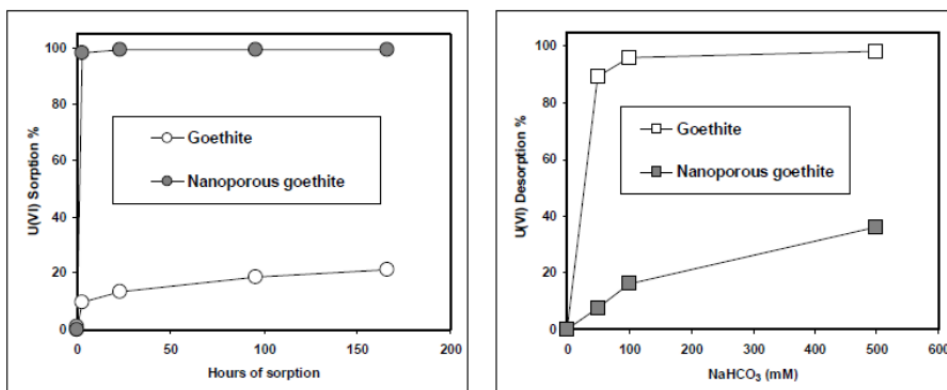


Fig. 6: Sorption results show strong U(VI) sorption of nanoporous goethite, and weak sorption of non-porous goethite (left). Desorption results show U(VI) sorped on nonporous goethite cannot be desorbed easily due to its strong binding on the nanopore surfaces.

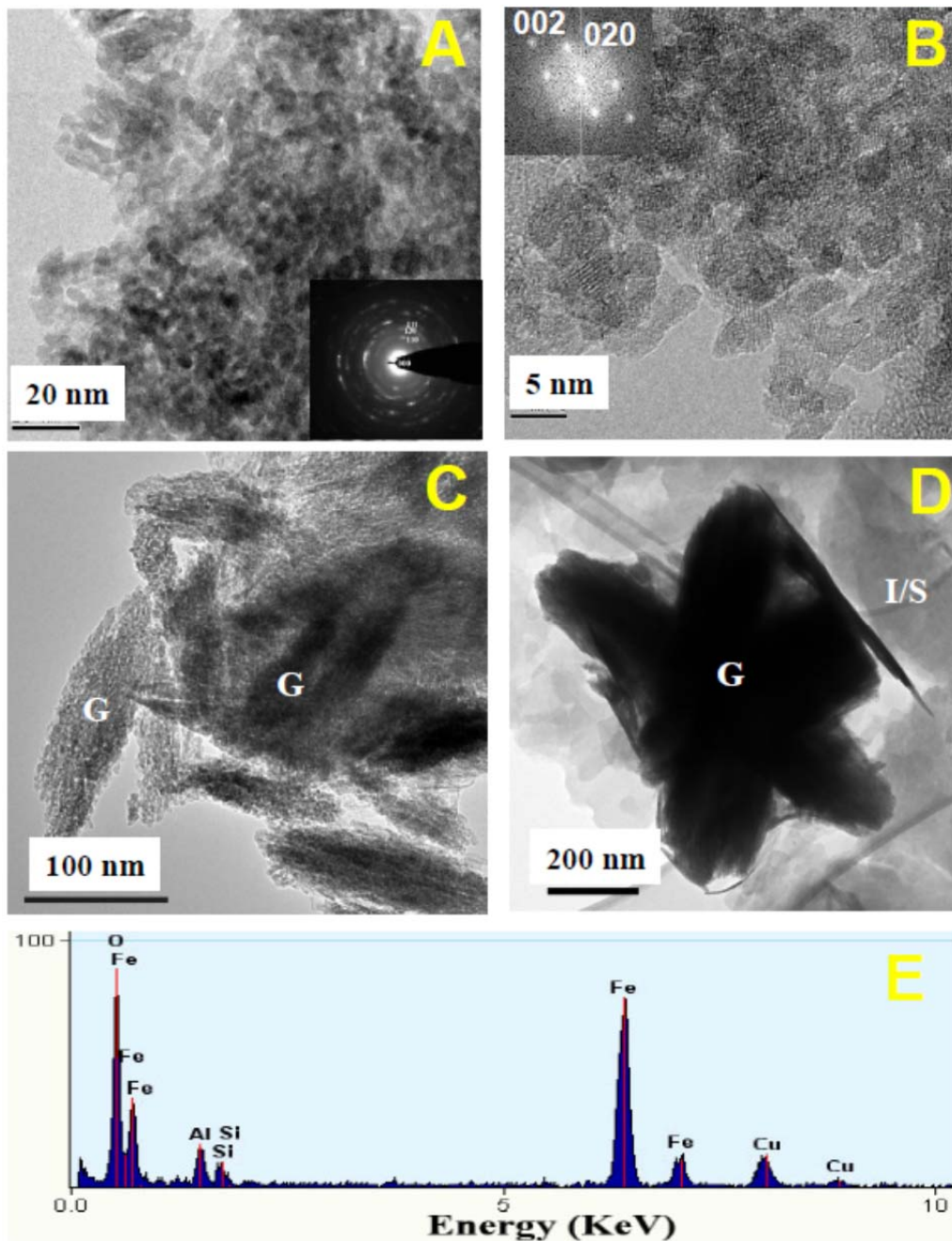


Fig. 7: TEM image showing nano-sized goethite in high-Fe(III) saprolite soil (A, B), twined goethite (V-shape) consisting of oriented aggregation of goethite nano-crystals in medium-Fe(III) saprolite soil (C), and low-Fe(III) saprolite soil (D) from ORFRC; Goethite nano-crystals and nanoporous structures ($< \sim 2$ nm) are evidently shown in high-resolution TEM image (Fig. 1B); I/S and G in TEM images indicate illite/smectite clay and goethite, respectively; X-ray EDS spectrum (E) shows small amount of Al in the goethite. Cu peak is from Cu grid holding the specimen. Si peak is from florescence peak of Li-drifted Si detector.

The results from the project provide advanced mechanistic, quantitative information on the physiochemical controls on uranium sorption and redox behavior in subsurface sediments. The influence of nanopore surfaces on coupled uranium sorption/desorption and reduction processes is significant in virtually all subsurface environments, because most reactive surfaces are in fact nanopore surfaces. We used both model system (synthetic nanopore alumina) and sediments from the ORNL Field Research Center for the proposed studies. The results will enhance transfer of our laboratory-based research to a major field research initiative where reductive uranium immobilization is being investigated. These activities directly addressed the need to develop quantitative understanding of the coupled physical, chemical and biological processes affecting contaminant transport, reactivity and stability in subsurface environments. Our results will provide the basic science for developing in-situ colloidal barrier of nanoporous alumina in support of environmental remediation and long term stewardship of DOE sites.

We carried out all the proposed studies with a slight modification in one proposed task for U(VI) reduction experiments. We used solutions of anthroquinone with well-defined redox potentials for the U(VI) reduction experiments instead of dissimilatory metal-reducing bacterium *Geobacter sulfurreducens*, because small molecules of anthroquinone are more effective for the reduction of U(VI) sorbed on nanopore surfaces.

Key word: nanopore, uranium, goethite, sorption, alumina, transport, subsurface, redox reaction, iron oxides, iron hydroxides, goethite, ferrihydrite

Products developed under the award

Publications

Jung, H. B., Boyanov, M. I., Konishi, H., Sun, Y., Mishra, B., Kemner, K. M., Roden, E. E., and Xu, H. (2012) Redox Behavior of Uranium at the Nanoporous Aluminum Oxide-Water Interface: Implications for Uranium Remediation. *Environmental Sci. & Tech.*, 46, 7301-7309.

Xu, H., and Jung, H. B. (2012) Role of Nanopores in Regulating Reactivity and Transport of Uranium in Subsurface Sediments. In A. S. Barnard and H. Guo eds. "Nature's Nanostructures." Pan Stanford Publishing, 195-221.

Konishi, H, Xu, H., and H. Guo (2012) Nanostructures of Natural Iron Oxide Nanoparticles. In A. S. Barnard and H. Guo eds. "Nature's Nanostructures." Pan Stanford Publishing, 75-113.

Wang, Y., Gao, H., and Xu, H. (2011) Nanogeochemistry: Nanostructures and Their Reactivity in Natural Systems. In "Frontiers in Geochemistry: Contribution of Geochemistry to the Study of the Earth," First edition. Edited by Russell S. Harmon and Andrew Parker, Blackwell Publishing Ltd. Blackwell Publishing Ltd. P 200-220.

Other products

Lecture materials (such as, characterization of nano-phases and nano-pores, roles of nanopores on chemical reactivity) developed from this project have been used in a graduate course of "Nano-geoscience".