Inorg. Chem. **2005**, *44*, 2986–2988

Inorganic Chemistry
Communication

Mica Surfaces Stabilize Pentavalent Uranium

Eugene S. Ilton,*,† Anca Haiduc,‡ Christopher L. Cahill,§ and Andrew R. Felmy†

*Pacific Northwest National Laboratory, Chemical Science Division, MSIN: K8-96,
902 Battelle Boulevard, Richland, Washington 99352, Shell Global Solutions International B.V.,
P.O. Box 38000, 1030 BN Amsterdam, The Netherlands, Department of Chemistry,
George Washington University, Washington, D.C. 20052, and Geophysical Laboratory,
Carnegie Institution of Washington, Washington, D.C. 20015*

Received September 12, 2004

High-resolution X-ray photoelectron spectroscopy was used to demonstrate that reduction of aqueous U^{6+} at ferrous mica surfaces at 25 °C preserves U^{5+} as the dominant sorbed species over a broad range of solution compositions. Polymerization of sorbed U^{5+} with sorbed U^{6+} and U^{4+} is identified as a possible mechanism for how mineral surfaces circumvent the rapid disproportionation of aqueous U^{5+}. The general nature of this mechanism suggests that U^{5+} could play an important, but previously unidentified, role in the low-temperature chemistry of uranium in reducing, heterogeneous aqueous systems.

Chemical processes at mineral−water and bacteria−water interfaces play a major role in the dissolution, precipitation, and sorption of heavy metals, such as uranium. In particular, both mineral surfaces and bacteria catalyze the slow reduction kinetics of U^{6+} in low-temperature aqueous systems.[1−8] Bacterial[1,2] and abiotic heterogeneous[3−8] reduction pathways have been intensively studied due to the vastly different solubility of hexavalent and tetravalent uranium. In all of these studies, the oxidation state of uranium was identified as U^{4+} and/or U^{6+}. Yet, the reduction of U^{6+} to U^{4+} is a two electron transfer process and it is likely that U^{5+} has some finite lifetime that depends, in part, on the reducing agent. Studies have discovered naturally occurring U^{5+},[9−11] but reports are rare and the conditions for its formation are not clear. As we shall discuss later, the lack of recognition of U^{5+} in aqueous systems could be real or a function of sampling bias, analytical difficulties, and the belief that U^{5+} is not stable. This latter predisposition concerning the stability of U^{5+} can be traced to the pioneering work on actinide chemistry performed under the aegis of the Manhattan Project which established the existence of U^{5+} in solution as UO_2^{+}, calculated the formal potential between UO_2^{+}, UO_2^{2+}, and U^{4+}(s), and discovered only a narrow stability field in water for U^{5+} between pH 2 and 4.[12−17] Outside this small stability field, extremely rapid disproportionation rendered solutions of U^{5+} difficult to maintain and impossible to study. These fundamental observations on the instability of U^{5+}, for solutions relevant to natural systems, have remained unchallenged.[18] However, because abiotic reduction of U^{6+} is catalyzed at mineral surfaces, the behavior of aqueous U^{5+} may not be relevant for reduction mechanisms at low temperatures. Indeed, although aqueous U^{5+} is unstable, numerous compounds containing U^{5+}, synthesized with solid-state methods at high temperature and controlled oxygen fugacities, show some remnant stability at ambient conditions.[9,19−22] Further, there is evidence[23] for U^{5+} in U_4O_9, a

---

* To whom correspondence should be addressed. E-mail: Eugene.Ilton@pnl.gov.

† Pacific Northwest National Laboratory.

‡ Shell Global Solutions International.

§ George Washington University and Carnegie Institution of Washington.

(1) Suzuki, Y.; Kelly, S. D.; Kemner, K. M.; Banfield, J. F. *Nature* **2002**, *419*, 134.
(2) Lovely, D. R.; Phillips, E. J. P.; Gorby, Y. A.; Landa, E. R. *Nature* **1991**, *350*, 413.
(3) Wersin, P.; Hochella, M. F., Jr.; Person, P.; Redden, G.; Leckie, J. O.; Harris, D. W. *Geochim. Cosmochim. Acta* **1994**, *58*, 2829−2843.
(4) Fiedor, J. N.; Bostic, W. D.; Jarabek, R. J.; Farrell, J. *Environ. Sci. Technol.* **1998**, *32*, 1466−1473.
(5) Liger, E.; Charlet, L.; Capellen, P. V. *Geochim. Cosmochim. Acta* **1999**, *63*, 2939−2955.
(6) Missana, T.; Maffiotte, C.; Garcia-Gutierrez, M. *J. Colloid Interface Sci.* **2003**, *261*, 154−160.
(7) Ilton, E. S.; Haiduc, A.; Moses, C. O.; Heald, S. M.; Elbert, D.; Veblen, D. R. *Geochim. Cosmochim. Acta* **2004**, *68*, 2417−2435.
(8) O'Loughlin, E. J.; Kelly, S. D.; Cook, R. R.; Csencsits, R.; Kemner, K. M. *Environ. Sci. Technol.* **2003**, *37*, 721−727.
(9) Burns, P. C.; Finch, J. F. *Am. Mineral.* **1999**, *84*, 1456−1460.
(10) Vance, E. R.; Mackey, D. J. *J. Phys. C: Solid State Phys.* **1974**, *7*, 1898−1908.
(11) Teterin, Y. A.; Utkin., I. O.; Melnikov, I. E.; Lebedev, A. M.; Teterin, A. Y.; Ivanov, K. E.; Nikitin, A. S.; Vukchevich, L. *J. Struct. Chem.* **2000**, *41*, 965−971.
(12) Heal, H. G. *Trans. Faraday Soc.* **1949**, *45*, 1−11.
(13) Heal, H. G.; Thomas, J. G. N. *Trans. Faraday Soc.* **1949**, *45*, 11−20.
(14) Nelson, F.; Kraus, K. A. *J. Am. Chem. Soc.* **1951**, *73*, 2157−2161.
(15) Kern, D. M. H.; Orlemann, E. F. *J. Am. Chem. Soc.* **1949**, *71*, 2102−2106.
(16) Kritchevsky, E. S.; Hindman, J. C. *J. Am. Chem. Soc.* **1949**, *71*, 2096−2102.
(17) Harris, W. E.; Kolthoff, I. M. *J. Am. Chem. Soc.* **1945**, *67*, 1484−1490.
(18) Grenthe, I.; Fuger, J.; Konings, R. J. M.; LeMire, R. J.; Muller, A. B.; Nguyen T. C.; Wanner, H. *Chemical Thermodynamics of Uranium*; North-Holland, Elsevier Science Publishers: Amsterdam, The Netherlands, 1992.

10.1021/ic0487272 CCC: $30.25

mixed valence U-oxide associated with oxidation of UO_2. Here, we demonstrate that heterogeneous reduction of aqueous U^{6+} at ferrous mica surfaces yields sorbed U^{5+} over a broad range of pH and ionic strength at 25 °C. The work is focused on micas because they are common minerals and one of the largest reservoirs of ferrous iron, a known U^{6+} reductant, in the Earth's crust.

Macroscopic single crystals of annite, the near-end member ferrous trioctahedral mica, were reacted at 25 °C with argon-sparged aqueous solutions containing 5 μM U^{6+} and variable NaCl, from pH 4.5 to 9.5. XPS spectra of the U4f level for U sorbed on annite edge orientations were fit with three components representing U^{6+}, U^{5+}, and U^{4+}. XPS yields information on the chemical state and composition of solid surfaces, where most of the signal was integrated over the top 80 Å of our sample.[7] The valence of U can be determined from the binding energies (BEs) and satellite structures associated with the $4f_{7/2}$ and $4f_{5/2}$ levels, and the 5f intensity.[7,19,20,23] Ilton et al.[7] did demonstrate that structural Fe(II) in micas can reduce sorbed U^{6+}, but modeled the $4f_{7/2}$ primary peak with only 2 components (assumed to be U^{4+} and U^{6+}). Good fits across a wide range of average U oxidation states were only possible by not including the satellite structure in the fitting and by allowing wide variations in both the full-width-at-half-maximum (fwhm) and BE separation of the component peaks. Here, we explicitly include the satellite structure and 3 components in fitting the spectra. Schoepite, $H_3O[(UO_2)O(OH)]$, and uraninite, UO_2, were used to derive peak parameters for the U^{6+} and U^{4+} components. The U^{5+} component was derived by fitting a (U^{5+}-U^{6+}) oxyhydroxide, synthesized hydrothermally,[24] with the U^{6+} component and solving for the U^{5+} peak parameters (Figure 1). The fwhm of the U^{6+} and U^{5+} primary peaks were set equal to each other; no other constraints were imposed on the U^{5+} component. The resulting best fit yielded a 1.04 eV separation between the U^{6+} and U^{5+} primary peaks, and 8.4 and 3.7 eV separations between the satellite and primary peaks for U^{5+} and U^{6+}, respectively (Figure 1), in agreement with the XPS of other $U^{5+}-U^{6+}$ compounds.[19,20,23] For greater detail on methods, see Supporting Information.

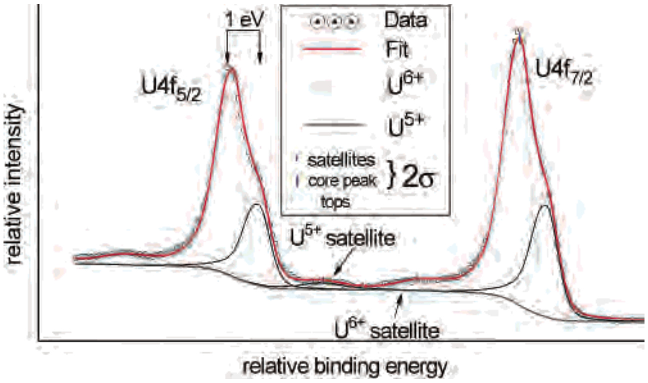

Figure 1. U4f XPS of synthetic $U^{5+}-U^{6+}$ oxyhydroxide.[24] The primary peak components are separated by 1.04 eV. Satellites for U^{5+} and U^{6+} are marked by arrows. The U^{6+} component is from schoepite, $UO_3 \cdot 3(H_2O)$, whereas the U^{5+} component is derived from the fitting procedure.

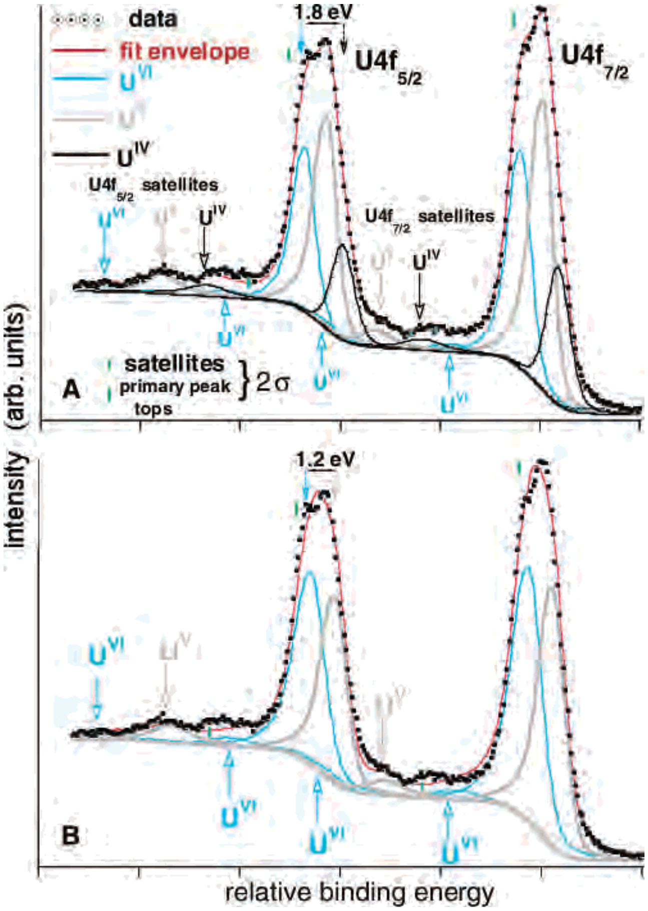

Figure 2. U4f XPS of annite edge orientations reacted with 5 μM U^{6+}_{aq} at pH 9.5 and 25 mM NaCl for 3 h. (A) Spectrum is modeled with U^{6+}, U^{5+}, and U^{4+} components with fwhms of 1.38 eV. The primary component peaks are separated by 1.8, 1.0, and 0.8 eV for $U^{6+}-U^{4+}$, $U^{6+}-U^{5+}$, and $U^{4+}-U^{5+}$, respectively. (B) Same spectrum modeled with only 2 components ($U^{6+}-U^{5+}$). Note that the fwhm of the primary component peaks broaden to 1.8 eV and that the 2 component model fails to reproduce the structure of the satellite and primary peaks.

Fitting the XPS of annite reacted with aqueous U^{6+} shows the need to consider 3 components with U^{6+}, U^{5+}, and U^{4+} characteristics (Figure 2). For example, Figure 2a shows that the primary peaks and satellite features are well fit with 3 components, where primary peak BEs are at 382.1, 381.0, and 380.3 (0.2 eV) for U^{6+}, U^{5+}, and U^{4+} (referenced to C1s at 285 eV), respectively. Both absolute and relative BEs for the primary component peaks are in agreement with literature values for mixed-valent and monovalent $U^{6+}-U^{5+}-U^{4+}$ compounds.[7,19,20,23] In contrast, the use of only 2 components (regardless of which 2) failed to model the satellites and the fine structure of the primary peaks (Figure 2b), despite letting component fwhms broaden by 30% relative to the 3 component model. In sum, only the 3

---

(19) Bera, S.; Sali, S. K.; Sampath, S.; Narasimhan, S. V.; Venugopal, V. *J. Nucl. Mater.* **1998**, *255*, 26−33.

(20) Van den Berghe, S.; Laval, J.-P.; Gaudreau, B.; Terryn, H.; Verwerft, M. *J. Nucl. Mater.* **2000**, *277*, 28−36.

(21) Fortner, J. A.; Kropf, A. J.; Finch, R. J.; Bakel, A. J.; Hash, M. C.; Chamberlain, D. B. *J. Nucl. Mater.* **2002**, *304*, 56−62.

(22) Finnie, K. S.; Zhang, Z.; Vance, E. R.; Carter, M. L. *J. Nucl. Mater.* **2003**, *317*, 46−53.

(23) Allen, G. C.; Holmes, N. R. *Can. J. Appl. Spectrosc.* **1993**, *28*, 125−130.

(24) Cahill, C. L.; Danek, J. 226th National Meeting of the American Chemical Society, New York, NY, Sept 7−11, 2003; INOR-219

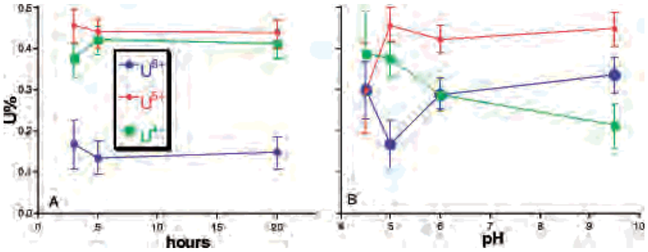

Figure 3. %U, U^{n+}/U(total), for U sorbed to mica edge orientations. Mole fraction valence states as a function of (A) time at pH 5 and 25 mM NaCl and (B) pH at 25 mM NaCl and 3 h. U valences were determined by XPS. Larger error at pH 4.5 is due to lower U sorption density.

component model can coherently fit primary and satellite peaks across a broad range of average U oxidation states.

A timed sequence of experiments at pH 5 and 25 mM NaCl showed that the relative proportion of sorbed U valence states is constant from 3 to 20 h (Figure 3a). U^{5+} (within error of U^{4+}) is the dominant valence state and appears to be stable at least up to 20 h of reaction time. Further, limited data at a 3 h time slice shows that U^{5+} is the dominant sorbed species from pH 5 to 9.5 (Figure 3b). Experiments at low ionic strength (no added alkali cation) record 25−35% U^{5+} from 1 to 20 h at pH 5 and from pH 4.5 to 9.5 at 3 h. Interestingly, both the high and low ionic strength experiments record a systematic decrease in %U^{4+} with increasing pH. The only qualitative difference is that the average U oxidation state is much higher in the low ionic strength experiments such that $U^{6+} > U^{5+} > U^{4+}$. In fact, measurable %U^{4+} goes to zero at pH 6−9.5 and no added NaCl. For a discussion on the effect of aqueous Na^+ on electron transfer at mica surfaces, see Ilton et al.[7]

The salient result requiring explanation is that U^{5+} is being preserved on mica surfaces, in some cases as the dominant U species, despite its well-known instability in solutions at pH values greater than 4. In fact, the founding experiments[12−17] and all subsequent work indicate that the concentration of aqueous U^{5+} at the experimental conditions is near zero. A clue to how this paradox can be resolved comes from solution chemistry, which indicates that formation of $U^{5+}-U^{6+}$ dimers at high concentrations of U^{6+} (>1 mM) can slow U^{5+} disproportionation.[25] Whereas sufficiently high concentrations of aqueous U^{6+} are rarely reached in nature or utilized in laboratory experiments (e.g., this study employed only 5 μM U^{6+}), locally high concentrations of U^{6+} and U^{4+} on mineral surfaces could induce polymerization and $U^{4+}-U^{5+}-U^{6+}$ linkages. In fact, polymerization is likely in some cases, given calculated U surface densities,[7] and has been observed for a subset of these samples by TEM.[7] In general, surface promoted polymerization is an increasingly documented phenomenon in undersaturated solutions.[26] Hence, heterogeneous reduction of sorbed U^{6+} to sorbed U^{5+} suggests a mechanism for preserving U^{5+} by circumventing the rapid disproportionation of aqueous U^{5+}: polymerization of U^{5+} with U^{6+}, and possibly U^{4+}, on a surface might interfere with disproportionation by limiting the direct interaction of U^{5+} species or inducing a metastable state. Sorption itself, possibly both to edge sites and in the hydrated near-surface interlayer region, might have the same effect. Although there are no studies of U^{5+} sorption, Np^{5+} (a U^{5+} analogue) is strongly sorbed by ferrihydrate at pH greater than 5, and by other oxides above circumneutral pH.[27] Spectroscopic evidence indicates that Np^{5+} forms inner-sphere sorption complexes, which is consistent with its sorption behavior.[28] However, the XPS measurements neither distinguish between the importance of sorption versus polymerization, nor between different possible sorption sites.

Consequently, heterogeneous reduction pathways coupled with surface induced polymerization of $U^{6+}-U^{5+}-U^{4+}$ and sorption on mineral surfaces could extend the significance of U^{5+} in natural and experimental systems. Still, until recently, the only reported evidence for naturally occurring U^{5+} was as a minor constituent in zircon[10] and possibly on the surface of coffinite, a U^{4+}-silicate.[11] The recent discovery of the first pentavalent mineral, wyartite, is instructive: wyartite (and by analogy U^{5+} in general) might only appear to be rare because it oxidizes to schoepite in air.[9] The corollary is that naturally occurring U^{5+} is under-reported, either because of sampling issues or a lack of rigorous analysis.

We have provided evidence for the stabilization of surface-bound U^{5+} during heterogeneous reduction of U^{6+} by ferrous micas in aqueous solutions from pH 4.5 to 9.5 at 25 °C. The results are surprising because aqueous U^{5+} rapidly disproportionates under these conditions. We propose that sorption itself or polymerization with co-sorbed U^{6+} and U^{4+} circumvents the instability and fast disproportionation of aqueous U^{5+}. Although the experiments were specifically performed with ferrous mica, we suggest that this reduction pathway might extend to other minerals and reductants. If so, U^{5+} is potentially underassessed in both heterogeneous experimental and natural systems. Further work, encompassing other minerals and more complex solution chemistry, including aqueous carbonate, is required to explore this hypothesis.

Acknowledgment. J. Rustad, E. Buck, K. Rosso and three anonymous referees provided insightful comments. Funding was from the Office of BES, Chemical Science Division, Geosciences Program (to E.S.I.); and from the NSF (DMR-0348982; CAREER Award) (to C.L.C.). A portion of this research was performed in the EMSL, a national user facility, located at PNNL.

Supporting Information Available: Additional experimental procedures and curve fitting methodology. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0487272

---

(25) Newton, T. W.; Baker, F. B. A. *Inorg. Chem.* **1965**, *4*, 1166−1170.
(26) Brown, G. E., Jr.; Henrich, V. E.; Casey, W. H.; Clark, D. L.; Eggleston, C.; Felmy, A.; Goodman, D. W.; Grätzel, M.; Maciel, G.; McCarthy, M. I.; Nealson, K. H.; Sverjensky, D. A.; Toney, M. F.; Zachara, J. M. *Chem. Rev.* **1999**, *99*, 77−174.
(27) Wang, P.; Anderko, A.; Turner, D. R. *Ind. Eng. Chem. Res.* **2001**, *40*, 4428−4443.
(28) Combes, J. M.; Chisholm-Brause, C. J.; Brown, G. E.; Parks, G. A.; Conradson, S. D.; Eller, P. G.; Triay, I. R.; Hobart, D. E.; Miejer, A. *Environ. Sci. Technol.* **1992**, *26*, 376−382.