Supporting Information for

U(VI) Sorption and Reduction by Fe(II) Sorbed on Montmorillonite

(Total number of pages for SI: 6)

SUDIPTA CHAKRABORTY, [$,∞,*] FABIENNE F. BOIVIN, [$,†] DIPANJAN BANERJEE, [§]

ANDREAS C. SCHEINOST, [§] MARTINE MULLET, [#] JEAN-JACQUES EHRHARDT, [#]

JOCELYNE BRENDLE, [‡] LOÏC VIDAL, [‡] AND LAURENT CHARLET [$]

[$]LGIT-OSUG, University of Grenoble-I, Grenoble, France

[§]Institute of Radiochemistry, FZD, Dresden, Germany

[#]LCPME, Université Henri Poincaré Nancy 1, France

[‡] Institut de Science des Matériaux de Mulhouse, LRC CNRS 7228, Université de Haute Alsace, Mulhouse, France

[∞]Department of Chemistry, Kanchrapara College, Kanchrapara 743145, West Bengal, India

[†]Ecole d'ingénieurs et d'architectes de Fribourg, HES-SO, CH-1705, Fribourg

* CORRESPONDING AUTHOR

Phone: +91 33 2585 8790; fax: +91 33 2826 3164; e-mail: chakrabortysudipta@hotmail.com

S1. Kinetic redox experiments

Fe(II)–U(VI) redox kinetics in the presence of 4.5 gL^{-1} MONT was studied in a closed reactor at room temperature with 0.05M $CaCl_2$ background electrolyte to minimize the exchange of interlayer cation by Fe(II) (*1*). The pH and Eh of the suspension were monitored in the suspension with a glass electrode and platinum electrode respectively both linked to a pH meter (Metrohm 781 pH/Ion Meter). The clay stock suspension was added to 0.05 M $CaCl_2$ ionic background solution and equilibrated overnight in a 350 ml glass reactor (with three neck, two for pH and Eh electrodes insertion and one for stock solution/suspension addition) wrapped with aluminium foil. Subsequently 0.7 mM Fe(II) solution was added and equilibrated for 72 h either at pH 6.2, 7.5 or 8.5 before addition of U(VI). Preliminary results (data not shown) on Fe(II) sorption do not show any difference between 3 days (in present study) and one week (*2*) equilibration with MONT prior to U(VI) addition. At time zero an aliquot of U(VI) stock solution was added to obtain an initial solution concentration of 0.04 mM and pH was readjusted. Given the reaction periods, a 10 ml sample of suspension was filtered through a 0.22-µm membrane filter syringe and analyzed for total Fe (Fe_T) and total U (U_T) concentrations in the filtrates. After filtration, the wet pastes were mounted into Teflon sample holders (SH01B) and sealed with Kapton tape for XAS measurements, immediately shock-frozen and transported in a Dewar filled with liquid N_2. At the beamline, samples were transferred within 2 min from the Dewar to closed-cycle He cryostat and cooled to 15 K within less than 20 min. At the XPS facility, the samples (as wet pastes) were transferred within 1 min from the Dewar to the vacuum chamber. The control sample (without Fe) containing clay and U(VI) was prepared at pH 5.9 in 50 ml vials by batch method (Table 1).

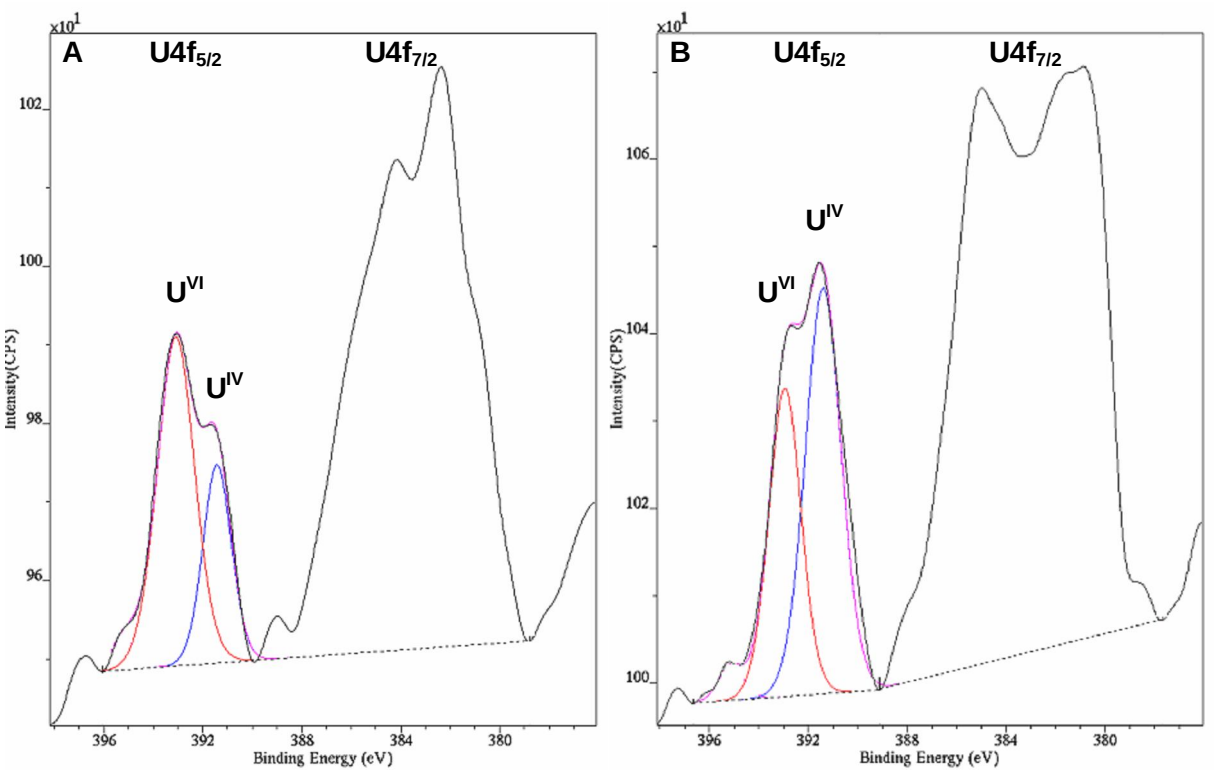

FIGURE S2.U4f XPS spectra of samples UF1 (A) and UF3 (B) recorded from kinetic experiment of U(VI) sorption onto MONT in presence of Fe(II) at initial pH 7.5.

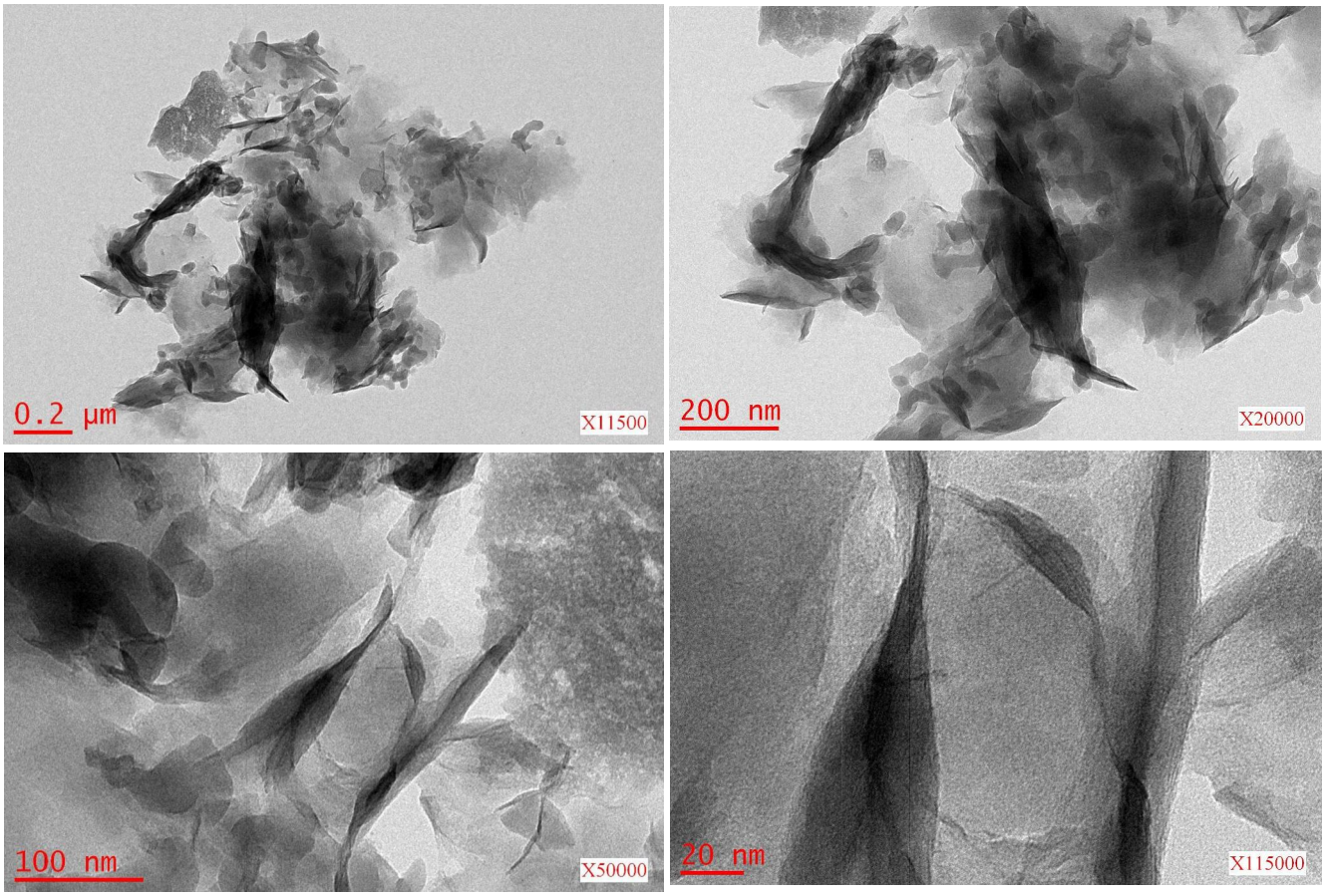

FIGURE S3. TEM micrographs of sample UF3 at different magnifications showing no formation/precipitation of mixed valence solids U_3O_8/β-U_3O_7/U_4O_9.

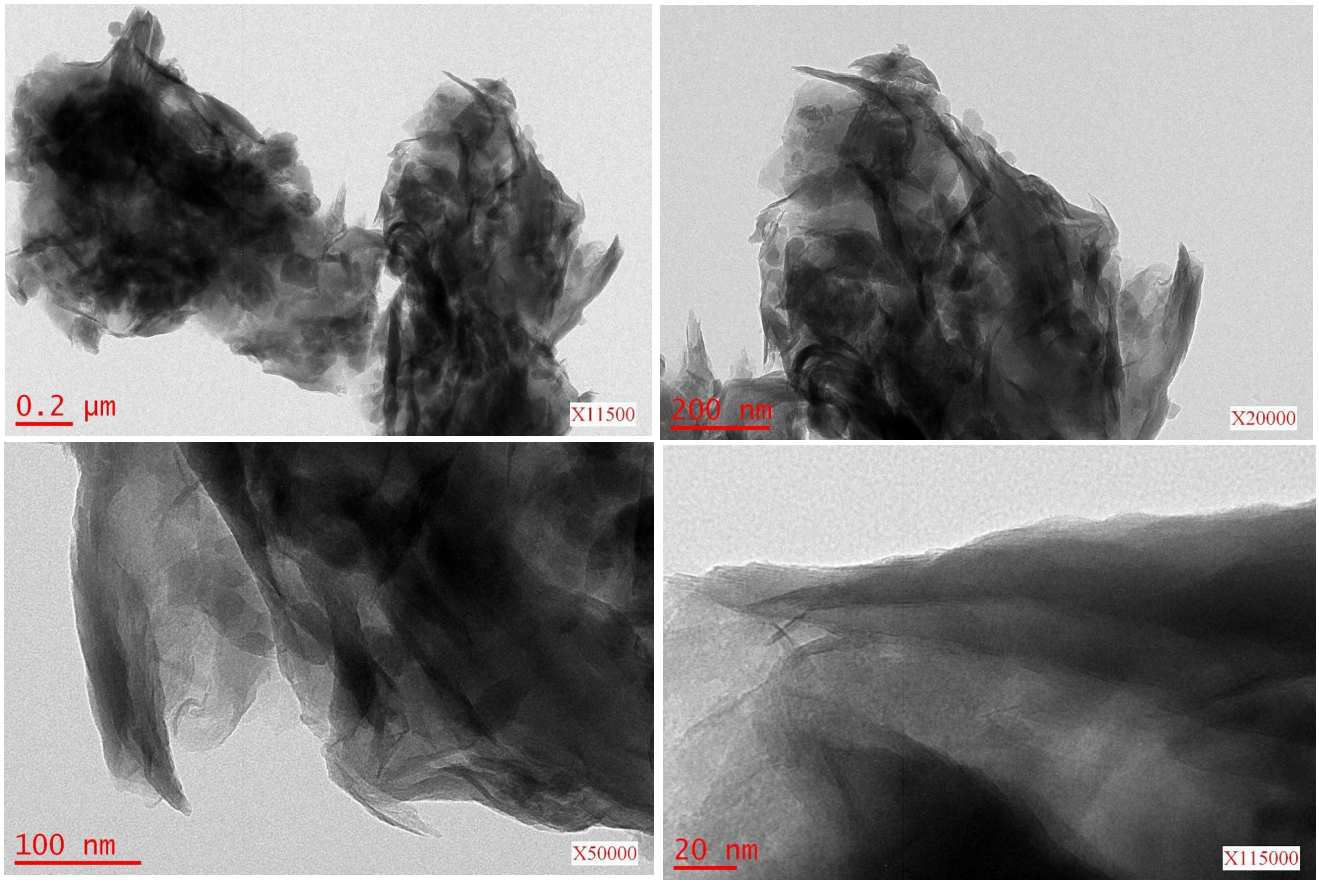

FIGURE S4. TEM micrographs of sample U3 at different magnifications showing no uranium bearing solid phase formation.

S5. Literature cited

(1) Charlet, L.; Tournassat, C. Fe(II)–Na(I)–Ca(II) cation exchange on montmorillonite in chloride medium; evidence for preferential clay adsorption of chloride–metal ion pairs in seawater. *Aquat. Geochem.* **2005**, *11*, 115–137.

(2) Charlet, L.; Scheinost, A. C.; Tournassat, C.; Greneche, J. M.; Géhin, A.; Fernández-Martínez, A.; Coudert, S.; Tisserand, D.; Brendle, J. Electron transfer at the mineral/water interface: selenium reduction by ferrous iron sorbed on clay. *Geochim. Cosmochim. Acta* **2007**, *71*, 5731-5749.