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**Assessing the reactivity of Fe(II) sorbed on smectite clays:  
U(VI) reduction**

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21

22 **ABSTRACT**

23 The reactivity of Fe(II) sorbed on three Ca-exchanged smectite clays was probed via U(VI)  
24 reduction at pH 6.0 ( $\pm 0.2$ ) under CO<sub>2</sub>-free, anoxic (O<sub>2</sub> <1 ppmv) condition. The clays varied  
25 with regard to structural Fe content from Fe-free (0 wt.%) montmorillonite (MONT), to Fe-poor  
26 (2.6 wt.%) montmorillonite (Fe-MONT), to Fe-rich (25.8 wt.%) nontronite (NAu-2). The U L<sub>III</sub>-  
27 edge XANES spectra showed no reduction of U(VI) in presence of Fe(II) sorbed on either Fe-  
28 MONT or NAu-2 after 72 h but a partial reduction (21%) on MONT after 24 h. U L<sub>III</sub>-edge  
29 EXAFS spectra further showed the formation of a soddyite-like surface precipitate on MONT in  
30 presence of sorbed Fe(II) after 72 h. The Mössbauer data further reveals that 10 ( $\pm 2$ ) % of the  
31 total sorbed Fe(II) was oxidized in presence of MONT before and an additional 6 ( $\pm 2$ ) % after  
32 addition of U(VI). The mechanism of U(VI) reduction involves Fe(II) specifically sorbed on  
33 oxidized and reduced strong edge sites of MONT. The non-reactivity of Fe(II) sorbed on Fe-  
34 MONT and NAu-2 towards U(VI) reduction is likely linked to the inter-valence charge transfer  
35 (IVCT) between surface Fe(II) and structural Fe(III). The present study demonstrates that the  
36 reduction capacity of Fe bound to the surface depends strongly on the nature of clay and  
37 correspondingly on the oxidation state of the sorbed Fe. Thus Fe(II) sorbed clay cannot be  
38 always considered as “universal reductant” for U(VI).

39

40

41 BRIEF: Clay catalyzed redox processes between aqueous U(VI) and surface bound Fe(II).

## 42 **Introduction**

43 The mobility and transport of hexavalent uranium, U(VI) in presence of clay have been studied  
44 for many years as possible remediation options in areas contaminated by uranium as well as for  
45 the evaluation of the performance of highly radioactive nuclear wastes (HLNW) repositories. As  
46 Fe(II) is common in both environments, the possible reduction of U(VI) to U(IV) and a  
47 comprehensive understanding of the Fe(II)-U(VI)-clay ternary system is necessary to mitigate  
48 the future possible risk in an anoxic uranium-polluted subsurface and to ensure long term  
49 stability of uranium at underground waste disposal sites.

50 Montmorillonite and nontronite are members of the smectite sub-group clay with structures  
51 similar to 2:1 phyllosilicates and are known to sorb Fe(II) and U(VI) present in solution. The  
52 mechanisms of U(VI) sorption on montmorillonite have been extensively investigated using  
53 surface complexation modeling,<sup>1-6</sup> spectroscopic analysis and molecular dynamics simulation  
54 methods,<sup>7-14</sup> while the information available on the nontronite system is limited.<sup>15-17</sup> Surface-  
55 bound Fe(II) commonly behaves as stronger reductant than corresponding aqueous species in  
56 both biotic and abiotic pathways, and therefore can transform organic (nitroaromatic explosives,  
57 pesticides and polyhalogenated solvents) and inorganic (Cr, Tc, Se, U) pollutants into nontoxic  
58 forms.<sup>18-20</sup>

59 The sorption of Fe(II) on montmorillonite has been well documented.<sup>21-23</sup> The sorption affinity  
60 of pH-dependent montmorillonite makes it possible to distinguish three types of edge sites: weak  
61 sites, oxidized strong sites and reduced strong sites. Strong “oxidized” sites refer to those that are  
62 linked with heterogeneous surface oxidation of Fe(II), while on strong “reduced” and weak sites  
63 only sorption takes place.<sup>21,23</sup> The sorption of Fe(II) on iron-rich nontronite (NAu-1 & NAu-2)  
64 has been studied in detail by Tsarev et al.<sup>15</sup> and Jaisi et al.<sup>24</sup>. In addition to pH dependence, both

65 montmorillonite and nontronite undergo heterogeneous surface oxidation of sorbed Fe(II) via  
66 different mechanisms. In montmorillonite, surface oxidation of Fe(II) may result in the formation  
67 of ferric hydroxide and lepidocrocite at lower and higher pH respectively<sup>25</sup> which, however,  
68 coupled to catalyze the reduction of U(VI),<sup>15,25</sup> Se(IV),<sup>19</sup> 4-chloronitrobenzene.<sup>26,27</sup> In the case of  
69 surface oxidation of Fe(II) on structural Fe(III)-bearing smectites, Fe(III)-montmorillonite and  
70 nontronite have a unique characteristic known as inter-valence charge transfer (ICVT) between  
71 sorbed Fe(II) and structural Fe(III). It has been proposed that Fe(III), which exists in clay  
72 tetrahedral (nontronite) and/or octahedral (montmorillonite) sites participates in the electron  
73 transfer reaction by a charge-shuttling process for redox mediation and catalysis or by edge and  
74 basal sites. Therefore, various secondary mineral phases like green rust, ferrihydrite,  
75 lepidocrocite and magnetite may be formed as oxidation products.<sup>28-31</sup> The reactivity of sorbed  
76 Fe(II) on structural Fe(III) bearing clays has been shown to vary in different cases. Jones et al.<sup>27</sup>  
77 observed a significant decrease of reactivity of Fe(II) sorbed on nontronite after 18 days in  
78 reduction of 4-chloronitrobenzene. Tsarev et al.<sup>15</sup> observed a partial reduction of U(VI) by Fe(II)  
79 sorbed on nontronite (NAu-1 and NAu-2) in presence of CO<sub>2</sub> while a partial oxidation of As(III)  
80 to As(V) was reported by Ilgen et al.<sup>32</sup>

81 Our previous study<sup>25</sup> has addressed the pH dependent abiotic reduction of U(VI) by Ca-  
82 exchanged montmorillonite (Fe-free, MONT) in the presence of Fe(II) and reported the  
83 formation of monomeric U(IV) as the most plausible sorbed reaction product rather than the  
84 commonly observed uraninite (UO<sub>2</sub>). By combining U and Fe speciation (following XANES and  
85 Mössbauer analyses) in this study, we suggest an U(VI) reduction mechanism by considering  
86 specific site sorption of Fe(II) on MONT. The Fe(II) reactivity related to the surface of Fe-poor  
87 montmorillonite (2.6 wt.% Fe-MONT) and nontronite (25.6% NAu-2) was compared to that of

88 Fe-free montmorillonite (0 wt.% MONT) probing U(VI) as a redox sensitive species under  
89 similar experimental conditions. All the experiments were performed in a CO<sub>2</sub>-free atmosphere  
90 to compare our results with those obtained in presence of CO<sub>2</sub> by Tsarev et al.<sup>15</sup> and also to  
91 exclude the effect of carbonate on uranium mobilization. The anoxic (O<sub>2</sub>-free) condition should  
92 preserve the oxidation state of ferrous iron and prevent the re-oxidation of reduced uranium  
93 species. A high ionic strength (0.05M CaCl<sub>2</sub>) was used to exclude Fe(II) sorption at cation  
94 exchange sites, and thus to take into account only for the reactivity of Fe(II) sorbed specifically  
95 in the reduction process.

96

## 97 **Materials and Methods**

### 98 **Chemicals**

99 All the solutions were prepared with boiled, argon (99.9992%) purged Millipore Milli-Q water.  
100 NaOH and HCl stock solutions were made from Titrisol ampoules. The Fe(II) stock solutions  
101 were freshly prepared from analytical grade FeCl<sub>2</sub> · 4H<sub>2</sub>O (Fluka Chemica), after transferring the  
102 required amount to a glove box (JACOMEX) under N<sub>2</sub> atmosphere (CO<sub>2</sub>, O<sub>2</sub> <1 ppmv),  
103 dissolved in deoxygenated water (dissolved O<sub>2</sub> <1 mgL<sup>-1</sup>) and acidified with 0.1 M HCl to pH <2  
104 to avoid oxidation.<sup>33</sup> <sup>57</sup>Fe(II) stock solutions were prepared by dissolving ~100 mg <sup>57</sup>Fe(0) in  
105 concentrated HCl at 100 °C and subsequent dilution with deoxygenated water in glove box.  
106 U(VI) solutions were prepared from 1000 mgL<sup>-1</sup> UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O (Alfa Aesar) standard  
107 solution.

### 108 **Clay minerals**

109 The synthetic Fe-free montmorillonite (MONT) ( $\text{Na}_{0.30}[(\text{Al}_{1.70}\text{Mg}_{0.30})\text{Si}_4\text{O}_{10}(\text{OH},\text{F})_2]_n\text{H}_2\text{O}$ ) was  
110 identical to that used in previous studies.<sup>19,21,25</sup> The synthetic structural Fe(III) bearing  
111 montmorillonite (Fe-MONT, 2.6 wt.% Fe) has the representative chemical formula,  $\text{Na}_{0.66}(\text{Si}_{8.0})$   
112  $(\text{Al}_{3.00}\text{Mg}_{0.66}\text{Fe}_{0.34}^{\text{III}})$ . The natural iron-rich nontronite (NAu-2, 25.8 wt.% Fe) [ $\text{Na}_{0.72}(\text{Si}_{7.55}\text{Al}_{0.50}$   
113  $\text{Fe}_{0.29}^{\text{III}})(\text{Mg}_{0.05}\text{Fe}_{3.54}^{\text{III}})$ ] was obtained from the Source Clay Minerals Repository, South  
114 Australia.<sup>34</sup> Approximately 1% calcite impurities in this clay was removed by using Na-  
115 acetate/acetic acid solution (pH 5) verified by XRD (not shown). All three clays in their Ca-  
116 exchanged forms were obtained by repeated saturation with 0.05 M aqueous solution of  $\text{CaCl}_2$   
117 and clay suspensions were then extensively argon-purged and transferred to the glove box.

#### 118 **Preparation of Fe(II) sorbed smectites**

119 To evaluate the reactivity of sorbed Fe(II) on smectites, three clay suspensions ( $10.6 \pm 0.2 \text{ gL}^{-1}$ )  
120 were reacted with  $1.2 \pm 0.2 \text{ mM}$  Fe(II) at  $\text{pH } 6.0 \pm 0.2$  for 72 h before U(VI) addition. The  
121 Mössbauer samples were prepared in a similar way using  $^{57}\text{Fe}(\text{II})$ . The experimental conditions  
122 are given in Table 1.

#### 123 **Kinetic redox experiments**

124 Fe(II)–U(VI) redox kinetic experiments in the presence of three Ca-exchanged smectite clays  
125 (MONT, Fe-MONT and NAu-2) were carried out in a closed reactor at room temperature ( $24 \pm 1$   
126  $^\circ\text{C}$ ) with 0.05 M  $\text{CaCl}_2$  ionic background as described in our previous study for MONT.<sup>25</sup> The  
127 control samples (without Fe) containing clay and U(VI) was prepared in 50 ml vials by batch  
128 method (Table 1).

129

#### 130 **$^{57}\text{Fe}$ Mössbauer spectrometry**



131  $^{57}\text{Fe}$  Mössbauer experiments were performed at 77K in transmission geometry with a 925 MBq  
132  $\gamma$ -source of  $^{57}\text{Co}/\text{Rh}$  mounted on a conventional constant acceleration drive. The samples  
133 containing about 5 mg  $\text{Fe}\cdot\text{cm}^{-2}$  were prepared and sealed in a glove box, and then transferred in a  
134 bath cryostay. The hyperfine structures were fitted using the MOSFIT program<sup>35</sup> involving  
135 quadrupolar components with lorentzian lines; the isomer shift values are referred to that of  $\alpha\text{-Fe}$   
136 at RT. The velocity of the source was calibrated using  $\alpha\text{-Fe}$  as the standard at RT.

### 137 **X-ray absorption spectroscopy**

138 X-ray Absorption Near-Edge Structure (XANES) and Extended X-ray Absorption Fine-  
139 Structure (EXAFS) spectra were collected at the Rossendorf Beamline at the European  
140 Synchrotron Radiation Facility (ESRF, Grenoble, France). The energy of the X-ray beam was  
141 tuned by a doubled crystal monochromator operating in pseudo channel-cut mode using a  
142 Si(111) crystal pair. Two platinum-coated Si mirrors before and after the monochromator were  
143 used to collimate the beam into the monochromator and to reject higher harmonics. Uranium  $L_{\text{III}}$ -  
144 edge spectra were collected in fluorescence mode using a 13-element high purity germanium  
145 detector (Canberra) together with a digital signal processing unit (XIA Xmap). Spectra were  
146 collected at 15K using a closed cycle He cryostat with a large fluorescence exit window  
147 (CryoVac). The energy was calibrated using the maximum of the first derivative of the yttrium  
148 K-edge (17038 eV). Between eight and ten scans were recorded for each sample. Dead time  
149 correction of the fluorescence signal, energy calibration and averaging of the individual scans  
150 were performed with the software package SixPack.<sup>36</sup> Normalization, transformation from  
151 energy into k space, subtraction of a spline background was performed with WinXAS using  
152 routine procedures.<sup>37</sup> Statistical analyses of XANES and EXAFS spectra was performed by  
153 Iterative Target-test Factor Analysis (ITFA) using the ITFA software package.<sup>38-40</sup>

154

## 155 **Results and Discussion**

### 156 **Sorption of Fe(II) and U(VI) on clays**

157 The experimental conditions with results from wet chemical analyses are shown in Table 1.  
158 Among three clays, NAu-2 has the highest affinity for Fe(II) sorption followed by Fe-MONT  
159 and MONT (Figure 1). The sorption of Fe(II) at pH 6 is attributed to cation exchange as well as  
160 site-specific sorption to clay edge sites.<sup>21,26</sup> In the absence of Fe(II), the extent of U(VI) sorption  
161 is less on Fe-MONT than MONT or Nau-2. The kinetic experiments (Fig. 1A & 1B) show a fast  
162 uptake of >80% of U(VI) from solution by the three clays with sorbed Fe(II) within 1 hr. The  
163 EXAFS results identified surface precipitation of soddyite-like phase only on MONT with  
164 sorbed Fe(II) after 72 h, a precipitate which was not observed for Fe-MONT and NAu-2. The  
165 removal of aqueous U(VI) by Fe(II) sorbed on MONT is therefore attributed primarily to a fast  
166 sorption of U(VI), followed by a slow precipitation of soddyite-like phases probably favored by  
167 dissolution of clay which will be discussed in the next section. In Fe(II) sorption experiment on  
168 NAu-2, a visible color change is observed from brown to pale green clearly different from  
169 commonly observed the deep green color of dithionite reduced NAu-2 (Figure S1 in supporting  
170 information). This color change is attributed to inter-valence charge transfer (IVCT) between  
171 sorbed Fe(II) and structural Fe(III) reported by other investigations.<sup>15, 28, 29</sup>

### 172 **Speciation of uranium in presence of Fe(II) sorbed on clays**

### 173 **XANES and EXAFS**

174 The normalized XANES spectrum of the U(VI) reference sample (NAu-2 + U(VI) at pH 6.2 i.e.  
175 N1) (Table 1) in Figure 2A shows the characteristic features of the uranyl ( $\text{U}^{\text{VI}}\text{O}_2^{2+}$ ) structure,  
176 including a white line peak centered at 17179 eV and a shoulder centered at approximately  
177 17190 eV. The feature at 17190 eV has previously been shown to result from multiple scattering  
178 resonances of the linear uranyl ion structure with the short  $\text{U-O}_{\text{ax}}$  bonds.<sup>42</sup> The XANES spectra  
179 of M1, M2, M3, F1, F2 and N2 samples are very similar to the U(VI) reference, implying that  
180 the dominating phase of uranium in these samples is in +VI oxidation state. This visual  
181 observation of the XANES spectra was further statistically verified with ITFA and a U(IV)  
182 reference spectrum, showing no coincidence. Therefore, no reduction of U(VI) by Fe(II) sorbed  
183 on three clays was observed after 72 h. ITFA analysis of the  $k^3$ -weighted EXAFS spectra  
184 revealed the presence of two structurally different components or species. One of the  
185 components, prevailing in samples M2 and M3, could be identified as samples an amorphous,  
186 soddyite  $[(\text{UO}_2)_2\text{SiO}_4 \cdot 2\text{H}_2\text{O}]$ -like surface precipitate forming in presence of Fe(II) on MONT.  
187 Using the spectrum of M1 as representative of the most likely pure U(VI) sorption complex, and  
188 that of a soddyite reference as representative of the surface precipitate, we could derive by  
189 Iterative Target Test the quantitative speciation of both components in the other sample spectra  
190 (Table 2). Only the M series starting after 24 h and increasing with reaction time showed  
191 evidence of surface precipitation. For samples F2 and N2, no reduction of U(VI) to lower  
192 valence state occurred suggesting that sorbed Fe(II) probably loses its reactivity while being  
193 involved in intervalence charge transfer (IVCT) with structural Fe(III) present in tetrahedral  
194 and/or octahedral sites for Fe-MONT and NAu-2 clays before reacting with aqueous U(VI).

195 To focus more on the kinetics of surface precipitation, we analyzed three samples M2a, M2b and  
196 M2c reacted at different time intervals. The XANES and EXAFS quantification (Table 2, 3)

197 shows that neither reduction of U(VI) nor surface precipitation occurred (Table 1) before 24 h in  
198 case of M2a and M2b. However, a partial reduction about 21% of total sorbed U(VI) was  
199 indicated by XANES in M2c (Table 3). However, the spectral characteristic of M2c with its  
200 absence of U-U backscattering is not similar to that of  $U_3O_8(s)$  with mixed U valence used as  
201 reference (not shown). Although we cannot unequivocally prove the presence of U-Al or U-Fe  
202 backscattering paths most likely masked by the strong multiple scattering peak at 2.9 Å  
203 (uncorrected for phase shift), the spectral features of M2c are in line with the formation of an  
204 inner-sphere complex like  $\equiv Fe(II)-O-U(VI)$  at the “reduced strong” edge sites coupled to a slow  
205 reduction step attributed to the surface oxidation of Fe(II) at the “oxidised strong” edge sites of  
206 MONT. No further increase in U(VI) reduction is observed before 72 hr. Moreover, in samples  
207 M2 and M3 we did not observe any U(VI) reduction probably due to the fact that surface  
208 precipitation starts between 24 h and 72 h and is clearly visible after 72 h (Figure 2 & 3). The  
209 total Si concentrations in solution in samples M2a, M2b and M2c show a slight upward trend up  
210 to 24 h due to the dissolution of MONT which, however, decreases in sample M2 due to surface  
211 precipitation of an uranium silicate-like soddyite solid phases (Table 3). So it is possible that the  
212 major part of the signals comes from the U(VI) bearing soddyite-like mineral phase showing no  
213 reduction in M2 and M3.

#### 214 **Speciation of sorbed Fe on clays with/out U(VI)**

#### 215 **Mössbauer analyses**

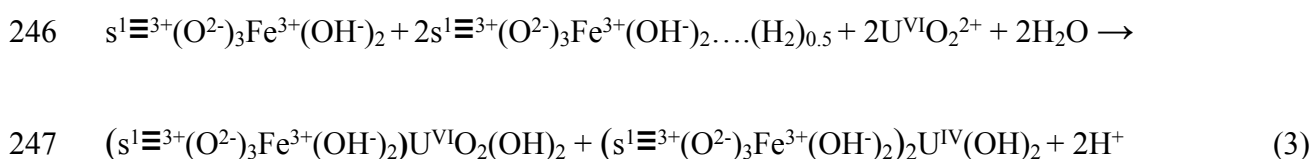
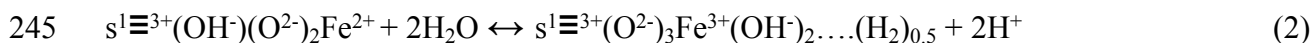
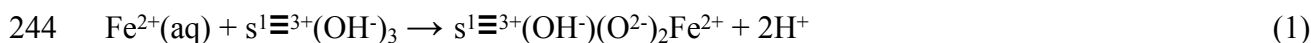
216 The 77K Mössbauer spectra of Fe(II) sorbed on MONT before and Figure 4B after U(VI)  
217 addition are compared in Figure 4. The corresponding refined values of the hyperfine parameters  
218 are listed in Table 4. According to the values of isomer shift, among four doublets, D1, D2 and

219 D3 are unambiguously assigned to Fe(II) species while D4 to Fe(III) species. The spectrum in  
220 Figure 4A must be deconvoluted into four quadrupolar doublets corresponding to (a)  
221 exchangeable  $\text{FeCl}^+$ , (b) exchangeable Fe(II), (c) Fe(II) sorbed on strong reduced site2 and (d)  
222 Fe(II) sorbed on strong oxidized site of MONT.<sup>21</sup> The presence of Fe(III) (D4 doublet) in sample  
223 M suggests that 10% of total sorbed Fe(II) is oxidized to Fe(III) by “oxidized strong edge sites”  
224 of MONT surface before U(VI) addition. This finding is well consistent with that previously  
225 found by Charlet et al.<sup>19</sup> and Gehin et al.<sup>21</sup> The spectrum shown in Figure 4B must be  
226 deconvoluted into at least five doublets. The new doublet D5 with higher quadrupole splitting  
227 value is assigned to the Fe(III) sorbed on strong reduced site2 which appeared to the detriment of  
228 the oxidation of sorbed Fe(II) of the “strong reduced” site2 of MONT after addition of U(VI).  
229 Thus the additional 6% oxidation of Fe(II) involves “strong reduced edge sites” concerned by the  
230 U(VI) reduction. On the basis of this result, two mechanisms of U(VI) reduction are proposed.

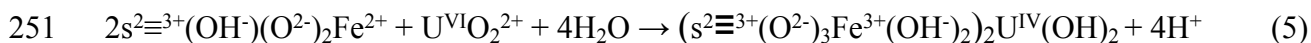
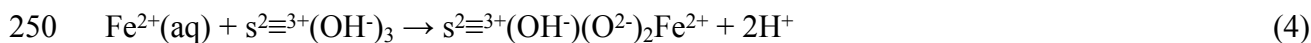
### 231 **Mechanistic approaches of U(VI) sorption-reduction by Fe(II)/MONT**

232 Our previous study<sup>25</sup> has shown that reduced uranium may exist on MONT and results in surface  
233 monomeric U(IV) complex species also shown in recent studies.<sup>15</sup> Therefore, U(VI) reduction  
234 mechanism is suggested by considering U(VI) and monomeric U(IV) surface complexes formed  
235 with Fe(II) specifically sorbed on oxidized and reduced strong sites of MONT. Furthermore,  
236 Mössbauer analyses of solid phase Fe speciation (Table 4) reveals that the reduction of U(VI)  
237 occurs in two steps: (1) a slow, diffusion controlled process involving  $\text{H}_2$ -like species formation  
238 resulting from the pre-oxidation of Fe(II) on oxidized strong sites of MONT<sup>19</sup> and (2) a relatively  
239 faster electron transfer to U(VI) through inner-sphere complexation between U(VI) and Fe(II)  
240 sorbed on “reduced” strong sites of MONT.

241 **Mechanism 1.** U(VI) reduction into monomeric U(IV) sorbed species by surface H<sub>2</sub> species  
 242 produced due to pre-oxidation of Fe(II) specifically sorbed on MONT oxidized strong  
 243 sites.<sup>19,21,42</sup>



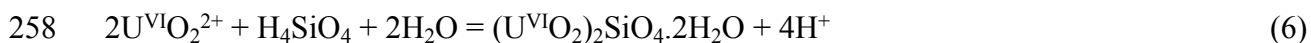
248 **Mechanism 2.** U(VI) reduction by Fe(II) sorbed on reduced strong sites of MONT by inner-  
 249 sphere complex formation.



252 where  $\text{s}^1\equiv^{3+}(\text{OH}^-)_3$  and  $\text{s}^2\equiv^{3+}(\text{OH}^-)_3$  represent one mole of MONT oxidized and reduced strong  
 253 sites respectively at pH 6. Equation (3) is attributed to a diffusion controlled process and is  
 254 therefore slow (days).

### 255 **Precipitation of Soddyite-like mineral phase on Fe(II) sorbed on MONT surface**

256 M2 and M3 suspensions are slightly oversaturated with respect to soddyite (saturation index  
 257 0.37) and precipitation may occur (Table 2) according to:



259 Previously it has been shown that redox potential of mineral/electrolyte suspension is useful in  
260 predicting end product reactivity of mineral when reacted with a contaminant.<sup>15,43</sup> In the present  
261 study, the redox potential of Fe(II) sorbed on Fe-MONT or NAu-2 suspension is lower than  
262 Fe(II)/Fe(III) in solution (Figure S2 in supporting information). Moreover, the amount of Fe(II)  
263 sorbed on these clays is nearly 10 times higher than the amount of sorbed U(VI), 5 times higher  
264 than stoichiometry would require for complete reduction to occur. However U(VI) reduction is  
265 not complete. In MONT 16% of the total sorbed Fe(II) is found to be active in electron transfer  
266 to U(VI). On the other hand, Fe(II) sorbed on Fe-MONT and NAu-2 shows stronger affinity to  
267 reduce structural Fe(III) before U(VI) addition and therefore loses its reactivity towards U(VI)  
268 reduction. One may form “dead-end” –Fe(III)-O-U(VI) complexes at both of these clay surfaces.

269 Working at higher concentration of clay, Fe(II) and U(VI) than those we previously used,<sup>25</sup>  
270 we do not show significant impact on the extent of U(VI) reduction but we observe a  
271 precipitation of soddyite-like phases on MONT. However, such precipitation is not observed in  
272 other systems containing either U(VI)-Fe(III)-bearing clays or Fe(II)-U(VI)-Fe(III)-bearing  
273 clays. It can therefore be concluded that the mobility of U(VI) is controlled by a coupled  
274 sorption-reduction and uranium silicate mineral phase precipitation reaction in the U(VI)-Fe(II)-  
275 MONT system whereas only redox-inactive sorption prevails when U(VI) is co-adsorbed on  
276 Fe(II)-Fe-MONT and Fe(II)-NAu-2 systems.

## 277 **Environmental implications**

278 The long-term stability of uranium present in nuclear waste disposal sites or bomb shells must be  
279 carefully assessed using MONT, Fe-MONT and NAu-2 considering that (1) mobility of U(VI) is  
280 mainly controlled by sorption-reduction on Fe(II) sorbed MONT surface coupled with the

281 precipitation of soddyite-like solids at higher U concentrations and (2) the reductive  
282 immobilization of U(VI) is not operative in Fe(II)-U(VI)-Fe-MONT and Fe(II)-U(VI)-NAu-2  
283 systems due to inter-valence charge transfer.

284

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289 Analytical Chemistry Platform at ISTERre (OSUG), the ESRF Radioprotection Group and the  
290 scientists of the Rossendorf Beamline (ROBL) for providing support during the XAS  
291 measurements.

292

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424 **TABLE 1.** Experimental conditions of sorption of U(VI) on Fe(II) sorbed onto smectite clays<sup>a</sup>

Sample No.	Clay type	[Fe(II)] <sub>0</sub> (mmolL <sup>-1</sup> )	pH <sub>i, Fe</sub>	[Fe(II)] <sub>sorb</sub> (mmolkg <sup>-1</sup> )	[U(VI)] <sub>0</sub> (mmolL <sup>-1</sup> )	pH <sub>i, -U</sub>	pH <sub>f, -U</sub>	[U(VI)] <sub>sorb</sub> (mmolkg <sup>-1</sup> )
M <sup>c</sup>		1.24	6.0	20.5	-	-	-	-
M1	Fe-free (0 wt%)	-	-	-	0.13	6.0	6.3	12.1
M2 <sup>c</sup>	montmorillonite (MONT)	1.15	5.9	19.7	0.13	6.0	6.1	12.0
M3		1.21	6.0	20.6	0.13	6.0	6.0	11.8
U1 <sup>b</sup>		0.69	6.2	20.0	0.04	6.1	5.5	8.3
F	Fe-poor (2.6 wt%)	1.50	5.9	87.3	-	-	-	-
F1	montmorillonite	-	-	-	0.11	5.8	5.7	9.5
F2	(Fe-MONT)	1.50	5.9	85.7	0.13	6.0	5.7	8.8
N	Fe-rich (25.8 wt%) nontronite	1.08	6.0	103.3	-	-	-	-
N1	(NAu-2)	-	-	-	0.13	6.2	5.1	11.8
N2		1.11	6.0	103.5	0.14	5.9	5.3	10.4

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426 <sup>a</sup> [clay] = 10.6 ± 0.2 gL<sup>-1</sup>, M & U = montmorillonite (MONT); F = Fe-montmorillonite (Fe-MONT)

427 and N = Nontronite (NAu-2); equilibration time of Fe(II) with clay before U(VI) addition = 72 h

428 and equilibration time of U(VI) after Fe(II) sorption on clay = 72 h.

429 <sup>b</sup> study by Chakraborty et al.<sup>25</sup>430 <sup>c</sup> samples prepared using <sup>57</sup>Fe(II)

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433 **TABLE 2.** Quantification of U(VI) precipitation molar fraction as soddyite-like mineral phase  
 434 and U(VI) sorbed as obtained by ITFA of XANES (12.10–12.25 keV).

<b>Sample No</b>	<b>pH</b>	<b>t (hr)</b>	<b>U(VI) precipitated as soddyite-like phase (UO<sub>2</sub>)<sub>2</sub>SiO<sub>4</sub>·2H<sub>2</sub>O</b>	<b>U(VI) sorbed onto Fe(II) sorbed on clays</b>	<b>Sum</b>
Soddyite	-	-	1.00	0.00	1.00
M1	6.0	72	0.00	1.00	1.00
M2a	5.8	0.16	0.02	0.97	0.99
M2b	5.7	1	0.05	0.92	0.98
M2c	5.5	24	0.08	0.87	0.95
M2	6.0	72	0.26	0.51	0.77
M3	6.0	72	0.75	0.00	0.75
F1	5.8	72	0.08	0.89	0.97
F2	6.0	72	0.03	0.92	0.95
N1	-	-	0.00	1.00	1.00
N2	5.9	72	0.04	0.99	1.03

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439 **TABLE 3.** Quantification of U oxidation states (molar fraction) by ITFA of XANES (12.10–  
 440 12.25 keV) and solution data (pH, [Si], [U] in  $\mu\text{molL}^{-1}$ ).

Sample No	pH	t (hr)	U(VI)	U(IV)	Sum	[Si] <sub>solution</sub> in $\mu\text{molL}^{-1}$	[U] <sub>solution</sub> in $\mu\text{molL}^{-1}$
M1	6.0	72	1.00	0.00	1.00	-	-
M2a	5.8	0.16	0.94	0.06	0.99	345	11
M2b	5.7	1	0.95	0.05	1.00	351	20
M2c	5.5	24	0.79	0.21	1.00	358	18
M2	6.0	72	0.91	0.09	1.00	335	3
U1 <sup>a</sup>	6.1	72	0.87	0.14	1.01	-	-

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442 <sup>a</sup> Study by Chakraborty et al.<sup>25</sup>

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451 **TABLE 4.** Refined values of  $^{57}\text{Mössbauer}$  hyperfine parameters estimated from the spectra  
 452 presented in Figure 4.

Sample No.	Site		$\delta \pm$ 0.02	$\Gamma \pm$ 0.02	$\Delta E_Q \pm$ 0.02	RA $\pm 2$
M (Fe(II)/MONT)	Fe(II)_exch_FeCl <sup>+</sup>	D1	1.37	0.41	3.40	36
	Fe(II)_exch_Fe <sup>2+</sup>	D2	1.32	0.34	3.03	33
	Fe(II)_strong_red2	D3	1.28	0.34	2.62	21
	Fe(III)_strong_ox	D4	0.47	0.49	0.58	10
M2c (Fe(II)/MONT+U(VI))	Fe(II)_exch_FeCl <sup>+</sup>	D1	1.37	0.28	3.42	39
	Fe(II)_exch_Fe <sup>2+</sup>	D2	1.34	0.38	3.04	32
	Fe(II)_strong_red2	D3	1.30	0.32	2.59	13
	Fe(III)_strong_ox	D4	0.47	0.46	0.58	10
	Fe(III)_strong_red2	D5	0.48	0.46	1.24	6

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 454  $\delta$  (mm s<sup>-1</sup>) isomer shift with respect to metallic  $\alpha\text{-Fe}(0)$  at 300K;  $\Delta E_Q$  (mm s<sup>-1</sup>) quadrupole  
 455 splitting; RA (%) relative abundance,  $\Gamma$  (mm s<sup>-1</sup>) full-width at half-height.

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462 **FIGURE CAPTIONS**

463 Figure 1. Kinetics of U(VI) sorption on (A) Fe(II)/MONT; (B) Fe(II)/Fe-MONT, Fe(II)/NAu-2.

464 [U(VI) added to Fe(II)/clay suspensions at  $t = 0$ ].

465 Figure 2. U  $L_{III}$ -edge XAS spectra of U(VI) sorbed on MONT, Fe-MONT and NAu-2 in the

466 presence of Fe(II) compared to the U(VI) and soddyite references, (A) fitted XANES; (B)

467 EXAFS and (C) Fourier transform of EXAFS.

468 Figure 3. U  $L_{III}$ -edge XAS spectra of kinetics of U(VI) sorption on MONT in the presence of

469 Fe(II) compared to the U(VI) (M1 sample in Table 1) and U(IV) colloid references, (A) fitted

470 XANES; (B) EXAFS and (C) Fourier transform of EXAFS.

471 Figure 4.  $^{77}\text{K}$  Mössbauer spectra of  $^{57}\text{Fe(II)}$  sorbed on MONT (A) before; (B) after U(VI)

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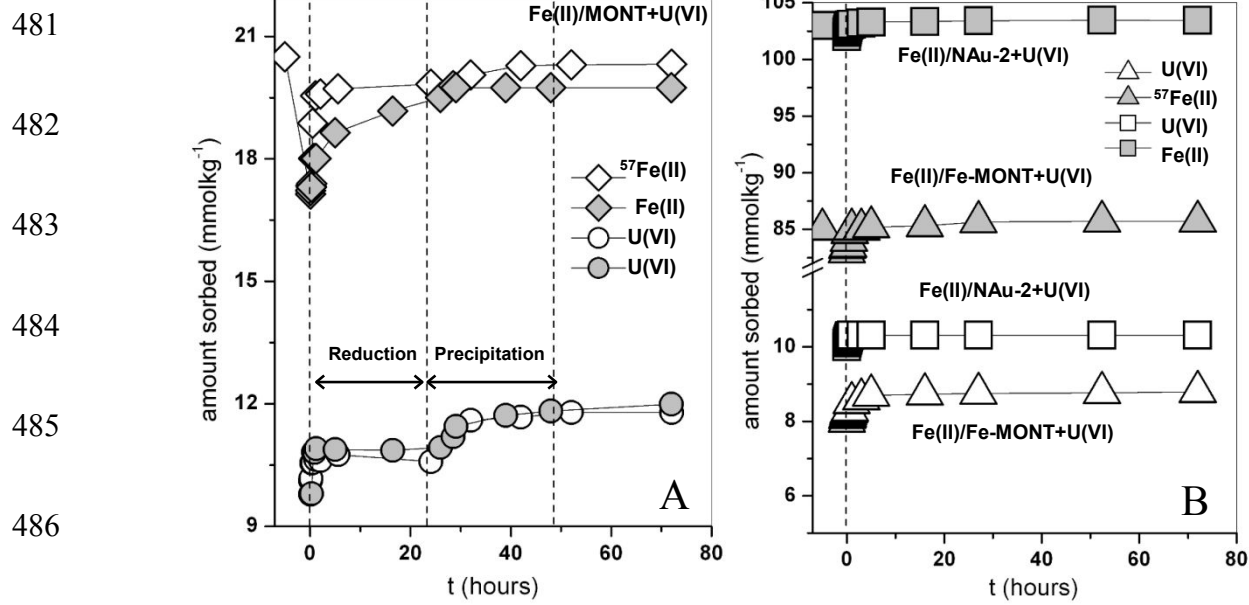
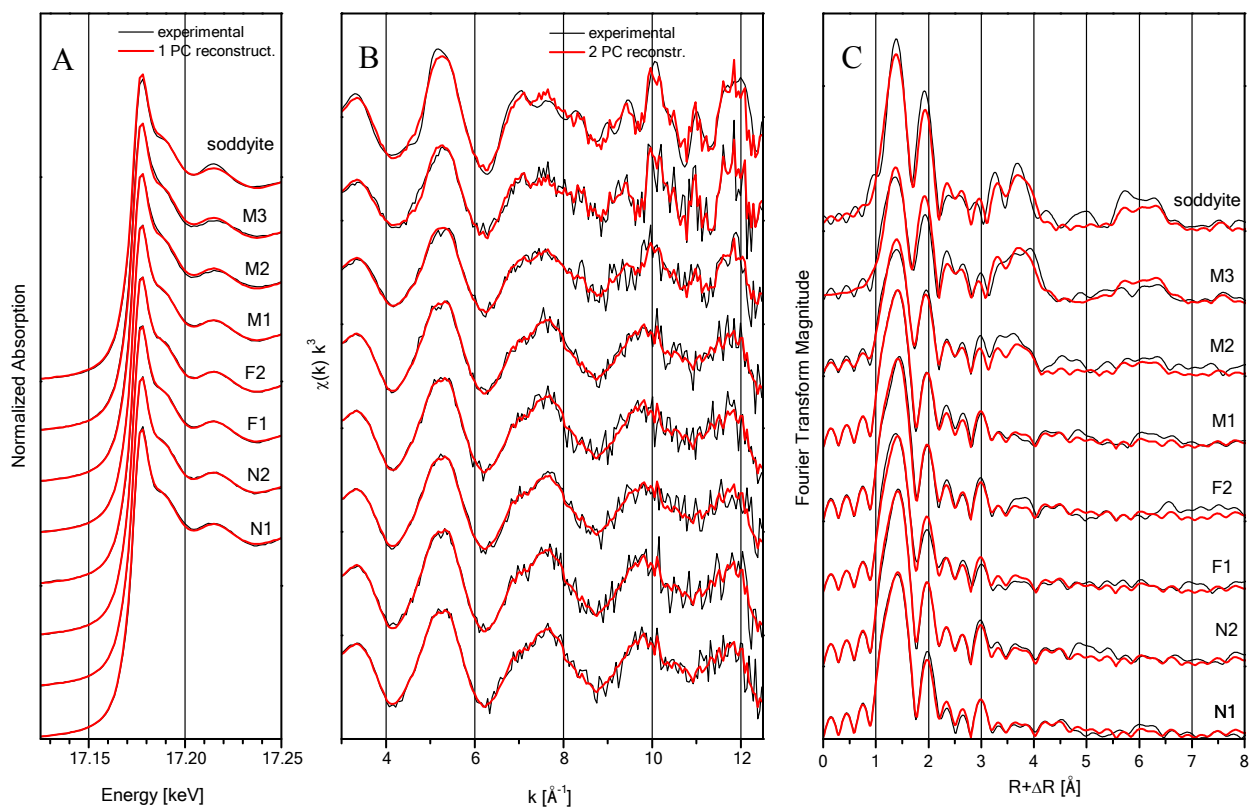


Figure 1

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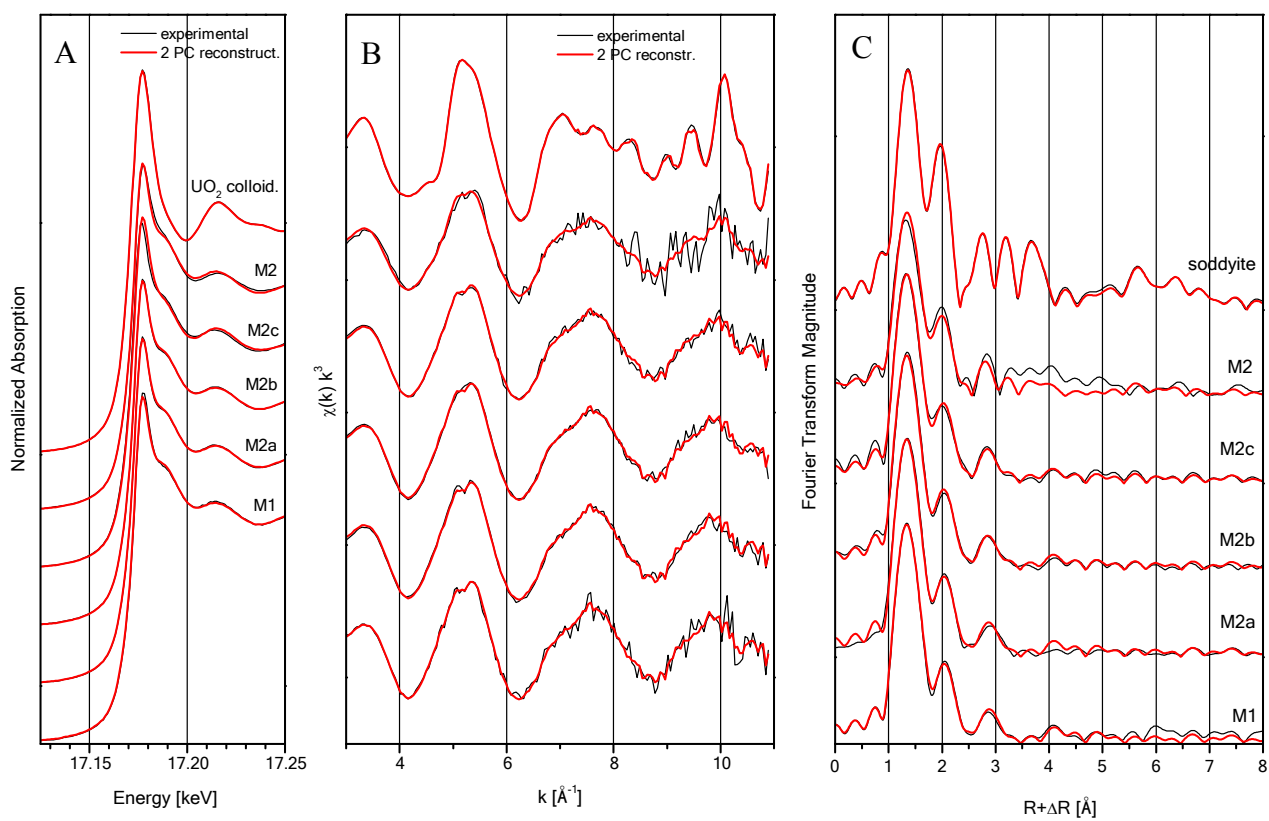
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**Figure 2**



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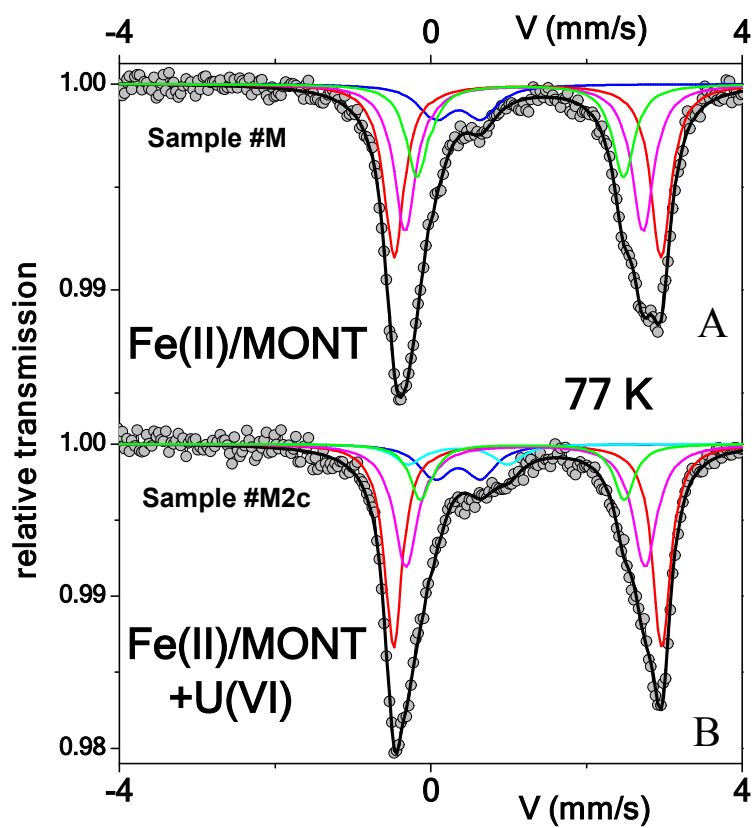
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**Figure 3**



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Figure 4