

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

Chakraborty, S.; Banerjee, D.; Scheinost, A.; Grenèche, J.-M.; Favre, F.; Géhin, A.; Charlet, L.;

Originally published:

April 2023

Journal of Materials Research 38(2023), 2752-2763

DOI: <https://doi.org/10.1557/s43578-023-00998-8>

Perma-Link to Publication Repository of HZDR:

<https://www.hzdr.de/publications/Publ-29864>

Release of the secondary publication
on the basis of the German Copyright Law § 38 Section 4.

This document is confidential and is proprietary to the American Chemical Society and its authors. Do not copy or disclose without written permission. If you have received this item in error, notify the sender and delete all copies.

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

Journal:	<i>Environmental Science & Technology</i>
Manuscript ID	es-2019-068495
Manuscript Type:	Article
Date Submitted by the Author:	12-Nov-2019
Complete List of Authors:	Chakraborty, Sudipta; Kanchrapara College, Department of Chemistry Banerjee, Dipanjan; KU Leuven, Department of Chemistry Scheinost, Andreas; The Rossendorf Beamline (BM20), European Synchrotron Radiation Lab Grenèche, Jean-Marc; Université du Maine, Institut des Molécules et Matériaux du Mans Favre, Fabienne; Ecole d'ingénieurs et architectes de Fribourg, Civil Engineering Géhin, Antoine; University Grenoble Alpes, ISTERre, Environmental Geochemistry Group, Observatory for Earth and Planetary Sciences Charlet, Laurent; Institut des Sciences de la Terre,

SCHOLARONE™
Manuscripts

1 Assessing the reactivity of Fe(II) sorbed on smectite 2 clays: U(VI) reduction

3 Sudipta Chakraborty,^{*,1,5} Dipanjan Banerjee,² Andreas C. Scheinost,³
4 Jean-Marc Grenèche,⁴ Fabienne Favre,^{1,6} Antoine Géhin,¹ Laurent Charlet¹

5 ¹ ISTerre, Environmental Geochemistry Group, Observatory for Earth and Planetary Sciences,
6 Grenoble University, 38041 Grenoble Cedex 9, France

7 ² Dutch-Belgian Beamline (DUBBLE), European Synchrotron Radiation Facility, 71 avenue des
8 Martyrs, CS 40220, 38043 Grenoble Cedex 9, France

9 ³ Institute of Resource Ecology, Helmholtz-Zentrum Dresden - Rossendorf, Dresden, Germany

10 ⁴ Institut des Molécules et Matériaux du Mans, IMMM, UMR CNRS 6283, Université du Maine,
11 72085 Le Mans Cedex, France

12 ⁵ Department of Chemistry, Kanchrapara College, West Bengal, India

13 ⁶ ITEC, HEIA-FR, HES-SO, University of Applied Sciences Western Switzerland, CH-1700,
14 Fribourg

15

16 chakrabortysudipta@hotmail.com; banerjee@esrf.fr; scheinost@esrf.fr; jean-
17 marc.greneche@univ-lemans.fr; Fabienne.Favre@hefr.ch; antoine.gehin@wanadoo.fr;
18 charlet38@gmail.com

19 * CORRESPONDING AUTHOR

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

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 (± 0.2) under CO₂-free, anoxic (O₂ <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_{III}-
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_{III}-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 (± 2) % of the
31 total sorbed Fe(II) was oxidized in presence of MONT before and an additional 6 (± 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,¹⁻⁶ spectroscopic analysis and molecular dynamics simulation
54 methods,⁷⁻¹⁴ while the information available on the nontronite system is limited.¹⁵⁻¹⁷ 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.¹⁸⁻²⁰

59 The sorption of Fe(II) on montmorillonite has been well documented.²¹⁻²³ 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.^{21,23} The sorption of Fe(II) on iron-rich nontronite (NAu-1 & NAu-2)
64 has been studied in detail by Tsarev et al.¹⁵ and Jaisi et al.²⁴. 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 respectively²⁵ which, however,
68 coupled to catalyze the reduction of U(VI),^{15,25} Se(IV),¹⁹ 4-chloronitrobenzene.^{26,27} 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.²⁸⁻³¹ The reactivity of sorbed
76 Fe(II) on structural Fe(III) bearing clays has been shown to vary in different cases. Jones et al.²⁷
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.¹⁵ observed a partial reduction of U(VI) by Fe(II)
79 sorbed on nontronite (NAu-1 and NAu-2) in presence of CO₂ while a partial oxidation of As(III)
80 to As(V) was reported by Ilgen et al.³²

81 Our previous study²⁵ 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 (UO₂). 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 CO₂-free atmosphere
90 to compare our results with those obtained in presence of CO₂ by Tsarev et al.¹⁵ and also to
91 exclude the effect of carbonate on uranium mobilization. The anoxic (O₂-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 CaCl₂) 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 FeCl₂ · 4H₂O (Fluka Chemica), after transferring the
102 required amount to a glove box (JACOMEX) under N₂ atmosphere (CO₂, O₂ <1 ppmv),
103 dissolved in deoxygenated water (dissolved O₂ <1 mgL⁻¹) and acidified with 0.1 M HCl to pH <2
104 to avoid oxidation.³³ ⁵⁷Fe(II) stock solutions were prepared by dissolving ~100 mg ⁵⁷Fe(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⁻¹ UO₂(NO₃)₂ · 6H₂O (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.^{19,21,25} 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.³⁴ 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 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 ± 1
126 $^\circ\text{C}$) with 0.05 M CaCl_2 ionic background as described in our previous study for MONT.²⁵ 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}Fe Mössbauer spectrometry**

131 ^{57}Fe Mössbauer experiments were performed at 77K in transmission geometry with a 925 MBq
132 γ -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 cryostat. The hyperfine structures were fitted using the MOSFIT program³⁵ 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_{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.³⁶ Normalization, transformation from
151 energy into k space, subtraction of a spline background was performed with WinXAS using
152 routine procedures.³⁷ Statistical analyses of XANES and EXAFS spectra was performed by
153 Iterative Target-test Factor Analysis (ITFA) using the ITFA software package.³⁸⁻⁴⁰

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.^{21,26} 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.^{15, 28, 29}

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 U-O_{ax} bonds.⁴² 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**

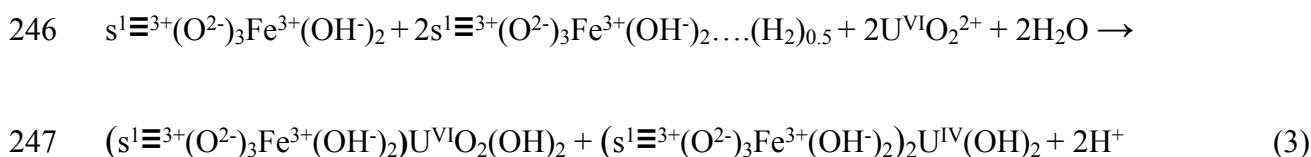
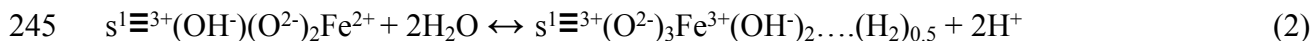
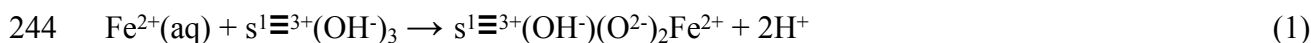
216 The 77K Mössbauer spectra of Fe(II) sorbed on MONT before and Figure 4B after U(VI)
217 addition are compared in Figure 4. The corresponding refined values of the hyperfine parameters
218 are listed in Table 4. According to the values of isomer shift, among four doublets, D1, D2 and

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 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.²¹ 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.¹⁹ and Gehin et al.²¹ 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.

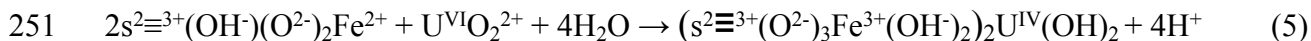
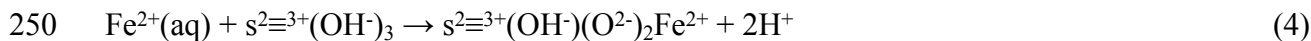
231 **Mechanistic approaches of U(VI) sorption-reduction by Fe(II)/MONT**

232 Our previous study²⁵ has shown that reduced uranium may exist on MONT and results in surface
233 monomeric U(IV) complex species also shown in recent studies.¹⁵ 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 H_2 -like species formation
238 resulting from the pre-oxidation of Fe(II) on oxidized strong sites of MONT¹⁹ 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 H₂ species
 242 produced due to pre-oxidation of Fe(II) specifically sorbed on MONT oxidized strong
 243 sites.^{19,21,42}



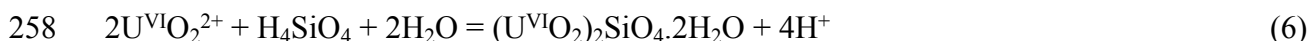
248 **Mechanism 2.** U(VI) reduction by Fe(II) sorbed on reduced strong sites of MONT by inner-
 249 sphere complex formation.



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.^{15,43} 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,²⁵
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

285 **ACKNOWLEDGMENT**

286 This research was funded by ANDRA (project no. #20072484). We are thankful to Dr. Jocelyne
287 Brendlé for synthesis of Fe-MONT and Dr. Laura Leone for Mössbauer analysis of Fe-MONT.
288 Delphine Tisserand and Florian Molton are acknowledged for their technical support within the
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

293 **Literature Cited**

294 (1) Bachmaf, S; Merkel, B. Sorption of U(VI) at the clay mineral-water interface. *Environ.*
295 *Earth Sci.* **2010**, 63 (5), 925-934.

296 (2) Bradbury, M.; Baeyens, B. Modelling the sorption of Mn(II), Co(II), Ni(II), Zn(II), Cd(II),
297 Eu(III), Am(III), Sn(IV), Th(IV), Np(V) and U(VI) on montmorillonite: Linear free energy
298 relationships and estimates of surface binding constants for some selected heavy metals and
299 actinides. *Geochim. Cosmochim. Acta* **2005**, 69 (4), 875–892.

- 300 (3) Pabalan, R.; Turner, D. R. Uranium (6+) sorption on montmorillonite: experimental and
301 surface complexation modeling study. *Aquatic Geochem.* **1998**, 2(3), 203-226.
- 302 (4) Turner, D. R.; Sassman, S. A. Approaches to sorption modeling for high-level waste
303 performance assessment. *J. Contam. Hydrol.* **1996**, 21, 311–332.
- 304 (5) McKinley, J. P.; Zachara, J. M.; Smith, S. C.; Turner, G. D. The influence of uranyl
305 hydrolysis and multiple site-binding reactions on adsorption of U(VI) to montmorillonite.
306 *Clays Clay Miner.* **1995**, 43, 586-598.
- 307 (6) Chisholm-Brause, C.; Conradson, S. D.; Buscher, C. T.; Eller, P. G.; Morris, D. E.
308 Speciation of uranyl sorbed at multiple binding sites on montmorillonite. *Geochim.*
309 *Cosmochim. Acta* **1994**, 58, 3625–3631.
- 310 (7) Schlegel, M.; Descostes, M. Uranium uptake by hectorite and montmorillonite: a solution
311 chemistry and polarized EXAFS study. *Environ. Sci. Technol.* **2009**, 43 (22), 8593-8598.
- 312 (8) Catalano, J. G.; Brown B. G. Jr. Uranyl adsorption onto montmorillonite: Evaluation of
313 binding sites and carbonate complexation. *Geochim. Cosmochim. Acta* **2005**, 69 (12), 2995-
314 3005.
- 315 (9) Greathouse, J. A.; Cygan, R. T. Molecular dynamics simulation of uranyl(VI) adsorption
316 equilibria onto an external montmorillonite surface. *Phys. Chem. Chem. Phys.* **2005**, 7 (20),
317 3580-3586.
- 318 (10) Kowal-Fouchard, A.; Drot, R.; Simoni, E.; Ehrhardt, J. J. Use of spectroscopic techniques
319 for uranium(VI)/montmorillonite interaction modelling. *Environ. Sci. Technol.* **2004**, 38 (5),
320 1399-1407.

- 321 (11) Zaidan, O. F.; Greathouse, J. A.; Pabalan, R. T. Monte Carlo and molecular dynamics
322 simulation of uranyl adsorption on montmorillonite clay. *Clays Clay Miner.* **2003**, 51, 372–381.
- 323 (12) Hennig, C.; Reich, T.; Dähn, R.; Scheidegger, A. M. Structure of uranium sorption
324 complexes at montmorillonite edge sites. *Radiochim. Acta* **2002**, 90 (9), 653-657.
- 325 (13) Sylwester, E. R.; Hudson, E. A.; Allen, P. G. The structure of uranium (VI) sorption
326 complexes on silica, alumina, and montmorillonite. *Geochim. Cosmochim. Acta* **2000**, 64 (14),
327 2431-2438.
- 328 (14) Dent, A. J.; Ramsay, J. D. F.; Swanton, S. W.; An EXAFS study of uranyl ion in solution
329 and sorbed onto silica and montmorillonite clay colloids. *J. Colloid Interface Sci.* **1992**, 150 (1),
330 45-60.
- 331 (15) Tsarev, S.; Waite, T. D.; Collins, N. R. Uranium reduction by Fe(II) in the presence of
332 montmorillonite and nontronite. *Environ. Sci. Technol.* **2016**, 50, 15, 8223-8230.
- 333 (16) Zhang, G.; Senko, J. M.; Kelly, S. D.; Tan, H.; Kemner, K. M.; Burgos, W. B. Microbial
334 reduction of iron(III)-rich nontronite and uranium(VI). *Geochim. Cosmochim. Acta* **2009**, 73
335 (12), 3523-3538.
- 336 (17) Ames, L. L.; McGarrah, J. E.; Walker, B. A.; Salter, P. F. Sorption of trace constituents
337 from aqueous solutions onto secondary minerals. I. uranium. *Clays Clay Miner.* **1983**, 31 (5),
338 321-334.
- 339 (18) Hofstetter, T. B.; Neumann, A.; Schwarzenbach, R. P. Reduction of nitroaromatic
340 compounds by Fe(II) species associated with iron-rich smectites. *Environ. Sci. Technol.* **2006**,
341 40, 235-242.

- 342 (19) Charlet, L.; Scheinost, A. C.; Tournassat, C.; Grenèche, J. M.; Géhin, A.; Fernández-
343 Martínez, A.; Coudert, S.; Tisserand, D.; Brendle, J. Electron transfer at the mineral/water
344 interface: selenium reduction by ferrous iron sorbed on clay. *Geochim. Cosmochim. Acta* **2007**,
345 *71*, 5731-5749.
- 346 (20) Neumann, A.; Hofstetter, T. B.; Skarpeli-Liati, M.; Schwarzenbach, R. P. Reduction of
347 polychlorinated ethanes and carbon tetrachloride by structural Fe(II) in smectites. *Environ. Sci.*
348 *Technol.* **2009**, *43*, 4082-4089.
- 349 (21) Géhin, A.; Grenèche, J. M.; Tournassat, C.; Brendlé, J.; Rancourt, D. G.; Charlet, L.
350 Reversible surface-sorption-induced electron-transfer oxidation of Fe(II) at reactive sites on a
351 synthetic clay mineral. *Geochim. Cosmochim. Acta* **2007**, *71*, 863–876.
- 352 (22) Schultz, C. A.; Grundl, T. J. pH dependence of ferrous sorption on two smectite clays.
353 *Chemosphere*, **2004**, *57*, 1301-1306.
- 354 (23) Soltermann, D.; Fernandes, M. M.; Baeyens, B.; Dähn, R.; Joshi, P. A.; Scheinost, A. C.;
355 Gorski, C. A. Fe(II) uptake on natural montmorillonites. I. macroscopic and spectroscopic
356 characterization. *Environ. Sci. Technol.* **2014**, *48* (15), 8688-8697.
- 357 (24) Jaisi, D.P.; Dong, H.; Morton, J. P. Partitioning of Fe(II) in reduced nontronite (NAu-2) to
358 reactive sites: reactivity in terms of Tc(VII) reduction. *Clays Clay Miner.* **2008**, *56* (2), 175-189.
- 359 (25) Chakraborty, S.; Favre, F.; Banerjee, D.; Scheinost, A. C.; Mullet, M.; Ehrhardt, J. J.;
360 Brendle, J.; Vidal, L.; Charlet, L. U(VI) sorption and reduction by Fe(II) sorbed on
361 montmorillonite. *Environ. Sci. Technol.* **2010**, *44* (10), 3779-3785.

- 362 (26) Schultz, C. A.; Grundl, T. J. pH dependence on reduction rate of 4-Cl-nitrobenzene by
363 Fe(II)/ montmorillonite systems. *Environ. Sci. Technol.* **2000**, 34, 3641-3648.
- 364 (27) Jones, A. M.; Murphy, C. A.; Waite T. D.; Collins, A. N. Fe(II) interactions with smectites:
365 temporal changes in redox reactivity and the formation of green rust. *Environ. Sci. Technol.* **2017**
366 51 (21), 12573-12582.
- 367 (28) Merola, R. B.; Fournier, E. D.; McGuire, M. M. Spectroscopic investigations of Fe²⁺
368 complexation on nontronite clay. *Langmuir* **2007**, 23 (3), 1223-1226.
- 369 (29) Schaefer, M. V.; Gorski, C. A.; Scherer, M. M. Spectroscopic evidence for interfacial
370 Fe(II)-Fe(III) electron transfer in a clay mineral. *Environ. Sci. Technol.* **2011**, 45, 540-545.
- 371 (30) Neumann, A.; Olson, T. L.; Scherer, M. M. Spectroscopic evidence for Fe(II)-Fe(III)
372 electron transfer at clay mineral edge and basal sites. *Environ. Sci. Technol.* **2013**, 47 (13), 6969-
373 6977.
- 374 (31) Latta, D. E.; Neumann, A.; Premaratne, W. A. J.; Scherer, M. Fe(II)-Fe(III) electron transfer
375 in a clay mineral with low Fe content. *ACS Earth Space Chem.* **2017**, 1 (4), 197-208.
- 376 (32) Ilgen, A. G.; Kruichak, J. N.; Artyushkova, K.; Newville, M. G.; Sun, C. Redox
377 transformations of As and Se at the surfaces of natural and synthetic ferric nontronites: role of
378 structural and adsorbed Fe(II). *Environ Sci Technol.* **2017**, 51 (19), 11105-11114.
- 379 (33) Morgan, B.; Lahav, O. The effect of pH on the kinetics of spontaneous Fe(II) oxidation by
380 O₂ in aqueous solution-basic principles and a simple heuristic description. *Chemosphere* **2007**,
381 68, 2080-2084.

- 382 (34) Gates, W. P.; Slade, P. G.; Manceau, A.; Lanson, B. Site occupancies by iron in nontronites.
383 *Clays Clay Miner.* **2002**, 50 (2), 223-239.
- 384 (35) Varret, F. ; Teillet, J. Unpublished Mosfit program, Université du Maine, France.
- 385 (36) Webb, S. M. SIXPack: a graphical user interface for XAS analysis using IFEFFIT. *Physica*
386 *Scripta* **2005**, T115, 1011-1014.
- 387 (37) Ressler, T. WinXAS: a program for X-ray absorption spectroscopy data analysis under MS
388 Windows. *J. Synchr. Radiat.* **1998**, 5, 118-122.
- 389 (38) Rossberg, A.; Reich, T.; Bernhard, G., Complexation of uranium(VI) with protocatechuic
390 acid - application of iterative transformation factor analysis to EXAFS spectroscopy. *Anal.*
391 *Bioanal. Chem.* **2003**, 376 (5), 631-638.
- 392 (39) Rossberg, A.; Ulrich, K.-U.; Weiss, S.; Tsushima, S.; Hiemstra, T.; Scheinost, A. C.,
393 Identification of uranyl surface complexes on ferrihydrite: Advanced EXAFS data analysis and
394 CD-MUSIC modeling. *Environ. Sci. Technol.* **2009**, 43 (5), 1400–1406.
- 395 (40) Lucks, C.; Rossberg, A.; Tsushima, S.; Foerstendorf, H.; Scheinost, A. C.; Bernhard, G.,
396 Aqueous Uranium(VI) Complexes with Acetic and Succinic Acid: Speciation and Structure
397 Revisited. *Inorg. Chem.* **2012**, 51 (22), 12288-12300.
- 398 (41) Allen, P. G.; Shuh, D. K.; Bucher, J. J.; Edelstein, N. M.; Palmer, C. E. A.; Silva, R. J.;
399 Nguyen, S. N.; Marquez, L. N.; Hudson, E. A. Determination of uranium structures by EXAFS:
400 schoepite and other U(VI) oxide precipitates. *Radiochim. Acta* **1996**, 75, 47–53.

401 (42) Truche, L.; Joubert, G.; Dargent, M.; Martz, P., Cathelineau, M., Rigaudier, T., Quirt, D.
402 Clay minerals trap hydrogen in the Earth's crust: Evidence from the Cigar Lake uranium deposit,
403 Athabasca. *Earth Planetary Sci. Lett.* **2018**, 493, 186–197.

404 (43) Chakraborty, S.; Bardelli, F.; Mullet, M.; Greneche, J. M.; Varma, S.; Ehrhardt, J. J.;
405 Banerjee, D.; Charlet, L. Spectroscopic studies of arsenic retention onto biotite. *Chem. Geol.*
406 **2011**, 281 (1-2), 83-92.

407

408

409

410

411

412

413

414

415

416

417

418

419

420

421

422

423

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

Sample No.	Clay type	[Fe(II)] ₀ (mmolL ⁻¹)	pH _{i, Fe}	[Fe(II)] _{sorb} (mmolkg ⁻¹)	[U(VI)] ₀ (mmolL ⁻¹)	pH _{i, -U}	pH _{f, -U}	[U(VI)] _{sorb} (mmolkg ⁻¹)
M ^c		1.24	6.0	20.5	-	-	-	-
M1	Fe-free (0 wt%)	-	-	-	0.13	6.0	6.3	12.1
M2 ^c	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 ^b		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

425

426 ^a [clay] = 10.6 ± 0.2 gL⁻¹, 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 ^b study by Chakraborty et al.²⁵430 ^c samples prepared using ⁵⁷Fe(II)

431

432

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).

Sample No	pH	t (hr)	U(VI) precipitated as soddyite-like phase (UO₂)₂SiO₄·2H₂O	U(VI) sorbed onto Fe(II) sorbed on clays	Sum
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

435

436

437

438

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 μmolL^{-1}).

Sample No	pH	t (hr)	U(VI)	U(IV)	Sum	[Si] _{solution} in μmolL^{-1}	[U] _{solution} in μmolL^{-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 ^a	6.1	72	0.87	0.14	1.01	-	-

441

442 ^a Study by Chakraborty et al.²⁵

443

444

445

446

447

448

449

450

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 ± 2
M (Fe(II)/MONT)	Fe(II)_exch_FeCl ⁺	D1	1.37	0.41	3.40	36
	Fe(II)_exch_Fe ²⁺	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 ⁺	D1	1.37	0.28	3.42	39
	Fe(II)_exch_Fe ²⁺	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

453
 454 δ (mm s⁻¹) isomer shift with respect to metallic $\alpha\text{-Fe}(0)$ at 300K; ΔE_Q (mm s⁻¹) quadrupole
 455 splitting; RA (%) relative abundance, Γ (mm s⁻¹) full-width at half-height.

456

457

458

459

460

461

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

472 addition.

473

474

475

476

477

478

479

480

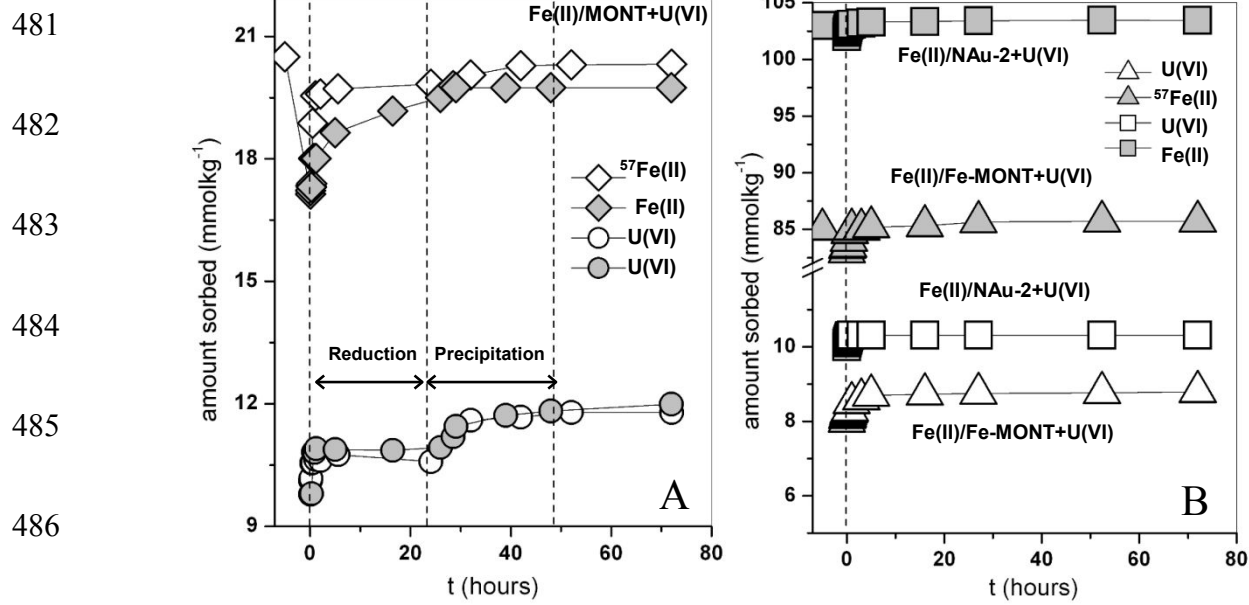
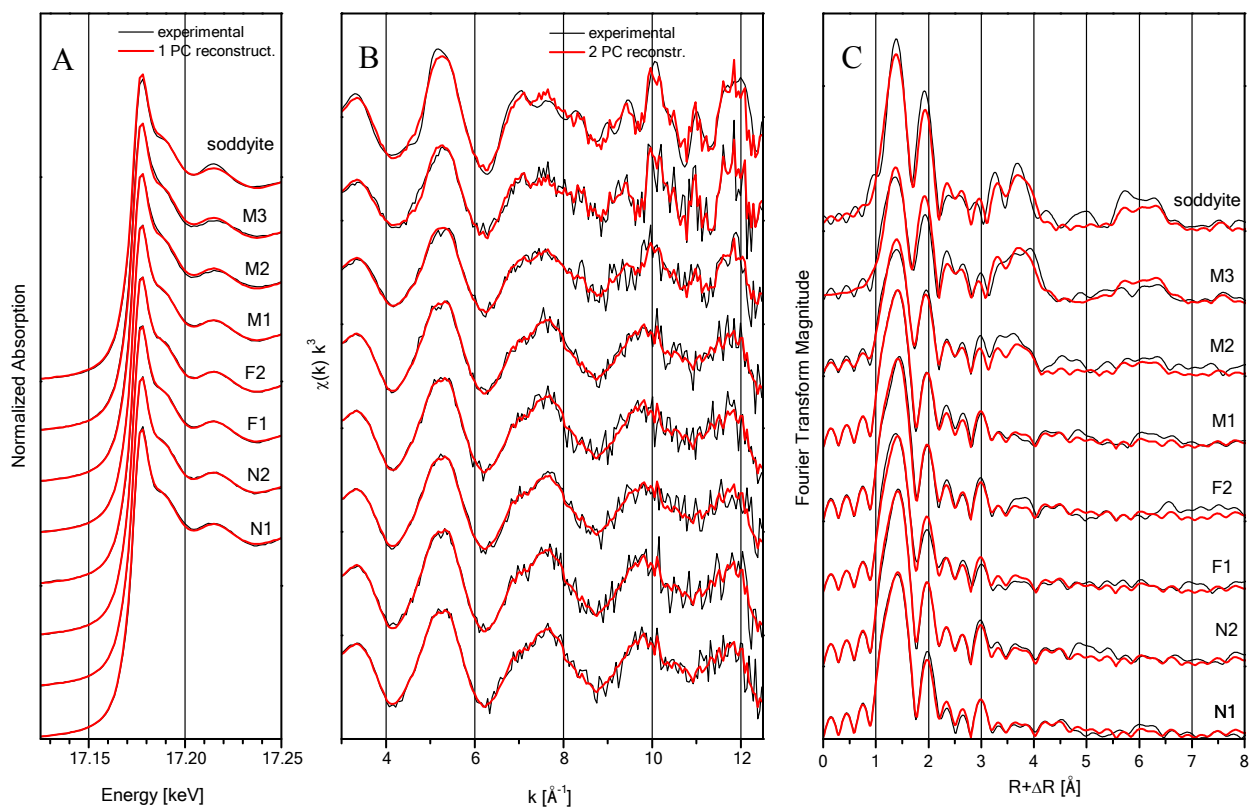


Figure 1

498
499

500

501

502

503

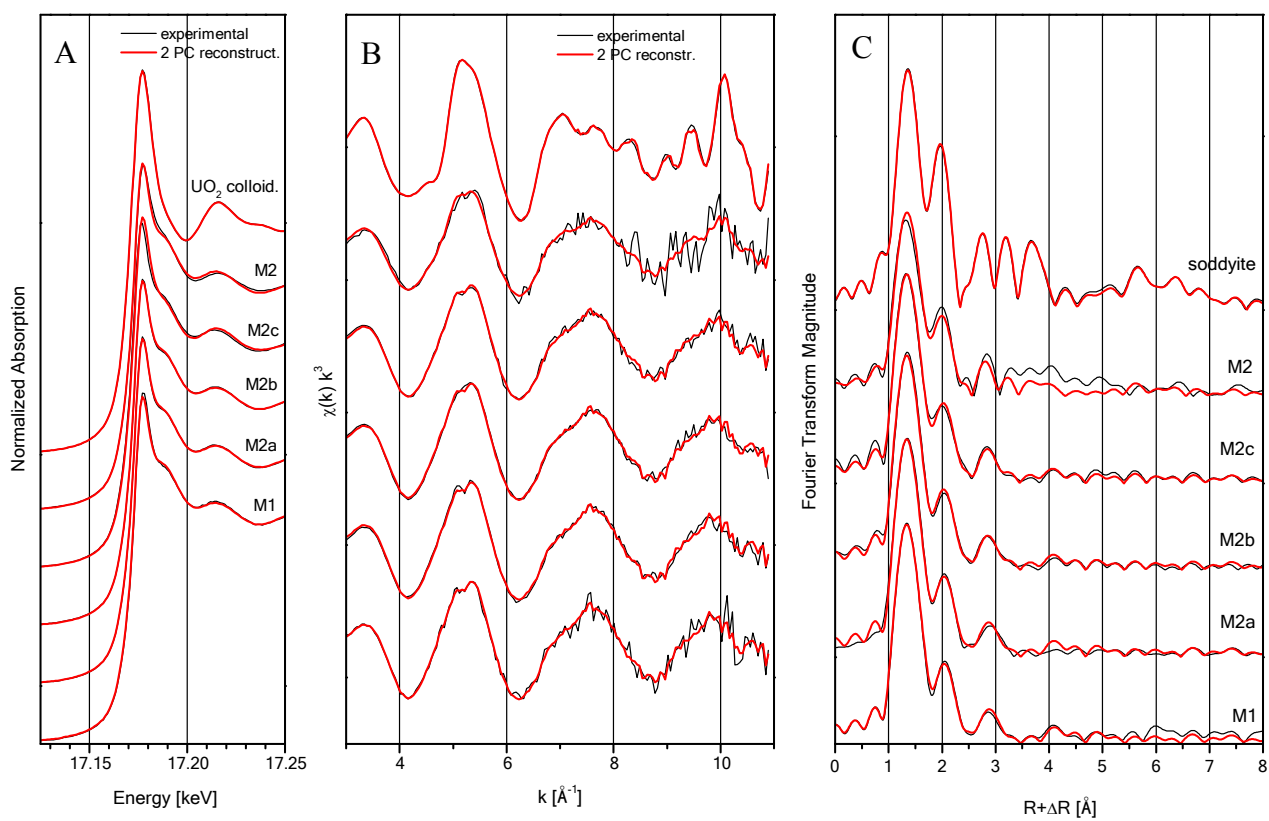
504

505

506

507

Figure 2



508
509

510

511

512

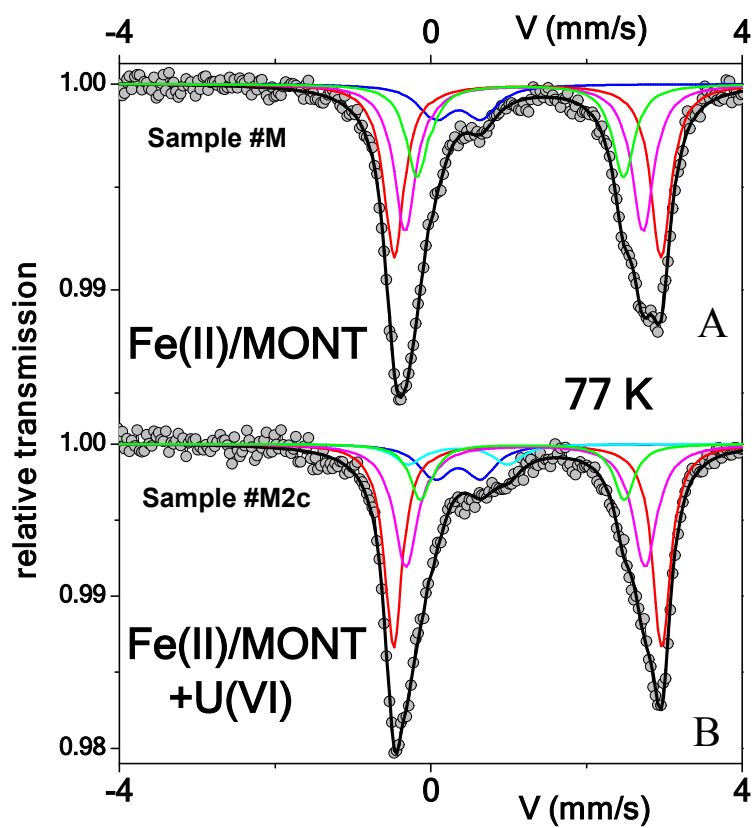
513

514

515

516

Figure 3



517

518

519

520

521

522

523

524

Figure 4