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# Neptunium sorption and redox speciation at the illite surface under highly saline conditions

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26 **ABSTRACT.** Neptunium (Np) uptake on illite is investigated in 1 and 3.2 molal (m) NaCl  
27 solutions under inert (Ar) atmosphere for  $4 < \text{pH}_m < 10$  ( $\text{pH}_m = -\log m_{H^+}$ ) and  $5 \times 10^{-8} <$   
28  $[\text{Np(V)}]_{\text{tot}} < 3 \times 10^{-4}$  M. In agreement with a previous study in 0.1 m NaCl solutions [Marsac et  
29 al. (2015) *Geochim. Cosmochim. Acta* 152, 39-51], Np(V) is the prevailing oxidation state in  
30 the aqueous solution, but Np uptake by illite is affected by surface induced reduction. The  
31 extent of Np(V) reduction to Np(IV) follows the measured redox potential (or the  $\text{pe} = -\log$   
32  $a_e$ ), which is influenced by the introduced Np(V) amount, because of the low redox capacity  
33 of the illite. The presence of Np(IV) on the solid phase is verified by X-ray Absorption Near  
34 Edge Spectroscopy (XANES). We can conclude that Np uptake by illite is not significantly  
35 affected by the variation of  $m_{\text{NaCl}}$  from 0.1 to 3.2 m and thus is in agreement with reports on  
36 tetravalent actinide and Np(V) sorption to clays at high ionic strength. The combination of (i)  
37 the two site protolysis non-electrostatic surface complexation and cation exchange model, (ii)  
38 the specific ion interaction theory to calculate activity coefficients for dissolved species and  
39 (iii) by accounting for redox equilibria and the stability of surface Np species, the overall Np  
40 uptake by illite can be simulated as a function of  $\text{pH}_m$ ,  $\text{pe}$  and  $m_{\text{NaCl}}$  using a single set of  
41 parameters. The present experimental and modeling results are particularly important in the  
42 context of deep geological nuclear waste disposal since many sedimentary rocks or clay  
43 formations that are deemed suitable for this purpose exhibit highly saline porewaters.

44 Keywords: Neptunium, illite, redox, saline, high ionic strength, surface complexation,  
45 spectroscopy, geochemical modeling.

## 1. INTRODUCTION

47           The final disposal in deep geologic formations is considered the most appropriate  
48 strategy to isolate high level nuclear waste (HLW) from the biosphere (e.g. OECD/NEA,  
49 2008). Sedimentary clay rock formations are potential host rocks for HLW in several  
50 European countries encompassing Opalinus Clay (OPA) in Switzerland (Nagra, 2002), Boom  
51 and Ypresian clays in Belgium (Ondraf, 2001), Callovo-Oxfordian (COx) clays in France  
52 (Andra, 2005) or Boda Claystone in Hungary (Lázár and Máthé, 2012). Indeed, clays exhibit  
53 low permeability, large surface areas and pronounced sorption capacity for many relevant  
54 radionuclides via ion exchange reactions as well as surface complexation to silanol and/or  
55 aluminol groups at the edges of clay particles. Illite and smectite are the most important  
56 components of the proposed claystone host rocks and may amount to about 50 wt.% of the  
57 material (Lauber et al., 2000; Gaucher et al., 2004; Bradbury and Baeyens, 2011; Pearson et  
58 al., 2011; Chen et al., 2014). Although actinide sorption to clays has been extensively studied  
59 (e.g. Bradbury and Baeyens, 2005; 2009a,b; and references therein), the underlying  
60 mechanisms were rarely investigated for ionic strengths above 0.1 M. While OPA and COx  
61 porewaters exhibit ionic strengths of 0.3-0.4 M, clay rock pore waters as e.g. in the Jurassic  
62 and lower Cretaceous clay rock in Northern Germany, which are also discussed as  
63 potentially appropriate host rock formations, may contain salt contents as high as about 5 M  
64 (Brewitz, 1980). Sedimentary rocks currently investigated in Canada are even in contact with  
65 brine solutions up to 6.5 M (Fritz and Frape, 1982). Therefore, detailed sorption investigations  
66 and the development of geochemical models that can predict actinide sorption and speciation  
67 in concentrated brine solutions are required (Vilks, 2011).

68           Neptunium (Np) is a minor constituent of high level radioactive waste. Yet, its  
69 environmental chemistry is of considerable interest due to the long half-life of its main  
70 isotope  $^{237}\text{Np}$  ( $t_{1/2} = 2 \times 10^6$  a) and the high solubility and mobility of its pentavalent state

71 ( $\text{NpO}_2^+$ ) under oxidizing conditions. Np is redox sensitive and its most relevant oxidation  
72 states in the geosphere are the penta- and tetravalent states (Kim, 1986). Both redox states  
73 show drastically different geochemical behavior concerning, for instance, complexation by  
74 organic and inorganic ligands, solubility, as well as sorption to minerals (e.g. Altmaier et al.,  
75 2013). Under reducing conditions, Np(IV) prevails and is considered rather immobile because  
76 of its strong sorption to minerals and its low solubility, as other tetravalent actinides (An; e.g.  
77 Th(IV)) or other tetravalent elements (e.g. Sn(IV)) (Bradbury and Baeyens, 2009a,b). Under  
78 oxidizing conditions, Np(V) prevails, which weakly sorbs to minerals and is regarded as  
79 rather mobile (e.g. Geckeis et al., 2013). However, partial reduction of Np(V) to Np(IV) when  
80 in contact with Opalinus Clay was suggested by comparing sorption data obtained under  
81 aerobic and anaerobic conditions: stronger Np sorption (Fröhlich et al., 2011) was found  
82 under anaerobic conditions and significant reduction to Np(IV) was observed using  
83 synchrotron based spectroscopic techniques (Fröhlich et al., 2012). A more recent Np-illite  
84 batch sorption study under oxygen-free argon atmosphere in 0.1 M NaCl showed that the  
85 strongly adsorbing Np(IV) is thermodynamically favored at a mineral surface compared to  
86 Np(V) (Marsac et al., 2015a). Although Np(V) prevailed in aqueous solution at  $\text{pH} \approx 7$ , as  
87 evidenced by liquid-liquid extraction method and by capillary electrophoresis hyphenated to  
88 inductively coupled plasma mass spectrometry (Graser et al., 2015), Np(IV) was observed at  
89 the illite surface by X-ray absorption near edge structure spectroscopy (XANES). When  
90 accounting for the uptake of both Np(V) and Np(IV) on illite and the redox potential of the  
91 illite suspension, Marsac et al. (2015a) were able to describe the overall Np uptake on illite  
92 for various redox conditions. The modeling approach was subsequently extended to the  
93 sorption behavior of plutonium, which exhibits an even more complex redox chemistry than  
94 Np. Pu can be found in the redox states +III to +VI under environmental conditions. The  
95 experimentally determined overall Pu uptake on kaolinite (Marsac et al., 2015b) and illite  
96 (Banik et al., 2016) in 0.1 M NaCl/ $\text{ClO}_4$  was successfully reproduced.

97           The above cited studies focused on aqueous solutions of low ionic strength. At high  
98 salt concentrations, activity coefficients of aqueous species change dramatically, whereas the  
99 effect of high ionic strengths on the surfaces properties of adsorbents and surface species is  
100 elusive. Previous work showed that non-electrostatic models are quite suitable to predict  
101 proton and metal ion sorption at high ionic strength to naturally occurring matrices that bear  
102 surface functional groups that are affected by pH and can be treated by the same formalism  
103 and with similar numerical models. This includes marine microalgae (Schjif and Herbling,  
104 2010; Zoll and Schjif, 2012) or bacteria (Ams et al., 2013). Eu(III) sorption to illite and  
105 smectite was investigated experimentally in  $0.1 < m_{NaCl} < 3.9$  molal (m) (Schnurr et al.,  
106 2015). The results obtained in the latter study showed that the 2 site protolysis non-  
107 electrostatic surface complexation and cation exchange (2 SPNE SC/CE) model coupled to  
108 either the specific ion interaction theory (SIT; Ciavatta, 1980) or the Pitzer formalism (Pitzer,  
109 1991) to account for activity coefficients in concentrated media was able to reproduce  
110 sorption data also at elevated ionic strength. By using the modeling approach of Schnurr et al.  
111 (2015), the Pu-illite study in 0.1 M NaCl of Banik et al. (2016) was extended to high ionic  
112 strength ( $0.1 < m_{NaCl} < 3.2$  m; Marsac et al., 2017). In the latter studies, the Pu(IV)/Pu(III) is  
113 involved. The present study is a similar extension of the work of Marsac et al. (2015a) on Np  
114 uptake on illite in 0.1 M NaCl to highly saline conditions (up to  $m_{NaCl} = 3.2$  m), but here a  
115 An(V)/An(IV) couple is involved. Together, the work of Marsac et al. (2017) and the present  
116 one should elucidate the actinide(III,IV,V) sorption and redox speciation at the illite surface  
117 under highly saline conditions. Classical batch experiments at various pH, total Np  
118 concentrations and  $m_{NaCl} = 1.0$  and  $3.2$  m were performed, and the redox potential was  
119 monitored. XANES was applied to determine the Np redox state at the illite surface. The  
120 coupling of the 2 SPNE SC/CE model with SIT was used to describe Np sorption and redox  
121 speciation on illite under saline conditions.

122

123

## 2. MATERIALS AND METHODS

124 All chemicals were of pro analytical quality or better and were obtained from Merck  
125 (Darmstadt, Germany) or Riedel de Haen (Seelze, Germany). Experiments were conducted  
126 with de-ionized “MilliQ” water (specific resistivity, 18.2 MΩ cm). The purified Na-illite was  
127 provided within the EC project CP CatClay. The source material derives from lacustrine  
128 continental sediments deposited at the Upper Eocene (~ -35 Ma) in the basin of Le Puy en  
129 Velay (Massif Central, France). The purification procedures and the characterization of the  
130 purified illite (<63 μm) were previously described in detail (Marsac et al., 2015). Concerning  
131 redox processes, it is noted that the iron content is 0.88 mol Fe per kg of illite (Marsac et al.,  
132 2015). The aqueous concentration of  $^{237}\text{Np}$  in sorption experiments after phase separation was  
133 determined by liquid scintillation counting (LSC) using the scintillation cocktail Ultima Gold  
134 XR (Packard Instruments Co., USA) and the liquid scintillation counter (LSC) Tri-Carb  
135 (Packard Instruments Co., USA). Results for  $^{237}\text{Np}$ - $\alpha$ -activities were corrected for  
136 interferences by the  $\beta$ -radiation from the daughter nuclide protactinium ( $^{233}\text{Pa}$ ) by applying  
137 the  $\alpha/\beta$  discrimination method. The procedure is described in detail by Marsac et al. (2015a)  
138 and will not be repeated here.  $^{233}\text{Pa}$  is a short-lived isotope ( $t_{1/2} = 27$  days) unlike  $^{237}\text{Np}$  ( $t_{1/2} =$   
139  $2.14 \cdot 10^6$  years). Since the  $^{233}\text{Pa}$  mass concentration is much smaller than that of  $^{237}\text{Np}$ , its  
140 competitive effect on Np sorption to illite can be neglected.

141

### 142 2.1. Neptunium stock solution

143 The initial  $^{237}\text{Np}$  solution was evaporated to dryness and dissolved in 8 M HCl. The  
144 solution was purified via anion exchange (BIO RAD<sup>®</sup> AG 1-X8). After a washing step with  
145 several milliliters of 8 M HCl, Pu contaminations were removed with a fresh solution of 150  
146 mg NH<sub>4</sub>I in 5 mL 8 M HCl. Subsequently, Np was eluted from the ion exchanger with 4 M  
147 HCl/0.05 M HF and evaporated to dryness in a PTFE beaker. The sample was fumed twice

148 with 1 M HClO<sub>4</sub> and the residue was dissolved in deionized water to obtain a solution  
149 containing only NpO<sub>2</sub><sup>+</sup>, as required for all our experiments, and its purity was verified by UV-  
150 Vis/NIR spectroscopy (Sjoblom and Hindman 1951). The final Np concentration was  
151 determined by LSC.

## 152 **2.2. Determination of pH and Eh**

153 pH in the clay suspensions was measured by an Orion 525A pH meter and a Ross electrode  
154 calibrated with 4 standard buffers (pH 3, 5, 7 and 9; Merck). The uncertainty of pH  
155 measurements is ± 0.05. For converting the pH value measured in saline solutions (I > 0.1 m)  
156 (pH<sub>exp</sub>) into a chemically meaningful quantity, a correction is applied in order to obtain the  
157 molal proton concentration, i.e. -log m<sub>H+</sub> (pH<sub>m</sub>). An empirical correction coefficient (A)  
158 which has been accurately determined by Altmaier et al. (2003) for NaCl solutions for our set-  
159 up with known -log m<sub>H+</sub> was added to pH<sub>exp</sub> values according to equations 1 and 2:

$$160 \quad pH_m = pH_{exp} + A_{NaCl} \quad (1)$$

$$161 \quad A_{NaCl} = 0.0013 \times m_{NaCl}^2 + 0.1715 \times m_{NaCl} - 0.0988 \quad (2)$$

162 where  $m_{NaCl}$  is the molality (mol kg<sup>-1</sup>) of the background electrolyte.

163 The redox potentials in the clay suspensions were measured using an Orion 525A (E<sub>h</sub>  
164 meter) and a Pt combined electrode with a Ag/AgCl reference (Metrohm). They were  
165 converted into Eh vs. standard hydrogen electrode (SHE) by correcting for the potential of the  
166 reference electrode. A commercial redox-buffer (220 mV, Schott instruments) was used for  
167 calibration. An equilibration time of 15 min was allowed for all Eh measurements, after  
168 having stirred the suspension. Uncertainties in Eh measurements are ± 50 mV (Altmaier et al.,  
169 2010; Kirsch et al., 2011). Eh was converted to the logarithm of the apparent electron activity,  
170  $pe = -\log a_e = 16.9 \times Eh(V)$  at 25°C. To our best knowledge, no ionic strength dependent  
171 correction needs to be performed for experimentally measured Eh values (as the one that has  
172 been described for pH measurements in brines above).

### 173 2.3. Batch sorption experiments

174 All sorption experiments were performed as batch type experiments with initial Np(V)  
175 concentrations in the range of  $5 \times 10^{-8}$  -  $3 \times 10^{-6}$  M. The batch experiments were carried out in 40  
176 mL polypropylene centrifuge tubes at room temperature in an argon glove box (< 1 ppm O<sub>2</sub>,  
177 absence of CO<sub>2</sub>). The sample volume was 25 mL. At a solid-to-liquid ratio of 2 g L<sup>-1</sup>, the  
178 suspensions were preconditioned at a given  $m_{NaCl}$  under continuous shaking for 4-5 days to  
179 achieve a given target pH<sub>m</sub> value by adding 0.1 M HCl or 0.1 M NaOH. After mixing the  
180 NpO<sub>2</sub><sup>+</sup> solution with the preconditioned illite suspension, pH<sub>m</sub> was readjusted by adding acid  
181 or base (HCl/NaOH). The samples were shaken end-over-end. According to Marsac et al.  
182 (2015a), Np(V) adsorption or reduction to Np(IV) does not significantly change with time  
183 after 7 days. Therefore, after 7 days, pH<sub>m</sub> and Eh were measured in the suspension and an  
184 aliquot of each sample was centrifuged in a Beckman L7 Ultracentrifuge at 90000 rpm for 1 h.  
185 The supernatant was analyzed for dissolved Np by LSC. Results obtained in batch  
186 experiments will be expressed throughout as distribution coefficients ( $R_d$  in L kg<sup>-1</sup>), calculated  
187 by the following equation:

$$188 R_d = ([Np]_{tot}/[Np]_{aq} - 1) \times V/m \quad (3)$$

189 where [Np]<sub>aq</sub> and [Np]<sub>tot</sub> (mol L<sup>-1</sup>) are the dissolved (final) equilibrium and total (initial)  
190 concentrations of Np in solution, respectively. The term V/m corresponds to the aqueous  
191 solution volume to illite mass ratio (L kg<sup>-1</sup>). An uncertainty of ± 0.3 is commonly associated  
192 with log R<sub>d</sub> determined for radionuclide sorption to clay minerals (Bradbury and Baeyens,  
193 2009a), although for low [Np]<sub>tot</sub> and high uptake, the uncertainty on log R<sub>d</sub> might be larger.

### 194 2.4. X-ray absorption near-edge spectroscopy (XANES)

195 One sample was prepared as described in the previous section for Np L<sub>3</sub>-XANES  
196 measurements for [NpO<sub>2</sub><sup>+</sup>]<sub>tot</sub> =  $3 \times 10^{-4}$  M, m/V = 20 g L<sup>-1</sup>,  $m_{NaCl}$  = 3.2 and pH<sub>m</sub> = 7.9 under

197 inert (Ar) atmosphere. The Eh measured after one week equilibration time was  $0.43 \pm 0.05$  V  
198 ( $pe = 7.3 \pm 0.8$ ). A similar experiment is described in Marsac et al. (2015a), however,  
199 performed in 0.1 m NaCl and at  $Eh = 0.40 \pm 0.05$  V ( $pe = 6.8 \pm 0.8$ ). Conditions for XANES  
200 measurements and the data treatment were identical to what has been described in detail in  
201 Marsac et al. (2015a). Briefly, an aliquot was centrifuged at 3000 g in a polyethylene vial  
202 (500  $\mu$ L). The supernatant was discarded, but an aliquot was taken for LSC. The wet illite  
203 paste was transferred into a vial, mounted inside an Ar-flushed cell, which acts as a second  
204 containment and keeps the sample vials in an anaerobic atmosphere (Brendebach et al., 2009).  
205 Measurements were performed at the 2.5 GeV synchrotron light source ANKA, KIT,  
206 Germany, at the INE-Beamline for actinide research (Rothe et al., 2006; 2012). A pair of  
207 Ge(422) crystals was used in the Lemonnier-type double crystal monochromator (DCM). The  
208 monochromatic radiation is focused by a Rh-coated toroidal mirror to a spot of  $< 1 \text{ mm} \times 1$   
209 mm at the sample position. Higher harmonic radiation in the incident beam was suppressed by  
210 detuning the parallel alignment of the DCM crystals to 70 % of photon flux peak intensity in  
211 the middle of the spectral range at the beginning of each scan. The incident flux was measured  
212 by an Ar-filled ionization chamber at ambient pressure and held constant by a digital  
213 MOSTAB feedback system. The Np  $L_3$ -edge spectra ( $E(\text{Np}^0 2p_{3/2}) = 17.61$  keV) were  
214 calibrated against the first derivative XANES spectrum of a Zr foil (energy of the first  
215 inflection point set to  $E(\text{Zr}^0 1s) = 17.998$  keV). All Np  $L_3$ -XANES spectra were recorded in  
216 fluorescence detection mode by registering the Np  $L_\alpha$  fluorescence yield at  $\sim 13.95$  keV as a  
217 function of the incident photon energy with a 5-pixel Ge solid state detector (Canberra LEGe).  
218 Up to 5 scans were collected at room temperature and averaged for each sample. The  
219 illuminated area of the sample was changed between each scan to minimize potential Np  
220 redox reactions induced by the beam. XANES spectra were extracted following subtraction of  
221 a linear pre-edge background function and normalization of the edge jump to unity using the  
222 Demeter Athena software (Ravel and Newville, 2005). The same energy range was

223 considered for the pre-edge and for the normalization of all XANES spectra (pre-edge: 17.30-  
224 17.55 keV; post-edge: 17.77-18.20 keV). Preliminary tests ensured that the differences in the  
225 XANES were not due to the normalization procedure.

226

## 227 **2.5. Thermodynamic modeling**

228 pe-pH diagrams for Np were obtained using PhreePlot (Kinniburgh and Cooper,  
229 2009), which contains an embedded version of the geochemical speciation program  
230 PHREEQC (Parkhurst and Appelo, 1999). PhreePlot also includes a parameter optimization  
231 procedure, which allows fitting a model to experimental data by minimizing the weighted sum  
232 of squares of the residuals. Thermodynamic constants for Np aqueous speciation were taken  
233 from the NEA thermodynamic database (Guillaumont et al., 2003). The specific ion  
234 interaction theory (SIT; Ciavatta, 1980) was used for the calculation of the activity  
235 coefficients of aqueous species. The 2 SPNE SC/CE model was used to simulate Np sorption  
236 to illite (Bradbury and Baeyens, 2009b). Cation exchange reactions of a metal ion with a  
237 charge +n ( $M^{n+}$ ) on Na-illite can be written as follows (Gaines and Thomas, 1953):



239 The cation exchange capacity (CEC) of the illite was set to 0.225 eq/kg. Surface complexation  
240 reactions can be written as follows:



242 where  $M^{n+}$  is a metal ion with a charge of +n and  $\equiv \text{SOH}$  is a protonated surface site.

243 Only the least abundant, i.e. strong, sites of the 2 SPNE SC/CE model were considered in the  
244 adsorption calculations with a site density of  $2 \times 10^{-3} \text{ mol kg}^{-1}$ , since the weak sites are  
245 irrelevant at trace levels of Np. Bradbury and Baeyens (2009b) determined a  $\text{NpO}_2^+ \text{-Na}^+$   
246 selectivity coefficient for illite as well as Np(V) surface complexation constants for illite  
247 within the 2 SPNE SC/CE model. Marsac et al. (2015a) determined surface complexation

248 constants for Np(IV). However, the fitted constants relied on the experimental Eh and,  
249 therefore, are subject to large uncertainties. Np and Pu are neighbors in the actinide series and  
250 the hydrolysis constants of Np(IV) and Pu(IV) are not significantly different (Guillaumont et  
251 al., 2003). On the basis of the linear free energy relationship determined for illite by Bradbury  
252 and Baeyens (2009b), the surface complexation constant for Np(IV) and Pu(IV) should not  
253 significantly differ. Recently, the surface complexation constants for Pu(IV) were refined for  
254 illite by Banik et al. (2016). The constants from the latter study were used here for Np(IV).  
255 No constants are available for Np(V) and Np(IV) surface complexation to the more abundant  
256 but weaker sites defined in the 2 SPNE SC/CE model. The complete aqueous thermodynamic  
257 database, SIT coefficients and the parameters for the 2SPNE SC/CE model are given in the  
258 supporting information.

259

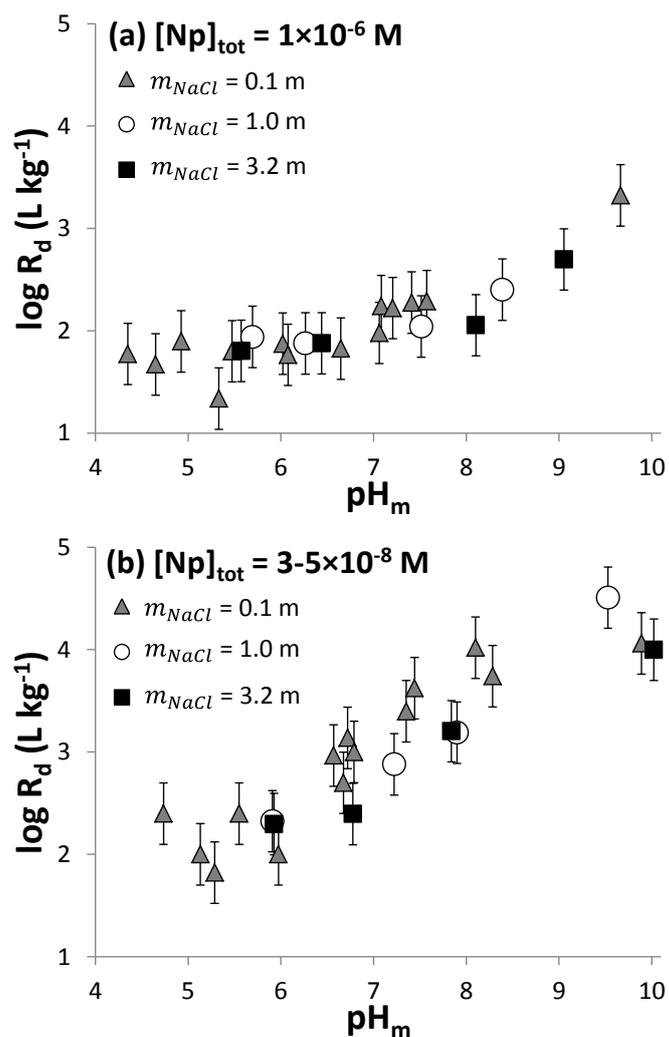
260

### 3. RESULTS

#### 261 *3.1. Experimental batch results*

262 Figure 1 presents experimental  $\log R_d$  ( $R_d$  in  $L\ kg^{-1}$ ) values versus  $pH_m$  for initial  
263 Np(V) concentrations of  $10^{-6}$  M (Fig. 1a) and  $5 \times 10^{-8}$  M (Fig. 1b), and  $m_{NaCl} = 1.0$  and 3.2 m.  
264 The results of Marsac et al. (2015a) in 0.1 m NaCl obtained after 1 week contact time are  
265 included for  $[Np(V)]_{tot} = 10^{-6}$  M (Fig. 1a) and  $3 \times 10^{-8}$  M (Fig. 1b). No data are available for  
266  $[Np(V)]_{tot} = 5 \times 10^{-8}$  M in 0.1 m NaCl. For both values of  $[Np(V)]_{tot}$ , no clear effect of the ionic  
267 strength on Np sorption is observed. This is consistent with the results of experiments related  
268 to the sorption of Np(V) onto illite, shale and bentonite (MX80) in NaCl/CaCl<sub>2</sub> solutions up to  
269 I~4.7 M (Nagasaki et al., 2016). For  $[Np(V)]_{tot} = 10^{-6}$  M,  $\log R_d$  slightly increases with  $pH_m$   
270 whereas, for  $[Np(V)]_{tot} = 3$  or  $5 \times 10^{-8}$  M, the increase in  $\log R_d$  with  $pH_m$  is more pronounced.  
271 As observed by Marsac et al. (2015a), Np sorption to illite is stronger for low  $[Np(V)]_{tot}$ . By  
272 comparison with the uptake of other cations on illite, it was demonstrated that this behavior

273 cannot be due to site saturation effects (see Figure 2 and corresponding text in Marsac et al.,  
274 2015a). In 0.1 m NaCl, the observations for Np were explained by the relatively low  $p_e$   
275 measured in the suspension and the formation of Np(IV) at the illite surface, with Np(V)  
276 prevailing in the aqueous solution. By addition of  $10^{-6}$  M Np(V) the overall concentration of  
277 oxidants in the suspension increases and apparently overcompensates the relatively low redox  
278 capacity of the illite suspension. As a consequence,  $p_e$  increases and a smaller fraction of  
279 Np(V) is reduced to Np(IV), which explains the observed reduced Np uptake at high  
280  $[\text{Np(V)}]_{\text{tot}}$ . Our results must be interpreted by taking into account the actual redox conditions  
281 in the system. Figure 2 shows the complete datasets for various  $[\text{Np(V)}]_{\text{tot}}$  (0.05, 0.09, 0.3, 0.5,  
282 0.9 and 3  $\mu\text{M}$ ) in 1.0 m (Fig. 2a,b) and 3.2 m NaCl (Fig. 2c,d). On the left side (Fig. 2a,c),  
283 uptake data are shown as  $\log R_d$  versus  $\text{pH}_m$  whereas, on the right side (Fig. 2b,d), the  
284 corresponding  $p_e$  versus  $\text{pH}_m$  data are given. As expected, the samples with the highest  
285  $[\text{Np(V)}]_{\text{tot}}$  show the highest  $p_e$  and the lowest  $\log R_d$ , whereas the highest  $\log R_d$  values are  
286 measured at the lowest  $p_e$  and the lowest  $[\text{Np(V)}]_{\text{tot}}$ . Although a small amount of Fe(II)  
287 contained in the illite was supposed to be responsible for the reduction of Np(V) to Np(IV)  
288 (Marsac et al. (2015a)), this could not be monitored experimentally. As calculated in the latter  
289 study, the amount of Fe(II) required for the reduction of Np(V) in the most concentrated  
290 sample (i.e. XANES sample:  $[\text{Np(V)}]_{\text{tot}} = 3 \times 10^{-4}$  M; 20 g/L illite) corresponds to about 0.08  
291 % of the total amount of Fe contained in the illite. Such small fractions are very likely below  
292 the detection limit of available experimental techniques.

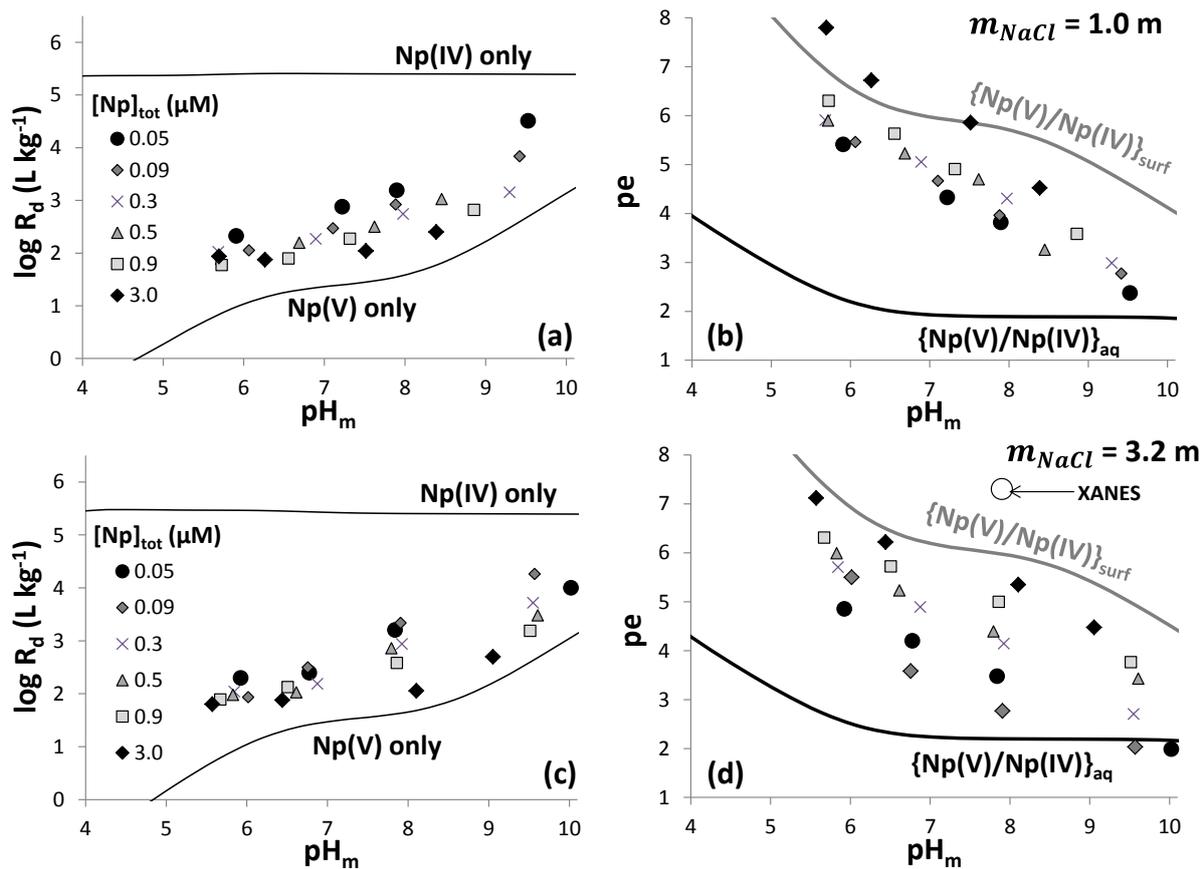


293  
 294 **Figure 1.** Np sorption to illite ( $\log R_d$  in  $\text{L kg}^{-1}$ ) after 1 week contact time in 1.0 and 3.2 m NaCl versus  $\text{pH}_m$  for  
 295  $[\text{Np(V)}]_{\text{tot}} = 10^{-6} \text{ M}$  (a) and  $5 \times 10^{-8} \text{ M}$  (b). The results obtained in 0.1 m NaCl are taken from Marsac et al. (2015a)  
 296 after 1 week contact time,  $[\text{Np(V)}]_{\text{tot}} = 10^{-6} \text{ M}$  (a) and  $3 \times 10^{-8} \text{ M}$  (b).  
 297

298 **3.2. Simulation of Np(V) and Np(IV) uptake**

299 Calculations are made using the 2 SPNE SC/CE model in combination with SIT and  
 300 the surface complexation constants for Np(V) and Pu(IV) determined by Bradbury and  
 301 Baeyens (2009b) and Banik et al. (2016), respectively, for  $[\text{NaCl}/\text{ClO}_4] \leq 0.1 \text{ m}$ . Np(IV)  
 302 sorption is considered to be identical to that of Pu(IV). The model is used to calculate the  
 303 uptake of Np(V) and Np(IV) without considering redox transitions. Results are shown in  
 304 figure 2a (for 1 m NaCl) and 2c (for 3.2 m NaCl). As for Pu(IV) (Marsac et al., 2017), no  
 305 significant ionic strength effect on Np(IV) sorption onto illite is observed for  $0.1 < m_{\text{NaCl}} <$

306 3.2 m. This is also consistent with the outcome of a previous study on Th(IV) sorption to  
307 montmorillonite between 0.1 and 1 m NaClO<sub>4</sub> (Bradbury and Baeyens, 2005). Also the Np(V)  
308 surface complexation to illite is found to be weakly affected by ionic strength for  $0.1 < m_{NaCl}$   
309  $< 3.2$  m (see also Nagasaki et al., 2016). As all metal ions, Np(V) is known to sorb to illite via  
310 cation exchange at low pH (pH < 6; for Np(V)) and at pH > 6 via inner sphere complexation.  
311 However, due to the small charge of the NpO<sub>2</sub><sup>+</sup> ion, and the multiple excess of Na<sup>+</sup>  
312 concentration, cation exchange becomes negligible and hence ionic strengths effects are not  
313 pronounced. In figures 2a (for 1 m NaCl) and 2c (for 3.2 m NaCl), our experimentally  
314 determined log R<sub>d</sub> values lie between those calculated for Np(V) and Np(IV) sorption data.  
315



316

317 **Figure 2.** On the left: experimental  $\log R_d$  data measured after 1 week versus the  $pH_m$  for the various  $[Np]_{tot}$   
 318 investigated (0.05, 0.09, 0.3, 0.5, 0.9 and 3  $\mu M$ ; shown as different symbols), for  $m_{NaCl} = 1.0$  m (a) and 3.2 m  
 319 (c). Calculated  $pH$ -edges for sorption of Np(V) and Np(IV) (no redox transition considered), respectively, are  
 320 shown as lines. On the right: corresponding  $pH_m$ - $pe$  values measured in  $m_{NaCl} = 1.0$  m (b) and 3.2 m (d) for the  
 321 different  $[Np]_{tot}$  are shown with the same symbols as on the left. The calculated Np(V)/Np(IV) redox borderlines  
 322 in solution ( $\{Np(V)/Np(IV)\}_{aq}$ ; black line) and at the illite surface ( $\{Np(V)/Np(IV)\}_{surf}$ ; grey line) are also shown.  
 323 Error bars are not shown for clarity but uncertainties for  $\log R_d$  (a,c) lie in the range of  $\pm 0.3$  and for  $pe$  (b,d) in  
 324 the range of  $\pm 0.8$ . The  $pH$ - $pe$  value for the sample analyzed by XANES ( $m/V = 20$  g  $L^{-1}$ ; 3.2 m NaCl;  $[Np]_{tot} =$   
 325  $3 \times 10^{-4}$  M) is also shown (d).

326

### 327 3.3. $pH$ - $pe$ diagrams in solution and at the illite surface

328 Redox borderlines between the predominance fields of Np(V) and Np(IV) in solution  
 329 (noted as  $\{Np(V)/Np(IV)\}_{aq}$ ) are shown in figures 2b (for 1.0 m NaCl) and 2d (for 3.2 m  
 330 NaCl) as black lines. The borderline between the predominance fields of Np(V) and Np(IV)  
 331 species adsorbed at the surface of illite (noted as  $\{Np(V)/Np(IV)\}_{surf}$ ) is described by:

$$332 \{Np(V)/Np(IV)\}_{surf} = \{Np(V)/Np(IV)\}_{aq} + (\log R_d(Np(IV)) - \log R_d(Np(V))) \quad (6)$$

333 and is plotted as well in figures 2b and 2d (grey lines). In eq. 6,  $\{Np(V)/Np(IV)\}_{aq}$  and  
334  $\{Np(V)/Np(IV)\}_{surf}$  correspond to  $pe$  values, where  $[Np(V)]_{aq}/[Np(IV)]_{aq}$  and  
335  $[Np(V)]_{surf}/[Np(IV)]_{surf}$  equal 1. They can vary with physico-chemical conditions ( $pH_m$ ,  $m_{NaCl}$ ,  
336  $T$ , etc) in a similar way as  $\log R_d(Np(IV))$  and  $\log R_d(Np(V))$ .

337 As shown in previous studies (Marsac et al., 2015a,b; Banik et al., 2016; Marsac et al.,  
338 2017), the stability fields of surface sorbed  $Np(IV)$  and  $Pu(IV)$  species are extended relative to  
339 those for dissolved species because of their stronger sorption relative to that of other redox  
340 states (i.e.  $Pu(III, V, VI)$ ;  $Np(V)$ ) under the conditions investigated in those studies. For  $pH < 6$ ,  
341 at elevated ionic strength (i.e. 1.0 and 3.2 m), we find a shift of  $\{Np(V)/Np(IV)\}_{surf}$  to  
342 significantly higher values because  $Np(V)$  sorption to illite is decreased.  $Np(V)$  and  $Np(IV)$   
343 inner-sphere surface complexation to illite is only weakly affected by ionic strength so that  
344  $\{Np(V)/Np(IV)\}_{surf}$  hardly varies between 0.1 and 3.2 m  $NaCl$  for  $pH > 6$ .

345 By comparing the experimental  $pH_m-pe$  values and the calculated values for  
346  $\{Np(V)/Np(IV)\}_{aq}$  and  $\{Np(V)/Np(IV)\}_{surf}$ , we expect  $Np(V)$  to prevail in solution while  
347  $Np(IV)$  predominantly exists as surface species. This qualitatively explains why the measured  
348  $Np$  sorption data lie between those calculated for pentavalent and tetravalent  $Np$  species.

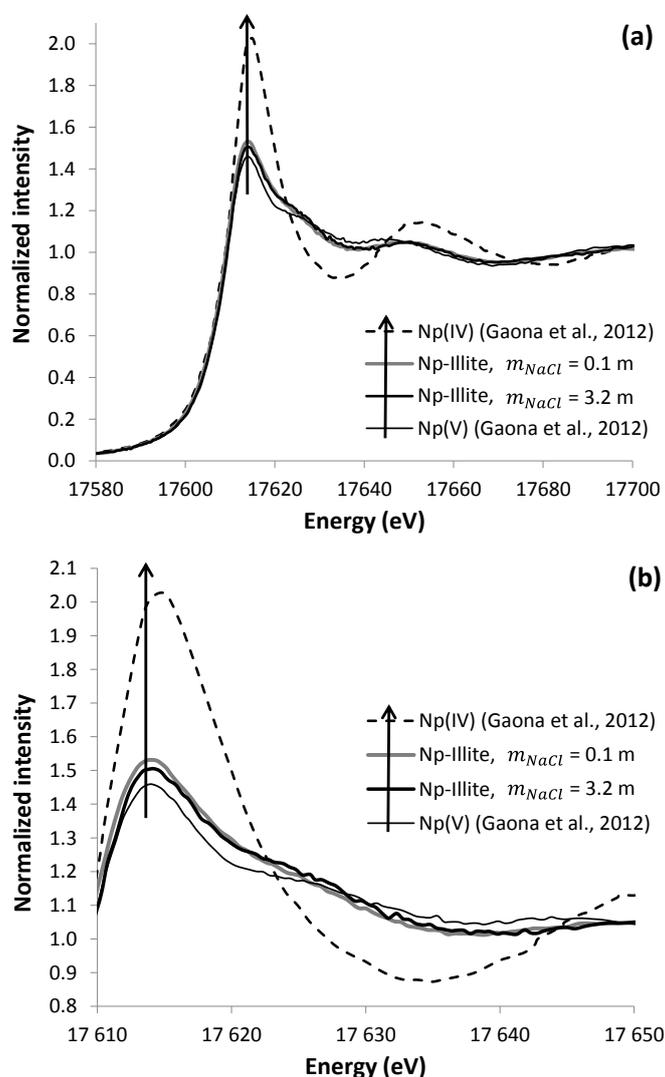
349

### 350 **3.4. Spectroscopic results**

351  $Np$  redox speciation at the illite surface was further investigated by XANES for  $pH_m =$   
352 7.9 ( $pe = 7.3 \pm 0.8$ ),  $m/V = 20 \text{ g L}^{-1}$ , 3.2 m  $NaCl$  and  $3 \times 10^{-4} \text{ M Np}$  (introduced as  $NpO_2^+$ ). In  
353 figure 3, the XANES spectrum recorded for the  $Np$ -illite sample prepared in 3.2 m  $NaCl$  is  
354 compared to the spectrum recorded in  $m_{NaCl} = 0.1 \text{ m}$  by Marsac et al. (2015a) under similar  
355 conditions ( $pH_m = 7.4$ ;  $pe = 6.8 \pm 0.8$ ). As explained before, phase separation was performed  
356 to remove the solution from the sample. Therefore, the following analysis of spectra pertains  
357 only to  $Np$  species associated to the solid phase. The  $Np$ -illite XANES spectra are compared  
358 to those reported for  $Np^{4+}$  and  $NpO_2^+$  aquo ions in 0.1 M  $HClO_4$  (Gaona et al., 2012),

359 measured at the same beamline. The presence of a shoulder at 17625 eV indicates multiple  
360 scattering of the outgoing Np  $2p_{3/2}$  electrons along the axis of the  $\text{NpO}_2^+$  dioxo cation. This  
361 indicates the prevalence of the +V redox state in both Np-illite samples. The “white line” (WL)  
362 position as well as the inflection point of Np redox states +IV and +V are similar and cannot  
363 be used as a conclusive probe for Np redox speciation. However, Np(V) and Np(IV) XANES  
364 show significant differences in the intensity of the WL. The WL intensity increases from the  
365  $\text{NpO}_2^+$  aquo ion to the Np-illite sample in 0.1 m NaCl. The sample prepared in 3.2 m NaCl  
366 shows intermediate intensity. As discussed in more detail in Marsac et al. (2015a) and  
367 Denecke et al. (2005), the WL of Np(V) sorbed to a mineral surface will be less intense than  
368 that of the Np(V) aquo-ion. Therefore, the present results indicate the presence of Np(IV). By  
369 fitting the 0.1 m NaCl Np-illite XANES spectrum with a linear combination of Np(V) and  
370 Np(IV) reference samples (i.e. aquo-ions), Marsac et al. (2015a) found that  $14 \pm 1\%$  (error  
371 provided by the Demeter Athena software; Ravel and Newville, 2005) of the adsorbed Np was  
372 Np(IV) (i.e. Np(V)-to-Np(IV) concentration ratio at the illite surface  $[\text{Np(V)}]_{\text{surf}}/[\text{Np(IV)}]_{\text{surf}} =$   
373  $6.1$ ). Repeating the same exercise for the 3.2 m NaCl sample yields the presence of at least  
374  $8 \pm 1\%$  of the Np existing as tetravalent species at the illite surface (i.e.  $[\text{Np(V)}]_{\text{surf}}/[\text{Np(IV)}]_{\text{surf}}$   
375  $= 11.5$ ). Although this value is small, it must be considered as a minimum value since the  
376 aquo-ions exhibit the most intense WLs. The same exercise with either a Np(V) or a Np(IV)  
377 reference, where Np is in a more condensed state (i.e. with a less intense WL), would lead to a  
378 larger fraction of Np(IV) (Marsac et al., 2015a). XANES analysis, therefore, yields a similar  
379 result compared to what has been obtained for the experiment at low ionic strength and  
380 provides a clear indication for partial reduction of Np(V), also at elevated ionic strength.  
381 Using experimental  $p_e$  and spectroscopically determined  $[\text{Np(V)}]_{\text{surf}}/[\text{Np(IV)}]_{\text{surf}}$  values, we  
382 find that  $\{\text{Np(V)/Np(IV)}\}_{\text{surf}} = 6.0$  (for  $m_{\text{NaCl}} = 0.1$ ) and  $6.2$  (for  $m_{\text{NaCl}} = 3.2$ ). These values  
383 compare very well with  $\{\text{Np(V)/Np(IV)}\}_{\text{surf}} = 5.9$  (for both 0.1 and 3.2 m NaCl), as  
384 determined by modeling (see e.g. the grey lines in Fig. 2b,d). This further confirms that the

385 Np(V)-Np(IV) redox transition at the illite surface is not substantially affected by ionic  
386 strength.



387

388 **Figure 3.** (a) Np L<sub>3</sub>-XANES measured for Np-illite samples ( $[Np]_{tot} = 3 \times 10^{-4}$  M,  $m/V = 20$  g L<sup>-1</sup>) prepared in 0.1  
389 m NaCl ( $pH_m = 7.4$ ;  $p_e = 6.8$ ; Marsac et al., 2015a) and 3.2 m NaCl ( $pH_m = 7.9$ ;  $p_e = 7.3$ ; present study).  
390 Reference XANES of aqueous Np(IV) and Np(V) in 1 M HClO<sub>4</sub> from Gaona et al. (2012) are shown for  
391 comparison. Arrows highlight the partial Np(V) reduction to Np(IV) in the present study. The area between  
392 17610 and 17650 eV is enlarged in (b). Results of the linear combination fit are shown in the supporting  
393 information (Figure S1).

394

395

## 4. DISCUSSION

### 4.1. *Effects of $pH_m$ , $pe$ and $m_{NaCl}$ on Np sorption to illite*

398 Because Np uptake on illite is sensitive to  $pH_m$  and  $pe$ , it appears difficult to study in  
399 detail the effect of a third parameter, namely  $m_{NaCl}$ . Figure 4 shows data for experimentally  
400 determined  $\log R_d$  plotted versus  $pe$  for  $m_{NaCl} = 0.1, 1.0$  and  $3.2$ . It is obvious that there is a  
401 strong correlation between  $R_d$  and  $pe$  showing that increasing the  $pe$  from 2 to 6 reduces  $R_d$  by  
402  $\sim 3$  orders of magnitude. In so far “ $pe$  edges” ( $\log R_d$  plotted vs.  $pe$ ) are more informative than  
403 the “ $pH$  edges” in Figures 2a and 2c ( $\log R_d$  vs.  $pH$ ). It appears that  $pe$  is the more relevant  
404 parameter determining Np retention under given conditions. A few experimental data do not  
405 fit into the trend and have been excluded from figure 4: (i) sorption data obtained at  $pH_m < 6$   
406 show a significant  $pH$  dependence because the Np(V)/Np(IV) borderlines in this range clearly  
407 evolve with  $pH$  (see Fig. 2b,d); (ii) at quite high  $pe$  values, where Np(V) prevails in solution  
408 and at the illite surface, the influence of  $pH$  on Np sorption is of course dominant (see the  $pH$ -  
409 edges of Np(V) in Fig. 2a,c). The exclusion of data points amount to  $\sim 20\%$  of the complete  
410 data set, and make sure that, for the selected data,  $pH$  has no significant effect.

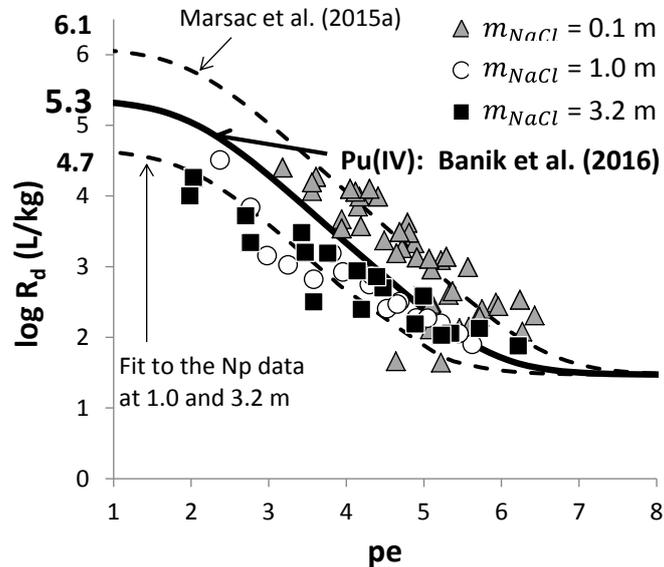
411 Figure 4 seems to suggest that Np sorption to illite is stronger in 0.1 than in 1.0 and  
412 3.2 m NaCl at least for  $pe < 4.5$ , an issue that does not occur on Figure 1. Recent experimental  
413 investigations did not show significant influence of ionic strength neither on tetravalent  
414 actinide ion ( $I = 0.1 - 3.2$  m; Bradbury and Baeyens, 2005; Marsac et al., 2017; results of both  
415 studies on Th(IV) and Pu(IV) sorption are shown in the supporting information) nor on Np(V)  
416 sorption to illite via inner-sphere surface complexation ( $I = 0.1$  to  $4.6$  M; Nagasaki et al.,  
417 2016). Moreover, our XANES results suggest no ionic strength effect on Np(V)-Np(IV) redox  
418 transition at the illite surface. In fact, the interpretation of the Np-illite results is strongly  
419 affected by the experimental  $pe$ . Unlike Np, Th(IV) is not a redox sensitive metal ion and its  
420 sorption on illite is independent of the ionic strength within the experimental uncertainties.

421 The same independency of the ionic strength is observed for Pu(IV) illite uptake. From these  
422 results it would appear difficult to assume, that the ionic strength has no significant influence  
423 on the Np(IV) uptake, although trends in average values could suggest such effects. Therefore,  
424 it is more probable that the variations of Np-illite uptake data are due to the uncertainties of  
425 experimental pe measurements.

426 To highlight the consistency between Np-illite and Pu-illite sorption data in 0.1, 1.0  
427 and 3.2 m NaCl (Banik et al., 2016; Marsac et al., 2017; present study), simulations are made  
428 with the 2 SPNE SC/CE model for  $pH_m = 7$  and the results are plotted in Figure 4. This  $pH_m$   
429 value is arbitrarily chosen because insignificant  $pH_m$  effect is expected for the selected dataset,  
430 as explained above. The surface complexation constant for Np(IV) given by Marsac et al.  
431 (2015a) (Table S3) describes sorption data determined for low ionic strength accurately, but  
432 overestimates sorption when comparing with experimental data determined in this study. In  
433 this case,  $\log R_d(\text{Np(IV)}) = 6.1$  (i.e.  $\log R_d$  values extrapolated to pe values where all Np(V)  
434 in the system is reduced to Np(IV) in solution and at the illite surface). Adjusting model  
435 parameters to fit our data in 1.0 and 3.2 m NaCl using PhreePlot leads to  $\log R_d(\text{Np(IV)}) = 4.7$   
436 (corresponding surface complexation constants are given in Table S3). In average, the model  
437 would give  $\log R_d(\text{Np(IV)}) = 5.4 \pm 0.7$  (which is also determined by Phreeplot when using the  
438 complete dataset in 0.1, 1.0 and 3.2 m NaCl; Table S3). This average value is in excellent  
439 agreement with  $\log R_d(\text{Pu(IV)}) = 5.3 \pm 0.3 \text{ L kg}^{-1}$  determined by Marsac et al. (2017) for  $0.1 <$   
440  $m_{\text{NaCl}} < 3.2 \text{ m}$ . Figure 4 shows that calculated  $\log R_d$  evolves linearly with pe for  
441 intermediate pe values (for  $\{\text{Np(V)/Np(IV)}\}_{\text{aq}} < pe < \{\text{Np(V)/Np(IV)}\}_{\text{surf}}$ , all the selected data  
442 are within this range in Figure 4). Therefore, an error of  $\pm 0.8$  on pe leads to an error of  $\pm 0.8$   
443 on the calculated  $\log R_d$  value, which compares well with the error on determined  $\log$   
444  $R_d(\text{Np(IV)})$  using Np-illite data at 0.1, 1 and 3.2 m NaCl ( $\pm 0.7$ ). These results suggest that it  
445 is reasonable to impose surface complexation constants for Np(IV) equal to those of Pu(IV)

446 and to attribute the trend of average Np-illite uptake with ionic strength effects to  
447 uncertainties in pe.

448



449

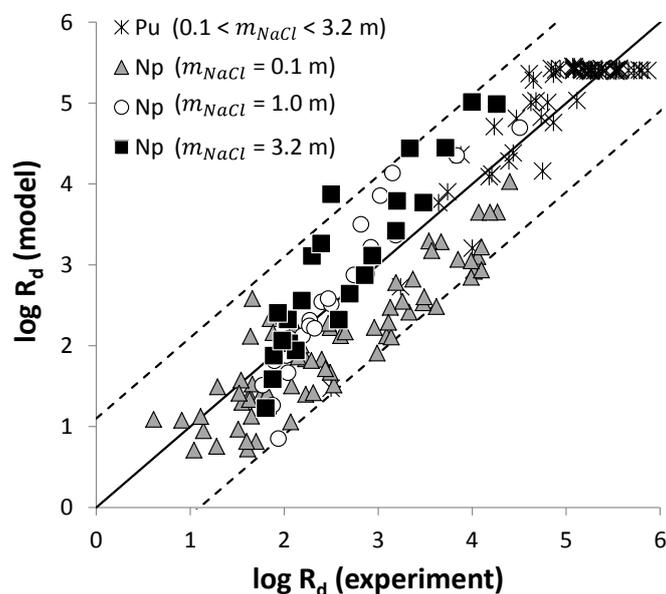
450 **Figure 4.** Np-illite sorption datasets from Marsac et al. (2015a;  $m_{NaCl} = 0.1$  m) and the present study ( $m_{NaCl} =$   
451 1.0 and 3.2 m) are plotted as  $\log R_d$  versus pe. Lines are calculations made with the 2 SPNE SC/CE model for  
452  $pH_m = 7$  using the surface complexation constants determined by Marsac et al. for Np(IV) (2015a; top dotted  
453 line), Banik et al. for Pu(IV) (2016; bold line) or fitting these constants to the 1.0 and 3.2 m NaCl data (bottom  
454 dotted curve). The corresponding  $\log R_d(Np(IV))$  is given on the y-axis.

455

#### 456 **4.2. Modeling An(III,IV,V) sorption to illite as a function of $pH_m$ , pe and $m_{NaCl}$**

457 Values of  $\log R_d$  are calculated for all the presently investigated conditions (including  
458 the conditions of Marsac et al., 2015a) using the experimental  $pH_m$  and pe values. The model  
459 results are plotted versus the experimental  $\log R_d$  in Figure 5. The results of Banik et al. (2016;  
460 0.1 m NaCl) and Marsac et al. (2017; 1.0 and 3.2 m NaCl), involving the Pu(IV)/Pu(III)  
461 couple, are also included. The 1:1 line shows the good agreement between model and  
462 experiment. Deviations of  $\pm 1.1 \log R_d$  unit are shown as dotted lines. This error for the  
463 calculated  $\log R_d$  accounts for both the error on pe ( $\pm 0.8$ ) and on experimental  $\log R_d$  ( $\pm 0.3$ ).  
464 For a wide range of  $pH_m$ ,  $[Np/Pu]_{tot}$ ,  $m_{NaCl}$  and pe investigated in these different studies (i.e.  
465 179 experimental  $\log R_d$  values) the discrepancies between model and the experimental

466 results rarely exceed 1.1 log  $R_d$  unit. The mean value of the deviation between experimental  
 467 and calculated log  $R_d$  values is 0.42. It is important to note that sorption data are highly  
 468 sensitive to the redox conditions and pe measurements are associated with considerable  
 469 uncertainties. We nevertheless conclude that the combination of (i) the 2 SPNE SC/CE model,  
 470 (ii) SIT and (iii) the approach developed by Marsac et al. (2015a,b), which accounts for redox  
 471 equilibria and the stability of surface species, allows to reasonably model actinide(III,IV,V)  
 472 uptake by illite as a function of  $pH_m$ , pe and  $m_{NaCl}$  up to highly saline conditions.  
 473



474  
 475 **Figure 5.** Modelled versus experimental log  $R_d$  values for Np (data from this study and Marsac et al., 2015a) and  
 476 Pu in  $0.1 < m_{NaCl} < 3.2$  m (data from Banik et al., 2016; Marsac et al., 2017). The 1:1 (solid) line is associated  
 477 with an uncertainty of  $\pm 1.1$  log  $R_d$  units (dashed lines).  
 478

#### 479 4. CONCLUSIONS

480 In agreement with previous studies performed at low ionic strength (Marsac et al.,  
 481 2015a), Np sorption increases with decreasing redox potential also at high  $m_{NaCl}$  (up to 3.2  
 482 m). Using a combined batch sorption, spectroscopic and geochemical modeling approach, the  
 483 strong interaction between Np and illite is attributed to the partial reduction of Np(V) to

484 Np(IV) at the illite surface driven by the higher thermodynamic stability of Np(IV) surface  
485 complexes as compared to Np(V) surface species. By the combination of the 2 SPNE SC/CE  
486 model with SIT, it is possible to reproduce experimentally obtained overall Np uptake data for  
487 illite as a function of  $pH_m$ ,  $pe$  and  $m_{NaCl}$  using a single set of parameters. The ionic strength  
488 has a relatively small impact on sorption of both Np(V) and Np(IV). Main parameters driving  
489 the sorption behavior of redox sensitive actinides are  $pH_m$  and  $pe$ .

490 Notably the role of the redox potential on the uptake of redox sensitive actinides on  
491 minerals is to be considered when applying laboratory derived conditional  $R_d$  values for  
492 performance safety assessment purposes. The applicability of such data is only justified, if  
493 redox conditions in laboratory experiments and those expected in the real system are identical.  
494 This is not always the case as extraction of natural materials from deep environments,  
495 transport to the laboratory and experimental handling are technically challenging and redox  
496 conditions may change due to e.g. access of oxygen. However, if the pH and redox potentials  
497 of *in situ* and laboratory conditions are known, mechanistic models as proposed here, are  
498 capable of assessing the overall uptake of redox sensitive actinides by natural adsorbents with  
499 reasonable accuracy. In agreement with recent studies, the use of non-electrostatic models  
500 appears suitable for the prediction of metal ion sorption to various types of surfaces even at  
501 elevated ionic strength, e.g. marine microalgae (Zoll and Schjif, 2012), bacteria (Ams et al.,  
502 2013), illite (Schnurr et al., 2015; Marsac et al., 2017) or smectite (Schnurr et al., 2015).  
503 Accordingly, the 2 SPNE SC/CE model is a reliable predictive tool for performance safety  
504 assessment for clays even under elevated saline conditions.

505

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512

513 **Supporting Information Available**

514 Additional material is provided in the supporting information section.

515

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- 648

649 **Figure caption**

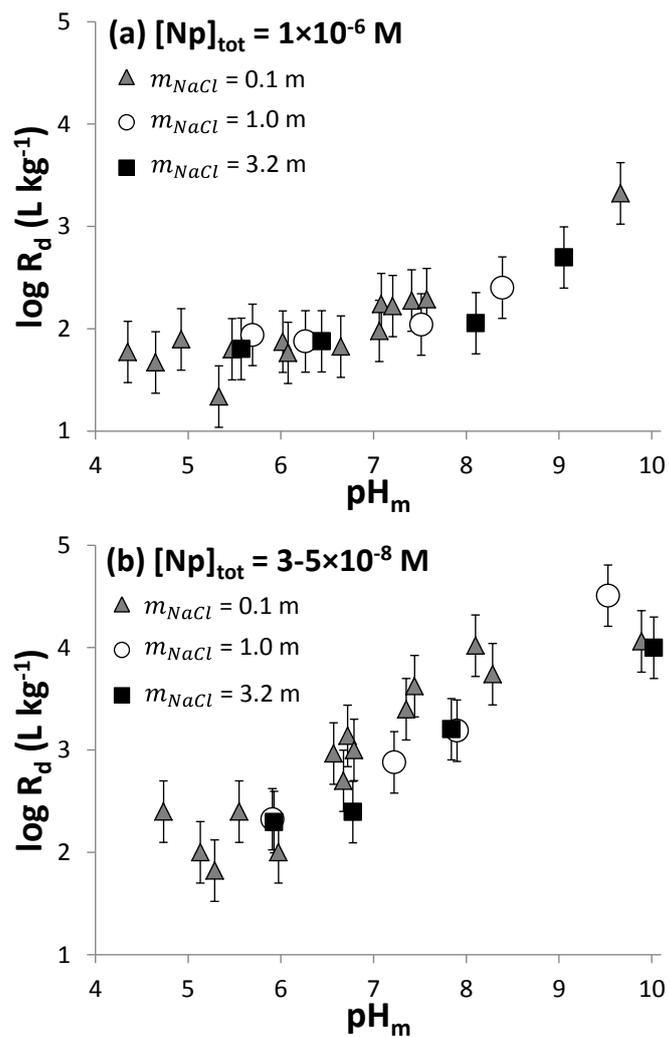
650 **Figure 1.** Np sorption to illite ( $\log R_d$  in  $L\ kg^{-1}$ ) after 1 week contact time in 1.0 and 3.2 m  
651 NaCl versus  $pH_m$  for  $[Np(V)]_{tot} = 10^{-6}$  M (a) and  $5 \times 10^{-8}$  M (b). The results obtained in 0.1 m  
652 NaCl are taken from Marsac et al. (2015a) after 1 week contact time,  $[Np(V)]_{tot} = 10^{-6}$  M (a)  
653 and  $3 \times 10^{-8}$  M (b).

654 **Figure 2.** On the left: experimental  $\log R_d$  data measured after 1 week versus the  $pH_m$  for the  
655 various  $[Np]_{tot}$  investigated (0.05, 0.09, 0.3, 0.5, 0.9 and 3  $\mu M$ ; shown as different symbols),  
656 for  $m_{NaCl} = 1.0$  m (a) and 3.2 m (c). Calculated pH-edges for sorption of Np(V) and Np(IV)  
657 (no redox transition considered), respectively, are shown as lines. On the right: corresponding  
658  $pH_m$ -pe values measured in  $m_{NaCl} = 1.0$  m (b) and 3.2 m (d) for the different  $[Np]_{tot}$  are  
659 shown with the same symbols as on the left. The calculated Np(V)/Np(IV) redox borderlines  
660 in solution ( $\{Np(V)/Np(IV)\}_{aq}$ ; black line) and at the illite surface ( $\{Np(V)/Np(IV)\}_{surf}$ ; grey  
661 line) are also shown. Error bars are not shown for clarity but uncertainties for  $\log R_d$  (a,c) lie  
662 in the range of  $\pm 0.3$  and for pe (b,d) in the range of  $\pm 0.8$ . The pH-pe value for the sample  
663 analyzed by XANES ( $m/V = 20\ g\ L^{-1}$ ; 3.2 m NaCl;  $[Np]_{tot} = 3 \times 10^{-4}$  M) is also shown (d).

664 **Figure 3.** (a) Np  $L_3$ -XANES measured for Np-illite samples ( $[Np]_{tot} = 3 \times 10^{-4}$  M,  $m/V = 20\ g$   
665  $L^{-1}$ ) prepared in 0.1 m NaCl ( $pH_m = 7.4$ ; pe = 6.8; Marsac et al., 2015a) and 3.2 m NaCl ( $pH_m$   
666 = 7.9; pe = 7.3; present study). Reference XANES of aqueous Np(IV) and Np(V) in 1 M  
667  $HClO_4$  from Gaona et al. (2012) are shown for comparison. Arrows highlight the partial Np(V)  
668 reduction to Np(IV) in the present study. The area between 17610 and 17650 eV is enlarged  
669 in (b). Results of the linear combination fit are shown in the supporting information (Figure  
670 S1).

671 **Figure 4.** Np-illite sorption datasets from Marsac et al. (2015a;  $m_{NaCl} = 0.1$  m) and the  
672 present study ( $m_{NaCl} = 1.0$  and 3.2 m) are plotted as  $\log R_d$  versus pe. Lines are calculations  
673 made with the 2 SPNE SC/CE model for  $pH_m = 7$  using the surface complexation constants  
674 determined by Marsac et al. for Np(IV) (2015a; top dotted line), Banik et al. for Pu(IV) (2016;  
675 bold line) or fitting these constants to the 1.0 and 3.2 m NaCl data (bottom dotted curve). The  
676 corresponding  $\log R_d(Np(IV))$  is given on the y-axis.

677 **Figure 5.** Modelled versus experimental  $\log R_d$  values for Np (data from this study and  
678 Marsac et al., 2015a) and Pu in  $0.1 < m_{NaCl} < 3.2$  m (data from Banik et al., 2016; Marsac et  
679 al., 2017). The 1:1 (solid) line is associated with an uncertainty of  $\pm 1.1$   $\log R_d$  units (dashed  
680 lines).

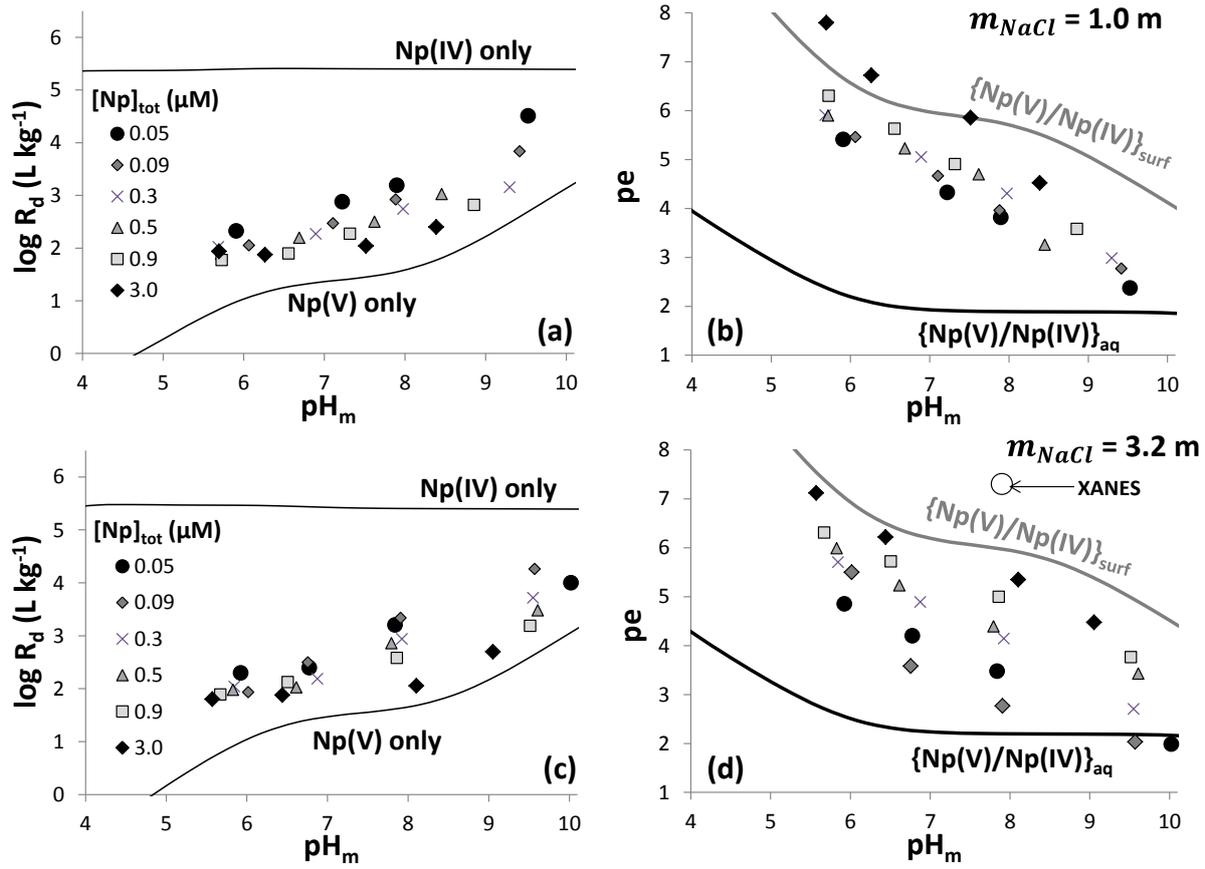


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**Figure 1**

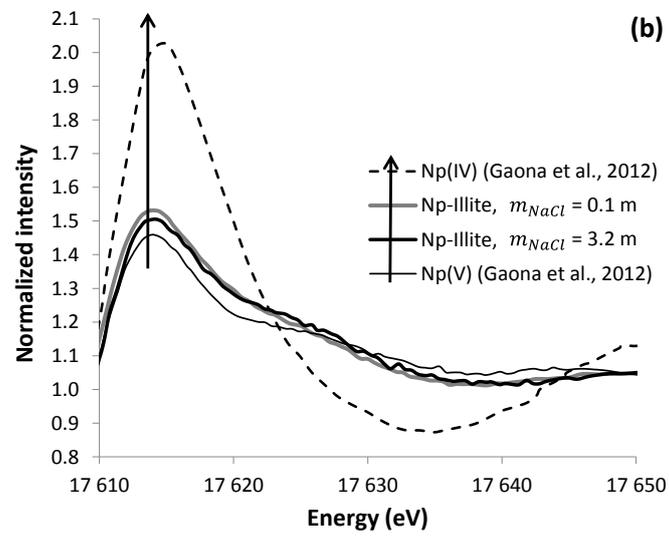
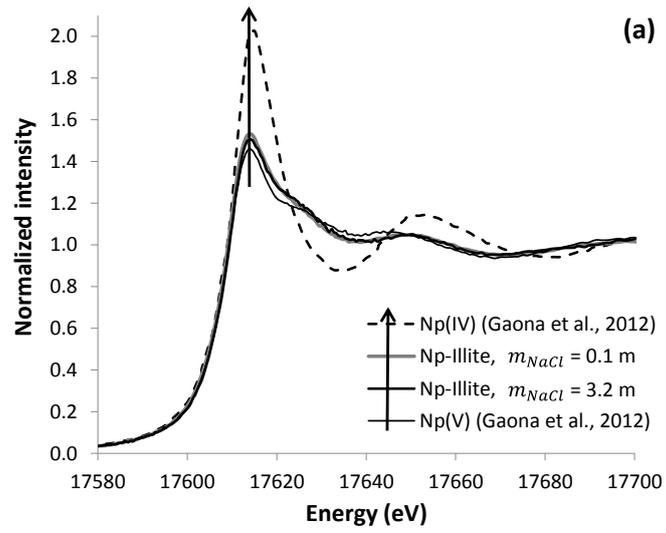


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Figure 2



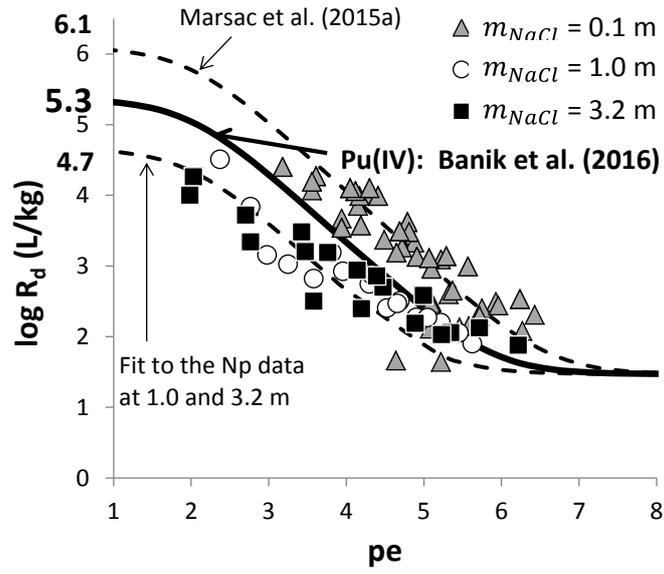
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**Figure 3**

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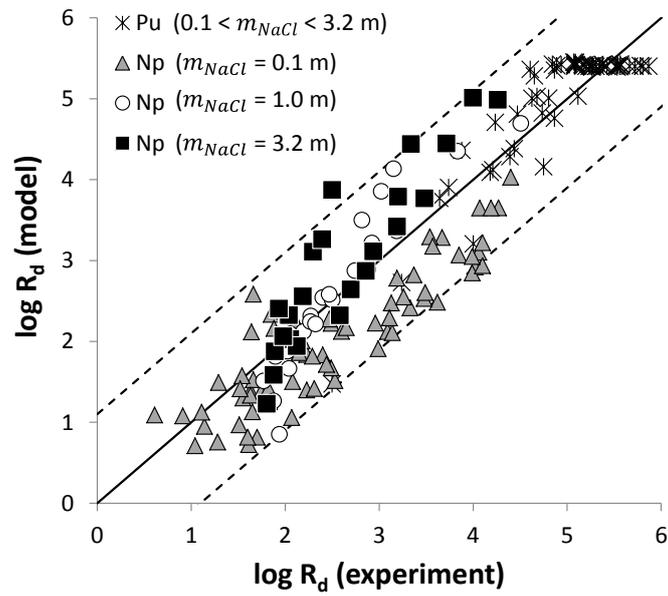


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Figure 4

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Figure 5