

**Geochemical Interactions of Plutonium with Opalinus Clay Studied by Spatially Resolved Synchrotron Radiation Techniques**

Kaplan, U.; Amayri, S.; Drebert, J.; Rossberg, A.; Grolimund, D.; Reich, T.;

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**Geochemical Interactions of Plutonium with Opalinus Clay Studied by Spatially Resolved Synchrotron Radiation Techniques**

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Complete List of Authors:	Kaplan, Ugras; Karlsruhe Institute of Technology (KIT), Institute for Nuclear Waste Disposal (INE); Johannes Gutenberg-Universität, Institut für Kernchemie Amayri, Samer; Johannes Gutenberg-Universität, Institut für Kernchemie Drebert, Jakob; Johannes Gutenberg-Universität, Institute of Nuclear Chemistry Rossberg, Andre; Forschungszentrum Dresden-Rossendorf, Institute of Radiochemistry Grolimund, Daniel; Paul Scherrer Institute, Swiss Light Source Reich, Tobias; Institut für Kernchemie, Johannes Gutenberg Universität Mainz

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1 **Geochemical Interactions of Plutonium with Opalinus Clay Studied by Spatially**  
2 **Resolved Synchrotron Radiation Techniques**

3

4 Ugras Kaplan<sup>1</sup>, Samer Amayri<sup>1</sup>, Jakob Drebert<sup>1</sup>, Andre Rossberg<sup>2</sup>, Daniel Grolimund<sup>3,\*</sup>,  
5 Tobias Reich<sup>1,\*</sup>

6

7 <sup>1</sup> Johannes Gutenberg-Universität Mainz, Institute of Nuclear Chemistry, Fritz-Strassmann-  
8 Weg 2, 55128 Mainz, Germany

9 <sup>2</sup> Helmholtz-Zentrum Dresden-Rossendorf (HZDR), Institute of Resource Ecology, Bautzner  
10 Landstraße 400, 01328 Dresden, Germany.

11 <sup>3</sup> Paul Scherrer Institute, Swiss Light Source, microXAS Beamline Project, 5232 Villigen PSI,  
12 Switzerland

13

14

15

16 \* Corresponding authors:

17 [treich@uni-mainz.de](mailto:treich@uni-mainz.de) (+49 6131 3925250); [daniel.grolimund@psi.ch](mailto:daniel.grolimund@psi.ch) (+41 56 310 4782)

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20

## 21 **Abstract**

22 Plutonium plays an important role within nuclear waste materials because of its long half-life  
23 and high radiotoxicity. The aim of this study was to investigate with high spatial resolution  
24 the reactivity of the more oxidized forms of Pu(V,VI) within Opalinus Clay (OPA) rock, a  
25 heterogeneous, natural argillaceous rock considered as potential repository host. A  
26 combination of synchrotron based X-ray microprobe and bulk techniques were used to study  
27 the spatial distribution and molecular speciation of Pu within OPA after diffusion and sorption  
28 processes. Microscopic chemical images revealed a pronounced impact of geochemical  
29 heterogeneities concerning the reactivity of the natural barrier material. Spatially resolved X-  
30 ray absorption spectroscopy documented a reduction of the highly soluble Pu(V,VI) to the  
31 less mobile Pu(IV) within the argillaceous rock material, while bulk investigations showed  
32 second-shell scattering contributions, indicating an inner-sphere sorption of Pu on OPA  
33 components. Micro-diffraction imaging identified the clay mineral kaolinite to play a key role  
34 in the immobilization of the reduced Pu.

35 The findings provide strong evidence that reduction and immobilization do not occur as  
36 linked processes on a single reactive phase but as decoupled, subsequent and spatially  
37 separated reactions involving different phases of the OPA.

38

39 **Keywords:** Plutonium, Opalinus Clay, micro-XANES, micro-XRD, micro-XRF,  
40 XANES/EXAFS, speciation, sorption, migration, synchrotron microprobe techniques

41

## 42 **1. Introduction**

43 The breach of the first containment and the resulting release of radionuclides out of the  
44 storage canisters and subsequent migration through the enclosing multi-barrier system  
45 corresponds to an accepted and considered incident within safety assessments of waste  
46 repositories<sup>1, 2</sup>. To assess the potential risk of impairing host rock formations, neighboring

47 aquifers and finally the biosphere, the mobility and immobilization behavior of radionuclides  
48 in multi-barrier systems have to be investigated. Beside other actinides, plutonium (Pu) will  
49 be a major contributor to the radiotoxicity of high-level nuclear waste after a storage time of  
50 more than 1,000 years due to the long half-lives and radiotoxicity of its isotopes  $^{239}\text{Pu}$  and  
51  $^{240}\text{Pu}$ <sup>3-7</sup>.

52 Considering the chemical properties of Pu, this element reveals a complicated redox behavior  
53 as it can exist in aqueous solution in different oxidation states (typically III-VI), depending on  
54 the chemical conditions such as pH, Eh, and ionic strength. Up to three oxidation states of Pu  
55 can coexist in natural waters. The oxidation states V and VI have low tendency for hydrolysis,  
56 precipitation, and sorption on natural minerals<sup>8-10</sup>. Accordingly, related species exhibit a  
57 pronounced mobility in subsurface systems. In contrast, the reduced oxidation states Pu(III)  
58 and Pu(IV) prevail as solids with low solubility and show a high affinity for mineral surfaces  
59 (strong adsorption or surface precipitations) resulting in a considerable retardation of the Pu  
60 spreading. Consequently, the migration behavior of Pu in the environment depends strongly  
61 on its oxidation state and related pore water chemistry (pH, redox potential, ionic strength,  
62 electrolyte composition, and complexing agents) but also on the geochemical characteristics  
63 of the host rock material, e.g., its mineralogy<sup>11</sup>.

64 Based on the typical initial waste forms and the reducing conditions in a nuclear waste  
65 repository, plutonium is expected to be present initially in its more reduced form of +IV in the  
66 repository<sup>12, 13</sup>. However, over time waters with increasing levels of dissolved oxygen may  
67 infiltrate the repository, potentially oxidizing Pu to its more mobile forms of +V and +VI.  
68 Accordingly, due to their increased mobility in subsurface systems and the resulting increased  
69 environmental risk, the present study focuses on the higher oxidized forms of Pu.

70 Based on their high cation retardation potential and advantageous physical properties – e.g.  
71 the self-sealing due to swelling – argillaceous rocks are considered as a potential host rock  
72 formation for the construction of high-level nuclear waste repositories in several European

73 countries <sup>4,5,6,7</sup>. In this study Opalinus Clay (OPA) rock, which is present in southern  
74 Germany and Switzerland, was used as a natural reference barrier material. Predominantly,  
75 OPA consists of different types of clay minerals, in particular illite, illite/smectite mixed  
76 layers, and kaolinite, with minor components such as calcite, quartz, and the Fe(II)-bearing  
77 minerals pyrite and siderite (see Supporting Information (SI). Regarding the potential  
78 application as host rock for a nuclear waste repository, OPA rock has favorable properties  
79 such as low hydraulic permeability as well as stable geochemical conditions and mechanical  
80 properties <sup>14</sup>. Several geological studies document that the present geological settings can be  
81 considered as being unchanged for several millions of years <sup>15</sup>.

82

83 In compacted clay barrier systems, diffusion – potentially retarded by sorption and/or  
84 precipitation – corresponds to the predominant transport phenomena determining the  
85 spreading of radionuclides <sup>16</sup> (while in advection dominated systems with larger transport  
86 pores colloid facilitated transport could become an additional relevant transport vector <sup>17, 18</sup>).  
87 Accordingly, the investigation of reactions occurring at the solid-solution interface is most  
88 fundamental towards an in-depth understanding of the retarded spreading of Pu in compacted  
89 reactive barrier systems. This topic received indeed considerable attention in the past.  
90 However, the vast majority of the corresponding investigations represent macroscopic scale  
91 studies employing a single, well defined solid, commonly pure or even synthetic mineral  
92 phase.

93

94 Several studies have been performed to investigate the interaction of Pu with pure clay  
95 minerals (e.g., kaolinite <sup>19, 20</sup>, illite <sup>21</sup>, or Na-montmorillonite <sup>22, 23</sup>). Pu sorption onto  
96 oxide/hydroxide mineral surfaces such as goethite and hematite <sup>24, 25</sup>, manganite and  
97 hausmannite <sup>26</sup>, or magnetite <sup>27</sup>, to sulfides (e.g., mackinawite <sup>27</sup>), or onto carbonates (e.g.,  
98 calcite <sup>28</sup> or chukanovite <sup>27</sup>) was also examined. These studies showed that the sorption

99 behavior of Pu depends indeed significantly on its oxidation state, the prevailing pH  
100 conditions, ambient CO<sub>2</sub> partial pressure, and the type of mineral surfaces present. For  
101 example, in the study of Sanchez et al.<sup>24</sup>, Pu(V) was reduced to Pu(IV) by a ‘surface  
102 mediated’ process and immobilized on the goethite surface (although without identification of  
103 the corresponding electron donor). Ionic strength variations in the range between 0.03 M and  
104 3.0 M did not influence the sorption of Pu(IV), indicative of a covalent bonding of Pu(IV) to  
105 the goethite. The sorption of Pu was further shown to decrease in carbonate media due to the  
106 formation of aqueous Pu-carbonate complexes documenting the importance of ligands (or  
107 pore water chemistry in general) in the context of subsurface Pu mobility.

108 Only a limited number of studies addresses the environmental reactivity of Pu(V) and Pu(VI)  
109 within complex natural barrier materials. Amayri et al.<sup>29</sup> studied the sorption of Pu and other  
110 actinides on OPA material by batch sorption experiments. This study showed that the affinity  
111 for the solid surfaces depends strongly on the oxidation state of the actinides. The determined  
112 sorption affinities for the tri- and tetravalent actinides such as Pu(III/IV) were almost 3 orders  
113 of magnitude stronger compared to actinide species of oxidation states +V and +VI.  
114 Compared to U(VI), that was stable during the experiments of Amayri et al., Pu(VI) expressed  
115 a more than 250 times higher uptake by OPA, a peculiarity construed by the authors as  
116 indication for a change in oxidation state of Pu(VI) during the sorption process. For the  
117 interaction of Pu(V) with bentonite, the time-dependent investigations of Begg et al.<sup>30</sup>  
118 revealed a slow, continuous uptake of Pu(V) over 300 days. Supported by indirect evidences,  
119 the authors attributed this observation to a slow reduction of Pu(V) on clay surfaces. Hixon et  
120 al.<sup>31</sup> observed ‘surface mediated reduction’ in case of Pu(V) reacting with Savannah River  
121 Site sediment material. Interestingly, Pu(V) was the dominant aqueous species, while the Pu  
122 reacted with the solid phase was determined to be Pu(IV).

123

124 While several field observations point to subsurface migration of Pu (see e.g., 2013 review by  
125 Kersting<sup>32</sup>), controlled laboratory-based or field-scale reactive transport studies investigating  
126 the spreading of Pu in subsurface porous media are scarce. In an early study, Ashida et al.<sup>33</sup>  
127 recorded and modelled diffusion profiles of Pu released by waste glass corrosion in  
128 compacted bentonite. In a series of transport studies, Kaplan and co-workers<sup>34,35</sup> documented  
129 the importance of redox processes for the mobility of Pu in porous media based on Savannah  
130 River Site sediment material.

131

132 While macroscopic investigations provide valuable (empirical) information regarding the  
133 composite behavior of a complex system, only limited information can be obtained  
134 concerning individual processes and mechanisms contributing to the final reactivity and  
135 corresponding evolution of a given system. However, in view of reliable safety assessments it  
136 is important to derive a mechanistic, process-based understanding. Consequently, it is  
137 mandatory to examine the interaction of Pu with geo-materials, additionally, on a microscopic  
138 scale as well as on a molecular level. In the literature only limited information can be found  
139 concerning the interaction of Pu with compacted barrier materials or their key components  
140 such as clay minerals on a molecular level. Briefly, Reich et al.<sup>36</sup> applied X-ray absorption  
141 fine structure (XAFS) spectroscopy to investigate the speciation of Pu after sorption on  
142 kaolinite in dependence on several experimental parameters such as Pu oxidation state (+III  
143 and +IV), ambient CO<sub>2</sub> partial pressure, and pH. The result showed an inner-sphere sorption  
144 of polynuclear Pu(IV) species on the kaolinite surface independent of the initial oxidation  
145 state<sup>36</sup>. Kirsch et al. used Pu L<sub>III</sub>-edge XANES (X-ray absorption near edge structure) and  
146 EXAFS (extended X-ray absorption fine structure) spectroscopy to investigate the reaction  
147 between aqueous Pu(III) or Pu(V) and different Fe(II)-bearing minerals (magnetite,  
148 mackinawite, and chukanovite), which are formed as corrosion products of nuclear waste steel  
149 containers under anoxic conditions. Pu(V) was reduced in the presence of all three minerals.

150 In the presence of mackinawite and chukanovite solid  $\text{Pu}^{\text{IV}}\text{O}_2$  phases were formed.  
151 Additionally, in the case of chukanovite and magnetite a significant fraction of plutonium was  
152 further reduced to Pu(III). In both cases, the observed spectroscopic signatures related to  
153 Pu(III) point to sorption complexes on the iron mineral phases rather than the precipitation of  
154 a Pu(III) solid phase<sup>27</sup>. Generally, reduced manganese and iron species present in different  
155 minerals have been reported to reduce Pu(V) and Pu(VI) to Pu(IV)<sup>25,26</sup>.

156

157 Applying molecular-level techniques to complex natural systems, Kaplan et al. investigated  
158 the mobility of Pu in different oxidation states (+III, +IV, +V, +VI) in red clay over a period  
159 of 2 - 11 years. Their studies showed that Pu mobility was influenced by both, the initial Pu  
160 oxidation state and occurring oxidation state transformations of Pu after coming in contact  
161 with the sediment. Using XANES spectroscopy and solvent extraction methods they found  
162 that the Pu oxidation state distribution in the sediments after 11 years was dominated by  
163 Pu(IV) and Pu(III) with minor amounts of Pu(V) and Pu(VI) as well as polymerized, neutral  
164 Pu species<sup>31,34</sup>.

165

166 A combination of synchrotron-based micro-analytical techniques can be used to gain a  
167 molecular-level understanding of the migration processes of actinides in heterogeneous  
168 materials and to detect the spatial distribution of immobilized actinides and other co-  
169 associated elements within geologic subsurface porous media. Duff et al. studied the sorption  
170 of dissolved Pu(V) on a natural zeolitic tuff<sup>37,38</sup>. Synchrotron-based micro-XRF showed that  
171 Pu is predominantly associated with manganese oxides and smectites but not with iron oxides.  
172 In-situ micro-XANES measurements on two highly enriched regions of Pu indicated that the  
173 average oxidation state of sorbed Pu was Pu(V) in one region and Pu(VI) in the other.  
174 Denecke et al. used micro-focused synchrotron radiation techniques to study a natural,  
175 uranium-rich tertiary sediment collected from Ruprechtov (Czech Republic). This study

176 evidenced AsFeS coating on framboid Fe nodules in the sediment to reduce the highly mobile  
177 aqueous U(VI) to less-soluble U(IV), thus immobilizing the uranium in the sediment <sup>39</sup>.  
178 Recently, Fröhlich et al. <sup>40</sup> used spatially resolved micro-XRF, X-ray absorption spectroscopy  
179 (micro-XAS), and micro-XRD to determine the reactivity of Np in natural Opalinus Clay. The  
180 results showed that Np(V) was reduced to Np(IV) by an Fe(II)-containing mineral identified  
181 by micro-XRD as pyrite.

182 Kaplan et al. <sup>34</sup> employed synchrotron-based micro-XRF imaging and micro-XANES to study  
183 lysimeter sediments amended with different Pu species. This study showed pronounced  
184 hotspots with high local Pu concentration. Interestingly, despite the documented reduction of  
185 Pu over the course of the long-term experiments, the distribution of Pu in the sediments was  
186 not correlated to Mn or Fe.

187 Until now, no comparable studies with high spatial resolution can be found in the literature  
188 investigating the reactivity of Pu within a natural reactive barrier material such as OPA.  
189 Therefore, our aim was to improve the understanding of the geochemical interaction of Pu  
190 with OPA on a molecular level. The focus was on the determination of the speciation of Pu  
191 immobilized by OPA during diffusion processes and to identify the most reactive constituents  
192 of the reactive barrier. Investigations with high spatial resolution by combining different  
193 synchrotron-based micro-analytical techniques were employed to unravel the complexity of  
194 the heterogeneous geological material. The spatial distribution of Pu and its correlation with  
195 other elements contained in OPA (i.e., Ca, Fe, Mn) were determined by micro-XRF mapping.  
196 The oxidation state and molecular structure of the sorbed Pu species were analyzed by micro-  
197 XAS spectroscopy, while the reactive crystalline constituents of the heterogeneous OPA were  
198 identified by micro-XRD. These microscopic investigations were complemented by Pu L<sub>III</sub>-  
199 edge EXAFS spectroscopy measurements of Pu reacted with powdered OPA material.

200 Such complementary, multimodal investigations are essential to decipher the fundamental  
201 reactive processes occurring in natural and engineered repository barriers and contribute

202 therefore in a fundamental manner to the safe disposal and long-term storage of hazardous  
203 radioactive materials.

204

205

## 206 **2. Materials and methods**

### 207 **2.1 Materials**

208 Details regarding the employed Opalinus Clay rock material and the preparation of the Pu(VI)  
209 stock solutions can be found in the SI.

210

### 211 **2.2. Sample preparation**

#### 212 **2.2.1. Sorption on OPA powder sample**

213 For EXAFS measurements, two powder samples were prepared based on batch sorption  
214 experiments. The sorption of Pu(IV) and Pu(VI) on OPA powder (Table S1) was investigated  
215 using synthetic OPA pore water <sup>41</sup> under anaerobic conditions (Ar-atmosphere). The sorption  
216 experiments were carried out in 50 mL centrifuge tubes (Beckman Coulter, USA) with a total  
217 solution volume of 40 mL. In each tube, OPA powder (240 mg) was preconditioned for  
218 72 hours with OPA pore water. After the preconditioning, the OPA suspensions were spiked  
219 with Pu(IV) or Pu(VI) from the <sup>239</sup>Pu stock solutions resulting in initial Pu concentrations of  
220 10 μM and 20 μM, respectively. During the equilibration time of 60 hours, the pH of the  
221 samples was adjusted to the desired value of about 7.6 by adding small amounts of NaOH or  
222 HClO<sub>4</sub> stock solutions, respectively. The pH measurements were performed using a pH meter  
223 (inoLab pH/Cond 720, WTW, Germany) equipped with a pH electrode (blue line 16 pH, SI  
224 Analytics GmbH, Germany). After equilibration, the suspension was separated by a two-step  
225 centrifugation procedure, first at 4025 g for 5 min (SIGMA 3K30, Sigma Laborzentrifugen  
226 GmbH, Germany), followed by 108'000 g for 1 h (Avanti J-30I, Beckman Coulter, USA).  
227 The Pu uptake was calculated based on the difference between initial and equilibrium Pu

228 concentrations in solution and the known solid-to-liquid ratio (6 g/L). The aqueous Pu  
229 concentrations were determined by liquid scintillation counting (LSC) using a home built  
230 scintillation counter measuring 1 mL sample in 10 mL scintillation cocktail Ultima Gold™  
231 XR (PerkinElmer, USA). Chemical conditions observed at the end of the equilibration period  
232 are reported in Table S2. The powder of each sample was dried under anaerobic conditions  
233 for 3 days at 26 °C, grinded, loaded into a special polyethylene sample holder, sealed, and  
234 transported to the European Synchrotron Radiation Facility (ESRF) either in an anaerobic jar  
235 (Schuett-biotec GmbH, Germany) purged with argon (for Pu(VI) sample) or in a special  
236 dewar filled with liquid nitrogen (Voyageur 12, AIR LIQUIDE Deutschland GmbH,  
237 Germany), in which the sample of Pu(IV) was kept at cryogenic conditions until the  
238 measurement.

239

240

241

#### 242 **2.2.2. Sorption on intact OPA thin section**

243 A thin section of OPA on a high-purity quartz glass slide (Heraeus Holding GmbH, Germany)  
244 was prepared at the Max-Planck-Institute for Chemistry, Mainz. This thin section had a  
245 thickness of ~25 µm and a total surface of approximately 1 cm<sup>2</sup>. A 20 µM <sup>242</sup>Pu solution  
246 (Millipore water, pH adjusted to 7.6, spiked with <sup>242</sup>Pu(VI) stock solution) was contacted with  
247 the thin section surface using an in-house engineered sorption cell. Pu(V) can be expected to  
248 be the predominant Pu species in the supernatant reservoir over the course of the experiment  
249 (see also SI). After a contact time of five days under ambient air conditions, the supernatant  
250 solution was removed. The final Pu concentration in the supernatant was measured by LSC  
251 and the amount of Pu sorbed per surface area OPA was determined. The surface area of the  
252 thin section contacted with Pu was sealed with Kapton foil immediately after removal of the

253 solution phase, loaded into a polyethylene sample holder and transported to the Swiss Light  
254 Source (SLS).

255

### 256 **2.2.3. Diffusion in OPA core**

257 One sample was produced by an in-diffusion experiment. A cylinder (25×11 mm [diameter ×  
258 height]) of aerobic OPA was placed in a stainless steel diffusion cell<sup>42</sup> and preconditioned  
259 with synthetic OPA pore water<sup>41</sup> (pH 7.6, I = 0.4 M, however without Sr<sup>2+</sup> to avoid spectral  
260 interferences between Sr (K<sub>α</sub> at 14165 eV) and Pu (L<sub>α</sub> at 14278 eV, see below)) for 6 weeks.  
261 The orientation of the clay rock core was chosen such that the direction of diffusion was  
262 parallel to the bedding planes of the clay. Prior to the in-diffusion of Pu, tritiated water (HTO)  
263 was used to characterize the OPA bore core by determining its porosity ( $\epsilon$ ) and the diffusion  
264 coefficient of water ( $D_e$ ) by means of a through-diffusion experiment. The obtained  $D_e$  value  
265 agrees well with literature values<sup>43, 44</sup>, while the porosity of the used OPA bore core is  
266 slightly higher (Table S3).

267 For a duration of one month, <sup>242</sup>Pu was diffusing from a reservoir into the OPA rock sample.  
268 Initial reservoir conditions were 20  $\mu\text{M}$  <sup>242</sup>Pu(VI) in OPA reference pore water with a pH of  
269 7.6 and a solution reservoir volume of 151 mL. However, Pu(V) can be expected to be the  
270 predominant Pu species in the supernatant reservoir over the course of the experiment (see  
271 also SI). The final Pu concentration in the reservoir was analyzed using LSC. About 90 % of  
272 the initial Pu diffused into the OPA core resulting in a final concentration of  $[\text{}^{242}\text{Pu}]_{\text{final}} =$   
273 1.9  $\mu\text{M}$ . The clay core was removed from the cell, dried at ambient conditions and cut into  
274 small pieces. These subsamples were placed in dedicated sample holders, sealed with Kapton  
275 foil, and transported to the Swiss Light Source (SLS).

276

277 A summary of the experimental methods, prepared samples, and related chemical conditions  
278 is provided in Tables S1 and S2.

279

280

**281 2.3. Measurements and data evaluation****282 2.3.1. XANES and EXAFS**

283 The Pu L<sub>III</sub>-edge (18057 eV) EXAFS data of the powder samples were recorded at ROBL  
284 (Rossendorf Beamline, ESRF, Grenoble, France). Data were measured in fluorescence mode  
285 using a 13-element Ge-detector (Canberra, USA). The X-ray beam was monochromatized by  
286 a Si(111) double-crystal monochromator. Higher order harmonic radiation was suppressed by  
287 two focusing mirrors. The sample was measured at 15 K using a He cryostat (CryoVac  
288 GmbH, Germany). The energy calibration was carried out by parallel measurement of a Zr  
289 foil (Zr K-edge at 17998 eV). Further details regarding EXAFS measurements at ROBL can  
290 be found in <sup>45</sup>. The EXAFS analysis was performed with the programs ATHENA <sup>46</sup> and  
291 EXAFSPAK <sup>47</sup>. Theoretical scattering phases and amplitudes were calculated with FEFF8.20  
292 <sup>48</sup> based on a hypothetical molecular cluster derived from the crystal structures of thorium  
293 iron phosphide oxide (Th<sub>4</sub>Fe<sub>17</sub>P<sub>10</sub>O<sub>1-x</sub>) <sup>49</sup>, where Th and P were replaced by Pu and Si/Al to  
294 model possible Pu-Si/Al and Pu-Fe interactions with the OPA surface. The average oxidation  
295 state of Pu in the bulk EXAFS samples was determined by fitting the XANES region between  
296 18050 and 18130 eV by a linear combination of standard spectra (Pu(III) <sup>50</sup>, Pu(IV) <sup>51</sup>, Pu(V)  
297 <sup>52</sup>, and Pu(VI) <sup>53</sup>).

298

299

**300 2.3.2. micro-XANES, micro-XRF, and micro-XRD**

301 All spatially resolved measurements were performed at the microXAS beamline at the SLS.  
302 The beamline is equipped with a Kirkpatrick-Baez mirror based microfocusing system and a  
303 double-crystal monochromator with three different crystal pairs (Si(111), Si(311), and  
304 Ge(111)). In our experiment only the Si(111) crystals were used. The energy calibration was

305 performed using a Zr foil. The X-ray fluorescence was measured using a single-element Si-  
306 drift detector (KETEK GmbH, Germany). To resolve the potential spectral interference  
307 between Pu ( $L_{\alpha}$  at 14278 eV) and geogenic Sr ( $K_{\alpha}$  at 14165 eV), the local Pu concentrations  
308 were reconstructed from the difference of two micro-XRF maps, recorded below (17900 eV)  
309 and above (18070 eV) the Pu  $L_{III}$ -edge (see also ref. <sup>37</sup>). Overview maps were recorded with  
310 pixel resolutions between 10 and 20  $\mu\text{m}$ . High-resolution mappings were collected with 1 to  
311 5  $\mu\text{m}$  pixel resolution using a focused X-ray beam size of  $3 \times 1.5 \mu\text{m}^2$  ( $h \times v$ ). Micro-XRF  
312 maps were processed and analyzed using facility provided MATLAB scripts.

313

314 X-ray diffraction images were recorded with a 100K Pilatus detector (DECTRIS Ltd.,  
315 Switzerland). The Pilatus XRD detector geometry was calibrated by measuring reference  
316 powder pattern of  $\alpha\text{-Al}_2\text{O}_3$ . Each area selected for micro-XRD imaging had a size of  
317  $11 \times 11 \mu\text{m}^2$  and was generally recorded with a step size of 1  $\mu\text{m}$  resulting in 121 patterns.  
318 Particular features have been measured in more detail using a pixel resolution of 0.5  $\mu\text{m}$ .  
319 Micro-XRD data were analyzed using the XRDUA software package <sup>54</sup>.

320 Pu  $L_{III}$ -edge micro-XANES investigations were performed on several Pu hot spots in  
321 fluorescence mode with an angle of 45 degrees between incoming X-ray beam and  
322 fluorescence detector. In each location multiple scans were collected. Background and energy  
323 corrections of the spectra were performed with the program ATHENA <sup>46</sup>. Linear combination  
324 fitting analysis based on reference spectra (see above) was used to determine the fractions of  
325 different Pu oxidation states in the measured hot spots.

### 326 3. Results and Discussion

#### 327 3.1. XANES and EXAFS measurements of OPA powder sample

328 XANES and EXAFS data obtained for Pu(V,VI) immobilized by powdered Opalinus Clay  
329 material are shown in Figure 1 (top) and Figure 2, respectively. Such spectroscopic data  
330 provide molecular-level information regarding the chemical speciation of Pu immobilized  
331 either as sorbed species at the solid-liquid interface or as secondary precipitate. However,  
332 such ('bulk') measurements provide system averaged information – an important point to  
333 consider, in particular in case of heterogeneous systems such as the OPA material.

334

335 The XANES spectrum depicted in Figure 1 (top) yields a Pu  $L_{III}$ -edge position of  
336  $18068 \pm 1$  eV. This value coincides with the Pu  $L_{III}$ -edge energy position measured for the  
337 Pu(IV) aquo ion<sup>55,56</sup>. A more detailed analysis employing linear combination fitting analysis  
338 (LCFA) based on reference spectra shows indeed that at least two thirds of the initial Pu(VI)  
339 were reduced to Pu(IV) ( $68 \pm 2$  %), while one fifth was detected to be Pu(V) ( $20 \pm 5$  %). The  
340 original oxidation state of Pu(VI) was detected only in trace levels ( $12 \pm 6$  %). Consequently,  
341 electron transfer reactions play an important role regarding the sequestration of Pu(VI) by  
342 OPA.

343

344 The Pu  $L_{III}$ -edge,  $k^3$ -weighted EXAFS spectrum of the same sample is presented in Figure 2  
345 together with the corresponding Fourier transform magnitude. In addition to the experimental  
346 data, the fitting results of two models, each of them considering two coordination spheres, are  
347 also included in the figure. The Fourier transform shows two main peaks. The first  
348 coordination shell is best described within these two fits by 6.8 or 7.1 oxygen atoms with an  
349 average Pu-O distance of 2.32 and 2.31 Å, respectively. The second peak can be modeled by  
350 various approaches involving different backscattering atoms, including Si, Al, or Fe for  
351 example. One first appropriate fit is obtained using a combination of Pu-Si/Al (at 3.10 Å) and

352 Pu-Fe/Mn (at 3.43 Å) scattering pairs in the second coordination shell (green line), while the  
353 second fit (red line) is based on two distinct sub-shells considering only Si/Al in the second  
354 shell (at 3.15Å and at 3.64 Å). Table S4 lists a summary of the molecular structure  
355 information obtained by the EXAFS fitting. Due to the restricted accessible k-range (limited  
356 to approximately 2-9 Å<sup>-1</sup>) and the noticeable noise in the experimental data, the chemical  
357 identity and relative importance of possible contributions in the second shell cannot be  
358 identified unambiguously. This deduction is emphasized by the close agreement of the two  
359 fits depicted in Figure 2.

360 However, in general, the molecular structural data measured for Pu reacted with OPA are in  
361 accord for example with results obtained by Kersting et al.<sup>57</sup> for Pu interacting with several  
362 Fe/Mn minerals and alumina-silicates. For the Fe/Mn containing minerals goethite, birnessite,  
363 and pyrolusite an averaged Pu–O distance of 2.30 ± 0.01 Å (modelled by two sub-shells) with  
364 coordination numbers of 6-8 are reported. Further, a Pu-Fe/Mn second-shell contribution at  
365 R=3.33-3.43 Å was identified. For the alumina-silicates the mentioned study reports Pu–O  
366 coordination numbers of 8-10 and distances of 2.28-2.37 Å and a Si second-shell contribution  
367 at 3.11-3.14 Å.

368 Any additional scattering contributions at larger distances as typically observed for Pu  
369 precipitations or polynuclear species<sup>36</sup> cannot be detected in the EXAFS data (Figure 2). For  
370 further elaboration, an additional EXAFS data set is shown in Figure S1 depicting the  
371 spectroscopic results for Pu(IV) interaction with OPA. Despite the higher susceptibility to  
372 form precipitates or polynuclear species, no corresponding evidence is observed in the  
373 spectrum. However, similar to the spectrum shown in Figure 2, a distinct second shell  
374 contribution is detected. The absence of polynuclear species or secondary Pu precipitates, but  
375 the detection of second shell scattering pairs in the EXAFS spectroscopic data is indicative of  
376 inner-sphere sorption (covalent bonding) of Pu to surfaces of minerals present in the Opalinus  
377 Clay. However, due to the geochemical complexity of the OPA – in particular the

378 simultaneous presence of Fe/Mn minerals and alumina-silicates<sup>41</sup> – the predominant reactive  
379 phase(s) and immobilization process(es) cannot be further refined based on the present bulk  
380 measurements of a powder sample.

381

382

### 383 **3.2 Spatially resolved investigations**

#### 384 **3.2.1. OPA thin section sample**

385 To develop a better understanding regarding the influence of geochemical complexity and  
386 (micro)heterogeneity on the local retention and chemical speciation of Pu in OPA, intact rock  
387 samples were examined with high spatial resolution. Multimodal microscopic chemical  
388 imaging and spatially resolved spectroscopy are employed to detect a possible variety of Pu  
389 species and to identify the reactive components of the OPA material. As a first type of intact  
390 rock samples, Figure 3 shows a thin section of OPA at different magnifications and probed  
391 with different microscopic tools. Figure 3a depicts a representative photograph of the OPA  
392 thin section. On this macroscopic scale the material appears to be rather homogeneous.  
393 However, already a moderately magnified view provided by visible light microscopy (Figure  
394 3b) reveals a heterogeneous structure (see also e.g.,<sup>58, 59</sup>). Increasing the spatial resolution  
395 further, microscopic chemical images obtained by X-ray microprobe analysis are shown in the  
396 two panels below in Figure 3 (c-g and h-l, respectively). Each of the two rows represents  
397 chemical information for a 120 x 120  $\mu\text{m}^2$  area. The two areas are separated by 500  $\mu\text{m}$  as  
398 schematically sketched by the red squares in Figure 3b. Both sets of chemical images reveal a  
399 characteristic micro-scale geochemical heterogeneity comparable to earlier evidences<sup>60-62</sup>.  
400 Following the exposure of the intact thin section to a Millipore water (pH adjusted to 7.6)  
401 spiked with Pu(VI), the resulting Pu retention pattern after reaction are far from homogeneous  
402 (Figure 3g and l). Pronounced differences in the local reactivity of the OPA rock material  
403 regarding the local retention of Pu can be observed. Two types of hierarchical pattern are

404 recognized. First, with a characteristic length scale of hundred(s) of micrometers, larger  
405 domains with elevated local Pu concentrations are surrounded by areas in which only lowest  
406 plutonium concentrations are measured ('patch pattern'). Corresponding boundaries are  
407 indicated by the white dashed lines in Figure 3 (g, l). Second, within the Pu-rich patches, the  
408 local Pu concentration reveals a characteristic 'speckle pattern'. Local Pu hot spots with an  
409 extension of less than  $\sim 10 \mu\text{m}$  are observed. Accordingly, large concentration gradients are  
410 expressed. Within a few micrometers, the local Pu concentration is changing by more than  
411 two orders of magnitude.

412

413 Comparing the observed distribution pattern of Pu to the elemental maps of the geochemical  
414 indicator elements Ca, Ti, Mn, or Fe, no unequivocal correlation can be established. The  
415 recorded elemental maps do not provide obvious reference towards the reactive phase(s)  
416 being involved in the immobilization processes of Pu in OPA.

417

418 To further detail the variability of chemical speciation and oxidation states of Pu immobilized  
419 at the OPA surfaces, micro-XANES measurements were performed on several Pu hot spots.  
420 As an example, Figure 1 (middle) shows the Pu  $L_{\text{III}}$ -edge micro-XANES spectrum of a  
421 selected hot spot in the thin section sample (see Figure 3g; marked by circle). The Pu  $L_{\text{III}}$ -edge  
422 peak energy occurs at  $18068 \pm 1 \text{ eV}$ , which is indicative of Pu being present predominantly in  
423 a +IV oxidation state<sup>56</sup>. The fractions of different Pu oxidation states in this particular hot  
424 spot were determined by LCFA to be  $80 \pm 3 \%$  Pu(IV) and  $20 \pm 4 \%$  Pu(V), respectively.  
425 Similar results were obtained for several other hot spots investigated on this sample.

426

427 The observed reduction from Pu(V, VI) to Pu(IV) requires at least one redox active electron  
428 donor couple (such as  $\text{Fe}^{2+}/\text{Fe}^{3+}$  or  $\text{Mn}^{2+}/\text{Mn}^{3+}$ ) to be present in the OPA material. For various  
429 iron- and/or manganese (hydr-)oxide phases the (surface mediated) reduction of Pu and

430 subsequent immobilization of the newly formed reduced Pu species by immediate adsorption  
431 to the reducing phase have been postulated, with a limited number of studies providing direct  
432 spectroscopic evidence<sup>26, 27, 57, 63</sup>. In these studies, the covalent bonding of Pu to the Fe/Mn-  
433 mineral surfaces is evidenced by the observation of a second shell contribution in the EXAFS  
434 spectra best fitted with a Pu-Mn/Fe scattering path. Such a mechanism would result in a  
435 superposed spatial occurrence of Pu with the Fe/Mn-bearing phase as Pu is proposed to be  
436 immobilized directly on the surface of the grains acting as electron donor. The expected  
437 pronounced spatial correlation between Pu and Fe or Pu and Mn, however, was not observed  
438 in the present system (Figure 3). Based on the same argumentation, the proposed uptake of Pu  
439 species by calcite<sup>28</sup> can be rejected to be the predominant process of Pu immobilization. The  
440 local Pu concentrations show no evident correlation with the calcium distribution.

441

442 To obtain further information related to the mineral phases responsible for the reduction and  
443 retention of Pu in the present experiment, selected areas including Pu hot spots were analyzed  
444 by combined two-dimensional micro-XRF and micro-XRD chemical imaging. First of all,  
445 despite a scattering volume as low as  $\sim 100 \mu\text{m}^3$ , the individual two-dimensional XRD pattern  
446 recorded in each pixel exhibit a pronounced complexity (Figure S2) reflecting the  
447 mineralogical micro-/nano-heterogeneity and intricacy of the OPA material. Nevertheless,  
448 comparing the average XRD pattern obtained for pixels with higher Pu local concentrations to  
449 the average XRD pattern observed at lower local Pu levels reveals one noticeable difference.  
450 Pixels with elevated Pu show increased intensities of a few selected reflections, which all can  
451 be assigned to kaolinite (001, 002, 003, 004 reflections; Figure S2). The spatial correlation of  
452 the local Pu concentration and the kaolinite distribution can be demonstrated by micro-  
453 XRF/XRD chemical imaging, as shown in Figure 4. The top panel depicts an image of the  
454 local distribution of Pu (see related yellow square in Figure 3), the corresponding zoom-in  
455 ( $11 \times 11 \mu\text{m}^2$  area) is depicted in the top left of the main panel of Figure 4. Below, the related

456 spatial distributions of the mineral phases kaolinite and illite are shown. The similarity of the  
457 Pu and kaolinite distribution is readily apparent. Opposite, Pu and illite (another clay mineral  
458 phase commonly considered as highly reactive in OPA <sup>21, 64-66</sup>) show a pronounced anti-  
459 correlation. Similarly, Fe, Mn, Ca (depicted in the right column of the main panel of Figure 4)  
460 and additional trace elements are not present in the location of immobilization of Pu.

461

462 The correlation between the local concentrations of Pu and local kaolinite content is shown in  
463 Figure S3. A clear positive correlation can be deduced. One has even to recognize that several  
464 experimental parameters or boundary conditions contribute to an easing of an existing  
465 correlation. First of all, in case of processes occurring at the mineral-solution interface being  
466 the dominant immobilization mechanism (such as adsorption or surface mediated secondary  
467 phase precipitation), the ratio of Pu XRF versus kaolinite XRD intensities is related to the  
468 local specific surface area of the kaolinite grains. Second, despite simultaneous data  
469 collection, the 'response' voxels for XRD and XRF are not identical. This is further amplified  
470 by the limited equilibration time of only 5 days resulting in enhanced Pu reactivity at the  
471 solution-side surface of the thin section, while XRD probes along the entire thickness of the  
472 thin section. Additional disturbances are caused by the established preferential orientation of  
473 the platelets in the kaolinite domains (Figure S2). OPA is known to be an anisotropic  
474 sedimentary rock <sup>67</sup>. Depending on the spatial alignment, certain kaolinite platelets are 'not  
475 visible' in the XRD measurements, while the related XRF based detection of the Pu  
476 concentration is not effected by the anisotropic nature of the porous medium. Despite these  
477 constraints, a convincing relation between Pu immobilization and local kaolinite appearance  
478 can be established. Consequently, the final immobilization of Pu is either directly related to  
479 kaolinite as reactive sorbent or to a geochemically linked (possibly highly disordered, X-ray  
480 amorphous) phase.

481

482 While kaolinite turns out to be involved in the final immobilization process, kaolinite cannot  
483 be expected to be responsible for the spectroscopically confirmed reduction of Pu(V,VI) to  
484 Pu(IV) prior to adsorption. Consequently, the reduction and the retardation do not occur as  
485 combined process on a single reactive surface. The immobilization of Pu(V,VI) in Opalinus  
486 Clay has to be represented by a multi-step mechanism with the two fundamental processes (i)  
487 reduction and (ii) sorption as two decoupled, subsequent, and spatially separated processes  
488 involving different reactive phases of the Opalinus Clay rock. First, the Fe(II)-bearing  
489 minerals siderite and pyrite present in significant quantities in Opalinus Clay possibly act as  
490 the redox active mineral phases. Evidence for the presence of siderite in the vicinity of the Pu  
491 hotspots is indeed provided by the micro-XRD imaging (Figure S2c). Second, kaolinite or a  
492 geochemically related phase present in the vicinity of the Fe(II)-bearing phase expresses the  
493 highest reactivity towards the sorption of the reduced Pu(IV).

494 An additional piece of evidence is provided by spectroscopic results obtained after sorption of  
495 reduced Pu(IV) to OPA powder (EXAFS data shown in Figure S1). This approach allows an  
496 isolated experimental investigation of the proposed second step, the immobilization of the  
497 reduced Pu(IV) by a reactive compound of OPA. The distinct second shell contribution can be  
498 fitted by a Pu-Al/Si second shell as one would expect for Pu sorbed to kaolinite. No  
499 additional, heavier backscatterer (such as, e.g., Fe) are required to obtain a satisfactory fit.

500

501

### 502 **3.2.2. OPA core diffusion sample**

503 To investigate sorption and diffusion processes under even more realistic conditions,  
504 Pu(V,VI) in-diffusion into OPA was examined experimentally. After an extended period of  
505 time (30 days), the Pu distribution and speciation at the surface of the OPA piece in contact  
506 with the Pu spiked reservoir solution were investigated.

507 Microscopic chemical images depicting the Pu distribution in relation to geochemical  
508 indicator elements such as Ca, Ti, Mn, or Fe are presented in Figure S4. The observed  
509 characteristic of the distribution pattern and the elemental correlations are analogous to the  
510 pattern observed and discussed for the thin section experiment (Figure 3).

511 Several spots of higher Pu concentration were analyzed by micro-XANES. A representative  
512 Pu L<sub>III</sub>-edge micro-XANES spectrum (Figure 1, bottom) shows that Pu(IV) is the dominating  
513 oxidation state ( $70 \pm 3 \%$ ). Only minor fractions of initial Pu(V) of about  $22 \pm 5 \%$  and  
514 Pu(VI) close to the detection limit ( $8 \pm 6 \%$ ) are observed. The Pu(V,VI) in-diffusion into a  
515 bulk clay rock piece - investigated at the reservoir-rock interface - yields results in agreement  
516 with the other two types of investigations discussed before.

517

#### 518 **4. Environmental implications**

519 The three different complementary types of investigations of this study yield coherent  
520 information relevant to the migration of Pu in engineered barrier systems and related  
521 geological subsurface systems. First, in all systems the Pu introduced as Pu(V,VI) was  
522 reduced by redox active components of the Opalinus Clay, to Pu(IV) with a smaller/minority  
523 fraction remaining as Pu(V). Chemical imaging shows the reduced Pu to be immobilized in  
524 the vicinity of the potentially redox active elements Fe and Mn. However, high resolution  
525 microscopic chemical imaging based on micro-XRF reveals unambiguously that the domains  
526 with immobilized Pu show only lowest local concentrations of Fe, Mn, Ti, or Ca. The  
527 domains reactive in terms of Pu immobilization are dominated by elements not detectable by  
528 the employed micro-XRF imaging configuration, in particular Al and Si. Accordingly, several  
529 geochemically reactive phases proposed in the context of surface mediated reduction and  
530 adsorption of Pu such as Mn(II) or Fe(II)-bearing oxides<sup>24, 25, 27</sup>, or calcite<sup>28</sup> can be rejected

531 as the reactive adsorption components (sorbents) in OPA under the conditions investigated in  
532 the present study. Further, possible secondary Pu phase precipitation (with high crystallinity)  
533 can be ruled out based on the EXAFS results. Consequently, in the present system Pu  
534 immobilization has to be based on a reactive process occurring at the pore water–rock  
535 interface such as adsorption to an Al/Si phase or the incorporation of Pu into a newly formed  
536 poorly crystalline (X-ray amorphous) Al/Si phase. This proposition is supported by the  
537 observed 2<sup>nd</sup> shell scattering contributions in the EXAFS data. Additional evidence is  
538 provided by combined micro-XRF/micro-XRD chemical imaging results revealing that the  
539 clay mineral kaolinite is consistently observed within the reactive micro-domains of high Pu  
540 retention. Opposite, no crystallographic evidence was found at these locations of high Pu  
541 concentration for enhanced localized availability of plausible electron donors, in particular  
542 Fe(II)-bearing mineral phases such as siderite or pyrite. This combination of findings provides  
543 strong evidence that at least two reactive components have to be involved in the observed  
544 ‘reductive immobilization’ of Pu in OPA. The electron donor and the immobilizing sorbent  
545 are two distinct, spatially separated components. Geological phases such as siderite or pyrite  
546 act as electron donor pools and buffer the redox potential locally, while a second OPA  
547 component exhibits a high sorption affinity for the reduced Pu(IV) species and acts as a strong  
548 sink affecting the stability field for the sorbed Pu(IV) compared to the aqueous species<sup>20</sup>.

549 Natural geological and engineered barrier materials are commonly complex and  
550 heterogeneous. In-situ multimodal microscopic studies under conditions relevant to deep  
551 geological formations are crucial to identify the reactive components and reaction pathways  
552 or to validate proposed mechanisms. The present study demonstrated that a simplistic  
553 description by a sole reactive component is not an adequate representation of the geochemical  
554 reactivity responsible for the immobilization of Pu(V,VI) within an Opalinus Clay barrier.

555 Studies on intact, undisturbed systems are absolutely essential to ascertain the geochemical  
556 reactivity for relevant geochemical conditions and settings.

557 In addition to providing essential information related to the safety assessment of nuclear waste  
558 disposal concepts, the presented observations contribute to advance our understanding of  
559 (redox-sensitive) radionuclide transport in the geosphere in general. Based on the employed  
560 chemical imaging, further progress can be expected by representing reactive transport even  
561 dynamically by a series of subsequent patterns.

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565

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567

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588

### 589 **Supporting Information**

590 Additional experimental details and supplementary results (PDF)

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594

595 **Figure Captions**

596

597 **Figure 1:**

598 Normalized Pu L<sub>III</sub>-edge XANES spectra of Pu(VI) interacted with different samples of  
599 Opalinus Clay rock material. top) OPA powder sample; middle) OPA thin section; bottom)  
600 OPA core diffusion sample. In each panel experimental data are compared to corresponding  
601 linear combination fits of Pu(III)<sup>50</sup>, Pu(IV)<sup>51</sup>, Pu(V)<sup>52</sup>, and Pu(VI)<sup>53</sup>. Contributions of  
602 individual components are included in the figures.

603

604 **Figure 2:**

605 Pu L<sub>III</sub>-edge k<sup>3</sup>-weighted EXAFS spectrum (left) and corresponding Fourier transform  
606 magnitude (right) of Pu(VI) interacted with Opalinus Clay powder. Experimental data are  
607 compared to two different two-shell fits consisting of a first Pu-O shell and the second shells  
608 correspond to different combinations of Pu-Si/Al and Pu-Fe/Mn backscattering pairs. The  
609 green line corresponds to a fit obtained using a combination of Pu-Si/Al and Pu-Fe/Mn  
610 scattering pairs in the second coordination shell, while the red line is based on two distinct  
611 sub-shells considering only Si/Al in the second shell (Table S4).

612

613 **Figure 3:**

614 Sorption experiment of a Opalinus Clay thin section sample reacting with Pu spiked Millipore  
615 water. a) photograph of a representative thin section, b) corresponding light microscope  
616 image, c-g) and h-l) elemental distributions of Ca, Ti, Mn, Fe, and Pu for two areas. Chemical  
617 images were obtained by synchrotron-based micro-XRF. A pronounced geochemical  
618 heterogeneity is observed on the micron-scale.

619 The rectangles sketch magnified zoom-in areas depicted in subsequent panels. The yellow  
620 circle in top-left corner of Figure 3g) indicates the location of the micro-XANES  
621 measurement shown in Figure 1 (middle).

622

623 **Figure 4:**

624 Multi-modal microscopic imaging of a domain with high local Pu retardation observed within  
625 the Opalinus Clay thin section. Elemental distribution maps of Pu, Fe, Mn, and Ca were  
626 recorded by micro-XRF while mineral distributions of illite and kaolinite are based on micro-  
627 XRD imaging.

628

629

## 630 REFERENCES

- 631 1. NEA/AEN, Features, Events and Processes (FEPs) for Geologic Disposal of  
632 Radioactive Waste - An International Database. Paris, 2000.
- 633 2. NAGRA, FEP Management for Safety Assessment (Project Opalinus Clay). Nagra  
634 Technical Report NTB-02-23, NAGRA Nationale Genossenschaft für die Lagerung  
635 radioaktiver Abfälle, Wettingen, Switzerland, 2002.
- 636 3. Gompper, K., Zur Abtrennung langlebiger Radionuklide. Forschungszentrum  
637 Karlsruhe: Karlsruhe, 2000.
- 638 4. ONDRAF/NIRAS, Technical overview of the SAFIR 2 report, Technical Report  
639 NIROND 2001. ONDRAF, Brussels, 2001.
- 640 5. OECD, Safety of geological disposal of high-level and long-lived radioactive waste in  
641 France - An international peer review of the "Dossier 2005 Argile" concerning disposal  
642 in the Callovo - Oxfordian formation. Organisation for Economic Co-operation and  
643 Development, Paris, 2006.
- 644 6. Hoth, P.; Wirth, H.; Reinhold, K.; Bräuer, V.; Krull, P.; Feldrappe, H., Endlagerung  
645 radioaktiver Abfälle in tiefen geologischen Formationen Deutschlands – Untersuchung  
646 und Bewertung von Tongesteinsformationen. In Bundesanstalt für Geowissenschaften  
647 und Rohstoffe (BGR): Berlin/Hannover, 2007.
- 648 7. NAGRA, Project Opalinus Clay: Safety Report – Demonstration of disposal feasibility  
649 for spent fuel, vitrified high-level waste and long-lived intermediate-level waste  
650 (Entsorgungsnachweis). Nagra Technical Report NTB-02-05, NAGRA Nationale  
651 Genossenschaft für die Lagerung radioaktiver Abfälle, Wettingen, Switzerland, 2002.
- 652 8. Lemire, R.; Fuger, J.; Nitsche, H.; Potter, P.; Rand, M. H.; Rydberg, J.; Spahiu, K.;  
653 Sullivan, J. C.; Ullman, W. J.; Vitorge, P.; Warner, H., Chemical Thermodynamics of  
654 Neptunium and Plutonium. Elsevier: Amsterdam, 2001.
- 655 9. Neck, V.; Altmaier, M.; Fanghanel, T., Solubility of plutonium hydroxides/hydrous  
656 oxides under reducing conditions and in the presence of oxygen. *C. R. Chim.* 2007, 10,  
657 (10-11), 959-977.
- 658 10. Runde, W., The chemical interactions of actinides in the environment. *Los Alamos*  
659 *Science* 2000, 26, 392-411.
- 660 11. Choppin, G. R., Actinide speciation in the environment. *J. Radioanal. Nucl. Chem.*  
661 2007, 273, (3), 695-703.
- 662 12. Runde, W.; Conradson, S. D.; Efurud, D. W.; Lu, N. P.; VanPelt, C. E.; Tait, C. D.,  
663 Solubility and sorption of redox-sensitive radionuclides (Np, Pu) in J-13 water from the  
664 Yucca Mountain site: comparison between experiment and theory. *Appl. Geochem.*  
665 2002, 17, (6), 837-853.
- 666 13. Kaplan, D. I.; Powell, B. A.; Demirkanli, D. I.; Fjeld, R. A.; Molz, F. J.; Serkiz, S. M.;  
667 Coates, J. T., Influence of oxidation states on plutonium mobility during long-term  
668 transport through an unsaturated subsurface environment. *Environ. Sci. Technol.* 2004,  
669 38, (19), 5053-5058.
- 670 14. NAGRA, Geologische Tiefenlagerung der abgebrannten Brennelemente, der  
671 hochaktiven und langlebigen mittelaktiven Abfälle — Darstellung und Beurteilung der  
672 aus sicherheitstechnisch-geologischer Sicht möglichen Wirtsgesteine und Gebiete.  
673 Nagra Technical Report NTB-05-02, NAGRA Nationale Genossenschaft für die  
674 Lagerung radioaktiver Abfälle, Wettingen, Switzerland, 2005.

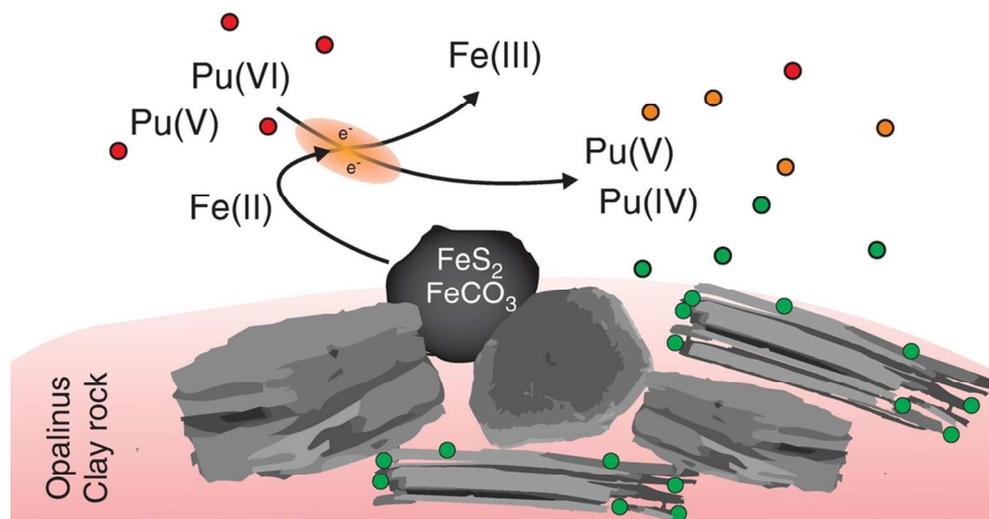
- 675 15. Mazurek, M.; Alt-Epping, P.; Bath, A.; Gimmi, T.; Waber, H. N.; Buschaert, S.; De  
676 Canniere, P.; De Craen, M.; Gautschi, A.; Savoye, S.; Vinsot, A.; Wemaere, I.;  
677 Wouters, L., Natural tracer profiles across argillaceous formations. *Appl. Geochem.*  
678 2011, 26, (7), 1035-1064.
- 679 16. Appelo, C. A. J.; Van Loon, L. R.; Wersin, P., Multicomponent diffusion of a suite of  
680 tracers (HTO, Cl, Br, I, Na, Sr, Cs) in a single sample of Opalinus Clay. *Geochim.*  
681 *Cosmochim. Acta* 2010, 74, (4), 1201-1219.
- 682 17. Missana, T.; Alonso, U.; Garcia-Gutierrez, M.; Mingarro, M., Role of bentonite colloids  
683 on europium and plutonium migration in a granite fracture. *Appl. Geochem.* 2008, 23,  
684 (6), 1484-1497.
- 685 18. Kersting, A. B.; Efurud, D. W.; Finnegan, D. L.; Rokop, D. J.; Smith, D. K.; Thompson,  
686 J. L., Migration of Plutonium in Ground Water at the Nevada Test Site. *Nature* 1999,  
687 397, 56-59.
- 688 19. Buda, R. A.; Banik, N. L.; Kratz, J. V.; Trautmann, N., Studies of the ternary systems  
689 humic substances - kaolinite - Pu(III) and Pu(IV). *Radiochim. Acta* 2008, 96, (9-11),  
690 657-665.
- 691 20. Marsac, R.; Banik, N. L.; Lutzenkirchen, J.; Buda, R. A.; Kratz, J. V.; Marquardt, C.  
692 M., Modeling plutonium sorption to kaolinite: Accounting for redox equilibria and the  
693 stability of surface species. *Chem. Geol.* 2015, 400, 1-10.
- 694 21. Banik, N. L.; Marsac, R.; Lutzenkirchen, J.; Diascorn, A.; Bender, K.; Marquardt, C.  
695 M.; Geckeis, H., Sorption and Redox Speciation of Plutonium at the Illite Surface.  
696 *Environ. Sci. Technol.* 2016, 50, (4), 2092-2098.
- 697 22. Zavarin, M.; Powell, B. A.; Bourbin, M.; Zhao, P. H.; Kersting, A. B., Np(V) and Pu(V)  
698 Ion Exchange and Surface-Mediated Reduction Mechanisms on Montmorillonite.  
699 *Environ. Sci. Technol.* 2012, 46, (5), 2692-2698.
- 700 23. Begg, J. D.; Zavarin, M.; Zhao, P. H.; Tumey, S. J.; Powell, B.; Kersting, A. B., Pu(V)  
701 and Pu(IV) Sorption to Montmorillonite. *Environ. Sci. Technol.* 2013, 47, (10), 5146-  
702 5153.
- 703 24. Sanchez, A. L.; Murray, J. W.; Sibley, T. H., The absorption of plutonium(IV) and  
704 plutonium(V) on goethite. *Geochim. Cosmochim. Acta* 1985, 49, (11), 2297-2307.
- 705 25. Powell, B. A.; Fjeld, R. A.; Kaplan, D. I.; Coates, J. T.; Serkiz, S. M., PU(V)O<sub>2</sub>(+)  
706 adsorption and reduction by synthetic hematite and goethite. *Environ. Sci. Technol.*  
707 2005, 39, (7), 2107-2114.
- 708 26. Shaughnessy, D. A.; Nitsche, H.; Booth, C. H.; Shuh, D. K.; Waychunas, G. A.; Wilson,  
709 R. E.; Gill, H.; Cantrell, K. J.; Serne, R. J., Molecular interfacial reactions between  
710 Pu(VI) and manganese oxide minerals manganite and hausmannite. *Environ. Sci.*  
711 *Technol.* 2003, 37, (15), 3367-3374.
- 712 27. Kirsch, R.; Fellhauer, D.; Altmaier, M.; Neck, V.; Rossberg, A.; Fanghanel, T.; Charlet,  
713 L.; Scheinost, A. C., Oxidation State and Local Structure of Plutonium Reacted with  
714 Magnetite, Mackinawite, and Chukanovite. *Environ. Sci. Technol.* 2011, 45, (17), 7267-  
715 7274.
- 716 28. Zavarin, M.; Roberts, S. K.; Hakem, N.; Sawvel, A. M.; Kersting, A. B., Eu(III),  
717 Sm(III), Np(V), Pu(V), and Pu(IV) sorption to calcite. *Radiochim. Acta* 2005, 93, (2),  
718 93-102.
- 719 29. Amayri, S.; Frohlich, D. R.; Kaplan, U.; Trautmann, N.; Reich, T., Distribution  
720 coefficients for the sorption of Th, U, Np, Pu, and Am on Opalinus Clay. *Radiochim.*  
721 *Acta* 2016, 104, (1), 33-40.
- 722 30. Begg, J. D.; Zavarin, M.; Tumey, S. J.; Kersting, A. B., Plutonium sorption and  
723 desorption behavior on bentonite. *Journal of Environmental Radioactivity* 2015, 141,  
724 106-114.

- 725 31. Hixon, A. E.; Hu, Y. J.; Kaplan, D. I.; Kukkadapu, R. K.; Nitsche, H.; Qafoku, O.;  
726 Powell, B. A., Influence of iron redox transformations on plutonium sorption to  
727 sediments. *Radiochim. Acta* 2010, 98, (9-11), 685-692.
- 728 32. Kersting, A. B., Plutonium Transport in the Environment. *Inorg. Chem.* 2013, 52, (7),  
729 3533-3546.
- 730 33. Ashida, T.; Kohara, Y.; Yui, M., Migration behavior of Pu released from Pu-doped  
731 glass in compacted bentonite. *Radiochim. Acta* 1994, 66-7, 359-362.
- 732 34. Kaplan, D. I.; Powell, B. A.; Duff, M. C.; Demirkanli, D. I.; Denham, M.; Fjeld, R. A.;  
733 Molz, F. J., Influence of sources on plutonium mobility and oxidation state  
734 transformations in vadose zone sediments. *Environ. Sci. Technol.* 2007, 41, (21), 7417-  
735 7423.
- 736 35. Powell, B. A.; Kaplan, D. I.; Serkiz, S. M.; Coates, J. T.; Fjeld, R. A., Pu(V) transport  
737 through Savannah River Site soils - an evaluation of a conceptual model of surface-  
738 mediated reduction to Pu (IV). *Journal of Environmental Radioactivity* 2014, 131, 47-  
739 56.
- 740 36. Reich, T.; Reich, T. Y.; Amayri, S.; Drebert, J.; Banik, N. L.; Buda, R. A.; Kratz, J. V.;  
741 Trautmann, N., Application of XAFS spectroscopy to actinide environmental science. In  
742 X-Ray Absorption Fine Structure-XAFS13, Hedman, B.; Painetta, P., Eds. Amer Inst  
743 Physics: Melville, 2007; Vol. 882, pp 179-183.
- 744 37. Duff, M. C.; Hunter, D. B.; Triay, I. R.; Bertsch, P. M.; Reed, D. T.; Sutton, S. R.;  
745 Shea-Mccarthy, G.; Kitten, J.; Eng, P.; Chipera, S. J.; Vaniman, D. T., Mineral  
746 associations and average oxidation states of sorbed Pu on tuff. *Environ. Sci. Technol.*  
747 1999, 33, (13), 2163-2169.
- 748 38. Duff, M. C.; Hunter, D. B.; Triay, I. R.; Bertsch, P. M.; Kitten, J.; Vaniman, D. T.,  
749 Comparison of two micro-analytical methods for detecting the spatial distribution of  
750 sorbed Pu on geologic materials. *J. Contam. Hydrol.* 2001, 47, (2-4), 211-218.
- 751 39. Denecke, M. A.; Somogyi, A.; Janssens, K.; Simon, R.; Dardenne, K.; Noseck, U.,  
752 Microanalysis (micro-XRF, micro-XANES, and micro-XRD) of a tertiary sediment  
753 using microfocused synchrotron radiation. *Microsc. Microanal.* 2007, 13, (3), 165-172.
- 754 40. Frohlich, D. R.; Amayri, S.; Drebert, J.; Grolimund, D.; Huth, J.; Kaplan, U.; Krause, J.;  
755 Reich, T., Speciation of Np(V) uptake by Opalinus Clay using synchrotron microbeam  
756 techniques. *Analytical and Bioanalytical Chemistry* 2012, 404, (8), 2151-2162.
- 757 41. Pearson, F. J.; Arcos, D.; Bath, A.; Boisson, J.-Y.; Fernández, A. M.; Gäbler, H.-E.;  
758 Gaucher, E.; Gautschi, A.; Griffault, L.; Hernán, P.; Waber, H. N. Mont Terri Project -  
759 Geochemistry of water in the opalinus clay formation at the Mont Terri rock laboratory.  
760 BWGG-5-E, Reports of the FOWG. Geology series; Federal Office for the Environment  
761 FOEN, Bern, 2003.
- 762 42. Wu, T.; Amayri, S.; Drebert, J.; Van Loon, L. R.; Reich, T., Neptunium(V) Sorption  
763 and Diffusion in Opalinus Clay. *Environ. Sci. Technol.* 2009, 43, (17), 6567-6571.
- 764 43. Van Loon, L. R.; Soler, J. M.; Jakob, A.; Bradbury, M. H., Effect of confining pressure  
765 on the diffusion of HTO,  $^{36}\text{Cl}$  and  $^{125}\text{I}$  in a layered argillaceous rock (Opalinus Clay):  
766 diffusion perpendicular to the fabric. *Appl. Geochem.* 2003, 18, (10), 1653-1662.
- 767 44. Joseph, C.; Van Loon, L. R.; Jakob, A.; Steudtner, R.; Schmeide, K.; Sachs, S.;  
768 Bernhard, G., Diffusion of U(VI) in Opalinus Clay: Influence of temperature and humic  
769 acid. *Geochim. Cosmochim. Acta* 2013, 109, 74-89.
- 770 45. Matz, W.; Schell, N.; Bernhard, G.; Prokert, F.; Reich, T.; Claussner, J.; Oehme, W.;  
771 Schlenk, R.; Dienel, S.; Funke, H.; Eichhorn, F.; Betzl, M.; Prohl, D.; Strauch, U.;  
772 Huttig, G.; Krug, H.; Neumann, W.; Brendler, V.; Reichel, P.; Denecke, M. A.; Nitsche,  
773 H., ROBL - a CRG beamline for radiochemistry and materials research at the ESRF.  
774 *Journal of Synchrotron Radiation* 1999, 6, 1076-1085.

- 775 46. Ravel, B.; Newville, M., ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-  
776 ray absorption spectroscopy using IFEFFIT. *Journal of Synchrotron Radiation* 2005, 12,  
777 537-541.
- 778 47. George, G. N.; Pickering, I. J. EXAFSPAK: A Suite of Computer Programs for the  
779 Analysis of X-ray Absorption Spectra, Stanford Synchrotron Radiation Laboratory.:  
780 Stanford, 1995.
- 781 48. Ankudinov, A. L.; Bouldin, C. E.; Rehr, J. J.; Sims, J.; Hung, H., Parallel calculation of  
782 electron multiple scattering using Lanczos algorithms. *Phys. Rev. B* 2002, 65, (10), 11.
- 783 49. Albering, J. H.; Jeitschko, W., The crystal structures of  $\text{Th}_4\text{Fe}_{17}\text{P}_{10}\text{O}_{1-x}$  and  $\text{ThFe}_5\text{P}_3$ . *J.*  
784 *Solid State Chem.* 1995, 117, (1), 80-87.
- 785 50. Schmeide, K.; Reich, T.; Sachs, S.; Bernhard, G., Plutonium(III) complexation by  
786 humic substances studied by X-ray absorption fine structure spectroscopy. *Inorg. Chim.*  
787 *Acta* 2006, 359, (1), 237-242.
- 788 51. Martin, P.; Grandjean, S.; Valot, C.; Carlot, G.; Ripert, M.; Blanc, P.; Hennig, C., XAS  
789 study of  $(\text{U}_{1-y}\text{Pu}_y)\text{O}_2$  solid solutions. *Journal of Alloys and Compounds* 2007, 444-445,  
790 410-414.
- 791 52. Di Giandomenico, M. V.; Le Naour, C.; Simoni, E.; Guillaumont, D.; Moisy, P.;  
792 Hennig, C.; Conradson, S. D.; Den Auwer, C., Structure of early actinides(V) in acidic  
793 solutions. *Radiochim. Acta* 2009, 97, (7), 347-353.
- 794 53. Reich, T.; Geipel, G.; Funke, H.; Hennig, C.; Rossberg, A.; Bernhard, G. Plutonium.  
795 XAFS measurements of plutonium hydrates, ESRF: Grenoble (F), 2000; pp 32-33.
- 796 54. De Nolf, W.; Vanmeert, F.; Janssens, K., XRDUA: crystalline phase distribution maps  
797 by two-dimensional scanning and tomographic (micro) X-ray powder diffraction. *J.*  
798 *Appl. Crystallogr.* 2014, 47, 1107-1117.
- 799 55. Conradson, S. D.; Abney, K. D.; Begg, B. D.; Brady, E. D.; Clark, D. L.; den Auwer,  
800 C.; Ding, M.; Dorhout, P. K.; Espinosa-Faller, F. J.; Gordon, P. L.; Haire, R. G.; Hess,  
801 N. J.; Hess, R. F.; Keogh, D. W.; Lander, G. H.; Lupinetti, A. J.; Morales, L. A.; Neu,  
802 M. P.; Palmer, P. D.; Paviet-Hartmann, P.; Reilly, S. D.; Runde, W. H.; Tait, C. D.;  
803 Veirs, D. K.; Wastin, F., Higher order speciation effects on plutonium L-3 X-ray  
804 absorption near edge spectra. *Inorg. Chem.* 2004, 43, (1), 116-131.
- 805 56. Conradson, S. D.; Al Mahamid, I.; Clark, D. L.; Hess, N. J.; Hudson, E. A.; Neu, M. P.;  
806 Palmer, P. D.; Runde, W. H.; Tait, C. D., Oxidation state determination of plutonium  
807 aquo ions using x-ray absorption spectroscopy. *Polyhedron* 1998, 17, (4), 599-602.
- 808 57. Kersting, A. B.; Zhao, P.; Zavarin, M.; Sylwester, E. R.; Allen, P. G.; Williams, R. W.,  
809 Sorption of Pu(V) on mineral colloids. . In *Colloidal-Facilitated Transport of Low-  
810 Solubility Radionuclides: A Field, Experimental, and Modeling Investigation*, A.B., K.;  
811 Remus, P. W., Eds. Lawrence Livermore National Laboratory Livermore, CA, USA,  
812 Vol. Report UCRL-ID-149688.
- 813 58. Houben, M. E.; Desbois, G.; Urai, J. L., A comparative study of representative 2D  
814 microstructures in Shaly and Sandy facies of Opalinus Clay (Mont Terri, Switzerland)  
815 inferred from BIB-SEM and MIP methods. *Marine and Petroleum Geology* 2014, 49,  
816 143-161.
- 817 59. Marschall, P.; Horseman, S.; Gimmi, T., Characterisation of gas transport properties of  
818 the Opalinus clay, a potential host rock formation for radioactive waste disposal. *Oil*  
819 *Gas Sci. Technol.* 2005, 60, (1), 121-139.
- 820 60. Wang, H. A. O.; Grolimund, D.; Van Loon, L. R.; Barmettler, K.; Borca, C. N.;  
821 Aeschmann, B.; Gunther, D., Quantitative Chemical Imaging of Element Diffusion into  
822 Heterogeneous Media Using Laser Ablation Inductively Coupled Plasma Mass  
823 Spectrometry, Synchrotron Micro-X-ray Fluorescence, and Extended X-ray Absorption  
824 Fine Structure Spectroscopy. *Anal. Chem.* 2011, 83, (16), 6259-6266.

- 825 61. Wang, H. A. O.; Grolimund, D.; Van Loon, L. R.; Barmettler, K.; Borca, C. N.;  
826 Aeschlimann, B.; Gunther, D., High Spatial Resolution Quantitative Imaging by Cross-  
827 calibration Using Laser Ablation Inductively Coupled Plasma Mass Spectrometry and  
828 Synchrotron Micro-X-ray Fluorescence Technique. *Chimia* 2012, 66, (4), 223-228.
- 829 62. Grolimund, D.; Wang, H. A. O.; Van Loon, L. R.; Marone, F.; Diaz, N.; Kaestner, A.;  
830 Jakob, A., Microscopic Chemical Imaging: A Key to Understand Ion Mobility in Tight  
831 Formations. In *CMS Workshop Lecture Series*, Society, C. M., Ed. 2016; pp 1-24.
- 832 63. Hu, Y. J.; Schwaiger, L. K.; Booth, C. H.; Kukkadapu, R. K.; Cristiano, E.; Kaplan, D.;  
833 Nitsche, H., Molecular interactions of plutonium(VI) with synthetic manganese-  
834 substituted goethite. *Radiochim. Acta* 2010, 98, (9-11), 655-663.
- 835 64. Bradbury, M. H.; Baeyens, B., A generalised sorption model for the concentration  
836 dependent uptake of caesium by argillaceous rocks. *J. Contam. Hydrol.* 2000, 42, (2-4),  
837 141-163.
- 838 65. Bradbury, M. H.; Baeyens, B., Predictive sorption modelling of Ni(II), Co(II), Eu(III),  
839 Th(IV) and U(VI) on MX-80 bentonite and Opalinus Clay: A "bottom-up" approach.  
840 *Appl. Clay Sci.* 2011, 52, (1-2), 27-33.
- 841 66. Joseph, C.; Stockmann, M.; Schmeide, K.; Sachs, S.; Brendler, V.; Bernhard, G.,  
842 Sorption of U(VI) onto Opalinus Clay: Effects of pH and humic acid. *Appl. Geochem.*  
843 2013, 36, 104-117.
- 844 67. Salager, S.; Francois, B.; Nuth, M.; Laloui, L., Constitutive analysis of the mechanical  
845 anisotropy of Opalinus Clay. *Acta Geotech.* 2013, 8, (2), 137-154.

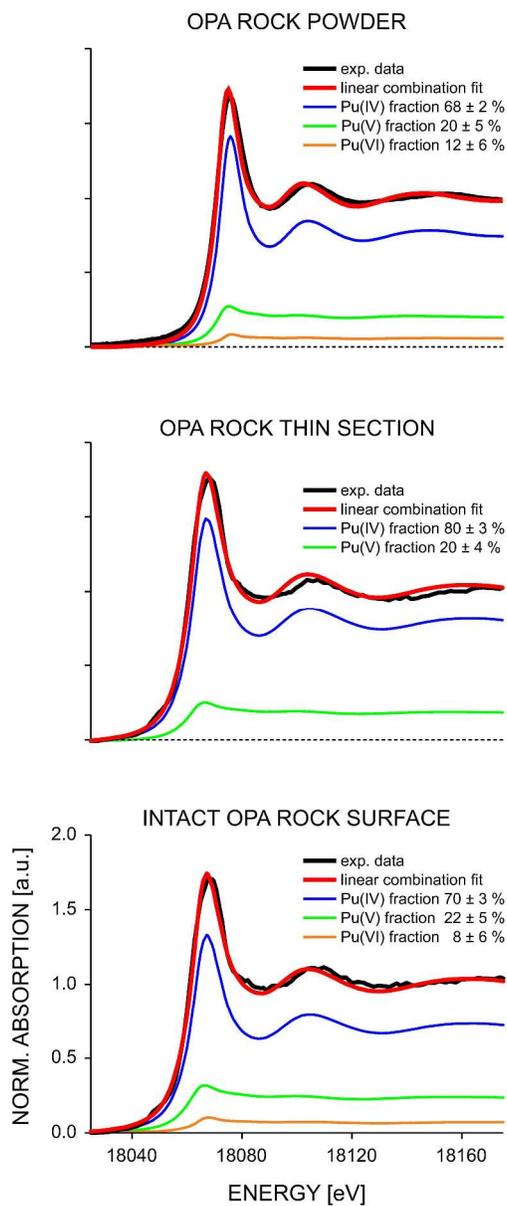
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### Reduction of Pu(VI), Pu(V) and immobilization of Pu(IV) in Opalinus Clay

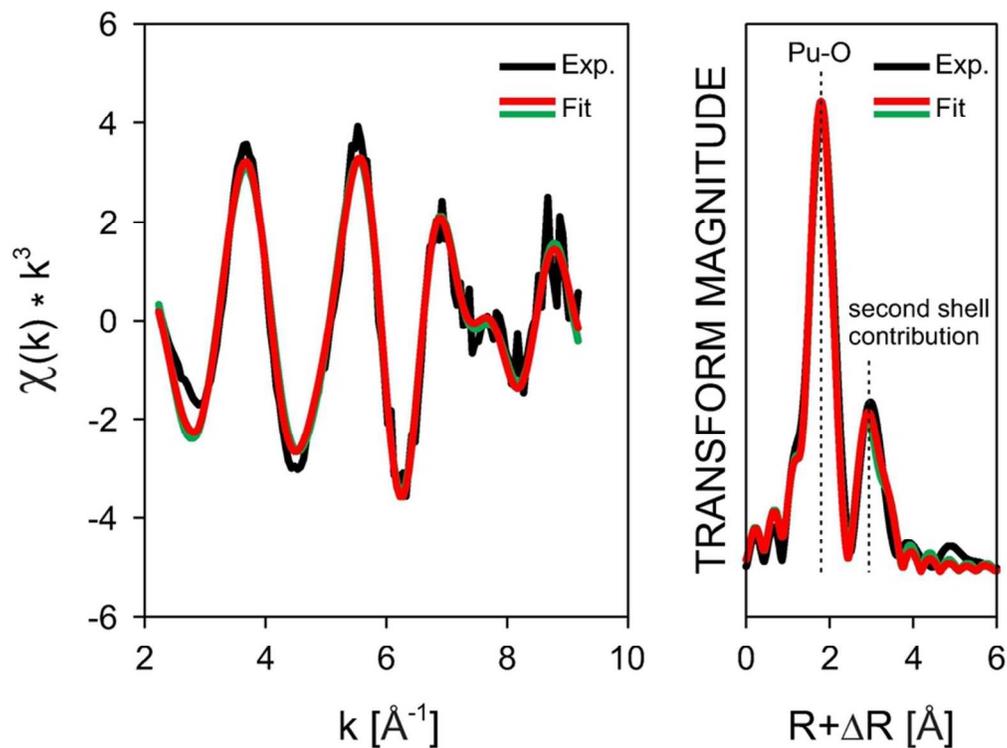
TOC entry

91x59mm (300 x 300 DPI)



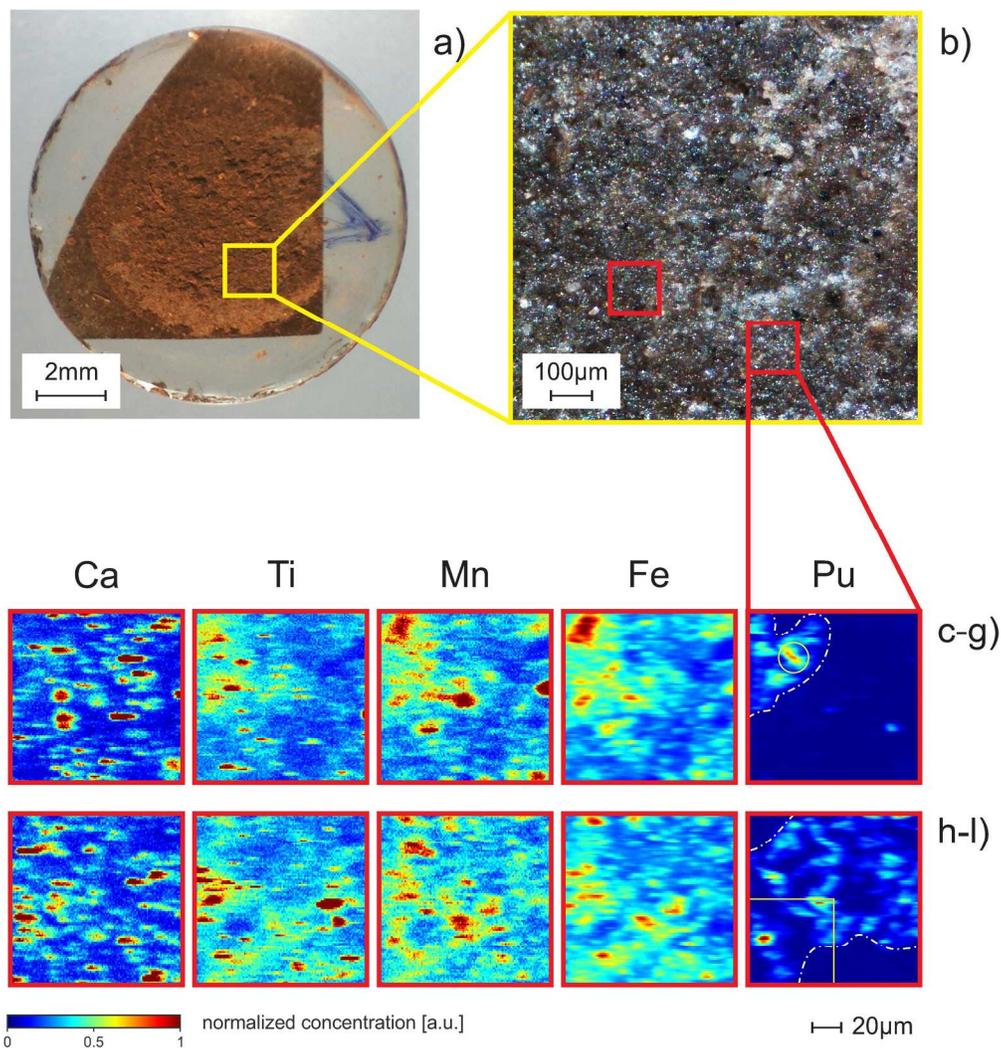
Normalized Pu LIII-edge XANES spectra of Pu(VI) interacted with different samples of Opalinus Clay rock material. top) OPA powder sample; middle) OPA thin section; bottom) OPA core diffusion sample. In each panel experimental data are compared to corresponding linear combination fits of Pu(III)50, Pu(IV)51, Pu(V)52, and Pu(VI)53. Contributions of individual components are included in the figures.

228x552mm (300 x 300 DPI)



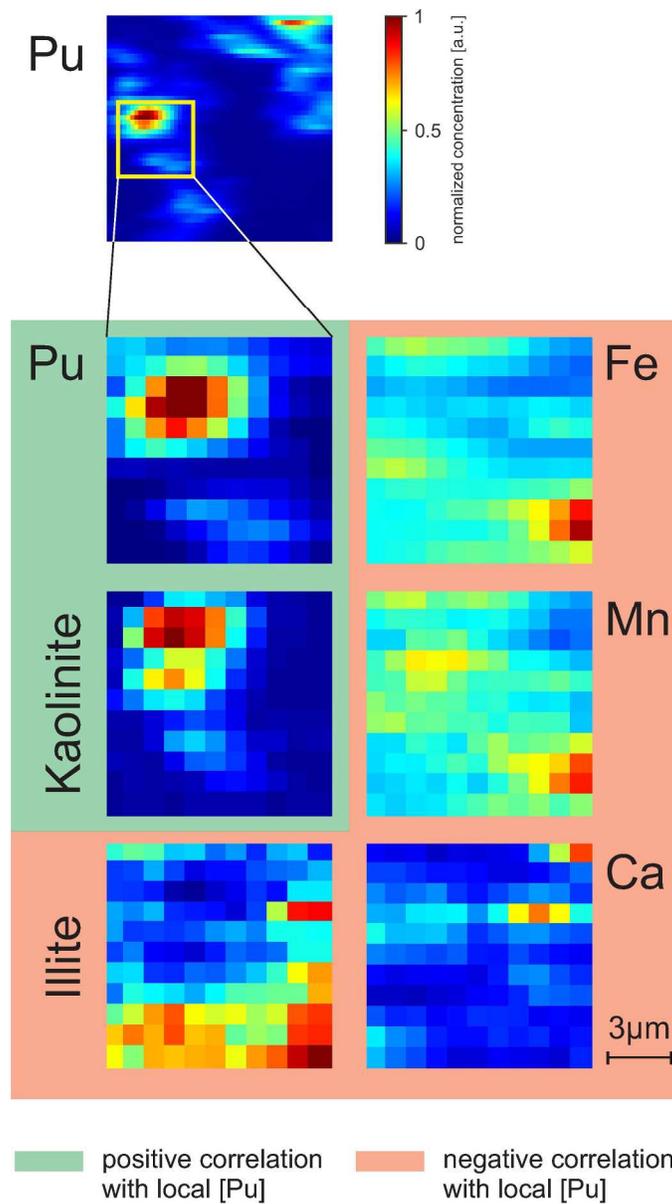
Pu LIII-edge  $k^3$ -weighted EXAFS spectrum (left) and corresponding Fourier transform magnitude (right) of Pu(VI) interacted with Opalinus Clay powder. Experimental data are compared to two different two-shell fits consisting of a first Pu-O shell and the second shells correspond to different combinations of Pu-Si/Al and Pu-Fe/Mn backscattering pairs. The green line corresponds to a fit obtained using a combination of Pu-Si/Al and Pu-Fe/Mn scattering pairs in the second coordination shell, while the red line is based on two distinct sub-shells considering only Si/Al in the second shell (Table S4).

77x57mm (300 x 300 DPI)



Sorption experiment of a Opalinus Clay thin section sample reacting with Pu spiked Millipore water. a) photograph of a representative thin section, b) corresponding light microscope image, c-g) and h-l) elemental distributions of Ca, Ti, Mn, Fe, and Pu for two areas. Chemical images were obtained by synchrotron-based micro-XRF. A pronounced geochemical heterogeneity is observed on the micron-scale. The rectangles sketch magnified zoom-in areas depicted in subsequent panels. The yellow circle in top-left corner of Figure 3g) indicates the location of the micro-XANES measurement shown in Figure 1 (middle).

181x189mm (300 x 300 DPI)



Multi-modal microscopic imaging of a domain with high local Pu retardation observed within the Opalinus Clay thin section. Elemental distribution maps of Pu, Fe, Mn, and Ca were recorded by micro-XRF while mineral distributions of illite and kaolinite are based on micro-XRD imaging.

158x281mm (300 x 300 DPI)