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Spectroscopic investigations of retention mechanisms**

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1 **U(VI) sorption on Ca-bentonite at (hyper)alkaline conditions – Spectroscopic investigations of**
2 **retention mechanisms**

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19

20 **Abstract**

21 Environmental conditions in deep geological repositories for radioactive waste may involve high pH
22 values due to the degradation of concrete. However, the U(VI) sorption at such (hyper)alkaline
23 conditions is still poorly understood. In this study, batch sorption experiments with Ca-bentonite in the
24 pH range 8-13 at different carbonate concentrations were combined with spectroscopic investigations
25 in order to gain insight into the underlying retention mechanisms. It was found that U(VI) sorption
26 strongly correlates with the aquatic U(VI) speciation determined by time-resolved laser-induced
27 luminescence spectroscopy (TRLFS). Increasing retention with increasing pH was accompanied by a
28 change in aquatic speciation from uranyl carbonates to uranyl hydroxides. The occurrence of
29 luminescence line narrowing and a decreased frequency of the symmetric stretch vibration, deduced
30 from site-selective TRLFS, indicate the presence of adsorbed U(VI) surface complexes. X-ray
31 absorption fine structure (EXAFS) spectroscopy confirms that surface precipitation does not
32 contribute to the removal of U(VI) from solution but that retention occurs through the formation of
33 two non-equivalent U(VI)-complexes on the bentonite surface. The present study demonstrates that in
34 alkaline environments, where often only precipitation processes are considered, adsorption can provide
35 effective retention of U(VI), despite the anionic character of prevailing aqueous species.

36

37 **Keywords:** uranium, Ca-bentonite, site-selective TRLFS, EXAFS, speciation, surface complexation

38 **1. Introduction**

39 Radioactive waste originating from nuclear power plants, military, industrial and medical applications
40 can pose a threat to human health due to its radio- and chemotoxic properties when migrating through
41 the subsurface and entering the food chain. Among the radionuclides contained in the nuclear waste
42 matrix, uranium is of special concern, since it represents by far the largest fraction of the waste and
43 features high chemotoxicity and isotopes with an extremely long half-life (i.e. U-238, U-235).
44 Therefore, a secure and effective disposal of such waste over long time spans within deep geological
45 repositories has to be guaranteed. Long-term safety assessment regarding the mobility of uranium in
46 the subsurface (safety case) requires profound understanding of uranium retention processes at mineral
47 surfaces under near-field repository conditions. Such conditions can involve high ionic strengths and
48 high pH values. Pore water chemistry of North German clay formations, which are considered as
49 potential host rocks, is characterized by high ionic strengths with salinities of approx. 150 g/L in the
50 lower cretaceous claystones at 800 m depth (Nowak and Maßmann, 2013; Wolfgramm et al., 2011).
51 Groundwaters in Japanese clay rocks and Canadian limestones, also possible host rocks, feature
52 similar ionic strengths (Hama et al., 2007; Mazurek, 2004). Such high salinities promote the
53 degradation of concrete within the geo-engineered barrier of the repository, leading to the evolution of
54 hyperalkaline cement pore waters ($10 < \text{pH} < 13$) (Berner, 1992; Gaucher et al., 2006; Seher and
55 Bracke, 2012). Such a shift in pore water chemistry can radically alter the retention potential of
56 mineral surfaces towards radionuclides. In this study the retention capability of Ca-bentonite is
57 investigated, as this material is considered as buffer and backfill material within deep geological
58 repositories (Lommerzheim and Jobmann, 2014).

59 While the sorption behavior of U(VI) by bentonite and its main constituent montmorillonite has been
60 extensively studied at up to weakly alkaline conditions, its sorption affinity and the underlying
61 mechanisms are largely unknown in the (hyper)alkaline regime. Under acidic conditions ($\text{pH} < 5$) and
62 low ionic strengths, the uranyl (here always used for $\text{U}^{\text{VI}}\text{O}_2^{2+}$ only), present as fully solvated ion, binds
63 via cation exchange on negatively charged surfaces with an overall low to moderate uptake. As the pH
64 increases to the circumneutral range, various U(VI) hydrolysis complexes dominate the solution

65 speciation, which further can form inner-sphere sorption complexes at the montmorillonite edge sites
66 (silanol and/or aluminol groups), resulting in a quantitative uptake of uranium by the clay mineral
67 (Maher et al., 2013; Stumm, 1992). The U(VI) surface speciation investigated in EXAFS
68 measurements confirmed a splitting of the equatorial oxygen shell of uranyl at circumneutral pH and
69 backscattering contributions from substrate atoms (Si/Al, Fe), indicative of inner-sphere complexation.
70 Shell fitting suggested bidentate coordination to aluminum octahedra and/or silicon tetrahedra
71 (Catalano and Brown, 2005; Chisholm-Brause et al., 1994; Hennig et al., 2002; Marques Fernandes et
72 al., 2012; Sylwester et al., 2000). In the presence of carbonate, sorption decreases drastically at $\text{pH} > 7$
73 due to the formation of negatively charged aqueous uranyl carbonate complexes. These complexes are
74 extremely stable in solution (Guillaumont et al., 2003) and have a low tendency to attach to mineral
75 surfaces (Fritsch, 2018; Maher et al., 2013; Marques Fernandes et al., 2012; Richter et al., 2016;
76 Tournassat et al., 2018). Nevertheless, modelling by Marques Fernandes et al. (2012) suggested that
77 uranyl carbonate complexes sorb at least to some extent to montmorillonite surfaces and also a number
78 of spectroscopic studies indicate the formation of ternary uranyl carbonate surface complexes on
79 montmorillonite, silica, Hanford sediment and ferrihydrite (Rossberg et al., 2009; Saleh et al., 2018;
80 Troyer et al., 2016; Wang et al., 2005). On the other hand, Marques Fernandes et al. (2012) could not
81 provide spectroscopic evidence for the formation of such surface complexes by EXAFS. Furthermore,
82 Tournassat et al. (2018) were able to model U(VI) retention behavior under a wide range of chemical
83 conditions without the introduction of uranyl carbonate surface complexes with the help of a refined
84 surface complexation model based on the consideration of surface charge spillover effects and precise
85 measurements of dissolved inorganic carbon (DIC). The presence of Ca^{2+} in the solution can further
86 modify the U(VI) retention behavior. Formation of highly soluble ternary $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ and
87 $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ complexes can additionally suppress U(VI) adsorption (Bernhard et al., 2001;
88 Joseph et al., 2013; Meleshyn et al., 2009; Schmeide et al., 2014).

89 None of the studies dealing with the formation of uranyl carbonate complexes address if such
90 complexes still prevail when further increasing the pH value. No clear upper pH boundary for their
91 formation has been shown experimentally as a function of DIC due to increasing competition of
92 carbonate with the hydroxyl ligand. Beside uranyl carbonates, the aqueous speciation in the pH range

8-13 is dominated by the higher hydrolysis complexes of uranyl ($\text{UO}_2(\text{OH})_3^-$ and $\text{UO}_2(\text{OH})_4^{2-}$) (Figure SM1). Generally, almost no studies were published on the adsorption of U(VI) by clay at $\text{pH} > 10$, describing surface complexes formed by contribution of these anionic aqueous U(VI) species. In his thesis, A. Schnurr (2015) quantified the U(VI) retention by illite and kaolinite up to $\text{pH} 12$. For both minerals almost complete sorption was maintained up to $\text{pH} 11$. At pH above that, a slight decrease in sorption was observed. Possible explanations for the observed retention behavior were not pursued spectroscopically. The mentioned study was performed in the absence of CO_2 . To our knowledge, no U(VI) sorption study on clay minerals at (hyper)alkaline pH exists, which would additionally consider the effect of carbonate in the solution at $\text{pH} 10$ -13. Studies concerning the U(VI) retention at hyperalkaline conditions mainly address colloid formation or precipitation processes. Generally, U(VI) solubility in (hyper)alkaline solutions is very low and (earth) alkali uranates are the solubility limiting phases (Altmaier et al., 2017; Bots et al., 2014; Tits and Wieland, 2018; Yamamura et al., 1998). In carbonate-free NaCl solutions at $\text{pH} 8$ -11, Altmaier et al. (2017) determined the U(VI) solubility, controlled by $\text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr})$, to be at nanomolar concentrations ($I=2.6 \text{ M}$). In Ca-containing solutions, U(VI) preferentially precipitates as Ca-uranate ($\text{CaUO}_4(\text{s})$) (Ochs et al., 2016; Tits et al., 2011; Tits and Wieland, 2018). Above $\text{pH} 11$, U(VI) solubility increases, reaching micromolar concentrations at $\text{pH} 13$ (Altmaier et al., 2017). Kaplan et al. (1998) investigated the U(VI) retention by sediments up to $\text{pH} 12$ and observed a number of heterogeneous precipitation processes. Kenney et al. (2017) attributed the removal of U(VI) from the solution above $\text{pH} 10$ to the precipitation of uranyl carbonates. Smith et al. (2015) observed the formation of U(VI) colloids and surface mediated precipitation processes in hyperalkaline calcite systems in most of their experiments. Indications for the formation of U(VI) surface complexes on calcite at $\text{pH} 10.5$ and 13.3 were only observed at sub-micromolar U(VI) concentrations. Also Bots et al. (2014) observed the formation of U(VI) nanoparticles at $\text{pH} > 13$. Considerable research has been performed concerning the U(VI) immobilization in cementitious systems at $\text{pH} > 13$. U(VI) is effectively retained in calcium silicate hydrate (C-S-H) phases and hardened cement paste (HCP) (Ochs et al., 2016; Tits et al., 2008; Wieland, 2014; Wolter et al., 2019) and uptake is facilitated by the presence of dissolved calcium (Pointeau et al., 2004; Tits and Wieland, 2018). Spectroscopic studies further investigated the nature

121 of the retained U(VI) complexes. TRLFS revealed the presence of surface complexes as well as
122 incorporated species and precipitation of Ca-uranates (Tits et al., 2011; Tits et al., 2015). EXAFS
123 investigations suggested a local coordination environment similar to U(VI) silicates (such as
124 uranophane) with a split equatorial oxygen shell and short and long silicon distances (Harfouche et al.,
125 2006; Macé et al., 2013). Despite all the above mentioned findings, U(VI) sorption in (hyper)alkaline
126 systems is still poorly understood as the existing studies provide only insight at very specific solution
127 conditions (pH, carbonate concentration, etc.), with even sometimes contradictory results, mostly
128 lacking information on the molecular level.

129 Due to the scarcity of thermodynamic data, so far no reliable model prediction can be made regarding
130 both the aquatic and the surface speciation of U(VI) under (hyper)alkaline conditions. Therefore, the
131 present work aims to provide a comprehensive and systematic description of the U(VI) sorption
132 behavior on Ca-bentonite in the pH range 8-13 as a function of pH and carbonate concentration. In
133 addition, laser luminescence spectroscopy and X-ray absorption spectroscopy applied in the present
134 study deliver information about the underlying retention mechanisms (i.e. distinguish between surface
135 complexation and surface precipitation) and the local U(VI) coordination environment of the retained
136 species.

137

138 **2. Material and Methods**

139 **2.1. Material**

140 The Ca-bentonite used as sorptive was of the type *Calcigel*® (Clariant, München, Germany). This
141 naturally occurring clay rock is mined in Bavaria (Germany) and was received as a powder with
142 particle sizes between 0.5 and 150 µm, the dominant fraction (90 %) of the particles being smaller
143 than 90 µm (laser granulometer HELOS Series KF + Quixel (SYMPATEC, Clausthal-Zellerfeld,
144 Germany), range "R3": 0.5-75 µm). The BET specific surface area was determined to be
145 $76.5 \pm 0.3 \text{ m}^2/\text{g}$ (Beckman Coulter, Fullerton, USA). The mineral composition according to the
146 supplier is 60-70 % montmorillonite, 6-9 % quartz, 1-6 % mica, 1-4 % feldspar, 1-2 % kaolinite and 5-
147 10 % others.

148 As background electrolyte a mixed salt solution (referred to as 'diluted Gipshut solution') was used in
149 all experiments, consisting of 2.5 M NaCl (p.a., Carl Roth, Karlsruhe, Germany), 0.02 M CaCl₂
150 (puriss. AppliChem, Darmstadt, Germany), 0.02 M Na₂SO₄ (p.a., Merck, Darmstadt, Germany) and
151 0.0051 M KCl (p.a., Merck). Featuring a total ionic strength of 2.63 M, it simulates in situ pore waters
152 of North German clay and salt formations at hypothetical repository depth (Wolfgramm et al., 2011).
153 All solutions were prepared with deionized water (18 MΩ cm⁻¹; mod. Milli-RO/Milli-Q-System,
154 Millipore, Schwalbach, Germany). For all experiments under N₂ atmosphere, water was additionally
155 degassed prior to solution preparation. U(VI) addition was realized with a 1×10^{-3} M stock solution
156 (U_{nat} in 0.005 M HClO₄). Carbonate was introduced to the samples by adding aliquots of 1 M NaHCO₃
157 (p.a., Carl Roth) or 2 M Na₂CO₃ (p.a., Merck) stock solutions.

158 **2.2. Bentonite characterization at (hyper)alkaline conditions**

159 In order to evaluate the stability of Ca-bentonite towards treatment with alkaline solutions, leaching
160 tests were performed as a function of pH. Duplicate samples of 10 g/L Ca-bentonite were contacted
161 with 0.1 M NaCl solution for three weeks at pH 8-13 (increments of 0.5). Frequent pH adjustments
162 (every two or three days) were done with NaOH (p.a., Carl Roth) and HCl (p.a., ACS, ISO, Carl

163 Roth). After centrifugation (6800×g, 30 min) in an Avanti J-20 XP centrifuge (Beckman Coulter,
164 Fullerton, USA), the supernatant was analyzed for Na, Mg, Al, Si, K and Ca with ICP-MS (NexION
165 350X, PerkinElmer, Waltham, USA), and for CO₃²⁻ with total inorganic carbon measurements
166 (multiN/C 2100, Analytik Jena, Germany). The centrifugate was analyzed with the powder X-ray
167 diffractometer Rigaku MiniFlex 600 (Tokyo, Japan), using Cu K α radiation and a Bragg-Brentano
168 geometry (in θ -2 θ geometry) with a step size of 0.02 °2 θ and a speed of 0.92 steps per second. For
169 mineral phase identification, the ICDD PDF database was used.

170 The surface charge of Ca-bentonite particles was determined by zeta potential measurements
171 (Zetasizer Nano ZS, Malvern Instruments, Malvern, United Kingdom). 11 bentonite suspensions (0.1
172 g/L) in the pH range 8-13 were prepared in 0.1 M NaCl, 2.5 M NaCl and 0.1 M NaCl + 0.02 M CaCl₂
173 in order to evaluate the effect of pH, ionic strength and calcium concentration. Potentials were
174 averaged over ten measurements consisting of 10-50 scans.

175 **2.3. Batch sorption experiments**

176 All samples were prepared in duplicate. Bentonite powder was weighed in polypropylene centrifuge
177 tubes and was suspended with 10 mL diluted Gipshut solution. As a result of experiments with
178 variable bentonite mass (Figure SM2), a solid to liquid (S/L) ratio of 10 g/L was selected for all
179 sorption experiments. Suspensions were pre-conditioned with frequent pH-adjustments with diluted
180 NaOH or HCl (every two or three days) until a constant pH value (± 0.05) was reached (approx. two
181 weeks). The pH was measured with an InoLab pH 7110 pH meter (WTW, Weilheim, Germany) and a
182 SenTix MIC glass electrode (WTW). Three point calibration of the pH meter was executed with WTW
183 buffer solutions (pH 6.865, 9.180 and 12.454) (WTW).

184 In solutions with high ionic strengths, the measured potential at the pH electrode, and accordingly the
185 derived pH_{exp}, deviates from the true potential due to the great discrepancy between the activity
186 coefficients of the sample and the electrolyte of the electrode (Altmaier et al., 2003). By introducing a
187 correction parameter A, the true pH can be derived according to:

$$-\log[\text{H}^+] = \text{pH}_{\text{exp}} + A \quad (1)$$

188 A was determined to be ~0.4 for this system by measuring the pH of solutions with an ionic strength
189 of 2.63 M and known H^+ or OH^- concentrations. During pre-equilibration, samples were placed in an
190 end-over-end shaker.

191 After pre-equilibration, U(VI) was added to the suspensions by pipetting calculated volumes of the
192 U(VI) stock solution. The initial U(VI) concentrations of each experiment are summarized in Table 1.
193 The sorption time was always seven days during which the samples were rotated in an end-over-end
194 shaker. This reaction time was based on kinetic sorption experiments (Figure SM3).

195 For phase separation, samples were centrifuged at $6800\times g$ for 30 min (see above). Photon correlation
196 spectroscopy (Zetasizer Nano ZS) showed that this procedure led to a sufficient phase separation,
197 leaving no measurable particle fraction in solution.

198 Uranium concentrations in the supernatants were determined by ICP-MS (see above). From the initial
199 (c_0) and the equilibrium (c_{eq}) U(VI) concentrations in solution [M], the sorption distribution coefficient
200 K_d was calculated according to equation (2), where V [L] is the volume of the solution and m [kg] the
201 mass of the solid.

$$K_d = \frac{c_0 - c_{eq}}{c_{eq}} \times \frac{V}{m} \quad (2)$$

202 Experiments were carried out both at carbonate-free conditions (N_2 inert gas box) and in the presence
203 of carbonate (at ambient air conditions). Low dissolved carbonate (LC = 1 mM) and high carbonate
204 (HC = 100 mM) concentrations were achieved by adding calculated amounts of NaHCO_3 or Na_2CO_3
205 to the solutions. These concentrations are representative of the lower and upper boundary for natural
206 carbonate concentrations expected in pore waters in the North German Basin at repository depth
207 (approx. 800 m). Analytical determination of the carbonate content (see above) confirmed stable
208 concentrations of dissolved carbonate within the time frame of the experiments. CO_2 from the ambient
209 air did not lead to an additional measurable increase of carbonate concentration within the time frame
210 of the experiments.

211 Samples without Ca-bentonite were prepared in order to investigate the solubility of U(VI) in the
 212 bentonite leachate under the given experimental conditions. As polypropylene centrifuge tubes showed
 213 significant uptake of U(VI) in the absence of Ca-bentonite (Text SM1), for these experiments
 214 fluorinated ethylene propylene (FEP) vials (Thermo Scientific Nalgene, Waltham, USA) were used,
 215 featuring an inert surface that minimizes uranium adsorption. Leachates of Ca-bentonite were
 216 produced at different pH values by contacting it with diluted Gipschut solution (10 g/L) for 2 weeks
 217 with continuous pH adjustments (pH 8-12.5, increments of 0.5). After phase separation, U(VI) was
 218 added to 10 mL of the leachate to reach a U(VI) concentration of 5×10^{-7} M. Seven days after U(VI)
 219 addition, the samples were ultracentrifuged (60 min, $187000 \times g$, Optima XL 100K, Beckman Coulter)
 220 and the supernatants were analyzed for uranium with ICP-MS.

221 In Table 1 all performed batch experiments and relevant experimental conditions are summarized.

222 *Table 1: Overview of performed batch experiments. Diluted Gipschut solution ($I=2.63$ M) was used as background electrolyte*
 223 *in all experiments. 'N₂' refers to experiments in the absence of CO₂ (minimal carbonate concentrations originating from*
 224 *bentonite leaching), 'LC' to low carbonate concentrations (1 mM) and 'HC' to high carbonate concentrations (100 mM).*

Experiment	S/L ratio [g/L]	atmosphere	c(U) [M]	pH
Solubility	-	N ₂	5×10^{-7}	8-13
Leaching	1-20	N ₂	-	8-13
		LC		
S/L ratio dependency	3-20	N ₂	1×10^{-6}	8
		LC		
Kinetics	10	N ₂	1×10^{-6}	8
		LC		
pH dependency	10	N ₂	5×10^{-7}	8-13
		LC	1×10^{-6}	
		HC	1×10^{-6}	

225

226

2.4. Time-resolved laser-induced luminescence spectroscopy (TRLFS)

In U(VI) luminescence spectroscopy, laser light is used to excite an electron from the covalently bound oxygen atoms of the “yl”-cation via a charge transfer mechanism to unoccupied molecular orbitals of uranium. The relaxation from the excited state to the electronic ground state will give rise to emission of photons (luminescence). The released energy of photons corresponds to the transition to the lowest vibrational level of the degenerated ground state (electronic transition line E) and to the higher vibronic levels of the electronic ground state (lines of vibronic progression S_1 , S_2 , etc.), yielding the characteristic multi-peak spectrum of uranyl. The spacing between E_1 and S_1 , defined as ν_s , represents the total symmetric stretch vibration frequency of the uranyl moiety (Tits et al., 2015; Wang et al., 2005). The magnitude of this frequency is sensitive to the number and type of ligands present in the equatorial plane and can be taken as a measure of the binding strength of coordinating ligands. An increased binding strength of equatorially bound ligands will withdraw electron density from the axial oxygens, reducing the strength of the “yl”-bond which in turn reduces the total symmetric stretch vibration frequency. Thus, a smaller E_1 to S_1 spacing is indicative of stronger bonding.

Conventionally, U(VI) luminescence is measured after indirect excitation with a high incident laser energy so that all U(VI) species contained in the sample are excited simultaneously. In case of a large heterogeneity of bonding environments (species or sorption sites) within the sample, this will lead to broadened and poorly resolved spectra. This broadening can be overcome by applying site-selective TRLFS at liquid helium temperatures. With this technique single species within the sample can be excited selectively by varying the excitation energy. At each wavelength within the inhomogeneously broadened absorption band only a small subset of uranyl ions is excited directly to the lowest vibrational level of the excited state, decaying radiatively to the ground state. For a more detailed explanation we refer to Tits et al. (2015), who applied this technique successfully for the first time for U(VI).

The aqueous speciation of uranium in the diluted Gipshut solution was investigated with non-selective TRLFS at $\lambda_{\text{ex}} = 266$ nm. Measurements were performed in the absence of CO_2 , at low and at high carbonate concentrations, equivalent to the pH-dependent sorption studies. Batch samples with

254 uranium concentrations of 5×10^{-7} M in diluted Gipshut solution were prepared in FEP vials at pH 8-
255 13. After 7 days, with frequent pH adjustments, 1 mL of each sample was filled in a polystyrene one
256 time cuvette (Carl Roth) and quick-frozen with liquid nitrogen. TRLFS measurements were
257 performed at 153 K by using a cryogenic cooling system. The laser system used was a Nd:YAG laser
258 (Minilite high-energy solid-state laser; Continuum, San Jose, USA) as described in Steudtner et al.
259 (2011) operating at an average pulsed energy of 0.3 mJ. The emission of the samples was recorded
260 using an iHR550 spectrograph (HORIBA Jobin Yvon, Bensheim, Germany) and an ICCD camera
261 (HORIBA Jobin Yvon). A gate width of 2000 μ s and a slit width to the spectrograph of 2000 μ m were
262 chosen. Spectra were recorded at different delay times (t_i), defined by the equation $t_i = 0.1 + 0.005 \cdot$
263 $x + i^{4/2000}$, with i being the step number. At each time step, 100 measurements were averaged. Peak
264 positions were identified from second derivatives of FFT-filter smoothed spectra by determining their
265 negative maxima. Luminescence lifetimes were obtained by plotting cumulative intensities at each
266 time step against delay time. Data points were then fitted exponentially.

267 Site-selective TRLFS was applied to investigate the U(VI) species sorbed on the Ca-bentonite surface.
268 Samples were prepared as described above in the batch sorption experiments, but with lower S/L ratio
269 (0.3 g/L) in order to increase the U(VI) surface coverage. Two samples were prepared in the absence
270 of CO₂ at pH 11, where sorption is at maximum: One with the same U(VI) concentration as in the pH-
271 dependent sorption experiments (5×10^{-7} M) and one with a U(VI) concentration two orders of
272 magnitude higher than that (5×10^{-5} M) to provoke U(VI) precipitation for comparison. After
273 ultracentrifugation (187000 \times g) (see above) each wet paste pellet was transferred into a copper sample
274 holder with a sealable quartz glass lid. Measurements were performed with a pulsed Nd:YAG
275 (Continuum Surelite II, San Jose, USA) pumped dye laser setup (Radiant Dyes Narrow Scan K,
276 Wermelskirchen, Germany). The emitted luminescence emission light was directed into a spectrograph
277 (Shamrock 303i, Andor Oxford Instruments, Abingdon, United Kingdom) equipped with a
278 polychromator with 300, 600, and 1200 lines/mm gratings, and the emission was monitored with an
279 intensified CCD camera (Andor iStar, Oxford Instruments) 10 μ s after the exciting laser pulse in a
280 time window of 10 ms. The laser pulse energy and the exact excitation wavelength were monitored in
281 every measurement with an optical power meter (Newport 1918-R, Irvine, USA) and a wavelength

282 meter (High Finesse WS-5, Tübingen, Germany), respectively. Spectra were recorded at excitation
283 wavelengths between 460 and 520 nm with a step size of 0.2 nm. Additionally, time-resolved
284 luminescence spectra were recorded at selected excitation wavelengths with a temporal step size of
285 10 μ s. To achieve the desired spectral resolution the solid samples were cooled to \sim 10 K in a helium-
286 refrigerated cryostat.

287 **2.5. Extended X-ray absorption fine structure (EXAFS) spectroscopy**

288 Batch sorption samples for the EXAFS measurements were prepared as described above. A total of 10
289 samples (Table SM1) with variable pH and carbonate concentration was prepared with a S/L ratio of
290 0.3 g/L, leading to sufficiently high surface coverage, despite the low initial U(VI) concentrations of
291 5×10^{-7} M in the absence of CO₂ and 1×10^{-6} M at low and high carbonate concentrations. Phase
292 separation was achieved by ultracentrifugation, after which the Ca-bentonite wet paste was transferred
293 into polyethylene (PE) sample holders. Samples were covered with capton tape, enclosed with a PE
294 cap and finally sealed by soldering.

295 The U L_{III}-edge (17166 eV) EXAFS spectra were recorded at the Rossendorf Beamline (ROBL,
296 BM20) at the European Synchrotron Radiation Facility (ESRF) (Matz et al., 1999), operated at 6 GeV
297 and an electron current of 200 mA. For rejection of higher harmonics two Rh-coated mirrors were
298 used and the incident white X-rays were monochromatized with a liquid nitrogen cooled Si(111)
299 double crystal monochromator. The sorption samples were measured under cryogenic conditions
300 (15 K) by using a closed cycle He-cryostat. In order to increase the signal-to-noise ratio for each
301 sorption sample, a maximum of eleven fluorescence spectra were recorded by counting the signal of
302 the U L $\alpha_{1,2}$ fluorescence lines with a 13-element Ge-detector. For energy calibration the absorption of
303 a Y metal foil at the K-edge (17038 eV) was measured simultaneously during each energy scan. The
304 incident photon flux and the absorption were measured with gas filled ionization chambers. For the
305 calculation of the photoelectron wave vector (k) the ionization potential (E_0) was set arbitrarily to $E_0 =$
306 17185 eV. EXAFSPAK (George and Pickering, 1995) and WinXAS (Ressler, 1998) were used for the
307 data treatment which included a correction for the dead-time of the 13 fluorescence channels, energy

308 calibration, averaging of the multiple sample scans, isolation of the EXAFS signal from the averaged
309 data and shell fit. As a reference for the aqueous $\text{UO}_2(\text{OH})_4^{2-}$ complex we used published data from
310 (Moll et al., 2014), where six absorption spectra were measured at room temperature. For the shell fit
311 theoretical scattering phase and amplitude functions were calculated with the ab-initio scattering code
312 FEFF 8.20 (Ankudinov et al., 1998) by using an arbitrary structural model of the sorption complex and
313 of the aqueous $\text{UO}_2(\text{OH})_4^{2-}$ complex (Figure SM4).

314 Iterative target transformation factor analysis (ITFA) (Rossberg et al., 2003) was applied in order to
315 quantify the structurally different sorption complexes and to isolate their spectra from the EXAFS
316 spectral mixtures of the sorption samples (Text SM2).

317

318 **3. Results and Discussion**

319 **3.1. Bentonite stability and surface charge**

320 Leaching experiments and consecutive powder X-ray diffraction (PXRD) measurements prove a
321 general stability of the minerals within the Ca-bentonite up to pH 12.5 over a time span of three
322 weeks, so that the U(VI) sorption processes can be discussed without consideration of substantial
323 disaggregation or alteration of the mineral surfaces. Ions leached from the Ca-bentonite to noticeable
324 amounts are Ca, Mg, Si and Al (Figure SM5). The most strongly leached element up to pH 12 is
325 calcium (~1.3 mM), which, however, is removed from the solution by calcite precipitation (in the
326 presence of carbonate, not shown) above pH 8.5 and by portlandite ($\text{Ca}(\text{OH})_2$) precipitation (in the
327 absence of carbonate) above pH 12. Magnesium precipitates as brucite ($\text{Mg}(\text{OH})_2$) above pH 9. Al and
328 Si concentrations in the leachates are very low up to pH 12.5. Only at pH 13 a significant increase in
329 concentration of both elements due to dissolution of montmorillonite can be observed. PXRD
330 diffractograms of Ca-bentonite leached between pH 8.5 and 12.5 have a very similar appearance and
331 feature the same main peaks (Figure SM6). Major identified phases are quartz and the clay minerals
332 montmorillonite, illite and muscovite. No significant alteration of mineral composition with increasing
333 pH could be detected. The observed stability of bentonite up to pH 12.5 is in accordance with
334 literature. Several studies describe that treatment with alkaline fluids of pH 12.5 only lead to minimal
335 alteration of smectites or leave the bentonite virtually unchanged (Fernández et al., 2009; Milodowski
336 et al., 2016; Vuorinen et al., 2006). Additionally, Schatz et al. (2013) found that Ca-montmorillonite is
337 more stable towards chemical erosion than Na-montmorillonite. Severe alterations only occur at even
338 higher pH values (>13), higher temperatures and over longer timespans.

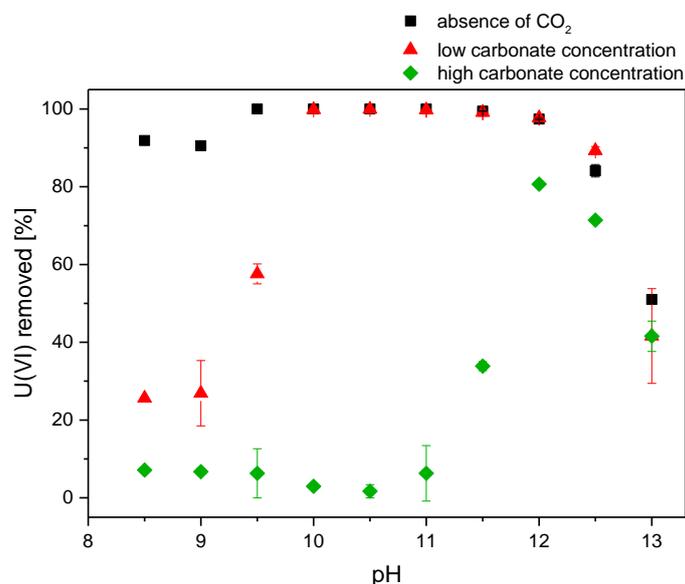
339 Zeta potential measurements show a negative surface charge of the Ca-bentonite over the entire pH
340 range in 0.1 M NaCl (Figure SM7), as it can be expected from the permanent negative charge of 2:1
341 clay minerals due to isomorphous substitution of cations within the octahedral and tetrahedral layers.
342 At high ionic strength (2.5 M NaCl) the potential is generally less negative because of the high density

343 of cations close to the surface. The addition of much smaller amounts of calcium (0.02 M) to 0.1 M
344 NaCl results in a similar effect, indicating the adsorption of calcium to the clay mineral surface.

345 **3.2. Batch sorption experiments**

346 Batch sorption experiments exhibit a complex U(VI) retention behavior depending on pH and the
347 amount of carbonate present in solution (Figure 1). In the absence of CO₂, U(VI) retention is approx.
348 90 % at pH 8-9 (squares in Figure 1). At higher pH, sorption even increases, forming a plateau of
349 complete retention from pH 9.5 to about pH 12. At pH ≥ 12, U(VI) sorption decreases again to only
350 50 % at pH 13. At low carbonate concentration (1 mM), U(VI) retention is low (approx. 20 %) at
351 pH 8-9. Going to higher pH values, the retention increases drastically, following a similar pH-
352 dependent trend as in the absence of CO₂. Also here a plateau of complete sorption is observed at pH
353 10-12, followed by a pronounced drop at pH ≥ 12 (triangles in Figure 1). When carbonate
354 concentration is high (100 mM), U(VI) retention remains on a very low level (< 10 %) up to pH 11.
355 Thereafter it increases, reaching 80 % at pH 12 (diamonds in Figure 1), before dropping again, similar
356 to the previously described series. The complete U(VI) retention in the absence of CO₂ and at low
357 carbonate concentrations corresponds to maximum log(K_d) values of approx. 5-6 log(L/kg), restricted
358 by the detection limit of the ICP-MS measurements (0.1 µg/L). At high carbonate concentrations, the
359 maximum retention at pH 12 corresponds to a log(K_d) value of 2.6 log(L/kg) (Figure SM8). The lower
360 U(VI) retention in the presence of carbonate at pH 8 to 9.5 is in accordance with literature and is
361 attributed to the predominant formation of weakly sorbing (calcium) uranyl carbonate complexes
362 (Bachmaf et al., 2008; Joseph et al., 2013; Maher et al., 2013; Marques Fernandes et al., 2012; Richter
363 et al., 2016; Tournassat et al., 2018). The higher the carbonate concentration is, the stronger the U(VI)
364 sorption decreases, as the relative abundance of uranyl carbonate species compared to uranyl
365 hydroxides or mixed uranyl carbonate hydroxo complexes is higher. An increase in retention with
366 further increasing pH has not been reported for such systems as none of these studies expands to the
367 hyperalkaline regime. Also in the absence of CO₂ published data is scarce (see section 1). Even
368 without discussing the underlying retention mechanism on a molecular level, the presented batch
369 results alone provide already substantial knowledge gain as they present for the first time a systematic

370 study of the U(VI) retention by clay rock from weakly alkaline to hyperalkaline pH. The results show
 371 that sorption can be very effective up to pH 12, also in the presence of carbonate. The decreased U(VI)
 372 retention in the presence of carbonate, reported previously in the literature, does only apply up to a
 373 certain pH and is highly dependent on the amount of carbonate in the solution.



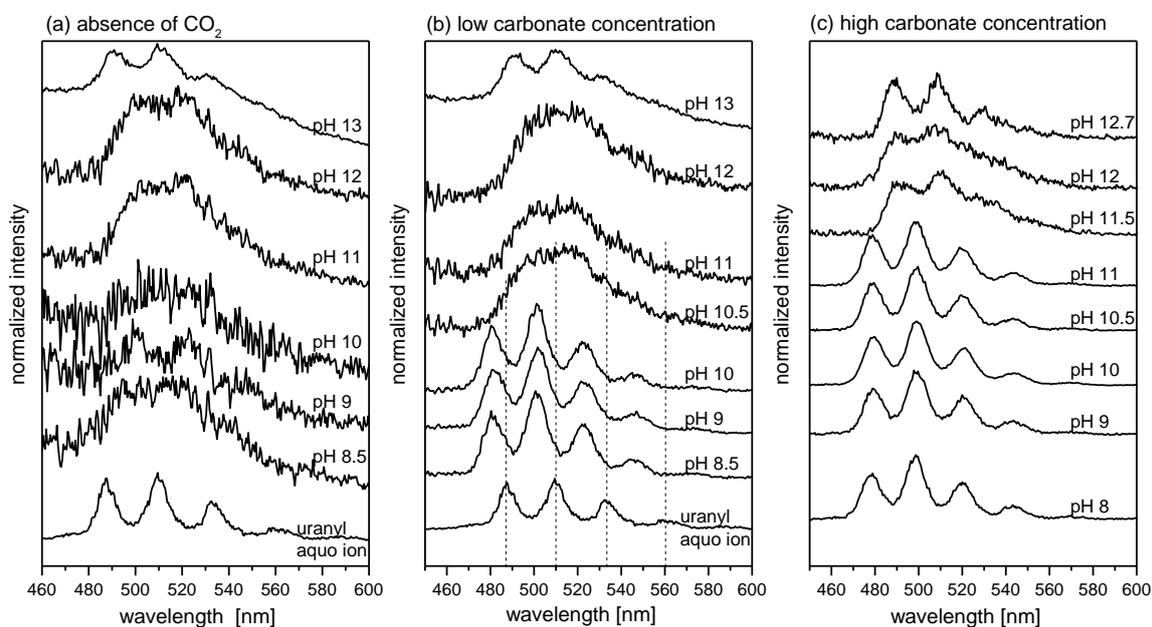
374

375 *Figure 1: Percentage of U(VI) sorbed on Ca-bentonite (10 g/L) in dil. Gipshut solution (I = 2.63 M) as function of pH and*
 376 *carbonate concentration (see section 2.3). Initial U(VI) concentrations were 1×10^{-6} M in the presence and 5×10^{-7} M in the*
 377 *absence of carbonate.*

378 3.3. Aqueous U(VI) speciation studied with TRLFS

379 In the absence of CO₂, the luminescence spectra of U(VI) in diluted Gipshut solution measured at
 380 153 K feature a low intensity with a poor spectral resolution (Figure 2a). Both phenomena are
 381 characteristic for uranyl hydroxide complexes at alkaline conditions. This has been reported by Drobot
 382 et al. (2016); Martínez-Torrents et al. (2013), and Moulin et al. (1998), where monomeric hydrolysis
 383 species UO₂(OH)₂, UO₂(OH)₃⁻ and UO₂(OH)₄²⁻ were shown to exhibit broadened spectra with weak
 384 spectral splitting. In spite of the low signal to noise ratio (particularly up to pH 10), the positions of the
 385 first two main peaks could be identified, situated at approx. 500 nm and 521 nm for the samples up to
 386 pH 12 (Table 2). Drobot et al. (2016) observed maxima at 499 and 520 nm for UO₂(OH)_{2(aq)} and at
 387 503 and 525 nm for UO₂(OH)₃⁻. Martínez-Torrents et al. (2013) and Moulin et al. (1998) described
 388 peaks for UO₂(OH)₃⁻ at 503 and 521 nm and at 499 nm and 519 nm, respectively. Luminescence

389 lifetimes depend on the presence of quenchers and, to a large degree, on the temperature of the sample.
 390 Therefore, comparing lifetimes obtained in different studies is difficult. From the aforementioned
 391 studies only Martínez-Torrents et al. (2013) performed measurements at cryogenic conditions (10 K).
 392 The reported luminescence lifetime of 198 μs for $\text{UO}_2(\text{OH})_3^-$ fits very well to the 208 μs obtained in
 393 the present work at pH 11 (measured at 153 K). At pH 13 the luminescence spectrum is shifted
 394 towards lower wavelength, having the first two maxima at approx. 490 and 511 nm (Table 2). These
 395 positions are in agreement with spectra measured by Tits et al. (2011) at very alkaline conditions (pH
 396 13.3), which were assigned to the higher hydrolysis species $\text{UO}_2(\text{OH})_4^{2-}$. The luminescence lifetime at
 397 pH 13 was measured to be somewhat shorter than at lower pH. This observation is consistent with the
 398 works of Martínez-Torrents et al. (2013) and Kitamura et al. (1998) in which shorter lifetimes are
 399 reported for $\text{UO}_2(\text{OH})_4^{2-}$ compared to $\text{UO}_2(\text{OH})_3^-$. Consequently, based on analysis of peak positions
 400 and luminescence lifetimes, anionic uranyl hydroxides (first $\text{UO}_2(\text{OH})_3^-$ and at very high pH
 401 $\text{UO}_2(\text{OH})_4^{2-}$) dominate the aqueous speciation of U(VI) in the diluted Gipshut solution in the absence
 402 of CO_2 between pH 8 and 13.



403
 404 *Figure 2: Luminescence spectra of uranyl ($[U(VI)] = 5 \times 10^{-7} M$) in the diluted Gipshut solution as a function of pH in the*
 405 *absence of CO_2 (a), at low carbonate concentration (b) and at high carbonate concentration (c).*

406 In the presence of carbonate, the recorded luminescence emission spectra vary strongly within the
 407 investigated pH range 8-13. Up to pH 10 at low carbonate concentration and up to pH 11 at high

408 carbonate concentration, the shape of the spectra is very similar, exhibiting a well-resolved spectral
409 splitting (Figure 2b,c). Compared to the uranyl aquo ion, these spectra are shifted towards lower
410 wavelengths, which is characteristic for uranyl carbonate complexes (Bernhard et al., 2001; Lee and
411 Yun, 2013; Steudtner et al., 2011; Wang et al., 2004). The obtained peak positions match very well
412 with literature data for $\text{UO}_2(\text{CO}_3)_3^{4-}$ and the ternary calcium uranyl carbonate complexes
413 $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ and $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ (Table 2). Luminescence lifetimes of these samples range
414 between 800 and 900 μs . As peak positions are very similar and the luminescence lifetimes depend on
415 temperature and solution composition, it is not possible to distinguish between $\text{UO}_2(\text{CO}_3)_3^{4-}$ and
416 ternary Ca-UO₂-CO₃ complexes here, based on the spectral properties. However, given that the diluted
417 Gipshut solution contains large amounts of calcium, the formation of ternary complexes with calcium
418 is expected. Another plausible complex is $\text{MgUO}_2(\text{CO}_3)_3^{2-}$, which was described by Lee et al. (2017)
419 with almost the same luminescence spectroscopic properties as $\text{UO}_2(\text{CO}_3)_3^{4-}$. The formation of this
420 complex might be favored when calcium is removed successively from the solution with increasing
421 pH due to calcite precipitation. Magnesium is then still available as brucite precipitation is initiated at
422 somewhat higher pH. At pH 10.5 at low carbonate concentrations and at pH 11.5 at high carbonate
423 concentration, an abrupt change in speciation is visible. The well resolved emission bands are not
424 detectable anymore. Instead, broad spectra with lower luminescence intensity are observed. Peak
425 positions and lifetimes compare very well to those that were obtained in the absence of CO₂ (for a
426 comparison, see Figure SM9) and are therefore also interpreted as monomeric uranyl hydroxide
427 complexes $\text{UO}_2(\text{OH})_3^-$ and $\text{UO}_2(\text{OH})_4^{2-}$. Consequently, uranyl carbonate complexes, which have been
428 widely reported to dominate the aqueous U(VI) speciation at alkaline conditions, prevail only up to a
429 certain pH, depending on the concentration of dissolved carbonate. At higher pH, the formation of
430 uranyl hydroxides is favored.

431 A clear correlation between changes in aqueous speciation and changes in the sorption behavior can be
432 observed. U(VI) retention is low in the pH range, where uranyl carbonate complexes dominate the
433 aqueous speciation according to the TRLFS measurements. The observed increase in retention in the
434 presence of carbonate above a certain pH coincides with the change in aqueous speciation from uranyl
435 carbonates to uranyl hydroxides. Generally, it can be stated that U(VI) retention is very high in

436 samples, where $\text{UO}_2(\text{OH})_3^-$ dominates the aqueous speciation. At $\text{pH} > 12$ the decrease in retention
 437 correlates with the formation of the higher hydrolysis species $\text{UO}_2(\text{OH})_4^{2-}$. In the light of electrostatic
 438 interactions, it has to be discussed if the very strong U(VI) retention at $\text{pH} 10\text{-}12$ can be attributed to
 439 adsorption of a negatively charged metal complex to the negatively charged bentonite surface, or if the
 440 retention under these conditions is rather caused by a precipitation of uranates.

441 *Table 2: Luminescence spectroscopic properties (band positions and luminescence lifetimes) of U(VI) in the diluted Gipshut*
 442 *solution of selected samples at different pH and carbonate concentrations. Literature data are given for comparison.*

Series	pH	Peak positions [nm]				Lifetime [μs]	T [K]
N ₂	9.0	502.1	522.9		-	153	
	11.0	499.3	521.0		208 ± 30	153	
	13.0	490.4	510.7	531.6	74 ± 17	153	
LC	9.0	481.2	502.1	523.4	546.9	877 ± 17	153
	11.0	497.0	519.2	542.8	569.6	149 ± 13	153
	13.0	490.4	510.3	532.5		89 ± 7	153
HC	9.0	478.8	499.6	521.4	544.1	804 ± 17	153
	11.0	477.9	499.2	520.5	544.1	808 ± 18	153
	12.7	488.1	508.9	530.2		112 ± 10	153
$\text{UO}_2(\text{CO}_3)_3^{4-}$ [a]		480.7	499.9	520.3	542.5	834 ± 9	153
$\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ [b]		480.5	501.2	522.7	546.0	1282	6
$\text{UO}_2(\text{OH})_3^-$ [c]		503.0	521.0	534.0	550.0	198 ± 8	10
$\text{UO}_2(\text{OH})_3^-$ [d]		503	525	547	572	3.4 ± 0	274
$\text{UO}_2(\text{OH})_4^{2-}$ [e]		491.4	510.5		140 ± 30	153	

[a] Steudtner et al. (2011); [b] Wang et al. (2004); [c] Martínez-Torrents et al. (2013); [d] Drobot et al. (2016); [e] Tits et al. (2011)

443 **3.4. U(VI) solubility**

444 Batch samples of U(VI) in leachates of Ca-bentonite in diluted Gipshut solution demonstrate that
 445 substantial amounts of the initial U(VI) (5×10^{-7} M) remained in solution over the entire pH range after

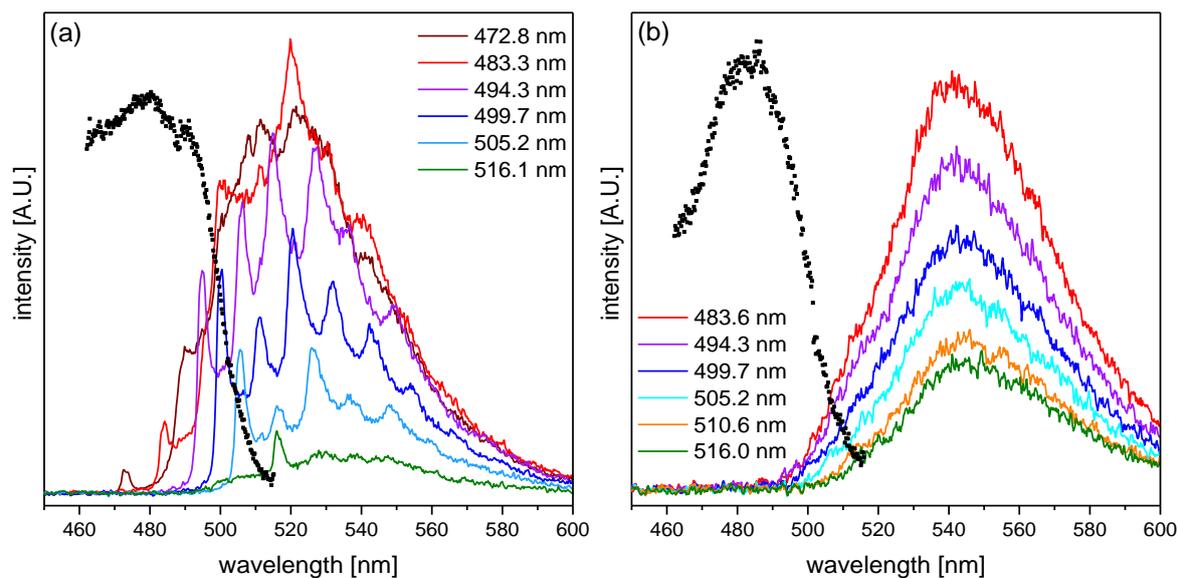
446 one week of contact time and after ultracentrifugation (Figure SM10). Hence, the complete removal of
447 U(VI) observed for the sorption samples at pH 10-12 cannot exclusively be attributed to precipitation
448 from the solution. This is in contrast to literature solubility studies, where U(VI) solubility is often
449 described to trend to nanomolar concentrations at alkaline conditions (Altmaier et al., 2017; Kitamura
450 et al., 1998). The solubility limiting phase between pH 8 and 13 is sodium di-uranate ($\text{Na}_2\text{U}_2\text{O}_7 \cdot \text{H}_2\text{O}$)
451 in pure sodium chloride solutions (Altmaier et al., 2017) and calcium uranate (CaUO_4) in the presence
452 of calcium (Bots et al., 2014; Moroni and Glasser, 1995; Smith et al., 2015; Tits et al., 2008; Tits et
453 al., 2011; Tits and Wieland, 2018). Due to the high calcium concentration in the diluted Gipshut
454 solution, the precipitation of Ca-uranates would be expected in the present study. However, the
455 solubility data given in literature were determined from undersaturation experiments, consistently
456 yielding lower equilibrium U(VI) concentrations compared to an oversaturation approach.
457 Furthermore, most solubility studies (e.g. (Altmaier et al., 2017)) were conducted over much longer
458 time spans, so that kinetics have to be considered. Under the given conditions, precipitation of
459 uranates might be a much slower process than U(VI) adsorption, making precipitation negligible
460 within the one-week sorption experiments. Tits and Wieland (2018) also found that at least up to
461 2×10^{-6} M U(VI) is stable in Ca-rich alkaline solutions for a time span of seven days. Having shown
462 that precipitation from the solution does not play a major role, surface-mediated precipitation
463 processes are still possible. Those could occur only when the Ca-bentonite is present, triggered by an
464 increased U(VI) concentration near the surface. In order to unambiguously distinguish between surface
465 precipitation and surface complexation, direct spectroscopic investigation of the U(VI) complexes
466 sorbed to the Ca-bentonite surface was necessary.

467

468 **3.5. U(VI) surface complexes studied with site-selective TRLFS**

469 Figure 3a shows the excitation spectrum (black data points) of U(VI) sorbed on Ca-bentonite at pH 11
470 in the absence of CO_2 and a series of selected emission spectra (in color), obtained at different
471 excitation wavelengths. The excitation spectrum does not contain much spectral information. The
472 absence of distinct maxima is attributed to great variety of sorption sites within the sample, leading to

473 an inhomogeneous broadening. This heterogeneity of sorption sites is not surprising as Ca-bentonite is
474 a very complex, multi-mineral material, where already montmorillonite can provide different
475 complexation sites (e.g. edge sharing, corner sharing) and aluminol/silanol functionalities. The variety
476 of sorption species can also be inferred from different emission spectra, which shift strongly,
477 depending on the excitation energy. At low excitation wavelength (e.g. 472.8 nm) the emission spectra
478 appear broadened and weakly resolved as the incident energy is high enough to excite all uranyl
479 moieties within the sample. At higher excitation wavelengths (in Figure 3a exemplarily shown for
480 $\lambda_{\text{ex}} = 494.3, 499.7$ and 505.2 nm), however, a clear luminescence line narrowing can be observed due
481 to resonant/direct excitation of single species. The occurrence of luminescence line-narrowing alone
482 already indicates the presence of adsorbed U(VI) surface complexes and eliminates U(VI)
483 precipitation as predominant retention mechanism. In U(VI) precipitates, such as Na,Ca-uranates, the
484 phenomenon of luminescence line narrowing is suppressed by homo-resonance energy transfer among
485 the U-atoms arranged in close distance to each other, leading to a mutual excitation and consequently
486 to a broadening of the signal (Lakowicz, 2006; Tits et al., 2015). Such signal broadening is observed
487 in our batch sample prepared with an initial U(VI) concentration of 5×10^{-5} M to provoke U(VI)
488 precipitation for comparison (Figure 3b). In fact, the obtained spectra show no luminescence line-
489 narrowing, irrespective of the excitation energy. Broad and unresolved maxima around 545 nm appear
490 at all excitation wavelengths, featuring luminescence lifetimes between 30 and 40 μs . Spectra with
491 similar appearance and lifetimes have been identified as Ca-uranate in Tits et al. (2015) and Tits et al.
492 (2011). No such features were observable in the sorption sample with 5×10^{-7} M uranium, implying that
493 adsorption can be considered to be the only relevant retention mechanism at these experimental
494 conditions.



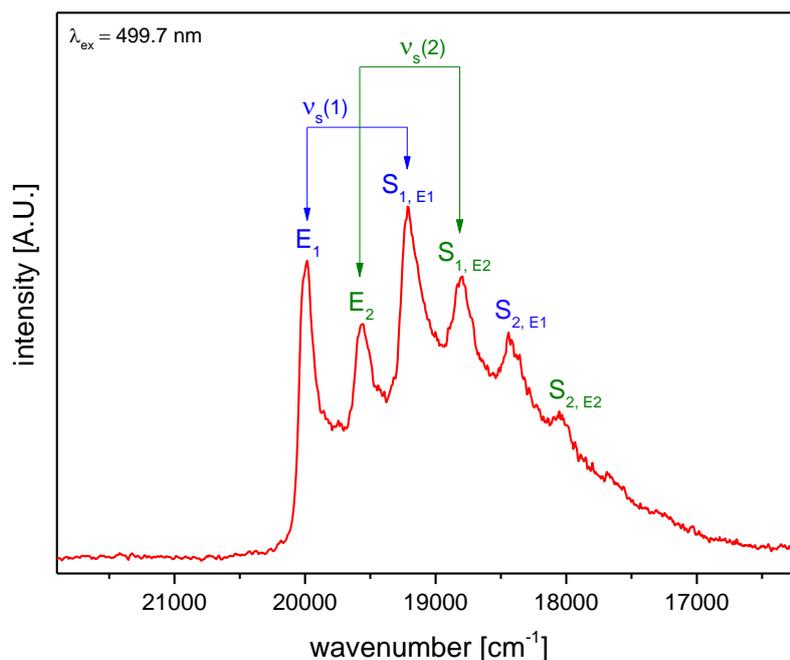
495

496 *Figure 3: Excitation (black dots) and emission spectra (colored lines) of U(VI) sorbed on Ca-bentonite in the absence of CO₂*
 497 *at pH 11 with [U(VI)] = 5 × 10⁻⁷ M (a) and [U(VI)] = 5 × 10⁻⁵ M (b) obtained with site-selective TRLFS at 10 K.*

498 From the absolute positions of the narrowed peaks of the emission spectra alone, not much
 499 information about the U(VI) surface speciation can be deduced. However, the relative position of the
 500 maxima (i.e. the distance of the different electronic and vibronic transition lines) provides insight into
 501 the structure of the uranyl unit. For that purpose, electronic and vibronic transition events were
 502 assigned to the single emission lines, exemplarily shown for the emission spectrum obtained at
 503 499.7 nm excitation wavelength (Figure 4). In phase with the incident laser energy, the resonant
 504 electronic transition line E₁ appears, followed by the lines of vibronic progression on E₁ (S_{1,E1} and
 505 S_{2,E1}) caused by the vibronic degeneracy of the electronic ground state. Furthermore, a second (non-
 506 resonant) U(VI) species with the non-resonant electronic transition line E₂ can be identified. Also this
 507 species is superimposed by the first two lines of vibronic progression (S_{1,E2} and S_{2,E2}). As already
 508 discussed in section 2.4, the spacing between the first two peaks of each species (i.e. between E₁ and
 509 S_{1,E1} and between E₂ and S_{1,E2}, respectively) corresponds to the total symmetric stretch vibration (ν_s) of
 510 the uranyl cation in the ground state. The spacing of the first (resonantly excited) species ν_s(1) is
 511 781 ± 5 cm⁻¹ (Table 3). With 758 ± 12 cm⁻¹, the stretch vibration ν_s(2) of the second, non-resonantly
 512 excited, species noticeably differs from the first one. Both frequencies lie in the typical range for
 513 U(VI) minerals and sorbed species (Wang et al., 2011; Wang et al., 2005), and are significantly

514 smaller than values found for aqueous species (Nguyen-Trung et al., 2000), such as $\text{UO}_2(\text{OH})_3^-$, which
515 is dominating the aqueous speciation at pH 11 (Table 3). Especially for species 2, this strong
516 weakening of the axial U-O bond implies strong bonding in the U(VI) equatorial plane upon
517 adsorption (i.e. inner-sphere surface complexation). The comparatively higher frequency for species 1
518 could then hint towards outer-sphere sorption.

519 Inner-sphere surface complexation of U(VI) at montmorillonite silanol and aluminol edge sites has
520 been previously demonstrated at neutral pH by TRLFS (Chisholm-Brause et al., 2004; Chisholm-
521 Brause et al., 2001; Kowal-Fouchard et al., 2004) and EXAFS (Catalano and Brown, 2005; Marques
522 Fernandes et al., 2012). Between pH 8 and 13, no spectroscopic studies dealing with U(VI) surface
523 complexation exist for comparison. The present study suggests that inner-sphere surface complexation
524 at pH 10-12 can occur in a similar way as at neutral pH. A couple of studies are available on U(VI)
525 sorption by cementitious systems above pH 13. The total symmetric stretch vibration of species 2 of
526 the present study compares very well to that of a surface complex detected on C-S-H phases at pH
527 13.3 by Tits et al. (2015). As $\text{UO}_2(\text{OH})_3^-$ is the dominant aqueous U(VI) species at pH 11, electrostatic
528 repulsion does not seem to prevent this anionic complex from adsorbing to the negatively charged clay
529 surface. A possible role of cations (i.e. Ca^{2+}) mediating between the anionic hydrolysis complex and
530 the mineral surface will be discussed below.



531
 532 *Figure 4: Luminescence emission spectrum of 5×10^{-7} M U(VI) sorbed on Ca-bentonite at pH 11 in the absence of CO_2 after*
 533 *laser excitation at 499.7 nm. Two U(VI) species could be identified based on their different electronic and vibronic*
 534 *transitions assigned with blue and green letters for species 1 and species 2, respectively. Spacing between the first two main*
 535 *peaks of each species $\nu_s(1)$ and $\nu_s(2)$ are indicated.*

536 *Table 3: Frequencies of the total symmetric stretch vibration (ν_s) deduced from the spacing between the luminescence*
 537 *emission lines of U(VI) (5×10^{-7} M) sorbed on Ca-bentonite at pH 11 in comparison to literature values.*

Uranyl species	ν_s [cm^{-1}]	Reference
1	781 ± 5	this study
2	758 ± 12	this study
UO_2^{2+}	870	Nguyen-Trung et al. (2000)
$\text{UO}_2(\text{OH})_3^-$	804	Nguyen-Trung et al. (2000)
U(VI) minerals and sorbed species	700-800	Wang et al. (2011); Wang et al. (2005)
Adsorbed on C-S-H	758	Tits et al. (2015)

538
 539 **3.6. Local U(VI) coordination environment studied with EXAFS**

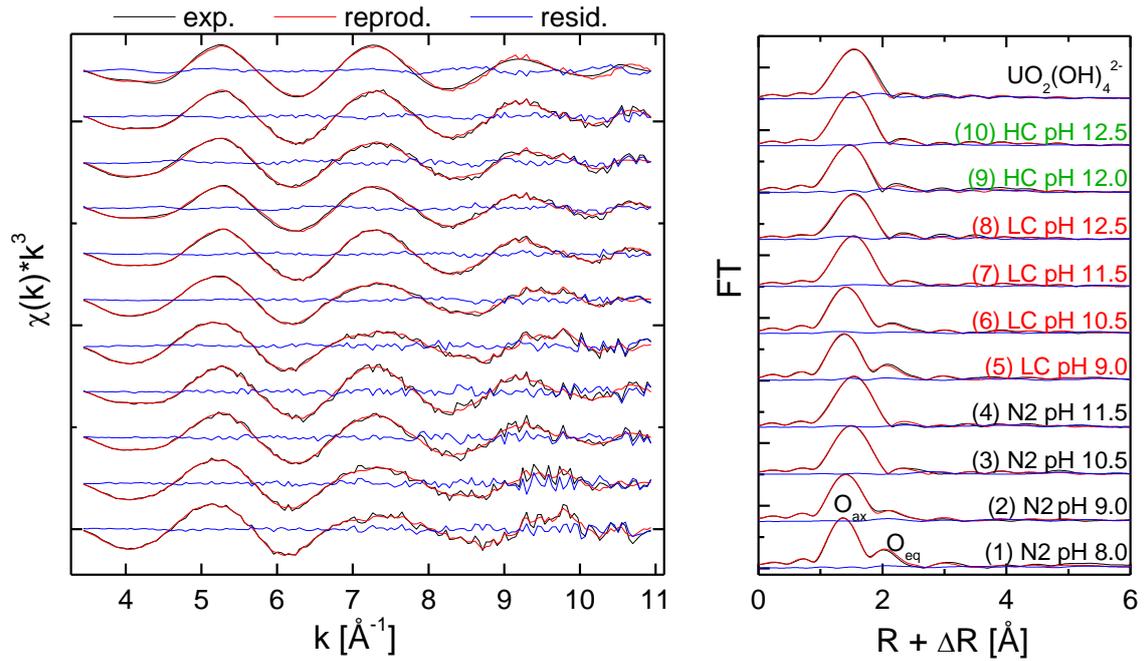
540 Figure 5 shows the EXAFS spectra and Fourier transforms (FT) of the sorption samples with different
 541 pH and carbonate concentrations (N₂, LC, HC), including a reference spectrum of the aqueous
 542 $\text{UO}_2(\text{OH})_4^{2-}$ complex. None of the spectra shows indications for U(VI) precipitation (i.e. no U-U
 543 backscattering paths detected). Consequently, as already deduced from site-selective TRLS, the
 544 predominant retention mechanism of U(VI) in Ca-bentonite under the given conditions is adsorption.

545 A trend of decreasing average equatorial oxygen (O_{eq}) distance with increasing pH is observed within
546 each sample series. While the peaks for O_{eq} and axial oxygen (O_{ax}) are clearly separated at pH 8 and 9,
547 at elevated pH only combined peaks for O_{eq} and O_{ax} can be observed in the Fourier transforms (FT).

548 The application of ITFA (Text SM2) showed that all ten EXAFS spectra can be reproduced with two
549 spectral components (Figure 5). Consequently, two structurally different sorption complexes are
550 present in the system with different fractions in each sample, depending on the pH. According to the
551 result of the iterative target test (ITT) component 1 is predominant at the lowest pH of each sample set
552 (i.e. sample 1 (N_2 , pH 8.0) or sample 5 (LC, pH 9)) and occurs independently of the presence or
553 absence of carbonate. Conversely, the fraction of component 2 is highest in the samples prepared at
554 high pH (Figure 6). According to the extracted single component spectra and the results of the ITFA,
555 component 2 matches to the $UO_2(OH)_4^{2-}$ reference. Hence, for the samples with high pH, both the
556 spectrum and the local atomic structure around U(VI) agree with those of the aqueous $UO_2(OH)_4^{2-}$
557 complex. Consequently, component 2 is a sorption species at the bentonite surface with a structure
558 similar to the aqueous $UO_2(OH)_4^{2-}$ complex.

559 An interaction of U(VI) with carbonate would lead to the detection of a third component in the sample
560 series LC and HC. However, only two components were detected. Consequently, no ternary U(VI)
561 carbonate sorption complexes are present on the Ca-bentonite surface. This observation is in
562 accordance with the work of Marques Fernandes et al. (2012), where no influence of carbonate on the
563 surface complexation could be detected with EXAFS, also supporting the hypothesis of Tournassat et
564 al. (2018) that uranyl carbonate complexes do not adsorb on montmorillonite surfaces to significant
565 amounts.

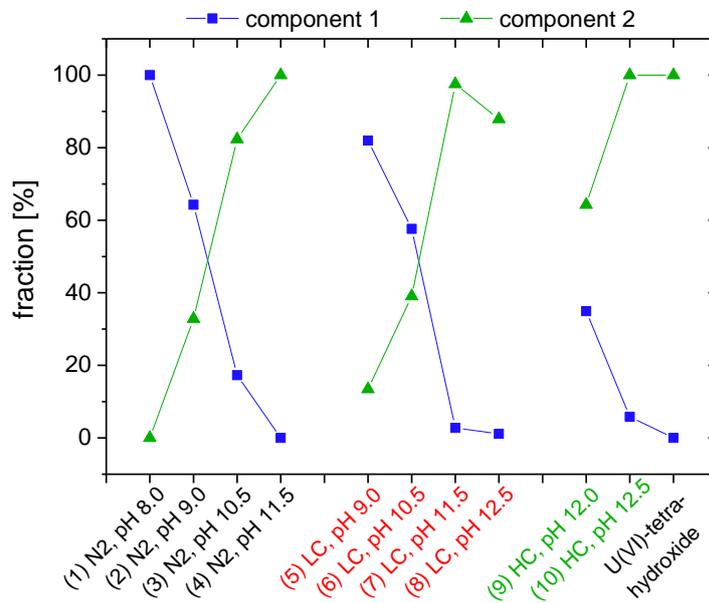
566 We performed a shell fit of the ITT isolated spectrum of component 1 and of the spectrum of the
567 aqueous $UO_2(OH)_4^{2-}$ complex, while the latter was selected instead of the ITT isolated spectrum of
568 component 2 in order to gain a higher resolution for the determination of radial distances due to the
569 larger available k -range. The fit of the spectra and the corresponding EXAFS structural parameters are
570 given in Figure 7 and Table 4.



571

572 *Figure 5: U L_{III}-edge EXAFS spectra (left, black) and corresponding Fourier transforms (right, black) with reproductions*
 573 *(red) and the residual (blue) of U(VI) sorption samples on Ca-bentonite in the absence of carbonate (N₂) and at low (LC) and*
 574 *high (HC) carbonate concentrations, including a reference spectrum of the aqueous UO₂(OH)₄²⁻ complex (Moll et al., 2014).*

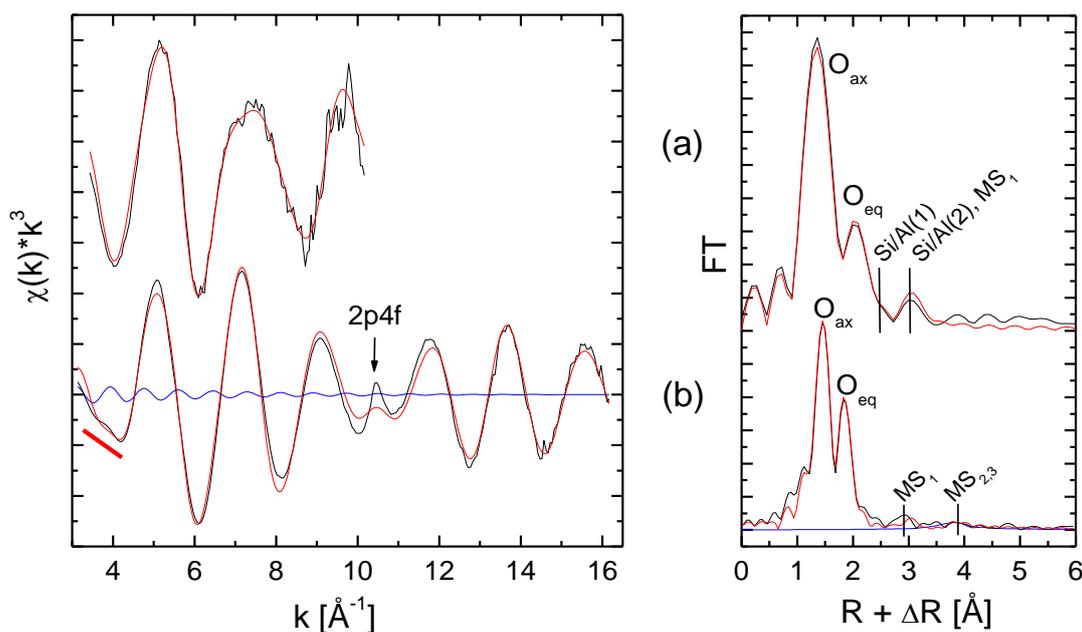
575



576

577 *Figure 6: ITT calculated fractions of component 1 and component 2 for U(VI) sorption samples on Ca-bentonite in the*
 578 *absence of carbonate (N₂) and at low (LC) and high (HC) carbonate concentration, including the reference of the aqueous*
 579 *UO₂(OH)₄²⁻ complex (Moll et al., 2014).*

580



581

582 *Figure 7: U L_{III}-edge EXAFS spectra of the ITFA isolated component 1 (a) and of the aqueous $UO_2(OH)_4^{2-}$ complex (b) (left)*
 583 *with corresponding Fourier transforms (FT) (right) together with the shell fit (red). Spectral contribution of MS_2 and MS_3*
 584 *(blue). $2p4f$ multi-electron excitation assigned with arrow (Hennig, 2007).*

585 For component 1 we obtained an equatorial oxygen shell ($U-O_{eq}$) at a distance of ~ 2.38 Å (CN fixed
 586 to 5). This shortened distance in comparison to $U-O_{eq}$ of hydrated outer-sphere sorption complexes on
 587 montmorillonite described in literature of ~ 2.43 Å ((Chisholm-Brause et al., 1994; Sylwester et al.,
 588 2000)) suggests the formation of inner-sphere surface complexes. Marques Fernandes et al. (2012)
 589 observed a splitting of the equatorial oxygen shell in sorption samples at pH 8 and obtained $U-O_{eq}$
 590 distances of ~ 2.3 Å and ~ 2.48 Å. Such a splitting cannot be resolved in the present study due to lower
 591 resolution in radial distances. However, when averaging the reported distances of Marques Fernandes
 592 et al. (2012), weighted by the coordination numbers (3.1 and 2.9), a mean $U-O_{eq}$ distance of 2.387 Å
 593 can be derived, which is in excellent agreement with our results. Furthermore, two Si/Al shells could
 594 be fitted in radial distances of 3.11 Å and 3.32 Å. Those are in good agreement with the Si/Al
 595 distances of 3.09 Å and 3.28 Å for the bidentate inner-sphere sorption complexes on montmorillonite
 596 at pH 8 described by Marques Fernandes et al. (2012). Therefore, the same type of U(VI) surface
 597 complex is proposed for our component 1.

598 Representative for component 2, the high symmetry of the $\text{UO}_2(\text{OH})_4^{2-}$ complex leads to the
599 appearance of a spectral feature at $k = 3.5 - 4.3 \text{ \AA}^{-1}$ (Figure 7, highlighted with red line) which
600 originates from the multiple scattering (MS) paths MS_2 ($\text{U}-\text{O}_{\text{eq}(1)}-\text{U}-\text{O}_{\text{eq}(2)}$) and MS_3 ($\text{U}-\text{O}_{\text{eq}(1)}-\text{U}-\text{O}_{\text{eq}(1)}$)
601 (Figure SM4). The scattering contribution of these inherent MS paths is strongly enhanced due to the
602 linear arrangement of the involved atoms, comparable with the arrangement in the linear “yl” chain of
603 U(VI) for which the MS_1 ($\text{U}-\text{O}_{\text{ax}(1)}-\text{U}-\text{O}_{\text{ax}(2)}$) shows a significant spectral contribution. Note that we
604 also tested the 4-fold degenerated 3-legged MS path $\text{U}-\text{O}_{\text{eq}(1)}-\text{O}_{\text{eq}(2)}$, but no further improvement of the
605 fit was obtained. The sum of the MS_2 and MS_3 scattering contributions causes a truncation of the
606 negative maximum of the EXAFS oscillation in this k -region (Figure 7). The distance of 4.55 \AA
607 measured for MS_2 and MS_3 matches, within the common error in determination of distances probed by
608 EXAFS (Li et al., 1995), the theoretically expected distance of 4.54 \AA which would be twice the O_{eq}
609 distance of 2.27 \AA (Table 4). The O_{ax} and O_{eq} distances and the corresponding Debye-Waller factors
610 (σ^2) are in good agreement with published data (Table 4) where the MS feature was not explored so
611 that only the coordination number (CN) and/or the O_{eq} distance could be used for the structural
612 interpretation of the aqueous $\text{UO}_2(\text{OH})_4^{2-}$ complex (Moll et al., 2000; Moll et al., 2014). However, the
613 error in determination of the CN is approximately 20 % (Li et al., 1995), hence the EXAFS determined
614 CN is not reliable enough to be used as a proof for the presence of a 4-fold coordinated U(VI)
615 complex. Thus, only the presence of the MS feature at $k = 3.5 - 4.3 \text{ \AA}^{-1}$ indicates univocally a
616 symmetric 4-fold coordination of U(VI). Due to the appearance at low k -values, the MS feature is
617 visible in the X-ray absorption near edge structure (XANES) at 17240 eV. Therefore, XANES can be
618 also used for the identification of a 4-fold coordination, as exemplary shown for the aqueous
619 complexes of the 5- and 4-fold coordinated U(VI)-hydrate ($\text{UO}_2(\text{H}_2\text{O})_5^{2+}$) and $\text{UO}_2(\text{OH})_4^{2-}$,
620 respectively (Figure SM11).

621 The MS feature at $k = 3.5 - 4.3 \text{ \AA}^{-1}$ is also present in case of the high pH sorption samples (Figure 5),
622 which is in line with the ITFA result (Figure 6) pointing to the prevalence of a sorption complex with
623 an $\text{UO}_2(\text{OH})_4^{2-}$ like structure. In the case of 5-fold coordinated U(VI) the $\text{O}_{\text{eq}(1)}-\text{U}-\text{O}_{\text{eq}(2)}$ angles are not
624 straight, so that the spectral contribution of MS_2 and MS_3 diminishes as observed for component 1

625 which covers the lower pH sorption samples. Thus, beside the fractions of the two sorption complexes
 626 the ITT shows also the transition from a 5-fold to a 4-fold coordination of U(VI) with increasing pH.

627

628 *Table 4: Shell fit EXAFS structural parameters for component 1 and the aqueous $\text{UO}_2(\text{OH})_4^{2-}$ complex.*

Shell	CN	$R / \text{\AA}$	$\sigma^2 / \text{\AA}^2$	$\Delta E_0 / \text{eV}$
Component 1				
O_{ax}	2*	1.797(3)	0.0010(2)	11.0(5)
MS_1	/2	/3.594	/0.002	/11.0
O_{eq}	5*	2.382(8)	0.0154(8)	/11.0
Si/Al(1)	1.5(2)	3.11(1)	0.003 ^a	/11.0
Si/Al(2)	1.2(2)	3.32(1)	0.003 ^a	/11.0
aqueous $\text{UO}_2(\text{OH})_4^{2-}$ complex				
O_{ax}	2*	1.8254(9)	0.00176(6)	3.6(3)
		1.83 ^b , 1.82 ^c	0.001 ^b , 0.0015 ^c	
MS_1	/2	/3.6508	/0.00352	/3.6
O_{eq}	4*	2.271(1)	0.0040(1)	/3.6
		2.25 ^b ,	0.0043 ^b ,	
		2.26 ^b , 2.27 ^c	0.0046 ^b , 0.004 ^c	
MS_2	/4	4.55(2)	0.005(3)	/3.6
MS_3	/4	/4.55	/0.005	/3.6

629 * - fixed parameter, / - linked parameter, CN – coordination number, R – radial distance, σ^2 – Debye-Waller factor, ΔE_0 – shift in energy
 630 threshold. The standard deviation of the fitted parameters is given in parentheses. Amplitude reduction factor $S_0^2 = 1.0$. Multiple scattering
 631 paths MS_1 (U- $\text{O}_{\text{ax}(1)}$ -U- $\text{O}_{\text{ax}(2)}$), MS_2 (U- $\text{O}_{\text{eq}(1)}$ -U- $\text{O}_{\text{eq}(2)}$), MS_3 (U- $\text{O}_{\text{eq}(1)}$ -U- $\text{O}_{\text{eq}(1)}$). ^a - σ^2 fixed at value taken from literature (Hennig et al., 2002;
 632 Marques Fernandes et al., 2012), ^b - (Möll et al., 2000), ^c - (Möll et al., 2014).

633 Despite the strong similarity with the aqueous $\text{UO}_2(\text{OH})_4^{2-}$ complex according to the shell fit, it can be
 634 ruled out that component 2 corresponds to an aqueous species, as U(VI) was almost completely
 635 removed from solution and the EXAFS samples were prepared as wet pastes with only a minor

636 amount of aqueous solution present. An aqueous species could therefore be present in the samples
637 only as a minor fraction, while component 2 accounts for up to 100 % in some of the samples.
638 Consequently, component 2 can definitely be assigned to an adsorbed species. Furthermore,
639 $\text{UO}_2(\text{OH})_4^{2-}$ is expected to be the dominant aqueous species only at $\text{pH} > 12$, as confirmed by our
640 TRLFS measurements. In our EXAFS samples between $\text{pH} 10$ and 12 , $\text{UO}_2(\text{OH})_3^-$ is the dominant
641 aqueous species prior to sorption. Owing to the difficulty to obtain $\text{UO}_2(\text{OH})_3^-$ as a single, isolated
642 species, no EXAFS reference spectra exist for this complex. Its structure, especially the coordination
643 number of equatorial oxygen, is not clarified. While sometimes referred to be 5-fold coordinated (3
644 OH and 2 H_2O), the DFT study of Ingram et al. (2006) proposed a 4-fold coordination (3 OH and 1
645 H_2O). Our finding of a 4-fold coordination of component 2 supports this hypothesis. Apparently, this
646 geometry is then preserved upon sorption, indicating relatively weak interaction with the substrate.
647 Also the fact that it was not possible to fit U-Si/Al scattering paths for component 2 indicates a larger
648 distance to the mineral surface. The complex could be bound via mediating cations such as Ca^{2+} ,
649 located between the negatively charged surface and the anionic uranyl hydroxide unit. Evidence for
650 Ca^{2+} attachment on the bentonite surface can be seen in our zeta potential measurements, where a
651 significant increase of the zeta potential was observed in the presence of Ca^{2+} (Figure SM7). Thus, the
652 sorption of negatively charged uranyl species would be realized by initial adsorption of Ca^{2+} to the
653 clay mineral surface (Gascó and Méndez, 2005; Missana and García-Gutiérrez, 2007; Pointeau et al.,
654 2004; Viallis-Terrisse et al., 2001), leading to a local charge inversion and facilitating attachment of
655 anionic uranyl hydroxides. Also the formation of aqueous ternary Ca-uranyl-hydroxides is possible,
656 which would have a neutral or even positive net charge and would be therefore capable of interacting
657 with the negatively charged bentonite surface. The existence of such ternary Ca-uranyl-hydroxide
658 complexes at (hyper)alkaline conditions is hypothesized but has not been explored yet in detail.

659 Based on the knowledge obtained from EXAFS, also an assignment of the two species detected with
660 site-selective TRLFS to the structurally different surface complexes is possible. Assuming a
661 $\text{UO}_2(\text{OH})_4^{2-}$ like structure for component 2, a theoretical frequency for the symmetric stretch vibration
662 can be calculated according to an empirical relationship for aqueous uranyl hydroxide complexes
663 found by Nguyen-Trung et al. (2000). With four equatorial oxygens a ν_s of 782 cm^{-1} is obtained, which

664 is almost identical to the ν_s of TRLFS-species 1 (781 cm^{-1} , Table 3). Accordingly, TRLFS-species 2,
665 with a lower ν_s of 758 cm^{-1} , has to correspond to the 5 fold-coordinated bidentate surface complex
666 (EXAFS-component 1). This assumption is reasonable as a decrease of ν_s (as a consequence of a
667 weakening of the axial U-O bonds) is a response to an increased electron density and increased ligand
668 bond strength in the equatorial plane (Di Pietro and Kerridge, 2016; McGlynn et al., 1961; Nguyen-
669 Trung et al., 2000; Tsushima, 2011). For EXAFS-component 1 this is a result of the bidentate binding
670 and the close proximity to substrate atoms (Si/Al) in contrast to EXAFS-component 2, where no
671 backscattering contributions from the substrate could be detected. Due to extensive σ donation from
672 the surface, Tsushima et al. (1998) and Morris et al. (1994) obtained similar values for ν_s for inner-
673 sphere surface complexes on silver nanoparticles (750 cm^{-1}) and smectite edge sites (751 cm^{-1}),
674 respectively.

675 **4. Conclusions**

676 Sorption experiments demonstrated that U(VI) retention on Ca-bentonite in the pH range 8-13 can be
677 very efficient, also in the presence of carbonate. Above a certain pH, which is determined by the
678 carbonate concentration, carbonate does not play a role in the U(VI) complexation in solution anymore
679 due to the dominance of hydrolysis. A clear correlation between sorption behavior and aqueous U(VI)
680 speciation in the diluted Gipshut solution was observed with TRLFS conducted at 153 K. Retention
681 reaches a maximum at conditions where $\text{UO}_2(\text{OH})_3^-$ is the predominant aqueous species. Solubility
682 tests have shown that the observed complete U(VI) removal at pH 10-12 cannot be attributed to
683 precipitation of (earth) alkali-uranates from the solution. In order to unambiguously distinguish
684 between surface precipitation and surface complexation as dominant retention mechanism, direct
685 spectroscopic investigations of the U(VI) complexes on the Ca-bentonite surface were performed with
686 site-selective TRLFS (at 10 K) and EXAFS. The occurrence of luminescence line narrowing and the
687 frequency of the total symmetric stretch vibration obtained from the TRLFS emission spectra, indicate
688 the presence of two U(VI) surface complexes. Also EXAFS spectra showed no indication of U(VI)
689 precipitation. With increasing pH, the nature of the retained U(VI) complexes shifts from inner-sphere
690 surface complexes with an overall equatorial coordination of five adsorbed on aluminol or silanol edge
691 sites to surface complexes with a 4-fold equatorial coordination which are presumably bound to the
692 surface via mediating cations (i.e. Ca^{2+}). For the first time, a 4-fold coordination in the equatorial plane
693 of U(VI) was univocally proven with the help of a multiple scattering feature originating from the
694 strong symmetry of the complexes, and without the need for error-prone shell fitting.

695 Consequently, by the combination of different spectroscopic methods, surface complexation was
696 unequivocally identified as the responsible process for the strong U(VI) retention by Ca-bentonite at
697 (hyper)alkaline conditions and low U(VI) concentrations. That means, that under certain alkaline
698 repository conditions, where precipitation of uranates does not occur (due to very low concentrations
699 or kinetic restraints), uranium is still effectively retained in argillaceous media by adsorption of
700 negatively charged metal complexes. The affinity towards the formation of surface complexes,
701 possibly by contribution of mediating cations such as Ca^{2+} , overrules the repulsive electrostatic forces

702 between the anionic aqueous complex and the negatively charged clay surface. This finding is of great
703 relevance, as also the migration of very small amounts of U(VI) out of waste repositories could lead to
704 a hazardous accumulation in the anthroposphere in the long term.

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714

715 **Appendix A. Supplementary material**

716 Supplementary data to this article can be found online at ...

717

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