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The Sorption Processes of U(VI) onto SiO₂ in the Presence of Phosphate: from Binary Surface Species to Precipitation

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1 ABSTRACT. The ternary system containing aqueous U(VI), aqueous phosphate and solid SiO₂
2 was comprehensively investigated using a batch sorption technique, *in situ* attenuated total
3 reflection Fourier-transform infrared (ATR FT-IR) spectroscopy, time-resolved luminescence
4 spectroscopy (TRLS), and Surface Complexation Modeling (SCM). The batch sorption studies
5 on silica gel (10 g/L) in the pH range 2.5 to 5 showed no significant increase in U(VI) uptake in
6 the presence of phosphate at equimolar concentration of 20 μM, but significant increase in U(VI)
7 uptake was observed for higher phosphate concentrations. *In situ* infrared and luminescence
8 spectroscopic studies evidence the formation of two binary U(VI) surface species in the absence
9 of phosphate, whereas after prolonged sorption in the presence of phosphate, the formation of a
10 surface precipitate, most likely an autunite-like phase, is strongly suggested. From SCM, excel-
11 lent fitting results were obtained exclusively considering two binary uranyl surface species and
12 the formation of a solid uranyl phosphate phase. Ternary surface complexes were not needed to
13 explain the data. The results of this study indicate that the sorption of U(VI) on SiO₂ in the
14 presence of inorganic phosphate initially involves binary surface-sorption species and evolves
15 towards surface precipitation.

16

17 INTRODUCTION

18 Sorption is a key process governing the mobility of radionuclides in the environment. The
19 sorption of uranyl(VI) on oxide and mineral systems and the effect of a wide range of parameters
20 (e.g. pH, ionic strength, contact time, surface area, etc.) have been the subject of many studies,
21 particularly as the migration behavior of uranium and other radionuclides is of relevance at low
22 level waste repositories, nuclear facilities, contaminated sites and uranium mine legacies.¹⁻⁴ The
23 effect of ligands on uranium(VI) sorption is also important because of the range of aqueous
24 organic and inorganic ligands found naturally in the environment, where the presence of a ligand
25 may impact on uranyl(VI) sorption by competing for sorption sites, form non-sorbing or weakly
26 sorbing uranyl(VI) ligand complexes in aqueous solutions, alter the electrostatic properties at the
27 solid/liquid interface, form a strongly sorbing uranyl(VI) ligand surface complex and/or precipi-
28 tate at the surface or in solution.⁵⁻⁷ One such ligand that has received much attention in recent
29 years is phosphate.⁸⁻¹⁰

30 Phosphate is ubiquitous in the environment, and its natural association with uranium is evident
31 in phosphate deposits important for the fertilizer industry, uranium contaminated sites and
32 uranium ores.⁹⁻¹³ This ligand has been shown to play an important role in determining the
33 environmental fate of uranium in subsurface environments due to its propensity to form sparing-
34 ly soluble phosphate minerals.^{8, 9, 14, 15} Phosphate injection has also been considered as a reme-
35 diation strategy for the immobilization of uranium and metals, in particular, the in-situ remedia-
36 tion of uranium contaminated environments.^{10, 15-19} This has led to a number of studies of ternary
37 systems containing U, P and model mineral surfaces, which have encompassed batch sorption
38 experiments, column studies, spectroscopic investigations and/or surface complexation modeling
39 (SCM).^{4-7, 17-25} These studies have also highlighted the complexity of this aqueous system which

40 includes the speciation of uranyl(VI) and tribasic phosphate, and the coupling of uranyl and
41 phosphate aqueous species to form uranyl(VI) phosphate complexes and precipitates both in
42 solution and at the mineral surface.^{9, 14, 17-21, 25-27} Nevertheless, an understanding of the behavior
43 of this ligand in the environment with respect to uranium(VI) sorption is paramount and a few
44 studies have attempted to distinguish adsorption from precipitation pathways.^{9, 19, 25, 27} While the
45 effect of phosphate on uranium(VI) adsorption has been investigated for a wide range of miner-
46 als, with the majority of studies conducted on iron oxides,^{1, 4, 7, 19, 23, 24} aluminum oxides²⁰⁻²² and
47 clays,^{4, 6, 25} there have been fewer studies conducted on SiO₂^{5, 28} although the latter is a predomi-
48 nant component of soils and host rocks. SiO₂ has different surface properties to these other
49 mineral surfaces, in particular a negatively charged surface over a wide pH range, as expected
50 from its low isoelectric point, which will impact on its binding and sorption capacity.²⁹

51 The binary sorption complexes of U(VI) onto silica have been investigated by different spec-
52 troscopic techniques to provide insight at the molecular level. These include extended X-ray
53 absorption spectroscopy (EXAFS), time-resolved luminescence spectroscopy (TRLS) and
54 vibrational spectroscopy.³⁰⁻³⁶ A general conclusion from these studies is that U(VI) predominant-
55 ly forms inner-sphere complexes at the silica surface. However, the surface speciation is still a
56 subject for discussion.^{30-33, 37} From SCM modeling, a mononuclear inner-sphere and a polynucle-
57 ar surface complex on the silica surface were proposed and the model tested with literature data
58 with consistent results.³⁸ The immobilization mechanism for uranium(VI) uptake in the presence
59 of phosphate at goethite and montmorillonite surfaces was recently investigated using EXAFS.^{25,}
60 ³⁹ These studies indicated the presence of U(VI) phosphate ternary surface complexes as well as
61 precipitation. To the authors' knowledge, no direct spectroscopic evidence has been presented

62 for the formation of ternary surface complexes and/or precipitation for the U(VI)/phosphate/SiO₂
63 ternary system.

64 The objective of the present study was to investigate the sorption processes of U(VI) onto SiO₂
65 in the presence of phosphate using a combination of batch, spectroscopic, and modeling tech-
66 niques, namely *in-situ* ATR FT-IR, TRLS, and SCM. The interactions of U(VI) and phosphate in
67 the absence of SiO₂ were also assessed. The macroscopic studies were conducted in the acid to
68 near neutral pH range whereas the spectroscopic investigations were focused at two discrete pH
69 values of 4 and 5.5. Silica gel has been used as a model substrate for SiO₂, with its higher BET
70 surface area promoting investigation of surface phenomena (*e.g.* enhanced sorption) compared to
71 quartz.⁴⁰ The present study is expected to have significant relevance in understanding radionu-
72 clide migration in geological systems and close knowledge gaps for this system, particularly with
73 respect to uranium(VI) sorption in the presence of phosphate.

74

75 MATERIALS AND METHODS

76 **Materials and Chemicals.** The SiO₂ used was Merck No 115111 SiO₂ with 90% of the parti-
77 cles between 15–40 μm, used without further pre-treatment.⁴⁰ The BET surface area was deter-
78 mined as 475 ± 30 m² g⁻¹ with an average pore diameter of 6.8 nm. Diluted U(VI) solutions were
79 freshly prepared prior to use from stock solutions of 0.05 M UO₂Cl₂ in 1 M HCl or 0.005 M
80 UO₂(ClO₄)₂ in 0.025 M NaClO₄, with ionic strength adjustment to 0.1 M. The adjustment of pH
81 was by addition of NaOH or HCl and HClO₄, respectively. NaH₂PO₄·H₂O was used to prepare
82 the phosphate solutions. All solutions were made up using Milli-Q water with a resistivity of
83 18.2 MΩ cm⁻¹.

84 **Batch Sorption Studies.** Batch sorption experiments were performed using a previously re-
85 ported technique.^{2, 4, 41} These experiments were conducted at a mass loading of 10 g L⁻¹ SiO₂,

86 20 μM [U(VI)], ionic strength of 0.1 M NaCl, normal atmospheric conditions and 25 $^{\circ}\text{C}$. The
87 effect of the phosphate ligand on U(VI) sorption was investigated for initial total phosphate
88 concentrations of 20 μM , 200 μM and 2 mM in the pH range 2.5 to 7. Radionuclide contact time
89 was maintained for 48 h where kinetic studies showed that the uptake of U(VI) was at steady-
90 state for the mesoporous silica gel (SI Fig. 1). The aqueous phase was separated by high speed
91 centrifugation at 8000 g for 20 minutes and subsequently acidified to pH < 2 prior to analysis for
92 uranium and total phosphorous by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)
93 and Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES), respectively.
94 Sorbent free control experiments for solutions containing 20 μM U(VI) and 20 μM P and a blank
95 experiment considering P sorption (20 μM) at the silica surface were also conducted. A sorption
96 isotherm experiment was conducted at pH 4, initial U(VI) concentrations ranging from 1 μM to
97 100 μM , both in the absence and presence of 20 μM P, to assess U(VI) equilibrium uptake
98 behavior and evidence of precipitation at this pH. A more detailed description of the sorption
99 experiments is provided in the Supporting Information.

100 ***In Situ* Attenuated Total Reflection Fourier-transform Infrared (ATR FT-IR) Spectros-**
101 **copy.** The principles of the methodology of recording *in situ* IR spectra of the (de)sorption
102 processes applying the ATR technique have been previously described.^{40, 42-44} The spectra were
103 measured on a Bruker Vertex 80/v vacuum spectrometer equipped with a mercury cadmium
104 telluride (MCT) detector. Each spectrum was averaged over 256 scans at a spectral resolution of
105 4 cm^{-1} . A more detailed description of the performance of the *in situ* sorption experiments at
106 different pH values is given in the Supporting Information.

107 **Time-Resolved Luminescence Spectroscopy (TRLS).** The TRLS experiments were per-
108 formed at room temperature. The luminescence of U(VI) was measured after excitation with

109 laser pulses at 266 nm and an averaged pulse energy of 0.3 mJ. The emitted light was detected
110 using a spectrograph and an ICCD camera. The TRL spectra were recorded from 370 to 670 nm
111 by accumulating 50 laser pulses using a gate width of 20 μs . For the time-resolved measurements
112 250 spectra were recorded until a maximum delay time of 6000 μs . The first time step started 50
113 ns after the excitation pulse. TRLS measurements were conducted for both aqueous systems and
114 sorption systems (10 g L⁻¹ SiO₂ present) in the absence and presence of 20 μM phosphate. In
115 accordance to vibrational spectroscopy, the experiments were performed at pH 4 and 5.5 (see
116 Supporting Information). The detailed preparation procedures of the aqueous and sorption
117 systems are given in the Supporting Information. All systems contained 20 μM U(VI). The
118 supporting electrolyte for the TRLS measurements was 0.1 M NaClO₄.

119

120 **Equilibrium Speciation Modeling and Surface Complexation Modeling (SCM).** Two
121 codes with complementary features were applied in this study. The aqueous speciation of U(VI)
122 in the absence of sorbent was calculated using the speciation code EQ3/6.⁴⁵ Since EQ3/6 is not
123 capable of handling SCM, the pH-dependent U(VI) sorption onto silica gel in the absence and
124 presence of phosphate was modeled with the geochemical speciation code PHREEQC (version
125 3.3.3- 10424).⁴⁶ Both codes used the same thermodynamic data for U(VI) compiled in the NEA
126 database.²⁶ For PHREEQC modeling, the PSI/Nagra Chemical Thermodynamic Database 12/07
127 (including the NEA data) was used.⁴⁷ Additional data for relevant solid phases (namely
128 Na-Autunite, Cejkaite, Clarkeite, Na-Compreignacite, and (UO₂)₃(PO₄)₂·6H₂O(s), which can
129 precipitate in the investigated U(VI)-P-silica system were included in the model and their
130 equilibrium reactions can be found in the Supporting Information (Table S1). For considering
131 surface complexation reactions of U(VI) onto silica gel, published data were used for predictive

132 modeling.³³ In this study, the Diffuse Double Layer Model was used for modeling surface
133 complexation reactions.⁴⁸ All relevant surface parameters and the surface complexation reac-
134 tions for the two considered binary surface complexes $\equiv\text{SiO}_2\text{UO}_2^0$ and $\equiv\text{SiO}_2\text{UO}_2\text{OH}^-$ are given
135 in the Supporting Information (Table S1). Species with carbonate were not considered as the
136 experimental conditions in the present study (pH 2.5–7) would not allow their formation.

137 In addition to the predictive modeling, all experimental data from batch sorption experiments
138 were fit to the ternary uranyl-phosphate surface complex $\equiv\text{SiO}_2\text{-UO}_2\text{PO}_4^{3-}$. For the estimation of
139 the surface complexation parameter (SCP, namely $\log K$ for this complex), PHREEQC was
140 coupled with the parameter estimation code UCODE.⁴⁹ A weighted residuals model was used to
141 fit the data. Fit quality was judged using the correlation coefficient R . The surface reaction of the
142 ternary complex and its obtained $\log K$ value is given in the Supporting Information (Table S1).

143

144 RESULTS AND DISCUSSION

145 **Batch Sorption Studies.** The sorption of U(VI) onto silica gel as a function of pH in the ab-
146 sence and presence of phosphate is shown in Figure 1 for a solid-liquid ratio of $10 \text{ g L}^{-1} \text{ SiO}_2$. In
147 the absence of phosphate, the U(VI) sorption curve shows a sorption edge between pH 3 and 5,
148 with a pH_{50} of 3.7. No increase in U(VI) sorption was observed with equimolar concentration (20
149 μM) of phosphate present, whereas for higher initial phosphate concentrations, an increase of
150 U(VI) sorption was observed, consistent with other reported studies.^{5, 28} No sorption of phos-
151 phate was observed in the absence of U(VI) which was demonstrated in a control experiment
152 (data not shown).

153 Chemical speciation modeling using the EQ3/6 code and the NEA database for aqueous solu-
154 tions containing $20 \mu\text{M}$ U(VI) and $20 \mu\text{M}$ phosphate in 0.1 M NaCl in the absence of SiO_2

155 predict that the solution speciation of U(VI) is predominantly UO_2^{2+} with minor amounts of
156 UO_2HPO_4 , UO_2Cl^+ , UO_2OH^+ and $\text{UO}_2\text{H}_2\text{PO}_4^+$ and the solution slightly oversaturated with a
157 solid phase such as chernikovite or autunite at pH 4.²⁶ A comparison of the experimental data
158 after 48 h equilibration time to the predicted equilibrium data is provided in the Supporting
159 Information (Fig. S2) and shows good agreement. In the presence of a sorbent, these equilibrium
160 conditions are likely to be impacted due to the decrease of aqueous U(VI) by sorption. Sorption
161 isotherms at pH 4 for U(VI) initial concentrations ranging between 1 to 100 μM , both in the
162 presence and absence of 20 μM phosphate, show sorption to be the dominant process and no
163 evidence of precipitation which would be indicated by a sharp break in the isotherm (see Sup-
164 porting Information Fig. S3A).²⁵ Nevertheless, the corresponding phosphate uptake curve at this
165 pH shows a gradual decrease in aqueous phosphate concentration for U(VI) concentrations
166 greater than 4.5 μM (see Supporting Information Fig. S3B), suggestive of some association
167 behavior between U(VI) sorbed at the surface and phosphate. Possible chemical speciation and
168 surface processes will be considered in more detail in the surface complexation modeling (see
169 below) following spectroscopic assessments, whereby more information about the molecular
170 events occurring during the sorption processes can be obtained from *in situ* vibrational and
171 luminescence spectroscopy, as performed in the present study.

172 **Vibrational spectroscopy of the aqueous U(VI)-phosphate complexes.** For an adequate
173 interpretation of the spectra obtained from sorption processes, a detailed knowledge of the
174 spectral properties of the aqueous species is necessary. However, the low solubility of U(VI)-
175 phosphate complexes in aqueous media hampers the acquisition of vibrational data. The aqueous
176 solutions containing U(VI) and phosphate at the lower micromolar concentration level, which
177 approach the detection limit of IR spectroscopy, are expected to remain homogenous only for a

178 relatively short time scale of a few hours. To ascertain the contribution from possible precipita-
179 tion, the IR spectra of a freshly prepared solution (pH 4) containing 20 μM U(VI) and 20 μM
180 phosphate was measured, as well as the precipitate obtained from an aged solution after ultracen-
181 trifugation. Surprisingly, both spectra reveal nearly identical spectral features at 1125, 994, and
182 919 cm^{-1} (Fig. 2A).

183 Considering the correlation of the molecular symmetry and the vibrational modes to be poten-
184 tially observed in IR spectra, the type of coordination of the phosphate ions to the uranyl(VI)
185 moiety can be derived. In the mid-IR region, different protonation states of the aqueous phos-
186 phate ions show different pattern of bands according to their prevailing molecule symmetry, that
187 is T_D , C_{3v} ($2x$), and C_{2v} symmetry for the PO_4^{3-} , HPO_4^{2-} , H_3PO_4 , and H_2PO_4^- ions, respectively
188 (see Supporting Information Fig. S4). For T_D symmetry, i.e. PO_4^{3-} , only one band representing
189 the triply degenerated ν_3 mode is observed, whereas two or three bands are expected to be
190 observed for ions of lower symmetries such as C_{3v} and C_{2v} , respectively, due to broken degener-
191 acy of the ν_3 mode. However, the extent of splitting of the $\nu_3(\text{PO}_4)$ mode deviates for the phos-
192 phate ions, HPO_4^{2-} and H_3PO_4 , sharing the same symmetry group (C_{3v}) but showing different
193 protonation states (see Supporting Information Fig. S4).

194 Thus, the overall molecule symmetry of the phosphate groups in the uranyl(VI) complex may
195 be derived from the number of bands observed in this spectral region. As the band at 919 cm^{-1}
196 can be assigned to the $\nu_3(\text{UO}_2)$ mode, the other two bands at 1125 and 994 cm^{-1} reflect modes of
197 the phosphate ions most likely showing a C_{3v} symmetry when coordinated to the uranyl(VI)
198 moiety, that is primarily a monodentate coordination.

199 Such a type of coordination for the phosphate ions has been also derived from crystal struc-
200 tures of U(VI) phosphate minerals. The corresponding IR spectra reveal the same pattern of

201 bands with maxima close to those in Fig. 2A, thus, a monodentate coordination in the aqueous
202 U(VI)-phosphate solution becomes evident. Additionally, this might reflect the presence of
203 polynuclear species.^{50, 51}

204 **Vibrational spectroscopy of the ternary sorption system U(VI)/phosphate/silica – Part A:**
205 **simultaneous sorption.** The spectra obtained for the sorption of a solution containing equimolar
206 (20 μM) U(VI) and phosphate at pH 4 obtained at an early and late stage of the sorption process
207 are shown in Figs. 2B and C, respectively. The tracking of the sorption processes by *in situ* IR
208 spectroscopy is accomplished by consecutive acquisition of spectra with a time resolution in the
209 sub minute range. These spectra are generally referenced to spectra of the solid phase recorded
210 before the sorption reaction was induced. Hence, the resulting spectra potentially show positive
211 and negative bands representing the appearance and disappearance of vibrational modes of
212 sorbed or released surface species occurring during the sorption processes, respectively. Moreo-
213 ver, contributions of modes of the stationary phase, such as surface or intrinsic lattice modes,
214 have to be considered in general, as they might occur during the sorption reactions. These modes
215 will be discussed where necessary.

216 At an early stage, i.e. within the first 10 minutes after sorption was induced, the spectrum ex-
217 hibits a weak positive band around 919 cm^{-1} reflecting the $\nu_3(\text{UO}_2)$ mode of the uranyl(VI) ion
218 (Fig. 2B). This band evolves with ongoing sorption and shows an increased intensity in the
219 spectrum of the late sorption process (Fig. 2C). In the frequency range above 950 cm^{-1} , bands
220 showing maxima at 1026 and 1000 cm^{-1} and a minimum at 1080 cm^{-1} are observed during the
221 early sorption stage (Fig. 2B). These bands are superimposed by two maxima revealing at 1125
222 and 994 cm^{-1} with ongoing sorption (Fig. 2C). A comparison with the spectra of the aqueous
223 solution and of the precipitate obtained after centrifugation (Fig. 2A) suggests the formation of

224 uranyl(VI) phosphate species on the SiO₂ surface. Moreover, from the relatively small band-
225 widths of the bands at 1125, 994 and 919 cm⁻¹ (Fig. 2C), the formation of a surface precipitate is
226 suggested. This is in accordance with other U(VI) sorption systems, where surface precipitation
227 occurs after prolonged time of sorption.^{52, 53}

228 **Vibrational spectroscopy of the ternary sorption system U(VI)/phosphate/silica – Part B:**
229 **sequential sorption.** In order to gain a deeper insight into the sorption processes sequential
230 sorption of U(VI) and phosphate, both at an initial concentration of 20 μM, was performed. For
231 an enhanced extent of sorption of U on the silica phase, the pH was increased to a value of 5.5.
232 After each sorption step, the solid phase was flushed with a blank solution for one hour. The
233 corresponding results are shown in Figs. 2D–G.

234 After exposure of a U(VI) solution to the silica phase for two hours, the spectrum obtained is
235 in good agreement with those of the previous sorption experiment recorded 10 minutes after a
236 solution containing U(VI) and phosphate was exposed to the silica phase (Figs. 2B,D). However,
237 in the absence of the phosphate, the band representing the ν₃(UO₂) mode is slightly shifted by
238 about 7 cm⁻¹ to lower wavenumbers and is now observed at 912 cm⁻¹, reflecting the binary
239 U(VI) surface species on silica. A decomposition of the asymmetric shape of the band reveals
240 two single components with maxima at 918 and 898 cm⁻¹ (Δν₃ = 20 cm⁻¹, see SI) reflecting the
241 formation of two different uranyl(VI) species at the SiO₂ surface. This is consistent with recent
242 vibrational spectroscopic findings of U(VI) sorption complexes on silica where two species were
243 formed revealing bands at 918 cm⁻¹ and 892 cm⁻¹.³⁶

244 In a previous study of the sorption processes of U(VI) onto gibbsite, investigated by vibration-
245 al and EXAFS spectroscopy under nearly identical conditions but at slightly higher pH (pH 6.0),
246 similar findings were shown to represent the formation of a dimeric carbonate containing ura-

247 nyl(VI) surface species.⁵² However, the absence of characteristic bands representing carbonate
248 surface species in the spectra of the present work makes the presence of species containing
249 carbonate ligands unlikely. Moreover, results from EXAFS investigations of the surface specia-
250 tion of U(VI) on silica demonstrate the presence of only monomeric species.^{30, 31} Thus, the two
251 species identified by vibrational spectrum decomposition are tentatively assigned to monomeric
252 (surface) species. A more detailed discussion of these species is given in the luminescence
253 spectroscopic section below.

254 An intermediate flushing of the sorption system with blank solution was performed as a next
255 step. Flushing the stationary phase after sorption processes have reached a steady state potential-
256 ly provides information of the reversibility of the sorption processes. From our previous investi-
257 gations, a high degree of reversibility was found to be strongly indicative of outer-sphere com-
258 plexation, whereas a different shape and significantly reduced amplitude of the spectra recorded
259 during the flushing step indicate the presence of several surface species and/or mainly inner-
260 sphere complexes.^{54, 55} After two hours of flushing, no significant release of uranyl(VI) species
261 was observed, because only a weak negative band at 912 cm^{-1} is observed in the respective
262 spectrum (Fig. 2E). In analogy to the sorption spectra, the decomposition of this negative band
263 reveals again two species showing the same band maxima as found for the sorption process.
264 With respect to the considerably reduced amplitude of the spectrum obtained after two hours of
265 flushing, the predominant formation of two U(VI) inner-sphere surface species is confirmed.

266 Subsequently, the silica film with adsorbed uranium was flushed with a $20\text{ }\mu\text{M}$ phosphate
267 solution. After one hour of exposure, the spectrum obtained shows three bands at 1127, 992, and
268 924 cm^{-1} (Fig. 2F) which are in good agreement to those of the aqueous systems (Fig. 2A) and of
269 the result from the simultaneous sorption experiment (Fig. 2C). An assignment of these bands to

270 a binary phosphate surface complex can be safely ruled out, as no interactions were observed in
271 corresponding IR experiments when the silica phase was flushed with phosphate ions only, as
272 expected from the low isoelectric point (pH_{IEP}) of the silica gel, and consistent with the macro-
273 scopic experiments showing no phosphate sorption at the SiO_2 surface in the absence of U(VI).
274 ^{29, 56}

275 The maximum of the band representing the $\nu_3(\text{UO}_2)$ mode appears at slightly higher frequen-
276 cies (now observed at 924 cm^{-1} , Fig. 2F) showing a considerably reduced bandwidth compared
277 to the spectrum of the binary sorption complex (Fig. 2D). Based on previous spectroscopic
278 experience with U(VI) surface precipitates on Al mineral oxides, such spectral characteristics
279 strongly suggest the formation of a precipitate at the silica surface.^{52, 53}

280 As a final step, the ternary sorption system was again flushed with a blank solution. The spec-
281 trum obtained after one hour of flushing reveals that no species at all are released from the
282 stationary phase (Fig. 2G). This result is consistent with the assumption that, due to the sorption
283 of phosphate, a sparingly soluble U(VI) phosphate phase is formed on the surface.

284 From the *in situ* IR experiments of the sorption processes, the formation of a solid uranyl(VI)
285 phosphate phase at the SiO_2 surface is strongly suggested. Thus, the findings of the macroscopic
286 batch experiments where an increased U(VI) uptake was observed at high P concentrations (
287 $> 20 \mu\text{M P}$) is interpreted in terms of the formation of a surface precipitate. Furthermore, the
288 high congruence of the spectra obtained after the sorption processes with those of naturally
289 occurring U(VI) phosphate minerals supports this conclusion.⁵¹ While the macroscopic batch
290 experiments for U(VI) sorption at the SiO_2 surface in the presence of $20 \mu\text{M}$ phosphate did not
291 show any differences compared to U(VI) sorption in the absence of phosphate, it is important to
292 acknowledge the differences in potential surface interactions between the batch experiments and

293 the IR experiments for the present studies. In the case of the latter, U(VI) and phosphate are in
294 excess, whereby the SiO₂ surface provides limited binding sites. Hence surface precipitation is a
295 strong possibility. In the case of the batch experiments, we have a much greater solid/liquid ratio
296 (by a factor up to approximately 10⁴) whereby there is an excess of binding sites relative to the
297 concentrations of U(VI) and P in solution, so evidence of surface precipitation is not apparent.

298 **Time Resolved Luminescence Spectroscopy (TRLS).** Luminescence spectroscopy of batch
299 samples potentially provides complementary information to the kinetic approach of in situ IR
300 spectroscopy. Although molecular structural information cannot be obtained from luminescence
301 spectra, the evaluation of both spectral position of emission bands and the luminescence lifetimes
302 provides information of the number of species and their prevalence in a sample. However, it has
303 to be noted that a comparison of lifetimes derived from different data sets published is not very
304 conducive to the identification of distinct species. This is due to the great variety of experimental
305 parameters applied, i.e. for sample preparation and instrumental set up. Thus, spectral positions
306 and the overall shape of bands represent more reliable features for the verification of the spectro-
307 scopic results.

308 The luminescence spectra of the precipitate obtained from aqueous solutions (pH 4 and pH
309 5.5) containing equimolar amounts of U(VI) and phosphate (20 μM) are shown in Fig. 3A. The
310 spectral characteristics and the lifetimes are summarized in Table 1. The spectra of the precipi-
311 tates and the parameters derived are in very good agreement irrespective of the prevailing pH
312 (Tab. 1) suggesting that the same dominating species is formed. According to data published
313 previously, this species is assigned to (solid or colloidal) (UO₂)₃(PO₄)₂·4H₂O.^{50, 57, 58} In analogy
314 to vibrational spectroscopy, the spectra of the binary aqueous system serve as references for
315 those of the sorption complexes.

316 TRLS spectra of the sorption samples of the binary system U(VI)/SiO₂ are shown in Fig. 3B.
317 The spectra obtained from samples equilibrated at pH 4 and 5.5 indicate the presence of one
318 uranyl(VI) surface complex species at pH 4 showing main emission bands at 498 and 518 nm
319 (species 1, $\Delta\nu_{\text{Emission}} = 775 \text{ cm}^{-1}$). At pH 5.5, additional band maxima occur around 504 and
320 524 nm ($\Delta\nu_{\text{Emission}} = 757 \text{ cm}^{-1}$), which are attributed to a second species occurring at this pH
321 level (species 2, Tab. 1). The spectral splitting of the main emission bands of these postulated
322 species is about 18 cm^{-1} lower for species 2 compared to species 1. This is nearly the same
323 frequency difference found for both species in the vibrational spectra ($\Delta\nu_3 = 20 \text{ cm}^{-1}$, see Fig. S5
324 in Supporting Information). Moreover, previous luminescence studies of the U(VI) sorption
325 complexes on silica also derived the presence of two surface species at circumneutral pH values,
326 where the species showing red-shifted band maxima becomes predominant at higher pH levels or
327 after prolonged incubation times.^{33,35}

328 A displacement of coordinated water molecules in the equatorial plane of the UO₂²⁺ unit, as it
329 occurs during complexation of ligand molecules or hydrolysis reactions, generally generates a
330 decrease of the frequencies of the spectral features in vibrational and luminescence spectra.
331 Consequently, in comparison to species 1, the spectral properties of species 2 suggest enhanced
332 interactions of the uranyl(VI) moiety with the solid phase due to the red-shifted maxima of the
333 absorption and emission bands in the IR and luminescence spectra, respectively. However, the
334 assignment of these species to mono- and bidentate inner-sphere species is not possible, because
335 such structural information cannot be derived from the spectroscopic techniques applied in this
336 work. Nevertheless, the reduced reversibility of the sorption reactions demonstrated by the
337 intermediate flushing step in the *in situ* IR experiment (Fig. 2E) reflects the predominant for-

338 mation of only inner-sphere complexes, in agreement with results discussed previously from X-
339 ray absorption spectroscopic studies.³⁹

340 In comparison to the spectra of the binary sorption system (Fig. 3B), the spectra of the ternary
341 sorption system, where U(VI) and phosphate were added simultaneously to silica, reveal only
342 small alterations of band intensities, peak positions and lifetimes (Fig. 3C and Tab. 1). Thus, a
343 similar molecular environment of the uranyl(VI) moiety at the solid silica phase, irrespective of
344 the presence or absence of phosphate, can be suggested. Again, this is consistent with vibrational
345 spectroscopic results where the band of the $\nu_3(\text{UO}_2)$ mode is only slightly changed in the pres-
346 ence of phosphate (Figs. 2B and 2C). These results suggest that the interaction of U(VI) with
347 silica is predominant even in presence of phosphate.

348 A different sorption mechanism, however, is observed after U(VI) and phosphate were allowed
349 to equilibrate for a prolonged time (3 days) in solution at pH 5.5. Sequential sorption onto silica
350 provides luminescence spectra shown in Fig. 3D. From these series of spectra, recorded immedi-
351 ately following contact and after prolonged incubation (3 and 5 days with SiO_2), again imply the
352 occurrence of two different species showing very similar spectral characteristics as the species
353 derived from the previous experiments. However, the decomposition of the spectra of the addi-
354 tional species after prolonged sorption (days 3 and 5) from the experimental data reveals consid-
355 erably reduced band widths compared to those of the species obtained from the previous experi-
356 ments (Fig. 3E, lower trace). This more concisely structured spectrum indicates the occurrence of
357 another species (species 3) prevailing under these conditions. Thus, the spectral differences of
358 species 2 and 3 most likely reflect structural rearrangements of the uranyl(VI) moiety due to the
359 extended formation of a surface precipitate after prolonged incubation time.

360 **Surface complexation modeling (SCM).** According to the spectroscopic results of this work
361 and literature data, the two binary uranyl(VI) surface species $\equiv\text{SiO}_2\text{UO}_2^0$ and $\equiv\text{SiO}_2\text{UO}_2\text{OH}^-$,
362 and relevant solid phases – most probably Na-Autunite – are likely to be formed under the
363 prevailing conditions and were considered during the predictive sorption modeling.^{33, 50} The
364 results clearly demonstrate that both processes, adsorption and precipitation, contribute to the
365 removal of U(VI) from the aqueous phase. Both binary surface species $\equiv\text{SiO}_2\text{UO}_2^0$ and
366 $\equiv\text{SiO}_2\text{UO}_2\text{OH}^-$ in addition with the surface precipitate Na-Autunite describe the experimental
367 data quite well as shown in Fig. 1 (dashed lines). For considering ternary U(VI)-phosphate
368 surface complexes the following surface complexation reaction was considered in the present
369 model.



371 The final SCM data set including specific surface site parameters are given in the Supporting
372 Information (Table S1). The obtained fitted $\log K(\equiv(\text{SiO})_2\text{-UO}_2\text{PO}_4^{3-})$ is 13.8 ± 0.16 . However,
373 the fitting procedure does not provide reasonable results for all batch curves presented in this
374 work. By considering the ternary surface complex an overestimation of the experimental data,
375 mainly for the 20 μM U, 20 μM P system, can be observed (see Supporting Information, Fig.
376 S6).

377 Hence, the predominant processes occurring in the sorption systems are identified as formation
378 of binary uranyl(VI) surface species and surface precipitation of a uranyl(VI) phosphate phase.
379 While the key findings of the present work shows that a uranyl phosphate ternary species is not
380 required to explain the experimental data, the formation of ternary surface species might occur
381 during the sorption processes as transient species which might become of some relevance only
382 under highly diluted conditions.

383 **Environmental Implications.** The fate and transport of uranium in subsurface environments
384 is an important consideration, particularly at many legacy nuclear sites. For a comprehensive
385 understanding of the migration behavior of U(VI) in aquifers, a detailed description of the
386 molecular scenarios comprising sorption and precipitation processes at mineral surfaces is
387 mandatory. In particular in the presence of strongly interacting ions, the environmentally relevant
388 parameters under which either of these processes becomes decisive in geochemical settings have
389 to be explored.

390 The focus of the present work at slightly acidic pH is very relevant to the environmental condi-
391 tions where phosphate remediation strategies are being considered.⁵⁹ Phosphate amendment to
392 mitigate the transport of uranium has received considerable attention over recent years, whereby
393 the precipitation of U(VI) by the addition of phosphate to contaminated groundwater can be used
394 as an alternative remediation approach to bioreduction of U(VI). As SiO₂ is a large component of
395 soils and host rocks, this work provides important information to assess the formation and
396 stability of uranyl phosphate precipitated at the SiO₂ surface. The information provided by the
397 combination of macroscopic and spectroscopic experiments described herein suggests the
398 predominant formation of a surface precipitate initiated by U(VI) binary surface complexes. The
399 surface-mediated formation of sparingly soluble solid uranyl(VI) phosphate phases initiated by
400 already sorbed uranyl(VI) species might represent a significant retention behavior of silica
401 towards aqueous U(VI) under environmentally relevant conditions.

402

403 SUPPORTING INFORMATION

404 Supporting Information provides detailed description of the performance of batch, IR and
405 TRLFS experiments. A scheme showing the kinetics of U(VI) sorption at the silica surface (Fig.

406 S1), equilibrium plots (experimental and predicted) for U uptake in the presence of P with no
407 sorbent present (Fig. S2), sorption isotherm for U(VI) uptake in the presence of 20 μM P at pH 4
408 (Fig. S3), splitting of the vibrational modes of the phosphate group according to the prevailing
409 symmetry group (Fig. S4), the decomposition of IR spectrum of binary uranyl(VI) surface
410 species (Fig. S5), and the SCM fitting curves considering a ternary phosphate complex (Fig. S6)
411 are provided. Table S1 provides all surface parameter and associated reactions for the modeling
412 of the U(VI)/Phosphate/SiO₂-system. This material is available free of charge via the Internet at
413 <http://pubs.acs.org>.

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419 **Author Contributions**

420 The manuscript was written through contributions of all authors. All authors have given approval
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601

602

603 TABLE

604 **Table 1.** TRLF spectral characteristics of the precipitate and surface species of
 605 U(VI)/phosphate/SiO₂.

Sample	Main emission bands / nm		τ / μ s	T / K	Assigned species	Ref.
U(VI)/ PO ₄ ³⁻ *	503	525	16.2 ± 0.4	298	(UO ₂) ₃ (PO ₄) ₂ ·6H ₂ O	This work (Fig. 3A)
	502	524	13.5 ± 0.3			
U(VI)/ SiO ₂ **	498	518	65 ± 6	n/s	UO ₂ H ₃ SiO ₄ ⁺	58
	494–496	514–516	—	4	≡SiO ₂ UO ₂ ⁰ Species 1	57
	498	518	170 ± 25	298		33, this work (Fig. 3B)
	—		180 ± 20	n/s	UO ₂ ²⁺ /SiO ₂	58
	501–503	522–526	—	4	≡SiO ₂ UO ₂ OH ⁻ Species 2	57
	504	524	360 ± 50	298		33, this work (Fig. 3B)
	506	528	400 ± 30	n/s	(UO ₂) _x (OH) _y ^{(2x-y)+} / SiO ₂	58
U(VI)/ PO ₄ ³⁻ / SiO ₂ **	497–498	519	105...137	298	Species 1	This work (Fig. 3C)
	498–504	525–527	210...358	298	Species 2	This work (Fig. 3C)
U(VI)/ PO ₄ ³⁻ / SiO ₂ ***	497	520		298	Species 1; 0 days	This work (Fig. 3D)
	503	526	285 ± 1.5	298	Species 3; ≥3 days	

606 * : precipitate obtained at pH 4 (upper line) and 5.5 (lower line); ** : sorption sample; *** : sorp-
 607 tion sample after pre-equilibration of U(VI) and phosphate; n/s: not available.

608

609 FIGURE CAPTIONS

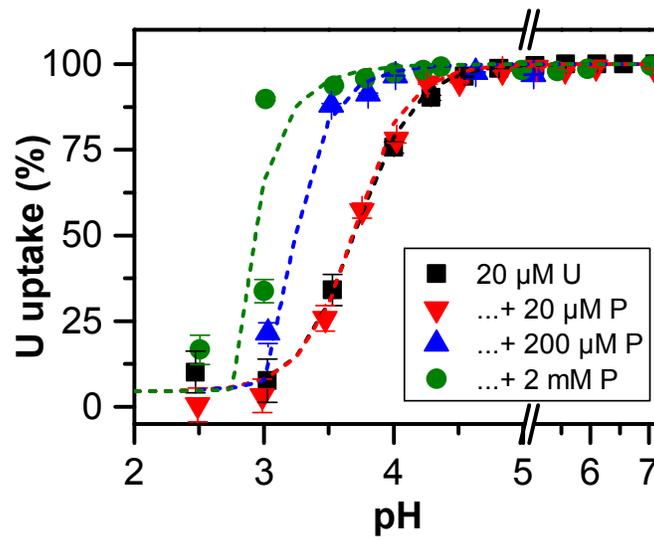
610 **Figure 1.** Uranium(VI) uptake onto SiO₂ in presence of different phosphate concentrations. Total
611 [U] = 20 μM; Total [P] = 0 μM (black squares), 20 μM (red triangles), 200 μM (blue triangles)
612 or 2,000 μM (green dots) (SiO₂ mass loading = 10 g L⁻¹; 0.1 M NaCl; equilibrium with air; 25
613 °C). Predictive results of Surface Complexing Modeling for the batch experiments performed at
614 given phosphate concentrations are plotted as dashed lines. Note that for clarity reasons an axis
615 break was added in the abscissa and only the largest error bars are shown at low pH values.

616 **Figure 2.** IR spectra of the aqueous U(VI)/phosphate phase (pH 4; black trace) and of the
617 precipitate (grey trace) obtained after ultracentrifugation (A). In situ IR spectra of the sorption
618 experiments of aqueous U(VI) and phosphate onto silica. Middle panel: spectra obtained within
619 the first 10 minutes (B) and after 60 minutes of exposure time of an aqueous U(VI)/P solution
620 (C) at pH 4. Note that the ordinate scaling of the latter spectrum is reduced by a factor of 0.3 for
621 clarity (1 mOD/tick). Lower panel: spectra obtained from sequential experimental steps as
622 indicated (pH 5.5). Exposure times are 120 and 60 minutes for steps I–II and III–IV, respectively
623 (ordinate scale: 20 mOD/tick). [U(VI)]_{init} = [P]_{init} = 20 μM, 0.1 M NaCl for all experiments.
624 Indicated values are in cm⁻¹.

625 **Figure 3.** Luminescence spectra of the U(VI)-phosphate precipitate (A) and the batch sorption
626 samples (B–D). The samples were adjusted to pH 4 (grey trace) and 5.5 (black trace) prior to
627 measurements (A–C). Spectra of the batch samples of the binary U(VI)/SiO₂ (B) and ternary
628 U(VI)/PO₄³⁻/SiO₂ (C) sorption systems. Spectra of the ternary U(VI)/PO₄³⁻/SiO₂ sorption sample
629 (pH 5.5) collected at different incubation times (zero, three, and five days, from below to top)
630 (D). Decomposed luminescence spectra (species 1, 2) obtained from spectra of sorption samples

631 (B, C) at pH 4 and 5.5 (E). Species 3 represents the second species obtained from spectra of aged
632 sorption sample (D).

633 FIGURES



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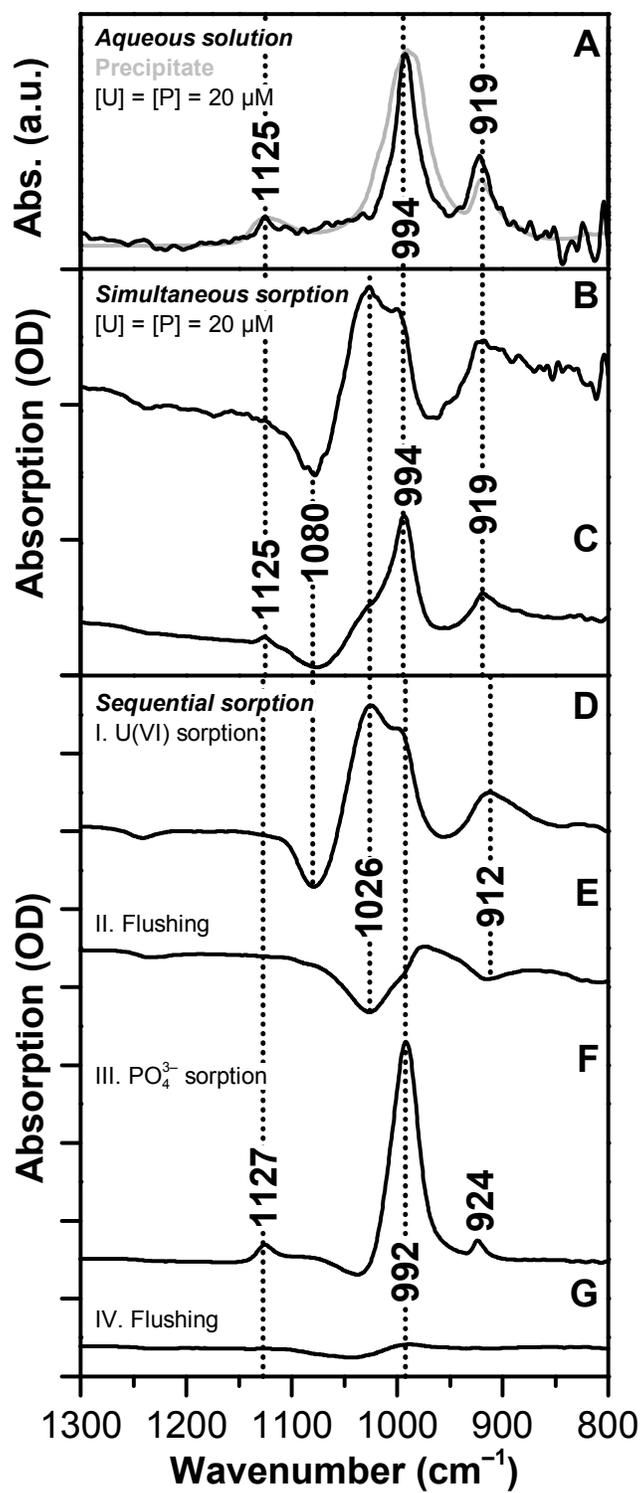
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Figure 1



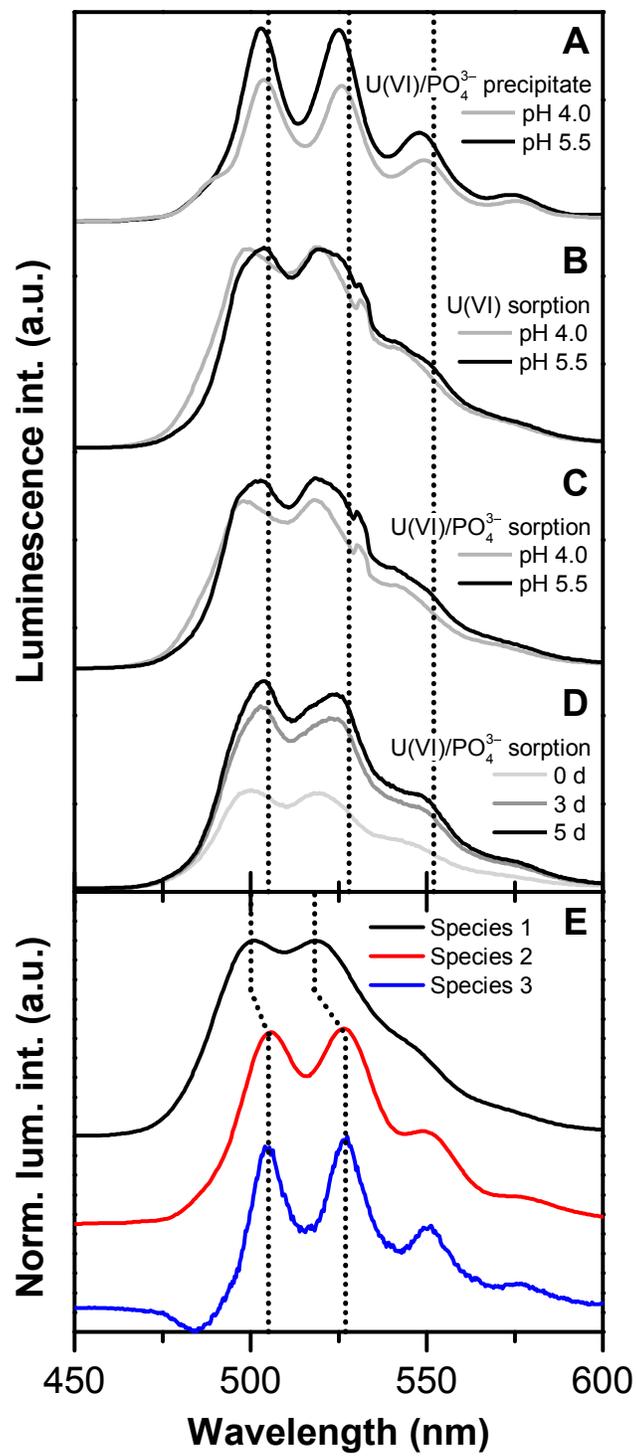
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Figure 2



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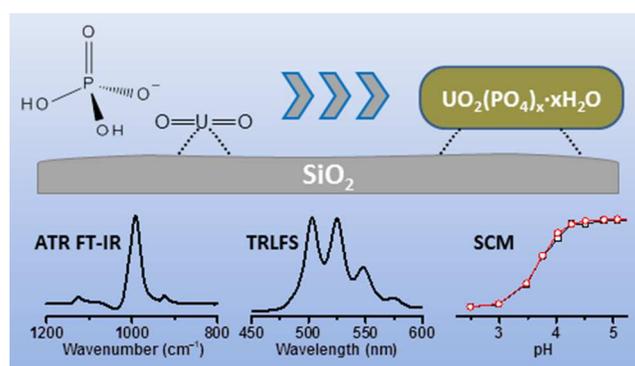
Figure 3

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TOC Artwork