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KEYWORDS

Uranium, redox state, magnetite, HR-XANES, EXAFS.

1 ABSTRACT

2 Uranium redox states and speciation in magnetite nanoparticles co-precipitated with U(VI) for
3 uranium loadings varying from 1000 to 10000 ppm are investigated by X-ray absorption
4 spectroscopy (XAS). It is demonstrated that the U M_4 high energy resolution X-ray absorption
5 near edge structure (HR-XANES) method is capable to clearly characterize U(IV), U(V) and
6 U(VI) existing simultaneously in the same sample. The contributions of the three different
7 uranium redox states are quantified with the iterative transformation factor analysis (ITFA)
8 method. U L_3 XAS and transmission electron microscopy (TEM) reveal that initially sorbed
9 U(VI) species recrystallize to non-stoichiometric UO_{2+x} nanoparticles within 147 days when
10 stored under anoxic conditions. These U(IV) species oxidize again when exposed to air. U M_4
11 HR-XANES data demonstrate strong contribution of U(V) at day 10 and that U(V) remains stable
12 over 142 days under ambient conditions as shown for magnetite nanoparticles containing 1000
13 ppm U. U L_3 XAS indicates that this U(V) species is protected from oxidation likely incorporated
14 into octahedral magnetite sites. XAS results are supported by density functional theory (DFT)
15 calculations. Further characterization of the samples include powder X-ray diffraction (pXRD),
16 scanning electron microscopy (SEM) and Fe 2p X-ray photoelectron spectroscopy (XPS).

17 INTRODUCTION

18 Uranium is the main constituent of spent nuclear fuel (SNF), but it can be also found in high
19 quantities in actinide (An) contaminated sites.¹ Developing the safety case for the safe disposal of
20 radioactive waste requires mechanistic understanding of the interaction of the waste products
21 with repository components. In case of water accessing the waste container, radionuclides will
22 react with the corrosion products, which potentially represent a very relevant reactive barrier
23 retaining pollutants release in the repository near field. Of particular interest is the detailed
24 understanding of An interactions with iron (Fe) oxides, e.g. magnetite (Fe_3O_4) considered as a

25 corrosion products of Fe based container materials.² A number of laboratory studies have been
26 performed to clarify the fate of uranium in such systems. Due to the complex redox processes
27 induced by Fe(II)/Fe(III) species, uranium is often found to exist in a mixture of redox states.
28 Uranium has two main environmentally relevant redox states, U(IV) and U(VI). U(V) is believed
29 to form as an intermediate redox species and exhibits a poorly understood geochemical behavior.
30 The only evidence of U(V) in nature is the uranium mineral wyartite.³ Whereas U(VI) and U(IV)
31 are usually found, depending on conditions, as a result of microbial and Fe(III)/Fe(II) driven
32 redox processes,⁴⁻¹⁰ only a few studies report U(V) as a relevant redox species. In earlier studies
33 U(V) was detected after Fe(II) catalyzed transformation of U(VI)-ferrihydrite to goethite (α -
34 FeO(OH))¹¹ and in different Fe (oxyhydr)oxides phases where Fe₃O₄ was considered as one of
35 the possible phases to stabilize U(V).¹² Also Nico et al. reported on the possibility of U(V) or
36 U(VI) incorporation into the octahedral position of the α -FeO(OH)/Fe₃O₄ after ferrihydrite
37 remineralization.¹³ Later studies attempted to specifically detect U(V) in different Fe systems
38 under controlled conditions with the aim to reconsider the relevance of U(V) for uranium
39 containing (geo)chemical systems.¹⁴⁻¹⁷ In most of the reported investigations, X-ray absorption
40 spectroscopy (XAS) based methods, i.e. U L₃ X-ray absorption near edge structure (XANES) and
41 extended X-ray absorption fine structure (EXAFS) as well as U 4f X-ray photoelectron
42 spectroscopy (XPS) are used to investigate the U speciation and redox states. XANES spectra
43 are sensitive to the U coordination environment and redox states but the spectra are dominated by
44 broad features due to large core-hole lifetime broadening effects.¹⁸ This challenges the
45 characterization and quantification of the different U redox states, especially when U(V) is also
46 present in the material. On the other hand, the XPS technique can successfully quantify mixed U
47 redox states if there is sufficiently high uranium content (> 1000 ppm) in the sample.^{12, 14, 16, 19}
48 However a clear identification of U(V) species can be hampered by low signal to noise ratio of

49 the spectra for low uranium contents. XPS has high surface sensitivity and is performed in ultra-
50 high vacuum, which can lead to potential changes of the samples. To handle these challenges,
51 complementary highly sensitive techniques are needed for thorough characterization of the U
52 redox states in such systems. The high energy resolution XANES (HR-XANES) method at the U
53 $M_{4,5}$ absorption edges was demonstrated to be very valuable for studies related to U redox state
54 analysis in complex uranium systems containing mixed U redox states.^{20, 21} The U M_4 HR-
55 XANES experiments need to be performed in He environment comprising the sample, analyzing
56 crystals and detector in order to avoid loss of intensity by scattering and absorption of photons in
57 air. Unlike XPS, vacuum conditions are not necessary. The samples can be investigated in the
58 form of solids, wet pastes, suspensions or liquids. U $M_{4,5}$ HR-XANES takes a great advantage
59 over the conventional U L_3 XANES. Reduced core-hole lifetime broadening results in better-
60 resolved spectral features allowing more precise redox state analysis. Due to the dipole selection
61 rule ($\Delta l = \pm 1$) the electrons are excited with high probability from U $3d_{3/2}$ to U 5f unoccupied
62 states. Therefore the U M_4 HR-XANES technique is also a direct probe of the unoccupied U 5f
63 valence states, which play a significant role in the chemical bonding of the An elements.²⁰⁻²⁴
64 In the present study we investigated the U redox states and speciation in the final product formed
65 by co-precipitation of U(VI) with Fe_3O_4 for variable U loadings (1000-10000 ppm). The U L_3/M_4
66 HR-XANES and U L_3 XANES/EXAFS as well as transmission electron microscopy (TEM) are
67 applied. Scanning electron microscopy (SEM), X-ray powder diffraction (pXRD), Fe $2p_{3/2}$ XPS,
68 geochemical calculations and density functional theory (DFT) are used to characterize the U
69 containing Fe_3O_4 samples. The main aim is to verify the presence of U(V) in this system. A long-
70 term study of samples kept under anoxic (up to 480 days) and oxidizing conditions (up to 226
71 days) was performed to elucidate the stability of the potential U(V) species in the Fe_3O_4
72 nanoparticles. We demonstrate that the applied U M_4 HR-XANES method is capable of detecting

73 U(IV), U(V) and U(VI) at relatively low (1000 ppm) total U concentrations being present
74 simultaneously in the same sample. The contributions of the three different U redox states are
75 quantified with the iterative transformation factor analysis (ITFA) method.²⁵

76 MATERIALS AND METHODS

77 **Preparation of the samples.** MilliQ-H₂O was used for the preparation of all samples. To remove
78 dissolved O₂ and CO₂ MilliQ-H₂O was bubbled for several hours with Ar outside and then for at
79 least one hour inside an argon (Ar) glovebox. Uranium containing Fe₃O₄ nanoparticles were
80 synthesized by direct precipitation²⁶⁻²⁸ inside an Ar glovebox equipped with pH, E_h electrodes
81 and a dropping funnel using the following procedure: to a 50 mL Teflon container the calculated
82 amounts of aqueous FeCl₃, FeCl₂ and an aliquot of aqueous U(VI)O₂Cl₂ (1000, 3000, 6000 and
83 10000 ppm U: Um1-Um10 samples) were added followed by dropwise addition of 0.5 M NaOH
84 (Backer, CO₂ free) to pH = 7.5-8.0. The suspension was stirred overnight, pH and E_h values were
85 recorded and pH was adjusted if necessary by adding 0.1 M NaOH. All samples were then stored
86 in the form of suspension in the Ar glovebox. The UO₂ (several μm particle size), U₄O₉ (used
87 from^{20, 29}) and 3000 ppm U(VI) adsorbed onto maghemite (γ-Fe₂O₃, spectra are named Umh)
88 serve as reference compounds. The γ-Fe₂O₃ was prepared by heating freeze-dried magnetite
89 nanoparticles at 200 °C during 2 hours in air.³⁰ 3000 ppm U as U(VI)O₂Cl₂ was then adsorbed on
90 the γ-Fe₂O₃. More than 99 % of U(VI) was adsorbed after 50 days as determined with inductively
91 coupled plasma mass-spectrometry (ICP-MS). Experimental details for U, Fe and salt
92 concentrations as well as pH, E_h measurements are given in Table S1.

93 For the U L₃/M₄ HR-XANES experiments, solids were separated from supernatant using a Nd
94 magnet. The supernatant was decanted and the solids were used in the form of a wet paste. All
95 samples were prepared in an Ar glovebox at 1-2 ppm O₂ level and less than 1 ppm CO₂. An inert
96 gas Plexiglas sample holder comprising a double containment (two separated 10 μm

97 polypropylene films) has been designed and used for the spectroscopic measurements. To avoid
98 contact of the samples with air they were transported one day prior to the experiments in a gas
99 tight aluminum cylinder filled with Ar and opened very shortly prior to the experiments.

100 For the U L₃ XAS experiments, subsamples Um1-Um10 from the same batch were separated
101 using a Nd magnet after 147 days of ageing in the Ar glovebox. After these experiments the Um1
102 sample was placed in a non-hermetically closed plastic vial and kept under ambient, aerobic
103 conditions (Um1a sample). The Um1a sample was investigated with the U M₄ HR-XANES (142
104 days in air, total 289 days) and with the U L₃ XAS (XANES and EXAFS) techniques (226 days
105 in air, total 373 days).

106 **X-ray absorption spectroscopy (XAS).** U L₃/M₄ HR-XANES experiments were performed at
107 the ID26 beamline, ESRF, Grenoble, France³¹ (Um1-Um10) and at the INE-Beamline, ANKA,
108 Karlsruhe, Germany²² (Um1a) with Johann type X-ray emission spectrometers.^{24, 32, 33} The U L₃
109 XAS (XANES and EXAFS) experiments were performed in fluorescence mode using a five
110 element Ge solid state fluorescence detector (Canberra) at the INE-Beamline. The ATHENA and
111 ARTEMIS program parts of the IFFEFIT program package were used for data reduction and
112 analyses of the EXAFS spectra.^{34, 35} Details on the experiments, the quantitative U oxidation
113 states analyses of the U M₄ HR-XANES spectra with the ITFA method for the 10 day aged
114 samples and the EXAFS analyses are given in the Supporting Information (SI).

115 **Additional characterization methods.** High resolution-TEM (HR-TEM) and SEM images were
116 recorded with a FEI Tecnai G2 F20 X-TWIN instrument operated at 200 kV and a FEI Quanta
117 650 FEG ESEM, respectively. pXRD patterns were measured with laboratory based Bruker AXS
118 D8 powder diffractometer and at the SUL-X-Beamline (ANKA, Karlsruhe, Germany) (SI).³⁶ The
119 FIT2D and DIFFRAC.EVA V3.1 programs were used to analyze the data.³⁷

120 **DFT calculations.** The experiments are supported by DFT calculations utilizing plane-wave
121 basis sets with periodic boundary conditions as implemented in the Vienna Ab initio Simulation
122 Package (VASP).³⁸⁻⁴⁴ Further details are given in SI.
123 Details on the thermodynamic calculations and the XPS experiments are reported in SI. Table S2
124 comprises the description of the studied samples and the applied characterization techniques.

125 RESULTS AND DISCUSSION

126 **Characterization of the Fe₃O₄ nanoparticles.** The formation of the Fe₃O₄ nanoparticles can be
127 described with reaction 1,



129 Measured E_h-pH values for samples containing 1000 ppm U (Um1) and 10000 ppm U (Um10)
130 are located inside the stability field of Fe₃O₄ according to the Fe Pourbaix diagram (Figure S1A);
131 redox conditions of the samples comprising 3000 ppm U (Um3) and 6000 ppm U (Um6) are
132 placed at the border of Fe₃O₄ – FeO(OH)(cr) (goethite) stability fields.⁴⁵ E_h-pH conditions are
133 such (E_h = -210 – -390 mV; pH = 7.5-8.0) that subsequent reduction of U(VI) to U(IV) would be
134 expected according to the U Pourbaix diagrams (Figures S1B, C). SEM images (Figure S2) and
135 powder XRD (pXRD) patterns (Figure S3) reveal that crystalline Fe₃O₄ nanoparticles with
136 octahedral shape and a size of 15-40 nm are formed. Energy dispersive X-ray analysis (EDX)
137 does not reveal segregated uranium precipitates. No goethite or any other Fe containing
138 crystalline phases are found. The Fe(II) content is slightly below that of stoichiometric Fe₃O₄
139 (Fe(II)/Fe_{TOT} = 0.33) at Fe(II)/Fe_{TOT} = 0.28 ± 3 % for all samples (Um1-Um10) aged for 310
140 days as indicated by the reduced intensity of the Fe(II) 2p_{3/2} peak of the Fe 2p XPS spectra
141 (Figure S4). There is no clear trend in the level of Fe(II) oxidation as a function of the U(VI)

142 concentration. In view of the low U/Fe mass ratios (0.0014-0.014), this is indeed not to be
143 expected.

144 **Redox states of U in the Fe₃O₄ nanoparticles aged for 10 days.** We characterized the U redox
145 state in the Um1-Um10 samples aged in inert atmosphere for 10 days with the U L₃ and M₄ HR-
146 XANES spectroscopy techniques. The U L₃ and M₄ HR-XANES spectra of the Um1-Um10
147 samples are depicted in Figures 1A and 1B, respectively.

148 The X-ray absorption spectra typically shift to higher energies by increasing the U redox state
149 due to the reduced screening of the 2p_{3/2} (L₃)/3d_{3/2} (M₄) core-hole by the decreased electronic
150 charge density on the U atoms. Smaller energy shifts of about ± 0.5 eV can be induced by
151 variations of the electronegativity of the bonding partner, changes in symmetry, short and long
152 range atomic order etc., for the same U redox state as suggested by U L₃ XANES studies.^{46, 47}

153 One exception of the general trend are the U L₃ XANES spectra of U(V) and U(VI) forming short
154 (< 1.9 Å) axial bonds with two O atoms (UO₂⁺/UO₂²⁺, U(V)/U(VI)-yl); the maxima of the most
155 intense absorption resonance (white line, WL) of the U(V)-yl and UO₂ spectra have similar
156 energy positions.¹⁹ The WL of the U(VI)-yl spectrum is only slightly shifted to higher energy and
157 it can potentially have the same energy position as e.g. U(V) species with more symmetric
158 coordination environments associated with loss of short uranyl bonds, i.e. uranate type of U(V)
159 species. This effect is induced by the large electronic density in the vicinity of U due to the strong
160 covalent bond of U(V)/U(VI) with the two axial O atoms. Such anomalous behavior is not
161 observed for U M_{4,5} HR-XANES spectra. Energy shifts within a range of ± 0.1 eV can be caused
162 by differences in short and long range atomic order around the absorbing atom as for example
163 observed for different UO₃ phases, but the spectra shift to higher energies for higher U oxidation
164 states.^{21, 48} For example the energy shift between UO₂ and U(V)-yl ([U(V)O₂(CO₃)₃]⁵⁻) is ~1.2

165 eV, whereas between U(V)-yl and U(VI)-yl ($[\text{U(V)O}_2(\text{CO}_3)_3]^{5-}$ and $[\text{U(VI)O}_2(\text{CO}_3)_3]^{4-}$) is ~ 1.0
166 eV.⁴⁹

167 The WL of the U L₃ HR-XANES spectrum of the Um10 sample is located at similar energy
168 position as the WL of the spectrum of Umh. U has oxidation state U(VI) in the Umh sample. In
169 addition, the feature marked with line c clearly visible in the U L₃ HR-XANES Umh and Um10
170 spectra (Figure 1A) is characteristic for the $\text{U(VI)O}_2^{2+}/\text{U(V)O}_2^+$ entity. These results suggest
171 predominant U(VI)-yl contribution in the Um10 sample. The absorption resonance marked with
172 line c becomes less intense in the spectra of the Um6-Um3 samples and it diminishes in the
173 spectrum of the Um1 sample. These spectra suggest that the Um1 sample if at all contains low
174 amount of uranyl species. In addition, the WL and the post edge absorption resonance marked
175 with line c' become broader and asymmetric from the Um10 to the Um1 spectrum. Such
176 asymmetric WLs have been previously described as being characteristic for uranate type of
177 U(V)/U(VI) species.^{19, 46, 50, 51} However it can not be excluded that this U species dominant in the
178 Um1 sample has redox state (IV). The local symmetry of these U(V)/U(IV) species should be
179 rather different compared to the U(V)/U(IV) in U₄O₉ since there is no resemblance between the
180 Um1 and the U₄O₉ spectra. It is clear that the U L₃ HR-XANES spectra are more sensitive to
181 small structural and oxidation states changes compared to the conventional U L₃ XANES.^{18, 52}
182 But the method is still limited by large core-hole lifetime broadening effects and does not allow
183 to reliably identify and quantify the U(IV), U(V) and U(VI) anticipated to be simultaneously
184 present in the samples.

185 Additional information on the U redox states is obtained by applying the U M₄ HR-XANES
186 method. Figure 1B depicts the U M₄ HR-XANES spectra of the Um1-Um10 samples and UO₂,
187 U₄O₉ as well as Umh for comparison. U₄O₉ contains U(IV) and U(V) visible by the two main
188 peaks separated by ~ 1 eV.²⁰ These spectral features are named d and e in the U M₄ HR-XANES

189 spectrum of U_4O_9 (Figure 1B). The main absorption peak *f* of the U_{M4} spectrum is shifted by ~
190 0.4 eV to higher energies as compared to peak *e* and it is assigned to U(VI). Spectral features *f*
191 and *f'* are also typical for U(VI)-yl ions with short (~1.77-1.91 Å) trans-dioxo bonds.^{23, 48, 53}
192 These features exist for U(V)-yl species but are considerably shifted (*f* ~0.6 and *f'* ~2.5 eV)
193 towards the main peak.⁴⁹
194 Much more clear compared to the U L_3 HR-XANES, the U M_4 HR-XANES spectrum obtained
195 for the U_{M1} sample demonstrates major contributions of U(V) (peak *e*) and minor fraction of
196 U(IV) (peak *d*) (Figure 1B). It is also evident that the intensity of feature *d* increases while
197 moving from the U_{M10} to the U_{M1} spectrum, the energy position of feature *e* shifts to lower
198 energies and features *f* and *f'* lose intensity. These spectral changes imply that the relative
199 contribution of U(VI) decreases, whereas the U(IV) content rises going from 10000 ppm U
200 (U_{M10}) to 1000 ppm U (U_{M1}) in the samples (Figure 1B).

201 **Quantification of the U redox states.** We performed quantitative analysis of the U M_4 HR-
202 XANES spectra by the ITFA method.²⁵ ITFA is used to decompose the spectral mixtures into the
203 spectra and the fractions of the components (Figure S5). The experimental spectra can be
204 sufficiently reproduced (Figure S5A) by using linear combinations of the three ITFA-extracted
205 component spectra (Figure S5B), so that the residual is similar to the expected experimental
206 error. Only the first three eigenvectors show a signal while the eigenvectors 4, 5 and 6 do not
207 contribute to the data (Figure S5C), hence only three components are necessary to describe the
208 variations in the spectral mixtures. The extracted component spectra correspond to the U(IV),
209 U(V) and U(VI) redox states. The analysis shows that the U_{M1} and U_{M10} samples contain 19 %
210 U(IV), 81 % U(V) and 0.7 % U(VI), 62.3 % U(V), 37 % U(VI), respectively (Table S3). The U
211 M_4 HR-XANES technique and the ITFA approach are clearly capable of detecting and

212 quantifying the three different redox states: U(IV), U(V) and U(VI), being present simultaneously
213 in the same sample.

214 **Redox states and local atomic environment of U in the Fe₃O₄ nanoparticles aged for 147**

215 **days.** We performed U L₃ XAS (XANES and EXAFS) studies for the magnetite suspensions
216 containing U stored for 147 days in anoxic conditions. For technical reasons, the redox states of
217 U in the Um1, Um3, Um6 and Um10 samples could not be analyzed with the U M₄ HR-XANES
218 method 147 days after the preparation of the samples.

219 The U L₃ XANES spectra of the Um10-Um1 samples are depicted in Figure 2A. The energy
220 positions of the WLs and the general shapes of the spectra of the Um10 sample and UO₂ are very
221 similar. We conclude that the initial U(VI)-yl has reduced mainly to U(IV) in the Um10 sample.
222 The spectra of the Um10-Um1 samples exhibit a trend and are shifted up to ~1.5 eV to higher
223 energies compared to UO₂ going from the Um10 to the Um1 sample (lines a and b in Figure 2A).
224 The WL becomes broader and the post-edge absorption resonance at ~17218 eV transforms from
225 a single asymmetric (c') to a broad peak shifted to higher energies observed also for the U L₃ HR-
226 XANES spectra of the 10 days aged samples (Figure 1A). We obtain additional insights from the
227 comparison of the conventional U L₃ XANES spectra measured for the Um1 samples aged for 10
228 and 147 days (Figure S6). The U L₃ XANES for the Um1 sample aged for 147 days is shifted
229 ~2,5 eV to lower energies compared to the spectrum of the sample aged for 10 days, which is an
230 evidence for higher U(IV) content (Figure S6). This result implies that reduction of U(V) to
231 U(IV) has continued for the Um1 sample 10 days after its preparation. We assume that the higher
232 oxidation state of U in the Um1 sample aged for 147 days is the U(V) species found for the 10
233 days aged Um1 sample. U(VI) was not found for the 10 day aged Um1 sample by the ITFA U M₄
234 edge HR-XANES analyses and since the Um1-Um10 samples were handled in the same way, i.e.

235 anoxic and reducing conditions, it is likely that U has reduced in all samples. Therefore the
236 observed energy shift can not be explained with major U(IV) and minor U(VI) contributions.
237 Alternatively, if the U has completely reduced to U(IV), this can be U(IV) in different
238 coordination environment compared to the U(IV) typical for the Um10 sample. However
239 published spectra for U(IV) in different coordination environments show no significant
240 differences in the energy positions of the WL maxima of the U L₃ XANES spectra.⁵⁴
241 The FT-EXAFS spectra and their best fits for the Um1, Um3, Um6 and Um10 samples after 147
242 days ageing are depicted in Figure 2B (see also Figures S7-9). The first coordination sphere of U
243 is best modeled with three U-O distances (R). R(U-O1) = 1.69(2)-1.73(2) Å is an untypically
244 short bond length for U(VI)-O_{axial}, which has been previously observed and controversially
245 discussed.^{55, 56} Particularly Conradson et al. proposed that these short U-O distances are
246 characteristic for U(VI) in a series of UO_{2+x} compounds.⁵⁵ The structural parameters obtained
247 from the fit to the FT-EXAFS are very similar with and without modeling these peaks; we chose
248 not to consider these very short U-O distances (< 1.75 Å) in our structural model since they can
249 be also part of a background signal. More detailed discussion on their potential structural
250 meaning is not in the scope of our study.
251 Due to the low signal to noise ratio of the EXAFS data particularly for the Um1 and Um1a
252 samples we have performed and report fits to the spectra for k range until 9.5 Å⁻¹ (Figure S10).
253 The main U-O2 distance obtained from the fits to the data continuously decrease from 2.26(1) Å
254 to 2.18(2) Å within the Um10-Um1 series, whereas the U-O3 distance remains within the range
255 R = 2.41(1) Å (Table S4, Figure S11). The coordination numbers (N) vary: N(U-O1) = 0.2(1)-
256 0.4(2), N(U-O2) = 2.2(2)-3.0(3) and N(U-O3) = 3.2(3)-1.8(2) (Table S4, Figure S11). The
257 observation that the first O coordination sphere of U splits into two dominant peaks was reported
258 for UO_{2+x} (x = 0-0.2) compounds where the split became more pronounced for large x.⁵⁵ We

259 therefore might assume that U in our samples exists mainly as non-stoichiometric UO_{2+x}
260 containing mixed U redox states. However, the trend for these two main U-O distances is
261 reversed compared to our EXAFS results since R-O2 and R-O3 grow as a function of the
262 increasing non-stoichiometric oxygen in UO_{2+x} with $R(\text{U-O2}) = 2.22\text{-}2.26 \text{ \AA}$ and $R(\text{U-O3}) = 2.36\text{-}$
263 2.42 \AA .⁵⁵ This can be explained by the presence of a second U site in our samples in addition to
264 U(IV)/U(V)/U(VI) constituents of UO_{2+x} particles. This U species becomes more relevant at low
265 uranium concentration (1000 ppm U), which agrees with the results from the U L_3 XANES data.
266 The $R(\text{U-O2}) = 2.18 \text{ \AA}$ for the Um1 sample is within the range $R = 2.05\text{-}2.20 \text{ \AA}$ reported in the
267 literature as typical for U(V) compounds.¹² These EXAFS results do not contradict to the
268 assumption that the U(V) found in the Um1 10 days aged sample is at least partially preserved.
269 This potential U(V) species is likely coordinated by Fe as the best fits to the FT-EXAFS spectra
270 reveal. This is based on the finding that coordination of U to Fe atoms is more prominent for the
271 Um1 compared to the Um10 sample. Two U-Fe interatomic distances are resolved: $N(\text{U-Fe1}) =$
272 $0.6(3)$, $R(\text{U-Fe1}) = 3.13(3) \text{ \AA}$ in Um10 and $N(\text{U-Fe1}) = 4.5(17)$, $R(\text{U-Fe1}) = 3.19(1) \text{ \AA}$ in Um1. A
273 U-Fe2 shell with a minor contribution ($N = 0.5(3)\text{-}1.0(8)$) is modeled too (Table S4). Somewhat
274 longer $R(\text{U-Fe}) (+ 0.04 \text{ \AA})$ and $N(\text{U-Fe}) = 6$ (fixed) values have been reported for U incorporated
275 into Fe octahedral sites.¹⁵
276 We still need to consider possible U(IV) species incorporated in Fe_3O_4 . Kerisit et al. calculated
277 similar $R(\text{U-Fe1}) = 3.18 \text{ \AA}$ for U(V) and $R(\text{U-Fe1}) = 3.19 \text{ \AA}$ for U(IV) incorporated in Fe_3O_4 .
278 The $R(\text{U-O}) = 2.10 \text{ \AA}$ is much shorter for U(V) compared to $R(\text{U-O}) = 2.23 \text{ \AA}$ for U(IV) and
279 closer to the experimental results for the oxidized Um1a sample with $R(\text{U-O}) = 2.13 \text{ \AA}$ (cf.
280 section Redox states of U in the Fe_3O_4 nanoparticles exposed to air).⁵⁷ As we discuss below the
281 U(V) species in Um1 and Um1a are very similar but there is less interference with near U-O
282 shells for the Um1a compared to the Um1 samples since $\text{UO}_2/\text{UO}_{2+x}$ is oxidized to form U(VI)-yl

283 in the former. To the best of our knowledge there is no report for U(IV) incorporated in
284 octahedral Fe_3O_4 sites. Based on these evidences, we conclude that U(V) not U(IV) is more likely
285 to be incorporated in the structure of Fe_3O_4 . (cf. DFT calculations).

286 In contrast, UO_{2+x} species dominate in the Um10 sample. The $R(\text{U-O}2) = 2.26 \text{ \AA}$ and $R(\text{U-O}3) =$
287 2.41 \AA obtained from the EXAFS analyses for this sample are very similar to the reported values
288 for $\text{UO}_{2.17}$ - $\text{UO}_{2.20}$.⁵⁵ The authors describe strong variations of the $R(\text{U-O})$ in the first coordination
289 sphere as a function of x in UO_{2+x} . In our system $R(\text{U-O}2)$ changes as a function of the U
290 concentration due to the increasing contribution of the second U(V) species, whereas $R(\text{U-O}3)$
291 remains constant. Hence it is apparent that the proposed UO_{2+x} has similar stoichiometry in all
292 samples. Presence of UO_{2+x} in the Um1-Um10 samples is also demonstrated by the intense peak
293 at about 3.84 \AA characteristic for the scattering of the photoelectron from U atoms in the second
294 U coordination sphere. The $N(\text{U-U}1)$ vary within $5.8(8)$ - $2.4(8)$ in the Um10-Um1 series. The
295 coordination numbers are significantly smaller than those found for bulk UO_2 : $N(\text{U-O}) = 8$ and
296 $N(\text{U-U}) = 12$. This can be due to structural disorder and the large contribution of U surface atoms
297 in the small nanoparticles, resulting in destructive interference and thus in decreasing amplitudes
298 of the EXAFS.^{41, 48} However, it can be also explained by the fraction of incorporated U atoms
299 versus UO_{2+x} nanoparticles. There is a distinct trend in the coordination numbers. The $N(\text{U-U}1)$
300 and $N(\text{U-O}3)$ decrease, whereas $N(\text{U-Fe}1)$ increases going from Um10 to Um1 (Figure S11). We
301 assume that minor redox changes have occurred for the Um1 sample since the characteristic for
302 UO_{2+x} : $N(\text{U-O}3) = 1.8(2)$, $N(\text{U-U}1) = 2.4(8)$ and for U incorporated in magnetite: $N(\text{U-Fe}1) =$
303 $4.5(17)$ correspond to about 19 % of U(IV) and 81 % U(V) found also from the quantitative
304 analyses of the U M_4 HR-XANES data for 10 days aging of the samples. Correspondingly, if the
305 about 37 % U(VI) found for the Um10 sample aged for 10 days has reduced to U(IV) and if we
306 take into account the initial 0.7 % U(IV), the coordination numbers will be similar to those

307 reported for the 147 day aged Um10 sample: $N(\text{U-O3}) = 3.2$, $N(\text{U-U1}) = 5.8$. The coordination
308 numbers obtained from EXAFS analyses can have uncertainties up to 30 %. But since we
309 compare them in a system with systematic structural variations, the magnitude of the uncertainty
310 is significantly reduced.

311 TEM analyses clearly confirm our interpretation of the EXAFS data since it detects crystalline
312 UO_2 nanoparticles with size of about 4-5 nm (Figure 3A) possibly grown on the surface of the
313 Fe_3O_4 particles (Figure 3B) with lattice parameters very close to stoichiometric UO_2 . Due to the
314 relatively large uncertainty for the obtained lattice parameter ($a = 0.271 \pm 0.004$ nm) it is not
315 possible to distinguish between UO_2 and UO_{2+x} . Considering also the EXAFS results, we
316 conclude that they are both likely.

317 It is useful to discuss potential formation of U(IV), U(V) or U(VI) inner sphere complexes sorbed
318 on Fe_3O_4 . Indeed U(IV) inner-sphere complexes stable within a few months have been reported
319 to form on Fe_3O_4 surfaces; the $R(\text{U-O})$ is elongated and the $N(\text{U-O})$ is higher ($R(\text{U-O}) = 2.42$ Å,
320 $N(\text{U-O}) = 9$) compared to UO_2 ($R(\text{U-O}) = 2.35$ Å, $N(\text{U-O}) = 8$).⁵⁴ For this U(IV) sorbed species
321 almost no U-U coordination is found similarly to U(IV) sorbed onto a Ti substituted Fe_3O_4 .
322 Moreover $R(\text{U-Fe}) = 3.56$ - 3.59 Å are reported, which are significantly longer compared to the
323 distances found in our system, $R(\text{U-Fe1}) = 3.13$ - 3.19 Å. Indeed the $R(\text{U-O}) = 2.42$ Å is
324 comparable to the $R(\text{U-O3})$ for our Um10-Um3 samples (Table S4). However, our EXAFS
325 analyses report higher $N(\text{U-U})$ for the Um10 sample, $N(\text{U-U1}) = 5.8$, which is in a good
326 agreement with the crystalline $\text{UO}_2/\text{UO}_{2+x}$ particles found by TEM. Latta et al. showed that UO_2
327 nanoparticles, are formed for high U surface coverage for samples aged for several months
328 under anoxic conditions.⁵⁴ They found systematic change of the only one U-O and the U-U
329 distances as a function of the U concentration not observed for our system. We conclude that

330 formation of crystalline $\text{UO}_2/\text{UO}_{2+x}$ nanoparticles is much more probable compared to sorbed
331 U(IV) species.

332 The possibility for U(V) stabilized on Fe(II) containing mineral surfaces as an inner sphere
333 complex has been discussed;⁵⁸ however no exact structural model was described. The
334 stabilization of U(V) seems to be more likely in the form of mixed U(V)-U(VI) oxyhydroxide.⁵⁹
335 For this compound two very long $R(\text{U}-\text{O}_{\text{axial}}) = 2.41\text{-}2.44 \text{ \AA}$ and four shorter equatorial O ligands
336 $R(\text{U}-\text{O}_{\text{equat}}) = 2.06 \text{ \AA}$ are found. Our EXAFS results do not report U-O bond distances, which
337 correspond to the distance obtained for the equatorial ligands therefore this model does not seem
338 to be appropriate.

339 U(VI) complexes sorbed on Fe oxides have two axial O atoms at about $\sim 1.79 \text{ \AA}$, six equatorial O
340 atoms at about $\sim 2.38 \text{ \AA}$ and $N(\text{U}-\text{Fe}) \sim 2(5)$, $R(\text{U}-\text{Fe}) > 3 \text{ \AA}$.⁶⁰ Since we find $N(\text{U}-\text{Fe}) \sim 4.5$ and no
341 strong evidence for stabilization of uranyl, we conclude that the formation of U(VI)-yl is not
342 likely.

343 **DFT calculations.** The aim of the calculations is to verify if it is energetically favorable to
344 incorporate U(V) into a magnetite site. In the DFT calculations with periodic boundary
345 conditions we used a $2 \times 2 \times 2$ super cell of magnetite and replaced one Fe^{2+} and one Fe^{3+} by U^{5+}
346 and one vacancy ($\text{Fe}^{2+} + \text{Fe}^{3+} \rightarrow \text{U}^{5+} + \square$). The Fe^{2+} and Fe^{3+} were chosen to be close to each other,
347 hence the presence of the vacancy allows the substitution of Fe by U to relax more easily. Since
348 U(V) is an open shell system we carefully monitored the occupation of the 5f orbitals and the
349 orientation of the spin of this electron. U(V) can be incorporated into a Fe^{2+} or Fe^{3+} octahedral
350 site, since both cases are energetically very close to each other (cf. Figure 3C). We found that the
351 orientation of the spin is important. The spin of the 5f electron points in the opposite direction
352 compared to the spins of the two replaced Fe ions. For the $R(\text{U}-\text{O}2)$ and the $R(\text{U}-\text{Fe}1)$ we
353 calculated theoretical values of $2.15(3) \text{ \AA}$ and $3.18(4) \text{ \AA}$, respectively, which are in excellent

354 agreement with the experimental results, $R(\text{U-O}2) = 2.18 \text{ \AA}$ and $R(\text{U-Fe}1) = 3.18 \text{ \AA}$, respectively
355 (Table S4).

356 **Redox states of U in the Fe_3O_4 nanoparticles exposed to air.** In order to verify possible
357 existence of U(V) in octahedral Fe_3O_4 environment the Um1 sample aged for 147 days in Ar
358 atmosphere was exposed for 142 days (U M_4 HR-XANES) and for additional 84 days (U L_3
359 XANES and EXAFS) to air. The U M_4 HR-XANES spectrum of Um1a (142 days in air) is
360 depicted in Figure 4A. The shoulder characteristic for U(IV) is not visible, whereas features f'
361 and f'' typical for U(VI)-yl appear in the spectrum. The main peak maximum has an energy
362 position very similar to the spectrum of the Um1 sample aged for 10 days in Ar, which confirms
363 that the main redox state of U is U(V) (Figure 4A). After exposing this Um1a sample to
364 additional 84 days in air U L_3 XAS (XANES and EXAFS) spectra were recorded. The U L_3
365 XANES is not as informative as the U M_4 HR-XANES but it can help to verify if any substantial
366 changes of the U oxidation state has taken place. The energy positions of the WL and the post
367 edge absorption resonance of the U L_3 XANES spectra of the Um1 aged for 10 days and the
368 Um1a (226 days in air) samples are comparable, which is an indication that the majority of the
369 U(V) remains stable in the Um1a sample exposed to air for additional 84 days (Figure S6).
370 The FT-EXAFS spectra of the Um1a (226 days in air) and the Um1 (aged for 147 days in Ar)
371 samples are compared in Figure 4B. It is apparent that the peaks characteristic for U coordination
372 to O and Fe are preserved: $N(\text{U-O}2) = 2.8(2)$, $R(\text{U-O}2) = 2.13(1) \text{ \AA}$; $N(\text{U-O}3) = 0.8(2)$, $R(\text{U-O}3)$
373 $= 2.36(2) \text{ \AA}$ and $N(\text{U-Fe}1) = 6.2(17)$, $R(\text{U-Fe}1) = 3.19(1) \text{ \AA}$, whereas the peak describing the
374 coordination to U is absent in the FT-EXAFS Um1a spectrum. The U(IV) in the UO_{2+x} particles
375 is likely oxidized to U(VI)O_2^{2+} as suggested from the $R(\text{U-O}1) = 1.78(1) \text{ \AA}$ with $N(\text{U-O}1) =$
376 $0.7(1)$. The disappearance of the peak characteristic for U at about 3.84 \AA can be explained by
377 increased disorder during the partial oxidation of U leading to destructive interference of the

378 scattered photoelectron waves. Alternatively, the U-U coordination can disappear due to a phase
379 transformation to a U(VI) phase, which does not contain U atoms at this distance. We did not
380 find crystalline U containing phases for the Um1a sample by applying pXRD. The relatively
381 long-term stability (142 days) of U(V) upon exposure to air (Um1a) can be explained by its
382 incorporation into the octahedral sites of Fe_3O_4 , where it is possibly protected against oxidation.

383 **U redox transformation model.** We propose the conceptual model presented in the abstract
384 graphics. More than 90 % of initially added U(VI) has adsorbed, most likely on ferrihydrite^{16, 61}
385 which is formed in the first stage after Fe(III) titration by NaOH solution and later recrystallizes
386 to Fe_3O_4 through intermediate Fe (oxyhydr)oxide phases.²⁷

387 Part of U(VI) stays adsorbed onto the Fe_3O_4 after 10 days of ageing time. We suppose that the
388 U(V) species have incorporated into the structure of Fe_3O_4 during the formation of the
389 nanoparticles as suggested by the more symmetric local coordination environment compared to
390 uranyl and coordination to Fe. Minor formation of U(IV) in the form of $\text{UO}_2/\text{UO}_{2+x}$ or sorbed
391 onto the surface is also possible.

392 After 147 days the U(VI) species have undergone phase transformation and reduction to
393 $\text{UO}_2/\text{UO}_{2+x}$, whereas major part of the incorporated U(V) species is preserved. When exposed to
394 air for more than 142 days U(IV) oxidizes to U(VI), whereas U(V) remains stabilized
395 incorporated into octahedral sites of Fe_3O_4 .

396 The experimental results illustrate that reduction of U(VI) to U(IV) is likely to take place,
397 expected from geochemical calculations, with apparently the highest U(IV) fraction for the
398 sample with the highest uranium content (10000 ppm). The relative fractions of U(IV), U(V) and
399 U(VI) depend on the initial uranium concentration while the kinetics of the uranium redox
400 processes depends on the pH/redox conditions, $\text{Fe(II)}/\text{Fe}_{\text{TOT}}$ ratio as well as the rate of electron
401 transfer between Fe^{2+} and Fe^{3+} ions in the octahedral sublattice.

402 The present study demonstrates the capability of U M_4 HR-XANES to clearly distinguish three
403 different U redox states, U(IV), U(V) and U(VI), in one sample and shows also the potential to
404 identify redox states for other actinides. Previously, U(V) was observed in different Fe(III)
405 (oxyhydr)oxides.¹¹⁻¹⁷ Our observation that U(V) can also be stabilized in Fe_3O_4 , which is a mixed
406 Fe(II)/Fe(III) phase, suggests that the U(V) stabilization range can be extended to more reducing
407 conditions. When exposed to air, apparently, the surrounding mineral matrix is able to protect
408 U(V) against oxidation. This might explain the observation of significant U(V) fractions in redox
409 systems where predominantly U(IV) or U(VI) would be expected considering thermodynamic
410 calculations. This shows that there is a lack of kinetical data to reliably describe and predict
411 uranium speciation in such complex systems. Further studies of U interaction with Fe phases with
412 varying Fe(II)/Fe(III) ratios will be of interest extending the redox/pH conditions where U(V) can
413 be stabilized.

414 Notably for the discussion on the relevance of U(V) species in the environment, U $M_{4,5}$ HR-
415 XANES combined with EXAFS and other techniques appears to be a powerful spectroscopic
416 tool, which is able to provide distinct answers. Another aspect of future studies is to analyze
417 systems with lower, environmentally relevant U concentrations, e.g. < 100 ppm U, and to
418 investigate a representative U-Fe containing natural system with a varying set of geochemical
419 conditions leading to different U redox and immobilization/mobilization scenarios.

FIGURES

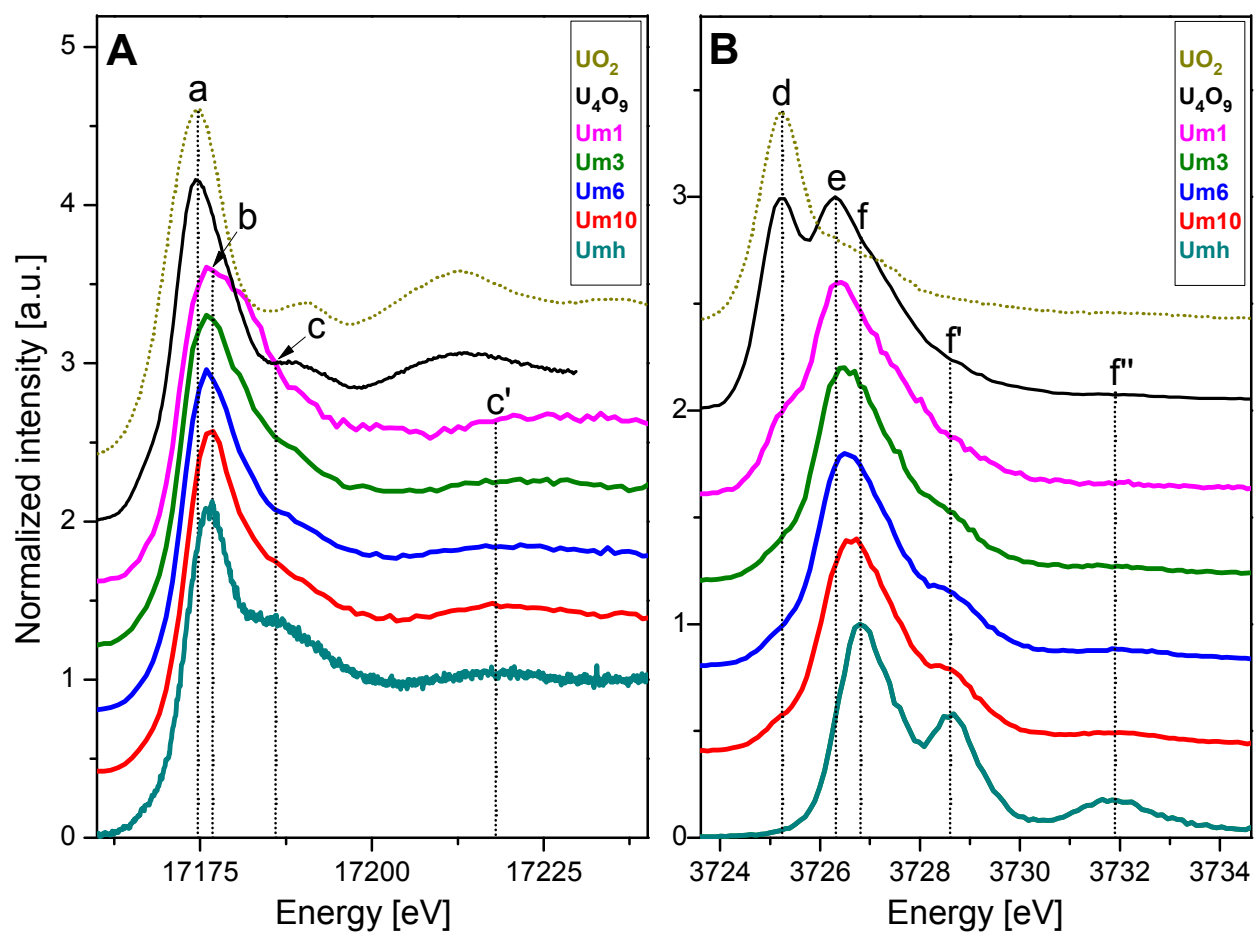


Figure 1. From bottom to top: U L₃ HR-XANES (A) and U M₄ HR-XANES (B) spectra of the Umh reference (U(VI) sorbed on maghemite for 55 days) and the Um10, Um6, Um3, Um1 samples aged for 10 days in anoxic conditions as well as the U₄O₉ and UO₂ references.

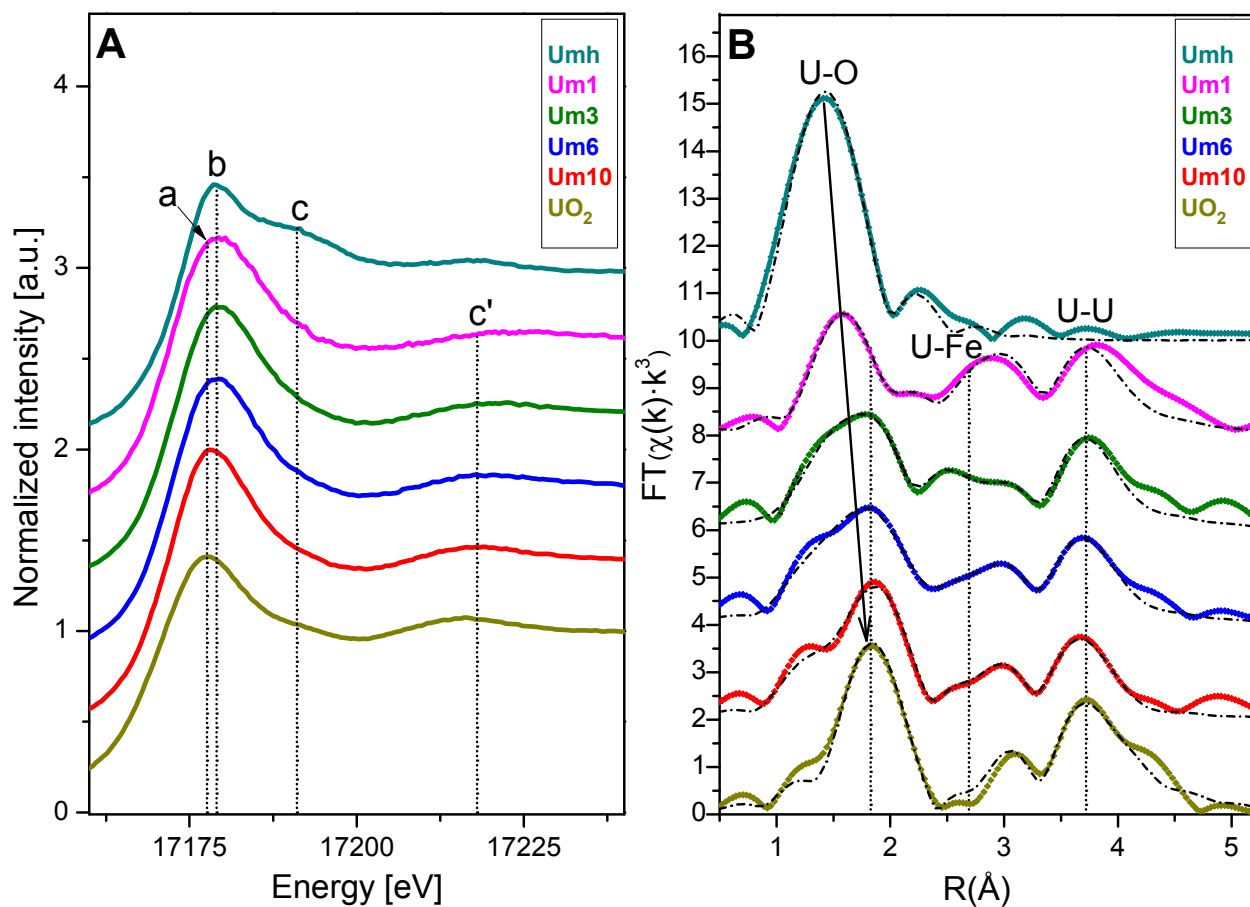


Figure 2. From bottom to top: U L₃ XANES (A) and FT-EXAFS spectra in R space (B) of the UO₂ reference and the Um10, Um6, Um3, Um1 samples aged for 147 days in anoxic conditions as well as the Umh reference (U(VI) sorbed on maghemite for 330 days). The FT-EXAFS and the best fit to the data are given in colored rhombs and in dash dot, respectively.

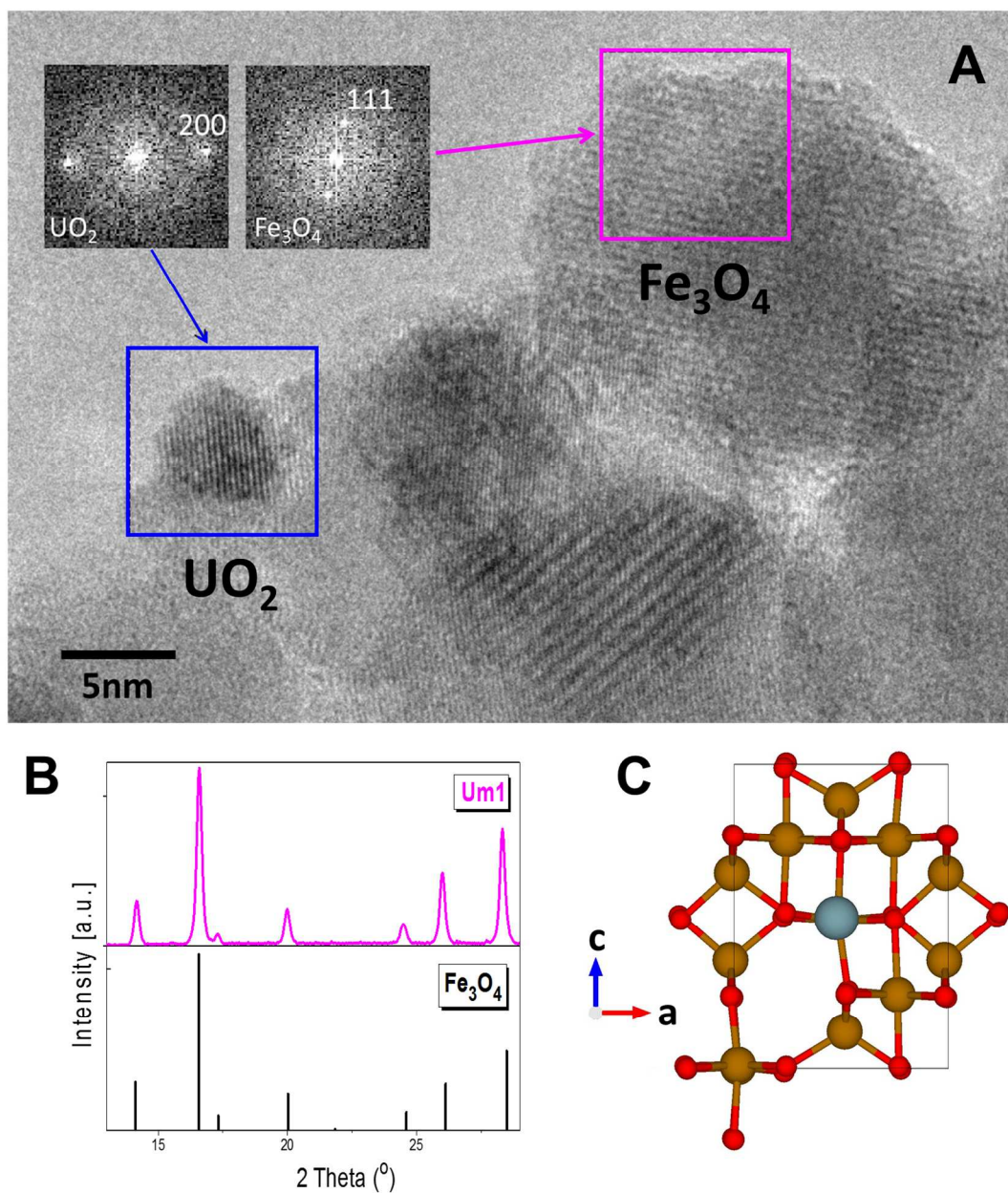


Figure 3. HR-TEM image of UO_2 nanocluster (blue box) and a Fe_3O_4 nanoparticle (magenta box) in the Um1 sample aged for 330 days in anoxic conditions (A). pXRD pattern of the Um1 sample aged for 480 days in anoxic conditions (top) and a reference pXRD pattern of Fe_3O_4 (ICSD 26410) (bottom) (B). U(V) incorporated into an octahedral iron site into the Fe_3O_4 structure as optimized by DFT; O atoms are in red, Fe atoms – brown and U atom – blue (C).

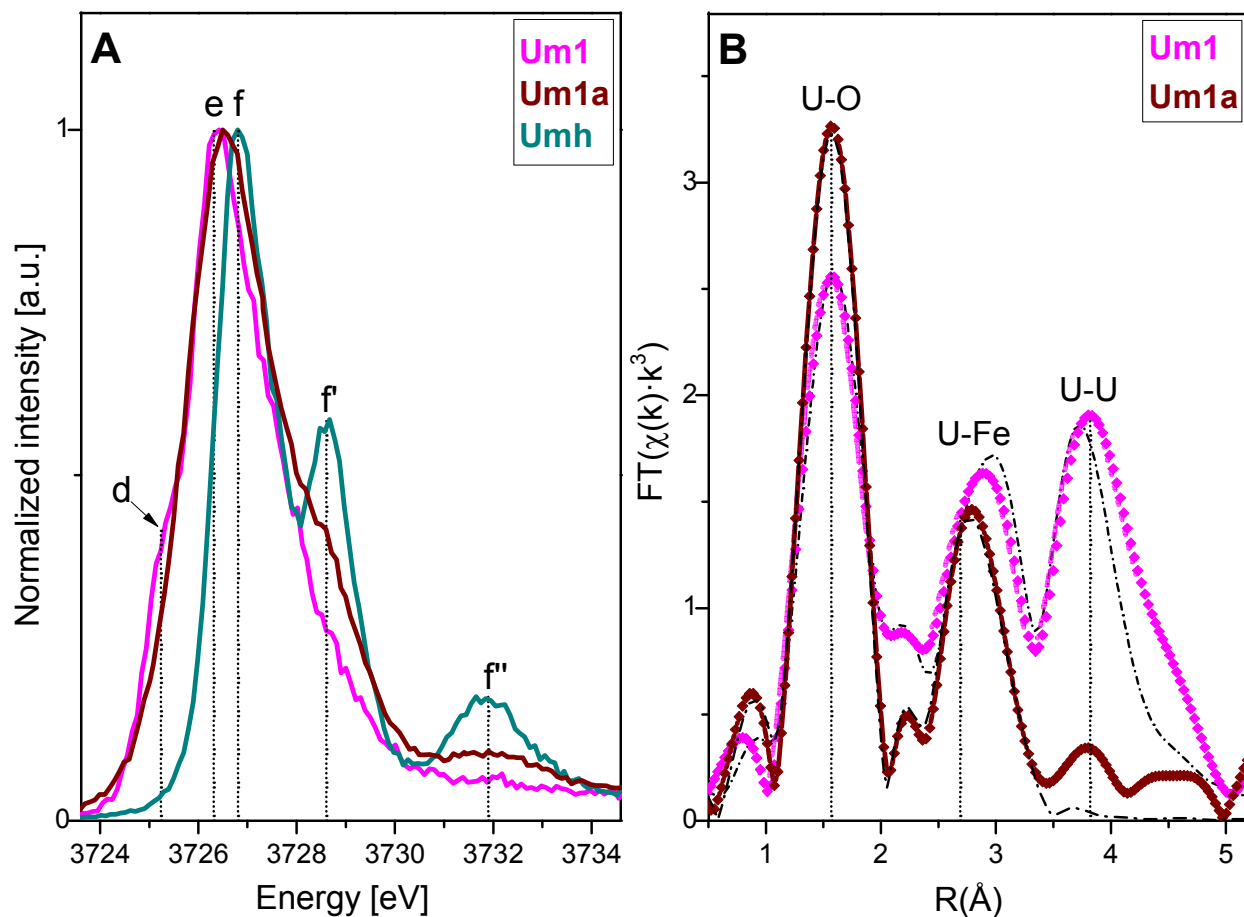


Figure 4. U M₄ HR-XANES spectra of the Um1 and Um1a samples as well as the Umh reference. The Um1 sample was aged for 10 days. The Um1a sample is the Um1 sample aged for 147 days exposed to air for additional 142 days (289 days total ageing time) (A). FT-EXAFS of the Um1 and Um1a samples. The Um1a sample is the Um1 sample aged for 147 days exposed to air for additional 226 days (373 days total ageing time) (B).

ASSOCIATED CONTENT

Supporting Information. Details on the preparation and characterization of the samples, the applied experimental as well as theoretical methods

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REFERENCES

1. Batuk, O. N.; Conradson, S. D.; Aleksandrova, O. N.; Boukhalfa, H.; Burakov, B. E.; Clark, D. L.; Czerwinski, K. R.; Felmy, A. R.; Lezama-Pacheco, J. S.; Kalmykov, S. N.; Moore, D. A.; Myasoedov, B. F.; Reed, D. T.; Reilly, D. D.; Roback, R. C.; Vlasova, I. E.; Webb, S. M.; Wilkerson, M. P., Multiscale Speciation of U and Pu at Chernobyl, Hanford, Los Alamos, McGuire AFB, Mayak, and Rocky Flats. *Environ Sci Technol* **2015**, *49*, (11), 6474-6484.
2. Schlegel, M. L.; Bataillon, C.; Benhamida, K.; Blanc, C.; Menut, D.; Lacour, J. L., Metal corrosion and argillite transformation at the water-saturated, high-temperature iron-clay interface: A microscopic-scale study. *Appl Geochem* **2008**, *23*, (9), 2619-2633.
3. Burns, P. C.; Finch, R. J., Wyartite: Crystallographic evidence for the first pentavalent-uranium mineral. *American Mineralogist* **1999**, *84*, (9), 1456-1460.
4. Dodge, C. J.; Francis, A. J.; Gillow, J. B.; Halada, G. P.; Eng, C.; Clayton, C. R., Association of uranium with iron oxides typically formed on corroding steel surfaces. *Environ Sci Technol* **2002**, *36*, (16), 3504-3511.
5. Duff, M. C.; Coughlin, J. U.; Hunter, D. B., Uranium co-precipitation with iron oxide minerals. *Geochim Cosmochim Acta* **2002**, *66*, (20), 3533-3547.
6. Latta, D. E.; Gorski, C. A.; Boyanov, M. I.; O'Loughlin, E. J.; Kemner, K. M.; Scherer, M. M., Influence of Magnetite Stoichiometry on U-VI Reduction. *Environ Sci Technol* **2012**, *46*, (2), 778-786.
7. O'Loughlin, E. J.; Kelly, S. D.; Cook, R. E.; Csencsits, R.; Kemner, K. M., Reduction of Uranium(VI) by mixed iron(II/iron(III) hydroxide (green rust): Formation of UO₂ nanoparticles. *Environ Sci Technol* **2003**, *37*, (4), 721-727.
8. O'Loughlin, E. J.; Kelly, S. D.; Kemner, K. M., XAFS Investigation of the Interactions of U-VI with Secondary Mineralization Products from the Bioreduction of Fe-III Oxides. *Environ Sci Technol* **2010**, *44*, (5), 1656-1661.
9. Suzuki, Y.; Kelly, S. D.; Kemner, K. M.; Banfield, J. F., Radionuclide contamination: Nanometre-size products of uranium bioreduction. *Nature* **2002**, *419*, (6903), 134-134.
10. Stewart, B. D.; Neiss, J.; Fendorf, S., Quantifying Constraints Imposed by Calcium and Iron on Bacterial Reduction of Uranium(VI). *Journal of Environmental Quality* **2007**, *36*, (2), 363-372.

11. Boland, D. D.; Collins, R. N.; Payne, T. E.; Waite, T. D., Effect of Amorphous Fe(III) Oxide Transformation on the Fe(II)-Mediated Reduction of U(VI). *Environ Sci Technol* **2011**, *45*, (4), 1327-1333.
12. Ilton, E. S.; Boily, J. F.; Buck, E. C.; Skomurski, F. N.; Rosso, K. M.; Cahill, C. L.; Bargar, J. R.; Felmy, A. R., Influence of Dynamical Conditions on the Reduction of U-VI at the Magnetite-Solution Interface. *Environ Sci Technol* **2010**, *44*, (1), 170-176.
13. Nico, P. S.; Stewart, B. D.; Fendorf, S., Incorporation of Oxidized Uranium into Fe (Hydr)oxides during Fe(II) Catalyzed Remineralization. *Environ Sci Technol* **2009**, *43*, (19), 7391-7396.
14. Ilton, E. S.; Pacheco, J. S. L.; Bargar, J. R.; Shi, Z.; Liu, J.; Kovarik, L.; Engelhard, M. H.; Felmy, A. R., Reduction of U(VI) incorporated in the structure of hematite. *Environmental Science and Technology* **2012**, *46*, (17), 9428-9436.
15. Marshall, T. A.; Morris, K.; Law, G. T. W.; W. Mosselmans, J. F.; Bots, P.; Roberts, H.; Shaw, S., Uranium fate during crystallization of magnetite from ferrihydrite in conditions relevant to the disposal of radioactive waste. *Mineralogical Magazine* **2015**, *79*, (6), 1265-1274.
16. Massey, M. S.; Lezama-Pacheco, J. S.; Jones, M. E.; Ilton, E. S.; Cerrato, J. M.; Bargar, J. R.; Fendorf, S., Competing retention pathways of uranium upon reaction with Fe(II). *Geochim Cosmochim Acta* **2014**, *142*, 166-185.
17. Boland, D. D.; Collins, R. N.; Glover, C. J.; Payne, T. E.; Waite, T. D., Reduction of U(VI) by Fe(II) during the Fe(II)-Accelerated Transformation of Ferrihydrite. *Environ Sci Technol* **2014**, *48*, (16), 9086-9093.
18. Vitova, T.; Kvashnina, K. O.; Nocton, G.; Sukharina, G.; Denecke, M. A.; Butorin, S. M.; Mazzanti, M.; Caciuffo, R.; Soldatov, A.; Behrends, T.; Geckeis, H., High energy resolution x-ray absorption spectroscopy study of uranium in varying valence states. *Phys Rev B* **2010**, *82*, (23), 235118-1-6.
19. Huber, F.; Schild, D.; Vitova, T.; Rothe, J.; Kirsch, R.; Schäfer, T., U(VI) removal kinetics in presence of synthetic magnetite nanoparticles. *Geochim Cosmochim Acta* **2012**, *96*, 154-173.
20. Kvashnina, K. O.; Butorin, S. M.; Martin, P.; Glatzel, P., Chemical State of Complex Uranium Oxides. *Physical Review Letters* **2013**, *111*, (25), 253002.
21. Popa, K.; Prieur, D.; Manara, D.; Naji, M.; Vigier, J.-F.; Martin, P. M.; Dieste Blanco, O.; Scheinost, A. C.; Prumann, T.; Vitova, T.; Raison, P. E.; Somers, J.; Konings, R. J. M., Further

insights into the chemistry of the Bi-U-O system. *Dalton Transactions* **2016**, 45, (18), 7847-7855.

22. Rothe, J.; Butorin, S.; Dardenne, K.; Denecke, M. A.; Kienzler, B.; Löble, M.; Metz, V.; Seibert, A.; Steppert, M.; Vitova, T.; Walther, C.; Geckeis, H., The INE-Beamline for actinide science at ANKA. *Review of Scientific Instruments* **2012**, 83, (4), 043105.

23. Vitova, T.; Green, J. C.; Denning, R. G.; Löble, M.; Kvashnina, K.; Kas, J. J.; Jorissen, K.; Rehr, J. J.; Malcherek, T.; Denecke, M. A., Polarization Dependent High Energy Resolution X-ray Absorption Study of Dicesium Uranyl Tetrachloride. *Inorganic Chemistry* **2015**, 54, (1), 174-182.

24. Walshe, A.; Pru; Vitova, T.; Baker, R. J., An EXAFS and HR-XANES study of the uranyl peroxides $[\text{UO}_2(\eta^2\text{-O}_2)(\text{H}_2\text{O})_2] \cdot n\text{H}_2\text{O}$ ($n = 0, 2$) and uranyl (oxy)hydroxide $[(\text{UO}_2)_4\text{O}(\text{OH})_6] \cdot 6\text{H}_2\text{O}$. *Dalton Transactions* **2014**, 43, (11), 4400-4407.

25. Rossberg, A.; Reich, T.; Bernhard, G., Complexation of uranium(VI) with protocatechuic acid - application of iterative transformation factor analysis to EXAFS spectroscopy. *Anal Bioanal Chem* **2003**, 376, (5), 631-638.

26. Baumgartner, J.; Dey, A.; Bomans, P. H. H.; Le Coadou, C.; Fratzl, P.; Sommerdijk, N. A. J. M.; Faivre, D., Nucleation and growth of magnetite from solution. *Nat Mater* **2013**, 12, (4), 310-314.

27. Jolivet, J. P.; Chaneac, C.; Tronc, E., Iron oxide chemistry. From molecular clusters to extended solid networks. *Chem Commun* **2004**, (5), 481-487.

28. Vayssieres, L.; Chaneac, C.; Tronc, E.; Jolivet, J. P., Size tailoring of magnetite particles formed by aqueous precipitation: An example of thermodynamic stability of nanometric oxide particles. *J Colloid Interf Sci* **1998**, 205, (2), 205-212.

29. Kvashnina, K. O.; Kvashnin, Y. O.; Butorin, S. M., Role of resonant inelastic X-ray scattering in high-resolution core-level spectroscopy of actinide materials. *Journal of Electron Spectroscopy and Related Phenomena* **2014**, 194, 27-36.

30. Cornell, R. M.; Schwertmann, U., *The Iron Oxides: Structure, Properties, Reactions, Occurrences and Uses*. Wiley: 2006.

31. Gauthier, C.; Sole, V. A.; Signorato, R.; Goulon, J.; Moguiline, E., The ESRF beamline ID26: X-ray absorption on ultra dilute sample. *J Synchrotron Radiat* **1999**, 6, 164-166.

32. Glatzel, P.; Bergmann, U., High resolution 1s core hole X-ray spectroscopy in 3d transition metal complexes—electronic and structural information. *Coordination Chemistry Reviews* **2005**, *249*, (1–2), 65-95.
33. Kvashnina, K. O.; Scheinost, A. C., A Johann-type X-ray emission spectrometer at the Rossendorf beamline. *J Synchrotron Radiat* **2016**, *23*, (3), 836-841.
34. Ankudinov, A. L.; Ravel, B.; Rehr, J. J.; Conradson, S. D., Real-space multiple-scattering calculation and interpretation of x-ray-absorption near-edge structure. *Phys Rev B* **1998**, *58*, (12), 7565-7576.
35. Ravel, B.; Newville, M., ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *J Synchrotron Radiat* **2005**, *12*, (4), 537-541.
36. Goettlicher, J.; Kotelnikov, A.; Suk, N.; Kovalski, A.; Vitova, T.; Steininger, R., Sulfur K X-ray absorption near edge structure spectroscopy on the photochrome sodalite variety hackmanite. *Z Kristallogr* **2013**, *228*, (3), 157-171.
37. Hammersley, A. P.; Svensson, S. O.; Hanfland, M.; Fitch, A. N.; Häusermann, D., Two-dimensional detector software: From real detector to idealised image or two-theta scan. *High Pressure Research* **1996**, *14*, (4-5), 235-248.
38. Kresse, G.; Furthmuller, J., Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys Rev B* **1996**, *54*, (16), 11169-11186.
39. Kresse, G.; Furthmuller, J., Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comp Mater Sci* **1996**, *6*, (1), 15-50.
40. Kresse, G.; Hafner, J., Ab-Initio Molecular-Dynamics for Open-Shell Transition-Metals. *Phys Rev B* **1993**, *48*, (17), 13115-13118.
41. Perdew, J. P.; Burke, K.; Ernzerhof, M., Generalized gradient approximation made simple. *Physical Review Letters* **1996**, *77*, (18), 3865-3868.
42. Blochl, P. E., Projector Augmented-Wave Method. *Phys Rev B* **1994**, *50*, (24), 17953-17979.
43. Kresse, G.; Joubert, D., From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys Rev B* **1999**, *59*, (3), 1758-1775.
44. Rollmann, G.; Rohrbach, A.; Entel, P.; Hafner, J., First-principles calculation of the structure and magnetic phases of hematite. *Phys Rev B* **2004**, *69*, (16), 165107-1-12.

45. Puigdomènech, I.; Colàs, E.; Grivé, M.; Campos, I.; García, D. In *A tool to draw chemical equilibrium diagrams using SIT: Applications to geochemical systems and radionuclide solubility*, Materials Research Society Symposium Proceedings, 2014; 2014; pp 111-116.
46. Soldatov, A. V.; Lamoen, D.; Konstantinović, M. J.; Van den Berghe, S.; Scheinost, A. C.; Verwerft, M., Local structure and oxidation state of uranium in some ternary oxides: X-ray absorption analysis. *Journal of Solid State Chemistry* **2007**, *180*, (1), 54-61.
47. Kosog, B.; La Pierre, H. S.; Denecke, M. A.; Heinemann, F. W.; Meyert, K., Oxidation State Delineation via U L-III-Edge XANES in a Series of Isostructural Uranium Coordination Complexes. *Inorganic Chemistry* **2012**, *51*, (14), 7940-7944.
48. Podkovyrina, Y.; Pidchenko, I.; Prüßmann, T.; Bahl, S.; Göttlicher, J.; Soldatov, A.; Vitova, T., Probing Covalency in the UO₃ Polymorphs by U M 4 edge HR- XANES. *Journal of Physics: Conference Series* **2016**, *712*, (1), 012092.
49. Pidchenko, I.; Green, J. C.; Fellhauer, D.; Bahl, S.; Prüßmann, T.; Bohnert, E.; Rothe, J.; Geckeis, H.; Vitova, T., Decrease of covalency in UO₂⁺. In preparation.
50. Nelin, C. J.; Bagus, P. S.; Ilton, E. S., Theoretical analysis of the U L₃-edge NEXAFS in U oxides. *RSC Advances* **2014**, *4*, (14), 7148-7153.
51. Van den Berghe, S.; Verwerft, M.; Laval, J. P.; Gaudreau, B.; Allen, P. G.; Van Wyngarden, A., The Local Uranium Environment in Cesium Uranates: A Combined XPS, XAS, XRD, and Neutron Diffraction Analysis. *Journal of Solid State Chemistry* **2002**, *166*, (2), 320-329.
52. Bès, R.; Rivenet, M.; Solari, P. L.; Kvashnina, K. O.; Scheinost, A. C.; Martin, P. M., Use of HERFD-XANES at the U L₃- and M₄-Edges to Determine the Uranium Valence State on [Ni(H₂O)₄]₃[U(OH,H₂O)(UO₂)₈O₁₂(OH)₃]. *Inorganic Chemistry* **2016**, *55*, (9), 4260-4270.
53. Pidchenko, I.; Heberling, F.; Kvashnina, K. O.; Finck, N.; Schild, D.; Bohnert, E.; Schäfer, T.; Rothe, J.; Geckeis, H.; Vitova, T., Aqueous U(VI) interaction with magnetite nanoparticles in a mixed flow reactor system: HR-XANES study. *Journal of Physics: Conference Series* **2016**, *712*, (1), 012086.
54. Latta, D. E.; Mishra, B.; Cook, R. E.; Kemner, K. M.; Boyanov, M. I., Stable U(IV) Complexes Form at High-Affinity Mineral Surface Sites. *Environ Sci Technol* **2014**, *48*, (3), 1683-1691.

55. Conradson, S. D.; Manara, D.; Wastin, F.; Clark, D. L.; Lander, G. H.; Morales, L. A.; Rebizant, J.; Rondinella, V. V., Local structure and charge distribution in the $\text{UO}_2\text{-U}_4\text{O}_9$ system. *Inorganic Chemistry* **2004**, *43*, (22), 6922-6935.
56. Debets, P. C., Structure of Beta- UO_3 . *Acta Crystallogr* **1966**, *21*, 589-&.
57. Kerisit, S.; Felmy, A. R.; Ilton, E. S., Atomistic Simulations of Uranium Incorporation into Iron (Hydr)Oxides. *Environ Sci Technol* **2011**, *45*, (7), 2770-2776.
58. Ilton, E. S.; Haiduc, A.; Cahill, C. L.; Felmy, A. R., Mica surfaces stabilize pentavalent uranium. *Inorganic Chemistry* **2005**, *44*, (9), 2986-2988.
59. Belai, N.; Frisch, M.; Ilton, E. S.; Ravel, B.; Cahill, C. L., Pentavalent Uranium Oxide via Reduction of $[\text{UO}_2](2+)$ Under Hydrothermal Reaction Conditions. *Inorganic Chemistry* **2008**, *47*, (21), 10135-10140.
60. Singer, D. M.; Chatman, S. M.; Ilton, E. S.; Rosso, K. M.; Banfield, J. F.; Waychunas, G. A., Identification of Simultaneous U(VI) Sorption Complexes and U(IV) Nanoprecipitates on the Magnetite (111) Surface. *Environ Sci Technol* **2012**, *46*, (7), 3811-3820.
61. Payne, T. E. L., G.R.; Waite, T.D. , Uranium(VI) sorption on model minerals. In *Sorption of Metals by Geomedia*, Jenne, E. A., Ed. 1998; pp 75-97.

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