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Complete List of Authors:	 Pidchenko, Ivan; Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal Kvashnina, Kristina; European Synchrotron Radiation Facility, Yokosawa, Tadahiro; Institute for Nuclear Waste Disposal, Karlsruhe Institute of Technology, Finck, Nicolas; Institute for Nuclear Waste Disposal, Bahl, Sebastian; Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal Schild, Dieter; Karlsruhe Institute of Technology (KIT), Institute for Nuclear Waste Disposal (INE) Polly, Robert; Research Centre Karlsruhe, Institute for Nuclear Waste Disposal Bohnert, Elke; Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal Bohnert, Elke; Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal Bohnert, Elke; Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal Bohnert, Elke; Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal Rossberg, Andre; Forschungszentrum Dresden-Rossendorf, Institute of Radiochemistry Göttlicher, Jörg; Forschungszentrum-Karlsruhe, Institute for Synchrotron Radiation Dardenne, Kathy; Institute for Nuclear Waste Disposal, Karlsruhe Institute of Technology Rothe, Jörg; Karlsruhe Institute of Technology, Institut für Nukleare Entsorgung Schäfer, Thorsten; Karlsruhe Institute of Technology (KIT), Institute for Nuclear Waste Disposal (INE) Geckeis, Horst; Karlsruhe Institute of Technology (KIT), Institute for Nuclear Waste Disposal (INE) Vitova, Tonya; Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal ,

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Uranium Redox Transformations after U(VI) Coprecipitation with Magnetite Nanoparticles

Ivan Pidchenko,^a Kristina O Kvashnina,^{b,c} Tadahiro Yokosawa,^a Nicolas Finck,^a Sebastian Bahl,^a Dieter Schild,^a Robert Polly,^a Elke Bohnert,^a André Rossberg,^c Jörg Göttlicher,^d Kathy Dardenne,^a Jörg Rothe,^a Thorsten Schäfer,^a Horst Geckeis,^a Tonya Vitova,^{a,*}

^a Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal (INE), P.O. 3640, D-76021 Karlsruhe, Germany
^b European Synchrotron Radiation Facility (ESRF), CS40220, 38043 Grenoble Cedex 9, France
^c Helmholtz-Zentrum Dresden-Rossendorf, Institute of Resource Ecology, P.O. Box 510119, D-01314 Dresden, Germany
^d Karlsruhe Institute of Technology, Institute for Photon Science and Synchrotron Radiation (IPS), P.O. 3640, D-76021 Karlsruhe, Germany

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 uranium loadings varying from 1000 to 10000 ppm are investigated by X-ray absorption 3 spectroscopy (XAS). It is demonstrated that the U M_4 high energy resolution X-ray absorption 4 near edge structure (HR-XANES) method is capable to clearly characterize U(IV), U(V) and 5 U(VI) existing simultaneously in the same sample. The contributions of the three different 6 uranium redox states are quantified with the iterative transformation factor analysis (ITFA) 7 method. U L₃ XAS and transmission electron microscopy (TEM) reveal that initially sorbed 8 U(VI) species recrystallize to non-stoichiometric UO_{2+x} nanoparticles within 147 days when 9 10 stored under anoxic conditions. These U(IV) species oxidize again when exposed to air. U M₄ 11 HR-XANES data demonstrate strong contribution of U(V) at day 10 and that U(V) remains stable over 142 days under ambient conditions as shown for magnetite nanoparticles containing 1000 12 ppm U. U L₃ XAS indicates that this U(V) species is protected from oxidation likely incorporated 13 into octahedral magnetite sites. XAS results are supported by density functional theory (DFT) 14 calculations. Further characterization of the samples include powder X-ray diffraction (pXRD), 15 scanning electron microscopy (SEM) and Fe 2p X-ray photoelectron spectroscopy (XPS). 16

17 INTRODUCTION

Uranium is the main constituent of spent nuclear fuel (SNF), but it can be also found in high quantities in actinide (An) contaminated sites.¹ Developing the safety case for the safe disposal of radioactive waste requires mechanistic understanding of the interaction of the waste products with repository components. In case of water accessing the waste container, radionuclides will react with the corrosion products, which potentially represent a very relevant reactive barrier retaining pollutants release in the repository near field. Of particular interest is the detailed understanding of An interactions with iron (Fe) oxides, e.g. magnetite (Fe₃O₄) 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 Fe ₃ O ₄ 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)/Fe ₃ O ₄ 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 L ₃ 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

the spectra for low uranium contents. XPS has high surface sensitivity and is performed in ultra-49 high vacuum, which can lead to potential changes of the samples. To handle these challenges, 50 complementary highly sensitive techniques are needed for thorough characterization of the U 51 redox states in such systems. The high energy resolution XANES (HR-XANES) method at the U 52 53 M_{4.5} absorption edges was demonstrated to be very valuable for studies related to U redox state analysis in complex uranium systems containing mixed U redox states.^{20, 21} The U M₄ HR-54 XANES experiments need to be performed in He environment comprising the sample, analyzing 55 crystals and detector in order to avoid loss of intensity by scattering and absorption of photons in 56 air. Unlike XPS, vacuum conditions are not necessary. The samples can be investigated in the 57 form of solids, wet pastes, suspensions or liquids. U M_{4.5} HR-XANES takes a great advantage 58 over the conventional U L₃ XANES. Reduced core-hole lifetime broadening results in better-59 resolved spectral features allowing more precise redox state analysis. Due to the dipole selection 60 rule ($\Delta l = \pm 1$) the electrons are excited with high probability from U $3d_{3/2}$ to U 5f unoccupied 61 states. Therefore the U M₄ HR-XANES technique is also a direct probe of the unoccupied U 5f 62 valence states, which play a significant role in the chemical bonding of the An elements.²⁰⁻²⁴ 63 In the present study we investigated the U redox states and speciation in the final product formed 64 by co-precipitation of U(VI) with Fe₃O₄ for variable U loadings (1000-10000 ppm). The U L_3/M_4 65 66 HR-XANES and U L₃ XANES/EXAFS as well as transmission electron microscopy (TEM) are applied. Scanning electron microscopy (SEM), X-ray powder diffraction (pXRD), Fe 2p_{3/2} XPS, 67 geochemical calculations and density functional theory (DFT) are used to characterize the U 68 containing Fe₃O₄ samples. The main aim is to verify the presence of U(V) in this system. A long-69 term study of samples kept under anoxic (up to 480 days) and oxidizing conditions (up to 226 70 days) was performed to elucidate the stability of the potential U(V) species in the Fe₃O₄ 71 72 nanoparticles. We demonstrate that the applied U M₄ HR-XANES method is capable of detecting

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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

Preparation of the samples. MilliQ-H₂O was used for the preparation of all samples. To remove 77 dissolved O₂ and CO₂ MilliQ-H₂O was bubbled for several hours with Ar outside and then for at 78 least one hour inside an argon (Ar) glovebox. Uranium containing Fe₃O₄ nanoparticles were 79 synthesized by direct precipitation ²⁶⁻²⁸ inside an Ar glovebox equipped with pH, E_h electrodes 80 and a dropping funnel using the following procedure: to a 50 mL Teflon container the calculated 81 amounts of aqueous FeCl₃, FeCl₂ and an aliquot of aqueous U(VI)O₂Cl₂ (1000, 3000, 6000 and 82 10000 ppm U: Um1-Um10 samples) were added followed by dropwise addition of 0.5 M NaOH 83 (Backer, CO_2 free) to pH = 7.5-8.0. The suspension was stirred overnight, pH and E_h values were 84 recorded and pH was adjusted if necessary by adding 0.1 M NaOH. All samples were then stored 85 in the form of suspension in the Ar glovebox. The UO₂ (several μ m particle size), U₄O₉ (used 86 from^{20, 29}) and 3000 ppm U(VI) adsorbed onto maghemite (γ -Fe₂O₃, spectra are named Umh) 87 serve as reference compounds. The γ -Fe₂O₃ was prepared by heating freeze-dried magnetite 88 nanoparticles at 200 °C during 2 hours in air.³⁰ 3000 ppm U as U(VI)O₂Cl₂ was then adsorbed on 89 the γ -Fe₂O₃. More than 99 % of U(VI) was adsorbed after 50 days as determined with inductively 90 coupled plasma mass-spectrometry (ICP-MS). Experimental details for U, Fe and salt 91 concentrations as well as pH, E_h measurements are given in Table S1. 92 For the U L_3/M_4 HR-XANES experiments, solids were separated from supernatant using a Nd 93 magnet. The supernatant was decanted and the solids were used in the form of a wet paste. All 94 samples were prepared in an Ar glovebox at 1-2 ppm O₂ level and less than 1 ppm CO₂. An inert 95 gas Plexiglas sample holder comprising a double containment (two separated 10 µm 96

polypropylene films) has been designed and used for the spectroscopic measurements. To avoid 97 contact of the samples with air they were transported one day prior to the experiments in a gas 98 tight aluminum cylinder filled with Ar and opened very shortly prior to the experiments. 99 For the U L₃ XAS experiments, subsamples Um1-Um10 from the same batch were separated 100 101 using a Nd magnet after 147 days of ageing in the Ar glovebox. After these experiments the Um1 sample was placed in a non-hermetically closed plastic vial and kept under ambient, aerobic 102 conditions (Um1a sample). The Um1a sample was investigated with the U M₄ HR-XANES (142) 103 days in air, total 289 days) and with the U L₃ XAS (XANES and EXAFS) techniques (226 days 104 in air, total 373 days). 105 X-ray absorption spectroscopy (XAS). U L₃/M₄ HR-XANES experiments were performed at 106 the ID26 beamline, ESRF, Grenoble, France³¹ (Um1-Um10) and at the INE-Beamline, ANKA, 107 Karlsruhe, Germany²² (Um1a) with Johann type X-ray emission spectrometers.^{24, 32, 33} The U L₃ 108 XAS (XANES and EXAFS) experiments were performed in fluorescence mode using a five 109 110 element Ge solid state fluorescence detector (Canberra) at the INE-Beamline. The ATHENA and ARTEMIS program parts of the IFFEFIT program package were used for data reduction and 111 analyses of the EXAFS spectra.^{34, 35} Details on the experiments, the quantitative U oxidation 112 states analyses of the U M₄ HR-XANES spectra with the ITFA method for the 10 day aged 113 samples and the EXAFS analyses are given in the Supporting Information (SI). 114 Additional characterization methods. High resolution-TEM (HR-TEM) and SEM images were 115 recorded with a FEI Tecnai G2 F20 X-TWIN instrument operated at 200 kV and a FEI Quanta 116 650 FEG ESEM, respectively. pXRD patterns were measured with laboratory based Bruker AXS 117 D8 powder diffractometer and at the SUL-X-Beamline (ANKA, Karlsruhe, Germany) (SI).³⁶ The 118 FIT2D and DIFFRAC.EVA V3.1 programs were used to analyze the data.³⁷ 119



- 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,

$$128 \quad \mathrm{Fe}^{2+} + 2\mathrm{Fe}^{3+} + 8\mathrm{OH}^{-} \to \mathrm{Fe}_{3}\mathrm{O}_{4} \downarrow + 4\mathrm{H}_{2}\mathrm{O} \tag{1}$$

Measured E_h-pH values for samples containing 1000 ppm U (Um1) and 10000 ppm U (Um10) 129 are located inside the stability field of Fe₃O₄ according to the Fe Pourbaix diagram (Figure S1A); 130 redox conditions of the samples comprising 3000 ppm U (Um3) and 6000 ppm U (Um6) are 131 placed at the border of $Fe_3O_4 - FeO(OH)(cr)$ (goethite) stability fields.⁴⁵ E_b-pH conditions are 132 such ($E_{\rm h} = -210 - -390$ mV; pH = 7.5-8.0) that subsequent reduction of U(VI) to U(IV) would be 133 expected according to the U Pourbaix diagrams (Figures S1B, C). SEM images (Figure S2) and 134 135 powder XRD (pXRD) patterns (Figure S3) reveal that crystalline Fe₃O₄ nanoparticles with octahedral shape and a size of 15-40 nm are formed. Energy dispersive X-ray analysis (EDX) 136 does not reveal segregated uranium precipitates. No goethite or any other Fe containing 137 crystalline phases are found. The Fe(II) content is slightly below that of stoichiometric Fe_3O_4 138 (Fe(II)/Fe_{TOT} = 0.33) at Fe(II)/Fe_{TOT} = 0.28 ± 3 % for all samples (Um1-Um10) aged for 310 139 days as indicated by the reduced intensity of the Fe(II) $2p_{3/2}$ peak of the Fe 2p XPS spectra 140 (Figure S4). There is no clear trend in the level of Fe(II) oxidation as a function of the U(VI) 141

Redox states of U in the Fe₃O₄ nanoparticles aged for 10 days. We characterized the U redox

142 concentration. In view of the low U/Fe mass ratios (0.0014-0.014), this is indeed not to be143 expected.

144

state in the Um1-Um10 samples aged in inert atmosphere for 10 days with the U L₃ and M₄ HR-145 XANES spectroscopy techniques. The U L₃ and M₄ HR-XANES spectra of the Um1-Um10 146 samples are depicted in Figures 1A and 1B, respectively. 147 The X-ray absorption spectra typically shift to higher energies by increasing the U redox state 148 due to the reduced screening of the $2p_{3/2}$ (L₃)/3d_{3/2} (M₄) core-hole by the decreased electronic 149 charge density on the U atoms. Smaller energy shifts of about ± 0.5 eV can be induced by 150 variations of the electronegativity of the bonding partner, changes in symmetry, short and long 151 range atomic order etc., for the same U redox state as suggested by U L₃ XANES studies.^{46, 47} 152 One exception of the general trend are the U L₃ XANES spectra of U(V) and U(VI) forming short 153 (< 1.9 Å) axial bonds with two O atoms $(UO_2^+/UO_2^{2+}, U(V)/U(VI)-yI)$; the maxima of the most 154 intense absorption resonance (white line, WL) of the U(V)-yl and UO₂ spectra have similar 155 energy positions.¹⁹ The WL of the U(VI)-vl spectrum is only slightly shifted to higher energy and 156 it can potentially have the same energy position as e.g. U(V) species with more symmetric 157 coordination environments associated with loss of short uranyl bonds, i.e. uranate type of U(V)158 species. This effect is induced by the large electronic density in the vicinity of U due to the strong 159 covalent bond of U(V)/U(VI) with the two axial O atoms. Such anomalous behavior is not 160 observed for U M_{4.5} HR-XANES spectra. Energy shifts within a range of \pm 0.1 eV can be caused 161 by differences in short and long range atomic order around the absorbing atom as for example 162 observed for different UO₃ phases, but the spectra shift to higher energies for higher U oxidation 163 states.^{21, 48} For example the energy shift between UO₂ and U(V)-yl ($[U(V)O_2(CO_3)_3]^5$) is ~1.2 164

185

165 eV, whereas between U(V)-yl and U(VI)-yl ($[U(V)O_2(CO_3)_3]^{5-}$ and $[U(VI)O_2(CO_3)_3]^{4-}$) is ~1.0 166 eV.⁴⁹

The WL of the U L₃ HR-XANES spectrum of the Um10 sample is located at similar energy 167 position as the WL of the spectrum of Umh. U has oxidation state U(VI) in the Umh sample. In 168 169 addition, the feature marked with line c clearly visible in the U L₃ HR-XANES Umh and Um10 spectra (Figure 1A) is characteristic for the $U(VI)O_2^{2+}/U(V)O_2^{+}$ entity. These results suggest 170 predominant U(VI)-yl contribution in the Um10 sample. The absorption resonance marked with 171 line c becomes less intense in the spectra of the Um6-Um3 samples and it diminishes in the 172 spectrum of the Um1 sample. These spectra suggest that the Um1 sample if at all contains low 173 amount of uranyl species. In addition, the WL and the post edge absorption resonance marked 174 with line c' become broader and asymmetric from the Um10 to the Um1 spectrum. Such 175 asymmetric WLs have been previously described as being characteristic for uranate type of 176 U(V)/U(VI) species.^{19, 46, 50, 51} However it can not be excluded that this U species dominant in the 177 Um1 sample has redox state (IV). The local symmetry of these U(V)/U(IV) species should be 178 rather different compared to the U(V)/U(IV) in U_4O_9 since there is no resemblance between the 179 Um1 and the U₄O₉ spectra. It is clear that the U L₃ HR-XANES spectra are more sensitive to 180 small structural and oxidation states changes compared to the conventional U L₃ XANES.^{18, 52} 181 But the method is still limited by large core-hole lifetime broadening effects and does not allow 182 to reliably identify and quantify the U(IV), U(V) and U(VI) anticipated to be simultaneously 183 present in the samples. 184

Additional information on the U redox states is obtained by applying the U M₄ HR-XANES

method. Figure 1B depicts the U M_4 HR-XANES spectra of the Um1-Um10 samples and UO₂,

- 187 U_4O_9 as well as Umh for comparison. U_4O_9 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

spectrum of U_4O_9 (Figure 1B). The main absorption peak f of the Umh spectrum is shifted by ~ 189 0.4 eV to higher energies as compared to peak e and it is assigned to U(VI). Spectral features f 190 and f" are also typical for U(VI)-yl ions with short (~1.77-1.91 Å) trans-dioxo bonds.^{23, 48, 53} 191 These features exist for U(V)-vl species but are considerably shifted ($f' \sim 0.6$ and $f'' \sim 2.5$ eV) 192 towards the main peak.⁴⁹ 193 Much more clear compared to the U L₃ HR-XANES, the U M₄ HR-XANES spectrum obtained 194 for the Um1 sample demonstrates major contributions of U(V) (peak e) and minor fraction of 195 196 U(IV) (peak d) (Figure 1B). It is also evident that the intensity of feature d increases while moving from the Um10 to the Um1 spectrum, the energy position of feature e shifts to lower 197 energies and features f' and f'' lose intensity. These spectral changes imply that the relative 198 contribution of U(VI) decreases, whereas the U(IV) content rises going from 10000 ppm U 199 (Um10) to 1000 ppm U (Um1) in the samples (Figure 1B). 200 Quantification of the U redox states. We performed quantitative analysis of the U M₄ HR-201 XANES spectra by the ITFA method.²⁵ ITFA is used to decompose the spectral mixtures into the 202 spectra and the fractions of the components (Figure S5). The experimental spectra can be 203 sufficiently reproduced (Figure S5A) by using linear combinations of the three ITFA-extracted 204 component spectra (Figure S5B), so that the residual is similar to the expected experimental 205

error. Only the first three eigenvectors show a signal while the eigenvectors 4, 5 and 6 do notcontribute to the data (Figure S5C), hence only three components are necessary to describe the

variations in the spectral mixtures. The extracted component spectra corespond to the U(IV),

209 U(V) and U(VI) redox states. The analysis shows that the Um1 and Um10 samples contain 19 %

210 U(IV), 81 % U(V) and 0.7 % U(IV), 62.3 % U(V), 37 % U(VI), respectively (Table S3). The U

211 M₄ HR-XANES technique and the ITFA approach are clearly capable of detecting and

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

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

days. We performed U L₃ XAS (XANES and EXAFS) studies for the magnetite suspensions

containing U stored for 147 days in anoxic conditions. For technical reasons, the redox states of

U in the Um1, Um3, Um6 and Um10 samples could not be analyzed with the U M_4 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

positions of the WLs and the general shapes of the spectra of the Um10 sample and UO_2 are very

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

energies compared to UO₂ going from the Um10 to the Um1 sample (lines a and b in Figure 2A).

The WL becomes broader and the post-edge absorption resonance at ~17218 eV transforms from

a single asymmetric (c') to a broad peak shifted to higher energies observed also for the U L_3 HR-

226 XANES spectra of the 10 days aged samples (Figure 1A). We obtain additional insights from the

comparison of the conventional U L₃ XANES spectra measured for the Um1 samples aged for 10

and 147 days (Figure S6). The U L₃ XANES for the Um1 sample aged for 147 days is shifted

 ~ 2.5 eV to lower energies compared to the spectrum of the sample aged for 10 days, which is an

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

oxidation state of U in the Um1 sample aged for 147 days is the U(V) species found for the 10

days aged Um1 sample. U(VI) was not found for the 10 day aged Um1 sample by the ITFA U M_4

edge HR-XANES analyses and since the Um1-Um10 samples were handled in the same way, i.e.

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

therefore might assume that U in our samples exists mainly as non-stoichiometric UO_{2+x} 259 containing mixed U redox states. However, the trend for these two main U-O distances is 260 reversed compared to our EXAFS results since R-O2 and R-O3 grow as a function of the 261 increasing non-stoichiometric oxygen in UO_{2+x} with R(U-O2) = 2.22-2.26 Å and R(U-O3) = 2.36-262 2.42 Å.⁵⁵ This can be explained by the presence of a second U site in our samples in addition to 263 U(IV)/U(V)/U(VI) constituents of UO_{2+x} particles. This U species becomes more relevant at low 264 uranium concentration (1000 ppm U), which agrees with the results from the U L₃ XANES data. 265 The R(U-O2) = 2.18 Å for the Um1 sample is within the range R = 2.05-2.20 Å reported in the 266 literature as typical for U(V) compounds.¹² These EXAFS results do not contradict to the 267 assumption that the U(V) found in the Um1 10 days aged sample is at least partially preserved. 268 This potential U(V) species is likely coordinated by Fe as the best fits to the FT-EXAFS spectra 269 reveal. This is based on the finding that coordination of U to Fe atoms is more prominent for the 270 271 Um1 compared to the Um10 sample. Two U-Fe interatomic distances are resolved: $N(U-Fe_1) =$ 0.6(3), R(U-Fe1) = 3.13(3) Å in Um10 and N(U-Fe1) = 4.5(17), R(U-Fe1) = 3.19(1) Å in Um1. A 272 U-Fe2 shell with a minor contribution (N = 0.5(3)-1.0(8)) is modeled too (Table S4). Somewhat 273 274 longer R(U-Fe) (+ 0.04 Å) and N(U-Fe) = 6 (fixed) values have been reported for U incorporated into Fe octahedral sites.¹⁵ 275 We still need to consider possible U(IV) species incorporated in Fe₃O₄. Kerisit et al. calculated 276 similar R(U-Fe1) = 3.18 Å for U(V) and R(U-Fe1) = 3.19 Å for U(IV) incorporated in Fe₃O₄. 277 The R(U-O) = 2.10 Å is much shorter for U(V) compared to R(U-O) = 2.23 Å for U(IV) and 278 closer to the experimental results for the oxidized Um1a sample with R(U-O) = 2.13 Å (cf. 279

- 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
- shells for the Um1a compared to the Um1 samples since UO_2/UO_{2+x} is oxidized to form U(VI)-yl

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

298

- In contrast, UO_{2+x} species dominate in the Um10 sample. The R(U-O2) = 2.26 Å and R(U-O3) =
- 287 2.41 Å obtained from the EXAFS analyses for this sample are very similar to the reported values
- for $UO_{2.17}$ - $UO_{2.20}$.⁵⁵ The authors describe strong variations of the R(U-O) in the first coordination
- sphere as a function of x in UO_{2+x} . In our system R(U-O2) changes as a function of the U
- 290 concentration due to the increasing contribution of the second U(V) species, whereas R(U-O3)
- remains constant. Hence it is apparent that the proposed UO_{2+x} has similar stoichiometry in all samples. Presence of UO_{2+x} in the Um1-Um10 samples is also demonstrated by the intense peak
- at about 3.84 Å characteristic for the scattering of the photoelectron from U atoms in the second
- U coordination sphere. The N(U-U1) 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 UO₂: N(U-O)= 8 and
- N(U-U) = 12. This can be due to structural disorder and the large contribution of U surface atoms
- in the small nanoparticles, resulting in destructive interference and thus in decreasing amplitudes
- versus UO_{2+x} nanoparticles. There is a distinct trend in the coordination numbers. The N(U-U1)

of the EXAFS.^{41, 48} However, it can be also explained by the fraction of incorporated U atoms

- and N(U-O3) decrease, whereas N(U-Fe1) increases going from Um10 to Um1 (Figure S11). We
- assume that minor redox changes have occurred for the Um1 sample since the characteristic for
- UO_{2+x} : N(U-O3) = 1.8(2), N(U-U1) = 2.4(8) and for U incorporated in magnetite: N(U-Fe1) =
- 4.5(17) correspond to about 19 % of U(IV) and 81 % U(V) found also from the quantitative
- analyses of the U M_4 HR-XANES data for 10 days aging of the samples. Correspondingly, if the
- about 37 % U(VI) found for the Um10 sample aged for 10 days has reduced to U(IV) and if we
- take into account the initial 0.7 % U(IV), the coordination numbers will be similar to those

reported for the 147 day aged Um10 sample: N(U-O3) = 3.2, N(U-U1) = 5.8. The coordination 307 308 numbers obtained from EXAFS analyses can have uncertainties up to 30 %. But since we compare them in a system with systematic structural variations, the magnitude of the uncertainty 309 is significantly reduced. 310 311 TEM analyses clearly confirm our interpretation of the EXAFS data since it detects crystalline UO₂ nanoparticles with size of about 4-5 nm (Figure 3A) possibly grown on the surface of the 312 Fe₃O₄ particles (Figure 3B) with lattice parameters very close to stoichiometric UO₂. Due to the 313 relatively large uncertainty for the obtained lattice parameter ($a = 0.271 \pm 0.004$ nm) it is not 314 possible to distinguish between UO_2 and UO_{2+x} . Considering also the EXAFS results, we 315 316 conclude that they are both likely. It is useful to discuss potential formation of U(IV), U(V) or U(VI) inner sphere complexes sorbed 317 on Fe₃O₄. Indeed U(IV) inner-sphere complexes stable within a few months have been reported 318 to form on Fe₃O₄ surfaces; the R(U-O) is elongated and the N(U-O) is higher (R(U-O) = 2.42 Å, 319 N(U-O) = 9 compared to UO₂ (R(U-O) = 2.35 Å, N(U-O) = 8).⁵⁴ For this U(IV) sorbed species 320 almost no U-U coordination is found similarly to U(IV) sorbed onto a Ti substituted Fe₃O₄. 321 Moreover R(U-Fe) = 3.56-3.59 Å are reported, which are significantly longer compared to the 322 distances found in our system, R(U-Fe1) = 3.13-3.19 Å. Indeed the R(U-O) = 2.42 Å is 323 comparable to the R(U-O3) for our Um10-Um3 samples (Table S4). However, our EXAFS 324 analyses report higher N(U-U) for the Um10 sample, N(U-U1) = 5.8, which is in a good 325 agreement with the crystalline UO₂/UO_{2+x} particles found by TEM. Latta et al. showed that UO₂ 326 nanoparticles, are formed for high U surface coverage for samples aged for several months 327 under anoxic conditions.⁵⁴ They found systematic change of the only one U-O and the U-U 328 distances as a function of the U concentration not observed for our system. We conclude that 329

formation of crystalline UO_2/UO_{2+x} nanoparticles is much more probable compared to sorbed U(IV) species.

The possibility for U(V) stabilized on Fe(II) containing mineral surfaces as an inner sphere complex has been discussed;⁵⁸ however no exact structural model was described. The stabilization of U(V) seems to be more likely in the form of mixed U(V)-U(VI) oxyhydroxide.⁵⁹ For this compound two very long R(U-O_{axial}) = 2.41-2.44 Å and four shorter equatorial O ligands R(U-O_{equal}) = 2.06 Å are found. Our EXAFS results do not report U-O bond distances, which correspond to the distance obtained for the equatorial ligands therefore this model does not seem to be appropriate. U(VI) complexes sorbed on Fe oxides have two axial O atoms at about ~1.79 Å, six equatorial O

339 U(VI) complexes sorbed on Fe oxides have two axial O atoms at about ~1.79 Å, six equatorial O 340 atoms at about ~2.38 Å and N(U-Fe) ~2(5), R(U-Fe) > 3 Å.⁶⁰ Since we find N(U-Fe) ~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 incorporate U(V) into a magnetite site. In the DFT calculations with periodic boundary 344 conditions we used a 2 \times 2 \times 2 super cell of magnetite and replaced one Fe²⁺ and one Fe³⁺ by U⁵⁺ 345 and one vacancy ($Fe^{2+}+Fe^{3+}\rightarrow U^{5+}+\square$). The Fe^{2+} and Fe^{3+} were chosen to be close to each other, 346 hence the presence of the vacancy allows the substitution of Fe by U to relax more easily. Since 347 U(V) is an open shell system we carefully monitored the occupation of the 5f orbitals and the 348 orientation of the spin of this electron. U(V) can be incorporated into a Fe^{2+} or Fe^{3+} octahedral 349 site, since both cases are energetically very close to each other (cf. Figure 3C). We found that the 350 orientation of the spin is important. The spin of the 5f electron points in the opposite direction 351 compared to the spins of the two replaced Fe ions. For the R(U-O2) and the R(U-Fe1) we 352 calculated theoretical values of 2.15(3) Å and 3.18(4) Å, respectively, which are in excellent 353

agreement with the experimental results, R(U-O2) = 2.18 Å and R(U-Fe1) = 3.18 Å, respectively
(Table S4).

Redox states of U in the Fe₃O₄ nanoparticles exposed to air. In order to verify possible 356 existence of U(V) in octahedral Fe₃O₄ environment the Um1 sample aged for 147 days in Ar 357 atmosphere was exposed for 142 days (U M₄ HR-XANES) and for additional 84 days (U L₃ 358 XANES and EXAFS) to air. The U M₄ HR-XANES spectrum of Um1a (142 days in air) is 359 depicted in Figure 4A. The shoulder characteristic for U(IV) is not visible, whereas features f 360 and f" typical for U(VI)-vl appear in the spectrum. The main peak maximum has an energy 361 position very similar to the spectrum of the Um1 sample aged for 10 days in Ar, which confirms 362 that the main redox state of U is U(V) (Figure 4A). After exposing this Um1a sample to 363 additional 84 days in air U L₃ XAS (XANES and EXAFS) spectra were recorded. The U L₃ 364 XANES is not as informative as the U M₄ HR-XANES but it can help to verify if any substantial 365 changes of the U oxidation state has taken place. The energy positions of the WL and the post 366 367 edge absorption resonance of the UL₃ XANES spectra of the Um1 aged for 10 days and the Um1a (226 days in air) samples are comparable, which is an indication that the majority of the 368 U(V) remains stable in the Um1a sample exposed to air for additional 84 days (Figure S6). 369 370 The FT-EXAFS spectra of the Um1a (226 days in air) and the Um1 (aged for 147 days in Ar) samples are compared in Figure 4B. It is apparent that the peaks characteristic for U coordination 371 to O and Fe are preserved: N(U-O2) = 2.8(2), R(U-O2) = 2.13(1) Å; N(U-O3) = 0.8(2), R(U-O3)372 = 2.36(2) Å and N(U-Fe1) = 6.2(17), R(U-Fe1) = 3.19(1) Å, whereas the peak describing the 373 coordination to U is absent in the FT-EXAFS Um1a spectrum. The U(IV) in the UO_{2+x} particles 374 is likely oxidized to $U(VI)O_2^{2+}$ as suggested from the R(U-O1) = 1.78(1) Å with N(U-O1) =375 0.7(1). The disappearance of the peak characteristic for U at about 3.84 Å can be explained by 376 increased disorder during the partial oxidation of U leading to destructive interference of the 377

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 ₃ O 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 ₃ O ₄ through intermediate Fe (oxyhydr)oxide phases. ²⁷
387	Part of U(VI) stays adsorbed onto the Fe ₃ O ₄ after 10 days of ageing time. We suppose that the
388	U(V) species have incorporated into the structure of Fe ₃ O 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 UO_2/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	UO_2/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 ₃ O 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, Fe(II)/Fe _{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 ₃ O 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.





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 U_4O_9 and UO_2 references.



 UO_2 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 UO₂ nanocluster (blue box) and a Fe₃O₄ 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 Fe₃O₄ (ICSD 26410) (bottom) (B). U(V) incorporated into an octahedral iron site into the Fe₃O₄ 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

AUTHOR INFORMATION

Corresponding Author

* tonya.vitova@kit.edu

Present Address

^a Institute for Nuclear Waste Disposal (INE), Karlsruhe Institute of Technology (KIT), P.O. 3640, D-76021 Karlsruhe, Germany

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