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PII: S0883-2927(20)30206-7

DOI: <https://doi.org/10.1016/j.apgeochem.2020.104714>

Reference: AG 104714

To appear in: *Applied Geochemistry*

Received Date: 24 March 2020

Revised Date: 4 June 2020

Accepted Date: 24 July 2020

Please cite this article as: Le Pape, P., Stetten, L., Hunault, M.O.J.Y., Mangeret, A., Brest, J., Boulliard, J.-C., Morin, G., HERFD-XANES spectroscopy at the U M_4 -edge applied to the analysis of U oxidation state in a heavily contaminated wetland soil, *Applied Geochemistry*, <https://doi.org/10.1016/j.apgeochem.2020.104714>.

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HERFD-XANES spectroscopy at the U M_4 -edge applied to the analysis of U oxidation state in a heavily contaminated wetland soil

Pierre Le Pape¹, Lucie Stetten^{1, 3}, Myrtille O.J.Y. Hunault², Arnaud Mangeret³, Jessica Brest¹, Jean-Claude Boulliard¹ and Guillaume Morin¹

¹ Sorbonne Université, Muséum National d'Histoire Naturelle, UMR CNRS 7590, IRD, Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, IMPMC, 75005 Paris, France

² Synchrotron SOLEIL, L'Orme des Merisiers, Saint Aubin BP 48, 91192 Gif-sur-Yvette, France

³ Institut de Radioprotection et de Sûreté Nucléaire, IRSN, 31 Avenue de la Division Leclerc, 92262 Fontenay-aux-Roses, France

Abstract

Determining U oxidation state in contaminated (sub)surface soils and sediments is essential to depict the geochemical processes affecting U in natural media. This information is also mandatory to infer the mechanisms governing the mobilization and transfer of this toxic radionuclide to the environment. Here, in attempt to detect U(IV), U(V) and U(VI) in wetland soil samples contaminated by past mining activities, we have performed high-resolution fluorescence detected X-Ray absorption near edge structure (HERFD-XANES) measurements at the U M_4 -edge. Linear combination fitting (LCF) analysis of the spectra have been conducted using reference samples representative of the wetland geochemistry, in which U occurs as U-phosphate minerals and mononuclear U complexes. Our experimental constraints for HERFD measurements at low energy (3.7 keV) implied to limit the thickness of the Kapton® foil used to protect the samples, which lead to slow oxidation by air during the measurements. In this context, U(IV) appeared to partly oxidize into U(VI) and/or U(V) within a few tens of hours. Nano-crystalline reference samples showed contrasted oxidation pathways for U(IV), transforming into U(V)/U(VI)-uranate in biogenic nano-uraninite, and into U(VI)-uranyl in nano-U(IV)-rhabdophane. In the wetland soils samples, uranium was mainly present as U(IV) and U(VI) with detection of minor U(V) (< 13 % of total U), possibly pristine and/or resulting from oxidation during the measurements. Our results thus show that U(V) may result from oxidation of mononuclear or nano-crystalline U(IV) after moderate air exposure, which challenges unambiguous detection of U(V) in environmental samples and calls for further U M_4 -edge HERFD-XANES measurements under strict anoxia.

keywords

uranium, wetland, speciation, oxidation state, HERFD-XANES at the U M_4 -edge

Graphical abstract

1. Introduction

Uranium (U) is a toxic contaminant that accumulates in continental reservoirs exposed to natural or anthropogenic sources (Coyte et al., 2018; Velasco et al., 2019; Hu et al., 2010). In particular, reducing zones in wetlands (Regenspurg et al., 2010; Li et al., 2014; Li et al., 2015; Wang et al., 2013; Mikutta et al., 2016; Stetten et al., 2018a; Stetten et al., 2019), rivers and lakes (Morin et al., 2016; Stetten et al., 2018b; Novotnik et al., 2018) may be important sinks for U. They can thus act as buffer zones protecting ecosystems from further spreading of this radiotoxic element downstream. Consequently, the geochemical reactivity of such contaminated material has to be carefully monitored, potential chemical reactions leading to U mobilization have to be elucidated, and if possible controlled to preserve the surrounding ecosystems. Due to cyclic hydrological fluctuations and the presence of organic matter, wetlands are subjected to intense biological activity and redox oscillations, parameters that exert a strong control on U chemistry (Stetten et al., 2018a, 2019; Gu et al., 2005; Akob et al., 2007; Li et al., 2015). Thus, spatio-temporal variations in U speciation are observed in wetland or peat soils (Mikutta et al., 2016; Stetten et al., 2018a, 2019; Gilson et al., 2015), eventually leading to U transfers from source minerals to more mobile forms, such as dissolved UO_2^{2+} ions or mononuclear U(IV) complexes (Stetten et al., 2019; Wang et al. 2013). In addition, microbial reduction of uranium is an important parameter to consider in environmental settings, as it can result in non-crystalline U(IV) (Boyanov et al., 2011; Bernier-Latmani et al., 2013; Rui et al., 2013), presenting poorly known geochemical reactivity when subjected to changes in local physico-chemical conditions. Among the parameters needed to depict the biogeochemical processes affecting U at the molecular scale in such reactive environments, the knowledge of the evolution of its oxidation state is of major importance (Stetten et al., 2018a, 2019; Roberts et al., 2017; Pidchenko et al., 2017). Even if rare occurrences of U(II) and U(III) have been observed in synthetic systems (La Pierre et al., 2014), only U(IV), U(V) and U(VI) oxidation states are considered as relevant to surface environments.

The intermediate oxidation state U(V) is reported to be weakly stable in solution as aqueous uranyl UO_2^+ ion since it rapidly disproportionates into U(IV) and U(VI) (Kern and Orlemann, 1949; Ekstrom, 1974), unless it is stabilized by complexing ligands

(Arnold et al., 2009), especially carbonates (Ikeda et al., 2007). Uranium(V) has also been recognized in rare natural minerals such as wyartite (Burns and Finch, 1999; Tsarev et al., 2017) but only in the uranate coordination (Arnold et al., 2009). U(V) has also been stabilized as uranate in the structure of uranium oxides (Stubbs et al., 2015), metal-uranium oxides (Guo et al., 2016) and iron-oxides (Ilton et al., 2012; Roberts et al., 2017; Pidchenko et al., 2017), as well as at the surface of iron oxides (Skomurski et al., 2011) and of Fe(II)-bearing micas (Ilton et al., 2005). However, U(V) has not yet been detected in soils or sediments sampled in natural media. This lack of detection could presumably be due to the transient character of U(V) (Kern and Orlemann, 1949; Ekstrom, 1974; Renshaw et al., 2005), but it is also clearly linked to the limited number of techniques able to unambiguously reveal its presence, *a fortiori* in diluted environmental samples. Indeed, most of the studies focusing on U oxidation state in environmental samples were based on X-ray absorption near-edge structure (XANES) spectroscopy performed at the U $L_{2,3}$ -edges (Li et al., 2015; Wang et al., 2013; Mikutta et al., 2016; Stetten et al., 2018a; Morin et al., 2016; Stetten et al., 2018b; Qafoku et al., 2009). Given the significant energy shift (~ 2.7 eV) of the absorption edge position between U(IV) and U(VI) when probing the U $6d$ unoccupied states, U L_3 -edge XANES spectroscopy, including high resolution fluorescence detected (HERFD) XANES, is sensitive to this valence change even in diluted environmental samples (Stetten et al., 2018a; Stetten et al., 2018b; Morin et al., 2016; Rui et al., 2013). Furthermore, although the shift between U(IV) and U(V) is smaller (≤ 1 eV), distinguishing between uranyl(VI) and uranate(V) is possible for pure compounds at the L_3 -edge (Chakraborty et al., 2010) especially because the spectrum of uranyl(VI) exhibits a shoulder on the high-energy side of the white line. Although uranyl(VI) and uranyl(V) both exhibit this characteristic shoulder, they can be distinguished by an energy shift at the L_3 -edge, reported to be 2.2 eV for aqueous UO_2^{2+} and UO_2^+ carbonato complexes (Ikeda et al., 2007). However, uranate U(V) is hardly distinguished from uranate U(VI) and U(IV) in uranium and iron oxides (Ulrich et al., 2009; Yuan et al., 2015). Thus, accurate determination of U oxidation states at the L_3 -edge in complex natural systems containing multiple U species remains difficult (e.g. Pidchenko et al., 2017), and in particular for U(V). Otherwise, X-ray Photoemission Spectroscopy (XPS), probing the $4f$ occupied states of uranium is a powerful option to detect U(V) (Ilton et al., 2005; Ilton and Bagus, 2011). Although limited to the surface of the samples analyzed under high-vacuum, this technique has

definitely proven the presence of U(V) in several oxide compounds, in which this intermediate species is thought to be stabilized by charge-transfers with neighboring metal ions (Stubbs et al., 2015), especially when it is restricted into 6 or 7-fold oxygen coordination (Ilton et al., 2012). Nevertheless, XPS analyses of the $5d$ orbitals should be preferred due to their high sensitivity to U oxidation state but require particularly high U concentrations (Ilton et al., 2017).

More recently, the use of HERFD-XANES has emerged in the field of environmental geosciences as a mean to improve spectral resolution and subsequently to decipher between chemical species (Proux et al., 2017; Le Pape et al., 2018). In particular, HERFD-XANES at the U M_4 -edge, probing the $5f$ unoccupied states, has been shown to be suitable to differentiate U(V) species from U(IV) and U(VI) (Kvashnina et al., 2013; Leinders et al., 2017; Kvashnina et al., 2017). Indeed, at the U M_4 -edge, the core-hole lifetime is significantly lower than at the U L_3 -edge (3.2 vs. 7.4 eV, Krause et al., 1979), and the use of HERFD-XANES spectroscopy measurement even more reduces the intrinsic spectral resolution to around 1 eV (Kvashnina et al., 2013), leading to a proper differentiation of U redox states (Roberts et al., 2017; Pidchenko et al., 2017). This approach has especially permitted to determine the proportion of U(V) in complex U oxide and intermetallic compounds (Kvashnina et al., 2013; Podkovyrina et al., 2016; Leinders et al., 2017; Kvashnina et al., 2017) and to clearly distinguish between uranyl(V) and (VI) complexes (Zegke et al., 2019). Combined with other techniques, this spectroscopic approach has also recently given evidence for U(V) in the products of microbial reduction of U(VI) (Vettese et al., 2020), as well as in natural U-minerals (Vitova et al., 2015). However, to date, this technique has not been applied to natural soils or sediments sampled on the field in which a complex mixing of U-bearing species and oxidation states are involved.

Here, we attempted to fill this gap by measuring HERFD-XANES spectra at the U M_4 -edge in environmental samples, collected in a heavily contaminated wetland located downstream from a former French U mine. In attempt to observe the U(V) oxidation state, we especially targeted two samples from soil cores previously analyzed at the U L_3 -edge by Stetten et al. (2018a). The first sample was collected at the redox water-table boundary in the wetland, *i.e.* in conditions propitious to electron transfers, and the second one was taken below the water-table, being representative of quasi-

permanent reducing conditions. In order to determine oxidation states in these field samples, we compared them with carefully chosen synthetic and natural reference samples. As air diffusion through the sample holder occurred during the experiment, oxidation of some samples was observed and the evolution of the HERFD-XANES spectral signatures overtime eventually brought to light details about the behavior of environmentally relevant U(IV)-bearing species during oxidation.

2. Material & Methods

2.1. Synthetic and natural samples

In this study, three samples of synthetic origin were used as model compounds. A lanthanum/calcium based nanocrystalline rhabdophane sample (nano-U(IV)-rhabdophane) was synthesized under anoxic conditions in the presence of U(IV) according to the protocol available in Stetten et al. (2018a), resulting in the following chemical formula : $(\text{La}_{0.98}\text{Ca}_{0.01}\text{U}_{0.01})\text{PO}_4 \cdot \text{H}_2\text{O}$. In this model compound each U^{4+} ion is 8-fold coordinated to oxygen atoms (4 $\text{U-O}@2.24(3)$ Å and 4 $\text{U-O}@2.39(5)$ Å) in a distorted hexagonal bipyramids sharing two edges and four corners with phosphate groups and two edges with La/Ca neighbors (Stetten et al., 2018a) (Figure 1). A biogenic nanocrystalline uraninite model compound (nano-uraninite), *i.e.*, a bio-uraninite with particles of ~3 nm in diameter as estimated by Scherrer analysis of the (111) XRD line width and consisting of pure U(IV), was produced under anoxic conditions at neutral pH by reducing U(VI)-acetate with *Shewanella oneidensis* MR-1 according to the protocol detailed in Morin et al. (2016). Shell-by-shell fitting of the U L_3 -EXAFS showed 8 $\text{U-O}@2.34$ Å as first neighbors and 8 $\text{U-U}@3.85$ Å as second neighbors for this model compound (Morin et al., 2016). The number of observed U second neighbors is lower than the expected value of 12 in the fluorite type structure because of the nanocrystalline character of the sample prepared through a biological pathway (Morin et al., 2016; Schofield et al., 2008). Triuranium octoxide (U_3O_8), containing theoretically 66 % U(V) and 33% U(VI) (Kvashnina et al., 2013) and exhibiting a layered structure, was taken from the IMPMC chemical stocks. As a model compound of uranyl phosphate mineral, an autunite $(\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10-12\text{H}_2\text{O})$ sample was provided by the IMPMC mineral collection. In this layered compound, each UO_2^{2+} ion is coordinated to four equatorial oxygen atoms forming a

square plane that shares each of its four corners with a phosphate group. Shell-by-fitting of the U L_3 -edge EXAFS spectrum of the autunite sample studied is available in Stetten et al. (2018a).

Finally, two environmental samples are considered in this study and originate from a wetland heavily impacted by former mine-water drainages from the Ty Gallen U mine, Brittany, France (Stetten et al., 2018a). Briefly, within the C2 core sampled, vacuum-dried and stored under anoxic conditions, one sample (C2-15cm; 1850 mg/kg U) was taken at the redox boundary between the saturated and non-saturated zones, and one sample was taken below at 30 cm (C2-30cm; 2255 mg/kg U) and is representative of quasi-permanent reducing conditions. Uranium speciation in those samples was previously determined using XANES and EXAFS analyses at the U L_3 -edge (Stetten et al., 2018a). The C2-15cm sample contained both U(IV) and U(VI) species with the respective contributions of $86\pm6\%$ and $14\pm6\%$ whereas in the C2-30cm sample, uranium was fully reduced to U(IV) species, in the form of both crystalline (U(IV)-phosphate minerals) and mononuclear U(IV) (associated to phosphoryl/carboxyl groups). Details on the location of the sampling site and other technical information about sampling procedures on the field are reported in Stetten et al. (2018a; 2019).

2.2. HERFD-XANES measurements at the U M_4 -edge

Uranium M_4 -edge (3728 eV) HERFD-XANES spectroscopy measurements were performed at the bending magnet MARS beamline at the SOLEIL synchrotron (Saint-Aubin, France), using a double Si(111) crystal monochromator equipped with a sagittal focusing of the second crystal. Higher harmonics rejection and vertical focusing was achieved by using the Si strip of each mirror inserted before and after the monochromator with a 4 mrad incidence angle. The Gaussian profile of the beam on the sample position showed vertical and horizontal full widths at half-maximum of 150 μm and 250 μm respectively. The incident energy was calibrated using the inflexion point of the absorption K -edge of potassium in a KBr pellet set at 3608 eV. To measure the $M\beta$ emission line of uranium, we used the 220 reflection of a Si(220) bent diced analyzer crystal with a curvature radius of 1m. A He-filled chamber was used to reduce the scattering of the emitted X-ray fluorescence by air between the

sample holder and the analyzer crystal, and between the analyzer crystal and the detector. The spectrometer resolution measured at the double energy (6676 eV) from the FWHM of the elastic scattering peak was 1.6 eV. Other details about the experimental procedure applied on the beamline can be found in Hunault et al. (2019).

All reference compounds were appropriately diluted in 50 mg of cellulose and pressed as pellets, to reach final U concentrations of 2.3, 3.5, 3.2 and 0.4 wt%U for $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{-}12\text{H}_2\text{O}$ (autunite), U_3O_8 (triuranium octoxide), UO_2 (nano-uraninite), and $(\text{La}_{0.98}\text{Ca}_{0.01}\text{U}_{0.01})\text{PO}_4 \cdot \text{H}_2\text{O}$ (nano-U(IV)-rhabdophane), respectively. The C2-15cm and C2-30cm wetland soil samples were pressed as pure pellets.

All sample pellets were sealed between two foils of thin Kapton® tape (12 μm thickness) and mounted in a single sample holder within an anaerobic chamber Jacomex™ (< 10 ppm O_2) at IMPMC laboratory. These Kapton® foils were clamped between the two hollowed plaques (Teflon®) of the 15 positions sample holder. Another thin Kapton® foil (12 μm thickness) was then crimped by an O-ring clamped by an aluminum frame on the front and back of the sample holder to serve as double containment. The choice of thin Kapton® tape to protect the samples was constrained by the necessity to minimize X-ray absorption through the double Kapton® containment, at both the incident (3.7 keV) and emission energies (3.3 keV), with an incident photon-flux on the sample delivered by a bending-magnet beamline. The sample holder was kept in an anoxic container until it was placed in front of the X-ray beam for the whole beamtime (6 days). Once the sample holder was mounted on the beamline, in air and in close contact with the He chamber, oxygen diffusion started in the sample holder through the thin Kapton® films with maximum flow estimated to 0.5 mL O_2 per 24 hours (<https://www.dupont.com/content/dam/dupont/products-and-services/membranes-and-films/polyimide-films/documents/DEC-Kapton-summary-of-properties.pdf>).

Measurements of HERFD-XANES spectra were performed at the maximum of the $\text{M}\beta$ emission line measured at 3337.5 eV on a pure U(VI) compound (Hunault et al., 2019). Between 3-9 and 20-25 scans of 20 minutes were collected for the reference compounds and wetland soil samples, respectively. Several consecutive scans on the same spot did not significantly alter the spectrum position nor shape, indicating that beam damage was negligible compared to air oxidation effects (Fig. S1). For the

U(IV) model compounds, nano-U(IV)-rhabdophane and nano-uraninite, the edge position and shape were observed to evolve as a function of time of air exposure (Fig. S1). Consequently, the first and 4 first scans only were merged to obtain the spectrum of the pristine model compound samples and the next scans were merged to characterize their oxidized counterparts. In contrast, no evolution in time was observed for the other samples, as further detailed in the results section.

2.3. Data processing

HERFD-XANES spectra obtained at the emission energy of 3337.5 eV were averaged using the Athena software (Ravel and Newville, 2005). The merged spectra were smoothed with the smoothing spline function in the Matlab® software using a spline parameter of $p = 0.9999$ while $p = 0$ is a least-squares straight-line fit to the data, and $p = 1$ is a cubic spline interpolant. Raw and smoothed data are plotted in Fig. S2. A straight background parallel to the pre-edge region was subtracted when necessary, and the spectra maxima were then normalized to 1, since the post-edge region of the wetland soil samples spectra was too noisy to reliably normalize them to their edge-jump height. To estimate the contribution of various U oxidation states in the environmental samples, wetland soil samples spectra were submitted to a linear combination fitting procedure using the reference compounds previously presented. HERFD-XANES least-square combination fits (LCF) were performed using a home-built program based on a Levenberg-Marquardt minimization algorithm (Stetten et al., 2018a, 2018b, 2019; Morin et al., 2016). The fit quality was estimated by a R-factor, $R_f = \sum [\mu_{\text{exp}} - \mu_{\text{calc}}]^2 / \sum \mu_{\text{exp}}^2$ and by a reduced chi-square, $\chi^2_R = N/(N-Np) \sum [\mu_{\text{exp}} - \mu_{\text{calc}}]^2$ where Np is the number of fitting components and N is the number of independent parameters corresponding to the energy range divided by assuming an intrinsic resolution of U M_4 -edge spectra of 1 eV (Kvashnina et al., 2013). The uncertainties on the fitting component proportions p were estimated to 98% confidence by $3 (\text{var}(p) \chi^2_R)^{1/2}$, where $\text{var}(p)$ is the variance of parameter p returned by the Levenberg–Marquardt routine for the lowest χ^2_R value (Ravel and Newville, 2005; Stetten et al., 2018a, 2018b, 2019; Morin et al., 2016). A statistical F-test, based on the Fisher-Snedecor distribution has been applied to compare the statistical significance of linear combination fits when adding a fitting component. To perform this test, the number of independent variables of the system, the number of

independent parameters considered for a spectrum is not the number of data points as classically considered, but the N value, i.e. ΔE (energy range of the spectrum) divided by an intrinsic resolution of U M_4 -edge spectra assumed to be of 1 eV (Kvashnina et al., 2013). Results of the F-test were then compared to a table of Fisher-Snedecor distribution considering a 95% confidence interval.

3. Results & Discussion

3.1. $U(IV)$, $U(V)$ and $U(VI)$ spectral signatures at the M_4 -edge

In previous studies on wetland soils contaminated by mine waters from the Ty-Gallen U mine (Brittany, France) (Stetten et al., 2018a; 2019), it has been shown that U chemistry in the wetland soil samples is mainly characterized by U association with phosphates, e.g. U-phosphate minerals such as ningyoite $(U,Ca,Ce)_2(PO_4)_2 \cdot 1-2(H_2O)$, lemontovite $(U(PO_4)(OH) \cdot (H_2O))$, and autunite $(Ca(UO_2)_2(PO_4)_2 \cdot 10-12H_2O)$. Thus, we have chosen a $U(IV)$ -phosphate (nanocrystalline $U(IV)$ substituted La-rhabdophane) and a $U(VI)$ -phosphate (autunite) as model compounds to be compared to the field samples. Figure 1A displays their HERFD-XANES spectra, obtained at the M_4 -edge. In autunite, 3 peaks are observed (3727.7, 3729.6, and 3733.4 eV, Table 1), corresponding to the splitting of the $5f$ orbitals of U when it occurs in uranyl coordination (Vitova et al., 2015; Vitova et al., 2017; Kolorenc and Kvashnina, 2018; Hunault et al., 2019; Zegke et al., 2019). For the nano- $U(IV)$ -rhabdophane model compound (Fig. 1A), only one peak is observed (3726.15 eV) and 3 shoulders are visible, corresponding to an early stage of $U(IV)$ oxidation to uranyl, that will be discussed in the next section. The energy shift observed between the $U(IV)$ and $U(VI)$ main peaks is 1.55 eV, which is roughly consistent with results reported in the literature (1.5 to 1.7 eV (Bès et al., 2016)). In Fig.1B, another $U(IV)$ model compound, nano-uraninite, accordingly exhibits a main peak at the same value as nano- $U(IV)$ -rhabdophane (3726.15 eV). Again, the little shoulder observed on the high-energy side of the white line is due to slight oxidation, as discussed in the next section. For the last model compound U_3O_8 , composed of 66% $U(V)$ and 33 % $U(VI)$, the spectral shape of our U_3O_8 model compound is consistent with previous observation at the U M_4 -edge (Leinders et al., 2017; Bès et al., 2016). Its maximum is positioned at 3727.55 eV, leading to a shift of 1.4 eV between UO_2 and U_3O_8 , which

is the same value as that reported in the recent publication by Leinders et al. (2017). However, a little shift is observed between U_3O_8 and the U(VI)-autunite reference ($\Delta E = 0.15$ eV), whereas it is not observed in the recent study of Leinders et al. (2017) ($\Delta E = 0$ eV). Such small discrepancies in reported energy shift values could be due to differences in experimental resolution or more likely to differences in the emission energies chosen in the RIXS plane for the measurements (Kvashnina et al., 2013; Le Pape et al., 2018). Despite this little difference, positions of the inflexion points of U_3O_8 and U(VI)-autunite spectra certify the presence of U(V) in our U_3O_8 reference sample as shown by the first derivative maxima (Fig. 1B).

Figure 1. HERFD-XANES spectra of reference compounds obtained at the U M_4 -edge at the emission energy of 3337.5 eV (A) and their first derivative (B). Energies of the main visible peaks are indicated by dotted lines and values are reported in Table 1. U(IV) in nano-U(IV)-rhabdophane (green, plain line); U(IV) in nano-uraninite (UO_2 , green, dotted line); U(V)/U(VI) in U_3O_8 (blue, plain line); U(VI) in autunite (orange, plain line). Crystal structures presented are taken from the work of Mooney (1950), Locock and Burns (2003), Wyckoff (1963), and Andersson et al. (2013) for rhabdophane, autunite, uraninite and triuranium octoxide, respectively.

338

<i>Uranium species</i>	<i>Theoretical oxidation state</i>	<i>Energy position of main peaks (eV)</i>
Nano-U(IV)-rhabdophane (La _{0.98} Ca _{0.01} U _{0.01})PO ₄ •H ₂ O	100% U(IV)	3726.15
Nano-uraninite – UO ₂	100% U(IV)	3726.15
U(VI)-Autunite Ca(UO ₂) ₂ (PO ₄) ₂ •10-12H ₂ O	100% U(VI)	3727.7 3729.6 3733.4
Triuranium octoxide U ₃ O ₈	66% U(V) - 33% U(VI)	3727.55

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Table 1. Theoretical oxidation state of uranium and corresponding energy positions of the main peaks on the HERFD-XANES spectra measured at the U M₄-edge for the model compounds presented in Figure 1.

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3.2. What is learnt from the oxidation of U(IV) reference minerals?

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Over the course of the measurements, which were performed in oxic conditions, but under double kapton containment (2x12µm thickness), we observed the progressive oxidation of the U(IV) model compounds overtime. In Figure 2A, oxidation of nano-uraninite is shown by comparing the average of the 3 first spectra vs. the average of the 4 next spectra performed few hours later, t₀ being the time at which the sample holder was removed from anoxic conditions. A net shift of the main peak is observed toward the higher energy (ΔE=1.2 eV) (Table 2). According to the energy position of the main peaks of our reference compounds, including U₃O₈ (Table 1), such observation is consistent with the oxidation of U(IV) to U(V)/U(VI). It is known that UO₂ oxidizes in air into UO_{2+x} minerals, such as U₄O₉ and U₃O₇ (Kvashnina et al., 2013; Leinders et al., 2017), which consist of a mixture of U(IV) and U(V) and have a cubic structure. Consequently, the presence of such mixed U(IV)/U(V) oxides is likely in our oxidized nano-uraninite sample (Kvashnina et al., 2013; Leinders et al., 2017; Bès et al., 2016). Moreover, the spectrum of our oxidized nano-uraninite can be reconstructed by the linear combination of the initial nano-uraninite plus U₃O₈ (Fig. 2B, Table 3). This result confirms the oxidation of U(IV) to U(V) and could also suggest the possible presence of a minor U(VI) contribution in uranate configuration, since U₃O₈ consists of both U(V) and U(VI) (Kvashnina et al., 2013; Leinders et al., 2017) (Fig. 2B; Table 3). However, fitting the spectrum of our oxidized nano-uraninite with pure U(IV), U(V) and U(VI) components would be necessary to confirm the

actual presence of U(VI) due to oxidation. Indeed, the transformation of bulk cubic U_3O_7 into the layered U_3O_8 compound is known to occur at temperatures higher than 200°C (Kvashnina et al., 2013) (typically at 500°C, Leinders et al., 2017) and is thus unlikely at room temperature. Nevertheless, our data suggest that further studies may be conducted to investigate the possibility of such transformation from nano-crystalline bio-uraninite at room-temperature. Interestingly, here, we show that nano-uraninite is very sensitive to air oxidation in comparison with the bulk compounds used in previous studies, synthesized at high temperature and whose surface had been treated with H_2 (Leinders et al., 2017; Kvashnina et al., 2013). This is also in line with the finding detailed in a previous study showing that oxidation of nano-uraninite in aqueous suspension lead to the formation of U(V) as a surface intermediate (Ulrich et al., 2009). Thus, the present results suggest that it could also occur in a solid-state at the contact with air. For this experiment, we can consider a ~1 micron penetration distance of X-rays in the samples at 3.7 keV, which is superior to the size of the nano-uraninite particles (~3 nm). This indicates that U speciation is not only measured at the particle surface but within entire nano-uraninite particles.

For nano-U(IV)-rhabdophane (Fig. 2C), an oxidation process is also observed. However, unlike the case of nano-uraninite, the oxidation gives rise to 3 shoulders (Table 2), that are specific of the uranyl U(VI) configuration (Vitova et al., 2015; Vitova et al., 2017; Kolorenc and Kvashnina, 2018; Hunault et al., 2019; Zegke et al., 2019) (Fig. 1A and Table 1). In addition, the LCF procedure applied to the oxidized sample shows that it can be reconstructed by using the initial nano-U(IV)-rhabdophane model compound plus the U(VI)-autunite model compound presenting an uranyl coordination (Fig. 2D, Table 3). This result suggests that no significant amount of U(V) can be observed as intermediate in the oxidation of U(IV)-phosphate minerals in which U ions are separated by phosphate groups. We can thus hypothesize that the absence of U or metallic second neighbor ion may have precluded U-O-U or metal-O-U charge transfers that have been proposed to stabilize U(V) in U- or metal- oxides (Stubbs et al., 2015; Ilton et al., 2012).

These observations of different oxidation pathways for our nano-uraninite and nano-U(IV)-rhabdophane model compounds upon air exposure may have important implications for environmental systems. Indeed, in (sub)surface reducing environments, both biogenic uraninite or non-uraninite U(IV) species can form (Bargar et al., 2008; Bernier-Latmani et al., 2010) and may then behave differently

upon re-oxidation processes. It can be inferred that U(V) likely forms upon oxidation of bio-uraninite, whereas the presence of phosphate minerals may rather turn U speciation to a U(IV)/U(VI) binary system. The consistency of this latter assumption would certainly require further work, and can be especially investigated in the contaminated wetland soil of Ty Gallen, in which U-phosphate minerals are submitted to redox cycling upon hydrological fluctuations (Stetten et al., 2018a, 2019), as detailed thereafter.

Figure 2. HERFD-XANES spectra at the U M_4 -edge measured at two different timesteps and showing the effect of oxidation by diffusion of air through the sample holder containing all the samples at the beginning of the experiment. t_0 is the time at which the sample holder was extracted from the anoxic box to be set up on the beamline.

A. HERFD-XANES spectra at the M_4 -edge of nano-uraninite and of oxidized nano-uraninite. **B.** LCF reconstruction of the HERFD-XANES spectrum of oxidized nano-uraninite using initial nano-uraninite plus U_3O_8 . The presence of U_4O_9 cannot be excluded as this transient species occurs during UO_2 oxidation to U_3O_8 (Leinders et al., 2017) **C.** HERFD-XANES spectra at the M_4 -edge of reduced nano-U(IV)-rhabdophane and of oxidized nano-U(IV)-rhabdophane. **D.** LCF reconstruction of the HERFD-XANES spectrum of oxidized nano-U(IV)-rhabdophane using initial nano-U(IV)-rhabdophane plus U(VI)-autunite. The presence of a low amount of U(V) cannot be excluded. Indicative contributions of the components used in linear combination fits are presented in Table 3.

Uranium species	Energy position of main peaks (eV)			
Initial nano-uraninite	3726.15			
Oxidized nano-uraninite	3726.15	3727.35		
Initial nano-U(IV)-rhabdophane	3726.15			
Oxidized nano-U(IV)-rhabdophane	3726.15	3727.7	3729.6	3733.4

Table 2. Position of the main peaks maxima on the HERFD-XANES spectra at the U M_4 -edge presented in Fig. 2 after U(IV)-bearing minerals were exposed to air.

	Initial nano-U(IV)-rhabdophane	Autunite	$R_f (.10^{-3})$	Red- $\chi^2 (.10^{-3})$
Oxidized nano-U(IV)-rhabdophane	96 (3.5)	14 (5)	0.49	1.002
	Initial nano-uraninite	U_3O_8	$R_f (.10^{-3})$	Red- $\chi^2 (.10^{-3})$
Oxidized nano-uraninite	68 (13)	48 (14.5)	1.99	5.03

Table 3. Indicative parameters of the linear combination fitting procedure applied to HERFD-XANES spectra at the U M_4 -edge for the oxidized reference samples. Graphical representation of the fits is presented in Fig. 2. The oxidized nano-U(IV)-rhabdophane is reconstructed using the initial nano-U(IV)-rhabdophane plus the U(VI)-autunite reference and the oxidized nano-uraninite is reconstructed using the initial nano-uraninite (UO_2) plus triuranium octoxide (U_3O_8).

3.3. Detailed analysis of U oxidation state in the wetland soil samples

The C2-15cm and C2-30cm wetland soil samples, containing 1850 and 2255 mg/kg U respectively, were chosen for X-ray absorption spectroscopy analysis at the U M_4 -edge because they are positioned at key depths in the C2 core (Stetten et al., 2018a). First, the C2-15cm sample is positioned at the redox boundary, materialized

by the water level separating the saturated and non-saturated zones of the wetland soil (Figure 3, left panel). In the previous study by Stetten et al. (2018a), LCF analysis of the U L_3 -edge XANES data for this sample, collected at 80K under strict anoxic conditions, indicated respective contributions of $86\pm 6\%$ and $14\pm 6\%$ for U(IV) and U(VI). Second, the C2-30cm sample is representative of a quasi-permanent reducing environment in which U was fully reduced (Stetten et al., 2018a). In both samples, U mainly occurred in the form of crystalline and mononuclear species, as indicated by U L_3 -EXAFS LCF analysis (Stetten et al., 2018a, Table 4). Figure 3 show the normalized U M_4 -edge XANES spectra of the two samples measured in the present study, with the main peaks in the absorption edge indicated by dotted lines. By comparison with the M_4 -edge XANES spectra of our reference compounds, both samples exhibit a peak at the U(IV) energy position as well as peaks belonging to U(VI)-uranyl (Table 1, Table 4). The obvious presence of U(VI) in C2-30cm suggests that oxidation of the sample has occurred during the exposure of the sample holder before the M_4 -edge HERFD-XANES spectra were collected, since previous L_3 -edge XANES data by Stetten et al. (2018a) indicated only U(IV) in this sample. In contrast successive M_4 -edge HERFD-XANES spectra of the soil samples exhibited close signals over the course of the measurements as shown in Fig S1, which indicated the absence of significant beam damage effect. Hence, for explaining the differences with Stetten et al. (2018a) L_3 -edge XANES results, we infer that the wetland soil samples in the form of pure pellets have oxidized before the measurements, after the multi-sample holder was extracted from its anaerobic containment and placed into the experimental hutch. Thanks to the first visual examination of the spectra (Fig. 3), it is noteworthy that the proportion of remaining U(IV) in the samples measured by LCF on HERFD-XANES at the M_4 -edge (Fig. 3 and Table 4) is roughly equal to the proportion of U(IV)-phosphate mineral initially present in the samples (Table 4). This observation suggests that, in contrast, mononuclear U(IV) complexes present in the samples may have been particularly sensitive to air oxidation during the experiment. Such an observation is in line with that made on a longer time scale in incubations experiments of wetland soil samples carried out by Stetten et al. (2019), showing the total oxidation of mononuclear U(IV) after 20 days under oxic air-conditions, whereas more massive U(IV)-phosphate minerals were not fully oxidized. Still, the U(IV) peak is higher in the C2-30cm than in C2-15cm sample, which would be consistent with the original speciation measured by XANES and EXAFS analysis at the L_3 -edge

(Stetten et al., 2018a, Table 4). These results would thus show that mononuclear U complexes are extremely sensitive to air oxidation.

In order to search for the presence of U(V) in the U M_4 -edge XANES spectra of the wetland soil samples, a linear combination fitting procedure using selected model compounds was used as a first approach. As our previous studies indicated the preponderant association of U with phosphates in these soils, U M_4 -edge XANES spectra of U(IV)-phosphate and U(VI)-phosphate reference compounds were selected as fitting components. To investigate the possible contribution of U(V), the U_3O_8 reference sample was chosen, containing 66% U(V) and 33% U(VI) (Leinders et al., 2017). Results presented in Fig. 3 and Table 4 show that adding a U_3O_8 contribution (23.5%, *i.e.* 19% normalized to sum of components) to the fit of the C2-15cm sample significantly improved the fit quality (R -factor changing from $4.6 \cdot 10^{-3}$ to $2.8 \cdot 10^{-3}$ and reduced chi-square changing from $10.3 \cdot 10^{-3}$ to $6.7 \cdot 10^{-3}$), as demonstrated by performing a F-test. Indeed, a F parameter of 8.37 was determined by comparing the reduced chi-squares obtained without or with the U_3O_8 components, which is superior to the critical value of 4.75 considering a 95% confidence interval. Assuming 66% of U(V) in U_3O_8 , the normalized U(V) contribution in the C2-15cm sample would not exceed 13% (Table 4), which remains low and within the uncertainty range on the fitting component, partly due to our careful mode of calculation for the number of independent parameters assigned to the spectra in the fitting routine. In the case of C2-30cm, the addition of a U_3O_8 contribution only slightly improves the R -factor and reduced chi-square parameters, which is not significant.

The possible presence of U(V) ($\leq 13\%$ of total U) suggested by our M_4 -edge analysis would be plausible in the C2-15cm sample since it is located at the redox boundary of the wetland, which is regularly subjected to dryness and air exposure periods (Stetten et al., 2018a). However, as detailed before for the model compounds, this putative U(V) component could also likely arise from oxidation of U(IV)-bearing phases due to air exposure of the sample through the Kapton® sealing during measurements at the beamline. Nevertheless, in both cases, the presence of U(V) could possibly be due to the oxidation of minor amounts of uraninite that is present in this sample, as shown by SEM-EDXS (see Figure SI-10a in Stetten et al. (2018a)). Also, a part of the putative U(V) component could results from the oxidation of certain

types of U(IV) mononuclear complexes, as those classically associated to iron-bearing minerals (Skomurski et al., 2011; Ilton et al., 2005; Yuan et al., 2015), if they account for part of the non-crystalline U(IV) present in the C2-15cm wetland soil sample (Stetten et al., 2018a). Besides, U(IV)-phosphate minerals present in the studied wetland are unlikely to host U(V), based on the results obtained here on our U-phosphate minerals model compounds.

In the C2-30cm sample, the oxidation of mononuclear U(IV) into U(VI) species would be the main explanation for the contributions obtained by fitting the M_4 -edge XANES spectrum (Table 4). However, due to the uncertainties previously mentioned, a minor and undetectable contribution of U(V) cannot be excluded.

Figure 3. HERFD-XANES spectra at the M_4 -edge for the two selected samples in the C2 core, C2-15cm (A) and C2-30m (B). Energies of the main visible peaks are represented as dotted lines and corresponding values are presented in Table 4. On the left panel, a brief scheme of the C2 core is given, presenting sample positions with respect to trends of uranium oxidation states determined according to XANES analyses at the L_3 -edge in Stetten et al. (2018a). Least-square linear combination fits (LCF) performed on the C2-15cm (C) and C2-30cm (D) samples using the model compounds nano-U(IV)-rhabdophane, U(VI)-autunite, and U_3O_8 , presented in Fig. 1. References compounds are represented as weighted components. For each sample, two cases of LCF are presented, including or not the U(V)-containing compound (U_3O_8 , 66% U(V) and 33% U(VI)). Indicative percentages for contributions of each model species are given in the Table 4.

		C2-15		C2-30	
	Energy position main peaks (eV)	3726.2		3726.3	
		3727.7		3727.6	
		3729.6		3729.6	
		3733.4		3733.4	
EXAFS U L ₃ -edge LCF contributions (%) (Stetten et al., 2018)	Nano-U(IV)-rhabdophane	55 (22)		56 (18)	
	U(IV)-Non-crystalline	40 (20)		44 (16)	
	U(VI)-autunite	15 (6)		-	
HERDF-XANES U M ₄ -edge LCF contributions (%) with or without U(V)-bearing component This study	Nano-U(IV)-rhabdophane	56 (12)	53 (10)	63 (12)	61 (11)
	U ₃ O ₈	-	23.5 (28)	-	18 (31)
	U(VI)-autunite	67 (12)	45 (28)	62 (12)	46 (30)
	R _f (.10 ⁻³)	4.85	2.84	4.46	3.35
	Red-chi ² (.10 ⁻³)	10.33	6.71	9.86	8.23

Table 4. Position of the main peaks on the HERFD-XANES spectra at the U M_4 -edge for the wetland soil samples C2-15cm and C2-30cm. Initial contributions of the U-bearing species in the C2-15cm and C2-30cm samples determined by linear combination fit of XANES and EXAFS spectra recorded at the U L_3 -edge in Stetten et al. (2018a). Results of the linear combination fitting procedure performed on the HERFD-XANES spectra recorded on the wetland samples at the U M_4 -edge and presented in Fig. 3. Indicative contributions of each U oxidation state in linear combination fits are indicated with their error bars presented between parenthesis. R -factor (R_f) and reduced χ^2 are given as estimators of the goodness of fit. Uncertainties on the fitting components are given to a 98% confidence, based on a 3 sigma evaluation (see text).

3.4. Experimental constraints for U(V) detection in environmental samples: conclusions and perspectives

In the present article, we show the first HERFD-XANES dataset at the U M_4 -edge on complex multicomponent environmental samples representative of a mining impacted site. Since oxidation occurred during the experiment despite the double Kapton® containment set up to protect the samples, the firm observation of U(V) could not be achieved in the original well-preserved environmental samples. However, the present results support that U(V) could form after moderate oxidation of nano-crystalline and mononuclear U(IV) species in both model compounds and environmental samples studied. In addition, we infer that the amount of U(V) may depend on the geochemical composition of the system investigated, e.g. uranium oxides vs. uranium phosphates.

Although these results are promising, further work is required to improve the experimental methodology and unambiguously unravel U(V) presence in undisturbed environmental samples. For future experiments, it will be valuable to overcome specific technical issues. In particular, performing the experiment under strict anoxic conditions turned out to be particularly challenging, even on undulator beamlines (Kvashnina et al., 2017). Still, even if progress has to be made in sample environments procedure during data collection as aforementioned, this study suggests that the presence of U(V) should be searched for, in particular, in (sub)surface soils and sediment systems presenting redox fluctuations.

4. Acknowledgments

The authors thank Pascale Blanchart and Anthony Julien for their help during the sampling of the wetland, as well as the site's owner for allowing access to the field. Georges Ona-Nguema and Rozimina Ibrahim are also greatly acknowledged for their work on the synthesis of the biogenic UO_2 model compound. This study was conducted within the framework of the IRSN/IMPMC collaborative research program number LS 20218/C151903-P150778. Lucie Stetten's PhD has been granted by Region Ile de France, DIM R2DS PhD grant number 2015-03. We thank SOLEIL synchrotron for providing beamtime.

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- HERFD-XANES measurements at the U M_4 -edge have been performed on soil samples from a heavily contaminated wetland (Brittany, France)
- Experimental constraints have implied sample oxidation over the course of the measurements
- Nano-uraninite reference transformed into U(V)/U(VI)-uranate upon oxidation
- Nano-U(IV)-rhabdophane reference transformed into U(VI)-uranyl upon oxidation
- Presence of U(V) cannot be excluded in wetland soil samples, pristine and/or resulting from oxidation by air during measurements

Declaration of interests

We, the authors, declare that we have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.