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Carbonate Facilitated Mobilization of Uranium from Lacustrine Sediments under Anoxic Conditions

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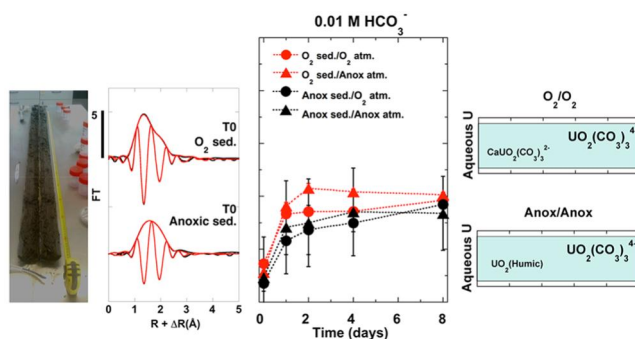
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ABSTRACT: Sorbed U(IV) species can be major products of U(VI) reduction in natural reducing environments as sediments and waterlogged soils. These species are considered more labile than crystalline U(IV) minerals, which could potentially influence uranium migration in natural systems subjected to redox oscillations. In this study, we examined the role of oxygen and carbonate on the remobilization of uranium from lake sediments, in which ~70% of the 150–300 ppm U is under the form of mononuclear U(IV) sorbed species. Our results show that both drying and oxic incubation only slightly increase the amount of remobilized U after 8 days, compared to anoxic drying and anoxic incubation. In contrast, the amount of remobilized U increases with the quantity of added bicarbonate even under anoxic conditions. Moreover, U L_{III}-edge XANES data show that a significant amount of the solid U(IV) is mobilized in such conditions. Thermodynamic speciation calculations based on the supernatant composition indicates the predominance of aqueous $\text{UO}_2(\text{CO}_3)_3^{4-}$ and, to a lesser extent, $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ complexes. These results suggest that monomeric U(IV) species could be oxidized into aqueous U(VI) carbonate complexes even under anoxic conditions via carbonate promoted oxidative dissolution, which emphasizes the need for considering such a process when modeling U dynamics in reducing environments.



1. INTRODUCTION

Uranium (U) pollution is a major concern to the environment and potentially to human health because of the chemical and radiological toxicity of this element.¹ Uranium has been released in terrestrial and aquatic ecosystems from natural sources and, during the last decades, from anthropogenic activities.² The contribution of former uranium mining activities is unequivocal for uranium and other metals as evidenced by local contaminations of lake sediments,^{3,4} aquifers,⁵ surface waters,⁶ soils,⁷ or wetlands.^{8,9} For instance, in France, sediments of several water bodies have been reported to be enriched in uranium as a consequence of former uranium mining activities from 1948 to 2001.¹⁰ Appropriate management of these U-enriched materials are currently investigated and developed in order to minimize the risks of U remobilization and therefore exposure to living organisms. Among existing management strategies for the treatment of U-impacted natural materials, remediation options mainly focus on microbial reduction of U(VI) to U(IV) processes such as biostimulation operations.¹¹ Indeed, U(IV) compounds are

mainly reported to be sparingly soluble in reducing conditions.^{12–14}

Another option consists of using former uranium mining sites for the storage of U-enriched fresh sediments after dredging operations, such as in France.¹⁰ As a result, these sediments might be exposed to variable physicochemical conditions that could influence the ultimate fate of uranium. For instance, the disposal of lacustrine anoxic sediments into open-air surface-storage facilities could induce U(IV) reoxidation to U(VI),^{15,16} which might then potentially facilitate uranium mobilization in the form of aqueous complexes of the uranyl ion UO_2^{2+} . Such unwanted reactions are expected to occur especially when uranium is present in the form of sorbed U(IV) species that are considered as being more labile than crystalline U(IV) minerals.^{17,18} Such sorbed U(IV) species

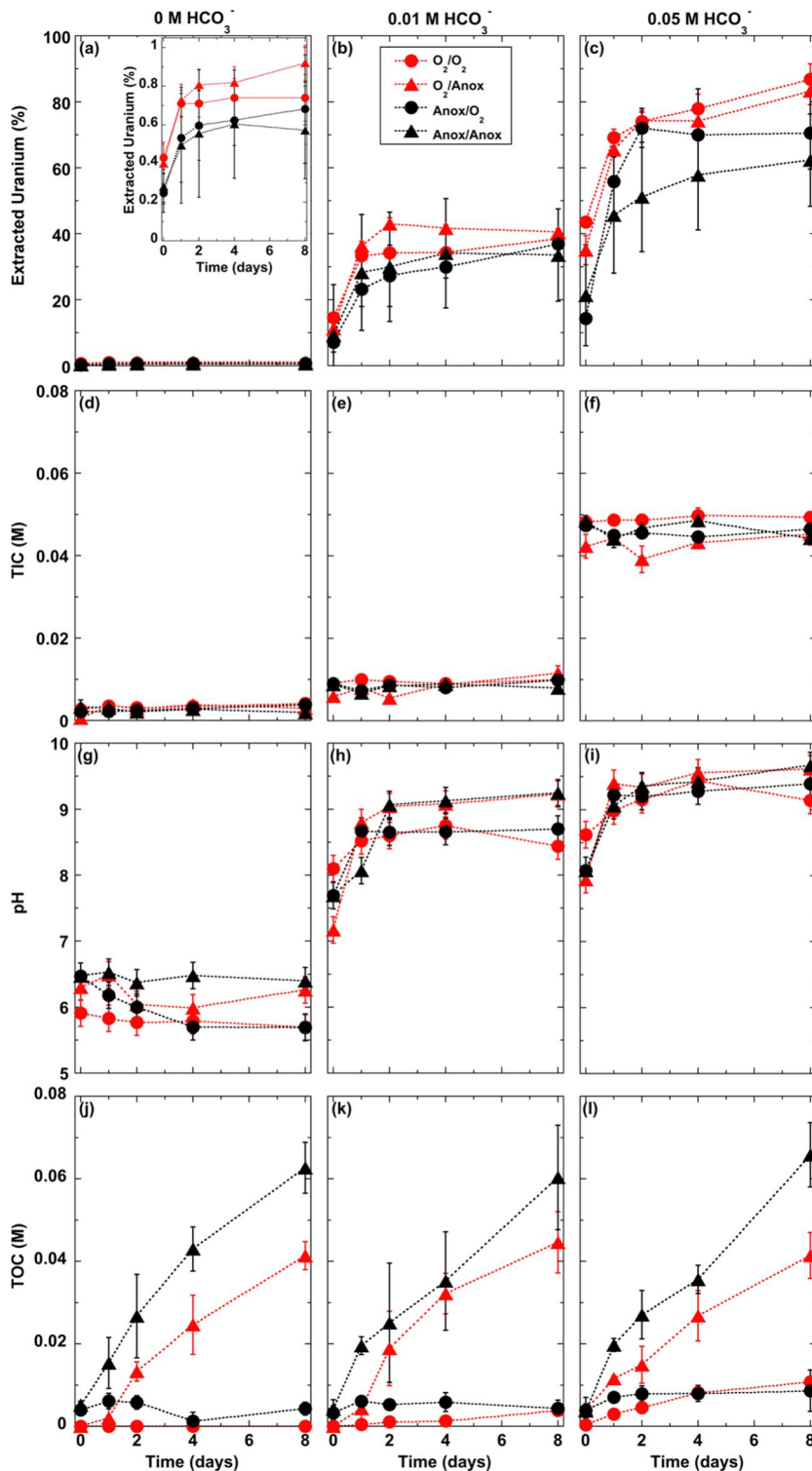


Figure 1. Extracted uranium, total inorganic carbon, pH, and total organic carbon measured for the three different studied HCO₃⁻ concentrations: left column (a, d, g, j), negative control at 0 M HCO₃⁻; center column (b, e, h, k), porewater-like alkalinity at 0.01 M HCO₃⁻, and right column (c, f, i, l), positive control at 0.05 M HCO₃⁻. For the four studied conditions: (red) O₂-dried samples dried under open-air conditions; (black) Anox-dried samples, dried under N₂-atmosphere; circles (●), incubation experiment under oxic conditions; triangles (▲), incubation experiment under anoxic conditions. Error bars represent the standard deviation over the 2011, 2012, and 2015 core samples.

have been recently identified in wetland soils,^{8,19} alluvial aquifer sediments,²⁰ and lake sediments.^{3,21}

To date, most studies about U(IV) remobilization are motivated by the concern of the long-term stability of both uraninite^{22,23} and nonuraninite species,⁹ especially for *in situ*

bioreduction strategies applied to remediation of subsurface uranium legacies.²² In such a context, nonuraninite U(IV) species have been shown to be less stable than uraninite under both oxic and anoxic conditions.^{17,23–27} Uranium mobility also largely depends on complexation of U(IV) and U(VI) with a

variety of ligands. For instance, mobilization of U(IV) in bioreduced sediments has been explained by uranium complexation to aqueous organic ligands,^{28,29} and U(IV) may be mobilized in wetland soils in the form of colloidal species.⁸ In addition, laboratory experiments have given evidence for carbonate promoted oxidative dissolution of UO₂ under reducing conditions.^{30,31} Evaluating the role of this latter mechanism on the dissolution of nonuraninite species may further help in deciphering among the various possible processes that control the long-term behavior of uranium in natural settings and repository sites.

In this study, we aimed at evaluating the influence of carbonates and redox conditions on the remobilization of uranium from lacustrine sediments in which 70% of U is present as mononuclear U(IV).³ We have investigated the influence of oxygenation during drying and incubation of the sediments in order to mimic dredging operations and surface storage of U-enriched sediments. In addition, we have evaluated the ability of aqueous carbonate species to remobilize U(VI) and U(IV) under such conditions. Because of the monitoring of both aqueous chemistry and U speciation in the solid phase, we show that aqueous U(VI) carbonate species as well as oxygenation conditions play a major role on U remobilization from the sediments.

2. MATERIALS AND METHODS

2.1. Sediment Samples. Sediments cores up to ~1.80 m length were collected in 2011, 2012, and 2015 in Lake Saint Clément, located at approximately 20 km downstream from the former uranium mine of the Bois Noirs – Limouzat in the Massif Central (France). The lake is supplied by the Besbre River, in which treated mine waters from the U-tailings pond and the former open-pit mine are discharged (Figure S1). Coring operations were conducted from a boat using an Uwitec gravity hand corer, at approximately 120 m upstream from the dam. The sediments were conditioned in a N₂-filled glovebag on the field. Special care was given to the preservation of the uranium oxidation state during sample transport to the laboratory, using aluminized plastic films heat-sealed within the glovebag in the field and conditioned below 4 °C for transportation. A previous study of the Lake Saint Clément sediments reported an increase in U concentration with depth, from 40 mg kg⁻¹ at the top of the sedimentary column to 360 mg kg⁻¹ at 180 cm depth.³

For this study, sediment samples containing between 150 and 300 mg kg⁻¹ of U were selected within the 110–150 cm depth interval of the cores, which takes into account the U concentration gradient in the sedimentary column of Lake Saint Clément.³ These sediments are characterized by a high organic content (12 wt % of total organic carbon) according to the previous chemical analyses.³ Within 48 h after field sampling, two types of drying conditions were applied to the fresh well-preserved sediment core samples in order to yield two types of starting samples for the incubation experiments: (i) oxidized sediments, referred to as O₂-dried samples that were dried under surface storage-like open-air conditions and (ii) anoxic sediments referred to as Anox-dried samples that were vacuum-dried under N₂ atmosphere in an anoxic glovebox. Once dried, samples were conditioned in glass vials sealed by butyl rubber stoppers and stored in a glovebox until the experiments. For each type of sample, O₂ or Anox, three replicate samples were used, corresponding to cores, respectively, collected in March 2011, October 2012, and

November 2015 at the same coring site, in order to integrate possible influence of seasonal conditions on U behavior. Extended X-ray absorption fine structure (EXAFS) analysis indicated that U was mainly present as mononuclear U(IV) in the Anox-dried sample.³ In the present study, EXAFS analysis showed that U was mainly present as mononuclear U(VI) in the O₂-dried sample (Figure S2 and Table S1).

2.2. Experimental Setup. In order to investigate the effect of oxygen on uranium remobilization, O₂-dried and Anox-dried samples were incubated under gentle stirring for 8 days, either under storage-like open-air conditions (referred to as O₂/O₂ and Anox/O₂ experiments, respectively) or inside a N₂-filled glovebox (referred to as O₂/Anox and Anox/Anox experiments respectively). A solid-to-liquid ratio of 1:100 was used for the experiments. For this purpose, 0.6 g of sediments were incubated for each condition with ultrapure water (O₂-free or not). At each sampling time, 0.75 mL was collected, filtered through 0.2 μm PTFE syringe filters, and acidified and diluted for analyses if needed. Dissolved oxygen concentration was monitored during the experiments and values were 8.90 ± 0.6 mg L⁻¹ (Cell Ox 325 O₂ electrode with a WTW Multi 340i hand-held meter) for O₂ incubation conditions and 0.0009 ± 0.0003 mg L⁻¹, calculated using Henry's law, based on P_{O₂} measured in the anoxic glovebox atmosphere (JACOMEX GPT3 glovebox, ±1 ppm) for Anox incubation conditions, respectively. Three concentrations of bicarbonate (0, 0.01, and 0.05 M HCO₃⁻) via initial addition of sodium bicarbonate were tested in order to assess their influence on uranium mobility. The first and latter values (0 and 0.05 M) correspond to negative and positive controls, respectively, and the 0.01 M value is a proxy for alkalinity concentration found in the sediment porewaters.²¹ Temperature (20 ± 2 °C) and relative humidity (28 ± 5%) (EL-USB-2, EasyLog, humidity and temperature logger) were constant through the experiments while pH varied freely from ~7 at the starting point to 6.2 ± 0.3, 8.5 ± 0.4, and 9.1 ± 0.4 for the three different HCO₃⁻ concentrations, respectively (Figure 1g–i).

Liquid samples were aliquoted during the incubation (time = 0, 1, 2, 4, and 8 days) and filtered through a 0.22 μm pore-size PTFE filter. Filtration was performed in an anoxic glovebox for the anoxic incubation experiments. Analyses of alkalinity³² and of dissolved iron speciation³³ were performed by colorimetric methods immediately after filtration. Samples were acidified with concentrated ultrapure HNO₃ for major and trace metals analyses by ICP-AES and ICP-MS. Non-acidified samples for TOC/TC/TIC measurements were stored at 4 °C until analyses.

In order to evaluate potential colloid-facilitated migration of uranium,³⁴ selected 0.22-μm filtrates of the 8-day incubation samples were refiltered at smaller cutoffs: 500 and 10 kDa, using poly-ether-sulfone ultrafiltration discs and an Amicon stirred cell. Total U, Fe, and C concentrations were measured after each filtration step.

Uranium in solution was determined using an ICP-MS 8800 Triple Quadrupole (Agilent). Relative standard deviation was below 10% as estimated from five measurements of the same sample, and limit of quantification was 0.03 ppm. Dissolved cations were measured using an ICP-OES iCAP 7600 Duo (Thermo Fisher Scientific). Relative standard deviation was below 10% as estimated from five measurements of the same sample, and detection limits were 10, 100, 40, 30, 100, and 10 ppb for Fe, Ca, K, Si, P, and Al, respectively.

Total organic carbon, total carbon, and total inorganic carbon (TOC/TC/TIC) were determined using a Vario TOC Cube analyzer (Elementar). Relative standard deviation was below 10% as estimated from five measurements of the same sample, and limits of quantification were 0.019 and 0.05 ppm for solid TC and TOC, respectively, and 0.5 ppm for dissolved organic carbon.

2.3. X-ray Absorption Spectroscopy. Since chemical extractions have not been reported efficient enough to discern changes in the oxidation state of uranium in the environmental samples,^{26–35} X-ray absorption spectroscopy (XAS) was used here to determine uranium oxidation state in the sediments after drying and during the incubation experiments. For this purpose, 10 samples were analyzed using XAS: (i) O₂-dried and Anox-dried samples used as starting samples and (ii) O₂/O₂, O₂/Anox, Anox/O₂, and Anox/Anox samples collected after 8 days of incubation with the addition of 0.01 and 0.05 M HCO₃⁻, samples with highest U extraction rates.

Solids were harvested by centrifugation (13000 rpm, 10 min, 10 °C) after 8 days of incubation, and the wet sediments were completely dried either at open air for the O₂ incubation conditions or inside the anoxic glovebox for the Anox incubation conditions. Samples were ground in an agate mortar, pressed as pellets, and sealed between two layers of Kapton tape. They were resealed with Kapton and stored within aluminized foil sealed bags (Protpack) under anoxic atmosphere preserved using GasPak during the transport to the synchrotron facility. Bags were opened in anoxic glovebox next to the beamline and rapidly transferred inside the cryostat, where they were placed under N₂ atmosphere.

Uranium L_{III}-edge X-ray absorption near edge structure spectroscopy (XANES) data of the sediment samples were collected in fluorescence detection mode using a 100-element solid state Ge array fluorescence detector at the high-flux 11–2 wiggler beamline of the Stanford Synchrotron Radiation Lightsource (SSRL, USA). The XANES spectrum of the Anox/Anox 0.01 M sample was recorded in high energy resolution fluorescence detection mode using the (777) reflection of Ge spherical crystals analyzers on the FAME-UHD BM16 beamline at the European Synchrotron Radiation Facility (ESRF, France). On both beamlines, the energy of the incident beam delivered by the Si(220) double-crystal monochromator, with sagittal focusing of the second crystal on BM16, was calibrated by setting the first inflection point of Y at 17038 eV, using a double transmission setup. Data were collected at 80 K (liquid N₂ cryostat) on 11–2, and at 20 K (liquid He cryostat) on BM16, in order to avoid photo-reduction of U(VI) under the X-ray beam.³⁶ A minimum of two scans were collected for each sample, and Sixpack³⁷ was used to average data and apply the dead time correction.

U L_{III}-edge XANES data of the sediment samples were fitted using Linear Combination Least Square (LC-LS) of the spectra of our purest U(IV) and U(VI) model compounds, namely, U(IV) citrate and U(VI) pyrophosphate.²¹ The Anox/Anox 0.01 M sample spectrum was fit using the HERFD-XANES spectra of a natural autunite “Ca(U^{VI}O₂)₂(PO₄)₂·10–12H₂O” from the University Pierre and Marie Curie collection (Paris, France) and of biogenic uraninite “U^{IV}O₂”³ that were recorded on the BM16 beamline. The quality of the LC-LS fits was estimated by a R-factor: $R_f = \frac{\sum [\mu_{\text{exp}} - \mu_{\text{calc}}]^2}{\sum y_{\text{exp}}^2}$, where μ is the normalized absorbance. The uncertainty on XANES LC-LS fitting components was estimated

by $3 \times \sqrt{\text{VAR}(p)\chi_R^2}$, where $\text{VAR}(p)$ is the variance of component p for the lowest χ_R^2 value; with $\chi_R^2 = N/(N - N_p) \sum [\mu_{\text{exp}} - \mu_{\text{calc}}]^2$, where N_p is the number of fitting components and N is the number of independent parameters corresponding to the energy range divided by the natural width of the U L_{III} levels.³⁸

2.4. Aqueous Speciation Calculations. The geochemical code JChess³⁹ was used for the calculation of aqueous U(VI) and U(IV) speciation for samples collected at the end of each experiment. Thermodynamic data are detailed in Table S6.^{13,40–45} Aqueous speciation of uranium was calculated on the basis of the following input data: total aqueous U, Ca, P, dissolved organic, and inorganic carbon and pH. Total dissolved Fe was implemented as aqueous Fe²⁺ since Fe aqueous speciation was difficult to predict regarding the presence of organic and inorganic ligand complexation and significant colloidal fraction as shown hereafter. Dissolved oxygen concentration was fixed at 8.9 and 0 mg L⁻¹ for O₂/O₂ and Anox/Anox experiments, respectively. For these latter experiments, equilibrium redox potential values returned by the JChess code were then directly related to the Fe²⁺ aqueous concentrations. The pH values were fixed to the input values.

3. RESULTS

3.1. Aqueous Chemistry. Dissolved concentrations of uranium and carbon were analyzed in the liquid phase after filtration at 0.22 μm. The major elements Fe, Ca, K, Si, P, and Al were also analyzed, and values are reported in Figures S3 and S4. The oxidation state of dissolved Fe (<0.2 μm) was measured for two of our experimental conditions (O₂/O₂ and Anox/Anox) using colorimetric methods (Figure S5). Iron was mostly present as Fe³⁺ in the oxic experiments, with half of this pool in colloidal form as show thereafter. In contrast, as expected, aqueous Fe²⁺ was high in the anoxic experiments.

Figure 1 shows the proportion of uranium released from the solid phase, together with the dissolved inorganic and organic carbon concentrations and the pH, as a function of incubation time for the various drying and incubation conditions investigated. Corresponding aqueous U concentrations are reported in Tables S2–S5. Less than 1% of total U was released from the solid phase (Figure 1a) when no HCO₃⁻ was added to the system (Figure 1d), and the pH was the lowest, ~6 (Figures 1g). In contrast, ~40% U was released (Figure 1b) when 0.01 M HCO₃⁻ was added (Figure 1e), and the resulting pH was 8.5 (Figure 1h). Likewise, ~60%–90% of U was released from the solid phase (Figure 1c) when 0.05 M HCO₃⁻ was added (Figure 1f) and when the pH increased up to ~9.5 (Figure 1i). In all cases, even for 0 M HCO₃⁻ (Figure 1a, insert), the sediments initially dried under open-air conditions (O₂-dried samples) yielded a higher U release than those dried under a N₂ atmosphere (Anox-dried samples), displayed in red and black symbols, respectively, in Figure 1.

As shown in Figure 1j, k, and l, organic carbon was preferentially released when sediments were incubated under anoxic conditions whatever the drying conditions, i.e., O₂/Anox and Anox–Anox experiments. The proportion of released organic carbon represented ~60% of the initial carbon in the sediment for the three HCO₃⁻ concentrations tested when sediments were incubated under anoxic conditions. On the contrary, when incubated under oxic conditions, only a small fraction (≤10%) was extracted. No correlation could then be found between U and organic carbon

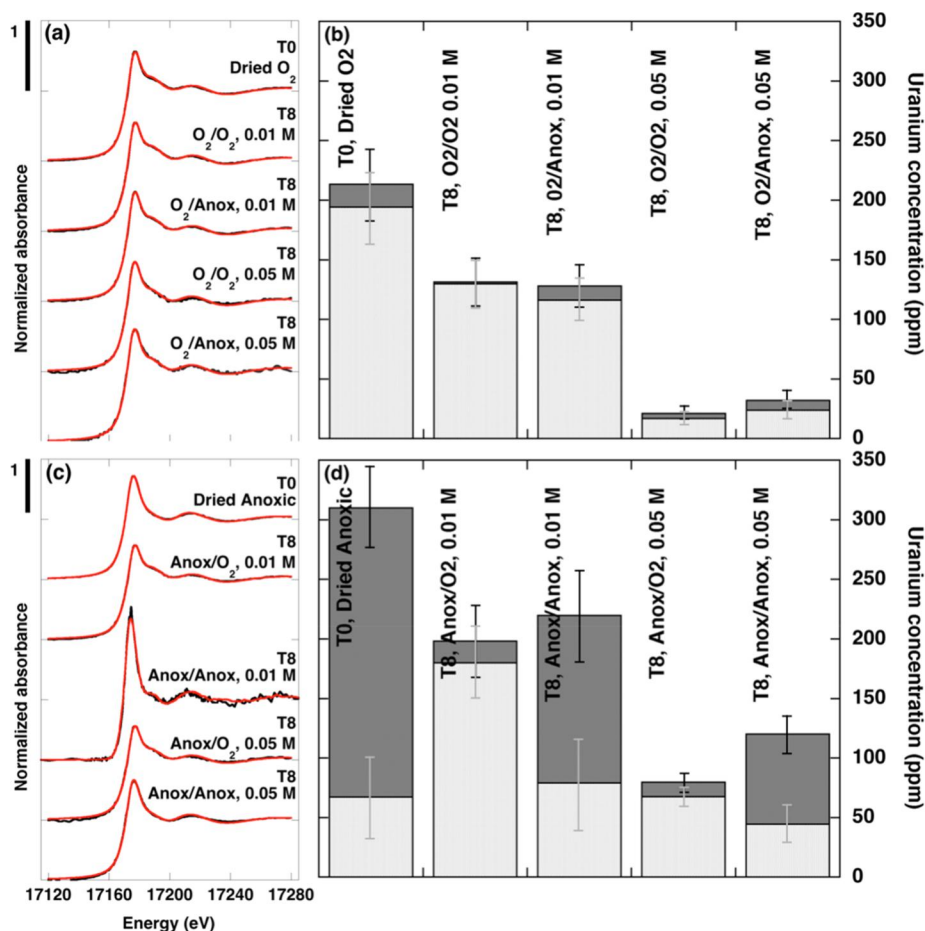


Figure 2. U L_{III}-edge XANES data fit (left) and uranium concentration and speciation in the solid phase (right). Dark gray for U(IV) and light gray for U(VI). (a),(b) Sediments dried under surface storage-like open-air conditions incubated for 8 days under surface storage-like open-air conditions or in anoxic atmosphere at pore water-like alkalinity (0.01 M HCO₃⁻) and positive control (0.05 M HCO₃⁻). (c),(d) Sediments dried in anoxic atmosphere incubated for 8 days under surface storage-like open-air conditions or in anoxic atmosphere at pore water-like alkalinity (0.01 M HCO₃⁻) and positive control (0.05 M HCO₃⁻). Error bars correspond to the uncertainty on XANES LC-LS fitting components. Data available in Supporting Information, Tables S2–S5.

releases, which suggests that organic carbon was likely not responsible for U mobility. In contrast, the growth in U release with increasing inorganic carbon concentrations suggests that bicarbonate ions could have played a key role in the remobilization of U, whether the incubation conditions were oxidizing (due to O₂ drying or O₂ incubation) or reducing (in Anox-drying, Anox-incubation systems).

3.2. Solid-Phase Analyses. We used XANES spectroscopy at the U L_{III} edge to evaluate the changes in U redox state that could have been caused by the sample drying and those that occurred during the incubations. In the O₂-dried sediment samples that initially contained 215 ppm U (Figure 2ab), U was almost fully oxidized before the incubation experiments (U(IV) < 10%). After 8 days of incubation under oxic and anoxic conditions, U remained oxidized in all cases, and the U concentrations decreased to 130 and 20–30 ppm in the solid phase, with the addition of 0.01 and 0.05 M of HCO₃⁻, respectively (Figure 2b).

In the Anox-dried samples that initially contained 310 ppm U (Figure 2cd), ~80% of U was under its reduced form (U(IV)), in agreement with previous XAS analyses.³ After 8 days of incubation under oxic conditions, U got almost fully oxidized (≤10% of U(IV)), and the remaining U concentration in the solid decreased down to ~200 and ~80 ppm,

with the addition of 0.01 and 0.05 M HCO₃⁻, respectively (Figure 2d). When these Anox-dried sediments were incubated under anoxic conditions, the extraction rate decreased, resulting in solid total U concentration of ~215 and ~120 ppm (Figure 2d). At the same time, the proportion of U(IV) in the solid did not vary significantly after 8 days of incubation under anoxic conditions (Table S5), which resulted in a net decrease in the absolute amount of U(IV) in the solid after the 0.01 and 0.05 M HCO₃⁻ experiments (Figure 2d). This result suggests that a significant fraction of the initial U(IV) solid pool was solubilized in these experiments. Further assessment of U speciation in the aqueous phase was then performed through size fractionation and thermodynamic modeling.

3.3. Size Distribution of Aqueous Species. In order to better understand the mechanism of U(VI) and U(IV) mobilization from the solid to the liquid phase, a sequential ultrafiltration procedure was applied to the aqueous samples obtained at the end of the experiments that yielded the lowest and the highest U release, i.e., those conducted without HCO₃⁻ and with the addition 0.05 M HCO₃⁻. Aqueous concentrations of U, Fe, total organic carbon, and total inorganic carbon were then measured for the <10, 10–500, and 500 kDa 0.22 μm size fractions at the end of the O₂/O₂ and Anox/Anox experiments that represented the most distinct

redox settings (Figure 3). These size fractionation results indicate that $100 \pm 10\%$ of U was present in the smaller size

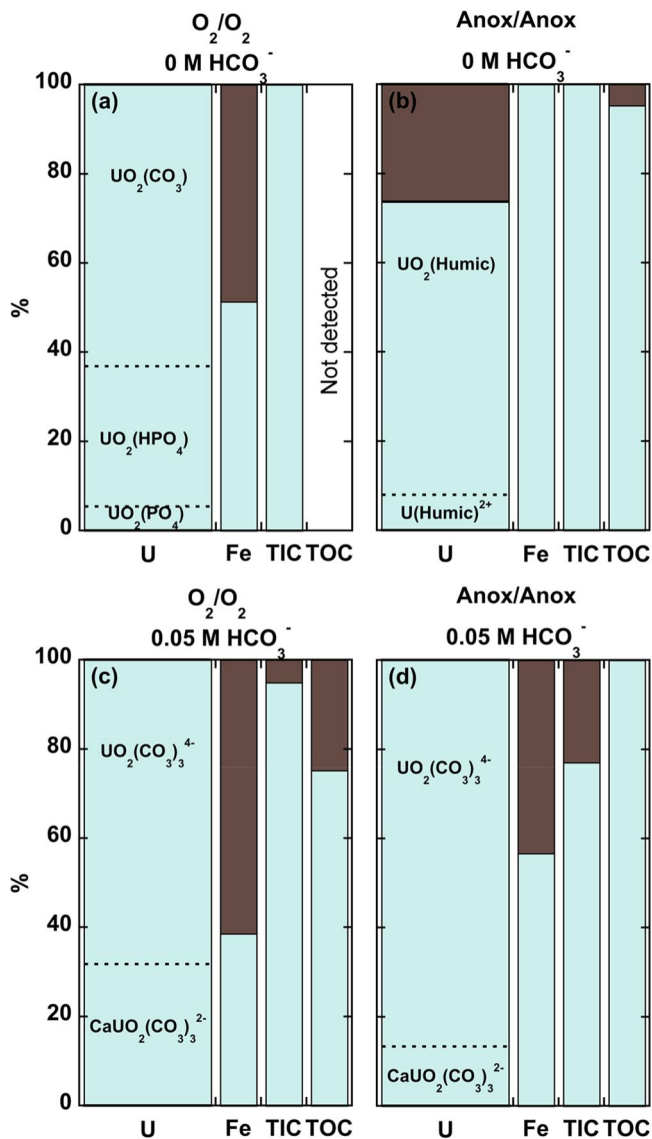


Figure 3. Distribution of aqueous species after filtration for samples with the lowest and the highest rate of uranium extraction (0 and 0.05 M HCO₃⁻, respectively). Brown, 500–10 kDa; blue, <10 kDa. Aqueous phase after 8 days (a) and (c) from sediments dried and incubated under surface storage-like open-air conditions (O₂/O₂) at 0 and 0.05 M HCO₃⁻, respectively, and (b),(d) from sediments dried and incubated under N₂ atmosphere (Anox/Anox) at 0 and 0.05 M HCO₃⁻, respectively.

fraction (<10 kDa), except for the Anox/Anox 0 M HCO₃⁻ experiment, in which $26 \pm 3\%$ of U was in the colloidal fraction (10–500 kDa). This result suggested that U was mainly mobilized in the form of aqueous complexes in all experiments, which was further investigated through equilibrium thermodynamic calculations reported in the next section. In contrast, iron was almost equally partitioned between the <10 kDa and colloidal (10–500 kDa) fractions, except for the Anox/Anox 0 M HCO₃⁻ experiment in which no colloidal iron was detected. Inorganic carbon for both HCO₃⁻ concentrations was mainly in the <10 kDa fraction, except for 0.05 M HCO₃⁻ Anox/Anox experiment where $23 \pm$

1% was in the colloidal fraction. Organic carbon was found to be mainly in the smaller size fraction (<10 kDa) especially for the Anox/Anox experiments, in which less than 5% of the large amount of organic carbon released was in the colloidal fraction (10–500 kDa). For oxic experiments, the small amount of organic carbon detected in the 0.05 M HCO₃⁻ experiment was also present in the <10 kDa fraction, with only 25% in the colloidal fraction. As the largest fractions of inorganic and organic carbon were the <10 kDa, we further investigated the respective role of dissolved inorganic and organic carbon in U mobilization through equilibrium thermodynamic calculations reported in the next section.

3.4. Thermodynamic Equilibrium Modeling of Aqueous Uranium Speciation. In order to further elucidate the mechanisms of U extraction in our experiments, the amount of U(IV) and U(VI) aqueous species were calculated with the geochemical code JChes,³⁹ using the chemical composition of the aqueous phase at the end of the O₂/O₂ and Anox/Anox experiments conducted with 0, 0.01, and 0.05 M HCO₃⁻. For the O₂/O₂ experiments, redox conditions were considered to be controlled by dissolved oxygen (8.9 mg L⁻¹), while for the Anox/Anox experiments dissolved Fe²⁺ concentrations were used for controlling redox conditions. Comparison of ferrozine assay (Figure S5) and size fractionation results (Figure 3) indicated that in the Anox/Anox experiments the colloidal fraction likely contained both Fe³⁺ and Fe²⁺. Dissolved Fe³⁺ was particularly low in the Anox/Anox 0.05 M HCO₃⁻ experiment, which justified neglecting dissolved Fe³⁺ in the prediction of the redox potential in this experiment. This observation and the complex Fe speciation in the other samples motivated our choice to consider total Fe as aqueous Fe²⁺ in our modeling of dissolved U speciation.

Our thermodynamic equilibrium calculations indicated that dissolved uranium was present only as U(VI) at the end of both O₂/O₂ and Anox/Anox experiments (Figure 3; Tables S7 and S8), except for the 0 M HCO₃⁻ Anox/Anox experiment, where ~8% of dissolved U was under the U(IV) form. In the 0 and 0.01 M HCO₃⁻ Anox/Anox experiments, neglecting the dissolved Fe³⁺ species may have led to underestimate the predicted redox potential since dissolved Fe³⁺ was present in the system (Figure S5). Even though, our modeling resulted mostly in the absence of dissolved U(IV).

Specific attention was also paid to the aqueous complexation of U(IV) and U(VI) with dissolved inorganic and organic carbon, including humic substances (Figure 3; Tables S7 and S8). For the O₂/O₂ experiments, our thermodynamic equilibrium calculations indicated that aqueous U was fully present as U(VI) mainly complexed by carbonate ligands. The UO₂(CO₃)₃⁴⁻ aqueous complex dominated in the 0.01 and 0.05 M HCO₃⁻ experiments (>60%), while the UO₂(CO₃) complex represented more than 60% of the total dissolved U in the 0 M HCO₃⁻ experiment (Figure 3; Table S7). Similar results were obtained for the 0.01 and 0.05 M HCO₃⁻ Anox/Anox experiments with even higher proportions of the UO₂(CO₃)₃⁴⁻ aqueous complexes, i.e., 100% and 87.5% of the total dissolved U, respectively (Figure 3; Table S8). In contrast, for the 0 M HCO₃⁻ Anox/Anox experiment, organic complexation of U was calculated to be dominant (Figure 3) but corresponded to a low U release (<1% of the total solid U) (Figure 1).

4. DISCUSSION

4.1. Effects of Dissolved Organic Carbon on U

Remobilization. In our incubation experiments of U-bearing lacustrine sediments, a significant amount of dissolved organic carbon was released under anoxic incubation, whereas this release was four to six times lower under fully oxygenated incubation conditions. Moreover, dissolved organic carbon was released to the same extent regardless of the bicarbonate concentrations added in the experiments (Figure 1j,k,l). These results are in agreement with a study of wetland soils,⁴⁶ in which large quantities of dissolved organic matter were reported to be solubilized under reducing conditions. Three hypotheses were formulated by the same authors to explain their observation: (i) desorption of organic matter due to pH rise, (ii) destabilization of organic matter–metal (oxyhydr)-oxides complexes via reductive dissolution of Fe and Mn oxyhydroxides, or (iii) production of organic metabolites due to microbes. The first hypothesis based on the pH rise is not validated in our anoxic experiments because of the similar dissolved organic carbon concentrations released at three different final pH values corresponding to different added bicarbonate amounts (respectively pH 6.3 for 0 M; 9.2 for 0.01 M, and 9.6 for 0.05 M HCO_3^-) (Figure 1j,k,l). Regarding the second hypothesis, the observation of aqueous Fe^{2+} in Anox/Anox experiments (Figure S5) could suggest that the reductive dissolution of Fe(III) solid phase in our anoxic experiments could have occurred. Indeed, a previous study of early diagenesis of Lake Saint Clément sediments have shown that anoxic conditions prevailing below the sediment–water interface were propitious to reduction of clay-associated Fe(III) accompanied by a significant *in situ* release of aqueous Fe^{2+} in the sediment pore waters at depth.²¹ Here, Fe release after 8 days does not exceed 4–5 mg L^{-1} , which suggests that, if any, microbial reduction in our incubation experiments was limited. Concerning the third hypothesis, the contribution of microbial activity to organic carbon release in the aqueous phase cannot be excluded, but microbial production of biomass should have been limited after only 8 days of incubation, especially in our sediments that had been stored in a dry state for several years. Finally, drying conditions of sediment samples could also partly explain the solubilization of organic carbon that we observed under reducing conditions. Indeed, dissolved organic carbon concentrations at $T = 0$ days were under the detection limit (DL) for the O_2 -dried samples, while significant concentrations of dissolved carbon were already measured from the beginning for the Anox-dried samples, whatever the incubation conditions (Figure 1j,k,l).

In our incubation experiments, the extent of organic carbon released did not play a major role in the transfer of uranium to the aqueous phase. Indeed, the pattern of dissolved organic carbon concentration was similar for all HCO_3^- conditions (Figure 1j,k,l), while the amount of extracted uranium drastically increased with the amount of added bicarbonate (Figure 1abc). This result is in line with the fact that the colloidal fraction of U did not contribute to U mobilization except in the Anox/Anox 0 M HCO_3^- experiment (Figure 3). Moreover, our thermodynamic equilibrium calculations predicted that U was mainly in the form of carbonate uranyl aqueous complexes in all experiments except the Anox/Anox 0 M HCO_3^- experiment. In this latter experiment, in which the amount of released U was more than 60 times lower than in the Anox/Anox 0.05 M HCO_3^- experiment, U complexation

to both dissolved and colloidal organic carbon likely explains U solubilization. In all other experiments, the contribution of dissolved organic carbon to U aqueous speciation is predicted to be negligible (Figure 3; Tables S7 and S8).

These results are in accordance with the study,²⁸ where only 0.04% of total U (0.8 g.kg^{-1}) from the solid phase was remobilized by low concentrations ($<10 \text{ mg L}^{-1}$) of humic acids in column experiments. Moreover, low U extraction rates were reported when using EDTA and citrate as complexing agents under reducing conditions.^{29,47} Organic species such as humic acids are effectively known to complex U(VI) and U(IV) as, respectively, aqueous and solid complexes.^{42,48} However, our calculations suggest that such complexes do not dominate aqueous U speciation in our incubation experiments, except in the absence of added carbonate and when anoxic conditions favored the release of large amounts of dissolved organic carbon (Anox/Anox 0 M HCO_3^- experiment). Minor complexation of U to aqueous organic carbon species in the other experiments cannot be excluded, but this mechanism does not explain the dramatic increase of uranium mobilization observed in our incubations conducted with added bicarbonates.

4.2. Effect(s) of Bicarbonate on U Remobilization. Our results suggest that inorganic carbon played a key role in uranium remobilization even under anoxic conditions. When inorganic carbon was not added to the system, the uranium release was minimal (Figure 1a) and did not exceed 1% of the 150–300 ppm U solid pool, represented by 70% of mononuclear species.³ In contrast, a large fraction (~60%–90%) of the uranium solid pool was mobilized to the aqueous phase when bicarbonate ions were added to the system at the beginning of the experiment. In this case, our speciation calculations suggest that dissolved U(VI) carbonate complexes were largely predominant, even under reducing conditions (Table S8). Carbonate facilitated dissolution of U in our oxic experiments is consistent with the well-known ability of uranyl to form soluble complexes with carbonate ions.⁴⁹ However, our results also show a massive release of U, likely in the form of aqueous U(VI) carbonate complexes, from our sediments that still contain a large fraction of U(IV) at the end of the Anox/Anox experiments (Figure 2). This result suggests that oxidative dissolution of U(IV) solid species could have occurred during our anoxic incubation experiments. Such a mechanism was previously proposed³⁰ for explaining the dissolution of biogenic and chemogenic uraninite under reducing conditions. According to these authors, the oxidation processes of U(IV) could be promoted by carbonate complexation due to the well-known stability of U(VI) carbonate aqueous complexes.^{49–51} This process, referred to as carbonate promoted oxidative dissolution of U(IV), was shown previously in the case of UO_2 dissolution.^{30,31} Our results thus give further insight into possible mechanisms that could explain the bicarbonate extractability of noncrystalline U(IV) previously reported.^{17,18} It could be especially favored in our experiments at alkaline pH, including the Anox–Anox experiment with 0.05 M of bicarbonate (Table S8).

4.3. Environmental Implications. Our results show that carbonate ions not only increased U(VI) mobility, as it has been reported earlier,^{49,51–53} but can also favor U(IV) carbonate promoted oxidative dissolution^{30,31,54–56} from contaminated sediments under both reduced and oxidizing conditions, as previously observed for pure biogenic and nonbiogenic uraninite in laboratory experiments.³¹ Indeed, the

present study demonstrates that mononuclear U(IV) can be remobilized from contaminated sediments, regardless of redox conditions, at alkaline pH, even at bicarbonate concentrations that can be encountered in lacustrine sediment pore waters (i.e., 0.01 M HCO_3^-).²¹ Our results thus have potential implications for the fate of uranium in contaminated soils and groundwater as well as in surface storage sites.^{3,8,19,20} Indeed, leaching of concrete in low level (LLW) radioactive waste has been reported to generate alkaline waters with high dissolved carbonate contents, which enhanced the mobility of U(VI).⁵⁶ Hence, although the dramatic uranium release that we observed in our high HCO_3^- experiments (0.05 M HCO_3^- , pH 8.5–9.5) cannot be extrapolated to natural media, these results could be useful for LLW waste studies. In addition, moderate to significant uranium release is expected at pH < 8.5, according to our experiments conducted at 0 and 0.01 M added HCO_3^- , respectively. Further studies would then be needed in order to assess the long-term remobilization of U at circumneutral pH. We also show that U remobilization processes observed here are effective under both oxic and anoxic conditions, in contrast with a recent study that reported that monomeric U(IV) remobilization from sediments is minimized in an oxic simulated natural media.²⁶ Our emerging results suggest that further investigations are necessary to better evaluate the relative importance of carbonate promoted oxidative dissolution and organic complexation in the remobilization of U(IV) under reducing conditions, especially in complex natural systems in which U(IV) speciation includes ill-defined mononuclear species. Better understanding the interactions between dissolved and solid U(IV) and organic and inorganic carbon is crucial to improve the evaluation and prediction of uranium remobilization processes in natural systems and thus to improve the storage management strategies for U-enriched materials.

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Notes

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