

and contaminated freshwaters. Moreover, our results raise issues concerning the long term fate of mononuclear U(IV) complexes and U(IV) phosphate nano-minerals, especially with respect to re-oxidation events.

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## Introduction

Redox cycling of uranium exerts a major control on its mobility in the environment because of the low solubility of U(IV) phases compared to that of U(VI) ones (Bargar *et al.*, 2008). In natural anoxic environments such as estuarine and coastal sediments, early diagenesis conditions favour the reduction of U(VI) species into low solubility U(IV) species, which decreases uranium concentrations in overlying waters and sediment pore-waters (Barnes and Cochran, 1993). Researchers addressing remediation of U-contaminated groundwaters have focused on *in situ* biostimulation strategies involving microbial reduction of U(VI) (Wu *et al.*, 2007; Yabusaki *et al.*, 2007) into biogenic uraninite (Suzuki *et al.*, 2005; Bargar *et al.*, 2008) as well as non-uraninite U(IV) phases (Kelly *et al.*, 2008; Bargar *et al.*, 2013; Alessi *et al.*, 2014a; Newsome *et al.*, 2014). *Ex situ* incubations of aquifer sediments under anoxic conditions have highlighted the importance of non-crystalline U(IV) species as major products of microbial reduction of U(VI) (Sharp *et al.*, 2011; Alessi *et al.*, 2014b). In laboratory bioassays, mononuclear U(IV)-phosphate complexes, in which a U(IV) ion coordinates to a PO<sub>4</sub> group, have been especially observed as products of microbial U(VI) reduction (Bernier-Latmani *et al.*, 2010; Fletcher *et al.*, 2010; Sivaswamy *et al.*, 2011). U(IV)-phosphate mineral phases as ningyoite CaU(PO<sub>4</sub>)<sub>2</sub>•2H<sub>2</sub>O have also been identified after microbial reduction of dissolved U(VI) in the presence of phosphate (Bernier-Latmani *et al.*, 2010; Lee *et al.*, 2010) or after reduction of U(VI) phosphate mineral phases (Khijniak *et al.*, 2005; Rui *et al.*, 2013). The occurrence and distribution of non-uraninite U(IV) phases in natural systems is however scarcely documented (Qafoku *et al.*, 2009). Recently, Campbell *et al.* (2012) showed that non-crystalline mononuclear U(IV) is present in aquifer sediments at the Rifle site. On the basis of this observation, it can be suspected that non-crystalline U(IV) species may form in other reducing environments, among which lacustrine sediments have a global environmental significance since they represent major uranium accumulation reservoirs in freshwater watersheds. Studies of uranium distribution in lacustrine environments suggested associations of U with organic matter in bottom lake sediments (Ueda *et al.*, 2000; Chappaz *et al.*, 2010) as well as in the water column (Alberic *et al.*, 2000) but no direct determinations of uranium speciation in such environments have been yet reported.

Here we used a combination of X-ray absorption spectroscopy, electron microscopy and selective chemical extraction to investigate uranium speciation in contaminated lake sediments. We show that uranium occurs mainly in the form of mononuclear U(IV)-phosphate/silicate complexes, and to a lesser extent

## Mononuclear U(IV) complexes and ningyoite as major uranium species in lake sediments

G. Morin<sup>1\*</sup>, A. Mangeret<sup>2</sup>, G. Othmane<sup>1</sup>, L. Stetten<sup>1,2</sup>,  
M. Seder-Colomina<sup>1,2</sup>, J. Brest<sup>1</sup>, G. Ona-Nguema<sup>1</sup>,  
S. Bassot<sup>2</sup>, C. Courbet<sup>2</sup>, J. Guillevic<sup>2</sup>, A. Thouvenot<sup>3</sup>,  
O. Mathon<sup>4</sup>, O. Proux<sup>5</sup>, J.R. Bargar<sup>6</sup>



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### Abstract

Natural attenuation of uranium in subsurface environments is usually assigned to immobilisation processes due to microbially mediated reduction of U(VI). Recent laboratory studies have established that the end products of such a process include both low solubility biogenic uraninite and more labile non-crystalline U(IV) species. Indeed, biogenic uraninite formation may be inhibited in the presence of organic or inorganic phosphoryl ligands, leading to the formation of non-crystalline U(IV)-phosphate complexes or nanoscale U(IV)-phosphate solids. Such species have been observed in shallow contaminated alluvial aquifers and can thus be suspected to form in other important environments, among which lacustrine sediments have a global environmental significance since they may represent major uranium accumulation reservoirs in riverine watersheds. Here, on the basis of microscopic, spectroscopic and chemical extraction analyses, we report the occurrence of mononuclear U(IV)-phosphate/silicate complexes, accompanied by nano-crystalline ningyoite-like U(IV)-phosphate minerals, as major scavengers for uranium in lacustrine sediments downstream from a former uranium mine in France. This observation reveals that uranium trapping mechanisms during early diagenesis of lacustrine sediments can virtually exclude uraninite formation, which has important implications for better modelling uranium cycling in natural

1. Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie (IMPMC), UMR 7590 CNRS-UPMC-IRD-MNHN, case 115, 4 place Jussieu, 75252 Paris Cedex 5, France

\* Corresponding author (email: guillaume.morin@impmc.upmc.fr)

2. Institut de Radioprotection et de Sûreté Nucléaire, IRSN, PRP-DGE, 31 avenue de la Division Leclerc, 92262 Fontenay-aux-Roses, France

3. Université de Clermont Ferrand, Athos Environment, 63171 Aubière, France

4. European Synchrotron Radiation Facility (ESRF), BP 220, 38043 Grenoble Cedex, France

5. Observatoire des Sciences de l'Univers de Grenoble (OSUG), UMR CNRS 832, Université Grenoble-Alpes, 38041 Grenoble Cedex 9, France - BM30B/CRG-FAME, ESRF, Polygone scientifique Louis Néel, 71 avenue des Martyrs, 38000 Grenoble, France

6. Stanford Synchrotron Radiation Lightsource (SSRL), SLAC National Accelerator National Laboratory, MS 69, 2575 Sand Hill Road, Menlo Park, CA 94025, USA



as nano-crystalline U(IV)-phosphate of the ningyosite-rhabdophane group. This result has major implications for better predicting the behaviour and fate of uranium in lacustrine environments.

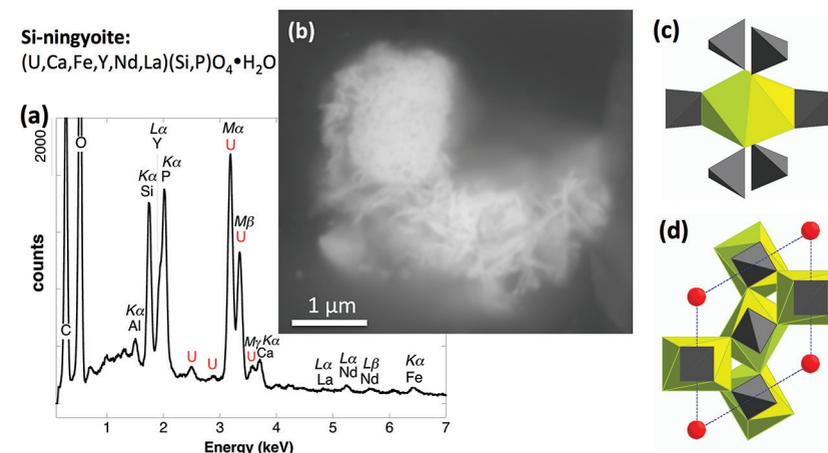
## Sampling Site and Analytical Methods

Sediment cores were sampled in March 2011 and October 2012, with an Uwitec® gravity corer, in the lake Saint-Clément, in a high U geological background area located ~20 kilometers downstream from the former uranium mine of Bois Noirs/Limouzat in the Massif Central, France (Fig. S-1). Core sections were immediately placed in a glove bag, purged with N<sub>2</sub>, sealed in hermetic containers, transported below 4 °C, and dried under vacuum in a glove-box at the IMPMC laboratory 24 hours after sampling. Samples were preserved under anoxic conditions until and during mineralogical and spectroscopic analyses, and during chemical extractions. For SEM-EDXS analyses, sediments were embedded in epoxy resin and prepared as thin sections. Here, we studied the most concentrated samples collected at 120-123 cm and 143-146 cm depth in the 2012 core and at 190-194 cm depth in the 2011 core, with total bulk U contents of ~200, 275 and 360 mg/kg (Fig. S-1; Table S-1). To determine uranium solid-state speciation, we used X-ray Absorption Near Edge Structure (XANES) spectroscopy, Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy at the U L<sub>III</sub>-edge, and Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDXS) analyses. In addition, we used 1M NaHCO<sub>3</sub> O<sub>2</sub>-free solution extraction (Alessi *et al.*, 2012) for evaluating the proportion of non-crystalline U(IV) species in the same samples. See Supplementary Information for detailed procedures.

## Identification of U-bearing Minerals in the Sediment Samples

X-ray diffraction indicated that the sediments consisted mainly of quartz, feldspar, micas and chlorite, in agreement with their chemical composition (Table S-1) and with the granitic geological substratum (Fig. S-1). The high organic carbon content ~12 wt % was related to fresh organic matter including vegetal debris. Barite [BaSO<sub>4</sub>] was detected under SEM-EDXS analyses, and pyrite [FeS<sub>2</sub>] was present as rare submicron sized crystals. Systematic SEM observations and EDXS analyses of the 143-146 cm sample revealed scarce U-bearing minerals (Table S-2): zircon, thorite (Fig. S-2), monazite (Fig. S-3), rhabdophane (Figs. S-4, S-5), and a nano-crystalline U-rich phosphate mineral of the ningyosite group (Figs. 1, S-6). Ningyosite was the most concentrated U phase identified in the sample, with the following approximate structural formula: [(U<sub>0.95</sub>Ca<sub>0.3</sub>Fe<sub>0.15</sub>Al<sub>0.15</sub>Y<sub>0.4</sub>Nd<sub>0.05</sub>)(PO<sub>4</sub>)(SiO<sub>4</sub>)•nH<sub>2</sub>O] (Table S-2, Fig. S-6). According to Muto *et al.* (1959), powder XRD data of ningyosite [CaU(PO<sub>4</sub>)<sub>2</sub>•2H<sub>2</sub>O] indicate that this mineral is isostructural to rhabdophane [REE<sup>3+</sup>PO<sub>4</sub>•H<sub>2</sub>O], with an equivalent amount of U<sup>4+</sup> and

Ca<sup>2+</sup> ions substituting for the REE<sup>3+</sup> ions. In the mineral phase identified here, the excess of U<sup>4+</sup> over Ca<sup>2+</sup> is likely compensated by SiO<sub>4</sub><sup>4-</sup> for PO<sub>4</sub><sup>3-</sup> substitution, as in Si-rich ningyosite (Doinikova *et al.*, 2014). Most ningyosite ore deposits are suspected to have formed in reducing zones close to the anoxic-oxic boundary, possibly via microbial activity (Doinikova, 2007) as suggested by laboratory experiments (Khijniak *et al.*, 2005; Bernier-Latmani *et al.*, 2010; Lee *et al.*, 2010; Rui *et al.*, 2013). In the sediments studied here, evaluating the importance of the U(IV) mineral phases with respect to other uranium species required both bulk XANES and EXAFS analyses and selective chemical extractions assays.

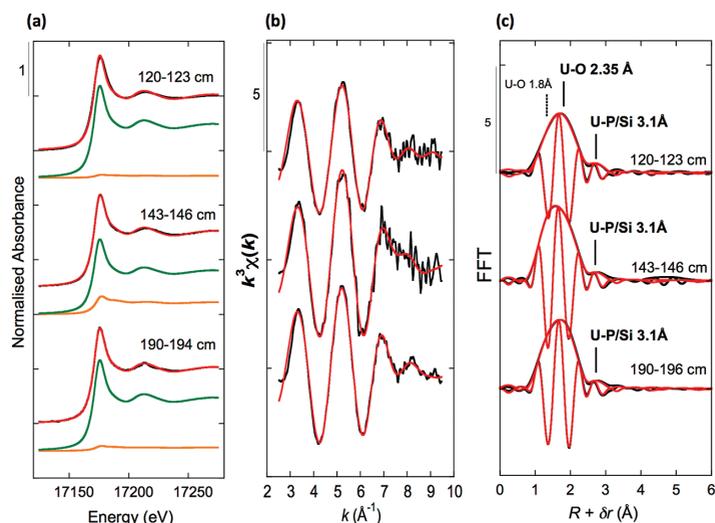


**Figure 1** (a) EDXS analysis (Table S-2) and (b) Backscattered electron SEM image of Si-ningyosite in sample 143-146 cm with nano-sized acicular shaped crystals characteristic of the ningyosite and rhabdophane group minerals. Coordination of the (c) U<sup>IV</sup>O<sub>8</sub> polyhedron (yellow) to phosphate tetrahedra (gray), and (d) cation polyhedra in the ningyosite/rhabdophane structure (Table S-4).

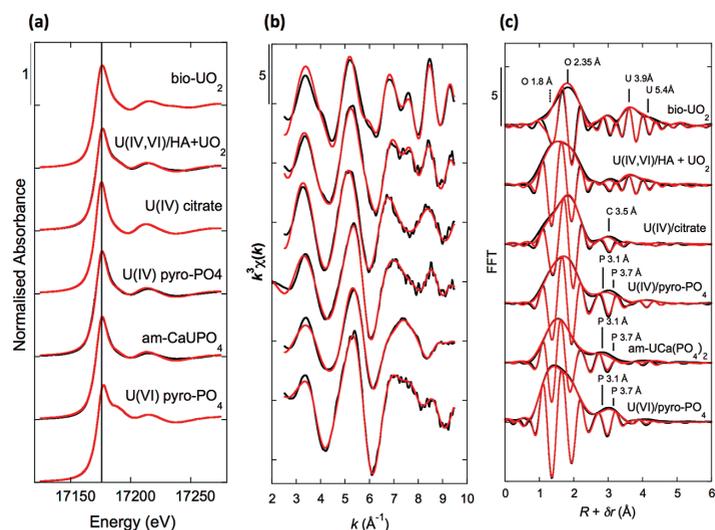
## Uranium Oxidation State

XANES analyses at the U L<sub>III</sub>-edge indicated that uranium was mainly present as U(IV) in the sediment samples studied (Fig. 2a). Indeed, the shoulder at ~17190 eV that is characteristic of the uranyl ion, *e.g.*, in U(VI)-pyrophosphate (Figs. 3a, S-7), was not observed in the XANES spectra of the sediment samples (Figs. 2a, 7a). Linear Combination Fitting (LCF) of the XANES spectra indicated that the proportion of U(VI) accounted at most for 20 % of total U in the 143-146 cm sample and was below 10 % of total U in the two other sediment samples (Fig. 2a, Table S-3).





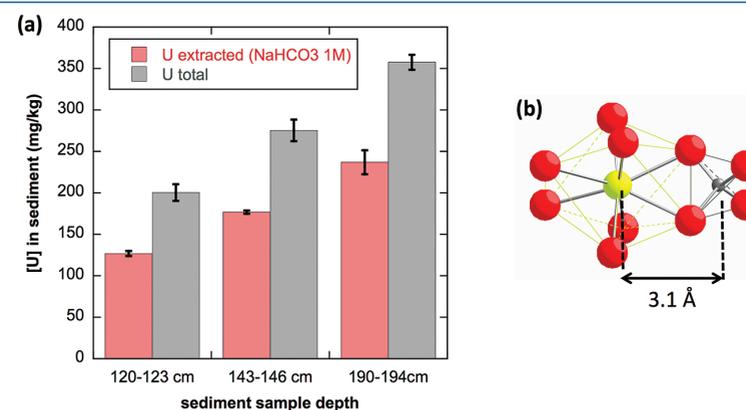
**Figure 2** Uranium L<sub>III</sub>-edge XANES and EXAFS data of the lake sediment samples (black). **(a)** Linear Combination Fits (red) of the XANES spectra included U(IV) citrate (green) and U(VI) pyrophosphate (orange) as components. **(b)** Shell-by-shell fits (red) of the unfiltered  $k^3\chi(k)$  EXAFS spectra and **(c)** their Fast Fourier Transforms. See Table S-3 for fitting parameters.



**Figure 3** Uranium L<sub>III</sub>-edge XANES and EXAFS data of relevant model compounds (black). **(a)** Linear Combination Fits (red) of the XANES spectra, **(b)** shell-by-shell fits (red) of the unfiltered  $k^3\chi(k)$  functions and **(c)** their Fast Fourier Transforms. See Table S-3 for fitting parameters.

### Chemical Extraction as a Probe for Mononuclear U(IV) Species

The proportion of mononuclear U(IV) species in the sediment samples was evaluated by selective chemical extraction using a 1 M NaHCO<sub>3</sub> O<sub>2</sub>-free solution under anoxic conditions using the protocol of Alessi *et al.* (2012) (Supplementary Information). As shown in Figure 4a, 65 ± 5 % of the total uranium content was extracted from the three samples by this method, and could be assigned to mononuclear U(IV). Indeed, non-crystalline U(IV) species may include mononuclear and polymerised U(IV)-complexes, the latter being less extractable than the former (Alessi *et al.*, 2014b). U(IV)-bearing minerals identified by SEM-EDXS, including ningyoite, rhabdophane, thorite and zircon, thus likely accounted at most for 35 ± 5 % of the total uranium in the sediment samples.



**Figure 4** **(a)** Concentration of U(IV) extracted by O<sub>2</sub>-free NaHCO<sub>3</sub> (1M) solution compared to total bulk U. **(b)** Local structure of mononuclear U(IV)-phosphate/silicate bidendate edge-sharing complexes determined by EXAFS analysis as major solid state species of uranium in the sediments studied (Fig. 2, Table S-3). The phosphate/silicate tetrahedron could be connected to either organic or inorganic substrates.

### EXAFS Evidence for Mononuclear U(IV)-phosphate/silicate Complexes as Major U Species

U L<sub>III</sub>-edge EXAFS data of the three sediment samples were rather similar to each other (Fig. 2b,c), and significantly different from that of biogenic nano-uraninite (Fig. 3b,c). Indeed, best fits of the sediment sample data were obtained with 8-9 U-O scattering paths at ~2.35 Å and ~1 U-P or U-Si path at ~3.1 Å, with similar fit quality for a P or Si neighbour (Figs. 2c, S-8, Table S-3). The U-O paths were consistent with U<sup>4+</sup> ions 8-fold coordinated to oxygen atoms (Table S-4). A minor U-O path at a distance of ~1.8 Å improved the fits, accounting for <5-20 % of uranyl ions identified by XANES analysis (Fig. 2a, Table S-3).



The observed U-P/Si distance of  $\sim 3.1$  Å corresponds to edge-sharing bidentate bridging of the  $\text{UO}_8$  group to a  $\text{PO}_4/\text{SiO}_4$  tetrahedron (Rui *et al.*, 2013) (Fig. 4b, Table S-4), such U-P distance being characteristic of non-uraninite U(IV) species identified as products of microbial (Bernier-Latmani *et al.*, 2010; Lee *et al.*, 2010; Boyanov *et al.*, 2011) or abiotic (Veeramani *et al.*, 2011) U(VI) reduction. Moreover, a sole P/Si atom was detected beyond the first oxygen coordination sphere of the U absorber, which contrasts with the higher number of second neighbours observed for amorphous U(IV) phases (Table S-3, Fig. S-9). This result demonstrated that uranium was mainly present as mononuclear U(IV)-phosphate/silicate complexes in the sediment, likely accounting for most of the extractable U(IV) fraction ( $65 \pm 5$  % of total U in Fig. 4).

Neither the U-U paths of the uraninite structure (Fig. 3), nor the U-P/Si at 3.7-3.8 Å (Fig. 1c) and U-U/Th/Ca/REE paths at 3.6-4.1 Å (Fig. 1d) that are characteristic of crystalline (Table S-4) and amorphous (Fig. S-9) U(IV)-bearing phosphate and silicate mineral phases, were detected around the U absorber in the sediments (Fig. 2c, Table S-3). Owing to the sensitivity of EXAFS to minor components (Alessi *et al.*, 2012), crystalline phases thus accounted for less than 10 % of U, suggesting that the non-extractable U fraction in the sediments ( $35 \pm 5$  % of total U in Fig. 4) consisted of nano-crystalline or amorphous U(IV) phases. For instance, biogenic nano-crystalline U(IV) is not easily extracted by 1M  $\text{NaHCO}_3$  (Alessi *et al.*, 2014b). We thus infer that a fraction of the primary U(IV)-bearing uranium minerals identified by SEM-EDXS, as zircon and thorite are likely metamict because of their high U and Th contents (Table S-2), which would make such phases difficult to detect by EXAFS as minor phases in a mixture with mononuclear U(IV) complexes. Accordingly,  $\sim 1$  instead of 4 Pu-Zr paths at 3.6 Å were reported for Pu L<sub>III</sub>-edge EXAFS analysis of highly metamict zircon (Begg *et al.*, 2000). In the same way,  $\sim 2$  to 4 times less P and U neighbours were observed by EXAFS in our amorphous U(IV) model compounds (Table S-3, Fig. 3) than in their crystalline analogues (Table S-4).

Finally, Continuous Cauchy Wavelet Transform analysis of the EXAFS data confirmed that mononuclear U(IV) was mainly complexed to phosphate or silicate groups, even if a minor contribution from carboxylic/phenolic or carbonate groups could not be excluded (Fig. S-8). Hence, our EXAFS results indicated that uranium was mainly in the form of mononuclear U(IV)-phosphate/silicate complexes in the sediments studied and thus provide a direct clue of the importance of such species in lacustrine systems.

## Environmental Implications

The knowledge of uranium speciation in natural sediments impacted by anthropogenic activities is essential for predicting the fate of uranium during and after sediment deposition. In that context, lacustrine sediments are of particular importance because they represent important accumulation reservoirs for this element in continental watersheds. The present study yields evidence for

mononuclear U(IV)-phosphate complexes as the main uranium species in lake sediments impacted by a former uranium mine. This observation reveals that uranium trapping mechanisms during early diagenesis of lacustrine sediments can virtually exclude uraninite formation, which has important implications for modelling uranium cycling in natural and contaminated freshwater systems. The absence of uraninite in the sediments studied here supports previous laboratory studies attesting that phosphate ions can inhibit uraninite precipitation (Khijniak *et al.*, 2005; Bernier-Latmani *et al.*, 2010; Lee *et al.*, 2010; Boyanov *et al.*, 2011; Rui *et al.*, 2013), and suggest that silicate could act similarly in natural systems. Our results also indicate that U(IV)-phosphates such as ningyoite, although present, account for a minor fraction of the total U(IV). Such a phase could have formed in the sediment after bioreduction of either soluble U(VI) (Bernier-Latmani *et al.*, 2010) or, more likely, of a secondary U(VI)-phosphate/silicate mineral inherited from the uranium ore (Rui *et al.*, 2013) (Fig. S-1).

Importantly, we show the predominance of mononuclear U(IV)-phosphate/silicate species, in agreement with results of laboratory studies involving U(VI) reduction in the presence of phosphate (Bernier-Latmani *et al.*, 2010; Fletcher *et al.*, 2010; Sivaswamy *et al.*, 2011; Boyanov *et al.*, 2011; Veeramani *et al.*, 2011; Sharp *et al.*, 2011; Alessi *et al.*, 2014b). Such U(IV) mononuclear species could either be sorbed to the surface of phosphate (Veeramani *et al.*, 2011) as well as silicate minerals, or be bound to organic phosphoryl groups (Alessi *et al.*, 2014b). The major occurrence of such species in lacustrine sediments has important environmental implications since mononuclear U(IV) species are potentially more labile than uraninite (Cerrato *et al.*, 2013; Alessi *et al.*, 2014a) and polymerised non-crystalline U(IV) phosphate phases (Alessi *et al.*, 2014b). Such lability raises issues concerning the long term fate of the mononuclear U(IV) species, especially when subjected to sharp redox changes, for example in sediment remediation strategies as dredging operations.

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## Additional Information

**Supplementary Information** accompanies this letter at [www.geochemicalperspectivesletters.org/article1610](http://www.geochemicalperspectivesletters.org/article1610)

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