Metaschoepite Dissolution in Sediment Column Systems—Implications for Uranium Speciation and Transport

William R. Bower, Katherine Morris, Francis R. Livens, J. Frederick W. Mosselmans, Connaugh M. Fallon, Adam J. Fuller, Louise Natrajan, Christopher Boothman, Jonathan R. Lloyd, Satoshi Usunomiya, Daniel Grolimund, Dario Ferreira Sanchez, Tom Jillbert, Julia Parker, Thomas S. Neill, and Gareth T. W. Law

Centre for Radiochemistry Research, School of Chemistry, The University of Manchester, Manchester, U.K., M13 9PL
Research Centre for Radwaste Disposal and Williamson Research Centre, School of Earth and Environmental Sciences, The University of Manchester, Manchester, U.K., M13 9PL
Radiochemistry Unit, Department of Chemistry, The University of Helsinki, Helsinki, Finland, 00014
Diamond Light Source, Harwell Science and Innovation Campus, Didcot, U.K., OX11 0DE
Kyushu University, Department of Chemistry, 744 Motooka, Nishi-ku, Fukuoka Japan, 819-0395
Swiss Light Source, Paul Scherrer Institute, Villigen, Switzerland, 5232

Ecosystems and Environmental Research Programme, Faculty of Biological and Environmental Sciences, The University of Helsinki, Helsinki, Finland, 00014

Supporting Information

ABSTRACT: Metaschoepite is commonly found in U-contaminated environments and metaschoepite-bearing wastes may be managed via shallow or deep disposal. Understanding metaschoepite dissolution and tracking the fate of any liberated U is thus important. Here, discrete horizons of metaschoepite (UO₃·nH₂O) particles were emplaced in flowing sediment/groundwater columns representative of the UK Sellafield Ltd. site. The column systems either remained oxic or became anoxic due to electron donor additions, and the columns were sacrificed after 6- and 12-months for analysis. Solution chemistry, extractions, and bulk and micro/nano-focus X-ray spectroscopies were used to track changes in U distribution and behavior. In the oxic columns, U migration was extensive, with UO₂²⁻ identified in effluents after 6-months of reaction using fluorescence spectroscopy. Unusually, in the electron-donor amended columns, during microbially mediated sulfate reduction, significant amounts of UO₂-like colloids (>60% of the added U) were found in the effluents using TEM. XAS analysis of the U remaining associated with the reduced sediments confirmed the presence of trace U(VI), noncrystalline U(IV), and biogenic UO₂, with UO₂ becoming more dominant with time. This study highlights the potential for U(IV) colloid production from U(VI) solids under reducing conditions and the complexity of U biogeochemistry in dynamic systems.

INTRODUCTION

Uranium (U) has been released into the environment through mining activities, weapons use, and via authorized discharges and accidents at nuclear sites. It is typically the largest radionuclide by mass in many higher activity radioactive wastes. Uranium is radiotoxic, chemotoxic, long-lived (²³⁵U half-life = 703.8 × 10⁶ years, ²³⁸U 4.468 × 10⁶ years), and persists in the subsurface; thus, it poses a significant environmental and human health risk. As such, understanding U behavior in the geosphere is essential.

Uranium is redox-active and its speciation typically controls its solubility and hence mobility. In oxic environments, relatively soluble complexes of U(VI) are typically present. Under anoxic conditions, lower solubility U(IV) species tend to dominate, with reaction end-products including UO₂ and noncrystalline U(IV). U(V) species have also been documented in environmental studies, but it typically disproportionates. Uranium also readily sorbs to a range of minerals (e.g., Fe/Mn-oxy(hydr)oxides, -sulfides, or phyllosilicates) and cell surfaces, or it can become incorporated into the lattices of neo-forming mineral phases. Interestingly, incorporation of U(V) into neo-forming Fe oxy(hydr)oxides appears to stabilize its redox state.
Overall, U(VI) reduction, sorption, or incorporation reactions in the geosphere can limit U migration in the environment, but to date, U biogeochemistry studies have largely focused on mechanisms controlling U(VI)\(_{(aq)}\) removal from solution (for example, see the review of Newsome et al., 2015). However, U(VI) solids have also been released to the environment (often in particulate form), or they can concentrate naturally (e.g., from U ores, placer deposits etc.). Our understanding of how these U solid phases behave in the environment, and how they contribute to U transport is not well-defined.

Metaschoepite (a U(VI) oxide) is a primary product of depleted uranium munition corrosion in former war zones (e.g., Gulf and Balkan Wars) and at military test sites. It also forms upon oxidation of UO\(_2\) in the environment, and UO\(_2\) can be formed at U contaminated sites during U(VI)\(_{(aq)}\) biostimulation, or be dispersed in the environment during mining activities or through nuclear accidents. Large volumes of uranium wastes, which include significant amounts of metaschoepite, may also be managed by either shallow or deep disposal in the UK. Despite this, the environmental behavior of metaschoepite, and its impact on U transport in complex, dynamic environmental systems is poorly constrained.

The objective of this study was therefore to track the stability of metaschoepite and the biogeochemistry of any liberated U in complex sediment/synthetic groundwater systems, under realistic environmental conditions (i.e., flowing groundwater, variable redox, dynamic sediment microbial communities). To do this, sediment columns representative of the UK Sellafield Ltd. site were doped with discrete horizons of metaschoepite particles. The metaschoepite was then subjected to groundwater flow for periods of up to 12-months; here, the columns either remainedoxic or became progressively reducing due to the addition of electron donors. Column effluent sampling during the experiments showed that the metaschoepite was readily dissolved; however, in the electron donor amended system, there was significant production of UO\(_2\)-like colloids during microbially mediated sulfate reduction. Sacrificial sampling of the sediments after 6- and 12-months of reaction and bulk, micro- and nanofocus XAS and XRF analyses was used to track changes in solid U speciation over time. Here, in oxic sediments, U(VI) binding to Fe-bearing mineral phases was shown to be important for longer term U(VI) retention. In the reducing sediments, a mix of noncrystalline U(IV) and biogenic UO\(_2\) governed U retention, but UO\(_2\) appeared to be more prevalent over time. Trace U(VI) was also detected in the reducing sediments, despite 10-months of sustained sulfate-reduction. The study highlights the potential for U(IV) colloid production from U(VI) solids under anoxic conditions and the complexity of U speciation in sediment systems.

**MATERIALS AND METHODS**

**Metaschoepite Source.** Synthetic metaschoepite powder was used as a metaschoepite source in sediment column studies. Prior to use, the metaschoepite was sieved to 25–50 μm; the “particles” in this size fraction were aggregates of micron-scale platelets that formed electrostatically bound clusters. Uranium comprised 77 wt % of the solid, yielding an average stoichiometry of UO\(_2\)·1.3H\(_2\)O. Further detail on the metaschoepite is provided in the Supporting Information (SI section 1).

**Sediment and Synthetic Groundwater.** Sediment representative of the UK Sellafield Ltd. site subsurface was collected from a well-characterized field site in Cumbria (SI section 2). The sediments were sampled from the unsaturated near surface (~5–10 cm depth) and were confirmed to be oxic at the point of collection and at the start of experiments (>97% of the 0.5 N HCl extractable Fe was present as Fe(III)). Prior to use in experiments, the sediment was sealed and stored at 4 °C for <2-months under a normal atmosphere. Auto clave synthetic groundwater representative of the Sellafield region, was used in the experiments (Table S1).

**Column Design and Experimental Approach.** A sediment/flowing groundwater column system was used so that the metaschoepite would be reacted under conditions that are representative of those found in the environment, for example, where solid contaminants would likely undergo gradual burial in soils/sediments, and experience water flow, ephemeral redox conditions, and the influence of dynamic microbial communities. A schematic of the column setup is provided in the SI (Figure S4). The columns were made from acrylic tubing (18 cm × 4 cm; total volume = ~214 cm\(^3\)) and were packed with 240 g (12 cm vertical, ~151 cm\(^3\)) of sediment. Metaschoepite (227 mg, 174 mg U) was added into a 2 cm (vertical) horizon of the sediment (40 g sediment). The columns were terminated at each end with layers of quartz sand (1 cm vertical) and glass wool (2 cm vertical), and then sealed with Duran GL45 screwcaps with GL14 connectors. This setup meant that the metaschoepite horizon was placed 5 cm above the groundwater inlet and 2 cm from the sediment base (see Figure S4). A peristaltic pump (Watson-Marlow 205-U) was used to pump synthetic groundwater into the base of the columns, with effluents then collected from the top of the columns. The groundwater pumping rate was 1.8 ± 0.2 mL h\(^{-1}\) (1.14 × 10\(^{-6}\) m s\(^{-1}\)).

Two groundwater treatments were used: (i) oxic and (ii) electron-donor amended. For the oxic treatment, an air bubbler was used to maintain O\(_2\) in the groundwater; for the electron-donor amended treatment, 1 mM (total) of acetate and lactate (50:50) was added, and the groundwater was sparged with N\(_2\) (30 min L\(^{-1}\)). Prior work with these sediments has shown that similar electron-donor addition readily promotes microbially mediated bioreduction. Throughout the experiment, the pH of the influent groundwaters was held between 7.2 and 7.4 via HCl addition. In the groundwater reservoirs, the concentrations of NO\(_3\)\(^–\), Fe, Mn, and U to track microbially mediated terminal electron accepting processes, changes in sediment geochemistry, and U dissolution/migration from the metaschoepite source. Effluent pH was measured using calibrated electrodes (Mettler-Toledo). Solution concentrations of NO\(_3\)\(^–\), SO\(_4\)\(^2–\), and Br\(^–\) (inert tracer) were measured by ion chromatography (Dionex DX120) on filtered (<0.2 μm PES) samples. Iron, Mn, and U concentrations were measured by ICP-MS (Agilent 7700x) from acidified (2% HNO\(_3\)) samples.
LIII-edge μ quartz wafers for subsequent autoradiography and synchrotron
resulting resin-embedded core was then cross-sectioned, and
were collected from wafers (extracted perpendicular from the
(see SI section 4 for further details).
Diamond Light Source and X05-LA at the Swiss Light Source
resin embedded sediment thin-sections on beamlines I18 at
Arsenic (PerkinElmer Optima 5300), or leached in 0.5 N HCl for
and sectioned at 0.5 cm intervals; the resulting sections were
then digested in boiling aqua regia for elemental analysis by ICP-
exchanged, was resin embedded with Spurr resin under Ar, using a
which had small perforations in the Al tubing to allow
subcores were immediately
ASH-frozen in
liquid N2 to preserve the sediment matrix, and then stored under
Ar at −80 °C before further work. One subcore was extruded
and sectioned at 0.5 cm intervals; the resulting sections were
then digested in boiling aqua regia for elemental analysis by ICP-AES (PerkinElmer Optima 5300), or leached in 0.5 N HCl for
60 min to estimate the proportion of bioavailable Fe(II) in the
sediments.40 Sections were also taken and kept frozen
(−80 °C) for bulk U LIII-edge XAS measurements. The other subcore, which had small perforations in the Al tubing to allow fluid exchange, was resin embedded with Spurr resin under Ar, using a method designed to maintain the redox chemistry of the
sediment and permit synchrotron X-ray based microanalysis.

Arrows indicate the time point of effluent sampling for investigations of solution U speciation using TEM and luminescence spectroscopy. Iron was
measured in the effluents and was at or close to the method detection limit without a discernible trend, so these data are not presented.

Figure 1. Effluent porewater (A) NO3−, (B) Mn, (C) SO42−, and (D) U for the oxic (no added electron-donor) groundwater system (blue, open
symbols), and electron-donor amended groundwater system (red, closed symbols). Squares (open and closed) denote “control” systems that did not
contain any added U, diamonds and circles (open and closed) denote duplicate metaschoepite-doped column systems, where one of each of the
duplicate columns was sacrificially sampled after 6- and, then, 12-months. No effluent U was detected in the “control” systems. Vertical dashed lines
show time points at 6- and 12-months, where columns were sacrificed, and solid-phase geochemistry and microfocus analysis was then completed.

At experimental end-points (182- and 364 days), columns
were uncapped under an Ar atmosphere and subcores (18 × 1.5
cm) were taken along the length of each column using thin-
walled Al tubes. The subcores were immediately flash-frozen in
liquid N2 to preserve the sediment matrix, and then stored under
Ar at −80 °C before further work. One subcore was extruded
and sectioned at 0.5 cm intervals; the resulting sections were
den was sacrificially sampled after 6- and, then, 12-months. No effluent U was detected in the “control” systems. Vertical dashed lines
show time points at 6- and 12-months, where columns were sacrificed, and solid-phase geochemistry and microfocus analysis was then completed.

Bulk and Spatially Resolved XAS/XRF Mapping. Bulk U LIII-edge fluorescence XAS data were collected on selected samples at 77 K on beamline B18 at Diamond Light Source, UK (Si 111 double-crystal monochromator). Spectra were collected using either a 9 or 36 element Ge detector and calibrated using a Y-foil
standard.

μXRF maps and discrete-area XAS data were collected from
resin embedded sediment thin-sections on beamlines I18 at
Diamond Light Source and X05-LA at the Swiss Light Source
(see SI section 4 for further details). μXRF and XANES maps
were collected from wafers (extracted perpendicular from the
thin-sections using a focused ion beam) on beamline I14 at Diamond Light Source (SI section 4).

Autoradiography. Autoradiographs, showing the distribution
of radioactivity across the polished sections, were collected using
a Typhoon 9410 variable mode imager. Samples were exposed for 24–72 h to a BAS-IP MS storage phosphor screen (Amersham Biosciences) and scanned at 50 μm resolution.

Fluorescence Spectroscopy. Uranyl emission spectra
from selected aqueous samples were collected at 77 K, following
excitation at 420 nm using a FP920 Phosphorescence Lifetime
Spectrometer (Edinburgh Instruments), with a 450 W steady
state Xe lamp and a Hamamatsu R928P red-sensitive photo-
multiplier in air-cooled housing. All spectra were corrected for
the detector response and excitation source using the instrument
correction files.

Transmission Electron Microscopy. TEM imaging with
selected area electron diffraction (SAED) of nanoparticulate phasess present in effluent samples was performed using a FEI Tecnai TF30 FEG analytical electron microscope with EDX spectrometer. Effluent solutions from the columns were prepared for analysis on holey-carbon TEM grids (Agar Scientific) using the method of Neill et al., (2018).43 Briefly, 2–3 drops (5 μL) of centrifuged (5 min, 1.44 × 104 g) effluent solution were pipetted onto the TEM grid and left to dry under an Ar atmosphere. This process was repeated 2–3 times to
accumulate sufficient colloids on the grid to permit analysis. The grid was then gently rinsed with a few drops of isopropyl alcohol and
finally fully dried (again under Ar) prior to TEM analysis. TEM images/SAED patterns were processed and indexed using Fiji.44
DNA Extraction and Microbial Community Characterization. DNA was extracted from select sediment samples from each column system to examine changes in the microbial community structure during experimentation. Further details for microbial community analysis are provided in SI section 5.

Results and Discussion

Column Effluent Geochemistry and Microbial Ecology. A pore volume of ~62 mL for the column sediment was calculated from the Br\(^-\) tracer analysis (SI section 3). This represented ~35% of the column’s volume, giving a flow rate of ~0.7 pore volumes/day. Breakthrough occurred after 112 h (Figure S5). In all experiments, the effluent pH dropped marginally (lowest ~6.5 in the oxic system) during the first month of reaction, presumably due to sediment buffering (SI section 6). After 1-month, all of the effluents buffered to a pH between 7.5 and 7.9 for the remainder of the experiment, likely due to bicarbonate alkalinity in the influent groundwaters (Table S1) or alkalinity generation in the microbially active sediment. It is unlikely that this small change in pH during the first month of groundwater flow would have had a significant impact upon carbonate complexation of U, metaschoepite dissolution, or mineral surface chemistry in this experiment. Stanley and Wilkin (2019)\(^45\) have demonstrated comparable metaschoepite solubility between pH 6–8.5 in the presence of 1 mM sodium bicarbonate.

In the columns exposed to oxic groundwater with no added electron-donor (both control and U-containing column systems), negligible changes in groundwater NO\(_3^-\), Mn, Fe, and SO\(_4^{2-}\) concentrations occurred (Figure 1). This suggests that these systems remained predominantly aerobic during the entire reaction period. Uranium breakthrough from the oxic, metaschoepite amended columns was observed between approximately 136 and 157 days (90–110 pore volumes; Figure 1D). In comparison, breakthrough of the conservative Br\(^-\) tracer occurred after 112 h (Figure S5), indicating that while the metaschoepite was undergoing dissolution, U(VI) transport through the sediment was retarded. The first of two columns for this system was sacrificed for solid phase analysis after 182 days, shortly after the initial U breakthrough (open circles, Figure 1D). Effluent data indicated that after 182 days, ~3% of the initial metaschoepite source U (~5.5 mg) had been eluted from the column via dissolution and groundwater transport (Figure 1). By the experiment end-point (364 days), ~85% of the initial

Figure 2. TEM analysis of the nanoparticulate U-bearing phase eluted from the electron-donor amended columns, sampled from effluent groundwater after 70 injected pore volumes (100 days of groundwater flow). (I–III) are a series of TEM images at sequentially increasing magnification. Dashed circles in panel II denote individual nanoparticles for context. A selected-area electron diffraction (SAED) pattern was collected from panel II (see inset), and the two primary reflections have been indexed according to the UO\(_2\) structure. An approximate lattice constant of 0.546 nm was calculated based on SAED analysis, close to that of UO\(_2\) (~0.547 nm at ambient temperature).\(^54\) Panel III shows a high-resolution image of a single colloid, with interplanar angles indicative of the UO\(_2\) structure superimposed. (IV) FFT of the area displayed in panel III. (V) EDX analysis across an aggregation of colloids showed U as one of the most abundant elements, after C and Cu (as inherent components of the TEM grid); further, K, Ca, and Mg were present likely as precipitated salts from the synthetic groundwater. Trace amounts of Mn, Si, and Fe were also measured as expected from complex environmental samples.
U (~148 mg) had been transported out of the column. The microbial community in this U-doped column system, after 6- and 12-months of oxic groundwater flow, remained remarkably similar to the microbial community of the fresh sediment, but a slight decrease in the proportion and diversity of Fe(III)- and sulfate-reducing bacteria was apparent (SI section 5.2).

Continuous addition of 0.5 mM acetate and 0.5 mM lactate to the electron-donor amended column system resulted in a cascade of microbially mediated terminal electron accepting processes. This was evidenced by clear trends in the effluent groundwater chemistry (Figure 1) and changes in the microbial community (SI section 5.2). Dissimilatory NO$_3^-$ reduction was apparent after 14–28 days (~10–20 pore volumes), with NO$_3^-$, which was continuously added at 0.3 mM, largely absent in the effluent groundwater after 58–100 days until the end of the experiment (Figure 1A). Here, it is likely that a stable denitrifying community had developed within the column, although given the sample resolution for microbial community analysis (SI section 5), it was not possible to quantify this. As well as denitrification, evidence for metal-reducing conditions was also observed, with soluble Mn appearing in the effluent after 36–58 days (~20–40 pore volumes) (Figure 1B). Metal-reducing conditions were also reflected in an increased contribution from dissimilatory metal-reducing bacteria in the microbial community at 182 days compared to the oxic control and starting material (SI section 5.2). This was also accompanied by signs of microbially mediated sulfate reduction, evidenced by a reduction in the effluent sulfate concentration (continuously added at 0.5 mM) after 35–100 days (~40–70 pore volumes) (Figure 1C) and concurrent blackening of the sediment reflecting Fe-sulfide precipitation (Figure 4). Indeed, near-total removal of sulfate was maintained from ~3-months until the end of the experiment (Figure 1). Additionally, after 58 days, the sediment clearly blackened from the base of the column upward (Figure 4), indicating that a dynamic and robust sulfate-reducing zone had developed after the exhaustion of bioavailable NO$_3^-$, Mn(III/IV), and Fe(III) in parts of the column. The microbial community analysis data mirrored the column geochemistry, with a marked increase in deltaproteobacteria apparent in the electron-donor amended columns after 182- and 364 days compared to microbial communities in the fresh sediment and oxic column system (SI section 5.2 and Figure S7). Data showed a relative increase in the diversity and abundance of sulfate-reducing bacteria and methanogens in the electron-donor amended columns, alongside a concurrent reduction in certain α-proteobacteria when compared to the fresh sediment and the oxic column system (Figure S7).

Uranium was also present in the effluent from the electron-donor amended columns between 71 and 171 days (~50–120 pore volumes) when clear evidence for strongly reducing, sulfidic conditions was apparent (Figure 1D). Surprisingly, U was eluted earlier than in the oxic column system. Indeed, the amount of U in the electron-donor amended column effluent was significant, with ~60% (~106 mg) of the added U eluted by 182 days and ~70% (~124 mg) eluted by 364 days.

**Uranium Solution Chemistry/Colloid Analysis.** The speciation of U in a sample of the groundwater from the oxic columns (taken after 234 days, U concentration = 0.20 mM) was analyzed using luminescence spectroscopy (Figures 1D and S9). Here, the spectrum was dominated by the characteristic vibrationally resolved emission profile of UO$_2^{2+}$ between 450 and 600 nm, confirming the solution speciation as dominantly UO$_2^{2+}$. In contrast, a sample with a similar U concentration (0.19 mM) taken from the electron-donor amended system after 100 days had a 76% reduction in the UO$_2^{2+}$ emission intensity compared to the oxic experiment when the same instrument settings were used (Figure S9). This indicates a reduced U(VI)$_{aq}$ contribution to this spectrum compared to the oxic sample. In addition, TEM and SAED analysis of the electron-donor amended effluent after 100 days confirmed the presence of nanocrystalline U-bearing solids (Figure 2), with the SAED data having a structural match to nanocrystalline, biogenic UO$_2$, as observed by other studies. Taken together, the luminescence and TEM data suggest that the electron-donor amended column effluent contained both aqueous U(VI) and nanocrystalline UO$_2$-like solids. However, the possible presence of U(VI) in/on the colloids cannot be ruled out, and possible quenching of luminescence from colloid-bound U(VI) may have contributed to the reduced intensity observed from this sample (Figure S9). The presence of colloids was not tested in the groundwater effluents of the oxic column systems.

The observation of significant UO$_2$-like colloid production from the metaschoepite source under sulfate reducing conditions is unusual and suggests a significant pathway to U(VI) colloid formation compared to biostimulation studies. Numerous authors have detailed the presence of U(VI)-bearing colloids in laboratory studies, for example refs 47–53. Suzuki et al. (2002) reported on the formation of biogenic UO$_2$ colloids from pure-cultures of *Desulfsporosinus* spp. challenged with U(VI)$_{aq}$ and electron donors, and from natural U contaminated sediments. In the pure culture work, the UO$_2$ colloids (~1–3 nm in diameter) were attached to the bacterial cell walls, indicating that they form at or near to the point of U(VI) bioreduction. Discrete UO$_2$ colloids and aggregates were also found in this study. Similar work by Lee et al. (2010) documented biogenic UO$_2$ colloid formation, growth, and aggregation, and TEM analysis demonstrated that biogenic polymers caused the aggregation. UO$_2$ colloids have also been documented to form on the surface of mackinawite (FeS) in the presence of sulfate-reducing bacteria. In that study, the authors proposed a model where U(VI)$_{aq}$ sorbed onto the FeS surface. The U(VI) is reduced to U(IV) via a redox reaction with mineral bound Fe(II); then, microbially mediated regeneration of the Fe(II) allows for continued U(IV) accumulation on the FeS surface. In turn, this leads to UO$_2$ colloid nucleation and growth. Finally, UO$_2$ colloids have been reported to form from corroding nuclear fuel, for example, ref 52, and in experiments where U(VI)$_{aq}$ is reacted with highly reactive Fe(III)-bearing minerals, for example, ref 53.

In this study, the use of a dynamic column system, combined with the complex biochemistry of the sediments (i.e., competing biotic and abiotic processes), means it is not possible to discern how the UO$_2$-like colloids formed from the metaschoepite in the electron donor amended system. However, the morphology and grain size of the U(VI)-solid may have played a significant role in forcing colloid formation. For example, rapid metaschoepite dissolution would likely lead to high localized U concentrations for bacteria, or at reactive mineral surfaces, encouraging colloid nucleation and growth. In turn, the groundwater flow in the columns could have destabilized colloid growth/aggregation (e.g., concentration or physical effects), and the propensity for colloid formation from the metaschoepite source may have outstripped the local supply of aggregating agents, such as biogenic polymers. Recent work in model abiotic systems has also shown that Si can passivate UO$_2$ colloid surfaces, preventing their aggregation. Si was not added to the synthetic...
groundwater used in the column experiments (Table S1), but Si would have been present at trace concentrations in the groundwater due to silicate dissolution, and Si was present in the EDX analysis of the UO$_2$-like colloids (Figure 2). As such, Si may also have also played a role in passivating the surface of the UO$_2$-like colloids in this study.

Irrespective of the mechanisms, extensive UO$_2$-like colloid formation from metaschoepite under sulfate-reducing conditions is novel and additional work is now required to underpin a mechanistic understanding of their formation and stability. Here, the impact of the U(VI) solid source (e.g., composition, grain size, morphology), biological interactions with this material, and colloid passivation mechanisms are clear areas for further research.

**Acid Extractions and Solid Phase Geochemistry.** Sediment samples from two time points (182 and 364 days) from each of the oxic and electron-donor amended systems were assessed for bioavailable Fe(II) using 0.5 N HCl extractions (Figure S10A). Here both oxic columns showed only trace Fe(II) present in the sediments. This, coupled to the effluent and microbial community data (Figure 1 and SI section 5.2) confirmed that both of the columns remained oxic throughout the experiment. In contrast, after 182 days of electron-donor amendment, this column system showed 75−95% 0.5 N HCl extractable Fe(II) throughout the length of the column (Figure S10A), confirming significant reduction of Fe(III) to Fe(II) and retention of the Fe(II) within the sediments (>90% Fe(II) after 364 days). Additionally, aqua regia extractions confirmed that in both electron-donor amended columns the sediment-associated Mn concentrations were generally lower than comparable oxic columns (Figure S10C), consistent with the observed reductive mobilization of Mn (Figure 1).

Sediment associated U profiles were also measured from aqua regia lixiviant and highlighted differences in gross U retention and migration/U loss under the different groundwater treatments. After 182 days flow under oxic conditions, ∼70% of the U originally added in the metaschoepite source was recoverable from the column sediments. The U had migrated from the source throughout the entire length of the column (U concentrations varied between 500 and 1000 mg kg$^{-1}$ up to 6 cm beyond the initial metaschoepite source) (Figure S10D). However, the U mass balance between the sediment extractions and effluents for this system after 182 days was poor (∼27% of the added U was unaccounted for). This may reflect heterogeneity in U distribution in the sediments after metaschoepite dissolution (see Figure 3) relative to the coarse-nature of sediment sampling for the aqua regia extractions. After 364 days under oxic conditions, the solid-phase U concentration had then fallen to between ∼150−250 mg kg$^{-1}$ throughout the column (Figure S10D), presumably as a result of the continued dissolution or mobilization of particle associated/sediment-bound U(VI). This meant that ∼21% of the originally added U remained extractable from the sediment after 1 year of oxic groundwater flow. The U mass balance between the sediment and effluents for this time point was better (∼106% of the added U accounted for); as such, the majority of the metaschoepite derived U had been transported out of the columns.

In the electron-donor amended columns after 182 days of reaction, the transport of UO$_2$-like colloids out of the columns (Figure 1D and Figure 2) meant that the total sediment extractable U was significantly lower than its oxic counterpart (only 30% of the U added in the metaschoepite remained in the sediments). This decreased to 21% after 364 days. The U mass balance (sediment extractions and effluents) for the two electron donor amended columns was 90% and 91%, respectively.

**Bulk X-ray Absorption Spectroscopy.** Select samples were analyzed using bulk U L$_{3}$-edge XANES and EXAFS. In the oxic systems, at 182 days, the sediments downstream from the initial metaschoepite horizon were sampled. For the bioreduced systems, sediments from both within and downstream of the horizon were sampled at 182 and 364 days (see Figures 3, 4, S11, and S12, spectra A−E). To gain insights into the U oxidation state changes in these complex samples, XANES data were analyzed by iterative target factor analysis (ITFA) (Figure S11). Sediments from the oxic system showed U(VI) speciation as expected, and sediments from the electron-donor amended systems showed evidence for partial reduction, with...
ITFA suggesting between 30% and 80% U(IV) across the samples. Here, the amount of sediment associated U(IV) varied with distance from the metaschoepite source, and the overall proportion of U(IV) increased from 182 to 364 days (Figure S11). For the oxic system, bulk EXAFS fitting parameters and best-fit results confirmed uranyl-like adsorption to the sediment in a sample taken from within the metaschoepite source horizon. Scattering contributions from C and Fe shells indicated uranyl complexation at the surface of Fe-oxy(hydr)oxides in the presence of carbonate. U–C/Fe distances correlate to expected distances for edge sharing carbonato-complexes at the surface of iron oxy(hydr)oxides.\(^{57}\) Uranyl retention by sediments in this manner is well documented, as U(VI) has been widely shown to sorb (bidentate edge/corner sharing) to a range of Fe/Mn-oxy(hydr)oxides.\(^{2,10,57-61}\) The dominant Fe-oxides in the sediment used in this study are hematite and goethite, which appear to be effective at sorbing U(VI) released from metaschoepite.\(^{57-59}\)

For the electron-donor amended systems, a contribution to the spectra from an axial O shell at \(\sim 1.8\) Å (uranyl coordination) was varied based on ITFA fitting of the XANES (Table S3) and this approach provided good fits. In the electron-donor amended column system after 182 days of groundwater flow, a uranyl contribution to the bulk EXAFS could still be modeled for samples taken from within the initial metaschoepite source horizon, as well as 3–3.5 cm downflow from the source, but its importance was reduced relative to U(IV)-O coordination (Figure S12 and Table S4, spectra B and C). Both spectra could also be modeled with an improved fit that included contributions from Fe and C shells. An oscillation was also visible in the Fourier transform at \(\sim 3.8\) Å for the 182-day metaschoepite source horizon sample (spectrum B, Figure S12); this may be indicative of a U–O shell from nanocrystalline UO\(_2\);\(^{10,11,26,48}\) however, the addition of a U–O shell did not yield a significant statistical improvement to the overall model fit for this spectrum.

After 364 days of reaction in the electron-donor amended column system (Figure S12 and Table S4, spectra D and E), the inclusion of partial uranyl O coordination was still statistically significant, suggesting that even after 10-months under sulfate-reducing conditions, some U(VI) was still present in the sediments. The sample within the original metaschoepite source horizon was modeled with a significant U–U backscatter shell at \(\sim 3.8\) Å for this spectrum.

**Figure 4.** For each time point (182 and 364 days) from the electron-donor amended column system: (I) Color photographs showing the sediment profiles (10 cm vertical). Note the ingrowth of FeS (blackening) along the flow direction (base to top). (II) Full-length autoradiographs of the resin-embedded, cross sectioned sediments showing radioactivity distribution in the columns (acquisition times varied for clarity, see Figure S11 for U concentrations in digests). Solid horizontal lines denote the region of initial metaschoepite source emplacement, dashed horizontal lines denote the horizons from which bulk U LIII-edge XANES and EXAFS data were collected (spectra B–E in relevant figures and tables). Numbered boxes within the autoradiographs correspond to \(\mu\)-focus XRF maps in panel III. Maps in panel III are either displayed as element-specific color panels (where warmer colors denote relative higher concentrations) or as multielement RGB maps (where green = U, red = Fe, blue = Mn, and color intensity denotes relative proportions of each element). XRF map 6A is a nanofocus map (pixel size 100 nm) of a FIB section extracted perpendicular to white line in XRF map 6 (see Figure S15 for details). Boxes marked J–S within the XRF maps denote regions from which \(\mu\)-focus U LIII-edge XAS data were collected, with EXAFS shown in (IV) \(k^3\) weighted Fourier transforms displayed for clarity, full data sets and XANES are presented in SI section 9). Asterisk (*) denotes that the Fourier transform is nonphase corrected. Bracketed regions above the plots show the expected peak positions for O, C, and Fe and U scatterers (nonphase corrected). (V) Scatter plots denote correlations between major elements (Fe, Mn, Zn, Cu) and U from broad-scale maps over areas that encompass those shown. Positive correlations denote colocation of the elements at differing concentrations.
The formation of biogenic, noncrystalline U(IV)\textsuperscript{10,11} as a U(VI) reductive end-point, separate from that of UO\textsubscript{2}, formation, is influenced by the species present in the experiment. The concentration of organic ligands, phosphate and the availability of surfaces of certain Fe(II)-minerals promote formation of noncrystalline U(IV) over UO\textsubscript{2} formation.\textsuperscript{10,12,62–65} An Fe backscattering shell could also be modeled for all bulk EXAFS spectra collected from the electron-donor amended columns except for spectrum D (Table S4).

Overall, bulk EXAFS fitting for samples from the electron-donor amended column system shows a decrease in U(VI) like coordination with time. After 1 year, at the base of the column where sulfate-reducing conditions have existed for the longest, UO\textsubscript{2} ingrowth dominates; with monomeric or noncrystalline U(IV) present further from the initial U and groundwater (and hence sulfate) source.

**High-Resolution Autoradiography and \(\mu\)-Focus XRF and XAS.** Data from the oxic column thin-section, sampled after 182 days of groundwater flow, are shown in Figure 3. At the 50 \(\mu\)m pixel resolution provided by the autoradiographs, U migration from the metaschoepite source along the groundwater flow-path is clear. After 182 days in the oxic column, a concentrated zone of radioactivity extends for \(\sim\)4 cm beyond the metaschoepite source region (Figure 3II). Beyond this, the activity becomes diffuse. \(\mu\)XRF mapping of selected areas within this zone showed a nonuniform distribution of U throughout the sample. Many areas showed U enrichment in regions also rich in Fe and Mn (e.g., Figure 3; map 1) as well as in the sediment matrix between larger mineral grains (i.e., clay/organic rich areas) (e.g., Figure 3, panel 4). Clays and organic matter commonly sorb U(VI).\textsuperscript{60} The area of highest U retention in the thin-section was found along a horizontal, linear feature in the autoradiograph. XRF mapping of this feature (Figure 3; maps 2 and 3) indicate it is a root fragment because of the presence of life-supporting nutrients, such as Cu and Zn,\textsuperscript{67,68} and consistent with organic material acting as sorption sites for U(VI) in sediments.\textsuperscript{59,70} Elemental correlation plots from broad-scale maps (Figure 3IV) reveal that, of the elements resolvable by \(\mu\)XRF mapping, Fe and Mn show the strongest positive correlations with U in theseoxic systems. This is also reflected in bulk EXAFS modeling where fits show Fe backscatters are possible, suggesting sorption to Fe-oxides\textsuperscript{60} (Table S4). Zinc and Cu also give an indication of possible U uptake onto organic matter, and a correlation between U and Sr may be indicative of uranyl association with carbonate or clay minerals.\textsuperscript{70}

\(\mu\)-focus XANES measurements from the same thin-section (Figure S11, spectra F–I) showed that U(VI) was dominant (\(>90\%\)) throughout the column. Corresponding \(\mu\)EXAFS measurements could be modeled with uranyl O coordination, similar to that described for the bulk-EXAFS measurement from this column system (see SI section 9 for the full data set and fitting parameters). Further, \(\mu\)-focus spectra F–I (Figures 3 and S13 and Table S5) could be modeled as uranyl complexes binding to the surfaces of Fe-bearing minerals consistent with U(VI) sorption to Fe-oxides.\textsuperscript{56–60} The fit for spectrum I, collected from the root fragment, was significantly improved by the incorporation of a U–C scattering path at 2.91 ± 0.02 Å; this may also reflect carbonato-complexed U(VI).\textsuperscript{21,57,71} Evidence for a U–C path is also apparent in the Fourier transforms of spectra F and H, but the incorporation of this path was not statistically valid (Table S5).

In the electron-donor amended column systems and consistent with bulk geochemical measurements (Figures 1 and S10), the autoradiographs (Figure 4) displayed a “patchy” distribution of radioactivity in both the 182- and 364-day columns, highlighting discrete regions of U retention following the onset of sulfate-reducing conditions. XRF maps revealed that after 182 days of groundwater flow, U was found in discrete zones in the sediment matrix (Figure 4, maps 1–4) in a similar manner to that described for the oxic system (U correlated with Fe- and Mn-rich phases, as well as biomarker elements like Zn and Cu). Further, more diffuse areas of U enrichment were found with distance from the metaschoepite source region, as well as additional areas of discrete U enrichment (Figure 4; maps 1–3).

After 364 days, most of the U retained on the sediments was largely present in a discrete horizon \(\sim\)1 cm above the initial metaschoepite source. Here, some U was colocated with Fe-rich mineral grains (Figure 4; maps 6 and 7), indicating that U may interact with reactive Fe at mineral surfaces. A proportion of the U was also matrix-bound (i.e., not associated with mineral surfaces), possibly being retained by clays and/or organic matter along groundwater flow paths (Figure 4, map 7).

\(\mu\)XANES measurements from the 182-day, electron-donor amended system (Figure S11, spectra J–N) showed that U(IV) accounted for 40–60% of the U on the solid phase. \(\mu\)EXAFS also revealed a range of mixed U(IV)/U(VI) species (Figures 4 and S13 and Table S6). Structures indicative of noncrystalline U(IV) could be modeled for several spectra. Only spectrum K, collected from a U hotspot \(\sim\)7.5 cm from the sediment base, could be confidently modeled using a U–U backscatter. Most spectra collected from the 182-day thin-section could be modeled with C or Fe backscattering shells (Table S6). Combined, the bulk and \(\mu\)EXAFS data suggest that noncrystalline U dominates in this sediment system during the early stages of bioreduction. Again, Fe surfaces have also been implicated as important sites for both U(IV) and U(VI) retention.\textsuperscript{72}

After 364 days in the electron-donor amended system, the residual U in the column was primarily contained within the black-colored zones where sulfate reduction had occurred (Figure 4). The proportion of U(IV) in this region, as modeled from the \(\mu\)XANES data (Figure S11, spectra O–S), was higher (63–80%) likely due to longer periods under reducing conditions. Corresponding \(\mu\)EXAFS data (Figures 3 and S13 and Table S7) were best modeled with small contributions from uranyl-like O backscatters emphasizing that only residual U(VI) remained in this system. Backscattering shells of C or Fe and increased contributions from UO\textsubscript{2} like U–U backscatters could also be modeled. For example, spectra O, P, Q, and S (Figure 4) could all be modeled with a U–U path concurrent with nanocrystalline, biogenic UO\textsubscript{2}. Evidence for noncrystalline U(IV) in these horizons was scarce; only spectrum R (65% U(IV)) showed no evidence of a U–U scattering contribution. When considered alongside the bulk EXAFS data for this column system, it appears there is a preferential growth of nanocrystalline UO\textsubscript{2} near the base of this system with sustained bioreduction.

Mechanisms for the preferential formation of “noncrystalline” U(IV) vs biogenic UO\textsubscript{2} are complex. Studies have shown the end-product of microbial U(VI) reduction to be dependent both upon the local microbiology and geochemistry. Indeed, systems containing higher ion strength media (elevated concentrations of...
of chlorides and phosphates) have yielded an increased contribution from noncrystalline U(IV) from the same bioreducing cell cultures. Studies have also suggested that UO$_2$ formation is prohibited due to the retention of U by cell biomass during reduction. In phosphate-free systems, Gram-positive bacteria preferentially produced noncrystalline U(IV) in direct contrast to Gram-negative bacteria, which produced nanoparticulate UO$_2$ under the same conditions, the differences proposed to be a result of cell envelope architecture. The formation of discrete U(IV) phosphate and carbonate phases must also be considered in dynamic systems like those presented here, although no evidence is apparent in the µEXAFS, and no P was supplied in the groundwater. Significant variations in binding site, local biomass, local porewater chemistry, and microbiology are, therefore, competing factors within discrete microenvironments to favor the formation of a specific end-member. Here, the interplay of all these factors on the micro-to-nano scale must be considered, however it is difficult to isolate a specific mechanism of noncrystalline U(IV) formation in these dynamic systems. In this case, as observed previously, residence time (i.e., aging of the noncrystalline U(IV) fraction) likely accounts for the increase in noncrystalline UO$_2$.

**Nanofocus XRF and XANES Mapping.** Variations in U speciation were also present at the nanometer scale (Figure S14). The extraction of a wafer of U contaminated sediment from the electron-donor amended column sediment (364 day) thin-section, along a Fe-oxide grain boundary (Figure 4, map 6A), permitted nano-XRF and XANES mapping at the newly commissioned Diamond Light Source Hard X-ray Nanoprobe (Figure S14). Discrete U L$_{III}$-edge XANES data from this sample have been grouped by subtle differences in the spectra, and the result is a nanometer-scale U speciation map. Figure S14 indicates the presence of up to three discrete groups of spectra identified within the 10 μm × 5 μm FIB section; the most oxidized (blue and green) are more closely associated with the regions of highest U concentration, along the boundaries of Fe-oxide grains.

**Implications.** This work has shown that an array of competing mechanisms control U migration and fate in complex sediment systems during metaschoepite dissolution. Under oxic conditions, metaschoepite dissolution resulted in significant U(VI)$_{(aq)}$ transport; however, U(VI) reaction with Fe-bearing sediment species retarded groundwater U transport and resulted in long-term (~1 year) U(VI) retention. During metaschoepite dissolution under anoxic conditions, significant amounts of UO$_2$-like colloids were produced. As colloids are known to enhance contaminant transport through the geosphere, this finding may be significant (e.g., for the management of sites contaminated with depleted U penetrators, mining sites, or for the geodisposal of metaschoepite containing wastes). However, further work is required to document the colloid formation mechanism(s) and stability, and this should include defining the role that the solid U source (i.e., chemical composition, surface morphology, etc.) plays in controlling instigating U colloid production, and the relative importance of biotic vs. abiotic UO$_2$ colloid formation mechanisms. Under anoxic conditions, micro-to-nanofocus XAS also revealed that U(VI), noncrystalline U(IV), and UO$_2$ were all retained in the sediment after metaschoepite dissolution, and UO$_2$ appeared to be a more important U(IV) product with added time. This may be significant in terms of uranium’s general biogeochemistry, as it is thought that UO$_2$ may be more resistant to oxidative remobilization, but clearly in this study, this is tensioned against significant U(IV) colloid production. Combined, the results highlight the complexity of U biogeochemistry in dynamic, evolving, environmental systems. This complexity and how it can be modeled at the macroscale needs to be considered for contaminated sites and in nuclear waste disposal.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.9b02292.

Contains additional information on sediment, groundwater, metaschoepite, microbial community characterization/composition, methods/techniques, pH data, and XAS data (PDF)

**AUTHOR INFORMATION**

**Corresponding Author**

*E-mail: gareth.law@helsinki.fi.*

**ORCID**

William R. Bower: 0000-0003-2070-2483
Katherine Morris: 0000-0002-0716-7589
J. Frederick W. Mosselmans: 0000-0001-6473-2743
Louise Natrajna: 0000-0002-9451-3557
Satoshi Utsunomiya: 0000-0002-6197-9705
Daniel Grolimund: 0000-0001-9721-7940
Gareth T. W. Law: 0000-0002-2320-6330

**Notes**

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