Environmental Science & Technology

Article

Cite This: *Environ. Sci. Technol.* 2019, 53, 3399−3409

pubs.acs.org/est

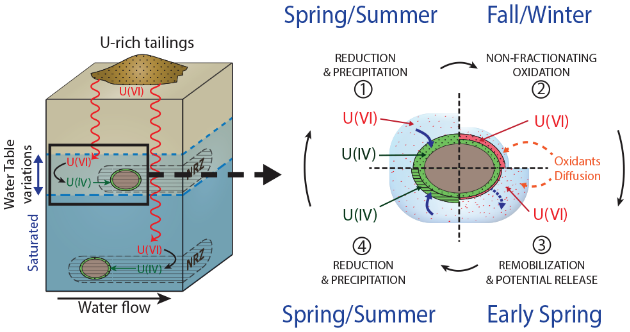
Isotopic Fingerprint of Uranium Accumulation and Redox Cycling in Floodplains of the Upper Colorado River Basin

Pierre Lefebvre,[*,†,‡,∇] Vincent Noël,[§] Kimberly V. Lau,[∥,○] Noah E. Jemison,[⊥,◆] Karrie L. Weaver,[†] Kenneth H. Williams,[#] John R. Bargar,[§] and Kate Maher[†]

[†]Department of Earth System Science, Stanford University, Stanford, California 94305, United States
[‡]Département de Géosciences, Ecole Normale Supérieure, Paris 75005, France
[§]Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, California 94025, United States
[∥]Department of Geological Sciences, Stanford University, Stanford, California 94305, United States
[⊥]Department of Geology, University of Illinois at Urbana−Champaign, Champaign, Illinois 61820, United States
[#]Earth Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

Supporting Information

ABSTRACT: Uranium (U) groundwater contamination is a major concern at numerous former mining and milling sites across the Upper Colorado River Basin (UCRB), USA, where U(IV)-bearing solids have accumulated within naturally reduced zones (NRZs). Understanding the processes governing U reduction and oxidation within NRZs is critical for assessing the persistence of U in groundwater. To evaluate the redox cycling of uranium, we measured the U concentrations and isotopic compositions (δ^{238}U) of sediments and pore waters from four study sites across the UCRB that span a gradient in sediment texture and composition. We observe that U accumulation occurs primarily within fine-grained (low-permeability) NRZs that show active redox variations. Low-permeability NRZs display high accumulation and low export of U, with internal redox cycling of U. In contrast, within high-permeability NRZs, U is remobilized under oxidative conditions, possibly without any fractionation, and transported outside the NRZs. The low δ^{238}U of sediments outside of defined NRZs suggests that these reduced zones act as additional U sources. Collectively, our results indicate that fine-grained NRZs have a greater potential to retain uranium, whereas NRZs with higher permeability may constitute a more-persistent but dilute U source.



INTRODUCTION

Groundwater monitoring by US Department of Energy (DOE) as part of the Uranium Mill Tailings Remedial Action (UMTRA) shows persistent uranium (U) plumes at numerous sites across the Upper Colorado River Basin (UCRB), USA,[1−4] with concentrations of groundwater U above the Environmental Protection Agency (EPA) groundwater maximum concentration limit (MCL) of 30 μg/L.[5] Understanding the processes driving U plume persistence at legacy ore-processing sites is a major challenge at the regional scale. Recent studies[3,6,7] highlighted the importance of "*naturally reduced zones*" (NRZs), consisting of sulfidic sediments enriched in organic carbon, that foster the accumulation of solid-associated U(IV) (noted as $\text{U(IV)}_{\text{sol}}$)[3,6,8−11]. Release of U due to oxidation of these U pools accumulated in NRZs is suspected to contribute to plume persistence.[3,4,9] Recent studies[12,13] suggest microbially mediated reduction within NRZs as a mechanism for U accumulation, whereas U mobilization is thought to be driven by oxidative mechanisms.[3,9] Although U in contaminated sites across the UCRB has been thoroughly studied in terms of speciation,[3,6−10,14] only a few studies have used U isotopes (i.e., $^{238}\text{U}/^{235}\text{U}$) to trace biogeochemical processes. Most studies to date have focused on Rifle, CO, a well-studied site where bioremediation experiments were conducted,[12,15,16] or on in situ recovery (ISR) uranium mining.[17−19] In this study, we quantify the isotopic fingerprint of natural U(VI) reduction in these complex systems by measuring U isotopes ratios (δ^{238}U) of natural sediment and pore water samples from four UCRB sites.

Alluvial sediments in UCRB floodplains were shown to exhibit organic carbon (OC)-enriched lenses dispersed within the detrital sediment.[4,7,20,21] In these zones, oxygen consumption due to organic matter decomposition under water-saturated conditions can locally develop reducing conditions.[7] Aqueous U(VI) (noted as U(VI)_{aq}) diffusing from the legacy

Received: October 4, 2018
Revised: January 20, 2019
Accepted: February 26, 2019
Published: February 26, 2019

ACS Publications

DOI: 10.1021/acs.est.8b05593
Environ. Sci. Technol. 2019, 53, 3399−3409

U ore-processing hosting sites into NRZ lenses of floodplain sediments downstream from these sites can thus be locally reduced to U(IV)$_{sol}$, resulting in U concentrations >200-fold higher than background concentrations.[3,6,9,11,14] In NRZs, the solid fraction of U was shown to be dominantly "non-crystalline" U(IV) phases that are very sensitive to oxidation.[9,11] The permeability of NRZs to oxidants thus controls the potential remobilization of U(IV)$_{sol}$. As suggested in Noël et al.,[11] two types of NRZs can be described depending on their particle size: (i) "*fine-grained*" NRZs (enriched in the <150 μm grain size fraction) that display a very low permeability and result in strong redox gradients and (ii) "*coarse-grained*" NRZs (with a similar grain size distribution to surrounding sediments) that are highly permeable and show greater penetration of oxidants, enhancing seasonal redox oscillations.[7,9]

Seasonal water table fluctuations are predicted to episodically expose NRZs to oxidants, such as aqueous species and dissolved gases, or directly to air[22−26] and may oxidize accumulated U(IV)$_{sol}$ and subsequently export solubilized U via groundwater transport. A recent model contradicts this assumption and proposes that redox oscillations, driven by annual water table fluctuations, could promote internal cycling of U because of diffusion limitations dominant in *fine-grained* NRZ sediments, minimizing export from the NRZ pore waters to groundwater.[10,11]

Thus, NRZs are nexuses of biogeochemical activity driven by hydrological dynamics that may dictate floodplain water quality at a regional scale.[7,11] Uranium behavior in response to hydrological variability remains poorly understood and is currently only estimated by its speciation. Complementary proxies of biogeochemical processes such as isotopes are required to improve predictions of U cycling and consequent short- and long-term impacts on water quality.

Reduction of U(VI) to U(IV) may occur either abiotically[27−35] or biotically when bacteria utilize U as an electron acceptor.[36−40] On the basis of experimental studies, reduction of U(VI) in the presence of abiotic reducing minerals, organics or sulfides, results in little to no enrichment of light isotopes (^{235}U) in the reduced product.[41,42] The exception is for magnetite, green rust, and aqueous Fe^{2+} that appear to cause preferential reduction of ^{235}U in experiments.[42] In contrast, biotic reduction by bacterial enzymes results in substantial enrichment of heavy isotopes (^{238}U) in the U(IV) product, corresponding to enrichment factors from +0.68‰ to +0.99‰ depending on the biological substrate.[42−46] Several strains of metal-reducing bacteria capable of reducing U have been observed in NRZs, including *Geobacter* and *Desulfobacteraceae*.[1,13] Biostimulation experiments at Rifle, CO displayed a putative biotic signature with consistent depletion of ^{238}U in the dissolved U(VI)$_{aq}$ phase,[12,15] underlining the major influence of biologically induced U reduction in response to artificial simulation.

Although biological reduction of U is thought to generate much of the observed fractionation,[42−46] a recent experimental study showed that abiotic reduction by mackinawite (FeS) in the presence of aqueous calcium (Ca) may induce similar enrichment factors by suppressing the overall removal rate, underlining the influence of aqueous speciation.[47] All of our sites display relatively high Ca levels (0.3−8.4 mmol/L, mostly >1 mmol/L). Consequently, although redox reactions should impart a clear isotopic signature, we cannot distinguish between biotic and abiotic reduction pathways. However, previous field studies infer reduction in these environments to be strongly mediated by microbial reactions.[3,6,8,12,15]

Adsorption of U(VI)$_{aq}$ is expected to cause a slight enrichment of light isotopes in the adsorbed pool,[46,48−50] with a fractionation of −0.15‰ for common aquifer minerals.[49] However, field studies of uranium desorption at Rifle, CO in response to bicarbonate amendment did not show any significant fractionation.[16] A major remaining uncertainty is the oxidative remobilization step, which has not been well constrained under natural conditions. On the basis of laboratory and field observations,[50,51] we infer that no fractionation occurs during oxidation. As demonstrated for Rifle, CO by Jemison et al.,[50] this would be in accordance with a "rind effect" as described by Wang et al.:[51] U isotopic fractionation appears to be limited by the complete oxidation of the outermost U(IV) layer before oxidizing the next layer. This kinetic limitation results in little to no fractionation.

To evaluate U cycling within NRZs, sediments and pore waters were collected from four field sites: Naturita, Grand Junction, Rifle, CO, and Shiprock, NM covering a linear distance of 410 km across a N−S transect through the central portion of the UCRB. Given our current understanding of uranium isotopes, we expect the isotopic signature of the NRZs to provide a measure of the amount of U reduction and, by extension, net U retention. When one assumes that U reduction in NRZ sediments leads to isotopic fractionation between the solid and pore waters,[42,46] whereas oxidation of U(IV) should not (see discussion in ref 50), the isotopic variability of sediments should provide a qualitative indication of the relative amount of U reduction within the different NRZs. In tandem, the pore waters are expected to provide unique information about the timing and extent of episodic sediment oxidation and U remobilization. This issue is critical for understanding U behavior in response to fluctuating redox conditions and is thus essential to improving bioremediation strategies.[8,15,52−56] Knowledge produced by this work ultimately supports the development of regional conceptual and numerical models of U behavior and transport within floodplains.

■ MATERIALS AND METHODS

Study Sites. U concentration and isotope measurements were performed on solid fractions of sediment cores that contain NRZs from four former U processing sites: Naturita (NAT-M8-1), Grand Junction (GJAST15B), Rifle (RFL 748 and RFL 749), CO, and Shiprock, NM (SR-DM-02) (Figure 1). We also analyzed pore waters collected from three cores (NAT-M8-1, GJAST15B, and SR-DM-02). All sites are located along riverbanks and show groundwater flow toward the river, causing progressive migration of the groundwater U plume. Naturita and Grand Junction sediments and pore waters were collected in October, when the water table is low, whereas Shiprock solid fractions and water samples were collected in April, when the water table is high. All pore waters were collected below the groundwater level. Groundwater was collected from well SR618 at Shiprock at the same date. Sample extraction and storage methods are described in the Supporting Information.

In addition to the sediment cores and pore waters, we analyzed a sample of the uranium ore concentrate from the Union Carbide Nuclear Corp, Uravan, CO. Although this site does not correspond directly to the study locations, it provides

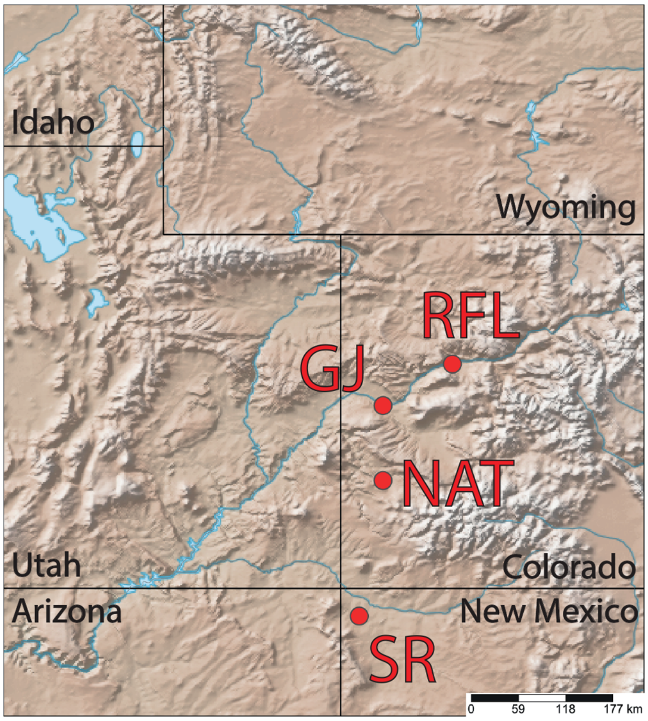


Figure 1. Map of the Upper Colorado River Basin and location of study sites: Grand Junction, CO (GJ); Naturita, CO (NAT); Rifle, CO (RFL); Shiprock, NM (SR). These four sites cover a linear distance of 410 km.

a constraint on the average isotopic composition of the original tailings, which are no longer available for analysis.

Naturita and Grand Junction NRZs are *coarse-grained* NRZs, whereas Rifle and Shiprock NRZs are *fine-grained*.[7,9,11] Because the Shiprock *fine-grained* NRZ is located in the zone of water table fluctuation, accompanied by strong evapotranspiration, and consequently partly and temporarily exposed to air, we refer to this NRZ as a *transiently saturated fine-grained* NRZ.[11] Conversely to Shiprock, the *coarse-* and *fine-grained* NRZs of Naturita, Grand Junction, and Rifle are referred to as *predominantly saturated* NRZs, although the shallower NRZ (300−400 cm) of Naturita may be considered as *seasonally saturated*.

Uranium speciation in the *fine-* and *coarse-grained predominantly saturated* NRZs is mostly noncrystalline U(IV) formed under water-saturated conditions and mainly complexed to organic carbon and mineral surfaces,[57−62] with minor crystalline U(IV) found in *coarse-grained* NRZs at Naturita and Grand Junction sites.[9] The U oxidation state in the *fine-grained transiently saturated* NRZs show that $U(VI)_{sol}$ is accumulated in similar proportions to $U(IV)_{sol}$. The $U(VI)_{sol}$ is suspected to be preferentially associated with solid phases that are kinetically stable against dissolution, i.e., sorbed to minerals and organic particles associated with evaporite mineral assemblages, or possibly precipitated as uranyl minerals.[11]

Chemical Analysis. Bulk sediments were analyzed for their organic composition,[13] chemical and mineralogical composition,[7,11] and U concentration and speciation.[9,11] Uranium concentrations reported here were analyzed using X-ray fluorescence spectrometry with a XEPOS (Spectro X Lab) X-ray fluorescence spectrometer. The speciation of sulfur (S) in the sediment cores included in this study[13] was used here to indicate the sediment redox state. Sulfur mineralogical composition was determined using X-ray absorption spectroscopy combined with X-ray microprobes.[7]

Uranium and calcium concentrations from pore waters were measured on an inductively coupled plasma mass spectrometer (ICP-MS). Aqueous concentrations correspond to the <0.2 μm dissolved and colloidal fraction.

Chemical Separation and Isotopic Analysis. Uranium in sediment samples corresponds to bulk solid-associated phases. Samples from Naturita, Grand Junction, and Shiprock, as well as U ore samples, were digested with a mix of Optima concentrated hydrofluoric, nitric, and hydrochloric acids. An aliquot was extracted for U concentration measurements on a Nu Attom ICP-MS at the Stanford University ICP-MS/TIMS Facility and/or by a Thermo X-series 2 ICP-MS at the EM-1 Facility. All water samples were acidified with concentrated HNO_3. Samples from RFL 748 and 749 cores were dissolved using a digestion method involving successive acid etching and heating before analysis of U concentrations on a Thermo iCAP ICP-MS at the University of Illinois at Urbana−Champaign (UIUC).

Samples were spiked with the IRMM 3636a $^{233}U-^{236}U$ tracer with sample/spike ratios of ~20 to correct for experimental and mass biases.[63] The samples were then purified via column chromatography using UTEVA resin (Eichrom Technologies, LLC). The separated, dried-down U fractions were further dissolved in 0.05 N nitric acid prior to isotopic analysis.

The $^{238}U/^{235}U$ ratios were measured on a Nu Plasma multicollector ICP-MS at Stanford University and at UIUC. The $^{238}U/^{235}U$ values are reported relative to the CRM-145 standard (certified value of $^{238}U/^{235}U = 137.837 \pm 0.015$[64]) according to eq 1.

$$\delta^{238}U = \left(\frac{\left(\frac{^{238}U}{^{235}U}\right)_{sample}}{\left(\frac{^{238}U}{^{235}U}\right)_{CRM\text{-}145}} - 1 \right) \times 1000\ ‰ \qquad (1)$$

Each sample was measured three times. Analytical errors (two standard deviations, 2SD) of $\delta^{238}U$ are equal to 0.12‰ and were determined using repeated measurements ($n = 72$) of bracketing standards CRM-145 and CRM-112a. United States Geologic Survey basaltic rock reference material BCR-2 was processed alongside samples from dissolution through analysis. Seven measurements resulted in a $\delta^{238}U$ of -0.27 ± 0.15‰ within the range of values reported in other studies.[63,65,66] Average uncertainties for U concentrations are based on several replicate samples that were digested and purified separately (external reproducibility) and are equal to 9.1% (2SD) for Naturita, Grand Junction, CO, and Shiprock, NM samples and equal to 13% for Rifle samples.

Further details about experimental and instrumental methods are available in the Supporting Information.

■ RESULTS

The concentration of sulfur (S) as iron sulfides (FeS and FeS_2) normalized to that of total S indicates NRZ horizons, as does enrichment in organic carbon,[13] and can be compared to vertical profiles of uranium concentrations and isotopic ratios for the cores from Naturita, Grand Junction, Rifle, and Shiprock (Figure 2). NRZs are identified either within the transiently saturated zone or in the deeper predominantly

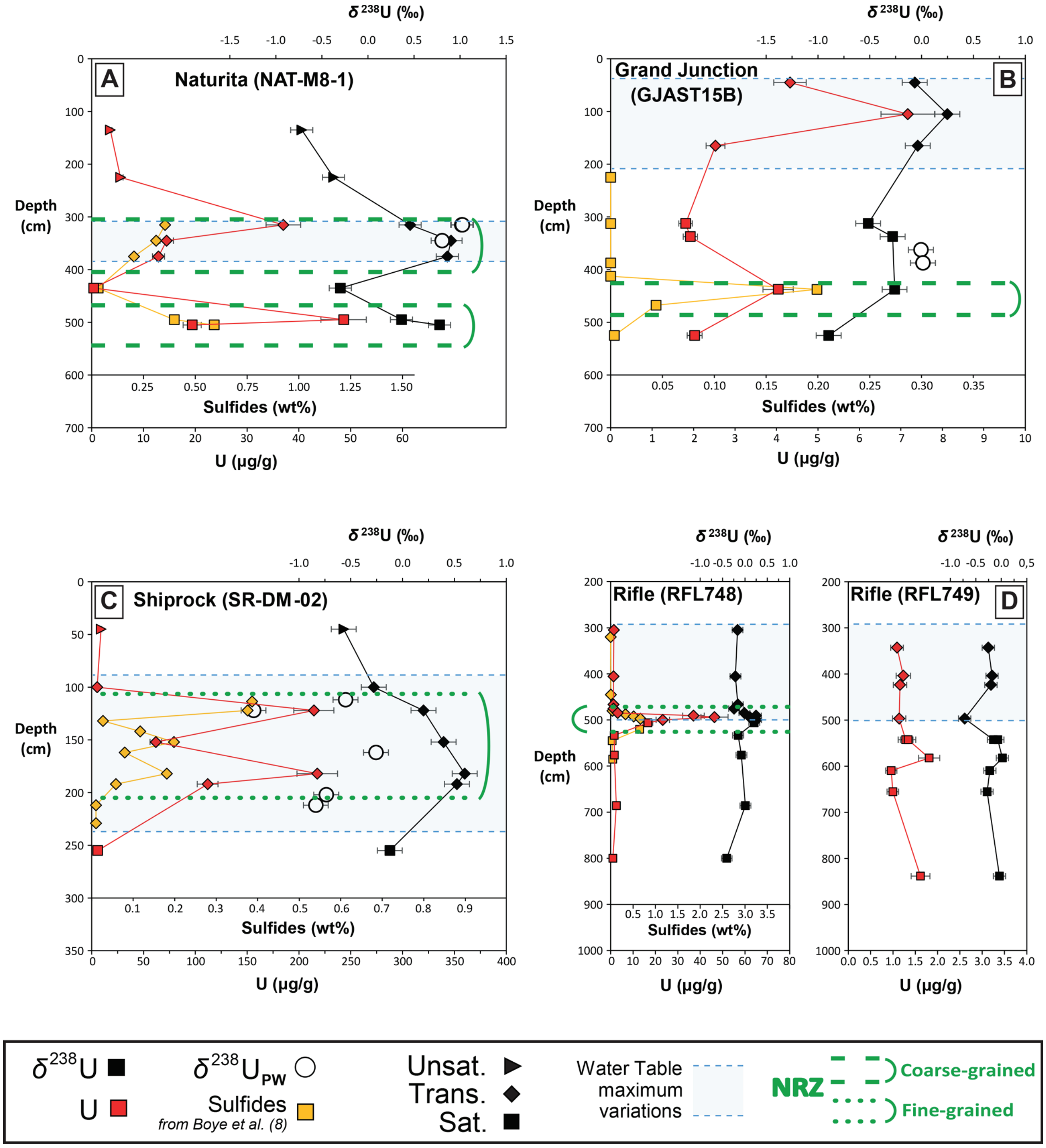


Figure 2. Sediment core vertical profiles of (A) NAT-M8-1, (B) GJAST15B, (C) SR-DM-02, and (D) RFL 748 and 749. Black points represent δ^{238}U values; red points are for uranium concentrations (U), and yellow are for sulfide concentration data from Boye et al.[13] Open circles represent δ^{238}U of pore waters ($\delta^{238}U_{PW}$). Filled symbols correspond to the position respective to the water table variation range (triangles for the predominantly unsaturated zone, diamonds for the transiently saturated zone, and squares for the deeper saturated zone). NRZ types and depth limits are represented by green dashed lines. The depth where sediments are seasonally saturated is shaded in blue.

saturated zone. High U concentrations are generally associated with high S levels, and U accumulation is especially substantial in the transiently saturated zone that is subject to intense redox variations. The range of U concentrations is greatest at Shiprock, where concentrations reach as high as 218 µg/g. In comparison, maximum concentrations in cores NAT-M8-1 and RFL 748 are on the order of 50 µg/g, with the lowest maximum concentrations measured in GJAST15B (7.17 µg/g) and RFL 749 (1.81 µg/g). U isotopic compositions (δ^{238}U) display variable ranges with maximum variations at Naturita (from −0.72‰ to 0.90‰) and intermediate variations at Grand Junction and Shiprock (from −0.90‰ to 0.25‰ and from −0.57‰ to 0.60‰, respectively). The lowest δ^{238}U ranges are measured in both cores RFL 748 and 749 from Rifle. The δ^{238}U values are systematically elevated in NRZs. Elevated U concentrations and δ^{238}U values are also observed in the shallow unsaturated zone at the Grand Junction site. The present study is focused on NRZs; geochemical results from this shallower zone will be described in a separate study. Samples collected in the upper unsaturated zone at Naturita and Shiprock display low U concentration and δ^{238}U values, indicating that no significant U accumulation and redox

DOI: 10.1021/acs.est.8b05593
Environ. Sci. Technol. 2019, 53, 3399−3409

processes are occurring within this oxic zone. In comparison, the δ^{238}U of the ore concentrate is 0.07 ± 0.21‰.

U concentrations ([U]) of pore waters are between 0.19 and 3.30 mg/L, which are up to 110 times above the EPA MCL of 30 μg/L (Figures 2 and 3). Calcium concentrations are lower at Naturita (0.42−0.92 mmol/L), intermediate at Grand Junction (0.30−3.4 mmol/L), and higher at Rifle (1.5−7.6 mmol/L) and Shiprock (2.0−8.4 mmol/L). Such Ca concentrations lead to the formation of neutrally charged Ca−U−CO_3 complexes that decrease U removal rate from solution and can cause abiotic isotopic fractionation comparable to biotic signatures.[47] Naturita pore waters (from the upper *coarse-grained* NRZ of the NAT-M8-1 core at 315 and 345 cm depths) that were collected at low water table conditions (October) have a mean δ^{238}U value of 0.95 ± 0.25‰ (Figures 2A and S1). This *coarse-grained* NRZ is suspected to be subject to diffusion of oxidants that cause U remobilization from the sediment to the associated pore water.[9] The pore water δ^{238}U value is in the same range (at 345 cm) or higher (at 315 cm) than the δ^{238}U of surrounding sediments. At Grand Junction, pore water sampling performed in October (collected at 350 and 375 cm depths, above the *coarse-grained* NRZ and within the saturated zone) showed an average δ^{238}U of 0.00 ± 0.03‰, slightly higher than that of the surrounding sediments (Figures 2B and S2). In contrast to Naturita and Grand Junction, pore waters from Shiprock that were collected in April within the *transiently saturated fine-grained* NRZ (between 107 and 207 cm) show δ^{238}U values (from −1.44‰ to −0.26‰) lower than those observed in the surrounding sediments (>0.20‰) (Figures 2C and S3). Shiprock groundwater from well SR618 sampled at the same time displays a higher δ^{238}U of 0.09‰. This is in the same range as Rifle groundwater measured in well CU-01 by Jemison et al.[50] (0.00 ± 0.04‰).

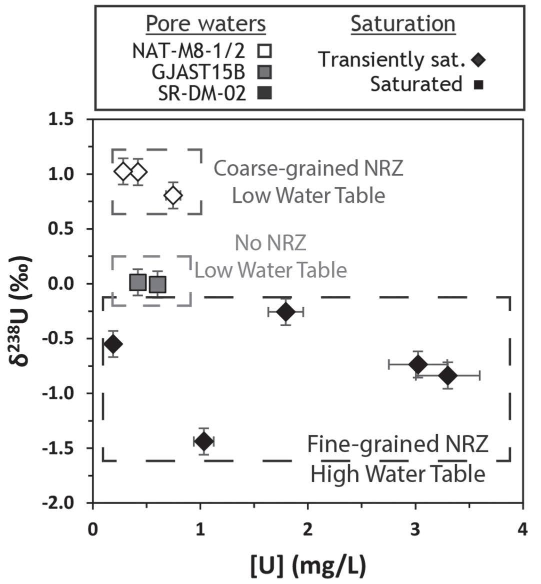


Figure 3. Isotopic composition (δ^{238}U, ‰) of pore waters from Shiprock, Naturita, and Grand Junction versus U concentrations (mg/L). Naturita and Grand Junction samples were collected in October, when the water table is low; Shiprock samples were collected in May, when the water table is high. Naturita and Shiprock samples were collected within a NRZ, whereas Grand Junction samples were collected from the oxic zone. Diamonds correspond to the transiently saturated zone, and squares represent the predominantly saturated zone.

DISCUSSION

NRZs Behavior and U Redox Dynamics. NRZs, which correspond to the main U reservoirs in sediments, exhibit different behaviors depending on the sampling time and on sediment permeability. At the time of pore water sampling, the Naturita and Grand Junction *coarse-grained* (high permeability) NRZs act as sources of U to the groundwater plume, with aqueous U release through remobilization of U from the solid reservoir. At Naturita, the similarity between aqueous and bulk sediment δ^{238}U inside the upper NRZ at 345 cm (0.81‰ and 0.90‰, respectively, Figures 2 and S1) suggests that U is being released from solid to dissolved forms without any significant fractionation and that the amount of released U is far greater than the preexisting amount of aqueous U. The difference between pore water and surrounding sediment δ^{238}U (+0.56‰ ± 0.23‰) observed near the water table interface at 315 cm, which suggests that an isotopically heavy U fraction is remobilized under oxidative conditions, does not correspond to any previously known mechanism. Given that the U oxidation process is not thought to enrich the aqueous fraction in heavy isotopes, this fraction may represent a more labile product of formerly reduced U with high δ^{238}U (around ∼1‰ as observed in deeper sediments). This fraction may be noncrystalline U(IV)$_{sol}$ that was shown to be dominant in these sediments[9] and easily remobilized.[67] If this fraction of U is released under oxidative conditions, δ^{238}U of the pore water would increase and δ^{238}U of the sediment would subsequently decrease, according to the amount oxidized. Although the presence of isotopically distinct U(IV)$_{sol}$ is consistent with observations of the distribution of U species,[9] the dissolved ^{238}U-enriched fraction could also have been transported from deeper in the *coarse-grained* NRZ where sediments display higher δ^{238}U.

As Grand Junction pore waters were sampled outside the NRZs, we conclude that they reflect the mobile U(VI)$_{aq}$ plume. The isotopically heavy U (0.00 ± 0.03‰) cannot originate from the low-δ^{238}U of the surrounding sediment (−0.28‰ and −0.26‰, Figures 2 and S2) and has probably been transported. This is consistent with oxidative remobilization of high-δ^{238}U U fractions (from upstream high-δ^{238}U NRZs) followed by transport, as described for Naturita and suggested by U speciation studies.[9]

The isotopic composition of Shiprock *transiently saturated fine-grained* NRZs suggests a very active redox system where U is locally remobilized and subsequently reduced, limiting U mobility. These *fine-grained* (low permeability) NRZs reside within the zone of water table fluctuations and are successively exposed to seasonal and episodic hydrological changes (wet−dry cycles), promoting redox cycling of the sediments.[11] Such conditions can drive localized remobilization of U(IV) pools with limited export of U from the reducing sediments,[10] because of the high capacity of *fine-grained* NRZs to maintain anoxic conditions[9,10,26] and low diffusion of remobilized U during oxidative cycling,[10,11] which is consistent with the elevated U concentration in the NRZ pore waters. The offset between δ^{238}U in the solid fraction and pore water (Figures 2 and S3) is consistent with a combination of abiotic and microbial reduction that depletes ^{238}U in pore water and enriches ^{238}U in the surrounding solid fraction.[42,46] The high Ca concentrations measured in pore waters (≥2.0 mmol/L)

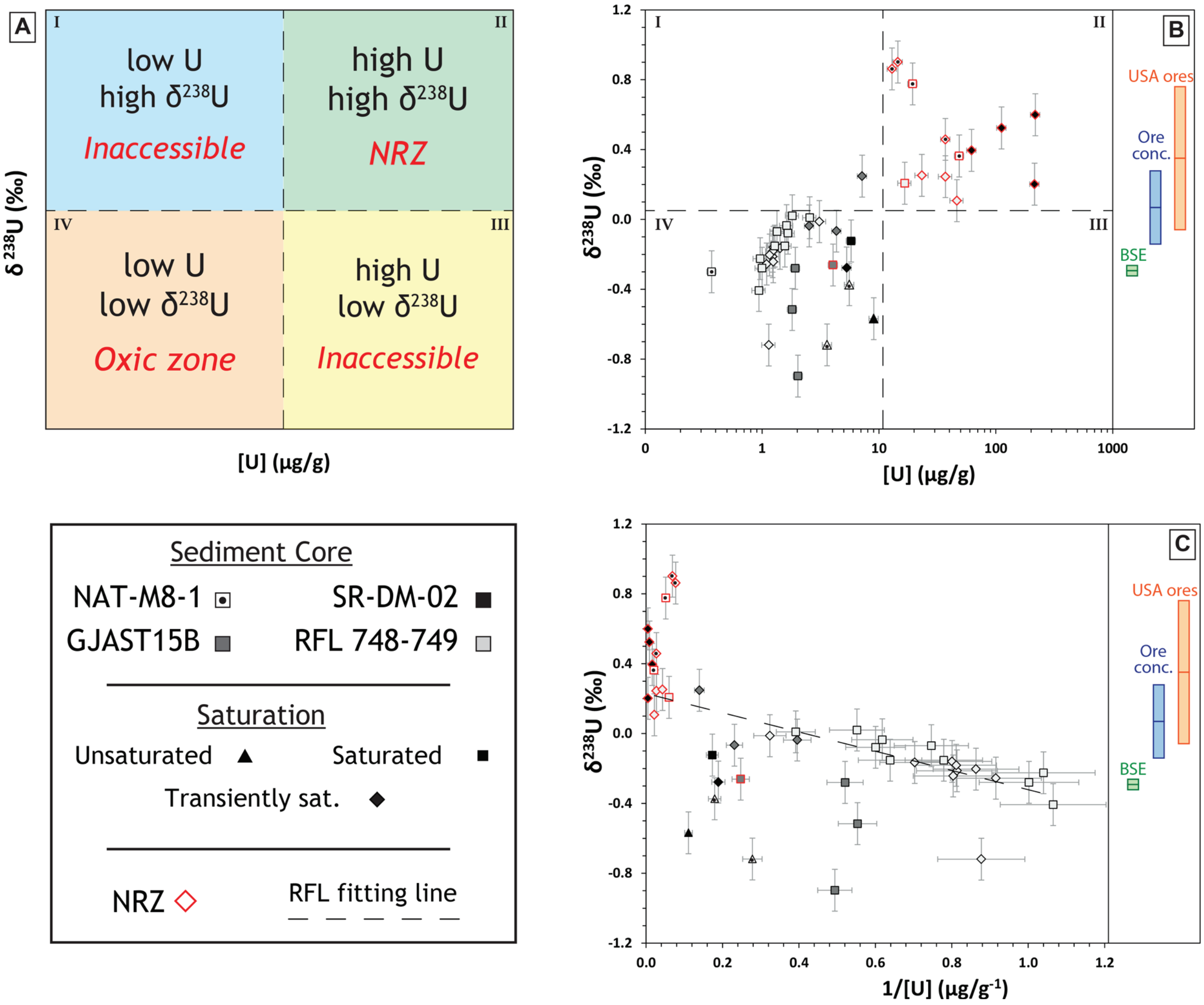


Figure 4. (A) Schematic repartition of δ^{238}U versus U concentrations into quadrants I to IV. (B) Isotopic composition of sediments (δ^{238}U, ‰) vs U concentrations (μg/g) on a log scale. (C) δ^{238}U vs inverse concentrations (1/U, in μg/g^{-1}). Triangles represent samples from the predominantly unsaturated zone; diamonds correspond to the transiently saturated zone, and squares are for the predominantly saturated zone. Samples located inside NRZs are in red. A linear regression through the Rifle samples is shown by a dashed line (right). Boxes on the right sides correspond to the average value (±2SD) for USA sandstone-type ores (orange box; see Discussion), the U ore concentrate analyzed in this study (blue), and the Bulk Silicate Earth value (green).[69]

may contribute to increasing the abiotic fractionation factor and thus the cumulative isotopic fractionation.[47] Applying a Rayleigh fractionation model (see the Supporting Information for more details), we estimate that a considerable amount of aqueous U is remobilized each year (up to 41 mg/L) and subsequently reduced (up to 97% of total aqueous U) with a fractionation factor of 1.0005. We thus infer that active redox cycling of U in the Shiprock NRZ was occurring at the time of sampling, substantially depleting ^{238}U in pore waters. A similar decrease in groundwater δ^{238}U, associated with extensive reduction, has also been observed at a larger scale in roll-front U deposits.[17,19]

The high δ^{238}U measured in well SR618 (0.09‰) should correspond to the well-mixed groundwater reservoir, in contrast to the pore waters, which reflect local conditions. Considering the low signature of NRZ pore waters (from −1.44‰ to −0.26‰), mass balance implies that water from outside the NRZ, where no active reduction is occurring, should have higher δ^{238}U (>0.09‰) than the average value given by groundwater. The signature of this water may be due to a fraction of remobilized U with a high δ^{238}U that was released from the NRZ that displays high solid-phase δ^{238}U signatures during the spring flooding event that occurred just before sampling. This fraction is thought to be small as U concentration in the well is very low (0.08 mg/L) compared to the NRZ pore waters (0.19 to 3.30 mg/L, Figure 3). A major fraction of the aqueous U remains within the *fine-grained* NRZ and is subsequently reduced, with substantial fractionation as observed in pore waters. This corroborates the results of Noël et al.,[11] which suggested that oxic geochemical conditions in *fine-grained* NRZs significantly resolubilize U with limited export from the NRZ pore waters to groundwater.

Isotopic Fractionation as a Measure of U Reduction. The accumulated U in NRZ sediments may originate from two main sources: geochemical background and tailings of the mining or milling site. Background U represents the major fraction of the samples with low U concentrations, of the order of 1 μg/g, in accordance with measurements in U.S.A. surface soils that showed a background value of ~1.5 μg/g (1.0 pCi/g[68]). Similarly, background δ^{238}U is expected to be similar to the δ^{238}U value of −0.29 ± 0.03‰ corresponding to the Bulk Silicate Earth (BSE) and continental crust estimated by Tissot and Dauphas.[69] Uranium from tailings is thought to represent the major component of U accumulation. Its isotopic signature remains unknown but is expected to be in the range of low-temperature sandstone-type U ores that were mined in the region. Sandstone-type deposits in the U.S.A. are variable but have an average isotopic ratio of 0.35 ± 0.41‰.[70−72] The δ^{238}U value of the uranium ore concentrate we analyzed (0.07 ± 0.21‰) suggests that the bulk tailings may have been on the low-end of this range.

The evolution pattern of U isotope fractionation during solid-phase U accumulation may be described by the relationship between U concentration and δ^{238}U (Figure 4): at low U concentrations (0−10 μg/g), δ^{238}U values remain below ∼0.05‰ (Figure 4A,B, quadrant IV), whereas high U accumulation in NRZs (>10 μg/g) is associated with substantial ^{238}U enrichment in the solid fraction (Figure 4A,B, quadrant II). No other U accumulation pathways seem to occur as samples do not plot in quadrants I (low U accumulation and high δ^{238}U) and III (high U and low δ^{238}U) shown in Figure 4A,B.

When highly reducing conditions occur in NRZs, resulting in high U accumulation (>10 μg/g), we observe a strong positive isotope fractionation (Figure 4B, quadrant II). Considering that the main primary source of uranium (mine tailings) is the same as for low U concentration sediments, the observed fractionation indicates that U reduction is not quantitative. If the entire U pool was reduced, δ^{238}U values would be equal to that of the source. This observation also suggests that reduction in NRZs occurs from a plentiful dissolved U reservoir that leads to high accumulation rates, up to more than 200 μg/g. These conclusions are consistent with our observations in Shiprock pore waters (Figure 3). Additionally, the inaccessible quadrant III in Figure 4B shows that high U accumulation rates require reducing immobilization of U with high supply.

Outside NRZs, less U accumulation and fractionation are observed (Figure 4A,B, quadrant IV), with δ^{238}U values lower than the range observed for U ores. In the case of Rifle, CO, we observe a strong mixing trend between two main sources of U (Figure 4C, linear relationship between δ^{238}U and inverse concentration) that may correspond to nonfractionating mixing between background and tailings U. Background U is represented by the local range of low concentration samples (0.9−1 μg/g) and has an approximate δ^{238}U signature of −0.3‰, consistent with the BSE value.[69] Uranium in concentrated samples from the *fine-grained* NRZ displays a higher signature of ∼+0.2‰, consistent with the U source. Uranium accumulation in Rifle sediments could be entirely attributed to mixing between pre-existing U and contaminated U that was weathered and transported from tailings, without any significant fractionation due to U reduction. Uranium reduction at Rifle may thus be driven by mixing and/or by quantitative U reduction that results in lower effective fractionation.

Non-NRZ samples from Naturita, Grand Junction, and Shiprock also display low δ^{238}U but no obvious mixing trend. The minimal to inverse fractionation observed outside of the NRZs, along with the low accumulation, may be partly explained by quantitative reduction of fractionated U that was transported out of the NRZs. Other factors that could suppress fractionation, such as shifting Ca concentrations and pH,[47] are unlikely to vary appreciably. However, adsorption of $U(VI)_{aq}$, which is thought to be on the order of a few percent of the total U pool,[9] may result in a slight decrease of δ^{238}U.[47−50] In addition, these nonreducing sediments are more affected by seasonal oxidation events than NRZs. These intense variations in redox conditions may cause substantial recycling of U that tends to attenuate potential isotope fractionation arising from reduction. This is consistent with the absence of high δ^{238}U in low U content sediments (Figure 4B, quadrant I). This mechanism could also explain the absence of significant U fractionation in the NRZ of GJAST15B, where the coarse-grained texture allows for penetration of oxidants.[9] Although we cannot exclude differences in the fractionation within the sediments, U that accumulates outside NRZs appears to partially originate from U release from NRZs that act as secondary U sources.

The highest U concentrations are observed in the *fine-grained* NRZ of Shiprock. This NRZ is subject to intense internal redox cycling, where noncrystalline U(IV) phases are thought to be seasonally oxidized to $U(VI)_{aq}$, subsequently forming stable U(VI)-bearing minerals or U(VI) trapped in insoluble evaporite minerals under saturated conditions.[11] The isotopic fractionation due to incorporation of U(VI) into secondary minerals is negligible for both experimental U(VI) coprecipitation with phosphate[46] and biological carbonate precipitation,[55,69,73,74] whereas U(VI) in abiotic experimental carbonate precipitates can be ca. ∼0.11‰ to 0.23‰ heavier than the dissolved U(VI), depending on carbonate speciation.[75] Building on the model of Noël et al.,[11] U cycling at Shiprock may thus be described by a sequence of (i) accumulation of ^{238}U-enriched $U(IV)_{sol}$ due to U reduction, followed by (ii) oxidation of $U(IV)_{sol}$ phases with no attendant fractionation and (iii) mixing of recently dissolved U with high δ^{238}U and preexisting aqueous U(VI) with lower δ^{238}U values. Subsequent adsorption (iv) of $U(VI)_{aq}$ is followed by (v) precipitation of U(VI) minerals with δ^{238}U values similar to the intermediate-δ^{238}U $U(VI)_{aq}$ reservoir. Thus, the total "surface" U has a lower δ^{238}U relative to $U(IV)_{sol}$. A substantial amount of solid-associated U is then dissolved (vi) during the spring flooding event, resulting in $U(VI)_{aq}$ heavier than before (i); (vii) a new step of reduction eventually occurs, enriching the new $U(IV)_{sol}$ fraction in ^{238}U. This cycle results in an overall increase in the δ^{238}U of the total U fraction with time that is limited by the presence of solid U(VI) with a lower δ^{238}U than solid U(IV). The incoming flux of ^{238}U, satisfying isotope and mass balance, is supported by the continuous and slow groundwater flow (with a relatively high δ^{238}U of 0.09‰ at well SR618).

In NAT-M8-1, similar δ^{238}U values are measured in two different *coarse-grained* NRZs, one of which is *seasonally saturated* and another that is *predominantly saturated* (Figure 2A). A comparable pattern is observed in the Grand Junction NRZ, which has similar characteristics.[7] This suggests that seasonal variability in NRZ moisture does not significantly influence the fractionating processes in these *coarse-grained* NRZs. Within the *transiently saturated fine-grained* NRZ in SR-DM-02, similar δ^{238}U values are observed in the zone of variable saturation regardless of U concentration (Figure 2C). This pattern may be due to attenuation of the fractionation along with accumulation (isotope distillation). Another possible explanation is that mixing effects may homogenize the U pool: the NRZs are close in depth (∼60 cm), and small-scale water table depth variations, caused by one-time events (such as intense precipitation) as well as annual water table variations, may induce a substantial vertical water flow in tandem with dissolution−precipitation processes.

Model for U Cycling in the NRZs. We propose that redox cycling of U in NRZs mirrors that of S and Fe described by Noël et al.[7] Iron sulfides can be partly oxidized into sulfates, elemental sulfur, and iron oxides during low water table conditions and then subsequently reduced back to Fe-sulfides during saturated periods.[76,77] Reduction of $U(VI)_{aq}$ within NRZs, likely microbially mediated, enriches ^{238}U in the $U(IV)_{sol}$ product.[42,46] In contrast, U oxidation does not cause any significant fractionation as shown above and in Jemison et al.[50] Furthermore, U oxidation is thought to be slow and retarded by a combination of low permeability and the presence of biomass, which fuels microbial sulfate reduction, and solutes that act as reductants, such as Fe(II) and S(-II).[10,78]

At all sites, the spring flooding causes a substantial increase in dissolved U, produced by mobilization of labile U in overlying sediments and/or in the upgradient aquifer. This event is immediately followed by a decrease in dissolved U concentration down to the background level, due to dilution of groundwater by continuous water flow and advection. This cycle is expected to partly affect Rifle and Shiprock NRZs,[11,26] with the mobility of dissolved U being limited by the low permeability and high reducing capacities of fine-grained sediments.[9,10,26]

Uranium accumulation generally occurs to a greater extent in *fine-grained*/low-permeability NRZs (Rifle and Shiprock) compared to *coarse-grained*/high-permeability NRZs (Naturita, Grand Junction). Moreover, maximum U accumulation is observed in *transiently saturated* NRZs, showing that the combination of (i) low permeability and (ii) intense redox cycling controls U accumulation.

Annual variations in the depth of the water table therefore cause deposition of ^{238}U-enriched $U(IV)_{sol}$ (mainly as noncrystalline U(IV) and to a lesser extent as weakly sorbed U(IV) or uraninite[9]) during late spring/early summer reductive saturation periods. Subsequently, this pool of $U(IV)_{sol}$ may be remobilized slowly during late summer/fall/winter and faster at the time of the spring flooding event, remobilizing aqueous U with similar isotopic composition to the ^{238}U-enriched U(IV). After U release, the dissolved U pool is then slightly enriched in heavy isotopes compared to the previous year. This accumulation cycle of U should lead to significant accumulation of ^{238}U in the solid fraction, consistent with the high $\delta^{238}U$ we observe in the bulk sediment and in accordance with known fractionation factors.[42−46] This model can also be applied to Shiprock, assuming U(VI) mineral precipitation does not significantly affect U isotope ratios. In summary, considering that U reduction is the only significant fractionating mechanism, redox cycling ultimately leads to the accumulation of heavy isotopes in the solid fraction, while pore waters inherit low $\delta^{238}U$ that is exported outside the NRZs.

We conclude that U cycling occurs within NRZs that are subject to dynamic redox conditions.[7] The persistence of U contamination is thus partly a function of episodic U release/dissolution and sorption/precipitation that releases small amounts of dissolved U each year when NRZs undergo oxidation.

Environmental Implications. The behavior of U isotopes provides new insights about the fate of U in contaminated sediments across the UCRB floodplain. NRZs appear to be active locations for U redox transformations. U accumulation into NRZs is driven by a combination of reduction pathways depending on the hydrologic conditions at the sites, with mixing of U from background and tailings that is variably overprinted by redox fractionation. U release is controlled by the NRZ texture and redox cycling.

Nonetheless, there remains a crucial need for experiments combining microbial and abiotic oxidation to refine the existing model and to improve our understanding of U cycling.

The localization of U cycling in the transiently saturated zone suggests potential improvements in U remediation strategies, such as focusing remediation efforts on this zone to increase efficiency. When remediation plans involve microbial reduction of U to decrease the dissolved $U(VI)_{aq}$ fraction,[8,15,52−56] further studies that monitor the evolution of U isotope signatures from sediments may help to track remediation progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b05593.

> Additional information (study sites, pore water−sediment comparison), additional methods (sampling, chemistry, measurements), and data tables (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: pierre.lefebvre@sorbonne-universite.fr.

ORCID

Pierre Lefebvre: 0000-0003-2298-4234

Vincent Noël: 0000-0002-5387-8664

Noah E. Jemison: 0000-0002-2557-716X

John R. Bargar: 0000-0001-9303-4901

Present Addresses

∇P.L.: Institut de Minéralogie, de Physique des Matériaux et Cosmochimie, Sorbonne Université, Paris 75005, France.

○K.V.L.: Department of Geology and Geophysics, University of Wyoming, Laramie, Wyoming 82072, United States.

◆N.E.J.: Earth and Environmental Sciences Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, United States.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the DOE-BER Climate and Environmental Sciences Division through the SLAC Groundwater Quality Science Focus Area (SFA) program and by DOE-BES through its support for SSRL. SSRL and SLAC are supported by the DOE-BES under Contract No. DE-AC02-76SF00515. This material was partially supported by the Lawrence Berkeley National Laboratory's Genomes-to-Watershed Scientific Focus Area that funded the work under contract DE-AC02-05CH11231 (Lawrence Berkeley National Laboratory; operated by the University of California). We thank the teams of U.S. DOE Office of Legacy Management and Environmental Sciences Laboratory of U.S. DOE Office at Grand Junction. We are very grateful to William Dam, Ray Johnson, and Sarah Morris for helping to manage the field sampling activities. The authors also thank Kristin Boye, Juan

S. Lezama Pacheco, Emily Cardarelli, and Sharon Bone of SLAC National Accelerator Laboratory for their assistance with planning and conducting field sampling activities. We thank the SLAC radiation protection program for their assistance with radioactive sample handling and Guangchao Li (EM1 Laboratory, Stanford University) for his help during analyses by ICP-MS.

REFERENCES

(1) Zachara, J. M.; Long, P. E.; Bargar, J. R.; Davis, J. A.; Fox, P. M.; Fredrickson, J. K.; Freshley, M. D.; Konopka, A. E.; Liu, C.; McKinley, J. P.; Rockhold, M. L.; Williams, K. H.; Yabusaki, S. B. Persistence of uranium groundwater plumes: Contrasting mechanisms at two DOE sites in the groundwater-river interaction zone. *J. Contam. Hydrol.* **2013**, *147*, 45−72.

(2) Dam, W. L.; Campbell, S.; Johnson, R. H.; Looney, B. B.; Denham, M. E.; Eddy-Dilek, C. A.; Babits, S. J. Refining the site conceptual model at a former uranium mill site in Riverton, Wyoming, USA. *Environ. Earth Sci.* **2015**, *74* (10), 7255−7265.

(3) Janot, N.; Lezama Pacheco, J. S.; Pham, D. Q.; O'Brien, T. M.; Hausladen, D.; Noël, V.; Lallier, F.; Maher, K.; Fendorf, S.; Williams, K. H.; Long, P. E.; Bargar, J. R. Physicochemical heterogeneity of organic-rich sediments in the Rifle aquifer, CO: impact on uranium biogeochemistry. *Environ. Sci. Technol.* **2016**, *50* (1), 46−53.

(4) Johnson, R. H.; Dam, W. L.; Campbell, S.; Noël, V.; Bone, S., Bargar, J. R.; Dayvault, J. Persistent Secondary Contaminant Sources at a Former Uranium Mill Site, Riverton, Wyoming USA. In *Proceedings of International mine water association*, Freiberg/Germany, 2016.

(5) U.S. Environmental Protection Agency. National Primary Drinking Water Regulations; Radionuclides; Final Rule. *Fed. Regist.* **2000**, *65*, 76708−76753.

(6) Campbell, K. M.; Kukkadapu, R. K.; Qafoku, N. P.; Peacock, A. D.; Lesher, E.; Williams, K. H.; Bargar, J. R.; Wilkins, M. J.; Figueroa, L.; Ranville, J.; Davis, J. A.; Long, P. E. Geochemical, mineralogical and microbiological characteristics of sediment from a naturally reduced zone in a uranium contaminated aquifer. *Appl. Geochem.* **2012**, *27* (8), 1499−1511.

(7) Noël, V.; Boye, K.; Kukkadapu, R.; Bone, S.; Lezama Pacheco, J. S.; Cardarelli, E.; Janot, N.; Fendorf, S.; Williams, K. H.; Bargar, J. R. Understanding controls on redox processes in floodplain sediments of the Upper Colorado River Basin. *Sci. Total Environ.* **2017**, *603*, 663−675.

(8) Noël, V.; Boye, K.; Lezama-Pacheco, J. S.; Bone, S. E.; Janot, N.; Cardarelli, E.; Williams, K. H.; Bargar, J. R. Redox controls over the stability of U(IV) in floodplains of the Upper Colorado River Basin. *Environ. Sci. Technol.* **2017**, *51* (19), 10954−10964.

(9) Bone, S. E.; Cahill, M.; Jones, M.; Fendorf, S.; Davis, J. A.; Williams, K. H.; Bargar, J. R. Oxidative uranium release from anoxic sediments under diffusion-limited conditions. *Environ. Sci. Technol.* **2017**, *51* (19), 11039−11047.

(10) Bargar, J. R.; Williams, K. H.; Campbell, K. M.; Long, P. E.; Stubbs, J. E.; Suvorova, E. I.; Lezama-Pacheco, J. S.; Alessi, D. S.; Stylo, M.; Webb, S. M.; Davis, J. A.; Giammar, D. E.; Blue, L. Y.; Bernier-Latmani, R. Uranium redox transition pathways in acetate-amended sediments. *Proc. Natl. Acad. Sci. U. S. A.* **2013**, *110* (12), 4506−4511.

(11) Noël, V.; Boye, K.; Kukkadapu, R. K.; Li, Q.; Bargar, J. R. Uranium storage mechanisms in wet-dry redox cycled sediments. *Water Res.* **2019**, *152*, 251−263.

(12) Shiel, A. E.; Johnson, T. M.; Lundstrom, C. C.; Laubach, P. G.; Long, P. E.; Williams, K. H. Reactive transport of uranium in a groundwater bioreduction study: insights from high-temporal resolution $^{238}U/^{235}U$ data. *Geochim. Cosmochim. Acta* **2016**, *187*, 218−236.

(13) Boye, K.; Noël, V.; Tfaily, M. M.; Bone, S. E.; Williams, K.; Bargar, J. R.; Fendorf, S. Thermodynamically controlled preservation of organic carbon in floodplain. *Nat. Geosci.* **2017**, *10* (6), 415−419.

(14) Qafoku, N. P.; Gartman, B. N.; Kukkadapu, R. K.; Arey, B. W.; Williams, K. H.; Mouser, P. J.; Heald, S. M.; Bargar, J. R.; Janot, N.; Yabusaki, S.; Long, P. E. Geochemical and mineralogical investigation of uranium in multi-element contaminated, organic-rich subsurface sediment. *Appl. Geochem.* **2014**, *42*, 77−85.

(15) Bopp, C. J., IV; Lundstrom, C. C.; Johnson, T. M.; Sanford, R. A.; Long, P. E.; Williams, K. H. Uranium $^{238}U/^{235}U$ isotope ratios as indicators of reduction: results from an in situ biostimulation experiment at Rifle, Colorado, USA. *Environ. Sci. Technol.* **2010**, *44* (15), 5927−5933.

(16) Shiel, A. E.; Laubach, P. G.; Johnson, T. M.; Lundstrom, C. C.; Long, P. E.; Williams, K. H. No measurable changes in $^{238}U/^{235}U$ due to desorption−adsorption of U (VI) from groundwater at the Rifle, Colorado, integrated field research challenge site. *Environ. Sci. Technol.* **2013**, *47* (6), 2535−2541.

(17) Basu, A.; Brown, S. T.; Christensen, J. N.; DePaolo, D. J.; Reimus, P. W.; Heikoop, J. M.; Woldegabriel, G.; Simmons, A. M.; House, B. M.; Hartmann, M.; Maher, K. Isotopic and geochemical tracers for U(VI) reduction and U mobility at an in situ recovery U mine. *Environ. Sci. Technol.* **2015**, *49* (10), 5939−5947.

(18) Brown, S. T.; Basu, A.; Christensen, J. N.; Reimus, P.; Heikoop, J.; Simmons, A.; WoldeGabriel, G.; Maher, K.; Weaver, K.; Clay, J.; DePaolo, D. J. Isotopic evidence for reductive immobilization of uranium across a roll-front mineral deposit. *Environ. Sci. Technol.* **2016**, *50* (12), 6189−6198.

(19) Murphy, J. M.; Stirling, C. H.; Kaltenbach, A.; Turner, S. P.; Schaefer, B. F. Fractionation of $^{238}U/^{235}U$ by reduction during low temperature uranium mineralisation processes. *Earth Planet. Sci. Lett.* **2014**, *388*, 306−317.

(20) Gardner, P.; Solomon, D. K. *Investigation of the hydrologic connection between the Moab mill tailings and the Matheson wetland preserve*. Report to the Utah DEQ Moab Millsite Groundwater Subcommittee, Salt Lake City, Utah, USA, 2003.

(21) Davis, J. A.; Curtis, G. P.; Wilkins, M. J.; Kohler, M.; Fox, P. M.; Naftz, D. L.; Lloyd, J. R. Processes affecting transport of uranium in a suboxic aquifer. *Phys. Chem. Earth, Parts A/B/C* **2006**, *31* (10−14), 548−555.

(22) Lair, G. J.; Zehetner, F.; Fiebig, M.; Gerzabek, M. H.; Van Gestel, C. A. M.; Hein, T.; Hohensinner, S.; Hsu, P.; Jones, K. C.; Jordan, G.; Koelmans, A. A.; Poot, A.; Slijkerman, D. M. E.; Totsche, K. U.; Bondar-Kunze, E.; Barth, J. A. C. How do long-term development and periodical changes of river-floodplain systems affect the fate of contaminants? Results from European rivers. *Environ. Pollut.* **2009**, *157*, 3336−3346.

(23) Weber, F.-A.; Voegelin, A.; Kaegi, R.; Kretzschmar, R. Contaminant mobilization by metallic copper and metal sulphide colloids in flooded soil. *Nat. Geosci.* **2009**, *2*, 267−271.

(24) Lynch, S. F. L.; Batty, L. C.; Byrne, P. Environmental risk of metal mining contaminated river bank sediment at redox-transitional zones. *Minerals* **2014**, *4*, 52−73.

(25) Schulz-Zunkel, C.; Rinklebe, J.; Bork, H.-R. Trace element release patterns from three floodplain soils under simulated oxidized−reduced cycles. *Ecol. Eng.* **2015**, *83*, 485−495.

(26) Yabusaki, S. B.; Wilkins, M. J.; Fang, Y. L.; Williams, K. H.; Arora, B.; Bargar, J. R.; Beller, H. R.; Bouskill, N. J.; Brodie, E. L.; Christensen, J. N.; Conrad, M. E.; Danczak, R. E.; King, E.; Soltanian, M. R.; Spycher, N. F.; Steefel, C. I.; Tokunaga, T. K.; Versteeg, R.; Waichler, S. R.; Wainwright, H. M. Water Table Dynamics and Biogeochemical Cycling in a Shallow, Variably-Saturated Floodplain. *Environ. Sci. Technol.* **2017**, *51* (6), 3307−3317.

(27) Liger, E.; Charlet, L.; Van Cappellen, P. Surface catalysis of uranium(VI) reduction by iron(II). *Geochim. Cosmochim. Acta* **1999**, *63*, 2939−2955.

(28) Behrends, T.; Van Cappellen, P. Competition between enzymatic and abiotic reduction of uranium(VI) under iron reducing conditions. *Chem. Geol.* **2005**, *220*, 315−327.

(29) Jeon, B.-H.; Dempsey, B. A.; Burgos, W. D.; Barnett, M. O.; Roden, E. E. Chemical reduction of U(VI) by Fe(II) at the solid-

water interface using natural and synthetic Fe(III) oxides. *Environ. Sci. Technol.* **2005**, *39*, 5642−5649.

(30) Nico, P. S.; Stewart, B. D.; Fendorf, S. Incorporation of oxidized uranium into Fe (hydr)oxides during Fe(II) catalyzed remineralization. *Environ. Sci. Technol.* **2009**, *43*, 7391−7396.

(31) Chakraborty, S.; Favre, F.; Banerjee, D.; Scheinost, A. C.; Mullet, M.; Ehrhardt, J.-J.; Brendle, J.; Vidal, L.; Charlet, L. U(VI) sorption and reduction by Fe(II) sorbed on montmorillonite. *Environ. Sci. Technol.* **2010**, *44*, 3779−3785.

(32) Boland, D. D.; Collins, R. N.; Payne, T. E.; Waite, T. D. Effect of amorphous Fe(III) oxide transformation on the Fe(II)- mediated reduction of U(VI). *Environ. Sci. Technol.* **2011**, *45*, 1327−1333.

(33) Veeramani, H.; Alessi, D. S.; Suvorova, E. I.; Lezama Pacheco, J. S.; Stubbs, J. E.; Sharp, J. O.; Dippon, U.; Kappler, A.; Bargar, J. R.; Bernier-Latmani, R. Products of abiotic U(VI) reduction by biogenic magnetite and vivianite. *Geochim. Cosmochim. Acta* **2011**, *75* (9), 2512−2528.

(34) Hyun, S. P.; Davis, J. A.; Sun, K.; Hayes, K. F. Uranium(VI) reduction by iron(II) monosulfide mackinawite. *Environ. Sci. Technol.* **2012**, *46* (6), 3369−3376.

(35) Veeramani, H.; Scheinost, A. C.; Monsegue, N.; Qafoku, N. P.; Kukkadapu, R.; Newville, M.; Lanzirotti, A.; Pruden, A.; Murayama, M.; Hochella, M. F. Abiotic Reductive Immobilization of U(VI) by Biogenic Mackinawite. *Environ. Sci. Technol.* **2013**, *47*, 2361−2369.

(36) Lovley, D. R.; Phillips, E. J. P.; Gorby, Y. A.; Landa, E. R. Microbial reduction of uranium. *Nature* **1991**, *350* (6317), 413−416.

(37) Lovley, D. R.; Phillips, E. J. Reduction of uranium by Desulfovibrio desulfuricans. *Appl. Environ. Microbiol.* **1992**, *58* (3), 850−856.

(38) Cai, C. F.; Dong, H.; Li, H.; Xiao, X.; Ou, G.; Zhang, C. Mineralogical and geochemical evidence for coupled bacterial uranium mineralization and hydrocarbon oxidation in the Shashagetai deposit, NW. *Chem. Geol.* **2007**, *236* (1−2), 167−179.

(39) Cai, C. F.; Li, H.; Qin, M.; Luo, X.; Wang, F.; Ou, G. Biogenic and petroleum-related ore-forming processes in Dong- sheng uranium deposit, NW China. *Ore Geol. Rev.* **2007**, *32* (1−2), 262−274.

(40) Chen, Z.; Cheng, Y.; Pan, D.; Wu, Z.; Li, B.; Pan, X.; Huang, Z.; Lin, Z.; Guan, X. Diversity of microbial community in Shihongtan sandstone-type uranium deposits, Xinjiang. *Geomicrobiol. J.* **2012**, *29* (3), 255−263.

(41) Rademacher, L. K.; Lundstrom, C. C.; Johnson, T. M.; Sanford, R. A.; Zhao, J.; Zhang, Z. Experimentally determined uranium isotope fractionation during reduction of hexavalent U by bacteria and zero valent iron. *Environ. Sci. Technol.* **2006**, *40* (22), 6943−6948.

(42) Stylo, M.; Neubert, N.; Wang, Y.; Monga, N.; Romaniello, S. J.; Weyer, S.; Bernier-Latmani, R. Uranium isotopes fingerprint biotic reduction. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112* (18), 5619−5624.

(43) Stylo, M.; Neubert, N.; Roebbert, Y.; Weyer, S.; Bernier-Latmani, R. Mechanism of uranium reduction and immobilization in Desulfovibrio vulgaris biofilms. *Environ. Sci. Technol.* **2015**, *49* (17), 10553−10561.

(44) Basu, A.; Sanford, R. A.; Johnson, T. M.; Lundstrom, C. C.; Löffler, F. E. Uranium isotopic fractionation factors during U (VI) reduction by bacterial isolates. *Geochim. Cosmochim. Acta* **2014**, *136*, 100−113.

(45) Stirling, C. H.; Andersen, M. B.; Warthmann, R.; Halliday, A. N. Isotope fractionation of ^{238}U and ^{235}U during biologically-mediated uranium reduction. *Geochim. Cosmochim. Acta* **2015**, *163*, 200−218.

(46) Dang, D. H.; Novotnik, B.; Wang, W.; Georg, R. B.; Evans, R. D. Uranium isotope fractionation during adsorption, (co)-precipitation, and biotic reduction. *Environ. Sci. Technol.* **2016**, *50* (23), 12695−12704.

(47) Brown, S. T.; Basu, A.; Ding, X.; Christensen, J. N.; DePaolo, D. J. Uranium isotope fractionation by abiotic reductive precipitation. *Proc. Natl. Acad. Sci. U. S. A.* **2018**, *115* (35), 8688−8693.

(48) Brennecka, G. A.; Wasylenki, L. E.; Bargar, J. R.; Weyer, S.; Anbar, A. D. Uranium isotope fractionation during adsorption to Mn-oxyhydroxides. *Environ. Sci. Technol.* **2011**, *45* (4), 1370−1375.

(49) Jemison, N. E.; Johnson, T. M.; Shiel, A. E.; Lundstrom, C. C. Uranium isotopic fractionation induced by U(VI) adsorption onto common aquifer minerals. *Environ. Sci. Technol.* **2016**, *50* (22), 12232−12240.

(50) Jemison, N. E.; Shiel, A. E.; Johnson, T. M.; Lundstrom, C. C.; Long, P. E.; Williams, K. H. Field Application of ^{238}U/^{235}U Measurements To Detect Reoxidation and Mobilization of U(IV). *Environ. Sci. Technol.* **2018**, *52*, 3422−3430.

(51) Wang, X.; Johnson, T. M.; Lundstrom, C. C. Isotope fractionation during oxidation of tetravalent uranium by dissolved oxygen. *Geochim. Cosmochim. Acta* **2015**, *150*, 160−170.

(52) Lovley, D. R.; Phillips, E. J. Bioremediation of uranium contamination with enzymatic uranium reduction. *Environ. Sci. Technol.* **1992**, *26* (11), 2228−2234.

(53) Finneran, K. T.; Anderson, R. T.; Nevin, K. P.; Lovley, D. R. Potential for bioremediation of uranium-contaminated aquifers with microbial U (VI) reduction. *Soil Sediment Contam.* **2002**, *11* (3), 339−357.

(54) Campbell, K. M.; Davis, J. A.; Bargar, J. R.; Giammar, D. E.; Bernier-Latmani, R.; Kukkadapu, R. K.; Williams, K. H.; Veramani, H.; Ulrich, K.-U.; Stubbs, J. E.; Yabusaki, S.; Figueroa, L.; Lesher, E.; Wilkins, M. J.; Peacock, A.; Long, P. E. Composition, stability, and measurement of reduced uranium phases for groundwater bioremediation at Old Rifle, CO. *Appl. Geochem.* **2011**, *26*, S167−S169.

(55) Williams, K. H.; Bargar, J. R.; Lloyd, J. R.; Lovley, D. R. Bioremediation of uranium-contaminated groundwater: a systems approach to subsurface biogeochemistry. *Curr. Opin. Biotechnol.* **2013**, *24* (3), 489−497.

(56) Campbell, K. M.; Gallegos, T. J.; Landa, E. R. Biogeochemical aspects of uranium mineralization, mining, milling, and remediation. *Appl. Geochem.* **2015**, *57*, 206−235.

(57) Fletcher, K. E.; Boyanov, M. I.; Thomas, S. H.; Wu, Q.; Kemner, K. M.; Löffler, F. E. U(VI) Reduction to Mononuclear U(IV) by *Desulfitobacterium* Species. *Environ. Sci. Technol.* **2010**, *44* (12), 4705−4709.

(58) Alessi, D. S.; Lezama-Pacheco, J. S.; Stubbs, J. E.; Janousch, M.; Bargar, J. R.; Persson, P.; Bernier-Latmani, R. The product of microbial uranium reduction includes multiple species with U(IV)-phosphate coordination. *Geochim. Cosmochim. Acta* **2014**, *131*, 115−127.

(59) Bone, S. E.; Dynes, J.; Cliff, J.; Bargar, J. R. Uranium(IV) adsorption by natural organic matter in anoxic sediments. *Proc. Natl. Acad. Sci. U. S. A.* **2017**, *114* (4), 711−716.

(60) Stetten, L.; Mangeret, A.; Brest, J.; Seder-Colomina, M.; Le Pape, P.; Ikogou, M.; Zeyen, N.; Thouvenot, A.; Julien, A.; Alcalde, G.; Reyss, J. L.; Bombled, B.; Rabouille, C.; Olivi, L.; Proux, O.; Cazala, C.; Morin, G. Geochemical control on the reduction of U(VI) to mononuclear U(IV) species in lacustrine sediments. *Geochim. Cosmochim. Acta* **2018**, *222*, 171−186.

(61) Stetten, L.; Blanchart, P.; Mangeret, A.; Lefebvre, P.; Le Pape, P.; Brest, J.; Merrot, P.; Julien, A.; Proux, O.; Webb, S. M.; Bargar, J. R.; Cazala, C.; Morin, G. Redox Fluctuations and Organic Complexation Govern Uranium Redistribution from U(IV)-Phosphate Minerals in a Mining-Polluted Wetland Soil, Brittany, France. *Environ. Sci. Technol.* **2018**, *52* (22), 13099−13109.

(62) Morin, G.; Mangeret, A.; Othmane, G.; Stetten, L.; Seder-Colomina, M.; Brest, J.; Ona-Nguema, G.; Bassot, S.; Courbet, C.; Guillevic, J.; Thouvenot, A.; Mathon, O.; Proux, O.; Bargar, J. R. Mononuclear U(IV) complexes and ningyoite as major uranium species in lake sediments. *Geochem. Perspect. Lett.* **2016**, *2*, 95−105.

(63) Weyer, S.; Anbar, A. D.; Gerdes, A.; Gordon, G. W.; Algeo, T. J.; Boyle, E. A. Natural fractionation of ^{238}U/^{235}U. *Geochim. Cosmochim. Acta* **2008**, *72* (2), 345−359.

(64) Richter, S.; Eykens, R.; Kühn, H.; Aregbe, Y.; Verbruggen, A.; Weyer, S. New average values for the n (238 U)/n (235 U) isotope ratios of natural uranium standards. *Int. J. Mass Spectrom.* **2010**, *295* (1), 94−97.

(65) Lau, K. V.; Maher, K.; Altiner, D.; Kelley, B. M.; Kump, L. R.; Lehrmann, D. J.; Silva-Tamayo, J. C.; Weaver, K. L.; Yu, M.; Payne, J.

L. Marine anoxia and delayed Earth system recovery after the end-Permian extinction. *Proc. Natl. Acad. Sci. U. S. A.* **2016**, *113* (9), 2360−2365.

(66) Cheng, H.; Edwards, R. L.; Shen, C.; Polyak, V. J.; Asmerom, Y.; Woodhead, J.; Hellstrom, J.; Wang, Y.; Kong, X.; Spötl, C.; Wang, X.; Calvin, A. J. Improvements in ^{230}Th dating, ^{230}Th and ^{234}U half-life values, and U-Th isotopic measurements by multi-collector inductively coupled plasma mass spectrometry. *Earth Planet. Sci. Lett.* **2013**, *371−372*, 82−91.

(67) Cerrato, J. M.; Ashner, M. N.; Alessi, D. S.; Lezama-Pacheco, J. S.; Bernier-Latmani, R.; Bargar, J. R.; Giammar, D. E. Relative Reactivity of biogenic and chemogenic uraninite and biogenic noncrystalline U(IV). *Environ. Sci. Technol.* **2013**, *47* (17), 9756−9763.

(68) Myrick, T. E.; Berven, B. A.; Haywood, F. F. Determination of concentrations of selected radionuclides in surface soils in the US. *Health Phys.* **1983**, *45* (3), 631−642.

(69) Tissot, F. L. H.; Dauphas, N. Uranium isotopic compositions of the crust and ocean: Age corrections, U budget and global extent of modern anoxia. *Geochim. Cosmochim. Acta* **2015**, *167*, 113−143.

(70) Brennecka, G. A.; Borg, L. E.; Hutcheon, I. D.; Sharp, M. A.; Anbar, A. D. Natural variations in uranium isotopes ratios of uranium ore concentrates: Understanding the ^{238}U/^{235}U fractionation mechanism. *Earth Planet. Sci. Lett.* **2010**, *291* (1−4), 228−233.

(71) Bopp, C. J., IV; Lundstrom, C. C.; Johnson, T. M.; Glessner, J. J. Variations in ^{238}U/^{235}U in uranium ore deposits: Isotopic signatures of the U reduction process? *Geology* **2009**, *37* (7), 611−614.

(72) Uvarova, Y. A.; Kyser, T. K.; Geagea, M. L.; Chipley, D. Variations in the uranium isotopic compositions of uranium ores from different types of uranium deposits. *Geochim. Cosmochim. Acta* **2014**, *146*, 1−17.

(73) Stirling, C. H.; Andersen, M. B.; Potter, E.-K.; Halliday, A. N. Low-temperature isotopic fractionation of uranium. *Earth Planet. Sci. Lett.* **2007**, *264*, 208−225.

(74) Romaniello, S. J.; Herrmann, A. D.; Anbar, A. D. Uranium concentrations and ^{238}U/^{235}U isotope ratios in modern carbonates from the Bahamas: Assessing a novel paleoredox proxy. *Chem. Geol.* **2013**, *362*, 305−316.

(75) Chen, X.; Romaniello, S. J.; Herrmann, A. D.; Wasylenki, L. E.; Anbar, A. D. Uranium isotope fractionation during coprecipitation with aragonite and calcite. *Geochim. Cosmochim. Acta* **2016**, *188*, 189−207.

(76) Charlet, L.; Markelova, E.; Parsons, C.; Couture, R.-M.; Madé, B. Redox oscillation impact on natural and engineered biogeochemical systems: chemical resilience and implications for contaminant mobility. *Procedia Earth Planet. Sci.* **2013**, *7*, 135−138.

(77) Colloff, M. J.; Baldwin, D. S. Resilience of floodplain ecosystems in a semi-arid environment. *Rangeland Journal* **2010**, *32* (3), 305−314.

(78) Campbell, K. M.; Veeramani, H.; Ulrich, K.-U.; Blue, L. Y.; Giammar, D. E.; Bernier-Latmani, R.; Stubbs, J. E.; Suvorova, E.; Yabusaki, S.; Lezama-Pacheco, J. S.; Mehta, A.; Long, P. E.; Bargar, J. R. Oxidative dissolution of biogenic uraninite in groundwater at Old Rifle, CO. *Environ. Sci. Technol.* **2011**, *45* (20), 8748−8754.