

No Measurable Changes in $^{238}\text{U}/^{235}\text{U}$ due to Desorption–Adsorption of U(VI) from Groundwater at the Rifle, Colorado, Integrated Field Research Challenge Site

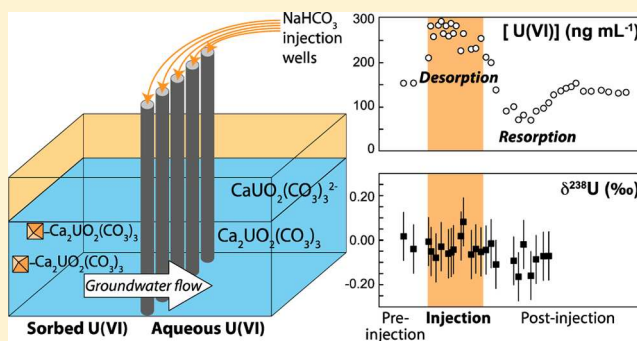
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Supporting Information

ABSTRACT: Groundwater samples were collected from the Integrated Field Research Challenge field site in Rifle, Colorado, over the course of a bicarbonate-induced U desorption–adsorption experiment. Uranium concentrations and high precision U isotopic compositions ($^{238}\text{U}/^{235}\text{U}$) of these groundwater samples were determined and used to assess the impact of bicarbonate-induced U(VI) desorption from contaminated sediments on the $^{238}\text{U}/^{235}\text{U}$ of groundwater. The $^{238}\text{U}/^{235}\text{U}$ of groundwater was not significantly impacted by bicarbonate-induced desorption of U(VI) from mineral surfaces or by adsorption of advecting U(VI) from upgradient locations onto those surfaces after the treatment. Assuming this absence of a significant shift in U isotopic composition associated with desorption–adsorption applies to other systems, reduction of U(VI) to U(IV) is expected to be the dominant source of U isotopic fractionation associated with removal of U(VI) from pore water as a result of natural and stimulated reductive pathways. Thus, changes in the $^{238}\text{U}/^{235}\text{U}$ composition of uranium-bearing fluids should be useful in quantifying the extent of reduction.



INTRODUCTION

Uranium (U) is an element of considerable interest due to its importance for energy and weapons industries and its contribution to the risk associated with radioactive waste storage and disposal. The largest volume of waste associated with the nuclear fuel cycle comes from U mining and milling.¹ The prevalence of U contamination in groundwater has driven research efforts to seek ways to improve the efficiency of in situ remediation of U and to minimize associated costs.² To assess the long-term viability of U remediation methods, we need to be able to distinguish the fate of U sorbed to mineral surfaces or precipitated by bioreduction.

Uranium transport in aquifers is impacted by both the valence state and the speciation of U. In groundwater systems, U occurs as the soluble and mobile oxidized species, U(VI), and the relatively insoluble and immobile reduced species, U(IV). Thus, reduction of U(VI) is proposed as a remedial strategy for U contaminated waters. Groundwater U(VI) concentration and mobility is also affected by U(VI) speciation. Changes in U(VI) aqueous speciation related to changes in pH and bicarbonate and Ca concentrations have a large impact on U(VI) adsorption and thus mobility. In groundwaters, the uranyl ion (UO_2^{2+}) dominates at low pH, while uranyl carbonate species (primarily $\text{UO}_2\text{CO}_3(\text{aq})$, $[\text{UO}_2(\text{CO}_3)_2]^{2-}$ and $[\text{UO}_2(\text{CO}_3)_3]^{4-}$) and

calcium-uranyl carbonate ternary species ($\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ and $\text{CaUO}_2(\text{CO}_3)_3^{2-}$) dominate at neutral to high pH in the absence and presence of typical groundwater Ca concentrations ($>1\text{ mM}$).^{3,4} Limited adsorption of these uranyl carbonate complexes to sediments will occur with the effect exacerbated in the presence of calcium.^{3–5} Thus, groundwater amendment with bicarbonate leads to the desorption of U(VI) from mineral surfaces by impacting U(VI) speciation, that is, by increasing the relative abundance of highly stable calcium-uranyl carbonate species.^{4–6}

The Old Rifle site (Rifle, Colorado, USA) is the former location of vanadium and U milling operations, which ceased operations in 1957. Department of Energy (DOE)-funded experiments are now conducted at the site as a part of the Rifle Integrated Field Research Challenge (IFRC) projects. These experiments are designed to assess both stimulated (through organic carbon amendment) and naturally occurring U bioreduction in contaminated groundwaters. Previous work at the Rifle IFRC has demonstrated success in decreasing U concentration in groundwater by reduction of U(VI) to U(IV), via the stimulation of naturally

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present bacteria species in the aquifer (e.g., *Geobacter* and *Desulfovibrio* species).^{7–9} By injecting an electron donor (e.g., acetate), bioreduction of soluble U(VI) results in U sequestration as biogenic uraninite (UO₂) precipitates.^{7,10,11} However, it can be difficult to identify the mechanism responsible for removal of U from groundwater, since observed decreases in U concentration could indicate reduction, that is, relatively long-term immobilization as U(IV), or simply U(VI) adsorption. While U immobilization by U(VI) adsorption is chemically reversible under certain geochemical conditions, bioreduction produces a crystalline U phase (e.g., uraninite) that is relatively resistant to oxidation due to the incorporation of impurities, such as Ca, from groundwater.¹² Monomeric U(IV), a non-crystalline reduction product, may form along with uraninite and may be more easily remobilized than uraninite.^{13–18} The ability to distinguish between U removal due to U(VI) reduction to U(IV) and U(VI) adsorption is therefore critical for estimating rates of bioreduction of U(VI) in the subsurface and for distinguishing potentially concurrent removal mechanisms.

Isotopic measurement of ²³⁸U/²³⁵U is a promising method for quantifying U reduction.¹⁷ A previous study has demonstrated that ²³⁸U/²³⁵U varies systematically with concentration decrease in field biostimulation experiments using acetate injections.²⁰ The observed shift in the ²³⁸U/²³⁵U (~1‰) is interpreted to reflect an isotope effect by nuclear volume favoring reduction of the heavier isotopes of U(VI) dissolved in groundwater to U(IV).²⁰ However, it is possible that adsorption could also cause changes in ²³⁸U/²³⁵U, complicating the interpretation of U isotopic results. Indeed, laboratory measurements have found a small but measurable enrichment of the heavier isotope in the remaining U(VI) pool when as UO₂²⁺ adsorbs to the manganese oxide birnessite resulting in a shift in ²³⁸U/²³⁵U of ~0.2‰.²¹ In the case of adsorption, where the U redox state does not change, differences between the coordination environments of the adsorbed and dissolved U(VI) species are suggested to be responsible for the isotope effect.²¹ As sorption-related isotope effects have been measured only for birnessite, it is conceivable that other metal oxides (e.g., iron oxides, such as goethite and magnetite) present in aquifers could induce greater isotopic fractionation, particularly given their affinity for U(VI) uptake via chemisorption.²² Thus, if changes in ²³⁸U/²³⁵U are to be used as a tool for quantifying the extent of reduction, potentially confounding effects associated with adsorption to and/or desorption from native aquifer materials need to be evaluated as sources of U isotopic fractionation.

The aim of this study was to determine if significant shifts in ²³⁸U/²³⁵U occur during desorption–adsorption processes in the field. We examined this by measuring the ²³⁸U/²³⁵U of groundwater samples recovered over the course of a sodium bicarbonate (NaHCO₃) amendment at the Rifle IFRC site during the “Super 8” field experiment between August and October 2010. Preinjection, the dominant calcium-uranyl carbonate species, Ca₂UO₂(CO₃)₃(aq) and CaUO₂(CO₃)₃^{2–}, are estimated to represent 67.5–74.9% and 24.2–31.0% of the total U(VI) aqueous speciation, respectively.⁶ In this experiment, bicarbonate injection increased the relative abundance of calcium-uranyl carbonate species, desorbing U(VI) from mineral surfaces and increasing U(VI) concentrations in downgradient wells by a factor of 2 or more. U(VI) desorption associated with NaHCO₃ is attributed to increases in both the bicarbonate and Ca concentrations, the latter resulting from the cation exchange between injected Na (NaHCO₃) and exchangeable cations (e.g., Ca).⁶ Previous work at Rifle has determined the bicarbonate extractable fraction of U(VI) sorbed to Rifle IFRC aquifer sediments is ~50–60% of

the total acid extractable metals fraction.²³ After amendment ceased, concentrations decreased as U(VI) in unimpacted, up-gradient waters repopulated the sorption sites via advection into the bicarbonate-impacted zone. This pronounced desorption–adsorption sequence allowed us to assess whether changes in U isotopic composition were associated with these desorption–adsorption processes associated with natural materials within an alluvial aquifer. This study will facilitate the application of this new geochemical monitoring tool for assessing the efficacy of U bioreduction in the subsurface.

ANALYTICAL METHODS

Site Description, Experimental Design, and Sample Collection. At Rifle, experimental plots consist of wells in spatially coordinated patterns (Figure 1), which are emplaced

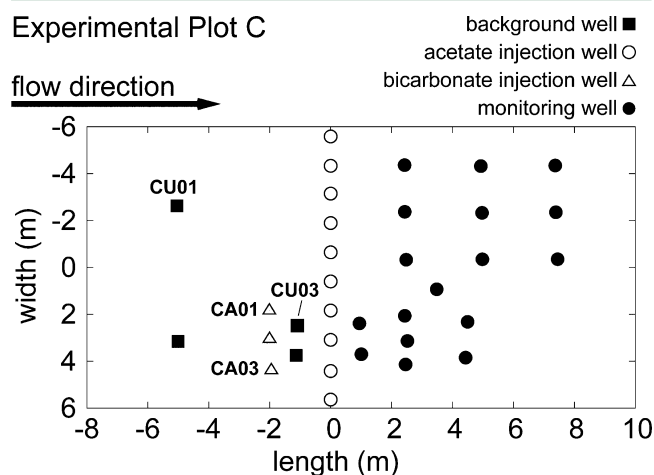


Figure 1. Map of experimental plot C. Wells relevant to this study (i.e., monitoring well CU01, injection wells CA01–CA03, and monitoring well CU03) are identified. Groundwater flow is denoted from left to right.

into an unconfined aquifer of unconsolidated sands, silts, clays, and gravel that overlies the relatively impermeable Wasatch Formation on the Colorado River floodplain.⁹ The aquifer materials are composed of Quaternary floodplain sediments dominated by quartz, with significant amounts of plagioclase and K-feldspar and smaller amounts of calcite, chlorite, kaolinite, smectite, Illite, and iron oxide minerals (primarily magnetite, goethite, and aluminum-substituted goethite).²⁴

During the Super 8 experiment, which began in August 2010 in plot C at Rifle (Figure 1), NaHCO₃ (12 000 L of 50 mM) was injected into the aquifer over a 21 day period (August 16–27 and August 29–September 7, 2010); a 2 day period was required to refill and remix the contents of the injection tank. The amended water was injected into wells CA01–CA03 and sampled at monitoring well CU03 located approximately 1 m downgradient from the region of injection (Figure 1). The injectate, consisting of NaHCO₃ and D₂O (as conservative tracer) additions to water from a nearby unimpacted well, was sparged daily with CO₂ to achieve and maintain a pH of ~7. The injectate was enriched with D₂O obtained from Cambridge Isotope Laboratories, Inc. (Andover, MA) by 500‰ δ²H to a δ²H of ~380‰.

For this study, we passed samples of groundwater (~20 mL) through 0.45 μm PTFE membrane filters and acidified to ~0.15 M with trace metal grade nitric acid (HNO₃). Groundwater samples were taken from background well CU01 and monitoring well CU03 (1) before the bicarbonate injection, (2) during

Table 1. Uranium Concentration and Isotopic Results for Background Well CU01, Monitoring Well CU03, and the Injectate

date	U conc (ng mL ⁻¹) ^a	$\delta^{238}\text{U}$ (‰) ^b	date	U conc (ng mL ⁻¹) ^a	$\delta^{238}\text{U}$ (‰) ^b
Well CU01			Well CU03		
7/31/2010 ^{cd}	183	0.11	9/7/2010 ^e	252	-0.05
8/18/2010 ^{cd}	158	0.06	9/9/2010	209	-0.03
9/6/2010	147		9/9/2010 dup. ^{df}	209	-0.06
9/22/2010 ^{cd}	147	0.08	mean $\pm$ 2SD		-0.05 $\pm$ 0.05
10/11/2010	141		9/11/2010 ^e	196	-0.02
10/21/2010 ^{cd}	140	0.02	9/13/2010	136	-0.14
11/2/2010	139		9/13/2010 dup. ^{df}	136	-0.09
11/10/2010 ^{cd}	140	0.06	9/13/2010 dup. ^{cdf}	136	-0.10
Well CU03			mean $\pm$ 2SD		-0.11 $\pm$ 0.05
8/7/2010 ^e	151	-0.02	9/20/2010 ^e	97.9	-0.09
8/7/2010 dup. ^f	151	0.05	9/22/2010 ^{cd}	68.9	-0.17
8/7/2010 dup. ^{cdf}	151	0.00	9/24/2010 ^d	79.5	-0.02
mean $\pm$ 2SD		0.01 $\pm$ 0.06	9/27/2010 ^e	68.2	-0.14
8/11/2010 ^e	151	-0.04	9/27/2010 dup. ^{cdf}	68.2	-0.19
8/17/2010 ^e	208	-0.01	9/29/2010	87.4	-0.04
8/18/2010	279	-0.05	9/29/2010 dup. ^{df}	87.4	-0.14
8/20/2010 ^e	300	-0.11	10/2/2010	95.3	-0.10
8/20/2010 dup. ^{cdf}	300	-0.05	10/2/2010 dup. ^{df}	95.3	-0.04
mean $\pm$ 2SD		-0.08 $\pm$ 0.09	10/2/2010 dup. ^{cdf}	95.3	-0.09
8/22/2010	289	-0.03	mean $\pm$ 2SD		-0.08 $\pm$ 0.06
8/22/2010 dup. ^{df}	289	0.02	10/4/2010 ^e	108	-0.07
8/22/2010 dup. ^{cdf}	289	-0.09	10/6/2010	125	
mean $\pm$ 2SD		-0.03 $\pm$ 0.11	10/9/2010	133	
8/25/2010	256	-0.05	10/11/2011	140	
8/25/2010 dup. ^{df}	256	-0.08	10/13/2010	143	
mean $\pm$ 2SD		-0.06 $\pm$ 0.05	10/15/2010	150	
8/26/2010 ^e	285	-0.06	10/18/2010	133	
8/27/2010	262	-0.01	10/21/2010	133	
8/27/2010 dup. ^{df}	262	-0.08	10/25/2010	135	
mean $\pm$ 2SD		-0.04 $\pm$ 0.09	10/28/2010	132	
8/30/2010	224	0.02	11/1/2010	128	
8/31/2010 ^e	262	0.08	Injectate		
9/3/2010	227	-0.15	8/16/2010 ^{cd}	127	-0.02
9/3/2010 dup. ^{df}	227	-0.01	8/16/2010 dup. ^{cdf}	127	-0.05
9/3/2010 dup. ^{cdf}	227	-0.03	8/24/2010 ^{cd}	108	-0.02
mean $\pm$ 2SD		-0.07 $\pm$ 0.15	9/3/2010 ^{cd}	155	-0.04
9/5/2010	229	-0.05	9/5/2010 ^{cd}	134	-0.07
9/5/2010 dup. ^{df}	229	-0.04	9/7/2010 ^{cd}	119	-0.02
mean $\pm$ 2SD		-0.04 $\pm$ 0.02			

^aConcentrations provided by the Lawrence Berkeley National Laboratory group. The instrumental uncertainty (RSD) on the concentration measurements is between 0.21% and 2.1%. ^b $\pm 0.11\%$ ($2 \times$ the square root of the rms uncertainty for 12 full procedural duplicates). ^cSamples were spiked to a $^{238}\text{U}/^{236}\text{U}$ ratio of ~ 30 – 50 . ^dSamples were prepared using the U purification technique of Weyer et al.,¹⁹ isotopic measurements were made using the two zeros method, and ^{238}U was measured in a collector equipped with a $10^{10} \Omega$ resistor rather than the standard $10^{11} \Omega$ resistor, as described in the Analytical Methods section. ^eMeasured relative to the IRMM REIMPE 18-A; reported relative to CRM 112-A. ^f“dup.” refers to a full procedural duplicate, inclusive of the analytical separation and isotopic analysis.

the injection phase, and (3) postinjection (Table 1). The injectate (bicarbonate-amended groundwater) was also sampled during the injection phase. The pH of CU01 and CU03 groundwater samples was monitored throughout the duration of the experiment. For CU01, the pH varied between 7.1 and 7.3 and for CU03 between 7.0 and 7.6.

Concentration Determinations. Groundwater U concentrations were determined using inductively coupled plasma–mass spectrometry (ICP-MS) (Elan DRCII, Perkin–Elmer, CA) at the Lawrence Berkeley National Laboratory. A subset of samples was selected for U isotopic analysis at the University of Illinois at Urbana–Champaign to monitor $^{238}\text{U}/^{235}\text{U}$ changes during (1) U desorption associated with the bicarbonate injection and (2) U adsorption after the injection ended. The U concentration and isotopic composition of the injectate were

also monitored throughout the duration of the injection phase of the experiment.

Stable Hydrogen Isotope Analysis. The $^2\text{H}/^1\text{H}$ ratio of groundwater samples from CU03 was used to monitor changes in $^2\text{H}/^1\text{H}$ associated with the injection of NaHCO_3 and D_2O . Hydrogen isotopic compositions are reported relative to the H isotopic standard VSMOW (Vienna Standard Mean Ocean Water) in the standard delta notation:

$$\delta^2\text{H} = \left(\frac{\left(\frac{^2\text{H}}{^1\text{H}} \right)_{\text{sample}}}{\left(\frac{^2\text{H}}{^1\text{H}} \right)_{\text{standard}}} - 1 \right) \times 1000 (\text{‰})$$

The $^2\text{H}/^1\text{H}$ ratios of water samples were measured using a method modified after Berman et al.²⁵ In brief, a field-deployable

liquid water isotope analyzer was used to measure water samples. This study utilized a newer version of the analyzer (LWIA V30d), which reduced the injection time from 120 to 80 s. Discrete water samples were collected and analyzed from 2 mL autosampler vials (Microanalytical Analysis Supplies, Suwanee, GA) using the CTC Analytics (Zwinger, Switzerland) LC PAL autosampler. To account for instrumental memory effects, 12 injections per sample (rather than 6) were used when analyzing the enriched samples.

Uranium Double Spike Correction and Sample Preparation. Previous work demonstrates high precision U isotopic analysis using a ^{233}U – ^{236}U double spike.^{19,20,26} We added a spike with a $^{233}\text{U}/^{236}\text{U}$ ratio of ~ 0.45 (prepared in-house from ^{233}U and ^{236}U isotope spikes) to all samples prior to analytical separation of U. The double spike allowed for the correction of instrumental mass bias and any isotopic fractionation associated with the sample preparation. The majority of reference materials and samples were spiked to give a $^{238}\text{U}/^{236}\text{U}$ of ~ 3 – 5 . Samples prepared later were spiked to give a ratio of ~ 30 – 50 (samples identified in Table 1). Spikes were equilibrated with sample solution ~ 16 h before they were dried and then redissolved in 8 or 3 M HNO_3 , in preparation for purification using anion-exchange or extraction chromatography, respectively.

The anion-exchange chromatography procedure for most samples follows that of Bopp et al.^{20,26} In brief, U was isolated using the anion-exchange resin AG 1-X8 (100–200 mesh) (Bio-Rad Laboratories, Inc.). Between 2 and 4 mL of the resin was loaded into columns and cleaned with successive washes of 1 M HCl and ≥ 18 M Ω cm water. The resin was conditioned with 8 M HNO_3 before loading the sample. Matrix elements were eluted with 8 M HNO_3 , before U was eluted with 1 mL of ≥ 18 M Ω cm water followed by 6 mL of 1 M HBr . Some of the samples were purified by extraction chromatography using the Eichrom UTEVA resin (~ 0.2 mL) and the method of Weyer et al.;¹⁹ these samples are identified in Table 1. Sample eluate solutions were dried and then treated successively two times with ~ 20 μL of 15 M HNO_3 to remove any organic residue. All samples were dissolved in 0.30 M HNO_3 in preparation for U isotopic analysis.

Uranium Isotopic Measurements. Samples were analyzed for U isotopic composition using a Nu Plasma HR (Nu 039; Nu Instruments, UK) multicollector inductively coupled plasma–mass spectrometer (MC-ICP-MS) housed in the Department of Geology at UIUC. A DSN-100 (Nu Instruments, UK) desolvator system was using for sample introduction. The measurement method was adapted from Bopp et al.^{20,26} and consisted of a single cycle that enabled collection of masses 233 to 238 (isotopes of U). For the majority of samples, ion beams were collected in Faraday collectors equipped with 10^{11} Ω resistors (collectors L3 to H1). For samples measured later (identified in Table 1), ^{238}U was measured in a collector equipped with a 10^{10} Ω resistor (allowing beam currents of up to 10^{-9} A), while the remaining isotope ion beams were measured in standard 10^{11} Ω collectors. An analysis comprised 5 blocks of 10×8 s integrations. For the majority of samples, an electronic baseline, measured by deflecting the ion beams off-axis, was used. However, the aforementioned samples measured after the H5 collector was equipped with a 10^{10} Ω resistor (identified in Table 1) were measured using a two zeros method, where zeros were measured at 0.5 amu above and below the measured mass for 30 s, and the average of those values was used to correct for

background signal and tailing from neighboring peaks. This is especially important for correcting potential tailing of the ^{236}U peak onto that of ^{235}U . For all reference materials and samples, ^{235}U signals were between 0.9 – 1.3×10^{-12} A and 0.6 – 4.8×10^{-12} A, and ^{238}U signals were between 1.1 – 1.7×10^{-10} A and 1.2 – 6.6×10^{-9} A, respectively, for the two methods using the different collector resistors for ^{238}U as described above. For reference materials and samples spiked to give $^{238}\text{U}/^{236}\text{U}$ of ~ 3 – 5 and ~ 30 – 50 , ^{233}U signals were between 1.0 – 4.6×10^{-11} A and 0.34 – 1.1×10^{-11} A, and ^{236}U signals were between 0.22 – 1.0×10^{-12} A and 0.74 – 2.4×10^{-11} A, respectively.

Uranium isotopic compositions are reported relative to the U isotopic standard CRM 112-A (New Brunswick Laboratory, U.S. DOE) in the standard delta notation:

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

Most samples were measured relative to CRM 112-A (New Brunswick Laboratory, U.S. DOE). Samples that were measured relative to IRMM REIMEP 18-A (JRC, Brussels, Belgium) have been renormalized to CRM 112-A (Table 1) using the average offset, 0.15‰, determined in-house from 14 measurements. IRMM REIMEP 18-A and CRM 129-A (New Brunswick Laboratory, U.S. DOE) were measured routinely. The running averages for IRMM REIMEP 18-A and CRM 129-A are $-0.15 \pm 0.09\text{‰}$ ($n = 14$) and $-1.67 \pm 0.06\text{‰}$ ($n = 21$), respectively. Twelve full procedural sample duplicates (Table 1) were analyzed and $2 \times$ the square root of the root-mean-square (rms) of the differences was calculated to determine the analytical uncertainty of the data, $\pm 0.11\text{‰}$ (95% confidence).

RESULTS AND DISCUSSION

U(VI) concentration results for groundwater from background well CU01, monitoring well CU03, and the bicarbonate injectate tank are given in Table 1 and Figure 2. The U(VI) concentration of the groundwater from background well CU01 varied from 139 to 183 ppb during the experiment (Table 1 and Figure 2a). Prior to the start of the bicarbonate injection (early August), the U(VI) concentration of groundwater from well CU03 was ~ 151 ng mL^{-1} . Bicarbonate in the well increased during the injection phase (August 16–September 7, 2010; Figure 2c), leading to an increase in the U(VI) concentration (Figure 2b) as U(VI) present in up-gradient groundwater coming into the site gained U(VI) desorbed from aquifer sediments. The U(VI) concentration doubled to a maximum concentration of ~ 300 ng mL^{-1} (Figure 2b), which corresponded to the highest value of $\delta^2\text{H}$ (conservative tracer of bicarbonate) four days after the start of the injection on August 20, 2010 (Figure 2c). After August 24th, the U(VI) concentration decreased, presumably as a result of waning desorption as adsorbed U(VI) was depleted from mineral surfaces (Figure 2b); indeed, elevated $\delta^2\text{H}$ values associated with conservative tracer confirm the presence of the injectate in the vicinity of CU03 throughout the injection phase (Figure 2c). As bicarbonate was flushed out of the experimental plot postinjection (after September 7, 2010), both the U concentration and the $\delta^2\text{H}$ value decreased (Figure 2b,c). Fifteen days after the injection ceased (September 22, 2010), U(VI) concentrations fell to a minimum concentration of 68.2 ng mL^{-1} (September 27, 2011), which is less than half that

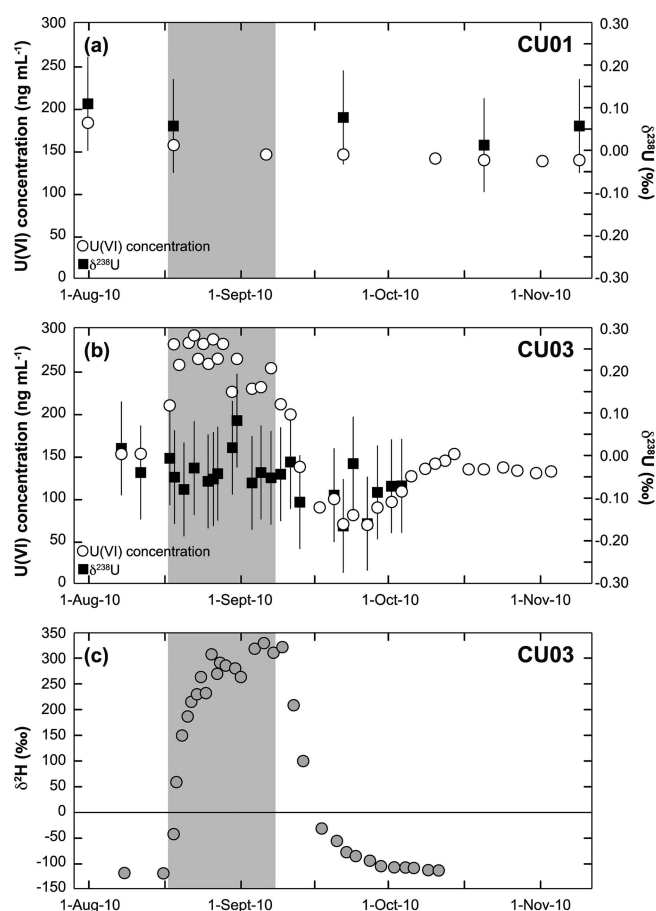


Figure 2. Uranium concentration and $\delta^{238}\text{U}$ measurement results for (a) background well CU01 and (b) monitoring well CU03 during the 2010 experiment. Bicarbonate (NaHCO_3) injection occurred from August 16, 2010 to September 7, 2010 with a break on August 28th, as denoted by the shaded area. Changes in the bicarbonate conservative tracer, D_2O , are shown as $\delta^2\text{H}$ in (c). While the uranium concentration for the background well CU01 during the 2010 experiment varies from 150 to 175 ppb, the $\delta^{238}\text{U}$ measurements results do not vary significantly. The CU01 $\delta^{238}\text{U}$ values fall within those (-0.10‰ to 0.19‰) reported for groundwater collected from the background wells by Bopp et al.²⁰ Over the course of the experiment, there was no significant change in the $\delta^{238}\text{U}$ of CU03 groundwater despite drastic concentration changes due to desorption.

observed in preinjection groundwater (Figure 2b). Assuming this groundwater advected into the experimental plot with a U(VI) concentration of approximately 150 ng mL^{-1} (similar to pre-experiment conditions), the water must have lost U(VI). We attribute this loss to adsorption of U(VI) onto sorption sites made available by the precursory bicarbonate flush. As these newly available sites became steadily repopulated with U(VI), U(VI) concentrations gradually increased until they returned to background values (174 ng mL^{-1}) late October/early November after the injection ended.

Measured U isotopic compositions for groundwater sampled from background well CU01, monitoring well CU03, and the bicarbonate injectate tank are given in Table 1 and Figure 2. The $\delta^{238}\text{U}$ values of groundwater from background well CU01 varied from 0.02‰ to 0.11‰ during the experiment (Table 1 and Figure 2a). Preinjection groundwater samples characterized by U concentrations of $\sim 151 \text{ ng mL}^{-1}$ exhibit $\delta^{238}\text{U}$ values of 0.01‰ and -0.04‰ ($n = 2$). The samples with increased dissolved U(VI) due to the bicarbonate-induced desorption

(characterized by higher U concentrations up to 300 ng mL^{-1}) have an average $\delta^{238}\text{U}$ value of $-0.03 \pm 0.09\text{‰}$ ($n = 12$, 2SD) (Figure 3). As U(VI) was adsorbed back onto aquifer materials

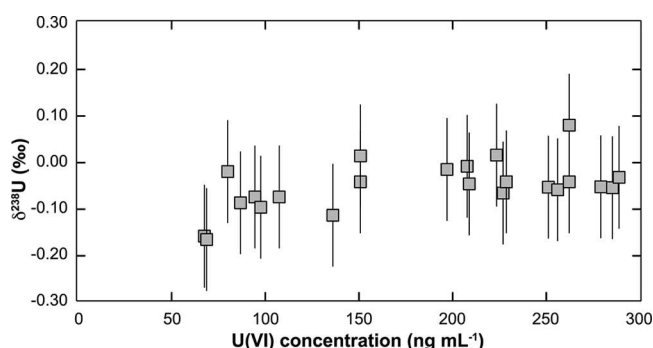


Figure 3. $\delta^{238}\text{U}$ measurements over the course of the experiment plotted against concentration changes. As concentration changed throughout the experiment, there was no significant change in $\delta^{238}\text{U}$ (0.11‰ , the 2SD on the mean, is the same as the reported uncertainty, 0.11‰).

postinjection and U(VI) concentrations decreased (with a minimum of 68.2 ng mL^{-1}) before recovering to background concentrations, samples had an average $\delta^{238}\text{U}$ value of $-0.09 \pm 0.10\text{‰}$ ($n = 10$, 2SD). The average $\delta^{238}\text{U}$ for all the samples from all three phases taken together is $-0.05 \pm 0.11\text{‰}$ ($n = 24$, 2SD). Thus, despite large variations in U concentration between samples collected during the preinjection, injection, and post-injection phases, all the variation in $\delta^{238}\text{U}$ among groundwater samples can be attributed to analytical uncertainty and is thus insignificant (Figure 3). Further, the absence of a correlation between the U concentration and $\delta^{238}\text{U}$ (Figure 3) suggests that a constant U isotopic fractionation for U adsorption to mineral surfaces cannot be assumed.

A recent study²¹ found that U(VI) adsorbed onto K-birnessite is isotopically lighter by $\sim 0.2\text{‰}$ relative to dissolved U(VI) in isotopic equilibrium with it. If similar U isotopic fractionation were observed in the Rifle field site, we would expect the groundwater $\delta^{238}\text{U}$ value to decrease significantly as U(VI) concentrations increased in response to the bicarbonate injection. Because the maximum concentration (300 ppb) was double the preinjection concentration, newly desorbed U(VI) must have been equal in abundance to U(VI) arriving with newly advected groundwater. If the desorbed U(VI) had a $\delta^{238}\text{U}$ value 0.2‰ less than the preinjection dissolved U(VI), we would expect the $\delta^{238}\text{U}$ value of the dissolved U(VI) to decrease by 0.1‰ for the highest concentration samples. Later, after the bicarbonate injection was stopped and the U(VI) concentration dropped to about one-half the preinjection value, about half the incoming U(VI) must have been lost as the sorption sites were repopulated. If the lost, adsorbed U(VI) was 0.2‰ less than the dissolved U(VI), mass balance demands an increase of about 0.1‰ for the lowest concentration samples. Thus, if the U isotopic fractionation observed in birnessite adsorption study occurred in the Rifle subsurface, this experiment should have generated a 0.2‰ range of $\delta^{238}\text{U}$ values in the dissolved U(VI). This range is considerably greater than our analytical precision, and given the large number of measurements, a significant trend in $\delta^{238}\text{U}$ versus U(VI) concentration would be apparent. Yet, no variation beyond the analytical precision, which is established firmly by the duplicate analyses, is observed.

The lack of isotopic fractionation observed in the Rifle IFRC aquifer indicates that adsorption at Rifle differs from that observed

for adsorption onto Mn-oxides in laboratory experiments.²¹ This discrepancy is probably related to differences in either the sorbents or the dominant U(VI) aqueous species present. Brennecke et al.²¹ argued that coordination changes between the dissolved UO_2^{2+} and U(VI) adsorbed onto birnessite are responsible for the isotopic fractionation they observed. Similar coordination changes have been reported for U(VI) adsorption to ferrihydrite, hematite, montmorillonite, quartz, and goethite^{27–31} suggesting that U isotopic fractionation during U(VI) adsorption to Rifle aquifer materials should be similar to that of birnessite.²¹ Thus, we suggest that the nature of the sorbent at the Rifle site does not cause the observed lack of fractionation. Rigorous laboratory experiments with a variety of silicate and oxide materials should be done to test this hypothesis.

However, U(VI) speciation considerations allow us to reconcile the observations. Sorption of $(\text{UO}_2(\text{H}_2\text{O})(\text{CO}_3)_2)^{2-}$ and $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ species onto quartz and calcite creates dominantly outer-sphere surface complexes as reported by Greathouse et al.³² and Doudou et al.,³³ respectively. We expect little isotope fractionation occurs with adsorption of uranyl carbonate and calcium-uranyl carbonate complexes, as outer-sphere complexes should not alter the local U(VI) environment. $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ complexes are the dominant U(VI) species in Rifle waters,⁶ and thus, a lack of isotopic fractionation under these conditions is quite reasonable. However, laboratory experiments measuring U isotopic fractionation for sorption of various U(VI) species including $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ are needed.

This study demonstrates that there is no significant change in the $\delta^{238}\text{U}$ associated with desorption and adsorption of U(VI) onto minerals present in the alluvial Rifle aquifer under the tested field conditions despite significant changes in the U(VI) concentration. These results have important implications for the interpretation of field U isotopic compositions. Significant U isotopic fractionation ($\sim 1\%$) has been interpreted to reflect the bioreduction of U during remedial activities.²⁰ The absence of U isotopic fractionation associated with adsorption allows isotopic variations to be ascribed to redox reactions alone, except when an isotopically distinct adsorbed U(VI) pool is desorbed. We observed from this study that adsorption of U(VI) is not associated with significant U isotopic fractionation under field conditions such as those at the Rifle IFRC site, thus simplifying the interpretation of $\delta^{238}\text{U}$ measurements from this and by extension similar field settings.

■ ASSOCIATED CONTENT

■ Supporting Information

$\delta^2\text{H}$ values for groundwater samples collected from well CU03 are given in Table S1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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