Low Temperature Equilibrium Isotope Fractionation and Isotope Exchange Kinetics between U(IV) and U(VI)

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Abstract

Measurements of the uranium (U) isotope ratio $^{238}\text{U}/^{235}\text{U}$ provide an emerging redox proxy in environmental and paleoredox studies, but many key parameters concerning U isotope fractionation are still poorly constrained. Here we report the equilibrium isotopic fractionation between dissolved U(IV) and dissolved U(VI), and rates of isotope exchange between solid-phase U(IV) and dissolved U(VI). We conducted one experiment at high concentration [35 mM U(IV) and 32 mM U(VI)] and low pH (0.2) in hydrochloric acid media at room temperature to determine the equilibrium isotopic fractionation between dissolved U(IV) and dissolved U(VI). Isotopic equilibrium was reached in about 19 days under such experimental conditions. The equilibrium isotope fractionation was determined to be $1.64 \pm 0.16\%$, with U(IV) being enriched in ^{238}U relative to U(VI). Applicability of the determined equilibrium fractionation is discussed.

We also conducted a set of experiments to determine isotopic exchange rates between

dissolved U(VI) and nanouraninite U(IV) under conditions closer to those in natural system, with lower concentrations and neutral pH. The exchange rate was found to conform to the rate law $R = k[\text{U(VI)}]_{\text{adsorbed}}$, in which R is the isotopic exchange rate ($\mu\text{M day}^{-1}$); k is the rate constant determined to be 0.21 day^{-1} ; and $[\text{U(VI)}]_{\text{adsorbed}}$ is the concentration of U(VI) adsorbed to nanouraninite (μM).

Our results, combined with consideration of the variables controlling U(VI)-U(IV) contact in natural settings, indicate that the timescale for significant isotope equilibration varies depending on environmental conditions, mostly uranium concentrations. In natural uncontaminated sediments with low uranium concentrations, equilibration is expected to occur on a timescale of hundreds to thousands of years. In contrast, in U-contaminated aquifers high U concentrations, significant equilibration could occur on timescales of weeks to years.

1 INTRODUCTION

Uranium (U) has attracted great interest in past decades due to its applications in nuclear energy and weapons industries, as well as the adverse environmental impacts of the waste associated with U mining and processing (Abdelouas et al., 1999b; Abdelouas, 2006; Parrish et al., 2008). The environmental impact is dependent on U bioavailability and mobility, which are strongly controlled by the oxidation state of U. Uranium exists mainly in two valence states in natural aqueous solutions: U(VI) and U(IV). Under typical natural conditions, U(VI) forms stable, soluble complexes with carbonate ions and other ligands, and is very mobile (Langmuir, 1978). Under reducing conditions, U(VI) can be reduced to

U(IV), which is highly insoluble. In modern U-contaminated environments, *in situ* reduction of U(VI) to U(IV) is a potential means to limit U mobility and bioavailability and thus mitigate U contamination (Lovley et al., 1991; Phillips et al., 1995; Liger et al., 1999; Anderson et al., 2003; O'Loughlin et al., 2003; Hua and Deng, 2008; Du et al., 2011; Hyun et al., 2012). Traditional monitoring of U(VI) reduction using concentration measurements alone is hindered by complexity, because the U concentration can also be influenced by adsorption, mixing with uncontaminated water, and advection of complex plumes past monitoring points.

The isotopic ratio $^{238}\text{U}/^{235}\text{U}$ is an emerging redox proxy (Schauble, 2007; Abe et al., 2008; Weyer et al., 2008) that can be an alternative method to detect and potentially quantify reductive immobilization of U(VI). Study of field biostimulation experiment found a systematic decrease in $^{238}\text{U}/^{235}\text{U}$ with decreasing U(VI) concentration as reducing conditions were generated (Bopp et al., 2010). This observation is confirmed by laboratory experiments on microbial reduction of U(VI) (Basu et al., 2014). The direction of the overall kinetic U isotope fractionation during microbial U(VI) reduction (Basu et al., 2014) is consistent with the one predicted by nuclear field shift (a.k.a., nuclear volume effect, NVE) (Schauble, 2007; Abe et al., 2008). Interestingly, in contrast to microbial reduction, abiotic reduction of U(VI) seems to generate undetectable fractionation in $^{238}\text{U}/^{235}\text{U}$ (Rademacher et al., 2006; Stirling et al., 2007; Stylo et al., 2014).

$^{238}\text{U}/^{235}\text{U}$ measurements also shows promise as a paleoredox proxy for early Earth's atmosphere and ocean (Montoya-Pino et al., 2010; Brennecka et al., 2011a; Kendall et al.,

2013). Throughout earth history, the geochemical behavior of U has depended greatly on redox conditions, with major changes in the global U cycle occurring as the earth transitioned from its early, reducing state to progressively more oxidizing conditions (Kendall et al., 2013; Lyons et al., 2014). The isotopic composition and concentration of U in seawater are sensitive to the redox state of the ocean. For example, both U concentration and $^{238}\text{U}/^{235}\text{U}$ of the anoxic Black Sea water were found to decrease systematically with increasing water depth (i.e., increasing anoxia), indicating U(VI) is gradually reduced to U(IV) accompanied by systematic U isotope fractionation (Romaniello et al., 2009). In addition, the long ocean residence time of U (about 500 kyr) makes the marine sedimentary U isotope record a good redox proxy candidate for the global ocean.

Given the growing interests in $^{238}\text{U}/^{235}\text{U}$ as a redox proxy, it is necessary to calibrate U isotope fractionations by various natural processes. Brennecka et al. (2011b) reported that U(VI) adsorbed to birnessite is depleted in ^{238}U by about 0.2‰ relative to coexisting dissolved U(VI). However, Shiel et al. (2013) did not observe an isotopically light adsorbed pool at the Rifle Integrated Field Research Challenge site when bicarbonate was injected into field wells to desorb U(VI) from aquifer sediments. Currently it appears that adsorption involves only a small isotope fractionation, which supports application of $^{238}\text{U}/^{235}\text{U}$ ratio to tracking redox processes. Wang et al. (2014) recently reported that oxidation of solid-phase U(IV) induces very little isotope fractionation, which supports the application of $^{238}\text{U}/^{235}\text{U}$ as a monitor of U(VI) reduction.

Besides reduction, adsorption and oxidation, isotopic exchange between coexisting U(IV)-

bearing phases and U(VI)-bearing phases is another possible process that could potentially alter $^{238}\text{U}/^{235}\text{U}$ ratios of aqueous U(VI) significantly. In this paper we will present results from laboratory experiments designed to determine the equilibrium fractionation between dissolved U(IV) and dissolved U(VI), and the isotope exchange rates between solid-phase U(IV) and dissolved U(VI).

2 ISOTOPE EXCHANGE REACTION

U(IV) and U(VI) bearing phases may be able to exchange isotopes with each other through the reaction

Importantly, the isotope exchange described here, which involves no net redox changes between U(IV) and U(VI), is different from previous isotope equilibration experiments (Florence et al., 1975; Nomura et al., 1996; Fujii et al., 2006), where oxidants and reductants were used to induce U redox cycling for nuclear enrichment purposes. The isotope exchange reaction given in **equation 1** is expected to be slow in solutions when both U(IV) and U(VI) are free ions in constant random motion. Two-electron transfer during one collision is deemed very slow (Linck, 1986). A more likely scenario is that U(VI) and U(IV) need to collide and form two separate U(V) ions, and the second electron transfer occurs only when intermediate U(V) ions collide again. This mechanism is inefficient when U concentration is very low. However, in the presence of electron shuttles such as quinones in natural organic matter (Brose and James, 2010), the isotope exchange mechanism may be different because electrons can be transferred between U(VI) and U(VI) by the “shuttles” and therefore no direct collision is needed. Alternatively, U(VI) and U(IV) collide and form a strongly complexed U(V)-U(V) dimer, which then quickly

disproportionate into U(VI) and U(IV) (Heal, 1946; Betts, 1948; Rona, 1950; Masters and Schwartz, 1961; Renshaw et al., 2005), and thus greatly enhancing the isotope exchange through the following reaction:

Given enough time, isotope exchange will force the $^{238}\text{U}/^{235}\text{U}$ of both U(IV) and U(VI) to be shifted toward equilibrium values. Accurate interpretation of U isotope data from any setting where U(VI) and U(IV) coexist for long periods of time requires knowledge of the size of equilibrium isotope fractionation and the rate at which isotopic exchange overprints original isotopic compositions. For example, during weathering, partially oxidized rock probably contains both solid U(IV)-bearing minerals and aqueous U(VI) in pore spaces. These two phases could possibly coexist for a long enough time to exchange isotopes. Similarly, in an aquifer with slow, natural reduction occurring, the mobile U(VI) may be exposed to U(IV) precipitates for years.

3 PREVIOUS STUDIES

Measurements of equilibrium isotope fractionation between U(IV) and U(VI) has been attempted previously, mostly for nuclear enrichment purposes (Florence et al., 1975; Nomura et al., 1996; Fujii et al., 2006). However, the experimental conditions (high concentrations in acid solutions, called “U(IV)_{aq}-U(VI)_{aq} exchange experiments” hereafter) were far from natural environmental conditions. Besides, since the experiments were designed to attain isotopic equilibrium via rapid reduction and oxidation, it is difficult to be completely sure isotopic equilibrium was attained. The presence of ion exchange resin during isotopic equilibration in these experiments may also have contributed to the isotope

fractionation. Accordingly, we designed an experiment to attain isotopic equilibrium via a more straightforward process and to determine a U(VI)-U(IV) equilibrium fractionation factor at precision higher than that attained in the previous studies.

Previous U(IV)_{aq}-U(VI)_{aq} exchange experiments (Betts, 1948; Rona, 1950; Masters and Schwartz, 1961; Tomiyasu et al., 1968; Ekstrom et al., 1974) yielded inconsistent results, with exchange half-lives ranging from less than 1 hr to more than 100 days. In addition, the forms of rate laws obtained from those experiments did not agree with each other, possibly because they were conducted in different acid media (sulfuric, hydrochloric, and perchloric acids). In most natural settings, U(IV) is in a solid state, and the isotopic exchange mechanism between solid U(IV) and aqueous U(VI) is likely to be fundamentally different. U(VI) can adsorb to the surface of solid-phase U(IV) and keep in contact, which can potentially facilitate the electron transfer.

In this study, we present one experiment (called “U(IV)_{aq}-U(VI)_{aq} exchange experiment” hereafter), with both U(IV) and U(VI) dissolved, to determine the equilibrium fractionation. We then present a set of laboratory experiments (called “U(IV)_s-U(VI)_{aq} exchange experiments” hereafter) designed to measure the isotope exchange rates between solid-phase U(IV) and dissolved U(VI) under conditions similar to environmental conditions (low U concentration and neutral pH). An isotope exchange rate law is proposed to predict isotope exchange rates under a wider range of concentrations.

4 EXPERIMENTS AND METHODS

4.1 Preparation of dissolved U(VI) and dissolved/solid U(IV)

U(VI) and U(IV) reagents used for all experiments were derived from a U metal (CRM112a, New Brunswick Laboratory, U.S. Department of Energy). The metal was first dissolved in double-distilled HNO_3 , evaporated to dryness, and then redissolved in 1 M HCl as the mother solution with a concentration of 0.42 M.

Generation of dissolved U(VI) and dissolved U(IV) stocks in hydrochloric acid media for determining the equilibrium isotope fractionation between two aqueous species is described below. Ten mL of the U(VI) mother solution was evaporated to dryness and redissolved in 20 mL 4.5 N HCl, which served as the U(VI) stock. Because U(IV) is prone to rapid oxidation when exposed to very small concentrations of O_2 , all containers and solutions used to synthesize U(IV) were purged with pure N_2 (passed through heated copper wire) to remove O_2 . All vials and serum bottles were sealed with thick blue butyl rubber stoppers and kept under positive N_2 pressure to exclude O_2 . U(IV) was reduced from U(VI) by zinc metal in sulfuric acid (Ondrejcin, 1961). Briefly, ten mL of the mother solution was evaporated to dryness and redissolved in 5 mL 2 M H_2SO_4 in a 30 mL glass vial sealed with a butyl stopper and purged with pure N_2 . Zinc metal pellets were placed in another sealed glass vial (30 mL) and also purged. The purged U(VI) + H_2SO_4 solution was transferred with N_2 -purged syringes and needles to the vial containing zinc pellets to start the reduction, which produced a green U(IV) solution. Excess hydrogen gas was released during the reduction by a needle piercing through the butyl stopper. The reduced U(IV) solution was then injected into excess 1 M O_2 -free ammonium hydroxide solution contained in another 30 mL glass vial, to precipitate U(IV) (Ondrejcin, 1961). A green

precipitate was immediately formed upon injection. Ammonium hydroxide was favored over sodium hydroxide because ammonia complexes with Zn^{2+} and prevents formation of Zn^{2+} -bearing precipitates, thereby minimizing solute contamination. The precipitate in the vial was centrifuged and the supernatant removed. To remove adsorbed sulfate, an O_2 -free 20 mM bicarbonate buffer was used to wash the solid-phase U(IV) three times. The solid-phase U(IV) was then dissolved in 40 mL O_2 -free 4.5 M HCl as the U(IV) stock for the U(IV)_{aq}-U(VI)_{aq} exchange experiment. The final concentrations of the dissolved U(VI) and dissolved U(IV) stocks were measured to be 0.20 M and 0.08 M. The yield for the U(IV) synthesis procedures was measured to be ~76%. Possible reasons for the <100% yield include incomplete reduction, incomplete precipitation, or U loss during washing. After going through the U(VI)-U(IV) separation and purification procedures as described in sections 4.5 and 4.6, the isotopic compositions [defined as $\delta^{238}\text{U} = (\text{R}_{\text{sample}}/\text{R}_{\text{CRM112a}} - 1)1000\text{‰}$, where R_{sample} and $\text{R}_{\text{CRM112a}}$ represent the $^{238}\text{U}/^{235}\text{U}$ ratios for samples and the standard CRM112a] of the dissolved U(IV) and dissolved U(VI) stocks were determined to be $0.05 \pm 0.08\text{‰}$ and $-0.04 \pm 0.08\text{‰}$. The small difference in the isotopic composition between U(VI) and U(IV) indicates that the low yield did not induce isotope fractionation.

For the U(IV)_s-U(VI)_{aq} exchange experiments where U concentrations were very low, isotopic exchange between U(IV) and U(VI) was expected to be slow. Therefore, the experiment was designed with a ^{235}U -enriched solid-phase U(IV) interacting with dissolved U(VI) having a natural isotopic composition ($\delta^{238}\text{U} = 0\text{‰}$), so that a small extent of isotopic exchange could be detected as a relatively large shift in $\delta^{238}\text{U}$. This set of experiments were conducted in 20 mM NaHCO_3 (adjusted to pH 7 by an O_2 -free $\text{N}_2\text{-CO}_2$

mixed gas) solution, which was used to buffer the pH and to minimize adsorption of U(VI).

The dissolved U(VI) and solid U(IV) stocks in bicarbonate solutions for the U(IV)_s-U(VI)_{aq} exchange experiments were made as follows. First, ten mL of the U(VI) mother solution was dried down and then dissolved in 20 mM NaHCO₃ solution to serve as the U(VI) stock for the U(IV)_s-U(VI)_{aq} exchange experiments. Second, to generate ²³⁵U-enriched solid U(IV) stock, a measured small amount of ²³⁵U-enriched U(VI) solution (U500, New Brunswick Laboratory) was added to the U(VI) mother solution. The mixture was evaporated to dryness and treated with the same U(VI) reduction and U(IV) precipitation procedures described above. The final ²³⁵U-enriched solid-phase U(IV) product was resuspended in O₂-free 20 mM NaHCO₃ buffer (pH 7). The stock U(IV) suspension and stock U(VI) solution were purged a second time with an O₂-free CO₂+N₂ gas mixture to make sure the pH was 7. The U(IV) stock suspension was stored for 2 weeks before use. This waiting period was to ensure the surface of the particles was relatively stabilized from potential aging processes that have been known to affect freshly precipitated chromium oxyhydroxide (Swayambunathan et al., 1989).

The XRD pattern for the solid-phase U(IV) generated using the above procedures is consistent with that of nano-uraninite with particle sizes of ~4 nanometer (XRD data presented in Wang et al, 2014). The concentrations of the dissolved U(VI) and solid U(IV) stocks were measured to be 0.21 M and 0.09M, respectively. After the U(VI)-U(IV) separation and purification procedures as described in sections 4.5 and 4.6, the $\delta^{238}\text{U}$ values of the dissolved U(VI) and solid-phase U(IV) stocks were measured to be $-0.04 \pm 0.08\%$ and

–87.75±0.27%, respectively.

4.2 Procedures for the U(IV)_{aq}-U(VI)_{aq} exchange experiment

In the U(IV)_{aq}-U(VI)_{aq} exchange experiment, we used relatively high concentrations [32 mM U(VI) and 35 mM U(IV)] so as to increase U(VI)-U(IV) interactions and thus to attain isotopic equilibrium within a reasonable amount of time. This experiment was conducted in hydrochloric media to keep U(IV) dissolved to avoid complications with adsorption. Separation of U(VI) and U(IV) using ion exchange chromatography in this experiment required about 30 minutes; significant oxidation of U(IV) solutions by exposure to air could occur in that time frame. To avoid oxidation, the entire experiment and U(IV)-U(VI) separation procedure were conducted in a glove box filled with 90% N₂ and 10% percent of H₂, with palladium as a catalyst to remove trace O₂. The O₂ concentration of the glove box atmosphere during the experiments was less than 1 ppm.

Measured amounts of the dissolved U(IV) and dissolved U(VI) stock solutions in 4.5 M HCl were injected into O₂-free ultrapure water (18 MΩ, Milli-Q) in a sealed serum bottle to obtain final concentrations of about 30 mM U(IV) and U(VI). The bottle was then wrapped in aluminum foil to avoid photochemical reactions and left standing at room temperature. Final U(IV) and U(VI) concentrations were measured to be 35 mM and 32 mM, respectively. The HCl concentration was found to be 0.625 M via acid-base titration. Immediately before each sampling event, the experimental bottle was shaken vigorously, and then the experimental solution was sampled by removing 40 μL of solution at time

intervals of 0.7 to 8 days, diluted into 0.5 mL 4.5 M HCl, and immediately loaded onto pre-cleaned and preconditioned AG1X8 anion exchange resin to separate U(IV) and U(VI) (see section 4.5).

4.3 Procedures for the U(IV)_s-U(VI)_{aq} exchange experiments

In the U(IV)_s-U(VI)_{aq} exchange experiments, separation of nanouraninite from dissolved U(VI) was accomplished by quick filtration. Therefore, those experiments were conducted in sealed, O₂-free serum bottles handled in the open air. Varying volumes of O₂-free 20 mM NaHCO₃ buffer solution (pH 7), U(VI) stock solution, and U(IV) solid suspension in the same buffer solution were sequentially injected into 100 mL serum bottles previously purged with the CO₂+N₂ mixed gas. U(IV) and U(VI) concentrations (Table 1) were varied among experiments so as to study the relationship between isotope exchange rate and concentrations. The serum bottles were wrapped in aluminum foil and constantly agitated on a shaker table at room temperature. Experimental suspensions were sampled at time intervals of a few minutes to a few days using purged, O₂-free syringes and immediately filtered with 0.1 µm syringe filters. The filtrate was saved for isotope analysis.

4.4 Double spike method

High precision ²³⁸U/²³⁵U measurements were obtained using a double spike approach, which corrects for instrumental mass bias during analysis and any isotopic fractionation induced by sample preparation steps (Chen and Wasserburg, 1981; Stirling et al., 2005; Weyer et al., 2008). The U double spike solution contained ²³³U and ²³⁶U (prepared in-house from ²³³U and ²³⁶U spikes) with a calibrated ²³³U/²³⁶U ratio of 0.46275±0.00001).

Timing of spike addition to samples is given in section 4.5 and 4.6. This double spike technique utilizes the measured $^{236}\text{U}/^{233}\text{U}$ ratios of the sample-spike mixture to determine the mass bias, and then to correct the measured $^{238}\text{U}/^{235}\text{U}$ ratio for the mass bias. The trace amount of ^{236}U contained in the U500 solution ($^{236}\text{U}/^{238}\text{U}=1.06\times 10^{-6}$) did not affect the double spike calculation. The technique also allows an isotope dilution calculation of ^{238}U concentration in a sample based on the measured $^{238}\text{U}/^{236}\text{U}$ ratio and the amount of ^{236}U added.

4.5 U(IV)-U(VI) separation by AG1X8 resin

For the $\text{U(IV)}_{\text{aq}}\text{-U(VI)}_{\text{aq}}$ exchange experiment, separation of dissolved U(IV) and dissolved U(VI) was carried out in the O_2 -free glove box immediately after sampling and dilution, using an anion exchange resin (AG1X8, 100–200 mesh, Eichrom). The resin was purged with pure N_2 for four hours to remove O_2 and resided inside the glove box for two weeks before use. Before using the resin, an oxygen indicator (resazurin) was passed through the resin to test the absence of oxygen on the surface of the resin beads. The separation relies on the fact that in 4.5 N HCl, U(VI) forms anionic complexes with Cl^- and adsorbs to the resin while U(IV) and other cations pass through the resin (Hussonnois et al., 1989; Ervanne, 2004). Briefly, immediately after dilution into 4.5 M HCl, samples were loaded onto 0.5 mL AG1X8 resin pre-cleaned by 4 mL 0.1 M HCl and pre-conditioned with 1 mL 4.5 M HCl. U(IV) was first eluted with 2 mL 4.5 M HCl and U(VI) was then released from the resin by 3 mL 0.1 M HCl.

Tests (data presented in Wang et al., 2014) showed undetectable isotopic fractionation

during this separation step by analyzing $^{238}\text{U}/^{235}\text{U}$ of different fractions of collected U(IV) and U(VI). Therefore, we did not need to double spike samples before the AG1X8 anion exchange step. The separated U(IV) and U(VI) solutions were taken out of the glove box and the U(IV) fraction allowed to oxidize by exposure to air.

4.6 U Purification by UTEVA resin

The concentrations of all samples including the separated U(IV) and U(VI) fractions from the U(IV)_{aq}-U(VI)_{aq} exchange experiment and the filtered U(VI) solutions from the U(IV)_s-U(VI)_{aq} exchange experiments, were measured on a Nu Plasma MC-ICP-MS (Nu 035; Nu Instruments, UK). Solution aliquots containing ~300 ng U were taken and doped with proper amount of the double spike to obtain $^{238}\text{U}/^{236}\text{U}$ of ~ 30. Spiked samples were evaporated to dryness on a hotplate in open air at about 60°C. Dried sample-spike mixtures were then dissolved in 1 mL 3 M HNO₃ and processed by a procedure modified from Weyer et al. (2008) that utilizes the UTEVA® U-specific ion exchange resin. Briefly, samples in 3 M HNO₃ were loaded onto columns filled with 0.3 mL UTEVA resin pre-cleaned with 4 mL 0.05 M HCl and conditioned with 1 mL of 3 M HNO₃. Matrix solutes were eluted with 2 mL 3 M HNO₃. U(VI) was finally released from the resin with 2.5 mL 0.05 M HCl. Purified U solutions were evaporated to dryness on a hotplate and redissolved in 0.3 M HNO₃ for isotope analysis.

4.7 Mass spectrometry

Purified U samples were analyzed for $^{238}\text{U}/^{235}\text{U}$ on the Nu Plasma MC-ICP-MS, with protocols modified from previous publications (Stirling et al., 2005; Stirling et al., 2007;

Weyer et al., 2008; Shiel et al., 2013; Wang et al., 2014). In brief, the sample solution was introduced the plasma by a DSN-100 desolvating system (Nu Instrument, UK). Ion beams (^{233}U , ^{235}U , ^{236}U , and ^{238}U) were measured simultaneously by Faraday collectors in 5 blocks of 10 integrations, each lasting eight seconds. Because tailing of the ^{236}U signal can potentially affect ^{235}U , a two-zeros method was used to correct for potential tailing of ^{236}U peak on ^{235}U peak. The background signal was measured 0.5 amu above and below the measured mass for 30 seconds before each block of 10 integrations and the average of those two values were subtracted from the measured peak signal.

The CRM 112-A standard was analyzed before and after every three samples. Despite the use of the double spike, drift in the measured standard value still occurred. This drift is presumably related to departure of the instrument's mass bias from the ideal exponential law assumed for the double spike technique, and affects samples and standards equally. The drift was smooth over time, typically occurred within a few hours after switching on the plasma, and gradually became small ($\sim 0.1\%$ over ~ 4 hours). Samples were analyzed only after the drift was less than about 0.1% per hour. Measured sample $\delta^{238}\text{U}$ values were normalized to the bracketing standards assuming linear changes in mass bias within a bracketing cycle.

An unprocessed secondary standard CRM 129-A (New Brunswick Laboratory, U.S. Department of Energy) analyzed during this study yielded an value of $-1.71 \pm 0.06\%$ (or $^{238}\text{U}/^{235}\text{U} = 137.6137 \pm 0.0036$, 2SD, $n = 10$), which agrees with previously published results (Weyer et al., 2008; Condon et al., 2010; Shiel et al., 2013). Standard CRM 112a in the

form of U(VI) was processed through the AG1X8 and UTEVA procedures and yielded unfractionated $\delta^{238}\text{U}$ value ($0.03 \pm 0.09\text{‰}$, 2SD, $n=6$). The blank of the AG1X8 and UTEVA resin procedures combined was measured to be 0.1 ± 0.3 ng (2SD, $n=12$), which was negligible compared to the 300 ng sample U.

We also routinely measured a purposefully underspiked ($^{238}\text{U}/^{236}\text{U}$ ratio of ~ 56) unprocessed standard IRMM 18-A (JRC, Brussels, Belgium), which yielded $\delta^{238}\text{U}$ of $-0.16 \pm 0.12\text{‰}$, or $^{238}\text{U}/^{235}\text{U} = 137.8277 \pm 0.0084$ (2SD, $n = 13$), which also agrees with previous published result (Weyer et al., 2008; Condon et al., 2010; Shiel et al., 2013). The larger 2SD on the IRMM 18-A was due to counting statistics on the lower intensity ^{233}U measurement.

The external uncertainties for samples were determined to be $\pm 0.08\text{‰}$ ($n=6$) and $\pm 0.27\text{‰}$ ($n=6$) for the $\text{U(IV)}_{\text{aq}}\text{-U(VI)}_{\text{aq}}$ exchange experiment and $\text{U(IV)}_{\text{s}}\text{-U(VI)}_{\text{aq}}$ exchange experiments, respectively, as twice the root mean square (RMS, 95% confidence level) of duplicate preparations and analyses (Hyslop and White, 2009). The larger uncertainty for the $\text{U(IV)}_{\text{s}}\text{-U(VI)}_{\text{aq}}$ exchange experiments was due to the use of the enriched tracer; very small amounts of contamination from natural U during sample preparation and measurement can significantly affect samples that are isotopically very different. The uncertainties on isotope dilution concentration measurements of experimental solutions were 6.5% ($n=6$) and 1.5% ($n=6$) for the $\text{U(IV)}_{\text{aq}}\text{-U(VI)}_{\text{aq}}$ exchange experiment and the $\text{U(IV)}_{\text{s}}\text{-U(VI)}_{\text{aq}}$ exchange experiments, respectively, the former being larger due to larger dilution factor from experimental solution to the solution to be spiked. The use of pipetting

for volume measurement, rather than gravimetric measurement, may also have contributed to the general high uncertainty on our concentration measurement.

5 RESULTS

5.1 Cross contamination

In the $\text{U(IV)}_{\text{aq}}\text{-U(VI)}_{\text{aq}}$ exchange experiment, cross contamination was determined by mixing dissolved U(IV) and dissolved U(VI) with distinctive isotopic compositions. The U(IV)-U(VI) mixtures were subject to separation procedures described in section 4.5. The percentage cross contaminations were then calculated by solving two mixing equations. These tests showed that 5% U(IV) mass was mixed with 96% U(VI) mass and 4% U(VI) mass mixed with 95% U(IV) mass. Results reported in the result section for the $\text{U(IV)}_{\text{aq}}\text{-U(VI)}_{\text{aq}}$ exchange experiment was corrected for cross-contamination using mass balance mixing equations. To avoid variation in the degree of cross contamination, volumes of resin and acids were kept constant between different sessions of sample preparation.

In the $\text{U(IV)}_{\text{s}}\text{-U(VI)}_{\text{aq}}$ exchange experiments, cross contamination can potentially be caused by traces of dissolved U(IV) and/or U(IV) particles breaking through the filters. The cross contamination caused by dissolved U(IV) is negligible because of the extremely low solubility of UO_2 at pH 7 (10^{-13} M, Langmuir 1978). In the presence of 20 mM bicarbonate, the solubility is still extremely low (10×10^{-11} M, calculated using MINEQL 4.62.2).

A separate test was also done to investigate potential passage of U(IV) particles through the

0.1 μm filter. In this test, the U(IV) stock suspension was filtered and the uranium masses in both the filtrate and the material caught on the filter were measured. The results showed that the filtrate contained 10.5% of the total U present in the original solid U(IV) stock. This U in the filtrate, which was measured to be isotopically indistinguishable from the original solid U(IV) stock, could have resulted from particle breakthrough, or presence of a dissolved U(VI) impurity in the solid U(IV) stock. To distinguish these two possibilities, the U(IV) particles caught by the first filtration were resuspended in O_2 -free 20 mM NaHCO_3 solution, stirred, and filtered again immediately. No U was detected in the second filtrate. If the U detected in the first filtrate was solid-phase U(IV), it is difficult to explain its absence in the second filtrate, because XRD data showed that the majority of the synthesized U(IV) was nano particles, which were much smaller than the 100nm filter paper pore size. The particles caught on the first filtration must be $>100\text{nm}$ aggregates of nano-uraninite particles (Abdelouas et al., 1999a). However, the vigorous shaking immediately before resuspending the solid residual during the first filtration should have broken apart the aggregates and resulted in some U in the second filtrate, which was not observed. Therefore, we attributed the 10.5% U detected in the first filtrate to U(VI) impurity, instead of particle breakthrough. Minor oxidation of U(IV) after the experiment started is discussed in [section 6.3](#).

Most importantly, U(VI) was recovered without significant contamination by U(IV). Immediately after the first filtration, the O_2 -free U(VI) stock ($-0.04 \pm 0.08\text{‰}$, in 20 mM NaHCO_3 solution) was quickly passed through the same syringe filter. The filtered U(VI) was measured to be $-0.39 \pm 0.28\text{‰}$ (2SE, $n=3$). This demonstrates insignificant

contamination of U(VI) by U(IV) during the filtration. In addition, the large and smooth changes in $\delta^{238}\text{U}$ (Fig. 2) during the course of the experiments could hardly be obtained if cross contamination was significant.

Measurement of $^{238}\text{U}/^{235}\text{U}$ in the uraninite particles caught by the filter were attempted in the beginning of the experiments but the results were irreproducible, presumably due to high vulnerability to contamination by blank uranium and U(VI) adsorption to the U(IV) precipitate and filter disk. For this reason, the solid-phase U(IV) was not measured for the rest of the experiments.

5.2 Results for the U(IV)_{aq}-U(VI)_{aq} exchange experiment

The results are presented in Table 2 and Fig. 1. The concentration of U(IV) and U(VI) remained unchanged within uncertainty during the entire experiment, indicating undetectable oxidation/reduction of U(IV)/U(VI). The $\delta^{238}\text{U}$ values of U(IV) and U(VI) started from 0‰ and gradually diverged from each other until isotopic equilibrium ($\delta^{238}\text{U}$ change became analytically indistinguishable) was reached in about 19 days. Both cross-contamination-corrected and -uncorrected $\delta^{238}\text{U}$ values are given in Table 2. The corrections are small, ranging from 0.01‰ to 0.09‰. The offset ($\Delta^{238}\text{U}_{\text{IV-VI}} = \delta^{238}\text{U}_{\text{IV}} - \delta^{238}\text{U}_{\text{VI}}$) was calculated using the corrected $\delta^{238}\text{U}$ values. At isotopic equilibrium, the offset (i.e., equilibrium fractionation) was 1.64 ± 0.16 ‰, with U(IV) being enriched in ^{238}U relative to U(VI).

5.3 Results for the U(IV)_s-U(VI)_{aq} exchange experiment

Results for the $\text{U(IV)}_s\text{-U(VI)}_{\text{aq}}$ exchange experiments are presented in Tables 1 and 3, and Fig. 2. The concentration data show that oxidation was very small; its impact on the isotopic composition of U(VI) is discussed in section 6.3. The fourth data point in Fig. 2A and the last data point in Fig. 2B sit beyond the uncertainty range, but the isotopic composition of these points did not deviate from the smooth trend shown in the middle column of Fig. 2. Therefore, we deemed these points as analytical outliers. The adsorbed U(VI) concentration was estimated by comparing measured dissolved U(VI) concentration with the expected values based on total U(VI) injected. The percentage of the adsorbed U(VI) out of total U(VI) ranged from 6% to 19%. The insensitivity of adsorbed U(VI) concentration [mol adsorbed U(VI) per mol exchangeable U(IV)] to dissolved U(VI) concentration (Fig. 3) suggests that the solid-phase U(IV) surface adsorption sites were saturated under the experimental conditions. The value of the saturated adsorbed U(VI) concentration is ~0.5 mole adsorbed U(VI) per mole of exchangeable U(IV). This value is reasonable given the point of zero charge (pH 5-5.5) for U(IV) dioxide (Olsson et al., 2002; Singer, 2008).

The $\delta^{238}\text{U}$ values of the first U(VI) samples in the $\text{U(IV)}_s\text{-U(VI)}_{\text{aq}}$ exchange experiments were negative ranging from -8.55 to -22.97‰, rather than the ~0‰ stock value. The first samples were taken 3 to 14 minutes after mixing U(IV) and U(VI), during which too little isotopic exchange could have occurred to explain the large shifts observed. Instead, the shift in the first sample was likely due to U(VI) impurity in the U(IV) solid, which was present prior to the stock's use in the experiments (see above). The variation in the measured initial values is consistent with the varying U(IV)/U(VI) ratios chosen for the

experiments. We stress that the shifts in the initial $\delta^{238}\text{U}$ values do not affect the calculation of exchange rates, since exchange rates are determined from the changes of $\delta^{238}\text{U}$ over time. The U(VI) concentration was also affected by the small amount of unintended U(VI) added with the U(IV) particles. However, this was accounted for by our measurements of the concentrations after the experiment started. All experiments showed significant progress toward isotopic equilibrium within 10 days (Fig. 2). For all experiments, the $\delta^{238}\text{U}$ plotted against time showed decreasing slopes over time, which is expected as isotopic equilibrium is approached.

6 DISCUSSION

6.1 Equilibrium fractionation: Comparison with previous studies

Uranium equilibrium isotope fractionation is a combination of the mass-dependent effect and nuclear volume effect (NVE) with fractionations occurring in opposite direction (Bigeleisen, 1996; Schauble, 2007; Abe et al., 2008). The overall U isotope fractionation can be expressed by the following equation (Nomura et al., 1996; Fujii et al., 2006):

$$\Delta = \frac{0.69}{T} - \frac{82}{T^2} \quad (3)$$

where the $0.69/T$ term is attributed to nuclear volume effect and the $-82/T^2$ term is attributed to nuclear mass effect. According to equation 3, at 298 K (25 °C) in hydrochloric media, the overall isotope fractionation is $1.4 \pm 0.3\text{‰}$ (Fujii et al., 2006), which is consistent with the $1.3 \pm 0.4\text{‰}$ (1σ) fractionation determined by Florence et al. (1975) in sulfuric acid. Our recent experiment (Wang et al., 2014) with oxidation of dissolved U(IV) by dissolved

oxygen in 0.1 N hydrochloric acid obtained an equilibrium-like (but not completely following an equilibrium model) isotope fractionation of $1.1 \pm 0.3\text{‰}$ (2σ), which is generally consistent with previous equilibration experiments involving net redox reactions (Florence et al., 1975; Nomura et al., 1996; Fujii et al., 2006).

The direct measurement ($1.64 \pm 0.16\text{‰}$, 2σ) of equilibrium isotope fractionation by our experiment at room temperature in hydrochloric acid media is, within the uncertainties, consistent with previous experiments involving multi-stage reduction and oxidation reactions (Florence et al., 1975; Nomura et al., 1996; Fujii et al., 2006). The equilibrium-like fractionation ($1.1\text{‰} \pm 0.3\text{‰}$) observed during oxidation of U(IV) by dissolved oxygen (Wang et al., 2014) in hydrochloric media is slightly smaller than the direct measurement of equilibrium fractionation reported in this study. Two hypotheses may explain the small discrepancy. First, it is possible that isotopic equilibrium was not fully reached during oxidation and the equilibrium-like trend observed during oxidation was due to kinetic fractionation accompanied by changing kinetic fractionation factor over the course of oxidation (Wang et al., 2014). Alternatively, the isotopic equilibrium was maintained during the oxidation experiment, and the discrepancy was due to a speciation effect. The oxidation experiment was conducted in 0.1 M HCl while the $\text{U(IV)}_{\text{aq}}\text{-U(VI)}_{\text{aq}}$ exchange experiment reported here was conducted in 0.625 M HCl. The uranium speciation in these two experiments is listed in Table 4, which shows that in stronger HCl, larger proportions of U(IV) and U(VI) are complexed with Cl ligand. A first-principle calculation suggests that U(IV)-U(VI) equilibrium fractionation is greater when U is complexed with Cl ligands (Abe et al., 2010), and we infer that U(IV)-U(VI) equilibrium fractionation is greater in

stronger HCl acid. Given the large overlapping uncertainties and different nature of experiments conducted so far (i.e., whether net reduction or oxidation is involved or not), it is difficult at this stage to isolate the speciation effect on equilibrium U isotope fractionation. More equilibrium isotope fractionation experiments conducted in different acid strength can be conducted in the future to test this hypothesis.

6.2 Extraction of exchange rates for the U(IV)_{aq}-U(VI)_{aq} exchange experiment

Isotopic exchange rates (R) were extracted by fitting the data via linear regression to the general isotopic exchange equation (McKay, 1938; Cole and Chakraborty, 2001):

$$-\ln(1 - F) = Rt \frac{[U(IV)] + [U(VI)]}{[U(IV)][U(VI)]} \quad (4)$$

where R is the rate of exchange (M day^{-1}); terms in brackets are U concentrations (M); t is time (day). F is the progress toward isotopic equilibrium, defined as:

$$F = \frac{\delta_{VI,t} - \delta_{VI,ini}}{\delta_{VI,eq} - \delta_{VI,ini}} \quad (5)$$

where $\delta_{VI,t}$, $\delta_{VI,ini}$, and $\delta_{VI,eq}$ are the isotopic composition of U(VI) at the time of sampling, the initial value, and the equilibrium value, respectively. For the U(IV)_{aq}-U(VI)_{aq} exchange experiment, the δ_{ini} value was -0.04‰ and the δ_{eq} value was determined to be -0.83‰ , the average of the last three cross-contamination-corrected $\delta^{238}\text{U(VI)}$ values (Table 2).

The exchange rate was calculated from the slope of the linear regression line on a plot of

ln(1-F) versus time (Fig. 1C) to be $3.8 \pm 1.1 \text{ mM day}^{-1}$. Our determined isotopic exchange rate agrees well with the rate law determined by Rona's (1950) experiment in an HCl solution, the same matrix as our experiment. Masters and Schwartz's (1961) rate law determined in sulfuric acid and Betts' (1948) rate law determined in perchloric acid yielded exchange rates two orders of magnitude lower and higher, respectively. This indicates that isotopic exchange rates between dissolved U(IV) and dissolved U(VI) are dependent on solution speciation.

6.3 Oxidation of U(IV) in the U(IV)_s-U(VI)_{aq} exchange experiments

Slight U(IV) oxidation appeared to have occurred in the U(IV)_s-U(VI)_{aq} exchange experiments (Table 3 and left column of Fig. 2), although most of the data points are within the measurement uncertainty. Because the U(IV) had a strongly negative initial $\delta^{238}\text{U}$, a small amount of oxidation could significantly alter the $\delta^{238}\text{U}$ of the dissolved U(VI). Table 3 shows hypothetical $\delta^{238}\text{U}$ values of U(VI) assuming there was only oxidation but no isotope exchange occurring. The oxidation-induced isotope shift was much less than the observed shift. Thus, oxidation could have only small effects on the overall results. Experiment 4 had the greatest potential impact, with oxidation potentially causing a maximum of 21% of the observed $\delta^{238}\text{U}$ shift. For experiments 2, 3, 5, and 6, oxidation could have caused 8%, 6%, 16%, and 17% of the observed shifts, respectively. The extraction of isotopic exchange rates below ignores possible oxidation effects, but we recognize that we may slightly overestimate the exchange rates due to the effects of net U(IV) oxidation.

6.4 Extraction of exchange rates for the U(IV)_s-U(VI)_{aq} exchange

experiments

The U(IV)_s-U(VI)_{aq} exchange experiments were conducted at neutral pH because this makes them more relevant to natural environments. However, the fact that U(IV) is in solid form at neutral pH complicates the interpretation of the experimental data, because only U atoms on the surfaces of the U(IV) particles are able to interact with U(VI). We refer to these exposed U atoms as exchangeable U(IV), and express their abundance as a molar concentration within the well-mixed suspension. Furthermore, we modeled the system assuming the exchangeable U(IV) is a fixed pool, i.e., no new U(IV) atoms are exposed to the solution during the course of the experiment. Accordingly, we used equation 4 and 5 to calculate exchange rates for the U(IV)_s-U(VI)_{aq} exchange experiments, and we set the U(IV) concentration equal to the exchangeable U(IV) concentration, not the total U(IV) concentration. We set the U(VI) concentration equal to the total concentration, including the dissolved and adsorbed forms. This was done based on an assumption that the dissolved U(VI) stays close to isotopic equilibrium with the adsorbed U(VI), and thus these two forms of U(VI) act as a single pool. $\delta_{VI.ini}$ was set equal to the initial measurements of the experiments; this varied between experiments, ranging from -6.38 to -22.97‰, due to the presence of the U(VI) impurity in the U(IV) stock. The $\delta_{VI.equ}$ values were calculated using the mass balance equation:

$$\delta_{IV.equ} - \delta_{VI.equ} = 1.64\text{‰} \quad (6)$$

$$m_{IV.exch} \delta_{IV.equ} + m_{VI.tot} \delta_{VI.equ} = m_{IV.exch} \delta_{IV.ini} + m_{VI.tot} \delta_{VI.ini} \quad (7)$$

in which “*m*” and “*exch*” stand for “*mass of uranium*” and “*exchangeable*”, respectively.

The actual equilibrium fractionation between solid U(IV) and dissolved U(VI) in the U(IV)_s-U(VI)_{aq} exchange experiments may be slightly different from the one (1.64‰) determined in the U(IV)_{aq}-U(VI)_{aq} exchange experiment, where both U(IV) and U(VI) were dissolved in HCl and thus had different speciation. Therefore, the value used in equation 6 may not be exact, but this does not cause a problem. If the actual fractionation departs slightly from 1.64‰, the error introduced when calculating progress toward equilibrium (equation 5) is very small, because the denominator is very large due to the very large initial isotopic difference between U(IV) and U(VI). In fact, using a fractionation of -1.0‰ alters the exchange rates by less than 10%. The use of the simple mixing equation (equation 7) caused less than 1‰ error in calculated equilibrium values.

In order to calculate exchange rates for experiments 2 through 6, the only remaining unknown parameter is the $m_{IV,exch}$. A rough estimate of the percentage of exchangeable U(IV) can be obtained from the particle size and uraninite crystal geometry. The U-U shell distance in nanoparticulate uraninite is ~0.38 nm (Suzuki et al., 2002; Senko et al., 2007; Komlos et al., 2008; Schofield et al., 2008). Therefore, only U atoms located much less than 0.38 nm from the particle surface are available for isotope exchange. Solid-state diffusion is ignored here owing to its long timescale compared to the isotope exchange timescale in our experiments. For ~4 nm particles, the volume of solid within 0.19 nm of the particle surface is ~30% of the total volume. The estimate has considerable uncertainty, but it provides a first-order estimate so that we could build a rate model. Later, we use a sensitivity test to assess how our rate model is affected by the uncertainty in the exchangeable fraction (section 6.5). In Fig. 2 (right column), the data fit straight lines reasonably well, and the exchange rates, calculated from the slopes (equation 4) are presented in Table 3. These results show that faster exchange rates are associated with

higher adsorbed U(VI) concentrations.

6.5 Isotopic exchange mechanisms

The isotopic exchange mechanism between solid U(IV) and dissolved U(VI) in a neutral-pH carbonate solution is likely to be fundamentally different than that in an acidic solution where both redox species are dissolved. At neutral pH, adsorption of U(VI) to the solid U(IV) surface will occur. Adsorption keeps the adsorbed U(VI) and exchangeable U(IV) in close proximity and makes electron transfer easier. This leads to a simple isotopic exchange rate law where the isotopic exchange rate is solely related to the amount of adsorbed U(VI):

$$R = k[U(VI)]_{adsorbed} \quad (8)$$

in which R is the isotopic exchange rate in $\mu\text{M day}^{-1}$; k is the rate constant in day^{-1} ; $[U(VI)]_{adsorbed}$ is the concentration of U(VI) adsorbed to U(IV) particles in μM . The exchangeable U(IV) concentration does not appear explicitly in this equation since it is already taken into account, because it determines the amount of adsorbed U(VI).

Fig. 4 is a plot of exchange rates as a function of adsorbed U(VI) concentration. The linearity suggests that the rate law proposed as **equation 8** is correct. The simple first reaction order with respect to adsorbed U(VI) concentration suggests that steps involving intermediate species U(V), if any, are not limiting the isotopic exchange rate.

Given the large uncertainty on the exchangeable fraction, we did a sensitivity test (**Fig. 5**) to examine its effect on the derived rate constant. Variation of the exchangeable fraction

from 0.29 to 0.45 leads to increase in the rate constant from 0.21 to 0.22 (an increase of ~5%). We also note that values far from our geometrical estimate destroyed the linear trends in plots of $-\ln(1-F)$ vs. time, like those given in Fig. 2, indicating that those values did not fit the rate model well. The best fit (least summed squared residual) between experimental data and the rate model is obtained with an exchangeable fraction of 0.31, consistent with the estimate based on particle size and crystal structure of the synthesized uraninite. The best-fit rate constant k is then calculated to be 0.21 day^{-1} at 25°C and pH 7.

7 APPLICATIONS AND LIMITATIONS

Our $\text{U(IV)}_{\text{aq}}\text{-U(VI)}_{\text{aq}}$ exchange experiment provides a first-order estimate of the maximum impact of isotopic exchange on the isotopic composition of U(VI) under given conditions. A mathematical expression for the maximum impact of isotope exchange on U(VI) can be obtained by calculating the shift in $\delta^{238}\text{U}$ of U(VI) by combining equations 6 and 7:

$$\delta_{VI.equ} - \delta_{VI.ini} = \frac{(\delta_{IV.ini} - \delta_{VI.ini}) - 1.64\text{‰}}{1 + m_{VI.tot} / m_{IV.exch}} \quad (9)$$

This shows that the maximum shift in $\delta^{238}\text{U}$ of U(VI) depends on (1) the initial difference in the $\delta^{238}\text{U}$ values between U(IV) and U(VI) , (2) the equilibrium fractionation between U(IV) and U(VI) (1.64‰ determined by our low pH experiment) and (3) the relative masses of U(VI) and exchangeable U(IV) . The use of the simple mixing equation (equation 7) causes negligible errors due to small isotope difference between U(IV) and U(VI) in natural environment.

An example calculation of the impact of U(IV)-U(VI) isotope exchange is given below. For the sake of illustration, the following assumptions are made: (1) an uncontaminated groundwater or soil setting with total soluble U(VI) and total solid U(IV) concentrations of 10 µg/L (current maximum contamination level is 30 µg/L) and 3 µg/g (average continental crust, McLennan, 2001), respectively; (2) a porosity of 30% and sediment density of 2 g/cm³; (3) all solid U(IV) minerals exposure to pore water; and (4) an exchangeable U(IV) fraction of 0.3. With these assumptions, $m_{VI,tot}/m_{IV,exch}$ is then estimated to be ~0.0024. For such a case where the mass of U(IV) dominates, equation 9 tells us that the maximum shift is mainly controlled by the denominator, i.e., the initial isotopic offset and the equilibrium isotope fractionation factor.

Our derived rate model (equation 8), combined with equation 4, can be used to obtain a first-order estimate of the half-life ($F=0.5$) of isotopic exchange:

$$t_{1/2} = \frac{0.693}{kf_s(1 + m_{VI,tot} / m_{IV,exch})} \quad (10)$$

where f_s is the fraction of total U(VI) that is adsorbed to solid U(IV) and k is the rate constant. If we adopt the rate constant determined from our experiments, the exchange half-life is dependent on f_s and relative amount of U(VI) and exchangeable U(IV).

An example calculation of the timescale is given as follows. In a uncontaminated aquifer, U(IV) particles would usually only account for a very small fraction of sediments. For the sake of illustration, we assume f_s equals the U(IV) concentration in sediments. This assumption is reasonable if U(VI) adsorbs to U(IV)-bearing solids and other solids equally

and the majority of U(VI) is adsorbed to particle surfaces. For an example, if the solid U(IV) concentration in the solid is 10 µg/g, this means then roughly 0.001% of U(VI) is adsorbed to U(IV), i.e., $f_s \approx 10^{-5}$. In Fig. 6, we plot the exchange half-life as a function of the wide range in possible U(IV) (and thus f_s values) and U(VI) concentrations. This demonstrates that the half-life of isotope exchange can vary dramatically, from <10 days to >1000 years, depending on U(IV) and U(VI) concentrations in the environment.

Fig. 6 provides an illustration of how the impact of U isotopic exchange could have important impacts under certain circumstances. However, we stress that quantitative prediction of exchange timescales in natural environment is not yet possible, due to uncertainties surrounding the exchangeable fractionation of U(IV) and the fraction of U(VI) that is adsorbed to U(IV) minerals. Several factors should be considered. First, U(IV) mineral grain sizes, which control the fraction of exchangeable U(IV), may vary owing to aging processes and conditions of formation (biogenic or abiogenic). Second, occlusion of U(IV) particles by organic matter or other oxides may hinder isotope exchange between U(IV) and U(VI). Third, competing anions against U(VI) for adsorption sites may decrease the adsorbed U(VI) concentration and thus isotope exchange rate. Fourth, electron shuttles (e.g. quinones) in natural systems may facilitate the isotope exchange. However, the results of this study indicate that isotopic exchange is potentially important in certain systems, and likely to have important impact on relatively short time scales in settings with large amounts of U(IV) particles or coatings.

8 CONCLUSIONS

The equilibrium isotopic fractionation between dissolved U(IV) and U(VI) at 25°C in 0.625 M HCl medium was determined to be $1.64 \pm 0.16\%$, with ^{238}U being enriched in U(IV) relative to U(VI). The uncertainty of this value is less than those determined in previous studies. Isotopic equilibration was attained after about 19 days, and the isotopic exchange rate under the experimental conditions was determined to be $0.0036 \pm 0.0011 \text{ M day}^{-1}$. The equilibrium isotope fractionation and the exchange rate agree with previous studies within the uncertainties.

Isotope exchange rates in experiments designed to more closely approximate natural conditions (neutral pH, solid U(IV), and much lower concentrations) were found to correlate linearly with the adsorbed U(VI) concentration with a rate constant of 0.21 day^{-1} at 25 °C. Our results, combined with consideration of the variables controlling U(VI)-U(IV) contact in natural settings, indicate that the timescale for significant isotopic equilibration between dissolved U(IV) and solid-phase U(IV) will vary dramatically in soils, sediments, and aquifers. In natural uncontaminated sediments with low U concentrations, equilibration is expected to occur on a timescale of hundreds to thousands of years. In contrast, U-contaminated aquifers with higher U concentrations could allow equilibration on the timescale of weeks to years.

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839 11 TABLES

840 Table 1: Concentration data for the $\text{U(IV)}_s\text{-U(VI)}_{\text{aq}}$ exchange experiments (experiments 2 to
841 6).

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Exp't	[U(IV)] total μM	[U(VI)] total μM	[U(VI)] dissolved μM	[U(VI)] adsorbed μM	[U(IV)] exchangeable μM
2	58.4	89.9	80.7	9.2	18.1
3	53.7	36.0	29.2	6.8	16.6
4	46.7	74.1	66.1	8.0	14.5
5	18.5	65.6	63.0	2.6	5.7
6	109.8	80.5	66.5	14.0	33.0

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Table 2: Result of the U(IV)_{aq}-U(VI)_{aq} exchange experiment (experiment 1).

Time day	[U(IV)] dissolved mM	[U(VI)] dissolved mM	$\delta^{238}\text{U}$ IV ‰	$\delta^{238}\text{U}$ VI ‰	$\delta^{238}\text{U}$ IV ^a ‰	$\delta^{238}\text{U}$ VI ^a ‰	Offset ^b IV-VI ‰	F ^c
0.0	38.1	33.9	0.06	-0.11	0.07	-0.12	0.19	0.10
0.7	32.9	32.8	0.25	-0.18	0.27	-0.20	0.47	0.21
2.0	35.2	31.3	0.33	-0.33	0.36	-0.37	0.66	0.42
6.7	35.5	30.8	0.62	-0.60	0.66	-0.68	1.34	0.81
10.8	35.0	31.8	0.71	-0.67	0.77	-0.76	1.53	0.91
14.7	34.4	31.2	0.69	-0.71	0.75	-0.80	1.55	0.96
19.1	33.9	30.7	0.74	-0.76	0.81	-0.84	1.65	1.02
27.9	33.7	32.3	0.75	-0.73	0.81	-0.82	1.63	0.98
35.8	33.7	33.3	0.75	-0.75	0.82	-0.83	1.65	1.00

R=0.0038±0.0011 M day⁻¹; half-life=3.1±0.9 day.

^a: Corrected for cross-contamination; ^b: Offset in $\delta^{238}\text{U}$ is calculated using cross-contamination-corrected values; ^c: F refers to the progress toward isotopic equilibrium. Uncertainties for $\delta^{238}\text{U}$ and concentrations are ±0.08‰ (2RMS) and 6.5% (2RMS), respectively.

Table 3: Results of the U(IV)_s-U(VI)_{aq} exchange experiments (experiments 2 to 6).

Exp't	Time day	[U(VI)] _{dissolved} μM	δ ²³⁸ U(VI) ‰	δ ²³⁸ U(VI)* ‰	F	R μM day ⁻¹	Half-life day
2	0.0	79.8	-8.55	-8.55	0.00	2.69±0.12	3.8±0.2
	0.9	78.6	-11.64	-8.67	0.23		
	3.0	78.1	-14.67	-8.94	0.43		
	5.1	86.5	-16.62	-9.21	0.61		
	10.9	80.5	-20.04	-9.94	0.87		
Estimated equilibrium			-21.75				
3	0.0	28.8	-22.97	-22.97	0.00	1.46±0.11	5.3±0.4
	2.1	28.5	-30.94	-23.62	0.39		
	4.0	29.1	-33.65	-24.17	0.52		
	6.8	29.2	-35.96	-25.00	0.63		
	10.8	30.2	-38.91	-26.15	0.78		
Estimated equilibrium			-43.51				
4	0.0	63.3	-10.61	-10.61	0.00	1.17±0.07	7.0±0.9
	1.8	65.9	-14.53	-10.85	0.31		
	3.8	64.7	-16.06	-11.11	0.43		
	5.9	65.5	-17.82	-11.40	0.58		
	7.8	66.7	-18.54	-11.64	0.63		
	11.7	65.8	-19.65	-12.14	0.72		
	14.0	67.3	-20.33	-12.44	0.78		
	15.8	65.3	-20.70	-12.68	0.81		
	19.9	66.8	-21.71	-13.19	0.89		
Estimated equilibrium			-23.15				
5	0.0	62.0	-6.38	-6.38	0.00	0.55±0.02	6.5±1.6
	1.8	62.2	-7.60	-6.46	0.19		
	3.8	62.7	-8.92	-6.56	0.39		
	5.9	64.1	-9.44	-6.66	0.47		
	7.8	62.3	-9.80	-6.75	0.53		
	11.7	63.3	-10.71	-6.93	0.67		
	14.0	62.7	-11.17	-7.04	0.74		
	15.8	62.6	-11.08	-7.13	0.73		
	19.9	63.4	-12.32	-7.32	0.92		
Estimated equilibrium			-12.84				
6	0.0	65.6	-17.39	-17.39	0.00	2.83±0.05	5.7±0.6
	1.8	65.0	-22.87	-18.03	0.26		
	3.8	66.8	-25.09	-18.72	0.37		
Estimated equilibrium			-38.32				

Uncertainties for δ²³⁸U and concentrations are ±0.27‰ (2RMS) and 1.5% (2RMS), respectively. The * represents hypothetical values as if there were no isotope exchange occurring and the δ²³⁸U value were only affected by oxidation (details in [section 6.3](#))

Table 4. Speciation of uranium in 0.625 N HCl (U(IV)_{aq}-U(VI)_{aq} exchange experiment in this study) and 0.1 M HCl [U(IV) oxidation experiment by Wang et al., 2014].

	0.625 M HCl		0.1 M HCl	
	Species	Percentage	Species	Percentage
U(VI)	UO ₂ ²⁺	51.7	UO ₂ ²⁺	86.1
	UO ₂ Cl ⁺	48.3	UO ₂ Cl ⁺	13.9
U(IV)	U ⁴⁺	3.3	U ⁴⁺	11
	UOH ³⁺	1.3	UOH ³⁺	27.9
	-	-	U(OH) ₂ ²⁺	5.9
	UCl ³⁺	95.4	UCl ³⁺	55.2

12 FIGURE CAPTIONS

Figure 1: Result of the $U(IV)_{aq}$ - $U(VI)_{aq}$ exchange experiment. Open circles and filled circles represent dissolved $U(VI)$ and dissolved $U(IV)$, respectively.

Figure 2: Result of the $U(IV)_s$ - $U(VI)_{aq}$ exchange experiments focusing on the isotopic exchange kinetics between dissolved $U(VI)$ and solid $U(IV)$. A, B, C, D, and E are for experiments 2, 3, 4, 5, and 6, respectively. Dashed lines in the middle column represent the predicted equilibrium value. The solid lines in the left column represent potential oxidation during the course of the experiment. These trends were used to estimate the impact of oxidation on the isotopic composition of $U(VI)$ (Table 3). The outlier in Fig. 2A1 was not used to estimate the oxidation curve.

Figure 3: Adsorbed $U(VI)$ concentration, in moles adsorbed $U(VI)$ per mole of exchangeable $U(IV)$, as a function of dissolved $U(VI)$ concentration. The insensitivity of adsorbed $U(VI)$ concentration to dissolved $U(VI)$ concentration indicates the particle surfaces were saturated by adsorbed $U(VI)$ in all $U(IV)_s$ - $U(VI)_{aq}$ exchange experiments. Exchangeable $U(IV)$ instead of total $U(IV)$ was used to calculate adsorbed $U(VI)$ concentration, because in this way, the plot tells us that about 0.5 moles of $U(VI)$ atoms were adsorbed to each mole of exposed $U(IV)$ atoms.

Figure 4: Plot of isotopic exchange rate R as a function the concentration of adsorbed $U(VI)$ for the $U(IV)_s$ - $U(VI)_{aq}$ exchange experiments.

Figure 5: Sensitivity analysis to test the influence of error in estimated exchangeable fraction on the extracted isotope exchange rate constant. An exchange rate constant of 0.21 day^{-1} is the best-fit value with the least summed squared residuals.

Figure 6: $U(IV)$ - $U(VI)$ exchange half-life as a function of varying total solid $U(IV)$ concentration (dashed curves left y-axis) or varying total $U(VI)$ concentration (solid curves, right y-axis). All axes are on logarithmic scale. The dashed and solid lines represent different $U(VI)$ and $U(IV)$ concentrations, respectively (numbers on the curves). The isotope exchange half-life can vary dramatically, from less than 10 days to more than 1000 years because the $U(VI)$ - $U(IV)$ contact is so widely variable in natural environments.

Figure 1

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