Isotope Fractionation During Oxidation Of Tetravalent Uranium By Dissolved Oxygen

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Abstract

We conducted laboratory experiments to investigate isotopic fractionations during oxidation of tetravalent uranium, U(IV), by dissolved oxygen. In hydrochloric acid media with the U(IV) dissolved, the $\delta^{238}\text{U}$ value of the remaining U(IV) increased as the extent of oxidation increased. The $\delta^{238}\text{U}$ value of the product U(VI) paralleled, but was offset to $1.1\pm 0.2\text{‰}$ lower than the remaining U(IV). In contrast, oxidation of solid U(IV) by dissolved oxygen in 20 mM NaHCO_3 solution at pH = 9.4 caused only a weak fractionation ($\sim 0.1\text{‰}$ - 0.3‰), with $\delta^{238}\text{U}$ being higher in the dissolved U(VI) relative to the solid U(IV). We suggest that isotope fractionation during oxidation of solid U(IV) is inhibited by a “rind effect”, where the surface layer of the solid U(IV) must be completely oxidized before the next layer is exposed to oxidant. The necessity of complete conversion of each layer results in minimal isotopic effect. The weak shift in $\delta^{238}\text{U}$ of U(VI) is attributed to adsorption of part of the product U(VI) to the solid U(IV) surfaces.

1. INTRODUCTION

Uranium mining and other applications in the energy and weapons industries over the past decades have caused contamination of groundwater and soils in many places around the world. This has raised public health concerns due to the chemical toxicity (mainly nephrotoxicity) of U (Bleise

et al., 2003).

U is a redox sensitive element, with two main valence states being stable in nature: U(VI) (hexavalent) and U(IV) (tetravalent). U(VI) is stable as dissolved uranyl ion (UO_2^{2+}) under a wide range of pH and often complexed by carbonate ions and other ligands in natural waters. In contrast, U(IV) is highly soluble only at very low pH (<2) in aqueous media (Langmuir, 1978). Thus, at circumneutral pH conditions, the reduction of mobile U(VI) to immobile U(IV) offers an efficient *in situ* method of mitigating U contamination (Bopp et al., 2010; Shiel et al., 2013). U(VI) can be reduced by both artificial and natural reductants, including Fe(II) species and microorganisms (Lovley et al., 1991; O'Loughlin et al., 2003; Hua et al., 2006; Du et al., 2011). In both cases, reduction needs to be monitored. Recent field and laboratory studies (Bopp et al., 2010; Basu et al., 2014) show that reduction of U(VI) causes a systematic shift in $\delta^{238}\text{U}$ that appears to be caused by a nuclear volume effect (Schauble, 2007; Abe et al., 2008). This allows the use of $^{238}\text{U}/^{235}\text{U}$ to monitor and potentially quantify reduction of U(VI).

However, studies have shown that the U(IV) product deposited by reductive remediation can be quickly reoxidized by natural oxidants such as oxygen and nitrate (Beller, 2005; Moon et al., 2009). Potential isotope fractionation during oxidation may complicate the application of $^{238}\text{U}/^{235}\text{U}$ measurements to indicate reduction.

Besides environmental applications, $^{238}\text{U}/^{235}\text{U}$ measurements have recently been used to trace ocean/atmosphere redox states (Montoya-Pino et al., 2010; Brennecka et al., 2011a; Kendall et al., 2013b). The long residence time of uranium in the ocean (about 500 ky) (Klinkhammer and Palmer, 1991) leads to homogeneous U concentration and isotopic composition of the open seawater (Delanghe et al., 2002; Stirling et al., 2007; Weyer et al., 2008). Therefore, $\delta^{238}\text{U}$ potentially offers a redox proxy on global scales.

The global U cycle on Earth is very sensitive to the oxygen content in the atmosphere. U in continental rocks is present mainly as U(IV), residing in feldspars, zircon, apatite, sphene, and

uraninite (Speer et al., 1981). U(IV) in minerals can only be oxidized to soluble U(VI) and carried to the ocean when the atmosphere O₂ is above a certain level. Absence of oxidative weathering leads to extremely small dissolved U concentrations in the ocean, given extremely low solubilities of U(IV) minerals under reducing conditions (Langmuir, 1978). Under these conditions, the global U cycle is dominated by sedimentary fluxes of reduced U contained in detrital grains, leading to essentially invariant marine sedimentary U isotope composition (Kendall et al., 2013a). With the onset of oxidative weathering, the increased U inventory in the ocean allows for partial reduction of U(VI), making ²³⁸U/²³⁵U variations possible. Therefore, variation of marine sedimentary U isotope composition may be used to trace paleoredox perturbations in earth's early surface environments.

This study aims to provide experimental data on U isotope fractionation during oxidation of dissolved U(IV) and synthetic solid U(IV). Laboratory experiments were designed with simplicity in mind, to obtain clear initial results with few complications.

2. EXPERIMENTAL AND ANALYTICAL METHODS

2.1. Synthesis of U(IV)

Tetravalent U is extremely sensitive to oxygen; therefore, U(IV) was protected from air by serum bottles and/or an glove box filled with nitrogen gas. A U(VI) stock solution, from which all U-bearing solutions and solids were created, was obtained by dissolving the metal U standard CRM 112a (New Brunswick Laboratory, U.S. Department of Energy) in concentrated nitric acid. Following previously reported methods (Ondrejcin, 1961), dissolved U(VI) was then reconstituted in 1 M sulfuric acid and reduced to U(IV) by zinc metal. The produced U(IV) was then precipitated in excess 1 M ammonium hydroxide. Ammonium hydroxide was preferred over sodium hydroxide because the latter introduces matrix cations. The U(IV) precipitate was centrifuged and washed three times with O₂-free 20 mM bicarbonate buffer (pH 7) to remove sulfate and Zn ions. The bicarbonate buffer solution was deoxygenated by passing mixed N₂-CO₂ gas through a 20 mM bicarbonate

solution. The purpose of this bicarbonate solution was to buffer pH, to minimize adsorption, and to simulate natural conditions. About half of the solid U(IV) was resuspended in O₂-free 20 mM bicarbonate buffer as the stock for the experiments focusing on oxidation of solid U(IV). The remainder was dissolved in O₂-free 4.5 M HCl as the stock for the experiments focusing on oxidation of dissolved U(IV). The synthesized solid U(IV) particles were stored in anaerobic serum bottles (pure N₂ headspace for the dissolved U(IV) stock and CO₂-N₂ mix gas for the solid U(IV) stock) for 2 weeks so that the particle surfaces were relatively stable and less prone to aging effects during the experiments. XRD analysis suggested that the synthesized U(IV) particles are ~4 nm uraninite (Fig. 1). Concentrations of the starting U(VI) solution, reduced U(IV) solution and solid U(IV) suspension were determined to be 0.2 M and , 0.1 M, and 1.2 mM, respectively. Since all experimental suspensions were homogenized by constant mixing, we reported molarity as the concentration unit for solid suspension for the sake of easy comparison with experiments on oxidation of dissolved U(IV). Isotopic compositions of the starting U(VI) solution, the reduced U(IV) solution and the solid U(IV) suspension were determined to be the same ($0.05 \pm 0.06\%$, expressed as $\delta^{238}\text{U}$ relative to CRM112a). This indicates that the reduction and precipitation processes used to make the starting materials did not fractionate U isotopes.

2.2. Experiment procedures

Two duplicate experiments examining oxidation of dissolved U(IV) (experiments 1 and 2) were conducted in 0.1 N HCl at room temperature in an anaerobic glove box with < 1ppm O₂ in order to facilitate immediate processing of the samples without exposure to air. A small measured amount of the dissolved U(IV) stock was added to 50 mL oxygenated 0.1 M HCl in 100 mL serum bottles sealed with butyl stoppers with air headspace and immediately mixed thoroughly. Solutions were sampled by withdrawing 0.5 mL volumes with needles and syringes at 0.1 to 3 day intervals. The sampled volume was replenished with an equal volume of air. Experimental solutions were

shaken at each sampling event but left standing the rest of the time. Immediately after sampling, 0.7 mL O₂-free 7.5 M HCl was added to the sampled 0.5 mL solutions to bring the HCl concentration to 4.5 M before separation of U(IV) and U(VI) by anion exchange (see below).

Two duplicate experiments examining oxidation of the synthetic, solid U(IV) oxide (experiments 3 and 4) were conducted in 20 mM NaHCO₃ solution at room temperature. These experiments required only filtration to separate dissolved U(VI) and solid U(IV) and thus were conducted in air. A measured amount of the synthetic solid U(IV) stock in 20 mM NaHCO₃ was filtered with a 0.1 µm filter, and the filtrate discarded, to remove potential dissolved U(VI) impurity produced during the precipitation step. The filter with solid U(IV) was then placed into a serum bottle containing 50 mL 20 mM NaHCO₃ (pH 9.4) and sealed with a butyl stopper with an air head space. The bicarbonate solution pH was originally made to be 7 (section 2.1), but changed to 9.4 after equilibration with air. A magnetic stir bar mixed the suspension during the entire duration of the experiment. 1 mL samples were taken using needles and syringes and filtered with 0.1 µm filters. The sampled volume was replaced with an equal volume of air. U(IV) on the filter was then placed in 2 mL of 2 M HCl to form dissolved U(IV). Because the suspension was mixed vigorously throughout the experiments, the ratio of solid U(IV) to dissolved U(VI) in withdrawn samples matched those of the sampled suspensions. Thus, sampling events did not alter the proportion of solid U(IV) and dissolved U(VI). In addition, the total U (dissolved plus solid) sampled at each sampling event remained constant over time, as shown in table 2. The exception was sample 1 of experiment 4, probably reflecting the heterogeneous nature of the suspension at the beginning of this experiment. However, all subsequent sampling events withdrew the same amount of total U.

2.3. Sample preparation

2.3.1. Double spike method

A double spike composed of ²³³U and ²³⁶U (²³³U:²³⁶U=0.46275) was used to correct

instrumental mass bias and potential isotope fractionation during sample preparation, based on previous published methods (Chen and Wasserburg, 1981; Stirling et al., 2005; Rademacher et al., 2006; Stirling et al., 2006; Stirling et al., 2007; Weyer et al., 2008; Bopp et al., 2010; Shiel et al., 2013). The timing of double spike addition is given below. The double spike technique also allows an isotope dilution calculation of U concentration based on measured $^{238}\text{U}/^{236}\text{U}$ and the known amount of double spike added.

2.3.2. Separation of dissolved U(IV) and U(VI)

Separation of dissolved U(IV) and U(VI) for experiments 1 and 2 was performed in an anaerobic glove box, via an anion exchange method modified from previous work (Hussonnois et al., 1989; Ervanne, 2004). In 4.5 M HCl, U(VI) is retained on the AG1X8 anion resin (100 – 200 mesh), while U(IV) passes through the resin. This method has been proven successful at separating U(VI) and U(IV) with ~95% recovery for U(IV) and ~99% recovery for U(VI) (Hussonnois et al., 1989). Samples in 4.5 M HCl were loaded onto 0.5 mL resin beds (~6 cm long), which were precleaned with 4 mL 0.1 M HCl and preconditioned with 1 mL 4.5 M HCl. U(IV) was then eluted with 2 mL 4.5 M HCl and collected. U(VI) was then released from the resin with 3 mL 0.1 M HCl. The separated U(IV) and U(VI) fractions were then taken out of the glove box for further purification (below).

Tests showed that this anion exchange step did not fractionate U isotopes and thus double spike was not added before this step. In this test, U(IV) and U(VI) were eluted, by 4.5 N HCl and 0.1 N HCl, respectively, in one resin-bed-volume increments, which were collected, purified, and analyzed separately. No difference in $\delta^{238}\text{U}$ between these increments was found (Fig. 2).

2.3.3. Purification of uranium

Uranium was extracted from samples and purified for isotopic analysis using a UTEVA resin method from published methods (Weyer et al., 2008; Shiel et al., 2013). Briefly, aliquots of the

separated U(VI) and U(IV) samples, containing 300ng U, were doped with a ^{233}U - ^{236}U double spike to obtain a $^{238}\text{U}/^{236}\text{U}$ ratio of ~ 30 , and then evaporated to dryness overnight at 80°C in the air. Tests showed that U(IV) was completely oxidized to U(VI) during the drying process.

Dried samples were redissolved in 1 mL 3 M HNO_3 and loaded onto 0.2 mL UTEVA resin columns precleaned with 4 mL 0.05 M HCl and preconditioned with 1 mL 3 M HNO_3 . Matrix ions were rinsed with 2 mL 3 M HNO_3 . Uranium was released from the UTEVA resin by 2.5 mL 0.05 M HCl . Samples were then dried completely and treated with one drop of heated concentrated HNO_3 , to destroy minor organics leached from the resin. Samples were finally dissolved in 0.3 M HNO_3 for isotope analysis.

2.4. Mass spectrometry

Purified U samples were analyzed for $^{238}\text{U}/^{235}\text{U}$ on a Nu Plasma MC-ICP-MS in the Department of Geology at the University of Illinois at Urbana-Champaign (Bopp et al., 2010; Shiel et al., 2013). Ion beams (^{233}U , ^{235}U , ^{236}U , and ^{238}U) were collected by Faraday collectors in a single cycle with five blocks of ten integrations, each lasting eight seconds. ^{238}U was collected in a Faraday collector with a $10^{10} \Omega$ resistor while all other beams were collected in collectors with $10^{11} \Omega$ resistors. Typical ^{238}U beam currents ranged from 300 to 500 pA, depending on daily instrument conditions. The tailing of the ^{236}U peak onto ^{235}U can cause errors on ^{235}U measurement. Therefore, we used a two-zeros method to correct for this potential tailing effect, where the signal was measured 0.5 amu above and below the measured mass for 30 seconds and the average of those two values was subtracted from the measured peak signal. Results are expressed as $\delta^{238}\text{U} = (\text{R}_{\text{sample}}/\text{R}_{\text{CRM112a}} - 1) \times 1000\text{‰}$, where R_{sample} and $\text{R}_{\text{CRM112a}}$ are the $^{238}\text{U}/^{235}\text{U}$ ratios of the sample and standard CRM112a respectively.

Despite using the double spike technique, we still found drift in the measured standard values. The drift is probably due to departure of the instrumental mass bias from the assumed exponential

law. However, the drift is independent of signal intensity, and therefore should affect samples and standards equally. The drift typically occurs in the first several hours after switching on the plasma. After tuning, we repeatedly analyzed (~10 times) unprocessed standard CRM112a until a relatively stable value (0.2‰ to 0.6‰, depending on the day) was obtained. Then we measured unprocessed standards (CRM129a (Brunswick Laboratory, U.S. DOE) and IRMM REIMEP 18a (JRC, Brussels, Belgium)), and processed standard CRM112a to assess accuracy, followed by samples. The measured average for unprocessed IRMM REIMEP 18a and CRM129a were -0.16 ± 0.04 ‰ (2SE, n = 6) and -1.72 ± 0.04 ‰ (2SE, n = 6), respectively, which agree with previously published results (Weyer et al., 2008; Shiel et al., 2013). The processed CRM112a yielded 0.00 ± 0.04 ‰ (2SE, n=5) after normalization by the unprocessed bracketing CRM112a standards. Throughout the actual sample measurement sessions, the drift was small (<0.1 ‰) within a bracketing cycle and followed a smooth curve over time. Accordingly, standard CRM112a was analyzed every three samples, and sample $\delta^{238}\text{U}$ values were normalized using the bracketing CRM112a standards assuming linear drift within a bracketing cycle. Even though the general time series of the CRM112a was not perfectly linear, the drift within a bracketing cycle is reasonably linear. The external uncertainty (2σ) for samples is ± 0.06 ‰, calculated as the root mean square (Supplementary Information) of 6 duplicate preparations.

3. RESULTS

3.1. Effect of cross-contamination during U(IV) and U(VI) separation

For the experiments focusing on oxidation of dissolved U(IV), U(IV) and U(VI) were separated by the anion exchange resin method, which caused minor cross-contamination. Tests showed that about 95% U(IV) was recovered in the 4.5 M HCl elution, and about 96% of U(VI) was released by 0.1 M HCl. This suggests that up to 5% of U(IV) was not eluted by 4.5 M HCl and was later collected together with U(VI) in 0.1 N HCl. Similarly, about 4% of U(VI) was not retained on

the resin upon loading and was collected together with U(IV) in 4.5 M HCl. The determined $\delta^{238}\text{U}$ values of U(IV) and U(VI) were subject to a cross-contamination correction (Table 1), assuming 5% of the U(IV) was mixed with 96% of the U(VI), and 4% of the U(VI) was mixed with 95% of the U(IV). To avoid variation in the extent of cross-contamination, volumes of resins and acids were kept constant between different sessions of sample preparation.

For the experiments focusing on oxidation of solid U(IV), U(IV) and U(VI) were separated by filtration. Therefore, U(VI) can potentially be cross-contaminated by very small concentrations of dissolved U(IV) and/or by U(IV) particles breaking through filters. On the other hand, U(IV) can potentially be contaminated by U(VI) adsorbed to U(IV) particles. The solubility of uraninite at circumneutral pH is extremely low, about 10^{-13} M (Langmuir, 1978). In the presence of 20 mM bicarbonate, the solubility is higher but is still low (about 10^{-11} M, calculated using MINEQL 4.62.2). The near-zero concentration of dissolved U observed in the first samples of experiment 3 and 4 (Fig. 4) indicates that the 0.1 μm filter retained essentially all of the U(IV) particles, despite their small sizes. Successful filtering of nanoscale uraninite particles is probably related to aggregation of those particles (Abdelouas et al., 1999; Burgos et al., 2008). Cross-contamination of U(IV) by adsorbed U(VI) will be discussed below.

3.2. Oxidation of dissolved U(IV)

Results for experiments 1 and 2, focusing on oxidation of dissolved U(IV), are summarized in Table 1 and Fig. 3. The rate of oxidation, represented by the slope of the U(IV) concentration vs. time plot, appeared to be constant throughout the oxidation, i.e., independent of U(IV) concentrations. The initial U(VI) product was isotopically lighter by about 1.1‰ relative to the remaining U(IV) in both experiments. As oxidation proceeded, the remaining U(IV) became progressively enriched in heavier isotope. The $\delta^{238}\text{U}$ of the product U(VI) formed a parallel trend to that of U(IV), offset by a nearly constant value. The offset is $1.1 \pm 0.3\text{‰}$ (2SD, n=7) for experiment 1

and $1.1 \pm 0.1\%$ (2SD, n=7) for experiment 2.

3.3. Oxidation of solid U(IV)

Results for experiments 3 and 4, focusing on oxidation of solid U(IV), are summarized in Table 2 and Fig. 4. In both experiments, the rate of reaction, represented by the slope of the U(IV) concentration vs. time plot, decreased over time as the remaining U(IV) concentration decreased.

In experiment 3, the $\delta^{238}\text{U}$ values of the remaining solid U(IV) first remained identical to the starting value (the dashed line) within analytical uncertainty, then gradually evolved to negative values after more than 80% of the U(IV) was oxidized (Fig. 4A). The $\delta^{238}\text{U}$ values of the dissolved U(VI) product were in all cases slightly higher than that of the concurrent solid U(IV), although the difference is within the uncertainties for some of the data points.

Experiment 4 was sampled more frequently than experiment 3, especially in the very early stages (<20% oxidation) of the experiment. The results mostly confirmed the basic observations in experiment 3. However, the results of this experiment revealed more details for the very early stages of oxidation of solid U(IV), showing that the $\delta^{238}\text{U}$ of the initially produced U(VI) was slightly negative (-0.13%), and then quickly increased to positive ($+0.34\%$), a total of about 0.5% increase, followed by gradual decrease to approach $\delta^{238}\text{U}$ of starting solid U(IV) ($+0.05\%$), represented by the dashed line. As in experiment 3, the U(IV) $\delta^{238}\text{U}$ value became negative in the late stages of the experiment.

The weighted average $\delta^{238}\text{U}$ of U(VI) and U(IV) for each sampling event in experiment 3, as shown in table 2, was $0.07 \pm 0.05\%$ (2SD, n = 7), which balances well with the starting isotopic composition of U(IV) (Fig. 4B). However, the weighted average was $0.11 \pm 0.12\%$ (2SD, n = 9) in experiment 4, which was higher than the starting U(IV) isotopic composition (Fig. 4D). Although this discrepancy is within the analytical uncertainty, it could have been caused by uneven withdrawing of solid U(IV) particles and dissolved U(VI) in the early sampling events, considering

the U(IV) particles tend to aggregate. The total concentration of U(IV) and U(VI) for experiment 4 (Table 2) did show that the first 2 samples withdrew more U than later samples. However, the slight lack of mass balance in experiment 4 does not affect the basic observation that oxidation of solid U(IV) caused only very weak isotopic fractionation.

4. DISCUSSION

4.1. Oxidation kinetics

The oxidation of dissolved U(IV) at low pH can be described by the following reaction (McCoy and Bunzel, 1909; Rollin and Eklund, 2000):

which indicates that the reaction rate is first order in terms of U(IV) concentration (Rollin and Eklund, 2000):

$$\frac{d[U(IV)]}{dt} = -k_{ox}[U(IV)] \quad (2)$$

where k_{ox} refers to the rate constant of oxidation. Therefore, one would expect an exponential decrease of U(IV) concentration with time. In contrast, we observed a linear decrease in U(IV) concentration (Fig. 3A), suggesting a zero reaction order in terms of U(IV) concentrations, i.e., $d[U(IV)]/dt = -k_{ox}$. We propose the reaction rate was likely limited by dissolved oxygen concentration. Even though the experimental solution was shaken before sampling, such brief shaking was probably insufficient to allow gas-liquid equilibrium. The 100 mL serum bottles contained 50 mL U(IV) solution and 50 mL air headspace. The starting U(IV) concentration in these two experiments was about 500 μM (Table 1). Assuming the solubility of O_2 in the experiments is the same as that in pure water, there would have been about 250 μM initial dissolved

oxygen, barely enough to oxidize all the U(IV). However, compared to pure water, electrolytic solutions such as HCl are expected to hold less dissolved oxygen. This may also have contributed oxygen shortage, limiting the oxidation rate.

In contrast to dissolved U(IV), oxidation of solid U(IV) in the presence of air and bicarbonate can be described by the following reaction (Grandstaff, 1976):

These two experiments were different from experiments 1 and 2 in that: 1) U(IV) was solid and therefore only surface U(IV) could interact with the oxidant; 2) dissolved oxygen was present in excess throughout the experiments because the starting U(IV) solid concentration (23 to 25 μM) was only about 10% of the initial dissolved oxygen concentration. Those factors indicate that oxygen was not limited in these two experiments and the U concentrations roughly followed first order kinetics. Assuming a first reaction order, integrating eqn 2 yields:

$$-\ln \frac{[U(IV)]}{[U(IV)_0]} = k_{ox} \cdot t \quad (4)$$

where $[U(IV)]/[U(IV)_0]$ represents the fraction of remaining U(IV). A natural log plot of the fraction of remaining U(IV) as a function of time is given in Fig. 5, which shows that experiment 3 concentration data can be approximated by a first order reaction with respect to U(IV) concentration. Data from experiment 4 (filled symbols) departed from the first-order model, but this only occurred in the last data point. One speculative explanation for the increased reaction rate in the later stages of experiment 4 is that the specific surface area increased as the uraninite particles became smaller. The difference between experiment 3 and 4 may be related to slight change of procedure. Because uraninite particles visibly stayed on the filter and failed to resuspend in experiment 3, i.e., the particles were aggregated and therefore specific surface area was much smaller, in experiment 4 the suspension was stirred at a much faster rate with a magnetic stir bar to

drive the particles off the filter paper. Despite of this difference, the isotope data of these two experiments were very similar.

4.2. Interpretation of experiments with both U(IV) and U(VI) dissolved

In experiments focused on oxidation of dissolved U(IV), the near constant offset between U(IV) and U(VI) (Fig. 3B) suggests isotopic equilibration between the two species. In other words, at any stage of the oxidation, it appears that the U(IV) and U(VI) pools in contact were close to isotopic equilibrium, with a constant equilibrium fractionation factor, defined as $\alpha_{\text{VI-IV}} = R_{\text{VI}}/R_{\text{IV}}$, and, to a very close approximation, a constant value of $\Delta^{238}\text{U}_{\text{IV-VI}} = \delta^{238}\text{U}_{\text{VI}} - \delta^{238}\text{U}_{\text{IV}}$ for the data considered here. An equilibrium fractionation model with $\Delta^{238}\text{U}_{\text{VI-IV}} = -1.1\text{‰}$ (solid lines in Fig. 3B) generally fit the data points well, but some data points, especially in experiment 1, fall outside of the equilibrium trend. The magnitude of the modeled equilibrium fractionation is comparable to most empirical and theoretical estimates at similar or slightly higher temperatures, ranging from $\sim -0.95\text{‰}$ to -1.39‰ (Florence et al., 1975; Bigeleisen, 1996; Nomura et al., 1996; Fujii et al., 2006; Abe et al., 2008).

Alternatively, the observed fractionation during oxidation of dissolved U(IV) could result from a complex kinetic fractionation, in which some steps in the overall multi-step oxidation reaction are close to isotopic equilibrium and some are kinetically controlled. We first constructed a simple Rayleigh distillation model, which applies to a closed system with no back reaction, where the instantaneous product U(VI) is related to the U(IV) pool by a constant kinetic fractionation factor, defined as $\alpha = R_{\text{VI}}/R_{\text{IV}}$ and conveniently approximately by $\epsilon^{238}\text{U}_{\text{VI-IV}} = (\alpha_{\text{VI-IV}} - 1) \times 1000\text{‰} \approx \delta^{238}\text{U}_{\text{VI.instantaneous}} - \delta^{238}\text{U}_{\text{IV.remaining}}$. The equations for the Rayleigh model are given in the supplementary information. As the oxidation proceeds, since there is no isotope exchange between U(VI) and U(IV), the remaining U(IV) became progressively isotopically heavier while the accumulated product U(VI) gradually approaches the starting isotopic composition of U(IV). In Fig.

3B, the dashed lines show a best-fit kinetic fractionation model, with $\epsilon^{238}\text{U}_{\text{VI-IV}} = -0.71\text{‰}$. The model does not fit the data within analytical uncertainty, and the misfit is greater than that observed with the equilibrium model.

However, this simple Rayleigh model assumes that the ϵ value does not change during the course of the experiments. A kinetic fractionation could change over time, for example in response to increasing U(VI) or U(V) concentrations. The oxidation reaction is a multi-step process with U(V) as an intermediate species. Rashid and Krouse (1985) examined kinetic fractionation induced by reduction of Se(IV) to Se(0) and found that the fractionation was larger in the early stages of the experiment and decreased as the reaction progressed. This change in fractionation was found to match closely a simple kinetic model consisting of two reaction steps, each with an invariant reaction rate constant and isotopic fractionation factor. The data of the present study are similar to those of Rashid and Krouse (1985), in that the initial reaction product was anomalously light relative to the trend of the later data. Thus, we conclude that changes in the magnitude of isotopic fractionation are possible in our experiments and that such changes can reproduce the observations. A kinetic model with an initial ϵ value of about -1.2‰ , decreasing to -0.7‰ as the reaction progressed, would fit the first few U(VI) data points and also reproduce the systematic downward curvature of the U(VI) data.

We recognize that the equilibrium model fits with only a small mismatch, but assert that this kinetic model is also plausible. However, the distinction between equilibrium and kinetic isotope effects here is not critical for practical application of these results. The U(VI) product is isotopically light and not far from equilibrium values; the only important difference is that a kinetic effect is likely to be variable, depending on reaction conditions.

4.3. Interpretation of experiments with solid U(IV)

Before interpreting the variation in $\delta^{238}\text{U}$ values in the experiments where UO_2 was

consumed, one must know if the $\delta^{238}\text{U}$ of the starting solid U(IV) was uniform from the center to the surface of each particle. We believe this was the case in our synthesized solid U(IV), since the precipitation of U(IV) did not involve a redox reaction and the local bonding environment around U(IV) atoms did not change greatly. Slight kinetic effects, for example related to differing diffusion rates, may have occurred, but these effects must be small because the relative mass differences of the relevant species are so small. Indeed, the invariant $\delta^{238}\text{U}$ of the U(IV) samples taken in the early to middle stages of the oxidation experiments is evidence of uniformity in the $\delta^{238}\text{U}$ values of U(IV) particles.

We attribute the lack of strong isotopic fractionation during oxidation of solid U(IV) to a “rind effect”, where the surface layer of solid U(IV) particles must be completely oxidized before the next layer is exposed to oxidant. Hence, nearly complete, congruent conversion of each layer of U(IV) to U(VI) results in minimal isotope fractionation. The exception to this rule is the earliest U removed from the solid surface. If the oxidative dissolution process involves kinetic fractionation, this would cause release of isotopically distinct U from the surface initially. However, this would last only a short time, as the U exposed on the solid surface would become increasingly fractionated in the opposite direction, negating the initial kinetic effect observed in the produced U(VI). It appears this occurred in experiment 4, which was sampled more frequently during the early stages to examine such effects. The initially produced U(VI) was about 0.1‰ lighter than the remaining solid U(IV) (Fig. 4D). As the oxidation proceeded, however, the $\delta^{238}\text{U}$ of the accumulated U(VI) increased to be isotopically heavier than the remaining solid U(IV).

The absence of large isotope fractionation during oxidative dissolution of solid U(IV) is in sharp contrast with the ~3‰ fractionation during reductive dissolution of solid Fe(III) (Crosby et al., 2005; Crosby et al., 2007; Wu et al., 2009). The large difference in $\delta^{56}\text{Fe}$ between product Fe(II) and remaining Fe(III) minerals was attributed to equilibrium fractionation between adsorbed Fe(II) and an active Fe(III) layer on the surface of the Fe(III) solid. However, no equilibrium fractionation

between adsorbed U(VI) and U(IV) solid was observed in our experiment. This could be due to an inability of the dissolved U(VI) to isotopically equilibrate with the solid U(IV) within the time frame of the experiments (a few hours). This is certainly a possible scenario, as the two electron transfers needed to drive this equilibration should be much slower than the single electron transfer needed in the Fe case.

In strong contrast to oxidation of dissolved U(IV) where the product U(VI) is isotopically lighter than the remaining U(IV), oxidation of solid U(IV) results in the product U(VI) being isotopically slightly heavier than the remaining U(IV), except for the very early stage of the oxidation of solid U(IV). Thus, an additional process must have occurred in experiments 3 and 4 to cause the observed sense of fractionation. We propose that the slightly elevated $\delta^{238}\text{U}$ in U(VI) for all but the early stages could have been caused by adsorption of a fraction of U(VI) to the U(IV) solid surfaces. Brennecka et al. (2011b) demonstrated that isotope fractionation occurs between dissolved U(VI) and U(VI) adsorbed to birnessite, with the adsorbed U(VI) being $\sim 0.2\text{‰}$ less in $\delta^{238}\text{U}$ than the dissolved U(VI). This fractionation was attributed to differences in the U-O coordination shell between adsorbed and dissolved U(VI) species. About 0.2‰ difference in $\delta^{238}\text{U}$ has also been observed between seawater U and U adsorbed to Mn-Fe crust (Weyer et al., 2008). However, recent experiments have found that adsorption of U(VI) to other mineral phases in the presence of bicarbonate could induce fractionations of different magnitudes (Jemison et al., 2014).

To illustrate that adsorption is one possible hypothesis to explain the observed isotope fractionation, We developed a simple mass balance model coupled with a Langmuir adsorption model, to match the observed isotopic evolution of U(IV) and U(VI) (Fig. 6, more details in Supplementary Information). In this model, the isotopic fractionation factor associated with adsorption is fit to be 0.3‰ (best fit value), with the adsorbed U(VI) (mainly complexed with carbonate) being isotopically lighter than the dissolved U(VI). This fractionation factor is slightly greater than the experiment data for adsorption of UO_2^{2+} and UO_2OH^+ onto birnessite (Brennecka et

al., 2011b); this slight difference is expected, considering the equilibrium fractionation between UO_2^{2+} and UO_2CO_3 (Schauble, 2006). The initial isotope fractionation between the first flux of product U(VI) and remaining U(IV) was fit to be 0.5‰, with the product U(VI) being isotopically lighter, which is consistent with the direction predicted by nuclear volume effect (Schauble, 2007; Abe et al., 2008). The negative $\delta^{238}\text{U}$ value of the initial U(VI) was subsequently quickly negated by a complementary shift of the surface layer of the uraninite particles toward positive values. Partial adsorption of the initially produced U(VI) in the early stages of the experiment should have elevated the isotopic composition of the dissolved U(VI), leading to an observed fractionation factor (-0.5‰) that is smaller than the fractionation (-0.71‰) observed in our experiment on oxidation of dissolved U(IV).

The different speciation of U(VI) in low-pH experiments and high-pH experiments was not likely to cause the different isotope fractionations between oxidation of dissolved U(IV) and solid U(IV). In the low-pH experiments, U(VI) was complexed with chloride (e.g., UO_2Cl^+), whereas in the high-pH experiments, U(VI) was complexed with carbonate (e.g., UO_2CO_3). However, this difference in speciation causes a relatively small difference (0.3‰, Schauble, 2006), and therefore does not explain the contrasting isotopic fractionation between low pH and high pH experiments.

4.4. Implications

The results of this study provide an initial assessment of isotopic fractionation induced by oxidation of U(IV) to U(VI) by dissolved oxygen; application of these results to natural settings should be done with caution. Our results for the oxidation of dissolved U(IV) show that the potential exists for significant isotope fractionation, with an isotopically light U(VI) product. However, the acidic conditions of these experiments are far from natural conditions. The results do advance our general understanding of U isotope systematics, and they may provide useful information in situations where U(IV) is complexed and solubilized by natural organic molecules, and oxidation of

such dissolved organic-bound U(IV) may induce significant fractionation.

The weak isotopic fractionation during oxidation of synthetic nano U(IV) particles should also apply to biogenic nanometer scale uraninite particles forming in biostimulated remediation sites. If true, the added U(VI) from oxidation should match the oxidizing U(IV), and therefore may be detected isotopically, assuming the reduced U(IV) is isotopically distinct from dissolved U(VI).

Even though our experiments indicate weak fractionation (about 0.1‰) during oxidation of synthesized solid U(IV) over a few hours, U(VI) and remaining uraninite minerals in natural settings, if in contact for long enough time, are potentially able to evolve toward isotopic equilibrium. However, in natural weathering environments, the weathering fluid is probably flushed away at rates dependent on local hydrogeological conditions such as permeability and precipitation. This may prevent significant isotope exchange due to prolonged contact between oxidized U(VI) and remaining U(IV) minerals. Further, since only surface U atoms on U(IV) minerals are able to exchange isotopes with dissolved U(VI), the impact of equilibrium fractionation on the dissolved U(VI) is limited by the small percentage of surface-active U(IV). This depends on the molecular structure and the sizes of U(IV) minerals, as well as concentrations of U(IV)-bearing minerals in rocks. This may explain the natural observation that $\delta^{238}\text{U}$ values in major rivers are similar to the average value of igneous rocks (Stirling et al., 2007; Weyer et al., 2008; Noordmann et al., 2010). Measurements of $^{238}\text{U}/^{235}\text{U}$ in various natural weathering environments should be undertaken to examine potential isotope fractionation during oxidation of U(IV)-bearing minerals.

5. CONCLUSIONS

Oxidation of dissolved U(IV) in low-pH solutions produced U(VI) with $\delta^{238}\text{U}$ values $\sim 1.1\text{‰}$ lower than the remaining dissolved U(IV). The data from our experiments show a fairly close, though not complete fit to a model in which isotopic equilibrium between U(VI) and U(IV) is maintained. However a kinetic fractionation process with isotopic fractionation initially at $\sim 1.2\text{‰}$

and later decreasing to $\sim 0.7\text{‰}$ also provide a plausible model for the data.

Oxidation of synthetic, solid UO_2 at neutral pH causes very little fractionation of U isotopes, with the $\delta^{238}\text{U}$ of the dissolved U(VI) being slightly greater than the remaining solid U(IV). This small shift can be explained by adsorption of isotopically light U(VI) onto the U(IV) solid.

These results suggest that although isotopic fractionation could occur during oxidation of U(IV), observed fractionation is likely limited if dissolution of solid U(IV) occurs in a congruent manner and/or if contact time between U(VI) and U(IV) phases is brief.

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8. TABLES

Table 1: Results for experiment 1 and 2 focusing on oxidation of dissolved U(IV) in 0.1 M HCl. [U(IV)] represents dissolved U(IV) concentration; [U(VI)] represents dissolved U(VI) concentration. F represents fraction of U(IV) remaining.

Exp't	Time	[U] _{IV}	[U] _{VI}	[U] _{total}	F	$\delta^{238}\text{U}(\text{‰})$					$\delta^{238}\text{U}^*(\text{‰})$				Offset*
		μM	μM	μM		U(IV)	2SE ^a	U(VI)	2SE	Mass balance ^b	U(IV)	2SE	U(VI)	2SE	U(IV)-U(VI)
1	0.0	515	44	559	0.92	0.07	0.06	-1.07	0.07	-0.02	0.12	0.06	-1.13	0.07	1.2
	0.4	461	93	554	0.83	0.11	0.06	-0.70	0.06	-0.03	0.15	0.06	-0.74	0.06	0.9
	3.3	315	223	538	0.59	0.42	0.06	-0.49	0.06	0.04	0.46	0.06	-0.54	0.06	1.0
	4.4	273	270	543	0.50	0.56	0.06	-0.40	0.06	0.08	0.60	0.06	-0.45	0.06	1.1
	5.4	223	307	530	0.42	0.64	0.06	-0.38	0.06	0.05	0.69	0.06	-0.43	0.07	1.1
	6.4	172	351	523	0.33	0.72	0.07	-0.38	0.13	-0.02	0.78	0.08	-0.43	0.14	1.2
	7.3	135	409	544	0.25	0.91	0.11	-0.29	0.06	0.01	0.98	0.12	-0.34	0.06	1.3
2	0.1	504	58	561	0.90	0.08	0.06	-0.90	0.06	-0.02	0.13	0.06	-0.95	0.06	1.1
	0.5	463	86	549	0.84	0.19	0.06	-0.78	0.06	0.03	0.24	0.06	-0.83	0.06	1.1
	2.3	368	167	535	0.69	0.33	0.06	-0.60	0.06	0.04	0.38	0.06	-0.65	0.06	1.0
	3.4	321	216	537	0.60	0.48	0.06	-0.49	0.06	0.09	0.53	0.06	-0.55	0.06	1.1
	4.4	274	265	539	0.51	0.56	0.09	-0.48	0.10	0.05	0.61	0.10	-0.53	0.11	1.1
	5.4	231	301	532	0.43	0.55	0.06	-0.38	0.06	0.03	0.60	0.06	-0.43	0.06	1.0
	6.3	186	359	545	0.34	0.73	0.06	-0.33	0.06	0.03	0.79	0.06	-0.38	0.06	1.2

*Corrected for cross-contamination during U(IV)-U(VI) separation. Correction was performed by solving two-end-member mixing equations.

a: Listed errors are either internal 2SE or external 2SE ($\pm 0.06\text{‰}$), whichever is greater.

b: Mass balance = $(\delta^{238}\text{U}_{IV} * [\text{U}]_{IV} + \delta^{238}\text{U}_{VI} * [\text{U}]_{VI}) / ([\text{U}]_{IV} + [\text{U}]_{VI})$.

Table 2: Results for experiment 3 and 4 focusing on oxidation of synthetic solid U(IV) in 20 mM NaHCO₃. [U(IV)] represents U concentration U mass retained on the filter divided by the sampled volume; [U(VI)] represents U concentration in the filtrate. F represents fraction of U(IV) remaining.

Exp'tTime		[U] _{IV}	[U] _{VI}	[U] _{total}	F	δ ²³⁸ U (‰)			Mass balance ^b	
	hour	μM	μM	μM		IV	2SE ^a	VI	2SE	‰
3	0.2	23.2	4.5	27.7	0.84	0.04	0.06	0.09	0.06	0.05
	0.4	19.4	8.4	27.8	0.70	0.00	0.06	0.15	0.06	0.05
	1.0	11.7	16.0	27.7	0.42	0.03	0.06	0.14	0.06	0.09
	1.6	6.4	21.4	27.8	0.23	0.00	0.06	0.11	0.06	0.08
	3.0	2.7	25.1	27.8	0.10	-0.05	0.06	0.15	0.06	0.13
	3.9	1.8	26.0	27.8	0.06	-0.14	0.06	0.10	0.06	0.09
4	0.1	24.8	1.4	26.2	0.95	0.02	0.12	-0.13	0.06	-0.02
	0.3	20.4	2.2	22.6	0.90	0.15	0.06	0.14	0.08	0.15
	0.4	16.9	3.5	20.4	0.83	0.06	0.06	0.26	0.06	0.10
	0.6	15.7	4.9	20.6	0.76	0.02	0.11	0.34	0.06	0.09
	0.8	14.2	6.6	20.8	0.68	0.14	0.06	0.26	0.06	0.18
	1.3	9.9	11.1	21.0	0.47	0.04	0.10	0.16	0.06	0.11
	1.8	6.7	15.1	21.8	0.31	0.08	0.06	0.17	0.06	0.14
	2.4	3.1	18.6	21.7	0.14	0.03	0.06	0.14	0.08	0.12
	3.0	1.2	19.8	21.0	0.06	-0.22	0.06	0.13	0.08	0.11

a: Listed errors are either internal 2SE or external 2SE (±0.06‰), whichever is greater.

b: Mass balance = $(\delta^{238}\text{U}_{IV} * [\text{U}]_{IV} + \delta^{238}\text{U}_{VI} * [\text{U}]_{VI}) / ([\text{U}]_{IV} + [\text{U}]_{VI})$.

9. FIGURE CAPTIONS

Figure 1. XRD result for the synthesized U(IV) particles. The high, narrow peaks represent standard uraninite; the low, wide peaks represent synthesized U(IV) particles. This XRD pattern is consistent with nano-crystalline uraninite (Singer et al., 2009). The XRD analysis also gives a rough estimate of the crystal size of ~4nm.

Figure 2. Test results for separation of dissolved U(IV) and dissolved U(VI) using AG1X8 resin (100–200 mesh). Filled symbols represent U(IV) rinsed by 4.5 M HCl; open symbols represent U(VI) released by 0.1 M HCl. Numbers with ‰ unit are the $\delta^{238}\text{U}$ values of corresponding elutions. Similar $\delta^{238}\text{U}$ values between different collected fractions indicate negligible isotope fractionation during separation.

Figure 3. Results for oxidation of dissolved U(IV) by air in 0.1 M HCl. A: Concentration changes over time. B: $\delta^{238}\text{U}$ as a function of the fraction of U(IV) remaining. Solid straight lines are modeled $\delta^{238}\text{U}$ for U(IV) and U(VI) as a function of F, assuming equilibrium fractionation $\Delta^{238}\text{U}_{\text{IV-VI}} = 1.1\text{‰}$. Dashed curves are the modeled trend with best-fit kinetic fractionation $\varepsilon^{238}\text{U} = -0.71\text{‰}$. Figure legends in B are the same as those in A.

Figure 4. Uraninite concentration (left) and $\delta^{238}\text{U}$ (right) vs. fraction of remaining U(IV) for oxidation of synthetic uraninite by air in 20 mM NaHCO_3 . The horizontal dashed lines in B and D represent the starting $\delta^{238}\text{U}$ of the synthetic solid U(IV).

Figure 5: Natural log plot of fraction of remaining U(IV) as a function of time, assuming first reaction order in terms of U(IV) concentration. The solid line together with the equation is the least square fit to the open square data points.

Figure 6: Result of the adsorption mass balance model. Oxidation kinetics are modeled to confirm to experiment 3. For convenience, the starting U(IV) concentration was arbitrarily set to be 1 (dimensionless), so that the fraction of remaining U(IV) and U(VI) concentrations share the same y-axis. See Supplementary Information for modeling details.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6