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Isotopic evidence for reductive immobilization of uranium across a roll-front mineral deposit

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Abstract

We use uranium (U) isotope ratios to detect and quantify the extent of natural U reduction in groundwater across a roll front redox gradient. Our study was conducted at the Smith Ranch-Highland *in situ* recovery (ISR) U mine in eastern Wyoming, USA, where economic U deposits occur in the Paleocene Fort Union formation. To evaluate the fate of aqueous U in and adjacent

to the ore body, we investigated the chemical composition and isotope ratios of groundwater samples from the roll-front type ore body and surrounding monitoring wells of a previously mined area. The $^{238}\text{U}/^{235}\text{U}$ of groundwater varies by approximately 3‰ and is correlated with U concentrations. Fluid samples down-gradient of the ore zone are the most depleted in ^{238}U and have the lowest U concentrations. Activity ratios of $^{234}\text{U}/^{238}\text{U}$ are ~5.5 up-gradient of the ore zone, ~1.0 in the ore zone, and between 2.3 and 3.7 in the down-gradient monitoring wells. High-precision measurements of $^{234}\text{U}/^{238}\text{U}$ and $^{238}\text{U}/^{235}\text{U}$ allow for development of a conceptual model that evaluates both the migration of U from the ore body and the extent of natural attenuation due to reduction. We find that the pre-mining migration of U down-gradient of the delineated ore body is minimal along eight transects due to reduction in or adjacent to the ore body, whereas two other transects show little or no sign of reduction in the down-gradient region. These results suggest that characterization of U isotopic ratios at the mine planning stage, in conjunction with routine geochemical analyses, can be used to identify where more or less post-mining remediation will be necessary.

Introduction

Nuclear power constitutes approximately 20% of electricity production in the United States and is considered an important component of current energy policy¹. Mining of U ore will continue to be necessary to maintain existing nuclear reactors and support any potential future expansion of nuclear energy. More than 90% of U.S. U production and nearly half of global output comes from *in situ* recovery (ISR) mines². The ISR method improves the economics of mining lower grade ore deposits and potentially reduces the environmental and public health effects relative to traditional underground or open-pit mining techniques. There is little to no

surface contamination from radioactive dust, leach ponds or tailings piles because the ore is extracted in an aqueous form.

Despite the advantages of ISR mining, there is considerable uncertainty surrounding the restoration of impacted aquifers to pre-mining (baseline) water quality³. A better understanding of the long-term fate of U and other contaminants from ISR mining, particularly fluid-sediment interactions that attenuate U concentrations, would enable industry and regulators to make more informed restoration plans and ensure the integrity of adjacent potable water supplies. For example, geologic formations that host U deposits suitable for ISR mining could have sufficient natural reductive capacity to sequester residual aqueous U after mining and restoration are completed. The reductive precipitation of U is preferred to other sequestration pathways such as sorption, because it is thought to limit U mobility over greater timescales⁴.

The reduction of hexavalent U has been widely cited but poorly documented in ISR restoration settings. For example, there is little known about the residual reducing capacity of the sediments and reduction pathways, how the kinetics of reduction reactions compare to groundwater velocities, the effects of aquifer heterogeneity on reduction, or whether the planned duration of groundwater monitoring is sufficient to ensure adequate natural attenuation². The purpose of this study is to highlight how pre-mining distribution of U and its isotopes can provide insights into the removal of U from groundwater. This type of background data and understanding of the natural system is a prerequisite to predicting the fate of U after mining-restoration.

The isotopic composition of dissolved U in groundwater is a promising tool for evaluating the fate of U down-gradient of ISR operations. There are two types of isotopic abundance variations: (1) variations in the relative abundance of ^{234}U in response to natural radioactive decay of ^{238}U and (2) mass-dependent variations in the $^{238}\text{U}/^{235}\text{U}$ ratio associated with the chemical reduction of

U. Changes in the abundance of ^{234}U , as reflected in the activity ratio of ($^{234}\text{U}/^{238}\text{U}$), arise due to α -recoil of the daughter ^{234}U isotope from mineral grains. The ^{234}U isotope has a recoil distance of 30-40 nm in most silicate minerals and can be either directly ejected from the mineral to groundwater or preferentially leached from radiation induced mineral defects⁵⁻⁷. Large variations of ($^{234}\text{U}/^{238}\text{U}$) in sandstone hosted U deposits have been recognized for more than 50 years but have not been utilized in environmental monitoring or restoration planning at ISR locations^{8,9 10-12}.

Recent research using environmental samples and laboratory experiments also documents small variations in $^{238}\text{U}/^{235}\text{U}$, a ratio that was long thought to be effectively invariant in most Earth materials¹³. Change of $^{238}\text{U}/^{235}\text{U}$ is primarily associated with reduction of U(VI) to U(IV)^{10,14}, where ^{238}U is preferentially reduced compared to ^{235}U . Experimental and field evidence suggest that the maximum magnitude of instantaneous U isotope fractionation during U(VI)-U(IV) reduction is approximately 1‰ of the $^{238}\text{U}/^{235}\text{U}$ ratio, but residual U that remains after extensive reductive removal can be shifted by several per mil relative to the starting composition^{10-12,14-17}.

Prior research on U mobility in fluvial sediments includes the US Department of Energy research sites at Hanford, WA and Rifle, CO¹⁸. At Hanford, the U isotopic compositions of groundwater and pore fluids have been used to trace contamination from nuclear waste storage into the vadose zone and water table, utilizing anthropogenic ^{236}U and variations in $^{238}\text{U}/^{235}\text{U}$ from the nuclear fuel cycle in addition to natural variations in ($^{234}\text{U}/^{238}\text{U}$)^{19,20}. In contrast to Hanford, the contamination at the Rifle site involves U with natural isotopic composition. Studies at the Rifle field site include analysis of variations in $^{238}\text{U}/^{235}\text{U}$ during reduction and desorption experiments^{17,21}. These studies find that $^{238}\text{U}/^{235}\text{U}$ is depleted in Rifle groundwater

during biostimulation-induced U(VI) reduction and not significantly fractionated by bicarbonate induced desorption. Thus $^{238}\text{U}/^{235}\text{U}$ was found to be a sensitive tracer of U reduction in the Rifle aquifer^{17,21}. Despite the limited natural reduction capacity and high groundwater pore velocities at the Rifle and Hanford sites, these locations are broadly relevant to ISR remediation because they too have artificially elevated U concentrations compared to natural conditions^{20,22} and provide the theoretical framework for research on the fate of aqueous U.

More recent work on U isotopes in low-temperature redox-type U deposits includes studies of the ore composition^{11,16,23,24} and studies of groundwater in and adjacent to ore deposits^{12,25-28}. For example, south Texas²⁵ and Australian¹² roll-front ore bodies have decreasing $^{238}\text{U}/^{235}\text{U}$ along the groundwater flow direction that are correlated with decreasing aqueous U concentrations. In the case of South Texas, the ($^{234}\text{U}/^{238}\text{U}$) is generally low in groundwater in contact with the U ore, with higher values up- and down-gradient of the ore body²⁵. The patterns for $^{238}\text{U}/^{235}\text{U}$ and ($^{234}\text{U}/^{238}\text{U}$) are similar for both mined and undeveloped portions of the ore zone. The south Texas and Australian studies identify U reduction as the primary process affecting the $^{238}\text{U}/^{235}\text{U}$ in groundwater and suggest a conceptual isotope fractionation model for interpreting the evolution of the $^{238}\text{U}/^{235}\text{U}$ ratio along the groundwater flow path.

Additional isotopic tracers including the short-lived U-series daughter isotopes ^{226}Ra and ^{228}Ra along with the sulfur and oxygen isotopes of sulfate provide additional information about processes influencing U mobility such as reduction and adsorption in the aquifer. Druhan and coworkers^{22,29} used the increasing $\delta^{34}\text{SO}_4$ during biostimulation experiments at the Rifle site to document the onset of microbial sulfate reduction. The $\delta^{34}\text{S}$ of aqueous SO_4 increases as sulfate-reducing microbes utilize the ^{32}S isotope preferentially to the ^{34}S isotope. The isotopes ^{226}Ra and ^{228}Ra are strongly adsorbed to clay minerals in low-TDS, low-chloride groundwater and can be

used to measure the sorption capacity of the sediments^{7,30}. The activity ratio of $^{222}\text{Rn}/^{226}\text{Ra}$, for example, can be used to infer the Ra sorption coefficient of the sediments³¹.

In this contribution, we present new ($^{234}\text{U}/^{238}\text{U}$) and $^{238}\text{U}/^{235}\text{U}$ data for groundwater samples and associated sediments to demonstrate that the isotopic composition of dissolved U in groundwater down-gradient of the ore zone at Smith Ranch, WY is consistent with partial attenuation through reduction of aqueous U. We also demonstrate that ore zone groundwater has distinct U isotopic compositions and that high precision measurements of U isotopes coupled with other geochemical tracers are a sensitive technique for evaluating the extent of U migration and reduction adjacent to an ISR well field.

Hydrogeologic setting

The Smith Ranch-Highland ISR mine is located approximately 50 miles northeast of Casper Wyoming, USA at the southern end of the Powder River Basin (Fig 1 inset). The U ore is concentrated in fluvial sandstones of the Paleocene Fort Union Formation (Fig S1). Regionally the strata dip to the East at $<0.5^\circ$ and groundwater flow is mostly eastward at 2-3 m/yr³². Uranium is concentrated at redox boundaries (roll fronts) that are typically 2-8 meters wide and at depths of 61-366 meters below the surface. Uranium typically occurs as uraninite (UO_2) and coffinite ($\text{U}(\text{SiO}_4)_{0.9}(\text{OH})_{0.4}$) coatings on sand grains and is commonly associated with pyrite and carbonaceous matter, which may have facilitated U reduction³³⁻³⁵. The U is thought to have been reduced from the soluble U(VI) to the insoluble U(IV) at a redox interface along the hydraulic gradient, forming crescent-shaped (roll-front) ore deposits.

The study area is mining unit 4a (MU4a; Fig 1), which consists of a perimeter ring of monitoring wells and a series of injection and production wells completed within the ore bearing sandstone. The area was mined between 1999 and 2005 using local groundwater fortified with

CO₂ and O₂. MU4a entered a restoration phase in 2013, however there were no remediation activities as of our sample collection time except for pumping from recovery wells to maintain negative hydraulic pressure, thus restricting down gradient migration of ore zone fluids. The groundwater analyses have never yielded concentrations of U in excess of the pre-mining values (Fig 1), which implies that the monitor well fluids are not affected by mining.

Prior to mining, the monitoring wells in the ore zone and perimeter ring were sampled as part of NRC licensing and characterized for major cations, anions, U, ²²⁶Ra and ²²⁸Ra³². Fluid samples from the wells up-gradient of the ore body had U concentrations of 10-17 ppb. Down gradient samples had concentrations as low as 5 ppb and up to 17 ppb (Fig 1). Aqueous U in the ore zone monitoring wells had 23-72 ppb U with the highest concentrations in the southeast end of the mining unit (Fig 1). The perimeter wells adjacent to the southeastern terminus of the mapped ore body have some of the highest U concentrations and may cross a lower grade portion of the roll front deposit.

Baseline wells in the ore zone have ²²⁶Ra activities of 366 to 1625 pCi/L whereas monitoring ring wells have 4.7-35.6 pCi/L down-gradient and 2.9-18.1 pCi/L up-gradient, although up-gradient well M436 has ²²⁶Ra activity of 193.8 pCi/L. The sharp contrast in U and radium concentrations between the ore zone and down-gradient monitoring wells is evidence that prior to mining there was little migration of U or daughter nuclides (such as ²²⁶Ra) down gradient of the ore zone. The mechanisms of radionuclide retention in the ore zone region are not evident from the concentration data alone; however, the apparent sharp gradient in ²²⁶Ra down gradient of the ore body requires processes in addition to reduction because Ra is not a redox sensitive element and the half life of ²²⁶Ra is 1600 years, many times greater than the inferred 50 to 100 year transit time of water between the ore zone and the down-gradient monitoring ring. This

implies that radium mobility is low, most likely because of adsorption and ion exchange with clays⁷, processes that may also impact U mobility³⁶⁻³⁸. The pre-mining groundwater composition data³⁹ (obtained from NRC website: <http://www.nrc.gov/info-finder/materials/uranium/licensed-facilities/smith-ranch/isr-wellfield-ground-water-quality-data.html>) summarized above are consistent with a local U mineralized zone surrounded by low U concentration sediments and low U concentration groundwater, an ideal situation for assessing U isotope fractionation associated with a redox boundary and groundwater transport.

Methods

Fluid samples were collected from monitoring wells in MU4a with dedicated down-hole pumps. Wells were purged and then the collected samples were filtered with a 0.45- μ m in-line filter and acidified in the case of U isotope aliquots. Samples for S and O isotopes of sulfate were filtered and then aqueous SO₄ was fixed by adding 20% BaCl₂ to precipitate BaSO₄. Sulfate samples were subsequently acidified with 6M HCl to remove any BaCO₃.

Sediments from the ore zone were recovered from an adjacent mining unit (MU4) by double tube coring and fractions were shipped to Los Alamos National Laboratory³⁵. Sediment aliquots were characterized for mineralogy, elemental composition and isotopic compositions of carbon, U and sulfur³⁵. Separate sediment aliquots were dissolved at UC Berkeley using nitric and hydrofluoric acids and prepared for $\delta^{238}\text{U}$ measurements using the same methods as aqueous samples.

Samples for $^{234}\text{U}/^{238}\text{U}$ analysis were purified using Eichrom Tru-Spec resin and analyzed on the GV IsoProbe at Lawrence Berkeley National Laboratory following well-established techniques²⁰. The $^{234}\text{U}/^{238}\text{U}$ ratio is usually discussed in terms of activity (A), where $A=n\lambda$ and n is the number of atoms and λ is the isotope decay constant. In a closed system, the activity of parent and

daughter isotopes will reach secular equilibrium ($A_{238\text{U}}=A_{234\text{U}}$). Thus, variations in $^{234}\text{U}/^{238}\text{U}$ are described by the activity ratio, [*i.e.*, ($^{234}\text{U}/^{238}\text{U}$), where the parentheses denote activity ratio], of the sample compared to secular equilibrium: $(^{n234}\text{U}\lambda_{234}/^{n238}\text{U}\lambda_{238})_{\text{sample}}/(^{n234}\text{U}\lambda_{234}/^{n238}\text{U}\lambda_{238})_{\text{secular equilibrium}}$. Measured $^{234}\text{U}/^{238}\text{U}$ ratios were corrected for ion counting-Faraday cup gain using a secular equilibrium standard and activity ratios were calculated using $\lambda_{234}=2.826\times 10^{-6}$ and $\lambda_{238}=1.551\times 10^{-10}$. The long-term external reproducibility of $^{234}\text{U}/^{238}\text{U}$ activity ratios at LBNL is better than $\pm 0.3\%$ (2σ).

Aliquots of the water samples that were used for $^{238}\text{U}/^{235}\text{U}$ analysis were spiked with the IRMM 3636a ^{233}U - ^{236}U tracer and purified using Eichrom UTEVA resin. The $^{238}\text{U}/^{235}\text{U}$ ratios were measured on the Nu Instruments MC-ICPMS at Stanford University and are reported as $\delta^{238}\text{U}$ relative to CRM145. Typical analyses had ^{238}U ion beams of $1.5\times 10^{-10}\text{A}$ and $^{238}\text{U}/^{235}\text{U}\sim 18\text{-}22$. The estimated external reproducibility (2σ) of $\delta^{238}\text{U}$ measurements is 0.1-0.15‰ based on 98 measurements of CRM145. Details of standard measurements are provided in the SI and by refs 25 and 40.

Sulfur and oxygen isotopes of SO_4 were measured using the Micromass Isoprime at UC Berkeley. Barium sulfate samples were mixed with vanadium oxide, loaded in tin capsules and combusted using the elemental analyzer. Sulfur was measured as SO_2 . Oxygen isotopes of sulfate were measured using pyrolysis and carbon monoxide to make SO_2 . Data were normalized to Canyon Diablo Troilite ($\delta^{34}\text{S}$) and SMOW ($\delta^{18}\text{O}_{\text{SO}_4}$).

Results and Discussion

Groundwater chemistry from 2012-2014 sampling campaign

The groundwater compositions for baseline (ore zone) and monitoring wells are reported in Table S1 and Figs 1 and S3. Our expectation is that the U ore body represents a redox boundary

and that the groundwater U concentration, $\delta^{238}\text{U}$ and ($^{234}\text{U}/^{238}\text{U}$) will all be affected by reactions such as reduction in the ore zone region. The up-gradient groundwater samples have moderate U concentrations 11-16 $\mu\text{g/L}$ and high ($^{234}\text{U}/^{238}\text{U}$) due to the combined effects of α - recoil and the weathering of silicate minerals^{6,41-43}. The $\delta^{238}\text{U}$ is depleted compared to most known groundwater and silicate minerals^{10,12,25,44}. The up-gradient groundwater ($^{234}\text{U}/^{238}\text{U}$) and $\delta^{238}\text{U}$ are tightly clustered varying from 5.12 to 5.61 and -0.88‰ to -1.08‰ respectively, with no discernable correlation with U concentrations.

In contrast to the up-gradient groundwater samples, the down-gradient samples display a large range in U concentrations, ($^{234}\text{U}/^{238}\text{U}$) and $\delta^{238}\text{U}$ (Fig 2). Most of the down-gradient samples have U concentrations <10 $\mu\text{g/L}$, lower $\delta^{238}\text{U}$ (-1.5‰ to -2.8‰) and lower ($^{234}\text{U}/^{238}\text{U}$) (< 3.70) compared to the up-gradient water samples (Fig 2). These observations are consistent with the hypothesis that the ore body represents an important reaction zone along the groundwater flow path. Two down-gradient samples from wells M458 and M452 have elevated $\delta^{238}\text{U}$ and U concentrations similar to the up-gradient samples (Fig 2) and thus lack the reduction signature typical of the other down-gradient wells.

Groundwater samples from the ore zone collected after mining have high residual U concentrations (13-40 ppm), have relatively high $\delta^{238}\text{U}$ compared to the up-gradient and down-gradient samples, (-0.41‰ to 0.15‰) and have ($^{234}\text{U}/^{238}\text{U}$) near secular equilibrium (0.97-1.11) (Fig. 2). These data are all consistent with residual oxidized U that came from dissolution of U oxide minerals³⁵. The high U concentrations in the ore zone are likely due to some residual oxidation of U and enhanced U(VI) stability in the presence of high bicarbonate concentrations after the completion of mining, at least adjacent to the borehole.

Additional inferences about the reducing conditions of the aquifer surrounding the ore zone can be derived from the concentrations of aqueous Fe and SO_4 . Fe(III) is largely insoluble, while Fe(II) is soluble in circumneutral pH groundwater, which implies that there should be increasing aqueous Fe concentrations in more reducing groundwater. Aqueous SO_4 concentrations, in contrast, tend to decrease in more reducing groundwater as SO_4 is reduced to HS^- and H_2S . The isotope ratios of S and O in aqueous SO_4 increase in response to microbial SO_4 reduction^{22,45}. Concentrations of aqueous Fe for MU4a are generally $<100 \mu\text{g/L}$ in the up-gradient wells and $>150 \mu\text{g/L}$ in the down-gradient wells, consistent with aquifer conditions being sufficiently reducing to cause Fe reduction across the ore body (Fig S2). In the monitoring ring, SO_4 concentrations vary between 68 and 157 mg/L while the ore zone well MP423, where there has been induced oxidation, has 896 mg/L SO_4 . The ore zone well MP423 is the most depleted in $\delta^{34}\text{S}$ (-14.1‰), likely due to sulfide mineral dissolution during mining, while the down-gradient wells are generally enriched in $\delta^{34}\text{S}$ compared to the up-gradient wells (Table 1). The sulfur isotopes indicate that aquifer conditions are sufficiently reducing to cause some sulfate reduction. However, the distribution of $\delta^{18}\text{O}_{\text{SO}_4}$ is less systematic compared to $\delta^{34}\text{S}$, with both the most depleted and enriched values found on the down-gradient side of the ore zone. Overall, the variability in $\delta^{34}\text{S}$ is fairly small compared to roll-front deposits in Texas, where $>30\%$ of variability is observed in both the fluid and solid phases^{46, 25}. Therefore we conclude that the relatively small variations in $\delta^{34}\text{S}$ of SO_4 suggest that the aquifer redox potential is just below the threshold for sulfate reduction and not sufficient for widespread or quantitative SO_4 reduction.

Core samples

Characterization of the ore body sediments provides information on the mineralogy and isotopic composition of the reactants in the redox reactions. The U concentrations and activity

ratios for core samples collected in previously mined sediments were reported by WoldeGabriel et al³⁵. The sediments have U concentrations from 3 to 25,000 µg/g U and the (²³⁴U/²³⁸U) varies systematically with depth between 1.5 near the top of the ore zone and 0.65 near the bottom of the ore zone. The ore-zone area from 235-238 m (769 to 779 ft) has nearly constant (²³⁴U/²³⁸U) of ca. 1.2 and this area also has the highest post-mining U concentrations (1000 to 25,000 µg/g). Three samples from the high U zone were analyzed for δ²³⁸U and are reported in Table 1. The sediment samples range in δ²³⁸U from -0.42‰ to -0.76‰ and are negatively correlated with U concentrations. The δ²³⁸U in the ore samples is intermediate between the up-gradient groundwater and the ore-zone groundwater (Table 1; Fig 2).

Chemical and isotopic evidence for U reduction

Recent research in sandstone hosted U ores and laboratory experiments suggest that ²³⁸U is removed from solution preferentially compared to ²³⁵U during partial reduction of U(VI) to U(IV) into minerals such as uraninite and coffinite^{12,15,47}. The preferential reduction of ²³⁸U(VI) results in decreasing ²³⁸U/²³⁵U in the fluid phase. The reduced and precipitated U(IV) has ²³⁸U/²³⁵U that is determined by the fluid composition and the fractionation factor α:

$$\alpha \equiv R_p / R_r \quad \text{Eq 1}$$

where R_p and R_r are the ²³⁸U/²³⁵U of the product and reactant respectively. With continued reductive precipitation the fluid U isotope composition should evolve according to a simple (Rayleigh) distillation model^{48,49}:

$$R_{fluid} = R_{initial} \times f^{(\alpha-1)} \quad \text{Eq 2}$$

Where R_{fluid} is the measured isotopic ratio in groundwater, $R_{initial}$ is the isotopic ratio of the

starting groundwater before reductive U removal, f is the concentration expressed as a fraction of the initial U(VI) reservoir and α is the fractionation factor defined above. According to the distillation model when $\alpha > 1$ and U is removed from solution, the $^{238}\text{U}/^{235}\text{U}$ and remaining U concentrations decrease. Though it is difficult to sample the initial dissolved U in natural systems, the quantity of interest is commonly α , which can be calculated by least squares fitting of the measured concentrations and isotopic ratios⁴⁸.

A distillation model for the isotopic evolution of the MU4a groundwater was calculated using a least squares regression model of the up-gradient and down-gradient values of $\delta^{238}\text{U}$ and U concentrations. The $\delta^{238}\text{U}$ values of the up-gradient waters are related to the fractionated down-gradient waters by $\alpha = 1.00078 (\pm 0.00012)$ when all monitoring well data is considered and $\alpha = 1.00103 (\pm 0.00010)$ when only MU4a monitoring wells are considered (Fig. 2; excluded wells are labeled as adjacent in Table S1). The apparent fractionation factor is likely a minimum value as fluid transport effects such as localized reduction, dispersion, and diffusive limitations tend to lessen the observed isotopic fraction compared to the intrinsic fractionation (i.e. observed in laboratory experiments or from theory)^{50,51}. The difference between the MU4a-only and all monitoring well $\delta^{238}\text{U}$ fractionation factors might arise from hydrology effects as the study area size is increased. We discuss this concept in more detail below. Additionally, because sorption does not strongly fractionate U isotopes, U removal by this process will also result in apparent fractionation factors shifted toward unity^{21,52}. The correlated [U] and $\delta^{238}\text{U}$ in MU4a groundwater suggests that U is removed by the reductive precipitation of U(VI) to U(IV).

The calculated U isotope fractionation factor is similar to equilibrium fractionation factors of 1.00095-1.0013, determined from *ab initio* calculations⁵³ and experiments^{54,55}. Similarly, microbial U reduction experiments have fractionation factors of $\alpha = 1.00068$ -1.00099^{47,56,57}.

Although the exact mechanism of fractionation of U isotopes during irreversible, kinetically controlled aqueous U(VI) reduction is not fully understood, fractionation in the Smith Ranch groundwater is similar in magnitude to both microbial reduction experiments and theoretical predictions of equilibrium inorganic reduction.

Other recent studies of roll front deposits have reported smaller fractionation factors of $\alpha=1.00048$ for a south Texas deposit²⁵, and $\alpha=1.00025$ - 1.00054 for deposits in South Australia (recalculated from published data for each aquifer¹²). The difference between the Smith Ranch fractionation factor and other roll front deposits might be related to the limited spatial extent of the MU4a study area (one sand unit and less than 4 km² area) compared to multiple sand units and greater geographic area at the South Texas and South Australia locations. Sampling over a more limited area may lessen the effects of hydrogeological dispersion and heterogeneity in the sediment lithology, reductants and isotope composition. Alternatively, the reduction mechanism may differ amongst the different roll front deposits. The Smith Ranch aquifers contain abundant fragments of organic carbon, a potential abiotic reductant³⁵, while the south Texas U deposits are thought to form as a result of H₂S gas incursion from stratigraphically lower hydrocarbon reservoirs^{46,58,59} and the south Australian deposits may be a mixture of these reducing materials¹².

Chemically reducing conditions between the ore zone and down-gradient monitoring wells in MU4a are also evident from the concentration and isotopic composition of sulfate. In MU4a the lowest [SO₄] and most enriched $\delta^{34}\text{S}$ occur in the same down-gradient wells as the depleted $\delta^{238}\text{U}$ (Table S1). The magnitude of $\delta^{34}\text{S}$ fractionation is less than 2‰, which is small compared to fractionations observed in many locations where bacterial sulfate reduction occurs^{22,45,60}. The relatively small degree of SO₄ isotope fractionation is consistent with the observation that sulfur

isotope fractionation factors are much smaller when SO_4 concentrations are ~ 1 mM or lower as in the Smith Ranch samples⁴⁵.

Uranium reduction mechanisms and U isotope fractionation

Recent experimental studies suggest that variations in $\delta^{238}\text{U}$ in low temperature environments arise primarily due to direct enzymatic U reduction by microbes and that $\delta^{238}\text{U}$ is not significantly fractionated during inorganic reduction^{56,57}. These inferences reflect the distinctly different U isotope fractionation observed in inorganic reduction experiments and microbial reduction experiments. The microbial experiments are thought to achieve a quasi-equilibrium condition for U isotopes, explaining the similarity to *ab initio* fractionation estimates with ^{238}U enrichment in the product (reduced) phase. In contrast, inorganic magnetite reduction experiments show ^{235}U enrichment in the product (reduced U(IV)) phase, possibly due to kinetic effects that are related to the absence of exchange between the reduced and oxidized reservoirs⁵⁶.

The U isotope variations in the MU4a groundwater can be used to infer possible U reduction mechanisms. The fractionation factor we derive is similar to the *ab initio* value, meaning the data could be interpreted as solely microbial U reduction or that the native mixture of inorganic and microbial reductants produce U isotope fractionation similar to the theoretical calculations and dissimilar from the recent inorganic experimental data. Evidence that redox conditions are favorable for inorganic U reduction occur in the relevant aquifer at Smith Ranch includes aqueous Fe(II) concentrations and observations of reduced U on the surfaces of pyrite grains in sediment cores from an adjacent mining area³⁵. The thermodynamic conditions for U reduction by aqueous Fe(II) are likely based on Fe(II) concentrations >100 ppb in the down-gradient wells (*e.g.*, 454, 455A, 458 and 452; Supporting Information Fig S3). The reduction of U by Fe(II) above $\sim \text{pH } 5.5$ is thermodynamically favorable and thought to be kinetically feasible in the

presence of abundant mineral surfaces including Fe sulfides⁶¹⁻⁶⁴. The presence of U reduced on the surfaces of lignite and pyrite in the Powder River Basin sediments suggest multiple possible inorganic reduction mechanisms³⁵. If there is a significant amount of non-fractionating U(VI) removal or an opposite sense of isotopic fractionation (*i.e.* ²³⁵U enrichment in remaining U(VI)) as observed in laboratory experiments⁵⁶ we should observe smaller apparent fractionation factors inferred from the fractionation model. The calculated fractionation factor for the Smith Ranch fluids is near the *ab initio* values and greater than calculated fractionation factors for South Texas²⁵ and South Australia¹² roll-front deposits, implying that the bulk U reduction process (microbial plus inorganic) both result in the reduced U having higher ²³⁸U/²³⁵U. The discrepancy in U isotope behavior between the Smith Ranch site and inorganic laboratory experiments may indicate that laboratory experiments have yet to capture the behavior of inorganic U reduction in a natural hydrogeologic setting. Alternately the proportion of inorganic U reduction in the reservoir could be small (<10%) compared to microbial reduction and be consistent with the experimental observations⁵⁶. Further experiments with conditions more closely matched to the aquifer mineralogy and fluid compositions may yield a better understanding of the relative roles for inorganic and microbial U reduction in roll front U deposits.

Insights into the spatial distribution of U reduction from ²³⁴U/²³⁸U_{AR}

Although there is evidence of reducing conditions down-gradient of the ore zone, a key question is if reduction is sufficiently fast so that U concentrations are reduced to regulatory limits within an acceptable distance. The observed changes in (²³⁴U/²³⁸U) can be used to estimate the distance over which U is removed by reductive precipitation processes. The model we use assumes that (²³⁴U/²³⁸U) in groundwater is determined by a balance between alpha-recoil related release of ²³⁴U from U-bearing minerals and dissolution of those minerals⁵⁻

^{7,41,65-70}. The data in Fig 3 show that the down-gradient groundwaters have (²³⁴U/²³⁸U) that is variable but intermediate between the values in the up-gradient water and the ore zone. However, the down-gradient waters all have lower U concentrations, suggesting net U removal. Removal can be the result of adsorption or reductive precipitation, but $\delta^{238}\text{U}$ values suggest that reductive precipitation is the mechanism. Hence a likely scenario is that the water leaving the ore zone has high [U] and low (²³⁴U/²³⁸U) like the ore zone fluids, and then acquires higher (²³⁴U/²³⁸U) as a consequence of alpha recoil effects as it moves down gradient. If we model this process using parameters that we can derive from the up-gradient waters, we can arrive at estimates of the lengthscale of reductive removal of U.

The equation that describes the change in ²³⁴U/²³⁸U with distance is:

$$\frac{d(^{234}\text{U}/^{238}\text{U})}{dx} = \frac{1}{L_{\text{weather}}} [A_s - (^{234}\text{U}/^{238}\text{U})] + \frac{1}{L_{\text{recoil}}} \quad (3)$$

Where x is the horizontal flow distance, A_s is the (²³⁴U/²³⁸U) of the sediments. L_{weather} and L_{recoil} are described by equations 4 and 5.

$$L_{\text{weather}} = qC_f / (\theta MC_s R_d) \quad (4)$$

$$L_{\text{recoil}} = qC_f / (\theta MC_s \lambda_{234} F_a) \quad (5)$$

where θ is the volumetric water content, M is the solid mass to groundwater volume ratio, C_f and C_s are the concentrations of U in the groundwater and the solid respectively, λ_{234} is the decay constant for ²³⁴U ($2.38 \times 10^6 \text{ yr}^{-1}$)⁷¹, q is the groundwater velocity, R_d is the mineral dissolution time constant and F_a is the fraction of ²³⁸U decays where the daughter isotope is lost from the mineral.

$L_{weather}$ and L_{recoil} control the steady state isotopic composition with distance, and the ratio of the U concentrations between the solid and the groundwater control the isotopic gradient and the rate of approach to isotopic steady state. For groundwater beyond the isotopic equilibration distance, the primary control on ($^{234}\text{U}/^{238}\text{U}$) is the ratio of $L_{weather}/L_{recoil} \sim \lambda_{234}F_d/R_d$ and for groundwater less than the isotopic equilibration distance, the ratio of $\theta MC_s/C_f$ is also important.

The U isotopic equilibration length scales $L_{weather}$ and L_{recoil} for Smith Ranch are on the order of 5 and 2 km respectively, meaning that water samples at the monitoring ring have not reached the steady-state ($^{234}\text{U}/^{238}\text{U}$). We assume that θMC_s is a property of the sediments and, similar to $\lambda_{234}F_d/R_d$, does not vary systematically over the study area, meaning that variations in ($^{234}\text{U}/^{238}\text{U}$) at the monitoring ring are related to the flow path distance and the groundwater U concentration between the ore zone and the monitoring ring.

The quasi-steady state ($^{234}\text{U}/^{238}\text{U}$) of groundwater can be described in terms of distance along the flow path⁶⁷:

$$(^{234}\text{U}/^{238}\text{U}) = (^{234}\text{U}/^{238}\text{U})_0 \exp\left(-\frac{x}{L_{weather}}\right) + (A_s + \frac{L_{weather}}{L_{recoil}} [1 - \exp\left(-\frac{x}{L_{weather}}\right)]) \quad (6)$$

where ($^{234}\text{U}/^{238}\text{U}$), ($^{234}\text{U}/^{238}\text{U}$)₀, and A_s are the ($^{234}\text{U}/^{238}\text{U}$) of the groundwater, initial groundwater and solid respectively.

We evaluate 3 scenarios that could describe U transport in the down-gradient region and compare the predicted ($^{234}\text{U}/^{238}\text{U}$) to the measured down-gradient water samples. Model 1 (M1) and model 2 (M2) have persistently high (50 $\mu\text{g/L}$) and low (2.5 $\mu\text{g/L}$) U concentrations from the ore zone to the down-gradient monitoring wells, respectively (Fig 4). These values approximate the range of [U] observed in the groundwater prior to mining. Model 3 (M3) has a 30 $\mu\text{g/L}$ U

concentration from 0-150 m and then 3 $\mu\text{g/L}$ past 150 m corresponding to an instantaneous precipitation event. Eq 6 is solved separately for both segments of M3. This assumes no mixing with upgradient U occurs down gradient of the ore zone. All other parameters are identical for the 3 models and are reported in the caption of Fig 4. Both M2 and M3 show that a decrease in U concentration down gradient is required to generate ($^{234}\text{U}/^{238}\text{U}$) similar to those observed at the monitoring ring (Fig 4). If U reduction is near quantitative in the pre-mining ore zone then the ($^{234}\text{U}/^{238}\text{U}$) at the monitoring ring will be relatively high (Fig 4). Conversely, if groundwater has high U concentrations as it migrates down gradient, this will result in low ($^{234}\text{U}/^{238}\text{U}$) at the monitoring ring.

The model results mean that the ($^{234}\text{U}/^{238}\text{U}$) can be used as a tracer to interpolate the fate of aqueous U between the ore zone wells and the monitoring ring and may be helpful for identifying transects where relatively high aqueous U concentrations have migrated down-gradient of the ore zone. In other words, the ($^{234}\text{U}/^{238}\text{U}$) at the monitoring wells will shift toward the ore zone value (in this case <2.5) if groundwater with relatively high aqueous U concentrations migrates toward the monitoring ring, increasing the effective L_{recoil} and L_{weather} equilibration distances. This effect will be detectable prior to U breakthrough at the monitoring wells.

The weathering- α -recoil model can be an effective tool for understanding the long-term fate of U mobility in ISR sites after mining-restoration activities are completed. The mining process imparts a distinct $\delta^{238}\text{U}$ -($^{234}\text{U}/^{238}\text{U}$) signature (Table 1; Fig 2), which is less heterogeneous than the pre-mining ore zone fluids and could be easily traced once the natural site hydrology is restored. Both mixing processes in the ore zone and α -recoil-weathering reactions in the down-gradient region require groundwater-mineral exchange reactions in the ore zone and down-

gradient regions. The existence of reactions that both add and remove U from the groundwater in the ore zone-down-gradient regions is additionally supported by the wide range of apparent ages for U ore minerals, which are produced by the decoupling of parent and daughter isotopes during dissolution-precipitation reactions⁷². The validity of this model could be more robustly examined with a series of groundwater wells aligned with the flow path and evaluation of the aqueous (²³⁴U/²³⁸U) prior to mining.

Uranium isotope implications for tracking the fate of aqueous ore zone U after remediation

Reduction of aqueous U on the down-gradient edge of the ore body will occur if there are sufficient reducing agents and will occur over a distance dictated by the kinetics of the reduction reaction relative to the fluid velocity. In natural roll-front deposits, the sharp boundaries between mineralized sediments and reduced, unmineralized sediments is evidence that the kinetics of reduction are relatively fast compared to fluid velocity and not a limiting factor for U reduction.

Natural attenuation as a component of ISR remediation strategy requires a demonstration that the aquifer down-gradient of mining operations is capable of reducing U and that the kinetics of reduction are sufficiently rapid that U transport is ideally restricted to within the monitoring well ring. We have demonstrated how $\delta^{238}\text{U}$ can be used to track the reduction of U while the (²³⁴U/²³⁸U), along with information about the host sediment and fluid velocities, can be used to estimate the degree to which U is transported down-gradient of the ore zone. Characterization of the pre-mining (²³⁴U/²³⁸U) in the ore zone groundwater would reduce the uncertainty in the model as the interpretation of (²³⁴U/²³⁸U) data in the down-gradient wells will change somewhat if (²³⁴U/²³⁸U) in the ore zone fluids is appreciably higher or lower (Fig 4). In the case of the MU4a study area, there is evidence for both minimal U transport out of the ore zone and substantial U reduction based on the U isotopic data (Figs. 2-4). Two exceptions may be the M458 and M452

wells, where the U appears to be a mixture of up-gradient-ore zone sources with little reduction. This suggests that extra attention to the remediation-restoration work up-gradient of the aforementioned wells may be necessary to mitigate down-gradient U transport compared to the rest of the well field. The ability to estimate the contribution of reduction to the overall U attenuation budget (reduction + adsorption) of the aquifer solids could be incorporated into reactive transport models constructed to predict down-gradient concentrations of U.

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Supporting Information

Details of the site background, ground- water major ion and trace element concentrations, and isotopic data ($\delta^{238}\text{U}$, ($^{234}\text{U}/^{238}\text{U}$), $\delta^{34}\text{S}$, and $^{87}\text{Sr}/^{86}\text{Sr}$). The Supporting Information is available free of charge on the ACS publications website

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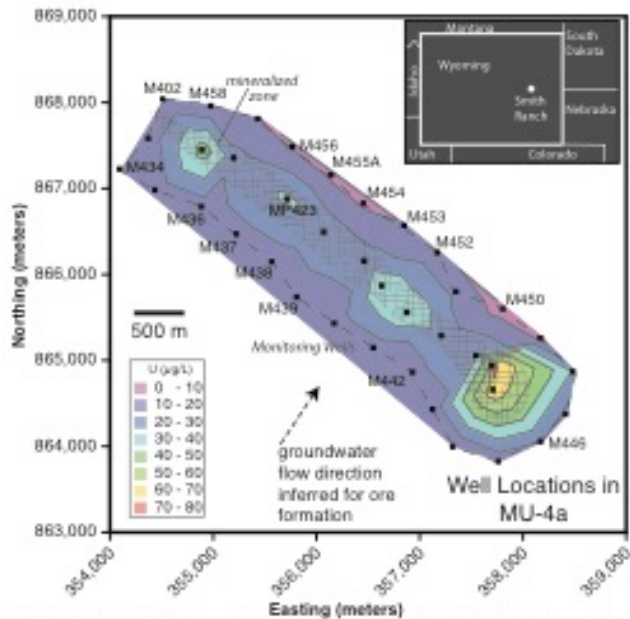


Fig 1. Map of the Smith Ranch MU4a well field in eastern Wyoming, USA. Wells in the perimeter ring are monitoring wells screened in the M sand up and down gradient of the mineralized sediments. Wells in the center area are baseline wells completed in the M sand inside the ore body. Contours show the pre-mining distribution of U. Wells in the southeast have the highest U concentrations while two zones on the presumed down-gradient side of the ore body are characterized by U concentrations less than 10 ppb (magenta color). Up-gradient wells are all between 10 and 20 ppb U.

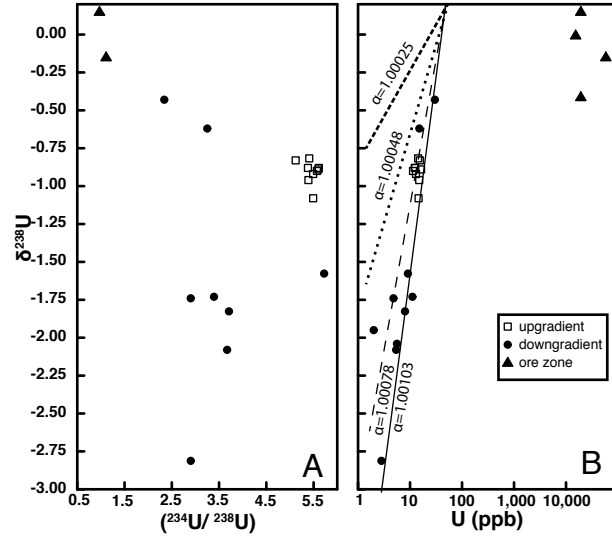
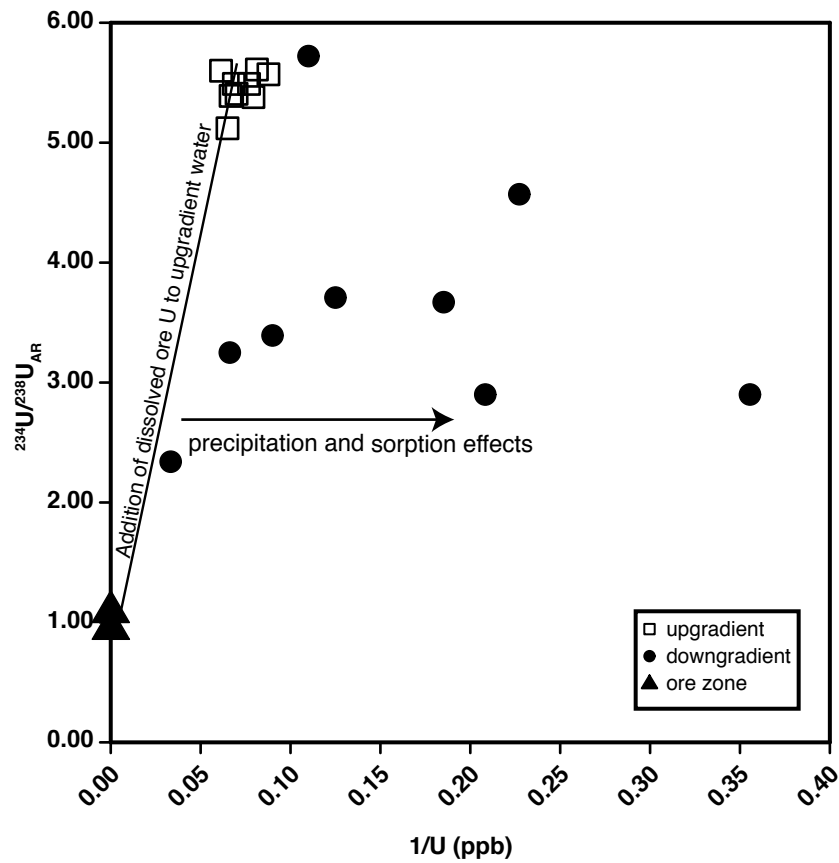


Fig 2. Distribution of U, $^{234}\text{U}/^{238}\text{U}_{\text{AR}}$, and $\delta^{238}\text{U}$ in groundwater in MU4a. Panel B shows the up-gradient and down-gradient $\delta^{238}\text{U}$ as a function of U concentration. Lines represent distinct isotopic fractionation factors based on least squares regression of the Smith Ranch data ($\alpha=1.00078$ and 1.00103), Rosita, TX ($\alpha=1.00048$) and South Australia ($\alpha=1.00025$).

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692 **Fig 3.** Mass balance model for the dissolution/desorption of ore zone U to the up-gradient water
 693 (legend as in Fig. 2). Notice the down-gradient samples largely fall off the mixing line, requiring
 694 sorption/precipitation to lower U concentration between the ore zone and the down-gradient
 695 sampling location.

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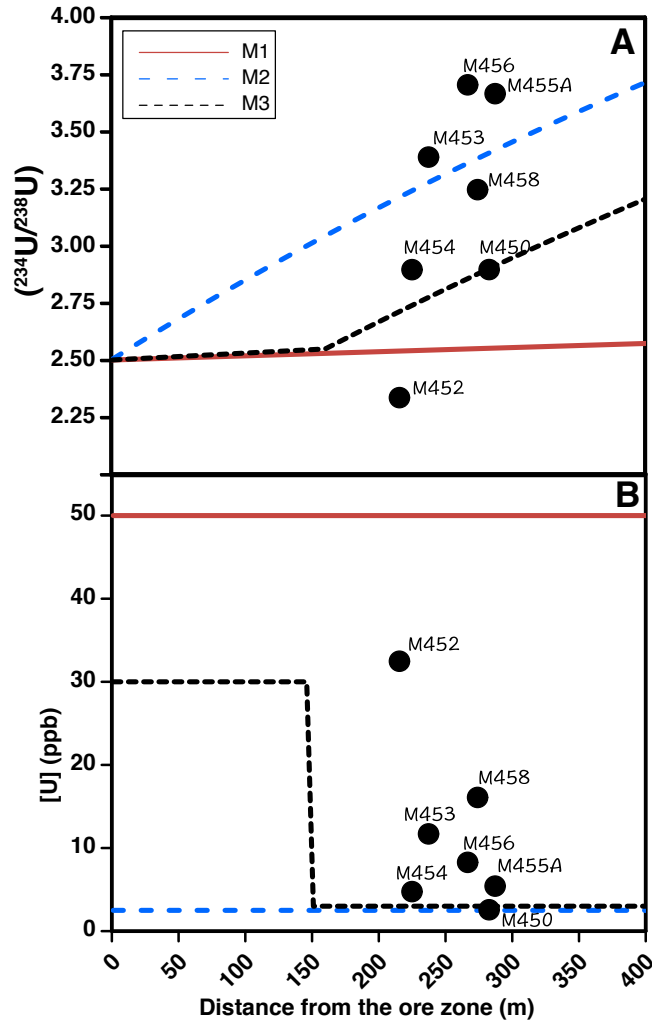


Fig 4. Down-gradient models for $(^{234}\text{U}/^{238}\text{U})$. (A) Models are based on equations presented in the text. All models use $R_d=8\text{e}^{-9} \text{ yr}^{-1}$, $\theta=0.25$, $F_a=0.015$, $C_s=30\text{ppm}$, $q=1 \text{ m/yr}$ and $M_s=25$. M1: $C_f=50\text{ppb}$, M2: $C_f=2.5 \text{ ppb}$, M3: $C_{f1}=30 \text{ ppb}$ and $C_{f2}=3\text{ppb}$. The strong dependence of the model curve on C_f demonstrates how down-gradient activity ratios can be affected by water-rock reaction in the down-gradient region. All model curves have $(^{234}\text{U}/^{238}\text{U})$ equilibration values of 6.5. The diamond symbols are the MU4a down-gradient water samples for reference. (B) modeled U concentrations for the models presented in panel A and $[\text{U}]$ for the down-gradient groundwater samples. The models M1 and M2 have constant U concentrations, while model M3 has a 90% decrease in aqueous U at 151 m.

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