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Se Isotopes as Groundwater Redox Indicators: Detecting Natural Attenuation of Se at an in Situ Recovery U Mine

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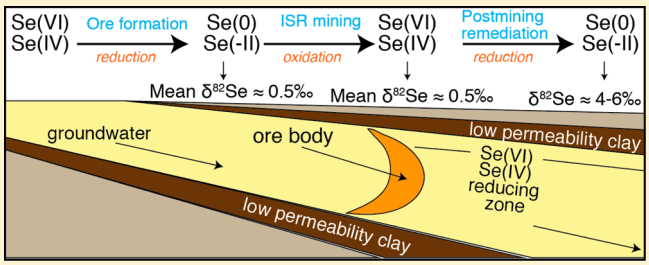
Supporting Information

ABSTRACT: One of the major ecological concerns associated with the in situ recovery (ISR) of uranium (U) is the environmental release of soluble, toxic selenium (Se) oxyanions generated by mining. Post-mining natural attenuation by the residual reductants in the ore body and reduced down-gradient sediments should mitigate the risk of Se contamination in groundwater. In this work, we investigate the Se concentrations and Se isotope systematics of groundwater and of U ore bearing sediments from an ISR site at Rosita, TX, USA. Our results show that selenate (Se(VI)) is the dominant Se species in Rosita groundwater, and while several up-gradient wells have elevated Se(VI), the majority of the ore zone and down-gradient wells have few or no Se oxyanions. In addition, the $\delta^{82}Se_{VI}$ of Rosita groundwater is generally elevated relative to the U ore up to +6.14‰, with the most enriched values observed in the ore-zone wells. Increasing $\delta^{82}Se$ with decreasing Se(VI) conforms to a Rayleigh type distillation model with an ε of −2.25‰ ± 0.61‰, suggesting natural Se(VI) reduction occurring along the hydraulic gradient at the Rosita ISR site. Furthermore, our results show that Se isotopes are excellent sensors for detecting and monitoring post-mining natural attenuation of Se oxyanions at ISR sites.



INTRODUCTION

The environmental mobility of the redox-active element Se is largely controlled by the high solubility contrast between its oxidation states. The oxidized Se species (i.e., Se(VI) and Se(IV)) are highly soluble, mobile, and toxic at elevated concentrations. Se immobilization in the environment occurs via chemical reduction to insoluble Se(0) or Se(-II). This redox-induced Se immobilization is common during the formation of roll-front uranium (U) ore deposits at redox interfaces in groundwater systems. Information about key reactions involving Se in redox-interface mineral deposits is crucial for understanding ore deposition mechanisms as well as pathways of Se cycling in aqueous environments.

Reductive immobilization of Se is an important reaction that tends to concentrate Se in roll-front type U ore deposits.[1,2] Commonly, ferroselite ($FeSe_2$) and pyrite are host minerals for Se in these U ore deposits.[1−4] Compared to its average crustal concentration (0.05 mg/kg), high concentrations of Se ranging from 0.5−500 mg/kg are reported from the roll-front deposits in Wyoming, Montana, and Utah in the United States.[5−7] These anomalously high Se concentrations have been used for U prospecting, particularly to characterize the location and shape of roll-front type deposits.[8] The similarity between the redox potential for reduction of Se oxyanions (Figure 1) and dissolved hexavalent uranium (U(VI))[9−11] leads to coprecipitation of Se minerals and U minerals.

In contrast, the oxidative dissolution of U ore enriched with Se minerals mobilizes Se and U in the environment in their toxic, oxidized forms. Se in the effluent from a traditional U mining and milling operation in northern Saskatchewan, Canada, led to the accumulation of toxic levels of Se in aquatic organisms.[12,13] Elevated Se concentrations in runoff or aquifers are reported from the regions of U mining and milling in the United States (e.g., Puerco River, Arizona; New Mexico; Rifle, Colorado).[14,15] At present, almost all recent U mining in the

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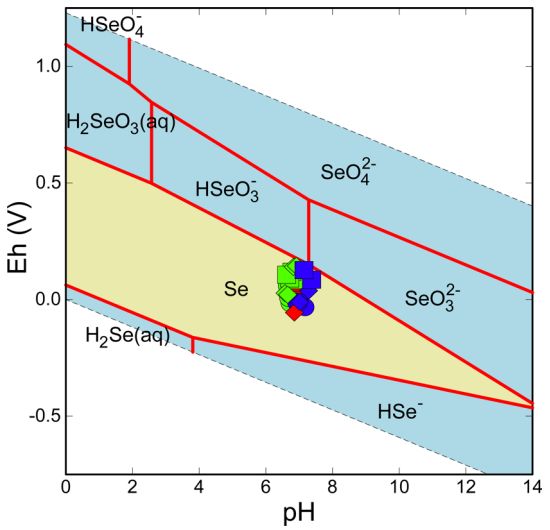

Figure 1. Pourbaix diagram for Se showing the thermodynamic stability of different Se species in the environment. Total Se concentration is 10^{-6} M. Light blue fields represent aqueous species, and golden field represents solid Se species. Red, green, and blue symbols represent groundwater from mining units PAA 1, PAA 2, and PAA 3, respectively. Squares, circles, and diamonds represent groundwater samples from up-gradient, ore-zone, and down-gradient wells, respectively.

United States and ~50% of global U mining employ a mining technique known as in situ recovery (ISR) that extracts U by oxidative dissolution of roll-front type sandstone-hosted ore deposits.[16,17] Despite several advantages such as the lack of mill tailings and radioactive dust, and its low CO_2 emission footprint, this mining method releases Se as toxic, mobile Se oxyanions along with U(VI) directly into groundwater.[18] Current strategies to mitigate Se(VI) in the groundwater after the completion of mining include groundwater sweep and occasionally active remediation by biostimulation or injection of abiotic reductants.[19]

Understanding naturally occurring reduction of Se oxyanions is critical for designing efficient remediation−restoration strategies at ISR sites. Natural attenuation of U(VI) by the existing reducing environments down-gradient of the redox interface at roll-front deposits has been proposed as an inexpensive but effective remediation strategy. Recent work from our group demonstrates conditions favorable for post-mining U(VI) reduction at ISR sites.[20,21] After the cessation of mining, the residual reducing capacity of the U ore and the prevailing reducing environments down-gradient of the ore should reduce mine-generated elevated concentrations of toxic Se oxyanions. At pH 7, the redox potential (Eh) required for the reduction of Se oxyanions (~0.4 V for Se(VI)−Se(IV) and ~0.2 V for Se(IV)−Se(0)) is higher than that for U(VI) (~0.0 V),[9−11] meaning that the reduction of Se(VI) and Se(IV) should precede U(VI) reduction. The challenge is to identify the active reduction of Se in the ore-zone or down-gradient groundwater and distinguish reduction from other processes that may affect aqueous Se concentration such as sorption and dilution.

An effective approach to better understand important reactions and possibly the reactions kinetics is the study of variations in stable isotope ratios. Se reduction can be detected by shifts in the relative abundance of its stable isotopes (^{82}Se, ^{80}Se, ^{78}Se, ^{77}Se, ^{76}Se, and ^{74}Se). The reduction of Se(VI) to Se(0) or Se(−II) via the intermediate product Se(IV) induces a kinetic isotopic fractionation resulting in the enrichment of heavier isotopes (i.e., ^{82}Se) in the remaining dissolved Se oxyanions.[11,22−24] This enrichment is described in terms of an isotopic enrichment factor ε, a per mil quantity, expressed as

$$\varepsilon = 1000‰ \times (\alpha - 1) \quad (1)$$

where α is the isotopic fractionation factor, defined as $\alpha = \frac{R_{product}}{R_{reactant}}$, and $R_{product}$ and $R_{reactant}$ are the ^{82}Se/^{76}Se in the reduction product and remaining Se oxyanions, respectively. Relatively large isotopic fractionation factors are observed during microbial reduction of Se(VI) to Se(IV) ($\varepsilon \sim -8‰$) and of Se(IV) to elemental Se ($\varepsilon \sim -14‰$).[25] Abiotic reduction of Se(VI) by green rust or of Se(IV) by FeS also induces large fractionations (up to −11‰).[22,23,26] In contrast, adsorption of Se(IV) to mineral surfaces results in a smaller fractionation (~−1‰).[26,27] Thus, Se stable isotope ratios in groundwater are a more reliable indicator of reduction of Se oxyanions than aqueous concentrations of the Se species, which are less easy to interpret because of the effects of dilution, removal by adsorption, or advection of heterogeneous plumes past sampling points.

Although the release of potentially toxic Se oxyanions by ISR activity is a widespread environmental risk, the fate of mobilized Se at post-mining ISR sites is not yet well-understood. In this article, we present species-specific Se concentrations and isotopic measurement data for U ore and 33 groundwater samples collected from wells located up-gradient, within, and down-gradient of a roll-front deposit located at an ISR site at Rosita, TX, USA. Sample locations include both previously mined and unmined parts of the site. The objective of our study is to demonstrate naturally occurring Se oxyanion reduction at the site using Se isotope ratios of groundwater samples collected across a groundwater redox interface. In addition, we discuss how the Se isotope data may provide additional information about the redox condition in the aquifer, particularly in the unmined part of the site, in relation to other geochemical indicators (i.e., Se concentrations, U concentrations, and U isotope data).

MATERIALS AND METHODS

Site Description and Groundwater Sampling. The study site is located at Rosita, TX, USA (Figure 2). A detailed description of the site can be found in Basu et al., 2015.[20] Briefly, the U roll-front deposit at this ISR site is defined by a poorly consolidated, mineralized sand unit bounded above and below by low-permeability clay units. For ISR mining, site groundwater fortified with O_2 and H_2O_2 was injected into the ore zone in three mining units or production area authorizations (PAA) to oxidize and dissolve the U ore utilizing the high natural bicarbonate concentrations to stabilize U−CO_3 complexes. The mining unit PAA 4 has a complete set of monitoring wells, but no mining has occurred to date. The mining was followed by a restoration process except in the most recently mined PAA 3, where the site groundwater treated by reverse osmosis was injected back into the aquifer. A network of existing wells, drilled within and up-gradient and down-gradient of the ore body, was used for post-mining monitoring of the site. The baseline (BL) wells located within the production zone was used for monitoring the water quality in the ore zone, while the up-gradient and down-gradient monitoring wells (MW) were used to ensure that there was no

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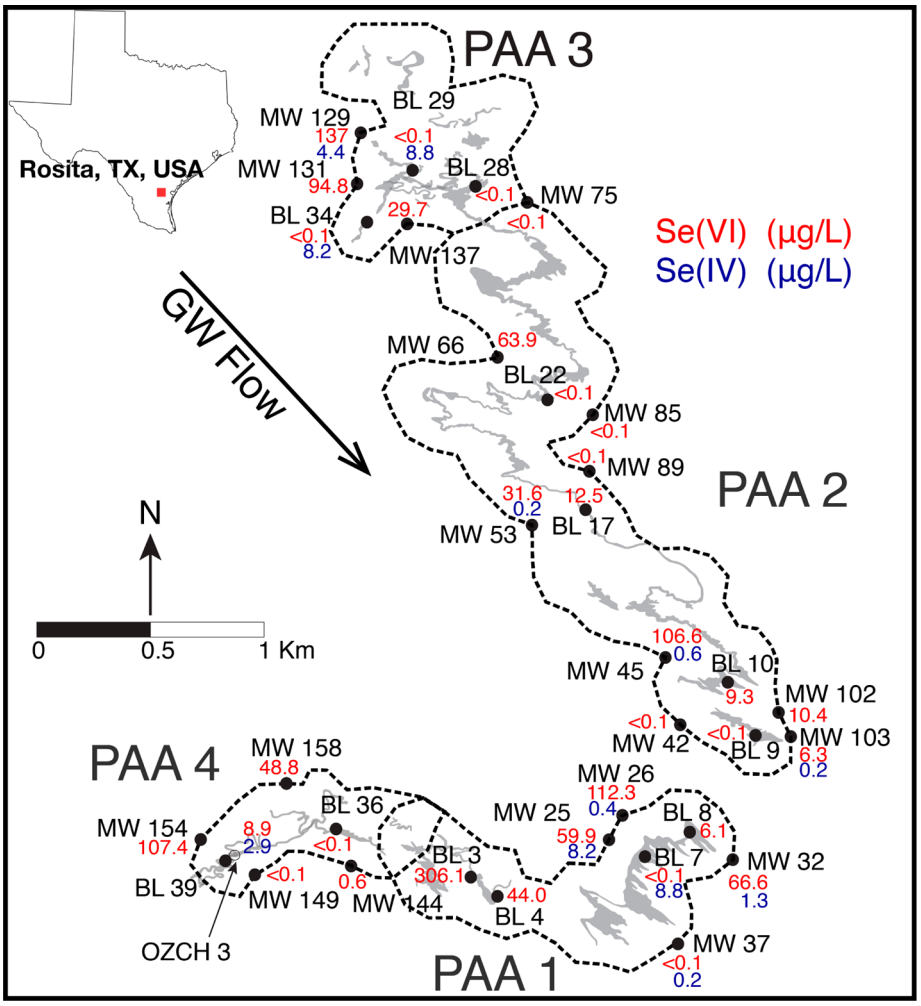

Figure 2. Map of the Rosita ISR site showing the mining units (PAA) and the distribution of Se(VI). Light gray areas define the roll-front U deposit. Black dots represent locations of wells sampled for Se oxyanion and Se isotope measurements, and the open circle shows the location of the borehole for the U ore sample. The dotted lines represent the perimeter ring of the monitoring wells. Numbers represent Se oxyanion concentrations, Se(VI) (red) and Se(IV) (blue) in μg/L.

excursion of the mining or restoration fluid leaving the ore zone.

Groundwater samples were collected from 33 wells along transects roughly parallel to the current groundwater flow direction. The wells were purged prior to sampling, and samples for Se oxyanion concentrations and Se isotopes were filtered using 0.45 μm in-line filters and collected in precleaned HDPE bottles with no headspace and no preservatives. The samples were stored at 4 °C prior to analysis.

Sediment Digestion. U ore samples were obtained from a borehole (OZCH 3) adjacent to BL 39 in PAA 4 (Figure 2). For Se concentration and isotopic analysis, 1.0 g aliquots of sediment samples from seven discrete depths were digested in an acid mixture (concentrated HCl + concentrated HNO_3, 3:1 v/v). First, each 1.0 g aliquot was treated with 4 mL of ∼7 M HNO_3 in Teflon beakers at 80 °C for about 12 h to remove any carbonate from the sediments. The remaining HNO_3 was then evaporated to near-dryness at 60 °C prior to addition of a freshly prepared acid mixture of HCl and HNO_3. The samples were digested at 80 °C for 24 h. After digestion, the acid mixture was removed by evaporating to near-dryness at 70 °C, and 5 mL of 0.1 N HCl was added. This solution was filtered using 0.45 μm PTFE filters to remove undigested particles.

Sample Purification and Mass Spectrometry. Se isotope ratios were measured using multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) at the Department of Geology, University of Illinois, Urbana–Champaign following the methods described in Schilling et al., 2014 and 2015.[28,29] For isotopic measurements, we used a double spike technique (^{74}Se + ^{77}Se) to correct for the isotopic fractionation during mass spectrometry and any that might occur during sample purification by ion exchange chromatography.[28,29] An aliquot of the double-spike solution of appropriate species (either Se(IV) or Se(VI)) was added to a carefully weighed aliquot of the sample (groundwater or digested U ore) containing approximately 100 ng of Se.

The Se oxyanion species was purified from other Se species and matrix elements by ion exchange chromatography.[29] For the separation of Se(VI), the samples were first acidified with HCl to a final strength not exceeding 0.1 M HCl. The acidified samples were passed through the anion exchange resin (Eichrom Technologies LLC, Lisle, IL), where Se(VI) was adsorbed onto the resin, while Se(IV) and other matrix elements (e.g., As and Ge) were rinsed out with 0.1 M HCl. Se(VI) was eluted from the resin by 6 M HCl and heated to 105 °C for 1 h. Finally, the samples were diluted to 2 M HCl,

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Table 1. Se Concentrations and Isotope Ratios in Rosita Groundwater and U Ore[a]

Rosita groundwater							
well	location	PAA	Se(VI) μg/L	$\delta^{82}Se_{VI}$	Se(IV) μg/L	$\delta^{82}Se_{IV}$	Eh (mV)
BL 3	ore zone	1	306.06	−1.46‰	<0.1		
BL 4	ore zone	1	44.02	0.97‰	<0.1		−6.0
BL 7	ore zone	1	<0.1		8.61	−1.36‰	−37.5
BL 8	ore zone	1	6.08	0.82‰	<0.1		46.4
BL 9	ore zone	2	<0.1		<0.1		9.2
BL 10	ore zone	2	9.32	0.97‰	<0.1		81.2
BL 17	ore zone	2	12.51	5.19‰	<0.1		−64.5
BL 22	ore zone	2	<0.1		<0.1		−42.6
BL 28	ore zone	3	<0.1		<0.1		−62.7
BL 29	ore zone	3	<0.1		3.18	0.51‰	−82.5
BL 34	ore zone	3	<0.1		8.22	0.73‰	−59.4
MW 25	up-gradient	1	59.87	0.58‰	8.17	−2.92‰	23.3
MW 26	up-gradient	1	112.27	0.9‰	0.4	ND	56.5
MW 32	down-gradient	1	66.56	0.45‰	1.29	−6.45‰	56.1
MW 37	down-gradient	1	<0.1		0.15	−2.63‰	−105.5
MW 42	up-gradient	2	<0.1		<0.1		34.0
MW 45	up-gradient	2	106.62	−0.47‰	0.61	ND	69.5
MW 53	up-gradient	2	31.59	0.83‰	0.24	ND	40.5
MW 66	up-gradient	2	63.87	0.7‰	<0.1		56.5
MW 75	down-gradient	3	<0.1		<0.1		−11.7
MW 85	down-gradient	2	<0.1		<0.1		−22.3
MW 89	down-gradient	2	<0.1		<0.1		−29.0
MW 102	down-gradient	2	10.38	1.12‰	<0.1		90.2
MW 103	down-gradient	2	6.26	0.59‰	0.2	−4.66‰	94.2
MW 129	up-gradient	3	137.01	0.43‰	4.35	−3.69‰	35.4
MW 131	up-gradient	3	94.84	0.54‰	<0.1		76.5
MW 137	down-gradient	3	29.72	0.51‰	<0.1		−59.5
BL 36	ore zone	4	<0.1		<0.1		
BL 39	ore zone	4	8.97	6.14‰	2.87	−0.61‰	
MW 144	down-gradient	4	0.6	ND	<0.1		
MW 149	down-gradient	4	<0.1		<0.1		
MW 154	up-gradient	4	107.44	2.22‰	<0.1		
MW 158	up-gradient	4	48.83	−1.12‰	<0.1		

Rosita U ore		
depth below ground surface (m)	Se (μg/kg)	$\delta^{82}Se$
60.66−60.96 (background)	24.3	−1.54‰
66.14−66.45	36.8	−1.28‰
66.45−66.75	33.8	−0.85‰
66.75−67.06	30.8	−0.62‰
67.06−67.21	31.7	−0.79‰
70.71−71.02	47.6	−0.64‰
71.02−71.32	39.0	−0.40‰

[a]ND: not determined. Eh measurements are from Basu et al., 2015.

sparged with N_2 to remove a volatile Br species, and equilibrated with Kr in the air for 12 h prior to isotopic analysis.

For Se(IV) extraction, the samples were not acidified before loading on the anion exchange resin. The Se(VI) was adsorbed onto the resin, and the effluent containing Se(IV) was collected by rinsing with 0.1 M HCl and then oxidized to Se(VI) by treatment with $K_2S_2O_8$ at 100 °C for 1 h. After oxidation, all samples were purified using the above procedure for Se(VI) purification.

For purification of Se from the digested U ore (as Se(IV)), we first evaporated the samples to near-dryness and then redissolved them in 5 mL of 0.1 M HCl. An aliquot of this solution containing ∼100 ng of Se was brought to a strength of 4−6 M HCl prior to purification by hydride generation described in ref 30. The H_2Se was trapped in a mixture of NaOH and H_2O_2 and converted to Se(VI). The excess H_2O_2 was removed from the samples by heating (∼100 °C) prior to purification using the procedure for Se(VI) described above.

Se isotope ratios are reported as $\delta^{82}Se$ relative to the isotopic standard reference material NIST SRM 3149,[31] defined as

$$\delta^{82}\mathrm{Se} = \left[\frac{(^{82}\mathrm{Se}/^{76}\mathrm{Se})_{\mathrm{sample}}}{(^{82}\mathrm{Se}/^{76}\mathrm{Se})_{\mathrm{SRM3149}}} - 1\right] \times 1000‰ \quad (2)$$

The uncertainty (2σ) of $\delta^{82}Se$ measurements, calculated from the twice the root mean square (RMS, 95% confidence level)[32] of 24 duplicate sample preparations and analysis, was 0.17‰. The value of the isotopic fractionation factor (α) was

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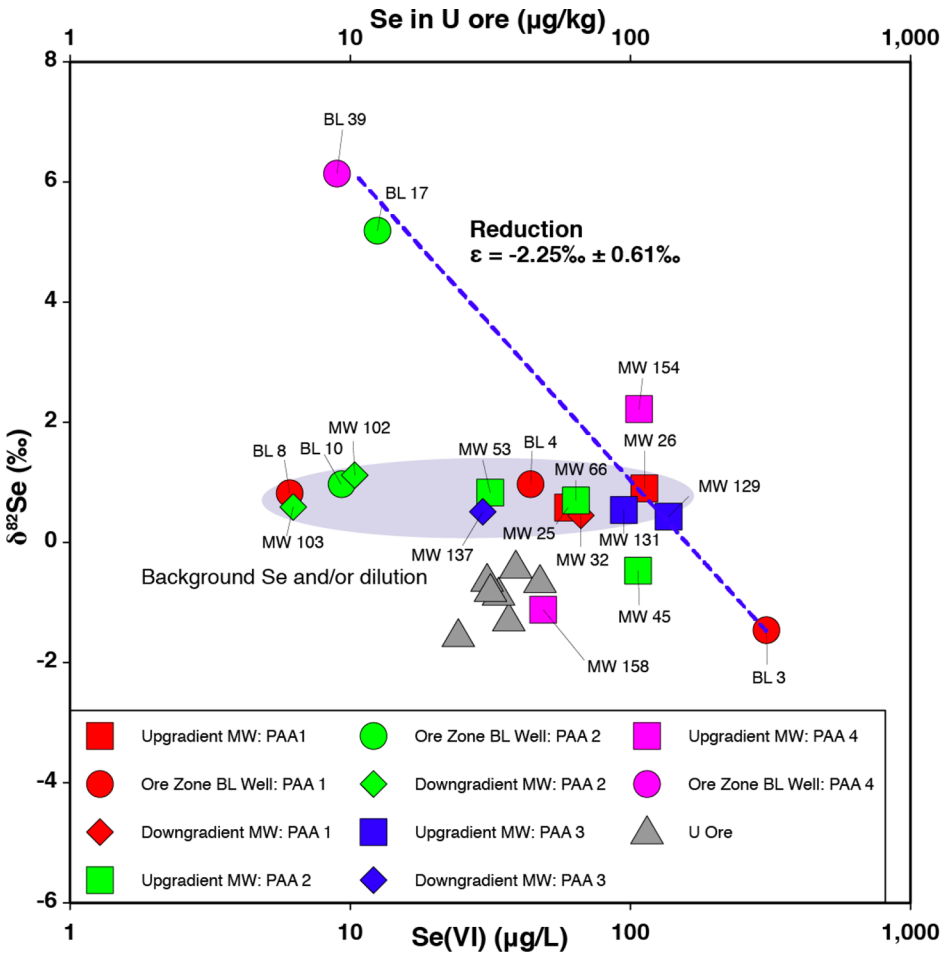

Figure 3. δ^{82}Se of aqueous Se(VI) in Rosita groundwater and Se minerals in the U ore vs Se concentration. Gray triangles represent the U ore, and red, green, blue, and pink symbols represent groundwater from mining units PAA 1, PAA 2, PAA 3, and PAA 4, respectively. The error bars (2 × SE) are smaller than the size of the symbols. The blue dotted line represent the modeled δ^{82}Se using a Rayleigh distillation model with ε = −2.25‰ ± 0.61‰, excluding the samples with NO_3^-.

determined from the slope of the best-fit line from the linearized plot of $\ln(\delta^{82}\text{Se} + 1000‰)$ versus $\ln(\text{Se(VI)})$.[33] The uncertainties (2σ) of ε were ±0.6‰, calculated from the scatter of the data points around the best-fit line using standard linear estimation methods.

RESULTS AND DISCUSSION

Se Concentrations in Rosita Groundwater and U Ore.

We have quantified Se(VI) and Se(IV) concentrations in the Rosita groundwater (Table 1) to understand the distribution pattern of the aqueous Se species at the study site. Se(VI) is the dominant species with concentrations up to 306 µg/L in the groundwater samples, while Se(IV) is found in fewer samples and only at concentrations below 9 µg/L. Generally, except for ore-zone wells BL 3 and BL 4, groundwater from the up-gradient monitoring wells has higher Se(VI) compared to that in the ore-zone or down-gradient monitoring wells. We did not observe any systematic pattern in the distribution of Se(IV) at the site. Out of 12 samples with measurable Se(IV), three ore-zone wells (BL 7, BL 29, and BL 34) and one down-gradient well, MW 37, contain only Se(IV), while the rest contain both Se(VI) and Se(IV). In the previously mined parts of the site, the down-gradient monitoring wells MW 37, MW 75, MW 85, and MW 89, contain little (<1 µg/L) or no Se oxyanions, either as Se(VI) or Se(IV). The wells MW 32, MW 102, MW 103, and MW 137, located directly down-gradient of the mapped discontinuities of the ore body (Figure 2), contain substantial amount of Se(VI) and, in some cases, Se(IV). In the unmined PAA 4, the down-gradient wells show little dissolved Se: MW 149 has no Se oxyanions, whereas MW 144 contains 0.6 µg/L Se(VI) and Se(IV) below detection level (<0.1 µg/L).

The Se concentrations in the U ore collected at seven discrete depths from borehole OZCH 3 adjacent to the ore-zone well BL 39 in the unmined PAA 4 area are low and vary from 24 to 48 µg/kg (Table 1). There is no apparent trend in the Se concentrations with depth. However, the samples with the highest U concentrations collected from 70.71−71.32 m below the ground surface also contain the highest amount of Se. The U ore was not characterized for the identity of Se bearing minerals, but previous work identified ferroselite and elemental Se as the dominant Se-bearing species in South Texas and other roll-front type U deposits.[1,2,34−37]

Se Isotope Ratios in Rosita Grondwater and U Ore.

The δ^{82}Se in groundwater samples from all PAAs and in the U ore are provided in Table 1. The δ^{82}Se of aqueous Se(VI) varies from −1.46‰ to +6.14‰, with most of the samples showing elevated δ^{82}Se relative to the Se isotope standard SRM 3149 (i.e., δ^{82}Se > 0.0‰) (Figure 3). The highest δ^{82}Se of Se(VI) is observed in groundwater from the ore-zone well BL 39 from the unmined PAA 4 area, while BL 3 from the already-mined

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PAA 1 exhibits the most-depleted δ^{82}Se value (−1.46‰). In a subset of samples, there is an apparent trend of increasing $\delta^{82}Se_{VI}$ with decreasing Se(VI) (Figure 3). Contrary to the δ^{82}Se values of Se(VI), δ^{82}Se of Se(IV) is substantially depleted by up to −6.45‰ except in samples from BL 29 ($\delta^{82}Se_{IV}$ = 0.51‰) and BL 34 ($\delta^{82}Se_{IV}$ = 0.73‰). Notably, these wells had no measurable Se(VI). In the samples containing both Se oxyanion species, Se(IV) is isotopically lighter than Se(VI) with Δ^{82}Se ($\approx\delta^{82}Se_{VI} - \delta^{82}Se_{IV}$) ranging from 3.5‰ to 6.9‰. We observe a weak correlation between Se(IV) concentration and $\delta^{82}Se_{IV}$ of the groundwater samples; the $\delta^{82}Se_{IV}$ decreases with decreasing Se(IV) (Figure S1).

The Se isotope compositions of the Se minerals in the U ore from seven discrete depths are provided in Table 1. The δ^{82}Se of the U ore ranges from −1.28‰ to −0.40‰. The median value of −0.72‰ is low relative to those of the majority of the groundwater Se(VI) samples (Figure 3). There is also an enrichment in δ^{82}Se in the ore with increasing depth.

Implication of Se Isotopic Signature of Rosita U Ore. Our observations of ^{82}Se depletion of the ore are limited to a single borehole (OZCH 3) in PAA 4, which does not provide the full extent of the spatial variability in δ^{82}Se of the ore body. Furthermore, the U ore samples from the borehole OZCH 3 are not representative of the Se-enriched portion of the roll-front system generated by reductive precipitation of Se. Lower Se concentrations of the U ore compared to that of up-gradient groundwater suggest a Se-rich sediment up-gradient of the borehole OZCH 3 (Table 1 and Figure 3). This is further supported by our observation of ^{82}Se depletion in the U ore. Ideally, reductive precipitation of Se oxyanions at the redox interface should produce ^{82}Se-depleted Se minerals at the up-gradient fringe of the roll-front deposit. With increasing distance along the hydraulic gradient, the Se minerals should become isotopically heavier. However, after complete removal of Se oxyanions from the groundwater, the Se concentrations and isotopic composition of the sediments should return to background values. The sediments collected 6 m above the ore-bearing zone contain 24.3 μg/kg of Se with a δ^{82}Se of −1.54‰, resembling the ore-zone sediments both in terms of Se concentrations and isotopic composition (Table 1). Therefore, we surmise that Se concentrations and isotopic compositions of our U ore samples reflect the primary Se content of the aquifer sediments.

Se Reduction in Groundwater: Se Concentration Distribution and Geochemical Conditions. The distribution of dissolved Se in Rosita groundwater is consistent with reduction of Se oxyanions, particularly Se(VI) reduction, by naturally occurring reducing environments within and down-gradient of the ore zone. The Se(VI) hotspots at the up-gradient wells or ore-zone wells in the mined part of the site resulted from the oxidation of Se minerals, either during mining or by interaction with the oxygenated recharge water. For example, high Se(VI) up to 107 μg/L in the up-gradient wells MW 158 and MW 154 in the unmined PAA 4 is likely to reflect natural dissolution of Se minerals in the aquifer. In the absence of any Se removal within or down-gradient of the ore zone, the down-gradient wells should show Se(VI) concentrations similar to that of the up-gradient wells. Few or no Se oxyanions in the down-gradient wells, particularly in MW 37, MW 75, MW 85, and MW 89, suggests Se removal before groundwater arrives at these wells.

The observed removal of Se along the hydraulic gradient suggests the geochemical conditions conducive to reduction of Se oxyanions within and down-gradient of the ore zone. At the study site, a progression from nitrate-reducing to Fe(III)-reducing and then to U(VI)-reducing conditions along the hydraulic gradient is inferred from concentrations of the redox species (e.g., NO_3^-, Fe(II), and U(VI)), Eh values, and isotopic measurements (e.g, δ^{15}N, and δ^{238}U) of groundwater samples.[20] Briefly, a general decrease in NO_3^- concentrations along the hydraulic gradient and a linear relation between the δ^{18}O-nitrate and δ^{15}N-nitrate (r^2 = 0.77, n = 11) with a slope ($\Delta\delta^{18}O/\Delta\delta^{15}N$) of 0.73 ± 0.13 is indicative of microbial denitrification. In addition, localized zones of Fe(III) and Mn(IV) reduction is suggested by elevated dissolved Mn (>0.05 mg/L) and Fe (>0.1 mg/L) concentrations in groundwater samples from PAA 1, PAA 2, and PAA 3. Furthermore, decreasing Eh of samples down-gradient of the ore zone (except MW 32, MW 102, MW 103, and MW 137) in all previously mined PAAs, also consistent with the pattern observed for redox-sensitive aqueous species. Among the down-gradient wells investigated by Basu et al. (2015), the samples from MW 37, MW 75, MW 85, and MW 89 exhibited low Eh (−11.7 to −105.5 mV), low U(VI) concentrations (<20 μg/L) and highly depleted δ^{238}U (−1.41‰ to −2.49‰) suggesting naturally occurring reducing environments capable of U(VI) and thus, Se(VI) reduction.

The overall range of Eh and pH suggests thermodynamic favorability of Se oxyanions reduction in Rosita groundwater (Figure 1). The decrease in Se(VI) along the hydraulic gradient is therefore consistent with the Se(VI) and perhaps Se(IV) reduction down-gradient of the ore zone suggested by Basu et al. 2015 on the basis of U isotopes and other evidence. Alternatively, Se(IV) could be strongly adsorbing and removed via sorption onto minerals.

Several down-gradient wells, however, do not follow the general trend of aqueous Se(VI) removal along the hydraulic gradient. These wells, MW 32, MW 102, MW 103, and MW 137, are located directly down-gradient of the mapped gaps in the ore body (Figure 2). These gaps may mark regions that lacked the reducing materials that were responsible for the formation of the ore body in the adjacent areas. This difference implies an unrestricted flow of the up-gradient water rich in Se(VI) and other oxidants (e.g., NO_3^-) (Figure S2) and with a high Eh to the down-gradient wells MW 32, MW 102, MW 103, and MW 137 through these gaps, which conforms to the observations reported in ref 20. The post-mining restoration fluid with high residual Se(VI) is unlikely to arrive at the down-gradient wells due to low groundwater velocity (3−6 m/year) and restriction of flow by net withdrawal of groundwater during restoration. However, the presence of the reduction product Se(IV) in MW 32 and MW 103 suggest existing Se(VI)-reducing conditions in these wells, which is also supported by our Se isotope data (see below).

Se Reduction in Groundwater: Se Isotope Ratios. If all of the variation of δ^{82}Se were due to reduction of Se from a single Se source by a single mechanism, a strong correlation between δ^{82}Se and concentrations of Se oxyanions would be expected. We did not observe a strong correlation between δ^{82}Se and Se(VI) concentrations, which suggests heterogeneous Se sources and complex Se cycling mechanisms. However, the samples that exhibit highly enriched δ^{82}Se (e.g., δ^{82}Se > 4‰) can only be generated by reduction of Se(VI). In the following paragraphs, we discuss the evidence of Se(VI) reduction from the δ^{82}Se data from Rosita groundwater along with potential alternative mechanisms with their limitations.

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In addition to the distribution of Se oxyanion concentrations, Se isotope data from Rosita U ore and groundwater samples help identify pathways of Se cycling and delineate Se(VI)-reducing zones at the study site. The up-gradient groundwater currently entering the roll-front system is Se(VI)-rich, with concentrations ranging from 32 to 137 μg/L (median Se(VI) = 94.84 μg/L). The δ^{82}Se of the up-gradient groundwater also varies from −1.12‰ to +2.22‰, with an average δ^{82}Se of 0.51‰. Because the roll-front system reduces and captures all incoming Se(VI), we hypothesize that the average δ^{82}Se of the U ore should be identical to the average δ^{82}Se of incoming groundwater, assuming that the Se inputs for the U ore were similar to that observed in the present system.

If dissolution of Se minerals were the only mechanism responsible for the observed distribution of Se(VI) in Rosita groundwater, we would expect the groundwater samples to be similar to the inferred average δ^{82}Se of the U ore (~0.5‰). The oxidative dissolution of U ore should yield aqueous Se(VI) with similar isotopic composition, as quantitative layer-by-layer dissolution of Se mineral grains results in negligible isotopic fractionation. However, it is possible for the post-mining groundwater to acquire Se with a range of δ^{82}Se values (e.g., −1.5‰ to ~2‰) because we expect the isotopic composition of Se minerals to exhibit spatial variability in the ore zone. Aqueous Se isotope compositions outside the −1.5‰ to +2.0‰ range suggest an alternate or additional process affecting the Se isotope composition of the groundwater.

The enrichments in δ^{82}Se of Rosita groundwater relative to the inferred average δ^{82}Se of the U ore are likely caused by Se(VI) reduction in Rosita groundwater. With ongoing reduction of Se(VI), the unreacted remaining Se(VI) exhibits ^{82}Se enrichment,[11,22−27,30] while the intermediate product Se(IV) is first enriched in the lighter isotopes (i.e., ^{76}Se) and later, upon further reduction to Se(0) and possibly complete removal of Se(VI), is enriched in ^{82}Se. The largest $^{82}Se_{VI}$ enrichments observed in the ore-zone wells BL 17 and BL 39 are 5.19‰ and 6.14‰, respectively, suggesting a maximum offset of ~6‰ from that of the inferred δ^{82}Se of the U ore. In all samples containing both Se(VI) and Se(IV), Se(IV) is isotopically lighter (i.e., enriched in ^{76}Se, − 6.38‰<δ^{82}Se < 0‰). This suggests that Se(IV) is a product of Se(VI) reduction rather than arising from the oxidation of the U ore. In addition, the two groundwater samples with $^{82}Se_{IV}$ enrichment (i.e., $\delta^{82}Se_{IV}$ > 0‰) have low Eh values ($Eh_{BL\ 29}$ = −82.5 mV and $Eh_{BL\ 34}$ = −59.4 mV) and no detectable Se(VI). This ^{82}Se enrichment in Se(IV) and a lack of Se(VI) suggests that extensive reduction of Se(IV) has occurred in the absence of production of Se(IV) via Se(VI) reduction.

The correlation between Se isotopic shifts and changes in Se oxyanion concentrations also suggests aqueous Se(VI) reduction. When Se(VI) data from all wells are pooled together, we observe two distinct trends in the relationship between δ^{82}Se values and Se(VI) concentrations (Figure 2). First, there is an increasing trend in δ^{82}Se with decreasing Se(VI). Second, for several wells such as BL 8, BL 10, MW 102, MW 103, MW 53, and MW 137, Se(VI) concentrations decrease with no major shift in the δ^{82}Se. In samples showing no major change in δ^{82}Se, particularly in BL 8, BL 10, MW 102, and MW 103, the decrease in Se(VI) may be attributed to a localized mixing with groundwater with relatively low Se, similar to that of MW 42, which is also consistent with relatively high Eh values and NO_3^- concentrations (Figure S2) in these wells.[20] Alternatively, a more likely scenario is that these samples may have acquired variable amounts of Se from the Se-rich zone in the roll-front, with a δ^{82}Se similar to the inferred average δ^{82}Se of the roll-front. The first trend in which δ^{82}Se in a subset of samples increased with decreasing Se(VI) conforms to a Rayleigh-type fractionation model with ε = −2.25‰ ± 0.61‰ calculated excluding Se data from the wells containing measurable NO_3^-. This strongly suggests Se(VI) reduction as the primary mechanism of Se(VI) concentration decrease in these samples.

A pair of alternative mechanisms, mixing and equilibrium isotopic exchange, with the potential to influence the Se isotopic signature of Rosita groundwater are unlikely to play any major role at the study site. The elevation in δ^{82}Se of Se(VI) in BL 39 and BL 17 above ~2‰ cannot be generated by mixing ore-zone groundwater with an average δ^{82}Se of 0.5‰, with the up-gradient water entering the system with a maximum δ^{82}Se of ~2‰. Therefore, mixing cannot account for the observed elevated δ^{82}Se values of Se(VI) in BL 39 and BL 17. Also, an equilibrium isotopic exchange between coexisting dissolved species Se(VI) and Se(IV) or more reduced Se species would lead to ^{82}Se enrichment in Se(VI). This seems highly unlikely under the prevalent geochemical conditions that are far from chemical equilibrium. The rates of exchange between Se(VI) and Se(IV), which requires the transfer of two electrons, have yet to be determined. However, on the basis of recent reports on U(VI)−U(IV) exchange also requiring two electrons transferred,[38] very slow exchange (100 to 1000 years) between Se(VI) and Se(IV) may be inferred at low concentrations (i.e., < 9 μg/L) of Se(IV). In addition, Se(VI)−Se(IV) exchange may further be inhibited by removal of Se(IV) by either adsorption or by reduction to Se(0).[11,39]

Se Isotopes as Redox Indicators in the Unmined Area. In addition to serving as an indicator for reduction of potentially toxic Se oxyanions in groundwater, the results from the unmined PAA 4 area demonstrate that stable Se isotope ratios aid in the precise determination of the redox state of the aquifer at Rosita ISR site (Table S1). Our previous work on U isotope ratios (^{238}U/^{235}U, expressed as δ^{238}U)[20] showed evidence of U(VI) reduction in the transect containing MW 158, BL 36, and MW 144 along the hydraulic gradient, particularly in the ore-zone BL and the down-gradient well, while there was a lack of U(VI)-reducing conditions along another transect (MW 154, BL 39, and MW 149) (Figure 2, Table S1). Along both transects, a decrease in NO_3^- in groundwater from ≥12 mg/L in the up-gradient wells to below detection in the ore-zone BL wells and down-gradient wells was also reported.[20] The western transect, where the lack of a large ^{238}U depletion in groundwater indicated the absence of U(VI) reduction in the ore-zone well BL 39 (δ^{238}U = 0.56‰) and down-gradient MW 149 (δ^{238}U = 0.48‰) shows an overall enrichment in δ^{82}Se of Se(VI) up to ~6‰ relative to the average δ^{82}Se (0.5‰) of the U ore, with BL 39 exhibiting a δ^{82}Se of 6.14‰. This δ^{82}Se of Se(VI) in BL 39 is ~4‰ higher compared to that of the up-gradient well MW 154 (δ^{82}Se = 2.19‰). Se(VI) in the down-gradient well MW 149 is below the detection limit (<0.1 μg/L). This suggests progressively stronger Se(VI)-reducing conditions along the hydraulic gradient.

In comparison, the up-gradient well MW 158 (δ^{238}U = −0.08‰) from the western transect shows ^{82}Se depletion ($\delta^{82}Se_{VI}$ = −1.12‰) with a lower Se(VI) concentration, suggesting spatial heterogeneity both in terms of background Se content and isotopic composition. However, the wells along the

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hydraulic gradient in this transect with highly fractionated U isotope ratios, BL 36 ($\delta^{238}U = -1.61‰$) and MW 144 ($\delta^{238}U = -1.96‰$), have very little or no detectable Se oxyanions, suggesting almost-quantitative reduction of Se(VI) and Se(IV) removal of Se(IV) via adsorption onto aquifer material, or both. Thus, the results from the unmined PAA4 demonstrate the effectiveness of Se isotope ratios in delineating Se(VI)-reducing environments and in providing additional information about existing redox conditions that can not be obtained from the U isotopic data alone.

Fractionation Mechanisms at Rosita and Comparison of ε with Previous Studies. The magnitude of the Se isotope fractionation observed at Rosita is more consistent with a microbial reduction mechanism than with abiotic reduction, but there is still sufficient uncertainty that abiotic reduction cannot be ruled out. Johnson et al. 2011 provides a detailed review of the magnitudes of Se isotope fractionation for various abiotic reductants and microbial species. Microbial reduction of Se oxyanions yields a range of ε values spanning from −0.3‰ to −7.5‰ for the reduction of Se(VI) to Se(IV) and from −1.7‰ to −12‰ for the reduction of Se(IV) to Se(0). The abiotic reduction of Se generally yields consistently large (>−10‰) isotopic fractionations. The ε for reduction of Se(VI) to Se(IV) by the Fe(II)−Fe(III) layered double hydroxide mineral "green rust", a likely reductant in soils and sediments, is ∼−11‰, while the reduction to Se(IV) to Se(0) by FeS and NH_2OH or ascorbic acid produces a fractionation (as ε) of −10‰ and −15.0 to −19.2‰, respectively. The ε determined from the groundwater samples from the Rosita ISR site (−2.25‰ ± 0.61‰) is much smaller in comparison to that observed during abiotic Se(VI) reduction and falls within the range observed during Se(VI) reduction by natural microbial consortia.[24] Despite some heterogeneities, the observed sequence of redox reactions along the hydraulic gradient from NO_3^- reducing to Fe(III)- and U(VI)-reducing environments is also consistent with the microbially mediated redox ladder in aquifers.[40] However, reservoir effects arising from the lack of chemical communication between the zones of reduction (e.g., biofilms or mineral surfaces in clay-rich zones) and the bulk dissolved Se(VI) in the more rapidly flowing parts of the sandy aquifer may limit the expression of overall isotopic fractionation in groundwater samples and thus lead to a diminished apparent ε value.[30] Future research involving similar sites should be directed toward identification of the Se-reduction mechanism and determination of ε at the site using analysis of the temporal trend of Se oxyanion concentrations with Se isotope ratios from the target wells. Additionally, the ε determined from the field data should be complemented by laboratory experiments for the site-specific reduction mechanism.

Implications for Monitoring of Se and U Reduction at ISR Sites. The results of this study demonstrate that Se isotope ratios are effective indicators of natural attenuation of Se(VI), a residual product of ISR mining and a potential water contaminant for several ISR sites. Furthermore, our results suggest that the Se isotope ratios record the redox environments precursory to U(VI)-reducing conditions that cannot be obtained from the concentration (e.g., Se(VI) or U(VI)) data alone.

A groundwater monitoring approach combining Se isotope ratios with U isotopic measurements is therefore advantageous in determining conditions conducive for post-mining natural attenuation of contaminants at ISR sites. For instance, naturally occurring aqueous and adsorbed Fe(II),[41,42] magnetite[43,44] and titanomagnetite,[45] and FeS[46,47] (both residual after mining and biogenic) may readily reduce U(VI) in aquifers. These abiotic reductants are also capable of reducing Se(IV).[48−51] Thus, in addition to $\delta^{238}U$, $\delta^{82}Se$ of groundwater would provide an improved characterization of the existing redox state and reducing capacity of the aquifer. In aquifers with a need for active remediation, the knowledge of the existing redox state is also important to determine the remediation strategy and the choice of reductant (if used) to avoid aggressive reductive remediation, which may mobilize contaminants such as arsenic.

Our measurements on Se speciation and stable Se isotopes reveal the spatial distribution at a single time and do not provide direct information on time-dependent changes in Se oxyanion concentrations and concomitant changes in Se isotope ratios. Efficient post-mining monitoring of reduction should include time-series measurements of Se oxyanion concentration and Se isotope ratios in samples from the target ore-zone BL wells or wells from the monitoring ring. This would enable more-accurate determination of the exact relationship between the changes in Se(VI) and Se(IV) concentrations in a target well and the associated shifts in $\delta^{82}Se$ (or the site-specific isotopic fractionation factor), which is required for the quantification of Se remediation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b01464.

Tables showing a comparison between Se(VI) and U(VI) concentrations in groundwater from PAA 4 along with Se ($\delta^{82}Se$) and U isotope ratios ($\delta^{238}U$). Figures showing the correlation between $\delta^{82}Se_{IV}$ and Se(IV) and the distribution of NO_3^- in Rosita groundwater. (PDF)

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Notes

The authors declare no competing financial interest.

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