Se isotopes as groundwater redox indicators: Detecting natural attenuation of Se at an in situ recovery U mine

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ABSTRACT

One of the major ecological concerns associated with in situ recovery (ISR) of uranium is the environmental release of soluble, toxic Se-oxyanions generated by mining. Postmining natural attenuation by the residual reductants in the ore body and reduced downgradient 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 upgradient wells have elevated Se(VI), the majority of the ore zone and downgradient wells have little 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 $-2.25‰ \pm 0.61‰$ 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 postmining 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 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 uranium 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 co-precipitation of Se-minerals and U minerals.

In contrast, the oxidative dissolution of U ore enriched with Se minerals mobilizes Se and U in the groundwater in their toxic, oxidized forms. Se in the effluent from a traditional U mining and milling operation in northern Saskatchewan, Canada, led to 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 USA (e.g., Puerco River, Arizona; New Mexico; Rifle,

CO)[14,15]. At present, almost all recent U mining in the USA and ~50% of global U mining employs 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 downgradient 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 downgradient 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/or Se(IV) should precede U(VI) reduction. The challenge is to identify the active reduction of Se in the ore zone and/or downgradient 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, ^{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

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

where α is the isotopic fractionation factor, defined as $\alpha = \frac{R_{product}}{R_{reactant}}$, where $R_{product}$ and $R_{reactant}$ are the ^{82}Se/^{76}Se ratios 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) (ε ~ –8‰) and of Se(IV) to elemental Se (ε ~ –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 postmining 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 upgradient, within and downgradient 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 3 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, upgradient and downgradient of the ore body, was used for postmining 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 upgradient and downgradient monitoring wells (MW) were used to ensure that there was no 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 pre-cleaned 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 adjacent to BL 39 in PAA 4 (Figure 2). For Se concentration and isotopic analysis, 1.0 g aliquots of sediment samples from 7 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 hrs 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 hr. 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 multi-collector 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, 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) where Se(VI) was adsorbed onto the resin

while Se(IV) and other matrix elements (e.g., As, Ge) were rinsed out by 0.1 M HCl. Se(VI) was eluted from the resin by 6M HCl and heated to 105 °C for 1 hr. Finally, the samples were diluted to 2 M HCl, sparged with N_2 to remove a volatile Br species, and equilibrated with Kr in the air for 12 hr 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, then oxidized to Se(VI) by treatment with $K_2S_2O_8$ at 100 °C for 1 hr. 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 re-dissolved them in 5 mL 0.1 M HCl. An aliquot of this solution containing ~ 100 ng 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 δ^{82}Se relative to the isotopic standard reference material NIST SRM 3149[31], defined as

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

The uncertainty (2σ) of δ^{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 determined from the slope of the best-fit line from the linearized plot of ln(δ^{82}Se + 1000‰) vs. ln(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 upgradient monitoring wells has higher Se(VI) compared to that in the ore zone or downgradient 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), 3 ore zone wells (BL 7, BL 29 and BL 34) and one downgradient 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 downgradient 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 downgradient 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 downgradient 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 7 discrete depths from borehole OZCH3 adjacent to the ore zone well BL 39 in the unmined PAA4 area, are low and vary from 24 μg/kg 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

193 Se bearing minerals, but previous work identified ferroselite and elemental Se as the dominant
194 Se bearing species in South Texas and other roll-front type U deposits[1,2,34-37].

195 **Se Isotope Ratios in Rosita Grondwater and U Ore.** The δ^{82}Se in groundwater samples from
196 all PAAs and in the U ore are provided in Table 1. The δ^{82}Se of aqueous Se(VI) varies from
197 −1.46‰ to +6.14‰, with most of the samples showing elevated δ^{82}Se relative to the Se isotope
198 standard SRM 3149 (i.e., δ^{82}Se >0.0‰) (Figure 3). The highest δ^{82}Se of Se(VI) is observed in
199 groundwater from the ore zone well BL 39 from the unmined PAA4 area, while BL 3 from the
200 already mined PAA1 exhibits the most depleted δ^{82}Se value (−1.46‰). In a subset of samples
201 there is an apparent trend of increasing $\delta^{82}Se_{VI}$ with decreasing Se(VI) (Figure 3). Contrary to the
202 δ^{82}Se values of Se(VI), δ^{82}Se of Se(IV) is substantially depleted by up to −6.45‰, except in
203 samples from BL 29 ($\delta^{82}Se_{IV}$ = 0.51‰) and BL 34 ($\delta^{82}Se_{IV}$ = 0.73‰). Notably, these wells had
204 no measurable Se(VI). In the samples containing both Se oxyanion species, Se(IV) is isotopically
205 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
206 weak correlation between Se(IV) concentration and $\delta^{82}Se_{IV}$ of the groundwater samples; the
207 $\delta^{82}Se_{IV}$ decreases with decreasing Se(IV) (Figure S1).

208 The Se isotope compositions of the Se minerals in the U ore from 7 discrete depths are
209 provided in Table 1. The δ^{82}Se of the U ore ranges from −1.28‰ to −0.40‰. The median value
210 of −0.72‰ is low relative to the majority of the groundwater Se(VI) samples (Figure 3). There is
211 also an enrichment in δ^{82}Se in the ore with increasing depth.

212 **Implication of Se Isotopic Signature of Rosita U ore.** Our observations of ^{82}Se depletion of
213 the ore are limited to a single borehole (OZCH3) in PAA4, which does not provide the full extent
214 of the spatial variability in δ^{82}Se of the ore body. Furthermore, the U ore samples from the
215 borehole OZCH3 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 upgradient groundwater suggest a Se rich sediment upgradient of the borehole OZCH3 (Table 1, 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 upgradient 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 6m above the ore-bearing zone contain 24.3 μg/kg of Se with a $\delta^{82}Se$ 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 downgradient of the ore zone. The Se(VI) hotspots at the upgradient 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 upgradient wells MW 158 and MW 154 in the unmined PAA 4 is likely to reflect natural dissolution of Se minerals in the aquifer. In absence of any Se removal within or downgradient of the ore zone, the downgradient wells should show Se(VI) concentrations similar to that of the upgradient wells. Little or no Se oxyanions in the downgradient 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 is consistent with the geochemical conditions conducive to reduction of Se-oxyanions within and downgradient 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, $\delta^{15}N$, and $\delta^{238}U$) of groundwater samples[20]. Briefly, a general decrease in NO_3^- concentrations along the hydraulic gradient and a linear relation between the $\delta^{18}O$-nitrate and $\delta^{15}N$-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 PAA1, PAA2, and PAA3. Furthermore, decreasing Eh of samples downgradient of the ore zone (except MW 32, MW 102, MW 103, MW 137) in all previously mined PAAs also consistent with the pattern observed for redox sensitive aqueous species. Among the downgradient wells investigated by Basu et al. (2015), the samples from MW 37, MW 75, MW 85, and MW 89 exhibited low Eh (–11.7 mV to –105.5 mV), low U(VI) concentrations (< 20 μg/L) and highly depleted $\delta^{238}U$ (–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 in downgradient the reducing environments suggested by Basu et al. 2015 based on U isotopes and other evidence. Alternatively, Se(IV) could be strongly adsorbing and removed via sorption onto minerals.

Several downgradient 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 downgradient 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 upgradient water rich in Se(VI) and other oxidants (e.g., NO_3^-) (Figure S2) and with a high Eh to the downgradient wells MW 32, MW 102, MW 103, and MW 137 through these gaps, which is consistent with the observations reported in reference 20. The postmining restoration fluid with high residual Se(VI) is unlikely to arrive at the downgradient 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 $\delta^{82}Se$ were due to reduction of Se from a single Se source by a single mechanism, a strong correlation between $\delta^{82}Se$ and concentrations of Se-oxyanions would be expected. We did not observe a strong correlation between $\delta^{82}Se$ and Se(VI) concentrations which suggests heterogeneous Se sources and complex Se cycling mechanisms. However, the samples that exhibit highly enriched $\delta^{82}Se$ (e.g., $\delta^{82}Se > 4‰$) can only be generated by reduction of Se(VI). In the following paragraphs, we discuss the evidence of Se(VI) reduction from the $\delta^{82}Se$ data from Rosita groundwater along with potential alternative mechanisms with their limitations.

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 upgradient groundwater currently entering the roll-front system is

Se(VI)-rich with concentrations ranging from 32 μg/L to 137 μg/L (median Se(VI) = 94.84 μg/L). The δ^{82}Se of the upgradient groundwater also varies from −1.12‰ to +2.22‰, with an average δ^{82}Se of 0.51‰. Since 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 postmining 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 $^{82}\varepsilon_{VI}$ 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

307 ^{76}Se, $-6.38‰ < \delta^{82}Se < 0‰$). This suggests that Se(IV) is a product of Se(VI) reduction rather than
308 arising from the oxidation of the U ore. In addition, the two groundwater samples with $^{82}Se_{IV}$
309 enrichment (i.e., $\delta^{82}Se_{IV} > 0‰$) have low Eh ($Eh_{BL\ 29} = -82.5$ mV and $Eh_{BL\ 34} = -59.4$ mV) and
310 no detectable Se(VI). This ^{82}Se enrichment in Se(IV) and a lack of Se(VI) suggests extensive
311 reduction of Se(IV) has occurred in the absence of production of Se(IV) via Se(VI) reduction.
312 The correlation between Se isotopic shifts and changes in Se oxyanion concentrations also
313 suggests aqueous Se(VI) reduction. When Se(VI) data from all wells are pooled together, we
314 observe two distinct trends in the relationship between $\delta^{82}Se$ values and Se(VI) concentrations
315 (Figure 2). First, there is an increasing trend in $\delta^{82}Se$ with decreasing Se(VI). Second, for several
316 wells such as BL 8, BL 10, MW 102, MW 103, MW 53, and MW 137, Se(VI) concentrations
317 decrease with no major shift in the $\delta^{82}Se$. In samples showing no major change in $\delta^{82}Se$,
318 particularly in BL 8, BL 10, MW 102, and MW 103, the decrease in Se(VI) may be attributed to
319 a localized mixing with groundwater with relatively low Se, similar to that of MW 42, which is
320 also consistent with relatively high Eh values and NO_3^- concentrations (Figure S2) in these
321 wells[20]. Alternatively, a more likely scenario is that these samples may have acquired variable
322 amounts of Se from the Se-rich zone in the roll-front with a $\delta^{82}Se$ similar to the inferred average
323 $\delta^{82}Se$ of the roll-front. The first trend where $\delta^{82}Se$ in a subset of samples increased with
324 decreasing Se(VI) conforms to a Rayleigh-type fractionation model with $\varepsilon = -2.25‰ \pm 0.61‰$
325 calculated excluding Se data from the wells containing measurable NO_3^-. This strongly suggest
326 Se(VI) reduction as the primary mechanism of Se(VI) concentration decrease in these samples.
327 Two alternative mechanisms, mixing and equilibrium isotopic exchange, with the potential to
328 influence the Se isotopic signature of Rosita groundwater are unlikely to play any major role at
329 the study site. The elevation in $\delta^{82}Se$ 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 upgradient 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 transfer of two electrons, have yet to be determined. However, based on recent reports on U(VI)-U(IV) exchange also requiring two electrons transferred[38], very slow exchange (100 to 1000 yrs) between Se(VI) and Se(IV) may be inferred at very 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 downgradient well, while there was a lack of U(VI) reducing conditions along another transect (MW 154, BL 39, MW 149) (Figure 2, Table S1). Along both transects, a decrease in NO_3^- in groundwater from ≥12 mg/L in the upgradient wells to below detection in the ore zone BL wells and downgradient 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 downgradient MW 149 (δ^{238}U = 0.48‰), shows an overall

enrichment in $\delta^{82}Se$ of Se(VI) up to ~6‰ relative to the average $\delta^{82}Se$ (0.5‰) of the U ore with BL 39 exhibiting a $\delta^{82}Se$ of 6.14‰. This $\delta^{82}Se$ of Se(VI) in BL 39 is ~4‰ higher compared to that of the upgradient well MW 154 ($\delta^{82}Se$ = 2.19‰). Se(VI) in the downgradient 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 upgradient well MW 158 ($\delta^{238}U$ = –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 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 either almost quantitative reduction of Se(VI) and Se(IV) and/or removal of Se(IV) via adsorption onto aquifer material. 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 that 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 small compared 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 postmining 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 would 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/or 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(VI) remediation.

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collection and drilling. The US Dept of Energy provided salary support for DJD and JNC during the study period under Contract No. DE-AC02-05CH11231. We thank two anonymous reviewers and Associate Editor Daniel Giammar for constructive comments that improved the quality of this manuscript.

Associated Content. Correlation between $\delta^{82}Se_{IV}$ and Se(IV), and distribution of NO_3^- in Rosita groundwater Comparison between Se(VI) and U(VI) concentrations in groundwater from PAA 4 along with Se ($\delta^{82}Se$) and U isotope ratios ($\delta^{238}U$), are provided in the Supporting Information. This information is available free of charge via the Internet at http://pubs.acs.org.

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572 Table 1. Se concentrations and isotope ratios in Rosita groundwater and U ore (ND = Not
573 determined). Eh measurements are from Basu et al., 2015.

Rosita Groundwater

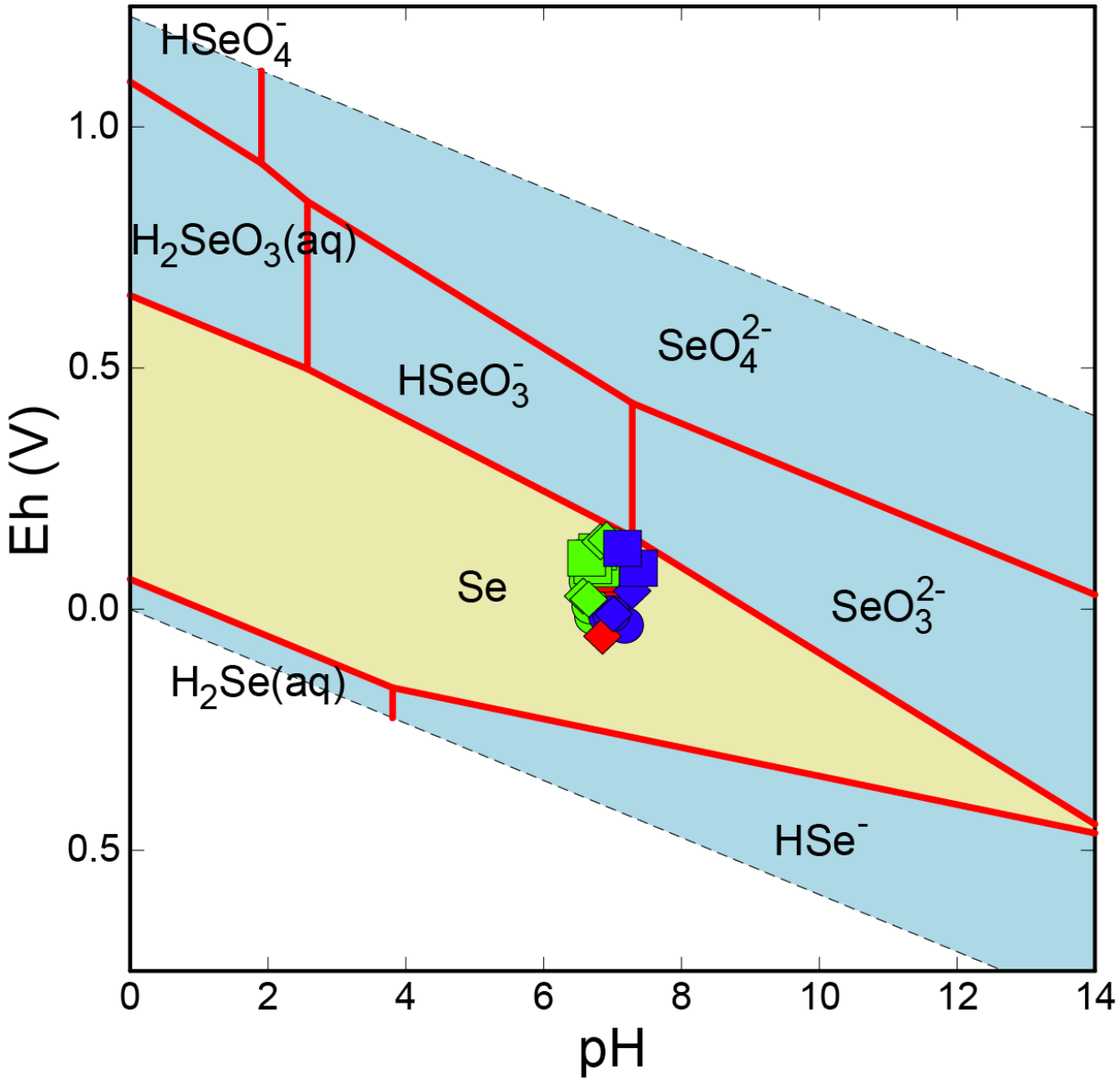
Well	Location	PAA	Se(VI) µg/L	$\delta^{82}Se_{VI}$	Se(IV) µg/L	$\delta^{82}Se_{IV}$	Eh (mV)
BL 3	Ore zone	1	306.06	-1.46‰	<0.1		
BL 4	Ore zone	1	44.02	0.97‰	<0.1		-6.0
BL 7	Ore zone	1	<0.1		8.78	-1.36‰	-37.5
BL 8	Ore zone	1	6.08	0.82‰	<0.1		46.4
BL 9	Ore zone	2	<0.1		<0.1		9.2
BL 10	Ore zone	2	9.32	0.97‰	<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	Upgradient	1	59.87	0.58‰	8.17	-2.92‰	23.3
MW 26	Upgradient	1	112.27	0.9‰	0.4	ND	56.5
MW 32	Downgradient	1	66.56	0.45‰	1.29	-6.45‰	56.1
MW 37	Downgradient	1	<0.1		0.15	-2.63‰	-105.5
MW 42	Upgradient	2	<0.1		<0.1		34.0
MW 45	Upgradient	2	106.62	-0.47‰	0.61	ND	69.5
MW 53	Upgradient	2	31.59	0.83‰	0.24	ND	40.5
MW 66	Upgradient	2	63.87	0.7‰	<0.1		56.5
MW 75	Downgradient	3	<0.1		<0.1		-11.7
MW 85	Downgradient	2	<0.1		<0.1		-22.3
MW 89	Downgradient	2	<0.1		<0.1		-29.0

MW 102	Downgradient	2	10.38	1.12‰	<0.1		90.2
MW 103	Downgradient	2	6.26	0.59‰	0.2	-4.66‰	94.2
MW 129	Upgradient	3	137.01	0.43‰	4.35	-3.69‰	35.4
MW 131	Upgradient	3	94.84	0.54‰	<0.1		76.5
MW 137	Downgradient	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‰	
MW144	Downgradient	4	0.6	ND	<0.1		
MW149	Downgradient	4	<0.1		<0.1		
MW154	Upgradient	4	107.44	2.22‰	<0.1		
MW158	Upgradient	4	48.83	-1.12‰	<0.1		

Rosita U ore

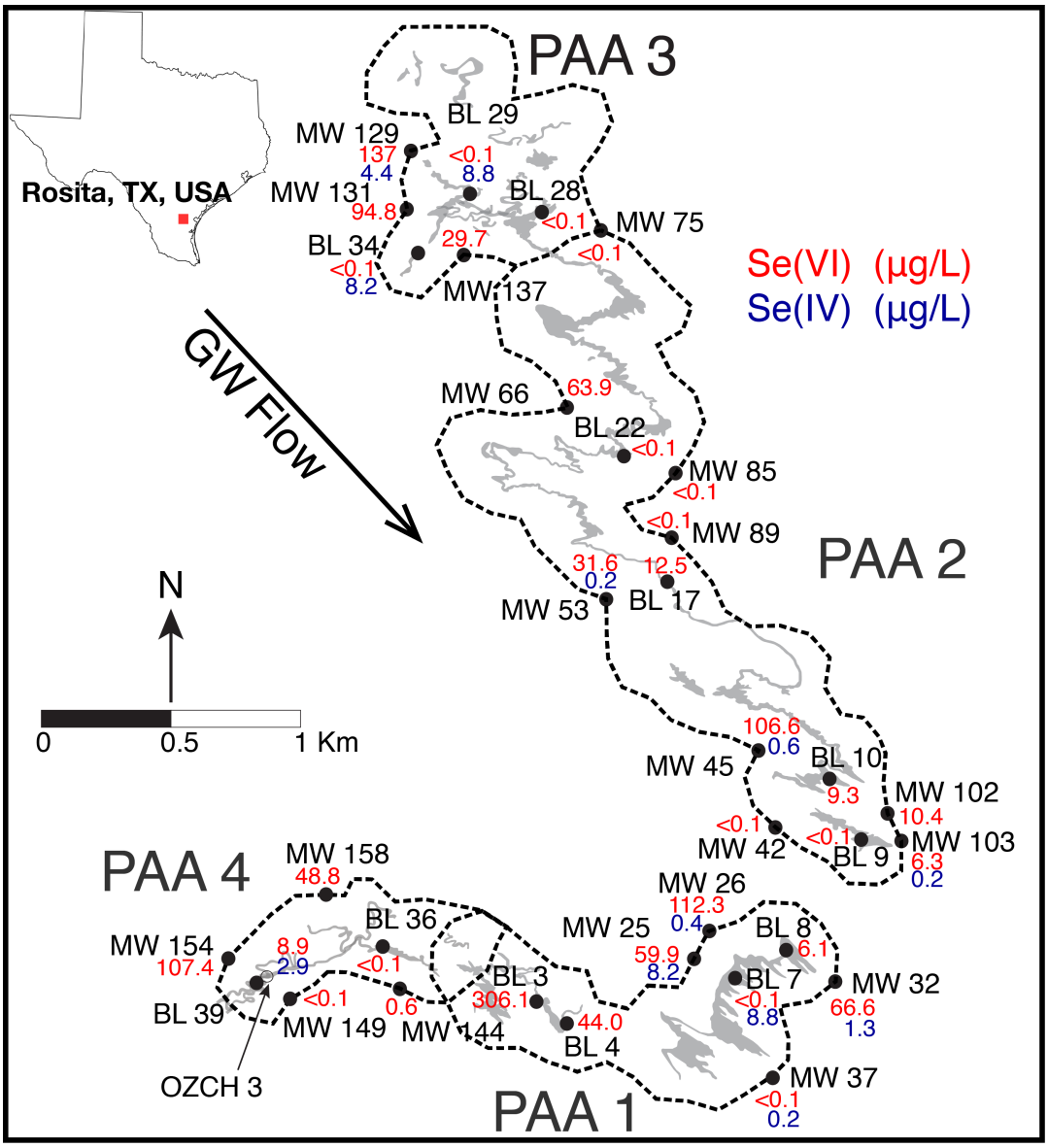
Depth b.g.s (m)	**Se (µg/kg)**	**δ^{82}Se**
60.66 - 60.96 (background)	24.3	-1.54‰
66.14 - 66.45	36.8	-1.28‰
66.45 - 66.75	33.8	-0.85‰
66.75 - 67.06	30.8	-0.62‰
67.06 - 67.21	31.7	-0.79‰
70.71 - 71.02	47.6	-0.64‰
71.02 - 71.32	39.0	-0.40‰

574

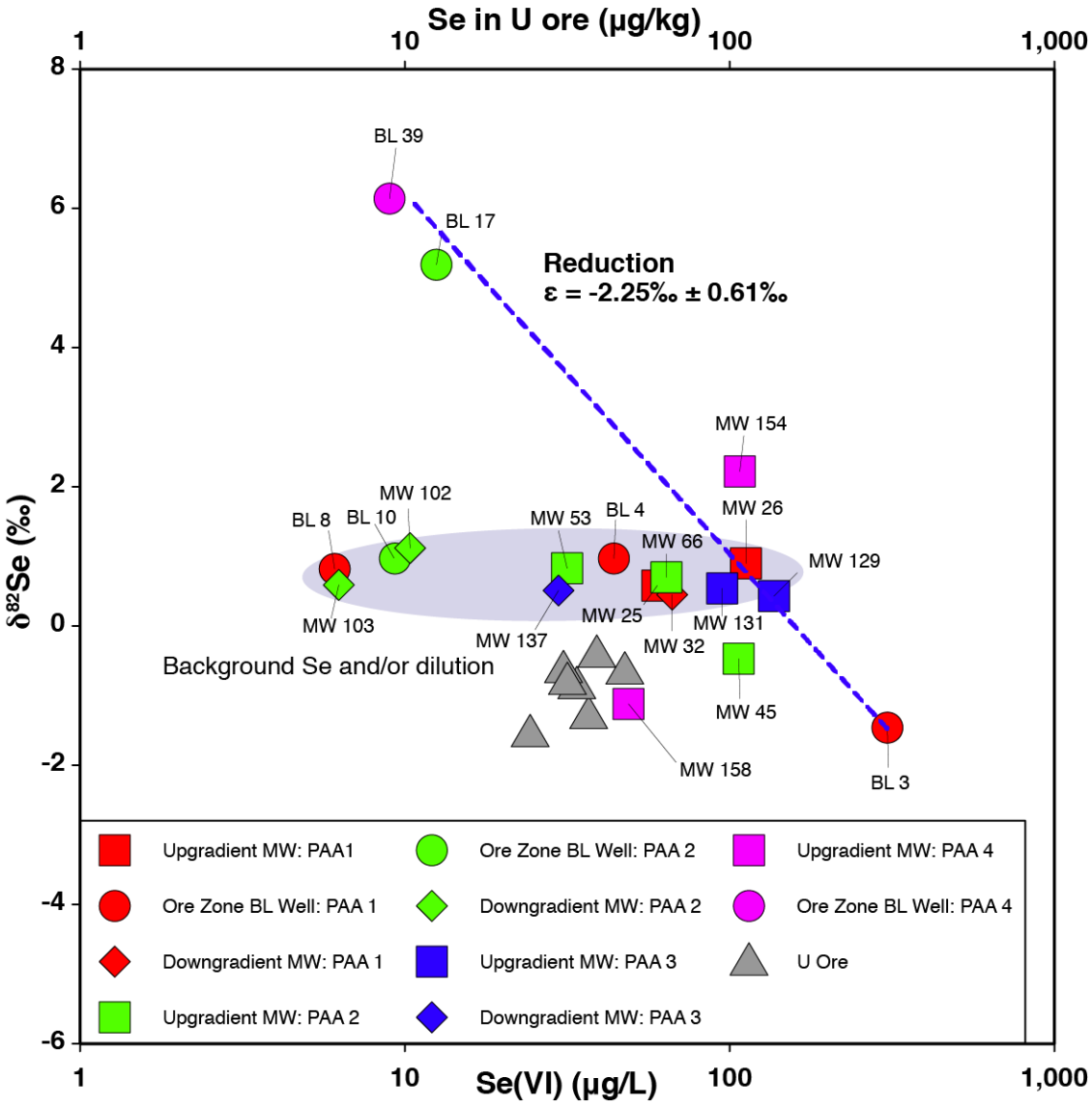


575

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

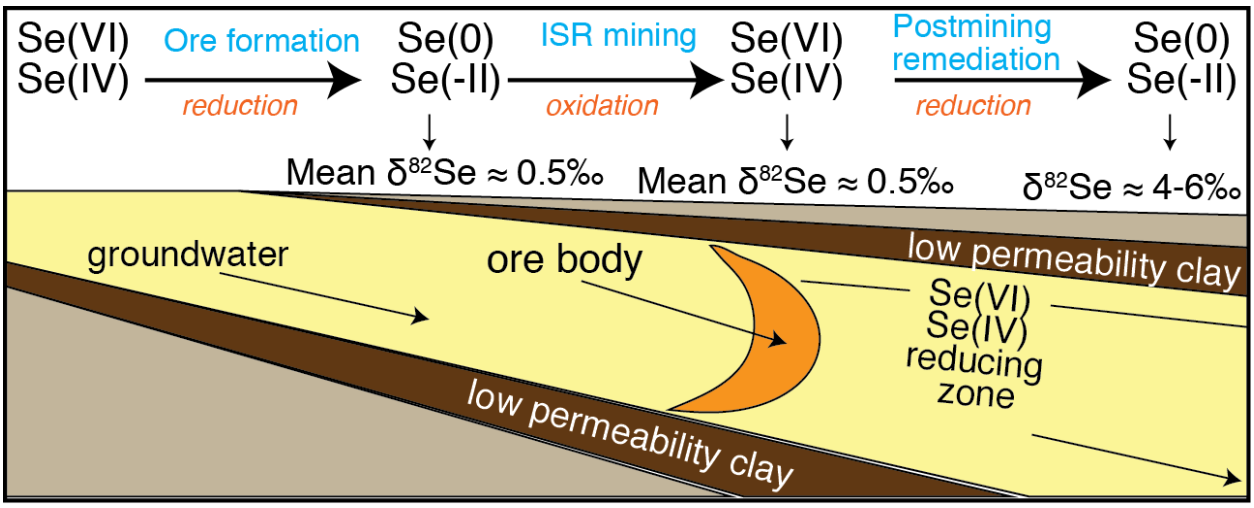


581
582 Figure 2. Map of the Rosita ISR site showing the mining units (PAA) and the distribution of
583 Se(VI). Light gray areas define the roll-front U deposit. Black dots represent locations of wells
584 sampled for Se oxyanion and Se isotope measurements and the open circle shows the location of
585 the borehole for the U ore sample. The dotted lines represent the perimeter ring of the monitoring
586 wells. Numbers represent Se-oxyanion concentrations - Se(VI) (red) and Se(IV) (blue) in µg/L.



587

588 Figure 3. δ^{82}Se of aqueous Se(VI) in Rosita groundwater and Se minerals in the U ore vs. Se
589 concentration. Gray triangles represent the U ore and red, green blue and pink symbols represent
590 groundwater from mining units PAA 1, PAA 2, PAA 3, and PAA 4, respectively. The error bars
591 (2*s.e.) for are smaller than the size of the symbols. The blue dotted line represent the modeled
592 δ^{82}Se using a Rayleigh distillation model with $\varepsilon = -2.25‰ \pm 0.61‰$ excluding the samples with
593 NO_3^-.


Se(VI)
Se(IV)
Ore formation
reduction
Se(0)
Se(-II)
ISR mining
oxidation
Se(VI)
Se(IV)
Postmining
remediation
reduction
Se(0)
Se(-II)
Mean δ82Se ≈ 0.5‰
Mean δ82Se ≈ 0.5‰
δ82Se ≈ 4-6‰
groundwater
ore body
low permeability clay
Se(VI)
Se(IV)
reducing
zone
low permeability clay

TOC art.