



Geochemical controls on arsenic and rare earth elements approximately along a groundwater flow path in the shallow aquifer of the Hetao Basin, Inner Mongolia

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ABSTRACT

Groundwaters and sediments were sampled approximately along a groundwater flow path in the shallow aquifer of the Hetao Basin, Inner Mongolia. Along a flow path with a length of about 9 km, groundwater evolves from $\text{Ca-HCO}_3\text{-SO}_4$ through $\text{Mg-Ca-HCO}_3\text{-Cl}$ to Na-Cl-HCO_3 from the recharge zone to the discharge zone. Eh and other redox indicators (i.e., dissolved Fe, H_2S , U and As concentrations) indicate that, except for those in the recharge zone and immediately to the southeast of a groundwater drainage canal, groundwaters are reducing and exhibit a progressive decrease in redox conditions along the flow path. Rare earth element concentrations exhibit less variation along the flow path, except that Eu concentration generally increases. Arsenic concentration is positively correlated with Eu concentration, while both of them are negatively correlated with Eh. North American Shale Composite (NASC)-normalized REE patterns are enriched in the HREEs relative to the LREEs for all groundwaters. They all have positive Eu anomalies ($\text{Eu}/\text{Eu}^* = \text{Eu}_{\text{NASC}}/(\text{Sm}_{\text{NASC}} * \text{Gd}_{\text{NASC}})^{0.5} = 3.42$ to 239) and slightly negative Ce anomalies ($\text{Ce}/\text{Ce}^* = \text{Ce}_{\text{NASC}}/(\text{La}_{\text{NASC}} * \text{Pr}_{\text{NASC}})^{0.5} = 0.39$ to 1.05). Reduction-oxidation, complexation, desorption and readsorption alter groundwater REE concentrations and fractionation patterns along the groundwater flow path. The positive Eu anomalies in groundwaters are probably due to preferential mobilization of Eu^{2+} relative to the trivalent REEs in the reducing condition. The same conditions causing the positive Eu anomalies probably also lead to As mobilization in the shallow aquifer.

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1. Introduction

High As groundwater has been widely found all over the world, including Bangladesh, India, China, Mexico, Hungary, Vietnam, Argentina and Chile (Smedley and Kinniburgh, 2002; Berg et al., 2007), which is considered as a serious worldwide problem. Extraction of As-affected groundwater through tubewells has led to tens of millions of people being at risk. In these aquifers, groundwater As is generally thought to have a natural source, and high As concentrations occur both in reducing (Bhattacharya et al., 1997; Nickson et al., 1998; Zobrist et al., 2000) and oxidizing conditions (Robertson, 1989; Peter et al., 1999). Reducing aquifers also are believed to be associated with groundwater As enrichment in some areas of Northwest China, especially in Xinjiang, Inner Mongolia (Smedley et al., 2003; Guo et al., 2008a; Deng et al., 2009; He et al., 2009), and Shanxi (Guo and Wang, 2004; Xie et al., 2009). Although Masscheleyn et al. (1991) found from laboratory experiments that some of the As was released before Fe, implying reductive desorption from Fe oxides rather than reductive dissolution, the precise mechanisms responsible for As mobilization in reducing aquifers remain uncertain.

Rare earth elements (REEs) are believed to be potential tracers for studying groundwater-aquifer rock interactions because of their generally coherent and predictable behavior (Tang and Johannesson, 2006). This coherent behavior of the REEs, combined with their sensitivity to changes in pH, redox conditions and adsorption/desorption reactions, makes the REEs particularly useful in hydrogeochemical studies (Wood, 1990). Because the REEs typically behave coherently, perturbations from the expected patterns can yield critical information on the types of processes occurring within a water-rock system. For example, Ce and Eu commonly behave differently compared to the other REEs because of their greater sensitivity to changes in redox conditions. Thus, anomalies in these elements have implications regarding the present (Ce) and/or past (Ce and Eu) redox state of the system (Leybourne et al., 2000). Since As mobilization is closely related to redox conditions in the aquifer, it is reasonable to expect that the ubiquitous and naturally occurring REEs may be used as chemical tracers for studying As behavior in natural waters. Tang and Johannesson (2006) observed that changing redox conditions along a groundwater flow path are accompanied by profound changes in REE concentrations and fractionation patterns.

The Hetao Basin is a typical sediment-filled basin, where high As groundwaters generally occur in shallow alluvial-lacustrine aquifers and inorganic As(III) is the dominant species (accounting for around 75% of total dissolved As) (Guo et al., 2008a). Li and Li (1994) and Tang et al. (1996) proposed that groundwater As naturally occurred

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under reducing conditions. Due to the coexistence of SO_4^{2-} and S^{2-} , Guo et al. (2008a) suggested that sulfate reduction has been an active process in these reducing aquifers.

However, no studies have focused on the geochemical processes that affect REE concentrations and fractionation patterns in this high As aquifer, and this investigation provides insights into the mechanisms of As mobilization in the aquifer. The main objectives are to 1) characterize geochemical behavior of the REEs along the groundwater flow path in the shallow aquifer of the Hetao Basin; 2) evaluate possible controls on their geochemical behavior; and 3) discuss implications of the REE patterns on mechanisms of As mobilization.

2. Hydrogeological setting

The study area lies along the front of the Yinshan Ranges and northwestern margin of the Hetao Basin (Fig. 1). The Yinshan Ranges are mainly composed of a metamorphic complex (slate, gneiss and marble) generally of Jurassic to Cretaceous age, which is folded and fractured (Li and Li, 1994). Due to continuous tectonic subsidence of the basin and uplift of the mountains, the sedimentation rate in the basin is continuously large. The aquifer dips towards the northwest. In the study area, shallow groundwaters mainly occur at depths between 5 and 50 m below land surface (BLS) in alluvial sediments in the northwest and alluvial-lacustrine sediments in the southeast (Fig. 1b). Alluvial sediments are present at the mountain front and in the piedmont and characterized by fine sand and silt, while lacustrine sediments sporadically occur at depths between 5 and 40 m BLS in the flatter part of the plain. The lacustrine sediments are mainly composed of silt and fine sand in Zone I-1, while silty sand and muddy clay with few interlayers of peat occur in Zone I-2 (Fig. 1b).

The aquifer conditions vary from unconfined to leaky-confined in the shallow deposits. Unconfined aquifers are mainly observed in Zones II and III, while leaky-confined aquifers are found in Zones I-1 and I-2 (Fig. 1b). The groundwater table depth ranges from 3 to 20 m, with a greater depth at the mountain front than in the flat plain.

The climate is semiarid-arid, with average annual precipitation of 130–220 mm (mainly during July to September) and annual evaporation rates of about 2000–2500 mm. Average annual temperatures range from 5.6 to 7.8 °C (Guo et al., 2008a). Groundwater is recharged by vertically infiltrating meteoric water in the basin and laterally penetrating fracture water from marble, slate and gneiss along the mountain front, as well as a little leaked water from natural lakes and a drainage canal, and irrigation return flow from farmland. It is discharged mainly via evapotranspiration and artificial extraction (Guo et al., 2008a). Because the groundwater table is very shallow in the flat plain, especially between wells 48 and 49, strong evaporation occurs and results in soil salinity. The general direction of groundwater flow is from northwest to southeast. Hydraulic conductivity decreases by a factor of 10 along the flow path ranging from ~20.0 m/d at the mountain front to ~2.2 m/d in the downdip regions. The flow rate is generally slow, and is a little greater in the northwest than in the southeast. There is a groundwater drainage canal cross the study area (Fig. 1b), which is used to locally lower the groundwater table and thereby reduce groundwater evaporation, for the purpose of land salinity remediation. Local groundwater flow is also controlled by the drainage canal (Fig. 2). Therefore, down-gradient of the evaporation zone (i.e., groundwater drainage canal), there are expected to be two shallow groundwater flow systems: one is a local groundwater flow system recharged by the drainage canal, and the other regional groundwater flow system is deeper and recharged from the mountain front (Fig. 2).

3. Materials and methods

3.1. Field sampling and field parameter measurement

Groundwater samples were collected along a flow path within Wulatehouqi and Hangjinhouqi counties in October, 2008. Parameters including water temperature, total dissolved solids (TDS), pH, Eh, H_2S and electrical conductivity (Ec), were measured at the time of groundwater sampling by using a multiparameter portable meter (HANNA, HI 9828). The Eh values reported in this study have not been corrected to the standard hydrogen electrode (SHE) but instead can be used as relative values. Alkalinity was performed on the sampling day and measured by the Gran titration method.

Water samples were also collected for subsequent laboratory analysis. Water samples for major and trace element analysis

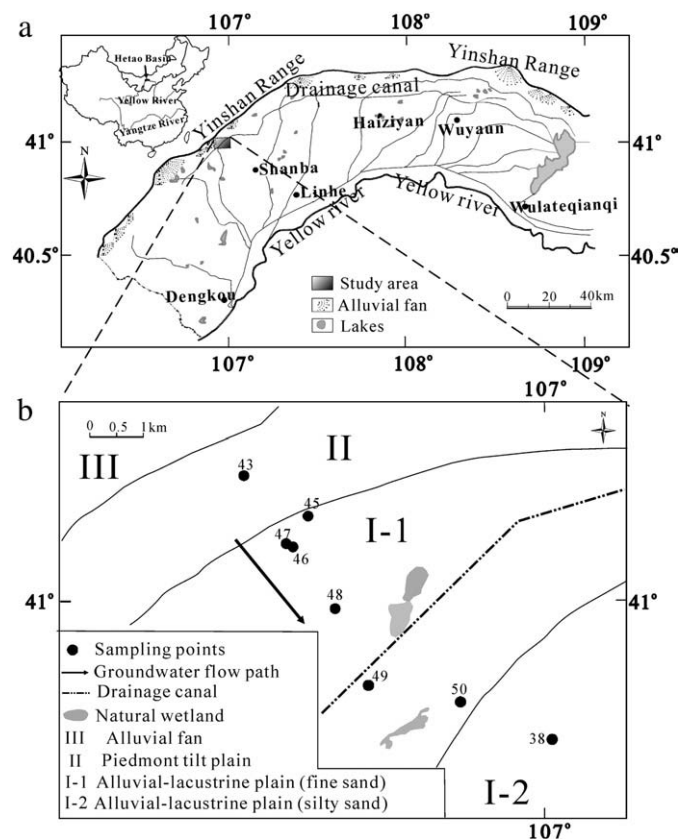


Fig. 1. (a) Location of study area. (b) Location of the wells sampled, groundwater flow path, and simplified sedimentation zones in the study area.

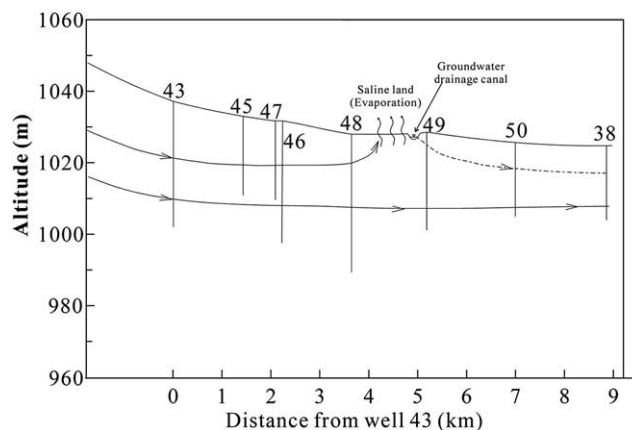


Fig. 2. Simplified hydrogeological section across the study area.

were filtered through a 0.45 µm millipore filter on site into 100 mL HNO₃-washed high density polyethylene (HDPE) bottles. Those for analysis of trace elements were acidified to pH<2 using 6 M HNO₃. Cation samples (Ca²⁺, Mg²⁺, K⁺ and Na⁺) were preserved immediately after on-site filtration with 6 M HNO₃, while anion samples were not acidified. Those for analysis of As species were preserved with 0.25 mol/L EDTA. Groundwater samples for determination of total aqueous REE concentrations were filtered using identical filters and immediately acidified to pH<2 with 6 M HNO₃. All samples were subsequently stored cold until analysis.

3.2. Analytical techniques

Unacidified aliquots were analyzed for F[−], Cl[−], NO₃[−], NO₂[−], NH₄⁺, HPO₄^{2−}, and SO₄^{2−} by Ion Chromatography with an instrument model DX-120 (Dionex). Concentrations of major cations and trace elements were determined by ICP-AES and ICP-MS, respectively. Concentrations of As and Se were determined by atomic fluorescence spectrometry (AFS) with hydride generation. In most cases, analytical charge imbalances were less than 5%.

Rare earth elements were quantified by ICP-MS (Agilent 7500C). There are several advantages of determining REE concentrations by the ICP-MS technique (Verplanck et al., 2001). The REE isotopes ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁶Nd, ¹⁴⁷Sm, ¹⁵³Eu, ¹⁵⁷Gd, ¹⁵⁹Tb, ¹⁶³Dy, ¹⁶⁵Ho, ¹⁶⁶Er, ¹⁶⁹Tm, ¹⁷⁴Yb, and ¹⁷⁵Lu were used to quantify the REEs in the groundwater samples that were prepared from NIST traceable standards. Interference from BaO⁺/Ba²⁺ on Eu was avoided by extraction of Ba from aliquots of each sample using diethylhexylphosphoric acid (Cerrai and Ghersini, 1966; Hodge et al., 1998). The ICP-MS was calibrated and the sample concentrations verified using a series of REE standards of known concentration (1, 2, 10, 100, 250, 500, and 1000 ng/L). The NIST Standard Reference Material (SRM) "Trace Elements in Water" (No. 1643b) was routinely run during analysis as an additional check on analytical quality.

The detection limits were 1 ng/L for all REEs. Analytical precision for the REEs, except for Ce and Pr, was better than 5% relative standard deviation (RSD); for Ce and Pr, the precision was 9% and 12% RSD, respectively.

Arsenic species in groundwater samples were analyzed using an HPLC-ICP-MS. A high performance liquid chromatograph (HPLC, 1100 Series, Agilent) consisting of a system controller, a solvent delivery module, a column oven and a six-port injection valve was used. A reversed-phase C18 column (Capcell, Pak, 250 mm × 4.6 mm, 5 µm particle size) was used for separation of As species. An ICP-MS (7500C, Agilent) was used as a detector, which was operated in the He mode for As determination to eliminate the possibility of an isobaric interference with ArCl.

4. Results

4.1. Groundwater composition along the flow path

Results show that groundwaters are chiefly Ca–Na–HCO₃–SO₄ type waters in and near the recharge zone. With flow down-gradient, the groundwater composition shifts towards Na–Cl–HCO₃. These groundwater compositions follow a general concept model for groundwater basins (Edmunds et al., 1982; Guo and Wang, 2004).

Concentrations of Cl[−], HCO₃[−], Na⁺, K⁺, Mg²⁺, and Ca²⁺ increase along the flow path up-gradient of the evaporation discharge zone (i.e., groundwater drainage canal), while SO₄^{2−} decreases (Table 1, Fig. 3a and b). Within the evaporation discharge zone, all composition concentrations drastically increase due to strong evaporation. In contrast, they decrease in their concentration down-gradient of the evaporation discharge zone. Since local wells with hand pumps screened at all depths were used for groundwater sampling, the mixing of local groundwater recharged from the drainage canal and

Table 1

Concentrations of major components, U, As species in groundwaters in the study area.

Well no.	43	45	47	46	48	49	50	38
Distance (km)	0	1.43	2.10	2.25	3.65	5.23	6.99	8.89
Well depth (m)	38	21	25	41	48	28	20	21
pH	7.14	7.42	7.68	8.03	8.32	7.86	7.96	8.38
Ec (µs/cm)	1080	551	702	647	770	4640	2910	1480
Eh (mV)	32	−140	−180	−200	−200	−66	−160	−180
T (°C)	13.2	11.6	11.5	11.4	11.4	10.8	10.7	10.2
Ca ²⁺ (mg/L)	91.5	49.6	71.4	65.1	56.0	129	36.8	15.9
Mg ²⁺	40.4	17.7	21.2	22.7	33.9	196	86.0	25.7
Na ⁺	71.0	44.5	42.9	37.8	52.5	764	586	329
K ⁺	5.0	4.0	3.8	3.5	4.7	8.3	7.6	5.9
HCO ₃ [−]	406	191	249	224	322	867	951	613
Cl [−]	47.7	27.4	45.5	36.4	83.9	864	547	306
SO ₄ ^{2−}	200	125	124	117	49.6	1115	41.2	2.80
F [−]	0.81	1.85	1.20	1.26	0.80	0.24	2.40	4.60
NO ₃ [−]	BDL	BDL	0.04	BDL	BDL	BDL	BDL	BDL
Fe _T	0.03	0.38	2.52	0.90	0.74	0.01	0.43	0.43
H ₂ S (µg/L)	BDL	–	–	18	17	7.0	2.0	6.0
Ba	74.5	86.2	56.0	100	134	18.9	150	91.7
U	104	0.44	0.34	0.48	0.14	1.32	0.22	0.14
As(III)	1.40	35.2	121	122	372	1.90	14.6	701
As(V)	0.80	19.1	8.70	22.3	22.2	0.60	34.0	80.6
As _T	2.16	54.2	129	144	395	2.50	48.6	781

"BDL" denotes below the detection limit.

"–" denotes the measurement were not done.

regional groundwater recharged from the mountain front would take place in the wells. The decrease is expected to result from groundwater mixing in the wells. In addition, NO₃[−] concentrations are mostly below the detection limit (i.e., 0.02 mg/L) (Table 1).

Oxidation–reduction potential (i.e., Eh) ranges from −200 mV to 32 mV. Generally speaking, Eh values were higher in the recharge zone groundwaters than in those from further down-gradient along the flow path, with exception of well 49 (Fig. 3c). At the down-gradient of the evaporation discharge zone, groundwater Eh drastically increases from −200 mV in well 48 to −66 mV in well 49 due to the recharge of drainage water.

Arsenic concentration initially increases along the flow path from the recharge zone to a distance of roughly 3.7 km (in well 48), up-gradient of the drainage canal, before drastically decreasing between well 48 (395 µg/L) and well 49 (2.5 µg/L) (Fig. 3c). Down-gradient of the drainage canal, As concentration increases again and reaches 781 µg/L in well 38.

Total Fe (Fe_T) concentrations range from 0.01 to 2.52 mg/L (Table 1). From the region nearest to the aquifer's recharge zone to about 9 km, Fe concentrations are variable. The highest Fe_T concentration (2.52 mg/L) occurs at a distance of 2.1 km (in well 47). Low Fe_T concentrations (<0.03 mg/L) were detected in wells 43 and 49. Groundwaters from these wells exhibit high concentrations of the redox-sensitive trace element U and low concentrations of H₂S (Table 1 and Supplementary Material S1). With flow down-gradient of well 49 (~5.3 km), Fe_T concentrations generally increase, reaching a value of 0.43 mg/L at about 9 km from the recharge zone.

Hydrogen sulfide concentrations range from below detection limit (i.e., 1.0 µg/L) to 18 µg/L (Table 1). From the aquifer sampled nearest to the recharge zone to a distance of 3.7 km (well 48), H₂S concentrations exhibit a progressive increase from below detection limit to 17 µg/L. Between 5 and 9 km down-gradient from the recharge zone (wells 49 to 38), dissolved H₂S generally increases (Supplementary Material S1).

4.2. REE concentrations

Rare earth element concentrations in the study area are low, and broadly similar to other circumneutral pH groundwaters (e.g. Johannesson et al., 2000; Tang and Johannesson, 2006). With the exception of Eu, the REE concentrations initially show small

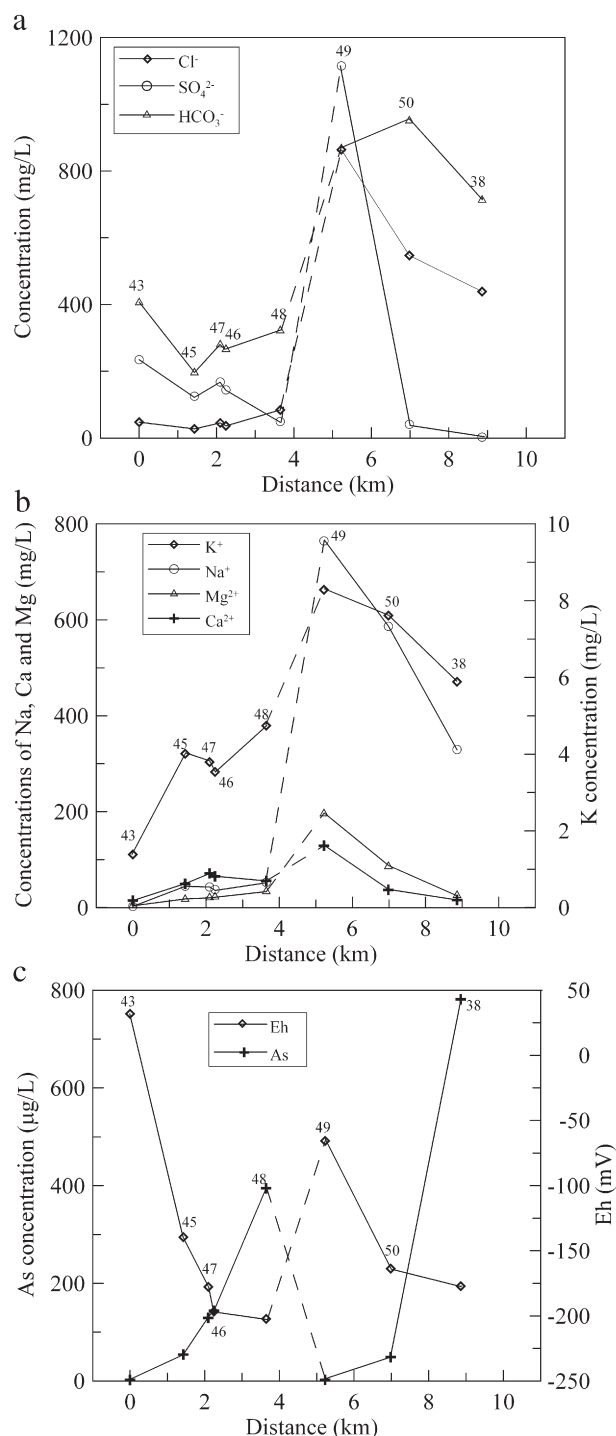


Fig. 3. Major anion concentrations (a), major cation concentrations (b), and As concentration and Eh (c) as functions of distance from the recharge zone (well 43).

fluctuations along the groundwater flow path until about 3.7 km (i.e., well 48), and keep relatively constant for the remainder of the flow path sampled (Table 2). The highest REE concentrations were found in the groundwater from well 46. Lanthanum and Ce concentrations, for example, reach 92.8 ng/L and 187 ng/L in this water sample. The groundwater at well 43 has higher La, Pr, Nd, Gd, Er, and Yb concentrations than its nearest down-gradient neighbor (well 45). Although most of the REEs shows less variation down-gradient of the evaporation discharge zone, Nd concentrations generally increase

Table 2

Concentrations of REEs (ng/L) in groundwaters from the study area.

Well no.	43	45	47	46	48	49	50	38
La	14.6	5.2	12.4	92.8	10.8	6.4	6.3	10.9
Ce	14.2	11.4	24.7	187	6.2	8.6	5.5	8.2
Pr	3.1	1.2	2.1	23.7	1.1	2.1	1.2	1.2
Nd	12.7	5.5	9.2	87.5	5.2	2.3	5.4	9.7
Sm	3.1	1.1	4.3	21.2	5.4	0.7	3.1	3.1
Eu	12.4	9.3	16.8	16.8	161	7.5	61.8	195
Gd	4.2	1.2	4.1	23.4	6.5	3.1	3.2	4.4
Tb	1.1	BDL	0.9	3.1	0.6	1.0	BDL	0.7
Dy	3.3	1.1	2.1	21.3	0.9	3.0	1.4	1.2
Ho	1.5	1.3	1.3	4.4	0.7	1.4	1.1	1.6
Er	2.5	1.2	3.4	8.1	1.2	1.2	1.3	1.1
Tm	1.2	BDL	0.6	2.1	0.8	0.9	0.8	0.7
Yb	5.8	1.1	1.1	5.7	4.6	3.5	1.1	5.5
Lu	1.1	0.7	1.2	1.3	1.3	1.0	1.2	1.2
(Er/Nd) _{NASC}	1.91	2.12	3.59	0.90	2.24	5.06	2.34	1.10
(La/Yb) _{NASC}	0.24	0.46	1.09	1.58	0.23	0.18	0.55	0.19
Ce/Ce*	0.46	0.99	1.05	0.87	0.39	0.51	0.44	0.49
Eu/Eu*	15.6	36.7	18.2	3.42	123	22.9	89.0	239

Ce/Ce* = $\text{Ce}_{\text{NASC}} / (\text{La}_{\text{NASC}} * \text{Pr}_{\text{NASC}})^{0.5}$.

Eu/Eu* = $\text{Eu}_{\text{NASC}} / (\text{Sm}_{\text{NASC}} * \text{Gd}_{\text{NASC}})^{0.5}$.

"BDL" denotes below detection limit.

from 2.3 ng/L for well 49 to 9.7 ng/L for well 38 in the direction of groundwater flow (Table 2).

Along the groundwater flow path, Eu concentrations remain essentially the same from well 43 to well 45, then increase to 161 ng/L for well 48. Following well 48, the next sample location along the direction of groundwater flow is well 49, which exhibits the lowest Eu concentration (7.5 ng/L). Further down-gradient, groundwaters show an increase in Eu concentration, reaching 195 ng/L in well 38 (Table 2).

4.3. NASC-normalized REE patterns

Normalized patterns with respect to the estimated average composition of the North American Shale Composite (NASC) (Taylor and McLennan, 1985) are displayed on Fig. 4 for groundwaters from the study area. The composite shale used to normalize these groundwater REE concentrations represents the mean of North American shales, and has been employed recently in groundwater studies (Leybourne et al., 2000; Dia et al., 2000; Rönnback et al., 2008).

The groundwaters mostly exhibit enrichment in the HREEs relative to the LREEs (Fig. 4). The (Er/Nd)_{NASC} ratios range from 0.90 to 5.06. The NASC-normalized Er/Nd ratios are all greater than unity, except for groundwater from well 46 which was a new well and has a greater

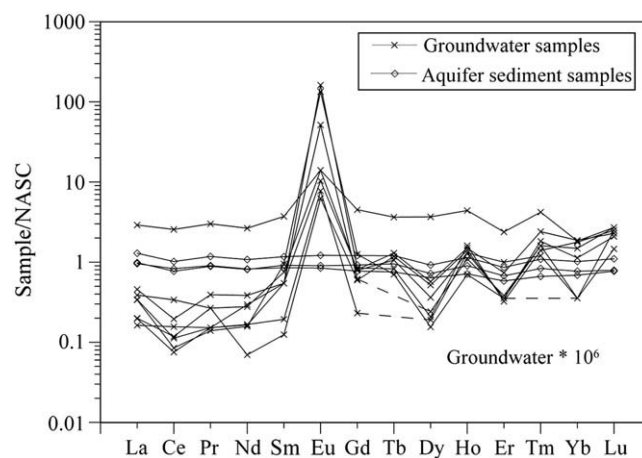


Fig. 4. NASC-normalized REE patterns for groundwaters and aquifer sediments from the study area.

depth (42 m). The $(\text{Er}/\text{Nd})_{\text{NASC}}$ ratios are high for groundwaters from shallower wells and/or wells in the recharge zone (e.g., 1.91–3.59). In comparison with other LREEs, the groundwaters possess relatively higher La concentrations.

All groundwaters have positive Eu anomalies ($\text{Eu}/\text{Eu}^* = \text{Eu}_{\text{NASC}} / (\text{Sm}_{\text{NASC}} \times \text{Gd}_{\text{NASC}})^{0.5} = 3.42\text{--}239$), and slightly negative Ce anomalies ($\text{Ce}/\text{Ce}^* = \text{Ce}_{\text{NASC}} / (\text{La}_{\text{NASC}} \times \text{Pr}_{\text{NASC}})^{0.5} = 0.39\text{--}1.05$) with except of the sample from well 47. The greatest difference in the Eu anomalies along the flow path occurs in groundwaters between wells 46 and 48, as indicated by the Eu/Eu^* ratios of 3.42 and 123, respectively. Beginning at a distance of ~5 km from well 43, the Eu/Eu^* ratios increase for the next three down-gradient wells. There is no correlation between the Eu anomalies and Ba concentrations, indicating that BaO^+ formation in the ICP plasma was insignificant. The Ce/Ce^* ratios initially increase with flow away from the recharge zone to a distance of about 2 km, then they are constant for the last four down-gradient wells.

5. Discussions

5.1. Redox conditions along the flow path

Geochemical analyses of shallow groundwaters from the study area show that the redox conditions change along the flow path, which are clearly evident in the fluctuating dissolved Fe and SO_4^{2-} concentrations, and the concentrations of redox-sensitive trace elements, U and As (Table 1 and Fig. 3). It should be noted that U behaves conservatively in oxic aquifers, occurring as the uranyl oxyanion (UO_2^{2+}) (Langmuir, 1978). Under reducing conditions, U is reduced and removed from solution via precipitation and/or scavenging by low solubility mineral phases (Langmuir, 1978; Hua and Deng, 2008; Moon et al., 2009). In contrast, As is readily mobilized in anaerobic aquifers (Smedley and Kinniburgh, 2002). Under reducing conditions, As is released from aquifer sediments by reductive desorption and/or reductive dissolution of Fe(III) oxides (Islam et al., 2004; Guo et al., 2008a,b).

Measured Eh values also indicate fluctuating redox conditions in the shallow aquifer along the flow path. Although the measured Eh value is generally not a quantitative measure of the actual equilibrium redox state in groundwater systems, Eh can be used with other redox indicators to ascertain, in a qualitative sense, the relative redox conditions of an aquifer (Runnells and Lindberg, 1990; Smedley and Edmunds, 2002).

Relatively oxidizing conditions are characteristic of groundwater from well 43, where As concentration is relatively low and U concentration is the highest. Between wells 43 and 48 (i.e., up-gradient of the evaporation discharge zone), groundwaters exhibit a progressive decrease in redox conditions as evidenced by Eh values, H_2S , U and dissolved Fe concentrations (Table 1 and Fig. 3c). It is important to note, however, that the redox potential drastically increases in groundwater from well 49, which is located immediately to the southeast of the groundwater drainage canal. The increase in Eh value in this well represents a pulse of more oxygen-rich groundwater that may have percolated down from the drainage canal. Simultaneously, As and dissolved Fe concentrations decrease. Along the groundwater flow path beyond well 49, Eh values and U concentrations decrease, whereas As and dissolved Fe concentrations increase again, demonstrating a renewed progressive decrease in redox condition.

The NO_3^- , dissolved Fe, and H_2S concentrations measured in groundwaters along the flow path are consistent with distinct redox zones in the aquifer (e.g., Chapelle and Lovley, 1992; Penny et al., 2003; Velasco Ayuso et al., 2009). Within the region of the aquifer nearest to the recharge zone (0–1 km), a variety of oxidation–reduction reactions are likely important, including aerobic respiration and denitrification. Beyond well 45 (~1.5 km), Fe(III) reduction generally predominates until well 47, where dissolved Fe concentration is the highest. At well 46, down-gradient neighbor of well 47,

sulfate reduction becomes the dominant redox reaction in the aquifer. The order of redox reactions follows the established sequence as suggested by Stumm and Sulzberger (1992). The H_2S concentration indicates that sulfate reduction becomes important between 2 and 4 km down-gradient along the flow path (i.e., between wells 46 and 48), where sulfide concentration is up to $18 \mu\text{g}/\text{L}$ (Supplementary Material S1). Although all groundwater samples are over-saturated with respect to pyrite with $\text{SI}_{\text{pyrite}} > 3.0$ (data not shown), the drop in dissolved Fe concentrations at wells 46 and 48 may be due to the removal of Fe(II) in sulfide minerals in the presence of higher dissolved H_2S concentrations as compared to groundwaters from other wells. Down-gradient of the evaporation discharge zone (beyond well 49), Fe(III) reduction gradually becomes dominant again, where sulfide concentration is relative low.

5.2. Controls on REE concentrations

Although the ultimate source of the REEs in natural water is the sediments through which the waters flow, the groundwaters have REE patterns that are totally different from those of the aquifer sediments (Fig. 4). This result indicates that the groundwaters do not inherit aquifer sediment-like REE signatures in the study area. Therefore, additional chemical weathering, adsorption, desorption, and solution complexation reactions are expected to control groundwater REE concentrations and fractionation patterns (Leybourne et al., 2000; Dia et al., 2000; Gruau et al., 2004; Johannesson et al., 2005).

Fig. 5 shows that the increase in REE concentration occurs in phase with a decline in the redox potential. Redox processes can contribute to the observed variations in groundwater REE concentration. As discussed above, reductive dissolution of Fe(III) oxyhydroxides occurs beyond well 45 along the flow path. Iron oxyhydroxides have the capacity to strongly adsorb or complex REEs (Ohta and Kawabe, 2001; Verplanck et al., 2004). Therefore, this result suggests that the reductive dissolution of Fe(III) oxyhydroxides in sediments would lead to a release of the REEs into groundwater.

Except for well 46, REE concentrations show a linear correlation with the free carbonate ion concentration (i.e., $[\text{CO}_3^{2-}]_{\text{f}}$) in groundwaters ($r = 0.72$). The high correlation coefficient indicates that the dissolved REE concentration is likely controlled by the amount of uncomplexed carbonate ion in the groundwater. Johannesson and Hendry (2000) suggested that higher carbonate ion concentrations would promote greater stability of the REEs in solution as dicarbonate complexes, and lead to their elevated concentrations. Carbonate

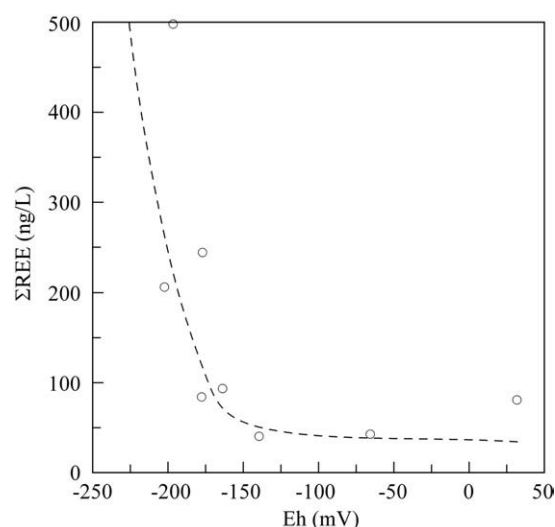


Fig. 5. Relationships between Eh and REE concentration in groundwaters from the study area.

complexation was also believed to be an important factor resulting in the elevated REE concentrations along the groundwater flow path within a shallow, basin-fill aquifer in southern Nevada (Johannesson et al., 1999).

5.3. Controls on REE patterns

Tang and Johannesson (2006) suggested that reductive dissolution of Fe oxyhydroxides would result in a release of preferentially scavenged LREEs into groundwater and lower $(\text{Er}/\text{Nd})_{\text{NASC}}$ ratios. Dissolved Fe concentrations have a weakly negative correlation with the $(\text{Er}/\text{Nd})_{\text{NASC}}$ ratios (not shown). Hence, the reduction of Fe oxyhydroxides would not be the reason for the HREE enrichment of the groundwaters from this region of the aquifer, although it is related to the elevated REE concentrations. Therefore, other processes, including complexation and readsorption, must be important to keep HREE enrichment in groundwaters.

The solution complexation of the REEs was calculated by the hydrogeochemical code PHREEQC (Parkhurst and Appelo 1999) using the LLNL database. Results of the REE speciation modeling show that dicarbonato ($\text{Ln}(\text{CO}_3)_2^-$) and carbonato complexes (LnCO_3^+) are the major dissolved species for all REEs, with the HREEs having a slightly higher portion of dicarbonato complexes as compared to the LREEs (Supplementary Material S2). The negatively charged mineral surface sites in aquifer sediments would have stronger affinities for the LREEs as positive charged carbonato complexes than the HREEs, for which the $\text{LnCO}_3^+/\text{Ln}(\text{CO}_3)_2^-$ ratios are slightly lower. Therefore, the large enrichments in the HREEs over the LREEs can be attributed to differences in solution complexation behavior across the REE suite, which leads to preferential release of the HREEs to groundwater and readsorption of the LREEs at sediment particle surfaces (Johannesson and Hendry, 2000). Besides, the $(\text{La}/\text{Yb})_{\text{NASC}}$ ratios are systematically lower in the high-bicarbonate waters than in the low-bicarbonate waters (Fig. 6). In a seawater study, Byrne and Kim (1990) also observed that the HREEs form stronger solution complexes with carbonate ions than the LREEs, and the LREEs are sequestered by a variety of organic and inorganic substrates. In addition, REE partitioning between solid and liquid would be another cause for the enrichment of the HREEs over the LREEs. Johannesson et al. (2000) found that solid–liquid partitioning coefficients (K_d) for REE decrease with increasing atomic number across the REE suite for the carbonate

and volcanic rock alluvial aquifer materials and concluded that the LREEs have greater affinities for aquifer surface sites than the HREEs.

The pH significantly dominates the REE fractionation patterns. It affects carbonate complexation of the REEs, with higher pH leading to the predominance of REE dicarbonato complexes. On the other hand, pH controls REE readsorption onto oxide surfaces. Groundwater pH is weakly alkaline (7.14–8.38) in the study area, with relatively higher pH in the down-gradient parts of the aquifer compared to the recharge zone. Readsorption of the REEs would be enhanced at higher pH, especially for the LREEs (Dupré et al., 1996). Therefore, the degree of LREE depletion is expected to be higher in groundwaters with higher pH (Leybourne et al., 2000).

Although most groundwaters have negative Ce anomalies, the Ce/Ce^* ratios are higher in groundwaters with lower Eh values. It is well known that both the oxidative precipitation as cerianite (CeO_2) and adsorption on Fe oxyhydroxides can contribute to Ce enrichment in oxidizing sediments (Bau, 1999; Dia et al., 2000). The possible explanation for slightly negative Ce anomalies would be that more Ce has been fixed as CeO_2 than that adsorbed on Fe oxyhydroxides in the sediment during sedimentation in an oxic environment. When conditions become more reducing (the actual situation), reduction of Fe oxyhydroxides first releases the adsorbed Ce, while reduction of CeO_2 is slower and only gradually mobilizes Ce into the waters.

5.4. Origin of Eu anomalies in shallow groundwater

According to the literature, three hypotheses have been proposed for explaining positive Eu anomalies in groundwaters: (i) positive anomalies in the aquifer sediments through which they flow; (ii) preferential dissolution of Eu-enriched minerals (e.g., plagioclase); and (iii) preferential mobilization of Eu^{2+} during water–mineral interaction compared to the trivalent REEs (Banks et al., 1999; Lee et al., 2003; Kharitonov et al., 2007; Leybourne and Johannesson, 2008).

Groundwaters have high positive Eu anomalies (Eu/Eu^* : 3.42–239). In contrast, aquifer sediments have flat NASC-normalized REE patterns with slight Eu anomalies (Eu/Eu^* : 0.98–1.04) (Fig. 4). The positive Eu anomalies of groundwaters are not related to the REE signatures of the source sediments through which they flow. As stated above, the aquifer sediments do not exert a dominant influence over the relative concentrations of the REEs in groundwaters.

To evaluate the second hypothesis, fourteen aquifer sediments obtained from the study area have been analyzed for mineralogical compositions and REE contents. Aquifers sediments have plagioclase contents ranging from 7.3% to 20.2%, clay mineral contents from 12.7% to 59.6%, and Eu from 0.60 $\mu\text{g/g}$ to 1.46 $\mu\text{g/g}$. Plagioclase contents have a positive correlation with Eu contents and their relationships depend on clay mineral contents (Fig. 7). It has been known that plagioclase preferentially accumulates Eu (Taylor and McLennan, 1988). Our results demonstrate that clay minerals could also enrich Eu in addition to plagioclase. The high Eu content of the clay minerals is due to their origin from alteration of feldspars. The two distinct trends observed in Fig. 7 may represent two distinct feldspar species and their distinct alteration products, respectively. However, it is observed that groundwater Eu concentrations vary over almost two orders of magnitude (6.5 to 195 ng/L), despite a nearly constant feldspar content (between 12% and 14%) in the aquifer sediments through which the groundwaters flow. Accordingly, the dissolution of plagioclase in the sediment is not expected to cause the positive Eu anomalies of groundwaters in the study area.

In the results of this study, Eu/Eu^* ratios have a negative correlation with Eh values (Fig. 8). The ratios are systematically higher in the lower Eh (reducing) groundwaters than in the higher Eh (oxidizing–mildly reducing) groundwaters suggesting that reducing conditions are the dominant factor contributing to the positive Eu anomalies. Europium is the only lanthanide that, under reducing conditions, can be divalent, and is thus segregated from other REEs

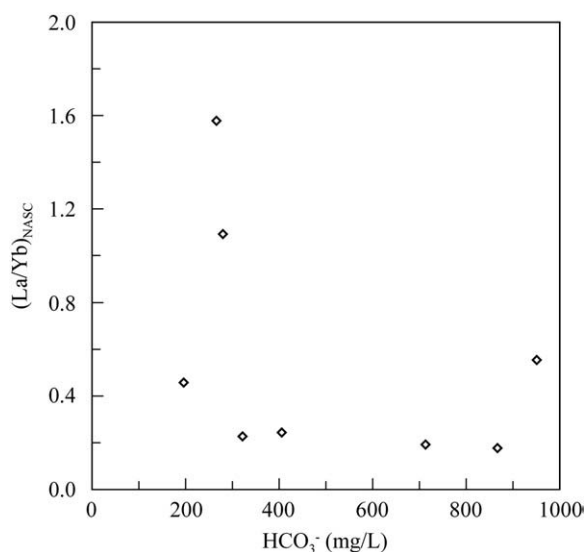


Fig. 6. Relationships between $(\text{La}/\text{Yb})_{\text{NASC}}$ and HCO_3^- concentration in groundwaters from the study area.

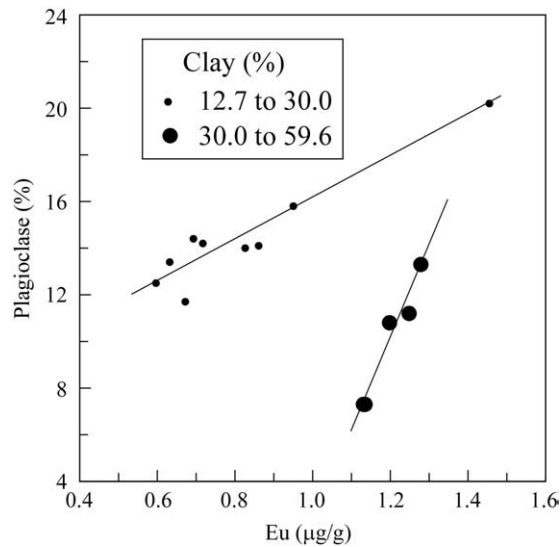


Fig. 7. Relationships between plagioclase contents and Eu contents in aquifer sediments with different clay mineral contents from the study area.

under such conditions (Lee et al., 2003). Although Eu speciation was not directly analyzed, it is expected that Eu^{2+} is the major Eu species mobilized from the aquifer sediments. Although Bau (1991) showed that Eu^{2+} is preferentially mobilized during water–rock interaction in high-temperature hydrothermal waters, it has also been proposed to contribute to Eu enrichments in stream water (Leybourne and Johannesson, 2008). The reason for Eu enrichment in the reducing groundwater of the study area would be preferential mobilization of Eu^{2+} relative to the more particle-reactive trivalent REEs. The mobilization would be related to reductive dissolution of Fe oxyhydroxides, as stated above. It remains unclear, however, when Eu^{3+} has been reduced to Eu^{2+} in the sediments. One possibility is that Eu^{2+} formed at the time of aquifer material sedimentation in a strongly reducing environment. The other is that Eu^{3+} is reduced to Eu^{2+} in the reducing aquifer during groundwater–rock interaction. Since it is generally believed that Eu^{2+} only occupies a very limited stability field at low temperature (Brookins, 1989), the latter seems to

be a less plausible explanation for the positive Eu anomalies in shallow groundwaters. The poor correlation between dissolved Fe and Eu/Eu^* suggests that the reductive dissolution of Fe oxyhydroxides should not be the only source for the Eu anomalies. The preferential desorption of $\text{Eu}(\text{II})$ should also play an important role.

5.5. Relationship between As mobilization and positive Eu anomalies

Arsenic concentrations are negatively correlated with Eh values (Table 1). The groundwaters with low Eh have high As concentrations. Therefore, As mobilization is closely related to reducing conditions. Due to limited diffusion of atmospheric O_2 into the aquifers, microbially mediated oxidation of organic matter can drive aquifers anoxic (Guo et al., 2008b). As stated above, Fe(III) reduction and/or sulfate reduction occur in the studied aquifer. In the Fe(III) reduction zone, Fe(III) oxyhydroxides have been reduced to Fe(II) forms, which results in As release via reductive dissolution of Fe oxides (Nickson et al., 1998; Islam et al., 2004; Guo et al., 2008b). Theoretically, the p_e value for As(V) reduction is lower than that for Fe(III) reduction, and higher than for sulfate reduction (Mukherjee et al., 2008). In the intermediate zone between Fe(III) reduction and sulfate reduction, As(V) is expected to be reduced, causing reductive desorption of As due to higher affinity for As(V) than As(III) onto aquifer sediments (Dzombak and Morel, 1990). Sulfide has been produced in the sulfate reduction zone, which would be precipitated with solution Fe(II) as diagenetic pyrite (or some other rapidly forming Fe-sulfide minerals) in groundwater being over-saturated with respect to pyrite. The diagenetic pyrite would also scavenge As from the waters (Lowery et al., 2007).

As discussed above, reducing conditions are the important factor leading to elevated REE concentrations along the groundwater flow path. Due to preferential mobilization of Eu^{2+} compared to the other trivalent REEs, large positive Eu anomalies are universally observed in groundwaters with low Eh values. It is also found that As concentrations vary in phase with Eu anomalies (Fig. 9). It is expected that As and Eu would be released simultaneously during reductive dissolution of Fe(III) oxyhydroxides, although As is also mobilized in the process of reductive desorption if As(V) is present on the sediment surface sites. The poor correlation between As and Fe concentrations may suggest that reductive desorption is involved in the process of As mobilization.

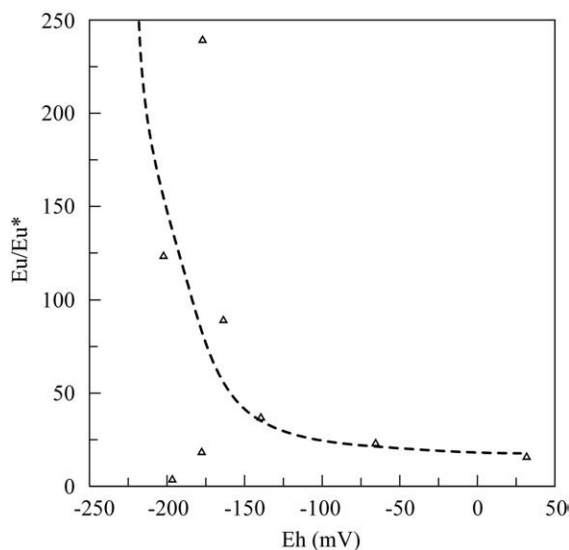


Fig. 8. Relationships between Eu/Eu^* ratios and Eh values in groundwater from the study area.

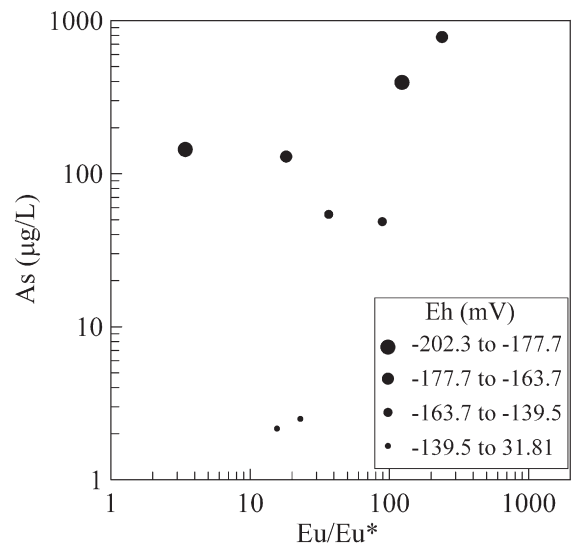


Fig. 9. Relationship between As concentration and Eu/Eu^* for the groundwaters with different Eh values in the study area.

6. Conclusion

In a study of the Hetao Basin, it was found that redox conditions change along the flow path. Eh and other redox indicators (i.e., dissolved Fe, H₂S, U and As concentrations) indicate that groundwaters, in the region of the aquifer proximal to the recharge zone and immediately to the southeast of the groundwater drainage canal, exhibits oxic–suboxic conditions. However, between ~1.5 and ~4 km along the flow path, and beyond well 49 (~5.5 km), groundwaters are reducing and exhibit a progressive decrease in redox conditions. Within the region of the aquifer nearest to the recharge zone (i.e., 0–1 km), a variety of oxidation–reduction reactions are possibly important, including aerobic respiration and denitrification. Between ~1 and ~2 km along the flow path, and beyond well 49 (~5.5 km), Fe(III) reduction occurs, whereas the increase in H₂S concentration between ~2 and ~3.5 km indicates sulfate reduction is important.

With exception of Eu, the REE concentrations initially show small fluctuations along the groundwater flow path until about 3.7 km (i.e., well 48), and keep relatively constant for the remainder of the flow path sampled. Generally, the increase in REE concentration occurs in phase with the decline in redox potential. Europium concentrations remain essentially the same from well 43 to well 45, and then fluctuate with groundwater flow beyond well 45, which are positively correlated with As concentrations. NASC-normalized REE patterns are characterized by HREE enrichment and LREE depletion for all groundwaters. The Eu/Eu* ratios of all groundwaters are greater than 3, showing groundwaters have positive Eu anomalies. The reducing condition is believed to favour Eu enrichment in groundwaters.

Changes in REE concentrations and shale-normalized patterns indicate that the REEs are not conservative tracers in shallow groundwater. Along the groundwater flow path, reduction, desorption and complexation account for the elevated groundwater REE concentrations, while carbonate complexation and readsorption result in enrichment of the HREEs relative to the LREEs. The major contribution to positive Eu anomalies in groundwaters is expected to be preferential mobilization of Eu²⁺ relative to the trivalent REEs. Since As concentrations vary in phase with Eu concentrations in groundwater, the geochemical controls on positive Eu anomalies imply similar mechanisms for As mobilization in the shallow aquifer in the study area.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.chemgeo.2009.11.010](https://doi.org/10.1016/j.chemgeo.2009.11.010).

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