The geochemical characteristics of aqueous rare-earth elements in shallow karst groundwater in Guiyang City, China

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Abstract   Fifty-seven shallow groundwater samples were collected from Guiyang karst basin, China, to analyze the aqueous rare-earth elements in low-water seasons and it is shown that the total amount of rare-earth elements (ΣREE) in karst groundwater is exceedingly low compared with that in carbonate rocks or weathering crusts of carbonate rocks, and ranges from 0.01 to 0.43, from 0.03 to 0.27, from 0.03 to 0.19 and from 0.05 to 1.38 $\mu g \cdot L^{-1}$ for dolomite, dolomitic & limestone, limestone and clastic rock aquifer, respectively. Both distributions and contents of rare-earth elements (REE) in karst groundwater reflect the lithology of host rocks or weathering crusts of carbonate rocks through which groundwater flows. The chondrite-normalized patterns show a non-flat profile with higher enrichment of slightly light rare-earth elements (LREE) than heavy rare-earth elements (HREE), prominent fractionation between LREE and HREE, negative Ce anomalies and negative or positive Eu anomalies. There is more obvious fractionation between LREE and HREE in groundwater than that in carbonate rocks and their weathering crusts due to high contents of HCO_3^- and PH in groundwater. In shallow karst groundwater, $REE(CO_3)_n^{2n-3}$ (n=1 and 2) is the main inorganic species of REE. But for a clastic rock aquifer, both $REESO_4^+$ and $REECO_3^+$ are the main inorganic species of REE. Species of REE in groundwater is closely associated with the hydrochemical type of groundwater which is predominated by the lithology of host rocks, groundwater-rock interaction and weathering-pedogenesis of carbonate rocks.

Key words   REE; karst groundwater; Ce and Eu anomalies; speciation; Guiyang

1 Introduction

The rare-earth elements (REE) comprise a series of elements including lanthanides with atomic numbers ranging from 57 to 71 (La to Lu) and have similar geochemical properties of the elements Sc and Y. The acronyms of REE are usually used to study different geochemical processes and acquire various significantly geochemical information. Generally, the lanthanides can be classified as three groups, light rare-earth elements (LREE) from La to Nd, middle rare-earth elements (MREE) from Sm to Ho and heavy rare-earth elements (MREE) Er to Lu. The elements of the same group have similar chemical and physical properties. However, the lanthanides can also be divided into two groups as LREE (from La to Eu) and HREE (from Gd to Lu) for diverse studies.

Because of similar physical or chemical properties but slight differences, these elements as groups have been extensively applied in the petrological studies involving igneous, sedimentary and metamorphic rocks and different geochemical processes on the earth's surface (Duddy, 1980; Huang Chengmin and Wang Chengshan, 2002; Li Jingyang et al., 1998; Wang Shijie et al., 2001; Zhu Lijun and Lin Jinye, 1996). Recently, inductively coupled plasma mass spectrometry (ICP-MS) has been extensively used in the field of geochemistry (Shabani et al., 1990; Stetzenbach et al., 1994). Investigations of the REE in groundwaters have been conducted in different regions (Banks et al., 1999; Dia et al., 2000; Fee et al., 1992; Gosselin et al., 1992; Janssen and Verweij, 2003; Johannesson and Hendry, 2000; Johannesson et al., 1996;

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Johannesson et al., 1997; 2000; Johannesson, 2005; Lee et al., 2003; Otsuka and Terakado, 2003; Smedley, 1991). Many investigations into the rare-earth elements have been carried out in karst regions involving weathering crusts of carbonate rocks (Huang Chengmin and Wang chengshan, 2002; Li Jingyang et al., 1998; Wang Shijie et al., 2001; Zhu Lijun and Lin Jinye, 1996). In karst regions, the geochemistry of karst rivers was predominated by the weathering-pedogenesis of carbonate rocks and characterized by the high concentrations of Ca^{2+} or Mg^{2+} and HCO_3^- and high pH values (Han Guilin and Liu Congqiang, 2007). The shallow karst groundwater aquifer is an open system under the oxidation condition, and characterized by the weathering-pedogenesis of carbonate rocks and interaction between groundwater and rocks. Scarcely, any related investigations on the geochemistry of REE have been carried out in this groundwater aquifer. In order to study the contamination and geochemical evolution of shallow groundwater systems in karst regions, in this study, REE study of karst groundwater involved relatively single lithology in shallow groundwater from the Guiyang Basin, China.

2 Materials and methods

2.1 Geographical and hydrogeological settings

Guiyang, the capital city of Guizhou Province where carbonate rocks are widespread in successive outcrop in the world , is located in the central part of Guizhou Province in the southwest of China, with the latitudes and longitudes ranging from 26°32′30″ to 26°40′00″ N and 106°35′40″ to 106°40′00″ E, respectively. The Guiyang Basin is characterized by high elevation and low latitude, a subtropical warm–moist climate, an average altitude of 1000 m, an annual average temperature of 15.3°C and an annual precipitation of 1200 mm. The Nanming River is the main river winding its way through the Guiyang Basin from the SW via the Xiaoche River, which have an annual average flow flux of 13.8 m^3/s and a low-water season flow flux of 4.9 m^3/s. Three reservoirs are located in the study region, i.e., the Aha Lake, and the Xiaoguan and Guanshan Reservoirs, and the Aha Lake is the main water storage resource for Guiyang City.

In the study region, chemical weathering and pedogenesis proceeded intensively, forming the unique karst geological and geomorphological features. The

main exposed strata belong to the Triassic (accounting for nearly 80% of the study region), with some being Permian and a few being Late Jurassic and Silurian in the east. Those are obviously controlled by geologic structures of S-N, N-N-E and E-W extending faults or folds. The rock types are predominated by carbonate rocks (dolomite and limestone) with a few of clastic rocks. The main aquifers in the study region are mostly composed of carbonate rocks (limestone and dolomite, accounting for more than 80% of the aquifers) with a few clastic rocks. The karst groundwater system in Guiyang is very complicated because carbonate rocks and clastic rocks of aquifers are usually interbedded-banded distributed (Han Zhijun and Jin Zhansheng, 1996). The Guiyang Basin is located in the central part of the study area. The altitudes in the north, west and south of the basin are higher than in the east. Therefore, surface water and groundwater are mainly flowing from north, southwest and south to the central part of the basin. The study region is divided into two hydrogeologic zones in terms of the characteristics of recharge, runoff and drainage (Fig. 1).

2.2 Sampling and measurement

In this study, fifty-seven shallow karst groundwater samples were collected from various types of springs and caves in the low-water season (January) (Fig. 1, Table 1). All high-density polyethylene (HDPE) bottles (50, 100 and 500 mL), filters and forceps for sampling were cleaned with acid and dried at 60°C before sampling. In the field, the following parameters were determined through a multi-parameter instrument (Model: Multi 340i) made by WTW (Wissenschaftlich Tlechnische Werkstatten Gmbh & Co. KG): water temperature, pH, electrical conductivity (EC) and dissolved oxygen (DO). The HCO_3^- was measured with the HCl titration method in the field sampling site.

2.3 Analytical procedure and methods

All of the groundwater samples were filtered by 0.22 μm synthetic acetate fabric filtering membrane prior to analysis for cations, anions and rare-earth elements. And all of the samples for the analysis of cations (K^+, Na^+, Ca^{2+} and Mg^{2+}) and rare-earth elements were kept in polythene bottles prior to being filtered, followed by adding ultra-pure HNO_3 to adjust pH lower than 2 and then were kept in an icebox. The samples for the analysis of anions (Cl^-, NO_3^- and SO_4^{2-}) were filtered and kept in polythene bottles. The cations (K^+, Na^+, Ca^{2+} and
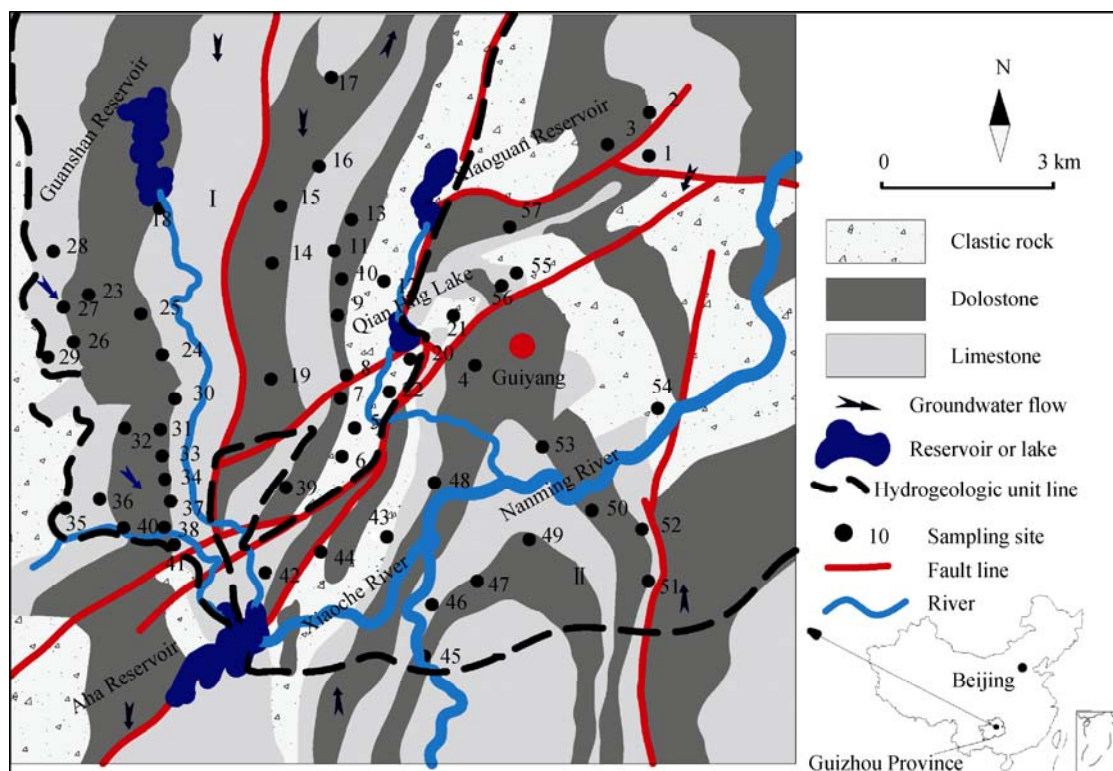
Fig. 1.   The hydrogeologic map showing the distribution of sampling sites in Guiyang karst basin, Guizhou Province, China, modified from the hydrogeologic map of Guiyang City (Han Zhijun and Jin Zhansheng, 1996).

Table 1   The description of sampling sites and aquifers in the Guiyang Basin, China

Sample No.	Description	Discharge (L/s)	Elevation (m)	Stratum	Aquifer
GY01	Gravity spring	0.2	1110	D_{2+3}	Dolomite
GY02	Gravity spring	1.52	1220	T_2g^1	Dolomite & limestone
GY03	Gravity spring	13.1	1220	P_1g+m	Dolomite
GY04	Artesian spring	0.03	1095	Tg^{1-1}	Dolomite
GY05	Gravity spring	0.005	1095	T_3+J	Clastic rocks
GY06	Gravity spring	0.007	1095	T_3+J	Clastic rocks
GY07	Gravity spring	5	1195	T_2g^{4-2}	Dolomite
GY08	Cave water	no data	1150	T_2g^3	Dolomite
GY09	Gravity spring	0.01	1260	T_2g^{4-3}	Dolomite
GY10	Gravity spring	0.01	1225	T_2g^{4-1}	Dolomite
GY11	Gravity spring	0.02	1250	T_2f	Dolomite & limestone
GY12	Gravity spring	0.06	1175	T_3+J	Clastic rocks
GY13	Gravity spring	0.1	1250	T_2g^{4-2}	Dolomite
GY14	Cave water	34	1250	T_2g^{1-2}	Dolomite
GY15	Gravity spring	8	1250	T_2g^{1-2}	Dolomite
GY16	Gravity spring	8	1250	T_2g^{1-1}	Dolomite & limestone
GY17	Artesian spring	7	1260	T_2g^{1-1}	Dolomite & limestone

(*to be continued on the next page*)

Sample No.	Description	Discharge (L/s)	Elevation (m)	Stratum	Aquifer
GY18	Artesian spring	1.2	1240	T_2g^3	Dolomite & limestone
GY19	Gravity spring	0.2	1220	T_2g^2	Dolomite
GY20	Gravity spring	1.5	1075	P_2l	Clastic rocks & minor limestone
GY21	Cave water	1.5	1140	P_2l	Clastic rocks & minor limestone
GY22	Artesian spring	0.2	1095	T_3+J	Clastic rocks
GY23	Artesian spring	67.2	1436	T_2g^{1-2}	Dolomite
GY24	Gravity spring	12	1230	T_2g^2	Dolomite & limestone
GY25	Artesian spring	8	1220	T_2g^2	Dolomite
GY26	Cave water	8	1240	T_2g^{1-1}	Dolomite & limestone
GY27	Cave water	0.42	1240	T_2d^2	Dolomite & limestone
GY28	Artesian spring	39.2	1260	T_2d^2	Limestone
GY29	Gravity spring	28	1290	P_2c	Limestone
GY30	Gravity spring	no data	1250	T_2g^{1-2}	Dolomite & limestone
GY31	Gravity spring	0.1	1210	T_2g^{1-2}	Dolomite
GY32	Gravity spring	0.1	1200	T_2g^{1-2}	Dolomite
GY33	Gravity spring	0.01	1180	T_2g^2	Dolomite
GY34	Gravity spring	1	1240	T_2g^{1-2}	Dolomite
GY35	Artesian spring	0.2	1240	P_2c	Limestone
GY36	Cave water	0.15	1230	T_2d^1	Limestone
GY37	Gravity spring	10	1190	T_2g^2	Dolomite & limestone
GY38	Gravity spring	0.3	1200	T_2g^{1-2}	Dolomite
GY39	Cave water	16	1180	T_2g^2	Dolomite
GY40	Gravity spring	100	1140	T_2g^{1-1}	Dolomite & limestone
GY41	Gravity spring	5	1150	T_2d^2	Dolomite & limestone
GY42	Gravity spring	0.16	1120	T_2g^{1-2}	Limestone
GY43	Gravity spring	5	1080	P_2d+T_1s	Clastic rocks & minor limestone
GY44	Gravity spring	0.25	1080	P_2l	Clastic rocks & minor limestone
GY45	Gravity spring	2.72	1100	T_2g^{4-1}	Dolomite
GY46	Gravity spring	6	1100	T_2g^{4-2}	Limestone
GY47	Gravity spring	6	1100	T_2g^{4-1}	Dolomite
GY48	Gravity spring	1	1020	T_2g^{1-1}	Dolomite & limestone
GY49	Gravity spring	0.5	1030	T_2g^{4-2}	Limestone
GY50	Gravity spring	3	1080	T_2g^{4-1}	Dolomite
GY51	Gravity spring	1.5	1000	T_2g^{1-2}	Dolomite & limestone
GY52	Gravity spring	2	1090	T_2g^{1-1}	Dolomite & imestone
GY53	Gravity spring	1	1050	T_2g^{1-2}	Dolomite & limestone
GY54	Gravity spring	37.5	1040	P_2l	Clastic rocks & minor limestone
GY55	Gravity spring	0.6	1040	T_2d^2	Limestone
GY56	Gravity spring	4	1060	T_2d^1	Limestone
GY57	Cave water	8.1	1100	T_2d^1	Dolomite

Mg^{2+}) were determined by atomic absorption spectrometry (AAS), while the anions (Cl$^-$, NO$_3^-$ and SO$_4^{2-}$) were determined by high-efficiency liquid chromatography. The hydrochemistry of shallow groundwater has been investigated adequately (Han Zhijun and Jin Zhansheng, 1996). The aqueous rare-earth elements (REE) in karst groundwater samples were measured by inductively coupled plasma mass spectrometry (ICP-MS, ELEMENT). However, the REE concentrations of groundwater samples are below the detection limit of the ICP-MS. Consequently, we used a series of extraction and back-extraction methods to analyze the REE in groundwater samples (Shabani et al., 1990). The REEs in shallow groundwater samples were concentrated 100 times at least. The analysis of dissolved REE concentrations includes the following steps: the REEs were extracted from water samples with 65% HDEHP (2-ethylhexyl hydrogen phosphate) and 35% H$_2$MEHP (2-ethylhexyl dihydrogen phosphate) in heptane, then back-extracted with 6N ultra-pure HCl and transformed into (REE) (NO$_3$)$_3$ for ICP-MS analysis. The following isotopes of REE were used for REE measurement: ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{151}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{167}Er, ^{169}Tm, ^{173}Yb, ^{175}Lu, and ^{89}Y. The detection limits are presented as follows: ^{139}La (0.018), ^{140}Ce (0.028), ^{141}Pr (0.005), ^{146}Nd (0.076), ^{147}Sm (0.009), ^{151}Eu (0.002), ^{157}Gd (0.021), ^{159}Tb (0.002), ^{163}Dy (0.009), ^{165}Ho (0.003), ^{167}Er (0.005), ^{169}Tm (0.002), ^{173}Yb (0.003), ^{175}Lu (0.0005), and ^{89}Y (0.022) µg/L. The entire analytical procedure was accomplished in the laboratory by using Millipore-Q water (18.2 QW cm) and ultra-pure reagents. The accuracy and precision of most REE measurements were kept within the range of ±3%, and those of the light REEs La and Ce were within the ranges of ±5% and ±10%, respectively (Han Guilin and Liu Congqiang, 2007). The rare-earth elements were analyzed at the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences (see the Appendix).

3 Results and discussion

3.1　The concentrations and distribution of REE in karst groundwater

In karst regions, the concentrations of aqueous REE in shallow groundwater are extremely low as compared with those in bedrock and weathering crust, whose ΣREE ranges from 0.01 to 0.43, from 0.03 to 0.27, from 0.03 to 0.19 , and from 0.05 to 1.38 µg·L^{-1} in dolomite, dolomite & limestone, limestone and clastic rock aquifers, respectively (Fig. 2). The REEs were usually absorbed by clay minerals and remained in carbonate weathering crusts, and a few REE were eluviated into aquifers by groundwater or interaction between water and rock in the process of weathering-pedogenesis of carbonate rocks. Consequently, the concentrations of REE in bedrock and weathering crusts are possible several orders of magnitude higher than those in karst groundwater systems. The concentrations and distribution of REE in karst shallow groundwater are obviously controlled by the geologic settings such as lithology and weathering-pedogenesis of carbonate rocks (Huang Chengmin and Wang Chengshan, 2002; Li Jingyang et al., 1998). However, the ΣREE of clastic rock aquifer varies widely due to the oxidation of iron-pyrites (FeS$_2$) in coal-seam strata or the weathering and dissolution of sulfatic-evaporite minerals (gypsum or anhydrite) and H$_2$SO$_4$ releasing. Strong weathering-pedogenesis and REE releasing from minerals enriched in REE would induce high REE concentrations in groundwaters. Samples GY06 and GY12T were collected from a clastic rock aquifer characterized by the high contents of REE. The distributions of REE in clastic rock aquifers also reflect the geologic environments through which groundwater flows. REEs are different in different Ca^{2+}/Mg^{2+} (molar ratio) aquifers through which groundwater flows and dominated by limestone, clastic rock and dolomite (Fig. 2).

3.2　Chondrite-normalized REE distribution patterns in groundwater

The REE composition of chondrite is usually used to normalize the values of REE concentration in different investigations in sedimentary rock regions. Groundwater is REE chondrite-normalized for different types of rock aquifers, showing a non-flat profile in distribution pattern. Although the concentrations of REE in karst groundwater are several orders of magnitude lower than those in bedrocks or weathering crust of carbonate rocks, the REE distribution patterns in groundwater have similar profiles to those in bedrocks and weathering crust of carbonate rocks. Compared with the weathering crusts of bedrocks and carbonate rocks, Ce is characterized by prominent negative anomalies and Eu is characterized by negative or positive anomalies in dolomitic, dolomitic & limestone, limestone and clastic rock aquifers (Fig. 3).
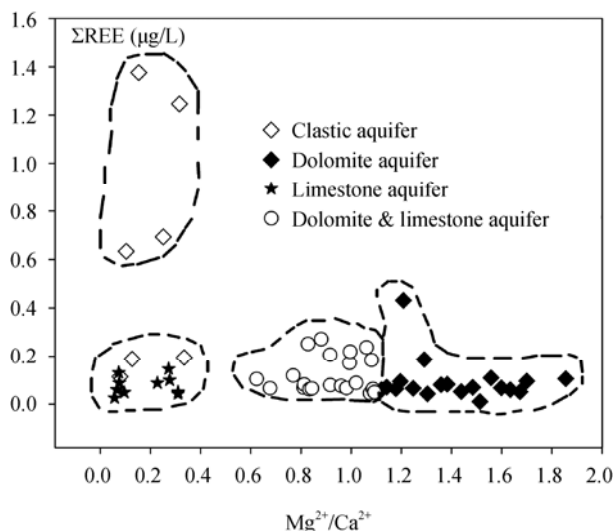
Fig. 2. Plot showing the concentrations and distribution of REE in different karst shallow groundwaters due to lithologic differences. For different karst aquifers, ratios of Ca^{2+}/Mg^{2+} (molar ratio) show differences in groundwater flowing through different geologic environments (limestone aquifer is characterized by high contents of Ca^{2+} and dolomite aquifer characterized by high concentrations of Mg^{2+}). It can be used to distinguish the type of aquifer through which groundwater flows (Han Zhijun and Jin Zhansheng, 1996). The hydrochemistry of shallow groundwater has been investigated adequately (Dong Zhifen et al., 2005).

In our investigations, the prominent fractionation between LREE and HREE was discovered in karst groundwater systems. For the chondrite-normalized REE patterns in groundwater, it can be found that the ratios of LREE/ HREE are within the range of 4.37–12.34 (7.18 on average), 3.60–10.32 (7.26 on average), 4.05–11.35 (7.46 on average) and 4.58–8.70 (7.11 on average) in dolomitic, dolomitic & limestone, limestone and clastic rock aquifers, respectively (Fig. 4). For the Permian and Triassic carbonate rocks or carbonate weathering crusts in the study region, which is characterized by slight LREE enrichment and HREE depletion (Li Jingyang et al., 1998; Nan Junya et al., 2002; Wang Shijie et al., 2001). Accordingly, the groundwater associated with these carbonate rocks or carbonate weathering crusts inherits their distribution patterns, yet is more fractionated through groundwater flowing (Han Guilin and Liu Congqiang, 2007; Johannesson et al., 2000). From LREE to HREE the ability of rare-earth elements to form carbonate complexes trends to increase, and the carbonate complexes might be removed by the adsorption of suspended complexes in groundwater flow (Johannesson et al., 1995; Johannesson, 2005). High
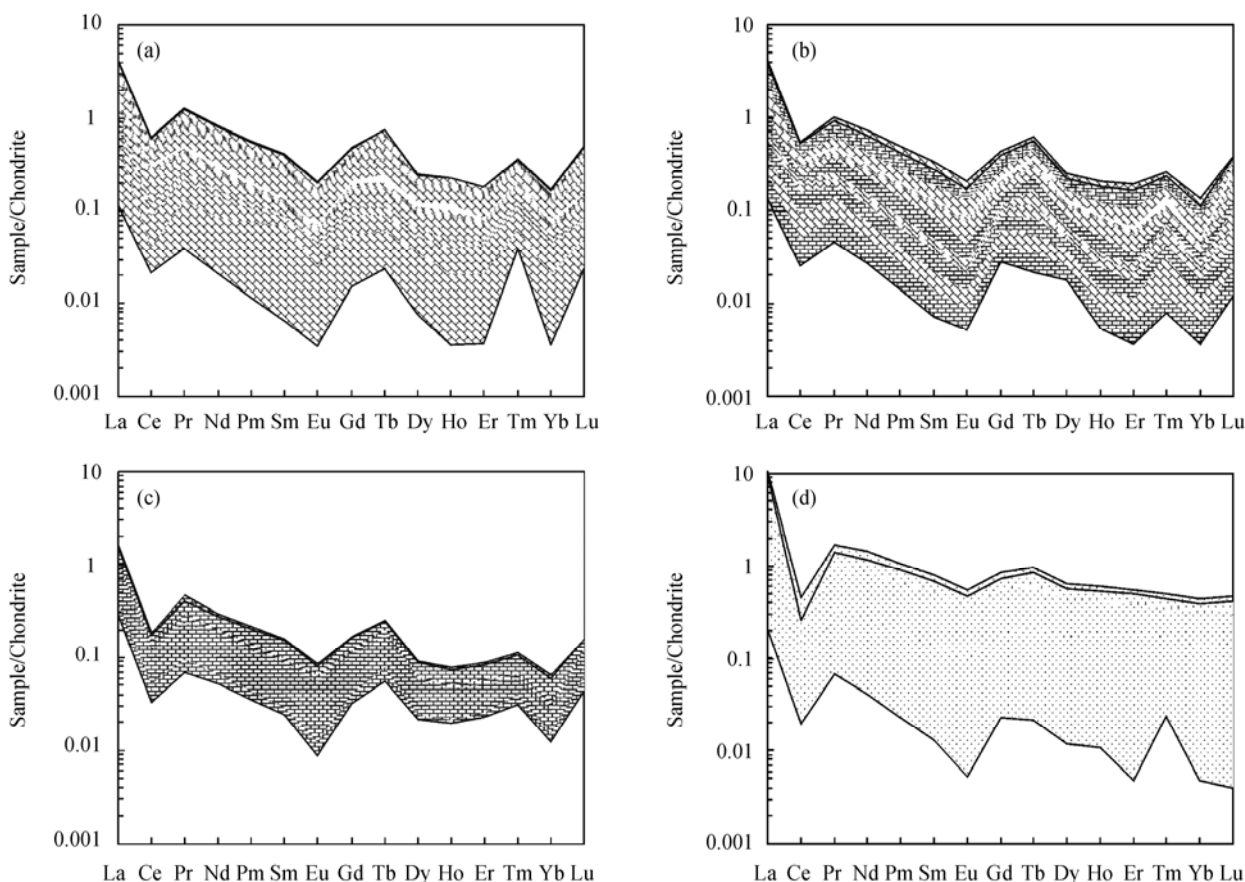
Fig. 3. The chondrite-normalized distribution patterns in different lithologic groundwater aquifers: (a) Dolomitic aquifer; (b) dolomitic & limestone aquifer; (c) limestone aquifer; and (d) clastic rock aquifer.

concentrations of HCO_3^- in groundwater in karst regions are regard as an important factor affecting the obvious fractionation between light rare-earth elements and heavy rare-earth elements.

3.3   Ce and Eu anomaly characteristics

Ce and Eu anomalies were found in carbonate rock aquifers, which may be closely associated with redox environment or processes. The Ce and Eu anomalies (δCe and δEu) were calculated from the following equations (Elderfield and Greaves, 1982; Winograd and Robertson, 1982):

$$\delta Ce = 2(Ce/Ce^*)/(La/La^* + Pr/Pr^*) \qquad (1)$$
$$\delta Eu = 2(Eu/Eu^*)/(Sm/Sm^* + Gd/Gd^*) \qquad (2)$$

In the above equations, La^*, Ce^*, Pr^*, Sm^*, Eu^* and Gd^* are the average concentrations of respective REE in chondrite, and La, Ce, Pr, Sm, Eu and Gd represent the contents of respective REE in karst groundwater. The REE are considered as being in trivalent state in low-temperature groundwaters, however, both Ce and Eu are sensitive to oxidative and reductive conditions. Ce^{3+} can be oxidized into Ce^{4+} and Eu^{3+} can be reduced into Eu^{2+} easily under oxidative or reductive conditions. Compared with carbonate rocks and weathering crusts of carbonate rocks, shallow karst groundwater shows more Ce prominent negative anomalies with δCe values within the ranges of 0.05 to 0.69, 0.06 to 0.55, 0.06 to 0.61 and 0.01 to 0.23 in dolomitic, dolomitic & limestone, limestone and clastic rock aquifers, respectively (Fig. 5). That might be induced from the fact that the shallow karst groundwater system is a chronically open system under oxidation condition, and Ce^{3+} is characterized by obvious negative anomalies and oxidized into Ce^{4+} easily (De Baar et al., 1988; Elderfield and Greaves, 1982; Winograd and Robertson, 1982). Moreover, pH is also an important factor affecting Ce anomalies (Akagi and Masuda, 1998; Han Guilin and Liu Congqiang, 2007; Otsuka and Terakado, 2003; Tricca et al., 1999):

$$Ce^{3+} + 2H_2O = CeO_2 + 4H^+ + e^- \qquad (3)$$
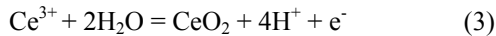
In the karst groundwater, the values of pH range from 5.68 to 9.15 with the mean value of 7.50, representing a neutral environment. Thus, the aqueous Ce^{3+} in groundwater is probably deposited as CeO_2 in solid phase and easily removed by absorption or groundwater flowing, which might be responsible for remarkable Ce depletion in karst groundwater. Therefore, the shallow karst groundwater is characterized by remarkable negative Ce anomalies under open and oxidation conditions with high pH. Furthermore, both negative and positive Eu anoma-

lies exist in the karst shallow groundwater with δEu values ranging from 0.25 to 0.94, from 0.28 to 0.92, from 0.22 to 1.23 and from 0.29 to 0.81 in dolomitic, dolomitic & limestone, limestone and clastic rock aquifers, respectively (Table 2, Fig. 5).
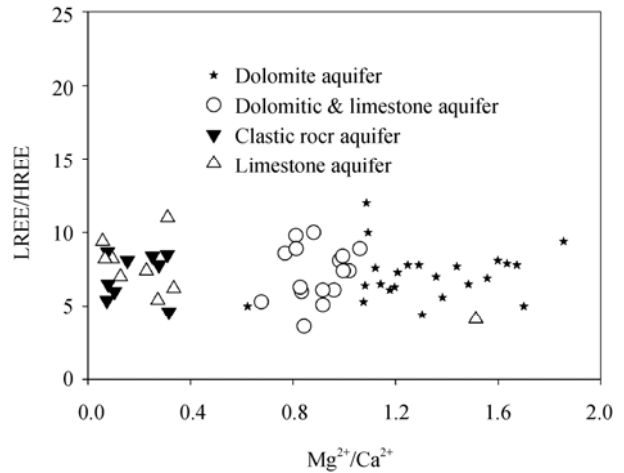
Fig. 4.   Plot of obvious fractionation between light rare-earth elements (LREE) and heavy rare-earth elements (HREE) in different lithologic shallow karst groundwaters.
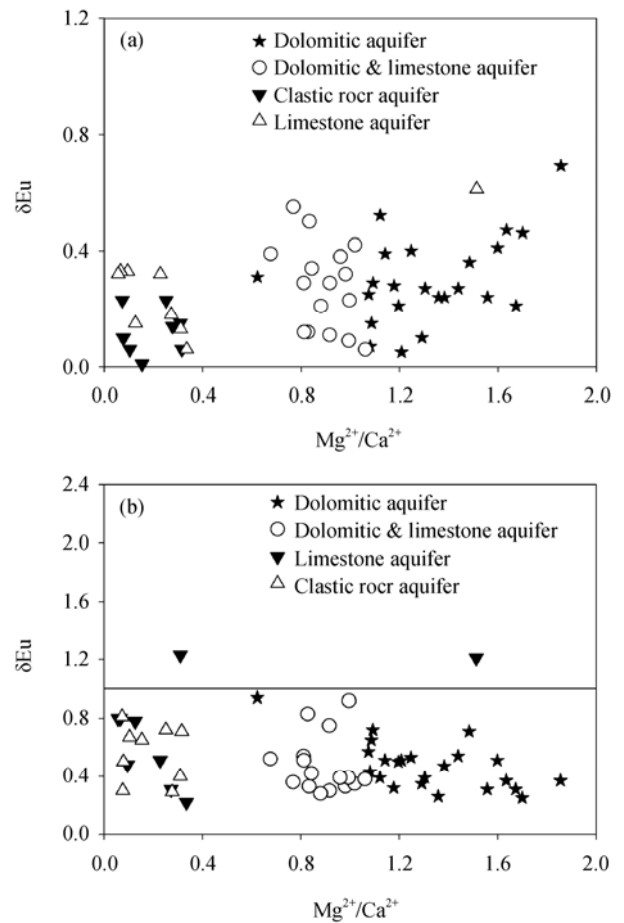
Fig. 5.   Plot of Ce and Eu anomalous characteristics in different lithologic shallow karst groundwaters.

Eu anomalies also exist in carbonate rocks or the weathering crusts of carbonate rocks (Li Jingyang et al., 1998; Nan Junya et al., 2002; Wang Shijie et al., 2001). Eu anomalies may be associated with the weathering-pedogenesis of carbonate rocks. During the process of weathering-pedogenesis of carbonate rocks, the rare-earth elements were released into groundwaters from weathering crusts by eluviation or groundwater-rock interaction. To sum up, both negative and positive Eu anomalies in groundwater inherit those from carbonate rocks and the weathering crusts of carbonate rocks. Both negative and positive Eu anomalies in karst shallow groundwaters also indicate that the rare-earth elements are dominated by the geological background and reflect the composition of their host rocks. (Johannesson et al., 2000; Smedley, 1991).

3.4　The species of REE in shallow karst groundwater

The species of REE in groundwater have been extensively investigated by using different geochemical methods and models (Johannesson et al., 1995; Johan-nesson et al., 1997; Johannesson et al., 2000; Lee and Byrne, 1993; Millero, 1992). The species of REE in different lithologic types of shallow karst groundwater were calculated with the geochemical speciation equilibrium model Visual MINTEQ ver.2.53 (Gustaffson, 2007) on the basis of MINTEQA2. In the dolomitic, dolomitic limestone and limestone aquifers, species of REE are similar, mainly including $REECO_3^+$ and $REE(CO_3)_2^-$. Total percentages of $REECO_3^+$ and $REE(CO_3)_2^-$ are within the ranges of 86.2% to 99.4%, 72.6% to 97.8% and 88.8% to 99.2% in dolomitic aquifer, dolomitic limestone aquifer and limestone aquifer, respectively [Fig. 6(a), (b), and (c)]. The species of $REECO_3^+$ decreases with increasing atomic number, but the species of $REE(CO_3)_2^-$ increases with increasing atomic number (Fig. 6).

Generally, the species of $REE(CO_3)_n^{2n-3}$(n=1 and 2) is the dominant compound in a single lithologic karst aquifer. It can be explained that similar rocks and minerals (such as dolomite or calcite) are weathered or dissolved in dolomitic, dolomitic & limestone and limestone aquifers and characterized by similar types of groundwater (Han Zhijun and Jin Zhansheng, 1996). The dissolution
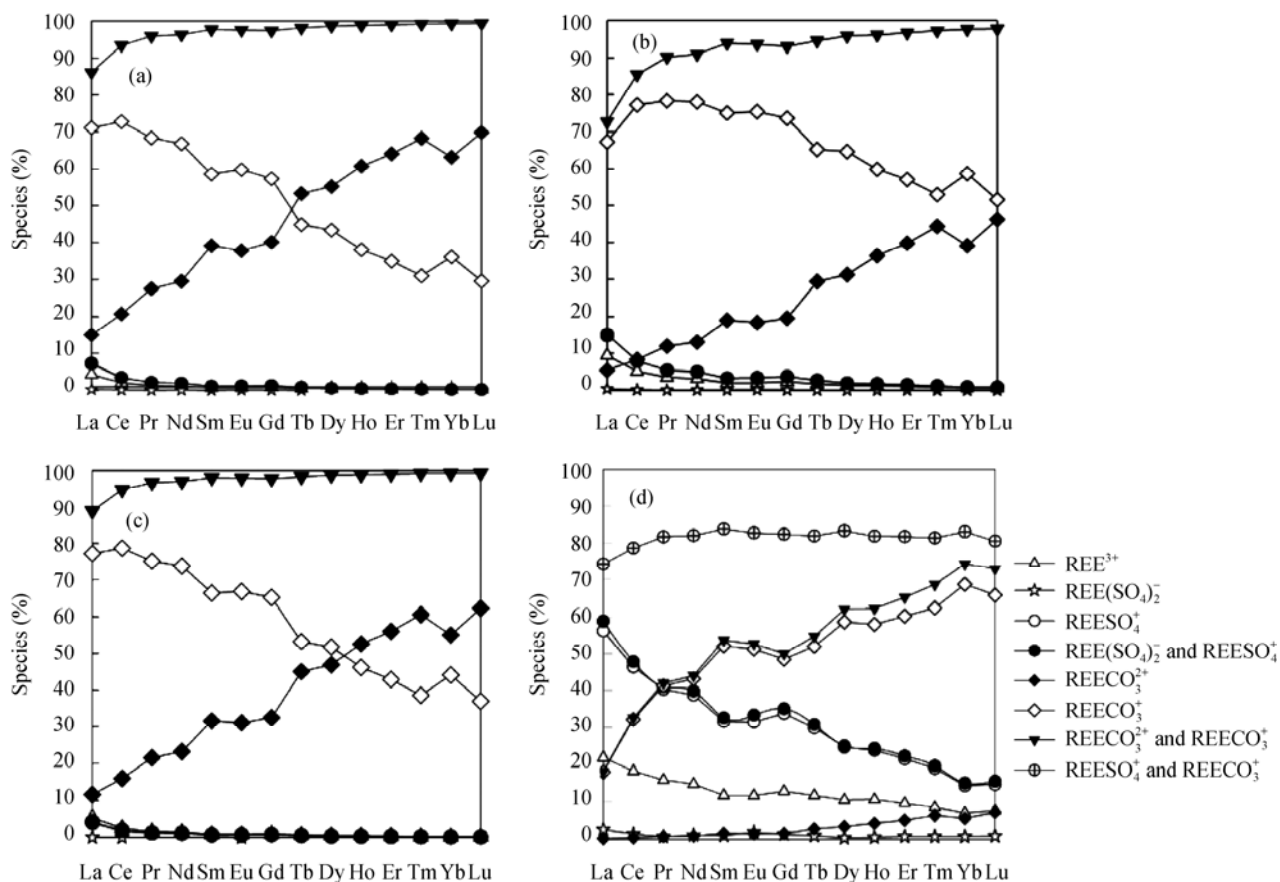
Fig. 6.　The inorganic species of REE in different lithologic shallow katst groundwaters; (a) Dolomitic aquifer; (b) dolomitic limestone aquifer; (c) limestone aquifer; and (d) clastic rock aquifer.

or weathering of minerals can be defined as the following equation:

$$Ca_nMg_{(1-n)}CO_3 + H_2O + CO_2(g) =$$
$$nCa^{2+} + (1-n)Mg^{2+} + 2HCO_3^- \qquad (4)$$
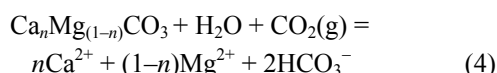
where, $0 < n \leq 1$, n and $(1-n)$ is the ratio of Ca/Mg in dolomite or calcite. The dissolution or weathering of dolomite or calcite in these aquifers controls the hydrochemical type of groundwater. And the hydrochemical type of groundwater is classified as HCO_3-Ca·Mg or HCO_3-Ca in karst aquifers, respectively. Previous investigations suggested that elevated carbonate ion concentrations in natural waters can facilitate the enhancement of dissolved REE concentrations via formation of REE carbonate complexes. Consequently, the species of $REE(CO_3)_n^{2n-3}$ ($n=1$ and 2) is the main REE compound in the karst groundwater.

$REESO_4^+$ and $REECO_3^+$ are the most dominant species of rare-earth elements in the clastic rock aquifer with the concentrations within the range of 74.2% to 80.5%. The species of $REESO_4^+$ decreases with increasing atomic number, but the species $REECO_3^+$ displays a reverse case [Fig. 6 (d)]. Higher contents of SO_4^{2-} in the crastic aquifer may induce the oxidation of iron-pyrite (FeS_2) in coal-seam strata or the weathering and dissolution of sulfatic-evaporite minerals (gypsum or anhydrite). The chemical reactions follow the following equations:

$$FeS_{2(s)} + 15/4 \, O_{2\,(g)} + 7/2 \, H_2O =$$
$$Fe(OH)_{3\,(s)} + 2SO_4^{2-} + 4H^+ \qquad (5)$$
$$CaSO_4 \cdot 2 \, H_2O_{(s)} = Ca^{2+} + SO_4^{2-} + 2H^+ \qquad (6)$$
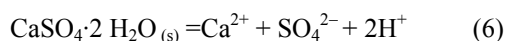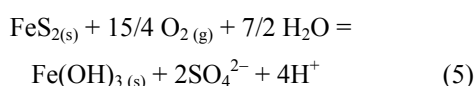
Therefore, the groundwater is characterized by the types of $HCO_3 \cdot SO_4^{2-}$-Ca or SO_4^{2-}-Ca, and the corresponding inorganic species of REE are $REESO_4^+$ and $REECO_3^+$. For the inorganic speciation of REE in shallow karst groundwater, the species of rare-earth elements is controlled by the hydrochemical type of groundwater which is controlled by lithology through which groundwater flows. The karst groundwater predominated by geologic environment and that by aquiferous materiales shows different REE geochemical characteristics. Accordingly, the species of rare-earth elements and Ce or Eu anomalies can be used as tracers to investigate karst groundwater-rock interactions and the evolution of groundwater systems.

4 Conclusions

The concentrations of rare-earth elements in the groundwater are exceedingly low in karst regions. The chondrite-normalize REE patterns show a non-flat profile, slight LEE enrichment as compared with HREE, prominent fractionation between LREE and HREE, negative Ce anomalies and negative or positive Eu anomalies.

(1) The distribution profiles of REE in groundwater inherit those from carbonate rocks and the weathering crusts of carbonate rocks. However, obvious fractionation between LREE and HREE can be explained that the ability of formation of complexes increases with increasing atomic number from LREE to HREE. And the HREE are easy to remove as carbonate compounds through precipitation of groundwater and characterized by obvious depletion.

(2) Remarkable negative Ce anomalies in karst groundwater can be explained that the karst groundwater system is a chronically open system under oxidation conditions, where aqueous Ce^{3+} might be easy to oxidized into Ce^{4+}. The value of pH might be also an important factor affecting Ce anomalies. Aqueous Ce^{3+} forms solid-phase CeO_2 is removed by absorption or groundwater flow easily, it might induce strong Ce depletion in karst groundwater. Both negative and positive Eu anomalies in karst groundwater reflect similar features in carbonate rocks or the weathering crusts of carbonate rocks.

(3) The species of $REE(CO_3)_n^{2n-3}$ ($n=1$ and 2) are the major inorganic species of REE in katst groundwater. However, in clastic rock aquifer, due to the oxidation of iron-pyrite (FeS_2) in coal-seam strata or the weathering-pedogenesis and dissolution of sulfit evaporite minerals (gypsum or anhydrite), both $REEO_4^+$ and $REECO_3^+$ are the main inorganic species of REE. Inorganic species of REE in groundwater are closely associated with the hydrochemical type of groundwater which is predominated by the geological environment through which groundwater flows, groundwater-rock interaction, and weathering-pedogenesis of carbonate rocks.

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Appendix

The REE composition of shallow karst groundwater from the karst basin (Guiyang), China (μg·L⁻¹)

Sample No.	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	ΣREE	LREE	HREE	L/H	δEu	δCe
Dolomite aquifer																				
GY01	0.0271	0.0131	0.0037	0.0096	0.001	0.0002	0.0031	0.0009	0.0019	0.0002	0.0006	0.001	0.0006	0.0006	0.0636	0.0547	0.0089	6.15	0.32	0.28
GY03	0.0976	0.0114	0.0087	0.0302	0.0097	0.0013	0.0083	0.0014	0.0071	0.0013	0.0029	0.0006	0.0029	0.0007	0.1838	0.1589	0.0249	6.38	0.43	0.07
GY04	0.0436	0.0212	0.0041	0.0156	0.0015	0.0008	0.004	0.0008	0.0037	0.0009	0.0031	0.0007	0.0037	0.0006	0.1043	0.0868	0.0175	4.96	0.94	0.31
GY07	0.0218	0.0089	0.0042	0.0094	0.0009	0.0002	0.0033	0.0002	0.0008	0.0001	0.0005	0.0003	0.0005	0.0001	0.0512	0.0454	0.0058	7.83	0.31	0.21
GY08	0.0379	0.0154	0.0044	0.0115	0.0012	0.0002	0.0033	0.0007	0.0008	0.0001	0.0008	0.0003	0.0007	0.0001	0.0807	0.0706	0.0101	6.99	0.26	0.24
GY09	0.0466	0.0199	0.0073	0.019	0.0024	0.0004	0.0039	0.0007	0.0037	0.0007	0.0012	0.0007	0.0009	0.0001	0.1094	0.0956	0.0138	6.93	0.31	0.24
GY10	0.0342	0.0277	0.005	0.0113	0.0011	0.0002	0.0041	0.001	0.0033	0.0013	0.0026	0.0012	0.0017	0.0008	0.0955	0.0795	0.016	4.97	0.25	0.46
GY13	0.0353	0.0405	0.0042	0.0136	0.0012	0.0002	0.0041	0.0008	0.0027	0.0005	0.0008	0.0002	0.001	0.0003	0.1052	0.0951	0.0101	9.42	0.37	0.69
GY14	0.0209	0.019	0.0029	0.0091	0.001	0.0002	0.0023	0.001	0.0013	0.0005	0.0006	0.0002	0.0007	0.0004	0.0601	0.0531	0.007	7.59	0.39	0.52
GY15	0.0441	0.0145	0.0038	0.0171	0.0013	0.0004	0.0039	0.0016	0.0037	0.0013	0.0009	0.0003	0.001	0.0002	0.0941	0.0812	0.0129	6.29	0.5	0.21
GY19	0.2255	0.0196	0.0235	0.0891	0.0187	0.0031	0.0178	0.0035	0.0119	0.0024	0.0075	0.0012	0.0066	0.0013	0.4317	0.3795	0.0522	7.27	0.51	0.05
GY23	0.0219	0.0111	0.0033	0.0077	0.0008	0.0003	0.0009	0.0009	0.0007	0.0002	0.0005	0.0002	0.0006	0.0003	0.0493	0.045	0.0043	10.5	0.72	0.29
GY25	0.0145	0.0086	0.0042	0.0061	0.0008	0.0003	0.0044	0.001	0.0007	0.0001	0.0004	0.0002	0.0004	0.0007	0.0424	0.0345	0.0079	4.37	0.39	0.27
GY31	0.0344	0.0139	0.0043	0.0158	0.0013	0.0004	0.0043	0.0023	0.0021	0.0008	0.0008	0.0002	0.0009	0.0011	0.0826	0.0701	0.0125	5.61	0.47	0.24
GY32	0.0256	0.0179	0.0034	0.0115	0.0011	0.0003	0.0048	0.0013	0.0013	0.0002	0.0006	0.0002	0.0006	0.0009	0.0672	0.0598	0.0074	8.08	0.51	0.41
GY33	0.0203	0.0179	0.0036	0.0099	0.001	0.0002	0.0025	0.0015	0.0008	0.0001	0.0005	0.0002	0.0005	0.0006	0.0596	0.0529	0.0067	7.9	0.37	0.47
GY34	0.0271	0.0179	0.0034	0.0112	0.0011	0.0003	0.0027	0.0022	0.0016	0.0002	0.0006	0.0002	0.0007	0.0012	0.0704	0.061	0.0094	6.49	0.51	0.39
GY38	0.0249	0.0173	0.0035	0.011	0.001	0.0002	0.0021	0.0021	0.0009	0.0001	0.0005	0.0002	0.0006	0.0002	0.0654	0.058	0.0074	7.84	0.53	0.4
GY39	0.0276	0.0164	0.0031	0.0114	0.0011	0.0004	0.0025	0.0014	0.0019	0.0002	0.0009	0.0002	0.001	0.0011	0.0692	0.06	0.0092	6.52	0.71	0.36
GY45	0.0232	0.0106	0.0028	0.0085	0.0009	0.0002	0.0027	0.001	0.0009	0.0002	0.0005	0.0001	0.0005	0.0001	0.0523	0.0463	0.006	7.72	0.54	0.27
GY47	0.0954	0.0149	0.0097	0.0338	0.0105	0.0011	0.0082	0.0015	0.0064	0.001	0.0019	0.0002	0.0012	0.0007	0.1865	0.1654	0.0211	7.84	0.35	0.1
GY50	0.0312	0.008	0.0041	0.0133	0.0011	0.0003	0.0018	0.0002	0.0009	0.0002	0.0006	0.0002	0.0007	0.0001	0.0627	0.058	0.0047	12.3	0.65	0.15
GY57	0.0152	0.0081	0.004	0.0086	0.0011	0.0004	0.0035	0.0011	0.001	0.0002	0.0007	0.0003	0.001	0.0002	0.0445	0.0374	0.0071	5.27	0.57	0.25
Dolomite & limestone aquifer																				
GY02	0.0319	0.0157	0.0043	0.0125	0.0011	0.0003	0.0057	0.0008	0.0045	0.0003	0.0006	0.0002	0.0006	0.0003	0.0788	0.0658	0.013	5.06	0.3	0.29
GY11	0.0271	0.015	0.0037	0.012	0.001	0.0002	0.003	0.0005	0.0022	0.0002	0.0005	0.0001	0.0005	0.0003	0.0663	0.059	0.0073	8.08	0.33	0.32
GY16	0.034	0.0254	0.005	0.0117	0.0013	0.0003	0.0043	0.0008	0.0028	0.0003	0.0008	0.0005	0.0009	0.0001	0.0882	0.0777	0.0105	7.4	0.35	0.42
GY17	0.0428	0.0394	0.0049	0.0167	0.0023	0.0004	0.0048	0.0011	0.0033	0.0006	0.0009	0.0003	0.001	0.0004	0.1189	0.1065	0.0124	8.59	0.36	0.55
GY18	0.0203	0.0182	0.0032	0.0096	0.0009	0.0002	0.0031	0.0012	0.0012	0.0004	0.0008	0.0006	0.0009	0.0006	0.0612	0.0524	0.0088	5.95	0.33	0.5
GY24	0.0248	0.0162	0.003	0.0098	0.0011	0.0003	0.0026	0.0017	0.0031	0.0002	0.0011	0.0002	0.0008	0.001	0.0657	0.0552	0.0105	5.26	0.52	0.39
GY26	0.0883	0.0132	0.0094	0.0361	0.0054	0.0008	0.0072	0.0025	0.0046	0.0009	0.0011	0.0005	0.001	0.0008	0.1715	0.1532	0.0183	8.37	0.39	0.09
GY27	0.1209	0.0391	0.0049	0.0212	0.0049	0.0019	0.008	0.0027	0.0069	0.0017	0.0036	0.0005	0.0012	0.0016	0.2191	0.1929	0.0262	7.36	0.92	0.23
GY30	0.0284	0.019	0.0041	0.0119	0.0012	0.0003	0.0038	0.0018	0.0017	0.0002	0.0009	0.0002	0.0008	0.0013	0.0756	0.0649	0.0107	6.07	0.39	0.38
GY37	0.0206	0.0139	0.0044	0.0103	0.0012	0.0004	0.0051	0.0014	0.0033	0.0004	0.0009	0.0008	0.0011	0.001	0.0649	0.0508	0.0141	3.6	0.42	0.34
GY40	0.1257	0.023	0.0116	0.0467	0.0079	0.0024	0.0098	0.0022	0.0078	0.0017	0.0058	0.001	0.0052	0.001	0.2518	0.2173	0.0345	6.3	0.83	0.12
GY41	0.0289	0.0138	0.0034	0.0141	0.001	0.0003	0.0026	0.0012	0.0009	0.0002	0.0006	0.0001	0.0006	0.0001	0.0678	0.0615	0.0063	9.76	0.54	0.29
GY48	0.149	0.0479	0.0098	0.0354	0.005	0.0006	0.0085	0.0015	0.0059	0.0014	0.0042	0.0004	0.0016	0.0004	0.2717	0.2477	0.024	10.3	0.28	0.21
GY51	0.1416	0.013	0.0108	0.0404	0.0066	0.0009	0.0081	0.0015	0.0063	0.0014	0.0042	0.0006	0.0015	0.0003	0.2372	0.2133	0.0239	8.92	0.38	0.06
GY52	0.0429	0.0085	0.0047	0.0156	0.0012	0.0004	0.0039	0.0004	0.0017	0.0002	0.0007	0.0002	0.0009	0.0002	0.0815	0.0733	0.0082	8.94	0.51	0.12
GY53	0.103	0.0182	0.0088	0.035	0.0099	0.0023	0.0083	0.0018	0.0073	0.0015	0.0049	0.0006	0.0041	0.0004	0.2061	0.1772	0.0289	6.13	0.75	0.11
Limestone aquifer																				
GY28	0.0684	0.0199	0.0066	0.0243	0.0037	0.0005	0.0065	0.0021	0.0054	0.0011	0.0038	0.0008	0.0021	0.0011	0.1463	0.1234	0.0229	5.39	0.31	0.18
GY29	0.0209	0.0116	0.0027	0.0065	0.0008	0.0002	0.0019	0.0008	0.0007	0.0001	0.0005	0.0002	0.0005	0.0005	0.0479	0.0427	0.0052	8.21	0.48	0.33
GY35	0.035	0.0194	0.0046	0.0161	0.0017	0.0005	0.0046	0.0013	0.0022	0.0001	0.0008	0.0003	0.0007	0.0005	0.0878	0.0773	0.0105	7.36	0.51	0.32
GY36	0.0912	0.0221	0.0089	0.0343	0.0069	0.0019	0.0081	0.0025	0.0061	0.0012	0.0034	0.0003	0.0012	0.0008	0.1889	0.1653	0.0236	7	0.78	0.15
GY42	0.0246	0.0135	0.003	0.0106	0.001	0.0005	0.0031	0.001	0.0008	0.0002	0.0005	0.0001	0.0006	0.0002	0.0597	0.0532	0.0065	8.18	0.8	0.33
GY46	0.0099	0.0063	0.0022	0.0041	0.0008	0.0002	0.0007	0.0001	0.0005	0.0001	0.0005	0.0001	0.0004	0.0001	0.026	0.0235	0.0025	9.4	0.8	0.32
GY49	0.0016	0.0036	0.0012	0.001	0.0005	0.0002	0.0007	0.0001	0.0004	0.0001	0.0003	0.0001	0.0004	0.0001	0.0101	0.0081	0.002	4.05	1.21	0.61
GY55	0.1073	0.0106	0.0092	0.0315	0.0084	0.0006	0.0082	0.0014	0.0064	0.0012	0.0041	0.0009	0.0043	0.0007	0.1948	0.1676	0.0272	6.16	0.22	0.06
GY56	0.0241	0.0064	0.0056	0.008	0.0009	0.0004	0.0011	0.0002	0.0009	0.0002	0.0006	0.0002	0.0007	0.0001	0.0494	0.0454	0.004	11.4	1.23	0.13
Clastic rock aquifer																				
GY05	0.0493	0.0117	0.0064	0.0189	0.002	0.0003	0.0047	0.0008	0.003	0.0006	0.0008	0.0006	0.0008	0.0001	0.1	0.0886	0.0114	7.77	0.29	0.14
GY06	1.0439	0.0189	0.0259	0.1116	0.0191	0.0054	0.0333	0.0075	0.0407	0.01	0.0302	0.0038	0.0219	0.0036	1.3758	1.2248	0.151	8.11	0.65	0.01
GY12	0.5958	0.0558	0.0551	0.245	0.057	0.0145	0.0683	0.013	0.0631	0.0119	0.031	0.0035	0.0287	0.0037	1.2464	1.0232	0.2232	4.58	0.71	0.06
GY20	0.0758	0.0116	0.0054	0.0157	0.0015	0.0003	0.005	0.0015	0.004	0.0013	0.0038	0.0012	0.0027	0.001	0.1308	0.1103	0.0205	5.38	0.3	0.1
GY21	0.0478	0.0117	0.0046	0.0138	0.001	0.0003	0.004	0.0011	0.002	0.0002	0.0007	0.0002	0.0007	0.0002	0.0883	0.0792	0.0091	8.7	0.4	0.15
GY22	0.0208	0.008	0.0024	0.0054	0.0007	0.0002	0.0008	0.0011	0.0008	0.0001	0.0006	0.0001	0.0007	0.0002	0.0419	0.0375	0.0044	8.52	0.81	0.23
GY43	0.3525	0.0326	0.0252	0.1074	0.0204	0.0053	0.0286	0.0056	0.0249	0.005	0.0133	0.0015	0.0097	0.0015	0.6335	0.5434	0.0901	6.03	0.67	0.06
GY44	0.0493	0.0083	0.0067	0.0297	0.0039	0.0008	0.006	0.0014	0.0043	0.0008	0.0011	0.0004	0.0009	0.0002	0.1138	0.0987	0.0151	6.54	0.5	0.1
GY54	0.3253	0.116	0.0296	0.125	0.0183	0.0051	0.0256	0.0043	0.0178	0.0037	0.0103	0.0014	0.0095	0.0014	0.6933	0.6193	0.074	8.37	0.72	0.23

Note: L/H. LREE/HREE.