

Geochemistry of rare-earth elements in shallow groundwater, northeastern Guangdong Province, China

YUAN Jianfei^{1,2}, MAO Xumei^{1,2}, WANG Yanxin^{1*}, DENG Zhide³, and HUANG Leihui³

¹ School of Environmental Studies, China University of Geosciences, Wuhan 430074, China

² State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan 430074, China

³ Guangdong Geological Engineering Company, Guangzhou 510425, China

* Corresponding author; E-mail: yx.wang@cug.edu.cn

Received March 5, 2013; accepted May 21, 2013

© Science Press and Institute of Geochemistry, CAS and Springer-Verlag Berlin Heidelberg 2014

Abstract Shallow groundwater and hot springs were collected from northeastern Guangdong Province, Southeast China, to determine the concentrations and fractionation patterns of rare-earth elements (REE). The results show that the La, Ce and Nd of REEs are abundant in groundwater and rock samples, and the Σ REE contents in groundwater and rock samples range from 126.5 to 2875.3 ng/L, and 79.44 to 385.85 mg/L, respectively. The shallow groundwater has slightly HREE-enriched PAAS-normalized patterns. However, the granitic rocks PAAS-normalized patterns, with remarkable negative Eu anomalies, are different from that of shallow groundwater. The enrichment of HREE is considered to be controlled by REE complexation and readsorption for most groundwater has Ce and Eu positive anomalies. The Ce and Eu anomalies in groundwater are controlled by redox conditions. Moreover, the Fe-containing sediments dissolution and/or the reduction of Fe oxyhydroxides are another factor contributing to Ce anomalies. The Eu anomalies in groundwater are controlled by the preferential mobilization of Eu^{2+} during water-rock interaction compared to Eu^{3+} .

Key words Rare-earth element (REE); geochemistry; shallow groundwater; Guangdong

1 Introduction

In the natural environment, the rare-earth elements (REE) are ubiquitous with stable and long-lived isotopes. REE has been used to trace many geological processes including crust evolution, weathering processes, paleoclimate change, and water-rock interaction (Guo Huaming et al., 2010a; He Shuoyang et al., 2011; Johannesson et al., 2006; Johannesson et al., 1997; Kralj and Kralj, 2009; Tweed et al., 2006). At the same time, more and more attention has been focused on aqueous REE accompanying with the improvement of analysis accuracy, for example, river, lake, sea and groundwater (Dia et al., 2000; Hannigan et al., 2010; Johannesson et al., 2011; Johannesson et al., 2006; Ojiambo et al., 2003; Ronnback et al., 2008; Zhao Fenghua et al., 2007). Because of the complexity

of the aquifer, REE in groundwater is mainly controlled by aquifer minerals, pH, redox condition, water type, organic or inorganic complexation, colloidal and particulate matter transport (Johannesson and Lyons, 1995; Leybourne and Johannesson, 2008; Sun Linhua et al., 2011; Tricca et al., 1999).

REE is abundant in granitoid weathering crust (Chen Binghui and Yu Shoujun, 1998; Ling Hongfei et al., 2006). Although granitic rocks is ubiquitous in Guangdong province, the drinking groundwater for local residents is derived from these weathering granitoid (Chen Binghui and Yu shoujun, 1998; Wu Meixian, 2003; Wu Meixian et al., 2003). Many geological studies have been done in this region (Chen Binghui and Yu Shoujun, 1998; Ling Hongfei et al., 2006; Wu Meixian, 2003). And some of earlier studies are focus on geochemistry of REE in weathering

granitoid, but few attentions have been paid on REE in groundwater and thermal water.

Here, we present the concentrations of REE, aqueous speciation, and PAAS-normalized patterns of shallow groundwater, and discuss the controlling factors of REE concentrations, fractionation patterns, and Ce and Eu anomalies. This study aims to improve the understanding of REE geochemistry of shallow groundwater from granitic aquifer.

2 Hydrogeology

The study area is located in the east part of the Pearl River Delta Regions. It is a sub-tropical monsoon climate with an average annual temperature of 23.3°C. The local annual precipitation is 1336 mm, but the annual evaporation is up to 1100 mm (Song Gang et al., 2011, 2005). The geological characteristic

of this study area is affected by regional geological history of three broad stages (Sinian-Silurian, Devonian-Mid Triassic, and Later Triassic-Present). There is a complicated tectonic background and a complete stratigraphic sequence which has undergone frequent metamorphism and intense magmatism (Fig. 1). Granite is the most extensive parent rock, accounted for more than 40% of the area of Guangdong Province (Song Gang et al., 2011).

There are three groups of aquifers in the study area: the first group is composed of coarse-medium sand and gravel, which belongs to pore groundwater; the second group is composed of granitic rocks, which is defined bedrock fracture water; and the third one is composed of limestone, gypsum and dolomite, which are the formation of carbonates fissure water. Along the fault belts of Heyuan and Zijin-Boluo, groundwater is abundant and thermal water emerges occasionally.

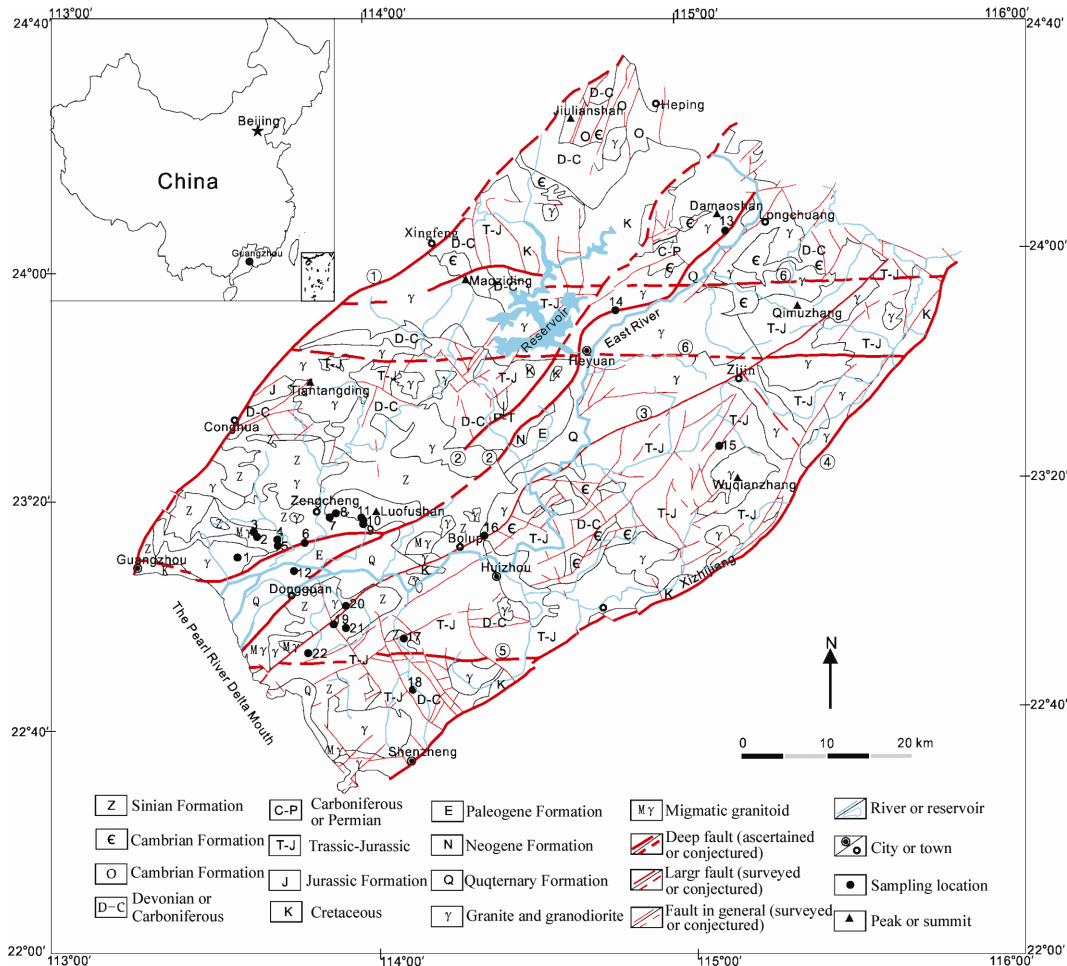


Fig. 1. Simplified map of geology and tectonic structure of northeastern Guangdong. The fault serials: ① Enping-Xinfeng fault; ② Heyuan fault; ③ Zijin-Boluo fault; ④ Lianhuashan fault; ⑤ Gaoyao-Huilai fault; and ⑥ Fogang-Fengliang fault. Water samples are also plotted in this map as numbers 1, 2, 3, etc.

3 Sampling and methods

3.1 Sampling

Four hot spring samples (named DG-13, DG-14, DG-15 and DG-16), thirteen cold groundwater samples (named DG-02, DG-03, DG-04, DG-06, DG-07, DG-08, DG-09, DG-10, DG-17, DG-18, DG-19, DG-20 and DG-22), and one stream water sample (named DG-11) were collected from wells and springs in northeastern Guangdong Province in September, 2010. Water temperature (T), electrical conductivity (EC), dissolved oxygen (DO), and pH were measured *in-situ* with a multi-parameter portable meter (520M-01 model).

All water samples were filtered through a 0.45 μm millipore filter *in-situ*, and stored into 50 ml HNO_3 -washed density polyethylene bottles. The samples of cation (Ca^{2+} , Mg^{2+} , Na^+ , and K^+) and trace elements (Ba, Mn and Fe) were preserved immediately after on-site acidification with ultra-pure HNO_3 , while anion samples (SO_4^{2-} , Cl^- , NO_3^- , and F^-) were not acidified. Water samples for determination of total aqueous REE concentrations were filtered with identical filters and immediately acidified to $\text{pH} < 2$ with ultra-pure HNO_3 .

3.2 Determination methods

Major anion concentrations were analyzed with an Ion Chromatography of DX-120 model (Dionex). Concentrations of major and trace elements were determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES; IRI INTER II XSP) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS; Agilent 7500a Plasma Mass Spectrometer). The uncertainties of measurements for major and trace elements are all within 5%.

Rare-earth elements were determined by ICP-MS. The REE isotope of ^{139}La , ^{140}Ce , ^{141}Pr , ^{146}Nd , ^{147}Sm , ^{153}Eu , ^{157}Gd , ^{159}Tb , ^{163}Dy , ^{165}Ho , ^{166}Er , ^{169}Tm , ^{174}Yb and ^{175}Lu were used to quantify the REEs in water samples. The ICP-MS was calibrated and the samples concentrations were verified using a series of REE standards. These REE standards were prepared from the National Institute of Standards and Technology (NIST) with known concentrations (1, 2, 10, 100, 250, 500 and 1000 ng/L). Moreover, The NIST Standard Reference Material (SRM) "Trace Elements in Water" (No. 1643b) was routinely used for quality control.

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

Granitic rock samples, including R-1, R-2 and R-3, were collected accompanied with groundwater sampling in the study area. These samples were dissolved with $\text{HNO}_3 + \text{HF}$ and analyzed for the REEs by ICP-MS. The measurement of rock REE were controlled with five USGS standards (i.e., AGV-2, BHVO-2, BCR-2, RGM-1 and GSR-1) with RSD not higher than 10%.

3.2 REE aqueous speciation

The aqueous speciation of REEs was calculated with the hydrogeochemical code of PHREEQC 2.18 with LLNL database (Guo Huaming et al., 2010a; Tweed et al., 2006).

4 Results and discussion

4.1 Water chemistry

The concentrations of major ions in shallow groundwater are presented in Table 1. The values of pH range from 5.52 to 8.12 with an average of 6.69. The dissolved oxygen (DO) vary from 0.95 to 9.15 mg/L with an average of 4.84 mg/L. The contents of the total dissolved solid (TDS) are from 20.10 to 411.28 mg/L. The concentrations of major ions are also plotted onto Piper diagram (Fig. 2). It shows that the water types vary from Ca-HCO_3 , $\text{Ca-(Na+K)-HCO}_3\text{-Cl}$, $(\text{Na+K)-Ca-HCO}_3\text{-Cl}$ to $(\text{Na+K)-Ca-Cl-HCO}_3$. Most of them are $(\text{Na+K)-Ca-HCO}_3\text{-Cl}$ type.

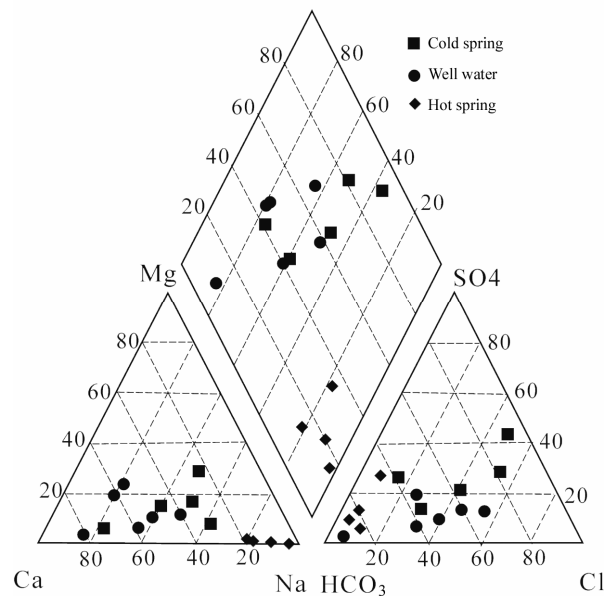


Fig. 2. Piper diagram for all water samples from the study area.

Some trace elements, such as Fe, Mn and Ba, are also listed in Table 1. The mean concentrations of Fe, Mn and Ba are 0.28 mg/L, 73.27 and 48.06 $\mu\text{g/L}$, respectively. The concentrations of F in groundwater vary from 0.16 to 15.26 mg/L, with an average of 3.27 mg/L.

Interestingly, the concentrations of major ions, F and Mn in hot springs (with water temperature from 56.70 to 78.60°C) are higher than those in cold groundwater, probably owing to intense water-rock interaction at high temperature.

4.2 REE concentrations

4.2.1 REE concentrations in groundwater

The total REE (ΣREE) concentrations in groundwater range from 126.5 to 2875.3 ng/L, with an average of 922.7 ng/L (Table 2). La, Ce and Nd of REEs are abundant in groundwater (Fig. 3). Moreover, the abundance of REEs decreases with increasing atomic number, indicating that the concentrations of light rare-earth elements (LREEs) are higher than that of the heavy rare-earth elements (HREEs) in groundwater (Fig. 3).

The ΣREE concentrations in hot springs, except of DG-16, range from 126.5 to 136.2 ng/L. It is striking that the ΣREE concentrations in hot springs (except DG-16) are lower than that in cold groundwater. However, DG-16 has the highest ΣREE concentration (up to 1886 ng/L) among hot springs, and is higher than that of most cold groundwater. Sample DG-16 may experience different chemical processes comparing with the other hot springs. For example, the mixing between thermal waters and cold groundwater (with high REE contents) can cause REE concentrations increased in DG-16.

Cluster analysis method was used for further understanding of REE in groundwater. Based on

Q-cluster analysis of REE in groundwater, water samples can be divided into two groups: group A and group B (Fig. 4a). All cold groundwater, except of DG-08 and DG-18, belong to group A. Furthermore, hot spring samples DG-13, DG-14 and DG-15 also fall into this group. Group B contains hot spring sample DG-16 and cold groundwater samples DG-08 and DG-18. It is obvious that the ΣREE concentrations in sample DG-08, DG-16 and DG-18 are higher than other samples (Table 2). The distinct REE concentrations make them fall into a different group.

R-cluster analysis of REE in groundwater was also conducted (Fig. 4b). The result indicates that REE can be grouped into two types: type A includes La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu, while Ce belongs to type B. Ce is the most abundant element in groundwater (Table 2 and Fig. 3). And it has one to three orders of magnitude higher than other REEs in water samples.

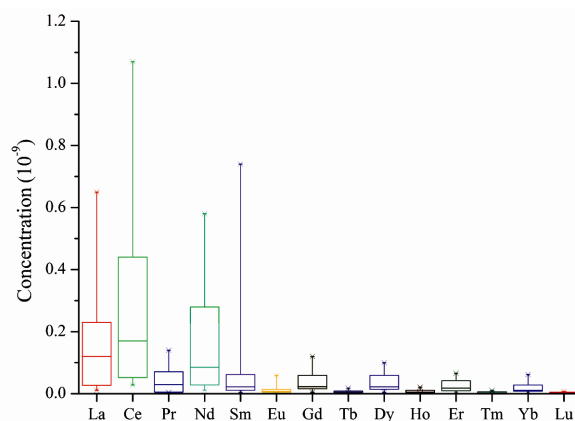


Fig. 3. Box-and-Whisker plot of concentrations (unit: 10^{-9}) for groundwater. The box represents the 25th, 50th and 75th percentile of the data and the whiskers the maximum and minimum of the data.

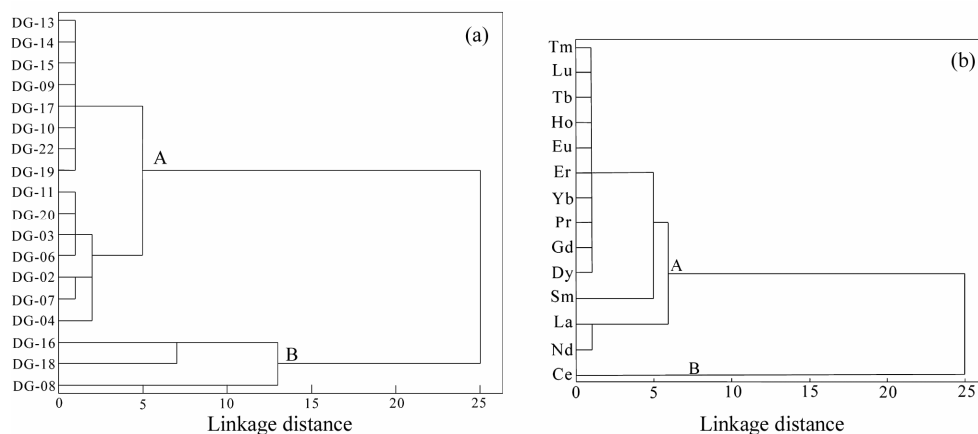


Fig. 4. Results of Q-cluster analysis (a) and R-cluster analysis (b) of 14 rare-earth elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb and Lu) of all water samples.

Table 1 Hydrochemistry of water samples in the study area

No.	DG-02	DG-03	DG-04	DG-06	DG-07	DG-08	DG-09	DG-10	DG-11	DG-13	DG-14	DG-15	DG-16	DG-17	DG-18	DG-19	DG-20	DG-22
Water type	Spring	Spring	Well	Well	Spring	Well	Spring	Spring	Stream	Hot spring	Hot spring	Hot spring	Hot spring	Well	Well	Spring	Well	Spring
T	24.40	24.00	24.10	25.70	ND	25.40	ND	22.20	ND	63.20	56.70	78.60	59.80	24.80	24.20	25.70	28.40	23.00
pH	5.78	7.60	6.20	5.52	ND	6.03	ND	6.11	7.02	7.04	7.20	8.12	7.55	7.24	5.95	6.71	7.04	6.24
DO	8.85	6.20	4.79	2.66	ND	7.48	ND	7.53	ND	5.38	0.95	1.15	1.81	1.70	3.18	7.08	4.76	9.15
TDS	54.80	22.89	75.99	154.08	ND	48.95	ND	21.09	ND	318.23	381.79	293.94	358.33	176.55	100.37	48.65	411.28	20.10
K ⁺	4.26	0.76	4.73	14.11	4.76	0.96	2.80	1.74	1.97	5.90	5.94	5.84	6.29	3.35	2.50	1.91	21.92	1.97
Na ⁺	7.28	5.33	10.46	24.87	10.85	7.14	10.48	3.81	3.12	101.10	123.60	113.30	129.30	11.91	8.73	3.92	35.56	3.17
Ca ²⁺	7.17	2.05	12.01	17.77	31.18	10.47	13.19	2.09	2.62	22.52	22.39	2.74	12.46	50.51	20.31	10.69	87.88	1.36
Mg ²⁺	1.43	0.46	1.52	3.18	10.95	0.69	3.31	0.73	0.55	0.82	0.64	0.19	0.38	1.49	5.09	1.91	7.10	1.03
Cl ⁻	7.06	5.48	11.63	34.21	11.17	15.24	17.88	5.00	6.16	9.68	17.81	16.63	16.26	6.64	18.73	6.98	39.00	5.70
SO ₄ ²⁻	4.52	6.70	5.51	12.89	6.59	5.08	6.35	3.46	5.31	24.92	77.51	13.72	37.46	6.89	7.67	7.29	89.37	4.32
HCO ₃ ⁻	25.32	1.45	40.86	53.80	ND	15.93	ND	7.45	ND	287.82	245.95	225.02	282.59	186.43	48.54	27.10	259.04	3.39
NO ₃ ⁻	10.24	1.15	9.063	19.73	0.38	1.40	5.46	0.37	1.20	0.26	0.94	0.88	0.37	0.26	12.67	2.15	0.31	0.69
F ⁻	0.18	0.23	0.64	0.41	0.25	--	0.71	0.17	0.34	9.12	9.99	15.26	14.51	2.28	0.40	0.24	0.62	0.16
Mn	19.40	3.56	7.92	96.80	92.10	24.90	12.80	3.96	10.70	100.00	69.60	8.57	88.90	648.00	97.00	0.83	32.50	1.28
Fe	0.08	0.21	0.02	0.07	0.25	0.35	0.05	0.09	0.46	0.28	0.12	0.01	0.23	2.76	0.07	0.01	0.08	0.02
Ba	84.40	7.76	155.00	47.70	37.5	11.40	72.10	17.20	9.82	6.38	15.00	18.20	5.64	40.80	219.00	17.90	73.20	26.00

4.2.2 REE concentrations in granitic rock

The \sum REE of rock samples vary from 79.44 to 385.85 mg/L, with an average of 198.89 mg/L (Table 2). The elements of La, Ce, and Nd are more abundant than other REE elements, and Ce is the most abundant element of REEs (Fig. 5). So, it also seems that the abundance of REE decreases with increasing atomic number, resulting that the concentration of LREEs higher than that of the HREEs in granitic rocks.

It is obvious that the plot trends of REE in groundwater and granitic rock samples are similar, and the abundant of REE decreases with increasing atomic number (Figs. 3 and 5). Earlier studies suggest that the ultimate source of the REE in groundwater is the mineral of aquifer (Johannesson et al., 1999; Johannesson and Hendry, 2000; Biddau et al., 2002; Sun Linhua et al., 2011). So, the REE concentrations of groundwater are mainly associated with groundwater-mineral interaction in aquifer along groundwater flowing.

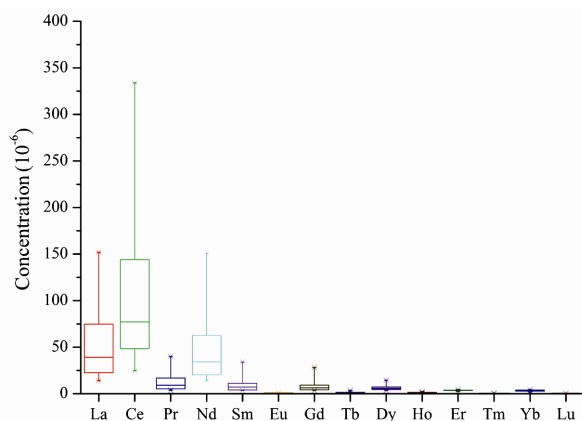


Fig. 5. Box-and-Whisker plot for granitic rock samples (unit: 10^{-6}) in the study area. The box represents the 25th, 50th and 75th percentile of the data and the whiskers the maximum and minimum of the data.

4.3 REE aqueous speciation

The aqueous speciation of REE was calculated by hydrogeochemical code of PHREEQC with LLNL database. The results demonstrate that carbonate complexes [LnCO_3^+ and $\text{Ln}(\text{CO}_3)_2^-$] and the free metal ions (Ln^{3+}) are dominated among the dissolved forms of REE in groundwater. Fluoride complexes (LnF^{2+}) also show significant in both cold groundwater and hot springs. Fig. 6 illustrates the results of aqueous speciation calculated for La, Nd, Gd and Yb in all water samples. It is obvious that free metal ions (Ln^{3+}), carbonate (LnCO_3^+) and/or dicarbonato [$\text{Ln}(\text{CO}_3)_2^-$] are the main aqueous species for REE in groundwater. The aqueous speciation of REE in cold groundwater is significantly different from those in hot springs. The

dicarbonato complexes [$\text{Ln}(\text{CO}_3)_2^-$] is negligible in cold groundwater but high in hot spring. On the contrary, the free ions (Ln^{3+}) are abundant in cold groundwater but negligible in hot springs.

In general, the aqueous speciation of REE in groundwater is controlled by pH (Fig. 6). It is predicted that the proportion of Ln^{3+} decreases with increasing pH, and Ln^{3+} becomes the dominant specie in water when pH is between 5.5 and 6.5. Carbonato complexes (LnCO_3^+) dominate in groundwater when pH ranges from 6.5 to 7.5. Dicarbonato complexes [$\text{Ln}(\text{CO}_3)_2^-$] increase with pH in alkaline groundwater. Furthermore, Ln^{3+} decreases but LnCO_3^+ increases with increasing atomic number of REE in groundwater when $\text{pH} < 7$; while $\text{Ln}(\text{CO}_3)_2^-$ increases but LnCO_3^+ decreases with increasing atomic number of REE increasing in groundwater when $\text{pH} > 7$. The changes of La, Nd, Gd and Yb are illustrated in Fig. 6. These results are consistent with other studies of REE aqueous speciation in groundwater (Biddau et al., 2002; Tang Jianwu and Johannesson, 2006).

It is worth noting that the aqueous speciation of REE in hot spring DG-15 is distinct from cold waters, even the other hot springs. For DG-15, the percentages of Ln^{3+} , $\text{Ln}(\text{CO}_3)_2^-$, LnCO_3^+ and LnF^{2+} are lower than 30%, indicating that these forms are not main solution species for REE. It is speculated that REE form complexation with other ions in groundwater for DG-15 has the highest temperature and pH (Table 1).

4.4 PAAS-normalized REE patterns

The Post Archean Average Shale (PAAS) is used to normalize REE concentrations in groundwater and granitic rocks. The values of PAAS composite are tabulated in Peter Kralj (Kralj and Kralj, 2009). It has been employed extensively in groundwater studies (Biddau et al., 2002; Johannesson et al., 1997; Tang Jianwu and Johannesson, 2006).

Most of the shallow groundwater exhibits HREE-enriched PAAS-normalized patterns in Fig. 7 for the normalized Nd/Yb ratios range from 0.03 to 0.97, with the average of 0.79. However, in some groundwater, such as DG-06, DG-07, DG-08, DG-11, DG-15, DG-18 and DG-22, the normalized Nd/Yb ratios vary from 1.07 to 2.53, indicating LREE slightly enriched in these water samples. Most of the water samples show slightly negative anomalies of Ce. The PAAS-normalized Ce anomalies range from -0.47 to -0.01, with an average of -0.19 (Fig. 7c). The values of δEu vary from 0.10 to 0.61 (Fig. 7a). Almost all groundwater present positive anomalies of Eu except the samples of DG-03, DG-08, DG-11 and DG-16 with negative anomalies of PAAS-normalized Eu (Fig. 7b).

Table 2 Concentrations of REE in groundwater and granitic rock samples in the study area

No.	DG-02	DG-03	DG-04	DG-06	DG-07	DG-08	DG-09	DG-10	DG-11	DG-13	DG-14	DG-15	DG-16	DG-17	DG-18
La	0.2900	0.1800	0.2100	0.1500	0.3400	0.3400	0.0160	0.0540	0.1200	0.0180	0.0180	0.0270	0.2300	0.0110	0.6500
Ce	0.3500	0.3700	0.1700	0.3000	0.4400	1.0700	0.0420	0.0940	0.5000	0.0350	0.0410	0.0520	0.8900	0.0280	0.9800
Pr	0.0710	0.0490	0.0510	0.0210	0.0810	0.0830	0.0052	0.0160	0.0290	0.0044	0.0041	0.0043	0.0710	0.0038	0.1400
Nd	0.3000	0.1900	0.2300	0.0790	0.3400	0.3500	0.0370	0.0780	0.1300	0.0180	0.0110	0.0280	0.2800	0.0130	0.5800
Sm	0.0650	0.0450	0.0420	0.0110	0.0730	0.7400	0.0110	0.0180	0.0290	0.0053	0.0040	0.0055	0.0620	0.0073	0.1100
Eu	0.0230	0.0075	0.0240	0.0075	0.0200	0.0130	0.0130	0.0092	0.0052	0.0023	0.0035	0.0042	0.0055	0.0070	0.0590
Gd	0.0920	0.0360	0.0520	0.0120	0.0630	0.0590	0.0300	0.0210	0.0240	0.0073	0.0047	0.0043	0.0660	0.0160	0.1200
Tb	0.0150	0.0063	0.0096	0.0016	0.0088	0.0078	0.0051	0.0041	0.0037	0.0014	0.0016	0.0007	0.0140	0.0033	0.0180
Dy	0.0950	0.0360	0.0590	0.0068	0.0610	0.0500	0.0420	0.0220	0.0220	0.0096	0.0140	0.0037	0.1000	0.0430	0.0910
Ho	0.0190	0.0092	0.0150	0.0017	0.0093	0.0094	0.0110	0.0051	0.0046	0.0039	0.0032	0.0007	0.0210	0.0110	0.0180
Er	0.0620	0.0230	0.0520	0.0043	0.0290	0.0240	0.0310	0.0180	0.0110	0.0096	0.0110	0.0024	0.0660	0.0420	0.0590
Tm	0.0066	0.0035	0.0068	0.0011	0.0035	0.0024	0.0047	0.0022	0.0015	0.0015	0.0015	0.0005	0.0110	0.0064	0.0070
Yb	0.0420	0.0210	0.0280	0.0026	0.0260	0.0190	0.0230	0.0110	0.0097	0.0082	0.0100	0.0022	0.0620	0.0370	0.0380
Lu	0.0059	0.0032	0.0058	0.0009	0.0032	0.0028	0.0034	0.0014	0.0016	0.0020	0.0015	0.0007	0.0075	0.0070	0.0053
ΣREE	1.4365	0.9797	0.9552	0.5995	1.4978	2.7704	0.2744	0.3540	0.8913	0.1265	0.1291	0.1362	1.8860	0.2358	2.8753
δCe	-0.25	-0.04	-0.42	0.08	-0.21	0.17	0.02	-0.14	0.29	-0.04	0.04	0.04	0.20	-0.01	-0.13
δEu	0.13	-0.06	0.38	0.48	0.14	-0.78	0.46	0.34	-0.03	0.23	0.57	0.61	-0.40	0.44	0.38
(Nd/Yb) _{SN}	0.59	0.75	0.68	2.53	1.09	1.53	0.13	0.59	1.11	0.18	0.09	1.06	0.38	0.03	1.27
No.	DG-19	DG-20	DG-22	R-1	R-2	R-3	R-4 ^a	R-5 ^a	R-6 ^a	R-7 ^a	R-8 ^a	R-9 ^a			
La	0.0790	0.1400	0.0690	74.8	31.5	89.2	22.59	13.95	14.48	53.71	39.16	50.47			
Ce	0.0730	0.4300	0.1000	144	62.5	170	48.36	29.40	24.67	82.71	77.13	88.86			
Pr	0.0300	0.0340	0.0200	16.9	7.32	18.7	5.32	3.57	3.58	12.14	9.10	11.01			
Nd	0.0140	0.1200	0.0850	62.6	28.4	64.9	20.21	14.99	14.07	41.91	34.23	39.25			
Sm	0.0180	0.0240	0.0220	11.9	5.63	11.2	3.97	3.49	3.54	7.16	7.42	7.61			
Eu	0.0056	0.0140	0.0061	1.12	1.44	1.12	0.88	0.25	0.50	0.58	0.61	1.07			
Gd	0.0230	0.0190	0.0160	9.92	5.17	9.21	4.18	3.47	3.81	6.42	6.34	7.05			
Tb	0.0027	0.0026	0.0024	1.44	0.78	1.45	0.61	0.53	0.63	0.89	0.87	0.97			
Dy	0.0140	0.0180	0.0120	7.28	4.31	8.03	4.58	3.56	4.43	5.83	5.73	6.40			
Ho	0.0029	0.0030	0.0030	1.31	0.84	1.55	1.10	0.79	1.02	1.23	1.18	1.30			
Er	0.0079	0.0110	0.0071	3.56	2.33	4.62	3.60	2.42	3.47	3.73	3.61	3.54			
Tm	0.0010	0.0015	0.0009	0.49	0.32	0.66	0.55	0.38	0.54	0.56	0.55	0.49			
Yb	0.0068	0.0100	0.0066	3.17	2.04	4.51	3.85	2.84	4.06	3.60	3.59	2.84			
Lu	0.0012	0.0032	0.0008	0.51	0.32	0.7	0.62	0.43	0.65	0.55	0.57	0.39			
ΣREE	0.2791	0.8303	0.3509	339.00	152.90	385.85	120.42	80.07	79.44	221.01	190.10	221.23			
δCe	-0.47	0.16	-0.21	-0.03	-0.02	-0.02	0.01	-0.02	-0.10	-0.13	-0.03	-0.06			
δEu	0.10	0.49	0.18	-0.31	0.10	-0.28	0.01	-0.48	-0.20	-0.40	-0.38	-0.16			
(Nd/Yb) _{SN}	0.17	1.00	1.07	1.64	1.16	1.20	0.44	0.44	0.29	0.97	0.79	1.15			

Units: 10^{-9} for water samples, the sample number is shown in the table with the prefix "DG"; 10^{-6} for rock samples, the sample number is shown in the table with the prefix "R". $\delta\text{Ce}=\log\{2\text{Ce}_{\text{SN}}/(\text{La}_{\text{SN}}+\text{Pr}_{\text{SN}})\}$; $\delta\text{Eu}=\log\{2\text{Eu}_{\text{SN}}/(\text{Sm}_{\text{SN}}+\text{Gd}_{\text{SN}})\}$. ^a Concentrations of REE for biotite-granite, data from Lin Hongfei et al. (2006). SN=Shale-normalized. The Post Archean Average Shale, data from Kraji and Kraji (2009).

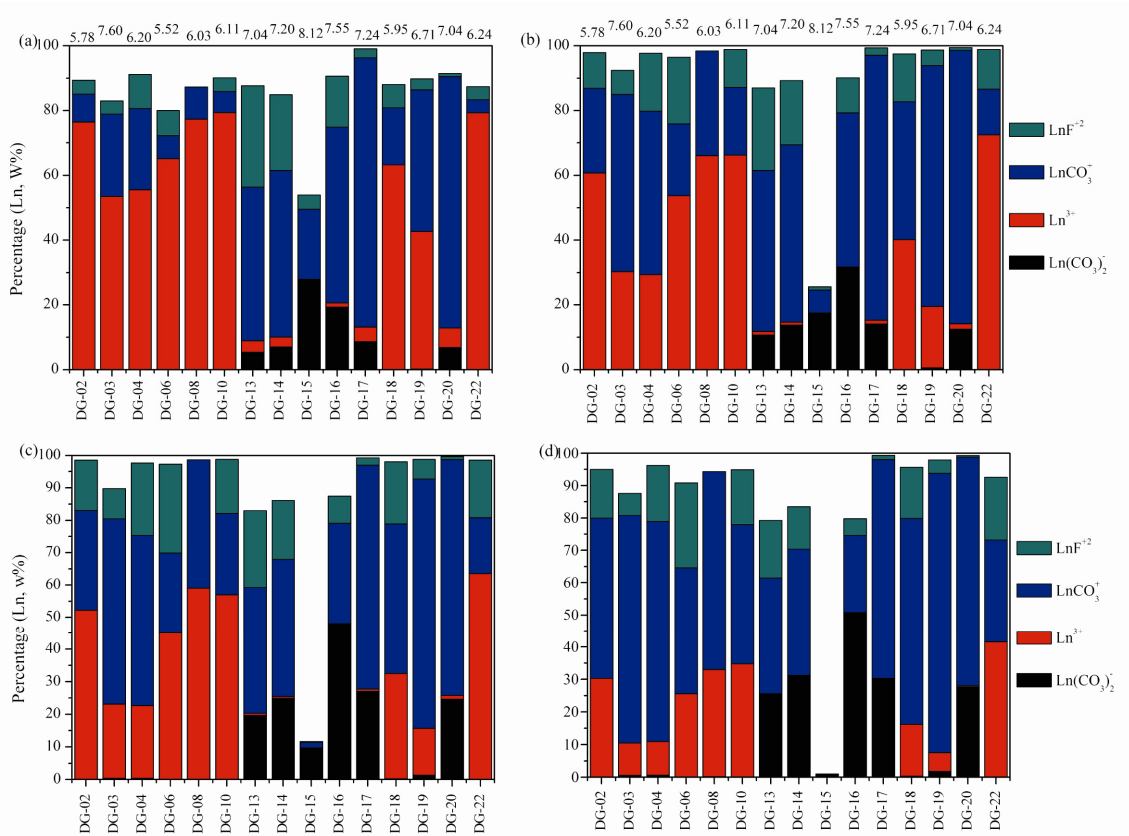


Fig. 6. Results of the aqueous speciation model for La (a), Nd (b), Gd (c) and Yb (d) in weight percentage for groundwater in the study area. Ln means La, Nd, Gd and Yb. The numbers at the top horizon are pH values for each sample.

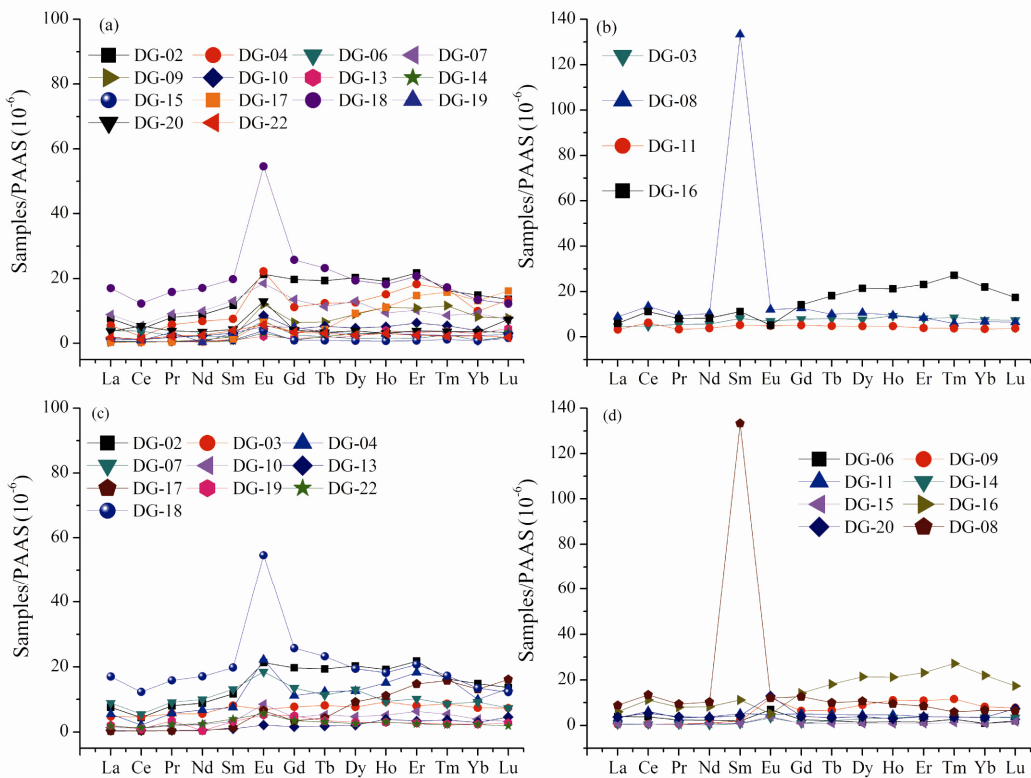


Fig. 7. PAAS-normalized REE patterns for water samples. (a) groundwater with positive Eu anomalies; (b) water samples with negative Eu anomalies; (c) groundwater with negative Ce anomalies; (d) water samples with positive Ce anomalies.

The granitic rocks have complex PAAS-normalized REE patterns (Fig. 8). LREE is enriched in the rock samples R-1, R-2, R-3 and R-4 because the normalized Nd/Yb ratios range from 1.15 to 1.64 with an average of 1.29. However, HREE is enriched in the other rock samples for the normalized Nd/Yb ratios lower than 1. Most of the samples have negative Eu anomalies and negative Ce anomalies.

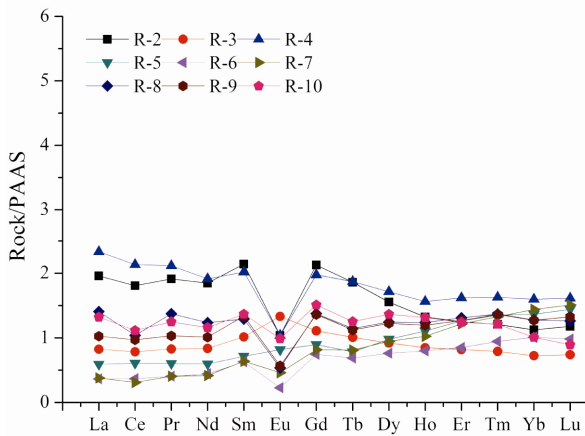


Fig. 8. PAAS-normalized REE patterns for granitic rock samples from the study area.

4.5 Influence on REE patterns

REE of groundwater are mainly derived from water-mineral interaction in aquifer along groundwater flowing, and then the REE pattern of groundwater should be similar to that of granitic rocks. However, significant difference on REE pattern between groundwater and granitic rocks are observed, indicating that some factors make influence on the concentration and pattern of aqueous REE, such as complexation and readsorption, resulting in HREE enriched in groundwater.

Free metal ions (Ln^{3+}) and carbonato complexes (LnCO_3^+) are major aqueous species with little or no dicarbonate [$\text{Ln}(\text{CO}_3)_2^-$] complex in cold groundwater. But carbonato complexes (LnCO_3^+) and dicarbonate [$\text{Ln}(\text{CO}_3)_2^-$] complex are abundant in hot springs with few or no the free metal ions (Ln^{3+}). Nevertheless, carbonato complexes (LnCO_3^+) are major species for all groundwater, and increase with increasing atomic number for each element. The negatively charged surface site in aquifer sediment would have stronger affinities for LREE as positive charged carbonato complexes (LnCO_3^+) than the HREE (Guo Huaming et al., 2010a). So, LREE with carbonato complexes (LnCO_3^+) would be absorbed onto the surface site in aquifer sediment, which results in HREE enrichment.

In addition, REE partitioning between solid and liquid phase would be another factor to the enrichment

of HREE. Johannesson et al. (1999) analyzed the partitioning coefficients (K_d) for REE between solid and liquid phase in the alluvial aquifer of volcanic rock, and found that K_d decreased with increasing atomic number for all REE. So, the LREE have closer contact to aquifer surface than the HREE.

4.6 Ce anomalies

Most cold groundwater inherit granitic rock Ce signature for negative Ce anomalies in almost all granitic rocks. But other chemical parameters or factors may also influence the Ce anomalies.

Most cold groundwater has negative Ce anomalies, while most hot springs have positive Ce anomalies (Fig. 7). The oxidative precipitation as cerianite (CeO_2) and desorption on Fe oxyhydroxides can account for negative Ce anomalies and positive Ce anomalies, respectively. The dissolved oxygen (DO) in groundwater has obvious indication to redox condition (Tang Jianwu and Johannesson, 2006). Negative relationship between DO and δCe are observed (Fig. 9), indicating redox condition as an important factor controlling Ce anomalies in groundwater. In addition, positive relationship between (Mn+Fe) and δCe occurs, probably indicating that the adsorbed Ce releases with Fe-contain sediments dissolution and/or the reduction of Fe oxyhydroxides (Fig. 10).

Some research suggested pH as a factor controlling Ce anomalies (Lei Liangqi et al., 2008; Olias et al., 2005). The results show that the aqueous speciation of REE in groundwater is controlled by pH (Fig. 6), indicating pH is a factor controlling REE complexation. However, there is no direct lineal relationship between pH and δCe in groundwater, indicating that pH is not the main factor controlling Ce anomalies.

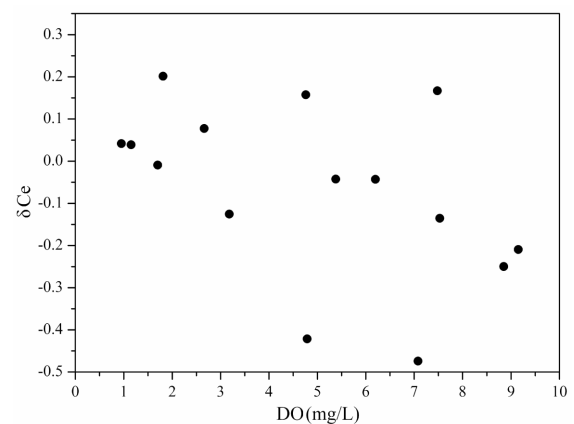


Fig. 9. Relationship between δCe and dissolved oxygen (DO) for groundwater in the study area.

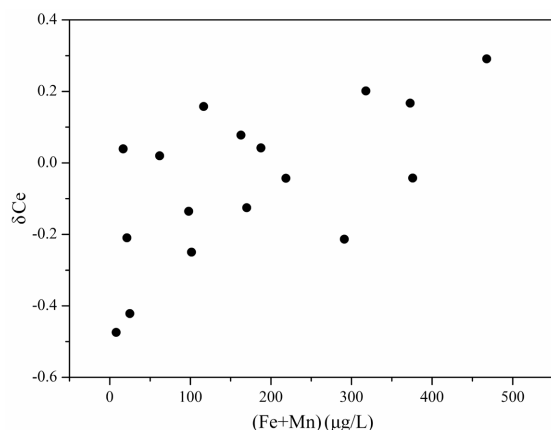


Fig. 10. Plot of δCe versus (Fe+Mn) of groundwater in the study area.

4.7 Eu anomalies

Earlier studies provided three hypotheses for explaining positive Eu anomalies, positive Eu anomalies in the aquifer sediments, preferential dissolution Eu-enriched minerals, such as plagioclase, and preferential mobilization of Eu^{2+} during water-rock interaction compared to Eu^{3+} (Banks et al., 1999; Guo Huaming et al., 2010a; Lee et al., 2003; Leybourne and Johannesson, 2008).

In this study, water samples are collected from granitic rocks or weathering granitic rocks. Most groundwater has positive Eu anomalies (Fig. 7a); while most granitic rocks have negative Eu anomalies (Fig. 8). The results suggest that positive Eu anomalies of most groundwater are not related to the granitic rocks of aquifer.

Guo Huaming et al. (2010a) suggest that plagioclase preferentially accumulates Eu. Plagioclase contents of granitic rock samples vary from 25% to 30% (Ling Hongfei et al., 2006). However, groundwater and granitic rocks have different Eu anomalies (Fig. 7 and Fig. 8). The dissolution of plagioclase of granitic rocks is not expected to cause the positive Eu anomalies of groundwater in the study area.

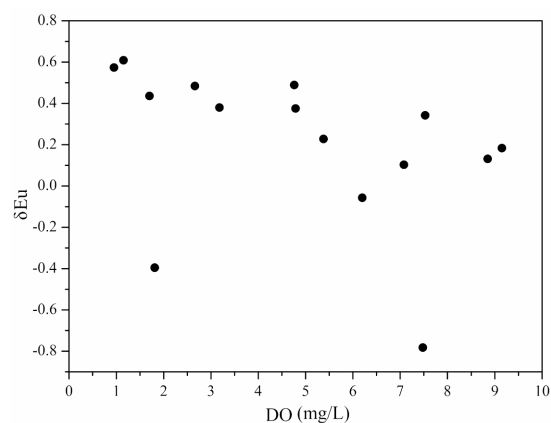


Fig. 11. Relationship of δEu and DO for groundwater in the study area.

The δEu have a negative correlation with DO. The values of δEu are higher in low DO groundwater than that in high DO groundwater (Fig. 11). Reducing condition (with low DO value) is probably the dominant factor contributing to the positive Eu anomalies because Eu^{3+} can be reduced to Eu^{2+} in reducing conditions (Guo Huaming et al., 2010a, 2010b). Leybourne and Johannesson (2008) suggest that Eu^{2+} is preferential mobilized during water-rock interaction in stream water. Earlier studies suggested that Eu enrichment in reducing groundwater would be preferential mobilization of Eu^{2+} relative to more particle-reactive trivalent REEs, and the mobilization would be related to reductive dissolution of Fe oxyhydroxides. However, the negative correlation between dissolved Fe and δEu shows that the reductive dissolution of Fe oxyhydroxides should not be the reason for Eu anomalies (Fig. 12). Therefore, the preferential mobilization of Eu^{2+} may play an important role in shallow groundwater.

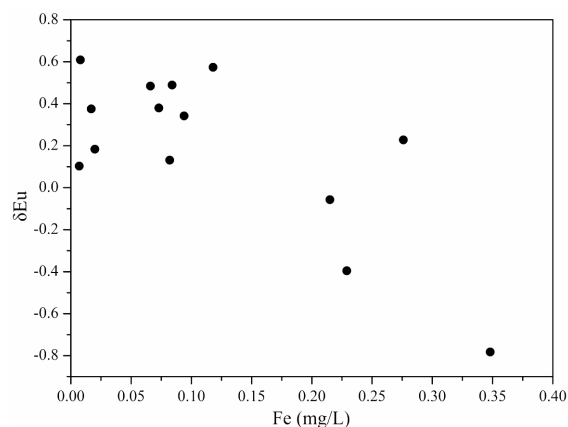


Fig. 12. Plot of δEu and Fe for groundwater in the study area.

5 Conclusions

Shallow groundwater and hot springs were collected from northeastern Guangdong Province, China for REE analysis. The groundwater types are mainly (Na+K)-Ca- HCO_3 -Cl. The $\sum\text{REE}$ contents vary from 126.5 to 2875.3 ng/L, and La, Ce and Nd are abundant in groundwater. Comparing with water samples, the $\sum\text{REE}$ concentrations vary from 79.44 to 385.85 mg/L in granitic rocks, and La, Ce, and Nd are also abundant elements in rock samples. The results indicate that the source of REE in shallow groundwater is the granitic rocks.

The dominated aqueous speciation of REE in cold groundwater are carbonato complexes (LnCO_3^+ , Ln is a certain element of lanthanide) and the free metal ions (Ln^{3+}), while that in hot springs are LnCO_3^+ and $\text{Ln}(\text{CO}_3)_2^-$. In addition, Fluoride species (LnF^{2+}) are also shown to be of significance in both cold waters and hot springs. The aqueous speciation of

REE in groundwater is controlled by pH. The proportion of Ln^{3+} decrease with increasing pH, and it becomes the dominant specie in water samples when pH is between 5.5 and 6.5. Carbonato complexes (LnCO_3^+) dominate REE speciation in groundwater when pH ranges from 6.5 to 7.5. And $\text{Ln}(\text{CO}_3)_2^-$ increase with pH in alkaline groundwater.

The shallow groundwater has slightly HREE-enriched (the average of the normalized Nd/Yb ratio is 0.79) PAAS-normalized patterns. But it is different from that of granitic rocks with remarkable negative Eu anomalies. REE complexation and readsorption are probably important factors to keep HREE enrichment in groundwater. Most groundwater has Ce and Eu positive anomalies. The Ce and Eu anomalies in groundwater are controlled by redox conditions. Moreover, the Fe-enriched sediments dissolution and/or the reduction of Fe oxyhydroxides are another factor accounting for Ce anomalies. The Eu anomalies in groundwater are controlled by the preferential mobilization of Eu^{2+} during water-rock interaction compared to Eu^{3+} .

Acknowledgements This research project was financially jointly supported by the National Natural Science Foundation of China (No. KZ09W312) and the Program for China Geological Survey (No. 1212011220014). The authors would like to thank Li Liang, Zhang Xiaofang for their great help in field sampling. Moreover, the manuscript benefited a lot from the constructive comments of anonymous reviewers.

References

- Banks D., Hall G., Reimann C., and Siewers U. (1999) Distribution of rare-earth elements in crystalline bedrock groundwater: Oslo and Bergen regions, Norway [J]. *Applied Geochemistry*. **14**, 27–39.
- Biddau R., Cidu R., and Frau F. (2002) Rare-earth elements in waters from the albitite-bearing granodiorites of Central Sardinia, Italy [J]. *Chemical Geology*. **182**, 1–14.
- Chen Binghui and Yu Shoujun (1998) Fractionation of rare-earth elements and its effecting factors in weathering crusts in South China [J]. *Acta Scientiarum Naturalium Universitatis Sunyatseni*. **37**, 92–96 (in Chinese with English abstract).
- Dia A., Gruau G., Olivie-Lauquet G., Riou C., Molenat J., and Curmi P. (2000) The distribution of rare-earth elements in groundwater: Assessing the role of source-rock composition, redox changes and colloidal particles [J]. *Geochimica et Cosmochimica Acta*. **64**, 4131–4151.
- Guo Huaming, Zhang Bo, Wang Guangcai, and Shen Zhaoli (2010a) Geochemical controls on arsenic and rare-earth elements approximately along a groundwater flow path in the shallow aquifer of the Hetao Basin, Inner Mongolia [J]. *Chemical Geology*. **270**, 117–125.
- Guo Huaming, Zhao Boyi, Yuan Weiliang, and Zhang Yang (2010b) Concentrations and patterns of rare-earth elements in high arsenic groundwater from the Hetao Plain, Inner Mongolia [J]. *Earth Science Frontiers*. **17**, 59–66 (in Chinese with English abstract).
- Hannigan R., Dorval E., and Jones C. (2010) The rare-earth element chemistry of estuarine surface sediments in the Chesapeake Bay [J]. *Chemical Geology*. **272**, 20–30.
- He Shuoyang, Zhu Lijun, Yang Ruidong, Shen Zheng, and Yu Xiaohong (2011) The geochemical characteristics of aqueous rare-earth elements in shallow karst groundwater in Guiyang City, China [J]. *Chinese Journal of Geochemistry*. **30**, 114–124 (in Chinese with English abstract).
- Johannesson K.H., Chevis D.A., Burdige D.J., Cable J.E., Martin J.B., and Roy M. (2011) Submarine groundwater discharge is an important net source of light and middle REEs to coastal waters of the Indian River Lagoon, Florida, USA [J]. *Geochimica et Cosmochimica Acta*. **75**, 825–843.
- Johannesson K.H., Farnham I.M., Guo C.X., and Stetzenbach K.J. (1999) Rare-earth element fractionation and concentration variations along a groundwater flow path within a shallow, basin-fill aquifer, southern Nevada, USA [J]. *Geochimica et Cosmochimica Acta*. **63**, 2697–2708.
- Johannesson K.H., Hawkins D.L., and Cortes A. (2006) Do archean chemical sediments record ancient seawater rare-earth element patterns [J]. *Geochimica et Cosmochimica Acta*. **70**, 871–890.
- Johannesson K.H. and Lyons W.B. (1995) Rare-earth element geochemistry of Colour Lake, and acidic freshwater lake on Axel Heiberg Island, Northwest Territories, Canada [J]. *Chemical Geology*. **119**, 209–223.
- Johannesson K.H., Stetzenbach K.J., and Hodge V.F. (1997) Rare-earth elements as geochemical tracers of regional groundwater mixing [J]. *Geochimica et Cosmochimica Acta*. **61**, 3605–3618.
- Kralj P. and Kralj P. (2009) Rare-earth elements in thermal water from the Sob-1 well, Murska Sobota, NE Slovenia [J]. *Environmental Earth Sciences*. **59**, 5–13.
- Lee S.G., Lee D.H., Kim Y., Chae B.G., Kim W.Y., and Woo N.C. (2003) Rare-earth elements as indicators of groundwater environment changes in a fractured rock system: Evidence from fracture-filling calcite [J]. *Applied Geochemistry*. **18**, 135–143.
- Lei Liangqi, Song Cian, Xie Xiangli, and Li Yanhong (2008) REE behavior and effect factors in AMD-type acidic groundwater at sulfide tailings pond, BS nickel mine, WA [J]. *Transactions of Nonferrous Metals Society of China*. **18**, 955–961.
- Leybourne M.I. and Johannesson K.H. (2008) Rare-earth elements (REE) and yttrium in stream waters, stream sediments, and Fe-Mn oxyhydroxides: Fractionation, speciation, and controls over REE plus Y patterns in the surface environment [J]. *Geochimica et Cosmochimica Acta*. **72**, 5962–5983.
- Ling Hongfei, Shen Weizhou, Sun Tao, Jiang Shaoyong, Jiang Yaohui, Ni Pei, Gao Junfeng, Huang Guolong, Ye Haimin, and Tang Zhengzhong (2006) Genesis and source characteristics of 22 Yanshanian granites in Guangdong Province: Study of element and Nd-Sr isotope [J]. *Acta Petrologica Sinica*. **22**, 2687–2703 (in Chinese with English abstract).
- Ojiambo S.B., Lyons W.B., Welsh K.A., Poreda R.J., and Johannesson K.H. (2003) Strontium isotopes and rare earth elements as tracers of groundwater-lake water interactions, Lake Naivasha, Kenya [J]. *Applied Geochemistry*. **18**, 1789–1805.

- Olias M., Ceron J.C., Fernandez I., and De la Rosa J. (2005) Distribution of rare-earth elements in an alluvial aquifer affected by acid mine drainage: The Guadiamar aquifer (SW Spain) [J]. *Environmental Pollution*. **135**, 53–64.
- Ronnback P., Astrom M., and Gustafsson J.P. (2008) Comparison of the behaviour of rare-earth elements in surface waters, overburden groundwater and bedrock groundwater in two granitoidic settings, eastern Sweden [J]. *Applied Geochemistry*. **23**, 1862–1880.
- Song Gang, Wang Xinming, Chen Diyun, and Chen Yongheng (2011) Contribution of ^{222}Rn -bearing water to indoor radon and indoor air quality assessment in hot spring hotels of Guangdong, China [J]. *Journal of Environmental Radioactivity*. **102**, 400–406.
- Song Gang, Zhang Boyou, Wang Xinming, Gong Jingping, Chan Daniel, Bernett J., and Lee S.C. (2005) Indoor radon levels in selected hot spring hotels in Guangdong, China [J]. *Science of The Total Environment*. **339**, 63–70.
- Sun Linhua, Gui Herong, and Chen Song (2011) Rare-earth element geochemistry of groundwater from coal bearing aquifer in Renlou coal mine, northern Anhui Province, China [J]. *Journal of Rare Earths*. **29**, 185–192.
- Tang Jianwu and Johannesson K.H. (2006) Controls on the geochemistry of rare-earth elements along a groundwater flow path in the Carrizo Sand aquifer, Texas, USA [J]. *Chemical Geology*. **225**, 156–171.
- Tricca A., Stille P., Steinmann M., Kiefel B., Samuel J., and Eikenberg, J. (1999) Rare-earth elements and Sr and Nd isotopic compositions of dissolved and suspended loads from small river systems in the Vosges mountains (France), the river Rhine and groundwater [J]. *Chemical Geology*. **160**, 139–158.
- Tweed S.O., Weaver T.R., Cartwright I., and Schaefer B. (2006) Behavior of rare-earth elements in groundwater during flow and mixing in fractured rock aquifers: An example from the Dandenong Ranges, Southeast Australia [J]. *Chemical Geology*. **234**, 291–307.
- Wu Meixian (2003) *Groundwater from the Fogang Granitoid Weathering Crust, Guangdong Province* [C]. pp.1–14. Guangzhou Institute of Geochemistry Chinese Academy of Science (in Chinese with English abstract).
- Wu Meixian, Li Xianhua, Liu Ying, and Wei Keqin (2003) Rare-earth elements in groundwater from Fogang Granitoid weathering crust of Baisha, Yingde, Guangdong Province, China [J]. *Geochimica*. **32**, 335–342 (in Chinese with English abstract).
- Zhao Fenghua, Cong Zhiyuan, Sun Hongfu, and Ren Deyi (2007) The geochemistry of rare-earth elements (REE) in acid mine drainage from the Sitai coal mine, Shanxi Province, North China [J]. *International Journal of Coal Geology*. **70**, 184–192.