

Geochemical characteristics of deep groundwater from sandstone aquifer in Qianyingzi mine, northern Anhui province, China

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Abstract

Major ions, trace elements and isotope concentrations for eight groundwater samples were tested, which collected from sandstone aquifer in Qianyingzi mine, northern Anhui province, China. The Geochemical characteristic of groundwater samples were studied based on the conventional graphical and multivariate statistical approach, and the resulted showed: two types of groundwater could be identified through the Piper diagram, which have high concentrations total dissolved solids (1,164–5,165 mg/L), with alkaline environment (pH = 8.02–8.90) in nature; the rare earth element of groundwater samples are characterized by enrichment of HREEs compared to LREEs when normalized to PAAS, which presented from the Nd_{SN}/Yb_{SN} ratios ranging from 0.042 to 0.121, with an average 0.075; groundwater characterized by negative Ce anomalies and positive Eu anomalies, what could be caused by the Ph conditions and exchange reaction between Eu^{2+} and Sr^{2+} , respectively; $\delta^{18}O$ and δ^2H of groundwater varied from -8.78 to -8.36‰ and -68.5 to -59.5‰ , respectively. The detritus and the exchange reaction between groundwater and alkyl could be the reason of obviously drift of δ^2H .

Key words: deep groundwater, geochemical characteristic, mining area, Northern Anhui province

INTRODUCTION

Many studies, focusing on the hydro-geochemical process, groundwater quality and water rock interaction, have great significance for the exploitation of groundwater (Kumar *et al.* 2009; Ramkumar *et al.* 2013). Especially for these days, with the development of society and economy, deep groundwater plays a key role for the natively character without any anthropogenic influences. However, the studies which devoted to the hydro-geochemical process in deep groundwater (depth > 400 m) are limited, for the sample collection is difficult.

Deep coal mining provides opportunities for the sample collection of deep groundwater. Deep groundwater in mining area has two typical characters for the specific district. First, it is the nicer and abundant water resource; in addition, it is the hidden danger for coal mine safety. Thus, deep groundwater investigations, such as major ions, trace elements, as well as isotopic studies, have been carried out in mining area (Chen *et al.* 2011; Gui *et al.* 2011; Sun *et al.* 2011). Especially with the evolution of analytical techniques, the rare earth elements (REEs) concentrations in groundwater have been studied for many scientists. REEs have the unique characteristics in diverse geological processes, what could be as the indicator in the water source discrimination (Chen *et al.* 2011; Sun *et al.* 2011).

Qianyingzi mine is located in northern Anhui Province, China, where has abundant coal resources. For the coal mine safe exploitation, water source discrimination is of great interest for the scientists and producer. Thus, so many studies what focused on the hydro-geochemical character, and then as basis to discuss the discrimination of groundwater have been carried out (Sun & Gui 2012). However,

these studies frequently to discuss only one or two type chemical elements, such as major elements, trace elements or isotope, the studies about the hydro-geochemical process combining the major ions and trace element with isotopic composition are limited. Especially in Qianyingzi mining, the information about hydro-geochemical has not been printed. The purpose of the study is to discuss the geochemistry character of groundwater from sandstone aquifer, using the major, trace element and isotopic data. The major targets are to (1) define the geochemical evolution of sandstone aquifer system in coal bearing; (2) understand the REEs characteristic of groundwater and its source; (3) identify the origin of isotope in groundwater samples. These results could be used as a basis for making sustainable groundwater development schemes and tracing the origin of deep groundwater.

MATERIALS AND METHODS

The Qianyingzi Coal Mine is located in the southern part of the Huaibei coalfield, which constituted by 23 active underground coal mines. Huaibei coalfield is one of the major coalfields in China, being located in the northern Anhui province, China. The basement of coal mine in the district is composed by Archean and Proterozoic metamorphic rock, with cover strata are stable sedimentation between late-Proterozoic and Permian (Gui *et al.* 2011). Groundwater system in the district from shallow to deep could be subdivided into four aquifers: the Quaternary aquifer, the Permian aquifer (Coal bearing aquifer), the Carboniferous aquifer (Taiyuan Formation limestone aquifer), and the Ordovician aquifer.

The groundwater samples were collected from sandstone aquifer in coal bearing of Qianyingzi mine, northern Anhui province, China (Figure 1). A total eight samples were collected from the Qianyingzi mining area. Water samples were collected via drainage holes in alleys, and then filtered through 0.45 μm pore-size membrane and collected into polyethylene bottles that had been cleaned using trace element clean procedures. All the eight samples were analyzed for major ions, trace elements and isotope.

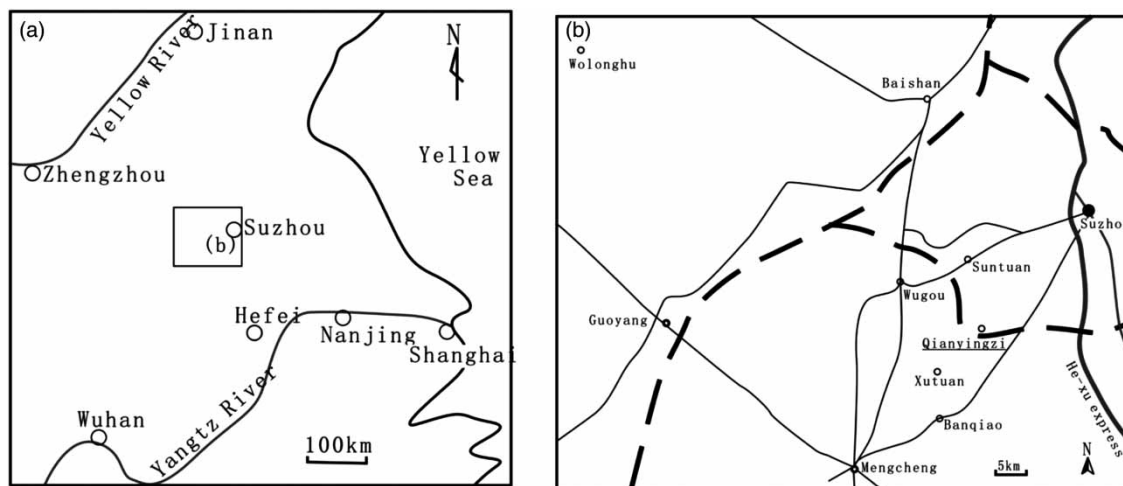


Figure 1 | Location of study area in northern Anhui Province, China.

Major ions were analyzed in the analysis testing center of department of coal geology of Anhui province, China. The K^+ and Na^+ were analyzed by atomic absorption spectrometry, SO_4^{2-} and Cl^- by ion chromatography, Ca^{2+} and Mg^{2+} by EDTA titration and alkaline by acid-based titration. The trace element and isotopic compositions were analyzed in the laboratory of Institute of Karst Geology, Chinese Academy of Geological Sciences. Trace element concentrations were determined after

pre-concentration by liquid-liquid extraction and analyzed by inductively coupled plasma mass spectrometry (ICP-MS, POEMS III) in the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences (Wuhan). The analytical precision for all trace elements was 10% relative standard deviation or better. The isotopic compositions were analyzed in the laboratory of Institute of Karst Geology, Chinese Academy of Geological Sciences. The isotopic data are reported with respect to standard mean ocean water, and $\delta^{18}\text{O}$ and δD have an overall precision of 0.2 and 2‰, respectively.

The piper diagram and calculates about carbonate equilibrium, total dissolved solids (TDS), density, conductivity and hardness were accomplished by software Aqqa, the statistical of samples data were completed by Excel (version 2007) and the SPSS (version 17).

RESULTS AND DISCUSSION

Major ions

The chemical data of groundwater samples are listed in Table 1, which used to discuss the geochemical characteristics of groundwater. The $\text{Na}^+ + \text{K}^+$ are dominant in the cation, whereas the SO_4^{2-} and HCO_3^- are mainly anion in the samples, with the low degree content of Cl^- (Table 1, Figure 2). In general, the pH values of groundwater varied from 8.02 to 8.90, with an average value 8.42, which indicates water is alkaline in nature. The amount of TDS of groundwater ranges from 1,164 to 5,165 mg/L, with an average of 2,428.8 mg/L. The geochemical data of groundwater were plotted on a Piper diagram (Figure 2), it can be seen almost all the ground water could be described the $\text{Na} \cdot \text{K} \cdot \text{SO}_4 \cdot \text{HCO}_3$ type. Eight groundwater samples could be subdivided into two types in detail, the $\text{Na} \cdot \text{K} \cdot \text{HCO}_3$ and $\text{Na} \cdot \text{K} \cdot \text{SO}_4$ types.

If the dissolution of calcite, dolomite and gypsum are dominant reaction in hydro-geochemical process, the ratio between $\text{Ca}^{2+} + \text{Mg}^{2+}$ and $\text{SO}_4^{2-} + \text{HCO}_3^-$ will be close to the 1:1. Ion exchange tends to shift the points to right due to an excess of $\text{SO}_4^{2-} + \text{HCO}_3^-$ (Fisher & Mulican 1997). The plot of $\text{Ca}^{2+} + \text{Mg}^{2+}$ versus $\text{SO}_4^{2-} + \text{HCO}_3^-$ (Figure 3(a)) shows that almost all the groundwater sample below the 1:1 line which indicate ion exchange is obviously. In addition, all the sample points are placed below the 1:1 line, what combined with the high concentrations of $\text{Na}^+ + \text{K}^+$, indicating the silicate weathering in the hydro-geochemical process.

The plot of Ca^{2+} versus Mg^{2+} of the groundwater suggests the dominance of the dissolution of calcite and dolomite that present in the sandstone aquifer with some Coal bearing strata (Figure 3(b)). If the points near to the 1:1 line, dissolution of dolomite should occur, whereas a high ratio is indicative of great calcite contribution. Most of the samples near to the line 1:1, which two samples above the line 1:1, what should be indicated that the dissolution of dolomite is exited, whereas the calcite weathering is dominant.

Rare earth element

The REE concentrations of groundwater samples are listed in Table 1 and the PAAS (Post Archean Average Shale) normalized REE patterns are presented in Figure 4 (Taylor & McLennan 1985). The total REE concentrations ($\sum\text{REE}$) are varied from 0.047 to 0.086 mg/L, with an average 0.066 mg/L. The normalized $\text{Nd}_{\text{SN}}/\text{Yb}_{\text{SN}}$ ratios (SN means PAAS normalization) varied from 0.042 to 0.121, with an average 0.075, what combined with the feature presented from Figure 4 revealed that all of the groundwater samples are characterized by enrichment of HREEs compared to LREEs when normalized to PAAS. In addition, the groundwater samples have weak negative PAAS normalized Ce anomalies, with the Ce/Ce^* values rang from -0.71 to 0.002, with an average

Table 1 | Major (mg/L), trace element ($\mu\text{g/L}$) and isotopic composition and other relations parameter of groundwater samples from sandstone aquifer in Qianyingzi mine, northern Anhui province, China

Parameter	QYZ1	QYZ2	QYZ3	QYZ4	QYZ5	QYZ6	QYZ7	QYZ8
$\text{K}^+ + \text{Na}^+$	652.33	582.45	1178.38	1718.35	543.67	471.82	524.29	949.88
Ca^{2+}	4.75	3.17	24.54	26.13	6.33	5.54	16.63	102.13
Mg^{2+}	3.84	3.36	4.8	11.53	3.84	3.84	19.2	87.37
Cl^-	181.67	282.21	199.31	149.93	188.73	146.4	407.44	287.5
SO_4^{2-}	375.79	4.53	1687.97	2837.57	125.13	21.4	8.64	1899.53
HCO_3^-	738.59	817.06	736.28	687.81	853.99	860.91	817.06	290.82
CO_3^{2-}	115.78	129.4		70.38	70.38	72.65		34.05
Hardness	27.68	21.75	81.05	112.68	31.63	29.65	120.59	614.81
Alkalinity	798.75	885.81	603.79	681.4	817.67	827.14	670.04	296.27
PH	8.54	8.9	8.05	8.55	8.31	8.65	8.02	8.36
TDS	1714	1425	3675	5165	1377	1164	1394	3516
La	0.0031	0.0041	0.0016	0.0029	0.0026	0.0033	0.0067	0.0032
Ce	0.0086	0.012	0.0032	0.004	0.0022	0.006	0.0036	0.0047
Pr	0.0013	0.0017	0.0008	0.0009	0.0019	0.0009	0.0017	0.0008
Nd	0.0032	0.0079	0.0061	0.01	0.0072	0.0079	0.0053	0.0059
Sm	0.0054	0.0072	0.012	0.01	0.008	0.013	0.0048	0.0071
Eu	0.0025	0.0037	0.0034	0.0069	0.0044	0.0082	0.03	0.0027
Gd	0.0028	0.0063	0.0035	0.0057	0.0067	0.0044	0.0049	0.0049
Tb	0.0009	0.0009	0.0013	0.0022	0.0038	0.0014	0.001	0.0018
Dy	0.0034	0.005	0.0046	0.0069	0.0012	0.0045	0.0076	0.002
Ho	0.0016	0.0014	0.0046	0.01	0.0011	0.002	0.0008	0.0025
Er	0.0095	0.0079	0.0062	0.0099	0.0079	0.0079	0.0042	0.0045
Tm	0.001	0.0012	0.0013	0.002	0.0017	0.0017	0.0006	0.0009
Yb	0.0022	0.0091	0.0059	0.012	0.0143	0.01	0.0052	0.0086
Lu	0.0015	0.0011	0.0013	0.0029	0.0028	0.0014	0.0018	0.0009
Zr	0.26	0.13	0.1	0.24	0.2	0.14	0.18	0.15
$\sum\text{REE}$	0.047	0.070	0.056	0.086	0.066	0.073	0.078	0.051
$\text{Nd}_{\text{SN}}/\text{Yb}_{\text{SN}}$	0.121	0.072	0.086	0.069	0.042	0.066	0.085	0.057
Ce/Ce^*	-0.024	0.002	-0.217	-0.248	-0.710	-0.097	-0.609	-0.169
Eu/Eu^*	0.47	0.41	0.33	0.63	0.45	0.66	1.46	0.33
δD	-58.5	-64.8	-68.5	-64.8	-64	-67.8	-64.2	-66.9
$\delta^{18}\text{O}$	-8.58	-8.59	-8.59	-8.58	-8.36	-8.75	-8.7	-8.78

-0.26, what calculated by $\text{Ce}/\text{Ce}^* = \log (2 * \text{Ce}_{\text{SN}} / (\text{La}_{\text{SN}} + \text{Pr}_{\text{SN}}))$. Whereas the Eu presented positive anomalies, with the Eu/Eu^* values varied from 0.33 to 1.46, with an average 0.59, what calculated by $\text{Eu}/\text{Eu}^* = \log (2 * \text{Eu}_{\text{SN}} / (\text{Sm}_{\text{SN}} + \text{Gd}_{\text{SN}}))$.

The negative Ce anomalies may reflect oxidative conditions of the aquifer, for Ce^{3+} is oxidized to the Ce^{4+} , reducing the concentrations of soluble Ce (Leybourne *et al.* 2000). However, there are no obviously proof supporting this view, for the groundwater collected from sandstone aquifer in coal bearing, where are regard as deoxidize environment for abundant coal resource. Another possible explanation is that the Ce anomalies of groundwater reflect differences in solubility of Ce redox species related to pH conditions in the aquifer system. Previous studies showed that degree of negative Ce anomalies varied with increasing pH, for Ce^{3+} is more stable in low pH conditions (Johannesson *et al.* 2005). The plot of Ce anomalies between pH showed that the degree of Ce anomalies varied

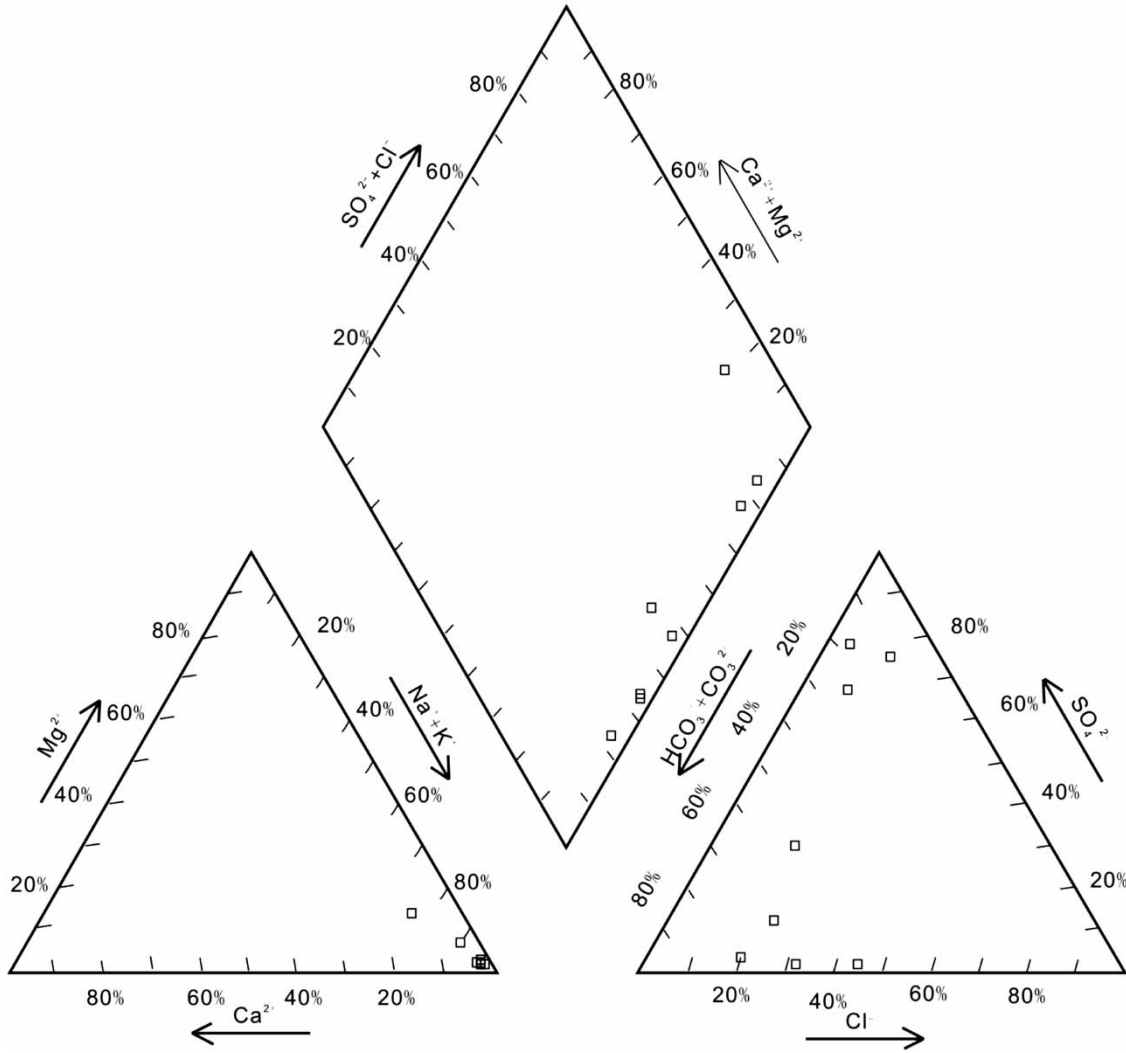


Figure 2 | Piper diagram of groundwater from sandstone aquifer in Qianyingzi mining, northern Anhui province, China.

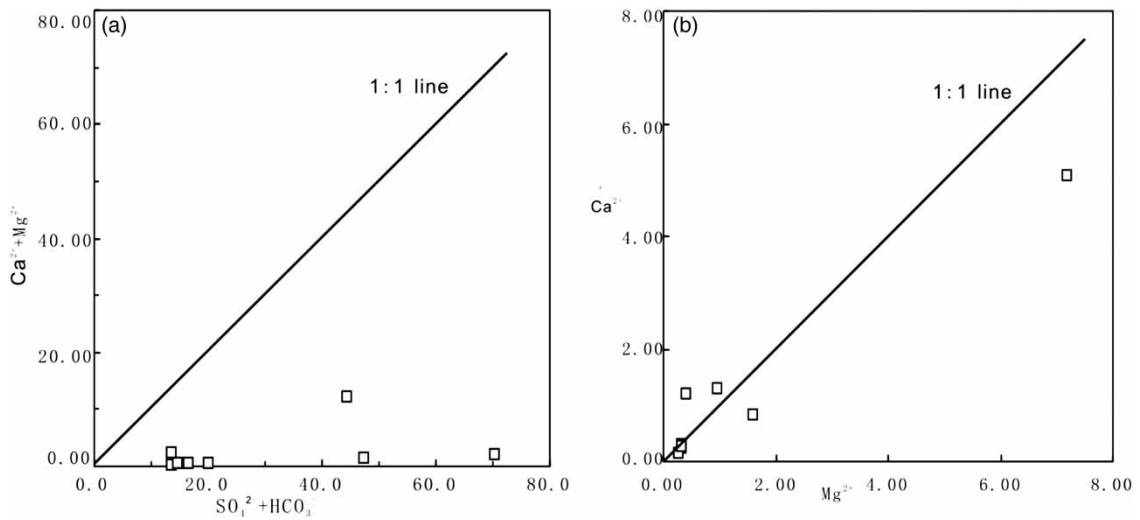


Figure 3 | The scatter diagrams of $Ca^{2+} + Mg^{2+}$ versus $SO_4^{2-} + HCO_3^-$, Ca^{2+} versus Mg^{2+} of groundwater from sandstone aquifer in Qianyingzi mine, northern Anhui province, China.

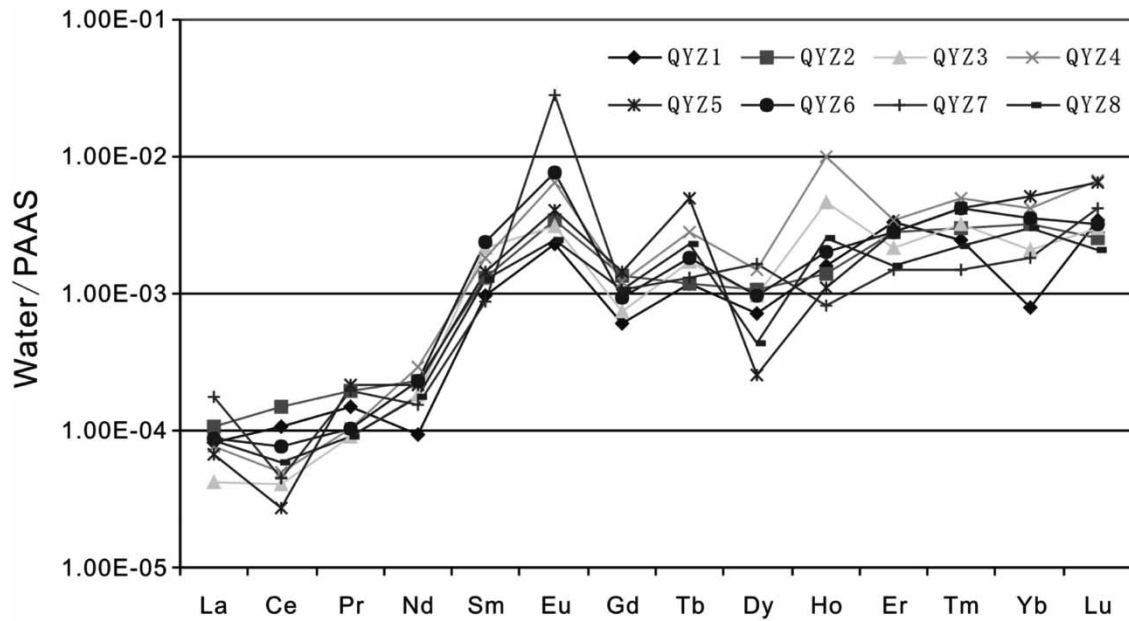


Figure 4 | PAAS normalized REE patterns of groundwater from sandstone aquifer in Qianyingzi mine, northern Anhui province, China.

along with the pH values (Figure 5), indicating that such a mechanism could be main reason for Ce depletion. The positive Eu anomalies in groundwater were related to the redox conditions (Jeong 2001). The positive Eu anomalies in deep groundwater possibly due to the exchange reaction between Eu^{2+} and Sr^{2+} in reducing conditions, for the chemical properties of Eu^{2+} and Sr^{2+} are similar (Yan *et al.* 2012). Therefore, if the concentration of Sr^{2+} is high in groundwater, the exchange reactions between Eu^{2+} and Sr^{2+} might occur. Consequently, Sr^{2+} is readily precipitated, whereas the concentration of Eu^{2+} is still high in groundwater. This mechanism possibly contributes to the positive Eu anomalies in groundwater in this study.

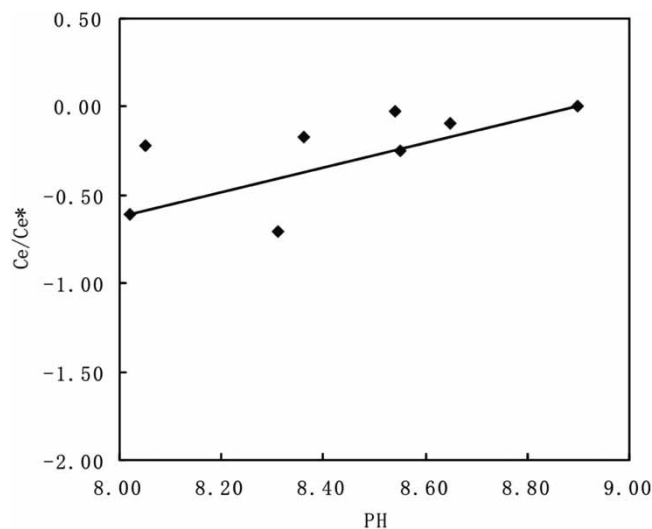


Figure 5 | Scatter diagram between pH versus Ce/Ce^* of groundwater from sandstone aquifer in Qianyingzi mine, northern Anhui province, China.

Zr and Sr are always considered to be representative of terrigenous and marine material in marine-terrigenous facies (e.g. the sandstone in the coal bearing strata), although Sr can also represent plagioclase in terrigenous detritus. Previous study showed that the REEs concentrations in sandstone are

dominated by the Zr (Gui *et al.* 2011). The REEs concentrations and fractionation in groundwater from sandstone aquifer are also expected be controlled by Zr, and the positive correlation between REEs and Zr are expected exiting too. This view was supported from the Figure 6, what presented positive correlation between Zr and REEs with the correlation coefficient 0.83. And the low positive coefficient (0.31) between Sr and REEs revealed that the contribution of REEs from marine material is limited.

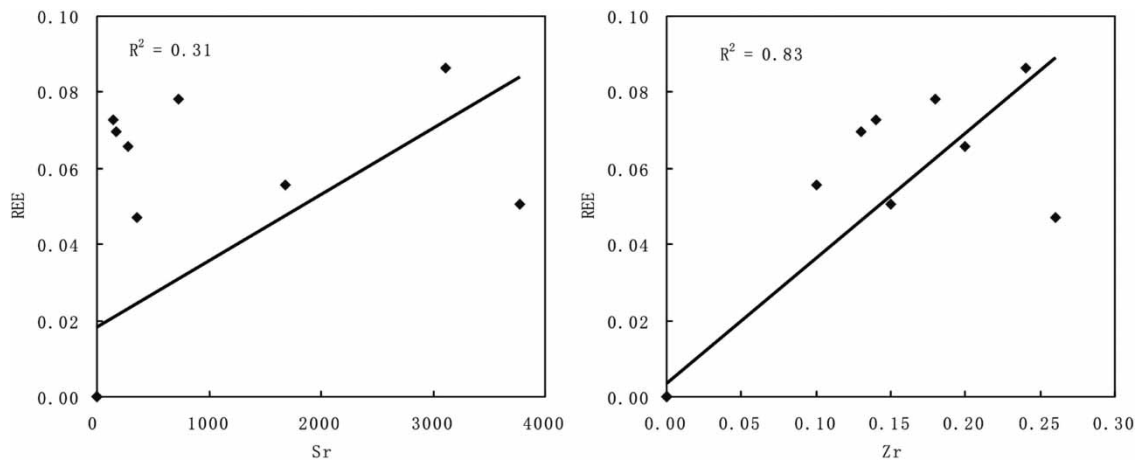


Figure 6 | Scatter diagram between REE versus Sr, Zr of groundwater from sandstone aquifer in Qianyingzi mine, northern Anhui province, China.

Isotope character

The results of the δD and $\delta^{18}O$ analysis for groundwater from sandstone aquifer are plotted in Figure 7 (a). The stable isotope values for groundwater samples were found be varied between -8.78 to -8.36 ‰ in $\delta^{18}O$ with an average of -8.62 ‰ and from -68.5 to -59.5 ‰ in δ^2H with an average of -64.94 ‰, respectively. In order to identify more information about the isotopic feature of groundwater samples, the other data are required. Thus, global meteoric water line (GMWL), local meteoric water line (LMWL) and local surface water line (LSWL) about the δD and $\delta^{18}O$ were gathered. The GMWL was described by $\delta D = 8 * \delta^{18}O + 10.56$, which defined by Craig (1961); the LMWL was characterized as $\delta D = 7.9 * \delta^{18}O + 8.2$, which summarized from the measured data of the stable

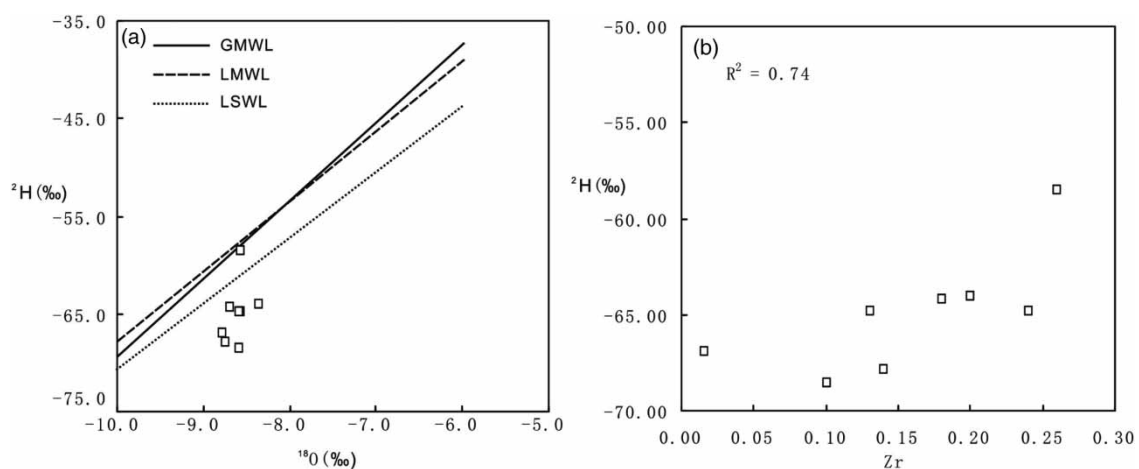


Figure 7 | Diagram between $\delta^{18}O$ and δD of groundwater from sandstone aquifer in Qianyingzi mine, northern Anhui province, China.

isotopes (Zhang 1989) and the LSWL is printed as the formula $\delta D = 6.74 \cdot \delta^{18}O - 3.33$ (Gui *et al.* 2005). All the lines and the isotopic message of the groundwater samples are plotted in Figure 7. The LSWL are below the LMWL and GMWL, which are presented from Figure 7, indicating that the surface water was shaped through the evaporation (Barth 2000).

Seven groundwater samples are plotted below the LSWL, LMWL and GMWL, except one groundwater sample be on the GMWL, what combined with the feature one sample among the LMWL and LSWL, indicating that the groundwater from sandstone aquifer be supplied from the meteoric water, with varied degree evaporation or not. In addition, the $\delta^{18}O$ and δ^2H are slightly variety, and the relationship between $\delta^{18}O$ and δ^2H in the groundwater from sandstone aquifer could be defined as $\delta D = 7.54 \cdot \delta^{18}O + 0.0005$. Further more, the values of δ^2H are variety obviously, whereas the $\delta^{18}O$ are stabilization reversely. The plots upward movement with a direction vertical or approximate to vertical, and all the plots are not exceed the LMWL, what revealed that the δ^2H have been drifted obviously.

Generally speaking, the variety of $\delta^{18}O$ and δ^2H could be caused by such factors as evaporation, reservoir temperature, residence time and water-rock interaction (Truesdell & Hulston 1980). The sight presented in Figure 7(a) could be interpreted by the sandstone aquifer being reducing environment, where exchange reaction of δ^2H between groundwater and alkyl is more markedly, whereas the exchanging of $\delta^{18}O$ has been equilibrium. And the deduction could be supported by the previous study (Gui *et al.* 2005). However, the positive correlation between δ^2H and Zr (Figure 7(b)), with the correlation coefficient 0.74, what implying that the variety of δ^2H are relate to the concentrations of Zr. In another word, the character of δ^2H could be caused by the detritus which have high degree concentration of Zr. However, the concretely process and influencing mechanism need the further work.

CONCLUSIONS

The concentration of major ions, trace elements and isotopic in groundwater samples collected from sandstone aquifer in Qianyingzi mine, northern Anhui province, China had been tested, the geochemistry characteristic of groundwater were analyzed, a series of conclusion could be obtained:

Groundwater from the sandstone aquifer could be subdivided into Na·K-HCO₃ and Na·K-SO₄ types, what have high concentrations TDS (1,164–5,165 mg/L), with alkaline environment (Ph = 8.02–8.90) in nature. The silicate weathering is dominated in the hydro-geochemical process, and the dissolution of calcite and dolomite were also existed, what be obtained from the relation between Ca²⁺ + Mg²⁺ and SO₄²⁻ + HCO₃⁻, Ca²⁺ and Mg²⁺, and the high concentration of Na⁺ + K⁺.

∑REE concentrations are varied from 0.047 to 0.086 mg/L, with an average 0.066 mg/L, what could be contributed from the detritus with high concentrations of Zr. The normalized Nd_{SN}/Yb_{SN} ratios varied from 0.042 to 0.121, with an average 0.075, revealing all of the groundwater samples are characterized by enrichment of HREEs compared to LREEs when normalized to PAAS. Slight negative Ce anomalies and marked positive Eu anomalies are existed in all samples, what could be caused by the Ph conditions and exchange reaction between Eu²⁺ and Sr²⁺, respectively.

The value of $\delta^{18}O$ are varied between -8.78 to -8.36‰, with an average of -8.62‰, whereas the δ^2H ranging from -68.5 to -59.5‰, with an average of -64.94‰. In addition, the values of δ^2H are variety obviously, otherwise, the $\delta^{18}O$ are stabilization reversely. Groundwater from sandstone aquifer could be supplied from the meteoric water, with varied degree evaporation or not, what deduced from the feature of the relation between samples plots and LSWL, LMWL and GMWL. The drift of δ^2H could be caused by the detritus and the exchange reaction between groundwater and alkyl.

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