



Major Ions, Trace Elements and Isotope Characteristics of Groundwater from Coal Bearing Aquifer: A Case Study

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Abstract: Major ions, trace elements and isotope concentrations were determined in water samples collected from coal bearing aquifer and surface rivers in Suxian coalfield, China. The geochemical characteristics and ionic sources were discussed, and serious results could be obtained: The groundwater samples from coal bearing aquifers are mainly subdivided into Na-HCO₃ types, only one sample be Na-SO₄ type, presenting different features with surface river water. The total REE concentrations (\sum REE) in groundwater samples are low with average value of 0.29 mg/L. The light rare earth elements in groundwater are less compared with high rare earth elements, evidenced by the small value of Nd_{SN}/Yb_{SN}. The reduction environment and organic matter in coal bearing aquifers are the reasons deduced the positive Ce anomalies in groundwater samples, while the surrounding feldspar rocks controlled the positive Eu anomalies. The concentrations of $\delta^{18}\text{O}$ and δD in groundwater samples are lower than river water samples, reflected the river waters affected by the evaporation clearly, with the heavy isotope enrichment. The evaporation and rock weathering affection is the mainly factors on the ionic source in groundwater samples, evidenced by the Gibbs diagrams and other ionic group ratios such as HCO₃⁻/Na⁺- Ca²⁺/Na⁺ and Mg²⁺/Na⁺-Ca²⁺/Na⁺.

Keywords: hydrochemistry; groundwater; coal bearing aquifer; rare earth elements; suxian coalfield

1. Introduction

As an important part of the surface environment system in earth, deep groundwater system serving as major storage zones for fresh water resources, what also contains lots of geological information for long time remaining in rock aquifers. Thus, lots of studies about hydrochemistry information had been completed to understand water-rock interaction, tectonic background and hydrogeological conditions (Chae et al., 2006; Ayenew et al., 2008). Especially in coal mining area, deep groundwater not only be the fresh water resources, but also damage the exploitation of deep coal resources in high degree, the chemical composition and flow paths of deep groundwater need be further concerned. Thus, studies about the chemical characteristics, runoff law and water quality of deep groundwater in coal mine area were completed (Gui et al., 2011; Sun et al., 2011). Some information to efficient groundwater development schemes and help reduce coal mining hazards as well as water quality deterioration could be provided by these studies.

However, these studies always focused on a coal mine (small area) or a certain class of chemical composition (single test) (Chen et al., 2014; Gui et al., 2014). The studies about deep groundwater hydrochemistry in a larger coal area, basing on the measure of major ions, rare earth elements and hydrogen and oxygen isotope are relative absence. While such studies could not

only help to understand the relationships between macro and micro component in groundwater, but also constraint the influenced factors on hydrochemistry evolution in deep groundwater.

In this study, groundwater samples in coal bearing aquifer and surface river samples in Suxian coalfield, Anhui Province, China were collected and the major ions, trace elements and hydrogen and oxygen isotope compositions were tested. The main objectives of the study were (1) to define the geochemical characteristics of groundwater in coal bearing aquifers, (2) to constraint the controlled factors on the hydrochemistry compositions in groundwater.

2. Geological Background

Suxian coalfield mainly composed by Qidong, Qinan, Taoyuan, Qianyingzi, Zhuxianzhuang and Luling coal mines, located in northern Anhui Province, China (Fig. 1). The basement of coal mine in the area is composed by Archean and Proterozoic metamorphic rock, with cover strata are stable sedimentation. Previous studies have shown that the deep groundwater system in the Suxian coal mine district could be subdivided into four aquifers from shallow to deep, the Quaternary aquifer (QA), coal-bearing aquifer (CA), Taiyuan formation limestone aquifer (TA) and Ordovician limestone aquifers(OA), all of that influence the coal exploration safely (Gui et al. 2007). The coal bearing aquifer mainly composed by

mudstone, siltstone, coal seams and a small amount of limestone (Fig. 2). The area has a marine-continental climate, and annual average temperature of 14.9 °C.

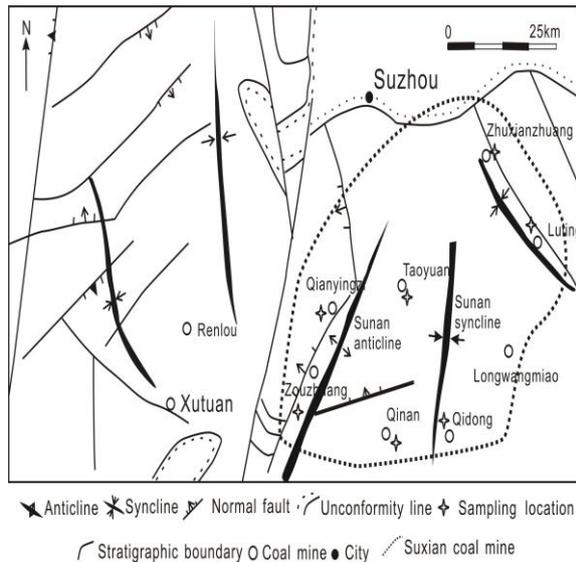


Figure 1 Location and geological setting of the study area in northern Anhui Province, China

3. Sampling and Test

The groundwater samples were collected in the same time (July, 2014), in order to exclude the problem such as groundwater chemical field changed in different time. In total five groundwater samples and seven river water samples were collected from coal bearing aquifers and surface rivers, respectively. Groundwater samples were collected via drainage holes in alleys, and then filtered into pre-cleaned and sterilized polyethylene bottles that had been cleaned following trace element cleaning procedures through a 0.45- μm membrane. All water samples were analyzed for major ions and hydrogen and oxygen isotopes, and only groundwater samples were measured for trace elements. Major ions were determined in the analysis testing laboratory of the Department of Coal Geology, Anhui Province, China. The isotopic compositions were determined in the laboratory of the National Engineering Research Center of Coal Mine Water Hazard Controlling. The isotopic data are reported relative to Standard Mean Ocean Water (SMOW), and the overall precisions of $\delta^{18}\text{O}$ and δD were 0.2 and 2 ‰, respectively. After liquid-liquid extraction, trace element concentrations were determined by inductively coupled plasma-mass spectrometry (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 % of the relative standard deviation or better.

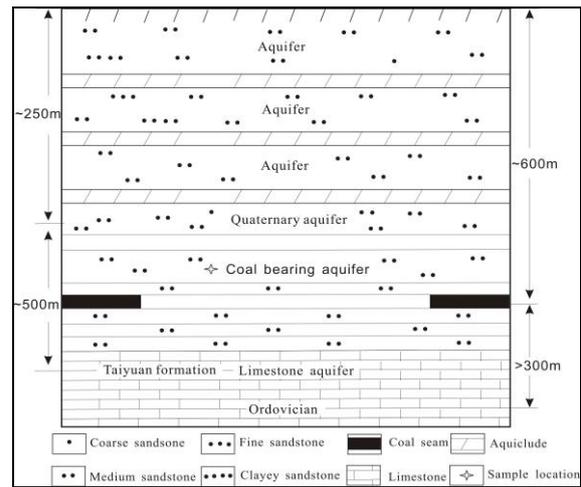


Figure 2 Hydrogeological profile and sampling location in the study area

4. Result and Discussion

4.1 Major ions chemistry

The major ions composition in water samples collected from Suxian coalfield are listed in Table 1. In general, the pH values of groundwater from coal bearing aquifer varied from 7.44 to 8.20, with an average value of 7.86, while the river water samples had a higher pH value with average value be 8.46, suggesting that all the water samples are alkaline in nature. The anionic compositions of Cl^- , SO_4^{2-} , and HCO_3^- in groundwater varied from 120.36 to 253.96, 40.34 to 2357.64 and 368.96 to 1981.93 mg/L, with the mean value be 180.85, 546.44 and 1088.59 mg/L, respectively. While the cationic compositions of K^+Na^+ , Ca^{2+} , and Mg^{2+} ranging from 449.26 to 1104.71, 4.05 to 105.25 and 3.91 to 109.23 mg/L, with average values be 706.28, 28.46 and 26.45 mg/L, respectively. In detail, the K^+Na^+ and HCO_3^- are the dominant ions in groundwater, thus, the groundwater samples are mainly subdivided into Na- HCO_3 types, only with one sample be Na- SO_4 type.

To further presented the chemical characters of groundwater from coal bearing aquifer and river water, the ionic concentrations were plotted on Piper diagrams (Fig 3). Some information could be obtained: all the alkali elements (K^+ and Na^+) exceeded the alkaline earth elements (Ca^{2+} and Mg^{2+}) in the groundwater samples. While the river water samples presented different characters with the groundwater samples. The concentrations of HCO_3^- are lower in river water samples, while the Cl^- and SO_4^{2-} content are higher comparing with the groundwater samples. In addition, the cationic compositions of Ca^{2+} and Mg^{2+} are higher in river water samples than the concentrations in groundwater samples. In conclusion, the groundwater samples from coal bearing aquifer have diverse characteristics with the surface river water.

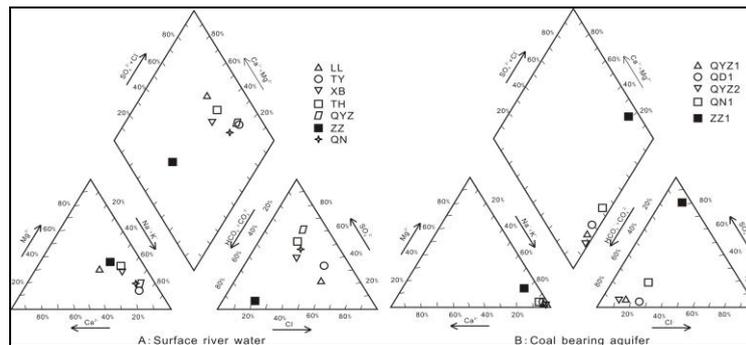


Figure 3 Piper diagrams in water samples from Ordovician limestone aquifer and river in Suxian coal mine, northern Anhui Province, China

Table 1 Major ions (mg/L) and isotope (‰) concentration in water samples from Suxian mining area

| No. | Source | K ⁺ +Na ⁺ | Ca ²⁺ | Mg ²⁺ | Cl ⁻ | SO ₄ ²⁻ | HCO ₃ ⁻ | CO ₃ ²⁻ | pH | TDS | TYPE | δD | δ ¹⁸ O |
|------|--------|---------------------------------|------------------|------------------|-----------------|-------------------------------|-------------------------------|-------------------------------|------|--------|---------------------|--------|-------------------|
| LL | River | 166.57 | 105.53 | 60.58 | 336.65 | 162.17 | 283.13 | 0.00 | 8.15 | 1300.0 | Na-Cl | -41.02 | -4.80 |
| TY | River | 470.40 | 72.06 | 46.64 | 490.75 | 432.39 | 211.20 | 37.54 | 8.91 | 2680.0 | Na-Cl | -52.41 | -6.69 |
| ZXZ | River | 176.94 | 45.34 | 49.58 | 142.42 | 260.54 | 244.27 | 17.52 | 8.44 | 983.0 | Na-SO ₄ | -33.36 | -3.01 |
| ZXZ | River | 314.68 | 80.15 | 97.21 | 223.07 | 637.98 | 394.40 | 0.00 | 8.12 | 1910.0 | Na-SO ₄ | -36.06 | -3.73 |
| QYZ | River | 483.39 | 62.03 | 65.46 | 237.22 | 847.07 | 226.99 | 43.21 | 8.60 | 2225.0 | Na-SO ₄ | -36.42 | -4.01 |
| QN | River | 420.17 | 65.58 | 59.40 | 269.40 | 560.60 | 363.87 | 35.04 | 8.53 | 2010.0 | Na-SO ₄ | -43.17 | -5.34 |
| ZZ | River | 75.53 | 29.96 | 31.42 | 51.48 | 20.58 | 295.17 | 20.02 | 8.48 | 204.2 | Na-HCO ₃ | -34.46 | -3.59 |
| QYZ1 | SA | 519.06 | 10.47 | 4.89 | 120.36 | 55.15 | 1156.96 | 0.00 | 7.8 | 1680 | Na-HCO ₃ | -63.24 | -8.43 |
| QYZ2 | SA | 865.38 | 10.47 | 4.89 | 144.78 | 96.73 | 1981.93 | 0.00 | 7.9 | 2870 | Na-HCO ₃ | -63.68 | -8.38 |
| QD1 | SA | 592.99 | 4.05 | 9.33 | 229.93 | 40.34 | 1185.75 | 0.00 | 8.1 | 2100 | Na-HCO ₃ | -63.57 | -8.48 |
| QN1 | SA | 449.26 | 12.08 | 3.91 | 155.24 | 182.34 | 749.33 | 0.00 | 8.2 | 1550 | Na-HCO ₃ | -64.48 | -8.28 |
| ZZ1 | SA | 1104.71 | 105.25 | 109.23 | 253.96 | 2357.64 | 368.96 | 0.00 | 7.7 | 4740 | Na-SO ₄ | -66.27 | -8.94 |

4.2 Rare earth elements

The rare earth elements and other trace elements of groundwater samples are listed in Table 2, and the Post Archean Average Shale (PAAS) normalized REE pattern diagrams are presented in Fig 4 (Taylor and McLennan 1985). Generally, the total REE concentrations (\sum REE) in groundwater are low, while the \sum REE in groundwater samples from coal bearing aquifers are more higher, with the value ranging from 0.049 to 0.65, with average value of 0.29 mg/L. The ratios Nd_{SN}/Yb_{SN} (SN indicates PAAS normalization) often used to indicate the fractionation between light and heavy rare earth elements, and the lower value of Nd_{SN}/Yb_{SN} reflected the light rare earth elements less in groundwater. Thus, the heavy REEs in groundwater samples are more enriched than light REEs, for the values of Nd_{SN}/Yb_{SN} in groundwater samples varied from 0.01 to 0.57, with average value 0.22, what also characterized by the Fig 4.

The anomalies of elements Ce and Eu, expressed by the formula $Ce/Ce^* = 2 * Ce_{SN} / (La_{SN} + Pr_{SN})$ and $Eu/Eu^* = 2 * Eu_{SN} / (Sm_{SN} + Gd_{SN})$, respectively, could reflected the relationship between elements with the adjacent elements. Previous studies showed Ce anomalies in groundwater generally controlled by such factors as pH values, oxidative conditions and surrounding rocks (Semedley 1991; Bau 1999). The Ce/Ce^* in groundwater samples varied from 0.81 to 1.39, with average value be 1.02, indicated the positive Ce anomalies are existed in the groundwater samples. In other words, the soluble cerium in

groundwater is the Ce^{3+} instead of Ce^{4+} , for the CeO_2 is easily to precipitation. Generally speaking, the Ce anomalies caused by pH value often presented good correlation with pH value, as Ce^{3+} is more stable in low pH conditions (Johannesson et al. 2005). However, the Ce in groundwater samples presented positive anomalies, without relationship with pH value, what suggesting the pH value is not the controlled factor influencing the Ce anomalies. The Ce anomalies in groundwater samples often presented similar feature as the surrounding rocks, when surrounding rock as the controlled factors. In the study, groundwater samples in coal bearing aquifer are surrounded by sandstone, limestone and coal beams. Thus, this mechanism is also not the mainly reason for positive Ce anomalies. In oxidative conditions, groundwater could presented negative Ce anomalies, as the Ce^{3+} is oxidized to Ce^{4+} , thereby reducing the concentrations of soluble Ce (Leybourne et al. 2000). However, the groundwater samples in coal bearing aquifer are remaining in reduction environment, what caused the soluble Ce existed in groundwater as Ce^{3+} . Thus, the reduction environment could be the mainly factors deduced the positive Ce anomalies in groundwater samples. In addition, organic matter also caused the positive Ce anomalies in groundwater, though the relative mechanism is not clear (Moller et al., 1993; Johannesson et al., 2004;). The groundwater samples collected from coal bearing aquifer had a high content of organic matter, thus, this factors also could be caused the positive Ce anomalies in groundwater samples.

The values of Eu/Eu^* in groundwater samples varied from 5.86 to 42.86, presented positive Eu anomalies. Water-rock interactions were confirmed as the reason for the positive Eu anomalies, especially for the minerals with higher Eu contents such as feldspar. In coincidence, the groundwater samples from coal bearing aquifer are surrounding by rocks such as sandstone, mainly composed by feldspar, suggesting the surrounding rock could be the reason for Eu anomalies. Positive Eu anomalies in groundwater could reflect an oxidative environment (Jeong 2001), whereas the aquifers in the study area have been confirmed as reduction environment, thus the oxidative environment could not be the reason for Eu anomalies.

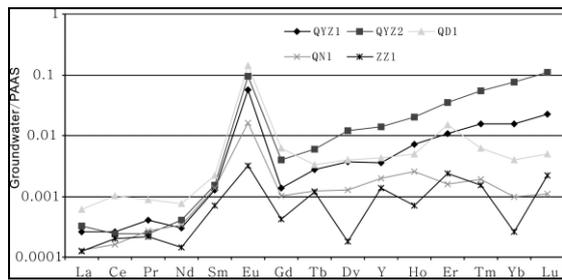


Figure 4 PAAS-normalized REE patterns in groundwater from Ordovician limestone aquifer in study area

Table 2 Trace elements ($\mu\text{g}/\text{L}$) concentrations in groundwater from limestone aquifer in Suxian mining area

| No. | QYZ1 | QYZ2 | QD1 | QN1 | ZZ1 |
|---------------------------|--------|--------|--------|--------|--------|
| Sr | 266 | 604 | 370 | 383 | 4610 |
| Y | 0.11 | 0.43 | 0.13 | 0.060 | 0.042 |
| Zr | 0.56 | 1.44 | 1.07 | 0.19 | 0.097 |
| La | 0.0100 | 0.013 | 0.023 | 0.0049 | 0.0048 |
| Ce | 0.021 | 0.019 | 0.081 | 0.013 | 0.016 |
| Pr | 0.0035 | 0.0022 | 0.0077 | 0.0024 | 0.0019 |
| Nd | 0.010 | 0.014 | 0.026 | 0.011 | 0.0050 |
| Sm | 0.0070 | 0.0086 | 0.012 | 0.0075 | 0.0039 |
| Eu | 0.061 | 0.10 | 0.15 | 0.017 | 0.0035 |
| Gd | 0.0063 | 0.019 | 0.028 | 0.0047 | 0.0019 |
| Tb | 0.0021 | 0.0046 | 0.0025 | 0.0010 | 0.0009 |
| Dy | 0.017 | 0.057 | 0.019 | 0.0059 | 0.0008 |
| Ho | 0.0071 | 0.020 | 0.0049 | 0.0025 | 0.0007 |
| Er | 0.031 | 0.098 | 0.043 | 0.0046 | 0.0068 |
| Tm | 0.0063 | 0.022 | 0.0025 | 0.0008 | 0.0006 |
| Yb | 0.044 | 0.22 | 0.011 | 0.0028 | 0.0007 |
| Lu | 0.011 | 0.053 | 0.0024 | 0.0005 | 0.0010 |
| REE | 0.2366 | 0.6490 | 0.4143 | 0.0788 | 0.0487 |
| Y/Ho | 15.04 | 21.24 | 26.87 | 23.79 | 58.74 |
| Y/Dy | 6.20 | 7.46 | 7.05 | 10.18 | 49.39 |
| Ce/Ce* | 0.81 | 0.85 | 1.39 | 0.85 | 1.23 |
| Eu/Eu* | 42.86 | 34.61 | 33.79 | 13.61 | 5.86 |
| Nd_N/Yb_N | 0.02 | 0.01 | 0.19 | 0.34 | 0.57 |

4.3 Isotope chemistry

The results of the δD and $\delta^{18}\text{O}$ analyses of ground- and river- water from the Suxian coalfield are plotted on Figure 5. The values of $\delta^{18}\text{O}$ in groundwater varied from -8.94‰ to -8.28‰, with an average of -8.50‰,

while the δD varied from -66.27‰ to -63.24‰, with an average of -64.25‰. Otherwise, the river water samples have the higher concentration of δD and $\delta^{18}\text{O}$, the value of δD and $\delta^{18}\text{O}$ are varied from -52.41 to -33.36‰ and -6.69 to -3.01‰, with an average value of -39.56‰ and -4.45‰, respectively.

Other data – e.g., the global meteoric water line (GMWL), local meteoric water line (LMWL) and local surface water line (LSWL) – were required to obtain more information about the isotope characteristics of the ground- and river- water samples in Suxian coalfield. The GMWL is characterized as $\delta\text{D}=8*\delta^{18}\text{O}+10.56$ (Craig, 1961); the LMWL as $\delta\text{D}=7.9*\delta^{18}\text{O}+8.2$, summarized from stable isotope data (Zhang, 1989), and the LSWL as $\delta\text{D}=6.74*\delta^{18}\text{O}-3.33$ (Gui et al., 2005). All these lines and the isotopic signatures of the river and ground- water samples are shown in Figure 5. All the water samples plotted below the LMWL and the GMWL, presenting the similar equal slope with the GMWL, indicated the groundwater samples from coal bearing aquifer were recharged from the precipitation and surface water. The groundwater samples have lower concentrations of $\delta^{18}\text{O}$ and δD comparing with river water, reflected the river water affected by the evaporation clearly, with the heavy isotope enrichment.

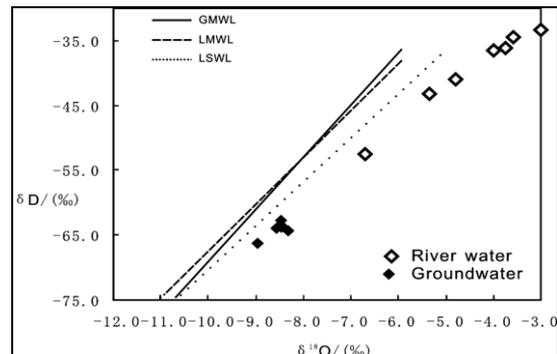


Figure 5 Plot of the $\delta^{18}\text{O}$ and δD values in water samples from the study area

4.4 Hydrochemistry process

Gibbs (1970) discussed the sources of ions in river water using a diagram comparing TDS and ionic group ratios – e.g., $\text{Na}^+(\text{Na}^++\text{Ca}^{2+})$, $\text{Cl}^-(\text{Cl}^++\text{HCO}_3^-)$, and in further applied to discussed the influenced mechanism of chemical composition in groundwater. In general, the water samples have low TDS contents and high ionic group ratios (close to 1), if river water is derived directly from precipitation, without the other influencing factor. In opposite, the ions source in water samples could be considered releasing from weathering of rocks, while the TDS content is higher and the ion ratio is less than 0.5. The plots diagram of $\text{TDS}-\text{Na}^+(\text{Na}^++\text{Ca}^{2+})$ and $\text{TDS}-\text{Cl}^-(\text{Cl}^++\text{HCO}_3^-)$ in water samples collected from study area were presented in Fig. 6. The higher ratio for $(\text{Na}^++\text{K}^+)/(\text{Na}^++\text{K}^++\text{Ca}^{2+})$ shown in Fig. 6 could have arisen during calculation, using the Na^++K^+ concentrations –

as determined – instead of the Na^+ concentration. It could be concluded, the higher TDS contents in water samples suggesting the ions in water samples is affected by the evaporation, with the rock weathering affection in a certain.

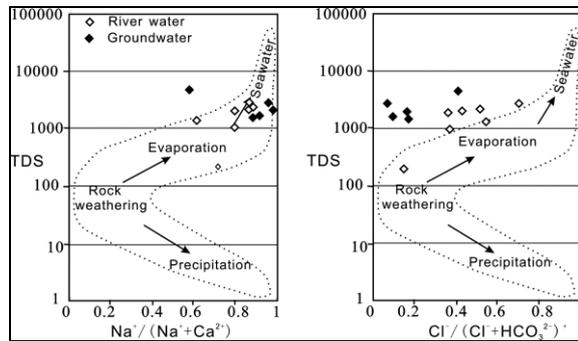


Figure 6 Gibbs diagrams of ground- and river- water samples in Suxian coalfield

Hydrogeochemistry of groundwater always influenced by such factors like water-rock interaction and recharging, and the degree of water-rock interaction controlled by the residence time within the aquifer (Gaillardet *et al.* 1999). In general, evaporate dissolution, carbonate dissolution and silicate weathering actions are three processes contributing to the generation of solutes in groundwater. As can be seen from Fig.7, the groundwater from coal bearing aquifer in the area is mainly controlled by silicate weathering and evaporate dissolution. This is also supported by the Gibbs diagrams and REEs features.

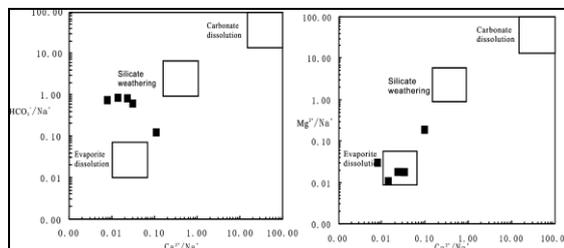


Figure 7 Scatter diagrams of $\text{HCO}_3^-/\text{Na}^+ - \text{Ca}^{2+}/\text{Na}^+$ and $\text{Mg}^{2+}/\text{Na}^+ - \text{Ca}^{2+}/\text{Na}^+$ in groundwater samples in study area

5. Conclusions

Several ground- and river- water samples were analyzed for major ions, trace elements and hydrogen and oxygen isotopes, collected from Suxian coalfield, Anhui Province, China, what as a basis to discuss the hydrochemistry characteristics and ionic source, a serious conclusion could be obtained:

The groundwater samples from coal bearing aquifers are mainly subdivided into $\text{Na}-\text{HCO}_3$ types, only with one sample be $\text{Na}-\text{SO}_4$ type, indicating the $\text{Na}^+ + \text{K}^+$, HCO_3^- and SO_4^{2-} were the dominant ions in the groundwater. While the river water samples have high concentrations of Cl^- , Ca^{2+} and Mg^{2+} compared with the groundwater.

The total REE concentrations ($\sum\text{REE}$) in groundwater samples varied from 0.049 mg/L to 0.65 mg/L, with average value of 0.29 mg/L. The lower ratios $\text{Nd}_{\text{SN}}/\text{Yb}_{\text{SN}}$ reflected the light rare earth elements are less in groundwater compared with high rare earth elements. The positive Ce anomalies in groundwater samples were controlled by the reduction environment and organic matter in coal bearing aquifers. While the positive Eu anomalies in groundwater samples were deduced by the surrounding feldspar rocks.

The values of $\delta^{18}\text{O}$ in groundwater varied from -8.94‰ to -8.28‰, with an average of -8.50‰, while the δD varied from -66.27‰ to -63.24‰, with an average of -64.25‰. While the river water samples have the higher concentration of δD and $\delta^{18}\text{O}$, the value of δD and $\delta^{18}\text{O}$ are varied from -52.41 to -33.36‰ and -6.69 to -3.01‰, with an average value of -39.56‰ and -4.45‰, respectively. The groundwater samples have lower concentrations of $\delta^{18}\text{O}$ and δD comparing with river water, reflected the river water affected by the evaporation clearly, with the heavy isotope enrichment.

Gibbs diagrams present high TDS contents and low ionic group ratios, indicating evaporation and rock weathering affection is mainly factors on the ionic source, what also supported by the diagrams of $\text{HCO}_3^-/\text{Na}^+ - \text{Ca}^{2+}/\text{Na}^+$ and $\text{Mg}^{2+}/\text{Na}^+ - \text{Ca}^{2+}/\text{Na}^+$.

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