Hydrochemistry Characteristics of Groundwater from Ordovician Limestone Aquifer in Suxian Coal Mine, Anhui Province, China

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Abstract*: Major ions, trace elements and isotope concentrations were measured in water samples collected from Ordovician limestone aquifer and surface rivers in Suxian coal mine district, China. The geochemical characteristics and hydrochemistry process were discussed, and serious results could be obtained: Groundwater samples from Ordovician limestone aquifer were mainly the Na-SO$_4$ and Na-HCO$_3$ types, the similar feature with the river water samples suggesting a certain relationship may be existed between groundwater and surface river water. The total REE concentrations ($\sum$REE) in groundwater samples varied from 0.0263 to 0.1348 mg/L, with an average value of 0.063 mg/L. The oxidative conditions are the mainly factors deduced the negative Ce anomalies and positive Eu anomalies. The groundwater samples, recharged by the precipitation and surface water, have lower concentrations of $\delta^{18}O$ and δD comparing with river water, reflected the river water affected by the evaporation clearly, with the heavy isotope enrichment. The negative correlation between $\delta^{18}O$ and TDS and Ca^{2+} indicated that the dissolution of limestone could be the factor influencing the oxygen isotope characters. Groundwater in Ordovician limestone is runoff from both sides to intermediate, with the Taoyuan coal mine as the subsidence center in study area, evidenced by the contour diagrams of TDS and $\delta^{18}O$. The hydrochemistry field and runoff field of groundwater in study area are mainly controlled by the tectonic field, especially the Sunan syncline.*

Keywords: *hydrochemistry; ordovician limestone; groundwater; isotope; suxian coal mine*

1. Introduction

Deep groundwater system is the important parts of the surface environment in earth, serving as major storage zones for fresh water resources. In addition, deep groundwater also contains lots of geological information, what flow or remain in rock aquifers for long time. Thus, the studies about deep groundwater hydrochemistry and dynamics have important significance for understanding the regional hydrogeological conditions, water-rock interaction and tectonic setting. In coal mining area, the deep groundwater is damaged in a high degree with the exploitation of deep coal resources, the chemical composition and flow paths of deep groundwater should be further concerned. In recent years, studies about the chemical characteristics, water quality, runoff law and hydrological process of deep groundwater in coal mine area were completed (Gui et al., 2011; Sun et al., 2011; Lin et al., 2014). These studies provide supporting information to efficient groundwater development schemes and help reduce coal mining hazards as well as water quality deterioration.

However, these achievements frequently focused on a coal mine (small area) or a certain class of chemical content (single test) (Chen et al., 2014; Gui et al., 2014). The studies of deep groundwater in a larger coal area based on the test of conventional elements, trace elements and hydrogen and oxygen isotope, and discuss the relationship between the macro and micro component in groundwater in further are relative absence. While such studies could not only help to understand the relationship between macro and micro components in groundwater, but also constraint the relationship between the flow field and chemical field.

Based on this knowledge, limestone aquifers groundwater in Ordovician in Suxian coal mine district were selected as the research object, and some groundwater and surface river water samples were collected from seven coal mines in Suxian coal mine district, and the major elements, trace elements and hydrogen and oxygen isotope compositions were measured. The main objectives of the study were (1) to define the geochemical characteristics of groundwater collected from limestone aquifers, (2) to understand the relationships between macro and micro components, and (3) to constrain the influenced factors controlling on the hydrochemistry process in the groundwater flow paths.

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2. Geological background

The Suxian coal mine district is located in northern Anhui Province, China, mainly including Qidong, Qinan, Taoyuan, Qianyingzi, Zhuxianzhuang and Luling coal mines (Fig. 1). The area has a marine-continental climate, and annual average temperature of 14.9 °C. Previous studies have shown that the deep groundwater system in the Suxian coal mine district four main aquifers, the Quaternary aquifer (QA), coal-bearing aquifer (CA), Taiyuan formation limestone aquifer (TA) and Ordovician limestone aquifers(OA), all of which have influence on coal exploration (Gui et al. 2007). The Ordovician limestone aquifers composed of mainly limestone (Fig. 2).
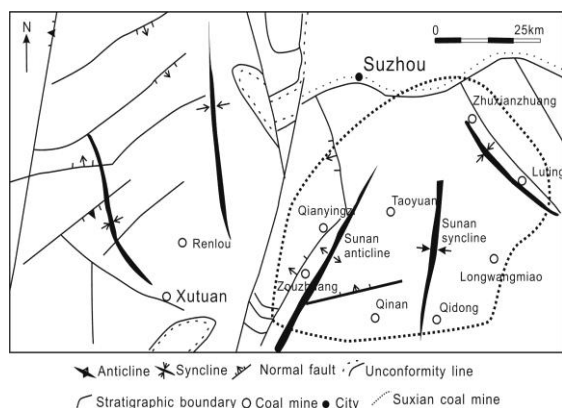

Figure 1. *Location and geological setting of the study area in northern Anhui Province, China*

3. Sampling and test

In order to exclude these problems such as groundwater chemical field changed in different time, the groundwater samples were collected in same time (July, 2014). In total thirteen water samples were collected from six coal mines, and six groundwater samples and seven river water samples were collected from Ordovician limestone aquifers and surface river, 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 groundwater samples were also measured for trace elements. Major ions were determined in the analysis testing laboratory of the Department of Coal Geology, Anhui Province, China. The $K^+ + Na^+$, SO_4^{2-} and Cl^-, Ca^{2+} and Mg^{2+}, and alkaline concentrations were determined by atomic absorption spectrometry, ion chromatography, EDTA titration, and acid-based titration, 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. 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 $\delta^{18}O$ and δD were 0.2 and 2 ‰, respectively.
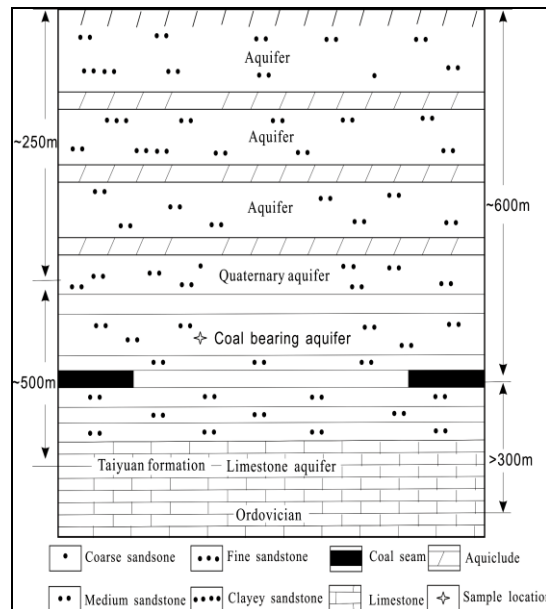

Figure 2. *Hydrogeological profile and sampling location in the study area*

4. Result and discussion

4.1 Major ions chemistry

The tested results of water samples collected from Suxian coal mine district are listed in Table 1, and the ionic balance between anions and cations was checked by AqQa software. In general, the pH values of groundwater from Ordovician aquifer ranged from 8.8 to 10.5, and had a mean value of 9.54, while the river water samples had a lower pH values with average value of 8.46, indicating that all the water samples were alkaline in nature. The anionic concentrations (Cl^-, SO_4^{2-}, HCO_3^-, and CO_3^{2-}) in the groundwater ranged from 32.60 to 181.89, 2.47 to 562.45, 3.56 to 207.63, and 7.51 to 81.09 mg/L, with average values of 78.93, 155.0, 86.45, and 31.87 mg/L, respectively. The cationic concentrations ($K^+ + Na^+$, Ca^{2+}, and Mg^{2+}) ranged from 62.78 to 190.39, 4.05 to 117.39, and 2.95 to 62.35 mg/L, with average values of 116.73, 38.58, and 17.43, respectively. The groundwater samples were mainly the Na-SO₄ and Na-HCO₃ types, indicating that Na^+, SO_4^{2-}, and HCO_3^- were the dominant ions in the groundwater. The ionic concentrations were plotted on a Piper diagram(Fig3 A) to further understand the hydrochemical characteristics of the groundwater from Ordovician limestone aquifer, and almost all the alkali elements (K^+ and Na^+) exceeded the alkaline earth elements (Ca^{2+} and Mg^{2+}) in the groundwater samples.

In addition, the river water samples were also plotted on a Piper diagram (Fig 3 B), and the diagram shows the similar characteristics with the water samples colleted from Ordovician limestone aquifer, suggesting a certain relationship could be exited between groundwater in Ordovician limestone aquifer and surface river water.
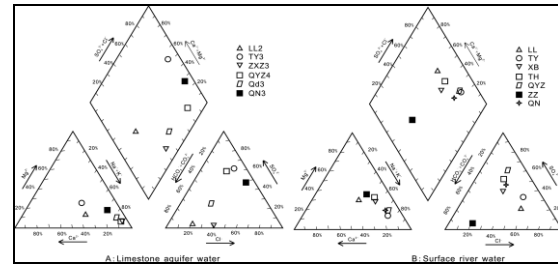
Figure 3. *Piper diagrams in water samples from Ordovician limestone aquifer and surface rivers in Suxian coal mine, Anhui Province, China*

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	$\delta^{18}O$
LL-2	Ordovician	141.61	78.84	17.43	54.91	4.32	207.63	81.09	9.43	587	Na-HCO$_3$	-42.76	-5.4
TY-3	Ordovician	190.39	117.39	62.35	181.89	562.45	132.32	7.51	8.80	1310	Na-SO$_4$	-60.23	-8.071
ZXZ-3	Ordovician	77.07	4.05	2.95	56.63	2.47	100.76	23.53	9.13	279	Na-HCO$_3$	-50.57	-6.732
QYZ-4	Ordovician	130.13	9.31	4.66	49.76	181.72	3.56	39.04	10.45	691	Na-SO$_4$	-47.98	-6.936
QD-3	Ordovician	62.78	5.67	3.93	32.60	42.39	43.26	32.54	10.54	276	Na- HCO$_3$	-47.69	-6.502
QN-3	Ordovician	98.38	16.19	13.26	97.81	136.65	20.36	7.51	8.90	446	Na-SO$_4$	-55.8	-7.512
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

4.2 Trace elements chemistry

The trace elements of groundwater samples are presented in Table 2 and the Post Archean Average Shale (PAAS) normalized REE patterns are presented in Fig 4 (Taylor and McLennan 1985). The total REE concentrations ($\sum$REE) varied from 0.0263 to 0.1348 mg/L, with an average value of 0.063 mg/L. The ratios Nd_{SN}/Yb_{SN} (SN indicates PAAS normalization) could indicated the fractionation between light and heavy rare earth elements. The values of Nd_{SN}/Yb_{SN} in groundwater samples varied from 0.14 to 0.76, with an average value of 0.41, what combined with the features of Fig 4, suggesting the groundwater samples are more enriched in heavy REEs than light REES.

The anomalies of elements Ce and Eu could indicated the relationship between the Ce and Eu and the adjacent elements, and expressed by Ce/Ce* and Eu/Eu*, what could be calculated using the formula $Ce/Ce^*=2*Ce_{SN}/(La_{SN}+Pr_{SN})$ and $Eu/Eu^*=2*Eu_{SN}/(Sm_{SN}+Gd_{SN})$, respectively. The Ce/Ce* values ranged from 0.7 to 1.7 in groundwater samples, with an average value of 1.01, presented positive Ce anomalies when normalized by PAAS. Specifically, only the groundwater sample from Luling coal mine presented positive Ce anomalies clearly, with the Ce/Ce* values be 1.7, and the other groundwater samples are presented negative Ce anomalies in diverse degree. Previous studies showed such factors as pH values, oxidative conditions and surround rock type could reduced the Ce anomalies in

groundwater (Semedley 1991; Bau 1999). The degree of negative Ce anomalies varies as the pH increases, as Ce^{3+} is more stable in low pH conditions (Johannesson et al. 2005). In other words, the negative Ce anomalies could present good correlation with pH values, when the pH conditions play the key role. However, this relationship between Ce anomalies and pH value was not existed. The Ce anomalies in groundwater caused by surrounding rock could present similar feature as the surrounding rocks, with the long time water-rock interaction.

In the study, groundwater samples are collected from Ordovician limestone aquifer, which is often expressed as Ce negative anomalies. Thus, this mechanism could be the reason for Ce depletion, what also could deduced the good correlation between Ce anomalies with other characteristic elements in limestone such as Ca and Sr. 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). The groundwater samples in Ordovician aquifer were presented similar characteristics with surface river water, indicating the groundwater has a good circulation with surface water. Thus, the oxidative conditions and surround rock were the reason for the negative Ce anomalies.

The values of Eu/Eu* in groundwater samples ranging from 2.94 to 22.09, with an average value of 16.6, presented positive Eu anomalies. Water-rock

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interactions were confirmed as the reason for the positive Eu anomalies, especially for the minerals with higher Eu contents such as feldspar. However, the surrounding rock is composed by carbonate, suggesting the surrounding rock could not be the main reason for Eu anomalies. Positive Eu anomalies in groundwater may indicate an oxidative environment (Jeong 2001), whereas the aquifers in the study area have been confirmed as oxidative, thus the oxidative environment could be the reason for Eu anomalies.
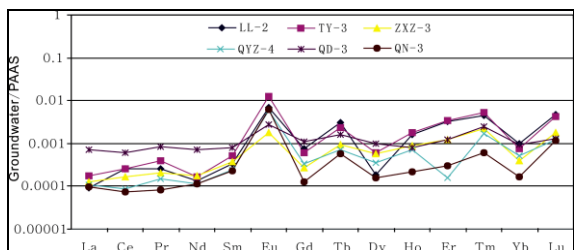

Figure 4. PAAS-normalized REE patterns in groundwater from Ordovician limestone aquifer in study area

For the nearly ionic radius, the geochemical behavior of the elements Y and Ho in the geological environment is alike. And the Y/Ho ratio is generally 27 in minerals and fresh river water. Seawater and limestone formed in the sea frequently present positive Y anomalies, what deduced by the higher removal rate of Ho, which is nearly double that of Y in seawater (Nozaki et al. 1997). Thus, the ratio Y/Ho is higher in groundwater collected from limestone aquifer, when the water-rock interaction were affected the rare earth elements concentrations in groundwater. While the Y/Ho ration in groundwater samples collected from study area ranging from 3.16 to 19.66, with an average value of 11.59, indicated the surrounding rock influence is lacked.

Table 2. *Trace elements (µg/L) concentrations in groundwater from limestone aquifer in Suxian mining area*

No.	LL-2	TY-3	ZXZ-3	QYZ-4	QD-3
La	0.0035	0.0068	0.0049	0.0041	0.027
Ce	0.021	0.021	0.014	0.0070	0.049
Pr	0.0023	0.0035	0.0018	0.0013	0.0073
Nd	0.0046	0.0058	0.0059	0.0038	0.025
Sm	0.0018	0.0029	0.0020	0.0013	0.0044
Eu	0.0075	0.013	0.0019	0.0065	0.0030
Gd	0.0036	0.0028	0.0013	0.0015	0.0052
Tb	0.0024	0.0018	0.0007	0.0006	0.0012
Dy	0.0009	0.0028	0.0026	0.0017	0.0046
Ho	0.0016	0.0017	0.0009	0.0007	0.0008
Er	0.0091	0.010	0.0036	0.0005	0.0035
Tm	0.0018	0.0021	0.0009	0.0007	0.0010
Yb	0.0027	0.0021	0.0011	0.0015	0.0027
Lu	0.0021	0.0018	0.0008	0.0005	0.0005
Y	0.0050	0.024	0.0051	0.0064	0.014

Sr	23.0	2742	38.9	410	26.9
Zr	0.20	0.20	0.11	0.088	0.12
REE	0.065	0.078	0.042	0.032	0.135
Y/Ho	3.16	13.53	5.86	9.11	18.25
Y/Dy	5.672	8.360	1.951	3.791	3.107
Ce/Ce*	1.70	0.98	1.05	0.70	0.81
Eu/Eu*	12.51	22.09	5.57	21.25	2.94
Nd_{SN}/Yb_{SNN}	0.14	0.23	0.45	0.22	0.76

4.3 Isotope chemistry

The results of δD and $\delta^{18}O$ analysis of groundwater and river water from the Suxian coal mine district are presented in table 1 and Fig. 5. The values of $\delta^{18}O$ in Ordovician limestone groundwater varied from -8.07 to -5.40 ‰, and had an average value of -6.86 ‰, while δD varied from -60.23 to -42.76 ‰, and had an average value of -50.8 ‰, respectively. Otherwise, the river water samples have the higher concentration of δD and $\delta^{18}O$, the values of δD and $\delta^{18}O$ 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.

In order to obtain more information about the isotopic characters of groundwater and river water samples, additional data are required. Thus, the global meteoric water line (GMWL), the local meteoric water line (LMWL), and the local surface water line (LSWL) for δD and $\delta^{18}O$ were collected as reference. The GMWL was defined by Craig in 1961, what described by $\delta D=8*\delta^{18}O+10.56$; the LMWL was characterized as $\delta D=7.9*\delta^{18}O+8.2$, which was summarized by Zhang (1989), and the LSWL was described by the formula $\delta D=6.74*\delta^{18}O-3.33$ (Gui et al. 2005). All the lines and the isotopic signatures of the groundwater samples are plotted in Fig.5. As the Fig.5 show, all the groundwater samples plotted below the LMWL and the GMWL, surrounding on the LSWL, and all the points distributed in a linear array, the equal slope of the line is similar with the GMWL. All the information indicated the limestone groundwater samples were recharged from the precipitation and surface water. The groundwater samples have lower concentrations of $\delta^{18}O$ and δD comparing with river water, reflected the river water affected by the evaporation clearly, with the heavy isotope enrichment.
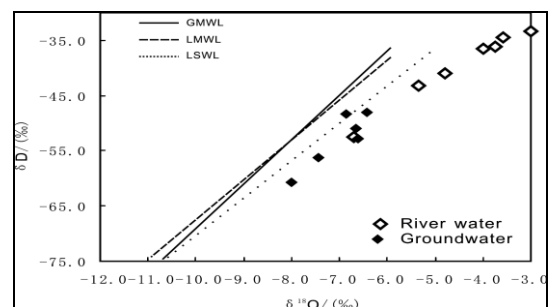

Figure 5. Plot of the $\delta^{18}O$ and δD values in water samples from the study area

4.4 Hydrochemistry process

Gibbs have been discuss the ion source in river water based on the diagram between TDS and the ions ratios such as $Na^+/(Na^++Ca^{2+})$, $Cl^-/(Cl^-+HCO_3^-)$ (Gibbs, 1970), and in further applied to discussed the influenced mechanism of chemical composition in groundwater. The water samples have low TDS content and high ratios (close to 1) generally, if the water samples directly recharged by precipitation without other influence. 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 TDS-$Na^+/(Na^++Ca^{2+})$ and TDS-$Cl^-/(Cl^-+HCO_3^-)$ in water samples collected from study area were presented in Fig. 6. 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.
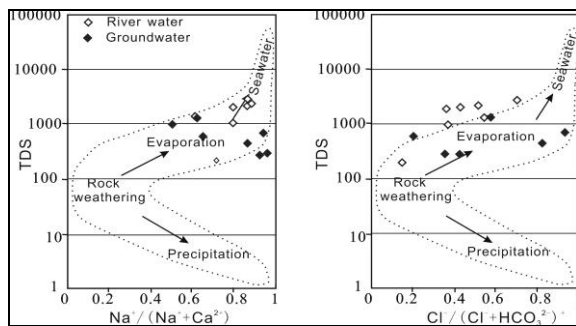

Figure 6. *Gibbs diagrams of ground- and river- water samples in Suxian coalfield*

4.5 Relationship between macro-micro components

Dissolved strontium (Sr) concentrations in the groundwater in the study area ranged from 23 to 2742 μg/L, with an average value 610 μg/L (Table 1). The elements Sr and Ca have similar geochemical behaviors for they are both alkaline earth elements. Generally speaking, the Sr concentration in water is approximately 1% that of Ca (Nakano 2014), the dominant element, and that the concentrations of the two elements are strongly correlated. Therefore, the positive correlations between Ca and Sr in the groundwater samples were expected. From Fig. 7, we observed that Ca and Sr are positively correlated, which indicates that the Sr in the groundwater is released by weathering (dissolution) of Ca-containing minerals, and that there are no other sources such as human activity.

As the total rare earth elements in groundwater are low, the source of REEs in groundwater are less to discussed, while the previous studies showed the water-rock interaction often changed the concentrations of REEs(Sun et al.,2011). Thus, the REEs could present positive correlation with Ca, if the water-rock interaction influenced the REEs concentrations. And the feature from Fig.7 also supported this view.

TDS is the reflection of accumulation of major ions in groundwater, indicating the salt water salinity. In general, the TDS gradually increased with the groundwater flow path, the correlations between TDS and isotope could understand the hydrochemistry process of groundwater in further. The diagram between TDS and $\delta^{18}O$ (Fig.7) showed that the content of $\delta^{18}O$ in groundwater presented decreasing trend with the TDS increasing. The negative correlation between TDS and $\delta^{18}O$ are existed, indicating the contents of $\delta^{18}O$ in groundwater samples are not only controlled by evaporation, but also influenced by water-rock interaction. In addition, the isotope exchange reaction between groundwater and carbonate rocks could cause light isotope enrichment (Chen et al., 2008). And the similar correlation ship between $\delta^{18}O$ and Ca^{2+} are also existed, indicated that the dissolution of limestone could be the factor influencing the oxygen isotope characters.
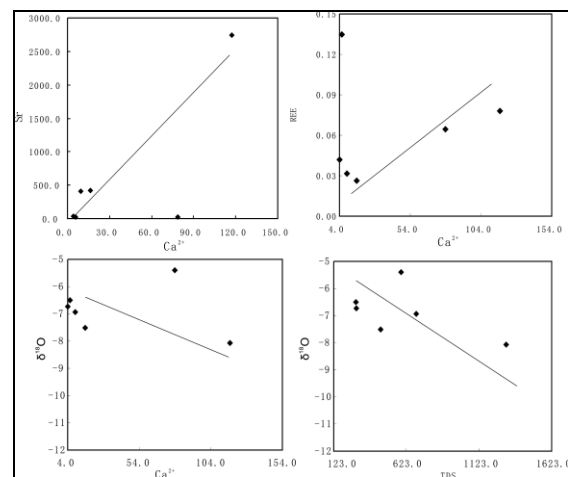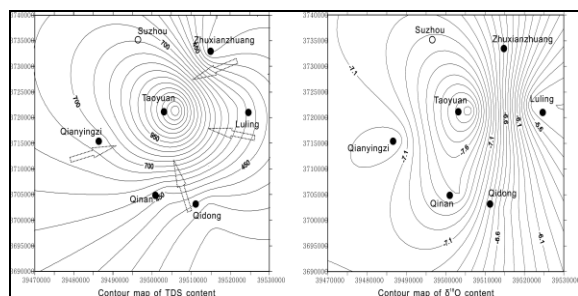

Figure 7. *Plots of elements in groundwater from Ordovician limestone aquifer in Suxian coalfield*

4.6 Distribution characteristics

As mentioned, major ions in groundwater could change in the process of circulation with the interaction between groundwater and surrounding rock. TDS is the total dissolved solids in groundwater, and the contour map of TDS is often used to simulate groundwater quality concentration gradient field. Generally speaking, the lower TDS in groundwater indicated the water-rock interaction is weak, and the groundwater residence time in aquifer is short, otherwise, the higher TDS contents in groundwater present the opposites course. Moreover, the groundwater flows from the lower TDS content to the higher TDS content, and the equivalent line density could reflects the dissolution degree of groundwater and surrounding rock. Thus, from the Fig.8, we could see, the contour diagrams of TDS showed the groundwater is runoff from both sides to intermediate, with the Taoyuan coal mine as the subsidence center, which is consistent with the hydrogeological data

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mentioned above. In detail, the contour diagram of $\delta^{18}O$ is also presented the similar feature compared with the diagram of TDS. More coincidentally, serious verdicts could be obtained based on the information presented by Fig.8 and Fig.1. The Sunan syncline is the main controlled factors influenced the groundwater flow and hydrochemistry characters in Ordovician limestone, and the Sunan anticline and Tongting anticline also have an effect on the groundwater. Thus, the hydrochemistry characteristics, especially the TDS and isotope feature could be used to identify the regional geological structure, for the hydrochemistry field and runoff field of groundwater are mainly controlled by the tectonic field.

***Figure 8.** Contour diagrams of TDS and $\delta^{18}O$ in groundwater from Ordovician limestone aquifer in Suxian coalfield*

5. Conclusions

Several water samples were analyzed for major ions, trace elements and hydrogen and oxygen isotopes, collected from Ordovician limestone aquifers and surface rivers in Suxian coal mine district, Anhui Province, China, what as a basis to discuss the hydrochemistry characteristics and groundwater flows, a serious conclusion could be obtained: The groundwater samples from Ordovician limestone aquifer were mainly the Na-SO$_4$ and Na-HCO$_3$ types, what have similar feature with the water samples collected from surface rivers, suggesting a certain relationship could be existed between groundwater in Ordovician limestone aquifer and surface rivers. The total REE concentrations ($\sum$REE) in groundwater samples varied from 0.0263 to 0.1348 mg/L. The heavy REEs in groundwater samples are enriched more than LREEs, evidenced by the values of Nd$_{SN}$/Yb$_{SN}$ varied from 0.14 to 0.76. The negative Ce anomalies in groundwater samples were controlled by the oxidative conditions and surround rocks. In addition, the oxidative environment also deduced the Eu anomalies.

The values of $\delta^{18}O$ and δD in groundwater varied from -8.07 to -5.40 ‰ and from -60.23 to -42.76 ‰, while the river water samples have the higher concentration of δD and $\delta^{18}O$. The river water samples influenced by the evaporation clearly, evidenced by the heavy isotope enrichment. The diagrams of δD-$\delta^{18}O$ presented groundwater samples

were recharged by the precipitation and surface water, what also evidenced by Gibbs diagrams. The positive correlations between Ca and Sr, REEs in the groundwater samples are exist, indicated the Sr in the groundwater is released by weathering (dissolution) of Ca-containing minerals, and the REEs concentrations in groundwater are affected by the water-rock interaction.

The content of $\delta^{18}O$ in groundwater samples are also influenced by water-rock interaction. And the negative correlation between $\delta^{18}O$ and Ca^{2+} indicated that the dissolution of limestone could be the factor influencing the oxygen isotope characters. The contour diagrams of TDS and $\delta^{18}O$ indicated the groundwater is runoff from both sides to intermediate, with the Taoyuan coal mine as the subsidence center in study area. The Sunan syncline is the main factors controlled the groundwater flow and hydrochemistry characters in Ordovician limestone.

Acknowledgements

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