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Original Research Paper

Strontium Isotope and Major Ions Chemistry of Groundwater from Sunan Coal-mining Region, Anhui Province, China

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ABSTRACT

In order to understand the major chemistry, strontium isotope characteristics of deep groundwater in a coal-mining area, eight typical groundwater samples were collected from the Sunan coal-mining region, Anhui Province, China, the geochemical characteristics of major ions, strontium, $^{87}Sr/^{86}Sr$ and source of strontium were discussed. The results showed that almost all the groundwater samples are described as Na-HCO_3 and Na-SO_4 types. The concentration values of Sr in groundwater samples are decreasing as follows: LA>QA>CA, however, the $^{87}Sr/^{86}Sr$ ratios in opposite. The Ca, Mg and Sr elements in the groundwater samples have the same sources, for the positive correlation between Ca/Sr and Mg/Sr. Sr in groundwater samples mainly originated from dissolution of carbonate rock, partially originated from weathering of silicate rock, especially in the coal bearing aquifer.

INTRODUCTION

Environmental isotopes could provide a sharper focus on underlying processes that control the chemical and physical behaviour of elements and compounds in the environment, thus many studies have been conducted about environmental isotopes. In the coal mine district, groundwater, being the mainly supply for human water, influencing the coal mine exploration safely. Thus, the research about hydrogeochemistry in the coal mining area could be as a basis for making sustainable groundwater development scheme and identifying the source of inrush water.

In recent years, many studies have been accomplished, that focused on the groundwater quality, ion source, hydrochemical characters and statistical analysis in the coal mining area (Chen et al. 2013, Ramkumar et al. 2013). When stable isotopes and hydrochemical data are examined for groundwater systems, important information about water-rock interaction are readily discernable (Marfia et al. 2004). Thus, so many researches about stable isotopes and the characteristics of hydrochemistry in surface water of shallow groundwater were also obtained. Whereas, the studies focused on deep groundwater are limited, as the groundwater sampling is difficult. But, deep coal mine exploitation provide an opportunity for deep groundwater sampling. In this study, we reported the latest chemical data about major ions and strontium isotopes, discussing the hydrogeochemical characteristics and source of strontium in the deep groundwater samples collected from the Sunan coal-mining region. The major targets are to (1) define the geochemical characteristics of groundwater collected from diverse aquifer, (2) identify the source of strontium in groundwater samples, (3) discuss the characters of strontium isotopes in groundwater samples. The results will be used as a basis for understanding the evolution of hydrochemistry of groundwater, making sustainable groundwater development schemes and identification of the groundwater source.

MATERIALS AND METHODS

The Sunan coal-mining district is mainly constituted by five coal mines (Qidong coal, Qinan coal, Qianyingzi coal, Taoyuan coal and Longwangmiao coal), which is situated in the north Anhui Province (Fig. 1). The region has a warm temperate monsoon climate with an annual temperature of 14.6°C. The average annual precipitation and evaporation in the area are 867.0 and 832.4mm, respectively. Groundwater is the main water supply source for drinking, irrigation and industry, as the surface water is scarce. Carboniferous and Permian are the coal-bearing formations with thickness more than 1300m in Sunan coal-mining area. Previous studies showed that Quaternary aquifer (QA), Coal bearing aquifer (CA) and Limestone aquifer (LA) are the main aquifers in the area (Gui & Chen 2007). The quaternary aquifer is mainly constituted by yellow mudstone, sandstone and conglomerate, with a depth between 280-300m. The coal bearing aquifer is featured by mudstone, sandstone and coal bed, with a depth ranging from 300 and 700m. Limestone aquifers are mainly composed of limestone with clastic rocks, which belongs to Taiyuan formation and Ordovician.

This study focused on the major chemistry and strontium characteristics of groundwater; eight typical groundwater samples were collected from the Sunan coal-mining district, Anhui Province. All samples were analysed for major ions, strontium, $^{87}Sr/^{86}Sr$, and collected from diverse aquifers in the Sunan coal-mining region. Water samples were collected via drainage holes in alleys, and then filtered through 0.45 mm pore-size membrane and collected in polyethylene bottles that had been cleaned using trace element clean procedures.

Major ion analysis was done in the analysis testing centre of the Department of Coal Geology of Anhui province, China. K^+ and Na^+ was analysed by atomic absorption spectrometry, SO_4^{2-} and Cl^- by ion chromatography, Ca^{2+} and Mg^{2+} by EDTA titration, and alkalinity by acid-based titration. A Piper diagram was used and calculations done for the carbonate equilibrium, total dissolved solids (TDS) content, density, conductivity and hardness using Aqqa software. For $^{87}Sr/^{86}$ Sr isotope ratios analysis, sufficient water to yield 2 µg of Sr was evaporated to dryness. Isotope analysis was determined at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences.

RESULTS AND DISCUSSION

Major ion chemistry: The analytical results for groundwater samples collected from the Sunan coal-mining region are listed in Table 1. In general, the pH values of the groundwater varied from 6.9 to 8.7, with an average value 7.7, which indicates that most of groundwater samples are alkaline in nature. The anionic concentrations (Cl^-, SO_4^{2-}, HCO_3^- and CO_3^{2-}) in the groundwater range from 146.4 to 328.0, 21.4 to 2837.6, 375 to 853.9 and 0 to 72.65 mg/L, with average values of 200.3, 849.7, 549.3 and 26.7 mg/L, respectively. The cationic concentrations (K^++Na^+, Ca^{2+} and Mg^{2+}) range from 295.05 to 1718.4, 5.54 to 360, and 3.84 to 73.7 mg/L, with average values of 574.9, 96.8 and 43.8, respectively.

In detail, the groundwater samples collected from QA are described as Na-HCO_3 types, for the Na^+ and HCO_3^- are the leading ions, whereas the other samples are presented Na-SO_4 types with the higher concentrations of SO_4^{2-}. Only one sample collected from LA is Ca-SO_4 type, for the higher content of Ca^{2+}. The ionic concentrations were plotted on a Piper diagram to characterize the geochemical nature of the groundwater in the Sunan coal-mining region (Fig. 2). It is detected from the Fig. 2 that almost all the alkali elements (K^++Na^+) exceed the alkaline earth elements (Ca^{2+}+Mg^{2+}). Also weak acids (HCO_3^-+CO_3^{2-}) exceed strong acids (Cl^- +SO_4^{2-}).

Sr and Sr isotopic characteristics: It can be seen from Table 1, dissolved Sr concentrations of the groundwater in the studied area, ranging from 278 to 1924µg/L, with an average value 1452.4µg/L. In detail, there is a clear difference between the Sr concentrations from the QA, LA and CA. In the LA, the Sr content is highest, varied from 1673 to 1924 µg/L, with the average value of 1810.5µg/L. However, the samples in CA presented lower content of Sr, with the average value 726µg/L. The concentrations of Sr in QA are among the CA and LA. In other words, the concentrations of Sr are decreasing as follows: LA>QA>CA.

The $^{87}Sr/^{86}Sr$ ratios varied from 0.710615 to 0.718776 in the studied groundwater samples, with the average value of 0.71223 (Table 1). The groundwater samples collected from diverse aquifers showed different $^{87}Sr/^{86}Sr$ ratios. The $^{87}Sr/^{86}Sr$ ratios in CA are highest, ranging from 0.71169 to 0.71878 with the average value 0.71523, whereas the $^{87}Sr/^{86}Sr$ in QA and La are lower, with the average value 0.71196 and 0.71087, respectively. In a word, the $^{87}Sr/^{86}Sr$ ratios in CA and LA have the highest and lowest values, with the QA between the two.

Sr and Ca are both alkaline earth elements, and as a consequence, their geochemical behaviours are very similar. Previous studies showed that the Sr concentration in water is approximately 1% that of the dominant element Ca, and the concentrations of the two elements are strongly correlated (Nakano 2014). Thus, the positive correlations between Ca and Sr are desired in the studied groundwater samples. From the Fig. 3(A), we can see the positive correlation between Ca and Sr existed, the correlation coefficient would achieve

Table 1: Major ions and strontium isotope composition of groundwater samples from Sunan coal mine.

No.	K^++Na^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	CO_3^{2-}	pH	Sr	Sr^{87}/Sr^{86}	Water type	Aquifer
SN1	543.7	6.3	3.8	188.7	125.1	854.0	70.4	8.31	278	0.718776	Na-HCO_3	QA
SN2	471.8	5.5	3.8	146.4	21.4	860.9	72.7	8.65	1174	0.71169	Na-HCO_3	QA
SN3	297.6	99.9	68.7	245.7	446.6	449.1	0.0	7.43	1859	0.710615	Na-SO_4	LA
SN4	295.1	80.4	52.9	219.3	414.1	390.5	0.0	7.16	1786	0.711086	Na-SO_4	LA
SN5	353.6	101.9	67.9	249.5	485.2	444.2	0.0	6.92	1924	0.711112	Na-SO_4	LA
SN6	338.0	360.0	73.7	328.0	1124.0	375.0	0.0	6.89	1673	0.710649	Ca-SO_4	LA
SN7	1718.4	26.1	11.5	149.9	2837.6	687.8	70.4	8.55	1267	0.712357	Na-SO_4	CA
SN8	581.3	94.3	67.6	74.9	1343.5	333.2	0.0	7.78	1658	0.711557	Na-SO_4	CA

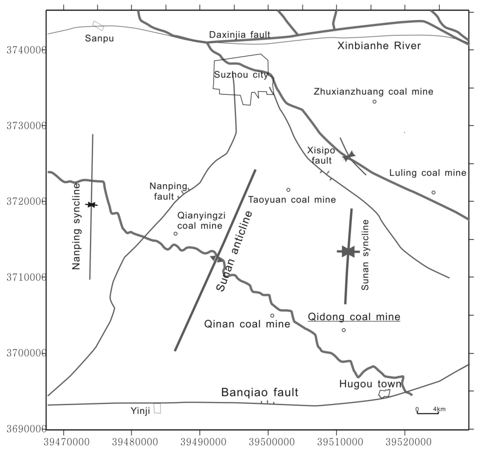

Fig. 1: Location of study area in northern Anhui Province, China.

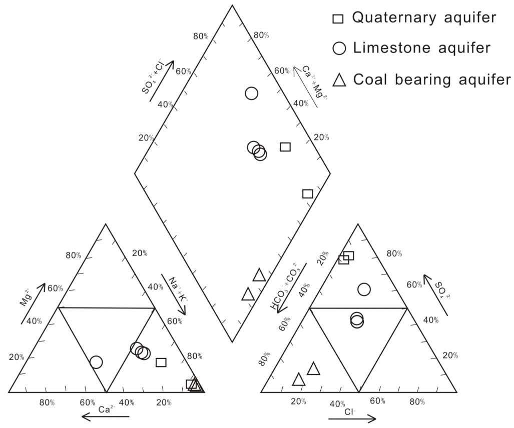

Fig. 2: Piper diagram of groundwater from Qinan coal mine in Anhui Province, China.

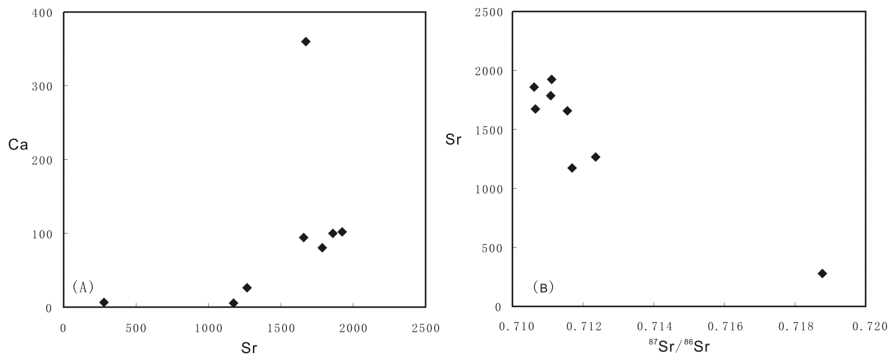

Fig. 3: Sr versus Ca and $^{87}Sr/^{86}Sr$ for groundwater collected from Sunan coal mine area.

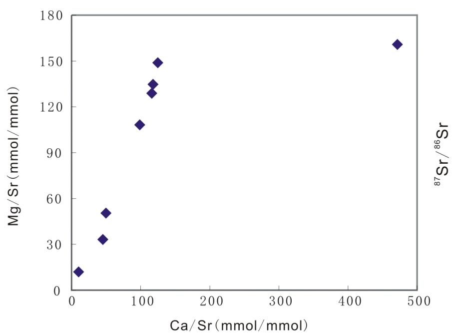

Fig. 4: Ca/Sr versus Mg/Sr for groundwater collected from the Sunan coal-mining region.

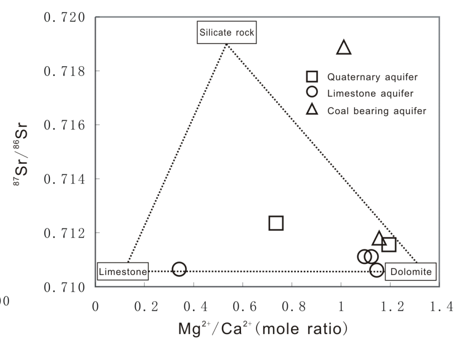

Fig.5: Mg^{2+}/Ca^{2+} versus $^{87}Sr/^{86}Sr$ for groundwater collected from the Sunan coal-mining region.

0.74, that indicated that the Sr in the groundwater is released from the weathering (dissolution) of Ca-containing minerals, without other source such as human activity. Thus, the $^{87}Sr/^{86}Sr$ ratio closely reflects the geologic environment.

As we know, four stable isotopes of strontium (^{84}Sr, ^{86}Sr, ^{87}Sr and ^{88}Sr) exist in the nature. ^{87}Sr also is generated by the radioactive decay of ^{87}Rb. Based on the fact the decay is extremely slow and strontium is found in rocks, the Rb-Sr method is widely used for geologic dating of rocks. For the ^{87}Sr concentrations in nature are stable in a short time scale, the groundwater samples have high concentration value of Sr could be desired to have the lower ratios about $^{87}Sr/^{86}Sr$. In other words, the Sr and the ratios $^{87}Sr/^{86}Sr$ would present the negative correlation, the Fig. 3(B) confirmed this view.

Source of strontium: In nature, the primary sources of dissolved Sr in groundwater are from the atmosphere and dissolution of Sr-bearing minerals. As the $^{87}Sr/^{86}Sr$ ratios in studied area are all higher than the $^{87}Sr/^{86}Sr$ ratios in rainfall (0.7060~0.7092) in the present study (Klaus et al. 2007), the atmospheric deposition is not thought to be a mainly source of Sr in this area. Thus, the Sr in groundwater samples, in this studied area, is considered released from surrounding rocks (carbonate, silicate and coal) through the water-rock interaction for a long time. However, previous studies shows that human activities also are an important source with the rapid economic and social development (Pu et al. 2012).

Dissolution of carbonate rock leading to the release of Ca, Mg and Sr into groundwater, what had been justified by the Ca/Sr and Mg/Sr ratios (Negrel & Petelet-Giraud 2005). In other words, the Ca/Sr and Mg/Sr would present a positive correlation, if the Ca, Mg and Sr elements have the same source. Fig. 4 is the plot diagram of Ca/Sr versus Mg/Sr in groundwater samples collected from Sunan coal-mining region, showed positive correlation between Ca/Sr versus Mg/Sr. Thus, the Ca, Mg and Sr elements in the groundwater samples have the same sources.

As mentioned above, ^{87}Sr is formed by the radioactive decay of the naturally occurring element, rubidium (^{87}Rb), with the half-life (4.967×10^{10}a) (Kossert 2003). Moreover, the biological or geological fractionation of isotopes is negligible, therefore, the ^{87}Sr/^{86}Sr ratios are characteristic of diverse Sr source (Vilomet et al. 2001). Previous studies showed that ^{87}Sr/^{86}Sr ratios are widely used for tracing water-rock interaction in hydorgeology (Blum et al. 1994). The water-rock interaction of groundwater in diverse aquifers would change the content of Ca, Mg, Sr content and ^{87}Sr/^{86}Sr ratios. Previous studies showed that the main contribution of Sr derived from silicate and carbonate rock weathering (dissolution) (Shand et al. 2009). Numerous researches about natural water bodies showed that the ^{87}Sr/^{86}Sr ratios derived from silicate mineral (0.716~0.720) are higher than that originated from carbonate rocks (0.706~0.709) (Palmer & Edmond 1992, Shand et al. 2009). The ^{87}Sr/^{86}Sr ratios of weathering end members of silicate, carbonate rock were presented in Fig. 5. The Sr releasing from carbonate rock has lower ^{87}Sr/^{86}Sr ratio comparing with the silicate rock. Mg^{2+}/Ca^{2+} is lower in limestone aquifer, however it is higher in dolomite aquifer. As shown in Fig. 5, most of the groundwater samples located in the vicinity of the weathering line of carbonate, that indicates, Sr in groundwater samples mainly originated from dissolution of carbonate rock. However, one sample located at the silicate rock area, indicating partial Sr in groundwater originated from weathering of silicate rock, especially in a coal bearing aquifer, which is constituted mainly by silicate rock. The phenomenon would be used to identify the source of inrush water in the coal mine.

CONCLUSION

Eight deep groundwater samples were collected from the Sunan coal-mining region, Anhui Province, China, for the testing the major ion chemistry, strontium and ^{87}Sr/^{86}Sr, hydrogeo-chemical characteristics and source of Sr, and a series conclusion could be obtained:

All the groundwater samples collected from QA are described as Na-HCO_3 type, whereas the other samples are presented as Na-SO_4 type with the higher concentrations of SO_4^{2}. Only one sample collected from LA is Ca-SO_4 type. The concentration values of Sr in groundwater samples are decreasing as follows: LA>QA>CA. However, the ^{87}Sr/^{86}Sr ratios in CA and LA have the highest and lowest values, with the QA between the two. Concentrations of Sr are presented positive and negative correlation with the Ca and the ratios ^{87}Sr/^{86}Sr in the studied groundwater samples.

The Ca, Mg and Sr elements in the groundwater samples have the same sources, for the positive correlation between Ca/Sr and Mg/Sr. Sr in groundwater samples mainly originated from dissolution of carbonate rock, partially originated from weathering of silicate rock, especially in Coal bearing aquifer.

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