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Original Research Paper

# Geochemical Characteristics of Groundwater from Limestone Aquifer in Sunan Coal-mining Region, Anhui Province, China

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## ABSTRACT

Major ion concentrations were analysed for twenty eight groundwater samples collected from limestone aquifers in the Sunan coal-mining area, Anhui Province, China. The conventional graphical and multivariate statistical approach was used to discuss the geochemical characteristics, ion source and hydrogeochemical process of groundwater, and the applicability of groundwater is also evaluated based on a series of index. The results showed that the groundwater samples are mainly featured alkaline in nature, with the high value of TDS ranges from 789 to 2753 mg/L. The concentration of $Cl^-$ is low compared to the concentrations of $SO_4^{2-}$ and $HCO_3^-$, otherwise, the cations are mainly composed of $Na^+$ and $Ca^{2+}$. Therefore, the hydrochemical type of groundwater samples is mainly divided into Ca-$SO_4$ and Na-$SO_4$ types. The dissolution of gypsum, weathering of dolomite and calcite are the main hydro-geochemical processes, which contribute most ions to groundwater. The groundwater samples could not meet the demand of drinking water, as compared to the standards of WHO. However, all the groundwater samples are suitable for irrigation, with a better calculated index.

## INTRODUCTION

As a most important fresh water storage, groundwater system plays a key role at present. Especially, in the North China plains, as the surface water storage problem is becoming serious, exploration of groundwater has been the main water supply for agricultural, domestic and industrial use. Otherwise, the formation and evolution of groundwater was affected by factors such as physical, chemical and biological conditions. Moreover, the characters of surrounding rock could change the chemical composition and the quality of groundwater through water-rock interaction over a long period of time. Thus, the studies on the hydro-geochemistry and its geological significance on groundwater, are necessary for understanding the geochemical characteristics of groundwater and its applicability.

Previous studies showed that the hydro-geochemical research could contribute to the understanding of groundwater quality, ion source and its formation process (Kumar et al. 2009, Ramkumar et al. 2013). So many studies focused on the groundwater quality, hydro-geochemical process and anthropogenic influences on the groundwater system, have been completed, for better exploitation and utilization of groundwater. In addition, deep groundwater in the coal mine area could be a threat for the coal mining exploration safety. So, many investigations on major ions, rare earth elements, stable isotopes of deep groundwater have been carried out in the coal mine area. Taking for instance, studies about discriminating the source of inrush water to avoid the mining accident has been accomplished in northern Anhui Province, China (Chen et al. 2013). However, the studies about quality evaluation of deep groundwater are limited. Water quality evaluation is one of the most important aspects in the deep groundwater analysis, which will always be used as a basis to talk about utilizing groundwater.

The purpose of this study is to discuss the geochemical characteristics of deep groundwater collected from limestone aquifers in Sunan Coal mine, Anhui Province, China, which can form a basis to evaluate the quality of groundwater and reveal the influenced factors of the groundwater, using hydrochemical and multivariate statistical methods. The results can be used for making sustainable groundwater development schemes and understanding the applicability of deep groundwater.

## MATERIALS AND METHODS

The Sunan coal-mining district, belonging to the Huaibei mining area, 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 is 867.0 and 832.4 mm, respectively. Groundwater is the main water supply source for drinking, irrigation and industry, as the sur-

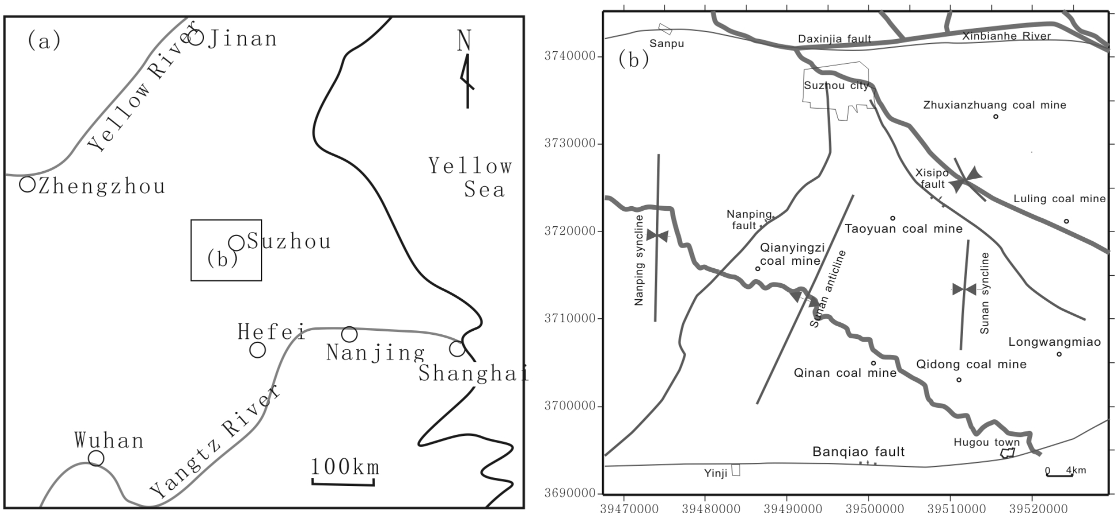


Fig. 1: Location of the study area.

Table 1: Composition of major ions in groundwater samples collected from a Limestone aquifer in Sunan mining area (The values are in mg/L except pH).

| No. | $K^++Na^+$ | $Ca^{2+}$ | $Mg^{2+}$ | $Cl^-$ | $SO_4^{2-}$ | $HCO_3^-$ | $CO_3^{2-}$ | pH | Water type | TDS |
|---|---|---|---|---|---|---|---|---|---|---|
| TY1 | 292.0 | 357.0 | 122.0 | 357.0 | 1119.0 | 440.0 | 0.0 | 7.42 | $SO_4$-Ca | 2687.0 |
| TY2 | 172.0 | 368.0 | 104.0 | 341.0 | 886.0 | 391.0 | 0.0 | 6.93 | $SO_4$-Ca | 2262.0 |
| TY3 | 349.0 | 363.0 | 65.1 | 334.0 | 1134.0 | 350.0 | 0.0 | 7.12 | $SO_4$-Ca | 2595.1 |
| TY4 | 406.0 | 376.0 | 42.1 | 339.0 | 1163.0 | 374.0 | 0.0 | 7.35 | $SO_4$-Ca | 2700.0 |
| TY5 | 338.0 | 360.0 | 73.7 | 328.0 | 1124.0 | 375.0 | 0.0 | 6.89 | $SO_4$-Ca | 2598.7 |
| TY 6 | 299.0 | 305.0 | 106.0 | 308.0 | 1006.0 | 452.0 | 0.0 | 6.87 | $SO_4$-Ca | 2476.0 |
| TY7 | 266.0 | 385.0 | 119.0 | 339.0 | 1180.0 | 396.0 | 0.0 | 6.78 | $SO_4$-Ca | 2685.0 |
| TY8 | 273.0 | 374.0 | 109.0 | 327.0 | 1123.0 | 423.0 | 0.0 | 6.87 | $SO_4$-Ca | 2629.0 |
| TY9 | 263.0 | 350.0 | 119.0 | 324.0 | 1129.0 | 369.0 | 0.0 | 7.82 | $SO_4$-Ca | 2554.0 |
| TY10 | 271.0 | 359.0 | 117.0 | 331.0 | 1144.0 | 378.0 | 0.0 | 7.91 | $SO_4$-Ca | 2600.0 |
| TY11 | 246.0 | 335.0 | 114.0 | 312.0 | 1013.0 | 425.0 | 0.0 | 6.89 | $SO_4$-Ca | 2445.0 |
| TY12 | 330.0 | 402.0 | 83.7 | 353.0 | 1222.0 | 363.0 | 0.0 | 7.40 | $SO_4$-Ca | 2753.7 |
| QD1 | 297.0 | 99.9 | 68.7 | 245.7 | 446.6 | 449.1 | 0 | 7.80 | $SO_4$-Na | 1607 |
| QYZ | 460.0 | 235.0 | 98.8 | 996.0 | 224.9 | 334.4 | 0 | 7.30 | Cl-Na | 2349 |
| QN1 | 279.5 | 19.9 | 14.6 | 220.9 | 27.2 | 463.8 | 0 | 8.50 | $HCO_3$-Na | 1025.9 |
| QN2 | 28.0 | 24.6 | 18.6 | 220.8 | 49.4 | 425.4 | 23.0 | 8.44 | $HCO_3$-Mg | 789.9 |
| QN3 | 268.9 | 21.8 | 15.1 | 225.4 | 8.2 | 418.4 | 23.7 | 8.63 | $HCO_3$-Na | 981.5 |
| QN4 | 297.6 | 99.9 | 68.7 | 245.7 | 446.6 | 449.1 | 0 | 7.44 | $SO_4$-Na | 1607.5 |
| QN5 | 261.3 | 100.8 | 85.1 | 242.3 | 448.2 | 441.8 | 0 | 7.34 | $SO_4$-Na | 1579.5 |
| QN6 | 353.6 | 101.9 | 67.9 | 239.5 | 455.2 | 444.2 | 0 | 6.89 | $SO_4$-Na | 1662.3 |
| QN7 | 375.9 | 104.2 | 50.0 | 232.6 | 561.1 | 453.9 | 0 | 7.78 | $SO_4$-Na | 1777.7 |
| QN8 | 258.1 | 141.5 | 82.3 | 511.3 | 257.3 | 600.9 | 418.8 | 8.68 | Cl-Na | 2270.0 |
| QN9 | 192.5 | 103.2 | 67.6 | 234.4 | 269.2 | 422.3 | 0 | 7.30 | $HCO_3$-Na | 1289.2 |
| QN10 | 349.5 | 110.7 | 71.4 | 239.6 | 591.9 | 461.3 | 0 | 7.21 | $SO_4$-Na | 1824.5 |
| QN11 | 295.1 | 80.4 | 52.9 | 219.3 | 414.1 | 390.5 | 0 | 7.16 | $SO_4$-Na | 1452.3 |
| QN12 | 284.3 | 157.1 | 87.1 | 256.3 | 646.2 | 410.7 | 0 | 7.15 | $SO_4$-Na | 1841.7 |
| QN13 | 236.0 | 210.7 | 91.9 | 542.0 | 252.9 | 672.9 | 451.6 | 8.35 | Cl-Ca | 2458.2 |
| LWM | 484.4 | 56.2 | 10.1 | 173.7 | 33.8 | 0 | 383.7 | 11.6 | $HCO_3$-Na | 1142.0 |

face water is scarce. Carboniferous and permian are the coal-bearing formations with thickness more than 1300 m in the Sunan coal-mining area. Previous studies showed that Quaternary aquifer, coal bearing aquifer and limestone aquifer 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 280-300 m. The coal bearing aquifer is featured by mudstone, sand-

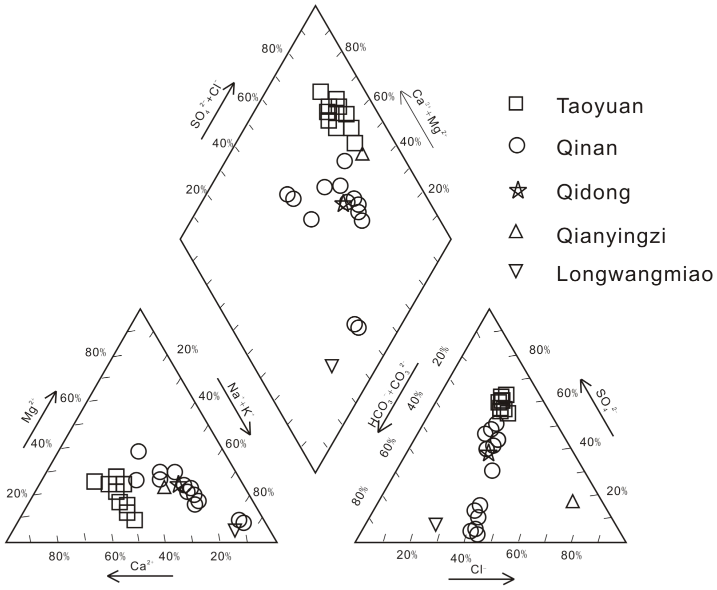


Fig. 2: Piper diagram of groundwater from LA in Sunan mining area.

stone and coal bed, with a depth ranging from 300 and 700 m. Limestone aquifer is mainly composed of limestone with clastic rocks, which belongs to Taiyuan formation and Ordovician.

This study was focused on the geochemical characteristics of groundwater from limestone aquifers in the Sunan coal-mining district, Anhui Province. Twenty eight groundwater samples were analysed for major ions, which were collected from limestone aquifers in five coal mines. Water samples were collected via drainage holes in alleys, and then filtered through 0.45 mm pore-size membrane and collected in polye-thylene bottles that had been cleaned using trace element clean procedures.

Major ion analysis was done in the analysis testing center 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 were made about the carbonate equilibrium, total dissolved solids (TDS) content, density, conductivity and hardness using Aqqa software, while statistical analysis of the sample data was carried out with SPSS software (version 19). Groundwater quality was assessed based on the chemical comparison with drinking water standard for World Health Organization (WHO 1993) and a series of indices like residual sodium carbonate (RSC), sodium adsorption ratio (SAR) and percent sodium (Eaton 1950, USSL 1954).

## RESULTS

**Descriptive statistics:** The analytical results for groundwater samples collected from the limestone aquifer are listed in Table 1. In general, the pH values of groundwater varied from 6.8 to 11.6, with an average value 7.6, which indicates that most of groundwater samples are alkaline in nature. The amount of total dissolved solids (TDS) in groundwater, ranges from 790 to 2754 mg/L, with an average of 2023 mg/L. The anionic concentrations ($Cl^-$, $SO_4^{2-}$, $HCO_3^-$ and $CO_3^{2-}$) in the groundwater range from 173.7 to 996, 8.2 to 1222, 0 to 672.9 and 0 to 451.6 mg/L, with average values of 322.8, 656.3, 413.4 and 46.5 mg/L, respectively. The cationic concentrations ($K^+$+$Na^+$, $Ca^{2+}$ and $Mg^{2+}$) range from 28.0 to 484.4, 19.9 to 402.0, and 10.1 to 122 mg/L, with average values of 293.8, 214.4 and 75.9, respectively. The hydrochemical type of groundwater samples are mainly divided into Ca-$SO_4$ and Na-$SO_4$ types, with few samples be of Na-$HCO_3$ type.

In order to obtain more information about the hydrochemical characters, the groundwater geochemical data were plotted on a Piper diagram (Fig. 2). In detail, groundwater samples from Taoyuan coal mine are characterized by high concentrations of $SO_4^{2-}$ and $Ca^{2+}$, otherwise, the other groundwater samples are mainly constituted by $K^+$+$Na^+$ and $HCO_3^-$. The concentration of $Cl^-$ are low in all groundwater samples relative to the $SO_4^{2-}$ and $HCO_3^-$.

**Multivariate statistical analysis:** Previous studied showed that multivariate statistical analysis was an efficient way to

Table 2: Correlation matrix of major ions for limestone aquifer groundwater in Sunan mining area.

| Parameters | $K^+$+$Na^+$ | $Ca^{2+}$ | $Mg^{2+}$ | $Cl^-$ | $SO_4^{2-}$ | $HCO_3^-$ | $CO_3^{2-}$ |
|---|---|---|---|---|---|---|---|
| $Na^+$+$K^+$ | 1.00 | | | | | | |
| $Ca^{2+}$ | 0.23 | 1.00 | | | | | |
| $Mg^{2+}$ | 0.02 | 0.70 | 1.00 | | | | |
| $Cl^-$ | 0.01 | 0.50 | 0.48 | 1.00 | | | |
| $SO_4^{2-}$ | 0.39 | 0.94 | 0.68 | 0.27 | 1.00 | | |
| $HCO_3^-$ | -0.15 | -0.37 | -0.01 | 0.54 | -0.53 | 1.00 | |
| $CO_3^{2-}$ | -0.16 | -0.12 | 0.06 | 0.79 | -0.35 | 0.88 | 1.00 |

Table 3: Variance explained and component matrixes for LA groundwater in Sunan mining area.

| Parameter | PC1 | PC2 | PC3 |
|---|---|---|---|
| $Na^+$+$K^+$ | 0.22 | -0.15 | 0.99 |
| $Ca^{2+}$ | 0.97 | -0.08 | 0.30 |
| $Mg^{2+}$ | 0.84 | 0.16 | 0.00 |
| $Cl^-$ | 0.53 | 0.81 | 0.01 |
| $SO_4^{2-}$ | 0.94 | -0.30 | 0.46 |
| $HCO_3^-$ | -0.29 | 0.92 | -0.24 |
| $CO_3^{2-}$ | -0.08 | 0.98 | -0.21 |
| Initial eigen value | 3.03 | 2.56 | 0.95 |
| Percentage of variance | 43.29 | 36.73 | 13.54 |
| Cumulative % of variance | 43.29 | 79.91 | 93.45 |

display complex relationships among many variables and their roles (Chen et al. 2013). In order to reveal the relation between the parameters, the multivariate methods of statistical analysis (PCA and CA) were obtained in the study, the results are presented in Table 2 and Table 3.

It could be concluded that strong positive correlations between $SO_4^{2-}$ and $Ca^{2+}$ were observed for the correlation matrix 0.94, which suggests that dissolution of gypsum existed in the hydro-geochemical process. The positive correlations also exist between $Ca^{2+}$-$Mg^{2+}$ and $Cl^-$-$CO_3^{2-}$ with the correlation matrix 0.70 and 0.79. All this indicate that weathering of dolomite and calcite are also contributing cations to groundwater, and the weathering process was caused by sulphuric acid, as there is so much sulphur dioxide in coal bed.

The rotated PCA loading is presented in Table 3, which could be usually used for obtaining the detailed statistical information. Three principal components were emerged, with more than 93.45% of cumulative variance. The parameters of $SO_4^{2-}$, $Ca^{2+}$ and $Mg^{2+}$, all have a high value in PC1, with the values 0.94, 0.97 and 0.84, which could be revealed as the factor is the dissolution of gypsum, limestone and dolomite. In detail, the aquifer rock could provide the $Ca^{2+}$, which is composed of limestone. Thus, the PC1 is the major factor for the ions formed in the groundwater samples, as the PC1 accounts for 43.29% of the total variance, with the initial Eigen value 3.91. PC2 accounts for 36.73% of the total variance, with a high loading for $HCO_3^-$, $CO_3^{2-}$ and $Cl^-$, which suggests that the weathering action of carbonate acid and chloride acid existed, and the influence factor is explained by PC2. PC3 accounts for 13.54% of the total variance, indicating the process of feldspar weathering by the sulphuric acid, as the $Na^+$+$K^+$ and $SO_4^{2-}$ have high values.

In summary, the dissolution of gypsum and weathering of limestone are the main hydrochemical processes, otherwise, the feldspar weathering action based on carbonate acid and chloride acid also existed.

## DISCUSSION

**Quality evaluation:** In order to further understand the applicability of the groundwater, the analytical results of ground-water samples were compared with the WHO standard (WHO 1993). The results showed that the average concentration of magnesium (77.9 mg/L) and pH values could meet the demand of WHO, however, the other parameters have all exceeded the boundary value. Especially, almost all the TDS values of groundwater samples are higher than 1000 mg/L, which suggests that the groundwater is not suitable for drinking before being processed.

The higher concentration of $Na^+$ in the groundwater could affect the crop growth, when used for irrigation. The irrigation usability of groundwater is usually evaluated by few index values, such as Residual Sodium Carbonate (RSC) and Sodium Adsorption Ratio (SAR) (USSL 1954), which could be calculated by the formula RSC=$HCO_3^-$+$CO_3^{2-}$-$Ca^{2+}$-$Mg^{2+}$ and SAR=Na+/SQRT [($Ca^{2+}$-$Mg^{2+}$)/2] respectively. Previous studies showed that three degrees could be divided on the basis of the RSC value: perfect (<1.5), permissible (1.5-2.5) and unsuitable (>2.5) (USSL 1954). The calculated results showed that the groundwater samples collected from the limestone aquifers in the area could be used for irrigation, as the average value of RSC is 0.77. Four groundwater types could be determined by the SAR value, which are as follows: perfect (<10), gould (10-18), sealed (18-26) and unsuitable (>26). And the calculated results about SAR also indicated that the groundwater samples are better for irrigation, with the average value as 4.75. And the results could be supported by the previous analysis.

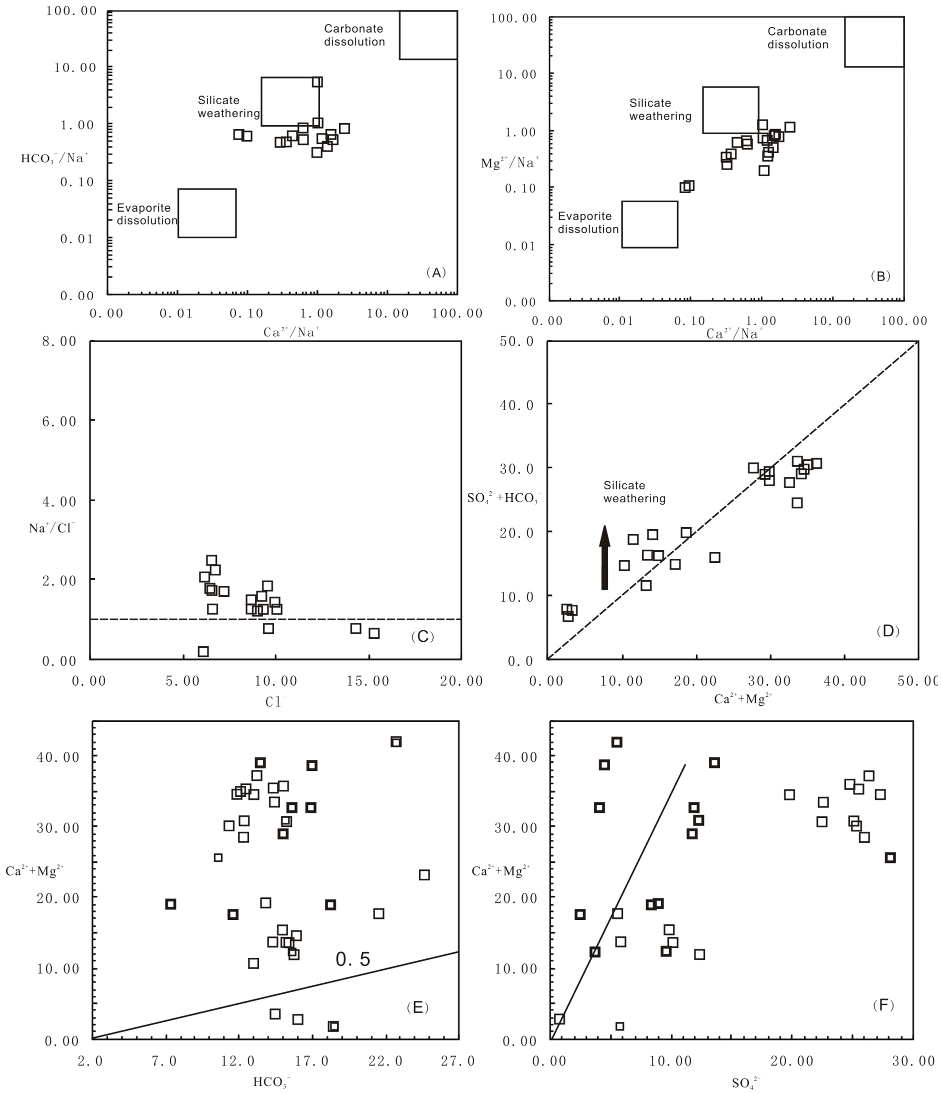


Fig. 3: Plots of major ions of limestone aquifer in Sunan mining area.

**Ions source:** Hydrogeochemistry of groundwater is always influenced by such factors like recharging and water-rock interaction, and the degree of interaction being controlled by the residence time within the aquifer (Gaillarde et al. 1999). Evaporite dissolution, carbonate dissolution and silicate weathering are three general processes contributing to the generation of solutes in groundwater. As can be seen from Fig. 3, the groundwater in the area is mainly controlled by silicate weathering and carbonate dissolution.

The dissolution of halite in groundwater, releases equal concentrations of $Na^+$ and $Cl^-$ into the solution, and mechanisms by which salinity is acquired in groundwater systems can be identified using the Na-Cl relationship (Sami et al. 1992). Therefore, the ratio $Na^+/Cl^-$ can be represented by a line with a value of $Na^+/Cl^-$ close to one, if the $Na^+$ and $Cl^-$ present came solely from halite dissolution. However, Fig. 3C presented the different characteristics, with the $Na^+/Cl^-$ ratios of most samples higher than one. This could indicate an additional source of $Na^+$, which could be thought as the weathering of silicate minerals. This view would be supported by the fact that groundwater aquifer is constituted by some silicate mineral(s). And the weathering process often along with increased $HCO_3^-$ concentrations, which is presented in Fig. 3D.

The most probable source of $Ca^{2+}$ and $Mg^{2+}$ in groundwater can be determined using the equation $(Ca^{2+}+Mg^{2+})/HCO_3^-$, in which all of the chemical species are represented by their concentrations expressed in mg/L. The ratio would be about 0.5, if the $Ca^{2+}$ and $Mg^{2+}$ in the groundwater were derived only by the dissolution of carbonates in the aquifer or the weathering of pyroxene and amphibole (Meybeck et al. 1987). The ratios of almost all the groundwater samples are above 0.5 (Fig. 3E), which suggests that the balance between the concentrations of $Ca^{2+}$+$Mg^{2+}$ and $HCO_3^-$ must have changed somehow. The strong positive correlation between $Ca^{2+}$+$Mg^{2+}$ and $SO_4^{2-}$ shown in Fig. 3F, suggests that sulphate dissolution could be an important source of the extra $Ca^{2+}$+$Mg^{2+}$. On the other hand, the low ($Ca^{2+}$+$Mg^{2+}$)/$HCO_3^-$ ratio seen in a few groundwater samples could be caused by $Ca^{2+}$+$Mg^{2+}$ depletion, arising from cation exchange.

## CONCLUSIONS

Twenty eight groundwater samples collected from limestone aquifers in Sunan coal-main area were tested, and the results were analysed by conventional graphical and multivariate statistical approach; the conclusions drawn are:

1. The groundwater samples are mainly featured alkaline in nature, with a high value of TDS ranging from 789 to 2753 mg/L. Compared with the concentrations of $SO_4^{2-}$ and $HCO_3^-$, the content of $Cl^-$ is low for almost all ground-water samples, whereas the content of $Na^+$ and $Ca^{2+}$ is higher than $Mg^{2+}$. The hydrochemical type of ground-water samples are mainly divided into Ca-$SO_4$ and Na-$SO_4$ types, with few samples of Na-$HCO_3$ type also.
2. The dissolution of gypsum and weathering of dolomite and calcite are the main hydro-geochemical process, which contribute most cations to groundwater. The weathering of feldspar by carbonate acid and sulphur acid also existed, even the action is weak.
3. The groundwater samples could not meet the demand of drinking water, compared to the standards of WHO. However, all the groundwater samples are suitable for irrigation, with the better calculated values.

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