



# Study on Hydrochemical Evolution Mechanism of Groundwater in Coal Mine

Shuangwei Chai\*

School of Resources and Environment Engineering, Henan Polytechnic University, 454000  
Jiaozuo, China

\*Corresponding Author: Shuangwei Chai

## ABSTRACT

In this paper, Pingdingshan coal mine is selected as the research area. Based on the conventional hydrochemical data of groundwater in coal mines, mathematical statistics and hydrogeochemical simulation are used to explore the evolution mechanism of groundwater hydrochemistry in the study area. It is indicated that the hydraulic connection of different water bodies is close, and there are many types of hydrochemical types, such as  $\text{HCO}_3\text{-Ca}\cdot\text{Mg}$  and  $\text{HCO}_3\text{-Na}$ . The formation of each hydrochemical component is mainly controlled by water-rock interaction. Among them,  $\text{Na}^+\text{+K}^+$  mainly come from the dissolution process of salt rock,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{HCO}_3^-$  mainly come from the dissolution of carbonate rock, and  $\text{SO}_4^{2-}$  mainly comes from the dissolution of gypsum.

## KEYWORDS

Hydrochemical Evolution; Aquifer; Hydrogeochemical Simulation; Water-Rock Interaction

## 1. INTRODUCTION

The groundwater environment is complex and interacts with the surrounding rock for a long time. The characteristics of the hydrochemical environment are constantly evolving in this process. Based on the results of sample collection and analysis, this paper quantitatively analyzes the source of groundwater hydrochemical ions in the study area by means of Origin and other drawing software and graphic analysis methods such as ion ratio diagram and chlor-alkali index diagram, and reveals its formation process. Quantitative simulation by PHREEQC software to explain the evolution mechanism of groundwater hydrochemical characteristics in coal mines is of great significance for in-depth understanding of the source, migration and transformation of groundwater components.

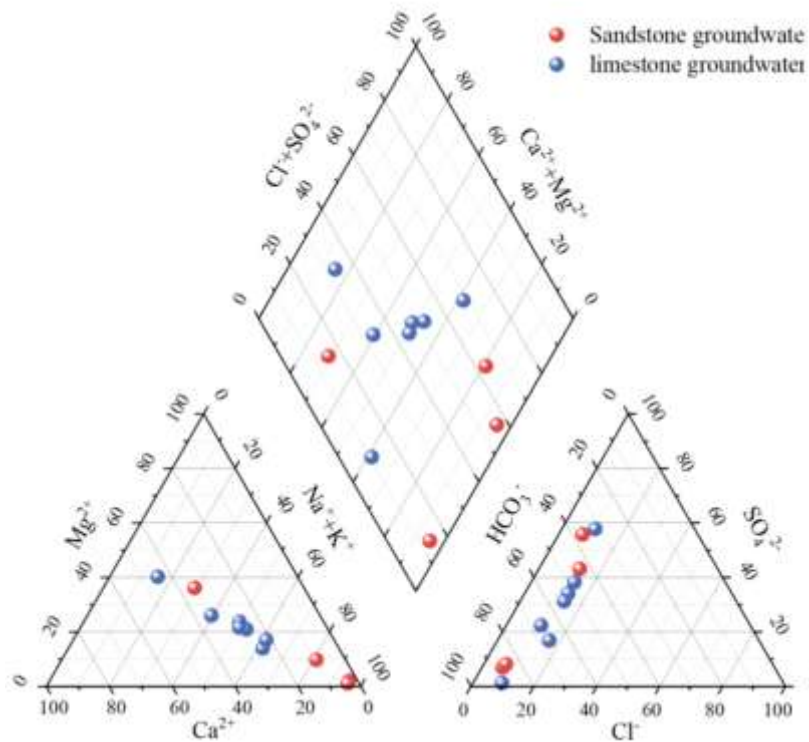
## 2. SAMPLE COLLECTION AND PROCESSING

When collecting samples, it is necessary to rinse the water sample bottle many times and fill the whole water sample bottle to ensure that the water sample bottle is quickly sealed and labeled without bubbles. GPS is used to locate the sampling position, and the surrounding environment is observed and recorded. The TDS, pH value and temperature of the water samples were measured on the spot by a portable tester. After the water samples were diluted and monitored after filtration, the conventional water chemical indexes such as  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  were measured by ion chromatograph and inductively coupled plasma emission spectrometer in Henan Polytechnic University.  $\text{HCO}_3^-$  was titrated with dilute sulfuric acid-methyl orange in the laboratory of the School of Resources and Environment, Henan Polytechnic University.

### 3. RESULTS AND DISCUSSION

#### 3.1. Hydrochemical type

According to the measured data of conventional hydrochemical ions such as  $K^+Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Cl^-$ ,  $SO_4^{2-}$  and  $HCO_3^-$ , the milligram equivalent percentage is calculated, and the Piper three-line diagram is drawn by origin software as shown in Figure 1.



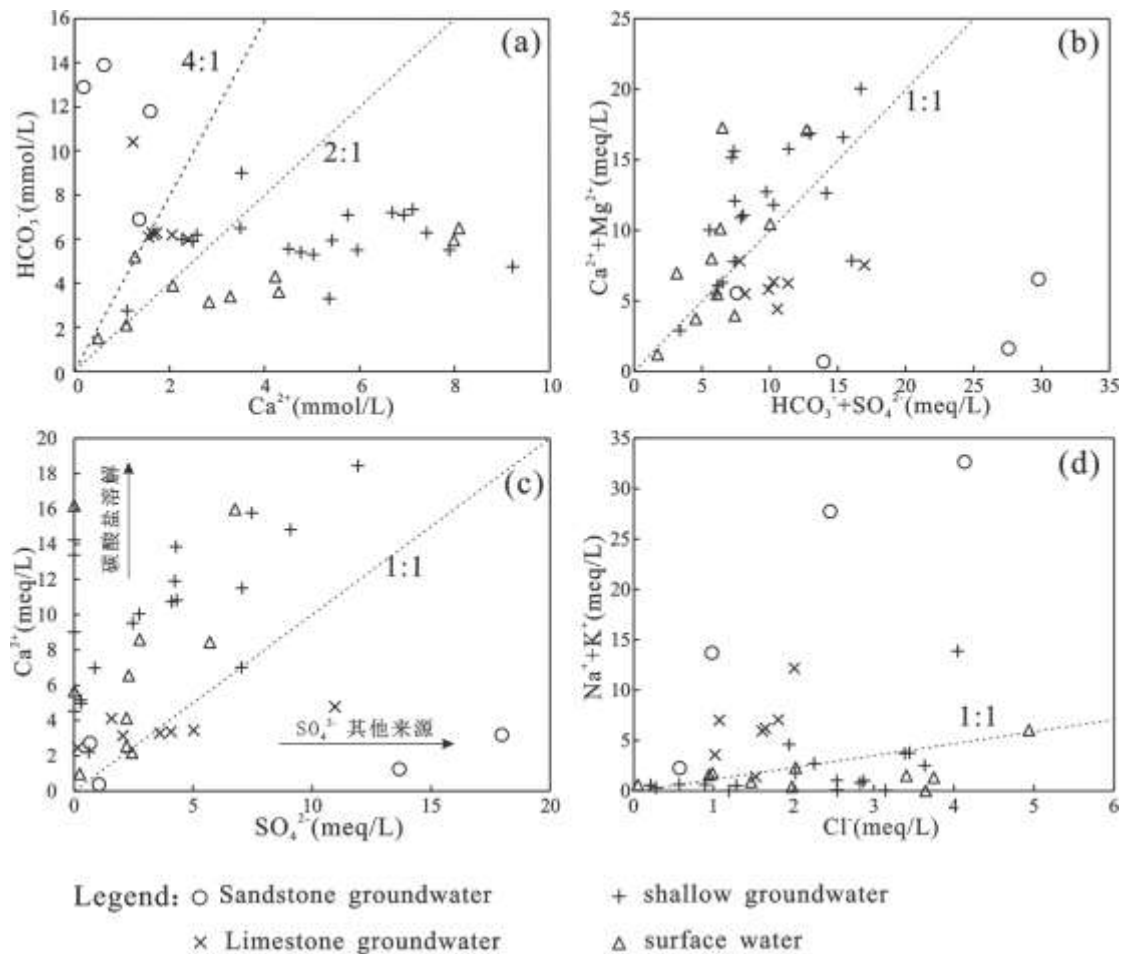
**Fig. 1** Piper three-line diagram of Coal Mine Groundwater

It can be seen from Fig.1 that the limestone water samples in the study area are mostly concentrated in the upper left of the diamond area, indicating that the hydrochemical type is mainly  $HCO_3^-Ca\cdot Mg$  type water. This is because limestone is rich in carbonate minerals such as calcium carbonate. Under the water-rock interaction, the dissolution of calcium carbonate makes the content of calcium, magnesium ions and bicarbonate ions in water higher. The distribution of sandstone water samples is more dispersed, and the coverage is wider in the diamond area, which shows that the hydrochemical types are more diverse, mainly  $HCO_3^-Na$  type, and some water samples show  $SO_4-Ca\cdot Mg$  type. In the cation triangle, the limestone water sample points are mostly close to the vertices of calcium and magnesium ions, indicating that the cation composition is dominated by calcium and magnesium ions. The distribution of water samples in sandstone water is discrete, not only near the vertex of calcium and magnesium ions, but also near the area of sodium and potassium ions, indicating that the cation composition of sandstone water is more complex. It may be due to the complex mineral composition of sandstone, which undergoes various geochemical processes such as mineral dissolution and ion exchange when interacting with water. In the anion triangle, the limestone water sample points are mostly concentrated in the bicarbonate ion area, indicating that the anion is mainly bicarbonate; the sandstone water sample points are distributed in the sulfate, chloride and bicarbonate ion regions, indicating that the anion composition is more abundant and may involve sulfur.

### 3.2. Qualitative characterization of hydrochemical evolution

The contents of  $\text{Na}^+\text{+K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$  in groundwater are affected by cation exchange adsorption, silicate rocks (albite ( $\text{NaAlSi}_3\text{O}_8$ ), montmorillonite ( $\text{Na}_{0.33}\text{Al}_{1.233}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2$ ), carbonate rocks (calcite ( $\text{CaCO}_3$ ), dolomite ( $\text{CaMg}(\text{CO}_3)_2$ )), and gypsum dissolution. When calcite ( $\text{CaCO}_3$ ) is dissolved in groundwater, the ratio of released  $\text{Ca}^{2+}$  to  $\text{HCO}_3^-$  is 1:2. When dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) is dissolved in groundwater, the ratio of released  $\text{Ca}^{2+}$  to  $\text{HCO}_3^-$  is 1:4. The dissolution of gypsum ( $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ ) in water will release the same amount of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$ .

It is of great significance to study the formation process of water chemical composition by using ion ratio analysis method to analyze the proportion relationship between various ions. Therefore, according to the measured data of water chemical ions in each water sample, the ion relationship diagram is further drawn as shown in the following figure.



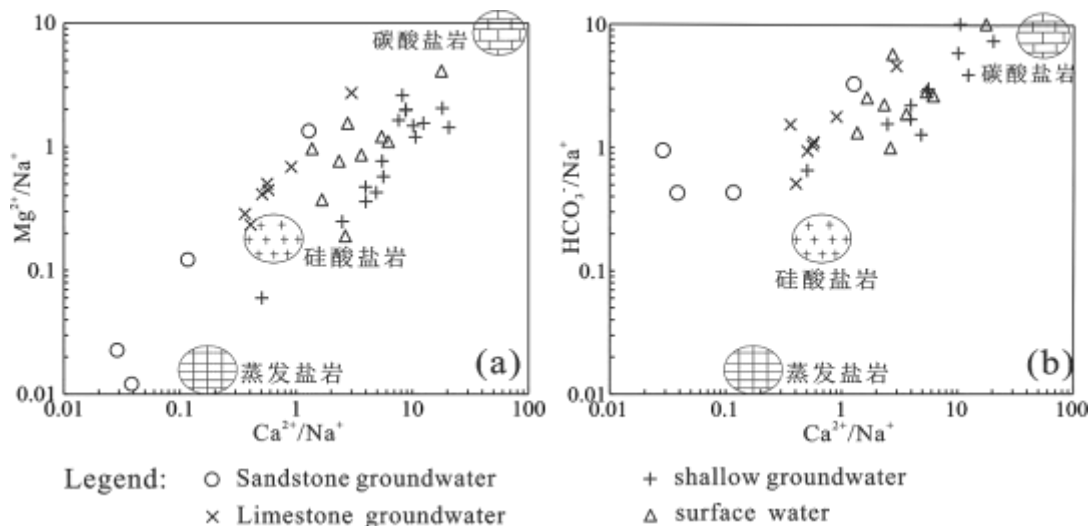
**Fig. 2** Relationship between the main ion ratios in groundwater and surface water in the study area

The relationship between  $\text{HCO}_3^-$  and  $\text{Ca}^{2+}$  content in coal mine groundwater is clearly shown in Fig.2(a). It can be seen that the content of  $\text{HCO}_3^-$  in limestone water samples is higher than that of  $\text{Ca}^{2+}$ . Most of the water sample points are concentrated between the 4:1 line and the 2:1 line, and are closer to the 4:1 line. There is a water sample point located in the upper left area. This is because the geological environment of limestone water is rich in carbonate rocks, so  $\text{HCO}_3^-$  and  $\text{Ca}^{2+}$  are closely related to the dissolution process of carbonate rocks. The water sample points of sandstone water are located in the upper area ( $\text{HCO}_3^- > 4 \times \text{Ca}^{2+}$ ), and the content of  $\text{HCO}_3^-$  is high, which indicates that the production of  $\text{HCO}_3^-$  in sandstone water is not only derived from the dissolution of carbonate rocks, but also from the dissolution of sulfate and silicate. At the same time, the decrease of  $\text{Ca}^{2+}$  content in sandstone water may be due to the fact that the weathering process of silicate minerals (such as feldspar or hornblende) in sandstone is usually slow, and cation exchange is also an important factor

affecting its content reduction. The water samples of phreatic water and surface water in the study area are mostly distributed in the lower area ( $\text{HCO}_3^- < 2 \times \text{Ca}^{2+}$ ), and the content of  $\text{Ca}^{2+}$  is high, which indicates that there may be a strong dissolution process of carbonate rocks in the phreatic water and surface water in this area, and there may be other factors affecting the content of  $\text{HCO}_3^-$ , resulting in a lower content than  $\text{Ca}^{2+}$ . In Fig.2(b), the limestone water sample points are mostly distributed below the 1:1 line, indicating that the value of  $(\text{Ca}^{2+} + \text{Mg}^{2+}) / (\text{HCO}_3^- + \text{SO}_4^{2-})$  in limestone water is less than 1, which can further explain that the calcium and magnesium ions in the limestone aquifer are mainly from the dissolution process of silicate and carbonate rocks<sup>[1-2]</sup>.

The water samples of phreatic water and surface water are distributed near the 1:1 line, in which calcium and magnesium ions are derived from the dissolution of gypsum and carbonate rocks. The dissolution of carbonate rocks will produce  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$ , and the dissolution of gypsum will increase  $\text{SO}_4^{2-}$ . The dissolution of silicate rocks may supplement a certain amount of  $\text{Mg}^{2+}$ , resulting in an approximately equal relationship between  $\text{Ca}^{2+} + \text{Mg}^{2+}$  and  $\text{HCO}_3^- + \text{SO}_4^{2-}$ . In Fig.2(c), limestone water and sandstone water samples are mostly distributed in the area below the 1:1 line,  $\text{Ca}^{2+} / \text{SO}_4^{2-}$  value  $< 1$ ,  $\text{SO}_4^{2-}$  content is higher, indicating that in addition to gypsum dissolution,  $\text{SO}_4^{2-}$  exists other sources such as sulfide oxidation or human input. The water samples of phreatic water and surface water are different, most of which are distributed in some areas above the 1:1 line, and the content of  $\text{Ca}^{2+}$  is higher. In Fig.2(d), the milligram equivalent ratio of  $\text{Na}^+ + \text{K}^+$  to  $\text{Cl}^-$  in limestone water and sandstone water is located above the 1:1 line, indicating that  $\text{Na}^+$  and  $\text{K}^+$  in limestone water and sandstone water are supplied by other sodium-containing silicate rock dissolution processes besides the salt rock dissolution process. In diving and surface water, the content of  $\text{Ca}^{2+}$  increases due to the cation exchange adsorption, and the content of  $\text{Na}^+ + \text{K}^+$  is less than that of  $\text{Cl}^-$ , which is consistent with the above analysis.

The weathering and dissolution process of carbonate rock, silicate rock and evaporite rock is an important source of solute in groundwater. Gaillardet et al. proposed a calculation model based on the normalized molar ratio of sodium ions. The  $\text{Ca}^{2+} / \text{Na}^+$  value was used as the abscissa, and the  $\text{HCO}_3^- / \text{Na}^+$  and  $\text{Mg}^{2+} / \text{Na}^+$  values were used as the ordinates, respectively. Based on this, the three major rock endmember diagrams were drawn, and further used to identify the potential sources of solutes in the water body, and the Gaillardet endmember diagrams of groundwater and surface water in the study area were drawn as follows.

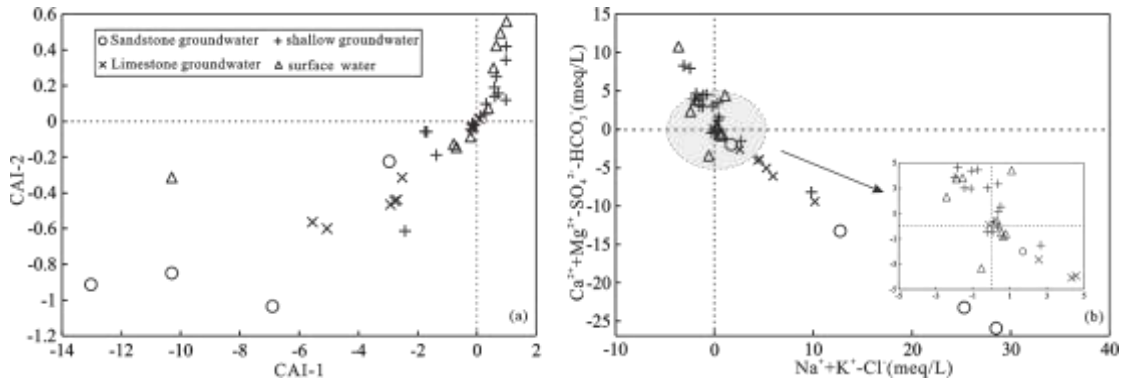


**Fig. 3** Gaillardet endmember diagram of groundwater and surface water in the study area

It can be seen from Fig.3 that most of the water samples in the study area are distributed between the end members controlled by silicate rocks and carbonate rocks. This phenomenon shows that the formation of water chemical components in the study area is mainly controlled by silicate weathering and carbonate dissolution. The groundwater sample point is close to the end of the silicate rock, and

the surface water sample point is close to the end of the carbonate rock, indicating that the groundwater is greatly affected by the weathering of the silicate rock, and the surface water is greatly affected by the weathering of the carbonate rock.

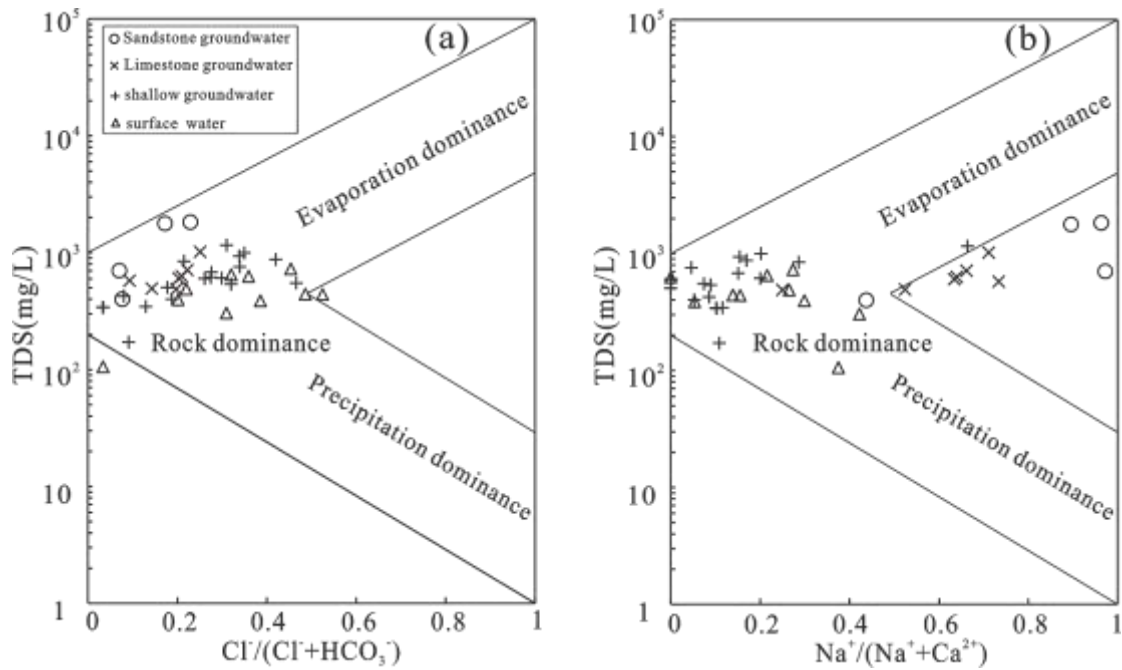
Through the analysis of the main ion ratio diagram, it can be known that the content of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Na}^+$  in groundwater will be affected by the alternating adsorption of cations. At the same time, using the chlor-alkali index method, it is possible to determine whether ion exchange adsorption occurs between the groundwater runoff and the rock and soil in the aquifer during the groundwater runoff process. It is also possible to evaluate the process of this effect and realize the quantitative analysis of the effect [3-4].



**Fig. 4** Cation alternating adsorption

From Fig.4(a), it can be seen that the distribution of water samples in CAI-1 and CAI-2 values are less than 0 side or greater than 0 side, which indicates that the positive and reverse cation exchange adsorption occurs. The limestone water sample points are distributed in the CAI-1 and CAI-2 values are less than 0 side ( $-5.55 < \text{CAI-1} < -2.52$ ,  $-0.60 < \text{CAI-2} < -0.31$ ), indicating that the cation exchange adsorption is strong, at the same time, through this feature, it is also verified that cation exchange is an important conclusion that leads to less  $\text{Ca}^{2+}$  content. Sandstone water shows the same characteristics as limestone water ( $-13.03 < \text{CAI-1} < -2.96$ ,  $-1.03 < \text{CAI-2} < -0.22$ ). There are water sample points distributed on the side of CAI-1 and CAI-2 values greater than 0 in phreatic water and surface water, and reverse cation exchange adsorption occurs.  $\text{Ca}^{2+}$  in aquifer medium enters into groundwater, making the content of  $\text{Ca}^{2+}$  increase. The relationship between  $(\text{Ca}^{2+} + \text{Mg}^{2+} - \text{SO}_4^{2-} - \text{HCO}_3^-)$  and  $(\text{Na}^+ + \text{K}^+ - \text{Cl})$  was further plotted, as shown in Fig.4(b). It can be seen that the distribution of all water samples shows a linear relationship and is located near the line with a slope of -1, which indicates that cation exchange has occurred significantly.

The Gibbs diagram is usually used to qualitatively determine the factors affecting the chemical composition of natural waters. The  $\gamma(\text{Cl}^-)/\gamma(\text{Cl}^- + \text{HCO}_3^-)$  and  $\gamma(\text{Na}^+)/\gamma(\text{Na}^+ + \text{Ca}^{2+})$  ( $\gamma$  is the milligram equivalent) values are used as abscissa, and the logarithm of total dissolved solids (TDS) is used as ordinate. According to the position of water sample points in the map, the factors controlling the formation of groundwater hydrochemical composition can be divided into three types: evaporation and concentration, water-rock interaction and atmospheric precipitation. When the ratio of  $\gamma(\text{Cl}^-)/\gamma(\text{Cl}^- + \text{HCO}_3^-)$  and  $\gamma(\text{Na}^+)/\gamma(\text{Na}^+ + \text{Ca}^{2+})$  in the water sample approaches 1 and the salinity content is higher than 1000mg/l, this means that the formation of such water samples is mainly affected by evaporation-crystallization. If the value of  $\gamma(\text{Cl}^-)/\gamma(\text{Cl}^- + \text{HCO}_3^-)$  or  $\gamma(\text{Na}^+)/\gamma(\text{Na}^+ + \text{Ca}^{2+})$  is less than or equal to 0.5, and the total dissolved solids (TDS) content is in the range of 100 mg/l to 1000 mg/l, it indicates that the characteristics of each hydrochemical component in the water sample are affected by water-rock interaction. If the value of  $\gamma(\text{Na}^+)/\gamma(\text{Na}^+ + \text{Ca}^{2+})$  or  $\gamma(\text{Cl}^-)/\gamma(\text{Cl}^- + \text{HCO}_3^-)$  is close to 1, and the TDS content is less than 100 mg / l, it indicates that the characteristics of each hydrochemical component in the water sample are affected by atmospheric precipitation. At the same time, the Gibbs diagram of groundwater and surface water in the study area is shown in Fig.5.



**Fig. 5** Gibbs diagram of groundwater and surface water in the study area

It can be seen from Fig.5 that the TDS of groundwater and surface water samples in the study area is moderate. Based on the above criteria, some sandstone water and limestone water samples are distributed in the water-rock interaction control area in the middle of the Gibbs diagram in the middle of the water-rock interaction area, indicating that there is a strong chemical reaction between groundwater and surrounding rock, and the dissolution of rock minerals affects the chemical composition of water samples. For example, the dissolution of carbonate rocks may increase the content of  $\text{HCO}_3^-$  in water, which in turn affects the ratio of  $\gamma(\text{Cl}^-)/\gamma(\text{Cl}^-+\text{HCO}_3^-)$ . In addition, some water samples of phreatic water and surface water are close to the boundary of evaporative crystallization area, indicating that these water bodies may have undergone a certain degree of evaporation process in the local environment, which makes the salt in the water relatively concentrated and the relative content of non-volatile ions such as Cl increased. Some water sample points are close to the evaporation crystallization area, which means that these water bodies have undergone an evaporation process and the salt is concentrated. Some water sample points fall in the precipitation control area, indicating that it is greatly affected by atmospheric precipitation, and the chemical composition is related to precipitation.

#### 4. CONCLUSIONS

(1) The hydrochemical characteristics of various types of water bodies were analyzed by mathematical statistics and Piper 's three-line diagram. The results showed that the hydraulic connections of different water bodies were close and the hydrochemical types were similar. The limestone water is mainly  $\text{HCO}_3\text{-Ca-Mg}$  type, and the sandstone water is mainly  $\text{HCO}_3\text{-Na}$  type.

(2) The ion ratio diagram, chlor-alkali index diagram and Gibbs diagram indicate that the chemical composition of groundwater in coal mines is mainly controlled by water-rock interaction. Among them,  $\text{Na}^+\text{+K}^+$  are mainly derived from the dissolution process of salt rock,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{HCO}_3^-$  are mainly derived from carbonate rock dissolution, and  $\text{SO}_4^{2-}$  is mainly derived from gypsum dissolution. The decrease of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  contents in sandstone water is due to cation exchange, desulfuration and silicate dissolution, respectively.

## CONFLICTS OF INTEREST

The authors declare that they have no conflict of interest.

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