

## **Hydro-chemical Characters and Ions Source of Groundwater from Qidong Coal Mine, Northern Anhui Province, China**

Herong Gui, Song Chen

*School of Earth Sciences and Engineering, Suzhou University, Suzhou, Anhui 234000, China*  
*hrgui@163.com*

**Abstract** Major ions were analyzed for twenty six groundwater samples collected from diverse aquifers in Qidong coal mine, northern Anhui province, China. Hydro-geochemical characters and ions sources of groundwater were discussed, the result showed that: the diverse groundwater samples have vary ions controlled by water-rock interaction, the concentrations of  $\text{Cl}^-$  are low for all groundwater samples, whereas the contents of  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$  are high with diversity degrees for groundwater. The concentrations of  $\text{Na}^+$  were decreasing as follows: LA (limestone aquifer) < QA (Quaternary aquifer) < CA (Coal-bearing aquifer), whereas the contents of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were increasing from CA to LA oppositely.

**Keywords** groundwater, ions source, hydrogeochemistry, Qidong coal mine

### **Introduction**

Deep groundwater is always reserving some information what inherit from the aquifer through the water-rock interaction over a long period of time. Thus, many studies, focusing on the groundwater quality, water-rock interaction and hydro-geochemical process have been completed, what based on the hydro-chemical analyzed (Kumar et al. 2009; Ramkumar et al. 2013). All these studies had revealed regional hydro-chemical process characteristics, and have important significance for the utilization of groundwater resources.

Qidong coal mine is located in northern Anhui Province, China, where has abundant coal resources. The studies about hydro-geochemical and groundwater source discrimination are weak. Especially, the printed information about different statistical methods using in groundwater source identification are blank. The purpose of this study is to identify the groundwater evolution for diverse aquifers, using hydro-chemical and statistical analysis. The major targets are to (1) constrain the hydro-geochemical process of groundwater for diverse aquifer, (2) recognize the ions source of groundwater.

### **Materials and methods**

Qidong coal mine, belonging to Huaibei mining area, is located at northern Anhui Province, China, which constituted by about thirty couples mines (fig.1). The climate in the area is marine-continental, with an annual average temperature of 14.9 °C.

Previous research showed Qidong coal mine mainly includes three aquifers: the Quaternary aquifers (QA), Coal bearing aquifer (CA) and Limestone aquifer (LA), all the three aquifers have threat to the coal mine exploration (Gui et al. 2007). The Quaternary aquifer is constituted by yellow mudstone, sandstone and conglomerate, with a depth ranging from 280 to 300 m. The Coal bearing aquifer is characterized by mudstone, siltstone and sandstone, with a depth between 300 and 700 m. Limestone aquifers are mainly composed of limestone with clastic rocks, which belong to Taiyuan formation and Ordovician.

A total twenty-six groundwater samples were collected from diverse aquifers in Qidong coal mine. All the groundwater samples are as flows: seven samples from QA, eleven samples from CA and eight samples from LA. Water samples were collected via drainage holes in alleys, and then filtered through 0.45  $\mu\text{m}$  pore-size membrane and collected into

polyethylene bottles that had been cleaned using trace element clean procedures. All the twenty-six samples were analyzed for major ions.

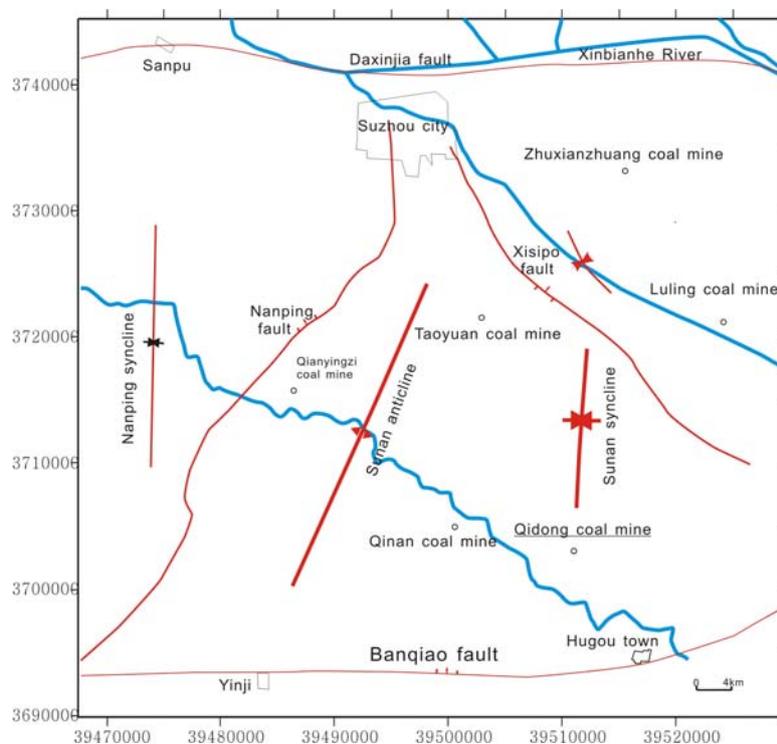


Fig. 1 Location of study area in northern Anhui Province, China

## Results and discussion

### Major ion chemistry

In general, the anion  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  concentrations in the groundwater range from 21 to 283 mg/L, 4 to 2064 mg/L, 188 to 630 mg/L and 0 to 93 mg/L, with averaged 211, 721, 397 and 11 mg/L, respectively. Otherwise, the cation  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations of the groundwater range from 1.0 to 940, 3.0 to 539, and 7.0 to 144 mg/L, with averaged 344, 147 and 68, respectively. The groundwater of QA is divided to Na- $\text{SO}_4$  or Na- $\text{HCO}_3$  type, however the LA groundwater is mainly be Ca- $\text{SO}_4$  or Ca- $\text{HCO}_3$ .

The geochemical data of groundwater were plotted on a Piper diagram (fig. 2), some information could be obtained. The concentrations of  $\text{Cl}^-$  are low for all groundwater samples, whereas the contents of  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$  are high with diversity degrees for groundwater collected from different aquifer. The cations also have the similar character with the anions. The most groundwater samples from coal bearing aquifer were characterized by the high concentrations of  $\text{Na}^+$ , and the anions are dominated by the  $\text{SO}_4^{2-}$  or  $\text{HCO}_3^-$ . Whereas, the groundwater samples from Quaternary aquifer have higher concentrations of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . The anions were consisted by  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$ , which were similar with the coal bearing aquifer. The contents of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were dominated in the groundwater from limestone aquifer, with high concentration of  $\text{SO}_4^{2-}$ . In conclusion, the concentrations of  $\text{Na}^+$  were decreasing as follows: LA<QA<CA, whereas the contents of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were increasing from CA to LA oppositely.

### Ions source

Hydrochemistry of groundwater always influenced by such factors: recharging and water-rock interaction, the degree of water-rock interaction controlled by residence time within the aquifer (Gaillardie et al. 1999). Generally, three general processes contribute to the generation of solutes in groundwater: evaporation dissolution, carbonate dissolution and silicate weathering. As can be seen from fig. 3(A, B), the groundwater in the area is mainly controlled by silicate weathering, the evaporate dissolution and carbonate dissolution also played important role on the groundwater from QA and LA, respectively. Especially, the groundwater samples of LA were influenced by the carbonate dissolution obviously.

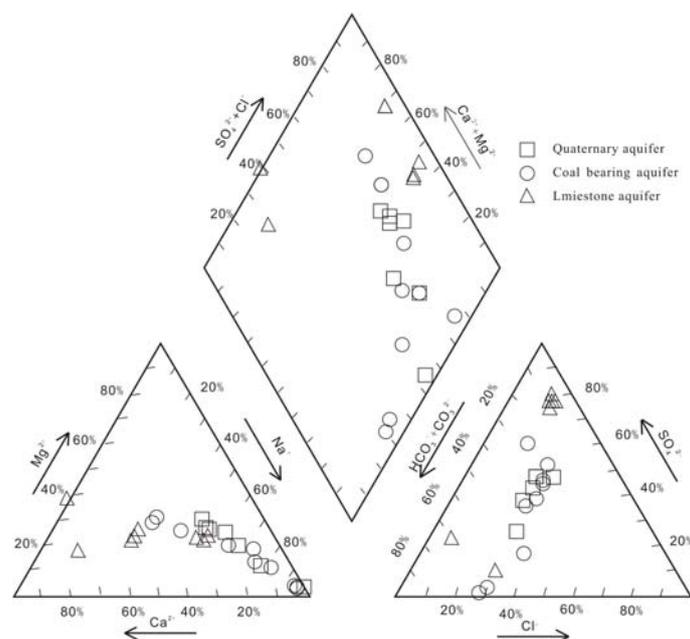
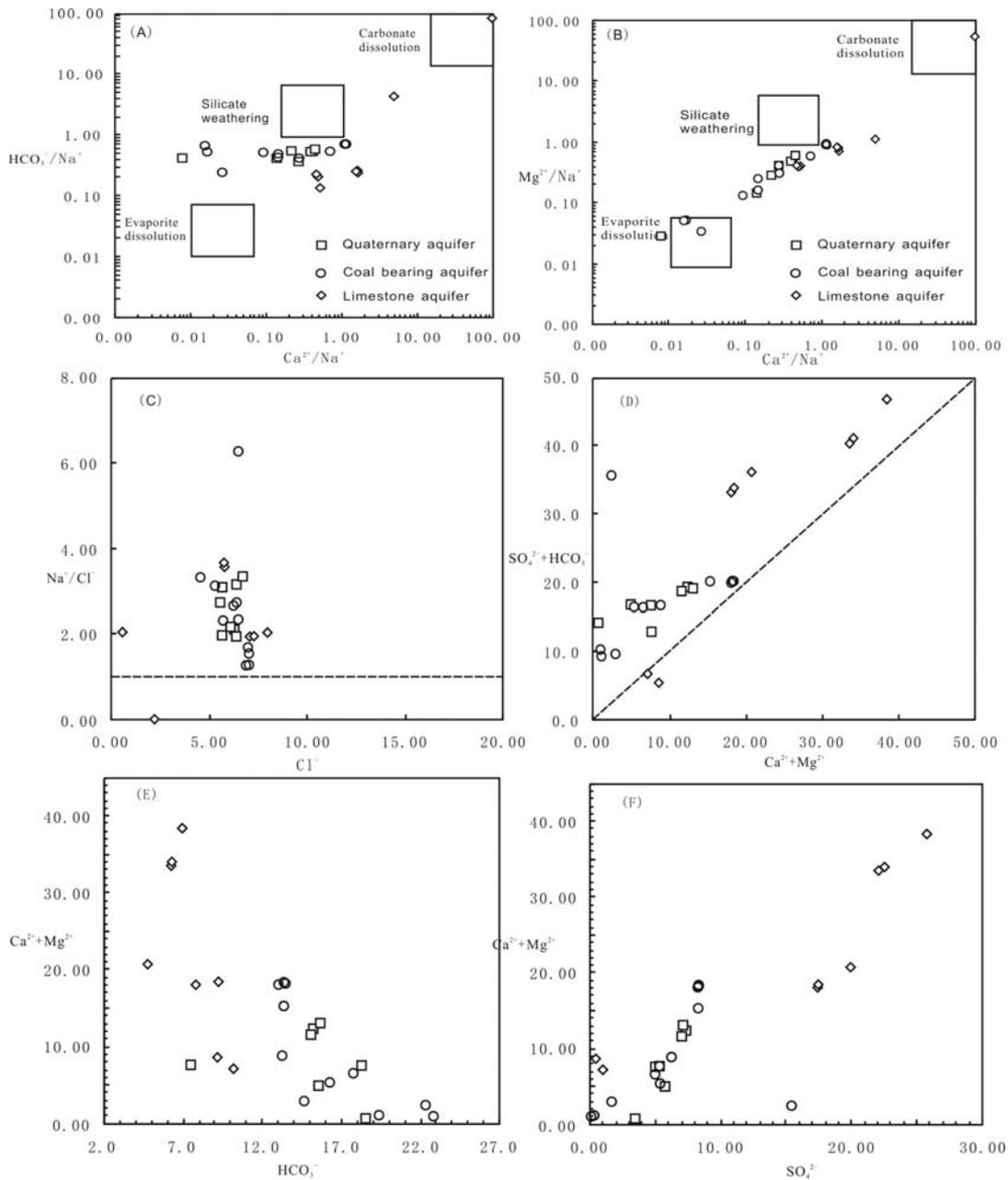


Fig. 2 Piper diagram of groundwater from Qidong coal mine in northern Anhui province, China.

Table 1 Chemical summary of groundwater samples from Qidong coal mine

	Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup>
Max	940	539	144	2064	283	630	93
Min	1	3	7	4	21	188	0
Mean	344	147	68	721	211	397	11
LA <sub>mean</sub>	317	287	98	1266	192	257	2
QA <sub>mean</sub>	341	72	57	466	213	422	10
CA <sub>mean</sub>	365	92	53	487	223	471	18

For the dissolution of halite in water releases equal concentration of Na<sup>+</sup> and Cl<sup>-</sup> into the solution, mechanism of acquiring salinity in groundwater systems could be identified using the Na-Cl relationship, (Sami et al. 1992). Thus, the value Na<sup>+</sup>/Cl<sup>-</sup> could be present a line and the value Na<sup>+</sup>/Cl<sup>-</sup> close to one, if Na<sup>+</sup> and Cl<sup>-</sup> came from halite dissolution only. However, the fig. 3C is presented different vision with Na<sup>+</sup>/Cl<sup>-</sup> ratios of most samples above one. What could be implied that additional Na<sup>+</sup>, probably from other source. Generally, the additional Na<sup>+</sup> in groundwater could be originated from weathering of silicate minerals, the views could be supported by some silicate mineral could be found in the aquifer rocks. And the weathering process often along with increased HCO<sub>3</sub><sup>-</sup> concentrations, what are presented from Figure 3D.



**Fig. 3** Plots of major ion for groundwater samples in Qidong coal mine (A and B are plots of  $\text{Na}^+$  normalized  $\text{Ca}^{2+}$ - $\text{HCO}_3^-$  and  $\text{Ca}^{2+}$ - $\text{Mg}^{2+}$ ; C and D are scatter of  $\text{Cl}^-$ - $\text{Na}^+/\text{Cl}^-$  and  $(\text{Ca}^{2+}+\text{Mg}^{2+})$ - $(\text{HCO}_3^-+\text{SO}_4^{2-})$ ; E and F are scatter of  $(\text{Ca}^{2+}+\text{Mg}^{2+})$ - $\text{HCO}_3^-$  and  $(\text{Ca}^{2+}+\text{Mg}^{2+})$ - $\text{SO}_4^{2-}$ )

The source of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in groundwater could be determined from the ratio of  $(\text{Ca}^{2+}+\text{Mg}^{2+})/\text{HCO}_3^-$ . The ratio would be about 0.5, if  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  come in groundwater only from dissolution of carbonates in the aquifer, or from the weathering of pyroxene and amphibole (Meybeck et al.1987). The ratio of the groundwater samples in the area are ranging from 0.09 to 9.7, with average value 2.66 (fig. 3E), revealing that the balance between concentration of  $\text{Ca}^{2+}+\text{Mg}^{2+}$  and  $\text{HCO}_3^-$  are changed by some reason. The strong positive correlation between  $\text{Ca}^{2+}+\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  are presented by fig. 3F, suggesting that sulfate dissolution could be important for the extra  $\text{Ca}^{2+}+\text{Mg}^{2+}$ . In additional, the low

$(\text{Ca}^{2+}+\text{Mg}^{2+})/\text{HCO}_3^-$  ratio of few groundwater samples could be the result of  $\text{Ca}^{2+}+\text{Mg}^{2+}$  depletion by cation exchange.

In a word, the groundwater samples in the area are mainly controlled by silicate weathering, especially in the Coal bearing aquifer. However, the dissolution of evaporate and carbonate are also played an important role on groundwater from QA and LA, respectively. Sulfate dissolution could be important for the extra  $\text{Ca}^{2+}+\text{Mg}^{2+}$ , for the best correlation between  $\text{Ca}^{2+}+\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$ .

### Conclusions

(1) The concentrations of  $\text{Cl}^-$  are low for all groundwater samples, whereas the contents of  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$  are high with diversity degrees for groundwater. The cations also have the similar character with the anions. In conclusion, the concentrations of  $\text{Na}^+$  were decreasing as follows:  $\text{LA}<\text{QA}<\text{CA}$ , whereas the content of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were increasing from CA to LA oppositely.

(2) The groundwater samples in the area are mainly controlled by silicate weathering, especially in the Coal bearing aquifer. Otherwise the dissolution of evaporate and carbonate also played important role on groundwater from QA and LA, respectively. Sulfate dissolution could be important for the extra  $\text{Ca}^{2+}+\text{Mg}^{2+}$ .

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