



# Statistical Analysis for Understanding Groundwater Chemical Variations

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## ABSTRACT

Understanding the hydro-chemical variation of groundwater is important for water usage in the coal mines. In this study, twenty-one and eleven samples have been collected from the coal bearing and limestone aquifer systems, respectively in a coal mine in northern Anhui Province, China. And their major ion concentrations have been analysed by statistical methods including correlation, factor and cluster analysis. The results indicate that the hydro-chemical characteristics of the groundwater samples from these two aquifer systems are different, the groundwater samples from the coal bearing and limestone aquifer systems are dominated by Na-HCO<sub>3</sub> and Ca-HCO<sub>3</sub> types, respectively. Correlation and factor analysis, as well as traditional hydro-chemical methods indicate that dissolution of evaporates and carbonates, as well as weathering of silicates are contributors for the chemical variations of the groundwater samples. In combination with traditional methods, the study demonstrated that statistical analyses are useful tools for understanding the hydro-chemical variation of groundwater.

## INTRODUCTION

Coals and its related products have played important role during the development of China. Previous studies revealed that coals accounted for 72.2% in China's primary energy consumption during 1980, and this proportion is still more than 60% in 2006 (Jiang 2008). Due to the large amount of consumption, the production capacity is also great. The coal production in 2006 was 2.3 billion tons, and it has been increased to 3 billion tons in 2009. However, in response to this high production, a large number of coal mining related disasters had occurred during the last two decades; more than 220 mines were flooded, more than 8000 persons died and the economic losses were up to 300 billion Yuan.

To be one of the most important coal producing areas in China, the annual production of coals is more than 100 million tons in the northern Anhui Province, China. The high coal production is also accompanied by a high occurrence of high water damage accident (Gui & Chen 2007). Under this condition, a large number of studies related to groundwater, especially the studies related to hydro-chemistry, have been brought to light (Gui et al. 2005, 2013, Chen et al. 2008, Sun et al. 2011, 2012). These studies demonstrated that hydro-chemistry of groundwater is good indicator for water source identification during water inrush.

However, the lack of water resource in the area is also serious, and the water discharged from the coal mines is concerned by the local government and the coal enterprises, because a reasonable application of these waters can reduce the potential threat for environmental protection and increase

the water resources in the area. However, the studies related to the qualities of these kinds of water are limited. Therefore, in this study, the major ion concentrations in groundwaters from two aquifers in the Zhuzhuang coal mine in northern Anhui Province, China have been analysed by statistical methods for understanding the processes controlling the groundwater chemistry. The study will be useful for the groundwater management in the area.

## HYDROLOGICAL BACKGROUND

The Zhuzhuang coal mine is located 9 km east to the Huaibei City, northern Anhui Province, China (Fig. 1) between the latitude 33°59'2"033"-33°56'2"373" and longitude 116°50'2"163"-116°52'2"523", and is bounded by the Yangzhuang coal mine in south and the Daihe coal mine in north. The coal mine is located in the centre of the Huaibei plain with continental-transitional climate. The winter is cold and windy, whereas the summer is hot and rainy. The annual average temperature is 14.5°C, and the average annual precipitation is 862 mm with most is concentrated in July and August.

The coal bearing strata in the coal mine include upper carboniferous and Permian, and the minable coal seams are only located in the Shanxi and Xiashihezi formations. There are four minable coal seams, including 3<sup>rd</sup>, 4<sup>th</sup>, 5<sup>th</sup> and 6<sup>th</sup>. To the end of 2009, the total production of coal was 7 million tons.

Previous exploration revealed that there are three aquifer systems in the coal mine. From shallow to deep, they are loose layer (LA), coal bearing sandstone (CA), limestone (TA) aquifer systems, and each system can be subdivided

into multi-aquifers. Characteristics of each aquifer are listed as follows:

The LA is a multilayer aquifer system, and is mainly recharged by precipitation and surface water infiltration. The cycling condition is good and its water table is changing with seasonal variations. The main route of excretion is evaporation and labour exploitation. Moreover, there is no hydraulic connection between LA and CA because of the thick aquifuge between them. The upper and lower parts of CA are confined by aquifuge, therefore, the CA is mainly recharged by in-layer runoff, and both the recharge and runoff in the aquifer system are poor. Under the condition of mining, the water in it is excreted by inrush or gushing. As to the rock compositions of the aquifer, they are mainly composed of sandstones. Moreover, the TA is a limestone dominant aquifer with multiple sources of recharge because it has a shallow outcrop. From the beginning of coal mining in the area, water inrush had occurred twelve times, and most of them were considered to be related to the TA.

### SAMPLING AND ANALYSIS

A total of thirty-two samples (twenty-one and eleven from CA and TA, respectively) have been collected in the Zhuzhuang coal mine, northern Anhui Province, China during June and July, 2012. Water pH values were measured in the field with a portable pH meter. Water samples were filtered through 0.45  $\mu\text{m}$  pore size membranes and collected

into 2-L polyethylene bottles that had been cleaned in the laboratory. Then, the samples were sent to the laboratory for analysis of major ions. Analytical processes were taken place at the Engineering and Technology Research Center of Coal Exploration in Anhui Province following the methods below:  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  were analysed by ion chromatography (CIC-200), whereas  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  were analysed by acid-base titration. Standard solutions were analysed simultaneously for calibration and the relative standard deviations are less than 5%.

Correlation and factor analyses were processed for tracing the source of major ions in the groundwater, and the plots of factor scores have been used for revealing the hydraulic connection between the CA and TA. All of these analyses were processed by the software SPSS (version 16).

### RESULTS

**Hydro-chemistry:** The analytical results of major ion concentrations of the groundwater samples in this study are listed in Table 1. As can be seen from the Table, the CA groundwater samples have pH values ranging from 6.5 to 7.9, with an average of 7.1, indicating their medium to slightly alkaline nature (four of them have pH values lower than 7). Their TDS range from 397 to 1014 mg/L (mean = 573 mg/L), and twelve and twenty of them have TDS lower than 500 and 1000 mg/L, respectively. In comparison to the standards of World Health Organization (WHO 2008), all

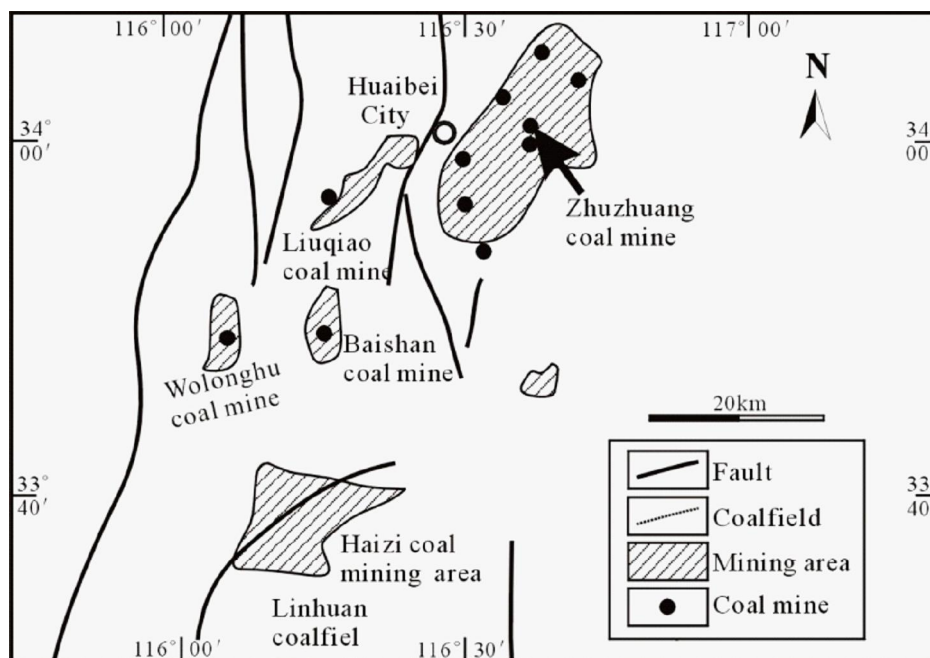


Fig.1: Location of the Zhuzhuang coal mine.

Table 1: Analytical results of major ions (mg/L) in the CA and TA.

ID	pH	Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	TDS	W-type
CA1	6.7	178	15	4	22	44	443	484	Na-HCO <sub>3</sub>
CA2	6.5	228	3	1	46	101	414	586	Na-HCO <sub>3</sub> -SO <sub>4</sub>
CA3	7.0	194	4	1	29	54	411	488	Na-HCO <sub>3</sub>
CA4	6.8	201	9	3	35	95	396	541	Na-HCO <sub>3</sub> -SO <sub>4</sub>
CA5	7.0	181	5	2	34	50	386	465	Na-HCO <sub>3</sub>
CA6	6.6	234	5	3	39	63	493	591	Na-HCO <sub>3</sub>
CA7	7.3	392	6	1	76	201	678	1014	Na-HCO <sub>3</sub> -SO <sub>4</sub>
CA8	7.5	365	11	3	63	117	760	939	Na-HCO <sub>3</sub>
CA9	7.1	100	55	15	58	52	339	448	Na-Ca-HCO <sub>3</sub>
CA10	7.0	133	17	9	30	20	376	397	Na-HCO <sub>3</sub>
CA11	7.2	150	19	2	28	58	342	428	Na-HCO <sub>3</sub>
CA12	7.4	217	2	2	40	8	515	527	Na-HCO <sub>3</sub>
CA13	7.0	214	2	2	24	27	508	523	Na-HCO <sub>3</sub>
CA14	7.0	219	2	2	24	49	490	541	Na-HCO <sub>3</sub>
CA15	7.0	207	3	2	26	27	490	511	Na-HCO <sub>3</sub>
CA16	7.0	70	64	23	24	44	394	421	Ca-Na-Mg-HCO <sub>3</sub>
CA17	7.2	341	9	8	127	41	703	877	Na-HCO <sub>3</sub> -Cl
CA18	7.2	178	16	9	31	31	470	499	Na-HCO <sub>3</sub>
CA19	7.4	212	2	1	31	50	458	525	Na-HCO <sub>3</sub>
CA20	7.3	175	12	3	44	63	359	476	Na-HCO <sub>3</sub>
CA21	7.9	158	31	15	20	18	500	492	Na-HCO <sub>3</sub>
TA1	6.8	49	76	21	26	45	363	399	Ca-Na-Mg-HCO <sub>3</sub>
TA2	7.1	26	93	28	17	73	363	418	Ca-Mg-HCO <sub>3</sub>
TA3	7.6	2	80	30	19	51	379	371	Ca-Mg-HCO <sub>3</sub>
TA4	7.8	88	51	17	17	59	367	416	Na-Ca-HCO <sub>3</sub>
TA5	7.0	78	62	16	27	45	374	416	Na-Ca-HCO <sub>3</sub>
TA6	6.8	52	76	19	27	41	367	398	Ca-Na-Mg-HCO <sub>3</sub>
TA7	6.8	54	75	21	21	49	367	404	Ca-Na-Mg-HCO <sub>3</sub>
TA8	6.9	65	62	19	23	49	359	398	Ca-Na-Mg-HCO <sub>3</sub>
TA9	7.1	47	70	18	23	36	344	365	Ca-Na-Mg-HCO <sub>3</sub>
TA10	7.3	71	60	17	24	36	307	362	Na-Ca-Mg-HCO <sub>3</sub>
TA11	8.0	2	48	12	20	33	437	333	Ca-HCO <sub>3</sub>

of the samples except one can be used for drinking according to their pH values and TDS contents. Moreover, Na<sup>+</sup> is the dominant cation followed by Ca<sup>2+</sup> and Mg<sup>2+</sup>, their concentrations are 70-392, 2-64 and 1-23 mg/L, respectively. As to the anions, HCO<sub>3</sub><sup>-</sup> is followed by SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup>, their concentrations are 339-760, 8-201 and 20-127 mg/L, respectively.

As to the TA groundwater samples, they also show medium to slightly alkaline nature with pH values in the range of 6.8 to 8.0 (mean= 7.2 and four of them have pH values lower than 7). However, different with those of the CA groundwater, they have low TDS contents (333-418 mg/L, mean = 387 mg/L), which can meet the desirable requirement of drinking water (WHO 2008). Their major ion concentrations are also different with those of the CA groundwater, they have Ca<sup>2+</sup> > Na<sup>+</sup> > Mg<sup>2+</sup> for cations; their mean concentrations are 69, 48 and 20 mg/L, respectively. However, they have similar trend of anion concentrations with those of the CA groundwater, the mean concentrations of HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> are 367, 48 and 22 mg/L, respectively.

**Hydro-chemical types:** The subdivision of Hydro-chemical

types is important for the study of groundwater, because of the dominant anion species of water change systematically from HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> as groundwater flows from the recharge zone to the discharge zone (Toth 1999). Therefore, Hydro-chemical water types give an indication for potential flow paths and connections of aquifers. Classification of groundwater in this study is based on the concentration of cations and anions by using Aquachem and two diagrams (Piper and Durov), and the results are given in Table 1 and Fig. 2. As can be seen from the table and figure, twenty of the CA groundwater samples are classified as Na-HCO<sub>3</sub> type, and only one is classified as Ca-HCO<sub>3</sub> type. However, eight of the TA groundwater samples are classified as Ca-HCO<sub>3</sub> type and three of them are classified as Na-HCO<sub>3</sub> type. These results indicate that these groundwater samples are probably located at the recharge or runoff zone, rather than the discharge zone (Toth 1999).

## DISCUSSION

**Correlation analysis:** The results of the correlation analy-

Table 2: Results of correlation analysis.

	Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
Ca <sup>2+</sup>	-0.83**				
Mg <sup>2+</sup>	-0.79**	0.96**			
Cl <sup>-</sup>	0.69**	-0.38*	-0.34		
SO <sub>4</sub> <sup>2-</sup>	0.50**	-0.17	-0.23	0.39*	
HCO <sub>3</sub> <sup>-</sup>	0.83**	-0.54**	-0.46**	0.68**	0.40*

Note: \*\* and \* mean correlation significant at the 0.01 and 0.05 levels, respectively.

Table 3: Results of factor analysis.

	FA1	FA2
Na <sup>+</sup>	-0.75	0.65
Ca <sup>2+</sup>	0.98	-0.17
Mg <sup>2+</sup>	0.96	-0.15
Cl <sup>-</sup>	-0.26	0.80
SO <sub>4</sub> <sup>2-</sup>	0.01	0.78
HCO <sub>3</sub> <sup>-</sup>	-0.46	0.74
Eigenvalue	2.70	2.27
Variance explained	45.0%	37.9%

sis are listed in Table 2. As can be seen from the table, Na<sup>+</sup> is negatively correlated with Ca<sup>2+</sup> and Mg<sup>2+</sup>, and positively correlated with Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>. The former relationship can be explained by ion exchange, whereas the latter relationships are considered to be indication of the dissolution of halite (NaCl) and mirabilite (Na<sub>2</sub>SO<sub>4</sub>). Moreover, the positive correlation between Na<sup>+</sup> and HCO<sub>3</sub><sup>-</sup> can be explained by the weathering of silicate minerals such as plagioclase, because this process can generate Na<sup>+</sup> and HCO<sub>3</sub><sup>-</sup> simultaneously (Meybeck 1987).

These considerations can be demonstrated by other Hydro-chemical methods. Firstly, the correlation between Na<sup>+</sup> and Cl<sup>-</sup> is often used for tracing the source of Na<sup>+</sup> in groundwater (Rogers 1989, Sami 1992), because dissolution of halite can generate Na<sup>+</sup>/Cl<sup>-</sup> (meq/L) equal to one. If there are other processes generating Na<sup>+</sup>, the ratio will be higher than one. As can be seen from Fig. 3, the TA groundwater samples are plotted near the 1:1 line, indicating that dissolution of halite is an important process controlling their Na<sup>+</sup> and Cl<sup>-</sup>. However, the CA groundwater samples have much higher Na<sup>+</sup> than Cl<sup>-</sup>, implying other processes. Because weathering of silicate mineral can generate HCO<sub>3</sub><sup>-</sup>, then the relationship between (HCO<sub>3</sub><sup>-</sup>+SO<sub>4</sub><sup>2-</sup>) and (Ca<sup>2+</sup>+Mg<sup>2+</sup>) in Fig. 3 demonstrated the contribution of silicate weathering for the Hydro-chemistry of the CA groundwater samples. Moreover, the ion exchange between Na<sup>+</sup> and Ca<sup>2+</sup> and Mg<sup>2+</sup> can be demonstrated by the high negative correlation between (Na<sup>+</sup>-Cl<sup>-</sup>) and (Ca<sup>2+</sup>+Mg<sup>2+</sup>-SO<sub>4</sub><sup>2-</sup>-HCO<sub>3</sub><sup>-</sup>) (r<sup>2</sup> = 0.95) (Schoeller 1965).

**Factor analysis:** Factor analysis is useful tool for revealing the potential information buried in the dataset including Hydro-chemical and environmental data (Kimball & Runkel 2009, Rapantova et al. 2012). In this study, factor analysis was performed on the dataset of all samples (Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>) and the result is presented in Table 3.

As can be seen from the table, two factors (FA1 and FA2) with total explanation of 82.9% have been obtained with Eigen value higher than one after varimax rotation. The first factor is responsible for 45.0% of the total variance and is dominated by Ca<sup>2+</sup> and Mg<sup>2+</sup>, whereas the explanation of the second factor is 37.9% and is mainly participated by Na<sup>+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup>. In considering about the hydrological background, the first factor can be explained to be a carbonate factor, which might be indication of dissolution of carbonate minerals such as calcite and/or dolomite. Whereas the second factor is considered to be a factor related to the dissolution of halite and mirabilite, as well as the weathering of silicate minerals. Moreover, the loading of Na<sup>+</sup> is high and negative in FA1, which might be an indication of ion exchange. These considerations can be demonstrated by other Hydro-chemical methods.

As can be seen from Fig. 4, the CA groundwater samples have Ca<sup>2+</sup>/Na<sup>+</sup> and Mg<sup>2+</sup>/Na<sup>+</sup> ratios in range of 0.01 to 1.05 and 0.005 to 0.613, respectively and suggest that dissolution of evaporate and weathering of silicate minerals are dominant in the CA. However, as to the TA groundwater samples, they have much higher Ca<sup>2+</sup>/Na<sup>+</sup> (0.67-57.9) and Mg<sup>2+</sup>/Na<sup>+</sup> (0.37-35.7) ratios, which indicate that dissolution of carbonate and weathering of silicate are the main processes controlling the groundwater chemistry, similar to the results obtained by factor analysis.

## CONCLUSIONS

Based on the statistical analysis of major ion concentrations in groundwater samples from two aquifer systems in the Zhuzhuang coal mine, northern Anhui Province, China, the following conclusions have been obtained:

The major ion concentrations of the groundwater samples from the coal bearing and limestone aquifer system are different with each other. They are dominated by Na-HCO<sub>3</sub> and Ca-HCO<sub>3</sub> types, respectively. Correlation and factor analysis indicate that dissolution of evaporate and weathering of silicate are responsible for the chemical variation of the groundwater samples from the coal bearing aquifer system, whereas dissolution of carbonate and weathering of silicate are responsible for the chemical variation of the groundwater samples from the limestone aquifer system. The results can be well confined by traditional Hydro-chemical methods.

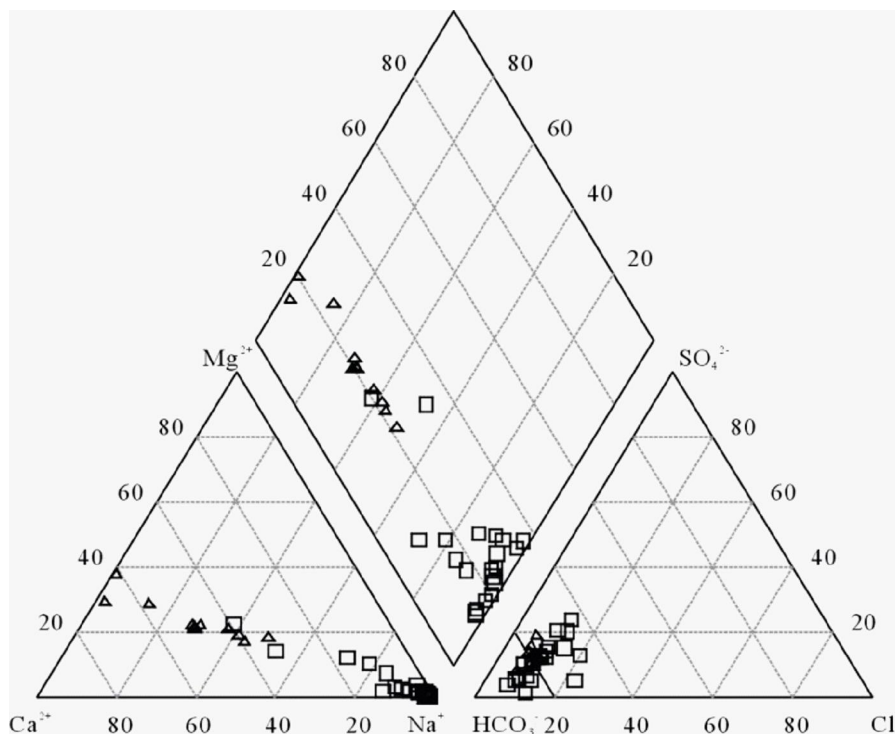


Fig.2: Piper diagram (Square - CA groundwater, Triangle - TA groundwater).

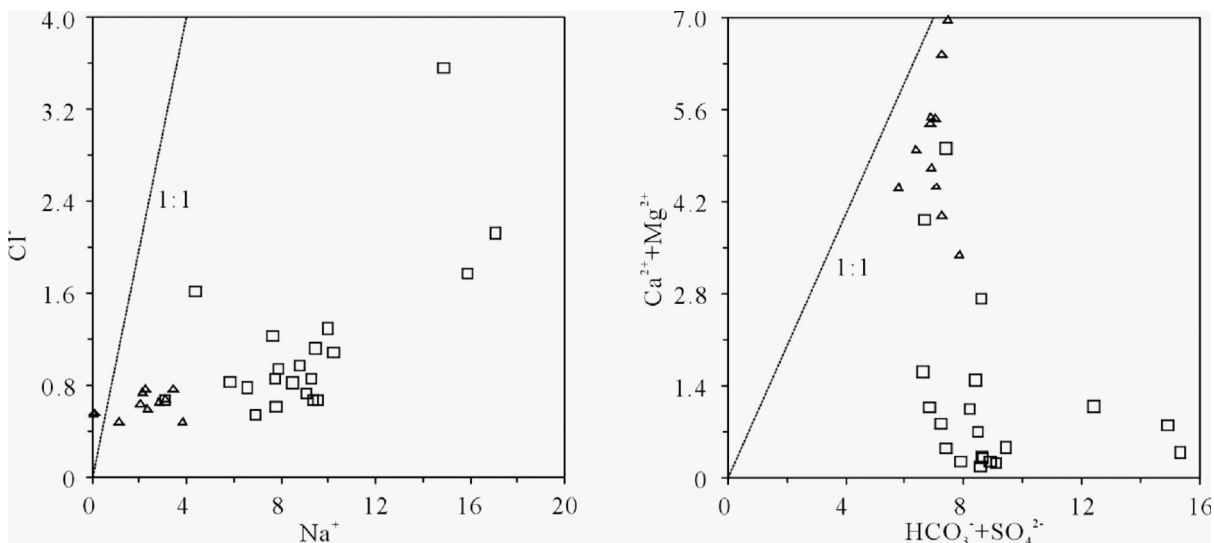


Fig. 3: Na<sup>+</sup> versus Cl<sup>-</sup> and (HCO<sub>3</sub><sup>-</sup> + SO<sub>4</sub><sup>2-</sup>) versus (Ca<sup>2+</sup> + Mg<sup>2+</sup>) diagrams.

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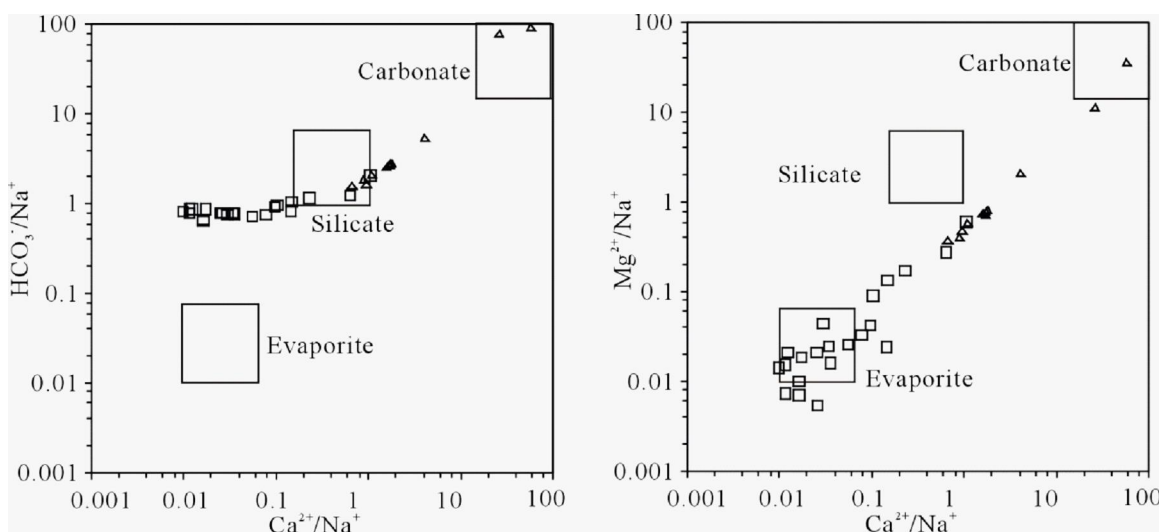


Fig. 4:  $\text{Na}^+$  normalized  $\text{Ca}^{2+}$  versus  $\text{HCO}_3^-$  and  $\text{Ca}^{2+}$  versus  $\text{Mg}^{2+}$  plots.

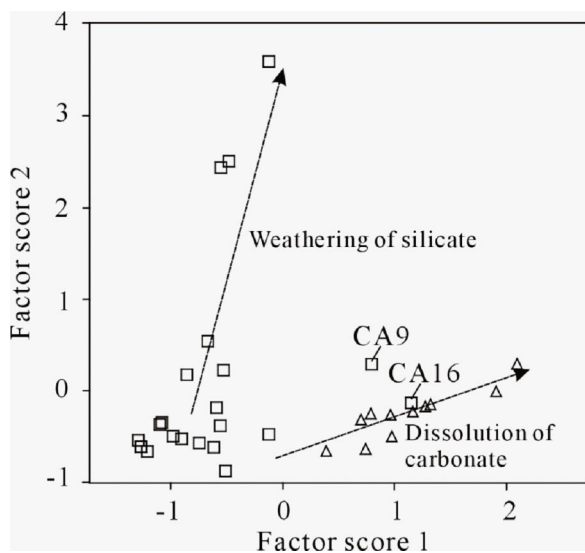


Fig. 5: Plots of factor scores.

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