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Geochemical study of groundwater mineralization in Guanzhong Basin, Shaanxi province, NW China

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ABSTRACT

The objective of this study is to determine the main geochemical processes that affect the formation and genesis of geothermal water in the Guanzhong Basin. Samples in different zone and different depth are taken and analyzed to reflect the variety of chemical characteristics of geothermal water in the area. Based on the chemical analysis, the main water chemical actions are the decarbonation and desulfurization function. Dissolution, Decarbonation reaction is happened widely in Guanzhong basin while desulfurization function is only found in deep stratum of Xi'an. Dissolution of calcite results in the Ca-HCO_3 type water of mountainfront recharge area.

Keywords: Guanzhong basin; Groundwater; Hydrochemical characteristics; Mineralization; Geochemical process; Dissolution

1. Introduction

Groundwater from the Guanzhong Basis is one of the most important sources for the industrial and agricultural activities in Xi'an. Problems, such as the decrease in water levels exist because of the groundwater exploiting, especially the exploiting of geothermal water. Scientists have carried out a number of studies, and most of them focus on exploitation and management of groundwater source. Zhang et al. analyzed groundwater storage system and provided suggested measures for the sustainable development of groundwater resources for the Guanzhong basin [1]; Wang et al. simulated the regulation capacity of groundwater reservoirs in the piedmont of the Qinling Mountain for Guanzhong Basin [2]. Isotopic methods were used in indentifying characteristics such as the formation of geothermal water, storing temperature, and circulation depth [3,4]. But systemic geochemical mechanism research for Guanzhong Basin is rare and it is necessary.

The purpose of this paper is to study all the geochemical processes in different location and different depth in Guanzhong basin. The geochemical processes are responsible for the spatiotemporal variations in groundwater chemistry [5]. Understanding the geochemical processes of groundwater is important for sustainable development and effective management of groundwater resources in Guanzhong basin.

2. Background

Guanzhong basin is located in the central of Shaanxi province, north eastern China, covering an area of

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19,000 km^2. It is bordered in the east by the Yellow River, in the north by the Bei Mountain and in the south by the Qinling Mountain, and extends to Baoji in the west. The climate of Guanzhong basin is between arid and semiarid. The mean annual precipitation is 530–700 mm, and the mean annual evaporation rate is as high as 900–1200 mm. Most precipitation in the Guanzhong basin occurs during July, August and September. Wei River is the main river in the area, which has collected hundreds of tributaries.

The aquifers of the area are mainly Quaternary gravel aquifer and tertiary fracture aquifer. Quaternary aquifer is more than 800 m deep, consists of porous, Aeolian, alluvial and diluvial Quaternary sediments, overlaid by an aquitard of sandy and silty clay. The tertiary aquifer is thousands of meters thick, consisting of brown-red mudstone, silty mudstone imbedded with medium-grained feldspar sandstone [6]. The major geothermal reservoirs include the Zhangjiapo group stratum, the Lantian–Bahe group stratum and the Gaolingqun group stratum of Tertiary System from the top to down. The Lantian–Bahe group, as the main exploitation geothermal aquifer in the basin, is fluvial and lacustrine sediments. The upper lithology is made up of brown mudstone, mudstone with fine sandstone, middle sandstone and grey slitstones. The bottom lithology takes on an uneven interbedded structure formed by light-brown mudstone, off white and dark fine sandstone, middle sandstone and grit. They have average depth of 2127.85 m, temperature of 88.6°C and artesian flux of 2.7574 m^3 h^{-1}. In this paper, most of the geothermal water samples were taken from this aquifer. All the sampling stations of cold water are in Quaternary gravel aquifer while the geothermal water samples are from tertiary fracture aquifer.

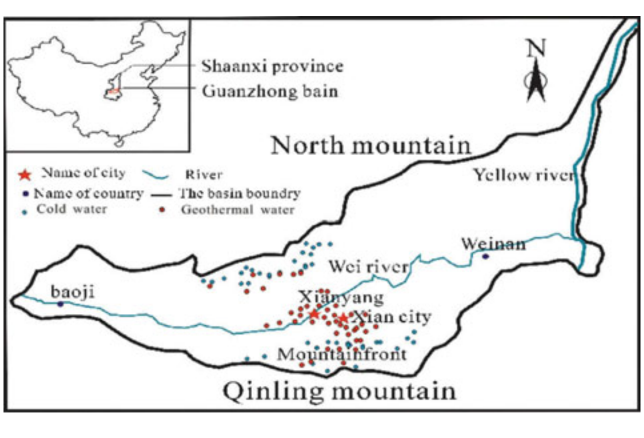

Fig. 1. Location map of the study area.

The sampling zone and sampling points are showed in Fig. 1. The hollow round which has light color represent cold water while the solid round which has a dark color represent geothermal water.

Based on the geographic location, water types and geological structure, the Guanzhong Basin is classified into 5 small zones and sampling areas. From north to south, these zones are Wei Bei, North of Xianyang, South of Xianyang, Xi'an and mountainfront. Mountainfront, refers to the suburbs area north of Qinling Mountain, such as Chang'an county, Zhouzhi county, Lan Qian county. Xi'an, Xianyang sampling area is the urban area of Xi'an and Xianyang cites. F.1 fault lie across Xianyang city, and the area in the North of the fault is signed as North of Xianyang while the South of it is signed as South of Xianyang. Wei Bei sampling area also include portion of Xianyang suburb lying south of North Mountain. All the legends of the paper adopt abbreviations; for example, Xi'an represents Xi'an geothermal water, mountainfront represents mountainfront geothermal water. All the geothermal water samples were labeled in bold character style while the cold water samples were labeled in tint character style.

3. Hydrochemical characteristics of groundwater

Major ions of groundwater are plotted on the Piper trilinear diagram [6] in order to distinguish the different water types in study area. The water in the area can be classed into four major types based on their hydrochemical properties. All the samples of cold water contain HCO_3^- anions. The cold water from mountainfront is Ca-HCO_3 type while the cold water from Wei bei belongs to Na-HCO_3 type. Geothermal water from Xi'an, mountainfront and the South of Xian Yang fall into Na-SO_4 or Na-HCO_3 categories. Geothermal water from Wei bei and North of Xian Yang belong to the Na-Cl type water (Fig. 2).

Schooler diagram was used in identifying the distribution of main ions. Cold water in the recharge area is in rich of Ca^{2+}, Mg^{2+} and HCO_3^- ions while the geothermal water of Xi'an and Xianyang are in rich of Na^+, Cl^-, which shows an obvious geochemical evolution process from the recharge water to discharge water. In the North of Fault 1(including Wei Bei and north of Xianyang), water composition is simpler and the main anion and cation are Cl^- and Na^+ respectively. However, in the South of Fault 1(including south of Xianyang and Xi'an), SO_4^{2-} ions are present in quantity. TDI and SO_4^{2-} (Fig. 3) are in linear relation indicating that SO_4^{2-} is the dominant ion in these area. It is necessary to discuss the source of SO_4^{2-} ions.

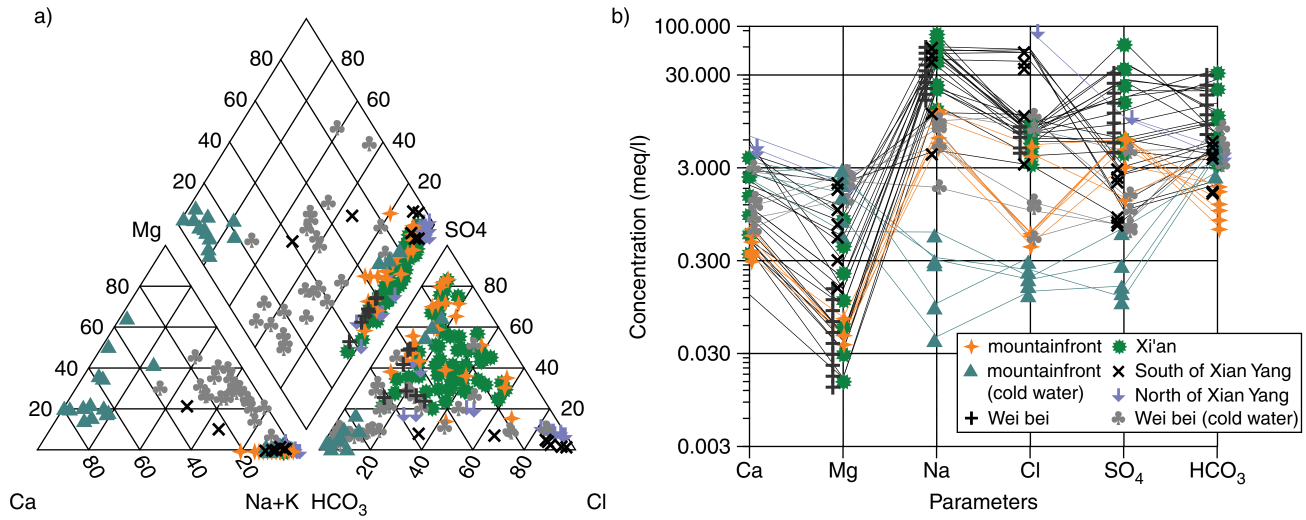

Fig. 2. Piper diagram and schooler diagram of the water samples in Guanzhong basin.

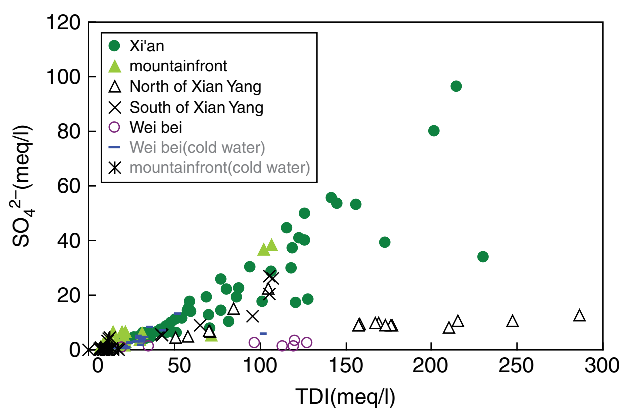

Fig. 3. The relationship between TDI, SO_4^{2-}.

4. Groundwater mineralization processes

4.1. Desulphurization and decarbonation reactions

In deep stratum, where groundwater storage environment is relatively closed, organic sediments undergo desulphurization reaction in closed environment as Eq. (1) showed. The desulphurization reaction increases the concentration of H_2S and decreases the concentration of SO_4^{2-} in the water. According to Fig. 4, the H_2S appears in the stratum deeper than 1500 m, because in shallow stratum environment is open and not suitable for desulphurization. Hence the concentration of H_2S is increasing as water depth increases in the Guanzhong basin:

$$SO_4^{2-} + 2C + 2H_2O \rightarrow H_2S + 2HCO_3^- \quad (1)$$

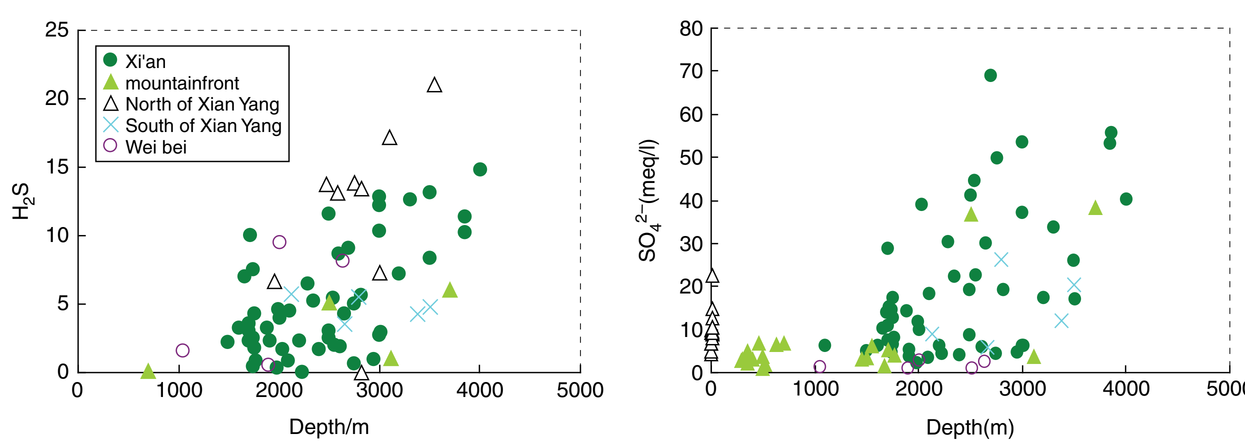

Fig. 4. The relationship between H_2S, SO_4^{2-} and depth.

Interestingly, SO_4^{2-} in Xi'an basin is not decreasing as the depth increases, and on the contrary, the concentration increases in deeper water. Therefore, it is concluded that SO_4^{2-} could have some other supply source in deep stratum. Samples of Xi'an has a strong linear relation but do not plot on the $[Ca^{2+}] = [SO_4^{2-}]$ line in diagram of Ca^{2+} ves. SO_4^{2-} (Fig. 6(b)), it inclines to the side of SO_4^{2-}. This indicates that the gypsum is not the only source of SO_4^{2-} in Xi'an geothermal water.

The diagram of $\delta^{34}S$ vs. $\delta^{18}O$ is used to identify different sources of SO_4^{2-}. According to the predecessors study results, different source of SO_4^{2-} has different isotope contents, with geothermal water in Xi'an plot near the land evaporate zone (Fig. 5). Hence, it is concluded that the other source of SO_4^{2-} in Xi'an geothermal water is from oxidation of land evaporation rock.

While the deep groundwater is flowing upward, calc-sinter is formed around the wells in a decarbonation process. During this process, Ca^{2+} and Mg^{2+} ions precipitates from groundwater as Eqs. (2), (3) showed, and consequently, Na^+ ions dominate groundwater. Field observation revealed the presence of calcite in the shallow stratum, and much CO_2 exist in the geothermal water, especially in Weibei and Xianyang. This observation suggests that decarbonation reaction has also occured in Guanzhong basin:

$$Ca^{2+} + 2HC0_3^- \rightarrow CaC0_3 \downarrow + H_2O + CO_2 \uparrow \quad (2)$$

$$Mg^{2+} + 2HC0_3^- \rightarrow Mg\,C0_3 \downarrow + H_2O + CO_2 \uparrow \quad (3)$$

4.2. Dissolution function

Fig. 6(a) shows a linear relation of increasing concentration between Ca^{2+} and HCO_3^- for samples of mountainfront cold water, which could be explained by dissolution of calcite that can be written as $CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^-$. On the other hand, samples of other areas did not display a clear linear relationship between concentrations of Ca^{2+} and HCO_3^- ions. This corresponds to the characteristics of high HCO_3^- in the water recharge zone.

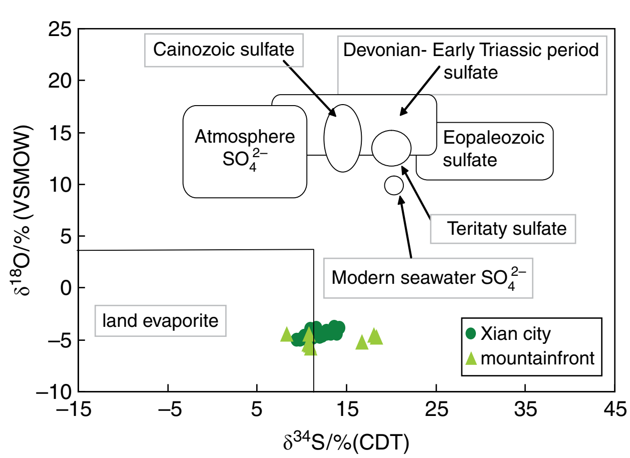

Fig. 5. Contrasting diagram of ^{34}S vs. ^{18}O in land evaporite, seawater and atmosphere source sulfate.

Fig. 6(b) shows the relationship between Ca^{2+} and SO_4^{2-} for the groundwater groups. Samples from North of Xian Yang plot close to the gypsum dissolve line, indicating the dissolution of gypsum in North of Xian Yang. Concentrations of SO_4^{2-} and Ca^{2+}ions in Xi'an has some linear relation, but the plots were far from $[Ca^{2+}] = [SO_4^{2-}]$ line and inclined towards greater SO_4^{2-} concentrations. Therefore, its SO_4^{2-} could have another source not only from gypsum dissolve.

The Na–Cl relationship has often been used to identify the mechanism for acquiring salinity and saline intrusions [7]. According to Fig. 6(c), geothermal water in Xi'an, mountainfront and Xian Yang have high Na^+ concentration; but the lack of Cl^- means that it could not be from dissolution of halite, because concentrations of Na^+ and C^- would have a good correlation if the water were from halite dissolution. The high Na/Cl ratio is probably due to water—rock reaction such as Eq. 4. Samples from Wei bei and North of Xian Yang plot close to the $[Na^+] = [Cl^-]$ line, so the dissolution of halite occurred in Wei bei and North of Xian Yang geothermal water:

$$2NaAlSi_3O_4 + 9H_2O + 2H_2CO_3 = Al_2Si_2O_5(OH)_4 + 2Na^+ + 2HCO_3^- + 4H_4SiO_4 \quad (4)$$

4.3. Cation exchange, mixing and evaporation

In Fig. 6(d), with Na^+ increasing, Ca^{2+} concentration is also increasing. This result contradict the characteristics of cation exchange process, since it is expected to observe the decrease in concentration of one cation and the increase in concentration of another cation in a cation exchange process. Dissolution reaction, is one of dominant reactions in the study area, which may cover the function of cation exchange.

Mixing reaction mainly refers to mixing of water of different depth in the study area when the geothermal water is pumped out from aquifer. The pressurized geothermal water is unlikely to recharge by cold water.

Evaporation is one of common geochemical processes of groundwater. Evaporation may make affect the contents of the groundwater and lead to a high content of TDI and Cl^-, but it is not a leading processes in the study area.

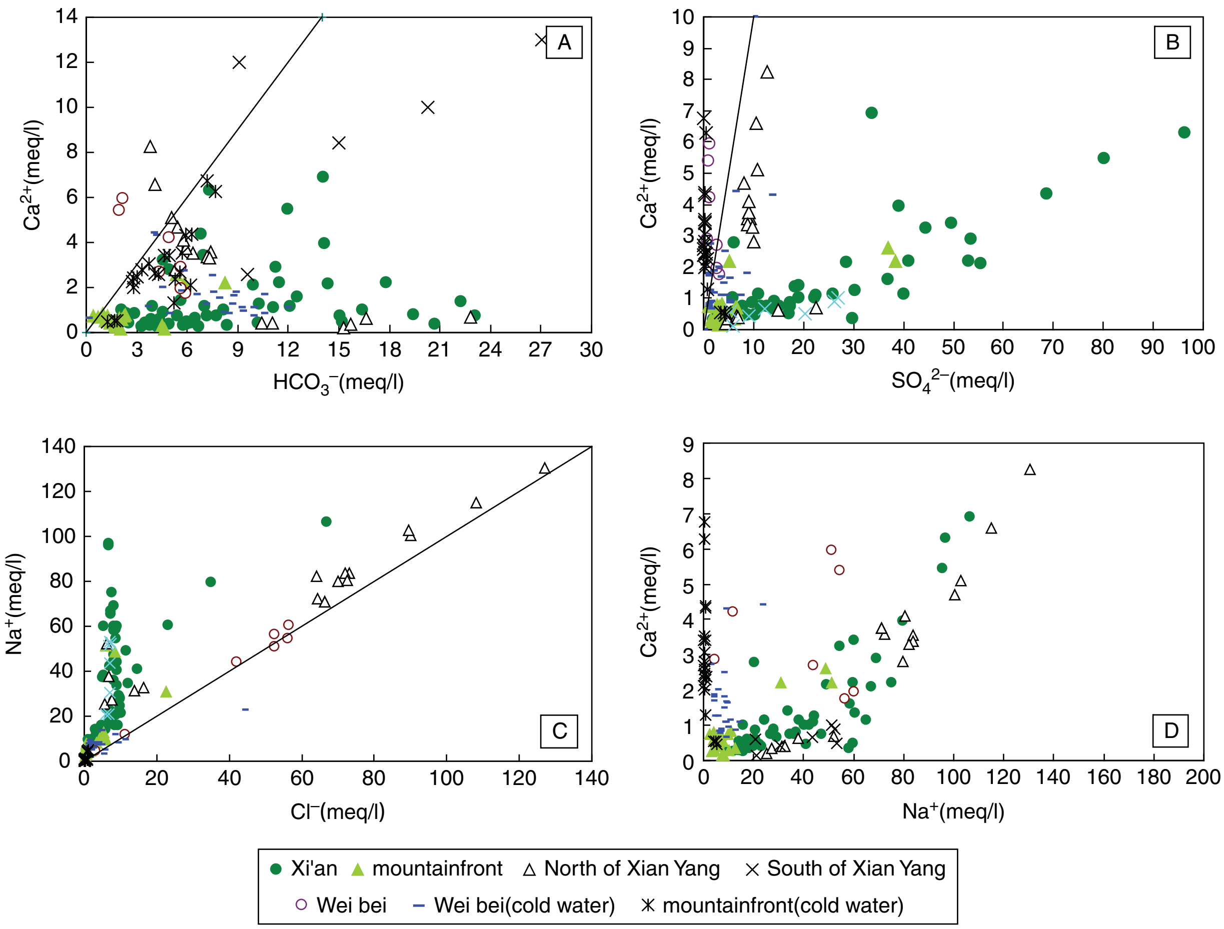

Fig. 6. The relationship between Ca^{2+} and HCO_3^-, Ca^{2+} and SO_4^{2-}, Na^+, and Cl^- concentration.

5. Conclusions

a. The groundwater in Guanzhong basin has a large variety of groundwater geochemistry; it can be classified into four main groups: Na–Cl (Wei bei and North of Xianyang geothermal water), Na–HCO_3 (cold groundwater from Weibei), Na–SO_4–HCO_3 (geothermal water of mountainfront and Xi'an), and Ca–HCO_3 (cold groundwater from mountainfront).

b. Dissolution reaction is the main geochemical processes taking place in Guanzhong basin. The dissolution of calcite mainly occurred in the mountainfront cold groundwater and the dissolution of halite was mainly found in Weibei and North of Xianyang geothermal water. High contents of Na^+ and Cl^- in North of Xianyan and Wei bei are derived from the dissolution of halite, and the dissolution of Albite is another potential source of Na^+. Water chemistry process in South of Xianyang and Xi'an is complex; chemical analysis indicates that SO_4^{2-} in Xi'an geothermal water is from oxidation of land evaporation rock and gymsum dissolution.

c. Desulphurization and decarbonation reaction is another geochemical process in Guanzhong basin. Decarbonation function happens commonly in geothermal water exploiting process. Desulphurization reaction is an important source for SO_4^{2-}.

d. Cation exchange, mixing, evaporation and anthropogenic activities are not the main geochemical processes in study area.

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