Hydrogeochemical features and origin of geothermal water of carbonate rocks in the NE Guanzhong Basin, China

Panpan Xu1,2, Qiying Zhang1,2 and Hui Qian1,2,3

1 School of Water and Environment, Chang’an University, Xi’an 710054, Shaanxi, China;

2 Key Laboratory of Subsurface Hydrology and Ecological Effects in Arid Region of the Ministry of Education, Chang’an University, Xi’an 710054, Shaanxi, China

3 Email: qianhui@chd.edu.cn

Abstract. A great number of geothermal waters in carbonate rocks are located in the NE Guanzhong Basin. Hydrogeochemical features and genesis of geothermal waters in carbonate rocks were investigated by hydrogeochemical and statistical methods. The results show that the geothermal water in carbonate rocks is basically fresh water with the dominant water type of Na-HCO3. The hydrogeochemistry of geothermal water is governed by water-rock interaction, and the reservoir environment of geothermal water is open. The origin of geothermal water can be the atmospheric infiltration water. This study is aimed to provide the scientific basis for the sustainable development and utilization of geothermal waters of carbonate rocks in Guanzhong Basin.

1. Introduction

With the exhaustion of oil, coal, natural gas and other traditional energy sources, geothermal energy is favored by people due to its rich resources, low environmental pollution and low operating costs [1-3]. Geothermal energy is clean and environmentally friendly, which has been extensively exploited and utilized for power generation, agricultural heating, fishery, and other purposes [4]. Nowadays, low to medium temperature geothermal resources are being investigated for potential exploitation in China. And the NE Guanzhong Basin is a case region [4-5].

Geothermal resources in the Guanzhong Basin were used as early as the Western Zhou Dynasty [4]. However, the water level in geothermal wells declines continuously since 1990, which indicates that the exploitation of geothermal water exceeds its recharge [6]. Therefore, it is very important to develop geothermal water resources reasonably. At present, there are a great number of studies on geothermal waters in Guanzhong Basin. For instance, Qin et al. [6] explored age and recharge source of geothermal waters in Xi’an area using hydrogeochemistry and isotopic properties. Qin et al. [7] explored the source of recharge and estimation of temperature for the Xi’an geothermal field, China. Ma et al. [8] determined the origin and classification of geothermal water in Guanzhong basin by geochemical and isotope methods. Xu et al. [4] identified the processes affecting the geothermal water compositions and gave a reliable estimation of temperatures of geothermal reservoirs in the Xi’an field. Nevertheless, the studies on geothermal water in carbonate rocks of the North Mountains in the Guanzhong Basin are relatively few. To meet this lack, the geothermal field in North Mountains was investigated by hydrogeochemical and statistical methods. Therefore, this study aims to explore hydrogeochemical features, natural evolution mechanisms and origin of geothermal waters in...
carbonate rocks of the North Mountains. It is intended to provide fundamental understanding for decision makers to pursue the development and utilization of geothermal resources in the North Mountains and the Guanzhong Basin.

2. Study area
The Guanzhong Basin (106°30′ ~ 110°30′E, 33°00′ ~ 35°20′N) is located in the middle of Shaanxi Province, China [4]. It is distinguished by an E-W length about 360 km and the N-S width 30-80 km with an area of 2×10^4 km^2 [6, 9]. It is a graben basin in a nearly E-W trend within the western Yellow River, eastern Baoji Canyon, northern Qinling Mountains and southern North Mountains. In this area, there is a warm temperate semi-humid continental monsoon climate with average annual temperature and precipitation of 13.7 °C and 569.6 mm, respectively [4]. Evaporation is generally between 1000-1200 mm/yr [10].

The geothermal waters in carbonate rocks are widely distributed in the northern part of the Guanzhong basin (Figure 1). In the study area, the reservoir rocks are of carbonate rocks and argillaceous carbonate rocks [9]. Geothermal water mainly occurs in Karst fissures of Paleozoic carbonate rocks [9].

Figure 1. Simplified geographic map and sampling locations of study area in the Guanzhong Basin, China.

3. Sampling and assessment methods
Totally, 20 water samples were collected from geothermal production wells with depths between 99 and 1215 m in the study area in 1999. The sampling locations are shown in Figure 1. The in-situ parameters such as temperatures, pH and TDS (total dissolved solids) of geothermal water samples were measured in the field using portable multiparameter equipment. SO_4^{2-} and Cl^- were measured by IC (ion chromatography), and HCO_3^- was determined by alkalinity titration. The cations (K^+, Na^+, Ca^{2+} and Mg^{2+}) and SiO_2 were analysed by an AA-100 atomic absorption spectrometer. The total amount of K^+ and Na^+ is approximately calculated as Na^+ content in data processing because of the content of K^+ much less than that of Na^+. The values of the charge balance error (CBE) within the range of ±5% are considered acceptable [11]. The CBE values of all water samples were between 0.47 % and 4.27 % with an average value of 1.87 %, suggesting that the analysis of ion contents is reliable.
4. Results and discussion

4.1. Physiochemical parameters

The statistical characteristics of physicochemical parameters of geothermal water samples are shown in Table 1. The temperatures of water samples ranged from 25.0 °C and 41.0 °C, with an average value of 30.1 °C. The pH of water samples was between 7.2 and 8.1 (mean=7.7) which indicates weak alkaline geothermal water in the study area. TDS values were low with the wide range of 423.5-1092.2 mg/L (mean=768.8 mg/L). 90% of the water samples were lower than 1000 mg/L belonging to freshwater. The SiO2 concentration varied from 0.1 to 24.1 mg/L with mean of 17.5 mg/L.

As shown in Table 1, the order of average cation contents was of Na⁺ + K⁺ > Ca²⁺ > Mg²⁺ with values of 143.0 mg/L, 83.0 mg/L and 40.9 mg/L, respectively. The mean abundance of anions in all samples was HCO₃⁻ > SO₄²⁻ > Cl⁻ with values of 335.4 mg/L, 219.7 mg/L and 113.5 mg/L, respectively.

Table 1. Physicochemical characteristics of geothermal water in study area.

| Parameters | T(°C) | pH  | TDS (mg/L) | K⁺+Na⁺ (mg/L) | Ca²⁺ (mg/L) | Mg²⁺ (mg/L) | Cl⁻ (mg/L) | SO₄²⁻ (mg/L) | HCO₃⁻ (mg/L) | SiO₂ (mg/L) |
|------------|-------|-----|------------|---------------|-------------|-------------|------------|-------------|-------------|-------------|
| Maximum    | 41.0  | 8.1 | 1092.2     | 242.3         | 113.1       | 50.1        | 230.0      | 393.8       | 466.7       | 24.1        |
| Minimum    | 25.0  | 7.2 | 423.5      | 88.6          | 48.1        | 22.5        | 12.5       | 67.2        | 249.9       | 0.1         |
| Mean       | 30.1  | 7.7 | 768.8      | 143.0         | 83.0        | 40.9        | 113.5      | 219.7       | 335.4       | 17.5        |

4.2. Hydrochemical facies

The Piper diagram [12] provides a tool for classification and comparison of water types excellently [13]. As shown in Figure 2, the Na-HCO₃ was dominant water type in the study area accounting for 60% of the water samples, with some minor hydrochemical facies of Na-SO₄, Ca-HCO₃ and Na-Cl. In general, these results show that geothermal water in study area belongs to carbonate water with low salinity.

Figure 2. Piper diagram of the geothermal water samples in the study area.
4.3. Natural evolution mechanisms
Gibbs diagrams are helpful to determine the main natural factors governing the formation mechanism of groundwater [14]. According to Gibbs diagrams, there are three major mechanisms: rock dominance, evaporation dominance, and precipitation dominance [15]. In Figure 3, the geothermal water samples were basically located in the zone of rock dominance suggesting the hydrogeochemistry of geothermal water dominated by water-rock interactions.

![Gibbs diagrams of the geothermal water samples in study area.](image)

**Figure 3.** Gibbs diagrams of the geothermal water samples in study area.

| Catalog | T | pH | TDS | K⁺+Na⁺ | Ca²⁺ | Mg²⁺ | Cl⁻ | SO₄²⁻ | HCO₃⁻ | SiO₂ |
|---------|---|----|-----|-------|------|------|-----|-------|-------|------|
| T       | 1 |    |     |       |      |      |     |       |       |      |
| pH      | -0.29 | 1 |     |       |      |      |     |       |       |      |
| TDS     | 0.55* | -0.13 | 1 |       |      |      |     |       |       |      |
| K⁺+Na⁺  | 0.45* | -0.07 | 0.91** | 1 |      |      |     |       |       |      |
| Ca²⁺    | 0.62** | -0.34 | 0.80** | 0.53* | 1 |      |     |       |       |      |
| Mg²⁺    | 0.25 | -0.00 | 0.69** | 0.46* | 0.57** | 1 |      |       |       |      |
| Cl⁻     | 0.65* | -0.17 | 0.94** | 0.88** | 0.81** | 0.47* | 1 |       |       |      |
| SO₄²⁻   | 0.48* | -0.05 | 0.92** | 0.72** | 0.80** | 0.80** | 0.79** | 1 |       |      |
| HCO₃⁻   | -0.59** | 0.01 | -0.55* | -0.34 | -0.71** | -0.26 | -0.66** | -0.69** | 1 |      |
| SiO₂    | 0.47* | -0.36 | 0.30 | 0.24 | 0.36 | 0.02 | 0.40 | 0.26 | -0.41 | 1 |

*Significant at the 0.05 level (2-tailed).
**Significant at the 0.01 level (2-tailed).

4.4. Correlation among parameters
The correlations among water parameters can define some related hydrogeochemical relationships [16]. As shown in Table 2, contents of the major ions (except for HCO₃⁻) were significantly and positively correlated with temperature and TDS. Concentration of Na⁺+K⁺ was correlated with Cl⁻ at
the 0.01 significant level (r=0.88), which indicates that their primary source can be halite dissolution. The correlation of Ca$^{2+}$ with SO$_4^{2-}$ was strongly positive (r=0.80), which suggests the dissolution of gypsum can be considered as the major source of Ca$^{2+}$ and SO$_4^{2-}$. HCO$_3^-$ showed a significantly negative correlation with Ca$^{2+}$ (r=-0.71), and a weakly correlation with Mg$^{2+}$ (-0.26). The possible reason for this phenomenon was that the cation exchange reaction resulted in the decrease of concentration of Ca$^{2+}$ and Mg$^{2+}$ and the increase of Na$^+$, which promoted the dissolution of calcite and dolomite providing a large number of HCO$_3^-$. 

4.5. Origin of geothermal water

Hydrochemical coefficients, for example $r_{Na^+/Cl^-}$, $r_{SO_4^{2-}\times100/Cl^-}$ and $r_{Mg^{2+}/Cl^-}$, were obtained for description of the origin of geothermal water. The calculation of these coefficients was presented in Table 3.

$r_{Na^+/Cl^-}$ ratio, called metamorphic coefficient, is an index reflecting the closure degree of hydrogeochemical environment [17]. This ratio is designed to determine the origin (including marine or meteoric) of groundwater [18]. The values of $r_{Na^+/Cl^-}$ ratio ranging from 1.24 and 12.85 (mean=2.75) were greater than 1 suggesting that the geothermal water in the study area have a meteoric origin with an open reservoir environment.

$r_{SO_4^{2-}\times100/Cl^-}$ ratio, named desulfurization coefficient is greater than10.26, which indicates that the geothermal water is generated in an open hydrogeochemical environment [17]. The $r_{SO_4^{2-}\times100/Cl^-}$ value varying 71.97 to 566.18 (mean=179.01) was larger than 10.26, suggesting that reservoir environment of geothermal waters is open.

$r_{Mg^{2+}/Cl^-}$ ratio is also an important indicator in detecting origin of groundwater, and its value above or below 0.5 indicates the fresh water and groundwater, respectively [19]. The $r_{Mg^{2+}/Cl^-}$ ratio of all water samples ranging from 0.52 to 9.10 (mean=1.65) was greater than 0.5, indicating that the geothermal water in the study area has a meteoric origin.

| Parameters | $r_{Na^+/Cl^-}$ | $r_{SO_4^{2-}\times100/Cl^-}$ | $r_{Mg^{2+}/Cl^-}$ |
|------------|-----------------|-----------------------------|-------------------|
| Range      | 1.24~12.85      | 71.97~566.18                | 0.52~9.10         |
| Mean       | 2.75            | 179.01                      | 1.65              |

5. Conclusions

This study was undertaken to explore hydrogeochemical features and origin of geothermal water in carbonate rocks of the Northeast of Guanzhong Basin by hydrogeochemical and statistical methods. The geothermal water of carbonate rocks in study area mainly occurs in Karst fissures of Paleozoic carbonate rocks. It basically belongs to freshwater with TDS less than 1000mg/L. The main anion and cation are HCO$_3^-$ and Na$^+$, followed by SO$_4^{2-}$ and Ca$^{2+}$. The Na-HCO$_3$ is dominant water type. Water-rock interaction of geothermal water is weak, and its governing role is rock weathering and leaching. The geothermal water is mainly meteoric origin within an open hydrogeochemical environment. This study can provide a scientific basis for the development and utilization of geothermal waters of carbonate rocks in NE Guanzhong Basin.

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