Application of geothermal thermometric scale in the study of deep reservoir temperature

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Abstract
The aim of this work is to determine the thermal storage temperature of a deep thermal reservoir, which has a great significance for the effective utilization of geothermal resources. The temperature of the reservoir was estimated by the cation ratio geothermometer and SiO₂ geothermometer methods. The results indicate that the K–Mg geothermometer is the best method of the cation ratio methods, with the calculated temperature of 108°C. The average value calculated by the SiO₂ method was 107°C. The measured temperature of the GRY1 drilling water sample in the Cangxian arch belt was 108°C. Because the calculated results of the geothermometers were consistent with the measured value of the borehole water, the K–Mg and SiO₂ geothermometers are suitable for the estimation of deep heat storage temperatures.

Keywords
Geothermometer, deep heat storage, Cangxian arch belt, water–rock balance, predict temperature

Introduction
China’s environmental problems caused by fossil fuels are severe and have affected human health and the ecosystem, particularly for the Beijing–Tianjin–Hebei region. China’s social
development is working closely with energy advancement by reducing the use of fossil fuels and focusing on clean energy. The potential for the development and utilization of geothermal resources is increasingly appealing due to geothermal’s environmental safety and sustainability.

Various Chinese researchers have investigated geothermal exploration (Wang and Sun, 2000). Due to the high risk and cost of deep-drilling exploration, geothermal research has been concentrated on shallow geothermal resources. Studies regarding the characteristics of deep heat storage are recognizably insufficient. Hydrogeochemistry, gas geochemistry, and the isotopic geochemical indicators of geothermal fluids contain information about the deep geological environment and geothermal fluid systems. These analyses are also the most cost-effective way to study underground thermal storage during geothermal exploration. Geothermometers are the most used methods to estimate a thermal reservoir’s temperature (Ding, 2013; Fournier and Ii, 1979; Wang, 2017).

The Cangxian arch belt is located in the central plains of Hebei Province and belongs to a geothermal anomaly area. The geophysical drilling data of the area show that the geothermal gradients vary in different depth sections. In the past, the study of heat storage temperatures primarily concentrated on shallow depths, generally between 500 and 3000 m. The hydrogeology team of the Hebei Coalfield Geology Bureau successfully completed the first deep thermal storage borehole in the entire Beijing–Tianjin–Hebei area, with a hole depth of 4025.82 m, exposing the Mesoproterozoic Jixian, with the final layer in the Changcheng system. Above the Gaoyuzhuang Formation, a medium-temperature thermal reservoir was found in the Changcheng system. The temperature at a depth of 4004.93 m reached 108°C, which has provided valuable information for the study of deep karts’ heat storage.

The aim of this study was to examine the equilibrium state between the minerals and fluids by using the results of the deep geothermal fluid tests. The PHREEQCI program and Na–K–Mg balance diagram were used, and the deep heat storage temperature of the Cangxian arch belt was estimated using geothermometer equations. The measured values of the pore heat reservoir temperature were compared with the calculated values, and the geothermometer methods were assessed for the appropriate evaluation of heat storage in this area. This method may provide a theoretical basis to predict the temperature within deep heat storage (including dry, hot rock formations).

**Overviews of study area**

The study area is approximately 6396 km², located in the middle of the Hebei Plain, with Cangzhou–Wuqiao bordering on the east and Wuyi–Xianxian–Dacheng County on the west. The northern boundary line is between Tianjin and Hebei, and the southern border is the Hengde Expressway. The first geothermal well in North China at a depth of 4000 m was drilled in Cangzhou City to ascertain the potential and distribution of heat storage at that depth, as can be seen in Figure 1.

**Geothermal fluid geothermometer**

When the minerals and the fluids in deep heat storage are in equilibrium, the fluid’s chemical composition does not change significantly although the temperature significantly decreases when the fluid reaches the surface. Therefore, the temperature of the heat storage can be estimated by comparing the chemical compositions with the chemicals’ equilibrium
temperatures (Armienta et al., 2014; Fournier, 1977; Helgeson, 1968; Lambrakis and Kallergis, 2005; Saibi and Ehara, 2010). Geothermometers have the advantage of economical speed, and these methods have been compared with the temperature measurement of the borehole. In 1966, Fournier and Mahon proposed the silica thermometer and presented the corresponding equations. White and Fournier demonstrated the Na–K thermometer equations in 1965 and 1979, respectively, and Fournier and Truesdell exhibited the Na–K–Ca thermometer equations in 1973. Research into geothermal fluid thermometers has since made considerable progress.

Cation ratio thermometer

The cationic geothermometer is an empirical approximation of temperature based on the cation exchange ratio. The ratio of the dissolved components in water is temperature-dependent, and this relationship of the geothermal water components is utilized (Giggenbach, 1988; Nieva and Nieva, 1987; Wu et al., 2006).

Many scholars have established the equations for the Na–K geothermometer and Na–K–Ca geothermometer successively (Kaasalainen and Stefánsson, 2012). In many medium–low temperature geothermal fluids, rich in Mg\(^{2+}\), the results of the Na–K–Ca geothermometer estimation have been noticeably higher. Because the Mg\(^{2+}\) correction was needed, Giggenbach established the K–Mg geothermometer in 1988.

Na–K geothermal temperature scale

The Na–K temperature scale is generally applied to hot water above at 150°C, especially in geothermal wells. The water-soluble Na\(^+\)/K\(^+\) under low-temperature conditions has not been generally controlled by the cation exchange reaction between symbiotic alkaline feldspars, which has the advantage of being less affected by dilution and vapor separation.
(Jin-Liang et al., 2014; Truesdell, 1976). In the deep underground hot water, the content of sodium and potassium ions changes regularly with the increase of temperature under natural.

The Na–K geothermal temperature standard generally requires the water sample to be neutral or weakly alkaline chloride and acidic water, it is not suitable for the Na–K geothermal temperature scale to estimate the temperature of its corresponding reservoir thermal. The following equations can be used

\[
t = \frac{1390}{1.75 + \log(Na/K)} - 273.15 \quad (\text{Na–K}^1)
\]  

or

\[
t = \frac{1217}{1.438 + \log(Na/K)} - 273.15 \quad (\text{Na–K}^2)
\]  

or

\[
t = \frac{856}{0.857 + \log(Na/K)} - 273.15 \quad (\text{Na–K}^3)
\]

In the equations, Na and K represent the mass concentrations of sodium and potassium ions in the water sample with units of mg/l.

**Na–K–Ca geothermometer**

The Na–K–Ca geothermometer is primarily used to treat calcium-rich geothermal fluids (Jin-Liang et al., 2014). When the fluids are removed from the high-pressure environment, they are prone to boiling, causing the estimated temperature value to be high because water will be lost through vaporization, and CaCO_3 could precipitate, affecting the calculation accuracy of the Na–K–Ca geothermometer (Wang, 2017)

\[
t = \frac{1647}{\log(Na/K) + \beta (\log \frac{Ca}{Na} + 2.06) + 2.47} - 273.15 \quad (\text{Na–K–Ca})
\]

(unit: mol/kg; \( T < 100^\circ C, \beta = 4/3; T > 100^\circ C, \text{ and } \log(Ca^{0.5}/Na) < 0, \beta = 1/3)\)

In the equation, Na, K, and Ca, respectively, represent the mass concentrations of sodium, potassium, and calcium ions in the water sample.

**K–Mg geothermometer**

The K–Mg geothermometer is suitable for low-temperature underground geothermal fluids (Feng et al., 2012). This geothermometer is based on the ion exchange reaction of potassium feldspar with muscovite and chlorite. This geothermometer not only reacts quickly to changes in temperature but also reaches equilibrium in solution (Wu et al., 2006). The relative content adjustment occurs much faster than with Na–K, even at low temperatures; the temperature scale equation is as follows
In the equation, K and Mg represent the mass concentrations of potassium and magnesium ions in the water sample.

**SiO$_2$ geothermometer**

The solubility of minerals such as quartz, chalcedony, and $\alpha$-cristobalite is a function of temperature (Pasvanoglu et al., 2012). The changes in pressure and salinity have little effect on the solubility of quartz and amorphous silicon below 300°C, so the concentrations can be directly used as a geothermometer. When estimating the underground heat storage temperature, the error is only ±3°C in many cases; the theoretical basis of its application is the dissolution–precipitation equilibrium theory of SiO$_2$ minerals in geothermal fluids. The solubility of SiO$_2$ increases consistently with increasing temperatures. Many scholars have established various SiO$_2$ geothermometer function relationships. These geothermometers are primarily applicable to temperatures ranging from 0 to 250°C. Considering the geothermal geological profile of the study area, the following relationships were selected for calculation and comparison.

**Quartz$^1$ geothermometer**

Quartz geothermometer without steam separation

$$ t = \frac{4410}{14.0 - \log \frac{K}{Mg}} - 273.15 \text{ (K–Mg)} \quad (5) $$

**Quartz$^2$ geothermometer**

Quartz geothermometer without vapor loss

$$ t = -42.198 + 0.28831 \text{ SiO}_2 - 3.6686 \times 10^{-4}(\text{SiO}_2)^2 + 3.1665 \times 10^{-7}(\text{SiO}_2)^3 $$
$$ + 77.034 \log \text{ SiO}_2 $$

**Quartz$^3$ geothermometer**

Quartz geothermometer with steam loss

$$ t = \frac{1309}{5.19 - \log \text{ SiO}_2} - 273.15 \quad (6) $$

**Chalcedony geothermometer**

$$ t = \frac{1032}{4.69 - \log \text{ SiO}_2} - 273.15 $$

**$\alpha$-Cristobalite geothermometer**
\[ t = \frac{1000}{4.78 - \log \text{SiO}_2} - 273.15 \]  

In the equations, SiO\(_2\) represents the mass concentration of silica in the water sample.

### Selection and calculation of geothermometer

Geothermometers to estimate reservoir temperatures such as Na–K, K–Mg, Na–K–Ca, and SiO\(_2\) geothermometer have many empirical equations. Only equation (10) has been used here, and the heat storage temperature has been compared and estimated according to the data in Table 1, with the results presented in Tables 2 and 3.

According to Table 2, the K–Mg geothermometer accurately estimated the thermal reservoir’s temperatures at 108 and 107\(^\circ\)C before and after fracturing, respectively. Combined with the previous Na–K and Na–K–Ca geothermometers, it can be found that the Na–K and Na–K–Ca geothermometers obtained higher values after fracturing than the pre-fracture estimates, while the K–Mg geothermometer had estimated after the fracturing than before the fracturing. This result may have been caused by the sample mixing with a large amount of cold water on the surface during the fracturing process, causing the sample not to meet the necessary conditions of the current geothermometer equation. Although the pumping had been carried out for a long time after fracturing, it is not guaranteed that the water used for fracturing had been removed entirely from the sample collection area, which

| Numbering     | Name                  | pH   | Temperature (°C) | K\(^+\) | Na\(^+\) | Ca\(^{2+}\) | Mg\(^{2+}\) | SiO\(_2\) |
|---------------|-----------------------|------|-----------------|--------|--------|-----------|-----------|---------|
| GRY1          | before hole fracturing | 7.02 | 107.56          | 109.96 | 1951.28| 207.98    | 43.78     | 76.56   |
| GRY1          | after pore fracture   | 7.78 | 107.56          | 112.64 | 1794.94| 234.58    | 49.24     | 112.04  |

| Numbering     | Name                  | Na–K\(^1\) | Na–K\(^2\) | Na–K\(^3\) | Na–K–Ca | K–Mg     | Average value |
|---------------|-----------------------|------------|------------|------------|----------|----------|----------------|
| GRY1          | before hole fracturing | 191.42     | 173.46     | 134.66     | 172.56   | 108.34   | 156.09         |
| GRY1          | after pore fracture   | 197.66     | 188.18     | 142.99     | 175.99   | 107.02   | 162.37         |

| Numbering     | Name                  | Quartz\(^1\) | Quartz\(^2\) | Quartz\(^3\) | Chalcedony | Cristobalite | Average value |
|---------------|-----------------------|--------------|--------------|--------------|-------------|--------------|----------------|
| GRY1          | before hole fracture  | 123.00       | 122.80       | 120.54       | 94.63       | 72.15        | 106.62         |
| GRY1          | after pore fracture   | 144.63       | 143.73       | 139.32       | 117.67      | 93.15        | 127.70         |
also could cause a change in the primary ion mass concentrations. Substantial changes within a specific range result in abnormally high or slightly low values from the calculations. In a low-temperature geothermal area, it is believed that chalcedony controls the content of SiO\textsubscript{2} (Sergio et al., 2014). Because the temperature estimates using chalcedony for medium–low temperature geothermal fluids can generally provide a more accurate value, the calculation results of the chalcedony geothermometer have been compared with the calculation results of the K–Mg geothermometer. The calculation of the K–Mg geothermometer uses the above cation ratios. The results were 108°C before fracturing and 107°C after fracturing. In this temperature calculation, the K–Mg geothermometer was more accurate than the chalcedony geothermometer, but the chalcedony geothermometer was used to analyze the water sample here. The temperature was more reasonable than other SiO\textsubscript{2} geothermometers, and the quartz geothermometer’s estimates were generally slightly higher. The estimated temperature before fracturing was closer to the measured value of the water temperature above the Gaoyuzhuang Formation. The temperature after fracturing had increased by approximately 20°C. The estimated temperature of the \(\alpha\)-cristobalite temperature standard was generally low, and the average temperature before fracturing estimated by the SiO\textsubscript{2} geothermometer was 107°C. The average temperature after fracturing was 128°C, which was higher than the water sample here. The measured temperature was slightly higher, which also confirms that the SiO\textsubscript{2} geothermometer demonstrates relatively high reliability in the estimation of underground geothermal fluid temperatures in this area.

As indicated by the SiO\textsubscript{2} geothermal thermometer in Table 3, the estimated temperature of the GRY1 borehole after fracturing was higher than before fracturing. This result could be due to the long-term high-strength fracturing process causing the pores in the upper part of the aquifer of the Gaoyuzhuang Formation to conduct heat, enhancing the hydraulic connection.

**Mineral–fluid chemical balance judgment**

Geothermal fluid geothermometers are used to estimate the reservoir temperature by geothermal borehole sampling (Moller et al., 2004). Each geothermometer has certain applicable conditions, and when determining which method to use, it is necessary to consider the following basic conditions: (1) the material must be sufficient, (2) the water–rock equilibrium must be balanced, and (3) the water (gas) does not rebalance during the migration to the sampling point. Therefore, it was necessary to study the equilibrium state of underground geothermal fluids and minerals to verify the reliability of the geothermometer method.

**Na–K–Mg triangle**

Due to low-heat storage temperatures and mixing with the upper layer of cold water, the chemical composition of the geothermal fluids does not reach a true water–rock equilibrium state. The Na–K–Mg triangle map determines if the groundwater in the area has reached this state. On this basis, this method was used to estimate the deep thermal reservoir temperatures in the study area. The Na–K–Mg triangle often has been used to evaluate the water–rock equilibrium state and to analyze the water samples suitable for its application (Zhao et al., 2010, 2007). This method depends primarily on the following two temperature-dependent reactions

\[
\text{K-Feldspar} + 1.6\text{H}_2\text{O} + \text{Mg}^{2+} = 0.8\text{K-Mica} + 0.2\text{Chloride} + 5.4\text{Silicon} + 2\text{K}^+ 
\]
The coordinates in the triangle can be calculated as follows

\[
\begin{align*}
S &= \frac{Na}{1000} + \frac{K}{100} + \sqrt[4]{Mg} \\
Na\% &= \frac{Na}{10S} \\
Mg\% &= \frac{100\sqrt[Mg]{Mg}}{S}
\end{align*}
\] (11)

In the equation, Na, K, and Mg represent the concentrations of sodium, potassium, and calcium ions in water, respectively.

The advantage of this method is that the equilibrium state of a large number of water samples can be simultaneously examined using the same picture, and the mixed water and balanced water can be sufficiently separated. In Figure 2, the percentage of the corresponding component’s content (mg/l) varies from 100 to 0% from each triangle point to its opposite side, and the percentage calculated by Na and Mg is parallel to the opposite side. The intersection point of the two straight lines indicates the concentration distribution of each water sample.

The Na, K, and Mg concentrations listed in Figure 2 could be used to establish if the water sample was suitable for the application of the ion geothermometer. In the figure, the water sample before the GRY1 fracturing falls on the side of the equilibrium water of the curve boundary line, which reflects that the equilibrium temperature of the water–rock reaction was low, and the water sample had not fully reached the equilibrium. Geothermal fluids may have come from a hotter environment and then diluted by the shallow cold water during the process of pumping the geothermal fluids to the surface, thereby lowering the concentrations of the elements in the geothermal fluids. The analysis of the geothermal fluid sediment’s composition from the GRY1 borehole indicated that the geothermal fluids were mixed with the relatively low-temperature water of the upper Mesoproterozoic Jixian Wumishan Formation during the upward migration process. In the figure, after the GRY1 fracturing, the water sample falls close to the Mg^{1/2} angle in the immature water section. This placement indicates that the Mg^{2+} content in these water samples was substantial, and the water–rock equilibrium temperature was not high.

Figure 2. GRY1 pore water sample Na–K–Mg triangle.
Therefore, the equilibrium temperature of the immature water sample estimated by the Na–K and Na–K–Ca geothermometers was unreasonable and can only be used as a reference.

**Multi-mineral balance method**

The multi-mineral balance method was used to determine the overall chemical equilibrium state between the hydrothermal fluid and minerals in the geothermal system (Niu et al., 2013). The principle was to regard the dissolved state of various minerals in the water as a function of temperature if the minerals were close to equilibrium simultaneously at a specific temperature. It could be determined that if the geothermal fluids and the set of minerals had reached equilibrium, the temperature at equilibrium was the deep geothermal temperature (Moller, 2000; Wang et al., 2007). It could be determined that geothermal fluids in this study had mixed with shallow cold water. It is impossible for water mixed with geothermal fluids that were not in equilibrium with the hydrothermal minerals to be in balance with a variety of minerals at a specific temperature.

In this study, two geothermal fluid samples from the Gaoyuzhuang Formation before and after GRY1 drilling and fracturing were selected. The saturation index (SI) values of various minerals calculated by the PHREEQCI program were used to select three groups of minerals based on the available data. The multi-mineral balance diagram is shown in Figure 3. The results of the analysis indicate that several minerals in the water sample before GRY1 drilling and fracturing were in two groups in the reference temperature range, and the chalcedony was close to saturation line. After the GRY1 fracturing, the minerals in the reference temperature range were in two groups in the supersaturation state.

The \( \alpha \)-cristobalite concentrations in the water samples before and after the fracturing were below the SI = 0 line, so the temperature of the thermal reservoir estimated by the \( \alpha \)-cristobalite geothermometer was lower than the actual value. The intersection with the line of SI = 0 would be after 150°C. The trending temperature was far from the measured value of the water sample above the Gaoyuzhuang Formation; the water samples before and after the fracturing were all above the SI = 0 line, so the temperature of the thermal reservoir.

![Figure 3. SI-T map for the water sample from GRY1 above the Gaoyuzhuang Formation. SI: saturation index.](image-url)
estimated by the quartz geothermometer was more than the actual value. The intersection with the line $SI = 0$ was approximately $104^\circ$C, indicating that the intersection temperature was close to the measured value of the water sample. The chalcedony was evenly distributed on both sides of the $SI = 0$ line before and after the fracturing. The index $SI$ value was close to zero, so the temperature of the thermal reservoir estimated by the chalcedony geothermometer was near to the actual value. The result estimated by this geothermometer was more reasonable than with other methods, and the intersection with the line $SI = 0$ was at approximately $110^\circ$C. This intersection temperature was also similar to the measured value of the water sample.

**SI method**

The mineral-solution equilibrium data calculated by the PHREEQC program were used to determine the minerals that have reached equilibrium. The program uses the geothermal fluid water quality analysis data to simulate the formation of the chemical components. The SI method quantitatively calculates the degree of equilibrium between the minerals in the deep reservoir and the water. The calculation results, as shown in Table 4, indicate that all of the mineral SIs of the water samples were greater than zero. In the saturated state, the geothermometer determined by the mineral was estimated as higher than the actual temperature. The SI was equal to zero

$$SI = \log Q - \log K = \log \frac{Q}{K}$$

where $K$ is the solubility of the mineral in the underground geothermal fluids (mol/l), and $Q$ is the actual ion activity (mol/l) of the mineral dissolved in the fluid.

The SIs of quartz, talc, barite, and serpentine in the fluids of the Gaoyuzhuang Formation were greater than zero before and after fracturing, indicating that the minerals were super-saturated. The estimated thermal reservoir temperature was higher than the actual value. Furthermore, the albite, anhydrite, anorthite, $\text{Fe(OH)}_3$, fluorite, gypsum, salt rock, illite, kaolinite, and $\text{SiO}_2$ SI values were less than zero before and after fracturing, indicating that the minerals were in the unsaturated state. The SI of rhodochrosite before fracturing was less

| Mineral                | $SI$ before fracturing | Mineral                | $SI$ before fracturing | Mineral                | $SI$ before fracturing | Mineral                | $SI$ before fracturing |
|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| Sodium feldspar        | -2.72                  | Salt rock              | -4.12                  | Sodium feldspar        | -1.54                  | Halite                 | -4.18                  |
| Anhydrite              | -0.30                  | Manganese ore          | -0.51                  | Anhydrite              | -0.16                  | Manganese ore          | 2.84                   |
| Calcium feldspar       | -4.22                  | Illite                 | -4.93                  | Calcium feldspar       | -2.32                  | Illite                 | -3.52                  |
| Barite                 | 0.14                   | Kaolinite              | -2.89                  | Barite                 | 0.31                   | Kaolinite              | -2.54                  |
| Chalcedony             | -0.08                  | Rhodochrosite          | -1.87                  | Chalcedony             | 0.06                   | Rhodochrosite          |                        |
| Serpentine             | 2.05                   | Quartz                 | 0.14                   | Serpentine             | 6.93                   | Quartz                 | 0.28                   |
| $\text{Fe(OH)}_3$      | -0.48                  | Sepiolite              | -1.43                  | $\text{Fe(OH)}_3$      | -1.05                  | Sepiolite              | 2.06                   |
| Fluorite               | -0.06                  | $\text{SiO}_2$        | 0.70                   | Fluorite               | -0.25                  | $\text{SiO}_2$        | -0.56                  |
| Plaster                | -0.88                  | Talc                   | 6.36                   | Plaster                | -0.74                  | Talc                   | 11.53                  |

Table 4. Geothermal fluid saturation before and after GRY1 hole fracturing.
than zero. The manganese ore concentrations had changed significantly before and after fracturing, changing from the unsaturated state to the supersaturated state, indicated by the substantial change in the mass concentration of ions, as presented in Table 5.

The calculated temperature of the water sample from the chalcedony geothermometer before GRY1 drilling and fracturing was lower than the measured temperature in the borehole. The SI of the chalcedony was less than zero, indicating an unsaturated state. The calculated temperature after fracturing was higher than the measured temperature value, as demonstrated by the supersaturated chalcedony SI value that was greater than zero. The SI values of the chalcedony before and after fracturing were nearly zero at 0.08 and 0.06, respectively, demonstrating that the reservoir temperature estimated by the chalcedony geothermometer was reasonable, with minimal error. The geothermometer estimation was distributed about 108ºC, above the measured temperature of the Gaoyuzhuang Formation, which indicates that the chalcedony in the geothermal system controls the balance between the geothermal fluids and silica.

Table 5. Comparison table before and after GRY1 water sample fracturing experiment (mg/l).

| Project                  | Fracture before the experiment | Fracture after the experiment | Difference | Project                  | Fracture before the experiment | Fracture after the experiment | Difference |
|--------------------------|--------------------------------|------------------------------|------------|--------------------------|--------------------------------|------------------------------|------------|
| Dissolved oxygen         | 6.68                           | 7.40                         | −0.72      | Total acidity            | 20.01                         | 5.73                         | 14.28      |
| K⁺                      | 109.96                         | 112.64                       | −2.68      | Zn                       | 0.024                         | 0.0100                       | 0.014      |
| Na⁺                      | 1951.28                        | 1794.94                      | 156.34     | Se                       | 0.0030                        | 0.0028                       | 0.0002     |
| Ca²⁺                    | 207.98                         | 234.58                       | −26.6      | Cu                       | 0.012                         | 0.0014                       | 0.0010     |
| SO₄²⁻                   | 558.48                         | 699.58                       | −141.1     | Ba                       | 0.18                          | 0.22                         | −0.04      |
| HCO₃⁻                   | 308.05                         | 348.96                       | −40.91     | Mn                       | 0.065                         | 0.0089                       | 0.0561     |
| Nitrate                 | 15.62                          | 0.00                         | 15.62      | PO₄³⁻                    | 0.00                          | 0.03                         | −0.03      |
| Free CO₂                | 17.62                          | 5.04                         | 12.58      | B                        | 7.69                          | 3.26                         | 4.43       |
| Sr                       | 13.02                          | 18.17                        | −5.15      | Cs                       | 0.0032                        | 0.036                        | −0.0328    |
| TDS                     | 6283.04                        | 6218.25                      | 64.79      | F⁻                       | 6.31                          | 4.80                         | 1.51       |
| SiO₂                    | 76.56                          | 112.04                       | −35.48     | Br⁻                      | 3.34                          | 3.63                         | −0.29      |
| NH₄⁺                    | 4.02                           | 17.75                        | −13.73     | I⁻                       | 0.25                          | 0.55                         | −0.3       |
| Nitrite                 | 0.09                           | 0.00                         | 0.09       | Al³⁺                     | 0.0066                        | 0.040                        | −0.0334    |
| Oxygen consumption       | 11.45                          | 19.64                        | −8.19      | High price iron          | 4.18                          | 1.86                         | 2.32       |
| Total alkalinity         | 252.65                         | 286.20                       | −33.55     | Total hardness           | 699.20                        | 789.19                       | −89.99     |

TDS: Total Dissolved Solvent.

Conclusion

In the research of water samples from the Gaoyuzhuang Formation in the Changcheng System’s Cangxian arch belt, the results of various geothermometers were compared and analyzed by standard methods. It was found that the temperature of the geothermal fluid reservoir in the area was suitable for using the chalcedony and K–Mg geothermometers. The two could accurately determine the temperature range of the heat storage, and the prediction results were consistent with the measured value of the water sample above the Gaoyuzhuang Formation. When using the Na–K–Mg triangle to evaluate the equilibrium state of the GRY1 borehole water sample, if the water sample has not reached equilibrium,
the heat storage temperature estimated by a cationic geothermometer will be abnormal. The PHREEQC program can calculate the mineral-solution equilibrium data to determine which minerals have reached equilibrium, and with these data, the temperature of the deep underground heat storage can be estimated. The combination of the PHREEQC program and the Na–K–Mg balance map is useful to evaluate the water–rock equilibrium state in the geothermal system, allowing accurate estimations of the geothermal temperatures.

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