Hydrogeochemical Characteristics of Huangshadong Geothermal Filed in Guangdong

Xiaoxue Yan¹, Wenjing Lin¹, Haonan Gan¹, Gaofan Yue¹ and Guiling Wang*¹

¹The Institute of Hydrogeology and Environmental Geology, CAGS, Shijiazhuang 050061, China
*Corresponding author’s e-mail: guilingw@yeah.net

Abstract: This paper analyzed genetic models of the geothermal water with middle low temperature in Huangshadong geothermal field which is one of the most important hydrothermal regions in the southeast coast of China. The flow pattern of geothermal water is replenished by precipitation, heated by circulation, and finally rises to the surface through cracks. The hydrochemical types of geothermal water in the study area is Na-HCO₃, and the hydrochemical types of non-geothermal water in the study area is Ca-HCO₃. The content of HSiO₂, Li, Sr, Ba and F were significantly enriched in geothermal water. Geothermal water in Huangshadong has larger circulation depth, longer flow time and smaller circulation rate, which make it obtain more heat than other geothermal water in the surrounding areas. According to the comprehensive analysis of the thermal field in the study area, there have two reservoirs for Huangshadong geothermal field, the shallow reservoir temperature is about 125°C, the deep reservoir temperature is about 180°C.

1. Introduction
Geothermal resource is one of the most realistic and competitive renewable energy resources [1]. In order to develop the energy and the useful components in the reservoir scientifically and rationally, hydrogeochemical methods are often used for analysis.

The study area located at the southeastern edge of Eurasia in Guangdong Province, which has been affected by the comprehensive action of plate movement for a long time. The development of fault structures is accompanied with the uplift of the crust and multiple periods of magmatic activities, which create a very favorable conditions for the storage of geothermal resources [2]. Therefore, Guangdong province has the richest geothermal resources and the largest number of geothermal springs. There are many scholars studied the genesis mechanism, hydrochemical characteristics, development and utilization of typical anomaly of geothermal in Guangdong Province by hydrochemical and geophysical methods [3-8]. As the geothermal area in Huangshadong geothermal field located in Guangdong Province has been designated as the target area for the development of dry hot rock resources, but the research is still in preliminary development and geothermal geological survey stage [9-11], and has not yet completed the conceptual model of geothermal water genesis model.

This paper analyzed the hydrogeochemical characteristics of Huangshadong geothermal field comprehensively basic on previous studies. The geochemical properties and evolution characteristics of geothermal water were studied by hydrochemical parameters and hydrogen and oxygen isotopes composition of the fluid; the water-rock interaction equilibrium was studied by equilibrium diagrams; finally, obtain the reservoir temperature by multiple methods, such as hydrochemical geothermometers,
silicon enthalpy method. These studies provide scientific reference for further exploration of geothermal fields in the area.

2. Geological settings
The study area lies in the eastern Guangdong, at the southeastern edge of the Eurasian plate, adjacent to the boundary between the Pacific plate and the Indian Ocean plate [12]. NE faults is the major regional faults in Guangdong area, the secondary fractures are mainly NW and EW faults. The faults associated with geothermal water is NE and NW faults, among which the NE structure is a compressional fracture which conductive the thermal from the deep reservoir; the NW structure is a tensile fault which controls the shallow discharge of geothermal water, as the rocks in the fault zone are more obviously broken than surrounding rocks. The geothermal water occurs in the junction of NE fault and NW fault. The strata exposed in the study area are Sinian (metasandstone, siltstone and shale), Cambrian (metamorphic fine sandstone, Siltstone, phyllitic shale), and Quaternary (clay, gravel-cobble) [13]. The intrusive rocks are mainly Jurassic and the lithology is medium-granule-biotite-adamellite, which output in stocks, providing the most suitable basement for the geothermal system (figure 1).

![Figure 1. Simplified geology map of the study area and sampling locations](image)

3. Sampling
Huangshadong were chosen as typical geothermal anomalous areas, from which 8 thermal water samples and 3 non-thermal water samples were collected in August 2017. The test items mainly include the major elements, trace elements, and hydrogen and oxygen isotopes. All samples were sent to the Institute of Hydrogeology and Environmental Geology, Chinese Academy of Geological Sciences within 2 weeks after sampling.

The temperature (T) and pH values of the geothermal water samples were measured using hand-held meters on site prior to sampling (WTW Multi 3400i). Cation ion concentration was detected by ICP method, anion was analyzed by ion chromatography, and the balance error between cation and anion was controlled within 3%. Hydrogen and oxygen isotope using wavelength scanning - light cavity ringdown spectroscopy in the temperature of 23°C, 50% humidity testing cases.

4. Results and Discussion
4.1 Water chemistry of the geothermal system
(1) The temperature of geothermal water in Huangshadong is 46.7 - 93°C, and the temperature of non-thermal water is 20-27.5°C. The thermal water is weakly alkaline (PH>7), the groundwater is neutral to slightly acidic water (mean pH level of 6.3), which related to the lithology of the strata.
(2) The TDS of geothermal water in Huangshadong is 560mg/l on average, and 83mg/l in non-thermal water on average, the value of TDS is in proportion to depth, indicating the more sufficient hydrolithogenesis with the increase of depth. The dissolved oxygen (DO) is generally lower in thermal water (1.4-6.24) than in non-thermal water (2.24-8.61), which may be due to the consumption of DO during the process of thermal water transport under water-rock action, or because the non-thermal water has obtained more precipitation supplies [8].

(3) The cation ions are mainly Na, anions is mainly HCO$_3^-$ in thermal water, and only a considerable amount of Ca exists in the shallow thermal water (H3) which may be caused by the mixing with shallow cold water (figure 2).

![Figure 2. Piper diagram showing the hot water samples in the study area](image)

(4) The trace elements in thermal water always have two main sources, one is from dissolving action, the other is from deep source. The content of HSiO$_2$, Li, Sr, Ba, F is in the thermal water is higher than that in the non-thermal water. Li is enriched in biotite, F in fluorite is enriched in biotite granite, and Ba and Sr are abundant in most medium-acidic granite. In addition, Sr and SiO$_2$ are abundant in silicate, feldspar and other minerals. Therefore the trace elements in thermal water is mainly affected by the dissolving of surrounding rock, in addition the high temperature and pressure may accelerates the reaction speed.

(5) As Cl$^-$ is neither easy to be absorbed by surrounding rocks nor affected by water-rock interaction in a natural water-rock system, it can be used to analyze which ions has a good correlation with it during the process of groundwater runoff [14-15]. In study area, the contents of Li, Sr, B, Ba, F show a strong positive correlation with Cl$^-$ in the thermal water ($R^2$>0.75), which indicated a deep source [16]. The content of SiO$_2$ which mainly sources from the dissolution of surrounding rocks, shows a positive correlation with Cl$^-$ ($R^2$=0.74), indicated a longer flow and a deep source. Generally, the linear relationship between the concentration of conserved components is considered as the best proof of the mixing of thermal water and non-thermal water [17]. The direct proportion between the conservative element SO$_4^{2-}$, HCO$_3^-$ show a strong positive correlation with Cl$^-$ ($R^2$>0.93), indicated the mixing of thermal and non-thermal water (figure 3) [18].
4.2 Isotopic characteristics of the geothermal system

Projected the hydrogen and oxygen isotopes onto the precipitation chart (figure 4), use the precipitation line of Pearl River Basin as local precipitation line ($D = 8.1 \times \delta^{18}O + 11.4$). The isotopes of non-thermal water distributed near the precipitation line with slight positive deviation, indicating that it recharged by nearby infiltration supply of meteoric precipitation and is affected by evaporation. The isotopes of thermal water is also close to the precipitation line, indicating that thermal water also recharged by the supply of meteoric precipitation, the value of isotope is lower, indicating that the thermal water recharged by meteoric precipitation at high altitudes [19].
4.3 Geothermometry
The geothermometry method are used to calculate the temperature of deep reservoir [20-21]. Some minerals can be used to calculate the temperature of deep reservoir, as these minerals had reached an equilibrium with thermal water in deep reservoir, and the content of the minerals is almost invariably, even though the temperature is dropped during the thermal water rose up [22-23]. In this paper, a variety of methods are combined to estimate the temperature of reservoir, and the results are shown in the table.

The Na-K geothermometer [24] yields very high temperature results within a wide range (142–290°C), as the reaction of the Na-K system is slow, it can be used to react with a deep high-temperature fluid. The K-Mg geothermometer [25] yields very low temperatures results (50°C - 125°C), which is closer to the measured temperature of the wellhead, because the reaction of the K-Mg system is faster and can reach equilibrium at low temperatures. The Na-K-Ca geothermometer [26] provides the temperature ranging from 145°C to 186°C.

As the cation geothermometer may make errors in the calculation of the temperature of thermal water which has not reach equilibrium, the silicon geothermometer was used to estimate the temperature of the reservoir. Before use the silicon geothermometer, it is necessary to judge the forms of heat transfer in reservoir, due to the temperature of the thermal water in study area is generally lower than the local boiling point, the results calculated of without steam loss is more suitable to estimate the reservoir temperature.

The calculated temperature of a quartz geothermometer is 78-170°C, the calculated temperature of a chalcedony geothermometer is 82-147°C.

The dissolution of SiO$_2$ is mainly controlled by quartz, chalcedony and amorphous SiO$_2$, the figure of logSiO$_2$ vs. logK$^2$/Mg (figure 5) can be used to judge the main mineral species which controlled the dissolution and estimate the reservoir temperature. In the study area, thermal water concentrated near the line of chalcedony, indicated the chalcedony may controlled the dissolution of SiO$_2$, and is more suitable to estimate the reservoir temperature. The temperature of reservoir estimated by this method is generally lower (50-140°C), which may be due to the influence of mixing with non-thermal water, and the shallower the well depth, the greater the mixing effect.

The silica-enthalpy mixing model can be used to evaluate the mixing ratio of thermal water and non-thermal water, and obtain the reservoir temperature before mixing [26]. In this model, thermal water is considered to be generated by mixing of deep thermal water with non-thermal water, assuming no steam or heat loss. Figure 6 presents the silica-enthalpy mixing model according to chalcedony and quartz solubilities, the cold water sample as one end member (t=21°C, SiO$_2$=20mg/l), and the thermal water as the other end member. The mixing line cuts through quartz solubility curve indicating the reservoir temperature of 182-263°C, mixing ratio is 70-95%; The mixing line cuts through chalcedony solubility curve indicating the reservoir temperature of 118-212°C, mixing ratio is 62-92%.

![Figure 5. Plot of log(SiO$_2$) versus log(K$^2$/Mg), concentrations in mg/L. The lines indicate the temperature dependence of the variables for silica minerals [27]](image1)

![Figure 6. Si-enthalpy model in study area](image2)
The Na-Ca-Mg diagram reflects that all of waters are immature, and the Na-K/Mg-Ca diagram reflects that all of thermal waters are immature except the water in borehole. These results indicated the effects of processes such as re-equilibrium and strong dilution/mixing with shallow non-thermal water [25, 28]. The Na-Ca-Mg diagram (figure 8) give the reservoir temperature of 188°C, the Na-K/Mg-Ca diagram (figure 7) give the reservoir temperature of 120°C.

![Figure 7. Plot of 10Mg/(10Mg + Ca) versus 10K/(10K + Ca) of the studied groundwater](image)

![Figure 8. Na-K-Mg diagram of the studied groundwater](image)

5. Summary of geothermometer applications

In conclusion, according to calculate by different thermometers the reservoir temperature have a wide range. The results of chalcedony, log (SiO₂) vs. log (K²/Mg) and k-mg geothermometer are very low and close to the measured temperature, so they cannot provide reasonable results. The results of Na-K is too high, and the silicon enthalpy diagram (quartz) gives a similar temperature, so they cannot provide reasonable results too. Due to the mixing of non-thermal water, the result of Na-K-Mg diagram is not appropriate [21]. It is observed that SiO₂ geothermometer, Na-K-Ca geothermometer, silicon enthalpy diagram (chalcedony) provide reasonable reservoir temperature which ranging from 120 to 180°C. The range include the deep reservoir temperature which eliminate the mixed effect (The deep thermal storage reservoir temperature is 142-212°C, averaged about 180°C), and the shallow reservoir temperature which had mixed with shallow non-thermal water (The average shallow reservoir temperature is 80-170°C, averaged about 125°C).

| Sample ID | Quartz (no steam loss) | Chalcedony (no steam loss) | K-Mg | Na-K | Na-K-Ca |
|-----------|------------------------|----------------------------|------|------|---------|
| H1        | 111.8                  | 85.9                       | 54.6 | 189.4| 145.4   |
| H2        | 129.3                  | 101.6                      | 79.4 | 187.4| 159.9   |
| H3        | 78.2                   | 55.6                       | 48.7 | 290.2| 186.6   |
| H4        | 134.2                  | 106.0                      | 91.2 | 147.9| 154.2   |
| H5        | 169.7                  | 147.1                      | 125.7| 142.8| 168.8   |
| ZK1       | 157.4                  | 126.8                      | 115.3| 183.6| 182.6   |
| ZK4       | 153.7                  | 123.5                      | 136.7| 156.8| 165.2   |
| ZK5       | 147.6                  | 118.1                      | 97.6 | 183.6| 171.5   |

6. Conclusion

The thermal water in the study area characterized by weakly alkaline and Na-HCO₃ type water, the non-thermal water characterized by neutral to slightly acidic water and Ca-HCO₃ type water. Based on the relationships of ions and Cl indicated the thermal water experience a longer and deeper flow and a
mixing process of thermal and non-thermal water. Hydrogen and oxygen isotopic compositions indicate that both thermal and non-thermal water have a main origin from meteoric precipitation. The reservoir temperature can be evaluated by using cation geothermometer, silication geothermometer, silica-enthalpy mixing model, log (SiO$_2$) vs log (K$_2$/Mg) diagram and equilibrium diagram. According to comprehensive analysis, the estimated mean deep reservoir temperature is 142-212°C, during the rise of the thermal water there is non-thermal water mixed, and the mix ratio is 62-91%, the temperature of thermal water which has been mixed is 80-170°C.

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