ISSN: 2414-1895 DOI: 10.6919/ICJE.202110_7(10).0066

Hydrochemical Characteristics of Geothermal Fluid in Guantao Formation in Tianjin Area

Huichuan Hu[1,2,a], Hui Tong[1,b], Zongjun Gao[1,*]

[1]College of Earth Science and Engineering, Shandong University of Science and Technology, Qingdao, Shandong, 266590, China;

[2]Tianjin Geothermal Survey, Development and Design Institute, Tianjin, 300250, China.

[a]303060543@qq.com, [b]thsdust@126.com, *gaozongjun@126.com

Abstract

In order to systematically understand the hydrochemical characteristics and genesis of the geothermal fluid in the Guantao Formation in Tianjin area, the hydrochemical characteristics, formation mechanism and occurrence environment of the geothermal fluid in the Guantao Formation were studied through mathematical statistics, Piper diagram, ion ratio, and geothermal temperature scale. The results show that there are obvious differences in the spatial distribution of the geothermal fluids in the Guantao Formation in the Tianjin area; the total mineralization in the Jizhong depression area in the west (772.3—1121.9 mg/L) is higher than the total mineralization in the Huanghua depression area in the east (1286.2—1972.6 mg/L) small; the hydrochemical type in the Jizhong depression area is HCO_3-Na type, and the hydrochemical type in the Huanghua depression area is Cl•HCO_3-Na type; The pH is between 7.61 and 8.63, all of which are weakly alkaline fresh water. The SiO_2 content in the geothermal fluid has reached the national drinking natural mineral water standard; the geothermal water in this area belongs to the category of low-temperature heat storage, and the method of using the chalcedony geothermal temperature scale to predict the temperature of the heat storage is more suitable; The analysis of the cause shows that the geothermal fluid originated from atmospheric precipitation, which belongs to the bromine-poor rock salt-bearing strata dissolved water and has the characteristics of terrestrial sedimentary water.

Keywords

Guantao Formation; Water Chemistry Characteristics; Thermal Storage Temperature; Origin; Tianjin.

1. Introduction

As a low-carbon, environment-friendly and renewable resource, compared with solar energy and wind energy, geothermal energy has the advantages of being free from climate, seasonal and diurnal changes, can be used efficiently, and is widely used in heating, medical treatment, power generation, aquaculture and other fields [1-2]. The geothermal water stored in the pores is formed after a long period of geological history, and its chemical composition varies greatly due to the influence of factors such as the geochemical environment and the state of migration and storage. Research on the hydrochemical characteristics of geothermal water can reveal its genesis, source, reservoir temperature,migration and storage status and other characteristics.

Tianjin is rich in geothermal resources and has a long history of development and utilization, dating back to the 1970s. Under the guidance of Li Siguang, a geothermal battle was conducted and a general survey of geothermal resources was conducted [3-4]. At present, the research on geothermal energy in Tianjin is mainly focused on the Miwushan Formation. Yue Dongdong and others have studied the hydrochemical characteristics of the Mishan Formation's thermal storage fluid. Liu Jie et al. Research on recharge of thermal storage geothermal in Miwushan Formation. However, there are relatively few studies on the thermal reservoirs of the Guantao Formation. This article systematically studies the hydrogeochemical effects of the Neogene Guantao Formation geothermal water through mathematical statistics, Piper three-line diagrams, ion ratios, and geothermal temperature scales, and summarizes them. Its water chemistry formation mechanism.

2. Overview of the study area and characteristics of thermal reservoirs

2.1 Overview of the study area

The Tianjin area is located at the northern margin of North China, the first-level structural unit. It is divided into the northern mountainous area and the southern plain area by the Ninghe-Baodi fault, and its geological structural characteristics have obvious differences. The northern mountainous area belongs to the second-level (level III) tectonic unit Jibaolong fold area of the Yanshan platform fold belt of the second-level structural unit, where Paleozoic and Pre-Palaeozoic are developed. The southern plain area belongs to the North China faulted depression area of the second-level structural unit, which is a Mesozoic and Cenozoic fault depression and depression basin. The geothermal resources in this area are mainly located in the southern plain. The third-level structural units in the area include one uplift and two depressions, namely the Cangxian Uplift, Jizhong Depression, and Huanghua Depression, including a total of 12 fourth-level structural units (Figure 1). The types of heat storage are Cenozoic pore-type heat storage (porous heat storage) dominated by continental clastic sediments, and Paleozoic, Meso-New Proterozoic carbonate karst fracture-type heat storage dominated by marine sediments (Bedrock thermal storage) [5]. The Neogene Guantao Formation (Ng) thermal reservoir in this study is one of the porous thermal reservoirs.

2.2 Thermal reservoir characteristics

From the perspective of structural pattern, the Neogene Guantao formation is missing in the core of shuangyao uplift in Tianjin. On both sides of the missing zone, due to different sedimentary environments, two completely different sets of Guantao formation thermal storage systems are formed: to the west of the missing zone is the Guantao formation thermal storage with Jizhong depression as the main body, with alternating River and lake facies accumulation, which is near the sedimentary center to Wuqing District and the north, Guantao formation fluid is in a deep circulation geological environment, and the permeability coefficient is small (0.23-0.74 m/d); On the east side of the missing zone, the thermal reservoir of Guantao formation with Huanghua depression as the main body forms a deep hydrostatic pressure system controlled by the sedimentary environment. It is fluvial alluvial and proluvial facies, and the permeability coefficient is significantly higher than that of Jizhong depression (1.71-2.18 m/d).

In terms of geomorphology, it belongs to fluvial facies clastic rock deposits, which are mostly coarse-fine-coarse sedimentary cycles. According to the characteristics of thermal reservoirs, they are divided into the upper Guan I sandstone thermal storage section and the lower Guan III sandstone thermal storage section. Pavilion I thermal storage section: thickness 100-200m, wellhead steady flow temperature 48-65℃; Pavilion III thermal storage section: wellhead steady flow temperature 60-82℃, unit water inflow 0.52-5.13 m^3/h·m, fluid chemical type It is HCO_3-Na, HCO_3·Cl-Na type, with a salinity of 0.8-1.9 g/L. Permeability coefficient: 0.3-2.2 m/d water conductivity: 40-212 m^2/d elastic release coefficient: 2.9-7.3×10^{-5}, porosity: 18-36.6%.

In this study, 17 groups of Neogene Guantao Formation geothermal fluid samples from different structural units in Tianjin plain area were collected, and the hydrochemical test results are shown in Figure 1; The test and analysis work is completed by Tianjin geological and mineral testing center.

ISSN: 2414-1895
DOI: 10.6919/ICJE.202110_7(10).0066

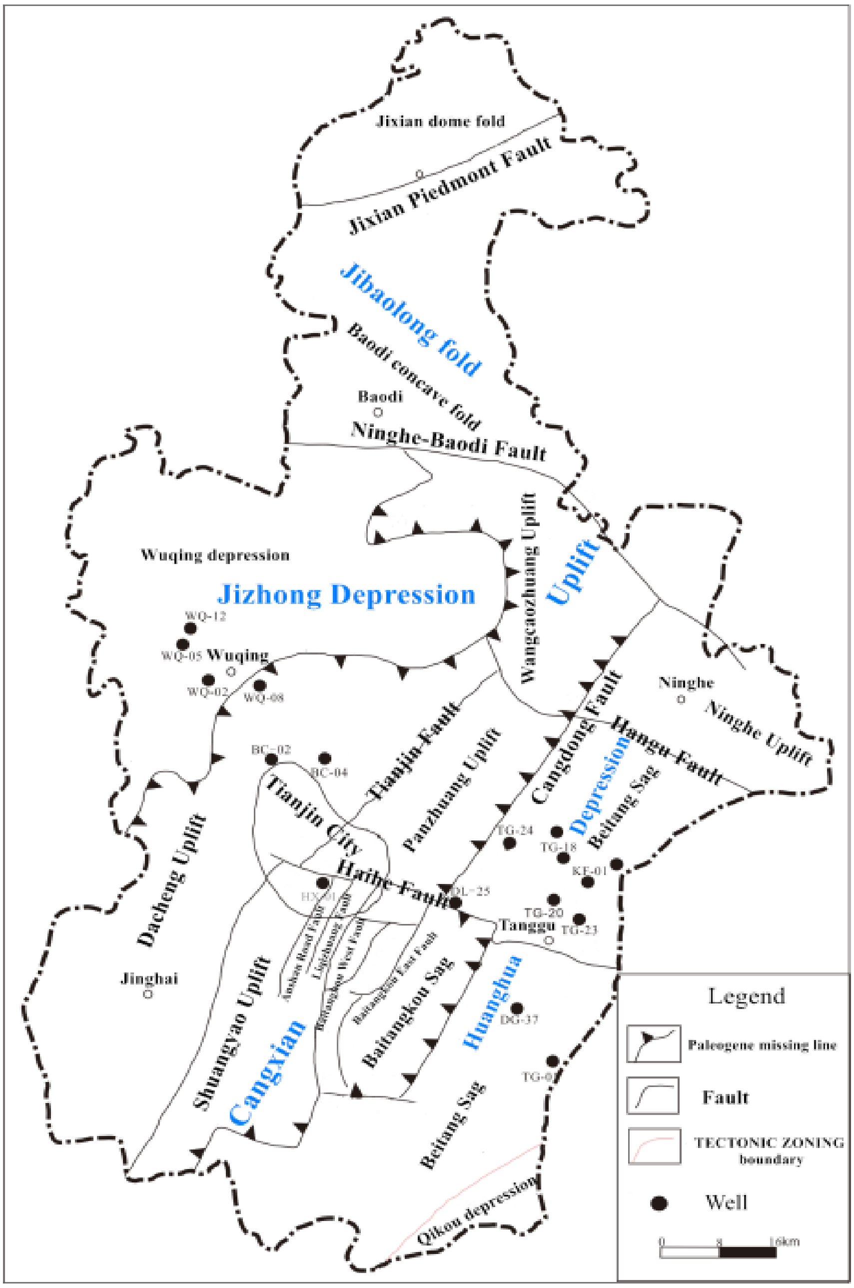

Figure 1. Zoning map of Tianjin tectonic units and distribution of sampling points

3. Water chemistry characteristics and analysis

3.1 Hydrogeochemical characteristics

Based on the characteristics of the geological structure of the Guantao Formation in the area, a regional analysis and evaluation of the area is carried out. The chemical composition of geothermal water in the study area is shown in Table 1. To the west of the missing zone is the Jizhong Depression. The cations are mainly Na^{+}, the anions are mainly HCO_3^{-}, the total salinity is 772.3-1121.9 mg/L, and the pH is 7.88-8.59, which is weakly alkaline freshwater. The water chemistry type is HCO_3-Na type; in the Huanghua depression area to the east of the missing zone, the main cations are Na^{+}, the anions are mainly HCO_3^{-}, $Cl^{-}$and SO_4^{2-}, the total salinity is 1286.2-1972.6 mg/L, and the pH is medium. From 7.61 to 8.55, it is weakly alkaline fresh water, and the water chemistry type is Cl·HCO_3-Na; in the uplift area of Cangxian County, the cations are mainly Na^{+}, the anions are mainly HCO_3^{-} and Cl^{-}, and the TDS is 1055.3-1276.2 mg/L, The pH is between 8.46 and 8.63, which is weakly alkaline fresh water. The water chemistry type is HCO_3-Na type and HCO_3·Cl-Na type water.

Table 1. Chemical compositions of geothermal water in the study area

number	K^+	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	HCO_3^-	SO_4^{2-}	pH	TDS	Groundwater type
BC-02	2	372.5	4.3	0	241.1	616.3	2	8.46	1276.2	HCO_3·Cl—Na
BC-04	1.3	304.4	2.1	0	115.2	573.6	11.7	8.63	1055.3	HCO3—Na
DG-37	4.7	624	9.1	0.2	561.9	530.9	141.5	8.55	1921.3	Cl·HCO3—Na
DL-25	57.6	445.5	28.8	6.2	390	463.8	240.9	7.61	1683.8	Cl·HCO3—Na
HX-01	19.7	498.5	30.9	6.1	372.2	524.8	239.7	7.86	1722.4	Cl·HCO3—Na
KF-01	4.7	518.4	10.9	0.8	343.9	561.4	231.5	7.87	1714.1	Cl·HCO3—Na
TG-01	4.4	641.3	12	0.9	632.8	463.8	176.8	8.38	1972.6	Cl·HCO3—Na
TG-16	4.6	482.6	9.1	0	322.6	537	206	8.42	1567.9	Cl·HCO3—Na
TG-18	6	509.6	10.7	0.5	342.1	512.6	215.1	8.43	1648.4	Cl·HCO3—Na
TG-20	5.8	549.7	12.8	0.5	379.3	546.1	226.7	8.42	1760.9	Cl·HCO3—Na
TG-23	5.2	418.7	18.5	4.2	297.8	408.8	200.2	8.54	1394.9	Cl·HCO3—Na
TG-24	16.4	359.4	13.5	2.4	205.6	524.8	128.1	8.34	1286.2	HCO_3·Cl—Na
TG-32	10.6	499.4	15.4	2.1	354.5	488.2	219.5	8.48	1635.9	Cl·HCO3—Na
WQ-02	3.4	254.9	3.1	0.4	53.2	570.5	23.5	8.59	979.5	HCO3—Na
WQ-05	4.4	283.4	4.5	0.4	63.8	674.3	27.1	7.88	1121.9	HCO_3—Na
WQ-08	2.2	200.8	4.5	0.5	40.8	436.3	38.2	8.33	772.3	HCO_3—Na
WQ-12	3.6	268.4	3.6	0.4	70.9	622.4	21.6	8.31	1045.9	HCO3—Na

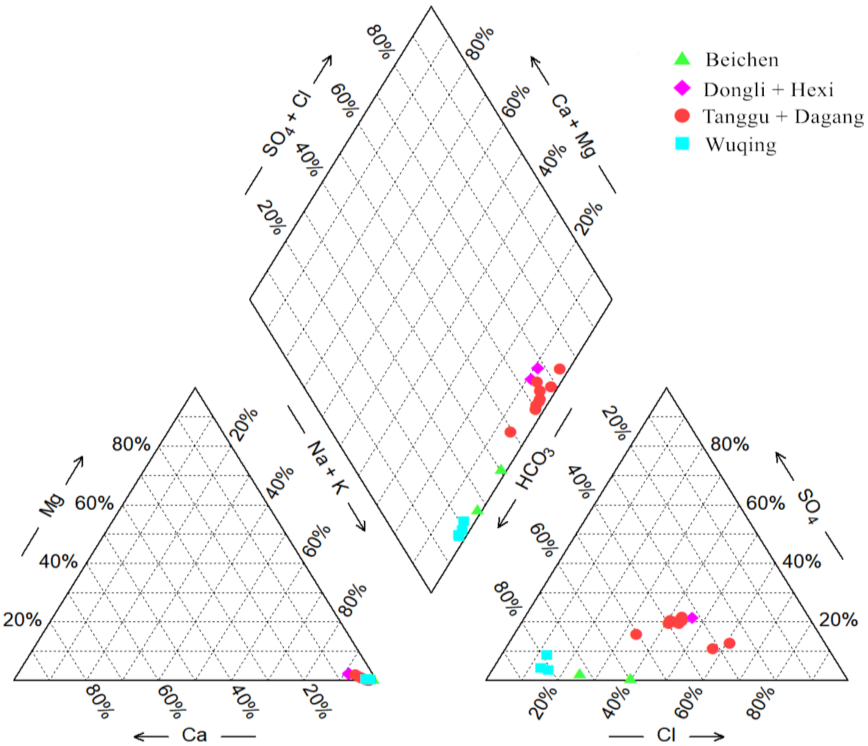

Figure 2. Piper plpt of Geothermal water

Tianjin has been exploiting geothermal heat for a long time, and monitoring of geothermal wells has been carried out for many years, taking the well WQ5 in the Jizhong depression area and the well TG16 in the Huanghua depression area as examples. The monitoring results are shown in Figure 3. The results showed that although some ion concentrations in Well TG16 fluctuated slightly, the main ion concentrations were generally stable; the main ion concentration and total salinity of Well WQ5 had large fluctuations in 2014. It is a small fluctuation but tends to be stable as a whole.The geothermal water of Neogene Guantao Formation in Tianjin has not changed significantly due to long-term artificial exploitation. To a certain extent, it can be explained that the hydraulic connection between thermal reservoirs is poor and there is no obvious mixing effect.

 Volume 7 Issue 10, 2021
DOI: 10.6919/ICJE.202110_7(10).0066

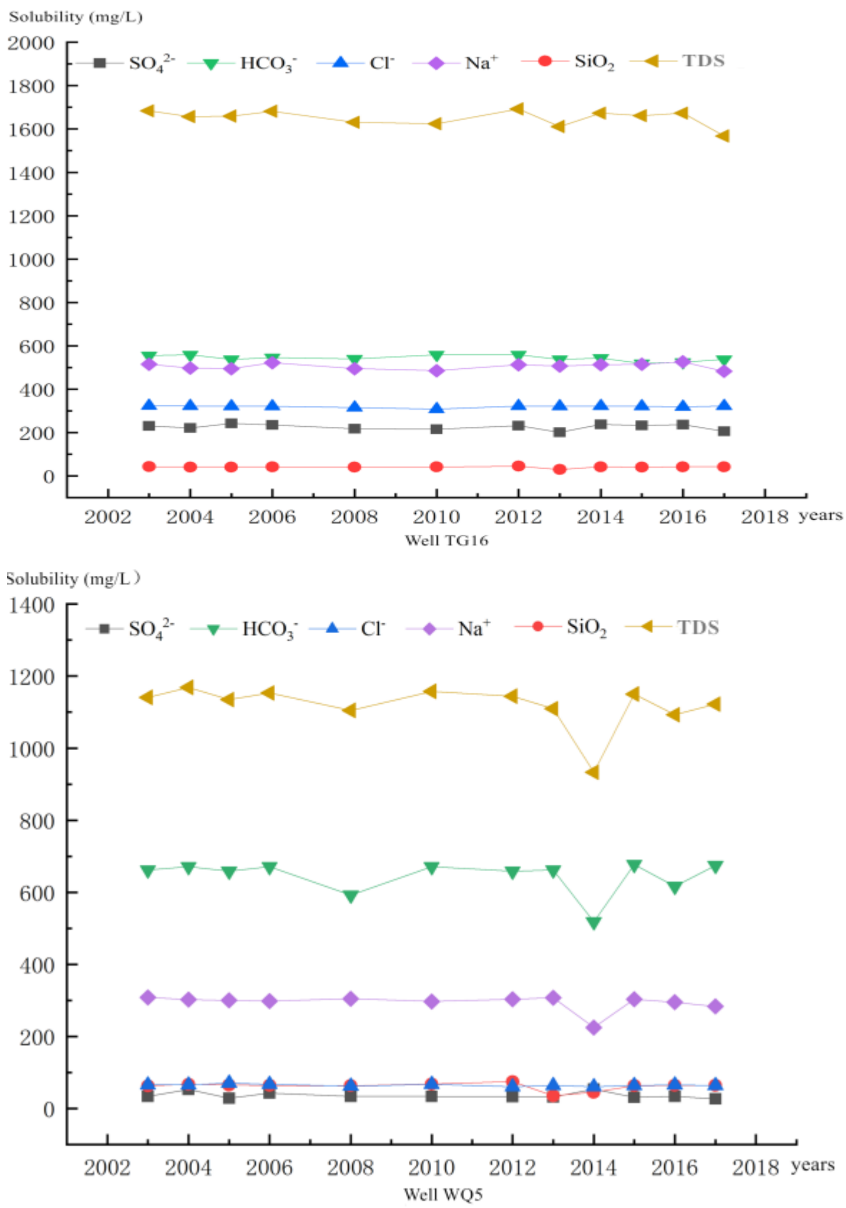

Figure 3. Dynamic monitoring chart of main ion content

3.2 Special components

The contents of some components such as silica, fluorine and metaboric acid in geothermal water of Neogene Guantao Formation in Tianjin are significantly higher than those in normal temperature groundwater. The SiO_2 content in most geothermal water reaches the national standard of the people's Republic of China drinking natural mineral water (GB 8537-2008) (≥ 25mg / L).

The F^- content in the geothermal fluid is generally high, between 3.89-10.0 mg/L, all exceeding the drinking water standard (GB5749-2006). The F^- content in the fluid increases in a positive correlation with the increase of the total salinity.

SiO_2 is abundant in stratum, and its solubility is mainly affected by temperature, so it can be used as a geochemical temperature scale to indicate the temperature of geothermal fluid. The content of SiO_2 in the geothermal water of the Neogene Guantao Formation in Tianjin is generally 29-64 mg/L, which is positively correlated with temperature, but has no obvious relationship with salinity. As a chemical component beneficial to human health, SiO2 often attracts people's attention. The content of soluble SiO_2 in most geothermal water of Neogene Guantao Formation in Tianjin reaches the national standard of the people's Republic of China drinking natural mineral water (GB 8537-2008).

Volume 7 Issue 10, 2021
DOI: 10.6919/ICJE.202110_7(10).0066

The content of HBO_2^- in geothermal fluid of Neogene Guantao Formation in Tianjin is different on both sides of the missing zone. The content of HBO_2^- in Huanghua depression is higher than that in Jizhong depression. The content of HBO_2^- in geothermal water in Jizhong depression is 0.12-9.29 mg/L, and the content of HBO_2^- in geothermal water in Huanghua depression is 17.23-28.95 mg/L, which is dozens of times higher than that of Quaternary cold water.

3.3 Hydrogen and oxygen isotopic characteristics

The δD range of the geothermal water in the Jizhong Depression in the study area is -77-69.3‰, the $\delta^{18}O$ range is -9.5-8.39‰, and the average values of the δD and $\delta^{18}O$ of the water samples are -69.4‰ and -9.07‰, respectively; The δD range of the geothermal water in the Huanghua Depression is -70.9-61.8‰, the $\delta^{18}O$ range is -9.07-8.79‰, and the average values of the δD and $\delta^{18}O$ of the water samples are 67.6‰ and -9‰ respectively. It can be seen that the stable hydrogen and oxygen isotopes of the Guantao Formation of the Neogene in Tianjin area have relatively small differences and have the same characteristics.

Hydrogen and oxygen stable isotopes are important indicators of geothermal water supply source. Through research, we can judge the source of geothermal water and determine the supply conditions of geothermal water and its connection with water in different circles [6]. The atmospheric precipitation line of hydrogen and oxygen stable isotope is an important basis for judging the source of water body, and its use is affected by meteorological and geographical factors [7]. Therefore, the precipitation line in Beijing is selected in this paper ($\delta D=7.5\ \delta^{18}O+8.1$) as the atmospheric drawdown line in the study area [8]. The hydrogen and oxygen isotope data of the study area are cast and compared with the precipitation line in Beijing (Fig.4). The results show that all water sample points are located near the precipitation line in Beijing, indicating that the main supply source of geothermal water in the study area is atmospheric precipitation.

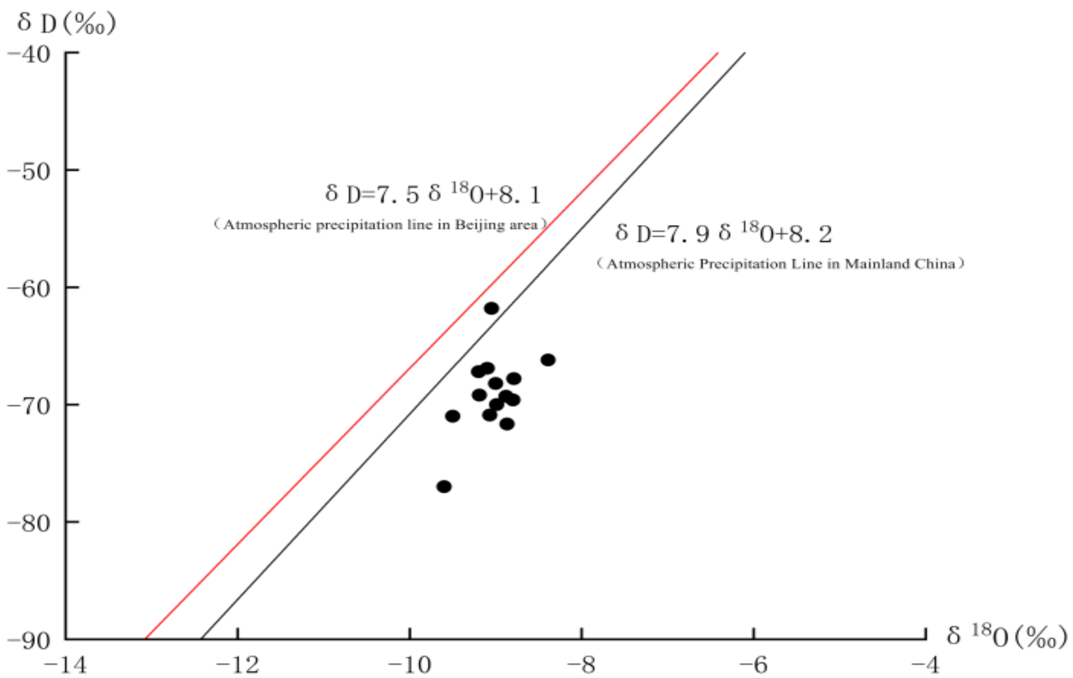

Figure 4. Hydrogen and oxygen isotopic composition of geothermal water of Guantao Formation in Tianjin area

3.4 Causes and sources of geothermal water

The milligram equivalent ratio of $\gamma Na^+/\gamma Cl^-$, also called metamorphism coefficient, can reflect the hydrogeochemical environment of the formation and the degree of concentration and metamorphism of groundwater. The sodium chloride and chlorine coefficient of standard seawater is 0.85. The ratio

ISSN: 2414-1895 DOI: 10.6919/ICJE.202110_7(10).0066

of $\gamma Na^{+}/\gamma Cl^{-}$ in the study area is higher than 0.85 of standard seawater, indicating that the geothermal water in this area dissolves through the rock salt-bearing strata and has typical dissolving water characteristics.

The chlorine bromine coefficient ($\gamma Cl^{-}/\gamma Br^{-}$) is a characteristic coefficient of seawater, and the chlorine bromine coefficient in seawater is about 300. When $\gamma Cl^{-}/\gamma Br^{-} <300$, the water belongs to marine sedimentary water (ancient storage water); if it is the filtered water of a bromine-poor salt-bearing formation, then $\gamma Cl^{-}/\gamma Br^{-}>300$ [9]. The chlorine-bromine coefficient of the study area is between 1490.41-184573.33, which is far greater than 300, which conforms to the characteristics of leaching water and belongs to the karst water of marine salt-bearing sediments.

$\gamma Br^{-}/\gamma I^{-}$ ratio: The coefficient of normal seawater is 1300, and the coefficient of geothermal water is much lower than this value, which has the characteristics of terrestrial sedimentary water. The bromine and iodine coefficient of the study area is between 0.05 and 3.05, far less than 1300, indicating that the geothermal water in this area has the characteristics of terrestrial sedimentary water.

Table 2. Chemical characteristic coefficient of Geothermal water

Sample serial number	$\gamma Na^{+}/\gamma Cl^{-}$	$\gamma Cl^{-}/\gamma Br^{-}$	$\gamma Br^{-}/\gamma I^{-}$
BC-02	2.38	2827.22	3.05
BC-04	4.08	89307.94	0.09
DG-37	1.71	65341.32	0.15
DL-25	1.76	113379.23	0.15
HX-01	2.07	144272.64	0.06
KF-01	2.33	184573.33	0.13
TG-01	1.56	129857.69	0.09
TG-16	2.31	56983.27	0.13
TG-18	2.30	176806.99	0.07
TG-20	2.24	19177.14	0.88
TG-23	2.17	6202.40	2.15
TG-24	2.70	15260.73	0.96
TG-32	2.17	13895.57	0.91
WQ-02	7.40	5265.05	0.10
WQ-05	6.86	1529.71	0.37
WQ-08	7.60	1490.41	0.98
WQ-12	5.84	10199.63	0.05

3.5 Thermal storage temperature

Thermal storage temperature is an important parameter that is indispensable for dividing the genetic types of geothermal systems and evaluating the potential of geothermal resources. It is of great significance for the effective use of geothermal resources [10]. The geothermal temperature scale method is an economical and effective means to determine the temperature of deep underground heat storage [11]. The geothermal temperature scale method mainly includes isotope geothermal temperature scale, silica geothermal temperature scale, gas temperature scale and cationic geothermal temperature scale. At present, there are more studies on cationic geothermal temperature scales and silica geothermal temperature scales at home and abroad, but few studies on isotopic geothermal temperature scales and gas temperature scales [12]. In this paper, the SiO_2 geothermal temperature scale and K-Mg temperature scale will be used to estimate the heat storage temperature of the Guantao Formation in the study area.

The SiO_2 temperature scale is the most commonly used and the earliest applied geothermal temperature scale. The theoretical basis of this method is that the content of SiO_2 in the geothermal fluid depends on the solubility of quartz in water at different temperatures and pressures [13]. Commonly used SiO_2 has chalcedony geothermal temperature scale and quartz conduction cooling temperature scale quartz geothermal temperature scale (no steam loss), of which chalcedony geothermal temperature scale is suitable for low temperature heat storage. The formula is:

ISSN: 2414-1895 | DOI: 10.6919/ICJE.202110_7(10).0066

$$t(℃) = \frac{1032}{1.69 - log\, C_{SiO_2}} - 273.15$$

In the formula: t is the temperature, ℃, C_{SiO2} is the solubility of SiO_2.

Giggenbach proposed the K-Mg temperature scale in 1988 [14]. In the water-rock system, K-Mg quickly reaches equilibrium, responds quickly to temperature changes, and is suitable for low-temperature heat storage. The formula is:

$$t(℃) = \frac{4410}{13.95 - \log \frac{C_k^2}{C_{M_g}}} - 273.15$$

In the formula: C_k and C_{Mg} are the mass concentrations of potassium and magnesium ions in the water, mg/L.

The actual water temperature in the Guantao Formation of the Neogene in the study area is between 48℃ and 86℃; the temperature calculated by the K-Mg temperature scale method is between 60.96 and 119.84, which is higher than the actual water temperature; the water temperature estimated by the chalcedony temperature scale is in Between 46.59 and 84.71, it is relatively close to the actual temperature, indicating that it is reasonable to use the chalcedony temperature scale method to predict the thermal storage temperature of the Neogene Guantao Formation in this area.

4. Conclusion

(1) The hydrochemical composition of the geothermal fluid in the Neogene Guantao Formation in the study area tends to be stable throughout the year. The dominant cation in the Jizhong depression area is Na^+, the anion is mainly HCO_3^-, and the water chemistry type is HCO_3-Na; the dominant cation in the Huanghua depression area is Na^+, the anion is mainly Cl^- and HCO_3^-, and the water chemistry type is Cl·HCO_3-Na type. The pH of the Jizhong Depression and Huanghua Depression is between 7.61 and 8.59, both of which are weakly alkaline freshwater.

(2) From the ion ratio and the hydrogen-oxygen stable isotope relationship, it can be seen that the Neogene Guantao Formation geothermal water belongs to the bromine-poor rock salt-bearing strata dissolved filtrate water, has the characteristics of terrestrial sedimentary water, and comes from atmospheric precipitation.

(3) The thermal storage temperature of the Neogene Guantao Formation in Tianjin is 48℃-86℃, which belongs to the category of low-temperature thermal storage. The method of using the chalcedony geothermal temperature scale to predict the thermal storage temperature is more suitable.

References

[1] Li D W, Wang Y X. Several major issues in the research and development of dry hot rock geothermal energy[J].Earth Science (Journal of China University of Geosciences),2015,40(11):1858-1869.(in China).

[2] Lund J W, Bjelm L, Bloomquist G, et al. Characteristics, development and utilization of geothermal resources [J]. Episodes, 2008, 31(1):140-147.

[3] Lu R, Du B J, Cai G Y, et al. Exploration report on Tianjin urban area and Wanglanzhuang geothermal field [R]. Tianjin: Tianjin Geothermal Exploration and Development Design Institute, 1987:23-49. (in China).

[4] Hou F Z. Li Siguang and Tianjin Geothermal Battle[J].Geothermal Energy,2010(6):23-25.(in China)

[5] He M C, Li C H, Zhu J L, et al. China's low and medium enthalpy geothermal engineering technology [M]. Beijing: Science Press, 2004.(in China).

[6] Qin D J, Sun J, Guo Y, et al. 2019. The impact of Yongding River on the karst water of Xishan Mountain and Yuquan Mountain Spring in Beijing[J]. Journal of Engineering Geology, 27(1):162-169.(in China).

[7] Gao Z J, Yu C, Tian Y, et al. Study on the Division of the Slope of the Atmospheric Precipitation Line in Mainland China and the Source of Water Vapor [J]. Groundwater, 2017, 39(06):149-152+177. (in China).

ISSN: 2414-1895 DOI: 10.6919/ICJE.202110_7(10).0066

[8] Lu Chang, Yang Jiang, Chen Zhi, Sun Fengxia, Zhou Xiaocheng, Li Ying. Geochemical characteristics of fluids in geothermal wells in the eastern part of the Capital Circle [C]. Seismological Fluid Professional Committee of China Seismological Society, Seismological Bureau of Qinghai Province. Seismic Fluid Professional Committee of China Seismological Society 2017 Abstract of the paper of the annual academic conference of the Chinese Seismological Society. Seismological Fluid Professional Committee of China Seismological Society, Qinghai Provincial Seismological Bureau: Seismic Fluid Professional Committee of China Seismological Society, 2017: 35.

[9] Sui H B, Kang F X, Li C S, et al. The relationship between Jibei geothermal water and Jinan spring water revealed by hydrochemical characteristics [J]. Karst China, 2017, 36(1): 49-58.(in China).

[10] Lu Z Q, Song H J, Cheng H Z. The application of geothermal temperature scale to estimate the thermal storage temperature of radon hot spring in Dasunzhuang, Pingyin County, Jinan City [J]. Geology of Chemical Minerals, 2020, 42(01):42-46.(in China).

[11] Wang Y, Zhou X, Yu Y, et al. Application of geothermal temperature scale to estimate the temperature of underground thermal storage [J]. Modern Geology, 2007, 21(4):605-612(in China).

[12] Liu J Q. Using the geothermal temperature scale to estimate the thermal storage temperature——Taking Shengzhou Chongren hot water as an example [J]. Western Exploration Engineering, 2014, 26(05): 129-132. (in China).

[13] Xu S G, Guo Y S. Foundation of Geothermal Science [M]. Beijing: Science Press, 2009:36-42 (in China).

[14] Giggenbach W F. Geothermal solute equilibria. Derivation of Na-K-Mg-Ca geoindicators [J]. Geochimica et Cosmochimica Acta, 1988, 52(12):2749-2765.